The University of Manitoba

The Mechanism of Extraction of Organic Compounds Using Polyurethane Membranes

by

Kathy Rzeszutek

A thesis submitted to the Faculty of Graduate Studies in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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THE UNIVERSITY OF MANITOBA

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Dedicated to:

Mom and my Sister

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Abstract

The main focus of this research has been to investigate the process by which organic compounds in solution are taken up by polyurethane membrane under various chemical and physical conditions. This extensive mechanistic study involved examining the effect of solution conditions on extraction (presence of salts, pH), the size and polarity of the organic species, the type and position of substituents on the molecule, membrane properties (active surface area, thickness), and temperature on the sorption of pollutants and industrially important compounds such as various phenols, benzoic acids, organic dyes, organometallic ion-association complexes, and organic solvents. It was found that the formation of a neutral species in solution and the ability to engage in hydrogen-bonding with the membrane is essential for extraction into polyurethane to occur. The size of the organic species is not as important as its overall polarity and the relative solubility in the solvent and in the membrane. Increased removal of species from solution can be attained by providing either a larger surface area exposed to the sample solution, a thicker membrane, or a receiving solution into which the compound can be desorbed from the membrane. Higher temperature can be used to accelerate the entire sorption process. The mechanism by which organic compounds are removed from solution by the polyurethane membrane can be subdivided into three separate phenomena, namely, the transfer of species from bulk solution to the solution-membrane interface and the reverse, adsorption onto the membrane surface, and transport into the bulk of the polymer.

Chapter 1: Introduction

1.1. Membrane separation technology

The abatement of environmental pollution is one of the biggest challenges of technology[1,2,3]. Many processing industries use large volumes of water in their operations, and therefore generate substantial quantities of wastewater. The textile, food and paper industries, for example, use extensive amounts of colorants in or on materials such as clothing, food, plastics, and paper products[4,5]. Industrial waste effluents contain a wide range of compounds such as organic solvents, dispersing agents, dyes, dyebath carriers, salts, emulsifiers, levelling agents, inorganic species and metals complexed with the dyes[6-27]. The presence of these chemicals in wastewater often has a pronounced effect on many water quality parameters such as pH, dissolved oxygen (DO), total organic carbon (TOC), total dissolved solids (TDS), and colour[28]. Over time, the contaminants can accumulate in aquatic animals and plants and reach dangerously high concentrations. Therefore, wastewater must be purified of these potentially toxic organic and inorganic species before it can be reintroduced back into the environment.

To produce acceptable final waste effluents, a variety of separation processes are used by the industries. In general, a separation process results in the division of a mixture into at least two fractions containing components that originally were in the mixture. Most commonly, the goal of separation is to increase the mole fraction of one component (or

more) of the original mixture in relation to the other components. The actual separation is usually achieved by physical means, although chemical reactions may be involved in the process. Separation can be attained by changing various thermodynamic conditions such as temperature and / or pressure or by using an extracting medium with which the individual components in a mixture can selectively interact. An ideal separation meets the following criteria:

a) high adaptability, i.e., it can be used for separating samples having a wide range of physical and chemical properties. For example, distillation cannot be considered an ideal technique because it is restricted in its adaptability as it can only separate stable volatile organic compounds.

b) variable load capacity, i.e., the separation should allow operation on the large production scale and on the smaller laboratory scale, i.e., it should effectively separate components regardless of their sample size.

c) selectivity and variable fraction capacity, i.e., the separation method should discriminate on the basis of the chemical structure of the components and be capable of separating multi-component samples into individual components.

d) high speed, convenience, and low cost, i.e., the technique should be rapid, allow automation, be easy to use, and of course be inexpensive.

Some examples of the separation technologies currently employed to purify aqueous waste effluents are shown in Table 1-1.

Table 1-1. Separations used in industry

Separation Technologies
distillation
mechanical separation
biological separation
chemical separation
ion exchange
adsorption
membrane separation

Distillation is effective at separating volatile compounds from non-volatile compounds, and sometimes at destroying bio-organisms. This technique is, however, expensive to operate and to maintain and may not completely separate mixtures of volatile compounds. Mechanical separation uses forces such as pressure, gravity, and heat to achieve the separation of components. Sedimentation and precipitation are two examples of mechanical separation. These types of methods are low cost and can be applied on a very large scale; however, at the same time, they can be time-consuming and ineffective at eliminating microbiological pollutants. Biological separation uses microbes and the enzymes they produce to digest,

transform, or degrade contaminants. This technique is convenient to use in hard to reach places such as rivers, but it is time-consuming and requires very specific conditions for the micro-organisms to be optimally functional. Furthermore, additional pollution can be created from an overdose of microbes and the entire operation can also be expensive. Chemical processing uses chemical substances to react with hazardous chemicals in the waste effluent by altering or transforming the compounds into non-harmful species. This technique is relatively inexpensive, but it can sometimes be ineffective because it often results in the production of additional waste in the form of reaction by-products. An ion exchange system is designed to absorb either cations or anions and to exchange certain ions. This process is low-cost but it is limited to removing only ionic chemical species and not micro-organisms. Adsorption most often uses activated carbon as a sorbent for chemicals. This method is universal and low-cost but non-selective. It also fails to remove micro-organisms and easily degrades in performance. The most recent separation technology involves the use of a variety of membranes to achieve the isolation of the desired organic and inorganic components.

All of the techniques described above fulfill the ideal criteria to some extent, however separation which fully meets all of those requirements has yet to be developed. Fortunately, the choice of different separation technologies is not mutually exclusive. In fact, the application of a combination of technologies usually yields a better final result at less expense. Therefore, a typical conventional separation process is often a multi-step process involving mechanical, biological and chemical treatments followed by carbon adsorption[2,29,30]. However, because of the many steps involved, the entire process is time-consuming, costly and may still not be fully effective.

Membrane technology is an attractive alternative to the conventional purification. Membrane separation is a single-step process that is capable of providing the same if not better final result than conventional purification[31-35]. Generally, membranes are thought of as films which can serve as physical barriers preventing passage of certain materials. This broad definition, however, says nothing about the membrane structure or function. In order to obtain a more informative understanding of the membranes, various classifications are used[34,35,36]. The first and perhaps the clearest distinction possible is by nature, namely biological vs. synthetic membranes. These two membrane types differ completely in structure and functionality.

Biological membranes surround the living cells and have very complex structures because they must accomplish specific functions in the cells. The main characteristic of biological membranes is that they contain a lipid bi-layer structure. Each lipid molecule possesses a hydrophobic and a hydrophilic part. The polar portion is situated at the water-membrane interface with the non-polar part being located in-between. Specific transport is accomplished by proteins incorporated within the bi-layer membrane.

The synthetic membranes can be subdivided into organic, inorganic, and liquid membranes[37-40]. The focus of this thesis is on the organic polymeric membranes. Two types of such membranes can be distinguished - symmetric and asymmetric, both of which can be either porous or non-porous. A symmetric membrane is made up of only one polymer and is uniform throughout. The thickness of the symmetric membranes ranges from 10 μm to 200 μm. Asymmetric membranes have a very dense top layer of 0.1 μm to 0.5 μm thick which is supported by a sub-layer 50 μm to 150 μm thick. If the top and the bottom layers differ

in their polymeric makeup, the membranes are known as composite membranes. The structural asymmetry of these membranes allows better selectivity in separation to be attained than that achieved with the symmetric membranes.

A membrane process uses a membrane to accomplish a particular separation. A commercially usable membrane must be semipermeable (i.e., allows one or more components to pass through), chemically and physically robust, non-biodegradable and inexpensive to manufacture. Examples of membrane materials used in current industrial operations are shown in Table 1-2[37-41].

Table 1-2. Membranes used in industry

Membrane Materials
Porous
cellulosic
polysulfone
polyamide
* "specific"
Non-Porous
poly(vinyl alcohol)
polybutadiene

* "specific" membranes have various metals or other species incorporated in their structure which increase the selectivity of the membrane

Separation and transport across a membrane occur when a driving force acts on the individual components in the system[33-36]. Both porous and non-porous membrane

separations in industrial processes today result most often from the pressure difference. Examples of pressure driven porous membrane separations are the reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF)[37,39,42-52]. The non-porous membranes are used in pervaporation applications[37,39,40].

When a membrane is placed between pure water and a salt solution, water flows into the cell filled with the salt solution, whereas the salt does not flow. The water level of the salt solution will increase until the flow of pure water stops at a steady state. The difference between the two levels can be converted to osmotic pressure. When a pressure higher than the osmotic pressure is applied to the salt solution, the flow of pure water is reversed and water will flow from the saline solution side into the pure water compartment. Again, no flow of salt through the membrane is observed. As a result, salt can be concentrated on one side and pure water collected on the other side. The same principle can be used with solutions other than salt solutions. Therefore, in processes such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration, substances can be concentrated and pure permeate, devoid of suspended solids, can be obtained. In all porous membrane processes, the separation of species is based on their molecular size and shape. The only difference exists in the pore size of the membranes used, and consequently the pressure applied. For example, a reverse osmosis membrane involves the smallest and most uniform pore construction and consequently the highest operational pressure (200-1200 psi) of the four processes is required. The membranes in the reverse osmosis processes concentrate low molecular weight organic and inorganic compounds (0.0001 to 0.0060 μm) and allow only the solvents to pass. Reverse osmosis is primarily used for water purification, including the

removal of specific ions and electrolytes. Nanofiltration operates at a pressure of 150 to 300 psi. The operational principles of this process are similar to reverse osmosis but this membrane allows the passage of monovalent ions and low molecular weight organic compounds. For example, nanofiltration can separate particles as small as 0.1 nm and as large as 10 nm. Ultrafiltration is essentially a low-pressure filtration (30-150 psi). The ultrafiltration membrane filters particles ranging from 1 nm to about 80 nm and allows the dissolved salts and low molecular weight compounds to pass through but it rejects macromolecules and proteins. Finally, microfiltration is used to filter out bacteria and yeast ranging from 100 nm to 10,000 nm in size, and to clarify the unprocessed feed solution. Microfiltration uses a very low pressure of 20-100 psi.

The non-porous membranes find applications in the pervaporation process[37,39,40]. Pervaporation is used to separate miscible aqueous and volatile organic mixtures and mixed organic solutions. For example, separation of alcohol from water can be obtained with pervaporation membranes. The membrane can either permeate organic solvents or permeate water depending on the polymer used. Separation is achieved by applying a lower pressure (vacuum) to the permeate side while maintaining the feed side at atmospheric pressure. A gradient is created due to the partial pressure of the permeate side being lower than the saturation pressure of the feed side. Solubility, diffusivity and desorption are important in this separation process.

Like any other technology, membrane separation processes have some flaws. Porous membrane separations (i.e., reverse osmosis, nanofiltration, ultrafiltration, and microfiltration) are affected by the so-called membrane fouling and concentration

polarization[53-57]. The occurrence of fouling affects the performance of the membrane by deposition of a layer of particulates onto the membrane surface or by blockage of the pores. This changes the effective pore size, and therefore the rejection characteristics of the membrane. Concentration polarization is another phenomenon that reduces the performance of the membrane. In fact, fouling can result from concentration polarization. When a driving force acts on the feed solution, the solute is partially retained by the membrane whereas the solvent permeates through. The retained solutes can accumulate at the membrane surface where their concentration will gradually increase. The consequence of this may be an increase in the retention of solutes and a reduction of the volume of permeate produced. Unlike the porous membrane process, the non-porous membrane separation (i.e., pervaporation) is a diffusion process and therefore the separation is only affected by the relative permeation rate of the components at the surface *vs.* the bulk of the membrane and by the relative volatility of the components in the mixture.

Several approaches are used to minimize the effects of fouling and concentration polarization and to prolong the optimal performance of the membrane. These may be direct methods examples of which are improvements of the hydrodynamics on the feed-side and the module design, or indirect methods which are concerned with the membrane surface design. In the early stages of membrane separations, a normal or tangential filtration mode has been used (Fig. 1-1)[58].

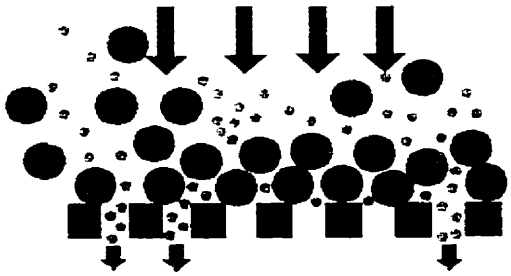


Fig. 1-1. Normal filtration mode

In this filtration mode, the influent flows directly against or perpendicular to the membrane surface. Water permeates through the membrane and the impurities are detained on the other side of the membrane. This mode is not used frequently because severe fouling and concentration polarization occur; the main advantage however is the high recovery of the permeate. In order to minimize the fouling and concentration polarization, the flow direction of the feed stream was changed to be parallel to the membrane wall (Fig. 1-2)[59].

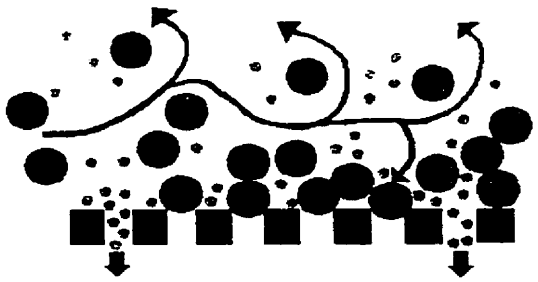


Fig. 1-2. Cross-flow filtration mode

In this mode, water still permeates through the membrane wall, but the contaminants are being continuously carried away from the membrane surface which minimizes the build-up of foulants. One disadvantage of this design is a lower recovery of the permeate than that obtained in the tangential mode. The cross-flow filtration is preferentially used in today's membrane separations. Another popular alternative is to use the tangential and the cross-flow filtrations in combination in order to achieve both high recovery and minimal fouling.

One of the latest solutions to the fouling and concentration polarization problems is the introduction of turbulence in the feed stream. There are many ways in which a pulsating flow can be created. For example, rotating disks can be positioned close to the membrane surface or abrasive particles can be introduced into the feed. Recently, an alternative method for producing turbulence has been developed which is more effective than the latter approaches. The technique is called Vibratory Shear Enhanced Processing (VSEP) (Fig. 1-3)[60].

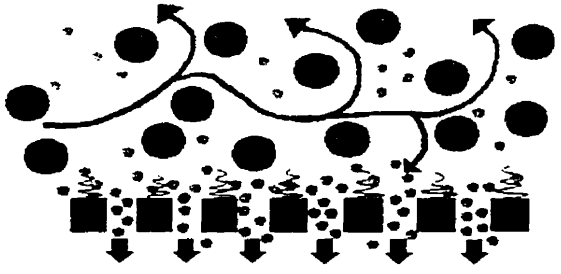


Fig. 1-3. Vibratory shear enhanced processing

Unlike in the previous filtration modes, the feed stream remains nearly stationary in the VSEP system. The membrane stack, on the other hand, moves in a vibratory motion which is tangential to the face of the membrane. The shear waves produced by the vibrations of the membrane cause solids and foulants to be repelled and the liquid to flow unhindered to the membrane pores. Because the VSEP filtration does not depend on the shearing forces of the feed flow, extremely viscous influents can be dewatered. This process also consumes less energy than the tangential and cross-flow filtrations. The limitation of VSEP lies in the disposal of the viscous concentrate.

Membrane processes require large areas of membranes to be exposed to the influent. In order to use membranes on a technical scale, the membranes are packed into units called modules[61,62,63]. The modules not only physically protect the membrane but also allow efficient separation of the permeate and the concentrate streams with minimal fouling and concentration polarization. The membrane's geometrical arrangement in a module must allow the passage of fluids past the membrane at a sufficient velocity to prevent excessive particulate deposits on the membrane surface so that fouling and concentration polarization are minimized. A number of module designs is possible and is based on two types of membrane configurations - flat and tubular membranes (Table 1-3). Examples of modules housing flat membranes are the plate-and-frame, spiral-wrap and VSEP modules. The common feature that these modules have is that they are built from several layers of membranes separated by feed and permeate spacers.

Table 1-3. Membrane modules

Membrane Configurations
plate-and-frame
spiral-wrap
hollow fibre
capillary
tubular
VSEP

The plate-and-frame modules are one of the earliest configurations on the market (Fig. 1-4)[64]. In these modules, sets of flat membranes are placed in a sandwich-like fashion with the permeate collection compartments on the inside. In each permeate and feed compartments a suitable spacer is placed to reduce concentration polarization and fouling and the membranes are built up to form a plate-and-frame stack. When feed solution is introduced, the permeate and the concentrate are collected in inside and outside compartments respectively.

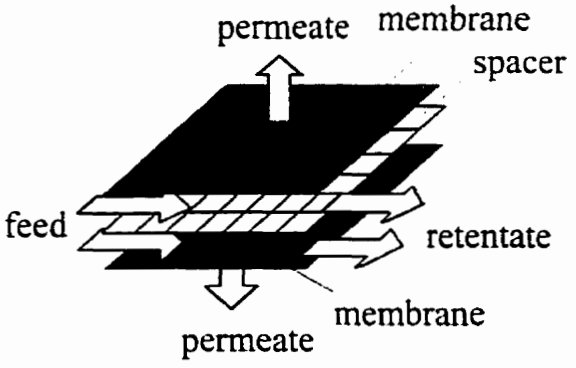


Fig. 1-4. The plate-and-frame module

The spiral-wrap format again utilizes flat sheet membranes (Fig. 1-5)[65]. It is in fact a plate-and-frame system wrapped around a porous central collection tube in a similar fashion to a sandwich roll. Waste water enters the spiral-wrap membrane from the surroundings and clean water permeates through the membrane to reach the permeate tube in the centre.

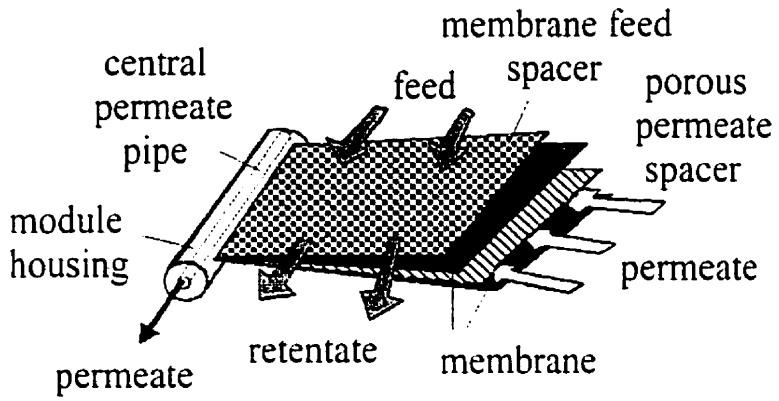


Fig. 1-5. The spiral-wrap module

In the VSEP module, membranes are arranged as parallel disks (Fig. 1-6)[66]. The membrane disk stack is spun in a torsional oscillation that produces shear forces at the membrane surface. One disadvantage of this design is that very large particulates can damage the membrane surface by abrasion and should be removed prior to using this module.

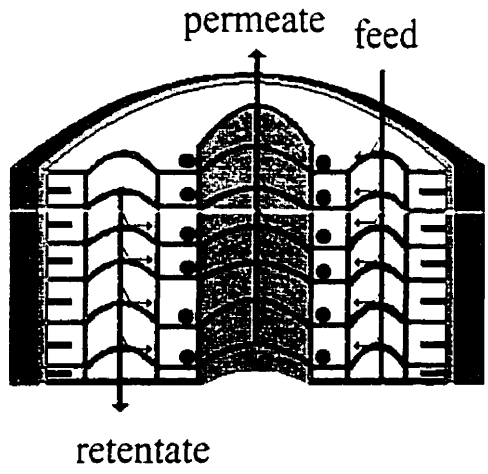


Fig. 1-6. The VSEP module

Another membrane configuration frequently used is the tubular configuration where the membrane is manufactured as a tube. Various tubular membrane configurations such as the hollow fibre, capillary and tubular arrangements differ mainly in the dimensions of the tubes used. The hollow fibre module has the smallest diameter tubes (< 0.5 mm), the capillary module is between 0.5 to 10 mm, and the tubular module is about 10 mm in diameter. The operational concepts for these three module types are the same and are illustrated in Fig. 1-7[67] with the hollow fibre module as an example.

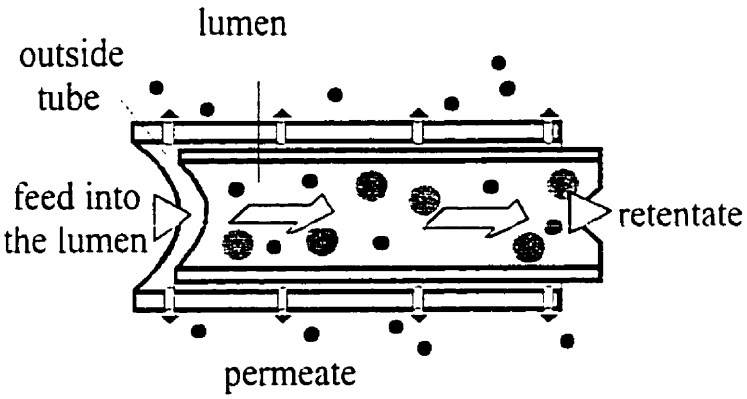


Fig. 1-7. The hollow fibre module

All tubular membranes have a dense selective layer on the inside of the tube and a support layer on the outside. In Fig. 1-7, the feed is shown to be pumped through the lumen of the membrane in which low molecular weight solutes are concentrated, and the permeate is collected outside the lumen. Alternatively, the feed solution can also enter the hollow fibre from the outside-in. In this case, pure permeate will be collected in the lumen. The first system mode is preferred because it offers more of the active membrane surface. The hollow fibre modules are used for reverse osmosis applications. The tubular and capillary modules are used for ultrafiltration and microfiltration applications.

A fundamental, but at the same time most challenging attempt at reducing fouling and concentration polarization, involves modification of the membrane surface properties to take into account the interactions of the membrane with the compounds that need to be separated[51]. For example, depending on the separation needs, the membrane may be made

hydrophobic or hydrophilic by coating or by depositing charged species on its surface. As a result, a better selectivity can be attained because the membrane system is tailored to the specific needs of the required separation.

Industrial processes which are presently fully operational are the porous membrane separations. Pervaporation which uses the non-porous membranes is being only used in some pilot plants[37,39,40,68-72]. For the porous membrane separations, the main research and development centre around the development of better membranes with long life, high stability and resistance to fouling. Another active area is oriented around the development of new applications, process control and optimization. The introduction of more strict pollution regulations will definitely accelerate the new developments in the membrane separations field.

1.2. Polyurethane membranes

In polymer chemistry, polymers are defined as high molecular weight materials which are made up of building blocks of repeat units or monomers. One of the most often used classifications segregates polymers on the basis of their chemical makeup and structure which are characterized by the elemental composition and types of monomer moiety within the polymer. For example, polymers composed of single repeat units are referred to as homopolymers. Heteropolymers or copolymers, on the other hand, contain more than one type of repeat unit within the polymer chains. Different types of heteropolymers exist which

are further classified based on the relative arrangement of each of the building blocks.

Polyurethane membranes are copolymers characterized by having the urethane group (-NHCO-O-) in their structure. The urethane group is formed by the reaction between isocyanate and hydroxyl groups. Due to the different polarity and chemical nature of the different parts of the polymer chain, the polymer separates into two phases designated as "soft" or amorphous and "hard" or microcrystalline segments (Fig. 1-8). The hard segments are made up of the more ordered regions of aromatic diisocyanates and are linked with the soft amorphous segments which are typically aliphatic polyether or polyester polyols[73].

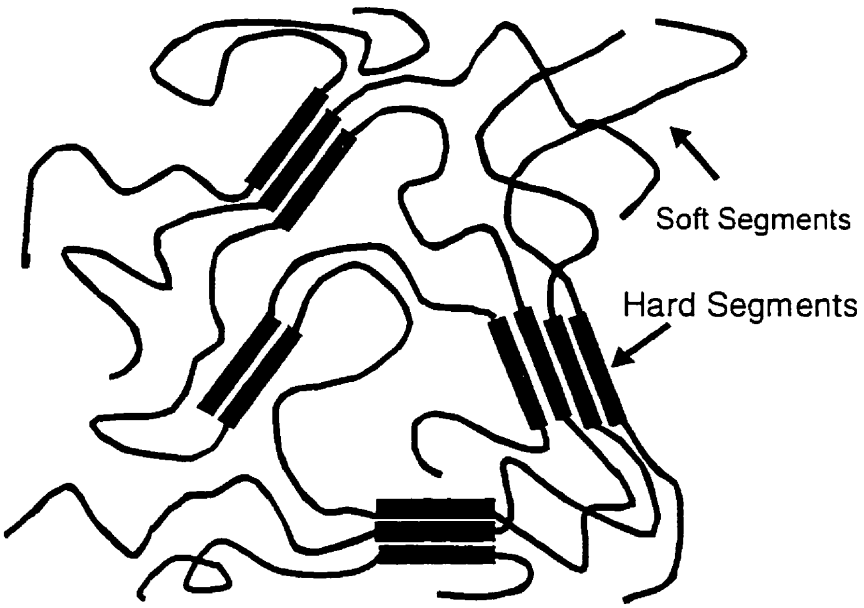


Fig. 1-8. Polyurethane structure

Both aliphatic and aromatic isocyanates can be used to synthesize the polyurethane hard

segments. The two most commonly used aromatic isocyanates in polyurethane synthesis are toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). These isocyanates are inexpensive and yield polyurethanes which have a more rigid and physically robust matrices than the polymers made from aliphatic isocyanates. Aliphatic polyols which are available for polyurethane synthesis include polyesters, polyethers, polycarbonates, hydrocarbons and polydimethyl siloxanes. However, the most commonly used polyols for the production of polyurethanes are the polyether or polyester-based compounds (Fig. 1-9)[74].

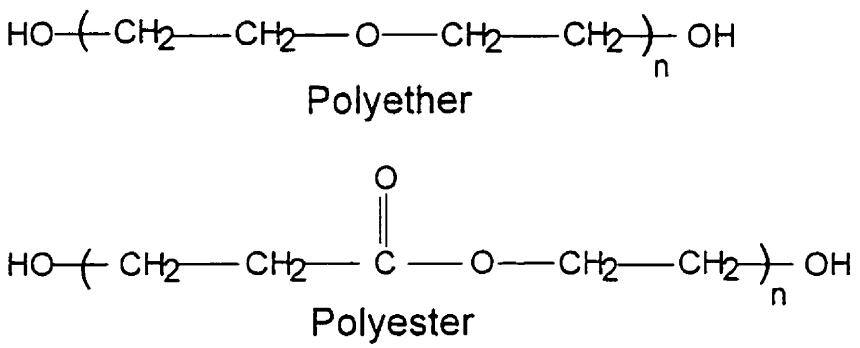


Fig. 1-9. Polyether and polyester polyol segments

Polyurethanes synthesised from the polyester polyols possess slightly better physical properties than the polyether polyol-based polymers but are susceptible to hydrolytic cleavage of the ester linkage. Because the polyether polyurethanes exhibit a high resistance to hydrolytic cleavage, they are favoured for the use in most industrial applications. In addition to being bound to polyols, the hard segments comprising diisocyanates can also be

linked with low molecular weight polymers called chain extenders which extend the length of the hard segments and increase the hydrogen-bond density and the molecular weight of the polyurethane. Chain extenders can be either aromatic diols and diamines, or the corresponding aliphatic diols and diamines. The polyurethane matrix can also contain other additives such as catalysts and plasticisers. The catalysts (e.g., dialkyl tin compounds) are used to increase the rate of the polymerisation reaction. Plasticisers, as the name suggests, add plasticity to the polymer by lowering the extent of intramolecular hydrogen-bonding interactions between the polymer chains. Such compounds are frequently various phthalate esters.

Due to the immiscibility of the hard and the soft segments and extensive hydrogen-bonding interactions, polyurethane membranes have a heterogenous structure. Hydrogen-bonding involves the N-H group in urethane as the donor and the urethane carbonyl, the ester carbonyl (in polyester polyurethanes), or the ether oxygen (in polyether polyurethanes) as the acceptor. Various hydrogen-bonding interactions that can be found in polyurethane membranes are schematically portrayed in Fig. 1-10[75].

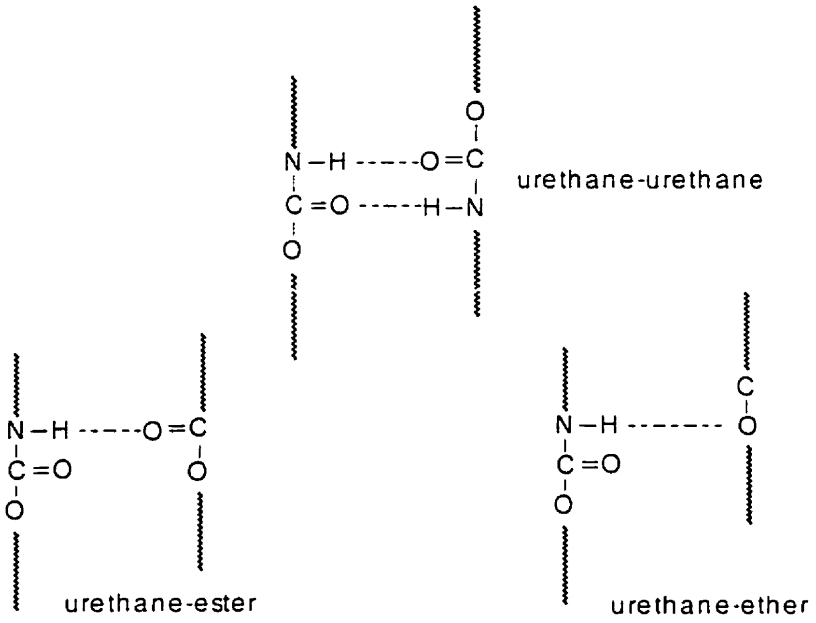


Fig. 1-10. Hydrogen-bonding in polyurethane membranes

The relative number of hydrogen bonds among the hard and the soft segments is determined by the degree of phase separation. For example, high phase segregation favours inter-urethane hydrogen-bonding (urethane-urethane). This two-phase polyurethane membrane matrix is responsible for the superior physical and mechanical properties of this polymer, namely flexibility with high strength, wear resistance, and a high degree of hardness. The numerous options available in selecting the chemistries and molecular weights of the various components, and the ratios in which they are reacted, allow the synthesis of polyurethanes having a broad range of physical properties. Overall, the domain structure of polyurethanes and their scope for structural diversity creates a wide variety of uses and applications for these materials.

1.3. General information on phenols, benzoic acids, organic dyes, and aqueous gold (III) halide complexes

Simple phenolic compounds were the first organic compounds used as models for studying the mechanism of extraction of organic compounds by the polyurethane membrane. Phenols have a general formula ArOH, where Ar is phenyl or substituted phenyl, and like alcohols contain the hydroxyl group (-OH). Phenols differ from alcohols in having the hydroxyl group attached directly to an aromatic ring. The nomenclature of phenols is based on derivatives of the simplest member of the family, the phenol, with the exception of methylphenols which are often given the special name of cresols. The simplest phenols are liquids or low-melting solids and because of extensive intermolecular hydrogen-bonding they have quite high boiling points. The aqueous solubility of phenols varies. For example, phenol itself is quite soluble in water because of hydrogen-bonding interactions with the water molecules, however, most other phenols are only sparingly soluble in water. The most important property of phenols is their acidity (Table 1-4)[76].

Table 1-4. Acidity values for some phenols

Phenol	Melting Point (°C)	Boiling Point (°C)	pK_a	
*acetic acid**			*4.75*	
2,4,6-trinitrophenol	122	-----	0.60	**Stronger Acid**
p-nitrophenol	115	-----	7.16	
o-nitrophenol	97	-----	7.21	
m-nitrophenol	45	216	8.36	
p-iodophenol	94	-----	9.30	
p-bromophenol	66	238	9.35	
p-chlorophenol	43	220	9.38	
phenol	43	182	10.00	
p-methoxyphenol	57	243	10.21	
p-methylphenol	35	202	10.26	
p-aminophenol	186	-----	10.46	**Weaker Acid**
*ethanol**			*16.00*	

* Values for acetic acid and ethanol are given for reference[76]

Because most phenols have acid constants (K_a) in the neighbourhood of 10^{-10}, they are considered to be weak acids. Consequently, in aqueous solution phenols dissociate to a small extent to give $H_3O^+$and a phenoxide ion, ArO^-. Aqueous hydroxides convert phenols into their salts and the aqueous mineral acids convert the salts back into free phenols (Table 1-5).

Table 1-5. Aqueous reactions of phenols

ArOH phenol	+	H_2O	⇌	ArO^- phenoxide	+	H_3O^+
ArOH phenol	+	NaOH base	→	ArO^-Na^+ salt		
ArO^- phenoxide	+	HCl acid	→	ArOH phenol		

The salts are soluble in water and insoluble in organic solvents. Substituted phenols can be either more or less acidic than phenol itself, depending on the nature of the substituents. For example, the presence of electron-withdrawing substituents on the phenol such as the halogens increases the acidity of the phenol. Conversely, electron-releasing substituents such as the alkyl groups decrease the phenol's acidity. Phenols occur widely throughout nature and serve as intermediates in the industrial synthesis of products as diverse as resins, adhesives and antiseptics. For example, phenols are used as raw materials for the manufacture of the explosives such as picric acid (2,4,6-trinitrophenol) and as starting materials for the synthesis of chlorinated phenols, food preservatives, herbicides and antiseptics. Because of the widespread use and toxicity of phenols there is a need for their recovery from waste solutions for recycling and for disposal of the industrial effluents.

The benzoic acids are another group of simple but versatile organic compounds for studying the extraction mechanism. Benzoic acids occupy a central place among carbonyl

compounds which can be found practically everywhere in nature. For example, the majority of biologically important molecules contain carbonyl groups as do most pharmaceutical agents and many synthetic chemicals. There are different kinds of compounds depending on what groups are bonded to the carbonyl, but the chemistry of the carbonyl groups (C=O) is similar regardless of their exact structure. The carbonyl compounds are planar about the double bond and the carbon-oxygen double bond is polarized because of the high electronegativity of oxygen relative to carbon, therefore all carbonyl compounds have quite high dipole moments and are polar. Benzoic acids contain the carboxyl group attached to an aryl group (ArCOOH) and are named as derivatives of the parent acid, benzoic acid, C_6H_5COOH. The benzoic acid molecules can form hydrogen bonds with each other and with other molecules and consequently have high boiling points and may form dimers. Aqueous hydroxides easily convert benzoic acids into their salts, and although benzoic acids with more than the six ring carbons are sparingly soluble in water, the salts of benzoic acids are quite water soluble because of their ionic structure. These salts are, however, insoluble in organic solvents. Aqueous mineral acids are used to convert the benzoic acid salts back into the benzoic acids. In aqueous solution, benzoic acid exists in equilibrium with the carboxylate anion (benzoate) and the hydrogen ion (Table 1-6).

Table 1-6. Aqueous reactions of benzoic acids

ArCOOH benzoic acid	+	NaOH base	→	$ArCOO^-Na^+$ salt		
$ArCOO^-Na^+$ salt	+	HCl acid	→	ArCOOH benzoic acid		
ArCOOH benzoic acid	+	H_2O	⇌	$ArCOO^-$ benzoate	+	H_3O^+

As shown in Table 1-7[77], the acidity of benzoic acids is related to the substituent groups on the benzoic acid molecules. For example, electron-withdrawing groups increase acidity by stabilizing the carboxylate anion and electron-donating groups decrease acidity by destabilizing the carboxylate anion.

Organic dyes can be either simple or complex in structure and morphology and have a wide range of chemical properties because of their structural diversity. These compounds are therefore very useful for a mechanistic study such as the one described in this thesis. The world-wide classification of organic dyes divides these compounds into groups shown in Table 1-8[78]. This classification is based primarily on the methods of applications of the dyes to various fibres in the textile industry and to a lesser extent on the molecular structure of the dyes.

Table 1-7. Effect of substituents on the acidity of *para* benzoic acids

Substituent on Benzoic Acid	K_a	pK_a	
			Weaker Acid
OH	2.8×10^{-5}	4.55	
OCH_3	3.5×10^{-5}	4.46	
CH_3	4.3×10^{-5}	4.34	
H	6.5×10^{-5}	4.19	
Br	1.1×10^{-4}	3.96	
Cl	1.1×10^{-4}	3.96	
CHO	1.8×10^{-4}	3.75	
CN	2.8×10^{-4}	3.55	
NO_2	3.9×10^{-4}	3.41	
			Stronger Acid

In this thesis, the sorption of various disperse, acidic and basic dyes is studied. Disperse dyes are small and compact with relatively low molecular weights. They are quite soluble in organic solvents but sparingly soluble in water. In aqueous solution, the solubilised disperse dye molecules exist as uncharged species which is why these dyes were selected for the mechanistic study of the sorption by polyurethane membrane. Under acidic conditions, protonation of the substituent groups on the disperse dye molecule may occur which results in formation of a charged species that is more soluble in aqueous solution. In the textile industry, disperse dyes are used for dyeing hydrophobic fibres.

Table 1-8. Classification of organic dyes

Dye Class	Fibre							
	Protein (wool)	Cotton Viscose	Cellulose Acetate	Cellulose Triacetate	Nylon	Polyester	Acrylic	Spandex
Acid	XX	NU	NU	NU	XX	NU	NU	XX
Direct	X	XX	NU	NU	X	NU	NU	X
Basic	NU	NU	NU	NU	NU	NU	XX	NU
Disperse	NU	NU	XX	XX	XX	XX	XX	XX
Sulphur	NU	XX	NU	NU	NU	NU	NU	NU
Vat	X	XX	NU	NU	NU	X	NU	X
Azoic	NU	XX	X	X	X	X	X	NU
Oxidative	NU	X	NU	NU	NU	NU	NU	NU
Mordant	XX	NU	NU	NU	X	NU	NU	XX
Reactive	XX	XX	NU	NU	X	NU	NU	XX

X while not of major importance for dyeing or printing, this class is of some interest for other uses e.g., tissue staining

XX this class of dye is of major importance for dyeing and printing

NU of no practical importance for dyeing or printing, but this does not mean that this class of dye does not stain the particular fibre under certain circumstances

Disperse dyes have quite diverse chemistries. but the two most often used classes of these dyes are based on the monoazoic and anthraquinone compounds (Fig.1-11)[78].

A) B)

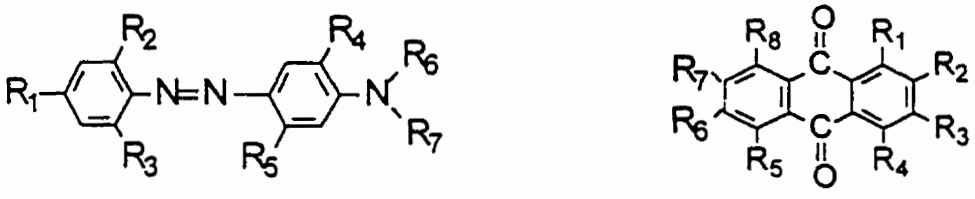
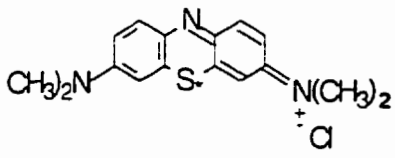
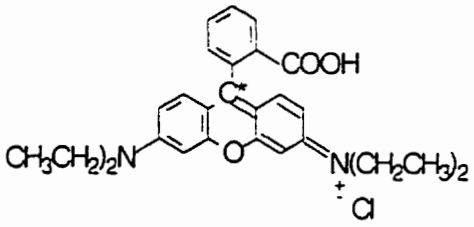


Fig. 1-11. A) Structural skeleton of the majority of monoazo disperse dyes: B) Structural skeleton of the majority of anthraquinone disperse dyes. R_1-R_8 are the various substituent groups

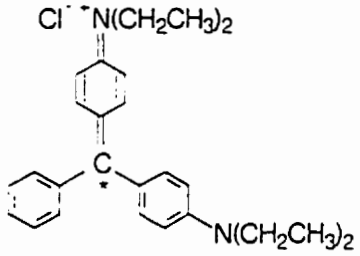
Acid dyes are water-soluble anionic dyes. They are often referred to as anionic because the chromophore part of the dye is negatively charged in aqueous solution. Basic dyes are defined by the Society of Dyers and Colourists as cationic dyes. A cationic dye dissociates in aqueous solution to give a coloured cation. The basic dyes used for this work are based on the thiazine. xanthene and triphenylmethane chromophores (Fig. 1-12)[78] which can specifically associate with gold (III) chloride to form an organometallic ion-pair.



Thiazines



Xanthenes



Triphenylmethanes

Fig. 1-12. Basic dyes which complex gold (III) chloride

* charge can be associated with these atoms as well

The complexes of gold (III) with halides are the most important of all gold complexes and they occur with chloride, bromide, and iodide. All halide complexes of gold (III) have the formula $(AuX_4)^-$ and possess square planar geometry (Fig. 1-13)[79]. In weakly acidic aqueous solution, the complex ions of gold halide may be hydrolysed to some extent. It has been shown that above 4×10^{-4} M HCl, the overwhelmingly predominant species is $(AuX_4)^-$ but below that concentration other gold complexes can also be present.

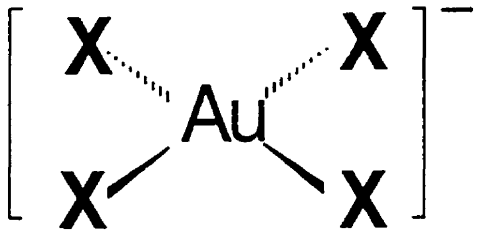


Fig. 1-13. Square planar structure of the halide complexes of gold

Previous research done in our laboratory on the sorption of inorganic species by the polyurethane membrane shows that gold (III) chloride complexes are extractable only from solutions having very high acidities in which the gold species exists as the neutral $HAuCl_4$. Unfortunately, the high solution acidity causes degradation of the membrane[79]. Because gold (III) chloride can form ion-pair association complexes with various organic dyes, it can perhaps be removed from solution by this polymer without having to be converted to $HAuCl_4$ which would eliminate the need for using highly acidic solution conditions and extend the operational life-time of the membrane. Information on the extraction of large ion-pair complexes can supplement what is already known about the mechanism of sorption of the organic and inorganic species by the polyurethane membranes. Furthermore, this technique can also have potential applications for the recovery of gold from aqueous solutions.

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Chapter 2: Experimental

2.1. Instrumental analysis

Weighing was done on either a Mettler PC440 Delta range balance or on a Mettler AE163 balance when more precise measurements were required. Solution pH measurements were made using an Orion Expandable Ion Analyzer EA 940. A modified Burrell Wrist-Action shaker was used for sample agitation at room temperature. A Fisher Versa-Bath® shaking water bath was used for experiments at higher temperatures.

Gas chromatographic data were obtained using a Hewlett-Packard 5710A gas chromatograph equipped with a 1 / 4 inch glass column packed with 60 / 80 Chromosorb W coated with 5% bentone 34 and 5% diisodecyl phthalate. The GC injection port and detector temperatures were 150 °C, the column temperature was held at 70 °C (separation of xylenes is based on their relative affinity for the packing material), and the carrier gas (hydrogen / helium) flow rate was approximately 5 mL / min.

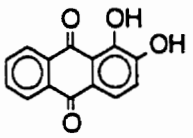
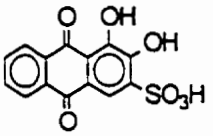
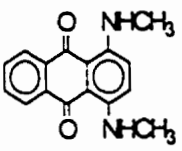
UV-vis spectra (190-820 nm) and absorbance readings of phenols, benzoic acids and organic dyes were taken using a Hewlett-Packard Model 8452A diode-array spectrophotometer. The wavelengths at which the readings were taken are shown in Table 2-1 and Table 2-2.

Table 2-1. UV-vis absorption wavelengths (λ_{max}) and molar absorptivities (ε) of phenols and benzoic acids used

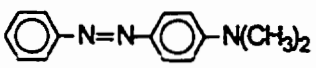
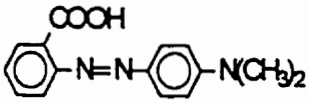
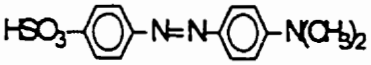
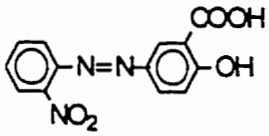
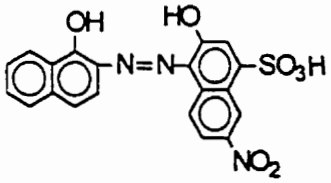
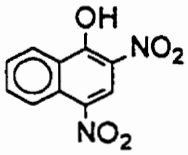
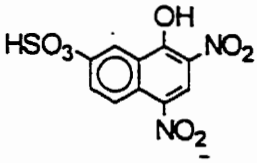
Compound Name	λ_{max} (nm)	ε (l mol^{-1} cm^{-1})
phenol	270	5630
ortho chlorophenol	274	40400
ortho bromophenol	274	28730
meta chlorophenol	274	31870
meta bromophenol	274	26130
para chlorophenol	280	3270
para bromophenol	280	1660
benzoic acid	274	4810
ortho bromobenzoic acid	280	1200
meta bromobenzoic acid	284	2950
para bromobenzoic acid	246	10660

Table 2-2. Structures, Colour Index numbers and UV-vis absorption wavelengths (λ_{max}) of organic dyes used in the transport study

A) Anthraquinone organic dyes

Name	Structure	C.I. Number	λ_{max} (nm)
Alizarin		58000	560
Alizarin Red S		58005	550
Disperse Blue 14		61500	640

B) Acidic organic dyes

Name	Structure	C.I. Number	λ_{max} (nm)
Solvent Yellow 2		11020	410
Methyl Red		13020	410
Methyl Orange		13025	510
Alizarin Yellow GG		14025	360
Eriochrome Black T		14645	680
Martius Yellow		10315	440
Naphthol Yellow S		10316	440

C) Basic organic dyes

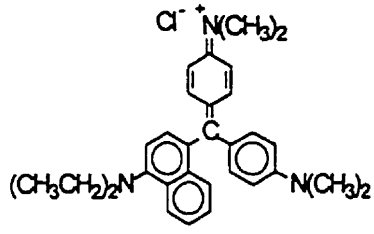
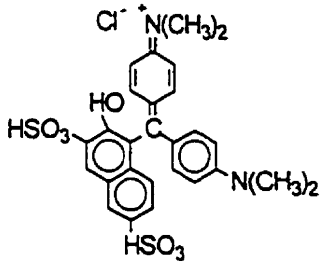
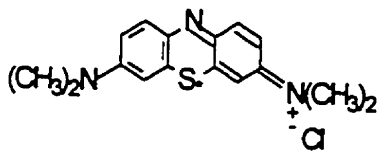
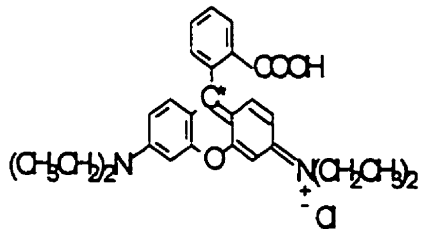
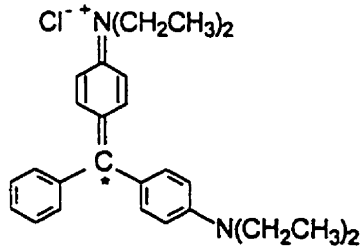
Name	Structure	C.I. Number	λ_{max} (nm)
Victoria Blue R		44040	580
Wool Green S		44090	610

Table 2-3. Structures, Colour Index numbers and UV-vis absorption wavelengths (λ_{max}) of organic dyes used in the transport study of organometallic ion-pairs

Compound Name	Structure	C.I. Number	λ_{max} (nm)
Methylene Blue		52015	636
Rhodamine B		45170	530
Brilliant Green		42040	625

Gold analyses were performed with a Varian SpectrAA-20 atomic absorption spectrometer equipped with an Instrumentation Laboratory VisimaxTM hollow cathode lamp and a Varian Mark VI burner head coupled with an air-acetylene flame. The maximum wavelength used was 242.8 nm with a slit width of 1.0 nm and a gold lamp current of 4 mA.

Thermal analyses of the polyurethane membranes were performed using a Perkin Elmer differential scanning calorimeter DSC 7 equipped with a Perkin Elmer thermal analysis controller TAC 7 / DX located at the Institut des Biomatériaux du Québec City. The data were collected and processed using Perkin Elmer Pyris software. The samples were heated from - 130.0 °C to 200.0 °C at 20.0 °C / min, cooled from 200.0 °C to -130.0 °C at 200.0 °C / min, and reheated using the previous heating profile. Helium was the purge gas at 20.0 ml / min., and liquid nitrogen was used for cooling the system.

Electron spectroscopy for chemical analysis (ESCA) surface analysis of the membrane was performed on a Perkin-Elmer PHI model 5600 (Physical Electronic Division), also located at the Institut des Biomatériaux du Québec using a monochromatic Al K_{α} X-ray source and a hemispherical analyzer with a pass energy of 187 eV. The X-ray gun was operated at 1486.6 eV and 18 mA with the sample chamber pressure below 10^{-8} Torr. The sample analysis area was 0.8 mm wide and 2.0 mm long.

Fourier transform infra-red spectrometry (FT-IR) was performed on a Bomem MB-series instrument with an attenuated total reflectance (ATR) attachment (Spectra Tech ATR part # 0012-482T).

Scanning electron microscopy (SEM) of the membranes was performed on a Cambridge Instruments Stereoscan 120 scanning electron microscope and an IBAS Kontron

Electronik image analyser with accompanying software located in the Department of Geology at the University of Manitoba. Sample coating (with Au / Pd) for SEM analysis was accomplished using an Edwards Sputter Coater #5150B.

2.2. Membrane materials used

The sorption of phenols and benzoic acids was studied using polyurethane membranes polyether-type PT6100S and PT6310S and polyester-type MP1495-SL (0.025 mm, 0.051 mm and 0.127 mm thick) obtained from Deerfield Urethane Inc. and Stevens Elastomerics / Urethane Products respectively.

The study of organic dyes and organometallic ion-pairs was done using only the Deerfield Urethane Inc. polyether-type polyurethane membranes PT6100S and PT6310S having thicknesses of 0.025 mm and 0.051 mm thick respectively.

2.3. Other reagents

All water used for experimentation was purified by a Barnsted Nanopure™ II system (using reverse osmosis-treated feedstock) and had a resistance of 18.1-18.3 MOhm/cm. Reagent grade HCl and NaCl and the organic solvents were supplied by Fisher Scientific. The phenols and benzoic acids were also supplied by Fisher Scientific and used without further purification. The *ortho*, *meta*, and *para* xylene solutions 99 + % pure were purchased

from Aldrich Chemical Company, Inc. and used without further purification. The organic dyes shown in Table 2-2 and Table 2-3 were obtained from a biological stain kit, Chem-Supply Model No. BS-100, provided by Chem Service, Inc. The purity of each dye was checked by TLC using a 50:10:15 ratio of *n*-butanol : ethanol : water mobile phase composition. Since these compounds appeared to be in their pure form, they were used without further purification. Gold solutions were prepared using $NaAuCl_4$ salt supplied by Johnson-Matthey.

2.4. Apparatus used for membrane testing

The apparatus used for studying the sorption of phenols and benzoic acids was a 40 mL Kimble Glass Inc. amber glass vial (60960A-912) with a plastic cap and a Teflon^{TM}-faced silicone liner. The polyurethane membrane was placed on the opening of the vial and covered with the Teflon^{TM} silicone disc and a screw cap and carefully tightened. The surface area exposed to the sample solutions was 2.54 cm^2. For experiments involving different surface areas of membrane exposed to solutions of phenols and benzoic acids, glass containers having larger caps were used.

The apparatus used for studying the transport of organic dyes and organometallic ion-pair complexes consisted of two separate glass "cells" (a starting and a receiving cell) having capacities of 260 mL (Fig. 2-1).

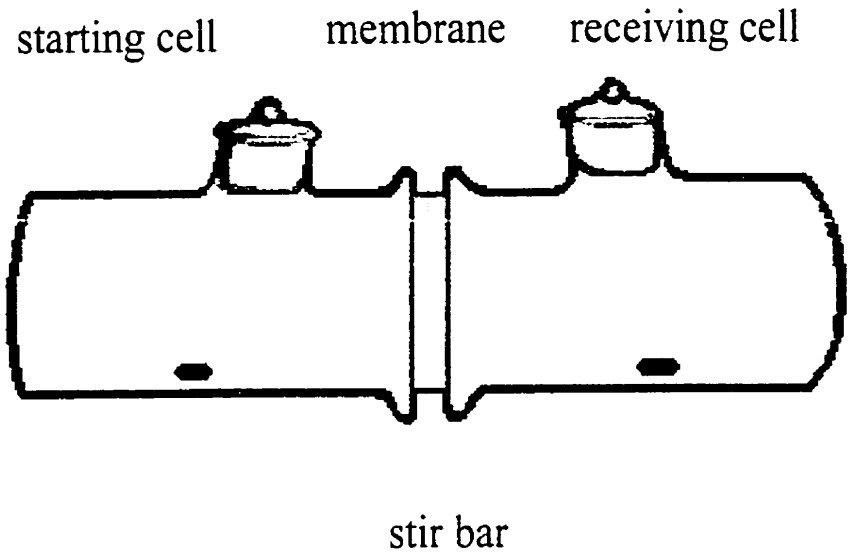


Fig. 2-1. The experimental apparatus for transport studies

The flanges of both cells were covered lightly with Dow Corning high vacuum silicone grease in order to obtain a better seal of the two cells. All cells had short sidearms which allowed access for solutions and sampling. The polyurethane membrane was cut into squares and placed between the flanges of the two cells which were then clamped together. The surface area of the membrane exposed to solutions was 23.8 ± 0.2 cm^2.

2.5. Experimental procedure

The stock solutions of benzoic acids and phenols were prepared by accurately weighing an appropriate amount of each compound, dissolving this in solvent and transferring to 500 mL volumetric flasks which were then filled to volume. Sample phenol solutions of about 2×10^{-4} M concentration and benzoic acid solutions of about 3×10^{-4} M concentration (unless otherwise specified in the data table) were prepared by transferring aliquots of the stock solutions to a 100 mL volumetric flasks. Parameters such as salt, acid, or base concentrations were adjusted prior to dilution to volume.

Sample solutions of *ortho*, *meta*, and *para* xylenes were prepared by diluting a known amount of a particular xylene isomer to 25 mL using hexane. 10 mL aliquots of the phenol, benzoic acid and xylene sample solutions were then transferred, using volumetric pipettes, into the sample vials covered with the membrane and a screw cap. The vials were then inverted to put the samples in contact with the membrane and shaken for a known amount of time. For each experiment, triplicate samples were prepared and the experiment was repeated several times to establish the reproducibility. The vials containing the samples were also weighed prior to and after the extraction to determine if any loss due to leakage may have occurred.

For the study involving transport of organic dyes through the polyurethane membrane, enough of each dye was weighed out to give a final solution concentration of about 1.9×10^{-5} M in 1.0 M HCl or in 1.0 M NaOH (unless otherwise specified in the data

table). The choice of this concentration was dictated by the solubility limit of the least soluble dye in 1.0 M HCl. Parameters such as salt, acid, or base concentrations were adjusted accordingly. The starting cell contained 250 mL of aqueous dye solution; the receiving cell contained 250 mL of 1.0 M HCl solution without the dye (unless otherwise specified in the data table). Teflon-coated stir bars were placed inside each cell to keep the solutions stirred throughout the experiment. Separate magnetic stirrers were needed for each cell. After the sample and the receiving solutions were transferred into the cells, the sidearm openings of the cells were closed with glass stoppers and Parafilm^{TM} to eliminate evaporation and pH variations. The entire apparatus was then wrapped in aluminum foil for the duration of the experiment to prevent any possible decomposition of the dye due to light. Each experiment was repeated at least twice to establish reproducibility.

The study of transport of organometallic ion-pair complexes of organic dyes with gold chloride species used aqueous solutions having about 3×10^{-6} M dye concentration and 11 ppm gold chloride concentration (unless otherwise specified in the data table). The remainder of the experimental procedure used was identical to that described earlier for the study of the transport of organic dyes through the polyurethane membrane.

The instrumental calibration for the DSC study of the polyurethane membranes was performed using mercury and indium standards. The mercury standard pellet was provided; the indium standard was made by weighing a known mass of indium into the conductive pellet and enclosing the metal in the pellet. All membranes used in the DSC study were cleaned with *meta* xylene in order to remove any silicone grease that may have been left over from the greased cell flanges. The membranes were cut into small pieces and enclosed within

the pellet. On average, 14 mg to 20 mg of the membrane material was needed to obtain a strong enough signal.

The ESCA analysis used the same membrane samples as the DSC analysis. Because this analysis is very sensitive to silicon, it was crucial to clean the membranes with xylene to remove any traces of silicone grease from the surface to aid in obtaining more accurate signals for the low concentration elements (e.g., nitrogen). The membranes were then cut into small pieces (about 1 cm x 1 cm) and placed on the ESCA sample holder. The analysis of all samples was performed in the automatic mode which is more time-efficient than the manual mode.

2.6. Mathematical treatment of the data

2.6.1 UV-visible analysis

The UV-vis spectra (190 nm-820 nm) of all sample solutions were taken and the absorbances (A_F) compared with the absorbances of the solutions prior to extraction (A_I). For phenols and benzoic acids, the degree of extraction is reported as the % E which is the % decrease of absorption from the solution using a Beer's Law (1) dependence.

$$\% E = (A_I - A_F) / A_I \qquad (1)$$

For the dye solutions, the absorbance of the initial solution (A_I) was compared with the absorbances of the starting and the receiving solutions taken after a known period of time (A_{FS}, A_{FR}). % Dye in Starting Cell and % Dye in Receiving Cell are the concentrations of dye in the starting and the receiving solutions respectively at a known time. The concentration of dye in the membrane at a specific time, reported as % Dye in Membrane, can be calculated.

$$\% \text{ Dye in Starting Cell} = A_{FS} / A_I \times 100\% \quad (2)$$

$$\% \text{ Dye in Receiving Cell} = A_{FR} / A_I \times 100\% \quad (3)$$

$$\% \text{ Dye in Membrane} = 100\% - (\% \text{ Dye in Starting Cell} + \% \text{ Dye in Receiving Cell}) \quad (4)$$

2.6.2 Gas chromatographic analysis

The sorption of the xylene sample solutions by the polyurethane membrane was quantified using gas chromatography. To determine whether a particular xylene was extracted by the membrane, ratios of the xylene being tested to the internal standard were obtained for the sample solutions and compared with those for the stock sample which was not exposed to the polyurethane membrane. A known amount of an internal standard, i.e., a xylene isomer different from that in the sample, was added to the sample solution after the extraction and to the same volume of the stock sample solution. *Ortho* xylene was used as

the internal standard for the analysis of *meta*, and *para* xylenes; *meta* xylene was used as the internal standard for the analysis of *ortho* xylene.

2.6.3. Atomic absorption analysis

Atomic absorption (AA) spectrophotometry was used for the quantitation of gold in solution. A calibration curve was created in the range of 1 ppm to 12 ppm of gold concentration. Initial (A_I) and final AA readings were obtained for the starting (A_{FS}) and the receiving(A_{FR}) solutions. The % gold in the final starting and receiving solutions was calculated using equations (5) and (6).

$$\% \text{ Gold in Starting Cell} = A_{FS} / A_I \times 100\% \quad (5)$$

$$\% \text{ Gold in Receiving Cell} = A_{FR} / A_I \times 100\% \quad (6)$$

The concentration of gold in the membrane was calculated from the difference (equation 7).

$$\% \text{ Gold in Membrane} = 100\% - (\% \text{ Gold in Starting Cell} + \% \text{ Gold in Receiving Cell}) \quad (7)$$

Chapter 3: Extraction of Phenols Using Polyurethane Membranes

3.1. Introduction

Polyurethanes have conventionally been used as elastic fibres, rubber foams, and coatings since the 1940s[1]. The use of these polymers as sorbents of various organic and inorganic species was proposed only in 1970 and ever since polyurethanes have been employed in many separation techniques[2]. Most recently, polyurethane polymers in the form of membranes have been used preferably to other polyurethane materials in a variety of industrial and environmental applications[3,4]. One example of such uses of polyurethane membranes is in the membrane separations technology for isolation of the inorganic and organic compounds from industrial effluents. The removal of inorganic species by polyurethane membranes has been shown to be feasible on the laboratory and industrial scales, and the mechanism of the sorption process has been addressed to some extent[5,6]. The extraction process of organic species by polyurethane membranes, on the other hand, has not been as extensively investigated. The very few existing publications on the extraction of organic compounds with polyurethane membranes have been concerned primarily with determination of the effects of several organic solvents on the membrane's physical and chemical stability for applications in industrial membrane separations and not with

elucidation of the sorption mechanism[7-10]. Polymers having high resistance to the physical and chemical stress are required for applications in the membrane purification technology because they must withstand high operational pressures and corrosive solution conditions. Because polyurethane membranes meet these criteria, they may eventually become more widely used for membrane separations. Detailed information on how chemical species in solution are extracted by the polyurethane membranes may allow one to design more efficient membrane purification systems for the removal of pollutants from industrial waste streams.

The study of the extraction mechanism of organic species by the polyurethane membrane was initiated with the investigation of the sorption of various phenols from solution. Phenols are widely used in industry and so far no single efficient method has yet been developed for their removal from waste effluents[3]. Understanding the mechanism of sorption of small and simple organic molecules such as phenols is important to studying the sorption of organic compounds in general because it can provide an insight into the extraction process by the polyurethane membrane of other more complex organic species.

3.2. Results and Discussion

3.2.1. Effect of phenol concentration on extraction

In some extraction processes, the concentration of the species in solution can affect

the efficiency with which the compound is removed by the extracting medium[11]. To determine whether the amount of phenol in solution has an effect on the sorption of phenol by the polyurethane membrane, solutions having various phenol concentrations were studied. The choice of solution concentration was limited by the solubility of phenols in the solvents and by the detection limit of the UV-visible spectrophotometer. Solutions having phenol concentrations of 2×10^{-6} M, 2×10^{-5} M, 1×10^{-4} M, and 3×10^{-4} M were extracted. For all solutions studied, no significant change in sorption was observed after about 3 h, but the percent phenol extracted from each solution by the polyurethane membrane varied. As shown in Table 3-1, the more concentrated phenol solutions were extracted to a greater extent by the polyurethane membrane than the less concentrated solutions. For subsequent experiments, 2×10^{-4} M phenol solutions were used.

During the extraction process three steps are occurring[12,13]: the transfer of phenol from the bulk solution to the solution-membrane interface; the penetration of phenol into the membrane surface; and the migration of phenol from the membrane surface into the bulk of the membrane:

phenol in solution ⇆ **phenol at solution-membrane interface** ⇆ **phenol in membrane surface** ⇆ **phenol in membrane bulk**

The amount of phenol sorbed from the solution is controlled by the slowest of the three steps which can be either the transfer of phenol from the solution-membrane interface into the

membrane surface or the migration of phenol from the membrane surface into the membrane bulk[12,14]. If the extraction efficiency is controlled by the distribution coefficient alone, an equal percent extraction of phenol can be expected regardless of the solution concentration. The fact that an increase in extraction was observed with the increase in the phenol solution concentration and that no change in sorption was observed after approximately 3 h for all solutions regardless of the phenol solution concentration indicates that the sorption is not controlled by the distribution coefficient alone.

Table 3-1. Effect of the concentration of phenols on extraction

Compound	*"natural" pH	2×10^{-6} M % E	2×10^{-5} M %E	1×10^{-4} M % E	3×10^{-4} M % E
o-bromophenol	5.25	12	22	37	39
m-bromophenol	5.42	29	34	37	39
p-bromophenol	5.11	32	37	41	41
o-chlorophenol	5.39	13	17	21	23
m-chlorophenol	5.40	24	30	34	35
p-chlorophenol	5.55	21	26	28	30

Conditions: 25.0 ± 2.0°C. 10 mL aliquot of an aqueous phenol solution, 0.051 mm ether-type membrane, active surface area of 2.54 cm^2, % E ± 2 % at observed equilibrium after 3 h

*"natural" pH is the pH of phenol (at all of the above concentrations) dissolved in water with no other adjustments e.g., no added acid, base or salt

Although equilibrium for the transfer of phenol from the lower phenol concentration solutions into the membrane surface was observed, equilibrium between phenol in the membrane surface and in the membrane bulk may not yet have been reached during that time. At the lower phenol solution concentration, the number of the phenol molecules entering the membrane surface is lower than at the higher phenol solution concentration (i.e., after equilibrium has been established between phenol in the bulk solution and at the solution-membrane interface). Because at the lower phenol solution concentration there are fewer molecules in the membrane surface, fewer phenol molecules interact with the membrane groups and there is less disruption of the intramolecular forces among the membrane groups. Consequently, migration of the phenol molecules deeper into the membrane is slower[14]. The slower rate of migration of the phenol molecules away from the surface into the membrane bulk affects the time after which equilibrium needs to be re-established at the solution-membrane surface interface. After the initial transfer of phenol from a low concentration solution into the membrane surface, the equilibrium at the solution-membrane surface is not re-established as quickly as when a high concentration solution is used because the phenol is not migrating from the surface into the membrane bulk as quickly. Therefore, a lower percentage of phenol was observed to be extracted from the less concentrated phenol solution at the observed solution-membrane surface equilibrium.

3.2.2. Effect of extraction time, surface area, and thickness of the membrane on extraction

In order to estimate the time needed for the extraction to reach equilibrium at room temperature, extraction of various phenol solutions (Table 3-1) having concentrations of 2 x 10^{-4} M was measured over a wide range of time. All solutions were mechanically shaken for the desired amount of time and then the samples were analysed after 30 min and subsequently at 1 h periods up to 10 h. Final readings were taken at 24 and 48 h. These experiments show that equilibrium was attained after approximately 3 h for all phenol solutions extracted with 0.051 mm thick ether- and ester-type polyurethane membranes. No significant increase in extraction was observed 45 h later as illustrated by the extraction of *m*-bromophenol (Fig. 3-1).

The effects of an increased membrane surface and thickness of the membrane on the extraction of phenols from solution were also investigated. The data in Table 3-2 show that an increase in surface area of the 0.051 mm thick membrane exposed to the phenol solution resulted in an increase in extraction nearly proportional to the increase in surface area. The thick membranes (0.051 mm and 0.127 mm) of identical surface area have a higher extracting capacity than the thin membranes (0.025 mm). This is exemplified by the results for the extraction of *m*-bromophenol (Table 3-3) over two time periods (3 h and 9 h) with both the ether- and the ester-type polyurethane membranes.

When species extract into the polyurethane membrane from a solution, three steps

take place, i.e., after equilibrium has been established at the solution-membrane surface interface, transfer of the phenol molecules occurs which is followed by migration of the phenol molecules into the bulk of the membrane. The majority of solid phase / liquid phase extractions are considered to be either adsorption or absorption processes. The overall extraction process by the polyurethane membrane is far more complex and cannot be classified as either adsorption or absorption alone.

Table 3-2. Effect of surface area on extraction of *m*-bromophenol

Active Surface Area (cm^2)	% E
2.00	36
2.54	44
7.07	85

Conditions: 25.0 ± 2.0 °C. 10 mL aliquot of ≈ 2 x 10^{-4} M aqueous phenol solution. 0.051 mm ether-type membrane. % E ± 3 % at equilibrium after approximately 3 h

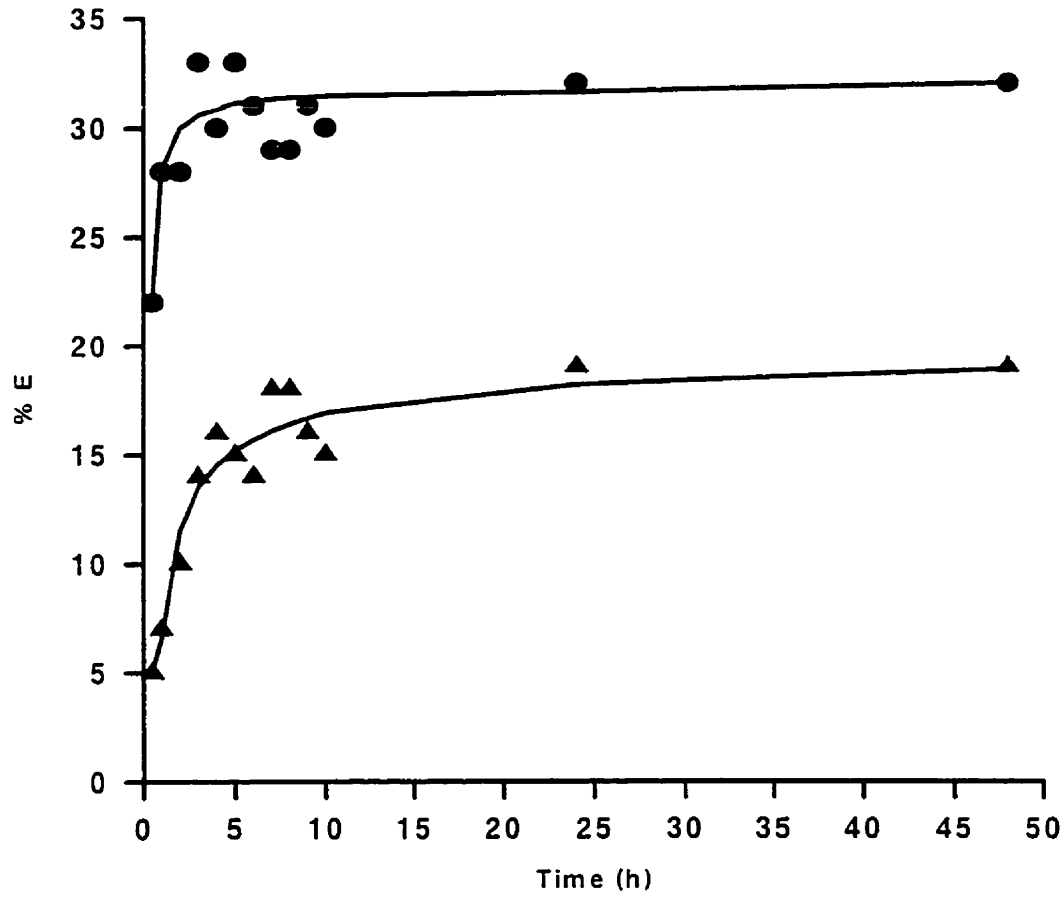


Fig. 3-1. Extraction of *m*-bromophenol with time using the ether- and ester-type polyurethane membranes. Conditions: 25.0 ± 2.0°C. 10 mL aliquot of ≈ 2 x 10^{-4} M aqueous phenol solution. 0.051 mm ether- and ester-type membranes. active surface area of 2.54 cm^2. % E ± 3 %. Extraction with the ether-type membrane: ●; extraction with the ester-type membrane: ▲

Table 3-3. Extraction of *m*-bromophenol by ether- and ester-type polyurethane membranes having thicknesses of 0.025 mm, 0.0.51 mm, and 0.127 mm

Membrane Type	Time	0.025 mm thick % E	0.051 mm thick % E	0.127 mm thick % E
Ether	3 h	26	42	59
	9 h	27	45	83
Ester	3 h	15	16	37
	9 h	16	23	46

Conditions: 25.0 ± 2.0°C, 10 mL aliquot of ≈ 2 x 10^{-4} M aqueous phenol solution, active surface area of 2.54 cm^2, % E ± 3 %

However, the first step in the extraction by the polyurethane membrane can be considered as adsorption and is analogous to the adsorption of gas molecules on a solid surface as described by Langmuir[15]. According to Langmuir, the extent of adsorption is determined by equilibrium that results from the adsorption of gas molecules on the surface and their evaporation from the surface and is proportional to the area of the surface exposed to the gas[15]. Assuming that the phenol molecules in solution behave similarly to the gas molecules,

the initial extraction of the phenol from solution into the membrane surface (y) can be represented by a modified Langmuir equation

$$y = b\, y_m\, C / (1 + b\, C) \qquad (1)$$

where y_m is the amount of phenol extracted from solution when the monolayer is complete, C is the concentration of phenol remaining in solution, and b is an extraction coefficient which is constant at a given temperature. Using the above analogy, the initial transfer of phenol from solution into the membrane surface can be expected to proceed rapidly until equilibrium is reached between the phenol in solution and the phenol in the membrane surface. This step is in part controlled by the solubility of the phenol in the aqueous phase and by the attraction of phenol to the membrane surface. If the extraction of phenol by the polyurethane membrane is only an adsorption process as the one described by Langmuir, no more phenol can be expected to be removed from the solution after equilibrium at the solution-membrane surface interface and the membrane surface has been attained. As shown in Table 3-3, the amount of phenol extracted by the thin membranes (0.025mm) does not significantly change with time, but membranes 0.051 mm and 0.127 mm thick extract more phenol when a longer extraction time is allowed. Because all of the membranes had an identical surface area exposed to the phenol solution, the observed increase in extraction for the thicker membranes implies that the phenol molecules must be migrating into the bulk of the thicker membranes and not back into the solution as in the Langmuir model. As the phenol molecules are migrating into the polymer matrix, the phenol concentration in the

membrane surface is depleted. In order to re-establish equilibrium between the solution-membrane surface interface and the membrane surface, more phenol is transferred from the solution into the membrane surface, and consequently more phenol is removed from the solution. No increase in the removal of phenol from solution with extended times was observed for the extractions with 0.025 mm thick ether- and ester-type membranes probably because the capacity of this amount of these membranes for phenol has been already reached at about 3 h.

The smaller variation in extraction over time (i.e., at 3 h vs. 9 h) observed for the 0.127 mm thick ester-type membrane (Table 3-3) indicates that migration of the phenol molecules through this membrane is probably much slower than through the 0.127 mm thick ether-type membrane. The difference in the rate of transfer of phenol through the two membrane types suggests that the structure of the membrane may be an important factor in the extraction process. The ester-type polyurethane has a more compact structure than the ether-type because the ester groups are more polar and have a better probability of forming intramolecular hydrogen bonds with other ester groups and with the hard segments than the ether groups. Thus, migration of phenol through the ester-type membrane may be hindered due to stronger and more extensive intramolecular interactions between the membrane ester groups. These interactions may be too strong to be disrupted effectively by the phenol and this can account for the consistently lower sorption obtained with the ester-type polyurethane membrane.

As is shown above, the extraction of phenol from solution using both types of the polyurethane membrane cannot be described solely as an adsorption process because it

involves migration of phenol into the bulk of the membrane and not just transfer of phenol into the surface of the polymer. This extraction process cannot be considered as absorption either because the extent of the removal of phenol from solution is controlled by the ability of phenol to interact with the membrane groups and not just by its solubility in the membrane. Because the extraction of organic compounds by the polyurethane membrane appears to result from molecular adsorption, absorption and various intermolecular interactions, the entire process is called sorption.

3.2.3. Effect of pH on extraction

Phenols can be involved in various equilibria with protons which result in neutral, positively, or negatively charged species. When the substituent groups on the phenol molecule are ionizable, the pH plays an important role in the extraction process by the polyurethane membrane (Table 3-4). The addition of base to phenol solutions resulted in a dramatic decrease in extraction due to the formation of a charged species. However, the addition of acid did not significantly alter the extraction which suggests that phenols must already exist as protonated species at the "natural" solution pH (Table 3-1) prior to the addition of acid. It can also be concluded that the oxygen present in the polyurethane membrane ether and ester groups does not become protonated with the addition of acid because the extraction capabilities of both membrane types did not change. If protonation of the oxygen took place, a decrease in extraction would have been observed due to formation

of a charged surface which would interact with the neutral phenols less favourably.

Table 3-4. Effect of base and acid addition

Acid or Base Added	Zero Addition	0.10 M Final Concentration	0.50 M Final Concentration	1.00 M Final Concentration	2.00 M Final Concentration
	% E	% E	% E	% E	% E
HCl	41	41	41	43	42
NaOH	41	9	0	0	0

Conditions: 25.0 ± 2.0 °C, 10 mL aliquot of ~ 2 x 10^{-4} M *m*-bromophenol solution, 0.051 mm ether-type membrane, active surface area of 2.54 cm^2, % E ± 3 % at equilibrium after 3 h

3.2.4. Effect of salts on extraction

The data for the extraction of phenols from salt solutions by the polyurethane membrane are shown in Table 3-5. It is known that charged species which are not extracted by the membrane sometimes can be extracted as ion-pairs[16]. The formation of ion-pairs can be accomplished using the "salting out" effect in which a highly concentrated salt solution is added to the sample solution so that ion-pairs are formed which can then extract.

Table 3-5. Effect of salt addition

Compound	Zero Addition	0.33 M NaCl Final Concentration	1.00 M NaCl Final Concentration
	% E	% E	% E
o-bromophenol	39	39	41
m-bromophenol	43	43	45
p-bromophenol	41	44	42
o-chlorophenol	21	21	23
m-chlorophenol	34	34	32
p-chlorophenol	29	29	28

Conditions: 25.0 ± 2.0 °C, 10 mL aliquot of ≈ 2 x 10^{-4} M aqueous phenol solution, 0.051 mm ether-type membrane, active surface area of 2.54 cm^2, % E ± 3 % at equilibrium after 3 h

As shown in Table 3-5, no change in extraction occurred with the addition of salt, which suggests that no ion-pair formation took place. This indicates that phenols must be present in a non-ionised form in aqueous solution prior to the addition of salt. Furthermore, the ether groups in the membrane probably do not have an initial electrostatic charge when in contact with water because the addition of salt had no effect on sorption. If the membrane

surface had been charged, the addition of salt would have resulted the formation of ion-pairs with the charged atoms on the membrane surface. Because the uncharged membrane surface is more capable of extracting the uncharged phenol molecules, an increase in sorption would have been observed.

3.2.5. Effect of solvent type on extraction

The initial experiments involved the extraction of phenols from water, however, the extraction from organic media can provide additional information about the mechanism. The results of the extraction of phenols from various solvents are presented in Table 3-6. The *meta* and *para* isomers did not show a significant difference in extraction from water, hexane or cyclohexane. The *ortho* isomer, on the other hand, extracted well from water, but very poorly from hexane and cyclohexane. None of the compounds extracted from acetonitrile or ethyl acetate.

Out of all of the solvents studied, water seems to be the best solvent from which to extract the halophenols using the polyurethane membrane. Water may be acting as a carrier for phenols which can interact with water through hydrogen-bonding. Water can bring the phenols closer in contact with the membrane groups and make transfer of phenols from the solution into the membrane surface more efficient.

Table 3-6. Extraction of phenols from various solvents

Compound	Water	Hexane	Cyclohexane	Acetonitrile	Ethyl Acetate
	% E	% E	% E	% E	% E
o-bromophenol	39	5	2	0	0
m-bromophenol	42	41	30	0	0
p-bromophenol	42	44	35	0	0
o-chlorophenol	22	2	1	0	0
m-chlorophenol	34	38	30	0	0
p-chlorophenol	30	25	28	0	0

Conditions: 25.0 ± 2.0°C, 10 mL aliquot of ≈ 2 x 10^{-4} M phenol solution, 0.051 mm ether-type membrane, active surface area of 2.54 cm^2, % E ± 3 % at equilibrium after 3 h

It has been shown that surface tension of the solvent has an effect on the liquid phase / solid phase extraction of organic compounds[17]. If the surface tension of the solvent is reduced by the solute, then the solute molecules will concentrate at the membrane surface, whereas if the surface tension is raised, the solute will move away from the membrane surface into the bulk of the solution. Most water-soluble organic compounds are known to reduce the surface tension of water[17]. Therefore, phenols in water may tend to accumulate in the regions of lower concentration, i.e., at the water-membrane interface and interact directly with the

membrane through non-specific attraction forces. Hexane and cyclohexane have lower surface tensions than water when in contact with the membrane, so phenols can be expected to extract comparably well from hexane and cyclohexane which was observed for the *meta* and *para* isomers but not for the *ortho* isomer. The *ortho* isomer possesses a higher localized charge than the other isomers since the hydroxyl and the halo substituents are closer together. Therefore, this isomer may not be solvated well by the hexane or cyclohexane molecules. Furthermore, because the surface of the membrane is more non-polar in these solvents (Chapter 7, ESCA analysis), the *ortho*-phenol may be repelled from the membrane surface and therefore less extraction will result. Extraction from polar organic solvents such as ethyl acetate and acetonitrile was not observed. All of the phenols studied are much more soluble in these solvents than in water or hexane. This suggests that in order for extraction to occur, the interactions of phenols with the membrane (which are responsible for the extraction) must be much weaker than the interactions of phenols with ethyl acetate and acetonitrile.

3.2.6. Importance of hydrogen-bonding and other non-specific interactions

Inter- and intramolecular hydrogen-bonding interactions are important in the extraction of phenols by the polyurethane membrane. One example of intermolecular hydrogen-bonding is the bonding between oxygen atoms on the membrane groups and the hydroxyl group or other substituents on the phenol molecule. Intermolecular hydrogen-bonding can also occur among the ether and the ester groups on the membrane segments, or

between the membrane groups and the solvent molecules. Intramolecular hydrogen-bonding interactions can occur within the phenol molecule itself, e.g., between the hydroxyl group and other substituents present on the phenol ring. Both inter- and intramolecular hydrogen bonds can only form if the two interacting atoms are very close to each other. These bonds can also be easily broken because they are quite weak[18].

The intra- and intermolecular hydrogen bonds appear to collectively influence the extraction of phenols by the polyurethane membrane. These effects are shown by comparing the extraction of halophenols, in which an intramolecular hydrogen bond is unlikely, with alkyl phenols which can form such bonds. As shown in Table 3-7, the dialkyl phenols extracted from water to a lesser extent than the halophenols (Table 3-6) and the extraction of the trialkyl phenols was comparable to that of halophenols. The trialkyl phenols have one methyl group that is not involved in the intramolecular hydrogen-bonding and which therefore is available for interactions with the membrane.

The isomers which can form the strongest intramolecular hydrogen bonds extract more poorly than those in which such bonding is less likely to take place. For example, halophenols which are unlikely to form intramolecular hydrogen bonds can be involved in intermolecular interactions with the membrane or the solvent through the hydroxyl group and through the halo substituents. Therefore, they extract better than the dialkyl phenols in which the intramolecular interactions may be competing with the intermolecular interactions. Phenols with trialkyl substituents or compounds that can form more intramolecular hydrogen bonds with the membrane extracted even better as is shown by the data in Table 3-7.

Table 3-7. Extraction of various organic compounds

Compound	Molecular Structure	Water % E	Hexane % E
2, 3-dimethylphenol	$(CH_3)_2C_6H_3OH$	20	4
2, 6-dimethylphenol	$(CH_3)_2C_6H_3OH$	17	3
3, 5-dimethylphenol	$(CH_3)_2C_6H_3OH$	17	6
2, 3, 5- trimethylphenol	$(CH_3)_3C_6H_2OH$	45	0
2, 4, 6- trimethylphenol	$(CH_3)_3C_6H_2OH$	34	0
2-*t*-butyl-5-methylphenol	$(t\text{-bu})(CH_3)C_6H_3OH$	90	20
phenol	C_6H_5OH	5	13
diphenol	$(C_6H_4)_2(OH)_2$	45	46
resorcinol	$C_6H_4(OH)_2$	20	0
benzoic acid	$C_6H_5CO_2H$	15	18
2, 4- dihydroxybenzoic acid	$(OH)_2C_6H_3CO_2H$	4	Not Soluble
3, 5-dihydroxybenzoic acid	$(OH)_2C_6H_3CO_2H$	0	Not Soluble
o-, *m*-, *p*-xylenes	$(CH_3)_2C_6H_4$	Not Tested	0*

Conditions: 25.0 ± 2.0 °C, ≈ 2 x 10^{-4} M solutions, 0.051 mm ether-type membrane, active surface area of 2.54 cm^2, 10 mL solution, % E ± 3 % at equilibrium after 3 h

* data were obtained using gas chromatography

The low extraction of alkyl phenols from hexane by the polyurethane membrane indicates that in this case the solubility has a larger effect on the extraction than the hydrogen-bonding interactions. Because the alkyl phenols are more soluble in hexane than in the membrane, they do not readily partition into the membrane.

Extractions obtained with the ether-type membrane are of a higher percentage than those with the ester-type membrane. This can be accounted for by the relative ability of the ester and the ether groups to form hydrogen bonds. The pK_a for the protonation of the ether oxygen is -3 and the pK_a for the protonation of the carbonyl oxygen is -6. The ether oxygen is more basic and therefore it is better at forming hydrogen bonds with phenols or with the solvent molecules[19].

From the observations discussed above it follows that the availability of the substituents on the compound for intermolecular interactions is as important in extraction by the polyurethane membrane as is the relative solubility of the compounds in the membrane and in solution. For example, the molecules having a certain balance between the polar hydrogen bond-forming substituents and the non-polar substituents are extracted. The molecules which are either very polar (e.g., 2,4-dihydroxybenzoic acid, or 3,5-dihydroxybenzoic acid) or very non-polar (e.g., xylenes) do not extract. Thus, sorption of phenols by the polyurethane membrane can be accounted for by a combined action of weak dispersion forces together with stronger hydrogen bond forces which depend on the proximity of the hydroxyl group to other substituents.

3.2.7. Effect of temperature on extraction

When phenols are sorbed by the polyurethane membrane, they can be thought of as distributing between the solution (a liquid phase) and the membrane (a solid phase). This can be represented by a distribution ratio, which is the equilibrium phenol concentration in a liquid phase, K_s, divided by the concentration of phenol in the solid phase, K_m. This ratio will change with temperature because the solubility of phenol in the two phases changes with temperature. The extraction of organic molecules from liquids into solids is usually expressed as standard affinity, $\Delta\mu^\circ$, which being a thermodynamic function, is exchangeable with Gibbs free energy, ΔG [20]. Thus, if $\mu_s + RT \ln [K_s]$ is the free energy of phenol in aqueous solution and $\mu_m + RT \ln [K_m]$ is the free energy of phenol in the membrane, these will be equal at equilibrium [20], i.e., $\mu_m + RT \ln [K_m] = \mu_s + RT \ln [K_s]$. Therefore, at any temperature T, the affinity of phenol for the membrane can be expressed by equation (2)

$$-(\mu_m - \mu_s) = -\Delta\mu^\circ = RT \ln [K_m] - RT \ln [K_s] = RT \ln [K_m] / [K_s] = RT \ln K \qquad (2)$$

where, K is the partition ratio.

The heat (ΔH°) and entropy (ΔS°) of sorption can be calculated from the partition ratios at two different temperatures or over a temperature range[20]. The assumption is that ΔH° and ΔS° are independent of temperature which holds if a plot of log K vs. 1 / T is a straight line.

Therefore,

$$\Delta H^{\circ} = -2.303\ R\ T_1T_2 / (T_2-T_1) \log K_1 / K_2 \quad (3)$$

$$\Delta S^{\circ} = -2.303\ R \log K_1 / K_2 \quad (4)$$

where T_1 and T_2 are the two temperatures, and K_1 and K_2 are the partition ratios at the two temperatures.

The percentage of extraction of bromophenols and chlorophenols was measured at the observed equilibrium at various temperatures. The results of the extraction of various phenols by the ester- and the ether-type membranes are presented in Table 3-8. The sample plots of log K vs. 1 / T for the bromophenols are shown in Fig. 3-2 and Fig. 3-3. Extractions of all bromo- and chlorophenols at low temperatures (4 and 12 °C) using the ester-type polyurethane membrane (Fig. 3-3) required 72 h rather than about 3 h to reach equilibrium. The values for K, ΔH°, and ΔS° for bromo- and chlorophenols calculated for the extractions with the ester- and the ether-type membranes are shown in Table 3-9. Extractions of all the bromophenol and chlorophenol isomers with the ether-type polyurethane membrane and the *meta* and *para* isomers with the ester-type membrane (Table 3-8) showed a gradual decrease in % E with an increase in temperature. Both ΔH° and ΔS° for these extractions are negative, and the entropy change for the sorption is quite small (Table 3-9).

Table 3-8. Effect of temperature

Compound	4 °C % E	12 °C % E	25 °C % E	37 °C % E	50 °C % E	70 °C % E	90 °C % E
o- bromophenol							
ether	30	31	39	21	19	17	13
ester	12	13	16	14	14	13	11
m-bromophenol							
ether	44	43	43	33	25	20	13
ester	32	28	24	20	18	13	11
p-bromophenol							
ether	42	44	41	27	20	16	6
ester	29	24	21	18	13	13	6
o-chlorophenol							
ether	23	23	21	16	15	14	12
ester	8	9	11	10	12	10	9
m-chlorophenol							
ether	34	32	34	21	17	10	9
ester	16	13	16	14	13	9	8
p-chlorophenol							
ether	29	31	29	20	14	11	8
ester	17	17	16	13	11	9	7

Conditions: 10 mL aliquot of ≈ 2×10^{-4} M aqueous phenol solution, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2, % E ± 3 % at equilibrium, temperature ± 1.0 °C (for extractions at 4 and 12 °C using the ester-type membrane, the observed equilibrium is reached after 72 h rather than after 3 h)

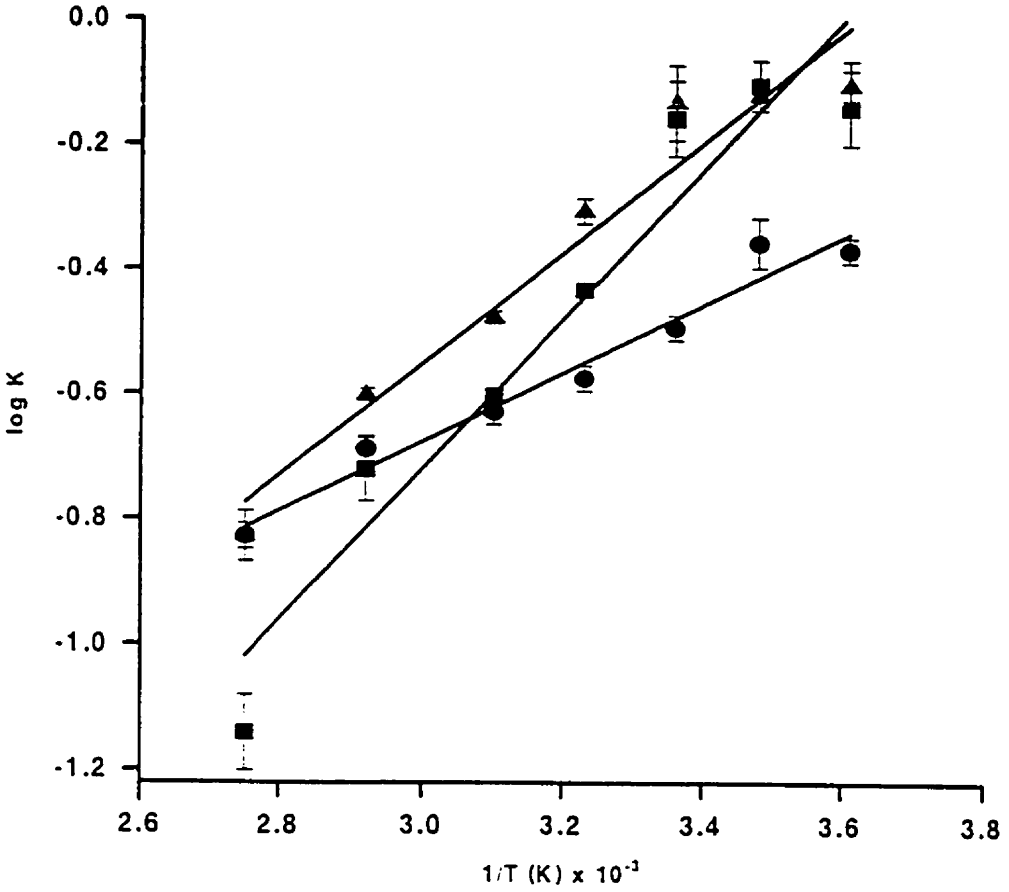


Fig. 3-2. Change in partition ratio with change in temperature for extraction of bromophenols using the ether-type polyurethane membrane. Extraction equilibrium was reached after 3 h
Bromophenols: ● *ortho-*, ▲ *meta-*, ■ *para-*

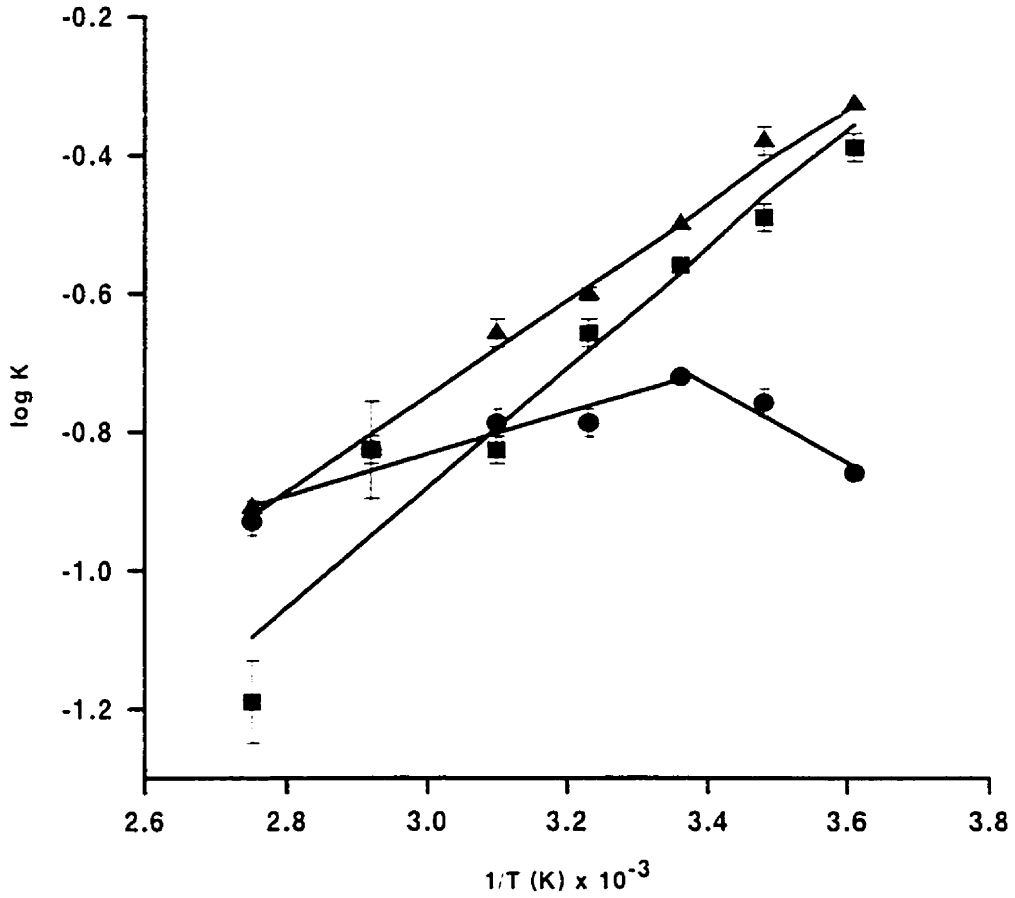


Fig. 3-3. Change in partition ratio with change in temperature for extraction of bromophenols using the ester-type polyurethane membrane. Extraction equilibrium was reached after 3 h except for solutions extracted at 4 and 12°C for which the equilibrium was attained after 72 h

Bromophenols: ● *ortho-*, ▲ *meta-*, ■ *para-*

Table 3-9. Partition ratio, enthalpy, and entropy change for extraction of phenols

Compound Membrane Type	K_1 / K_2	$\Delta H°$ (KJ mol^{-1})	$\Delta S°$ (J $mol^{-1}K^{-1}$)
***o*-bromophenol**			
ether (4 – 90 °C)	2.879	-10.28	-8.79
ester (4 – 25 °C)	0.716	10.85	-2.02
ester (25 – 90 °C)	1.545	-6.52	-7.85
***m*-bromophenol**			
ether (4 – 90 °C)	5.275	-16.17	-13.83
ester (4 – 90 °C)	3.829	-12.97	-11.16
***p*-bromophenol**			
ether (4 – 90 °C)	11.313	-23.19	-20.17
ester (4 – 90 °C)	6.375	-17.89	-15.40
***o*-chlorophenol**			
ether (4 – 90 °C)	2.199	-7.66	-6.55
ester (4 – 25 °C)	0.710	11.11	2.85
ester (25 – 90 °C)	1.265	-2.29	-1.96
***m*-chlorophenol**			
ether (4 – 90 °C)	5.867	-16.13	-13.80
ester (4 – 90 °C)	2.184	-7.54	-6.49
***p*-chlorophenol**			
ether (4 – 90 °C)	4.690	-15.02	-12.85
ester (4 – 90 °C)	2.720	-9.66	-8.32

Conditions: 10 mL of = 2×10^{-4} M aqueous phenol solutions, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2. Extraction equilibrium was reached after 3 h except for solutions extracted at 4 and 12 °C with the ester-type membrane for which the equilibrium was attained after 72 h

When these phenol isomers partition from the solution into the membrane, their motion becomes more restricted, and therefore a negative entropy is observed. Since the sorption process also involves a decrease in free energy then from the thermodynamic relationship $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ it follows that ΔH° should be negative which is confirmed by the data. Thus the sorption of these isomers by the membrane is an exothermic process and from LeChatelier's principle, it follows that the extent of sorption (under equilibrium conditions) should decrease with increasing temperature which is observed. Another explanation for the decrease in extraction with an increase in temperature is that the physical structure of the membrane may change at an increased temperature so that the matrix is less accessible to phenol molecules (Chapter 7). The higher energy of the membrane segments and of the phenol molecules provided by the increased temperature may prevent any stable interactions between the membrane groups and the phenol from forming, and therefore result in a lower extraction. A smaller change in entropy for the extraction with the ester-type membrane suggests that the freedom of motion of the bromo- and chlorophenol molecules in this membrane is higher. This indicates that during extraction with the ester-type membrane, the phenols are more solvated and not as tightly bound as they are to the ether-type membrane.

The *ortho* bromo- and chlorophenols showed a different sorption pattern when extracted with the ester-type polyurethane membrane over the 4 to 90 °C temperature range. Extractions of the *ortho* isomers with the ester-type membrane showed an extraction maximum at 25°C and a slight decrease at higher and lower temperatures. Two sets of data corresponding to two straight line plots for which equations (3) and (4) are valid at equilibrium are shown in Table 3-9. The non-linearity of the log K vs. 1 / T plot for the

extraction of the *ortho* isomers using the ester-type polyurethane membrane is due to the combined effect of the structure of the *ortho* isomers and the more polar nature of the ester-type polyurethane membrane. Unlike the *meta* and *para* isomers, the *ortho* isomer undergoes a so-called *ortho* effect[15]. The proximity of the substituents allows for intermolecular non-covalent interactions such as hydrogen-bonding and charge transfer which may result in the formation of a localized electronic field in the molecule[15]. The strength of this *ortho* effect is susceptible to temperature changes[15]. The overall sorption of the *ortho* phenols may be a result of a combined effect of the electrostatic interactions, the hydrophobic interactions and hydrogen-bonding. Because the ester-type membrane is more polar than the ether-type membrane, the electrostatic interactions between the phenol and the membrane may be stronger and may induce the formation of more resonance structures of the *ortho* phenol which in turn contribute to the non-linearity of the plot shown in Fig. 3-3. The extractions of the *ortho* phenols with both membrane types are generally lower compared to the extractions of the *para* and *meta* isomers most likely due to the *ortho* effect. In the *para* and *meta* isomers, the hydroxyl group is separated from the substituent by the largest distance. Therefore, the hydroxyl group can interact more freely with the membrane substituents through hydrogen-bonding interactions.

3.3. Conclusion

The study of the sorption of various phenols by the polyurethane membrane shows

that these compounds are extracted in their neutral form. Intra- and intermolecular hydrogen-bonding interactions of phenols appear to be important factors governing the extraction process. An increased sorption of phenols by the polyurethane membrane can be attained by providing either a larger surface area exposed to the phenol solution or a thicker membrane that has higher sorption capabilities. Strong intramolecular hydrogen-bonding reduces the intermolecular interactions between the phenol molecules and the membrane and results in a lower extraction. The relative solubility of phenol in the liquid phase and in the membrane can also affect the sorption. The ether-type polyurethane membrane shows a higher extraction capability for the phenols than the ester-type polyurethane membrane which is related to the differences in the molecular and microcrystalline structure of these two membrane types and their ability to interact with the phenol molecules. Room temperature is optimal for the extractions of phenols from solution by the polyurethane membrane.

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Chapter 4: An Investigation Into the Sorption of Benzoic Acids by Polyurethane Membranes

4.1. Introduction

The in-depth study of the sorption of substituted phenols from solution by the polyurethane membrane provided sufficient information to propose a preliminary mechanism for the sorption process[1]. Because the overall sorption appears to be very complex, the mechanism described in the previous chapter based only on data collected for such a narrow representative group of organic compounds cannot be applied to all other organic species. However, it is evident from the phenol study that the polyurethane membrane can be used to extract those organic compounds which are capable of engaging in hydrogen-bonding with the membrane. In order to acquire more representative information regarding the sorption mechanism, the extraction of a wider range of organic compounds had to be examined.

Benzoic acids belong to a very broad class of carboxylic acids and, like the phenols, are quite small and can form hydrogen bonds with themselves or with other species. It is advantageous to study the sorption of benzoic acids not only from the mechanistic perspective but also because of the wide industrial use of these compounds and the consequent need for their removal from waste effluents[2-6]. Information on the sorption of various benzoic acids can supplement the proposed mechanism and can allow us to compare

and contrast extractions of the phenolic and the carboxylic compounds by the polyurethane membrane.

4.2. Results and Discussion

4.2.1. Effect of benzoic acid concentration on extraction

The concentrations of the monobromobenzoic acid solutions used in this study were in the range of about 3×10^{-6} to 3×10^{-4} M as dictated by the solubility of the compounds in water and the detection limit of the UV-visible spectrophotometer (Table 4-1). When the solution concentration of *meta* monobromobenzoic acid was increased, higher extraction of this compound with both the ether- and the ester-type polyurethane membranes was observed. An increase in the solution concentration of *para* monobromobenzoic acid resulted in a significantly higher extraction only when the ether-type polyurethane membrane was the sorbing medium. Extraction of the *para* isomer with the ester-type membrane did not change with a higher solution concentration. At the "natural" solution pH (i.e., the pH of monobromobenzoic acid dissolved in deionized water without adjustment) of 3.27, *ortho* monobromobenzoic acid was not extracted by either of the membranes regardless of its solution concentration.

Before benzoic acid enters the membrane, equilibrium between the benzoic acid molecules in solution and at the solution-membrane interface is established. Next, transfer

of benzoic acid from the membrane-solution interface into the membrane surface takes place which is followed by migration of the benzoic acid molecules deeper into the membrane matrix.

Table 4-1. Effect of the concentration of monobromobenzoic acids on extraction

Compound	% E				
	"natural" pH	3 x 10^{-6} M	3 x 10^{-5} M	1 x 10^{-4} M	3 x 10^{-4} M
o-Bromobenzoic acid	3. 27				
Ether		----	0 ± 0	0 ± 0	2 ± 1
Ester		----	0 ± 0	0 ± 0	0 ± 0
m-Bromobenzoic acid	3.43				
Ether		----	0 ± 0	11 ± 1	27 ± 2
Ester		----	0 ± 0	6 ± 1	15 ± 2
p-Bromobenzoic acid	3.54				
Ether		3 ± 1	4 ± 1	10 ± 1	20 ± 2
Ester		7 ± 1	8 ± 1	9 ± 1	9 ± 1

Conditions: 25.0 ± 2.0 °C. 10-mL aliquot of an aqueous monobromobenzoic acid solution. 0.051 mm ether- and ester-type membranes. active surface area of 2.54 cm^2. n = 3

---- below an instrumental detection limit

The rate of removal of benzoic acid from solution by the polyurethane membrane is controlled by the slowest of the above steps, namely by transfer of benzoic acid from solution-membrane interface into the membrane surface or by migration of benzoic acid from the surface into the polymer bulk. Solvent extraction processes are controlled by the equilibrium distribution coefficient which is the ratio of the equilibrium concentration of the extractant in an aqueous phase to the concentration in an organic phase. For such processes, the equilibrium distribution coefficient remains unchanged regardless of the starting solution concentration of the extracting species. If sorption by the polyurethane membrane is analogous to a solvent extraction, the ratio of the concentrations of the extractant in aqueous solution and in the membrane should not change as one can expect the extraction coefficient to be independent of the original concentration. The results in Table 4-1 show that the extractant concentration did affect the distribution coefficient when the polyurethane membrane was the organic medium. Therefore, the sorption process by the polyurethane membrane cannot be considered a simple solvent extraction. The results obtained from the this study and the study of sorption of phenols indicate that all of the sorption steps, i.e., transfer of the organic species into the solution-membrane interface, partitioning of the organic species into the membrane surface, migration through the membrane bulk, plus the total capacity of the available membrane collectively determine the amount of the extracting species that is removed from solution. Therefore, the % extraction for the sorption of organic compounds by the polyurethane membrane does not simply represent the transfer of the extractant from an aqueous phase to an organic phase as in the solvent extraction, but it also provides information about the transport properties of the bulk membrane.

The time needed to attain the individual equilibria in solution, at the solution-membrane interface and in the bulk of the membrane may vary, which can account for the observed change in the % extraction with the change in concentration. At lower benzoic acid solution concentrations, the abundance of the benzoic acid molecules in the vicinity of the membrane surface is lower than at the higher solution concentration. Consequently, fewer benzoic acid molecules are transferred into the polymer surface. Because fewer molecules are entering the membrane, fewer molecules are interacting with the polymer. As a result, less disruption of the intermolecular interactions between the membrane domains takes place and migration of benzoic acid deeper into the body of the polymer is slower than at a higher solution concentration. Therefore, a lower percentage of benzoic acid was extracted from the less concentrated solution. These results are consistent with the data obtained for the sorption of various phenols from aqueous solutions of differing concentrations[1]. The extraction of benzoic acids by the polyurethane membrane is governed to some extent by the strength and number of the intermolecular interactions formed between the polymer and the extracting species (discussed in sections *4.2.2* and *4.2.6*). Therefore, the structure of the monobromobenzoic acids and the structure of the membrane can dictate the extent to which the intermolecular interactions occur. For example, the very low extraction of the *ortho* isomer with both membrane types and the relatively low and level extraction of the *para* isomer with the ester-type polyurethane membrane are most likely due to the ineffective intermolecular interactions of these isomers with the membrane.

4.2.2. Effect of extraction time and type of the polyurethane membrane

Extractions over a range of 0.5 h to 72 h using the ether- and the ester-type polyurethane membranes were measured to determine how much time is needed for the extraction of benzoic acids to reach equilibrium at room temperature. Sample solutions were mechanically shaken for the desired amount of time and analysed after 0.5 h and subsequently at 1-h periods up to 12 h. Final readings were taken at 25, 45, 65, and 72 h.

The change in extraction of benzoic acid with time is illustrated by the extraction of *meta* monobromobenzoic acid shown in Fig. 4-1. Extraction with both the ether- and the ester-type membranes increased very rapidly up to about 24 h, beyond which no further significant increase was observed. Therefore, it can be assumed that equilibrium was attained within approximately 24 h for solutions containing 3×10^{-4} M concentration of benzoic acids extracted with 0.051 mm thick ether- and ester-type polyurethane membranes.

The ether-type polyurethane membrane extracted a greater amount of each benzoic acid than the ester-type membrane which can be attributed to the efficiency with which the benzoic acid molecules can disrupt the hydrogen-bonding between the domains in each of the membranes. The ester-type membrane has a more compact and rigid internal structure than the ether-type membrane because the ester groups have a better probability of forming intermolecular hydrogen bonds than the ether groups due to the hard and the soft domains not being as segregated as in the ether-type polymer (Chapter 7). The benzoic acid molecules entering the ester-type membrane have to break a greater number of hydrogen bonds than in

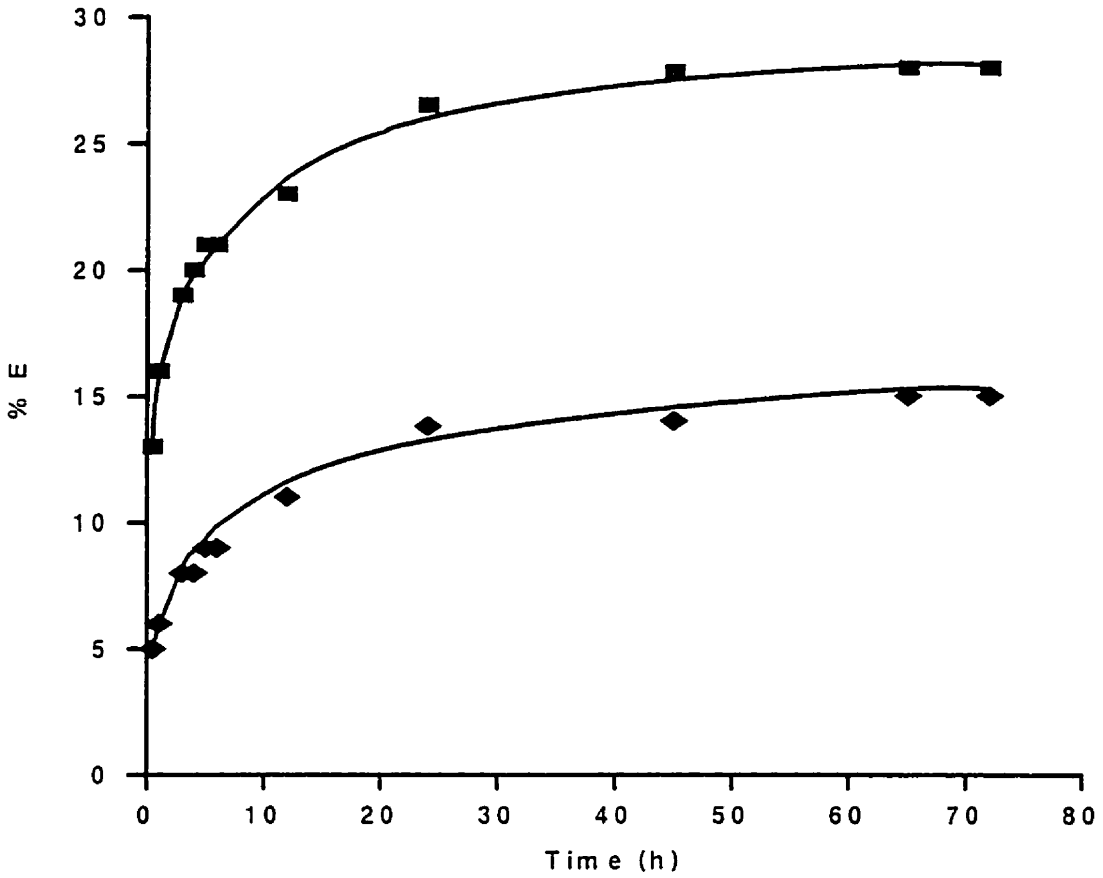

Fig. 4-1. Extraction of *m*-monobromobenzoic acid with time using the ether-and ester-type polyurethane membranes. Conditions: 25.0 ± 2.0 °C, 10-mL aliquot of ≈ 3 x 10^{-4} M aqueous monobromobenzoic acid solution, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2 Extraction with the ether-type membrane, ■; extraction with the ester-type membrane, ◆

the ether-type polymer in order to move deeper into the matrix. This can account for the slower migration of benzoic acids through the ester-type membrane, and hence the lower extraction obtained with this membrane.

4.2.3. Effect of surface area and thickness of the membrane

Extraction of benzoic acids with both membrane types can be increased by increasing the surface of the membrane exposed to the sample solution and / or by increasing the thickness of the membrane. When the surface areas of the 0.051 mm thick membranes exposed to *meta* and *para* monobromobenzoic acids solutions were increased, significantly greater extractions with both membrane types resulted (Table 4-2). Although, at the "natural" pH of 3.27, the *ortho* isomer was extracted very poorly by the ether-type membrane, an increase in extraction was still observed with an increase in the surface area (Table 4-2). However, when the ester-type polyurethane membrane was used, no extraction of the *ortho* isomer occurred regardless of the membrane surface area exposed to the sample solution. The thicker polyurethane membranes (0.051 mm and 0.127 mm) having identical surface areas were found to have higher extracting capacities for the *meta* and *para* isomers than the thinner membranes (0.025 mm) (Table 4-3). The extraction of *ortho* monobromobenzoic acid with the ether-type membrane was very low, but it also increased when a thicker membrane was used (Table 4-3).

Table 4-2. Effect of surface area on extraction of monobromobenzoic acids

Compound	% E		
	Active surface area (cm^2)		
	2.54	6.61	18.1
o-Bromobenzoic acid			
Ether	2 ± 1	3 ± 1	5 ± 1
Ester	0 ± 0	0 ± 0	0 ± 0
m-Bromobenzoic acid			
Ether	28 ± 3	47 ± 3	67 ± 3
Ester	15 ± 2	29 ± 3	58 ± 3
p-Bromobenzoic acid			
Ether	18 ± 2	34 ± 3	49 ± 3
Ester	8 ± 1	20 ± 2	36 ± 3

Conditions: 25.0 ± 2.0 °C, 10-mL aliquot of ≈ 3×10^{-4} M aqueous monobromobenzoic acid solution (pH 3.27, 3.43, and 3.54 for *o*-, *m*-, *p*- isomers respectively), 0.051 mm ether- and ester-type membranes, n = 3

Table 4-3. Extraction of monobromobenzoic acids by the ether- and the ester-type polyurethane membranes having thicknesses of 0.025 mm, 0.051 mm, and 0.127 mm

Compound	% E		
	Membrane thickness		
	0.025 mm	0.051 mm	0.127 mm
o-Bromobenzoic acid			
Ether	0 ± 0	2 ± 1	4 ± 1
Ester	0 ± 0	0 ± 0	0 ± 0
m-Bromobenzoic acid			
Ether	13 ± 2	25 ± 2	37 ± 3
Ester	3 ± 1	13 ± 2	17 ± 2
p-Bromobenzoic acid			
Ether	9 ± 1	21 ± 2	30 ± 3
Ester	4 ± 1	6 ± 1	12 ± 1

Conditions: 25.0 ± 2.0 °C, 10-mL aliquot of = 3 x 10^{-4} M aqueous monobromobenzoic acid solution (pH 3.27, 3.43, and 3.54 for *o*-, *m*-, *p*- isomers respectively), active surface area of 2.54 cm^2, n = 3

Similarly to the extraction of phenols, the results for the extraction of benzoic acids can be explained by looking more closely at the initial transfer of benzoic acid into the membrane surface and its subsequent migration through the membrane. After equilibrium between benzoic acid in solution and benzoic acid at the solution-membrane interface was achieved, the benzoic acid molecules transfer into the membrane surface and migrate through the bulk of the membrane. Similarly to the extraction of phenols, the first step in the overall extraction of benzoic acids can be considered as Langmuir adsorption[7], and the Langmuir equation can be used to describe it:

$$y = b\, y_m\, C / (1 + b\, C) \qquad (1)$$

where y is the membrane surface, y_m is the amount of benzoic acid adsorbed from solution when the monolayer is complete, C is the concentration of benzoic acid remaining in solution, and b is an adsorption coefficient which is constant at a given temperature. The adsorption of benzoic acid from solution into the membrane surface proceeds until equilibrium is reached between benzoic acid in solution and benzoic acid adsorbed in the surface of the membrane.

As previously observed for the extraction of phenols[1], the results obtained from studying the effect of the membrane thickness on the extraction of benzoic acids also show a proportional relationship between the amount of benzoic acid extracted and the membrane thickness (Table 4-3). This indicates that although initially adsorption is taking place, the subsequent process responsible for further removal of benzoic acid cannot be accounted for

by adsorption. A possible explanation is that the benzoic acid molecules like phenol, after being initially adsorbed into the membrane surface, begin to migrate deeper into the polymer as a result of hydrogen-bonding interactions with the soft segments of the membrane and the relative solubility in solution and in the membrane. Because of this migration, the concentration of benzoic acid at the solution-membrane interface and in the membrane surface is depleted and has to be restored to maintain equilibrium. The benzoic acid molecules continue to travel deeper into the membrane until the capacity of the membrane is reached. When benzoic acids were extracted with the 0.051 mm thick membrane, equilibrium was attained within 24 h. A shorter time needed to reach equilibrium can be expected for the extractions done with 0.025 mm thick membrane, and a longer time for the extractions with 0.127 mm thick membrane. Therefore, although equilibrium was reached more quickly with the thinner membrane, a lesser amount of benzoic acid was removed from solution because the thinner membrane became fully saturated with benzoic acid more quickly than the thicker membrane.

4.2.4. Effect of pH on extraction

The effect of solution pH on the extraction of monobromobenzoic acids by the polyurethane membrane was studied in order to confirm that neutral species extraction is occurring as was observed for the extraction of various phenols[1]. Benzoic acid solutions having an even slightly basic pH (0.001 M NH_4OH) did not show any extraction. In contrast,

the slightly acidic solutions (0.001 M HCl) showed significantly higher sorption than the sorption at the "natural" pH (i.e., at 0 M HCl solution concentration) (Table 4-4).

Table 4-4. Effect of acid on extraction

HCl Final Concentration (M)		% E		
		o-Bromobenzoic acid	*m*-Bromobenzoic acid	*p*-Bromobenzoic acid
0	Ether	2 ± 1	27 ± 2	19 ± 2
	Ester	0 ± 0	15 ± 1	7 ± 1
0.001	Ether	17 ± 2	45 ± 2	40 ± 2
	Ester	7 ± 1	24 ± 2	12 ± 2
0.01	Ether	20 ± 2	48 ± 2	40 ± 2
	Ester	8 ± 1	26 ± 2	22 ± 2
0.1	Ether	21 ± 2	47 ± 2	41 ± 2
	Ester	9 ± 1	26 ± 2	22 ± 2
0.5	Ether	20 ± 2	44 ± 2	40 ± 2
	Ester	8 ± 1	25 ± 2	20 ± 2
1	Ether	18 ± 2	48 ± 2	40 ± 2
	Ester	9 ± 1	26 ± 2	20 ± 2
2	Ether	12 ± 1	39 ± 2	40 ± 2
	Ester	9 ± 1	22 ± 2	20 ± 2

Conditions: 25.0 ± 2.0 °C. 10-mL of = 3 x 10^{-4} M aqueous bromobenzoic acid solution. 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2. n = 3

Benzoic acids are weak carboxylic acids which dissociate slightly in aqueous solution[8]. As a result, two forms are present in the "natural" pH solution - the undissociated neutral benzoic acid and the carboxylate anion of benzoic acid. The ratio of these two species is dependent on the dissociation constant, K_a, for the particular benzoic acid[9] (e.g., for *ortho*, *meta*, and *para* the K_a are respectively 140 x 10^{-5}, 15.4 x 10^{-5}, 10.7 x 10^{-5}). For example, because *ortho* monobromobenzoic acid has the highest K_a, it is dissociated in solution to a higher extent than the *meta* and *para* isomers. The addition of base to the benzoic acid solutions resulted in the formation of the carboxylate anion which was not extracted by the membrane. Conversely, the addition of acid resulted in the protonation of those benzoic acid molecules which may have been negatively charged at the "natural" pH and consequently in increased extraction. However, when the solutions were made very highly acidic (e.g., 2 M HCl final concentration), a positive charge may have been placed on the carbonyl oxygen or the formation of carboxylic acid dimers and homoconjugated anions may have occurred[10] which would account for the decrease in extraction. These results strongly confirm the hypothesis that benzoic acids like phenols are efficiently removed from solution by the polyurethane membrane only if present as neutral species.

4.2.5. Effect of salts on extraction

The addition of salt to an aqueous solution of an organic compound increases the ionic strength of the solution which has been shown to increase the efficiency of solvent

extractions and extractions with the polyurethane foam[11-13]. To determine the effect of salt on the sorption of benzoic acids, the sample solutions were acidified prior to the addition of salt and extraction to ensure that all of the benzoic acid molecules were exclusively in their "neutral" form (Table 4-5). No change in extraction was observed for solutions having 0.5 M salt concentration. When the concentration of salt was increased from 0.5 M to 2 M, the extraction slightly increased.

Table 4-5. Effect of NaCl concentration on extraction

Compound	%E			
	NaCl Final Concentration (M)			
	0.0	0.5	1	2
o-Bromobenzoic acid				
Ether	20 ± 2	18 ± 2	25 ± 2	31 ± 3
Ester	8 ± 1	8 ± 1	11 ± 1	15 ± 2
m-Bromobenzoic acid				
Ether	48 ± 3	48 ± 3	54 ± 3	55 ± 3
Ester	26 ± 2	24 ± 2	29 ± 2	40 ± 3
p-Bromobenzoic acid				
Ether	40 ± 3	42 ± 3	49 ± 3	59 ± 3
Ester	22 ± 2	25 ± 2	31 ± 3	34 ± 3

Conditions: 25.0 ± 2.0 °C, 10-mL aliquot of ≈ 3×10^{-4} M monobromobenzoic acid solution having 0.01 M HCl final concentration, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2, n = 3

In high ionic strength solutions, the activity of species is different from that in low ionic strength solutions. If the addition of salt had an effect on extraction of benzoic acids by the polyurethane membrane, the effect would be observed even at 0.5 M NaCl concentration. The slightly higher extraction of benzoic acid from solutions containing 1 M and 2 M salt concentrations may have a larger error associated with it than what is reported in Table 4-5 because at high salt concentrations benzoic acids are known to form various dimers and homoconjugated species[10].

4.2.6. Effect of solvent type on extraction

The most important solvent effects originate from interactions between the solvent and the solute, such as hydrogen-bonding, dipole-dipole, and hydrophobic-bonding interactions which are related to the molecular structure of the solvent and the solute[14]. Information on the extraction of monobromobenzoic acids from organic solvents having variable polarities may help to estimate the polarity of the membrane and therefore allow one to predict which compounds may be soluble in the membrane. The results for the sorption of monobromobenzoic acids from water and from polar and non-polar organic solvents are shown in Table 4-6. *Ortho* and *para* monobromobenzoic acids extracted much better from cyclohexane and hexane than from water. The *meta* isomer extracted equally well from the non-polar organic solvents as from water. Extraction from acetonitrile was very low for all benzoic acids studied, and no extraction of monobromobenzoic acids occurred from ethyl

acetate.

Table 4-6. Extraction of monobenzoic acids from various solvents

Compound	% E				
	Water	Hexane	Cyclohexane	Acetonitrile	Ethyl Acetate
o-Bromobenzoic acid					
Ether	2 ± 1	50 ± 3	38 ± 3	7 ± 1	0 ± 0
Ester	0 ± 0	36 ± 3	26 ± 2	4 ± 1	0 ± 0
m-Bromobenzoic acid					
Ether	28 ± 2	29 ± 2	30 ± 3	5 ± 1	0 ± 0
Ester	15 ± 2	15 ± 2	16 ± 2	0 ± 0	0 ± 0
p-Bromobenzoic acid					
Ether	18 ± 2	27 ± 2	30 ± 3	2 ± 1	0 ± 0
Ester	8 ± 1	12 ± 1	21 ± 2	0 ± 0	0 ± 0

Conditions: 25.0 ± 2.0 °C, 10-mL aliquot of ≈ 3×10^{-4} M organic and aqueous monobromobenzoic acid solutions (pH 3.27, 3.43, and 3.54 for *o*-, *m*-, *p*-isomers respectively), 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2, n = 3

Acetonitrile is a polar aprotic solvent with a strong dipole. This solvent has a low hydrogen bond acceptor strength and promotes ionization of benzoic acids which can result in ion-pairing and formation of homoconjugated species such as RCOOH....-OCOR[15]. The

low extraction of monobromobenzoic acids from acetonitrile can therefore be partially accounted for by the formation of ionic and dimeric molecules. Ethyl acetate is also a polar aprotic solvent, but unlike acetonitrile it can engage in hydrogen-bonding interactions. No extraction of benzoic acids occurred out of this solvent probably due to the stronger intermolecular hydrogen-bonding between the solvent and benzoic acids than between benzoic acids and the membrane.

Unlike acetonitrile and ethyl acetate, water is a protic solvent with a high dielectric constant. It can function in hydrogen-bonding both as donor and as acceptor, and its dielectric constant is high enough to exclude ion-pair formation[16]. Because benzoic acids are weak acids, they dissociate in water to some extent. *Meta* and *para* monobromobenzoic acids have lower K_a values than *ortho* monobromobenzoic acid and extracted well from water probably because the majority of their molecules are neutral species in water. *Ortho* monobromobenzoic acid is the strongest acid, and therefore it dissociates to the highest extent in aqueous solution which can account for its very low sorption.

Cyclohexane and hexane are inert solvents of low dielectric constant and prevent ionization of benzoic acids[16]. These solvents are poor at solvating anions and forming hydrogen bonds. *Ortho* monobromobenzoic acid is less ionized in hexane and cyclohexane than it is in water or in the polar organic solvents. Furthermore, because the *ortho* isomer carries more localized polarity, it is less likely to interact with hexane through hydrophobic interactions, and consequently it was observed to partition preferably into the more polar membrane. *Para* monobromobenzoic acid also showed increased extraction from hexane and cyclohexane as compared to that from water and the polar organic solvents. Again, this

indicates that the hydrogen-bonding interactions between the benzoic acid molecules and the membrane domains are stronger than the hydrophobic interactions with hexane or cyclohexane. Sorption of *meta* monobromobenzoic acid from water and from the non-polar organic solvents was similar which suggests that the solubilities of this benzoic acid isomer in water and in hexane and cyclohexane are comparable.

4.2.7. Effect of temperature on extraction

During the sorption process, the benzoic acid molecules partition between the solution and the polyurethane membrane. As with the phenols, the partitioning of benzoic acid between the two media can be mathematically expressed as a distribution ratio, which is a ratio of the equilibrium concentration of benzoic acid in solution, K_s, to the concentration in the membrane, K_m. This ratio changes with temperature because the solubility of benzoic acid in the two phases changes with temperature. Extraction of organic molecules from liquids into solids is conventionally represented as standard affinity, Δa°, and it is interchangeable with Gibbs free energy, ΔG[17]. The free energies of benzoic acid in the membrane and in aqueous solution are equal at equilibrium[17] and can be used to calculate the partition ratio, K (2):

$$-(a_m - a_s) = -\Delta a^{\circ} = RT \ln [K_m] - RT \ln [K_s] = RT \ln [K_m] / [K_s] = RT \ln K \qquad (2)$$

The heat (ΔH°) and entropy (ΔS°) of sorption can be calculated from the partition ratios at two different temperatures or over a temperature range[18] with the assumption that ΔH° and ΔS° are independent of temperature (i.e., if a plot of log K vs. 1 / T is a straight line).

$$\Delta H^\circ = -2.303\ R\ T_1T_2 / (T_2-T_1)\ \log K_1 / K_2 \quad (3)$$

$$\Delta S^\circ = -2.303\ R\ \log K_1 / K_2 \quad (4)$$

where T_1 and T_2 are the two temperatures, and K_1 and K_2 are the partition ratios.

The percent removal of monobromobenzoic acids from solution by the polyurethane membrane was measured after 24 h (at which equilibrium has been attained) at 4°, 10°, 25°, 37°, and 55°C. The results of extractions using the ether- and the ester-type membranes are shown in Table 4-7. The plots of log K vs. 1 / T for *ortho*, *meta* and *para* monobromobenzoic acids extracted with the ether- and the ester-type membranes at various temperatures are shown in Fig. 4-2 and Fig. 4-3 respectively. K, ΔH°, and ΔS° calculated for extractions of monobromobenzoic acids with both membrane types are shown in Table 4-8.

Extractions of all monobromobenzoic acid isomers with the ether-type membrane showed a gradual decrease in % E with an increase in temperature (Table 4-7). Both ΔH° and ΔS° for these extractions are negative (Table 4-8). The negative entropy obtained for extraction of benzoic acids with the ether-type membrane indicates that the freedom of motion of benzoic acids is more restricted in the membrane than in solution. Because the

sorption process involves a decrease in free energy, ΔH° can also expected to be negative which is confirmed by the data.

Table 4-7. Effect of temperature on extraction

Compound	% E				
	4°C	10°C	25°C	37°C	55°C
o-Bromobenzoic acid					
Ether	25 ± 3	21 ± 3	20 ± 2	17 ± 2	14 ± 2
Ester	2 ± 1	2 ± 1	6 ± 1	7 ± 1	2 ± 1
m-Bromobenzoic acid					
Ether	55 ± 2	50 ± 2	45 ± 2	36 ± 2	31 ± 2
Ester	15 ± 1	17 ± 1	23 ± 1	19 ± 1	14 ± 2
p-Bromobenzoic acid					
Ether	52 ± 2	48 ± 2	41 ± 2	32 ± 2	26 ± 2
Ester	14 ± 1	17 ± 1	23 ± 1	18 ± 1	14 ± 1

Conditions: 10-mL aliquot of ≈ 3×10^{-4} M aqueous monobromobenzoic acid solutions having 0.01 M HCl final concentration, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2, n = 3, temperature ± 1.0 C

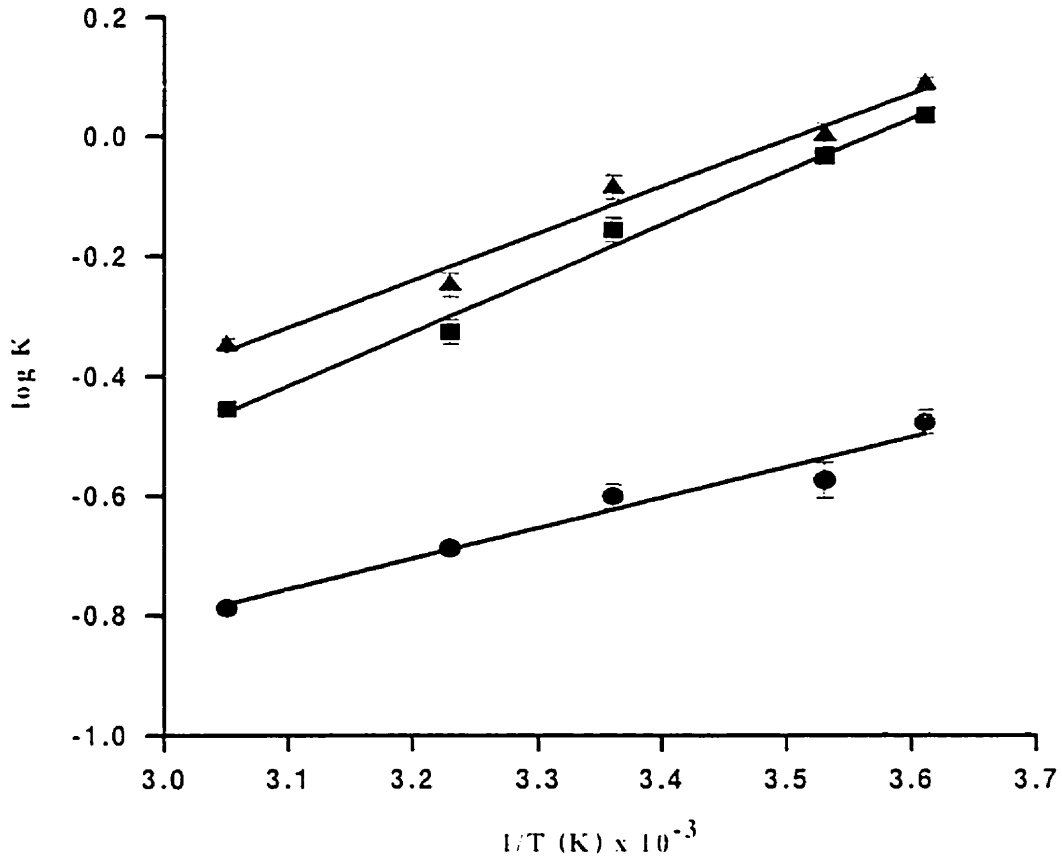

Fig. 4-2. Change in partition ratio with change in temperature for extraction of monobromobenzoic acids using the ether-type polyurethane membrane. Extraction equilibrium was reached after 24 h
Monobromobenzoic acids: ● *ortho-*, ▲ *meta-*, ■ *para-*

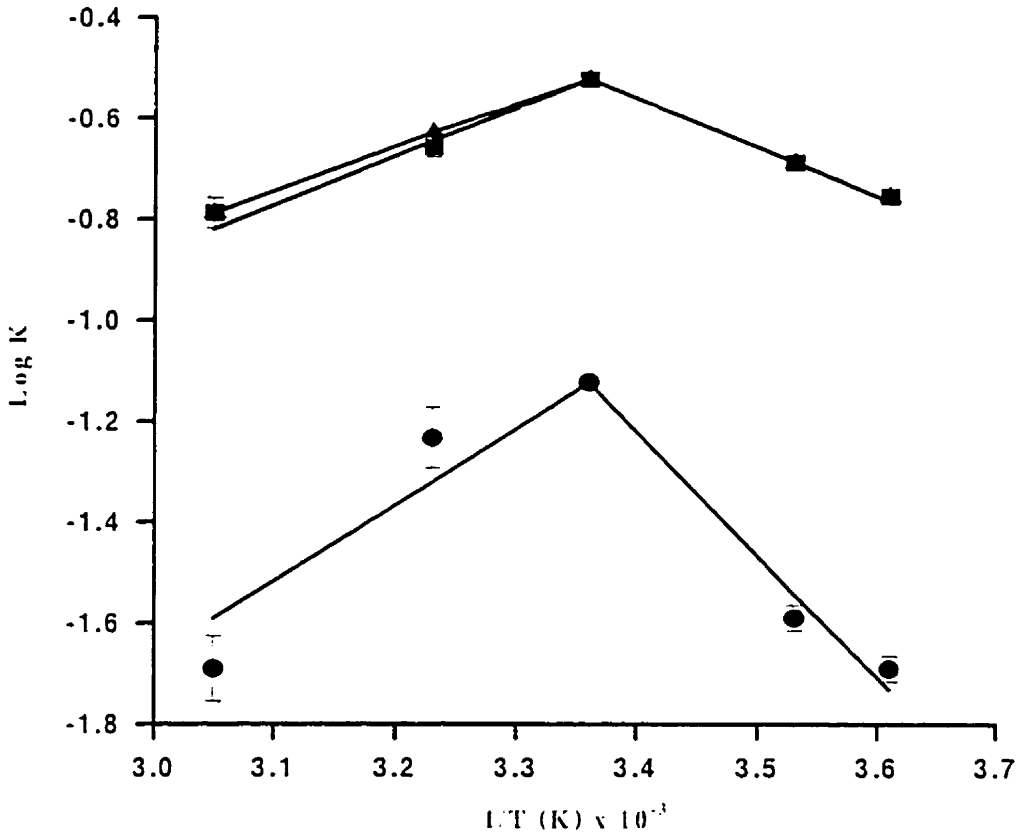

Fig. 4-3. Change in partition ratio with change in temperature for extraction of monobromobenzoic acids using the ester-type polyurethane membrane. Extraction equilibrium was reached after 24 h
Monobromobenzoic acids: ● *ortho-*, ▲ *meta-*, ■ *para-*

Table 4-8. Partition ratio, enthalpy, and entropy change for extraction of monobromobenzoic acids

Compound	K_1 / K_2	ΔH° (KJmol^{-1}l)	ΔS° (Jmol^{-1}K^{-1})
o-Bromobenzoic acid			
Ether			
4-55 °C	2.043	-11.56	-5.94
Ester			
4-25 °C	0.271	42.68	10.86
25-55 °C	3.691	-41.81	-10.86
m-Bromobenzoic acid			
Ether			
4-55 °C	2.722	-16.20	-8.33
Ester			
4-25 °C	0.589	17.30	4.40
25-55 °C	1.834	-19.42	-5.04
p-Bromobenzoic acid			
Ether			
4-55 °C	3.085	-18.22	-9.37
Ester			
4-25 °C	0.589	17.30	4.40
25-55 °C	1.834	-19.42	-5.04

Conditions: 10-mL aliquot of ≈ 3 x 10^{-4} M aqueous monobromobenzoic acid solutions having 0.01 M HCl final concentration, 0.051 mm ether- and ester-type membranes, active surface area of 2.54 cm^2, temperature ± 1.0 °C

Since the sorption of monobromobenzoic acids by the ether-type membrane is an exothermic process then, by applying LeChatelier's principle, the extraction (under equilibrium

conditions) can be expected to decrease with increasing temperature which was observed. Furthermore, as the temperature increases, the physical structure of the membrane matrix changes. As is demonstrated by the thermal transitions for the membrane exposed to a 60 °C solution (DSC data, Table 7-2), at higher temperature the soft and the hard segments in the membrane matrix become less segregated than for membranes exposed to a lower temperature (e.g. XPR at 4 °C, Table 7-2) which can affect the ability of the membrane domains to engage in stable hydrogen-bonding with benzoic acid molecules and in turn results in a lower extraction.

Extractions of monobromobenzoic acids with the ester-type membrane showed an extraction maximum at 25 °C, and a slight decrease at higher and lower temperatures (Table 4-7, Fig. 4-3). Two sets of data corresponding to two straight line plots for which equations (5) and (6) are valid at equilibrium are displayed in Table 4-8. The calculated enthalpy and entropy for extractions done over the 4°C to 25 °C range are positive and for the 25 °C to 55°C range, both are negative. A possible explanation is that at low temperatures, the ester membrane groups interact more strongly with each other, and therefore are not fully available for intermolecular interactions with the benzoic acid molecules. As the temperature increases, some of these interactions among the membrane domains may be weakened due to the increased energy of the individual segments. As a result, the domains are more available for interactions with benzoic acids in solution. However, because hydrogen-bonding interactions are weak and easily broken[19], at very high temperatures such interactions may not be stable, and therefore a decrease in extraction was observed. These observations agree with the results on the extraction of substituted phenols by the

polyurethane membrane and are supported by the DSC data (Chapter 7).

4.3. Conclusion

The sorption process of *ortho*, *meta* and *para* monobromobenzoic acids by the polyurethane membrane is governed by the strength of intermolecular hydrogen-bonding interactions. A combination of factors such as the physical structure of the membrane, solution conditions, the extracting species characteristics, the solvent type, and the solution temperature collectively influence the strength of the intermolecular interactions formed between the membrane domains and the benzoic acid molecules. All of benzoic acids are sorbed to a higher extent by the ether-type polyurethane membrane than the ester-type membrane. This is attributed to the stronger hydrogen-bonding occurring between the benzoic acid molecules and the ether segments of the membrane than the ester segments and to a higher segregation degree of the ether-type membrane domains. The benzoic acids must exist as neutral molecules in solution in order to be extracted by the membranes. This conclusion is supported by the pH effects on the extraction of benzoic acids from aqueous solution and by the extraction of benzoic acids from organic solvents. The extraction efficiency of the monobromobenzoic acid isomers from organic solvents is comparable to that from water only when the interactions of benzoic acids with the solvents are weaker than with the membrane and when no ionization of the benzoic acid molecule is taking place. For example, all of the isomers were observed to extract well from the non-polar organic solvents

but very poorly from the polar organic solvents. Benzoic acid having the substituent in the *ortho* position extracted more poorly from water than the *meta* and *para* isomers. This is attributed to the localized charge in the *ortho* compound which makes it more polar, and to the decreased possibility of engaging in interactions with the membrane domains due to steric effects. This is supported by the data for extractions of *ortho* monobromobenzoic acids from water and from polar and non-polar organic solvents. Sorption of benzoic acids by the ether-type membrane decreased when temperature was increased, and sorption by the ester-type membrane reached a maximum at room temperature and decreased at both lower and higher temperatures. The differences in the sorption obtained with the two membrane types most likely result from the differences in the chemical and microcrystalline structure of the two membranes and thus the variable strength of the intermolecular interactions formed among the membrane domains at the different temperatures (Chapter 7). The extraction of benzoic acids by the polyurethane membrane shows support for the mechanism proposed for the extraction of various phenols. An understanding of the factors governing the sorption of organic compounds can allow easier developments in the useful applications of the polyurethane membrane.

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Chapter 5: Transport of Organic Dyes Through Ether-Type Polyurethane Membranes

5.1. Introduction

The data collected from studying the extraction of phenols[1] and benzoic acids[2] by the polyurethane membrane show that this polymer can remove simple organic compounds from solution by hydrogen-bonding with the species in solution. To determine whether the size and the polarity of an organic compound have an effect on the sorption process by the polyurethane membrane, the extraction of various organic dyes having diverse structures and morphologies was studied. In existing industrial purification operations, the removal of organic dyes from waste effluents is accomplished primarily by using activated carbon as an adsorbent. However, this process is relatively ineffective due to a large difference in the polarities of the activated carbon and the dyes. Consequently, waste effluents containing organic dyes are very difficult to treat in industrial and environmental systems[3]. The purification of dye-containing effluents using membrane technology is not yet fully operational on the industrial scale due to the complex chemical nature of these effluents. In order to mimic industrial membrane separation processes more closely, transport of dyes through the polyurethane membrane and into a receiving solution was studied in addition to investigating the extraction of these compounds. An understanding of the extraction process

of phenols and benzoic acids made it possible to optimize the initial extraction solution conditions for the larger and more complex dyes. However, the factors affecting transport of the dyes through the polymer and their desorption into the receiving solution had to be fully investigated. Overall, this study provides further insight into the mechanism of sorption of organic compounds by the polyurethane membrane. This research also demonstrates that the polyurethane membrane can be utilized to effectively remove and recycle textile colorants in an experimental setup which resembles an industrial membrane separation process.

5.2. Results and Discussion

5.2.1. Effect of the solution pH on transport of organic dyes through the polyurethane membrane

The study of sorption of phenols and benzoic acids by the polyurethane membrane shows that two conditions must be met in order for extraction to occur. First, the organic compound must be transferred from solution into the membrane surface. Second, after the initial sorption has occurred, more of this compound can be removed from solution only if the species in the membrane surface can migrate deeper into the polymer. An increase in the degree of sorption occurs until the membrane becomes saturated. The extraction of phenols and benzoic acids shows that the polyurethane membrane can only retain uncharged organic species. Furthermore, the information on the extraction mechanism of phenols and benzoic

acids suggests that it can be possible to increase the amount of the organic compound removed from the starting solution if the extracted compound can be desorbed from the membrane into a receiving solution. To test this hypothesis, the transport of a series of organic dyes (Table 2-2) which are representatives of the dyes frequently used in the textile industry[4,5] was investigated.

The solution conditions chosen for these dyes were such that the majority of the dye molecules existed as a single form, either as charged or as neutral species. Both 1.0 M HCl and 1.0 M NaOH solutions were used for the extraction and transport of the anthraquinone dyes Alizarin and Alizarin Red S, all of the acidic dyes, and the basic dye Wool Green S. The anthraquinone dye Disperse Blue 14 is insoluble in a basic solution, and therefore it was tested only in 1.0 M HCl. The basic dye Victoria Blue R is also insoluble in a basic solution but it dissolves in water (pH ~5.0) and in 1.0 M HCl. Table 5-1 shows the qualitative results for the extraction and transport of the selected dyes from the corresponding starting solutions. The receiving solution for each dye had a similar acidity or basicity to the starting dye solution. The color of each dye in the starting solution, in the receiving solution, and in the membrane corresponds to the type of species present (i.e., charged vs. uncharged). The anthraquinone and the acidic dyes (with the exception of Methyl Orange) extracted and transported from an acidic solution but not from a basic solution. The acidic Methyl Orange and the basic dye Wool Green S showed no extraction or transport from either solution used. Basic Victoria Blue R extracted and transported from water but not from an acidic solution.

Table 5-1. Qualitative analysis of the transport of anthraquinone, acidic and basic organic dyes

Dye	Dye in Starting Solution		Dye in Receiving Solution	Dye in Membrane
Anthraquinone				
Alizarin	1.0 M HCl:	yellow	yellow	yellow
	1.0 M NaOH:	violet	none	none
Alizarin Red S	1.0 M HCl:	light yellow	light yellow	light yellow
	1.0 M NaOH:	purple	none	none
Disperse Blue 14	1.0 M HCl:	pink	pink	blue
Acidic				
Solvent Yellow 2	1.0 M HCl:	red	red	red
	1.0 M NaOH:	yellow	none	none
Methyl Red	1.0 M HCl:	red/pink	red/pink	red/pink
	1.0 M NaOH:	yellow	none	none
Methyl Orange	1.0 M HCl:	red	none	none
	1.0 M NaOH:	yellow	none	none
Alizarin Yellow GG	1.0 M HCl:	orange	orange	orange
	1.0 M NaOH:	yellow	none	none
Eriochrome Black T	1.0 M HCl:	burgundy	burgundy	burgundy
	1.0 M NaOH:	yellow	none	none
Martius Yellow	1.0 M HCl:	light yellow	yellow	yellow
	1.0 M NaOH:	orange	none	none
Naphthol Yellow S	1.0 M HCl:	light yellow	light yellow	light yellow
	1.0 M NaOH	dark yellow	none	none
Basic				
Victoria Blue R	1.0 M HCl:	yellow	none	none
	Water:	blue	blue	blue
Wool Green S	1.0 M HCl:	green	none	none
	1.0 M NaOH:	blue	none	none

Conditions: 25.0 ± 2.0 °C. 250-mL of ≈ 1.9 x 10^{-5} M dye solution in the starting cell. 250-mL of solvent in the receiving cell. 0.025 mm thick ether-type membrane. surface area of 23.8 ± 0.2 cm^2

In 1.0 M HCl, the anthraquinone dyes that have acidic substituents, e.g., Alizarin and Alizarin Red S, are neutral. During extraction and transport of these dyes from an acidic solution, the membrane had the same color as the starting dye solutions. In 1.0 M NaOH, Alizarin and Alizarin Red S are negatively charged. No extraction or transport was observed from basic solutions of these dyes. Organic dyes such as Disperse Blue 14 having basic substituents are positively charged in 1.0 M HCl. During the transport of Disperse Blue 14, the starting and the receiving solutions contained the charged species (pink), but the membrane was blue in color. The blue color of Disperse Blue 14 is observed when the dye molecules are uncharged (e.g., when the dye is dissolved in a non-polar solvent such as hexane). The data collected on transport of the anthraquinone dyes suggest that only a neutral form of these dyes is retained by the membrane. Clear visual evidence for this conclusion is the transport of Disperse Blue 14 during which a color change was observed when the dye was transferred from solution into the polymer and *vice versa*.

Similar conclusions can be reached from the extraction and transport of the acid dyes. In 1.0 M HCl, the majority of the acidic dye species are neutral. Similarly to the anthraquinone dyes, the acidic dyes were extracted and transported from and into an acidic solution but not from a basic solution. The acidic dye Methyl Orange, however, was an exception. The lack of extraction of this dye can be accounted for by the high probability that the dye never actually existed as an extractable uncharged species, i.e., the closest instance in which this dye resembled an uncharged species was when it formed a zwitterion. The net charge on the zwitterion is zero, but the individual ends of this species are either positively or negatively charged. Consequently, no initial transfer into the membrane surface could

occur, and hence no subsequent transport into the receiving cell was observed.

Similar reasoning can be used to account for the unextractability of basic Wool Green S. As with Methyl Orange, the probability of Wool Green S being uncharged is unlikely due to the presence of the basic substituents and the sulfonic acid group on the dye molecule. Under acidic conditions, the sulfonic acid group on the dye is neutral, but the amino groups (other than the ion-paired substituent which is not considered to be truly charged because the positive charge is closely associated with the negative ions) may be protonated. The opposite is true in a basic solution. Since no neutral species was formed, there was no extraction and therefore no transport. Basic Victoria Blue R has only basic substituents in addition to the ion-paired quaternary ammonium group. The majority of Victoria Blue R molecules are neutral in water (again, the ion-paired group is not considered to be charged), and therefore this dye was extracted and transported from water. No extraction or transport occurred from 1.0 M HCl due to the presence of the positively charged species.

These results further support the hypothesis that the presence of a neutral species of an organic compound is a deciding factor which determines whether the initial transfer of an organic compound from solution into the membrane surface can take place. After the successful initial sorption, transport through the membrane into a receiving solution can occur only if the receiving solution conditions are favorable for desorption of the organic species from the membrane. For example, the anthraquinone dyes were transported into the acidic receiving solutions but not into water in which they are only sparingly soluble. In conclusion, the transport of organic dyes from one solution into another using the polyurethane membrane as the transporting medium is contingent upon both the initial

sorption of the dye from solution into the polymer surface and the chemical properties of the receiving solution.

5.2.2. Effect of dye geometry, size, and chemical properties on transport through the polyurethane membrane

The first step in the overall transport process (Fig. 5-1) is the transfer of the dye from solution into the membrane surface. It is hypothesized that the efficiency with which this step occurs is dependent on the relative solubilities of the dye in the solvent and in the membrane which result from all the different possible specific and non-specific interactions[6]. After the initial sorption has taken place, the ability of the sorbed species to separate the individual segments of the polymer and migrate deeper into the polymer bulk is largely driven by the strength and the extent of the intermolecular interactions that can take place between the species and the constituent groups in the hard and the soft segments of the polymer[1,2]. Because all of the dyes used in this study are relatively non-polar with aromatic rings which are also found in the matrix of the membrane and with substituents capable of intermolecular interactions, they should be soluble in this polymer. The remainder of this discussion is referring to the neutral form of the dyes since it is the only species that is retained by the membrane. Based on what is known about the extraction and transport within the polyurethane membrane matrix, it can be anticipated that the rate of transport of the dye from the starting solution into the receiving solution may be affected by the morphology and the chemical characteristics of the dye molecule.

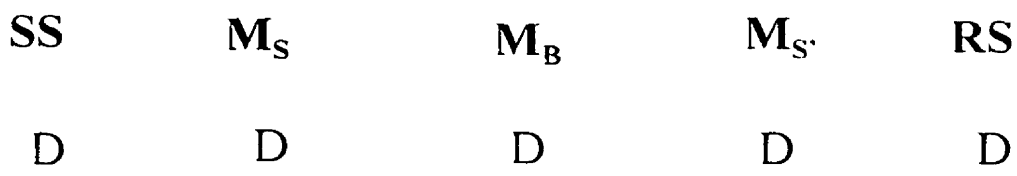

Fig. 5-1. A pictorial representation of transport of an organic dye through a polyurethane membrane

SS is the starting solution, **D** is the neutral dye species, $\mathbf{M_S}$ is the membrane surface on the starting solution side, $\mathbf{M_B}$ is the membrane bulk, $\mathbf{M_S}$ is the membrane surface on the receiving solution side, **RS** is the receiving solution

To test this hypothesis, the dyes were dissolved in the solvent from which extraction and transport occur (Table 5-1) to give a concentration of 1.9×10^{-5} M. The ether-type 0.025 mm thick polyurethane membrane was used in all instances. The results reported in Table 5-2 show the time at which no further change was measured in the receiving and the starting cells, the % dye that was detected in each of the cells at that time, and the % dye that was

calculated to be in the membrane.

Table 5-2. Effect of dye morphology and chemical properties on the rate of transport

Dye	Time (h)	% Dye in Starting Cell	% Dye in Receiving Cell	% Dye in Membrane
Anthraquinone				
Alizarin	163	48 ± 3	42 ± 4	10 ± 3
Alizarin Red S	929	50 ± 3	45 ± 3	5 ± 3
Disperse Blue 14	147	47 ± 1	46 ± 1	7 ± 1
Acidic				
Solvent Yellow 2	235	54 ± 1	45 ± 1	1 ± 1
Methyl Red	183	18 ± 2	15 ± 2	65 ± 1
Alizarin Yellow GG	240	14 ± 3	5 ± 2	81 ± 2
Eriochrome Black T	216	39 ± 3	15 ± 4	46 ± 3
Martius Yellow	43	29 ± 3	29 ± 3	42 ± 3
Naphthol Yellow S	408	90 ± 1	8 ±3	2 ± 1
Basic				
Victoria Blue R	733	30 ±1	26 ± 1	40 ± 1

Conditions: 25.0 ± 2.0 °C. 250-mL aliquot of ≈ 1.9×10^{-5} M aqueous dye solution in the starting cell in a solvent from which transport occurred (Table 5-1). 250-mL aliquot of solvent (identical to that in the starting cell) in the receiving cell. 0.025 mm thick ether-type membrane, n = 3, active surface area of 23.8 ± 0.2 cm^2

Unlike the other dyes, Eriochrome Black T and Naphthol Yellow S showed significantly lower concentrations in the receiving cell than in the starting cell at the reported times. This suggests that the transport of the two dyes must be very slow and therefore any change in the solution concentration at the time of measurement may be too small to detect. Dyes such as Alizarin, Disperse Blue 14 and Solvent Yellow 2 were not well retained by the membrane but were quite efficiently transported. Other dyes such as Methyl Red, Alizarin Yellow GG, Eriochrome Black T, Martius Yellow, and Victoria Blue R were very well retained and transported through the polyurethane membrane. Alizarin Red S and Naphthol Yellow S were very poorly extracted and transported by this polymer.

The dyes which showed very inefficient extraction and transport (Alizarin Red S and Naphthol Yellow S) are small, compact and both have a single sulfonic acid substituent (Table 2-2 A and B). Because of the small size of these dyes, the effect of the individual substituents on the chemical characteristics of the entire dye molecule is more significant than it would be for a larger dye. Thus, in the case of Alizarin Red S and Naphthol Yellow S, the presence of the sulfonic acid group imparts more polarity to both compounds. The relatively polar character of these dyes hinders an efficient initial sorption into the membrane surface and results in a very slow transport into the receiving solution. The dyes which were effectively retained and transported by the membrane are generally non-polar in nature (Table 2-2 B and C). For example Eriochrome Black T, in spite of having the sulfonic acid substituent group in its structure, remains quite non-polar because of a greater overall number of non-polar aromatic rings. Unlike Alizarin Red S and Naphthol Yellow S, this dye was sorbed and transported quite efficiently. Martius Yellow, which has a chemical structure

identical to that of Naphthol Yellow S (Table 2-2 B) but lacks the sulfonic acid group, was highly retained by the membrane and very quickly transported. This again indicates that it is the resultant polarity of the dye molecule (and therefore the solubility) and not the polarity of the individual substituents that plays a more important role in the transport process. Dyes which showed high extraction and efficient transport are quite diverse in geometry and size. Examples are large non-linear dyes such as Eriochrome Black T and Victoria Blue R, smaller linear Methyl Red and Alizarin Yellow GG, and even smaller Martius Yellow (Table 2-2). Based on the above observations, it can be concluded that the morphology and size of the dye alone are not important in controlling the transport process, i.e., the % concentration of the linear dyes, Methyl Red and Alizarin Yellow GG, in the membrane was significantly higher than that of, for example, Eriochrome Black T or Martius Yellow. This can be accounted for by the presence of the carboxylic acid groups on both Methyl Red and Alizarin Yellow GG which are also found in the polymer matrix. The presence of the carboxylic acid groups increases the probability for the occurrence of more hydrogen-bonding interactions between the dye and the polymer and increases the solubility of the dye in the polymer matrix. These results support the hypothesis on the importance of the intermolecular interactions in the sorption by the polyurethane membrane. Dyes such as Alizarin, Disperse Blue 14 and Solvent Yellow 2 (Table 2-2 A and B) were not well retained by the membrane, but they were transported quite efficiently. These dyes are capable of forming hydrogen bonds and are relatively non-polar. The low concentration of these dyes in the membrane, in spite of their effective transport, is probably a result of their relative solubility in the solvent and in the polymer. The strength of hydrogen-bonding of the dyes with the solvent

must have been slightly higher than with the polymer and therefore preferential partitioning of these dyes into the aqueous phase was observed.

In conclusion, the rate of transport is not controlled by the geometry or size of the dye molecule but rather by the relative solubility of the dye in the polymer and in the solvent which partially results from the strength and the extent of the intermolecular interactions with the polymer and the solvent. These findings are in agreement with the conclusions reached from the study of the mechanism of extraction of phenols and benzoic acids by the polyurethane membrane.

5.2.3. Dependence of the rate of transport on thickness of the polyurethane membrane

The relationship between the thickness of the polyurethane membrane and the rate of transport of the dye molecules through this polymer is exemplified by the transport of 1.9 x 10^{-5} M Disperse Blue 14 in 1.0 M HCl starting solution into 1.0 M HCl receiving solution using 0.025 and 0.051 mm thick ether-type polyurethane membranes. Fig. 5-2 and Fig. 5-3 show the time taken to achieve equilibrium between the starting cell, the receiving cell and the membrane when the 0.025 and 0.051 mm thick membranes were used respectively. Equilibrium was reached within about 195 h with the 0.025 mm thick membrane and within 219 h with the 0.051 mm thick membrane. At the observed equilibrium, the 0.025 mm thick

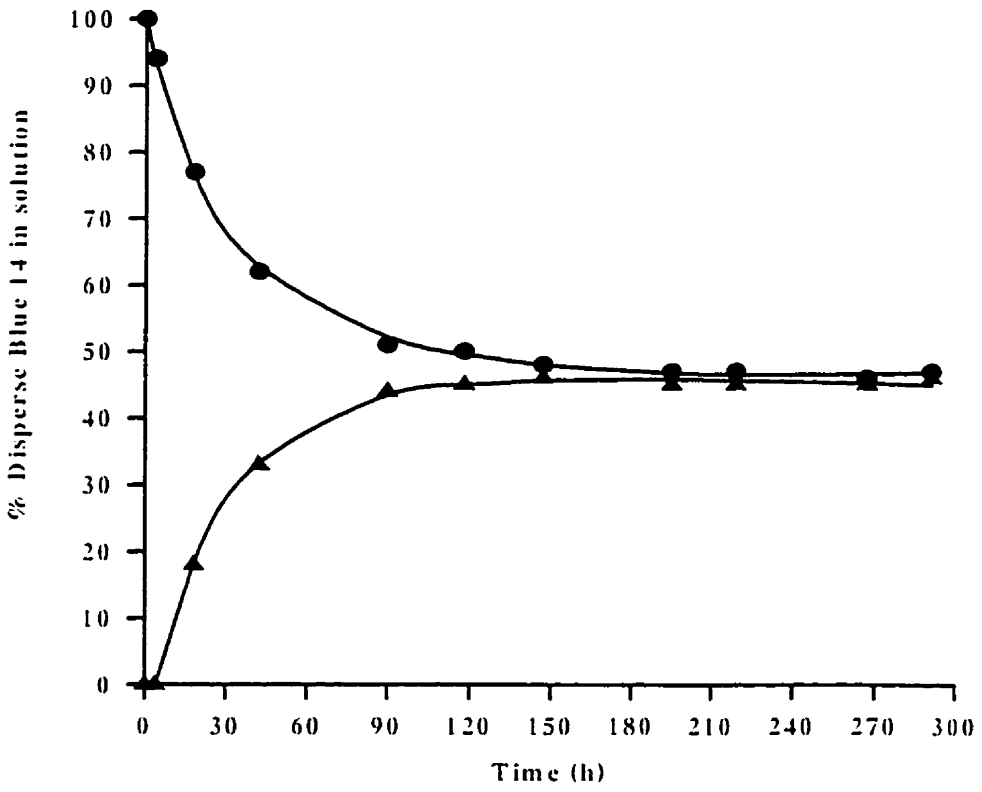

Fig. 5-2. Transport of Disperse Blue 14 through 0.025 mm thick ether-type polyurethane membrane. Conditions: 25.0 ± 2.0 °C. 250-mL aliquot of ≈ 1.9×10^{-5} M aqueous dye solution in 1.0 M HCl in the starting cell. 250-mL aliquot of 1.0 M HCl in the receiving cell. 0.025 mm thick ether-type membrane. active surface area of 23.8 ± 0.2 cm^2. Decrease in dye concentration in the starting cell. ●: increase in dye concentration in the receiving cell. ▲

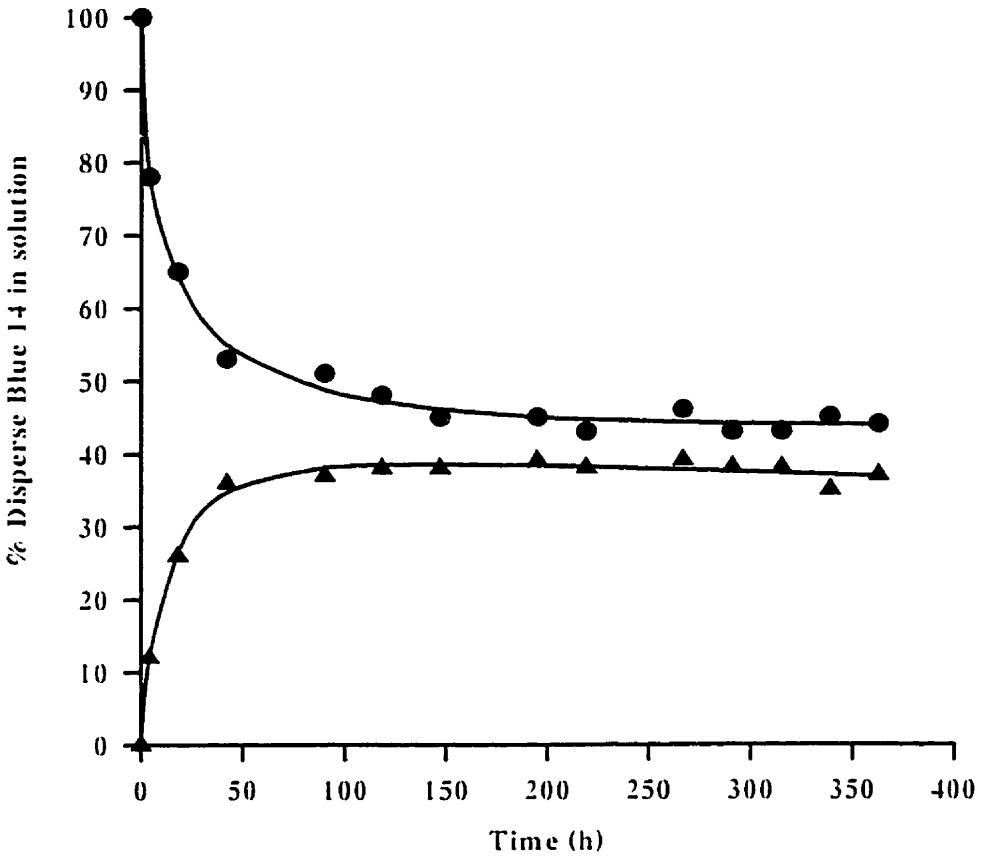

Fig. 5-3. Transport of Disperse Blue 14 through 0.051 mm thick ether-type polyurethane membrane. Conditions: 25.0 ± 2.0 °C. 250-mL aliquot of ≈ 1.9×10^{-5} M aqueous dye solution in 1.0 M HCl in the starting cell, 250-mL aliquot of 1.0 M HCl in the receiving cell, 0.051 mm thick ether-type membrane, active surface area of 23.8 ± 0.2 cm^2. Decrease in dye concentration in the starting cell, ●; increase in dye concentration in the receiving cell, ▲

membrane contained 6 ± 2 % of the starting concentration of the dye, and the 0.051 mm thick membrane contained 19 ± 1 % of the initial dye solution concentration. The masses corresponding to the active surface (23.8 ± 0.2 cm^2) of 0.025 mm and 0.051 mm thick membranes prior to being exposed to the dye were approximately 0.120 g and 0.235 g respectively.

An attempt was made to determine the overall diffusion coefficient for the transport process. At a steady state, the diffusion coefficient can be evaluated by using a so-called "time-lag" method[7,8]. Initially, in the non-stationary state, the amount of dye, Q, diffusing through the membrane is mathematically represented by

$$Q = F\,\Delta x\,C_A\left[\frac{D_t}{\Delta x^2} - \frac{1}{6} - \frac{2}{\pi_n^{\,2}}\sum\frac{(-1)^n}{n^2}\exp\frac{\left(-D_n^{\,2}\,n^2\right)}{x^2}\right] \qquad (1)$$

where F is the surface area of the membrane, Δx is the membrane's thickness, C_A is the extractant concentration in the starting solution, n is the number of membrane sheets, D_t is the diffusion coefficient at a certain time, D_n is the diffusion coefficient through n sheets of membrane, π is a constant.

As time increases and the equilibrium is approached, equation (1) can be simplified to

$$Q = \frac{D\,C_A\,F}{\Delta x}\left[t - \frac{\Delta x^2}{6\,D}\right] \qquad (2)$$

If the thickness of the membrane, Δx, and the time, t, taken to reach the steady state ("time-lag") are known, equation (2) can be further simplified which results in equation (3) from which the approximate diffusion coefficient can be calculated[7,8].

$$D = \frac{\Delta x^2}{6\,\Delta t} \qquad (3)$$

The transport of Disperse Blue 14 through the 0.025 mm thick membrane required about 195 h for the dye in the membrane to reach a steady state (i.e., when no further change in the dye concentration was observed in the starting and receiving solutions and in the membrane). The approximate diffusion coefficient calculated using equation (3) is 5.34×10^{-7} mm^2 h^{-1}. The transport of Disperse Blue 14 through the 0.051 mm thick membrane required about 219 h to reach a steady state. The approximate value of the diffusion coefficient is 1.98×10^{-6} mm^2 h^{-1}.

As expected, the overall equilibrium for the transport of Blue 14 was achieved more quickly when a thinner membrane was used. This can be accounted for by the shorter path that the dye has to diffuse through in order to reach the receiving cell solution. The more

quickly the dye appears on the receiving cell side of the membrane, the more rapidly it can be desorbed into the receiving solution. The concentration of the dye in the membrane increases until a steady state is reached where no further change in sorption or transport is observed. The amount of dye in the thinner membrane was calculated to be approximately one third of that in the thicker polymer. The thicker membrane can retain a higher amount of the dye because it has more of the polymer material by weight that is available for interactions with the dye molecules. The calculated diffusion coefficients for the transport are broad approximations of the true values. A true mathematical representation of the entire diffusion is beyond the scope of this work because it is too complex and requires extensive knowledge of differential equations.

5.2.4. Dependence of the rate of transport on the initial dye solution concentration

Disperse Blue 14 and Solvent Yellow 2 were used to study the effect of the initial concentration of the dye on the rate of transport through the polyurethane membrane. The choice of the initial dye concentrations in the sample cells was dictated by the solubility of the dyes in 1.0 M HCl and the detection limit of the UV-visible spectrophotometer. The starting concentrations for both Solvent Yellow 2 and Disperse Blue 14 are 1.9×10^{-6} M and 1.9×10^{-5} M. Table 5-3 and Table 5-4 show the time taken to achieve equilibrium at the two concentrations for both dyes, and the corresponding percentage of each dye in the starting and the receiving cells and in the membrane.

Table 5-3. Effect of the initial concentration of Disperse Blue 14 on the rate of transport

	Initial Concentration of Disperse Blue 14	
	1.9×10^{-6} M	1.9×10^{-5} M
Equilibrium Time (h)	146	146
% Dye in Starting Cell	27 ± 4	48 ± 1
% Dye in Receiving Cell	27 ± 4	45 ± 1
% Dye in Membrane	46 ± 4	7 ± 1

Conditions: 25.0 ± 2.0 °C, 250-mL aliquot of aqueous dye solution of appropriate concentration in the starting cell in 1.0 M HCl, 250-mL aliquot of 1.0 M HCl in the receiving cell, 0.025 mm thick ether-type membrane, n = 3, active surface area of 23.8 ± 0.2 cm^2

Table 5-4. Effect of the initial concentration of Solvent Yellow 2 on the rate of transport

	Initial Concentration of Solvent Yellow 2	
	1.9×10^{-6} M	1.9×10^{-5} M
Equilibrium Time (h)	235	235
% Dye in Starting Cell	55 ± 1	52 ± 1
% Dye in Receiving Cell	43 ± 1	47 ± 1
% Dye in Membrane	2 ± 1	1 ± 1

Conditions: 25.0 ± 2.0 °C, 250-mL aliquot of aqueous dye solution of appropriate concentration in the starting cell in 1.0 M HCl, 250-mL aliquot of 1.0 M HCl in the receiving cell, 0.025 mm thick ether-type membrane, n = 3, active surface area of 23.8 ± 0.2 cm^2

Regardless of the starting dye solution concentration, equilibrium was achieved within approximately 146 h for Disperse Blue 14 and within 235 h for Solvent Yellow 2. When 1.9 x 10^{-6} M Disperse Blue 14 solution was extracted, a higher percentage of the dye was retained by the membrane and lower final concentrations were detected in the starting and the receiving solutions than in the extraction of 1.9 x 10^{-5} M solution of this dye. This was not observed for the transport of the corresponding solutions of Solvent Yellow 2.

In the case of the extraction of the less concentrated solution of Disperse Blue 14, although the membrane contained a higher proportion of the original dye from solution, the calculated molar concentration of the dye in the membrane was approximately the same as for the extraction of the more concentrated solution. This indicates that the membrane continues to remove the dye from solution until its capacity for the dye is reached. In the case of Solvent Yellow 2, the capacity of the membrane is probably reached at 2% extraction even with the 1.9 x 10^{-6} M dye solution concentration. Therefore, a change in the percentage of this dye in the membrane was not observable as with the Disperse Blue 14.

To determine whether the polyurethane membrane already containing a dye can be used to transport more dye if a fresh receiving solution is provided, the stepwise removal of Disperse Blue 14 from solution was studied. The starting concentration of Disperse Blue 14 was 1.9 x 10^{-5} M. After equilibrium was achieved between the two cells and the membrane, the molar dye concentrations in both cells and in the membrane were calculated. Next, the receiving cell solution containing the dye was discarded and replaced with new 1.0 M HCl solution. The solutions in both cells were again allowed to come to equilibrium, and the concentrations were calculated. This process was repeated until an instrumental detection

limit for the dye was reached.

The calculated molar concentrations of Disperse Blue 14 in the starting and the receiving cells at equilibrium for each successive sorption are shown in Table 5-5. The concentration of Disperse Blue 14 in the membrane gradually increased during the initial extraction / transport until equilibrium. The membrane dye concentration remained constant for all subsequent extraction / transport experiments regardless of the time at which the measurements were taken and the dye solution concentration used. Furthermore, because the time needed to achieve equilibrium for all extractions was approximately the same, it can be concluded that the transporting properties of the membrane were not affected by the presence of the dye in the matrix. These results show that the membrane can extract the dye until its capacity for the dye is reached (i.e., the solubility limit for the dye in the membrane is reached). In order for this membrane to continue removing the remaining dye in the starting solution, a flow of dye through the membrane into the receiving solution must occur.

Table 5-5. Successive removal of Disperse Blue 14 from aqueous solution

	Dye Concentration in Starting Cell at Equilibrium (M)	Dye Concentration in Receiving Cell at Equilibrium (M)	Dye Concentration in Membrane at Equilibrium (M)
Initial Conditions	1.9×10^{-5}	0	0
Initial Transport	8.9×10^{-6}	8.7×10^{-6}	1.4×10^{-6}
Second Transport	4.3×10^{-6}	3.9×10^{-6}	1.6×10^{-6}
Third Transport	2.1×10^{-6}	2.3×10^{-6}	1.5×10^{-6}

Conditions: 25.0 ± 2.0 °C, 250 mL of dye solution in the starting cell in 1.0 M HCl, 250 mL of 1.0 M HCl in the receiving cell, 0.025 mm thick ether-type membrane, active surface area of 23.8 ± 0.2 cm^2

Note: Initial Conditions represent the initial concentration in the starting cell before any extraction or transport has occurred; the time required to reach equilibrium was approximately 147 h for all transports

5.2.5. Effect of salt on the rate of transport through the polyurethane membrane

Disperse Blue 14 and Solvent Yellow 2 were chosen to illustrate the effect of salt on the rate of transport of the dye through the polyurethane membrane. The extraction efficiency and the time taken to achieve equilibrium for the transport of both dyes (1.9×10^{-5} M) from

1.0 M HCl solutions containing 0.5 M LiCl were compared with the results for solutions without the salt. Aqueous salt solutions without the dye containing 0.5 M and 1.0 M concentrations of NaCl, KCl, RbCl, $CaCl_2$, and $Al_2(SO_4)_3$ in 1.0 M HCl and in water were also tested to determine whether any transport of the cations and / or anions was occurring. The percentages of the dyes in the starting and the receiving solutions and in the membrane at equilibrium for the sample solutions with and without salt are presented in Table 5-6. None of the cations and anions were transported through the membrane from any of the starting salt solutions as confirmed by analysis using atomic absorption spectroscopy. The extraction efficiency of Disperse Blue 14 and Solvent Yellow 2 from the starting solutions containing the salt and the rates of transport into the receiving cells were almost identical within experimental error (which was obtained by looking at the variability in the three readings for each of the dyes) to the corresponding solutions of these dyes without the salt. Furthermore, the presence of salt did not change the saturation amount of either of the dyes that could be retained by the polyurethane membrane.

As discussed in section *5.2.1*, the majority of Disperse Blue 14 species in 1.0 M HCl are positively charged. These positively charged species are, however, at equilibrium with a small percentage of the uncharged molecules of Disperse Blue 14. The opposite is true for the solution of Solvent Yellow 2 in 1.0 M HCl in which the predominant species is the uncharged dye molecule.

Table 5-6. Effect of salt on the rate of transport of Disperse Blue 14 and Solvent Yellow 2

	Equilibrium Time (h)	% Dye in Starting Cell	% Dye in Receiving Cell	% Dye in Membrane
Disperse Blue 14				
No Salt Added	147	48 ± 1	46 ± 1	8 ± 1
0.5 M LiCl	195	48 ± 2	40 ± 2	10 ± 2
Solvent Yellow 2				
No Salt Added	234	52 ± 1	46 ± 1	2 ± 1
0.5 M LiCl	234	58 ± 2	41 ± 2	1 ± 2

Conditions: 25.0 ± 2.0 °C. 250-mL aliquot of ≈ 1.9×10^{-5} M aqueous dye solution in the starting cell in 1.0 M HCl with salt concentration appropriately adjusted. 250-mL aliquot of 1.0 M HCl in the receiving cell. 0.025 mm thick ether-type membrane. n = 3. active surface area of 23.8 ± 0.2 cm^2

When salt is added to solutions containing charged organic species. ion-pair formation can take place[9,11] and the overall solution can become more polar. Because of the increased solution polarity in the presence of salts. a "salting out" effect can be expected where the non-polar uncharged species become more insoluble in the solvent. and therefore partition more efficiently into the non-polar membrane which can be expected to result in a more rapid

extraction and transport of organic compounds through the membrane. Because no significant changes in extraction and transport rates were observed, it can be concluded that the addition of salt did not cause a sufficiently high change in the relative solubility of the dye species in solution and in the membrane. These findings are in agreement with the conclusions from the investigation of the extraction of phenols and benzoic acids by the polyurethane membrane.

5.2.6. Dependence of the rate of transport on the solution temperature

1.9×10^{-5} M solutions of Disperse Blue 14 in 1.0 M HCl were transported into a 1.0 M HCl solution using 0.025 mm polyurethane membrane at 4 °C, 23 °C, 37 °C, and 66 °C. The percentages of Disperse Blue 14 in the starting and the receiving cells and in the membrane at 24 h for each of the temperatures are shown in Table 5-7. The percentage of this dye retained by the membrane was approximately the same at all four temperatures. However, the rates of removal of the dye from the starting cell and the rate of transport into the receiving cell increased with the increase in temperature.

The above results do not correlate with the temperature data that was collected for extraction only of phenols and benzoic acids by the ether-type polyurethane membrane. For the extraction of phenols and benzoic acids, as the temperature increased, the extraction decreased because of the exothermic nature of the extraction process. In this study, however, in addition to extraction, transport into a receiving solution occurred. Unlike the simple extraction, the transport is probably controlled not only by the thermodynamic factors but

also by the concentration gradient created during the process at the membrane-solution interface on the receiving solution side.

Table 5-7. Effect of temperature on the rate of transport of Disperse Blue 14

Temperature (°C)	% Dye in Starting Cell at 24 h	% Dye in Receiving Cell at 24 h	% Dye in Membrane at 24 h
4	88 ± 1	6 ± 1	6 ± 1
23	69 ± 1	24 ± 1	7 ± 1
37	58 ± 1	36 ± 1	6 ± 1
66	45 ± 1	43 ± 1	7 ± 1

Conditions: temperature ± 2.0 °C, 250-ml aliquot of ≈ 1.9×10^{-5} M aqueous dye solution in the starting cell in 1.0 M HCl, 250-mL aliquot of 1.0 M HCl in the receiving cell, 0.025 mm thick ether-type membrane, n = 3, active surface area of 23.8 ± 0.2 cm^2

The fact that the membrane retained approximately the same amount of dye at all of the temperatures suggests that the solubility of the dye in the polymer remained relatively the same. The increased rates of removal and transport of the dye at higher temperatures result from changes in the physical properties of the membrane matrix at those temperatures (see Chapter 7). Due to the higher energy in the membrane segments at the increased temperature, some of the intermolecular interactions among the individual segments within the polymer are weakened or broken; this results in the matrix being more mobile (i.e., more amorphous)

in nature and consequently more accessible to the dye species in solution. Based on the thermal transitions observed at the higher temperatures (e.g., 66 °C, see DSC analysis in Chapter 7), it can be concluded that the dye sorbed in the surface can migrate more freely through the bulk of the polymer and into the receiving solution. This is also evidenced by the significantly shorter time in which equilibrium was achieved (e.g., within 146 h at 23 °C vs. 24 h at 66 °C).

5.3. Conclusion

The rate at which the various organic dyes transport through the ether-type polyurethane membrane is dependent on the solution pH, the overall polarity and capability of the dye molecule to engage in hydrogen-bonding interactions with the polymer, the relative solubility of the dye in the polymer and in the solvent, and the solution temperature at which the transport is occurring.

In order to obtain an initial transport through the bulk of the membrane, the pH of the starting solvent must be favorable for the formation of a neutral species which is the only type of species soluble in the membrane. Furthermore, a flow of the species through the membrane into the receiving solution is observed only if a driving force resulting from the differences in dye concentration in the starting and receiving solutions and in the membrane (or a concentration gradient) is present. The rate of transport is dependent on the chemical factors such as the efficiency with which the dye can partition into the membrane surface and then migrate through the membrane bulk, and on the physical experimental conditions such

as the temperature. For example, compounds with comparable solubility in the polymer and in solution were transported from the starting cell into the receiving cell quite efficiently. On the other hand, if the solubility of the compound was relatively higher in one of the media, the transport may have been hindered due preferential partitioning. The partitioning of the dye between the solution and membrane surface phases and the rate of migration through the bulk of the membrane can be significantly altered by changing the temperature. The rate of transport of the dyes through the polyurethane membrane increased when higher temperatures were used. The increase in the transport rate at increased temperatures can be accounted for by change in the physical properties of the membrane matrix which becomes more amorphous, and therefore more accessible to the dye species in solution. Overall, the results from this study provided a deeper insight into the mechanism of extraction and transport process of organic compounds by the polyurethane membrane and showed that this membrane has considerable potential in commercial applications for the removal of organic compounds from aqueous solutions.

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Chapter 6: Extraction of Metal-Dye Ion-Association Complexes by Thin Ether-Type Polyurethane Membranes

6.1. Introduction

The vast majority of basic organic dyes are usually synthesized as salts. Consequently, in aqueous solution, the basic dyes are found as ion-pairs which are formed between the cation and the anion constituents of the dye molecule. The organic dyes chosen for this study are representatives of basic dyes from the thiazine, xanthene and triphenylmethane groups (Fig. 1-12) which are known to complex various metal ions, particularly the gold (III) chloride anion[1,2]. The basic dyes are frequently referred to as cationic dyes because the coloured part of the salt is a cation. The positive charge, however, can be associated with two different atoms on the dye structure. All of the groups of dyes mentioned above have positively charged amine substituents but, depending on the dye structure, the charge can also be found on another atom in the dye molecule[3]. For example, the thiazine dyes can be positively charged at the sulfur atom, the xanthene dyes can have a positive charge on the ring carbon, and the triphenylmethane dyes can have a positive charge on the central carbon. Because the charge can be within the ring in the xanthene and the thiazine cations, these dyes have more rigid structures than the triphenylmethane cations. The associated anion can be either a simple chloride or a more complex ion.

Although the polyurethane membrane has been used to remove the individual inorganic and organic compounds from solution, the feasibility of extracting large organometallic ion-association complexes has not been investigated. Gold has been shown to extract into the polyurethane membrane but only under highly acidic conditions which cause degradation of the membrane. The sorption of organometallic ion-pairs of gold (III) chloride and organic dyes, on the other hand, is feasible under mild solution conditions in which no degradation of the polymer occurred. This study further extends the understanding of the mechanism involved in the extraction of both organic and inorganic species from solution and can have potential applications for the removal of gold from aqueous solutions.

6.2. Results and Discussion

6.2.*1. Effect of salt*

The effect of salt on the sorption of ion-association complexes of the thiazine, Methylene Blue, the xanthene, Rhodamine B, and the triphenylmethane, Brilliant Green with the gold chloride species was studied by extracting the sample solutions from a 1 M NaCl starting solution into a 1 M NaCl receiving solution. First, the individual sorption of each dye and the gold species under these conditions was investigated. Extraction and transport of each organic dye from and into 1 M NaCl occurred quite readily. On the other hand, no extraction or transport of gold chloride was observed from 1 M NaCl solution. Next, the

sorption of solutions containing both the gold chloride species and one of the dye species together in solution was studied. Only in the presence of dyes was the extraction and transport of gold from 1 M NaCl possible (Table 6-1).

Previous work on the sorption of organic and inorganic compounds by the polyurethane membrane demonstrated that only neutral or uncharged species can be sorbed by this polymer[4-8]. The presence of salt favours the formation of a negatively charged complex ($AuCl_4^-$) which can account for the unextractability of gold from 1 M NaCl solution. In salt solution, the dye molecules are positively charged and associated with the negatively charged chloride as the counter-ion. As a result, the overall dye species is an uncharged ion-pair which can be extracted by the polymer. As shown in Table 6-1, the removal of Methylene Blue from the starting salt solution and its transport into the receiving salt solution was relatively slow as compared to those observed for Rhodamine B and Brilliant Green. The retention of Brilliant Green in the membrane was 57 % of the original solution concentration and that of Rhodamine B was 30 %, whereas only 1 % of Methylene Blue was retained in the polymer matrix. Methylene Blue is the most polar of the three dyes, therefore its transfer from the relatively polar aqueous solution into the non-polar membrane was not very efficient although it did occur to a small extent. Because the rates of removal and transport of this dye were not very rapid, the dye concentration that appeared in the receiving solution was low. Brilliant Green, on the other hand, is the most non-polar of the three dyes which can partially account for its high extraction by the polyurethane membrane. The appearance of this dye in the 1 M NaCl receiving solution was quite slow as compared to its rate of removal from the 1 M NaCl starting solution. At 48 h, 37 % of the original dye

concentration was left in the starting solution but only 6 % was detected in the receiving solution. The difference in the rates of removal and appearance of Brilliant Green in the starting and the receiving solutions respectively is probably due to the higher solubility of this dye in the polymer than in the 1 M NaCl solution.

Table 6-1. Effect of salt on extraction and transport of basic dyes and their ion-association complexes with gold chloride

	Time (h)	% Dye in Starting Solution	% Au Starting Solution	% Dye in Receiving Solution	% Au Receiving Solution	% Dye in Membrane	% Au in Membrane
Methylene Blue							
no gold	48	97	-----	2	-----	1	-----
*with gold	48	91	96	8	3	1	1
Rhodamine B							
no gold	48	62	-----	8	-----	30	-----
with gold	48	34	94	26	5	40	1
Brilliant Green							
no gold	48	37	-----	6	-----	57	-----
with gold	48	44	93	2	6	54	1

Conditions: 22 ± 2 °C. 250-mL aliquot of ≈ 3.0×10^{-6} M dye concentration in 1.0 M NaCl solution in the starting cell with 11 ppm gold chloride concentration where appropriate. 250-mL aliquot of 1.0 M NaCl in the receiving cell. 0.025 mm thick ether-type membrane, active surface area of 23.8 ± 0.2 cm^2. All values have an error of ± 1 %, n = 3

**see Fig. 6-1*

Unlike the other two dyes, Rhodamine B has a carboxylic acid substituent capable of engaging in hydrogen-bonding interactions with the membrane which should favour its retention within the polymer matrix. Rhodamine B, however, is more polar than Brilliant Green and therefore may not be as soluble in the membrane. This can explain the slower rate of removal of Rhodamine B from the polar 1 M NaCl starting solution and the lower % extraction into the polymer.

When a gold chloride anion is present in the dye solution, the chloride ion associated with the dye cation can exchange with the gold anion and result in the formation of an organometallic ion-pair. The success of forming such a complex will, however, depend on the ease with which the relatively large gold chloride species can associate with the dye which is determined by the stereochemistry of both the dye cations and gold chloride. Because transport of gold was observed with all the dyes from 1 M NaCl solution which otherwise is unfavourable for gold sorption, an ion-pair with each of the dyes must have been formed (Table 6-1). At 48 h, 3 % gold was transported with Methylene Blue, 5 % with Rhodamine B, and 6 % with Brilliant Green. In the presence of gold, transport of Methylene Blue increased but the low retention of this dye in the membrane remained unchanged. Transport of Rhodamine B increased significantly to 26 % (at 48 h) and its retention in the membrane increased to 40 %. Transport of Brilliant Green decreased in the presence of gold but the retention in the membrane remained relatively unchanged. The retention of the gold species in the membrane was quite low (about 1 %) regardless of the dye used.

Overall, the extraction and transport of the otherwise unextractable gold chloride anion was feasible in the presence of each of the studied dyes in solution. The percentage of

gold chloride transported with either Brilliant Green or Rhodamine B was comparable and it was higher than with Methylene Blue. This may, however, be due to the fact that those dyes were removed from the starting solution more quickly than Methylene Blue. If a higher concentration of the gold chloride-dye ion-pair enters the membrane and is transported through the polymer bulk, a higher concentration will also appear in the receiving solution.

The readings taken at a much later time, show that gold chloride continued to transport with Methylene Blue (Fig. 6-1) and with Brilliant Green but not with Rhodamine B. At about 400 h, all of Rhodamine B was removed from the starting solution but a considerably high gold concentration was still present. The remaining gold anions did not show further sorption by the membrane without Rhodamine B in solution. Because Methylene Blue and gold were removed from solution at slow and comparable rates, the dye molecules had a higher probability of associating with the gold and therefore a continuous transport of the charged gold species could occur. Brilliant Green extracted from the starting solution into the membrane at a faster rate than the gold and eventually the starting solution contained only gold chloride without the dye. Unlike with Rhodamine B, the presence of a high concentration of Brilliant Green in the membrane allowed the charged gold chloride species to continue to extract and transport through the membrane.

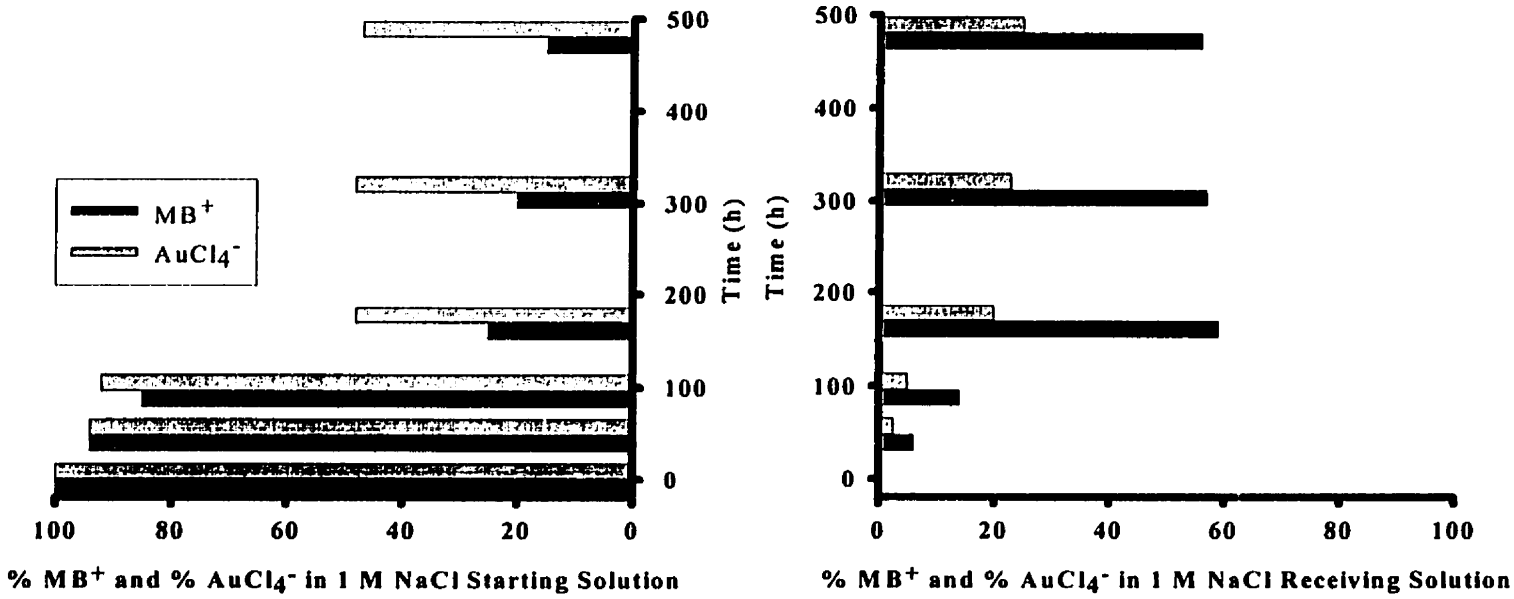

Fig. 6-1. Effect of salt

Conditions: 11 ppm gold chloride and 3 x 10^{-6} M Methylene Blue in 1 M NaCl starting solution; 1 M NaCl in receiving solution

6.2.2. Effect of acidic pH

The effect of solution acidity on sorption of the gold chloride-organic dye ion-pair was studied by looking at extraction and transport from sample solutions containing Methylene Blue and Rhodamine B in 1 M HCl. Brilliant Green solutions were prepared in 0.01 M HCl due to the sensitivity of this dye to high acidity. The results in Table 6-2 show that no extraction or transport of Methylene Blue was observed from 1 M HCl solution. Rhodamine B showed some transport from an acidic solution but it was quite slow (at 120 h, 6 % of Rhodamine B transported and only 1 % was retained in the membrane). Unlike the two other dyes, Brilliant Green extracted extremely well from 0.01 M HCl (at 24 h, 100% was removed). Although the acidic solution of Brilliant Green was yellow, the membrane containing the dye was green indicating that an uncharged species (an ion-pair) was present in the membrane. Gold chloride in acidic solution showed quantitative transport into the receiving acidic solution with all the dyes studied.

Under the acidic solution conditions, the gold chloride species was extracted and transported well and perhaps independently of the dye because a neutral $HAuCl_4$ complex could be formed. The dye molecules, on the other hand, may have been positively charged. For example, Methylene Blue could have had positively charged amine substituents or sulfur or nitrogen atoms on the ring and as a result the dye did not extract into the polyurethane membrane. The carboxylic acid substituent on Rhodamine B molecule is uncharged at the acidic pH.

Table 6-2. Effect of acid on extraction and transport of basic dyes and their ion-association complexes with gold chloride

	Time (h)	% Dye in Starting Solution	% Au Starting Solution	% Dye in Receiving Solution	% Au Receiving Solution	% Dye in Membrane	% Au in Membrane
Methylene Blue							
no gold	48	100	-----	0	-----	0	-----
*with gold	48	92	57	8	36	0	7
Rhodamine B							
no gold	48	98	-----	6	-----	2	-----
			-----		-----		-----
	120	93				1	
with gold	48	20	68	9	28	71	4
Brilliant Green**							
no gold	24	0	-----	0	-----	100	-----
with gold	24	0	82	0	6	100	12

Conditions: 22 ± 2 °C. 250-mL aliquot of ≈ 3.0 x 10^{-6} M dye concentration in 1.0 M HCl solution in the starting cell with 11 ppm gold chloride concentration where appropriate. 250-mL aliquot of 1.0 M HCl in the receiving cell. 0.025 mm thick ether-type membrane. active surface area of 23.8 ± 0.2 cm^2. All values have an error of ± 1 %. n = 3

**see Fig. 6-2; **for this dye 0.01 M HCl was used*

However, the amine substituents, the ring carbon and the oxygen atoms may be positively charged in 1 M HCl solution. Because some extraction and transport of this dye was observed, a small percentage of the dye molecules must have existed as neutral species (ion-pair) and therefore could be extracted by the membrane. Brilliant Green has two amine substituents which, in addition to the central carbon, may be protonated in an acidic solution. The fact that extraction under acidic pH occurred very readily indicates that a small percentage of this dye is uncharged and in equilibrium with the charged species. When the neutral species was removed, more of it was created to restore this equilibrium. This process continued until all the dye was sorbed from the starting solution. Because Brilliant Green is highly soluble in the membrane, it was not removed very effectively from the polymer matrix into the more polar receiving solution and therefore no transport was observed.

When gold chloride was added to the acidic solution of Methylene Blue, transport of this dye into the receiving solution occurred (Fig. 6-2, Table 6-2). When a solution of Rhodamine B in 1 M HCl was extracted in the presence of gold, retention of this dye in the polymer matrix significantly increased (at 48 h an increase from 1% extraction without gold to 71 % extraction with gold was observed). Furthermore, the rates of removal of Rhodamine B from the starting solution and transport into the receiving solution increased. The transport of gold compared to the transport of Methylene Blue and Rhodamine B was much faster which suggests that the majority of gold species must be transported as neutral $HAuCl_4$ molecules in acid solution and only a small percentage is charged and associated with the dye cations.

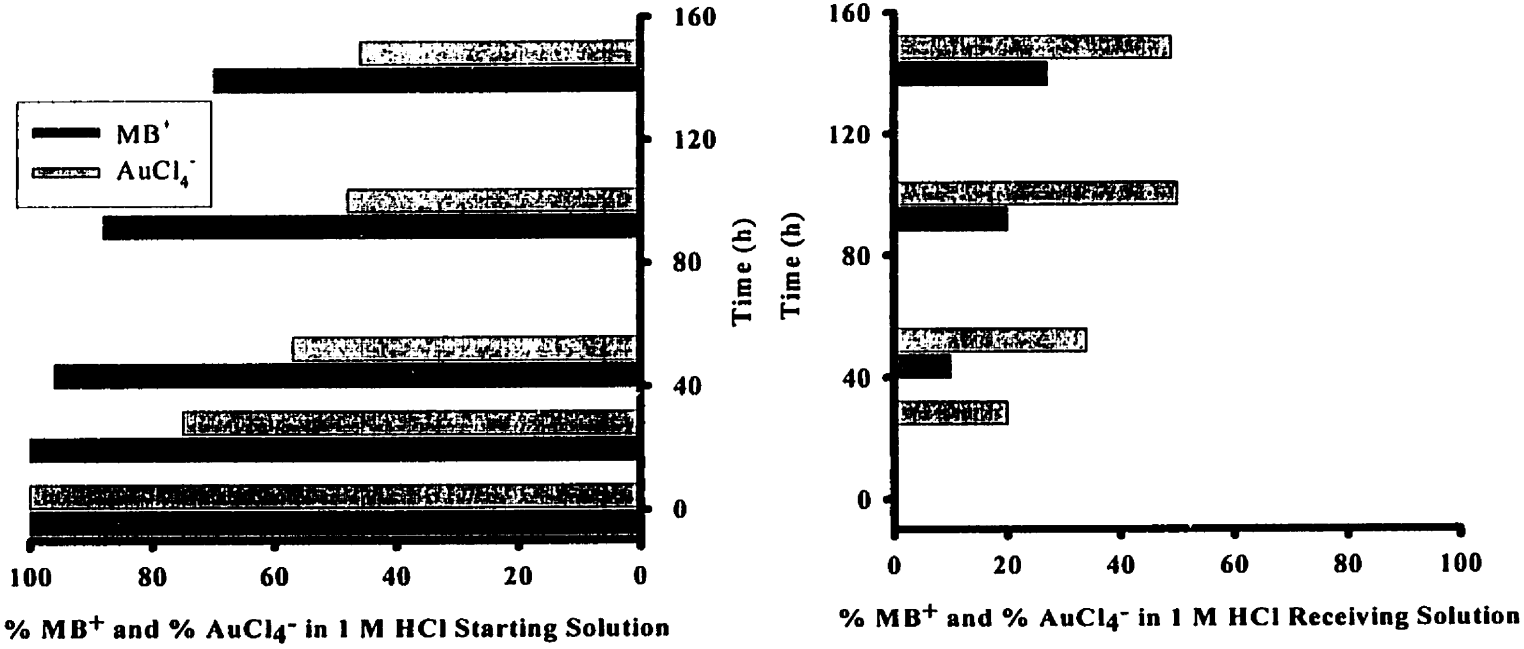

Fig. 6-2. Effect of acid

Conditions: 11 ppm gold chloride and 3 x 10^{-6} M Methylene Blue in 1 M HCl starting solution; 1 M HCl in receiving solution

If this is true, then the dye can be expected to show an increased transport at a higher gold chloride concentration. This hypothesis was tested by extracting solutions having identical Methylene Blue concentrations but varied gold chloride concentrations (Table 6-3). Indeed, the sample solution with 60 ppm gold concentration showed an increased rate of transport of Methylene Blue as compared to the dye solution containing only 11 ppm gold.

Table 6-3. Effect of the gold chloride concentration on extraction and transport of Methylene Blue through the polyurethane membrane

$[AuCl_4^-]$		% Concentration in the Starting Cell		% Concentration in the Receiving Cell		% Concentration in the Membrane	
		MB^+	$AuCl_4^-$	MB^+	$AuCl_4^-$	MB^+	$AuCl_4^-$
11 ppm	24 h	100	73	0	21	0	6
	160 h	70	45	28	50	2	5
60 ppm	24 h	81	70	17	25	2	5
	160 h	54	52	45	42	1	6

Conditions: 22 ± 2 °C; 250-mL aliquot of ≈ 3.0×10^{-6} M Methylene Blue and gold chloride in 1.0 M HCl solution in the starting cell; 250-mL aliquot of 1.0 M HCl in the receiving cell; 0.025 mm thick ether-type membrane having an active surface area of 23.8 ± 0.2 cm^2, all values have an error of ± 1 %, n = 3

Note: MB^+ stands for the Methylene Blue species in solution

This can be attributed to the availability of more of the negatively charged gold species for complexation with the dye. In 1 M HCl, the majority of gold chloride species exist as $HAuCl_4$ and are at equilibrium with a small percentage of the $(AuCl_4)^-$. Only the gold anions can interact with the dye cations and form an ion-pair. If the concentration of gold chloride is increased, the amount of the negatively charged gold species will also increase which, in turn, can interact with more dye cations. Therefore, the higher gold solution concentration increases the likelihood of the ion-pair complex with the dye being formed which results in an increased amount of dye transported. The sorption of Brilliant Green is different from that of Methylene Blue and Rhodamine B because this dye extracted very well from an acidic solution without the presence of gold. When the dye was combined with gold chloride in 0.01 M HCl, a shift in wavelength was observed which indicates an ion-pair formation. Although the dye and the gold may be entering the membrane as an ion-pair, the complex is probably not very stable because only gold was desorbed into the 0.01 M HCl receiving solution and the dye remained in the polymer.

6.2.3. *Effect of different starting and receiving solutions*

Up to this point the sorption of gold chloride-organic dye ion-association complexes has been studied when both the starting and the receiving solutions had identical composition. In this section, the results for sorption from a starting solution that is different in composition from the receiving solution are presented.

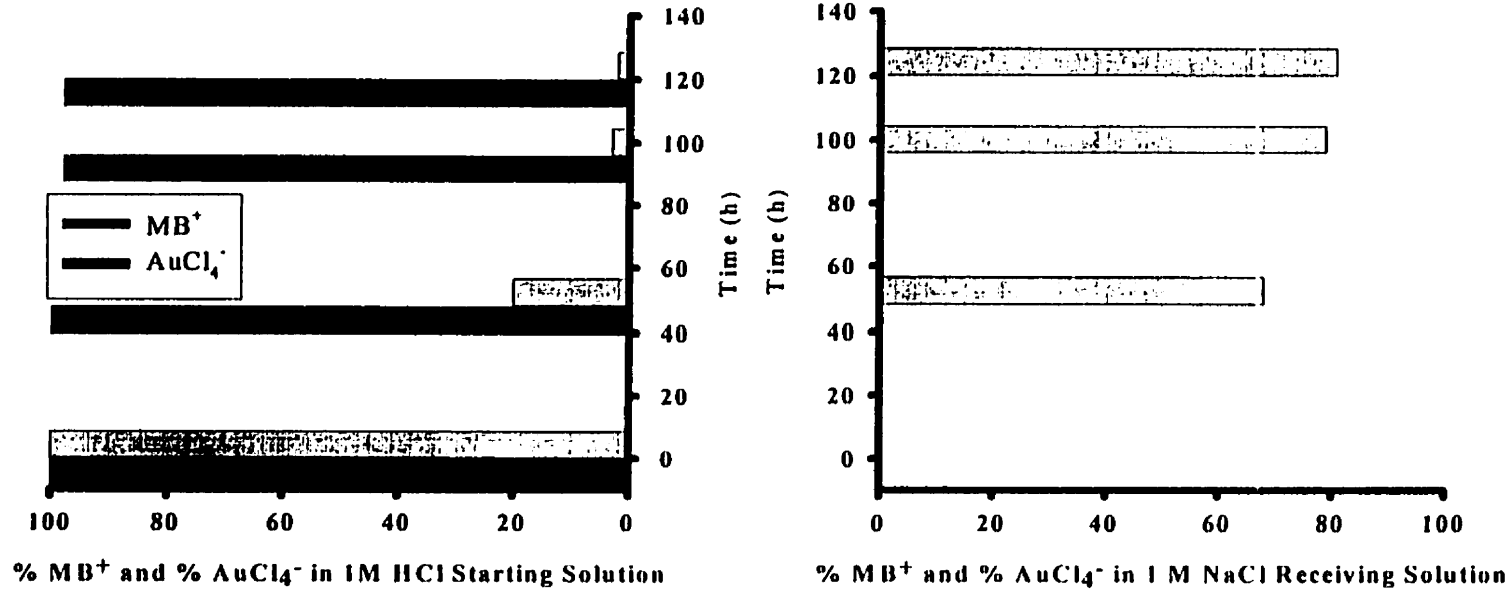

Fig. 6-3. Effect of acid in the starting solution and salt in the receiving solution

Conditions: 11 ppm gold chloride and 3 x 10^{-6} M Methylene Blue in 1 M HCl starting solution; 1 M NaCl in receiving solution initially

When the starting solution was 1 M HCl and the receiving solution was 1 M NaCl, a very slow transport of gold without the presence of dye in solution was observed. The rate of transport of gold would be expected to be quite slow at the 1 M HCl concentration because at this acidity a large proportion of gold remains charged and only a small percentage is neutral and can extract into the membrane[5]. Under the above solution conditions, Methylene Blue did not extract at all. A solution of Rhodamine B showed some extraction (2% at 288 h) but no transport. Brilliant Green extracted completely from 0.01 M HCl.

When gold chloride was added to the solution of Methylene Blue, still no extraction or transport of this dye was initiated but a very rapid and quantitative transport of gold occurred (Fig. 6-3). Addition of gold to a Rhodamine B solution resulted in an increased in extraction of the dye (17 % at 288 h) with no transport. Gold, again, transported quickly and quantitatively into the receiving 1 M NaCl solution. Thus, with both Methylene Blue and Rhodamine B a rapid transport of gold chloride from 1 M HCl into 1 M NaCl occurred as compared to the transport of gold from an identical solution but without the dyes. However, the presence of gold in solution did not induce any transport of either of the dyes. The complete extraction of Brilliant Green was not affected by gold or by the differing starting and receiving solution compositions. As was observed before, Brilliant Green showed no transport into the 1 M NaCl receiving solution.

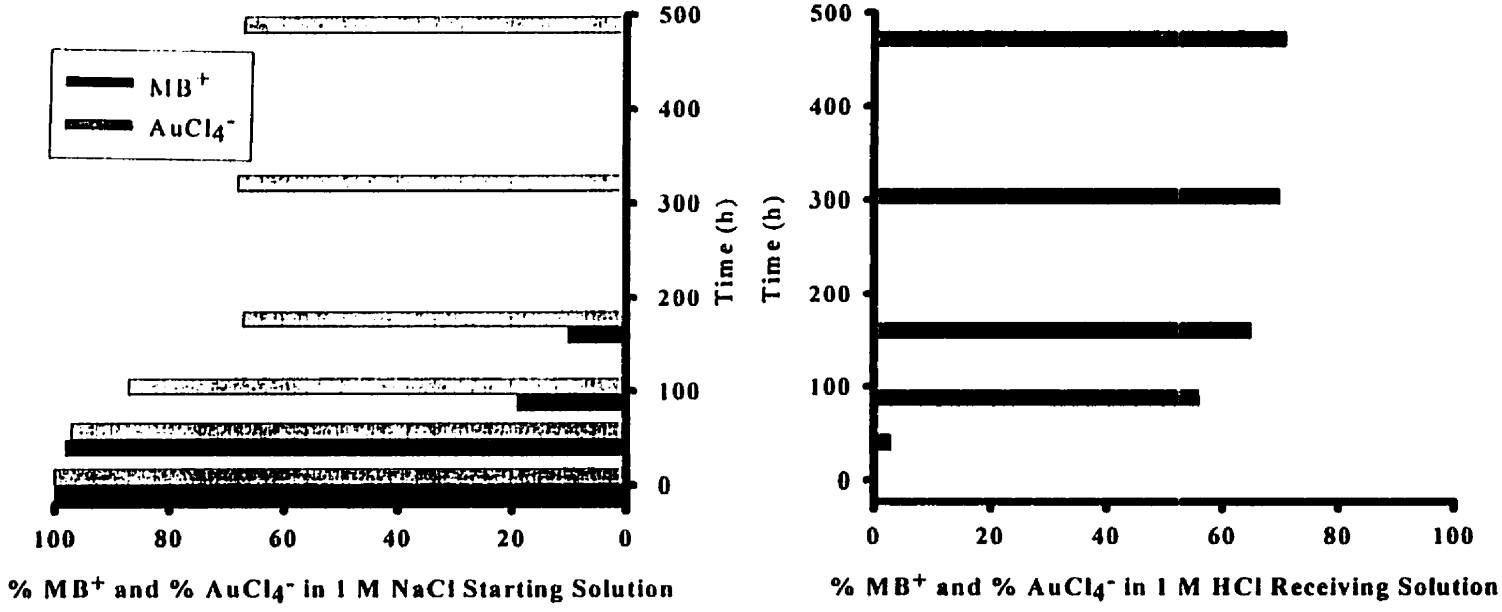

Fig. 6-4. Effect of salt in the starting solution and acid in the receiving solution

Conditions: 11 ppm gold chloride and 3 x 10^{-6} M Methylene Blue in 1 M NaCl starting solution; 1 M HCl in receiving solution initially

The conditions of the starting and receiving solutions were then reversed, i.e., the starting solution was now 1 M NaCl and the receiving solution was 1 M HCl. A solution of gold alone did not show any extraction or transport as expected since gold chloride is negatively charged in 1 M NaCl. Conversely, very rapid transport of Methylene Blue (Fig. 6-4) and Rhodamine B occurred in the presence of gold and the gold species was left behind in the starting solution. When Methylene Blue and Rhodamine B were present in solution alone, transport also took place but the rates of the removal and appearance of these dyes in the starting and receiving solutions respectively were very slow compared to those observed in the presence of gold. Again, an extraction of 100 % of the Brilliant Green occurred from 1 M NaCl starting solution and no transport into the 1 M HCl receiving solution was observed. Even though no Brilliant Green was left in solution, the transport of gold continued and at 288 h 23% of gold was detected in the receiving solution and 54 % in the membrane.

Based on the results presented in the previous sections of this chapter, the dyes and the gold would be expected to transport together as an ion-pair. Since this was not observed, it is possible that either the formation of the ion-pair did not occur or the complex formed was not stable. One other reason for the occurrence of selective transport of either the gold or the dye species when different starting and receiving solutions were used may be the large disparity in the rates of extraction of each of the species from the starting solution. If one species is being removed from the starting solution at a much faster rate, the probability of effective complex formation is reduced. Furthermore, a continuously decreasing availability of one of the species for complexation can influence the amount of the complex formed.

Therefore, even if an ion-pair was formed, its concentration would be quite low. The presence of Brilliant Green in the membrane appears to make the polymer permeable to the otherwise unextractable gold species. This was different from the sorption of gold with Methylene Blue and Rhodamine B in that gold was extracted and transported even though Brilliant Green was completely absent in the starting solution (but present in the membrane, i.e. 100 % extraction) before transport of gold has been initiated.

6.2.4. Effect of temperature

The effect of temperature on extraction and transport of gold chloride-organic dye ion-pair is exemplified with the sorption of Methylene Blue from 1 M NaCl starting and receiving solutions for which data are shown in Table 6-4. The results for the different temperatures were compared for different sorption time intervals to emphasize the differences in the rates of transport at the various temperatures. At 4 °C after 168 h, almost no transport of Methylene Blue was observed, but high extraction occurred. Similarly, gold showed no transport but about 11 % of its initial concentration was found in the membrane. At 25 °C at 48 h, some increase in the transport rate of Methylene Blue was observed but the amount of this dye in the membrane decreased drastically (2%). The gold began to show some transport (5%) but its retention in the membrane also decreased as for the dye (1%). At 60 °C at 16 h, high retention and transport of both Methylene Blue and gold took place.

Table 6-4. Effect of temperature on extraction and transport of Methylene Blue and gold chloride through the polyurethane membrane

Compound	% Concentration in the Starting Cell	% Concentration in the Receiving Cell	% Concentration in the Membrane
MB^+			
4 °C at 168 h	65	1	34
22 °C at 48 h	92	6	2
60 °C at 16 h	18	25	57
$(AuCl_4)^-$			
4 °C at 168 h	89	0	11
22 °C at 48 h	94	5	1
60 °C at 16 h	60	11	29

Conditions: temperature ± 2 °C; 250-mL aliquot of ≈ 3.0×10^{-6} M Methylene Blue and 11 ppm gold chloride in 1.0 M NaCl solution in the starting cell; 250-mL aliquot of 1.0 M NaCl in the receiving cell; 0.025 mm thick ether-type membrane having an active surface area of 23.8 ± 0.2 cm^2, all the values have an error of ± 2. n = 3

Note: MB^+ stands for the Methylene Blue species in solution

A DSC study of the polyurethane membrane exposed to solutions at the three temperatures (see Chapter 7) indicated that the matrix of the membrane after exposure to a solution at 60 °C becomes more homogenous in structure (i.e., the soft and the hard domains are less segregated). The other membranes which were exposed to solutions at lower temperatures showed greater segregation of the soft and the hard domains. Because at the higher temperature the hydrogen-bonding interactions within the membrane domains are weakened, the soft segments can become more exposed and available for interactions with the species in solution which can account for the consistently higher sorption and the increased rate of transport at the elevated temperature. Because at lower temperatures the polymer is more crystalline in nature, the individual domains may be too strongly engaged in intra- and intermolecular interactions with each other which would make the matrix less available for interactions with the species in solution. At 4 °C there was no transport although sorption occurred, which was probably due to the limited or very slow migration of the species through the highly segregated matrix.

6.3. Conclusion

Without the presence of organic dyes, gold chloride was extracted and transported from 1 M HCl but not from 1 M NaCl as a result of the formation of a neutral and weakly acidic $HAuCl_4$ complex[4]. Without gold, Methylene Blue and Rhodamine B extracted and transported from 1 M NaCl solution but not from 1 M HCl. Brilliant Green was completely

removed by the polyurethane membrane from both 1 M NaCl and 0.01 M HCl solutions regardless of the presence of gold.

Ion-association complexes of gold chloride with Methylene Blue and Rhodamine B were transported from both 1 M HCl and 1 M NaCl starting solutions into 1 M HCl and 1 M NaCl receiving solutions, respectively. When the composition of the starting and the receiving solutions was not identical, selective transport of the gold chloride or dye species occurred. Finally, increased temperature resulted in a higher retention of gold and dyes in the membrane matrix and in increased rates of transport into the receiving solution.

This study and the previous work on the mechanism of sorption of organic compounds by the polyurethane membrane show that three steps are taking place during the sorption of gold chloride-dye ion-association complexes from aqueous solution. First, the diffusion of the complex from solution into the membrane surface occurs which is dependent on the formation of an uncharged species. Next, transport of the sorbed species from the membrane surface into the bulk of the membrane takes place as a result of solubility and intramolecular interactions. The final step involves desorption of the species and diffusion away from the membrane surface into the receiving solution. This step is feasible only if appropriate receiving solution conditions are provided.

The investigation of the process of transporting a large metal-dye ion-pair through the membrane confirmed the separate conclusions that were reached from the extraction and transport of inorganic and organic compounds[4-8]. Furthermore, this study demonstrated that selective removal of each of the species constituting the ion-pair can be attained by changing the solution conditions. This information can be useful in textile membrane separation

applications where it can be important to obtain selective isolation of metal additives from the colorants for recycling or for purification of the final effluent.

References for Chapter 6

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Chapter 7: Membrane Characterization

7.1. Introduction

The two most important potential applications of the polyurethane materials are in the biomaterials science for the manufacture of various human implantation devices and in the membrane separations technology for the purification of solutions and for the recovery of organic and inorganic compounds. One of the biggest problems in studying commercially available polyurethanes is the difficulty for scientists outside the industry in obtaining information on their exact composition which in turn makes the development of new applications more difficult.

Detailed information on the chemical makeup of the polyurethane membranes used in this research was inaccessible from the manufacturer. Previous work done in this laboratory provided only very general information regarding the chemical composition of the ether- and the ester-type polyurethane membranes. Therefore elucidation of the mechanism of the polyurethane extraction process was quite challenging due to the limited knowledge of the exact polymer composition which is invaluable for a mechanistic study such as the one described in this thesis.

In order to determine whether any relative chemical or morphological changes occurred in the surface and the bulk of the polyurethane membrane when the membrane was subjected to various solution and physical conditions during sorption, various analytical

methods were used. The data obtained allowed for a greater understanding of the proposed extraction mechanism without the need to know the exact components used in the membrane synthesis. The methods used for the chemical characterization of the polyurethane membranes included differential scanning calorimetry (DSC), electron spectroscopy for chemical analysis (ESCA), and attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR). The surface topography of both the ether- and the ester-type membranes was qualitatively studied using scanning electron microscopy (SEM).

7.2. Results and Discussion

7.2.1. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique which is used to characterise the glass transition (T_g) and the melting (T_m) temperatures of a polymer, the degree of crystallinity, and the degree of phase separation and morphological changes within the bulk of the polymer[1]. In a DSC analysis, a polymer sample is placed inside the calorimeter and heated at a fixed rate. The amount of energy needed to maintain a fixed rate of temperature increase is measured, and changes in the specific heat denote changes in the mobility of the polymer chains. The glass transition temperature, T_g, is identified by a change in the heat capacity which appears as a baseline shift (an inflection point), and it is the temperature at which a large increase in the mobility of the polymer backbone occurs. An

endothermal peak in the DSC thermogram denotes the melting temperature of the polymer, T_m, at which disordering of the crystalline regions of the hard segments occurs. After initial heating, the polymer can be rapidly cooled, which is known in DSC analysis as quenching, and then heated again. This can provide additional information on the bulk morphology of the polymer independent of its previous thermal processing conditions.

Numerous[2,3,4] DSC studies on a variety of polyurethane materials show that as many as five transitions can be observed. The glass transition usually occurs in the range of -50 °C to -10 °C; the transitions corresponding to the disruption of the soft-hard domain interactions are in the range of 35 °C to 115 °C and 130 °C to 170 °C; the disruption of the hard segment domains and melting can occur anywhere from 160 °C to 225 °C. The DSC thermograms collected in this study are shown in Appendix 1. The data from the DSC thermograms are summarized in Table 7-1, Table 7-2, and Table 7-3.

Characterization of the thermal properties of the ether- and the ester-type polyurethane membranes used in this research indicates that both membrane types show multiple thermal transitions. For all of the membranes studied, three distinct transition regions were identified (Table 7-1, Table 7-2, and Table 7-3): the first group of transitions occurred at below zero temperatures, the second group of transitions was observed in the range of 0 °C to about 100 °C, and the last occurred above 100 °C. A general agreement with the literature values was observed[2,3,4].

Table 7-1. Comparison of DSC transitions for the ether-and the ester-type polyurethane membranes

	XPR untreated		*XPR xylene cleaned*		*MP untreated*		*MP xylene cleaned*	
	T	I	T	I	T	I	T	I
Initial Run	(-60 - 0)	(-38)	(-50 - -25)	(-45)	(-12 - 15)	(-10)	(-20 - 0)	(-6)
	(50 - 90)	(83)	(60 - 85)	(81)	(15 - 38)	(35)	(44 - 86)	(72)
	(90 - 143)	(142)	(90 - 170)	(159)	(38 - 45)	(40)	(90 - 170)	(140)
	(143 - 147)	(146)			(45 - 46)	(45)		
	(155 - 164)	(157)			(50 - 84)	(74)		
	(165 - 170)	(166)			(84 - 175)	(157)		
After 1st Quench	(-50 - 42)	(-1)	(-33 - 40)	(1)	(0 - 59)	(20)	(-5 - 58)	(19)
	(42 - 100)	(87)	(40 - 100)	(92)	(59 - 90)	(72)	(58 - 98)	(71)
	(100 - 175)	(168)	(100 - 170)	(165)	(110 - 150)	(130)	(98 - 113)	
					(150 - 170)	(160)	(113 - 142)	(137)
							(142 - 170)	(152)
After 2nd Quench	Was Not Collected		(-36 - 30)	(12)	(0 - 50)	(16)	(0 - 50)	(20)
			(120 - 170)	(160)	(50 - 80)	(60)	(50 - 98)	(61)
					(85 - 140)	(136)	(98 - 140)	(135)
					(140 - 170)	(159)	(140 - 170)	(156)

XPR is the ether-type membrane: MP is the ester-type membrane

Column T shows the temperature ranges for the transitions (°C)

Column I shows the temperatures at which inflection occurred (°C)

Table 7-2. DSC transitions for the ether-type polyurethane membranes exposed to solutions at 4 °C, 25 °C, and 60 °C

	XPR xylene cleaned		*XPR* 4 °C		*XPR* 25 °C		*XPR* 60 °C	
	T	I	T	I	T	I	T	I
Initial Run	-50 - -25	(-45)	(-60 - 0)	(-27)	(-66 - 25)	(-32)	(-50 - -23)	(-41)
	60 - 85	(81)	(35 - 95)	(87)	(44 - 64)	(56)	(-17 - -7)	(-17)
	90 - 170	(159)	(95 - 159)	(158)	(64 - 100)	(84)	(-2 - 1)	(-2) pk
			(159 - 162)	(161)	(100 - 175)	(165)	(2 - 6.7)	(2) pk
			(162 - 175)	(165)			(13 - 21)	(21, 72) pk
							(94 - 128)	(86, 112)
							(129 - 190)	(164, 175)
After 1st Quench	-33 - 40	(1)	(-35 - 44)	(2)	(-55 - 42)	(0)	(-35 - 43)	(1)
	40 - 100	(92)	(44 - 75)	(60)	(42 - 62)	(59)	(43 - 75)	(57)
	100 - 170	(165)	(75 - 90)	(83)	(62 - 88)	(84)	(75 - 92)	(89)
			(90 - 160)	(148)	(88 - 175)	(166)	(92 - 185)	(163)
			(160 - 175)	(165)				
After 2nd Quench	(-36 - 30)	(12)	(-15 - 37)	(1)	(-25 - 35)	(-1)	Was Not Collected	
	(120 - 170)	(160)	(37 - 62)	(46)	(35 - 57)	(50)		
			(62 - 93)	(88)	(60 - 90)	(85)		
			(93 - 175)	(167)	(90 - 175)	(164)		

XPR is the ether-type membrane

pk stands for peak: all membranes were cleaned with xylene

Column T shows the temperature ranges for the transitions (°C)

Column I shows the temperatures at which inflection occurred (°C)

Table 7-3. DSC transitions for the ether-type polyurethane membrane containing Brilliant Green (extracted from 1 M NaCl solution)

	XPR 25 °C		*XPR with Brilliant Green*	
	T	I	T	I
Initial Run	(-66 - 25)	(-32)	(-8 - -3)	(-6)
	(44 - 64)	(56)	(21 - 25)	(22)
	(64 - 100)	(84)	(43 - 46)	(44)
	(100 - 175)	(165)	(46 - 56)	(50) pk
			(57 - 65)	(60)
			(65 - 95)	(83)
			(115 - 180)	(138, 163)
After 1st Quench	(-55 - 42)	(0)	(-20 - 40)	(1)
	(42 - 62)	(59)	(50 - 94)	(88)
	(62 - 88)	(84)	(94 - 180)	(163)
	(88 - 175)	(166)		
After 2nd Quench	(-25 - 35)	(-1)	(-20 - 40)	(17)
	(35 - 57)	(50)	(100 - 180)	(88, 176)
	(60 - 90)	(85)		
	(90 - 175)	(164)		

XPR is the ether-type membrane

pk stands for peak: all membranes were cleaned with xylene

Column T shows the temperature ranges for the transitions (°C)

Column I shows the temperatures at which inflection occurred (°C)

Table 7-1 summarizes the transition regions for the ether- and the ester-type membrane samples which were not subjected to any cleaning treatments (i.e., untreated) and for the membranes which were cleaned with xylene (as was necessary for the subsequent ESCA analysis) in order to remove any traces of silicone grease which may have been transferred onto the membrane surface from the experimental apparatus. The observed transitions occurred approximately in the same regions for the untreated and the cleaned membranes, but the untreated membranes showed a few more small transitions in the upper temperature range. In all cases, the first quenching resulted in an upward temperature shift of the transitions. The transition regions after the second quench were almost identical to those observed after the first quenching. The below zero transitions for the ether-type polyurethane membrane were much lower than for the ester-type membrane. The mid-range positive transitions occurred at higher temperatures for the ester-type membrane, and the high temperature transitions were comparable for both membrane types.

As mentioned earlier, a glass transition temperature, T_g, is the temperature at which the polymer undergoes a change from a glassy material to a more elastic, rubbery material. The T_g not only indicates the temperature at which disruption of the weak interactions among the polymer soft segments takes place but also measures the degree of phase-separation of the polyurethane domains[2]. The T_g is affected by the purity of the phase, and so if the polyurethane is well phase-separated, the T_g will lie very close to that of the soft segment polymer. The larger the deviation from this value, the larger the degree of phase-mixing of the soft and the hard segments. The degree of order within the hard segments depends upon chemistry, rigidity and degree of hydrogen-bonding within the hard segment. The higher the

degree of order within the hard segments, the higher the melting point of the polyurethane. As is shown in Table 7-1, the transitions below zero degrees for both membrane types were well separated from the transitions above zero degrees which suggests that the soft segment domains in both membranes are quite pure and well segregated from the hard domains (the ether-type membrane showed a little more segregation than the ester-type membrane, i.e., a larger temperature gap existed between the transitions below and above zero degrees). Because the exact chemical compositions of the membranes are not known, the observed temperature transitions cannot be truly compared with the literature values[2,3,4]. However, relative comparisons can be made for the initial runs and after quenching has been performed for both membrane types. Because the T_g transitions for the ester-type membrane were lower than for the ether-type membrane, it can be concluded that stronger interactions occur among the soft segments of the ester-type polyurethane which confirms such assumptions made earlier throughout this thesis. The ester-type polyurethane showed a greater tendency for the hard segments to be surrounded by the polyester-rich soft segment phase probably because of the greater polarity of the polyester segments which makes them more miscible with the nitrogen-rich hard segments. The T_g transitions can shift upward to merge with the higher temperature transitions after annealing (quenching) has been performed. The increase in T_g of the soft segment after annealing indicates that a greater proportion of the hard segments is dispersed within the soft segments. A comparison of the initial run data and the first quench data in Table 7-1 shows that indeed a shift toward a higher temperature occurred when the membranes were rapidly cooled after the initial heating and then re-heated. Furthermore, the boundaries between the transitions after quenching were not as distinct,

which indicates that after quenching the membrane matrix was no longer well segregated into soft and hard regions but was more homogenous in nature. The temperature regions in which phase-mixing occurs are referred to in polymer chemistry as the microphase separation transition (MST) regions[2]. For polyurethanes, in general, MST is believed to occur in the range of 140 °C to about 200 °C. The MST marks the onset of microdomain mixing of the non-crystalline hard and soft segments which involves the disruption of microdomain structure to form a homogenous mixed phase. Above 200 °C, melting of the microcrystalline domain occurs which involves disruption of the strongest forces in the crystalline segments. The MST can certainly be observed after the first quench of the polyurethane membranes. The overall crystallinity of the polymer was not changed after the second quench (i.e., no significant change in transition regions was observed) which indicates that probably a higher temperature is needed to induce more mixing of the remaining segregated regions. A complete melting of the crystalline hard segments most likely did not occur because heating of the samples was terminated at 200 °C.

Table 7-2 summarizes the DSC data for the ether-type polyurethane membranes exposed to aqueous solutions at various temperatures. The data after the first and the second quench is reported in Table 7-2 only to show that again the initial phase segregation was highly decreased after quenching which, as was already discussed above, is indicative of a more homogenous membrane matrix. The T_g of the ether-type membrane exposed to an aqueous solution at 60 °C resembled most closely the T_g of the membrane which was not exposed to a solution (i.e., xylene cleaned XPR). The mid-temperature transitions for that membrane were more numerous and occurred at lower temperatures than for the control

membrane and for the other membrane samples: the high temperature transitions were again comparable for all samples. The membranes exposed to solutions at 4 °C and at 25 °C showed a distinct separation of the T_g from the other transitions as did the control. The membrane exposed to a solution at 60 °C, on the other hand, showed small clustered transitions until the high temperature range was reached. This indicates that the matrix of the membrane exposed to a solution at 60 °C was not as heterogenous in nature as the matrices of the control sample and the other two membranes exposed to solutions at the lower temperatures. The presence of phase segregation suggests that the soft segments must be highly hydrogen-bonded with other soft segments and not with the hard segments. Because the T_g of the polyurethane soft segments is quite low, the solution temperature of 60 °C which is above the T_g can accelerate the dissociation of the hydrogen-bonding by the increasing the molecular mobility in the polymer chains. All of the studied membranes were exposed to the solutions for the same time durations. The fact that at 4 °C and 25 °C no mixing of the soft and the hard domains was observed even though these temperatures were above the T_g of the soft segments suggests that the crystalline hard segments at those temperatures were still hydrogen-bonded. As the solution temperature was increased to 60 °C, most likely the hard segment-soft segment hydrogen bonds were disrupted because the inter-urethane hydrogen bonds formed with other hard segments are much stronger than the hydrogen bonds between the hard and the soft segments. The rigid aromatic structure of the hard segments leads to very strong hydrogen-bonding between the carbonyl in the urethane linkage and the N-H group of the urethane group on adjacent polymer chains. Consequently, temperatures lower than 200 °C are usually below the T_g or T_m of the hard segments and

therefore no disruption of these bonds is observed. However, some of the weaker bonds among the hard semi-crystalline domains may be broken. The observed high temperature transitions were roughly identical for all the samples as would be expected. A change in the slope in the region of 90 °C to 190 °C (i.e., inflection) can be attributed to the onset of the hydrogen bond dissociation (i.e., T_g) of the semi-crystalline hard segments. Because of the high aromatic content in the hard crystalline domains of both membrane types, the majority of these hard segments probably remained in a crystalline and highly hydrogen-bonded form around the 200 °C temperature.

Table 7-3 shows the effect of an organic dye Brilliant Green on the membrane matrix. The T_g for the dye-containing membrane shifted upwards in comparison to the control membrane, and more numerous transitions occurred in the mid-temperature region; the upper temperature transitions were unaffected. These results indicate that the presence of the dye in the soft segments added some crystallinity or hardness to the soft domain while the hard domain remained unaffected. This suggests that the transfer of an organic compound into the membrane matrix from solution occurs as a result of interactions of the organic compound with the soft segments of the membrane and not with the hard segments which supports the proposed sorption mechanism. This also supports the earlier explanation as to why a consistently lower sorption has been observed with the ester-type polyurethane membrane in comparison to the sorption obtained with the ether-type membrane. As shown in Table 7-3, after the first quench, the crystallinity imparted by the presence of Brilliant Green in the membrane matrix was lost. As a result of quenching, mixing of the hard and the soft segments occurred, and therefore the transition peak which was previously observed in the

soft domain is not detectable due to the formation of a more homogenous matrix.

7.2.2. Electron Spectroscopy for Chemical Analysis (ESCA)

There is a whole range of spectroscopic techniques that have been developed in order to probe the surface chemistry and structure of materials. One example is x-ray photoelectron spectroscopy (XPS) more commonly known as electron spectroscopy for chemical analysis (ESCA) which is considered to be one of the more powerful tools for surface analysis currently available[1]. In ESCA analysis, solid samples are placed in a special charger and excited with a large flux of monoenergetic radiation (e.g., Al Kα at 1486 eV). These x-rays interact with the 5 to 10 nm top layer of the sample and lead to emission of characteristic x-rays (electrons) each having an energy characteristic of the electron orbital from which it was ejected. The difference in energy between the exciting photons and the emitted electrons is equal to the binding energy of the electron. An ESCA spectrum is a plot of the photoelectron intensity against the kinetic energy (binding energy) of the ejected electrons. Since no two elements have the same set of binding energies, the energy distribution of the ejected electrons is characteristic of the atomic orbital, the valence state and electron distribution within the material. ESCA peaks are usually named according to the level from which the electron was emitted. This type of analysis can give information on coordination numbers, oxidation states and chemical bonding effects, but accurate characterization can sometimes be difficult to obtain due to the high sensitivity of this technique to the presence of certain

elements.

ESCA has been shown to be successful at determining the surface domain structure of various copolymers including the polyurethane materials[2,3,4]. Therefore, the surfaces of the ether- and the ester-type polyurethane membranes used in this research were studied using this technique. The detected % concentration of the elements present in the surface (or near surface) of the ether - (XPR) and the ester-type (MP) polyurethane membranes and the % concentration of the impurities are shown in Table 7-4. Table 7-5 and Table 7-6. The data obtained from the ESCA analysis are more informative when represented as ratios of the elements rather than as % elemental composition. The calculated ratios of the elements which were identified on the surface of the ether- and the ester-type polyurethane membranes are shown in Table 7-7. Table 7-8 and Table 7-9. An example of an ESCA spectrum is shown in Fig.7-1.

Table 7-4. Concentration of the elements present in the surface of the ether- and the ester-type polyurethane membranes

Membrane	C1s	N1s	O1s	Si2p	S2p	Ca2p	Na1s	Cl2p	Sn3d5
	%	%	%	%	%	%	%	%	%
xylene cleaned MP	88.11	3.73	7.22	0.70	0.05	-----	0.12	0.06	-----
untreated MP	79.31	2.35	11.13	7.20	-----	-----	-----	-----	-----
H_2O / *HCl MP	67.40	2.11	20.47	10.02	-----	-----	-----	-----	-----
	*82.67	*3.23	*10.48	*3.62	-----	-----	-----	-----	-----
xylene cleaned XPR	85.57	0.87	10.56	2.31	0.44	0.25	-----	-----	-----
untreated XPR	66.73	0.60	18.69	13.98	-----	-----	-----	-----	-----
H_2O / * HCl XPR	63.70	0.75	23.28	12.20	-----	-----	-----	-----	0.07
	*64.26	*0.61	*22.05	*13.09	-----	-----	-----	-----	-----

Table 7-5. Concentration of the elements present in the surface of the ether-type polyurethane membrane exposed to solutions having different temperatures

Membrane	C1s	N1s	O1s	Si2p	S2p	Ca2p	Na1s	Cl2p	Sn3d5
	%	%	%	%	%	%	%	%	%
4 °C XPR	70.18	1.63	21.32	6.87	-----	-----	-----	-----	-----
25 °C XPR	68.27	1.38	21.36	9.00	-----	-----	-----	-----	-----
60 °C XPR	49.03	0.51	31.94	18.52	-----	-----	-----	-----	-----

Conditions: All membranes were exposed to water

Table 7-6. Concentration of the elements present in the surface of the ether--type polyurethane membranes exposed to various solvents

Membrane	C1s	N1s	O1s	Si2p	S2p	Ca2p	Na1s	Cl2p	Sn3d5
	%	%	%	%	%	%	%	%	%
xylene cleaned XPR	85.57	0.87	10.56	2.31	0.44	0.25	-----	-----	-----
Aqueous									
H_2O / *H_2O XPR	58.14	0.57	23.80	17.40	-----	-----	-----	-----	-----
	58.23	0.60	23.64	17.00	-----	-----	-----	-----	-----
H_2O / *HCl XPR	63.70	0.75	23.28	13.09	-----	-----	-----	-----	-----
	*64.26	*0.61	*22.05	*13.09	-----	-----	-----	-----	-----
BG NaCl / NaCl XPR	56.20	0.63	27.13	15.99		0.05	-----	-----	-----
Mixed									
EtOH / *H_2O XPR (transport)	51.99	0.00	25.32	22.69	-----	-----	-----	-----	-----
	57.64	0.00	23.54	18.83					
EtOH / * HCl XPR (transport)	65.57	0.81	20.93	12.69	-----	-----	-----	-----	-----
	*64.36	*0.45	*20.74	*14.30	-----	-----	-----	-----	0.16
Hexane / *H_2O XPR (no transport)	49.01	0.00	27.66	23.33	-----	-----	-----	-----	
	*52.19	*0.00	*24.92	*22.89	-----	-----	-----	-----	-----
Hexane / *H_2O XPR (transport)	58.81	1.23	26.48	13.48	-----	-----	-----	-----	
	*56.76	*0.92	*28.08	*14.25	-----	-----	-----	-----	-----

Table 7-7. Comparison of the surface elemental composition of the ether- and the ester-type polyurethane membranes

Membrane	N / C ratio	O / C ratio	N / O ratio
xylene cleaned MP	0.0400	0.08	0.5000
untreated MP	0.0296	0.14	0.2110
H_2O / HCl MP	0.0313 / 0.0391	0.30 / 0.13	0.1030 / 0.3080
xylene cleaned XPR	0.0102	0.12	0.0821
untreated XPR	0.0090	0.28	0.0321
H_2O / HCl XPR	0.0102	0.65	0.0012 / 0.0100

Table 7-8. Effect of temperature on the membrane surface characteristics

Membrane	N / C ratio	O / C ratio	N / O ratio
4 °C XPR	0.0234	0.31	0.0751
25 °C XPR	0.0098	0.41	0.0235
60 °C XPR	0.0102	0.65	0.0157

Conditions: All membranes were exposed to water

Table 7-9. Effect of solvents on membrane surface characteristics

Solvent	N / C ratio	O / C ratio	N / O ratio
xylene cleaned XPR	0.0102	0.12	0.0821
Aqueous			
H_2O / H_2O XPR	0.0098	0.41	0.0239
H_2O / HCl XPR	0.0012 / 0.0100	0.37 / 0.34	0.0322 / 0.0276
BG NaCl / NaCl XPR	0.0011	0.48	0.0232
Mixed			
EtOH / H_2O XPR (transport)	0 / 0	0.49 / 0.41	0 / 0
EtOH / HCl XPR (transport)	0.0123 / 0.0070	0.32 / 0.32	0.0388 / 0.0217
Hexane / H_2O XPR (no transport occurred)	0 / 0	0.57 / 0.48	0 / 0
Hexane / H_2O XPR (transport occurred)	0.0209 / 0.0162	0.45 / 0.50	0.0464 / 0.0327

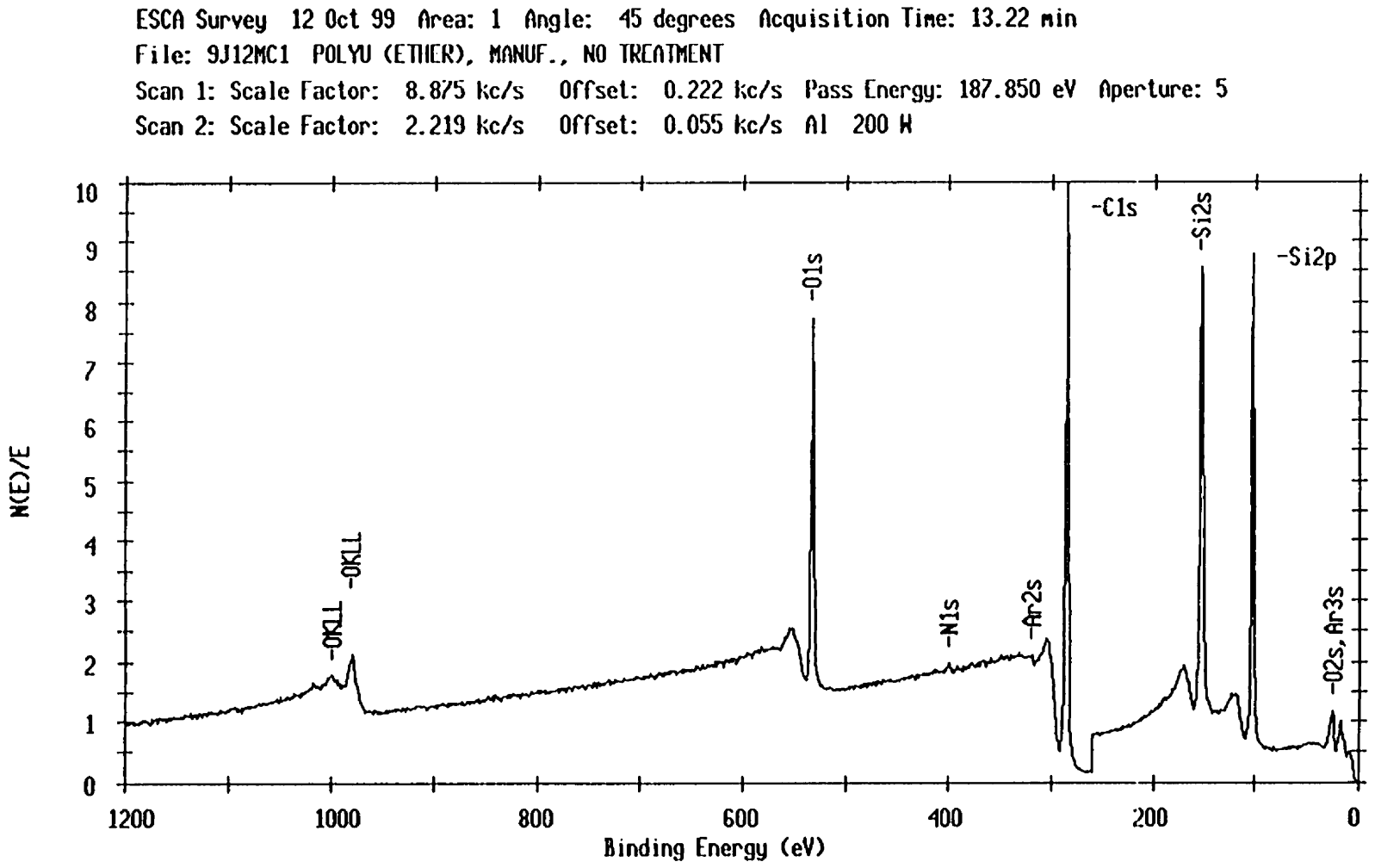

Fig. 7-1. An ESCA spectrum of the untreated ether-type polyurethane membrane

All membranes (with the exception of the membranes labelled "untreated") were cleaned with xylene prior to analysis in order to remove any silicone grease which may have been present on the membrane surface. The hard segments of the polyurethane contain nitrogen, carbon and oxygen, therefore the magnitude of the N / O and N / C ratios can be an indication of whether there are any hard segments near the surface. However, when the concentration of nitrogen is very small in comparison to the other elements, as is in the case of both the ether- and the ester-type membranes, there may be some error associated with the calculated ratios. The O / C ratio is an indication of the abundance of the polyurethane soft segments near the membrane surface.

Table 7-7 shows the calculated N / C, N / O, and O / C ratios for the untreated ether- and the ester-type membranes and the membranes which were cleaned with xylene prior to analysis or exposed to aqueous solutions. As indicated by the N / C and N / O ratios (which are not zero), all of the membranes studied have some hard segments present near the membrane surface. It is quite evident from this data that the ester-type membrane shows a much higher enrichment of the surface by hard segments than for the ether-type membrane. This observation is in agreement with the DSC data which indicated a higher phase-mixing in the ester-type membrane. The untreated membranes appear to have a lower aggregation of the hard segments near the surface than the membranes cleaned with xylene. However, the xylene-cleaned membranes may have more error associated with the readings due to a higher detected concentration of silicon which may have affected the readings for nitrogen. The membranes which were exposed to aqueous solutions showed a lower abundance of nitrogen near the surface and a significantly higher abundance of carbon and oxygen. This

implies that when the membranes are exposed to solution, the soft segments become more abundant near the surface (in the ESCA depth) and the hard segments are less abundant. This is again supported by the DSC results which indicated that membranes exposed to a solution at 25 °C had well segregated soft and hard domains.

Table 7-8 shows the effect of temperature increase on the surface composition of the ether-type polyurethane membrane. As the solution temperature was increased from 4 °C to 60 °C, the nitrogen content near the surface decreased whereas the carbon and oxygen concentrations increased as is implied by the magnitude of the calculated N / O, N / C and O / C ratios respectively. These results indicate that with the increase in temperature, the surface of the membrane (in the ESCA depth range) becomes more enriched by soft segments. The DSC results collected for these membranes showed that as the temperature was increased, less segregation of the matrix was observed, i.e., partial mixing of the soft and the hard segments occurred. Therefore, the observed decrease in the nitrogen content at the membrane surface might not in fact truly represent an enrichment of the surface by the soft segments. At increased temperatures, the soft segments become more mobile and perhaps can shield some of the nitrogen atoms from being detected.

Variable extractions of organic compounds by the polyurethane membrane have been observed with the use of different solvents (Chapters 3, 4, and 5). The data shown in Table 7-9 was collected in order to determine whether the solvent to which the membrane was exposed had an effect on the surface composition: the results for the membrane not exposed to any solution are reported for comparison (control). All membranes exposed to the solutions shown in Table 7-6 have the O / C ratios much higher than the O / C ratio for the

control membrane. Membranes exposed to solutions, in particular the aqueous solutions, also have significantly lower N / O and N / C ratios. Based on these results, it can be concluded that when the polyurethane membrane is immersed in a solution, the membrane surface becomes enriched in the soft segments. Because the membrane surface is highly concentrated in the soft segments, the soft segments and not the hard segments must be involved in the initial transfer of the organic species from solution into the membrane surface. This is further supported by the DSC data which also indicated increased segregation of the soft and the hard domains of the membranes exposed to a solution. The O / C ratio remained independent of the solution composition and the N / C and N / O ratios showed some variation but not significant enough to observe any trends.

7.2.3. Infrared Analysis

Infrared spectroscopy (IR) can be used to identify chemical groups within a compound. Chemical bonds within a material vibrate at characteristic frequencies and so when infrared radiation is passed through the material at certain frequencies, the molecule will absorb the energy and vibrate[1]. Each group is capable of a number of different modes of vibration such as stretching and bending for example, so a number of peaks can often be attributed to the presence of a particular chemical structure. Identification of these peaks and their magnitude can permit identification of the molecular structure. Unlike the traditional IR analysis which is based on transmission of the beam through the sample, in Fourier transform analysis (FTIR) the incident beam is partially transmitted and partially reflected.

Both internal and external reflection can be used to obtain spectra of absorbance vs. λ. In ATR - FTIR (attenuated total reflectance FTIR), attenuation of the total internal reflectance is produced. The ATR spectra are very similar to those obtained by FTIR but some peaks may be more intense or shifted.

The ATR-FTIR spectra for both the ether- and the ester-type polymer films having thicknesses of 0.025 mm and 0.051 mm are shown in Fig. 7-2 and Fig. 7-3. Fig. 7-4 is an overlay of the ATR-FTIR spectra of the ether- and the ester-type membranes 0.025 mm thick for which the peak assignments are shown in Table 7-10[2,5-7]. The spectra shown in Fig. 7-5, Fig. 7-6, Fig. 7-7, Fig. 7-8, Fig. 7-9, and Fig. 7-10 were acquired on the ether- and the ester-type membranes exposed to ethanol, hexane and acetone respectively.

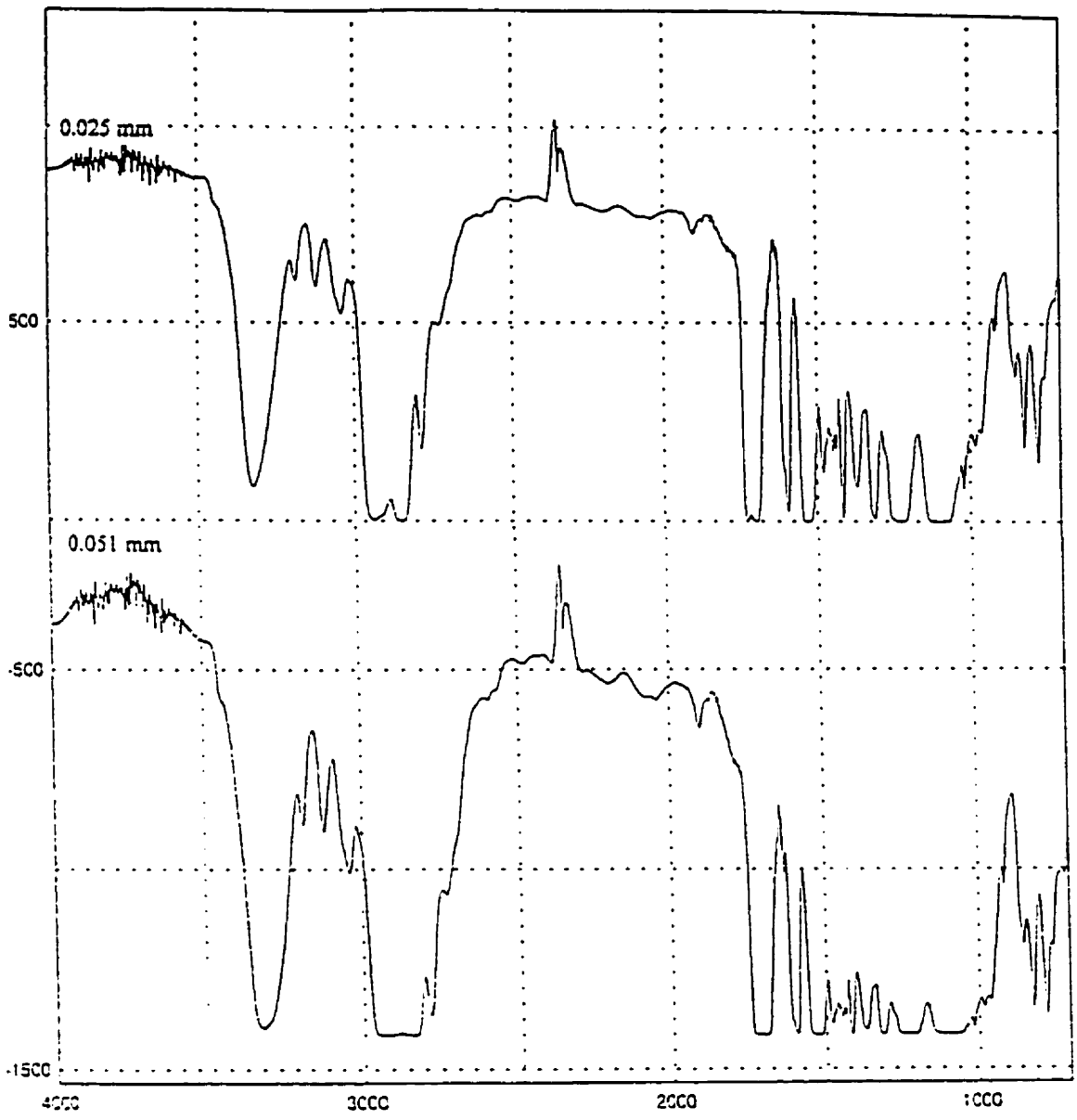

Fig. 7-2. ATR-FTIR spectra of the ether-type polyurethane membranes (untreated)

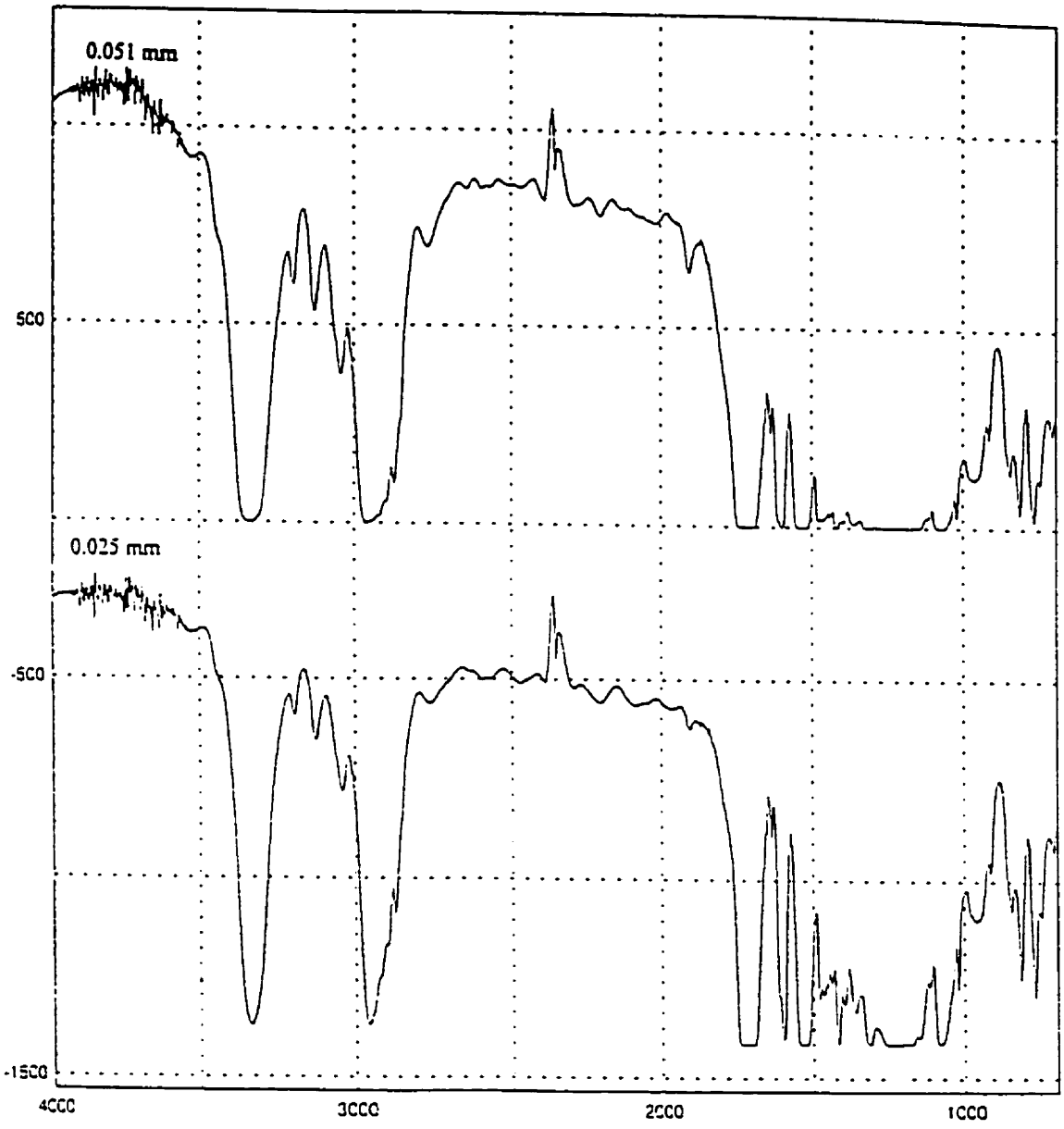

Fig. 7-3. ATR-FTIR spectra of the ester-type polyurethane membranes (untreated)

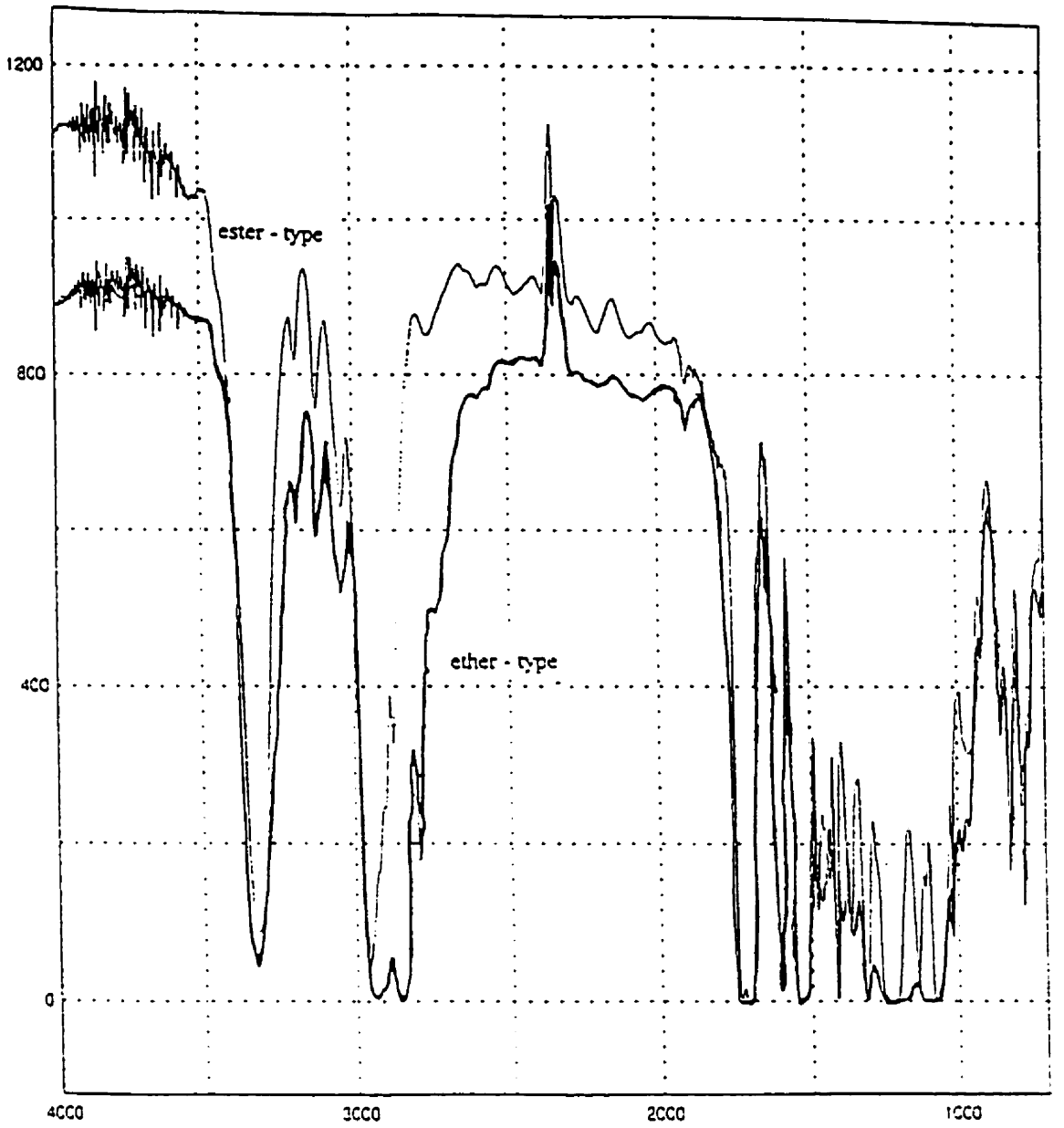

Fig. 7-4. A comparison of the ATR-FTIR spectra of the ether-and the ester-type membranes having thicknesses of 0.025 mm

Table 7-10. Peak wavenumber assignments of functional groups in the FTIR of the polyether-and polyester-type polyurethane membranes (see Fig. 7-4)

Wave Number (cm^{-1})		Peak Assignment
Polyether-type	**Polyester-type**	
495	495	out-of-plane ring bending
710	710	(O-C=O) bending
770	770	(C-H) aromatic out-of-plane deformation
815	815	(C-H) aromatic out-of-plane wag
960	958	(C-H) aromatic out-of-plane deformation
980	-----	(C-O-C) antisym stretch
1018	1018	(C-H) aromatic and (C-O-C) stretch
1073	1064	(O=C-O) stretch
1104	------	(C-O-C) antisym stretch
------	1141	(C-O-C) antisym stretch
------	1172	(C-O-C) antisym stretch
1221	1223	(C-N) and (N-H) stretch
1310	1310	(C-N) and (N-H) stretch
1365	1365	(C-H) symmetric deformation in CH_3
1420	1418	(C-N) stretch
1498	1498	(N-H) deformation
1596	1600	(C=C) stretch aromatic
1720	1720	(C=O) stretch in urethane
1740	1740	(C=O) stretch in urethane
2800	------	(C-H) stretching in CH_3
2850	2860	(C-H) antisym and sym stretch in CH_2
2920	2960	(C-H) antisym and sym stretch in CH_2
3338	3338	(N-H) stretch

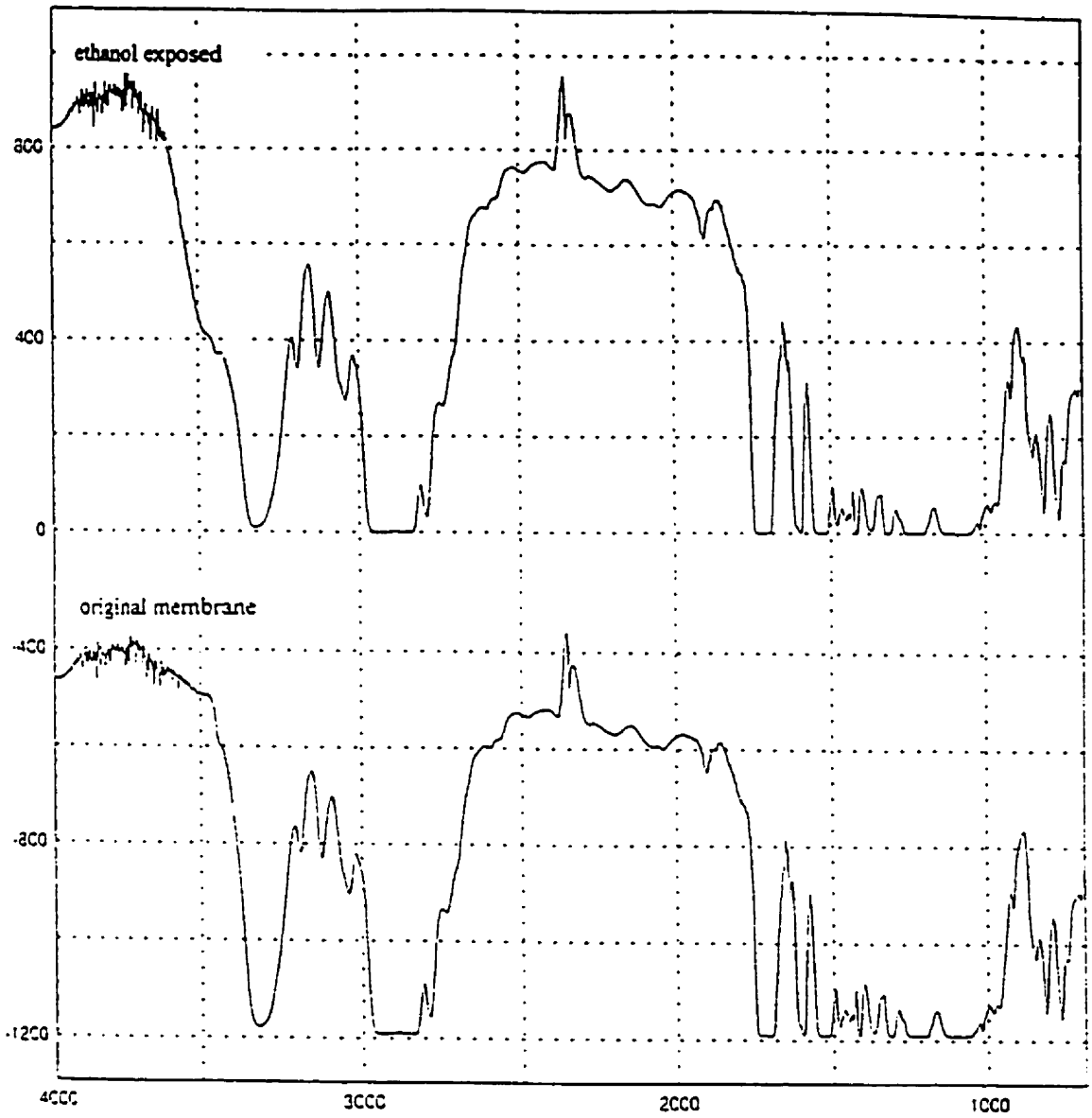

Fig. 7-5. The ATR-FTIR spectrum of the ether-type membrane exposed to ethanol and the spectrum of the untreated membrane

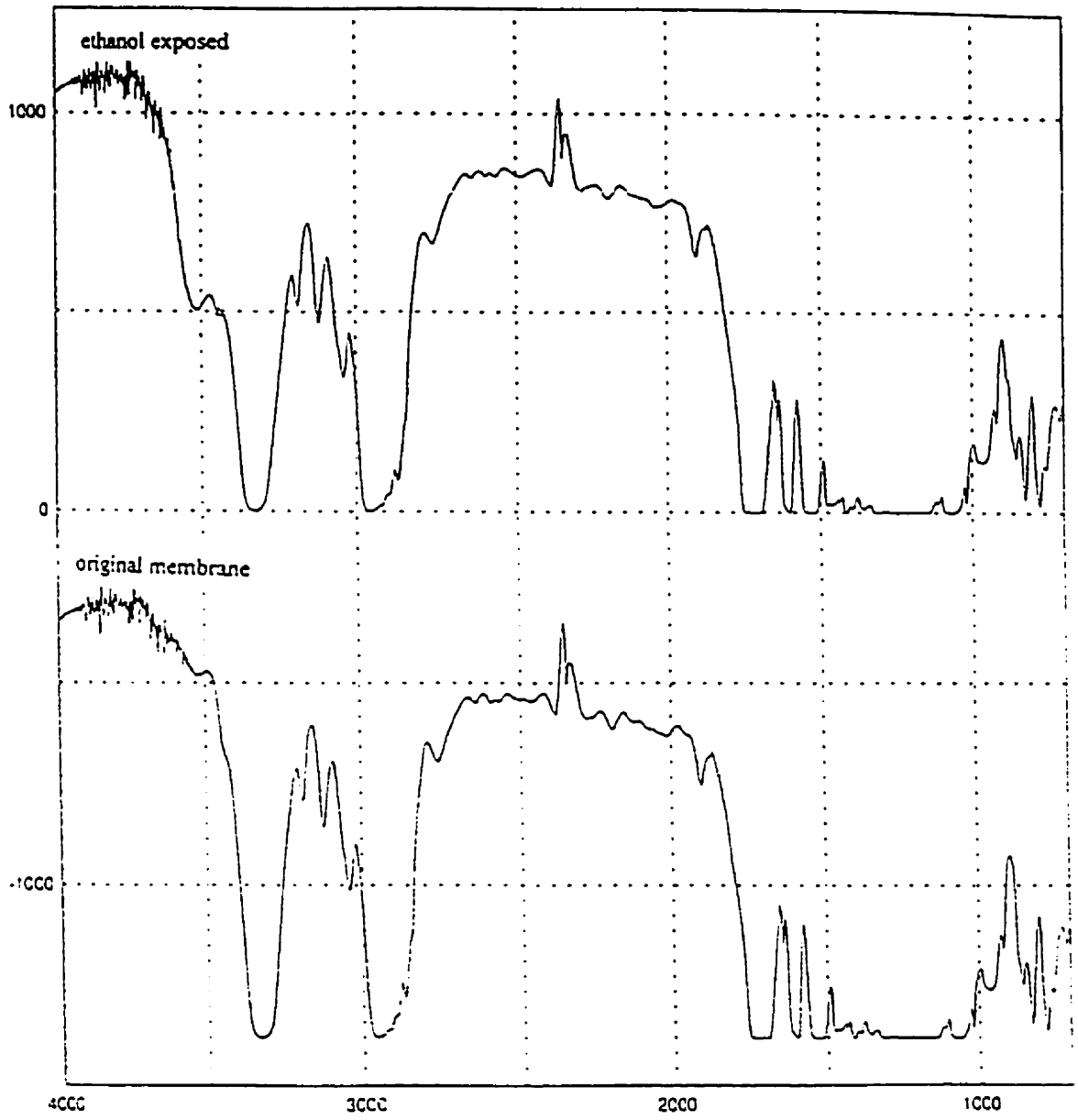

Fig. 7-6. The ATR-FTIR spectrum of the ester-type membrane exposed to ethanol and the spectrum of the untreated membrane

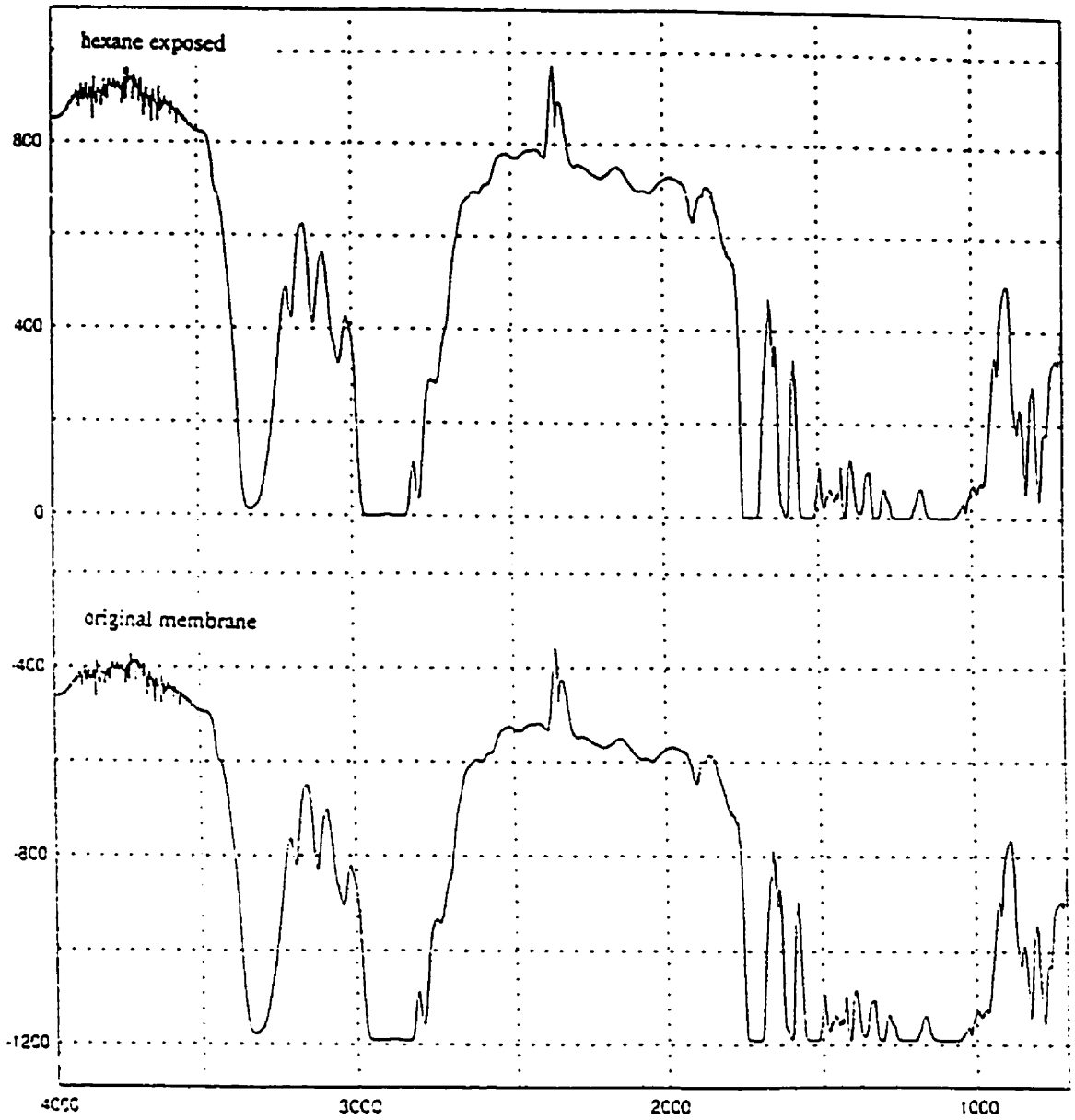

Fig. 7-7. The ATR-FTIR spectrum of the ether-type membrane exposed to hexane and the spectrum of the untreated membrane

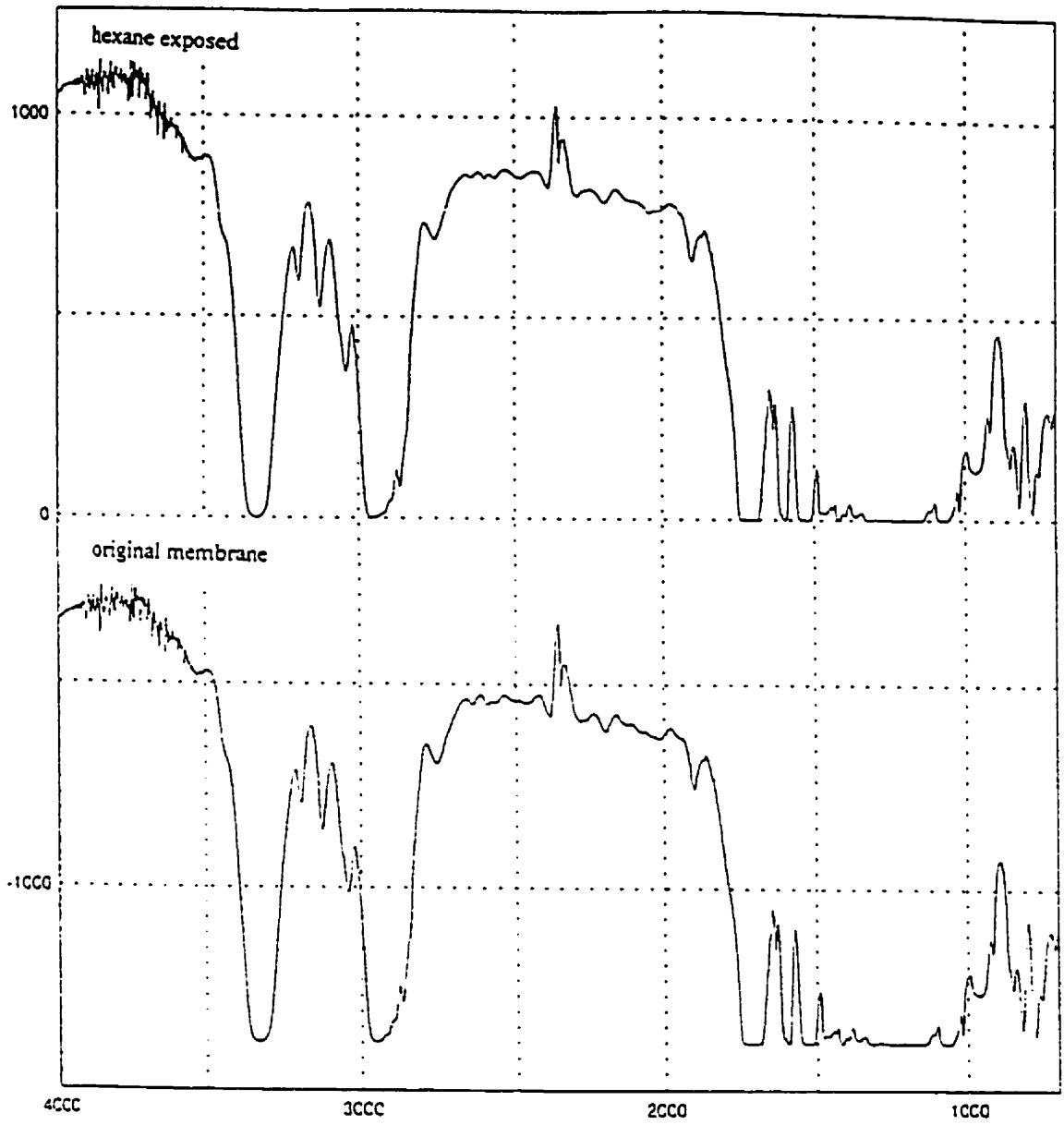

Fig. 7-8. The ATR-FTIR spectrum of the ester-type membrane exposed to hexane and the spectrum of the untreated membrane

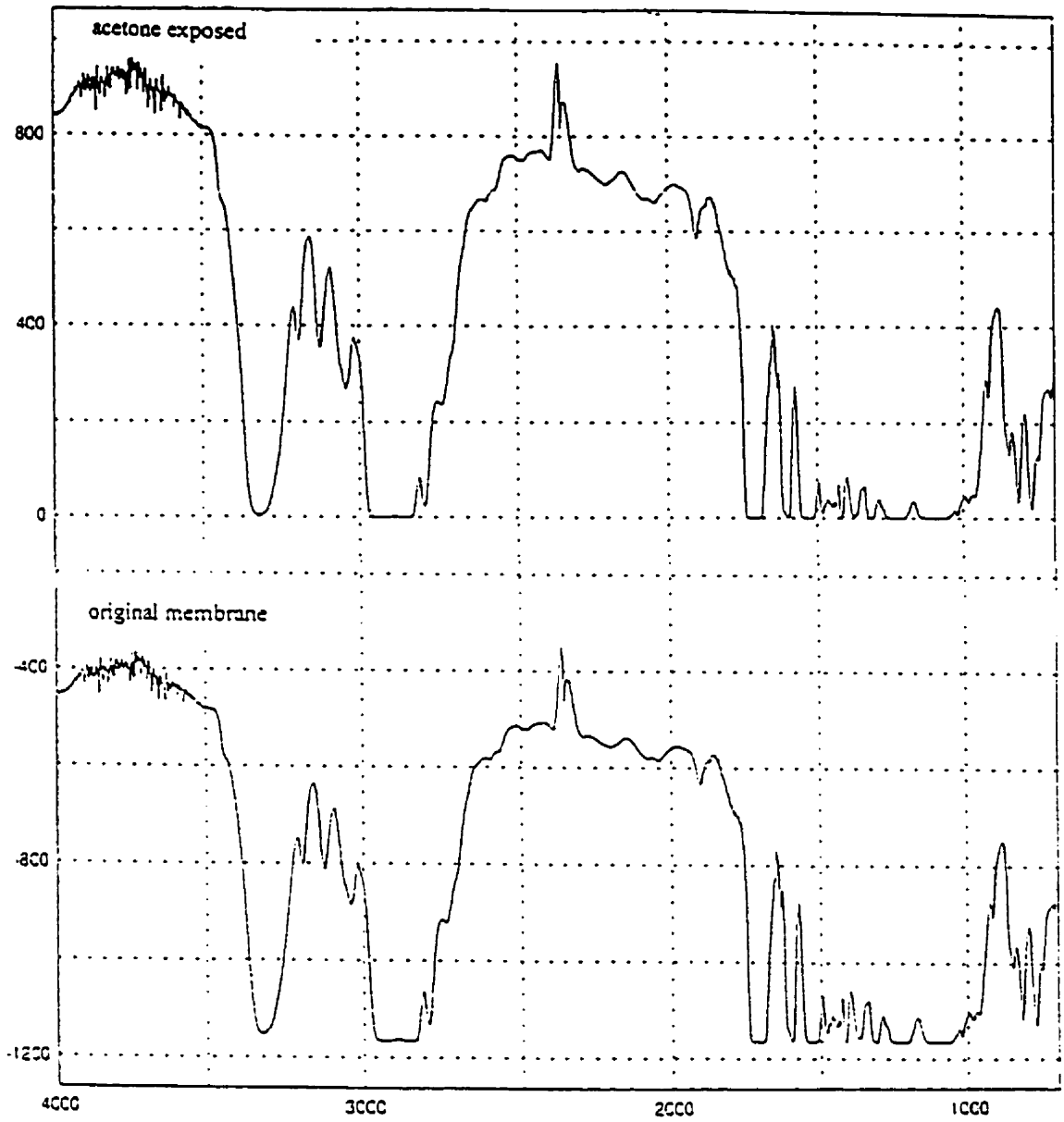

Fig. 7-9. The ATR-FTIR spectrum of the ether-type membrane exposed to acetone and the spectrum of the untreated membrane

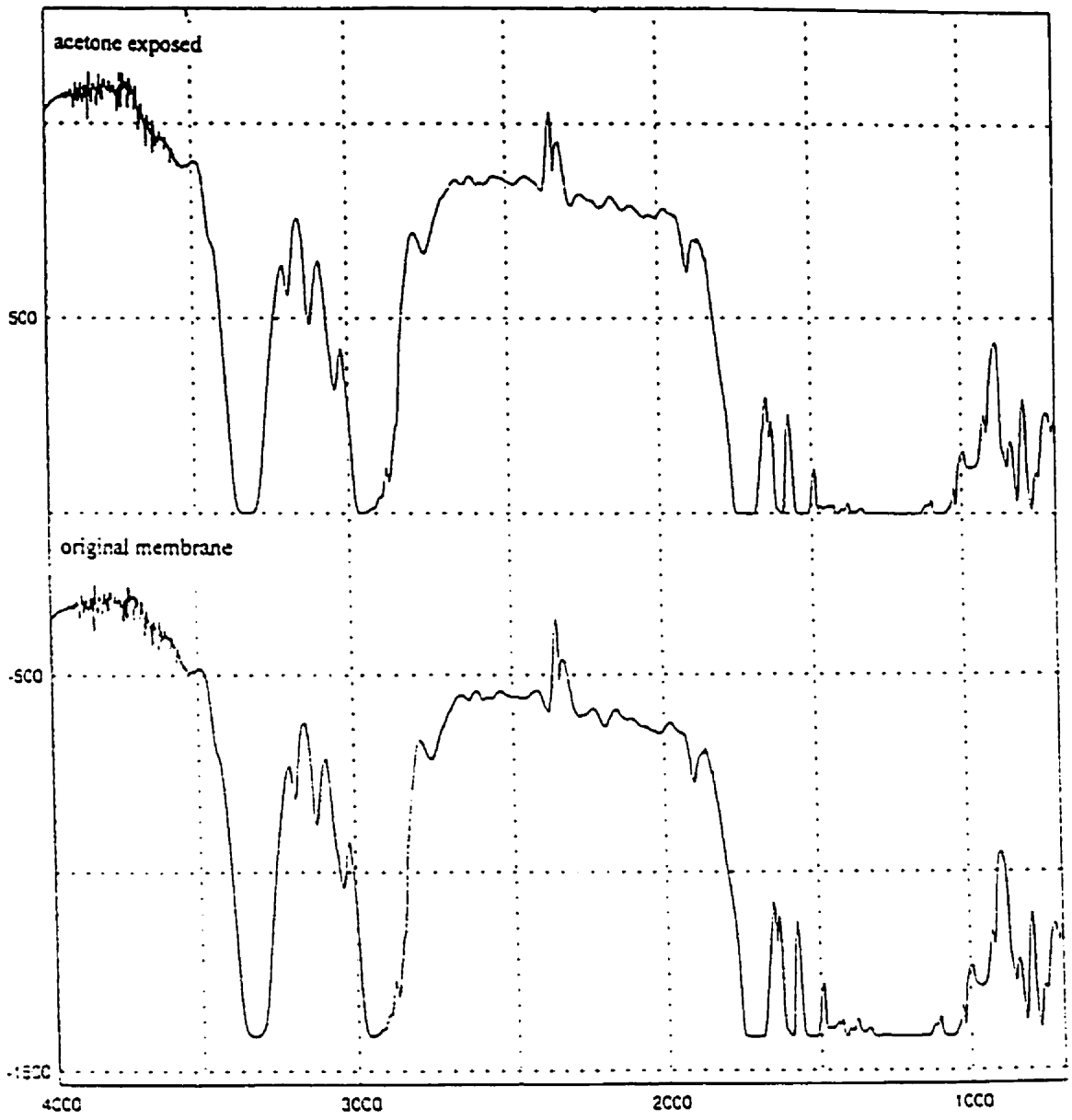

Fig. 7-10. The ATR-FTIR spectrum of the ester-type membrane exposed to acetone and the spectrum of the untreated membrane

As shown by Fig. 7-4 and by the peak assignments[2,5-7] in Table 7-10, the ATR-FTIR spectra of the ether-type and the ester-type polyurethane membranes are very similar except for the region in 2700 - 3000 cm^{-1} range and some minor differences in the shape of the peaks in the 600-1700 cm^{-1} range. These differences arise primarily from the presence of the ether group in the polyether soft segment of the ether-type membrane and the ester group in the polyester soft segment of the ester-type membrane. Absorption bands (1596 and 1600 cm^{-1}) in both membrane types indicate the presence of aromatic carbons which are found in the hard segments of both membranes. Scans of both membranes showed large peaks at 3338 cm^{-1} which are characteristic of the hydrogen-bonded N-H group and indicate that the membrane surfaces must contain some hard segments engaged in hydrogen-bonding which is also reflected by the DSC and ESCA analyses.

The ATR-FTIR spectra of both the ether- and the ester-type membranes which were exposed to hexane and acetone do not indicate any change in the polymer structure. However, when the membranes were exposed to ethanol, an increase in the peak at about 3550 cm^{-1} corresponding to a hydroxyl group from alcohols was observed. This indicates that although no decomposition of the membranes occurred, both membranes extracted and retained the alcohol in their matrix.

In conclusion, the ATR-FTIR analysis of the ester- and the ether-type membranes further confirmed the presence of the hard segments on the membrane surface. The membranes could be distinguished from each other using ATR-FTIR, and the spectra were generally in agreement with the peak assignments from the literature[2,5-7] with some minor shifts in peak positions which are due to the slightly different polymer compositions. The

ATR-FTIR data indicated that no decomposition of the membranes occurred due to exposure to organic solvents. Furthermore, the ATR-FTIR spectra for both the ether- and the ester-type membranes exposed to ethanol clearly showed that sorption of the alcohol by both membranes occurred.

7.2.4. Scanning Electron Microscopy (SEM)

Unlike the techniques used earlier to study the bulk and surface chemical compositions of the polyurethane membranes, surface characterization using scanning electron microscopy (SEM) can allow the collection of information on the polymer surface and the bulk morphology. SEM techniques have been widely used to study the surface topography of polymeric membranes. For example, the presence of large scale phase-separation, pores, voids, cracking can be detected by SEM. These physical characteristics or morphologies can also be individually examined in more detail and classified according to roughness, porosity and texture. The bulk of the membrane can be viewed using SEM by looking at the cross-sections of the samples. Differences in the membrane surface and bulk structures can result not only from differences in the bulk chemistry but also from the physical and chemical treatments to which the membrane is subjected. Furthermore, because a macro-scale analysis is being done, the sample consistency can also be assessed. For example, if large variations in the surface and bulk appearance exist within a sample, then these may partially account for any difficulties encountered in analysis of the membrane on

the small atomic scale.

In order to obtain the SEM images, all of the polyurethane membrane samples (cut with scissors) were first sputter coated with conductive Au / Pd prior to analysis. The coated samples were then placed in the sample compartment of the scanning electron microscope and the representative images of each sample were taken and stored for image analysis. Several selected SEM images of the membranes studied by the other techniques discussed in this chapter are shown in Fig. 7-11, Fig. 7-12, Fig. 7-13, Fig. 7-14, and Fig. 7-15. All of the images of the membrane surfaces were obtained at a magnification of 320 x. The images of the cross-sections of the membranes were obtained at a magnification of 1180 x and a tilt angle of 45 degrees. The three dimensional appearance of the micrographs is due to shading and varying levels of brightness. The shading and brightness occur because the surface of the membrane and the features on it are not flat and reflect the secondary electrons from the source at different angles. Features which are thin, such as the "bubbles" on the membrane surface, also appear brighter because the secondary electrons reflected from them and the membrane surface can be collected simultaneously, which shows as a rim lighting around these features. In SEM analysis the noise, which affects the clarity of the micrograph, is caused by the instability of the electron source or detector during the time required to scan an image. An attempt was made to reduce the noise, but it was very difficult to find a scan time that would completely eliminate the above effect. On some of the micrographs the brightness range was very small, therefore there was not enough contrast to give good visibility, although the noise was relatively low. Contrast manipulation was used to improve the visibility of some features but at the expense of other features. Consequently, some of

the images are not very sharp in appearance.

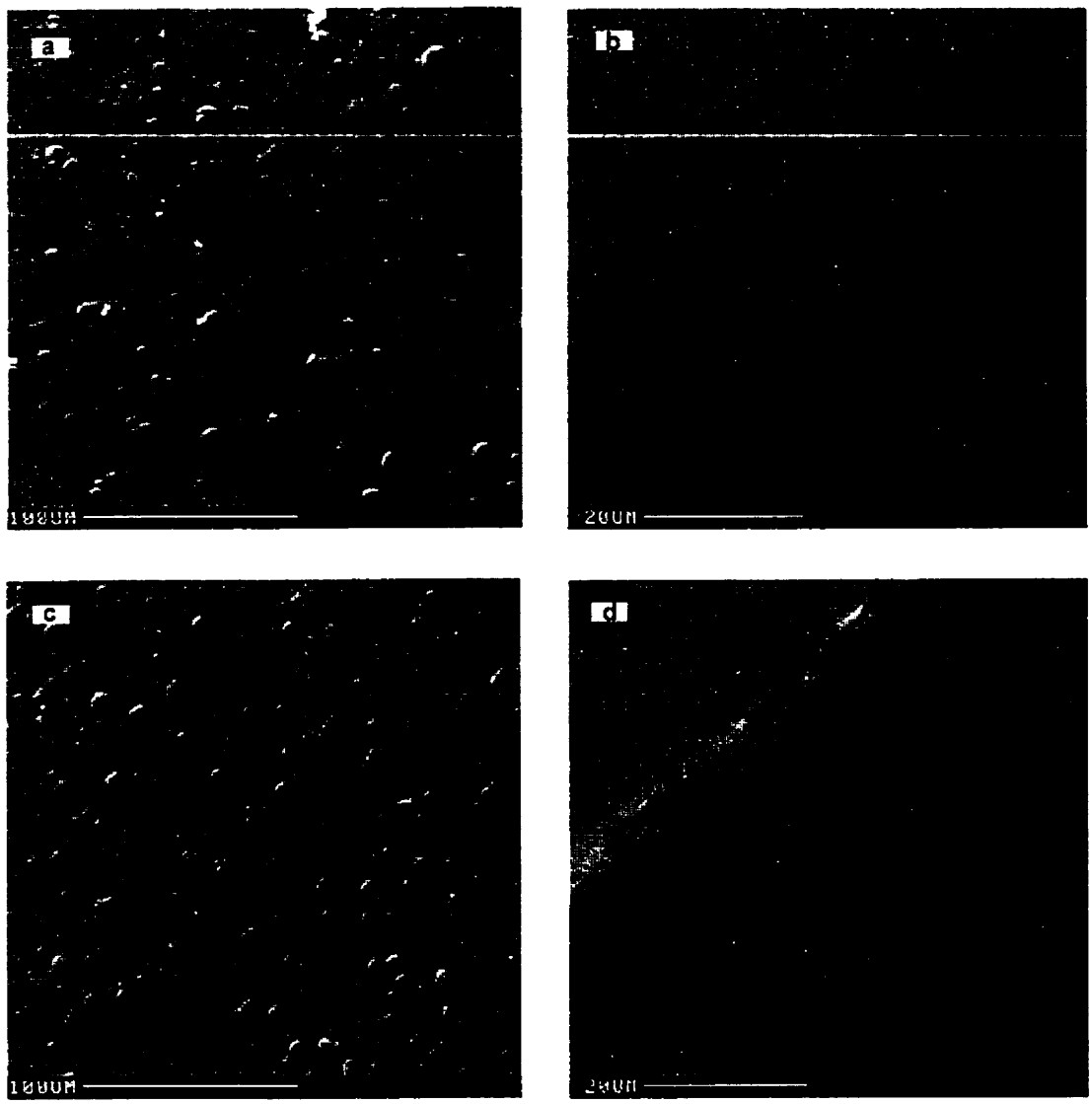

Fig. 7-11. The SEM images of the untreated ether-type membrane: (a) surface view, (b) edge view, and the xylene-cleaned membrane: (c) surface view, (d) edge view

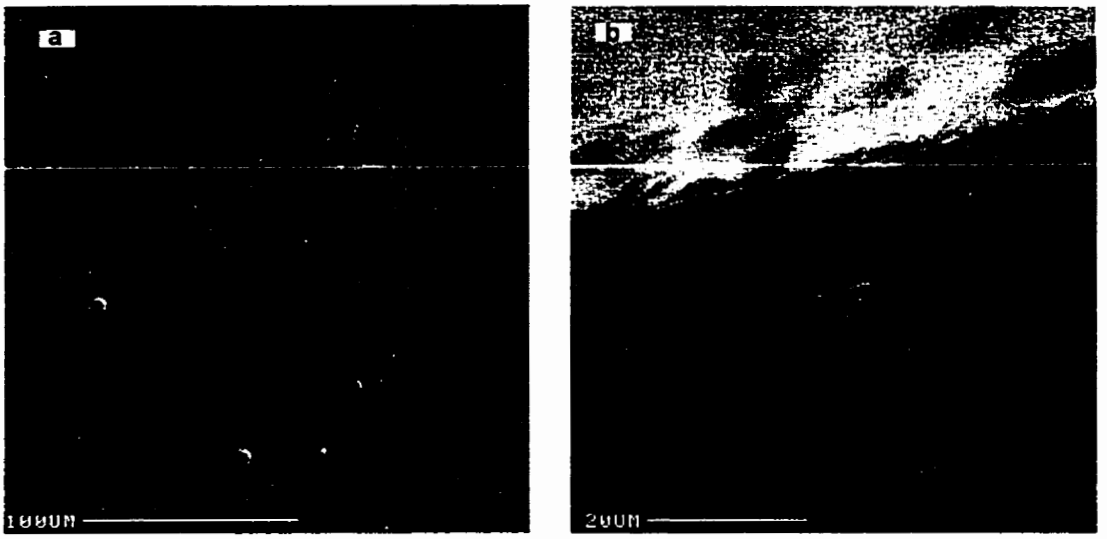

Fig. 7-12. The SEM images of the untreated ester-type membrane: (a) surface view, (b) edge view

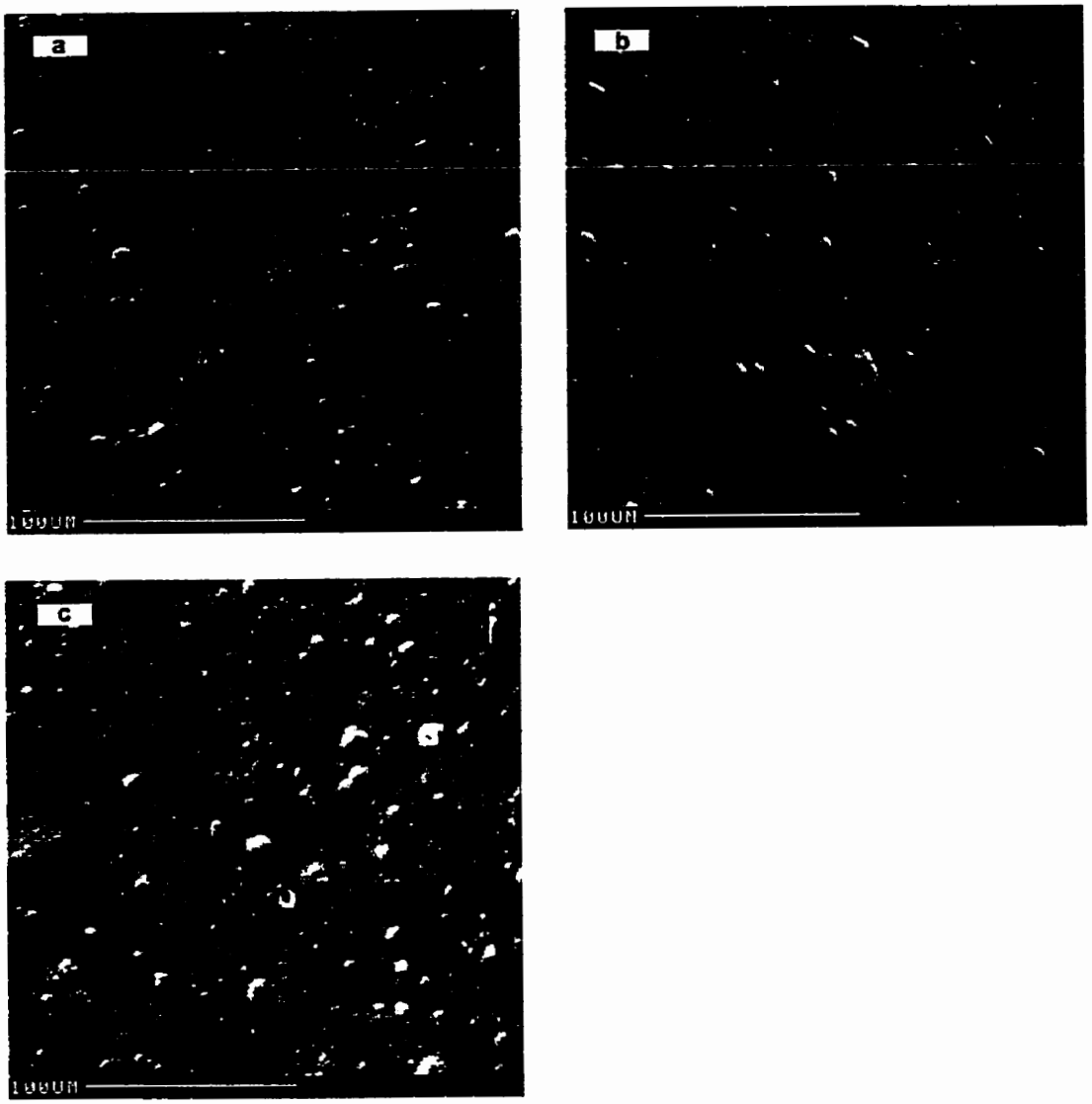

Fig. 7-13. The SEM images of the surfaces of the ether-type membrane exposed to aqueous solutions (water) at various temperatures: (a) 4 °C, (b) 25 °C, (c) 60 °C

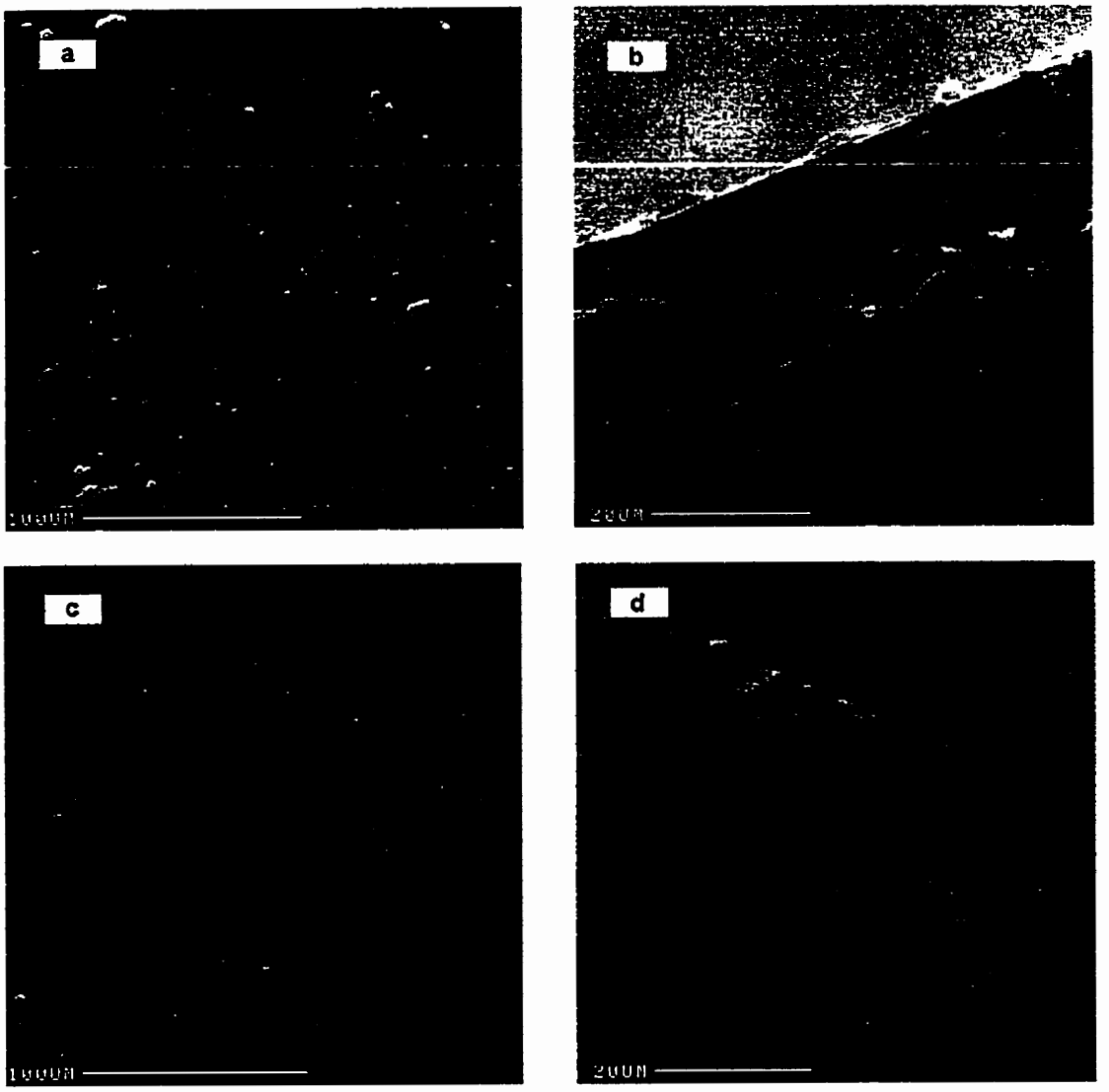

Fig. 7-14. The SEM images of the ether-type membrane exposed to: (a) 1 M HCl surface view, (b) 1 M HCl edge view, and the ester-type membrane exposed to: (c) 1 M HCl surface view, (d) 1 M HCl edge view

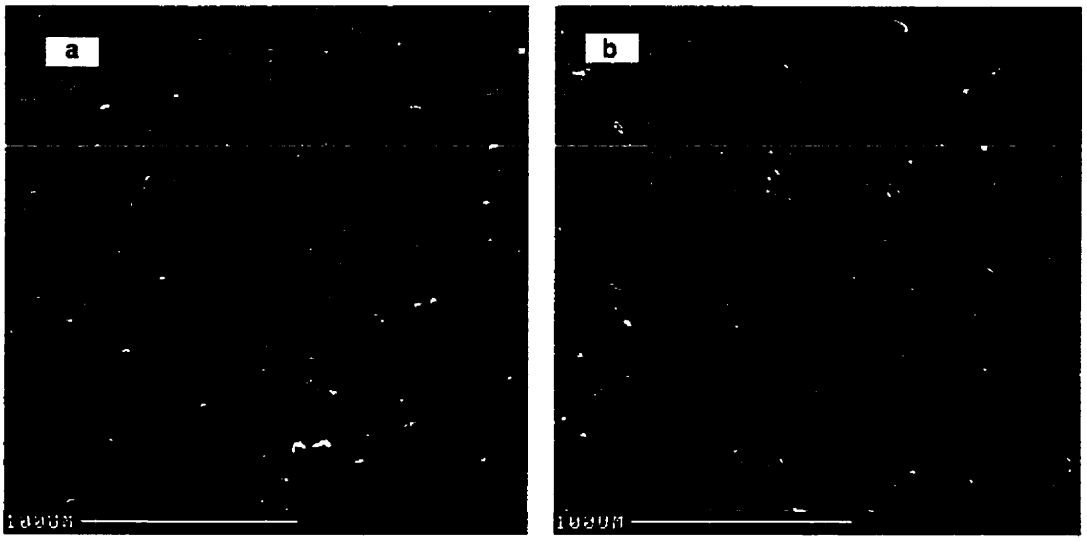

Fig. 7-15. The SEM images of the surfaces of the ether-type membrane exposed to: (a) hexane (b) an organic dye Brilliant Green in 1 M NaCl

The only apparent difference between the images shown in Fig. 7-10 to Fig. 7-14 exists between surfaces of the ether- and the ester-type polyurethane membranes. The ester-type membrane has a much less grainy appearance regardless of the experimental conditions used. The cross-sections of both membrane types look similar. The less smooth surface of the ether-type membrane may have resulted from its manufacturing process when more air may have been trapped in the polymer matrix. The relatively bright shading of the bubbles indicates that they are very thin and examination of the cross-section of the membranes shows that these bubbles do not completely perforate the membrane. The results obtained from the SEM study do not show any decomposition of the membranes which were exposed to several organic and aqueous solvents and to solvents at varying temperatures as is evidenced by the lack of cracks and tears and the roughly unchanged appearance and occurrence of the bubbles and holes. The SEM technique is useful for a qualitative macroscopic analysis of the surface and the bulk of the polyurethane membranes but it fails to provide any information on the domain structure of the membranes.

7.3. Conclusion

The chemical characterization of the ester- and the ether-type polyurethane membranes using DSC and ESCA techniques provided some useful insights into the domain structures of both membranes. Both the ether- and the ester-type membranes exposed to solutions at temperatures below zero or around the room temperature appeared to have well

segregated soft and hard domains. On the other hand, the membranes exposed to solutions at a higher temperature (e.g., 60 °C) had a more homogenous matrix resulting from mixing of the soft domains with the hard semi-crystalline or crystalline regions. The untreated ester-type polyurethane membrane had a less segregated matrix than the ether-type membrane. This can partially account for the consistently lower sorption of organic compounds observed with this membrane. Because in the ester-type membrane the soft and the hard segments are less well segregated, the intramolecular interactions between these segments may be stronger and the organic compounds in solution have more difficulty in accessing the overall matrix. Exposure of both membranes to solutions promoted accumulation of the soft segments at the surface and resulted in more extensive domain segregation which supports the hypothesis that it is the soft segment domain which is primarily involved in the intramolecular interactions with the organic compounds in solution. The ESCA analysis indicated that nitrogen is present near the surfaces of both membranes (a higher surface concentration of nitrogen was present in the ester-type membrane). The fact that nitrogen was found near the surface suggests that some hard segments are present at the surface; however because a small representative area of the polyurethane membrane was examined in this analysis, some error may be associated with these results. The ATR-FTIR analysis confirmed the presence of the ether and the ester segments in the membranes and also indicated the presence of nitrogen and aromatic species which are found in the hard domains of the polymer. No decomposition of either membrane exposed to organic and aqueous solutions was detected as indicated by the relatively unchanged appearance of the ATR-FTIR spectra. In fact sorption of ethanol by both membranes was evident in the obtained spectra. The SEM analysis also showed no

change in the macro-structure of the membranes exposed to various physical and chemical treatments.

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Chapter 8: Conclusions and Future Work

8.1. Extraction and transport of organic compounds using polyurethane membranes

The extraction of substituted phenols is the pioneering study in the investigation of the mechanism of sorption of organic compounds by the polyurethane membrane which clearly demonstrates the potential of this polymer for the removal of organic compounds from solution. The study of sorption of phenols shows that these compounds are extracted by the polyurethane membrane only if present in solution as neutral species. Furthermore, this research also indicates that the hydrogen-bonding interactions of phenols with the membrane are quite important in the entire sorption process. The extraction amount of phenols in the membrane can be increased by providing more polymer material to interact with the phenol molecules in solution which can be accomplished by either increasing the surface area of the membrane exposed to the phenol solutions or by using a thicker membrane. One other option may be to use the ether-type polyurethane membrane which gives consistently higher extraction of phenols than the ester-type polymer.

The feasibility of extracting phenols with the polyurethane membrane suggests that this polymer is also capable of removing other organic species from solution and therefore can potentially be used in the membrane separation technology for the purification of effluents. In order to obtain more detailed information regarding the sorption mechanism

(i.e., to determine the role of functional groups and solution conditions on the process) and to confirm the findings on the extraction phenols, sorption of benzoic acids and various organic dyes was studied. The extraction of simple monohalobenzoic acids confirms the importance of hydrogen-bonding interactions between the neutral extracting species and the membrane during sorption. The ether-type membrane again shows superior extraction capabilities for benzoic acids in comparison with the ester-type membrane. The temperature affects the extraction of benzoic acids to some extent, as with the phenols, and this effect varies with the membrane type. The investigation of extraction of benzoic acids from various solvents (aqueous and organic) confirms the conclusion that the entire sorption is collectively controlled by a combination of factors such as the composition of the membrane, chemical structure of the extracting species, the solution conditions, and solution temperature. It was advantageous to study the sorption of simple organic compounds such as phenols and benzoic acids not only from the mechanistic perspective but also because of the wide industrial use of these compounds and the consequent need for their removal from waste effluents. Furthermore, a good understanding of the extraction of these small and simple compounds provides a basis for studying the sorption process of other more complex organic species.

The study of the sorption mechanism of organic dyes demonstrates that in addition to removing organic species from solution, the membrane can serve as a transport medium. The knowledge of the extraction of phenols and benzoic acids has allowed the optimization of the initial solution conditions for the extraction of organic dyes. The factors which affect the transport of various anthraquinone, acidic and basic dyes through the polymer and the

desorption of the extracted dyes into a receiving solution had to be fully investigated. The effects of dye geometry and size, initial dye concentration, thickness of the membrane, and solution temperature on the rate of transport were examined. An increased rate of transport of the dyes occurs with increased solution temperature and with the use of a thinner polyurethane membrane. The differences in the rates of transport can be attributed to the relative solubility of organic dyes in the membrane and in solution, and to the strength and extent of intermolecular interactions with the membrane. Dye solution concentration, geometry and size, and the presence of salts in solution have no significant effect on the rate of transport. All of the studied dyes, as discussed with phenols and benzoic acids, exist in neutral form in the membrane. Overall, the results from this study provide further insight not only into the mechanism of extraction but also the transport of organic compounds by the polyurethane membrane. The feasibility of extraction and transport of organic dyes through the polyurethane membrane also suggests that this membrane could be utilized in an industrial membrane separation process to remove and recycle textile colorants. All of the above work is published in Talanta[1,2,3].

8.2. Extraction and transport of organometallic species using polyurethane membranes

In this laboratory, the polyurethane membrane has been shown to successfully remove both organic and inorganic species from solution. Therefore, studying the feasibility

of sorption of organometallic species which possess the characteristics of both organic and inorganic compounds was a good choice for completing the investigation of the mechanism of sorption of compounds from solution by the polyurethane membrane. The research on the extraction and transport of inorganic[4,5] and organic compounds shows that one of the key conditions that must be met in order to obtain sorption is the formation of a neutral species by the extracting compound. The majority of organometallic compounds are charged in basic or acidic solution due to their complex structure and therefore would not be extracted by the membrane. The organometallic ion-association complexes, on the other hand, can be neutral if appropriate solution conditions are provided. Such complexes can be formed between organic dyes and complex metallic ions. Examples of organometallic ion-association complexes are the complexes of gold chloride species, which extract into the polyurethane membrane under appropriate conditions[5], and several organic dyes which are known to complex the gold anion[6]. The study of sorption of these organometallic ion-association complexes again showed support for the proposed sorption mechanism of organic compounds. Furthermore, this study demonstrated that it is not necessarily only the neutral species that is extracted by the polyurethane but a species that has no localized charge associated with it. The organometallic ion-association complexes of gold chloride and the studied organic dyes have no charge associated with the molecule and therefore are sorbed by the membrane. In fact, sorption of species which are not otherwise extracted by the polyurethane membrane such as the charged gold chloride anion can be induced if a formation of a stable ion-pair complex can occur. This work has been submitted for publication in the *Journal of Membrane Science.*

8.3. Polyurethane membrane characterization

The chemical and morphological characterization of the polyurethane membranes has been performed in order to determine if any relative changes in the membrane surface and bulk occur during sorption due to exposure of the membrane to various chemical and physical experimental conditions. Throughout this thesis assumptions have been made about the changes occurring in the membrane matrix during sorption in order to explain the observed phenomena. The chemical characterization of the surface and the bulk of the ether- and the ester-type membranes provides the analytical support for these assumptions and further insight on some of the observed phenomena.

8.4. Future work

In the course of this extensive study, several related projects have been started which are quite promising and worth investigating in more detail. One example is the possibility of immobilizing an organic compound in the membrane matrix which can allow sorption of charged species which are not normally extracted by the polyurethane. For example, the presence of the organic dye Brilliant Green in the polyurethane membrane allows extraction of charged gold chloride species from solutions without the formation of a gold chloride-dye ion-association complex in solution. The presence of Brilliant Green in the membrane matrix

somehow makes the membrane permeable to the otherwise unextractable gold chloride. Without the dye in the membrane, charged gold complexes can be made extractable only if they are first converted into neutral species which often requires very acidic solution conditions which results in the degradation of the membrane[2]. Membrane degradation is undesirable from an industrial point of view, because it creates a need for a frequent replacement of the membranes used in the purification systems in order to maintain the efficacy of the separation process which in turn increases the operational costs. The possibility of extracting both charged and uncharged species with the same membrane without having to use harsh solution conditions is therefore economically very valuable.

Another quite promising project involves investigating the sorption of various alcohols from water. Preliminary studies of the sorption of ethanol, methanol, and butanol by the polyurethane membrane show that all of these alcohols can extract and transport through both the ether- and the ester-type membranes from aqueous and mixed organic solutions (e.g., ethanol extracted from hexane). Each alcohol as low as 1 % in an aqueous solution can be extracted by the membrane and desorbed into a receiving solution containing water. The major difficulty encountered in this study was the quantification of the amount of alcohol in the aqueous phase. Separation of alcohols from solutions using a polyurethane membrane can be a very economical alternative to the currently used pervaporation process because the energy consumption is much lower than in the latter operation. One application may be in the food industry for dealcoholization of beverages.

Because the polyurethane membranes possess strong chemical and thermal resistance, they are a viable option to the membranes presently being used in industrial purification

processes. The detailed knowledge of the extraction mechanism of organic compounds by the polyurethane membrane can perhaps allow a more effective design of a membrane separation system for the removal of various components in industrial effluents.

References for Chapter 8

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Appendix 1

Complete DSC Thermograms

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: xprm
Data Collected: Oct 13,1999 06:54:53 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc

Validation
- Validated: No

Sample ID: polyU *XPR Manufacturer Final Run*
Operator ID:
Comment:
Sample Weight: 14.780 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\Chosen Files\XPRMfbnc@991013110915.dsd

Initial Conditions
- Temperature: -130.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To -130.00°C
Total Points in Run: 2735

Method Steps:

1) Hold for 1.0 min at -130.00°C
   - Data Points: 60

2) Heat from -130.00°C to 200.00°C at 20.00°C/min
   - Data Points: 991

3) Cool from 200.00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

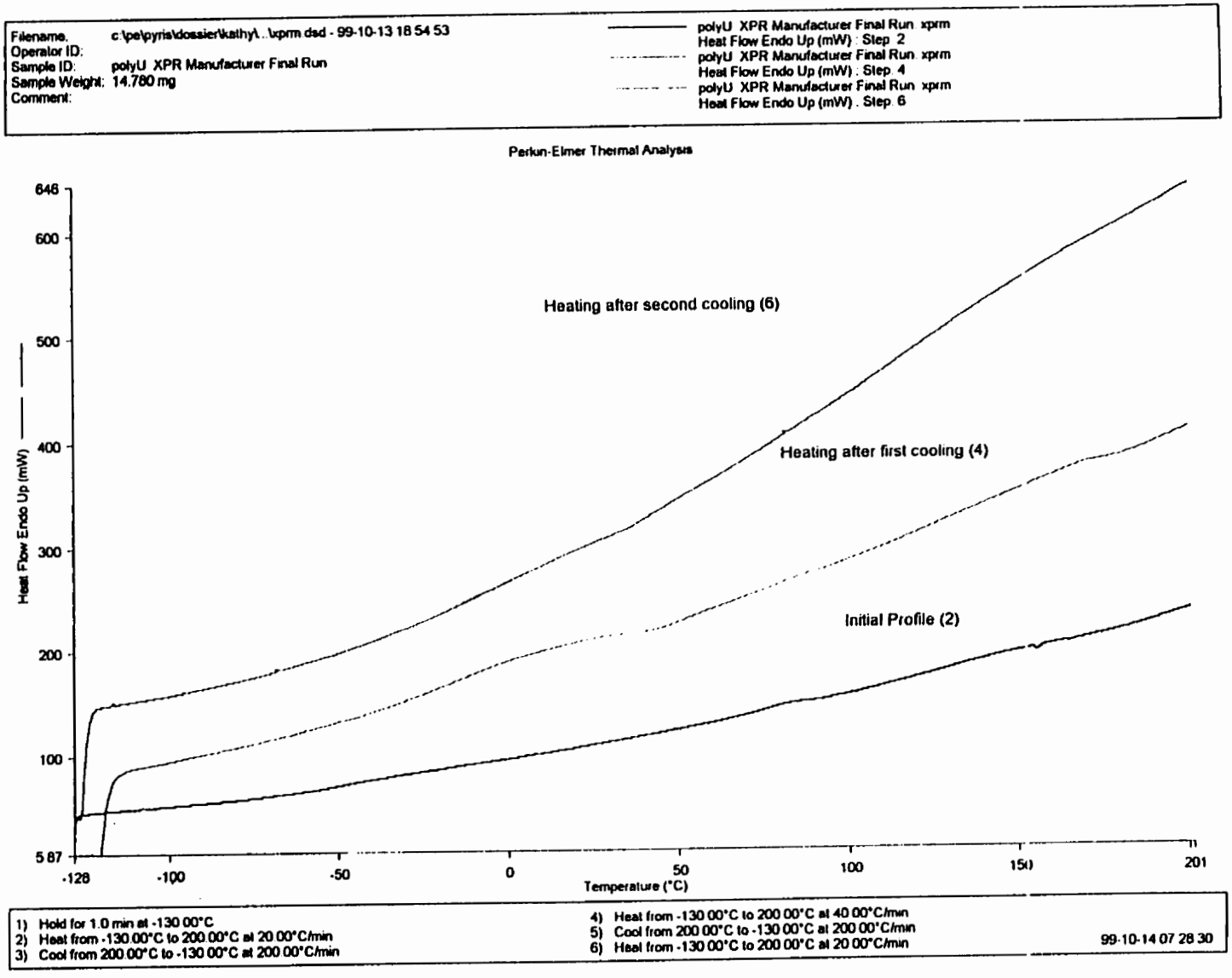
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991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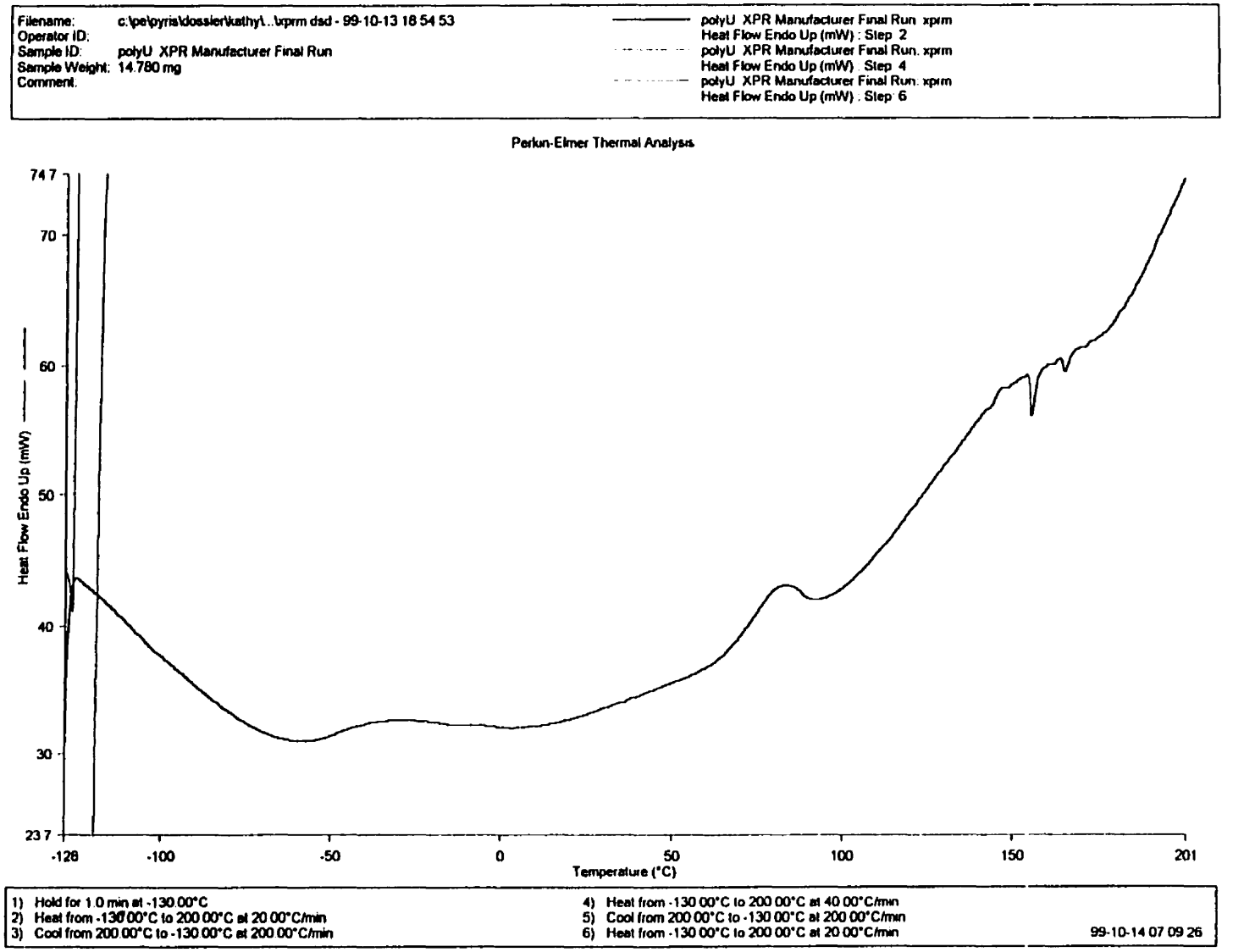
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 2
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 4
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
Heating after second cooling (6)
Heating after first cooling (4)
Initial Profile (2)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07 28 30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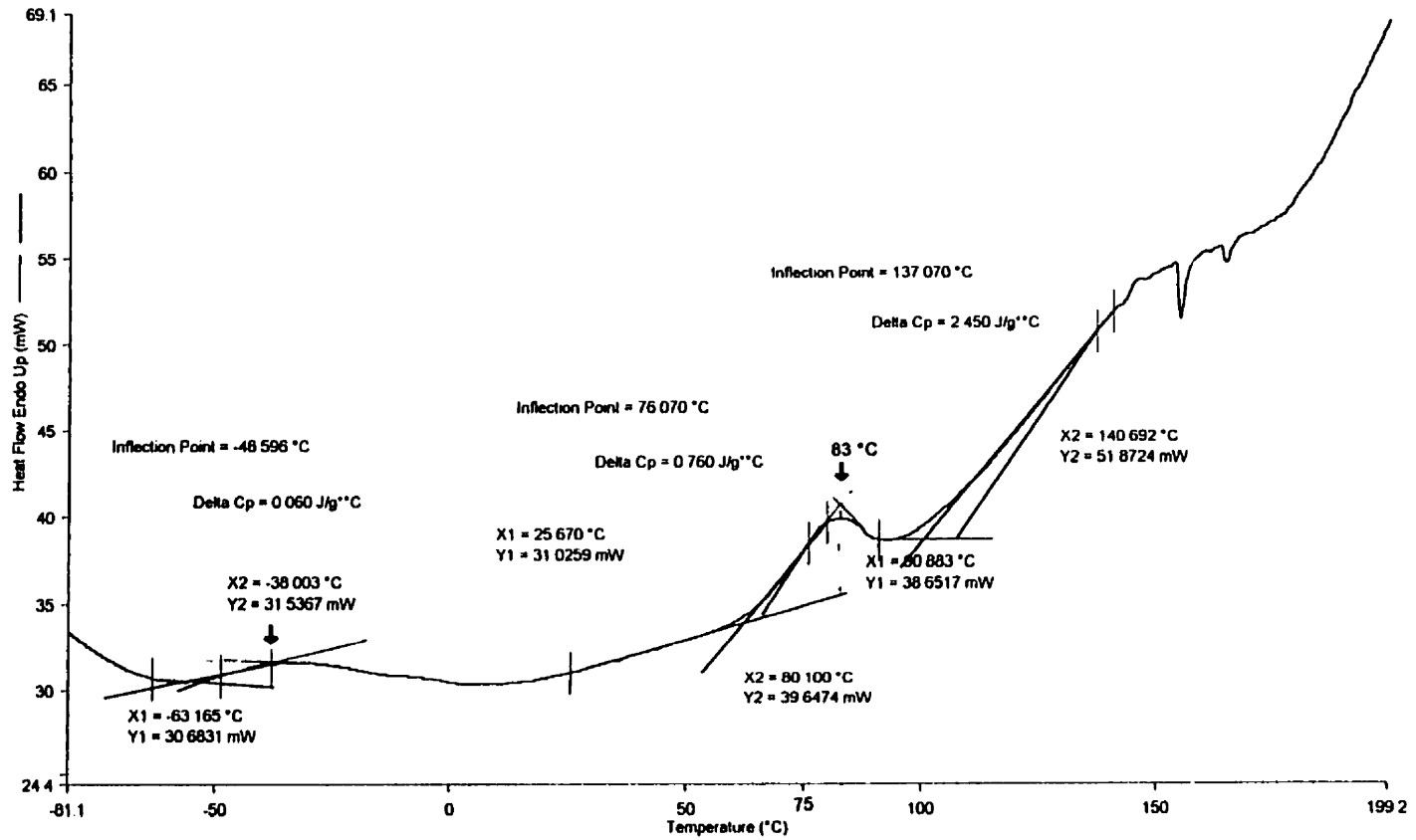
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 2
polyU XPR Manufacturer Final Run. xprm
Heat Flow Endo Up (mW) : Step 4
polyU XPR Manufacturer Final Run. xprm
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
74.7
70
60
50
40
30
23.7
Heat Flow Endo Up (mW)
-128
-100
-50
0
50
100
150
201
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07:09:26

Filename: c:\pe\pyris\dossier\kathy\ .\xprm dsd - 99-10-13 18 54 53
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:

polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 2
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 4
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 6

Perkin-Elmer Thermal Analysis



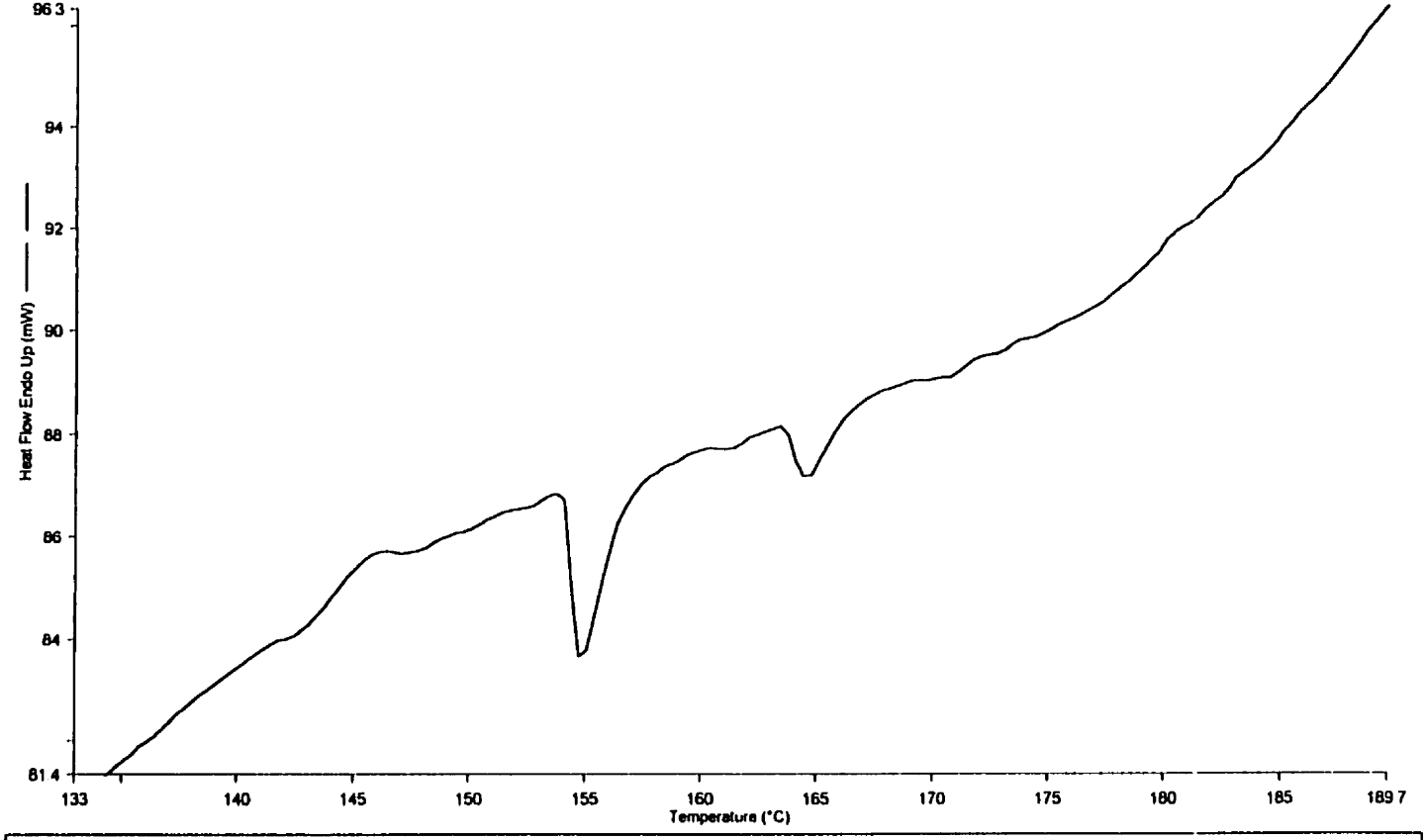
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 07:12:52

Filename: c:\pe\pyris\dossier\kathy\...\xprm dsd - 99-10-13 18 54 53
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:

polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 2
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 4
polyU XPR Manufacturer Final Run. xprm
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis

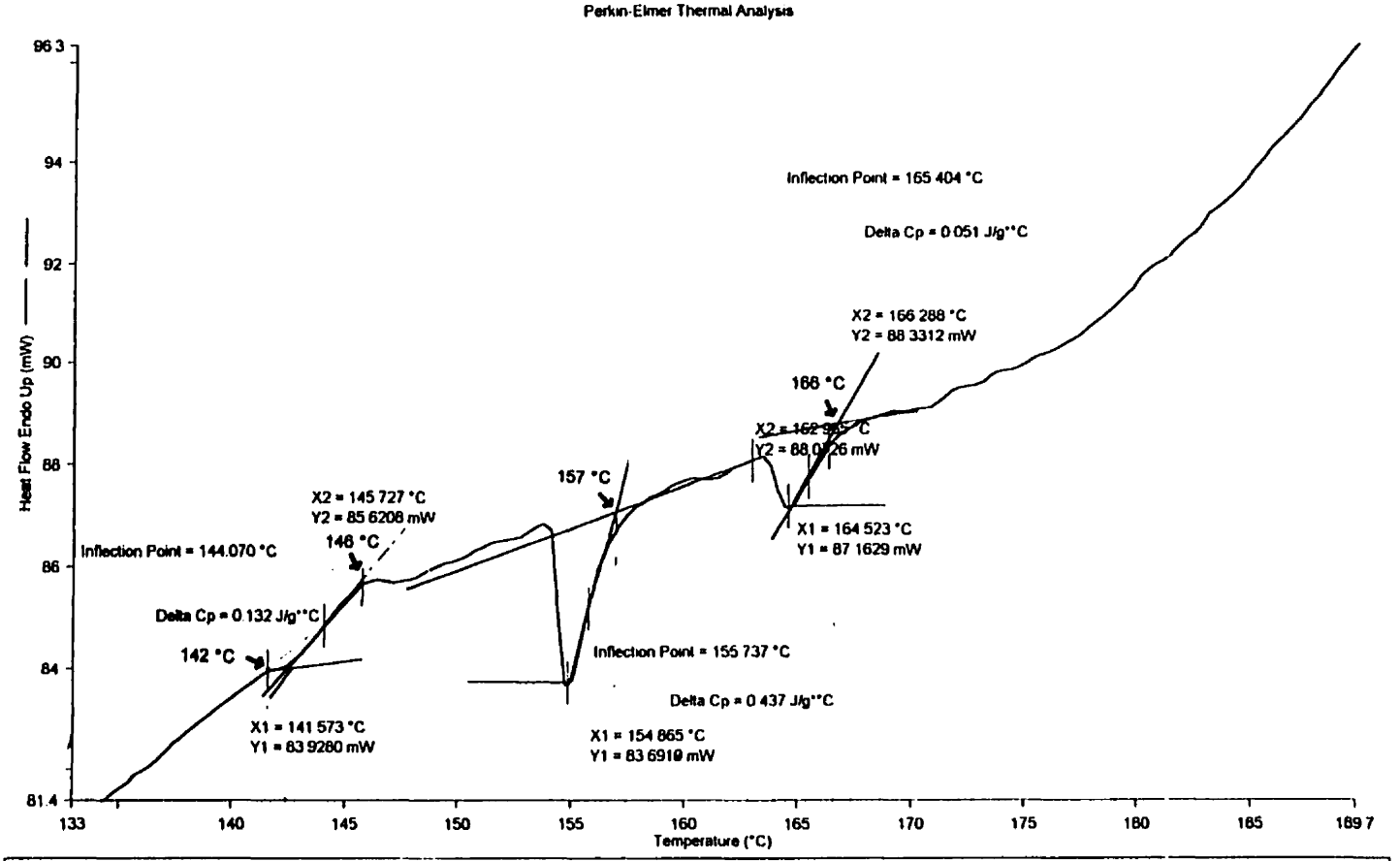


1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 07:17:05

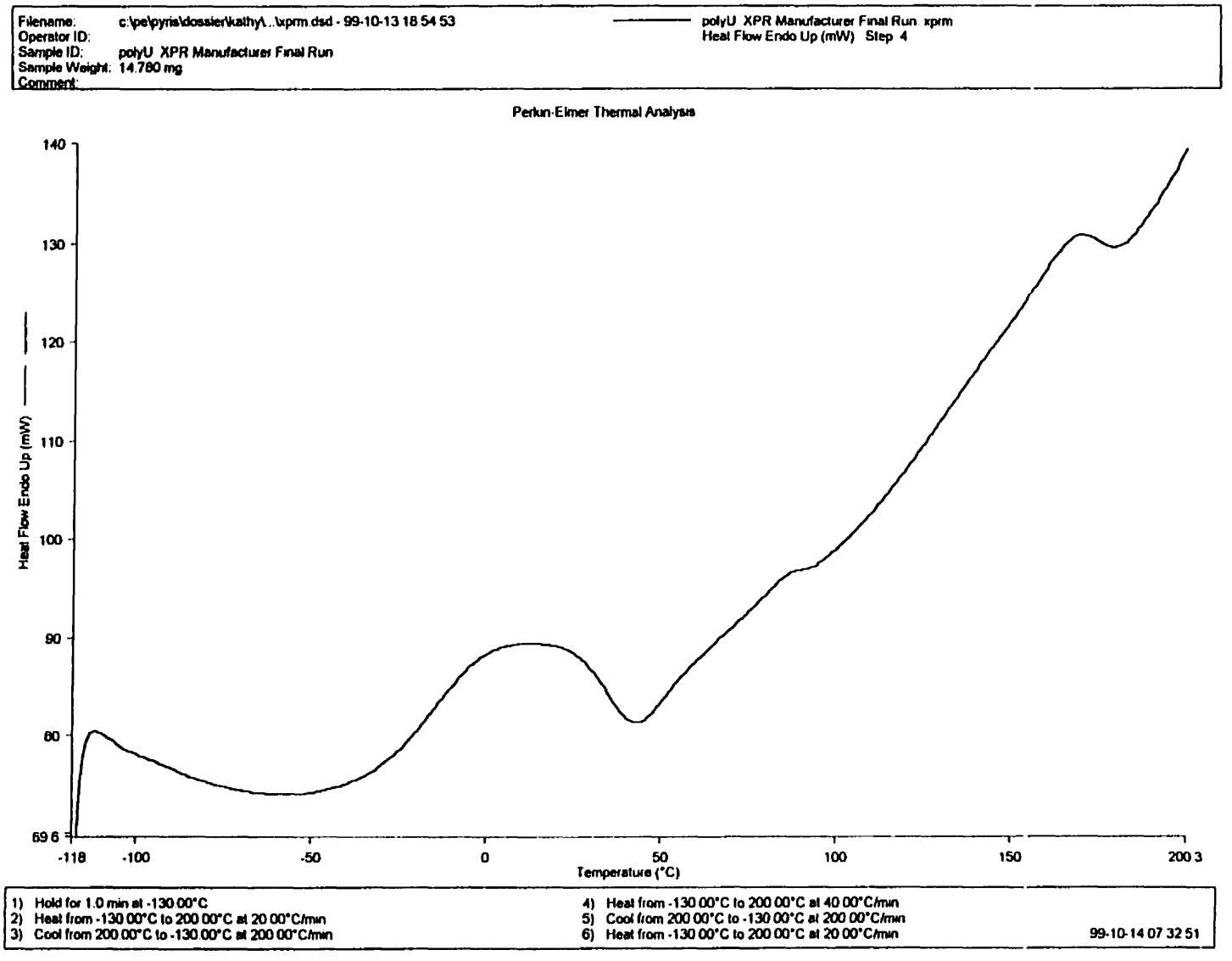
Filename: c:\pe\pyris\dossier\kathy\ \xprm dsd - 99-10-13 18 54 53
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:

polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 2
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 4
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) : Step 6



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 07:20:49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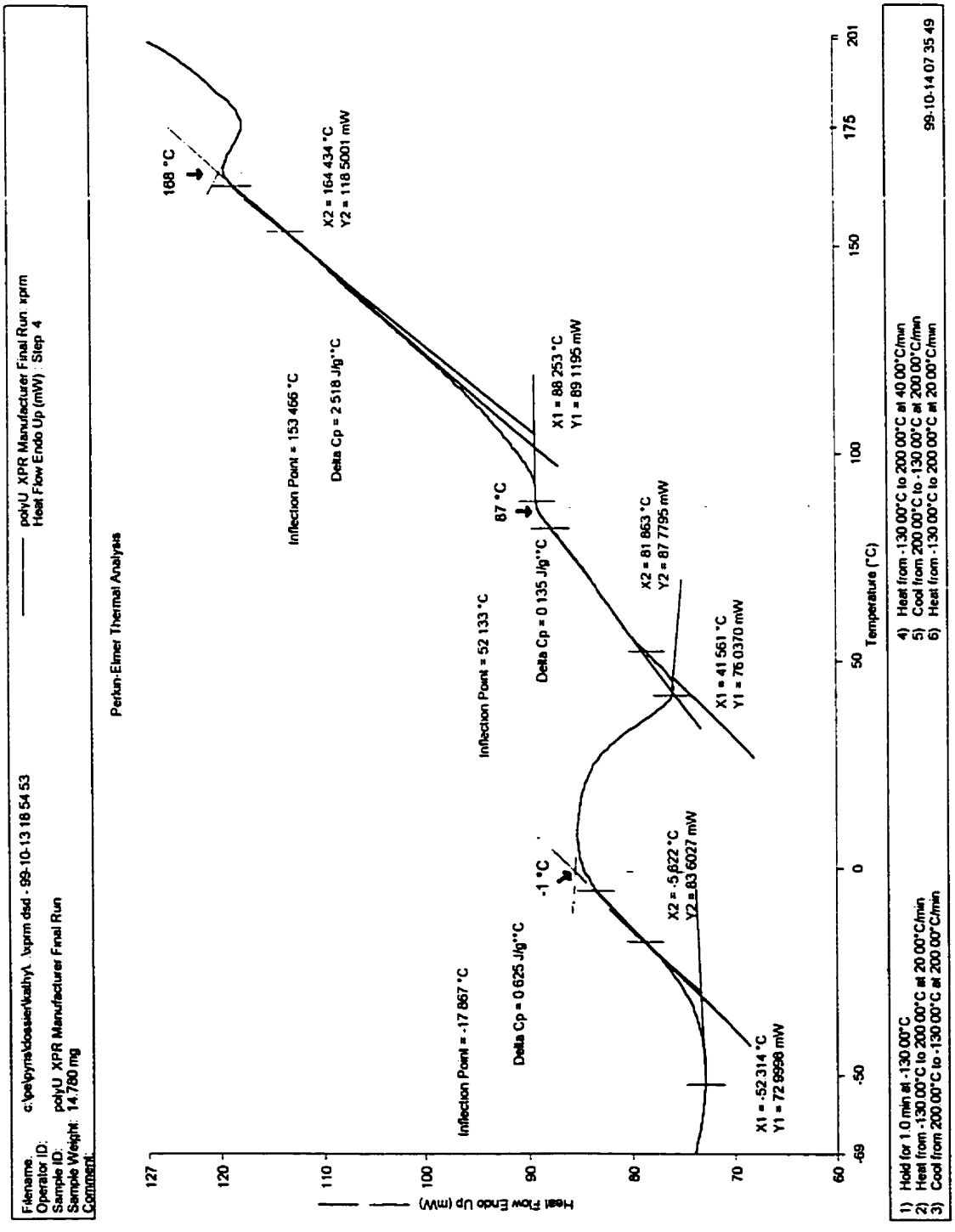
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:
polyU XPR Manufacturer Final Run xprm
Heat Flow Endo Up (mW) Step 4
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
140
130
120
110
100
90
80
69.6
-118
-100
-50
0
50
100
150
200.3
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07 32 51


Filename: c:\polyms\dossier\kathy\ \xprm dsd - 99-10-13 18 54 53
Operator ID:
Sample ID: polyU XPR Manufacturer Final Run
Sample Weight: 14.780 mg
Comment:
polyU XPR Manufacturer Final Run.xprm
Heat Flow Endo Up (mW) Step 4
Perkin-Elmer Thermal Analysis
188 °C
X2 = 164.434 °C
Y2 = 118.5001 mW
Inflection Point = 153.466 °C
Delta Cp = 2.518 J/g*°C
87 °C
X1 = 88.253 °C
Y1 = 89.1195 mW
Inflection Point = 52.133 °C
Delta Cp = 0.135 J/g*°C
X2 = 81.863 °C
Y2 = 87.7795 mW
X1 = 41.561 °C
Y1 = 76.0370 mW
-1 °C
X2 = -5.822 °C
Y2 = 83.6027 mW
Inflection Point = -17.867 °C
Delta Cp = 0.625 J/g*°C
X1 = -52.314 °C
Y1 = 72.9998 mW
Heat Flow Endo Up (mW)
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07:35:49

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: mpm
Data Collected: Oct 13,1999 07:58:32 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc

Validation
- Validated: No

Sample ID: polyU MP Manufacturer Final Run
Operator ID:
Comment:
Sample Weight: 14.480 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\Chosen Files\MPMfbnc@991013110915.dsd

Initial Conditions
- Temperature: -130.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To: 25.00°C
Total Points in Run: 2735

Method Steps:

1) Hold for 1.0 min at -130.00°C
   - Data Points: 61

2) Heat from -130.00°C to 200.00°C at 20.00°C/min
   - Data Points: 990

3) Cool from 200.00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

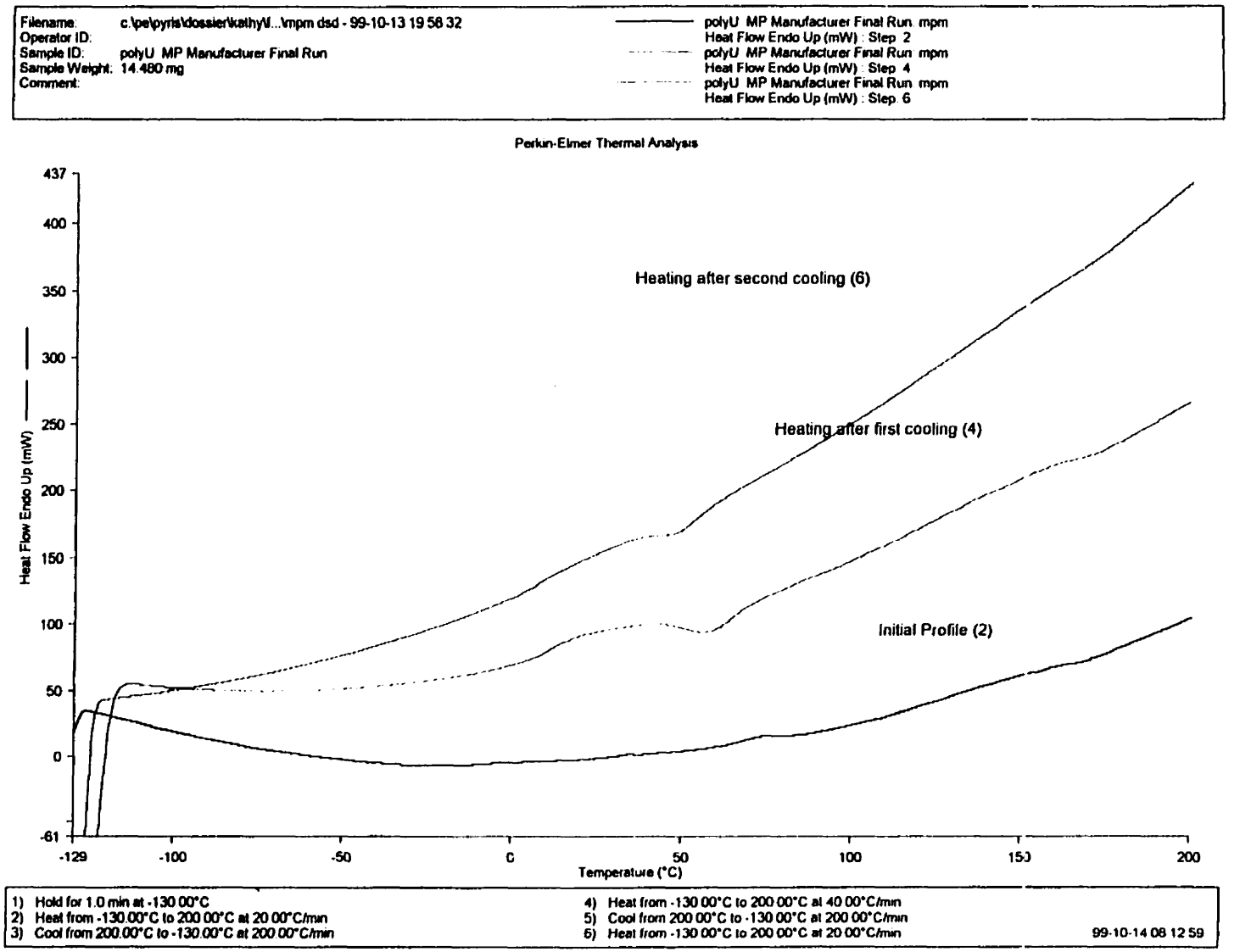
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991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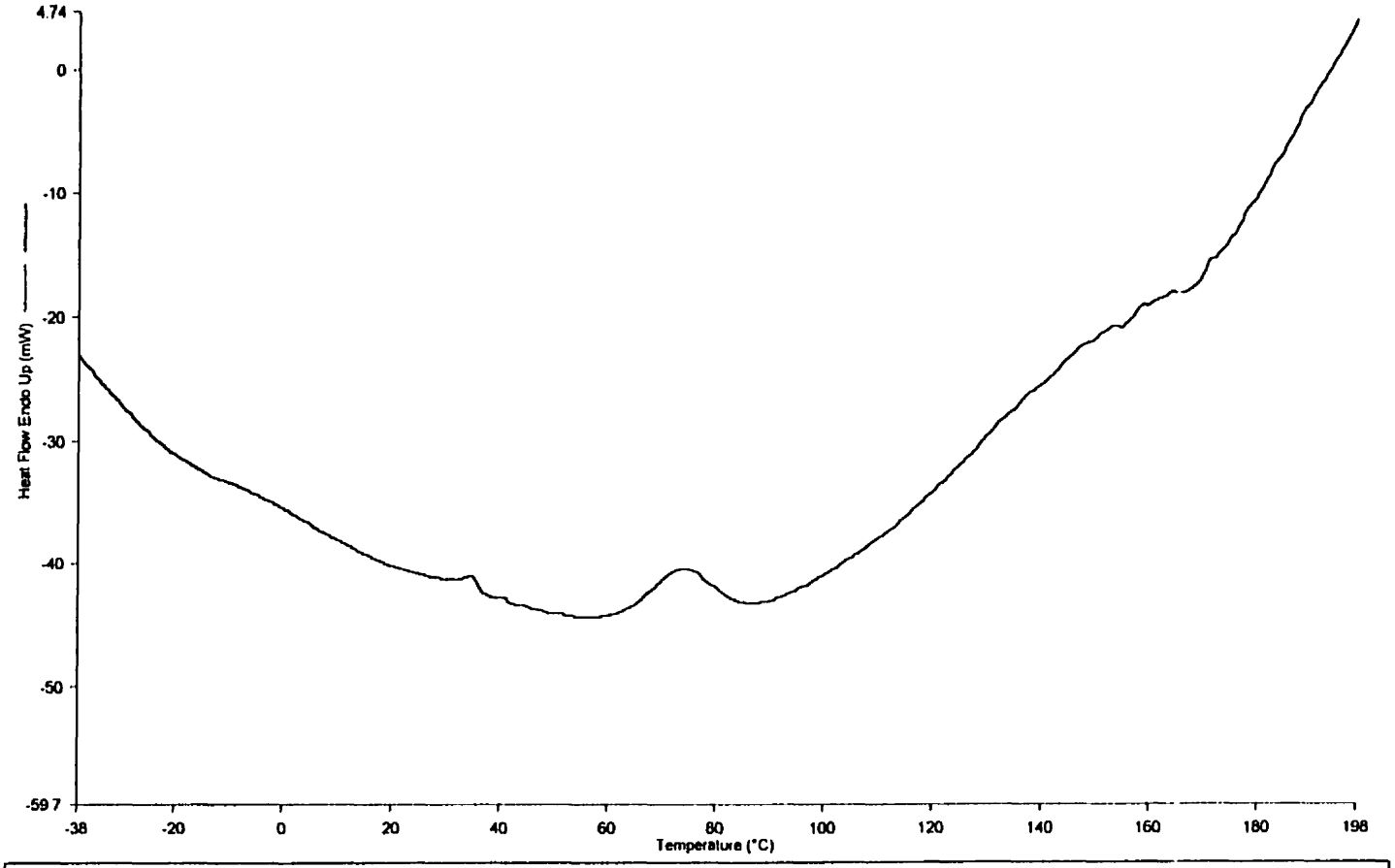
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 2
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 4
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heating after second cooling (6)
Heating after first cooling (4)
Initial Profile (2)
Heat Flow Endo Up (mW)
Temperature (°C)
437
400
350
300
250
200
150
100
50
0
-61
-129
-100
-50
0
50
100
150
200
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08 12 59

Filename: c:\pe\pyris\dossier\kathyl...\mpm dsd - 99-10-13 19:58:32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:

polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) Step 2

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -130.00°C at 200.00°C/mn
4) Heat from -130.00°C to 200.00°C at 40.00°C/mn
5) Cool from 200.00°C to -130.00°C at 200.00°C/mn
6) Heat from -130.00°C to 200.00°C at 20.00°C/mn

99-10-14 08:15:02

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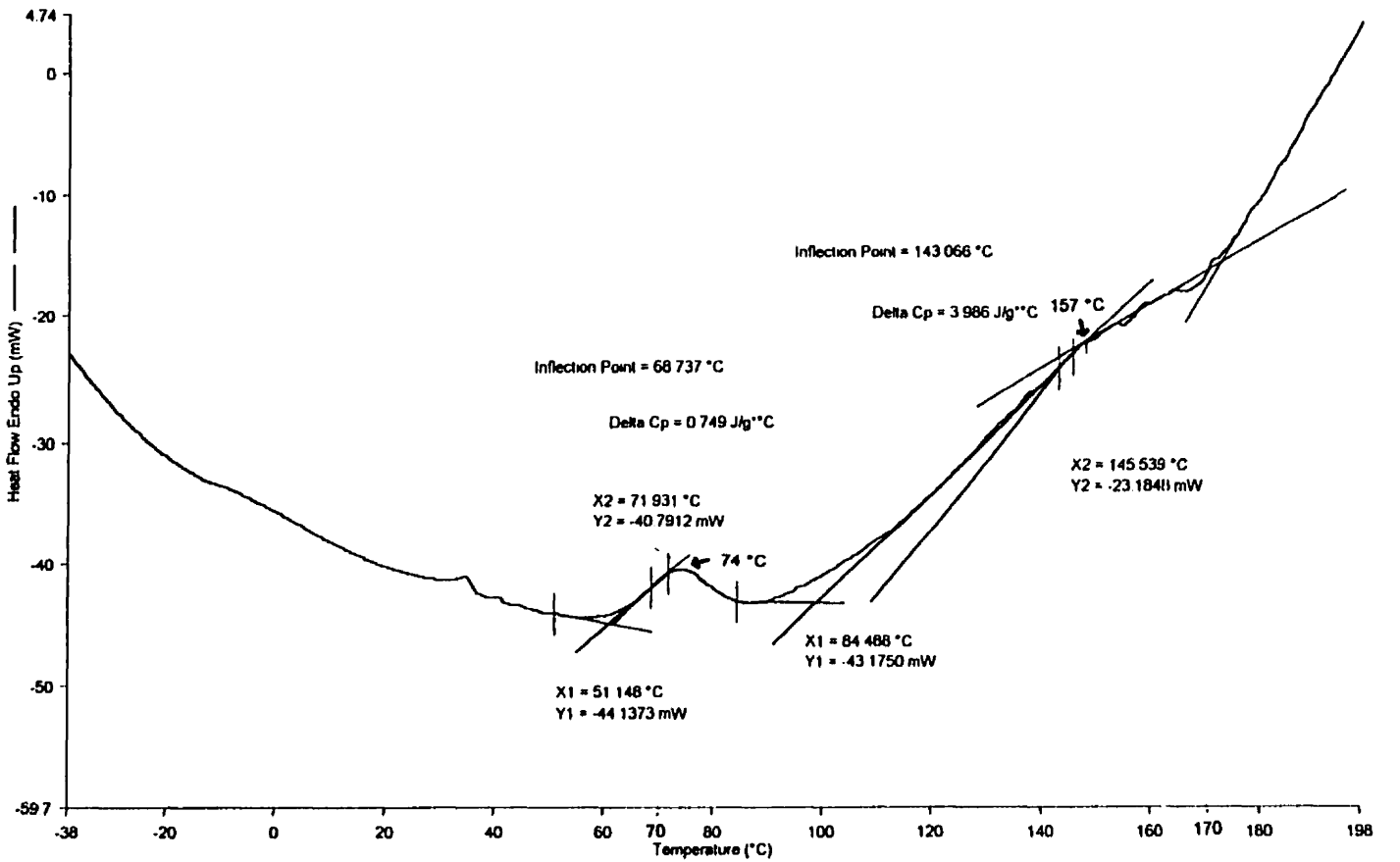
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:

polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) . Step 2

Perkin-Elmer Thermal Analysis



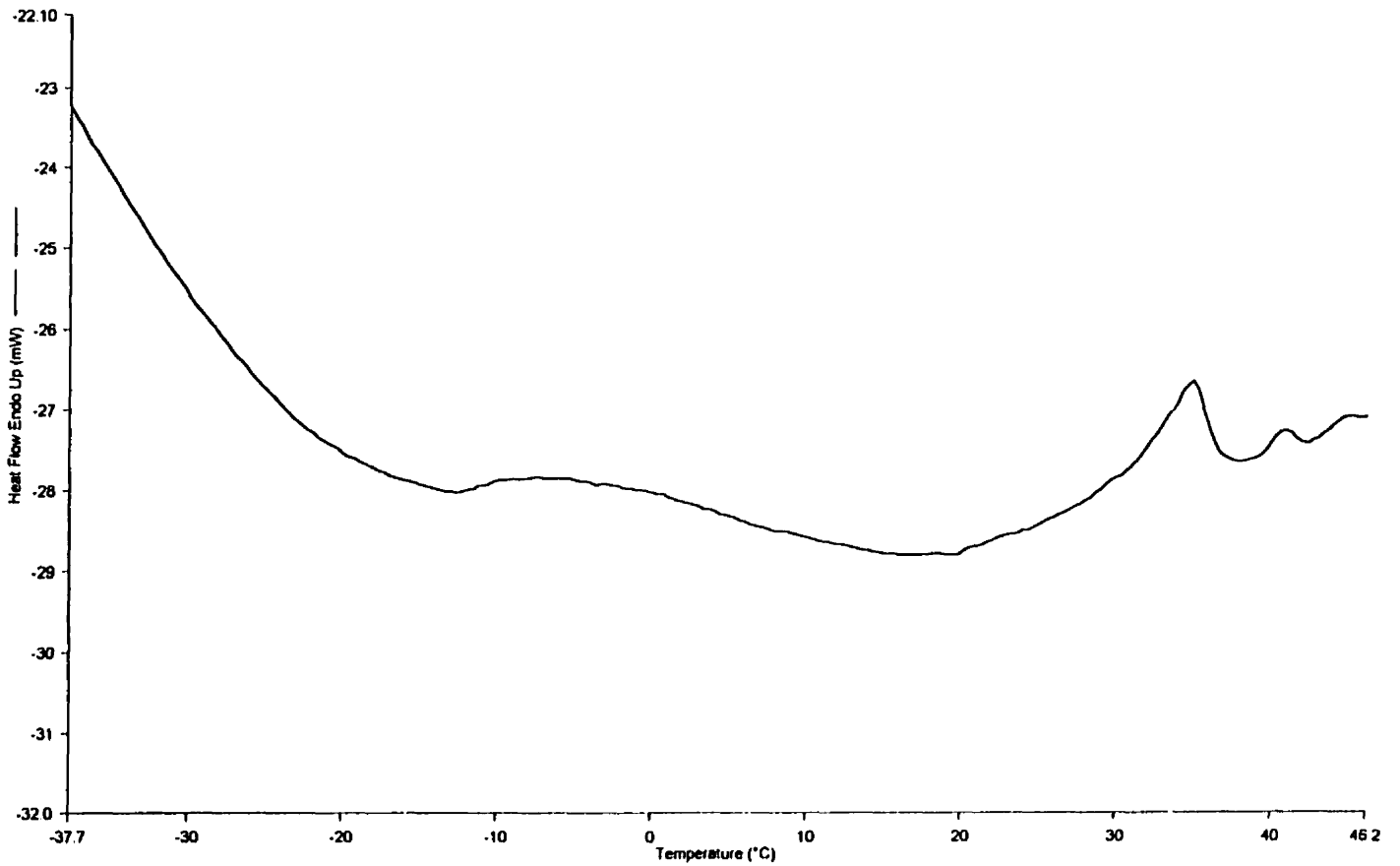
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/mn
5) Cool from 200.00°C to -130.00°C at 200.00°C/mn
6) Heat from -130.00°C to 200.00°C at 20.00°C/mn

99-10-14 08:17:23

Filename: c:\pe\pyris\dossier\kathyU \mpm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:

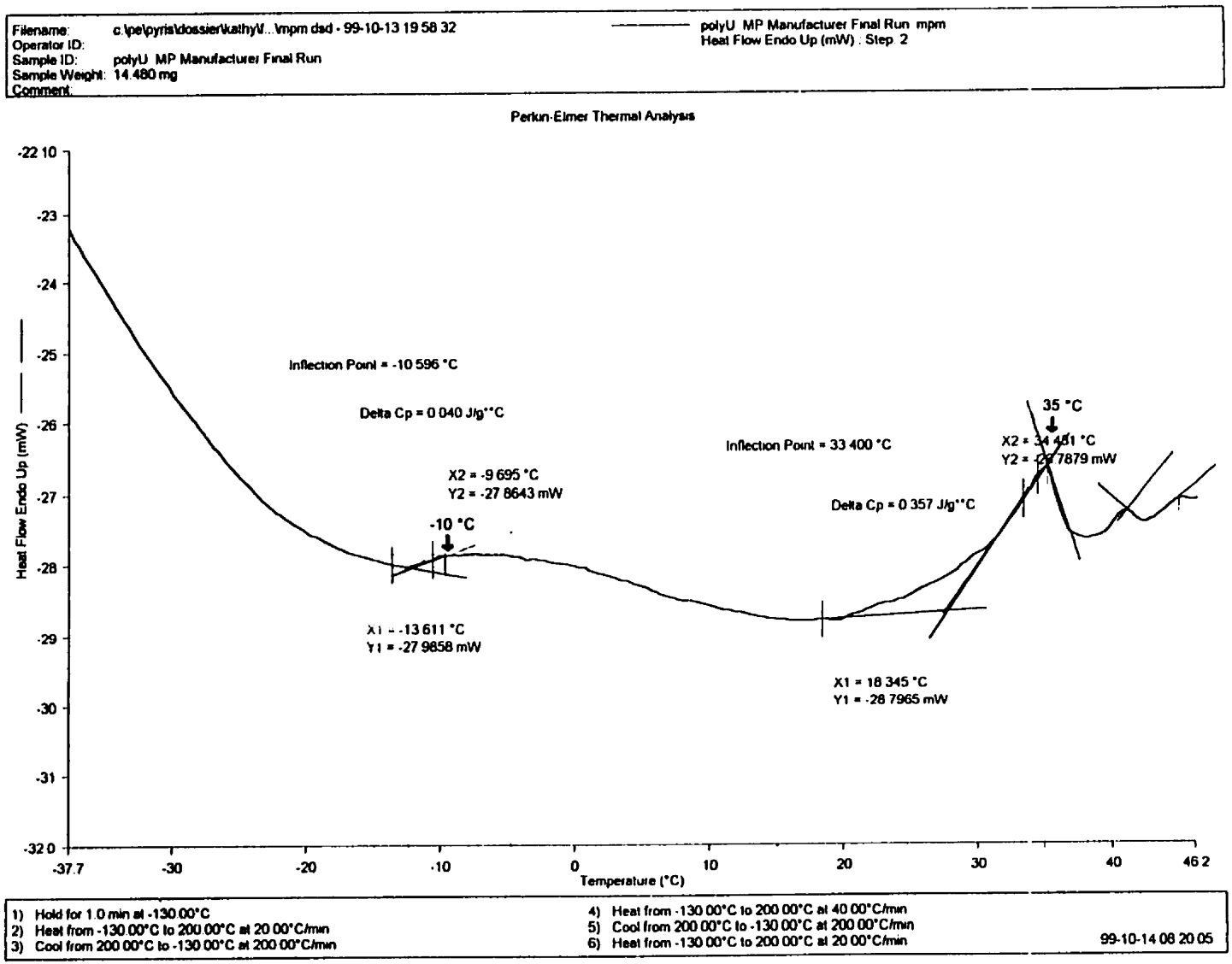
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 2

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

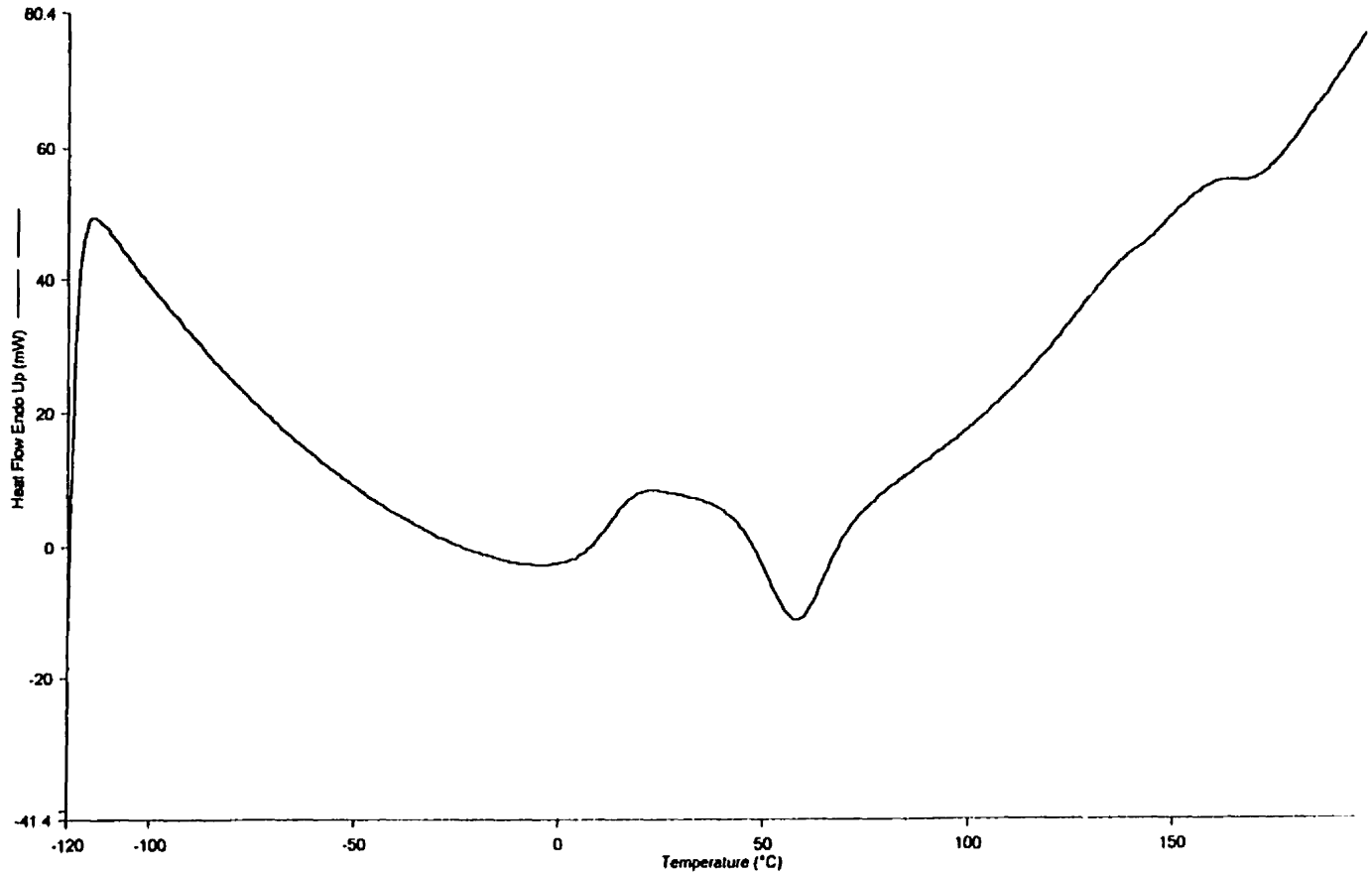
99-10-14 08 18 27


Filename: c:\pe\pyris\dossier\kathyU...\mpm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 2
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
-22.10
-23
-24
-25
-26
-27
-28
-29
-30
-31
-32.0
-37.7
-30
-20
-10
0
10
20
30
40
46.2
Inflection Point = -10.596 °C
Delta Cp = 0.040 J/g**C
X2 = -9.695 °C
Y2 = -27.8643 mW
-10 °C
X1 = -13.611 °C
Y1 = -27.9858 mW
Inflection Point = 33.400 °C
Delta Cp = 0.357 J/g**C
35 °C
X2 = 34.451 °C
Y2 = -27.7879 mW
X1 = 18.345 °C
Y1 = -28.7965 mW
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -130.00°C at 200.00°C/mn
4) Heat from -130.00°C to 200.00°C at 40.00°C/mn
5) Cool from 200.00°C to -130.00°C at 200.00°C/mn
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08:20:05

Filename: c:\pe\pyris\dossier\kathyW \m,xm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14 480 mg
Comment:

polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) Step 4

Perkin-Elmer Thermal Analysis



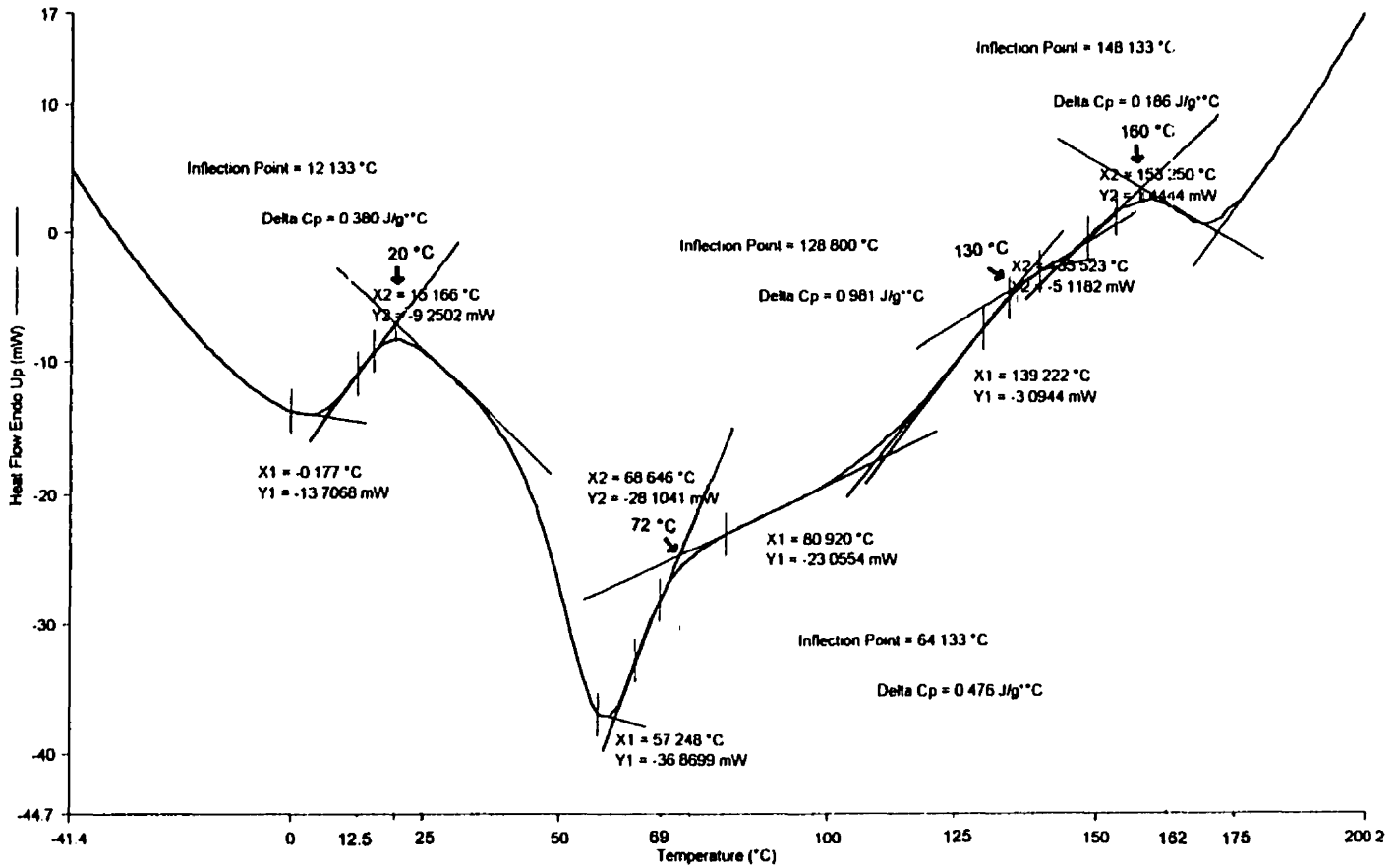
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 08

Filename: c:\pe\pyris\dossier\kathyl\ .\mpm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:

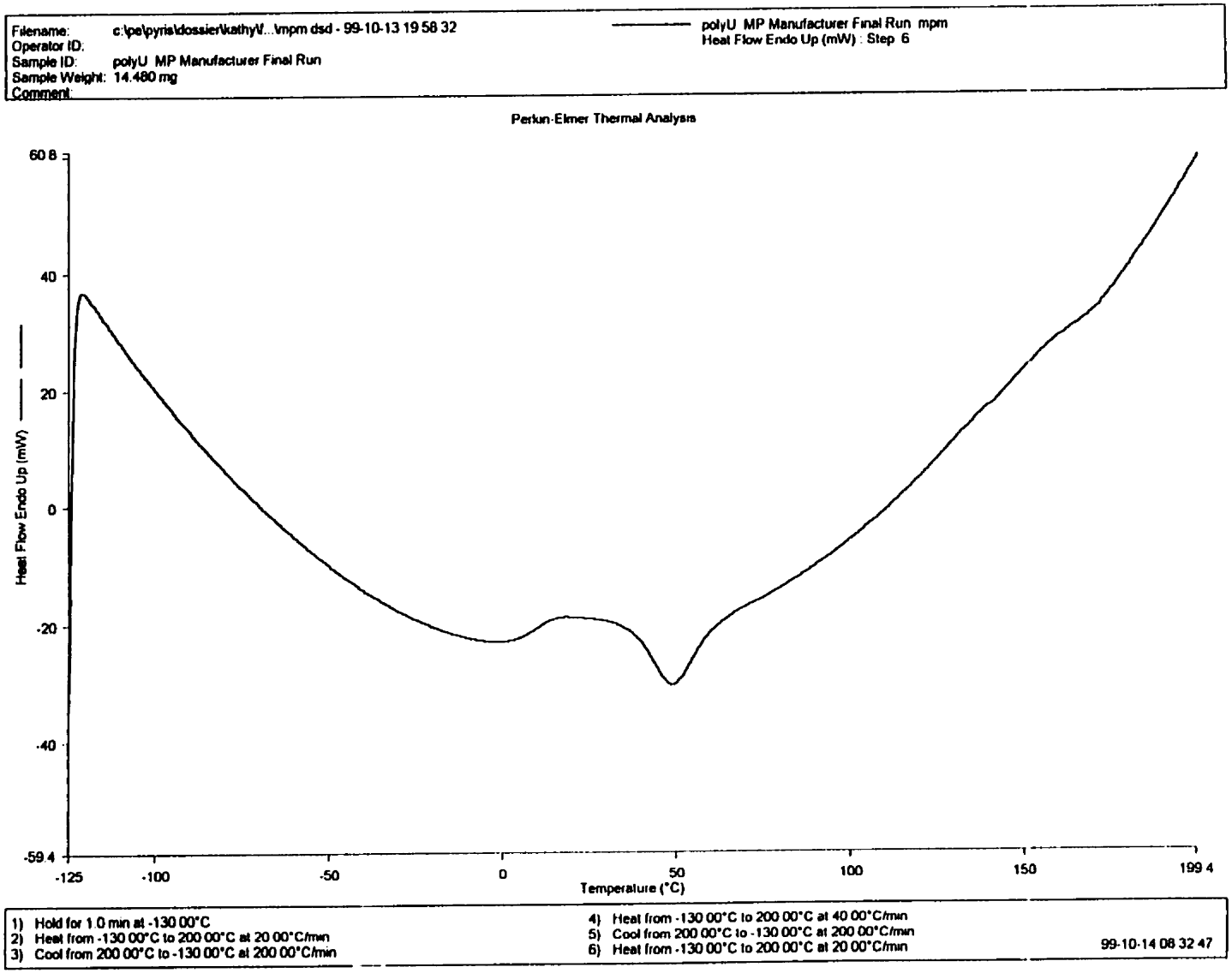
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 4

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

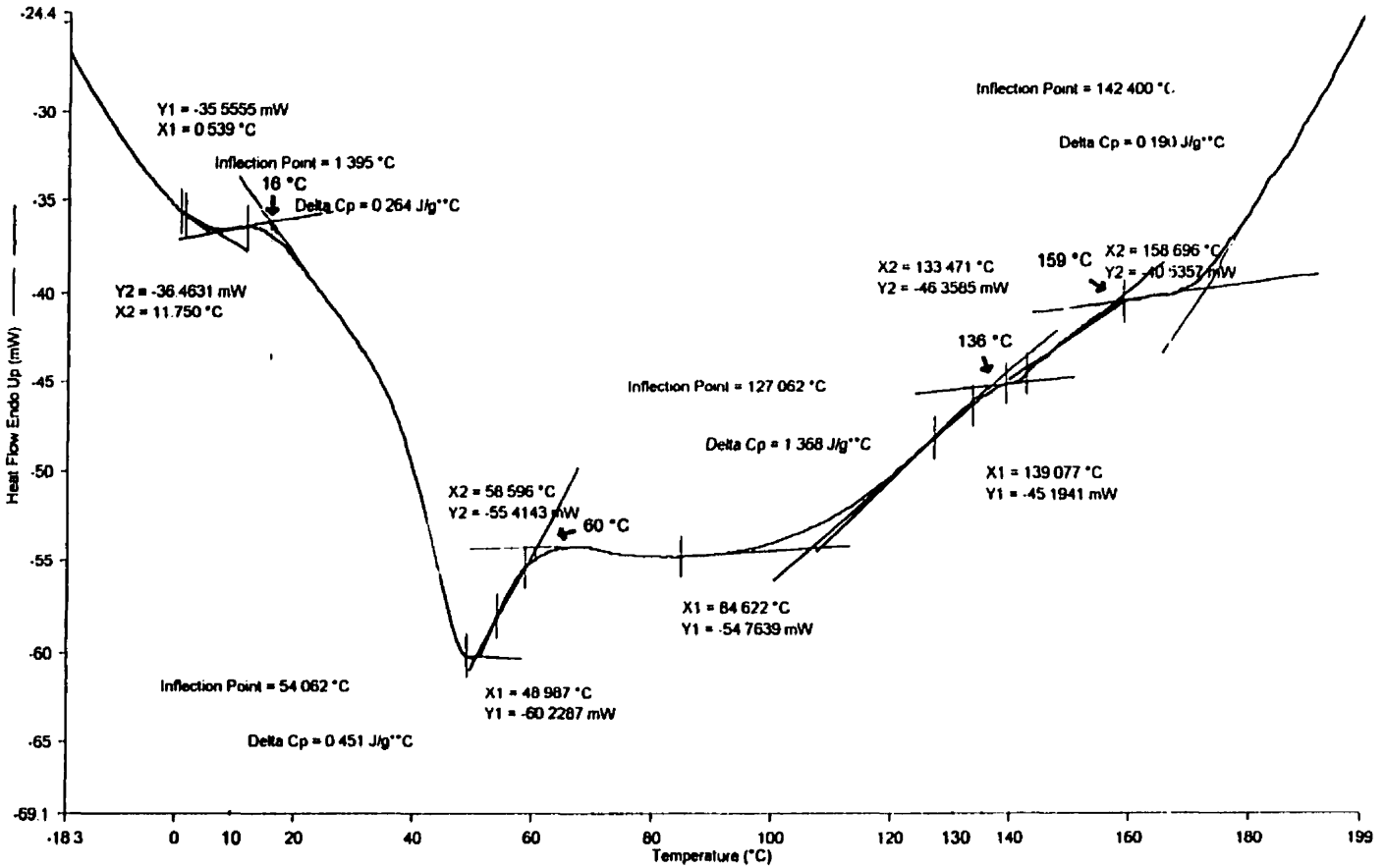
99-10-14 08:28:33


Filename: c:\pe\pyris\dossier\kathyV...\mpm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:
polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
60.8
40
20
0
-20
-40
-59.4
-125
-100
-50
0
50
100
150
199.4
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08 32 47

Filename: c:\pe\pyris\dossier\kathyW...\mpm dsd - 99-10-13 19 58 32
Operator ID:
Sample ID: polyU MP Manufacturer Final Run
Sample Weight: 14.480 mg
Comment:

polyU MP Manufacturer Final Run mpm
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/mn
3) Cool from 200.00°C to -130.00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/mn
5) Cool from 200 00°C to -130 00°C at 200 00°C/mn
6) Heat from -130 00°C to 200 00°C at 20 00°C/mn

99-10-14 08 37 44

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument	
Type:	DSC 7
Name:	DSC 7
Filename:	xprfbnc
Data Collected:	Oct 13,1999 04 50.11 PM
Calibration Info:	
Filename:	C \PE\Pyris\Dossier\Kathy\calibok1 dsc
Validation	
Validated:	No
Sample ID:	polyU XPR Xylene Cleaned Final Run
Operator ID:	
Comment:	
Sample Weight:	16 450 mg
Save Filename:	C \PE\Pyris\Dossier\Kathy\Chosen Files\XPRfbnc@991013110915 dsd
Initial Conditions	
Temperature:	-130 00 °C
Y Initial:	20 00 mW
Purge Gas:	Helium
Purge Gas Rate:	20 0 ml/min
Sample Rate:	Standard
Equilibrate Within	
Temperature:	0 01 °C
Heat Flow:	0 01 mW
Maximum Time:	3 00 min
End Condition:	Go To -130 00°C
Total Points in Run:	2735

Method Steps:

1) Hold for 1.0 min at -130 00°C
   Data Points: 60

2) Heat from -130 00°C to 200 00°C at 20 00°C/min
   Data Points: 991

3) Cool from 200 00°C to -130 00°C at 200 00°C/min
   Data Points: 99

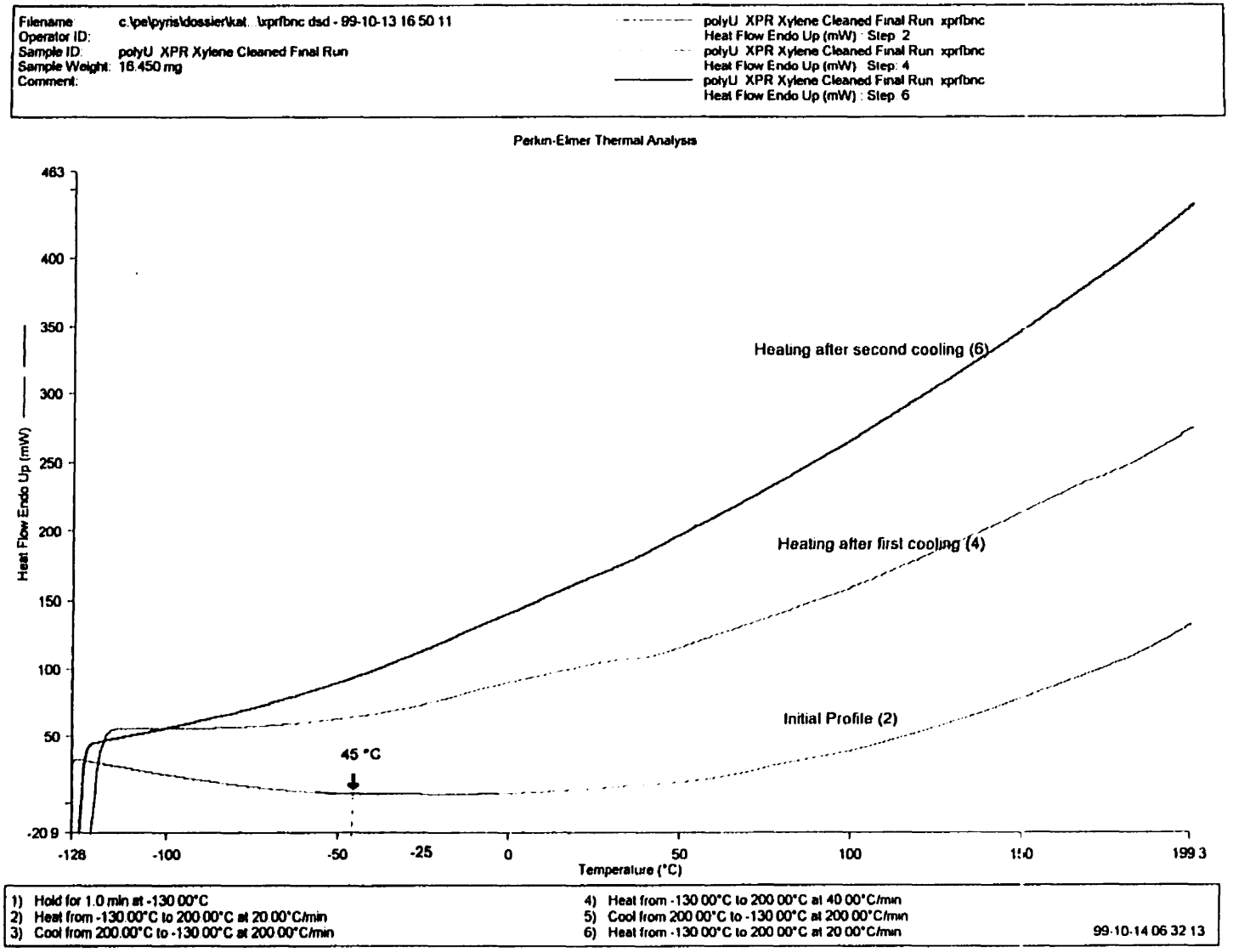
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
   Data Points: 495

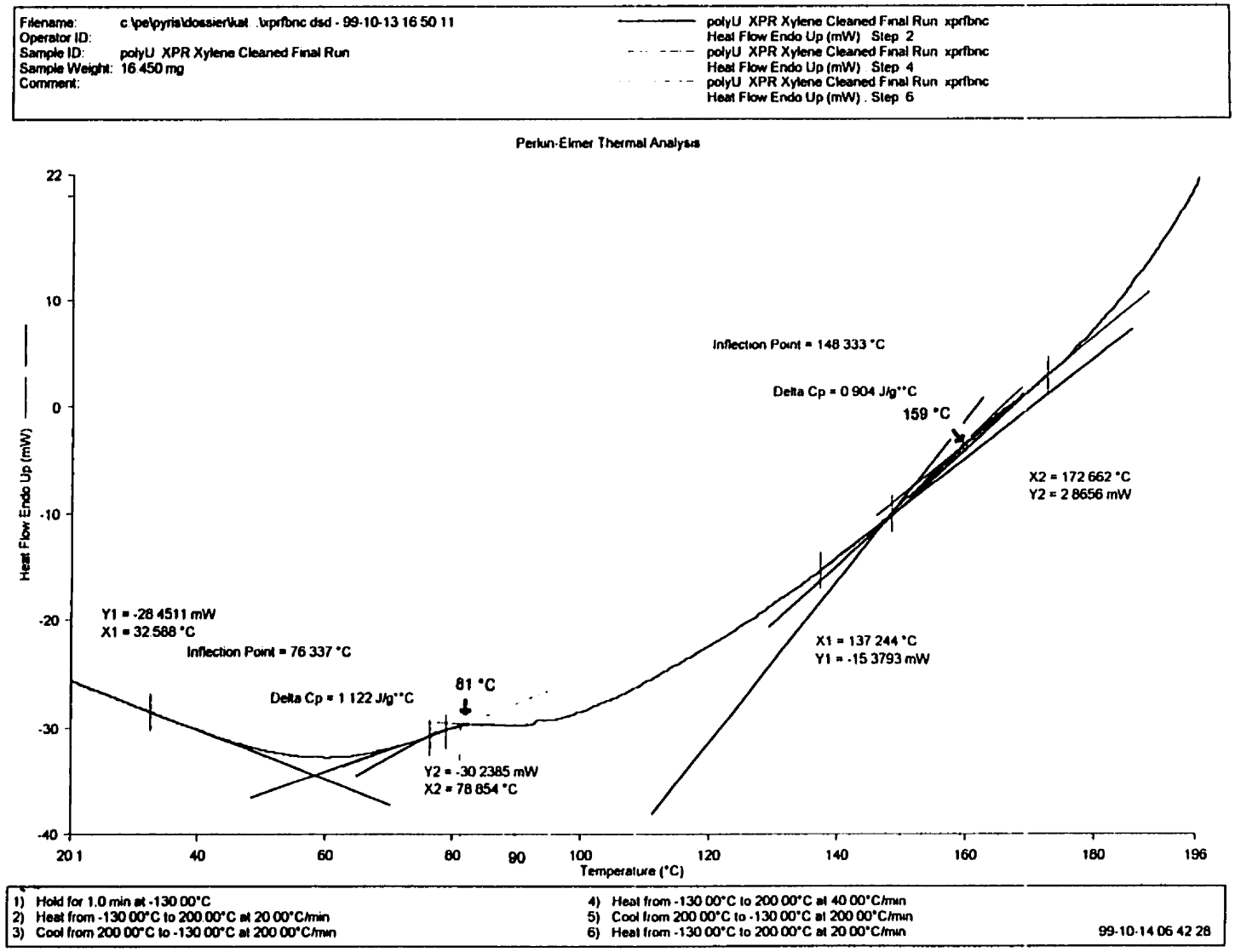
DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991

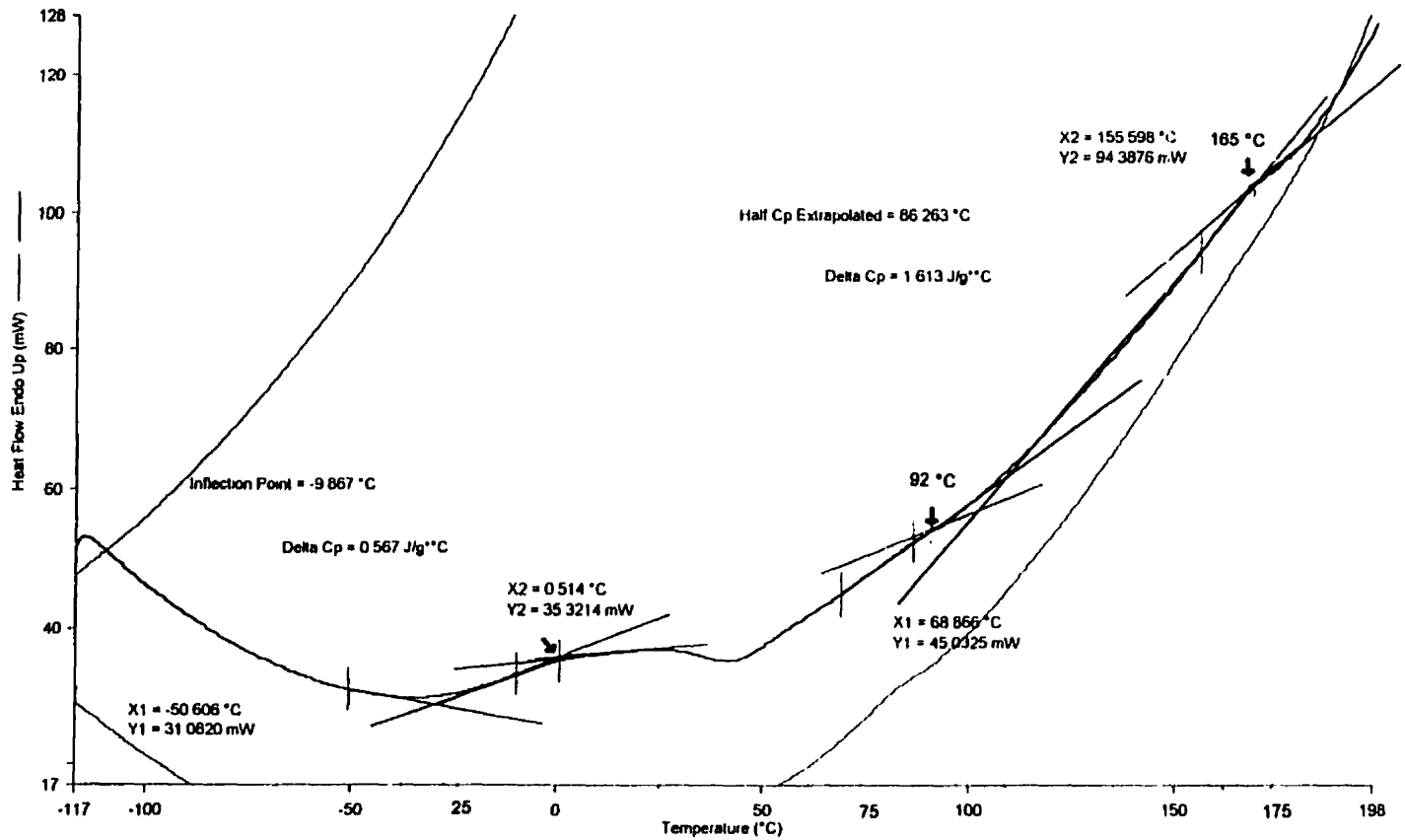

Filename: c:\pe\pyris\dossier\kat. \xprfbnc dsd - 99-10-13 16 50 11
Operator ID:
Sample ID: polyU XPR Xylene Cleaned Final Run
Sample Weight: 16.450 mg
Comment:
polyU XPR Xylene Cleaned Final Run xprfbnc Heat Flow Endo Up (mW) : Step: 2
polyU XPR Xylene Cleaned Final Run xprfbnc Heat Flow Endo Up (mW) Step: 4
polyU XPR Xylene Cleaned Final Run xprfbnc Heat Flow Endo Up (mW) : Step: 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
463
400
350
300
250
200
150
100
50
-20 9
-128
-100
-50
-25
0
50
100
150
199 3
Temperature (°C)
Heating after second cooling (6)
Heating after first cooling (4)
Initial Profile (2)
45 °C
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 06 32 13


Filename: c:\pe\pyris\dossier\kat .\xprfbnc.dsd - 99-10-13 16:50:11
Operator ID:
Sample ID: polyU XPR Xylene Cleaned Final Run
Sample Weight: 16.450 mg
Comment:
polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) Step 2
polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) Step 4
polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
Inflection Point = 148.333 °C
Delta Cp = 0.904 J/g°°C
159 °C
X2 = 172.662 °C
Y2 = 2.8656 mW
Y1 = -28.4511 mW
X1 = 32.588 °C
Inflection Point = 76.337 °C
Delta Cp = 1.122 J/g°°C
81 °C
Y2 = -30.2385 mW
X2 = 78.854 °C
X1 = 137.244 °C
Y1 = -15.3793 mW
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 06:42:28

Filename: c:\pe\pyris\dossier\kat \uprfbnc dsd - 99-10-13 16 50 11
Operator ID:
Sample ID: polyU XPR Xylene Cleaned Final Run
Sample Weight: 16 450 mg
Comment:

polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) : Step 2
polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) Step 4
polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



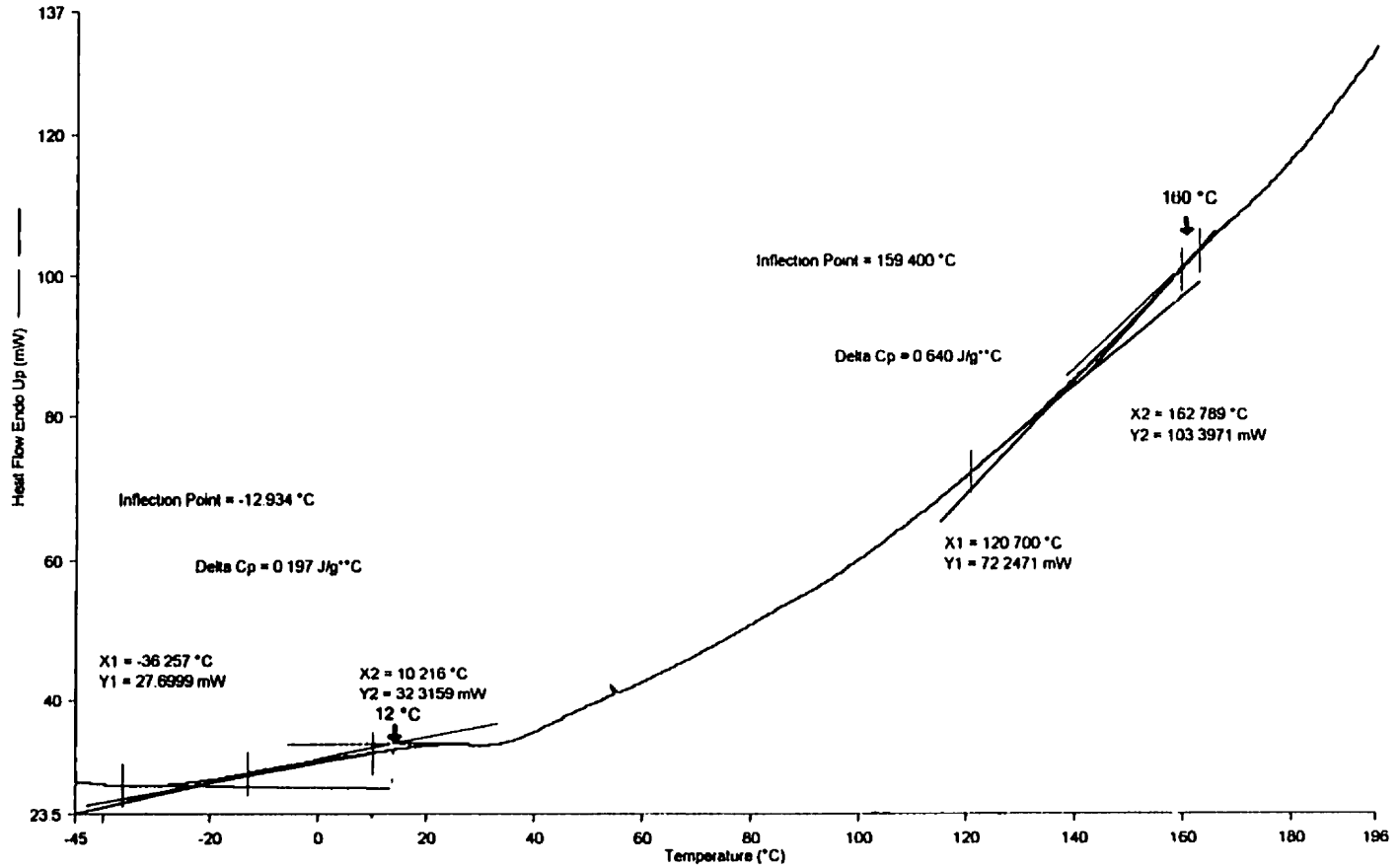
1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min

99-10-14 06 50 41

Filename: c:\pe\pyris\dossier\kat...\xprfbnc dsd - 99-10-13 16 50 11
Operator ID:
Sample ID: polyU XPR Xylene Cleaned Final Run
Sample Weight: 16.450 mg
Comment:

polyU XPR Xylene Cleaned Final Run xprfbnc
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 06:57:28

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: mpfbnc
Data Collected: Oct 13,1999 05:58:31 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc

Validation
- Validated: No

Sample ID: polyU_MP Xylene Cleaned Final Run
Operator ID:
Comment:
Sample Weight: 16.330 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\Chosen Files\MPfbnc@991013110915.dsd

Initial Conditions
- Temperature: -130.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To: -130.00°C
Total Points in Run: 2735

Method Steps:

1) Hold for 1.0 min at -130.00°C
   - Data Points: 61

2) Heat from -130.00°C to 200.00°C at 20.00°C/min
   - Data Points: 990

3) Cool from 200.00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

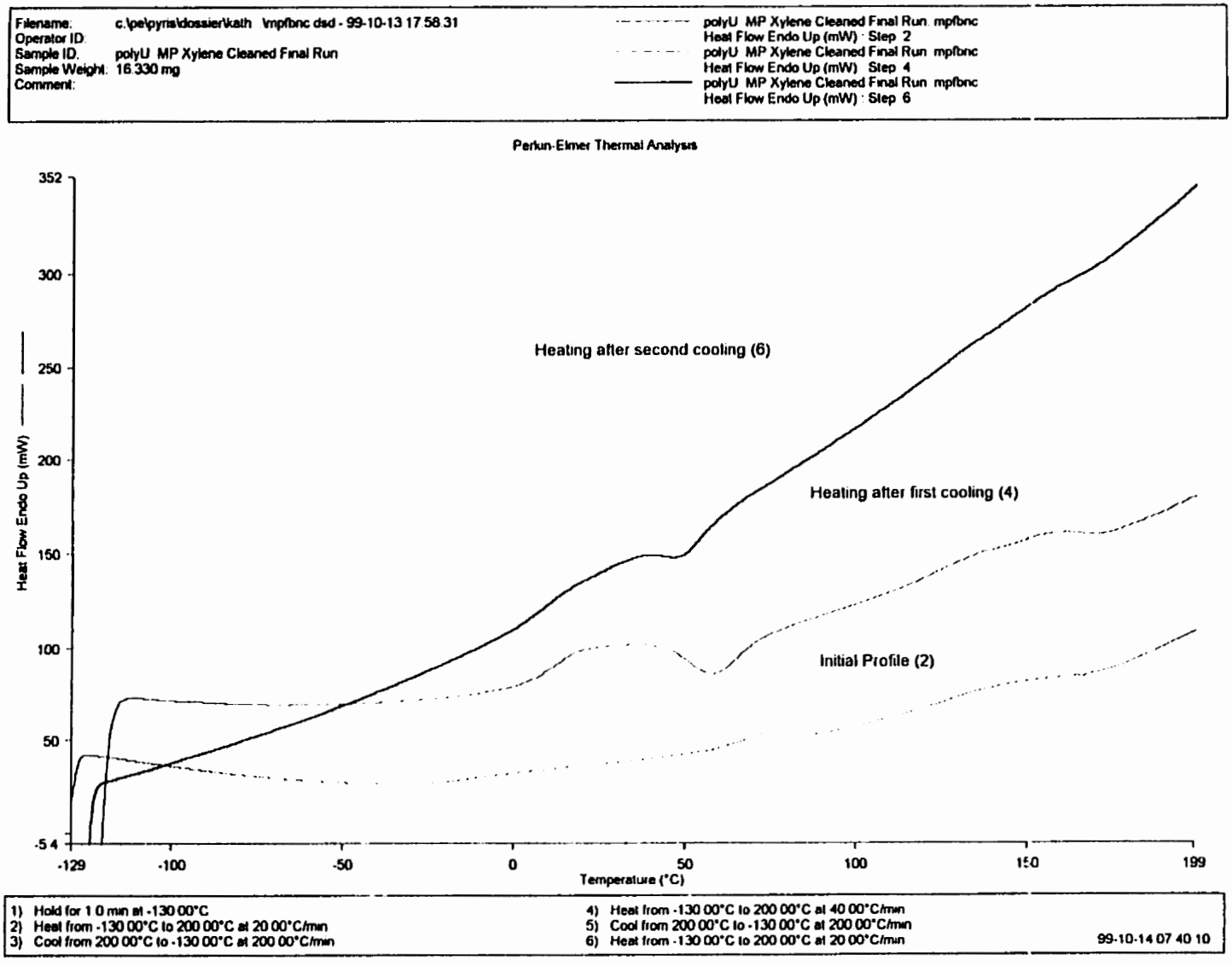
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

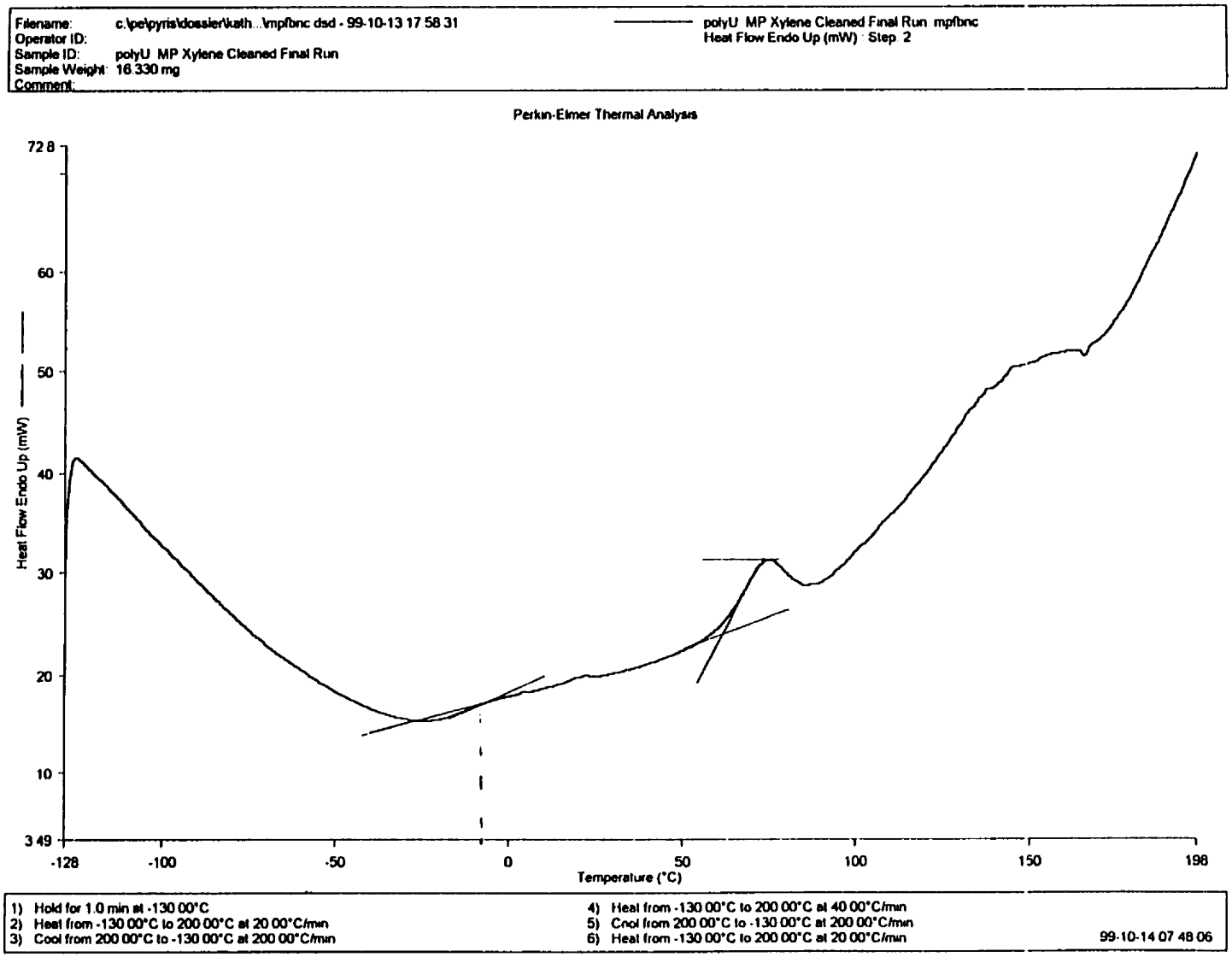
DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991

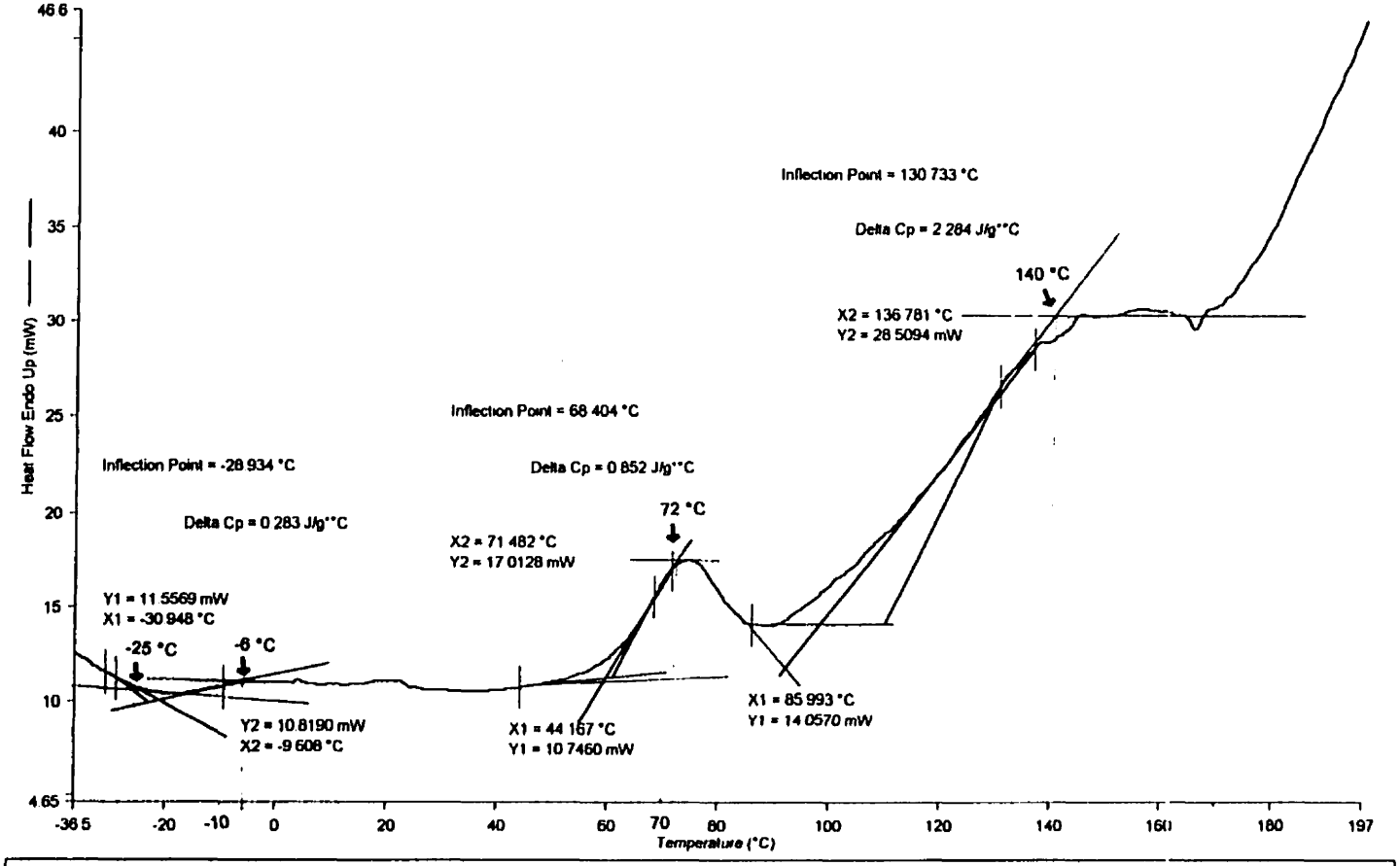

Filename: c:\pe\pyris\dossier\kath \mpfbnc dsd - 99-10-13 17:58:31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 2
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) Step 4
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
352
300
250
200
150
100
50
-5.4
-129
-100
-50
0
50
100
150
199
Temperature (°C)
Heating after second cooling (6)
Heating after first cooling (4)
Initial Profile (2)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07:40:10


Filename: c:\pe\pyris\dossier\kath...\mpfbnc dsd - 99-10-13 17 58 31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 2
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
72.8
60
50
40
30
20
10
3.49
-128
-100
-50
0
50
100
150
198
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07:48:06

Filename: c:\pe\pyris\dossier\kath . \mpfbnc.dsd - 99-10-13 17:58:31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:

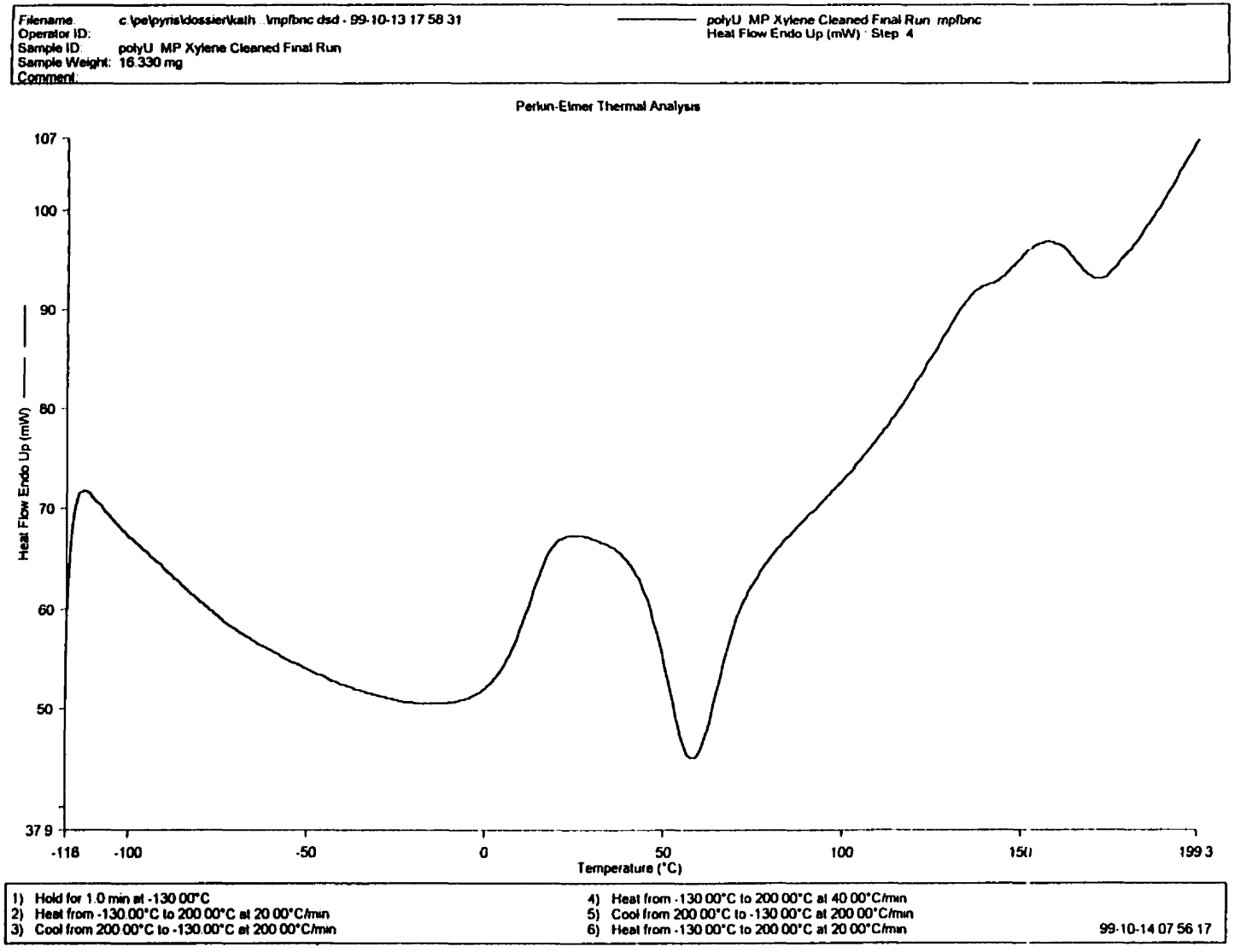
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 2

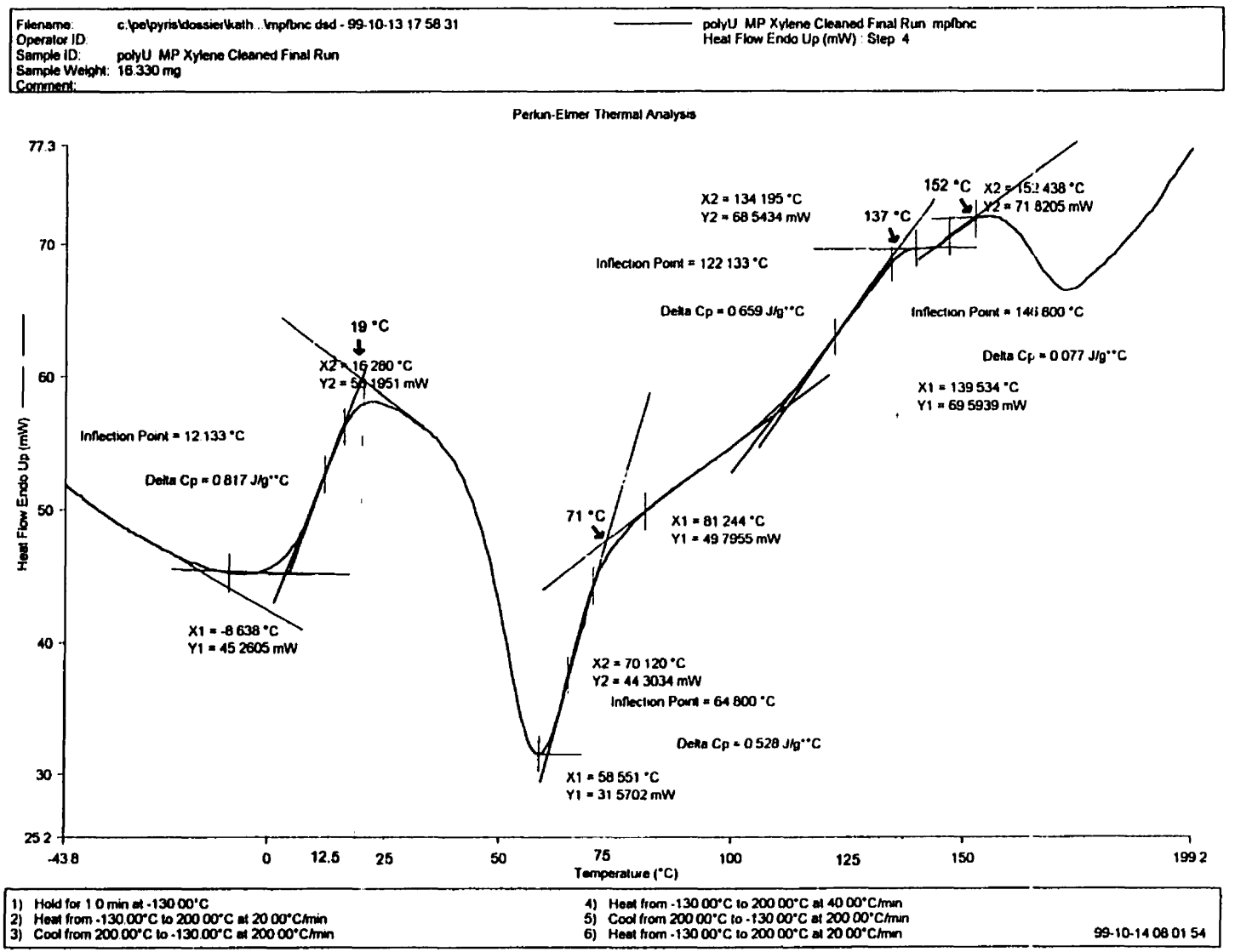
Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -130.00°C at 200.00°C/mn
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/mn
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 07:51:43

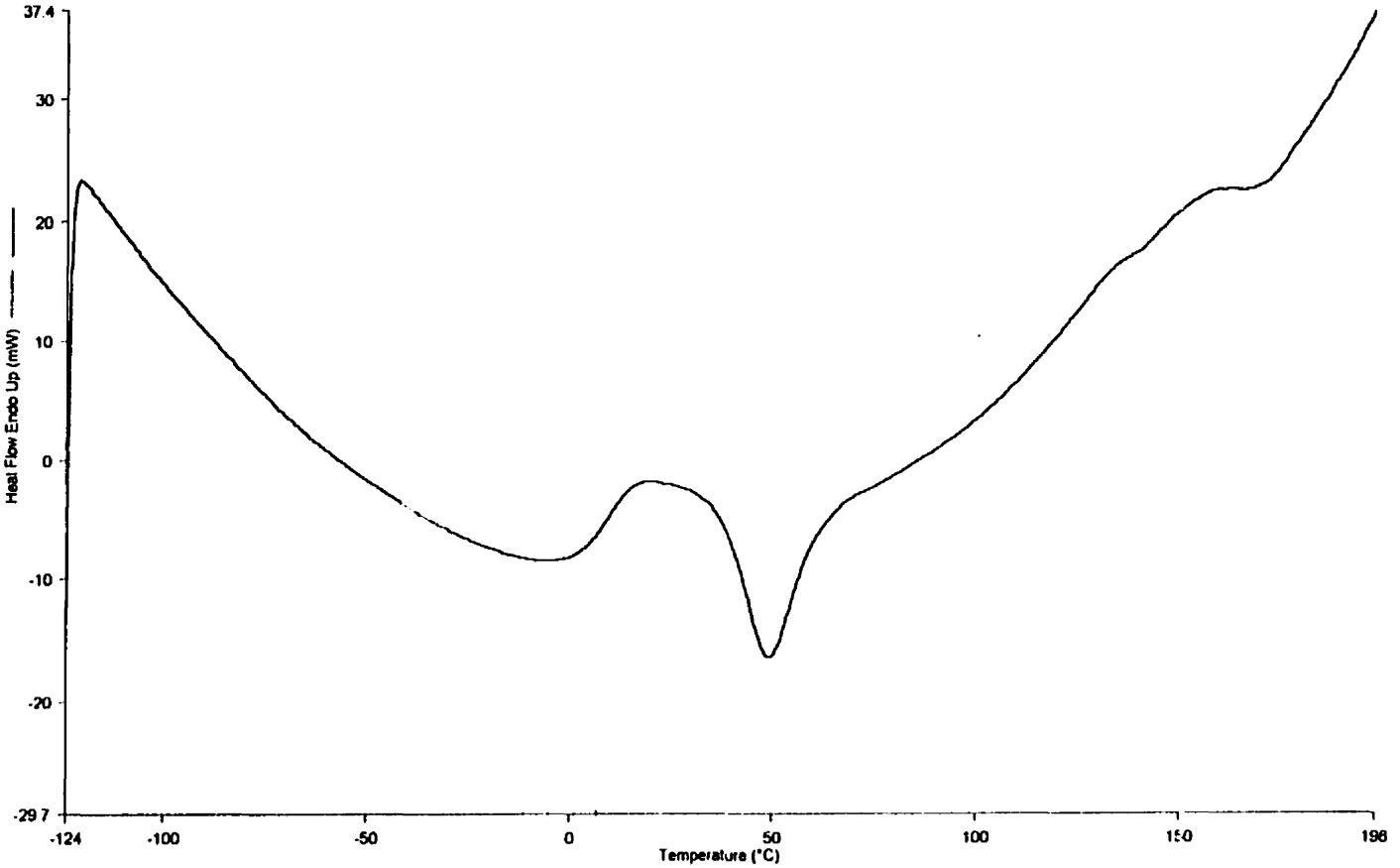

Filename: c:\pe\pyris\dossier\kalh...\mpfbnc.dsd - 99-10-13 17:58:31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 4
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
107
100
90
80
70
60
50
37.9
-118
-100
-50
0
50
100
150
199.3
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 07:56:17


Filename: c:\pe\pyris\dossier\kath..\mpfbnc dsd - 99-10-13 17 58 31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 4
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
77.3
70
60
50
40
30
25.2
-43.8
0
12.5
25
50
75
100
125
150
199.2
19 °C
X2 = 16.280 °C
Y2 = 54.1951 mW
Inflection Point = 12.133 °C
Delta Cp = 0.817 J/g°°C
X1 = -8.638 °C
Y1 = 45.2605 mW
71 °C
X1 = 81.244 °C
Y1 = 49.7955 mW
X2 = 70.120 °C
Y2 = 44.3034 mW
Inflection Point = 64.800 °C
Delta Cp = 0.528 J/g°°C
X1 = 58.551 °C
Y1 = 31.5702 mW
X2 = 134.195 °C
Y2 = 68.5434 mW
137 °C
Inflection Point = 122.133 °C
Delta Cp = 0.659 J/g°°C
152 °C
X2 = 152.438 °C
Y2 = 71.8205 mW
Inflection Point = 146.800 °C
Delta Cp = 0.077 J/g°°C
X1 = 139.534 °C
Y1 = 69.5939 mW
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08:01:54

Filename: c:\pe\pyris\dossier\kath .\mpfbnc dsd - 99-10-13 17 58 31
Operator ID:
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:

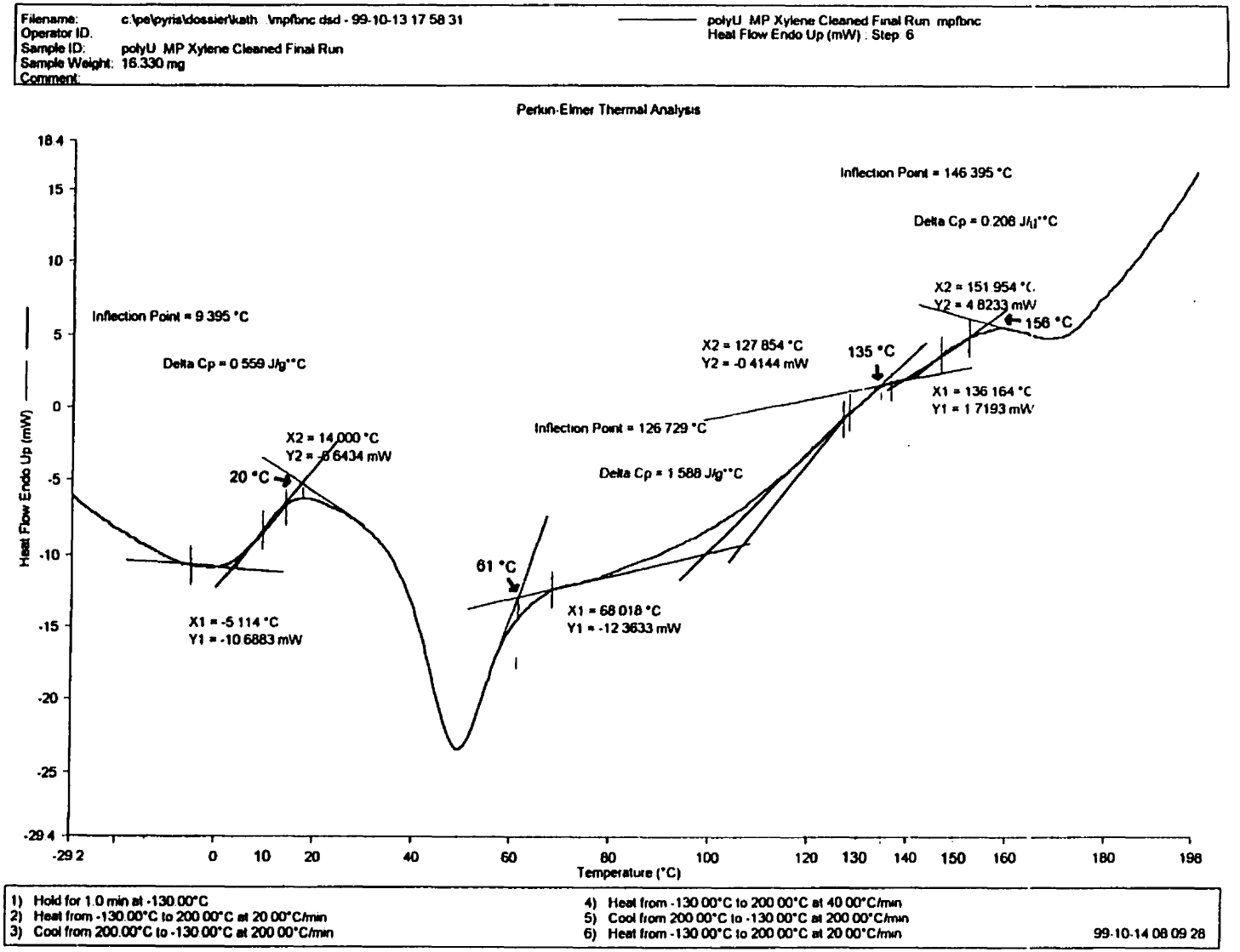
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) . Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 08:06:18


Filename: c:\pe\pyris\dossier\kath \mpfbnc dsd - 99-10-13 17 58 31
Operator ID.
Sample ID: polyU MP Xylene Cleaned Final Run
Sample Weight: 16.330 mg
Comment:
polyU MP Xylene Cleaned Final Run mpfbnc
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
Inflection Point = 9.395 °C
Delta Cp = 0.559 J/g°°C
X2 = 14.000 °C
Y2 = -5.6434 mW
20 °C
X1 = -5.114 °C
Y1 = -10.6883 mW
61 °C
X1 = 68.018 °C
Y1 = -12.3633 mW
Inflection Point = 126.729 °C
Delta Cp = 1.588 J/g°°C
X2 = 127.854 °C
Y2 = -0.4144 mW
135 °C
X1 = 136.164 °C
Y1 = 1.7193 mW
Inflection Point = 146.395 °C
Delta Cp = 0.208 J/g°°C
X2 = 151.954 °C
Y2 = 4.8233 mW
156 °C
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08:09:28

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: xpr4deg
Data Collected: Oct 13,1999 12:50 59 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1 dsc
- Date/Time: Oct 12,1999 03:33 02 PM

Validation
- Validated: No

Sample ID: polyU XPR 4 C
Operator ID:
Comment:
Sample Weight: 18 500 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\XPR4Cnc@991013110915 dsd

Initial Conditions
- Temperature: -130 00 °C
- Y Initial: 20 00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20 0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0 01 °C
- Heat Flow: 0 01 mW
- Maximum Time: 3.00 min

End Condition: Go To: -105 00°C
Total Points in Run: 2735

Method Steps:
1) Hold for 1.0 min at -130.00°C
   - Data Points: 61

2) Heat from -130.00°C to 200 00°C at 20 00°C/min
   - Data Points: 990

3) Cool from 200 00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

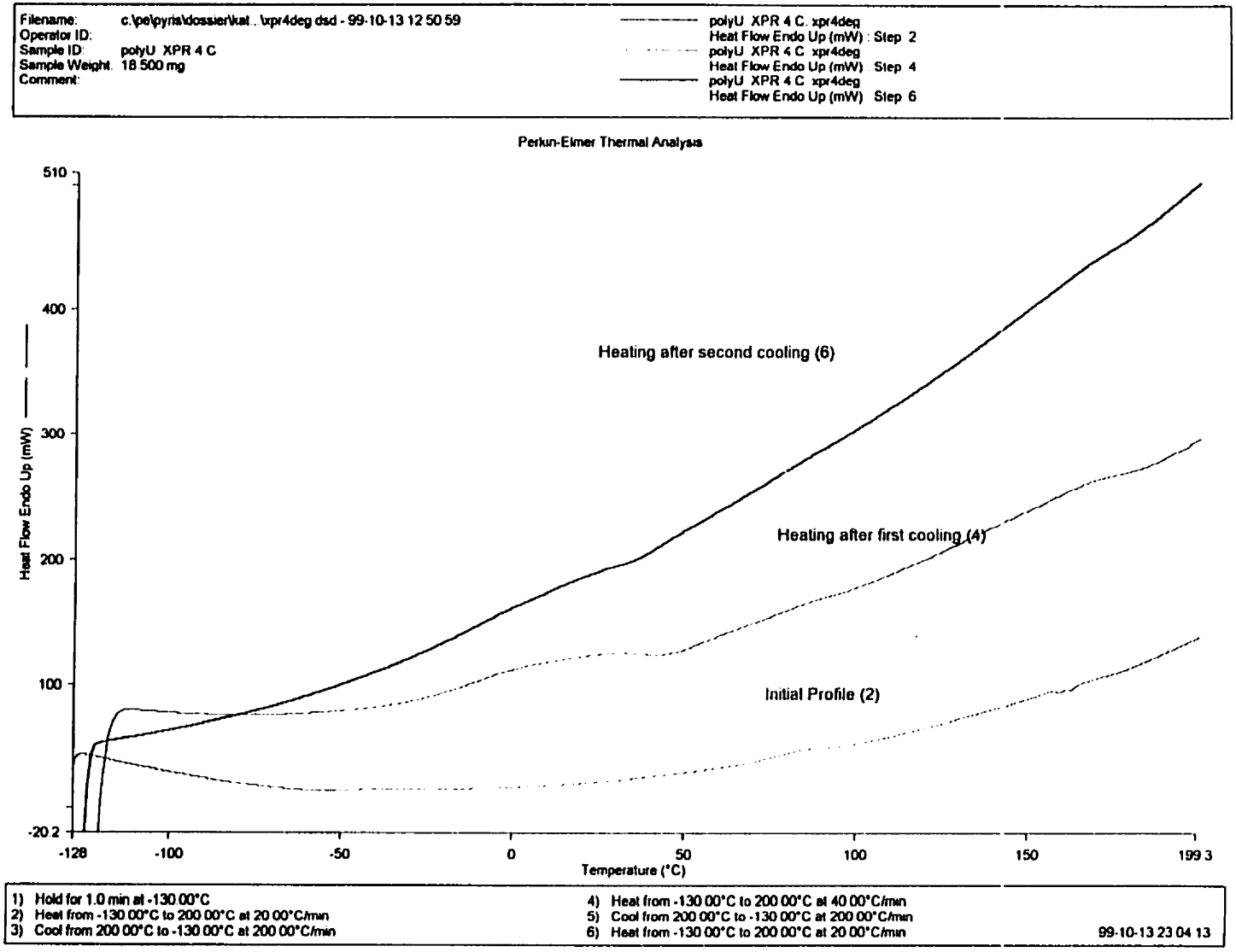
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

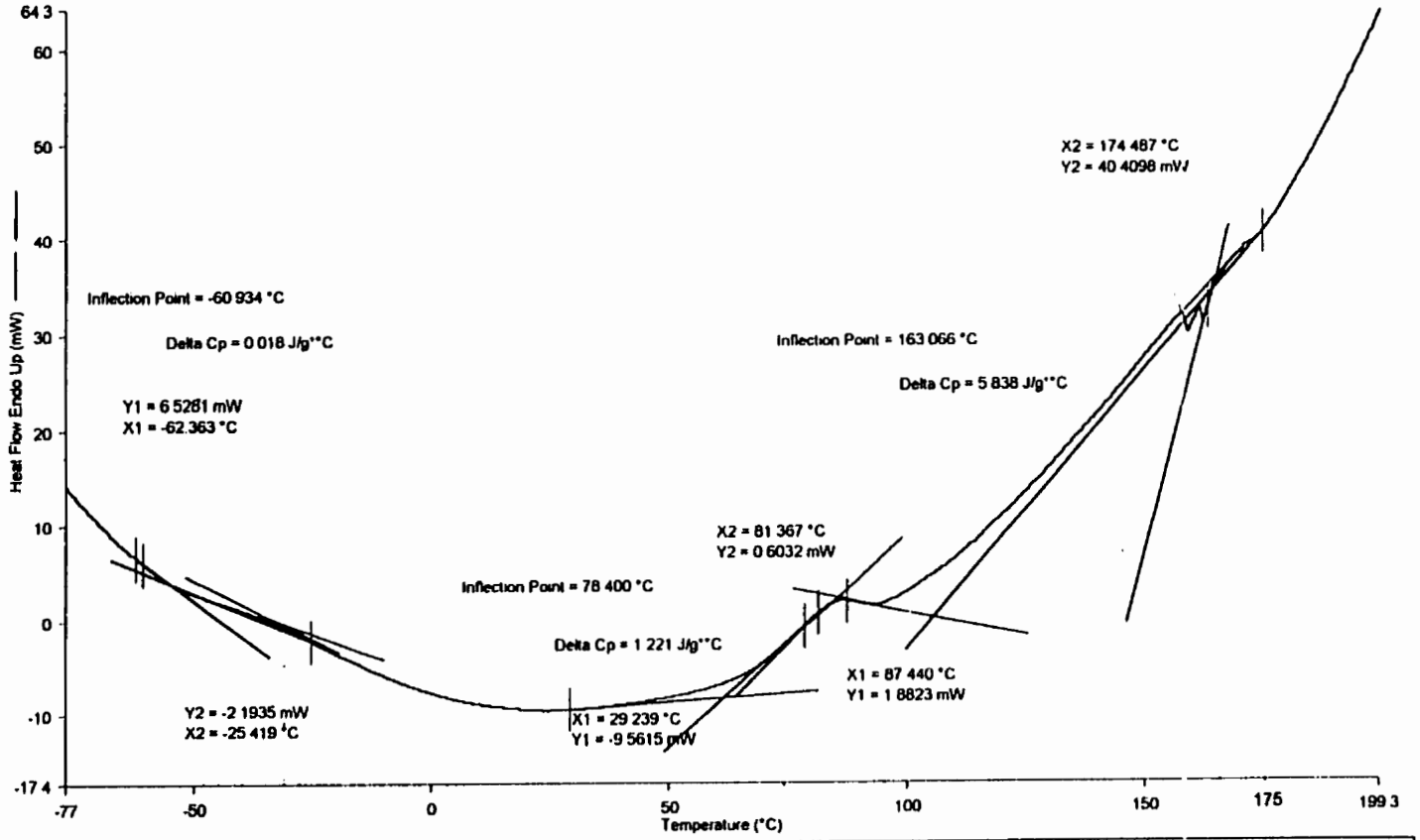
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991


Filename: c:\pe\pyris\dossier\kat..\xpr4deg dsd - 99-10-13 12 50 59
Operator ID:
Sample ID: polyU XPR 4 C
Sample Weight: 18.500 mg
Comment:
polyU XPR 4 C. xpr4deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 4
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
510
400
300
200
100
-20.2
Heating after second cooling (6)
Heating after first cooling (4)
Initial Profile (2)
-128
-100
-50
0
50
100
150
199.3
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-13 23:04:13

Filename: c:\pe\pyris\dossier\kat...\xpr4deg dsd - 99-10-13 12 50 59
Operator ID:
Sample ID: polyU XPR 4 C
Sample Weight: 18.500 mg
Comment:

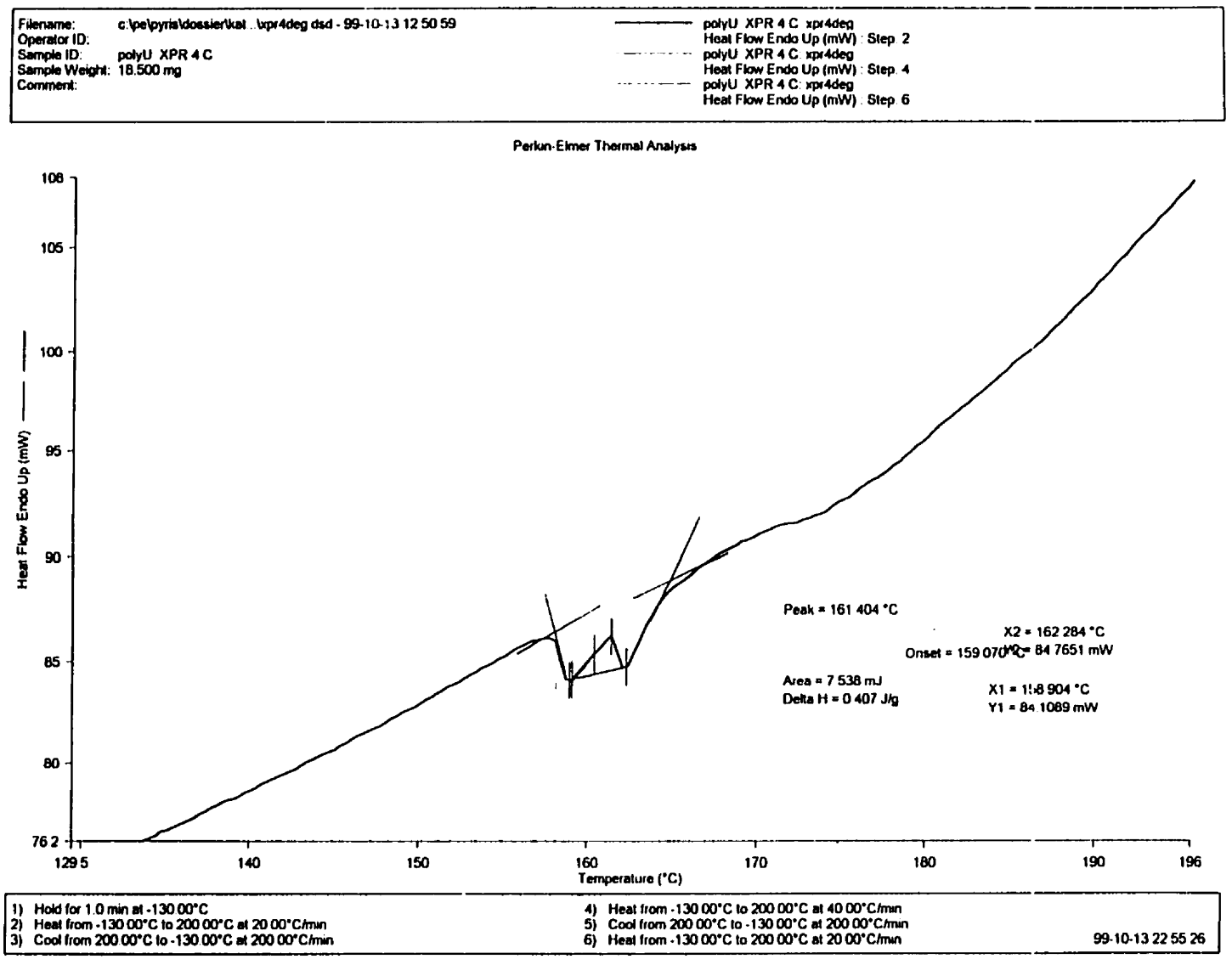
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 2
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 4
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min

99-10-13 22 49 31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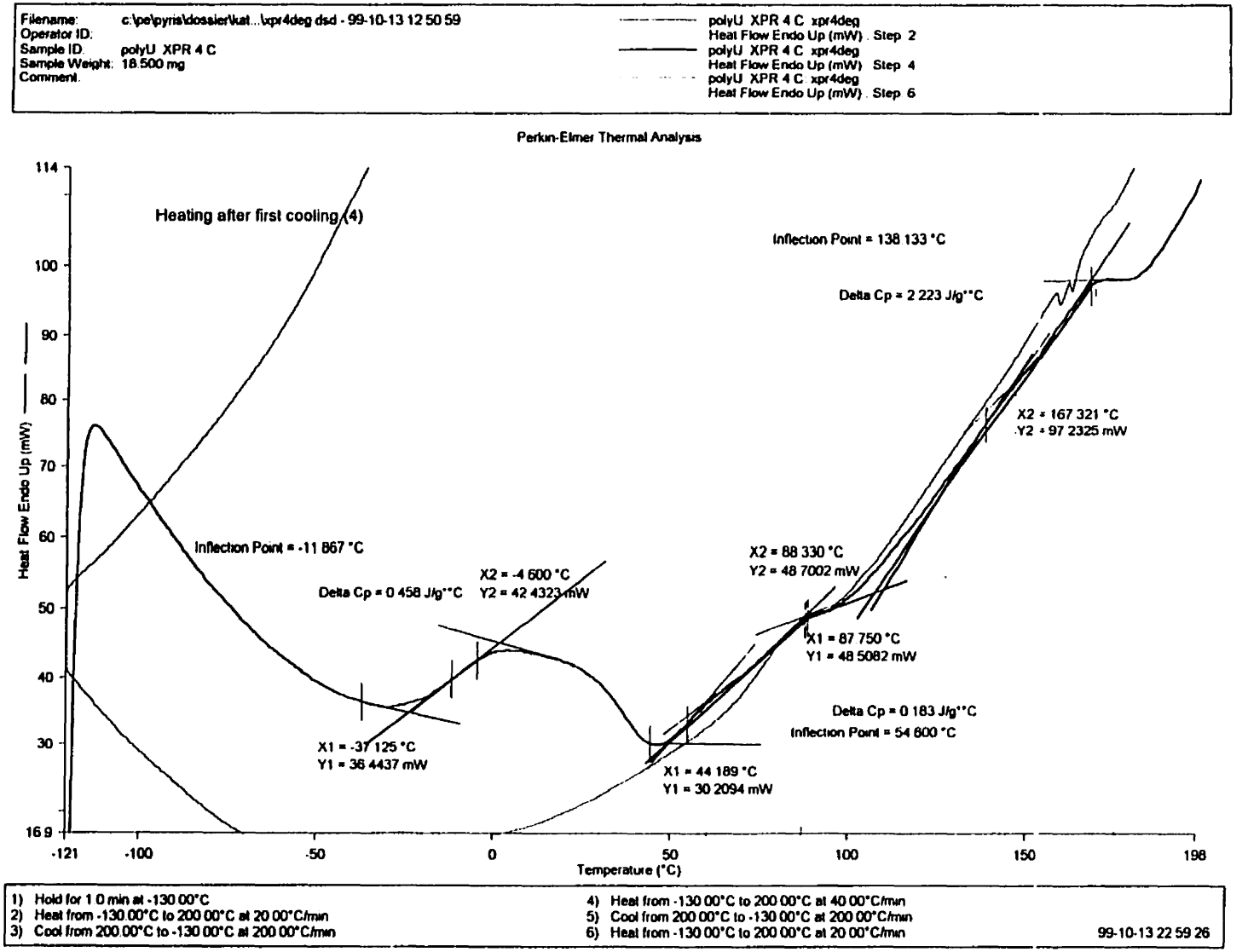
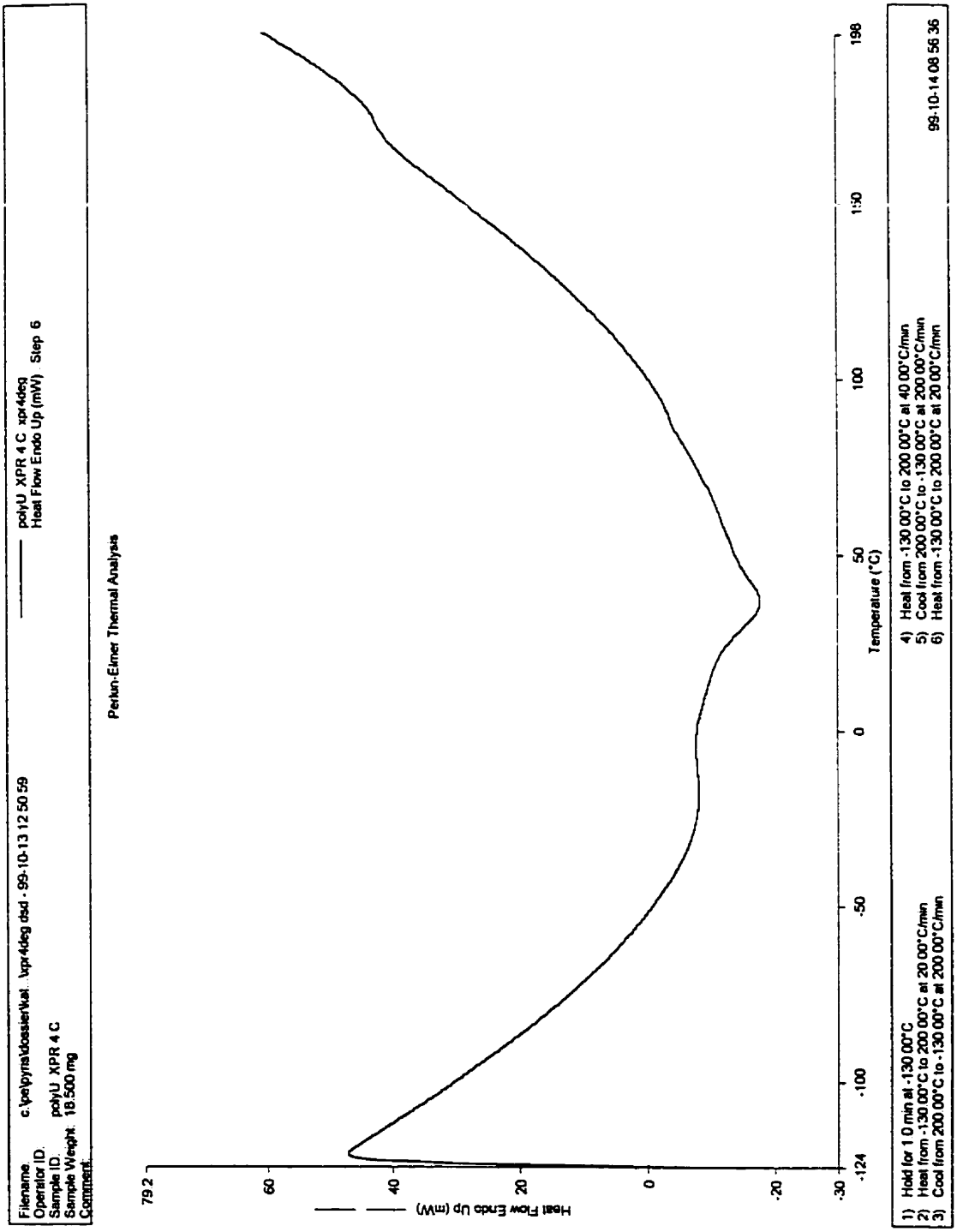
Operator ID:
Sample ID: polyU XPR 4 C
Sample Weight: 18.500 mg
Comment:
polyU XPR 4 C: xpr4deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 4 C: xpr4deg
Heat Flow Endo Up (mW) : Step 4
polyU XPR 4 C: xpr4deg
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
108
105
100
95
90
85
80
76 2
129 5
140
150
160
170
180
190
196
Temperature (°C)
Peak = 161 404 °C
X2 = 162 284 °C
Onset = 159 070 °C
Y2 = 84 7651 mW
Area = 7 538 mJ
Delta H = 0 407 J/g
X1 = 158 904 °C
Y1 = 84 1089 mW
1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min
99-10-13 22 55 26


Filename: c:\pe\pyris\dossier\kat...\xpr4deg dsd - 99-10-13 12 50 59
Operator ID:
Sample ID: polyU XPR 4 C
Sample Weight: 18.500 mg
Comment:
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) . Step 2
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) . Step 4
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) . Step 6
Perkin-Elmer Thermal Analysis
Heating after first cooling (4)
Inflection Point = 138 133 °C
Delta Cp = 2 223 J/g°°C
X2 = 167 321 °C
Y2 = 97 2325 mW
Inflection Point = -11 867 °C
X2 = -4 600 °C
Delta Cp = 0 458 J/g°°C
Y2 = 42 4323 mW
X2 = 88 330 °C
Y2 = 48 7002 mW
X1 = 87 750 °C
Y1 = 48 5082 mW
X1 = -37 125 °C
Y1 = 36 4437 mW
Delta Cp = 0 183 J/g°°C
Inflection Point = 54 600 °C
X1 = 44 189 °C
Y1 = 30 2094 mW
Heat Flow Endo Up (mW)
Temperature (°C)
114
100
90
80
70
60
50
40
30
16.9
-121
-100
-50
0
50
100
150
198
1) Hold for 1 0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min
99-10-13 22 59 26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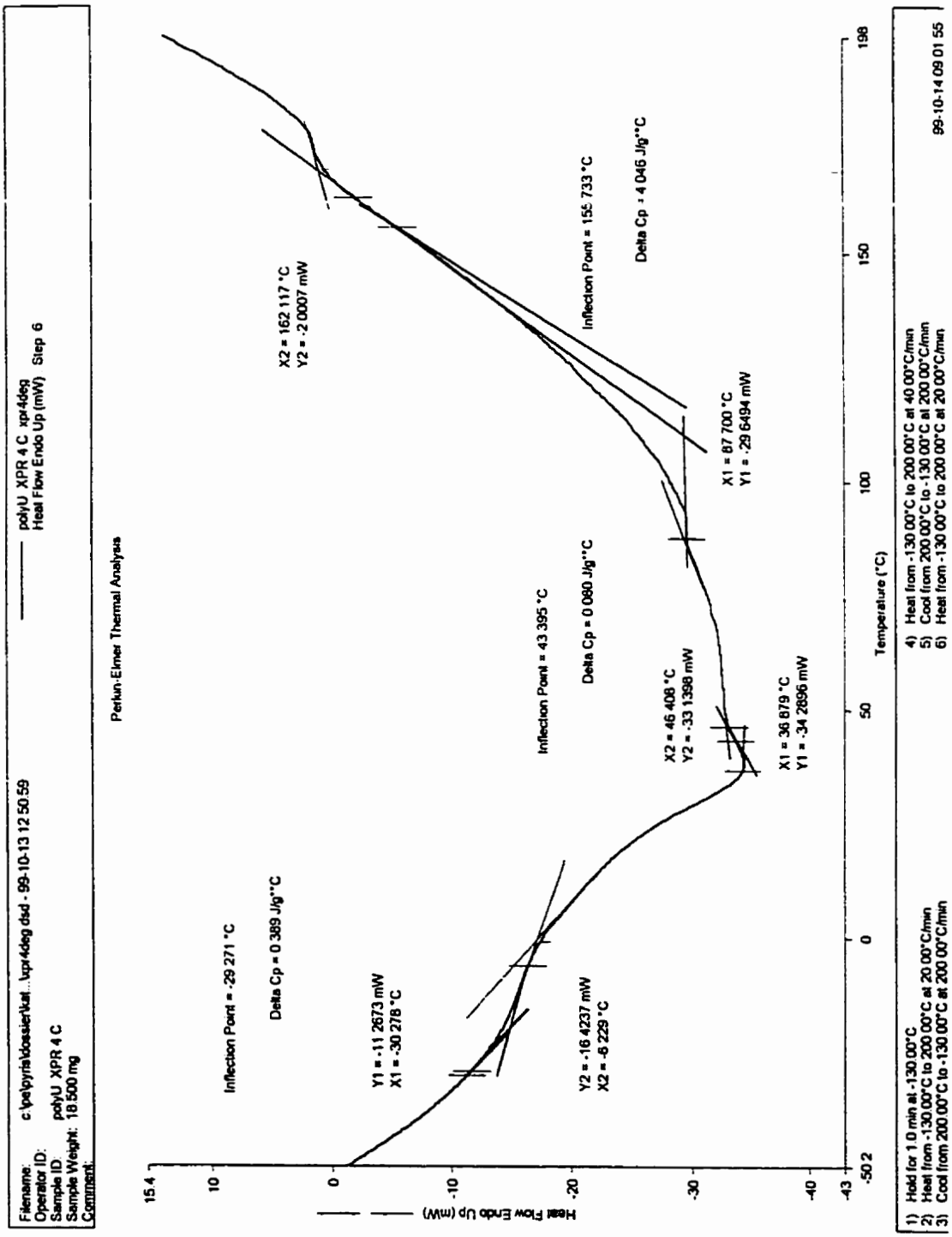
Operator ID:
Sample ID: polyU XPR 4 C
Sample Weight: 18.500 mg
Comment:
polyU XPR 4 C xpr4deg
Heat Flow Endo Up (mW) Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
79.2
60
40
20
0
-20
-30
-124
-100
-50
0
50
100
150
198
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 08:56:36



Not Enough Printer Memory -- See User's Guide

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: xpr25deg
Data Collected: Oct 13,1999 02:14:13 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc
- Date/Time: Oct 12,1999 03:33:02 PM

Validation
- Validated: No

Sample ID: polyU XPR 25 C reused with new cond
Operator ID:
Comment:
Sample Weight: 17.900 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\XPR25Cnc@991013110915.dsd

Initial Conditions
- Temperature: -130.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To: -130.00°C
Total Points in Run: 2735

Method Steps:

1) Hold for 1.0 min at -130.00°C
   - Data Points: 60

2) Heat from -130.00°C to 200.00°C at 20.00°C/min
   - Data Points: 990

3) Cool from 200.00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

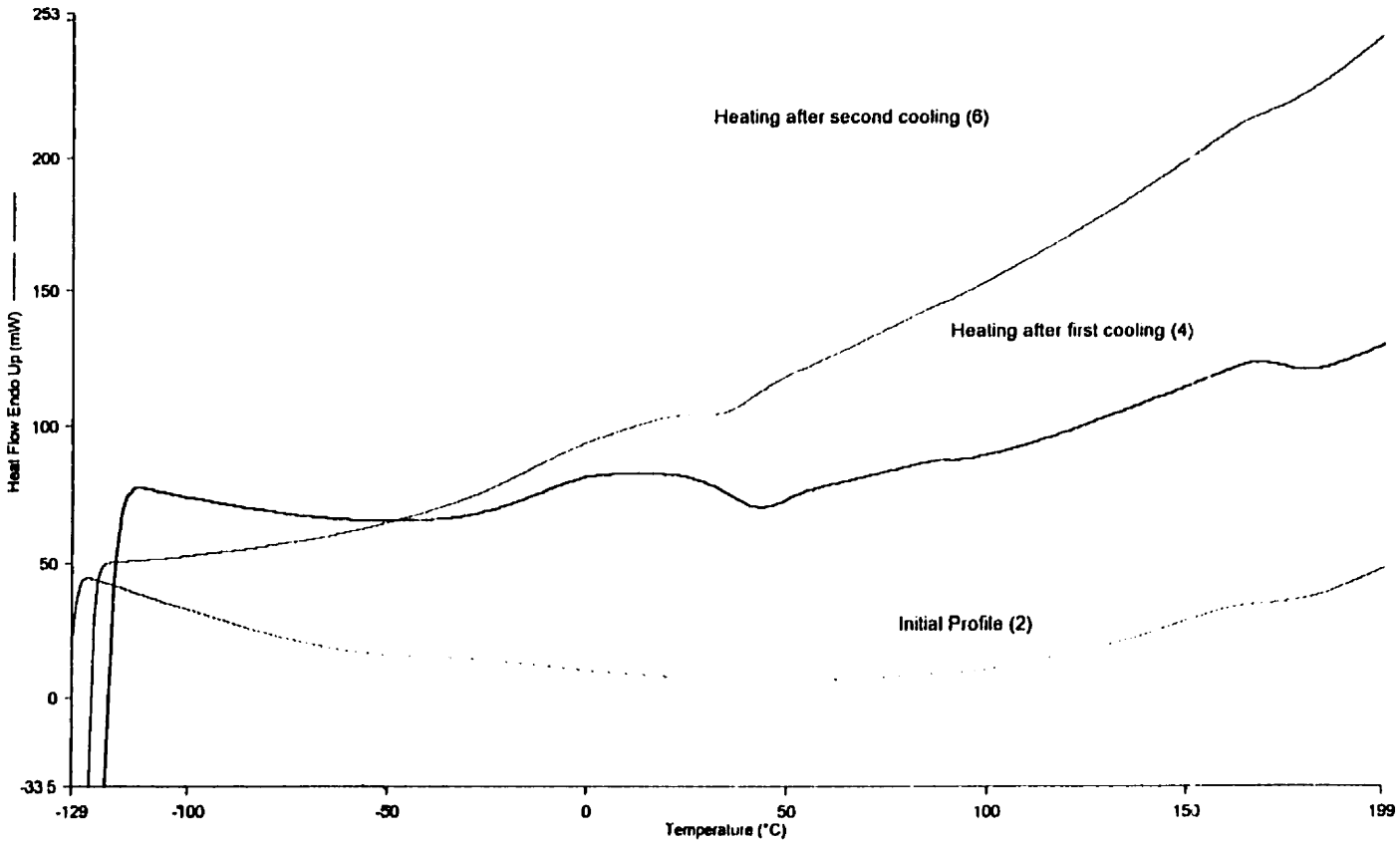
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991

Filename: c:\pe\pyris\dossier\ka...\xpr25deg dsd - 99-10-13 14.14.13
Operator ID:
Sample ID: polyU XPR 25 C reused with new cond
Sample Weight: 17.900 mg
Comment:

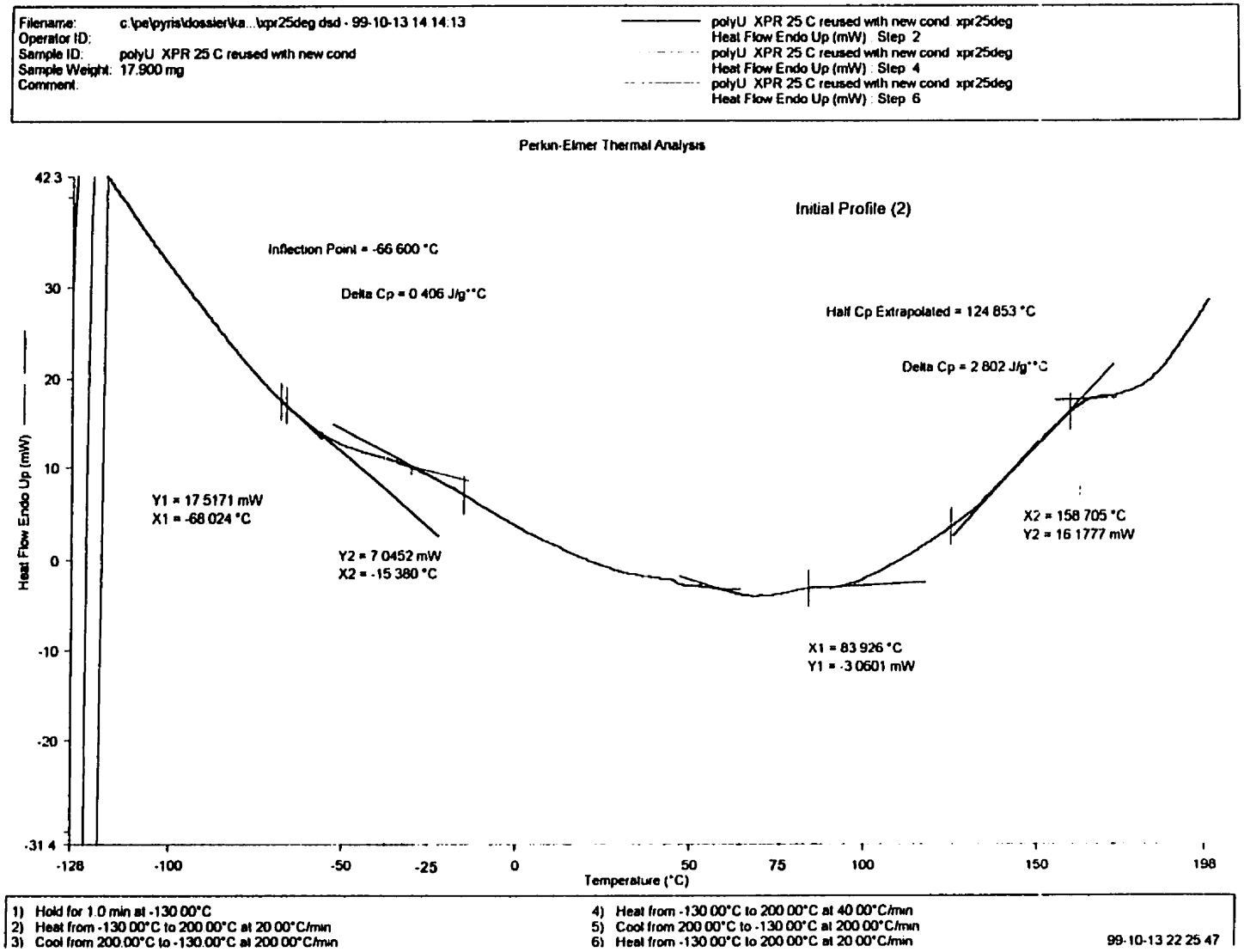
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step 4
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step 6

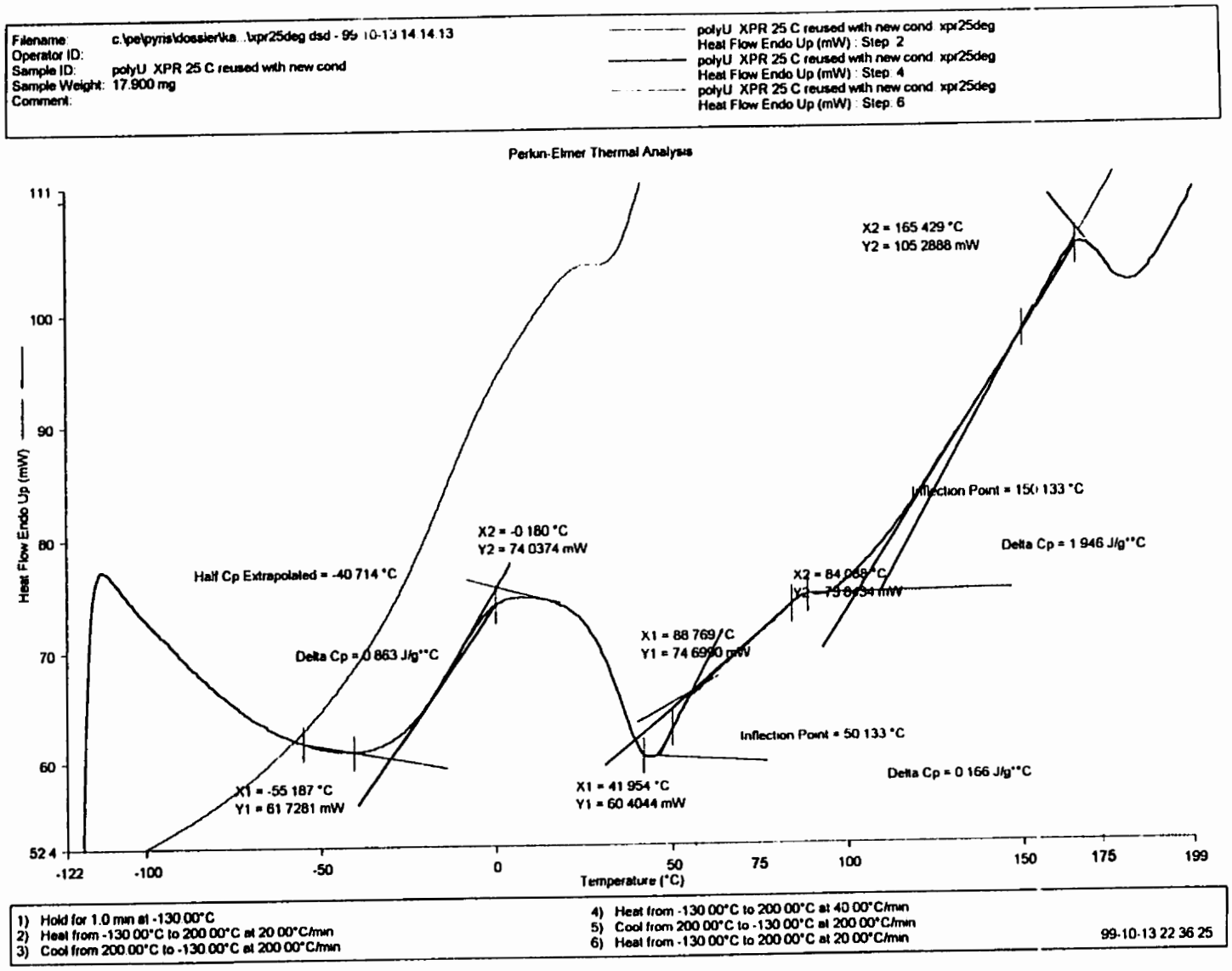
Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-13 22:14:22

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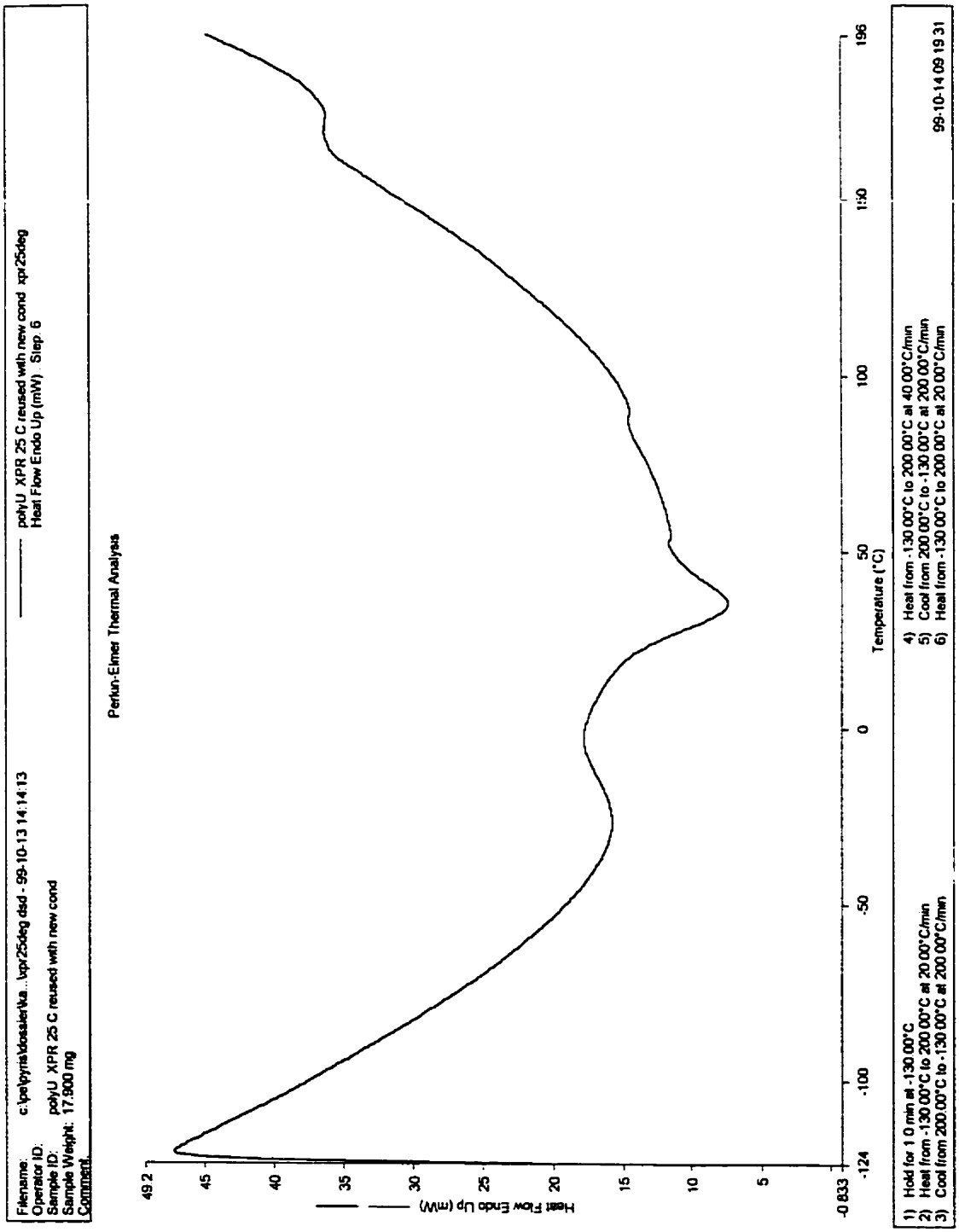
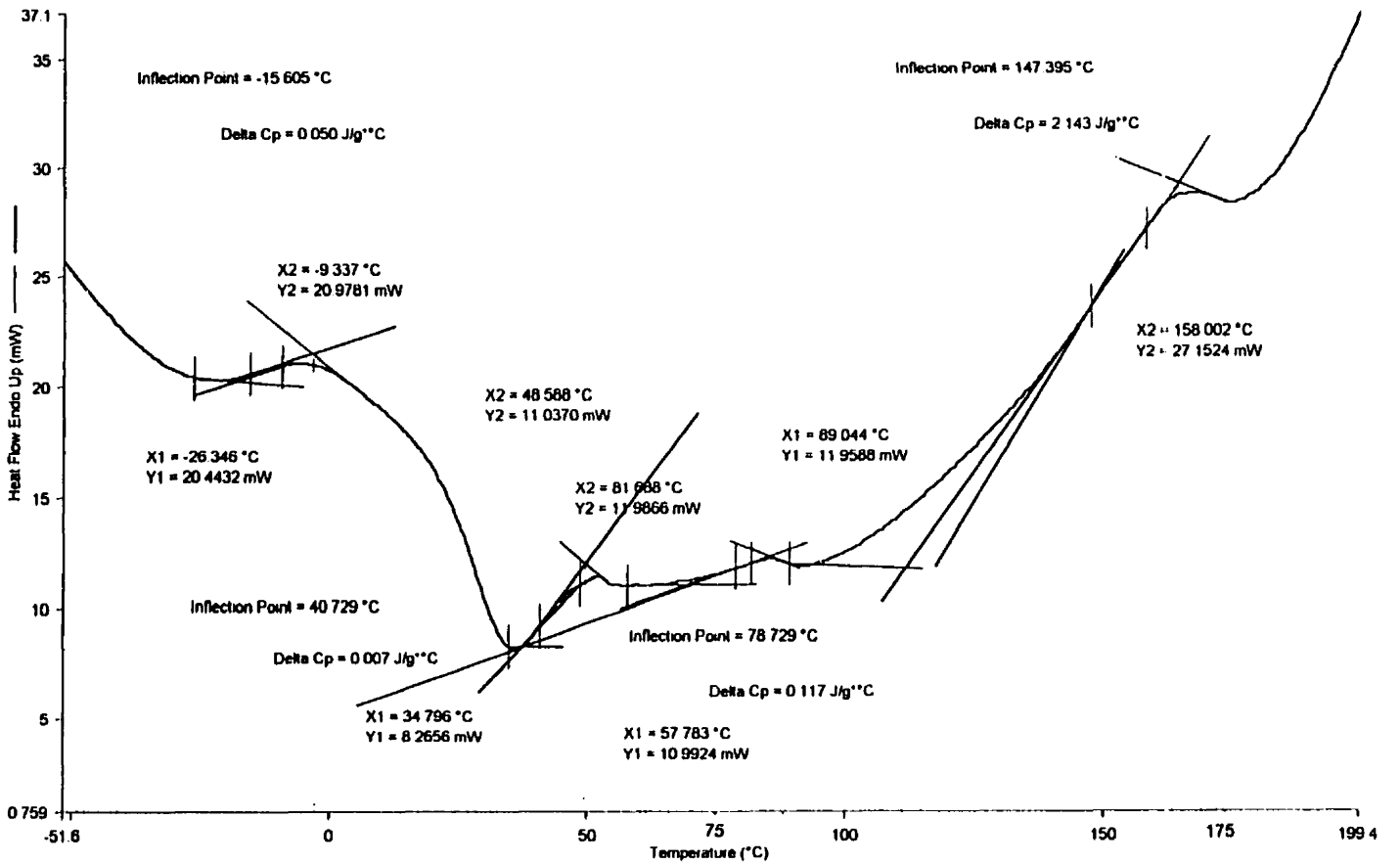
Operator ID:
Sample ID: polyU XPR 25 C reused with new cond
Sample Weight: 17.900 mg
Comment:
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step: 2
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step: 4
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step: 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
X2 = 165.429 °C
Y2 = 105.2888 mW
Inflection Point = 150.133 °C
Delta Cp = 1.946 J/g**C
X2 = 84.068 °C
Y2 = 75.8754 mW
X2 = -0.180 °C
Y2 = 74.0374 mW
Half Cp Extrapolated = -40.714 °C
Delta Cp = 0.863 J/g**C
X1 = 88.769 °C
Y1 = 74.6990 mW
Inflection Point = 50.133 °C
Delta Cp = 0.166 J/g**C
X1 = -55.187 °C
Y1 = 61.7281 mW
X1 = 41.954 °C
Y1 = 60.4044 mW
1) Hold for 1.0 mn at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -130.00°C at 200.00°C/mn
4) Heat from -130.00°C to 200.00°C at 40.00°C/mn
5) Cool from 200.00°C to -130.00°C at 200.00°C/mn
6) Heat from -130.00°C to 200.00°C at 20.00°C/mn
99-10-13 22:36:25


Filename: c:\pelpyrisk\dosaserka...\xpr25deg dsd - 99-10-13 14:14:13
Operator ID:
Sample ID: polyU XPR 25 C reused with new cond
Sample Weight: 17.900 mg
Comment:
polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) Step: 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
49.2
45
40
35
30
25
20
15
10
5
-0.833
-124
-100
-50
0
50
100
150
196
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-14 09:19:31

Filename: c:\pe\pyris\dossier\ka...\xpr25deg dsd - 99-10-13 14 14.13
Operator ID:
Sample ID: polyU XPR 25 C reused with new cond
Sample Weight: 17.900 mg
Comment:

polyU XPR 25 C reused with new cond xpr25deg
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 09:10:33

DSC 7 Method
Calibration 1

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: xpr60deg
Data Collected: Oct 13,1999 09:55:48 AM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc
- Date/Time: Oct 12,1999 03:33:02 PM

Validation
- Validated: No

Sample ID: polyU_XPR 60 C
Operator ID:
Comment:
Sample Weight: 15.980 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\XPR60C@991013093049.dsd

Initial Conditions
- Temperature: -100.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To: -105.00°C
Total Points in Run: 1502

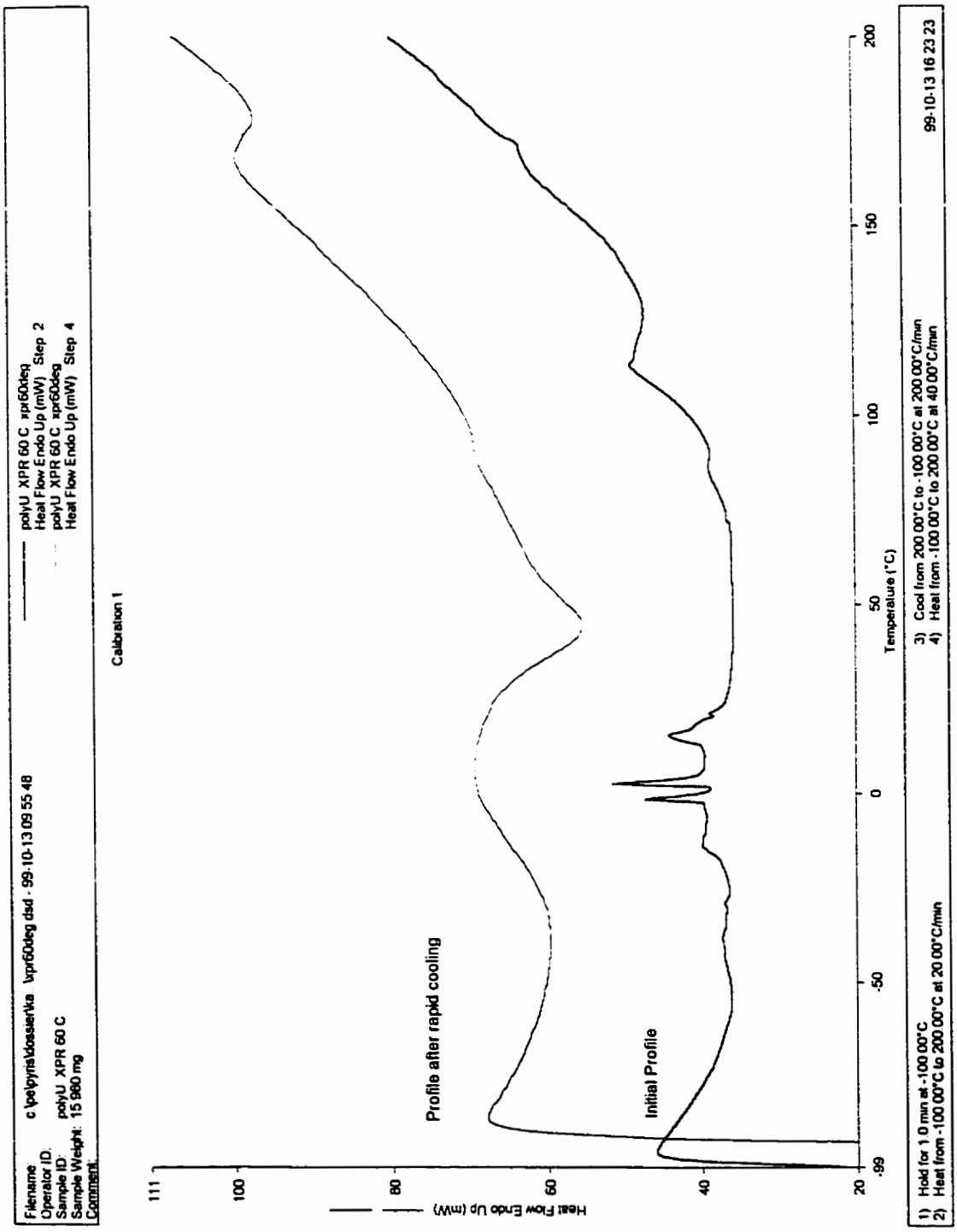
Method Steps:

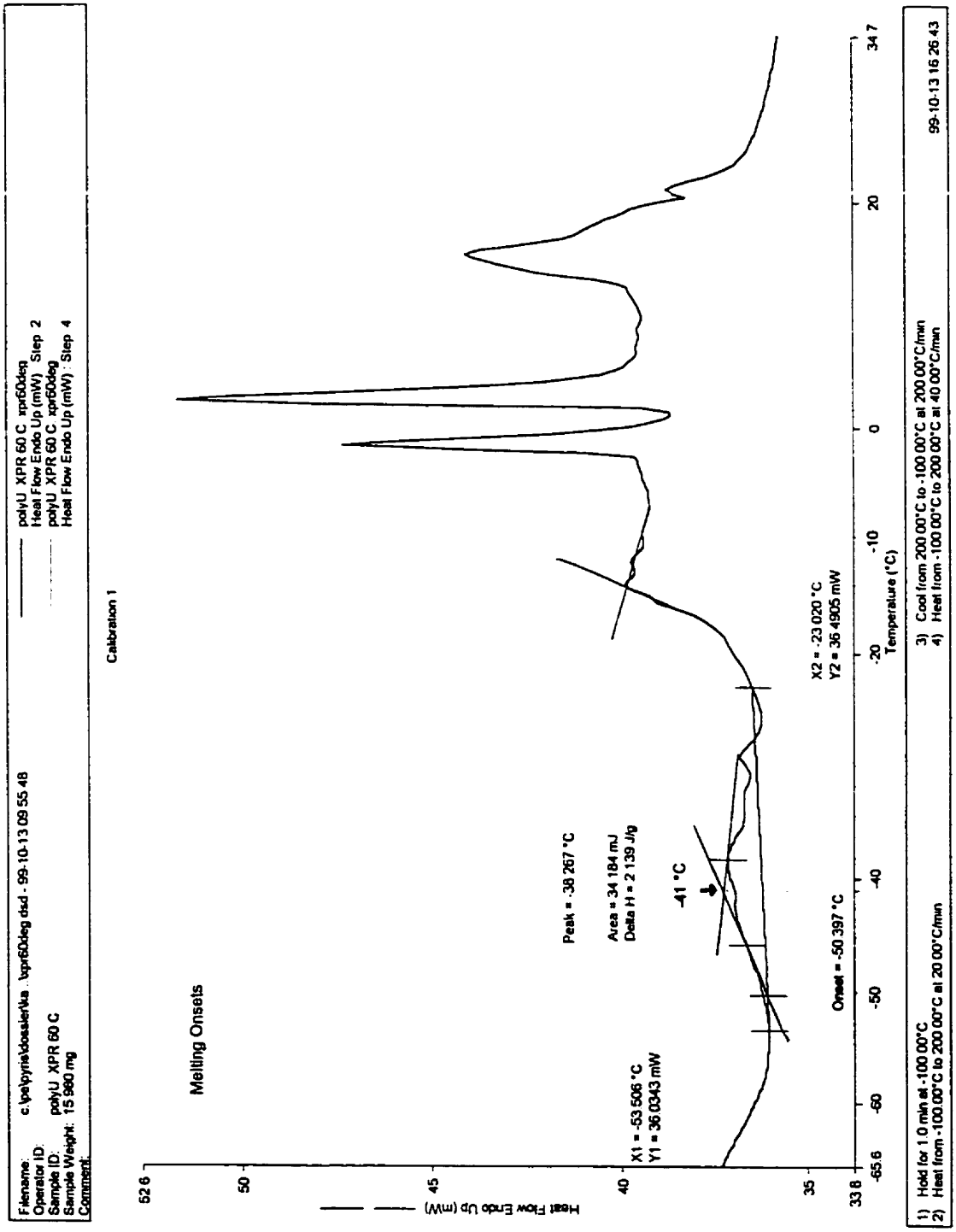
1) Hold for 1.0 min at -100.00°C
   - Data Points: 61

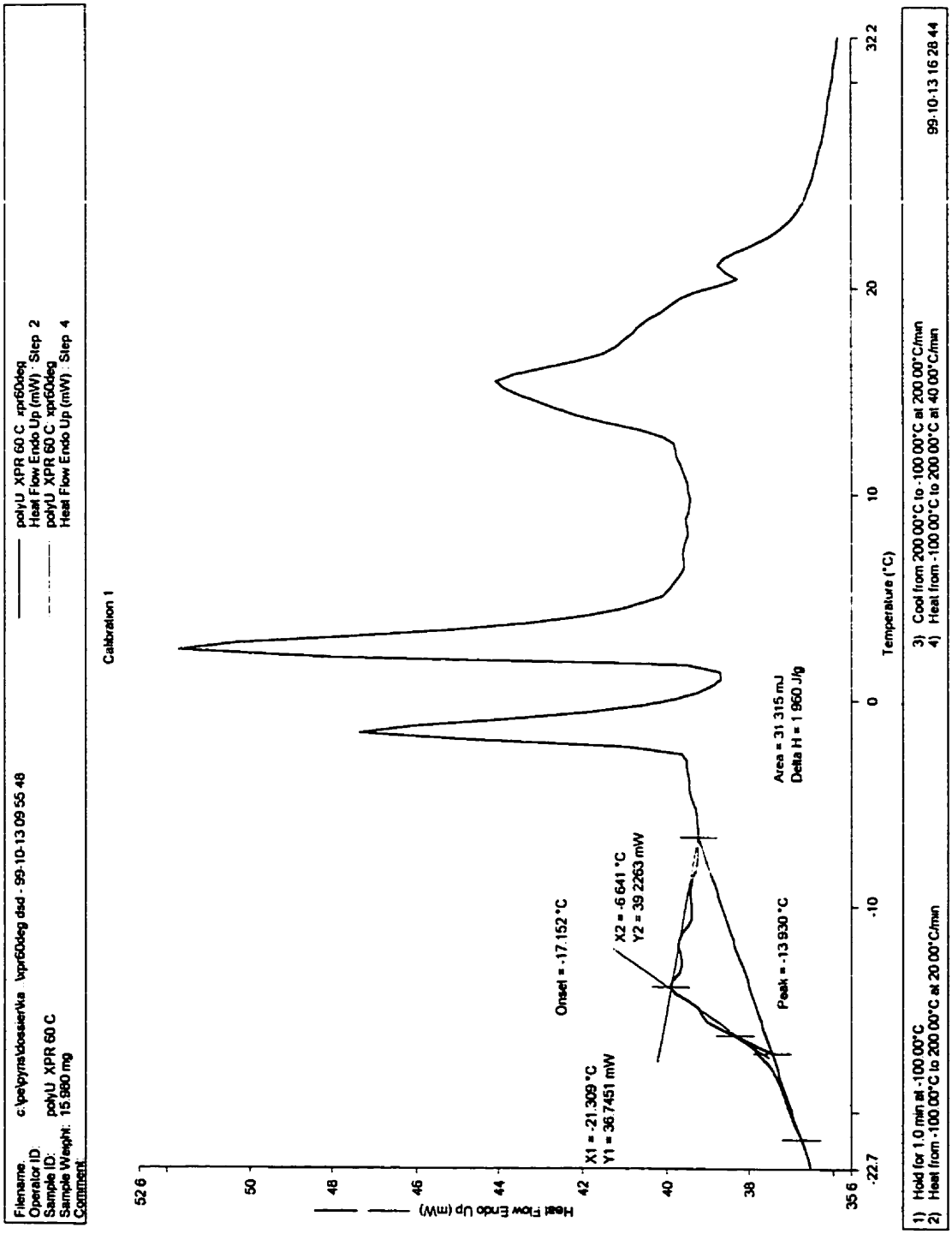
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
   - Data Points: 900

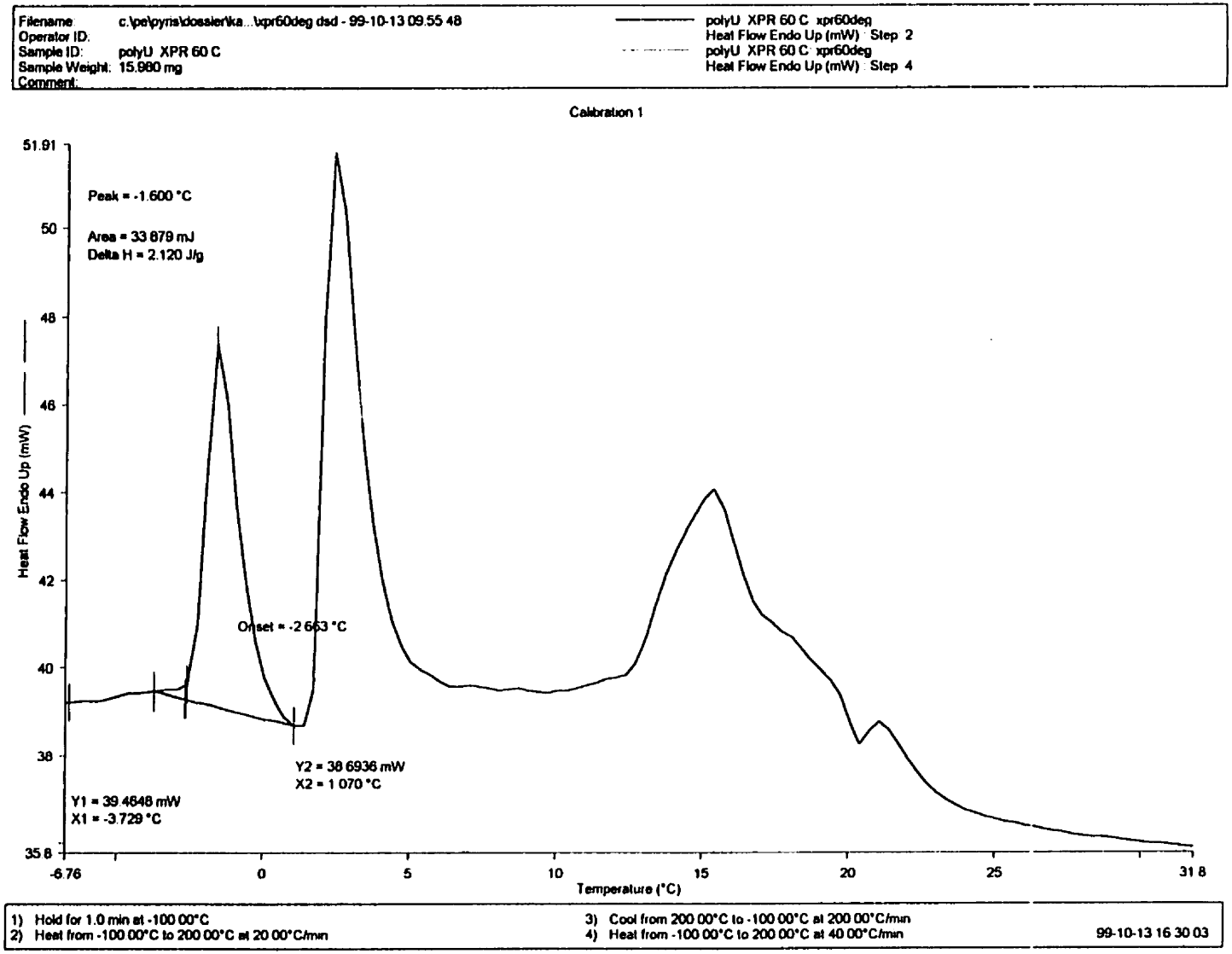
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
   - Data Points: 90

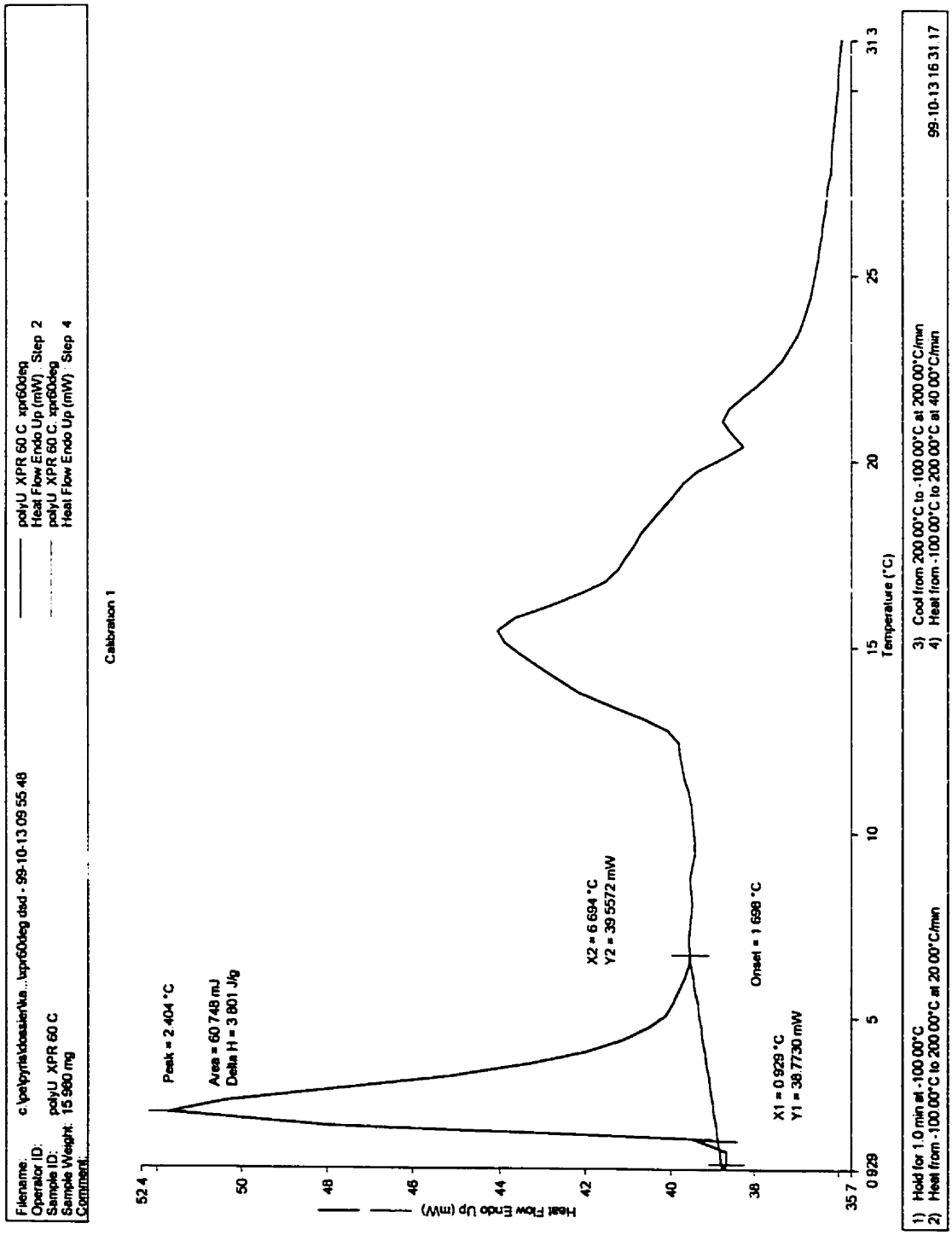
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
   - Data Points: 451

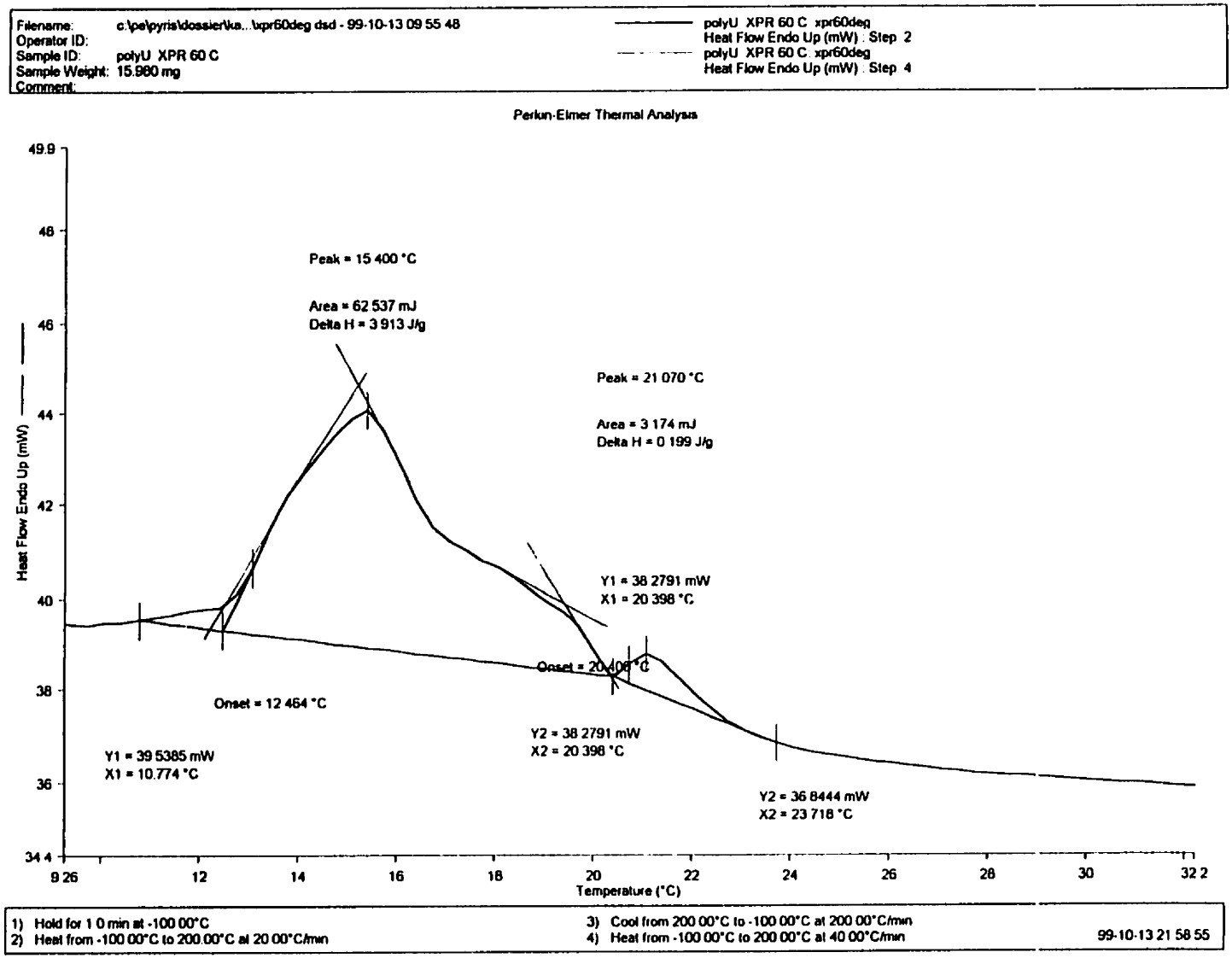

Filename: c:\polypyrrole\dsc\xrka \xpr60deg dsd - 99-10-13 09 55 48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 4
Calibration 1
Profile after rapid cooling
Initial Profile
Heat Flow Endo Up (mW)
Temperature (°C)
1) Hold for 1.0 mun at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 16:23:23

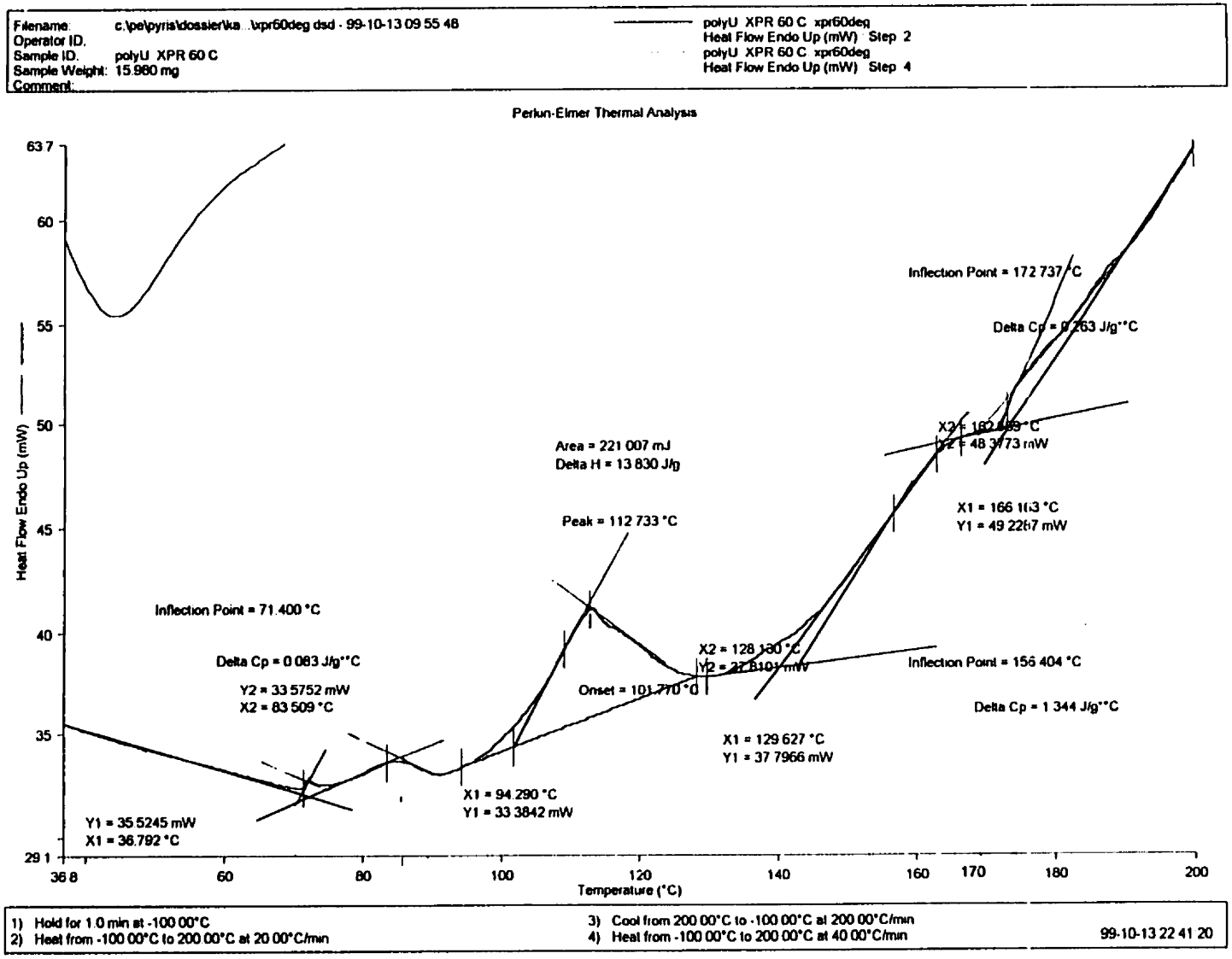

Filename: c:\polyris\dossier\ka...\xpr60deg dsd - 99-10-13 09:55:48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C xpr60dsq
Heat Flow Endo Up (mW) Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 4
Calibration 1
Melting Onsets
Peak = -38.267 °C
Area = 34.184 mJ
Delta H = 2.139 J/g
-41 °C
X1 = -53.506 °C
Y1 = 36.0343 mW
X2 = -23.020 °C
Y2 = 35.4905 mW
Onset = -50.397 °C
Heat Flow Endo Up (mW)
Temperature (°C)
52.6
50
45
40
35
33.8
-65.6
-60
-50
-40
-20
-10
0
20
34.7
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 16:26:43

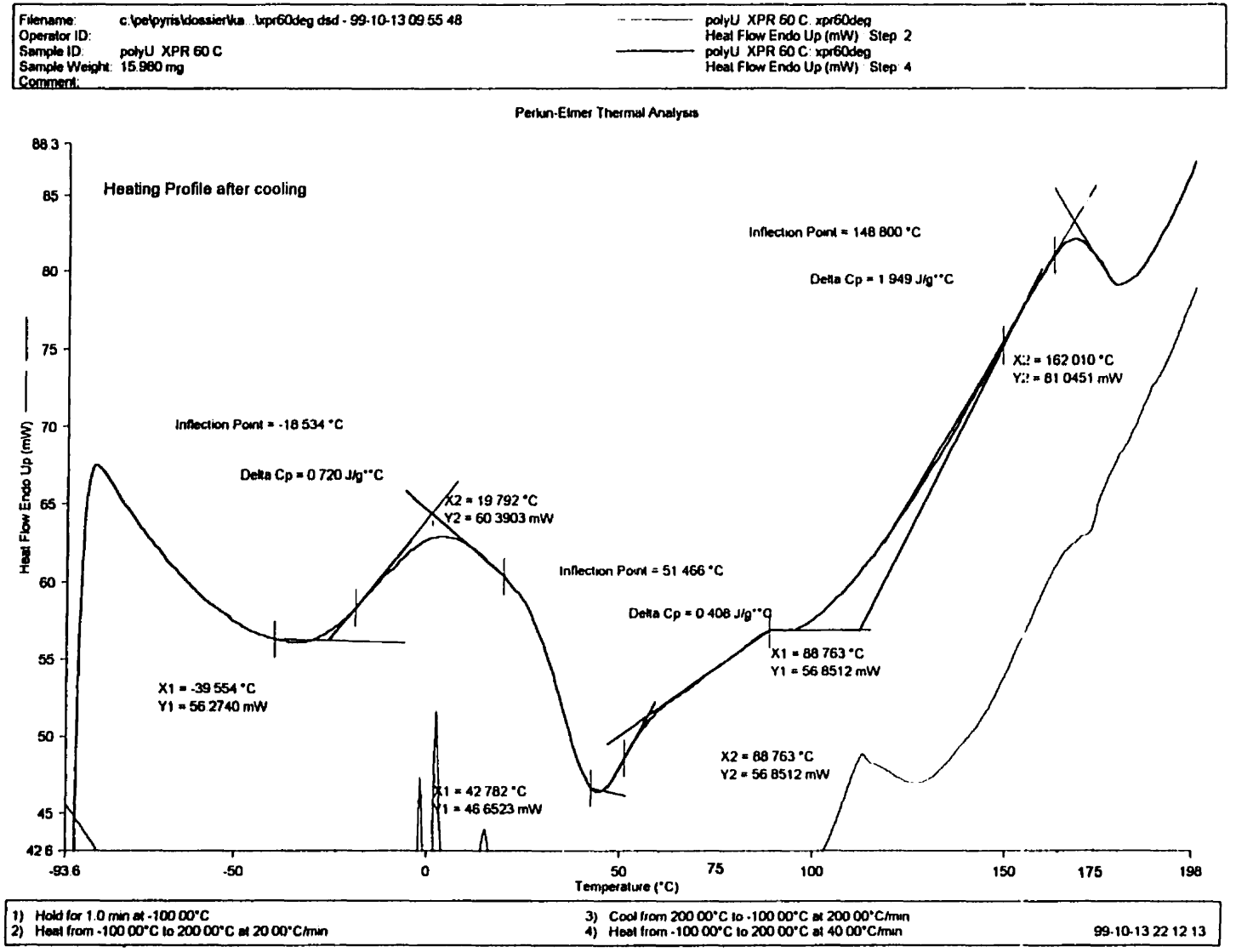

Filename c:\pelpyrrs\dosser\ka \xpr60deg dsd - 99-10-13 09 55 48
Operator ID
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) : Step 4
Calibration 1
Heat Flow Endo Up (mW)
Temperature (°C)
Onset = -17.152 °C
X1 = -21.309 °C
Y1 = 36.7451 mW
X2 = -6.641 °C
Y2 = 39.2263 mW
Peak = -13.930 °C
Area = 31.315 mJ
Delta H = 1.960 J/g
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 16:28:44


Filename: c:\pe\pyris\dossier\ka...\xpr60deg dsd - 99-10-13 09:55:48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) : Step 4
Calibration 1
Peak = -1.600 °C
Area = 33.879 mJ
Delta H = 2.120 J/g
Onset = -2.663 °C
Y2 = 38.6936 mW
X2 = 1.070 °C
Y1 = 39.4648 mW
X1 = -3.729 °C
Heat Flow Endo Up (mW)
Temperature (°C)
51.91
50
48
46
44
42
40
38
35.8
-6.76
0
5
10
15
20
25
31.8
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 16:30:03


Filename: c:\polypyrrole\dossier\ka...\xpr60deg dsd - 99-10-13 09:55:48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 4
Calibration 1
Peak = 2.404 °C
Area = 60.748 mJ
Delta H = 3.801 J/g
X2 = 6.694 °C
Y2 = 39.5572 mW
Onset = 1.698 °C
X1 = 0.929 °C
Y1 = 38.7730 mW
Heat Flow Endo Up (mW)
Temperature (°C)
52.4
50
48
46
44
42
40
38
35.7
0.929
5
10
15
20
25
31.3
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 16:31:17


Filename: c:\pe\pyris\dossier\ka...\xpr60deg.dsd - 99-10-13 09:55:48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C: xpr60deg
Heat Flow Endo Up (mW) : Step 2
polyU XPR 60 C: xpr60deg
Heat Flow Endo Up (mW) : Step 4
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
Peak = 15.400 °C
Area = 62.537 mJ
Delta H = 3.913 J/g
Peak = 21.070 °C
Area = 3.174 mJ
Delta H = 0.199 J/g
Y1 = 38.2791 mW
X1 = 20.398 °C
Onset = 20.406 °C
Onset = 12.464 °C
Y2 = 38.2791 mW
X2 = 20.398 °C
Y1 = 39.5385 mW
X1 = 10.774 °C
Y2 = 36.8444 mW
X2 = 23.718 °C
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/mn
3) Cool from 200.00°C to -100.00°C at 200.00°C/mn
4) Heat from -100.00°C to 200.00°C at 40.00°C/mn
99-10-13 21:58:55


Filename: c:\pe\pyris\dossier\ka...\xpr60deg dsd - 99-10-13 09 55 48
Operator ID.
Sample ID. polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 2
polyU XPR 60 C xpr60deg
Heat Flow Endo Up (mW) Step 4
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
63.7
60
55
50
45
40
35
29.1
36.8
60
80
100
120
140
160
170
180
200
Inflection Point = 172.737 °C
Delta Cp = 0.263 J/g°°C
X2 = 160.689 °C
Y2 = 48.3773 mW
Area = 221.007 mJ
Delta H = 13.830 J/g
Peak = 112.733 °C
X1 = 166.103 °C
Y1 = 49.2267 mW
Inflection Point = 71.400 °C
Delta Cp = 0.083 J/g°°C
Y2 = 33.5752 mW
X2 = 83.509 °C
X2 = 128.130 °C
Y2 = 37.8101 mW
Onset = 101.770 °C
Inflection Point = 156.404 °C
Delta Cp = 1.344 J/g°°C
X1 = 129.627 °C
Y1 = 37.7966 mW
X1 = 94.290 °C
Y1 = 33.3842 mW
Y1 = 35.5245 mW
X1 = 36.792 °C
1) Hold for 1.0 min at -100.00°C
2) Heat from -100.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -100.00°C at 200.00°C/min
4) Heat from -100.00°C to 200.00°C at 40.00°C/min
99-10-13 22 41 20


Filename: c:\pe\pyris\dossier\ka ..\xpr60deg dsd - 99-10-13 09 55 48
Operator ID:
Sample ID: polyU XPR 60 C
Sample Weight: 15.980 mg
Comment:
polyU XPR 60 C: xpr60deg
Heat Flow Endo Up (mW) Step 2
polyU XPR 60 C: xpr60deg
Heat Flow Endo Up (mW) Step 4
Perkin-Elmer Thermal Analysis
Heating Profile after cooling
Inflection Point = 148 800 °C
Delta Cp = 1 949 J/g°°C
X2 = 162 010 °C
Y2 = 81 0451 mW
Inflection Point = -18 534 °C
Delta Cp = 0 720 J/g°°C
X2 = 19 792 °C
Y2 = 60 3903 mW
Inflection Point = 51 466 °C
Delta Cp = 0 408 J/g°°C
X1 = 88 763 °C
Y1 = 56 8512 mW
X1 = -39 554 °C
Y1 = 56 2740 mW
X2 = 88 763 °C
Y2 = 56 8512 mW
X1 = 42 782 °C
Y1 = 46 6523 mW
Heat Flow Endo Up (mW)
Temperature (°C)
1) Hold for 1.0 min at -100 00°C
2) Heat from -100 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -100 00°C at 200 00°C/min
4) Heat from -100 00°C to 200 00°C at 40 00°C/min
99-10-13 22 12 13

DSC 7 Method
Perkin-Elmer Thermal Analysis

Instrument
- Type: DSC 7
- Name: DSC 7

Filename: bg
Data Collected: Oct 13,1999 03:50:54 PM
Calibration Info:
- Filename: C:\PE\Pyris\Dossier\Kathy\calibok1.dsc
- Date/Time: Oct 12,1999 03:33:02 PM

Validation
- Validated: No

Sample ID: polyU_BG xylene cleaned NaCl NaCl
Operator ID:
Comment:
Sample Weight: 15.780 mg
Save Filename: C:\PE\Pyris\Dossier\Kathy\BGnc@991013110915.dsd

Initial Conditions
- Temperature: -130.00 °C
- Y Initial: 20.00 mW
- Purge Gas: Helium
- Purge Gas Rate: 20.0 ml/min
- Sample Rate: Standard

Equilibrate Within
- Temperature: 0.01 °C
- Heat Flow: 0.01 mW
- Maximum Time: 3.00 min

End Condition: Go To -130.00°C
Total Points in Run: 2735

Method Steps:

1) Hold for 1.0 min at -130.00°C
   - Data Points: 61

2) Heat from -130.00°C to 200.00°C at 20.00°C/min
   - Data Points: 990

3) Cool from 200.00°C to -130.00°C at 200.00°C/min
   - Data Points: 99

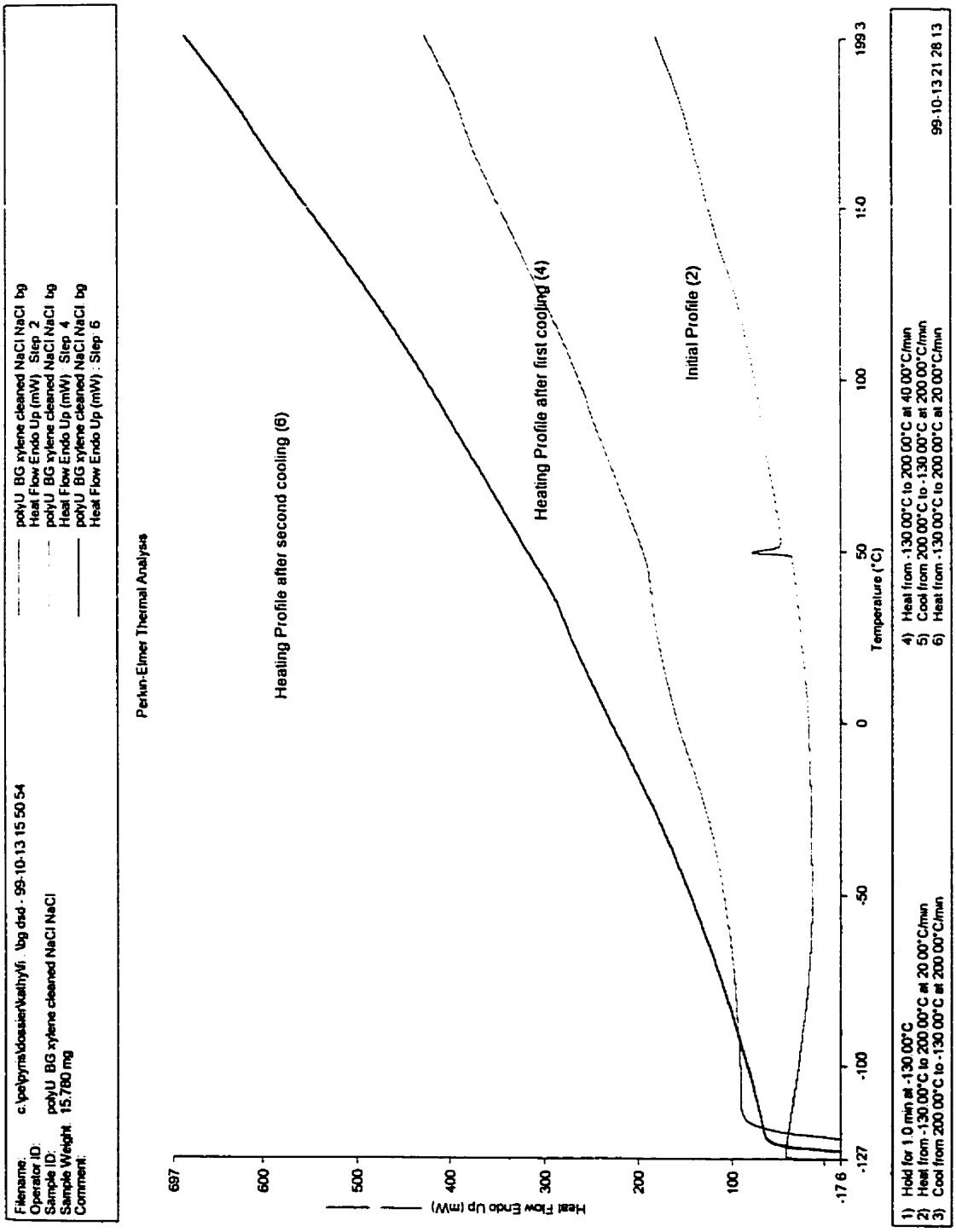
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
   - Data Points: 495

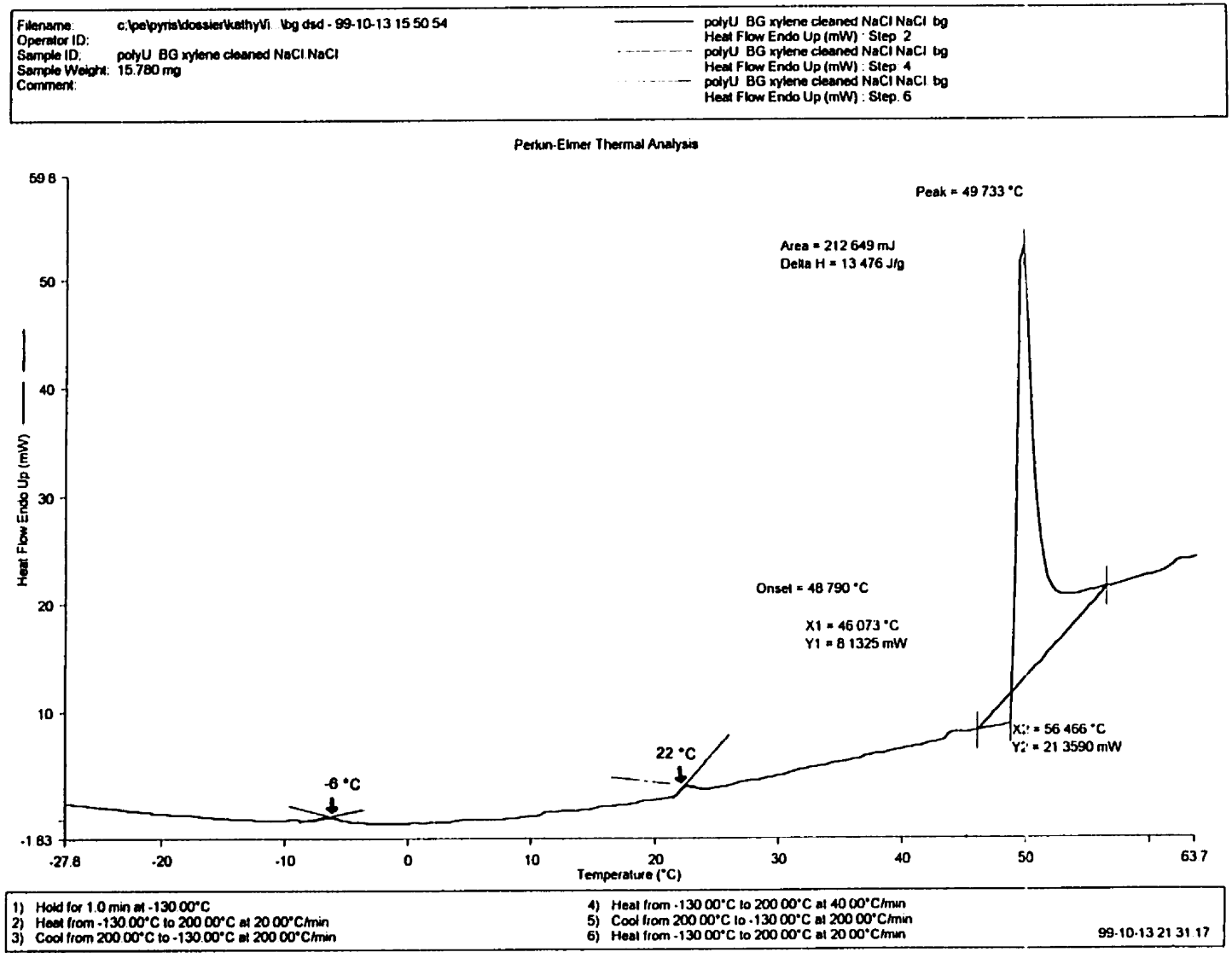
DSC 7 Method
Perkin-Elmer Thermal Analysis

Method Steps:

5) Cool from 200.00°C to -130.00°C at 200.00°C/min
   Data Points: 99

6) Heat from -130.00°C to 200.00°C at 20.00°C/min
   Data Points: 991

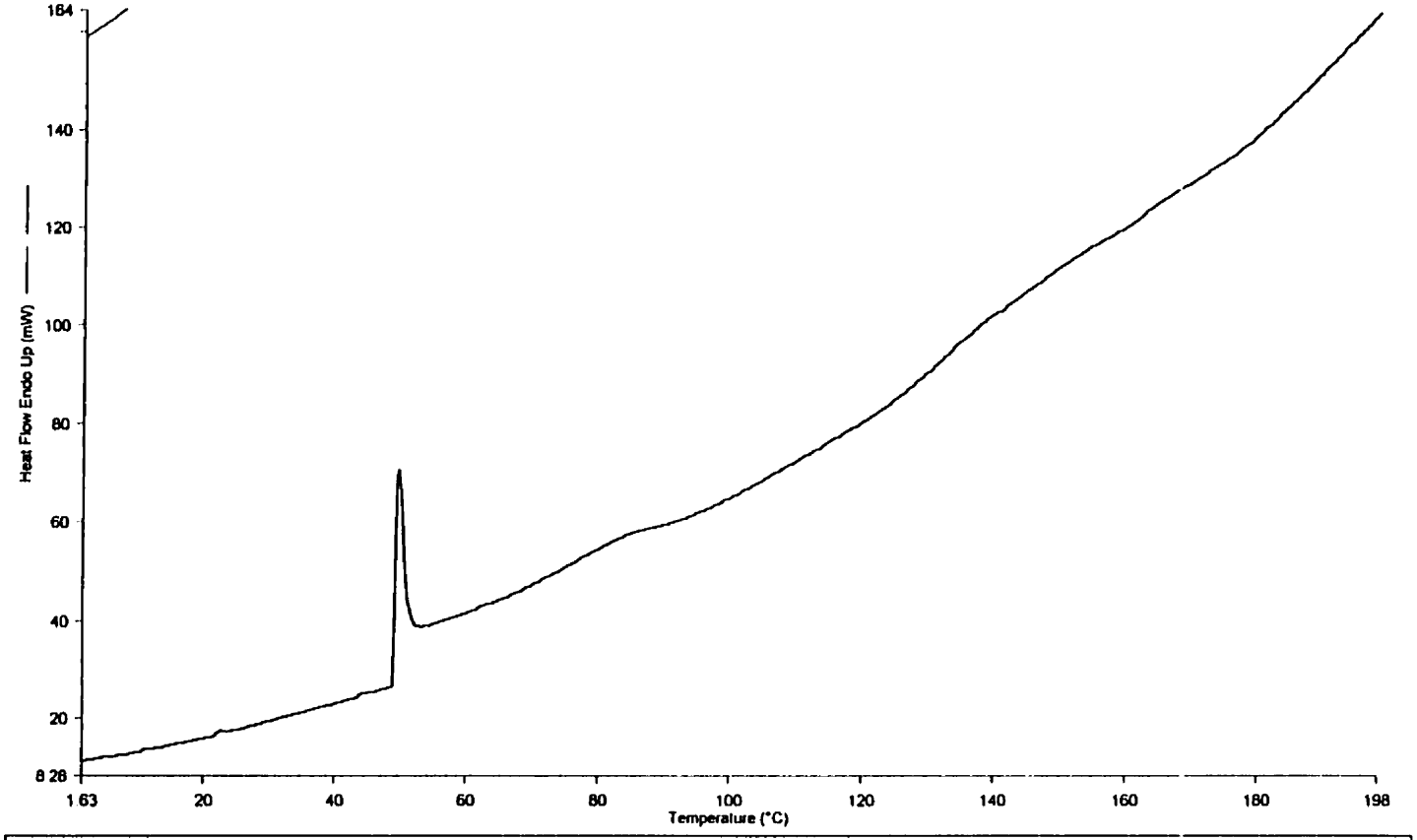

Filename: c:\polymis\dossier\vathyfi\ .\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 6
Perkin-Elmer Thermal Analysis
Heating Profile after second cooling (6)
Heating Profile after first cooling (4)
Initial Profile (2)
Heat Flow Endo Up (mW)
697
600
500
400
300
200
100
-176
-127
-100
-50
0
50
100
150
199.3
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-13 21:28:13


Filename: c:\pe\pyris\dossier\kathyVi \bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Peak = 49 733 °C
Area = 212 649 mJ
Delta H = 13 476 J/g
Onset = 48 790 °C
X1 = 46 073 °C
Y1 = 8 1325 mW
X2 = 56 466 °C
Y2 = 21 3590 mW
22 °C
-6 °C
Heat Flow Endo Up (mW)
Temperature (°C)
59 8
50
40
30
20
10
-1 83
-27.8
-20
-10
0
10
20
30
40
50
63 7
1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min
99-10-13 21 31 17

Filename: c:\pe\pyris\dossier\kathy\fi..\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

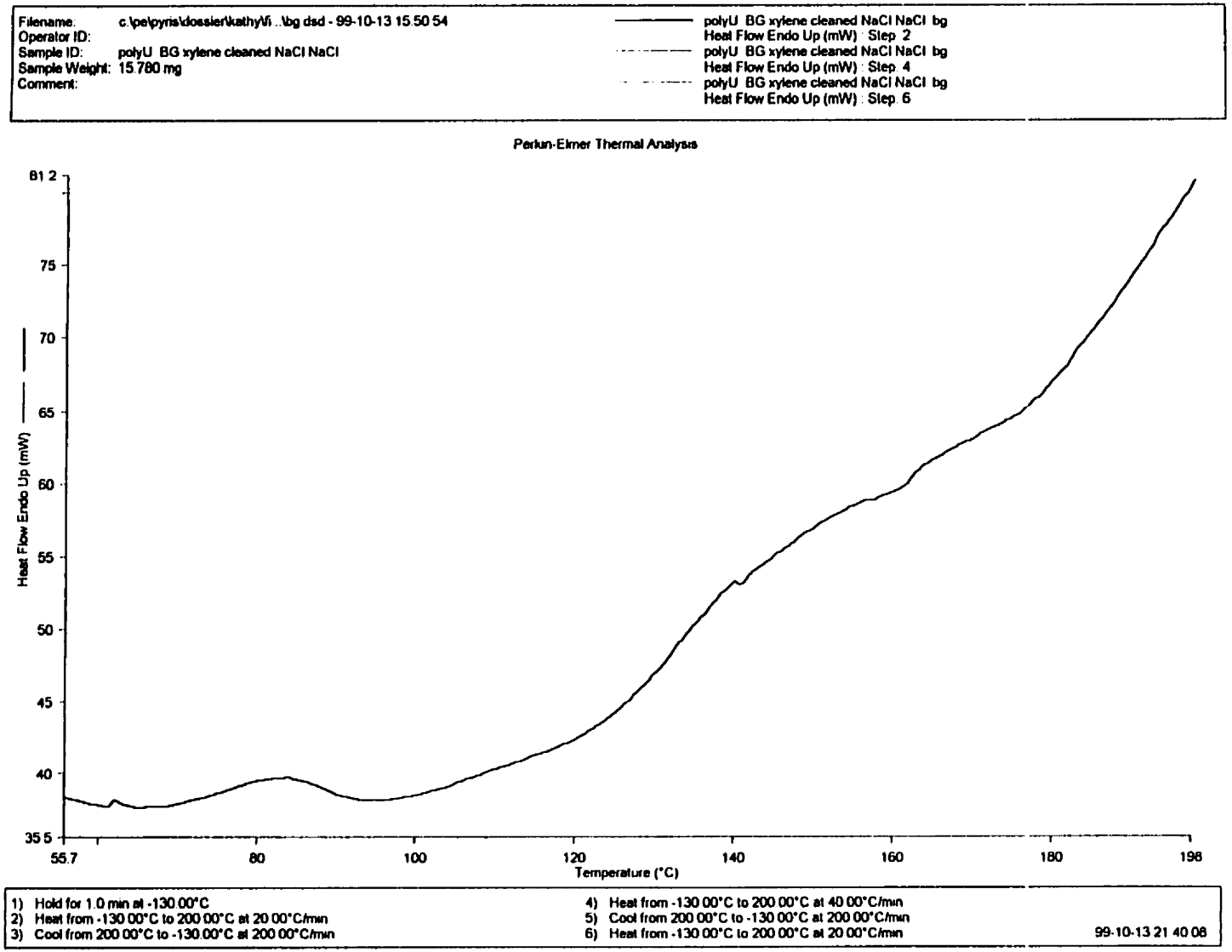
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

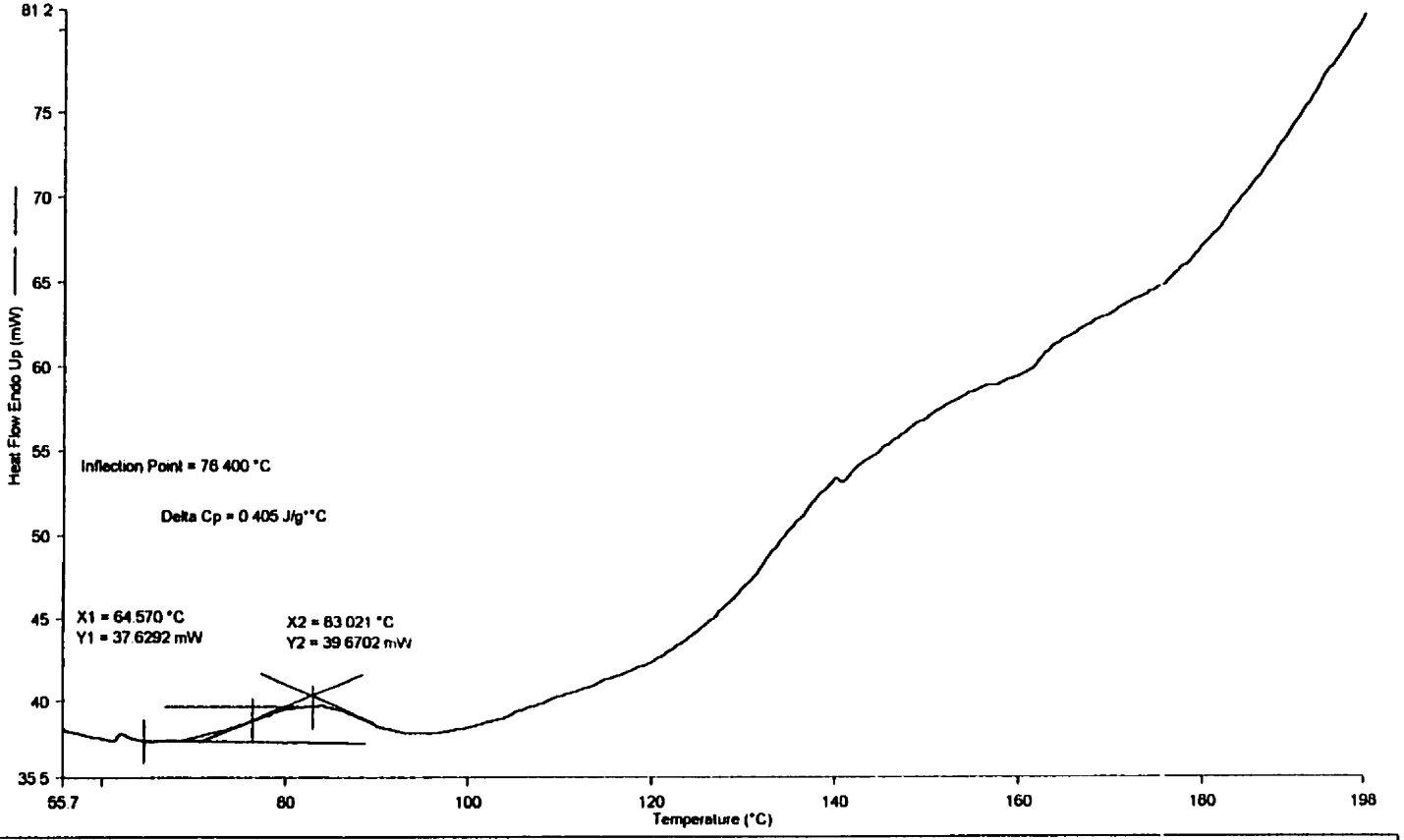
99-10-13 21:38:19


Filename: c:\pe\pyris\dossier\kathy\fi ..\bg dsd - 99-10-13 15.50.54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
81.2
75
70
65
60
55
50
45
40
35.5
55.7
80
100
120
140
160
180
198
Temperature (°C)
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min
99-10-13 21:40:08

Filename: c:\pe\pyris\dossier\kathy\i...\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



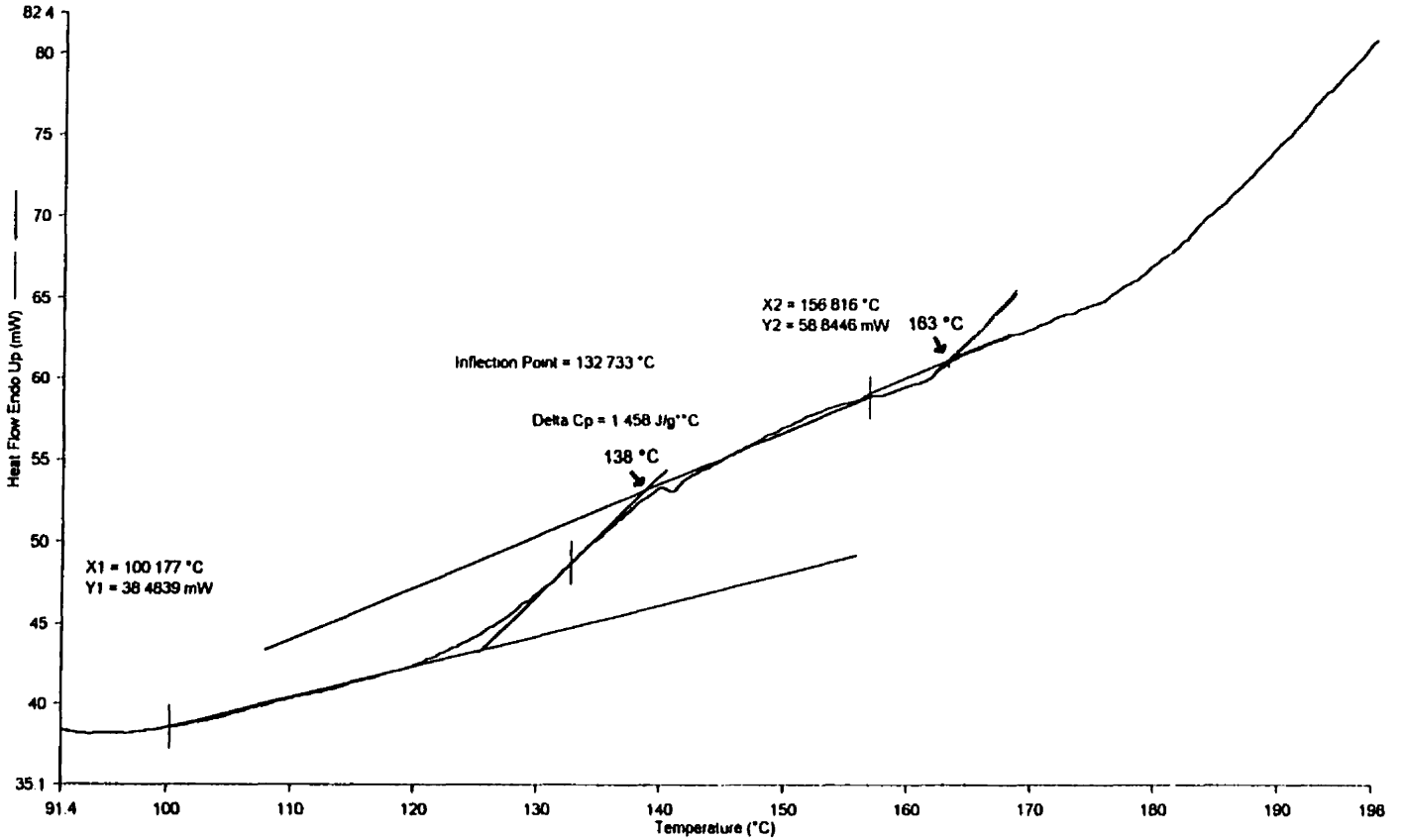
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-13 21 42 24

Filename: c:\pe\pyris\dossier\kathy\fi.. \bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 2
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 4
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 6

Perkin-Elmer Thermal Analysis



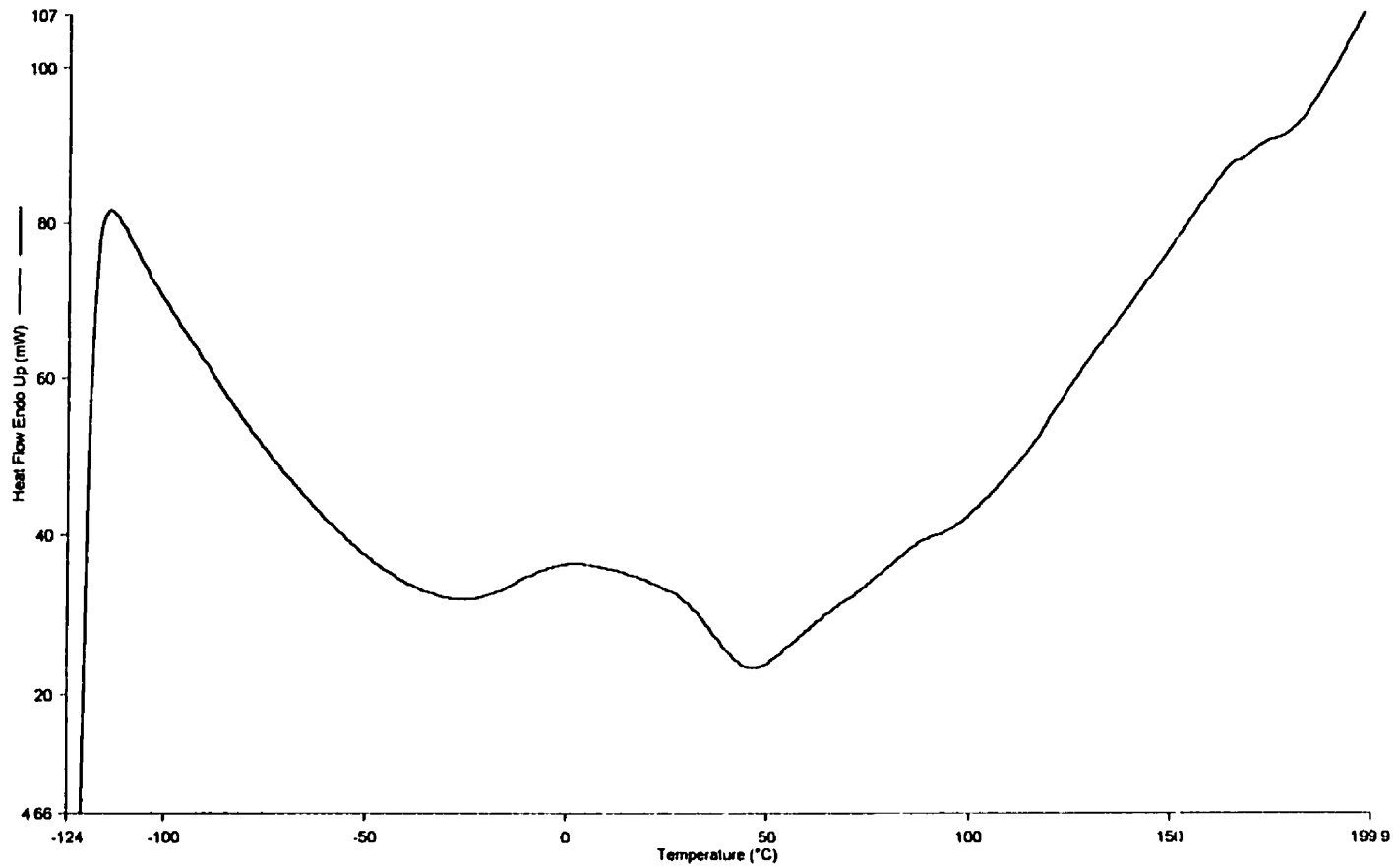
1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-13 21:45.15

Filename: c:\pe\pyris\dossier\kathy\fi ..\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 4

Perkin-Elmer Thermal Analysis



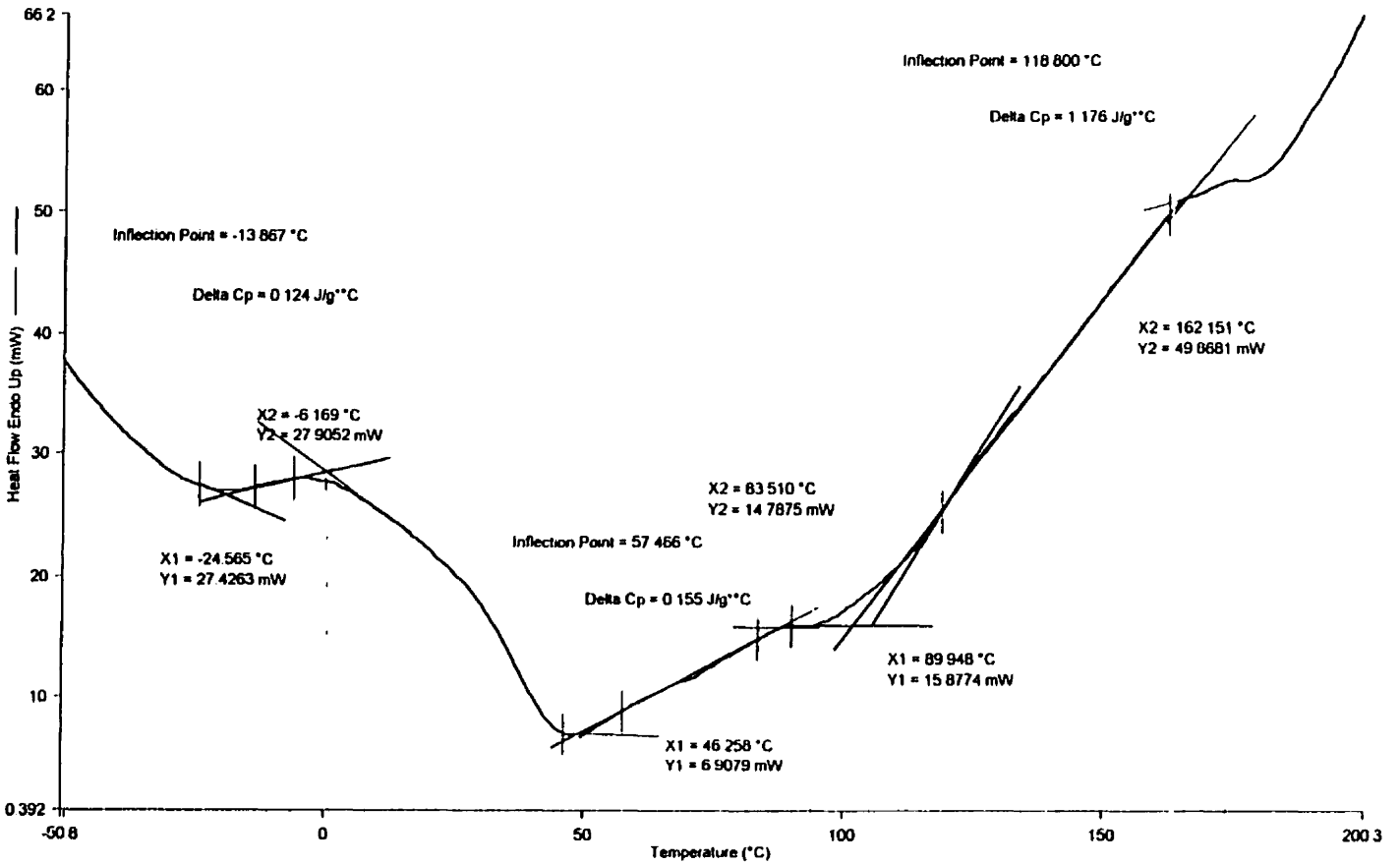
1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min

99-10-14 09 23 58

Filename: c:\pe\pyris\dossier\kathy\fi..\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 4

Perkin-Elmer Thermal Analysis



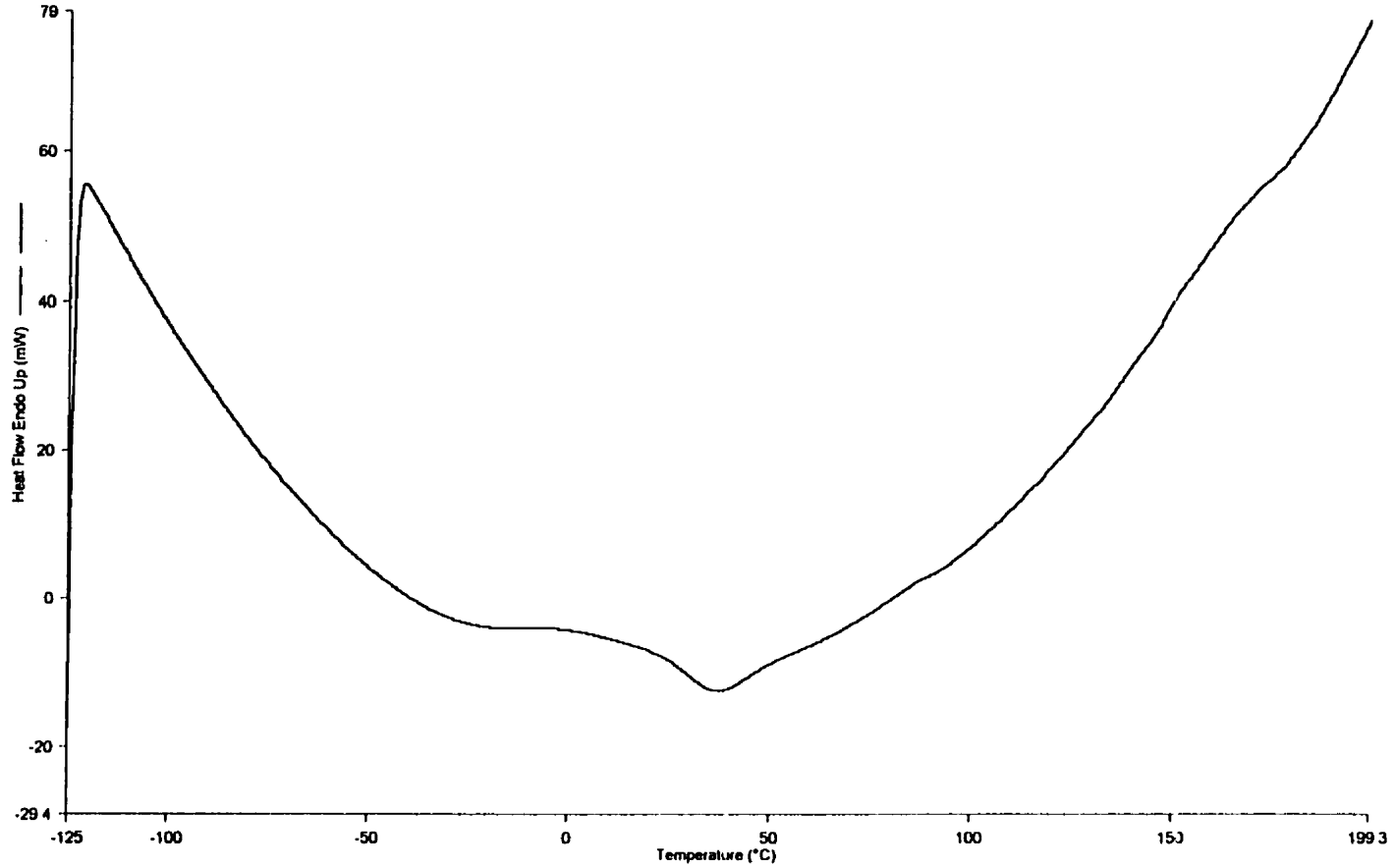
1) Hold for 1 0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min

99-10-14 09 26 53

Filename: c:\pe\pyris\dossier\kathy\fi . \bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:

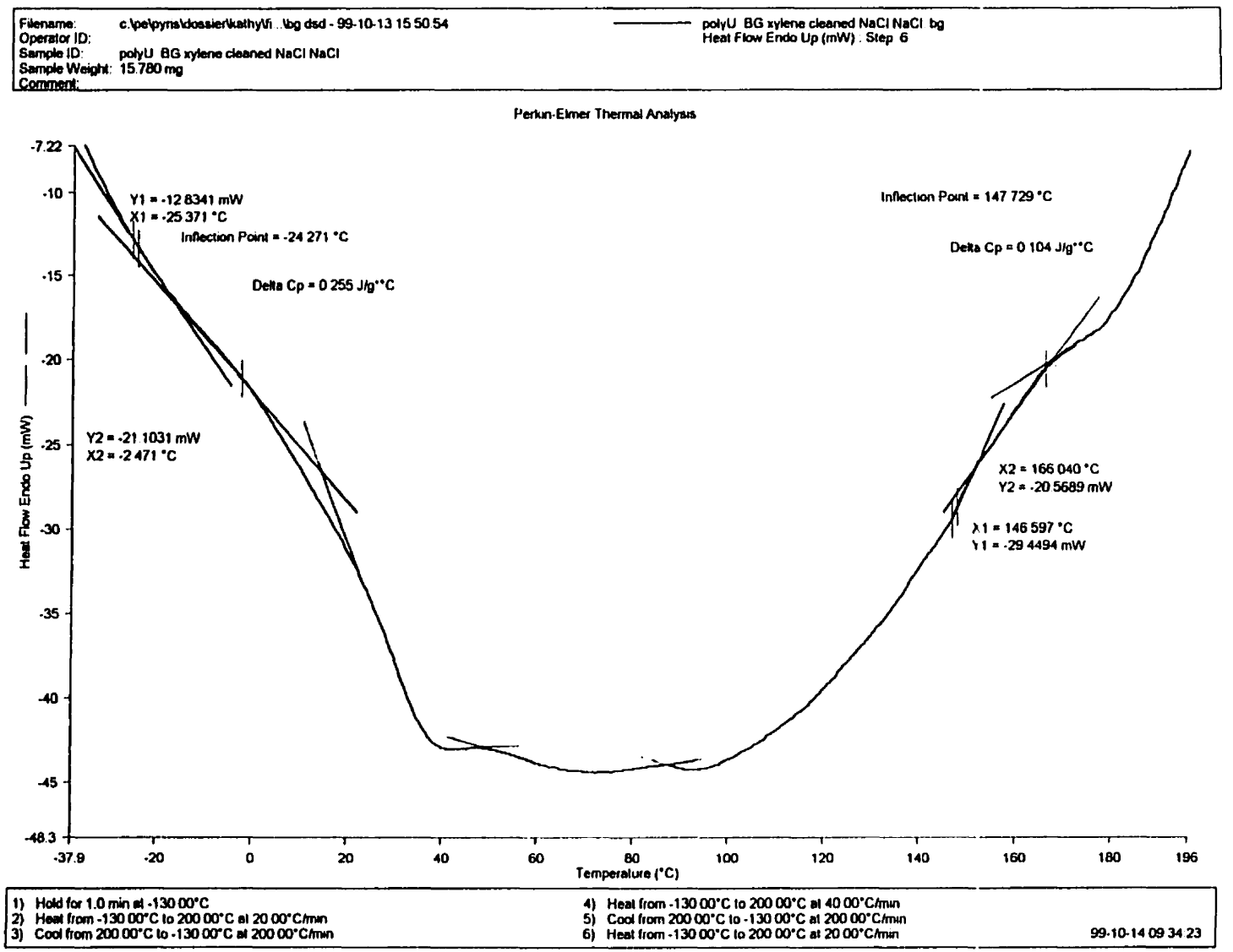
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) Step 6

Perkin-Elmer Thermal Analysis



1) Hold for 1.0 min at -130.00°C
2) Heat from -130.00°C to 200.00°C at 20.00°C/min
3) Cool from 200.00°C to -130.00°C at 200.00°C/min
4) Heat from -130.00°C to 200.00°C at 40.00°C/min
5) Cool from 200.00°C to -130.00°C at 200.00°C/min
6) Heat from -130.00°C to 200.00°C at 20.00°C/min

99-10-14 09 28 24


Filename: c:\pe\pyris\dossier\kathy\fi ..\bg dsd - 99-10-13 15 50 54
Operator ID:
Sample ID: polyU BG xylene cleaned NaCl NaCl
Sample Weight: 15.780 mg
Comment:
polyU BG xylene cleaned NaCl NaCl bg
Heat Flow Endo Up (mW) : Step 6
Perkin-Elmer Thermal Analysis
Heat Flow Endo Up (mW)
Temperature (°C)
Y1 = -12 8341 mW
X1 = -25 371 °C
Inflection Point = -24 271 °C
Delta Cp = 0 255 J/g°°C
Y2 = -21 1031 mW
X2 = -2 471 °C
Inflection Point = 147 729 °C
Delta Cp = 0 104 J/g°°C
X2 = 166 040 °C
Y2 = -20 5689 mW
X1 = 146 597 °C
Y1 = -29 4494 mW
1) Hold for 1.0 min at -130 00°C
2) Heat from -130 00°C to 200 00°C at 20 00°C/min
3) Cool from 200 00°C to -130 00°C at 200 00°C/min
4) Heat from -130 00°C to 200 00°C at 40 00°C/min
5) Cool from 200 00°C to -130 00°C at 200 00°C/min
6) Heat from -130 00°C to 200 00°C at 20 00°C/min
99-10-14 09 34 23