SYNTHESIS AND BASIC CHARACTERISTICS OF SEGMENTED POLY(ARYLENE ETHER SULFONE)-POLY(ARYLATE) COPOLYMERS

by

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(ABSTRACT)

Segmented copolymer systems composed of an amorphous glassy engineering polymer as one segment and a potentially anisotropic polyester as the second segment were synthesized and investigated. The engineering thermoplastic segment was based on various all aromatic poly(arylene ether sulfones) derived from the nucleophilic aromatic substitution reaction between hydroquinone, biphenol, and dichlorodiphenylsulfone. This reaction was conducted in the presence of potassium carbonate and anhydrous aprotic dipolar solvents. Poly(biphenol terephthalate) and poly(oxybenzoate) were synthesized in situ as the second, potentially anisotropic, semicrystalline segment. These segmented copolymers were synthesized either by solution, interfacial, or melt acidolysis techniques. The melt acidolysis technique was used to synthesize the segmented copolymers with high poly(arylate) contents. The morphology of the copolymers was found to be totally amorphous for those copolymers with low levels of the poly(arylates). They were semicrystalline when the poly(arylate)

contents were increased beyond a critical value of about 15 weight percent. Differential scanning calorimetry, optical microscopy, and wide angle X-ray scattering were used to probe the copolymer morphology. The chemical structures of the segmented copolymers were studied through the use of Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy (both ^{1}H and ^{13}C). As the weight percentage of the poly(arylate) was increased, a very significant improvement in the solvent resistance was noted. Evidence of anisotropy and liquid crystallinity in the copolymers was provided by optical microscopy, differential scanning calorimetry, and wide angle X-ray scattering.

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I give thanks to God for the spiritual uplifting given when needed. My roommate/technician/brother/friend gets a well deserved word of thanks for things too numerous to mention. I especially wish to thank my parents for their never-ending encouragement throughout my academic career.

Dedicated To

M. L. O.

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CHAPTER 1

INTRODUCTION

Copolymerization is one of the most important methods utilized to incorporate the properties of two immiscible homopolymers into the same material. Statistical, block, graft, and segmented copolymers are known as will be discussed in the literature review. Oftentimes an improvement in properties such as strength, toughness, solvent resistance and thermal resistance is realized as a function of copolymer structure and architecture. For example, high performance organic macromolecular materials known as engineering thermoplastics are replacing many traditional materials such as metals and ceramics in important and demanding applications. The replacement of traditional materials with lighter and more processible plastics will no doubt continue as research continues to improve upon the desirable properties and to eliminate the undesirable properties in these polymers.

Liquid crystalline polymers, which may be defined as macromolecules which display dimensional order in solution or the melt, have been increasingly studied in recent years due to their outstanding mechanical properties. However, processing of this class of polymers has been a problem. Copolymer technology has therefore been employed to retain or improve the desirable properties while rendering the polymers more processible.

This dissertation reports the research conducted to improve the properties of engineering thermoplastics by incorporating a potential liquid crystalline segment into a copolymer. Segmented copolymers formed from short blocks of poly(arylene ether sulfones) with short blocks of poly(arylates) were investigated. This research concentrated on retaining the high strength and good thermal properties of the anisotropic poly(arylate) while improving the mechanical properties and solvent resistance of the poly(arylene ether sulfone).

The synthesis of functionally terminated poly(arylene ether sulfones) and the synthetic techniques used to form segmented copolymers with polyarylate segments has been emphasized. The basic properties of these segmented copolymers were also investigated not only to confirm the structures of the synthesized polymers, but also to gain some understanding of the structure-property relationships inherent in these systems. The morphological aspects of the copolymers were also carefully studied, since the morphology is of the utmost importance in the final performance of the new segmented copolymers.

The following review of the pertinent literature will lay the foundation for the work discussed in this dissertation. The synthetic techniques employed in related systems will be examined. Solution and bulk reactions will be discussed and compared. The relationship between the structure of the polymer or copolymer and the resulting properties will also be presented. An emphasis will be placed on segmented copolymers where microphase separation can occur. The area

of liquid crystalline polymers, especially thermotropic liquid crystalline polyesters, will be reviewed. The discussion in this area, since it is a relatively new area, will focus not only on the synthesis and structure-property relationships but also on some of the theoretical aspects of liquid crystals. A discussion of some characterization procedures as related to the systems at hand will also be presented. These procedures will deal with the confirmation of structures of starting materials and oligomers as well as elucidation of structures and properties of copolymers.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

"I just want to say one word to you. Just one word. 'Plastics.'

"Exactly how do you mean."

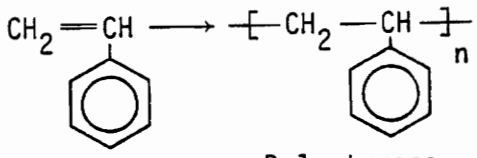
"There's a great future in plastics."

These quotes from the movie "The Graduate" were made in 1967 and are most appropriate for the discussion at hand. The time and money spent in the research of polymers and plastics have grown exponentially since this quote was made. It would appear the time and money has been well spent. Polymers and plastics are creeping, if not leaping, into every facet of one's life. In addition to the discoveries and developments in this area has been the coinage of a whole new language unique to the polymer world. The word "plastic" as used in the opening quote is synonymous with the term polymer although now plastics are a subclass of polymers. A polymer is a large molecule derived from a number of repeating units. These repeating units are made from monomers which are the starting materials used to build these polymers. The very word is actually derived from the Greek words "poly" meaning many and "mer" meaning unit. Thus, a polymer is composed of many units. In the same vein, a molecule composed of only a few repeating units is termed an oligomer. As mentioned, a polymer is made up of repeating units and if there is only one kind of

repeating unit the polymer is termed a homopolymer, such as polystyrene from styrene. A polymer composed of two kinds of repeating units is termed a copolymer with a terpolymer composed of three kinds of units and so on. An ambiguity in this terminology is shown in Scheme 1.

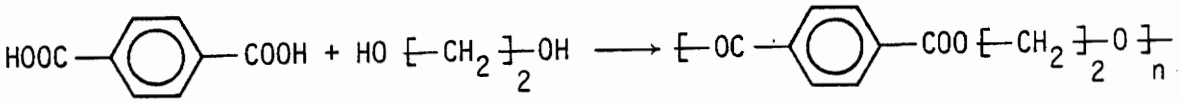
Both of the polymers shown in Scheme 1 are homopolymers and therein lies the ambiguity. Polymer 1, polystyrene, is composed of one monomer and thus is expected to be a homopolymer. On the other hand, polymer 2 is synthesized from two monomers and might be thought of as a copolymer. However, the polymer is composed of only one kind of repeat unit and is still considered a homopolymer. Thus, it is the number of kinds of repeat units in the polymer and not the number of monomers used which determines if a polymer is a homopolymer, copolymer, etc.

Another delineation point which can be drawn from Scheme 1 is that of the classification of the polymers. The two possible classifications are: step-growth and chain-growth. These classifications are based upon the mechanism of the polymerization. Focusing attention on the mechanism for the synthesis of polystyrene from styrene in Scheme 1, the mechanism for this polymerization is termed as chain-growth and is characterized by three distinct steps. Step 1 is an initiation step followed by a propagation step and finally a termination step.[1] There is the additional characteristics of attaining high molecular weight polymer immediately after initiation and of having a "living" polymer by delaying the termination step. In contrast, the mechanism for the synthesis of



Polystyrene

Polymer 1

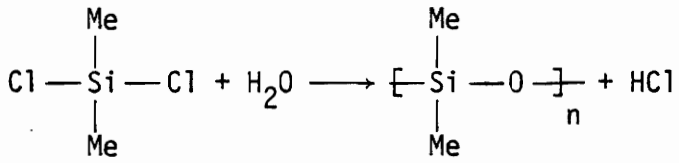


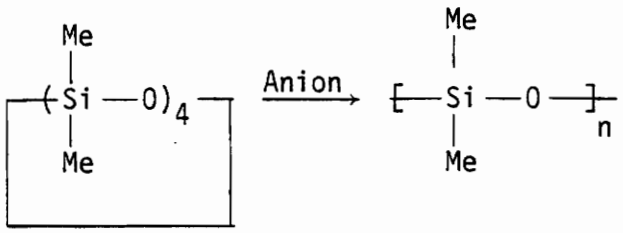
Polyethylene Terephthalate

Polymer 2

SCHEME 1. Examples of monomers and homopolymer repeat units derived from them.

polyethylene terephthalate is termed step-growth. In a step-growth polymerization, the molecular weight of the polymer builds up slowly through the reaction of the functional groups on the ends of the monomers, dimers, etc. Thus, two monomers can react to form a dimer, a dimer and another monomer molecule can react to form a trimer, and so forth until high molecular weight polymer is formed.[2] In a step-growth reaction, there is only one type of reaction responsible for the formation of polymer in contrast to the three distinct steps of initiation, propagation, and termination discernable in a chain-growth reaction. Professor Flory developed this classification [3] after an ambiguity developed with the terminology introduced by Carothers. Carothers divided polymers into two categories based upon their structures, [4] either an addition reaction or a condensation reaction. An addition reaction was defined as a polymer which had its repeat unit composed of the same chemical formula as that of the monomer. On the other hand, a condensation polymer was formed by losing some molecule to form a new linkage in the repeat unit. The term condensation comes from the fact that a water molecule was often the small molecule which was lost and "condensed" out on the wall of the reaction vessel. However, there are cases of the same polymer being made by two different routes--one where a small molecule is lost, another where it is not. See Scheme 2.





SCHEME 2. The synthesis of polydimethylsiloxane by step-growth and chain-growth reactions.

As mentioned earlier, one may define homopolymers as containing only one chemical repeat unit and copolymers as consisting of two. Copolymer can be further subdivided into several different types according to the arrangement of the repeat units within the polymer chain. If the arrangement of the repeat units is statistical or random in nature, the copolymer is termed a statistical or random copolymer. The IUPAC prefers the term "statistical." An alternating copolymer aptly describes the copolymer in which the repeat units alternate throughout the chain. If a copolymer is arranged such that one repeat unit is in the form of a long chain and the other repeat unit forms a side chain or branch off of the main chain, the polymer is termed a graft copolymer.[5] Special branch block copolymers are termed star copolymers. As the name implies, the copolymer has a central hub with arms emanating from it taking on the shape of a star. A linear copolymer that is composed of long sequences of each respective repeat unit is called a block copolymer.[6] There are also further subdivisions within the block copolymer class. If there is just one chemical bond between the dissimilar long sequences, the copolymer is defined as a diblock. Similarly, a triblock contains three blocks which may consist of either three different blocks or the two end blocks could be the same. If the sequences of the blocks are greater than three, one has a multiblock copolymer.[7,8] A multiblock copolymer may also be called a segmented copolymer if the blocks are of relatively short lengths. Moreover, these copolymers may have perfectly alternating sequences, may consist of randomly coupled oligomers, or even might be generated "in situ" by the reaction of two

monomers in the presence of one functional reactive oligomer. These various copolymers are schematically illustrated in Scheme 3.

The academic and industrial interest in these copolymers is due to the unique properties that can be achieved with these systems. The properties to be realized from copolymers might at first thought be expected also from a simple physical blend of the respective homopolymers. However, high molecular weight homopolymers for the most part are incompatible or immiscible with each other. This incompatibility takes the form of a macroscopic phase separation. Macroscopic phase separation can be thought of as trying to mix oil with water. Thermodynamically, this separation is explained by the familiar Gibbs equation for the free energy of mixing (ΔG):

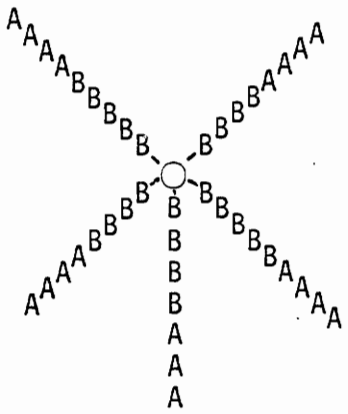
$$\Delta G = \Delta H - T\Delta S.$$

For two polymers to be compatible and hence mix at the molecular level, the free energy of mixing must be negative.[9] In order for ΔG to be negative, then the entropy of mixing (ΔS) must be positive and large enough to overcome any positive (endothermic) enthalpy of mixing (ΔH). Polymers, owing to their high molecular weights, generally have very small entropies of mixing and a small enthalpy of mixing will thus lead to a phase separated immiscible mixture. Such a macrophase separated mixture will usually produce less than desirable mechanical properties due to poor interfacial adhesion and other problems. Note that there are some exceptions to this generalization.[9] Copolymers circumvent macrophase separation

AABABBBABAAABA — Statistical or random copolymer

ABABABABABABABA — Alternating copolymer

AAAAAAAAAAAAAA
B B B
B B B
B B B
B B B
B B B — Graft Copolymer



Star block copolymer

AAAAAAAABBBBBBBB — Diblock copolymer

AAAAAABBBBBBCCCCCC — Triblock copolymer (A may equal C)

$(AAAAAAABBBBBB)_n$ — Multiblock or segmented copolymer

SCHEME 3. Schematic representation of the various types of copolymers.

because the "homopolymer" sequences (short or long) are linked together via a chemical bond. The two polymers cannot now separate on a macro scale but may separate on a molecular level called microphase separation, under the appropriate conditions.[10] The copolymers in turn may display better properties than the corresponding blends due to the microphase separation coupled with the intrinsically good interfacial coupling. The two phase copolymers have also been used as effective compatibilizers or emulsifiers in a blend of two incompatible homopolymers. This phenomenon can be visualized as analogous to an emulsion formed by adding a surfactant to the oil and water mixture. The surfactant stabilizes the oil-water mixture and the macro separation does not occur. An important consideration in block and graft copolymer technology is that phase separation will only occur when the molecular weight of the respective polymers reaches a critical value.[11] This critical value is referred to as the critical block molecular weight for phase separation.[10] The polymer-polymer interaction parameter also influences the onset of the microphase behavior.

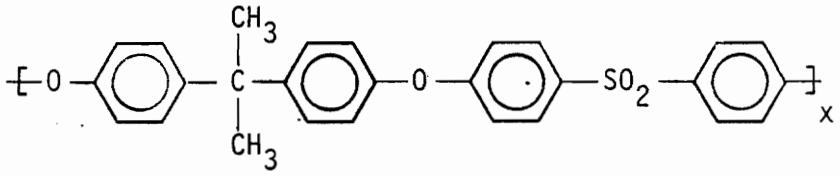
At first glance, it would appear that as long as the homopolymers are linked together through a chemical bond to form a copolymer the properties of the copolymer are fixed. However, in Scheme 3, one notes that there are a variety of ways a copolymer can be structured.[12] Architecture of the copolymer thus also plays a major role in the final properties of the copolymer. While the chemical nature of the segments essentially determines the chemical resistance, thermal characteristics, stability, and transport properties of the

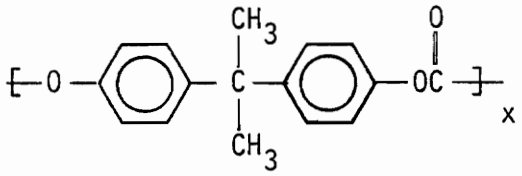
copolymer, the architecture of the copolymer affects the mechanical strength, rheological properties, and rubbery behavior if an elastomer.[7,10]

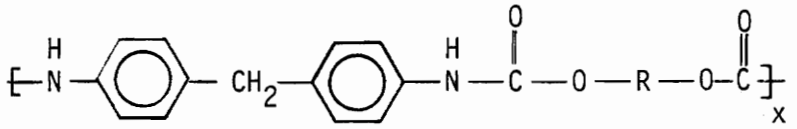
It is thus realized that copolymerization chemistry has allowed introduction of new materials and properties not only as copolymers but also as compatibilizers for polymer blends at a critical time when industrial economics have not favored the development of many compatible homopolymers. An emphasis will be placed in this thesis on copolymers of the alternating, random and segmented, or multiblock type. In order to discuss copolymer technology, the synthesis, characterization, and properties of the corresponding homopolymers will be presented.

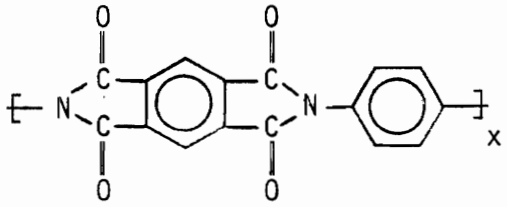
2.2 Engineering Thermoplastics

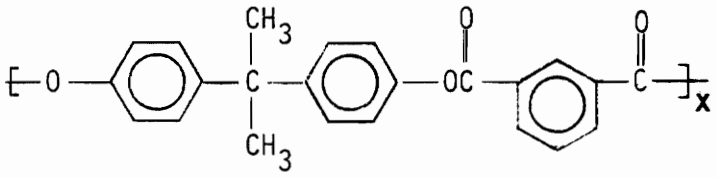
As a class, engineering thermoplastics are characterized as being tough, ductile materials with good thermal properties. Materials such as:

Polysulfones 

Polycarbonates 

Polyurethanes 

Polyimides 

Polyarylates 

are but a few examples of engineering thermoplastics. Thermoplastics are materials which are thermally stable above their glass transition or melting temperatures. They can be melted or dissolved and shaped into various products and subsequently can be remelted or redissolved to be processed again. This is in contrast to a thermoset material

which cannot be reprocessed once it has been shaped into its final form. An engineering thermoplastic is a thermoplastic with properties, either mechanical or thermal, which compare them favorably, at least in several ways, with metals or ceramics. Materials commonly called thermoplastics include the styrenic and olefinic polymers. A comparison of engineering thermoplastics to thermoplastics to metals will illustrate the enhanced properties to be gained from the engineering thermoplastics. Table 1 is a collection of typical properties of selected materials from each of the three classes of materials. As can be seen from Table 1, on a weight basis, an engineering thermoplastic is stronger than steel. In industries such as the aerospace industry, engineering thermoplastics become very attractive materials to replace the heavier metals. The lighter, but equally performing plastics, thus save weight and money in comparison to the heavier metals they replace. Oftentimes, plastics offer properties that metals can't compare with such as fatigue and chemical resistance.

The ultimate properties of a polymer are due to many intertwining parameters. There are basically seven polymer parameters. They are:

1. Chemical composition
2. Molecular weight
3. Topology
4. Morphology
5. Stereochemistry
6. Surface characteristics
7. Additives.

TABLE 1

TYPICAL PROPERTIES OF SELECTED COMMODITY PLASTICS, ENGINEERING THERMOPLASTICS AND METALS [13]

Material	Tensile Strength (psi)[1]	Elongation at Break (%)	Flexural Modulus (psi)x10^{-3}	Density (g/ml)
Polystyrene	5,200- 7,500	1- 3	380-490	1.05
Polyethylene	3,200- 4,500	10-1200	145-225	0.96
Polycarbonate	9,500	110	340	1.18
Polysulfone	9,000	40- 60	330-400	1.24
Polyamide-imide	17,000- 26,900	12- 15	520-665	1.39
Steel [14]	210,000-710,000	0.1	-	7.50

(1) Pounds per square inch (psi) values may be converted to the SI units, megapascals (MP), by multiplying by the factor 6.89×10^{-3}.

The chemical composition encompasses not only what molecules make up the polymer repeat units but also how these repeat units are arranged; that is, is it a homopolymer or copolymer? What type of copolymer is it? Block, graft, segmented, etc. After the molecular weight reaches a particular value, dependent upon the particular polymer, most properties level off although the properties are drastically dependent upon the molecular weight at the lower values. The molecular weight distribution is also important, especially in properties such as melt viscosity and tensile strength. Melt viscosity and other physical properties are also dependent upon the topology of the polymer especially if the polymer is branched, linear, or a crosslinked network. The thermal properties of a polymer are a function of the morphology of the system, whether it is an amorphous or crystalline polymer, extent of crystallinity, etc. Stereochemistry and other forms of chain isomerization in polymers play a very important role in polymer properties such as crystallinity and glass transition temperatures. Not only is there the possibility of cis-trans isomers (geometrical isomers) but also isotactic, syndiotactic, and atactic configurational isomers, and even head-head type placement. Polymer properties, such as friction and wear, are directly dependent on surface characteristics, as are adhesive and aesthetic properties. A much overlooked but nevertheless important polymer parameter is the additives in polymers. Most all of the other parameters can be influenced if not drastically altered by the addition of appropriate additives, such as fillers, plasticizers, stabilizers, etc.

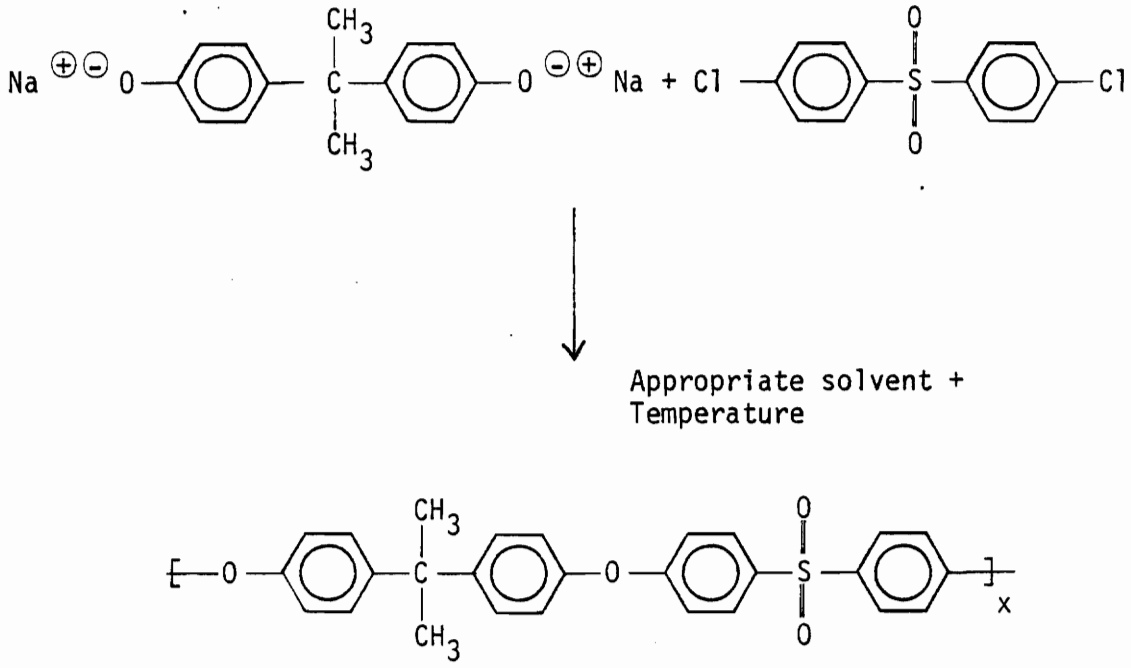
All of these parameters while important to engineering thermoplastics are of equal importance to all polymers. These parameters will be alluded to throughout the discussions on all of the polymers in this thesis.

2.3 Polysulfone Engineering Thermoplastics

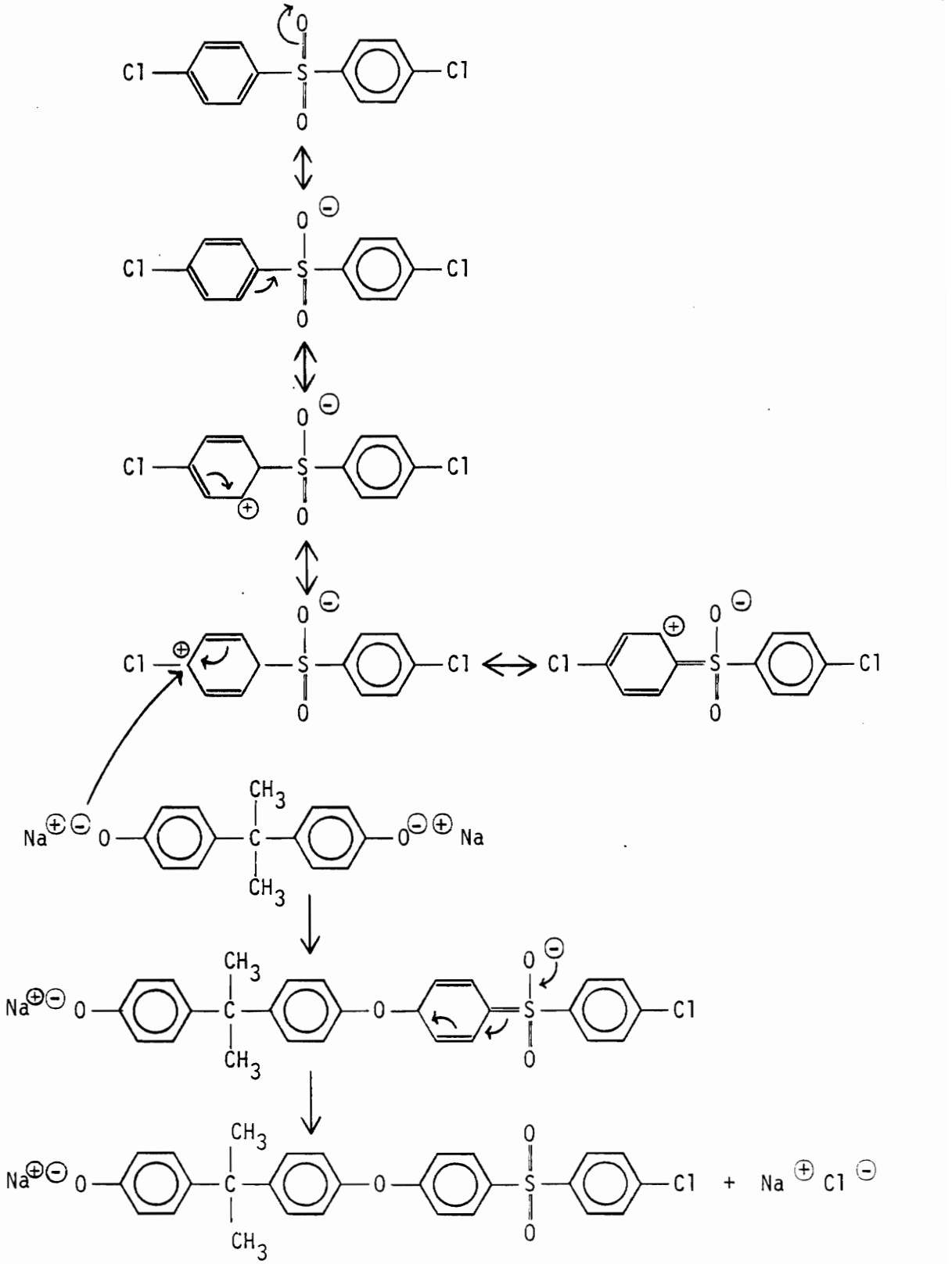
In order to fully evaluate the properties and uses that engineering thermoplastics are enjoying, an in-depth discussion of an appropriate choice in this area should be made. One such choice is poly(arylene ether sulfones) or more simply polysulfones. The commercial production and their widespread utility make these engineering thermoplastics an interesting subject. The synthetic routes employed in the making of polysulfones as well as the properties of the final product will be discussed. Particular emphasis will be placed on the structure-property relationships in this polymer as well as related copolymers and other materials.

2.3.1 Syntheses of Polysulfones

The synthetic method most commonly used to produce a polysulfone polymer is that of a nucleophilic aromatic displacement reaction. In a nucleophilic displacement reaction, an activated aromatic halide is reacted with the phenate form of a phenolic compound. An example of this synthesis is in the formation of the commercially produced polysulfone Udel developed by the Union Carbide Corporation and recently purchased by Amoco (Scheme 4). In this particular reaction, the disodium salt of bisphenol-A is reacted with the activated aromatic halide, 4,4'-dichlorodiphenylsulfone to form the poly(arylene ether sulfone).[15,16,17,18] The 4,4'-dichlorodiphenylsulfone is termed an activated aromatic halide due to the electron withdrawing nature of the sulfone group. Shown in Scheme 5 are the resonance forms for one side of the dichlorodiphenylsulfone and the mechanism



SCHEME 4. The synthesis of a polysulfone via a nucleophilic aromatic substitution reaction.



SCHEME 5. Resonance forms of 4,4'-dichlorodiphenyl sulfone and the mechanism leading to the formation of bisphenol-A polysulfone.

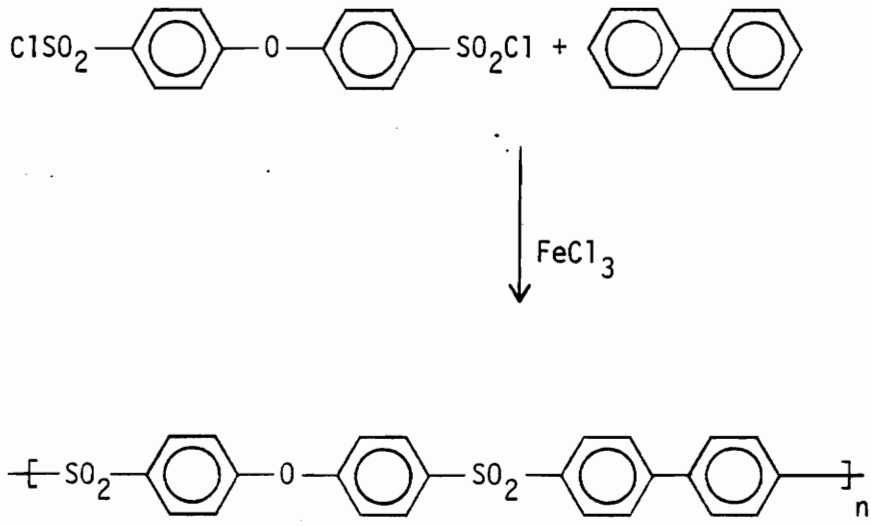
for the formation of the bisphenol-A polysulfone. As can be seen in Scheme 5, the sulfone group's electron withdrawing nature activates the ortho and para positions of the rings to which it is attached. However, the ortho positions are sterically hindered due to the bulky sulfone group and the para position becomes the predominant position of attack by the phenate of bisphenol-A. The leaving chlorine group also facilitates the arylene ether formation by forming the salt NaCl. One might envision the use of other activating groups besides the sulfone in this type of reaction. A carbonyl group can be used; however, the reaction is noticeably slower due to the weaker activation the carbonyl group provides. The substitution of the better fluorine leaving groups instead of chlorine greatly enhances this reaction. The choice of an appropriate solvent is an important parameter in this synthesis. The solvent must be able to dissolve the reactants and polymer product and yet be unreactive toward them. High temperatures (150-200°C) are used so the solvent must withstand these temperatures without decomposing. Typically, dipolar aprotic solvents such as dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), or sulfolane were used. Early work in the area of polysulfones used either aqueous caustic/DMSO [15] or potassium carbonate in DMAc.[19] These systems worked fine for the synthesis of bisphenol-A based polysulfone; however, they were found to be less suitable for other systems. Particularly, polysulfones based upon the bisphenols hydroquinone and biphenol were not synthesized in high molecular weights using DMSO. This is probably due to the low solubility of the phenate forms of the bisphenols in the DMSO and the relatively low

boiling point of DMAc (b.p.= 163°C). In order to circumvent the problem of a low boiling solvent, a higher boiling dipolar aprotic solvent was sought. Two solvents emerged as potential candidates: N-methyl-2-pyrrolidone (NMP, b.p.=202°) and cyclohexylpyrrolidone (CHP, b.p.= 290°C). Recently these solvents have been used with success to synthesize not only bisphenol-A polysulfones but also polysulfones based on hydroquinone and biphenol.[22,23] In the use of NMP and CHP, the phenates of the bisphenol(s) are formed in situ using potassium carbonate as the base. This phenate formation leads to the generation of water as a by-product in the reaction. Oftentimes, an additional solvent such as chlorobenzene or toluene is added to facilitate the removal of water by the formation of an azeotrope with the water.

Previously, the all aromatic polysulfones were synthesized by a completely different synthetic technique and mechanism. A Friedel-Crafts reaction [21] was used instead of the nucleophilic displacement reaction discussed above. An example of this reaction is shown in Scheme 6. Catalysts other than $FeCl_3$ such as $SbCl_5$ and $InCl_3$, can also be used. Unfortunately, small amounts of ortho substitution occurs, which tends to produce poorer mechanical behavior.

2.3.2 Properties of Polysulfones

The poly(arylene ether sulfones) became commercially viable materials due to their relative ease of synthesis, moldability, and myriad of useful properties. Bisphenol-A polysulfones are totally amorphous or glassy polymers, which display good mechanical strength



SCHEME 6. Friedel-Crafts synthesis of an all aromatic polysulfone.

and high thermal and oxidative resistance. They are tough ductile polymers which show good impact and creep resistance over a wide temperature range. Typically the temperature range is from as low as -150°C to as high as 160-170°C. The use of all aromatic polysulfones, such as the hydroquinone or biphenol based materials, can further extend the upper use temperature to above 200°C due to their higher glass transition temperatures. The low use temperature of polysulfones is attributed to a strong beta transition at -100°C. A beta transition is a secondary transition which involves the motion of a small segment of the polymer chain. This small scale motion is in contrast to the glass transition which is the onset of motion (bond rotation and conformational changes) of the whole polymer chain or a very large portion of the chain. The beta transition in polysulfones is attributed to the motion of the phenylene rings and sulfone groups as well as water bound to the polar groups within the chain.[24,25,26]

Polysulfones are generally resistant to most aqueous acids and bases; however, they are not very resistant to chlorinated solvents such as methylene chloride and chlorobenzene or to acetone. The use of hydroquinone or biphenol instead of bisphenol leads to polymers which are more solvent resistant. This increased solvent resistance is attributed to crystallinity induced by solvent treatment in these materials.

Polysulfones have also been studied as to their radiation stability.[27,28,29,30] The all aromatic polysulfones were found to be quite stable with good retention of mechanical properties with large doses of radiation. The bisphenol-A polysulfones though very

good tend to be somewhat less stable owing to the aliphatic isopropylidene unit which may be a source for the generation of free radicals. The free radicals then lead to polymer degradation via chain scission and crosslinking.

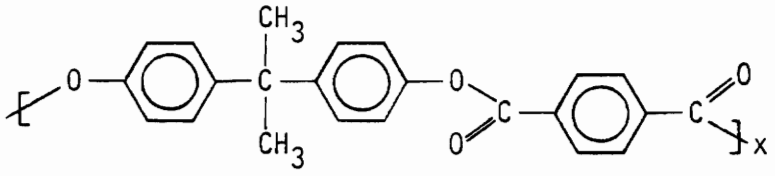
Another attractive feature of polysulfones is their processibility. The amorphous polysulfones can be molded and processed using conventional thermoplastic processing equipment.[16] Equipment such as extruders, injection molders, and calendars have been utilized.

2.4 Polyesters: Polyarylates and Liquid Crystal Polyesters

The breadth and scope of this discussion will be limited to predominantly aromatic polyesters. Predominantly aromatic polyesters are otherwise known as polyarylates. These polymers are characterized by ester bonds within the backbone of the polymer. This is in contrast to polymers such as polymethylmethacrylate which have the ester moieties as side groups on the polymer backbone (see Scheme 7). Polyarylates are also distinguished by having a predominance of aromatic groups in the backbone. These aromatic groups give rise to improved mechanical and thermal properties and in some cases improved environmental stability. The wide variety of synthetic techniques leading to the formation of polyarylates as well as their properties, both the mechanical and thermal, will be discussed.

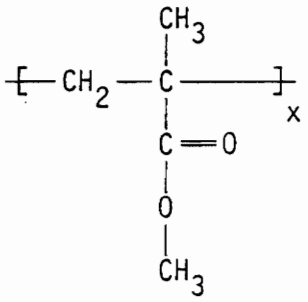
The nomenclature "liquid crystal" seems to be a contradiction in terms. A crystal is thought of as having three-dimensional order which is locked into a solid. A liquid on the other hand should have no order whatsoever. It would thus seem that these separate terms are mutually exclusive. However, it is theoretically (as well as being documented) possible to have some type of order which is intermediate between these two extremes. Thus, a material which has one- or two-dimensional order can flow like a liquid but have properties reminiscent of a crystal and was coined a liquid crystal. As there are many types of polymers, there are also many types of liquid crystals. Polyester liquid crystals will be the main area of focus in this portion of the discussion. However, since this is a relatively new area of research, a broad background will be included. While

"A"



Polyarylate

"B"



Polyacrylate

SCHEME 7. Schematic representation comparing a polyarylate (A) with a poly(acrylate) (B).

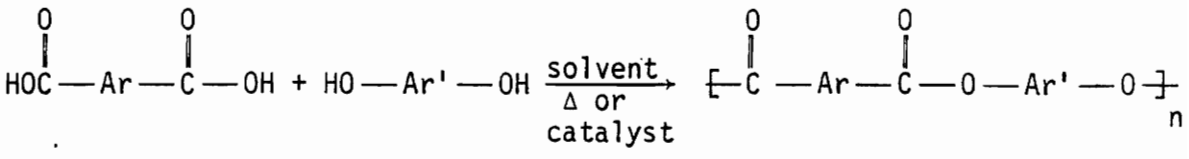
liquid crystals are still largely a laboratory curiosity, their unique structures and properties have led to some commercial applications. The DuPont Company commercialized the aromatic polyamide (aramid) Kevlar®. Kevlar has found applications as tire cords, reinforcing fibers in skis and tennis rackets, and protective body armor. The liquid crystalline polyester Xydar® made by Dartco Manufacturing Company has been used for high temperature cookware. The thrust of this discussion will therefore be in the structure-property relationships as applied to engineering thermoplastics.

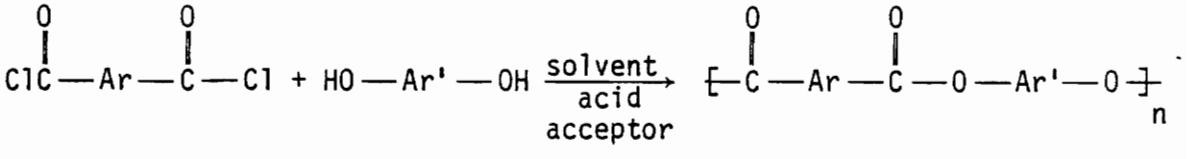
2.4.1 Syntheses of Polyarylates and Liquid Crystal Polyesters

There are a variety of synthetic techniques available for the synthesis of polyarylates and liquid crystal polyesters. The three basic types of synthetic procedures are: solution, interfacial, and bulk. Each one of these types can be further subdivided according to the reacting species used to form the polyester. Scheme 8 shows the three basic types of procedures and the subdivisions relating to each. The solution procedure involves the use of a solvent which will dissolve not only the monomers but also the final polyester. In the case of a solution reaction between a diacid chloride with an aromatic bisphenol, an acid acceptor must be employed to effectively remove the hydrogen chloride by-product.[31,32]

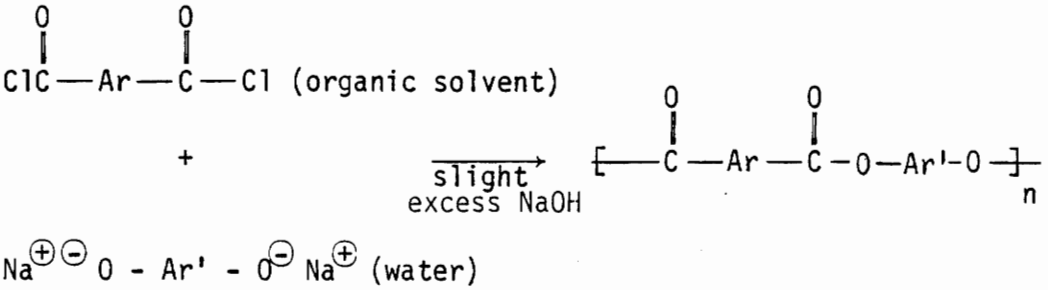
Tertiary amines such as triethylamine or pyrridine have been effectively used as both catalyst and acid acceptors. The synthesis of a polyarylate from a diacid and aromatic bisphenol generally requires either high temperatures or catalysts and activators of some

Solution





Interfacial



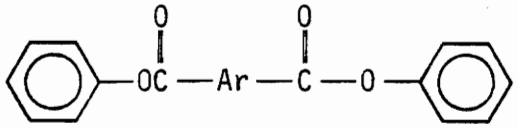
SCHEME 8. Three basic types of synthetic procedures used to synthesize polyarylates and liquid crystal polyesters. (Continued on next page.)

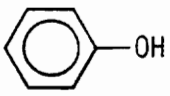
Bulk

1. $HOC-Ar-C(=O)-OH + HO-Ar'-OH \xrightarrow{\text{very slow}} \left[C(=O)-Ar-C(=O)-O-Ar'-O\right]_n + H_2O$

2. $HOC-Ar-COH + CH_3C(=O)-O-Ar'-OC(=O)-CH_3 \xrightarrow{\Delta}$

$$\left[C(=O)-Ar-C(=O)-O-Ar'-O\right]_n + CH_3COH$$

3.  $+ HO-Ar'-OH \xrightarrow{\Delta}$

$$\left[C(=O)-Ar-C(=O)-O-Ar'-O\right]_n + \text{  }$$

4. $CH_3-OC-Ar-C(=O)-O-CH_3 + HO-Ar'-OH \xrightarrow{\Delta}$

$$\left[C(=O)-Ar-C(=O)-O-Ar'-O\right]_n + CH_3-OH$$

5. $ClC-Ar-CCl + HO-Ar'-OH \xrightarrow{\Delta} \left[C(=O)-Ar-C(=O)-O-Ar'-O\right]_n + HCl$

SCHEME 8. (Continued.)

type. A high enough temperature must be achieved to remove the water formed as the reaction by-product in the former case. A solvent which can withstand these high temperatures without degrading or interfering with the polymerization must be found. In the latter case, the catalysts and activators play an extremely important role in the polyester synthesis since these reactions are generally carried out at ambient temperatures. The solvent in this case is usually a mixture of solvents with one being a dipolar aprotic solvent such as DMAc or NMP and the other solvent being pyrridine.[33,34]

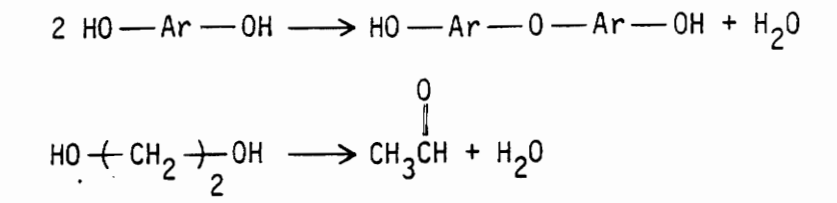
In an interfacial reaction.[31,32] a metal salt of the aromatic bisphenol is formed in the aqueous layer while the organic layer has the diacid chloride monomer dissolved in it. At the interface between the immiscible organic phase and aqueous phase, the bisphenol salt and diacid chloride react. The growing polymer chain is either soluble in the organic solvent or swollen by it. In some cases, the polymer is continuously removed from the interface mechanically. The by-product, a metallic salt usually NaCl or KCl, is effectively removed from the reaction because it is much more readily soluble in the aqueous layer than in the organic layer. This leads to more polymer formation due to LeChataliers principle (removal of a product shifts an equilibrium reaction toward products). A prime example of an interfacial reaction is the production of bisphenol-A polycarbonate from bisphenol-A and phosgene.[32,35] The bisphenol-A is dissolved in an aqueous alkali media, an organic solvent such as chlorobenzene or chloroform is then added, followed by the introduction of phosgene gas.

While solution and interfacial techniques are very feasible procedures to use in making polyesters, it is oftentimes necessary to make these polymers in bulk techniques. Sometimes a suitable solvent can't be found for the monomers and polymers. Commercially, a solvent is thought of as a necessary nuisance. After the polymer has been made, the polymer must be separated from the solvent and the solvent either disposed of or recycled. This then just adds an additional cost to the polymer. Thus, a bulk process may be an economical choice. However, a dominant factor in favor of a bulk technique is its simplistic nature. The monomers are heated together and when the polymer is formed it can usually be used as is. In addition to its simplistic nature, a bulk process overcomes one of the most common problems associated with solution and interfacial techniques, that of polymer precipitation due to crystallinity. Polyesters, especially aromatic polyesters, tend to be of crystalline morphology. The crystallinity then renders the polymer insoluble in many solvents. The bulk process overcomes this limitation. In a bulk technique, the reaction can be carried out at a temperature above the melting point of the final polymer. This process lends itself nicely to liquid crystal polymer synthesis also. By their very nature, liquid crystalline polymers are crystalline and thus relatively insoluble in many solvents. The bulk process can then be utilized to synthesize these novel materials which otherwise could not be synthesized in solution or interfacially.

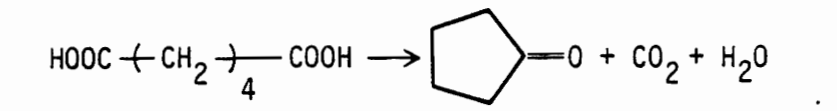
As can be seen from Scheme 8, there are a wide variety of bulk techniques.

The first of these reactions is the direct reaction between a diacid and di-alcohol (referred to as a diol). The temperature at which this reaction is carried out depends upon a number of factors. These factors include the melting point of the respective monomers since the reaction takes place in the molten state. The temperature is usually above the melting point of the final polymer although in the synthesis of some liquid crystalline polyesters this isn't necessarily true.[36] The dominant factor controlling the minimum temperature used is the by-product water. To facilitate the removal of the water so that high molecular weight polymer can be formed, the temperature is raised above the boiling point of water. This allows the removal of water by distillation. The control of temperature can be quite critical in this reaction. Many undesirable side reactions can take place at the elevated temperature commonly used in these reactions. Side reactions that involve the monomers are dehydration of the diol or decarboxylation of the diacid. An unsaturated alkene, aldehyde, or ether results from the dehydration of the diol.[35] Decarboxylation eliminates carbon dioxide from the diacid and usually only occurs when some other group activates a carboxyl group although this is not always the case.[35,37,38] The polymer or oligomers may also undergo side reactions yielding unsaturation in the polymer or many of the products to which the monomers convert. Scheme 9 illustrates some of these undesirable side reactions as well as other transformations.

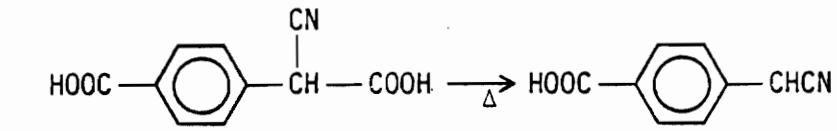
Not all side reactions are undesirable. The last reaction in Scheme 9 illustrates one such potentially beneficial side reaction.

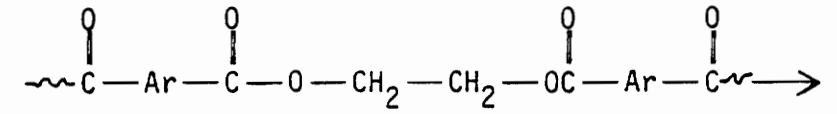


Dehydration

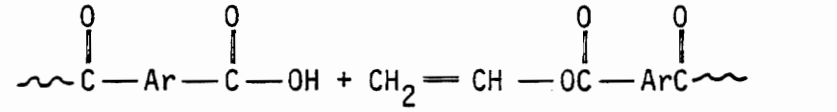


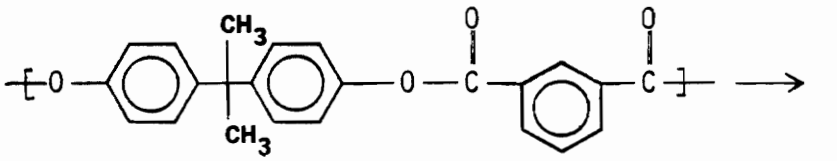
Decarboxylation



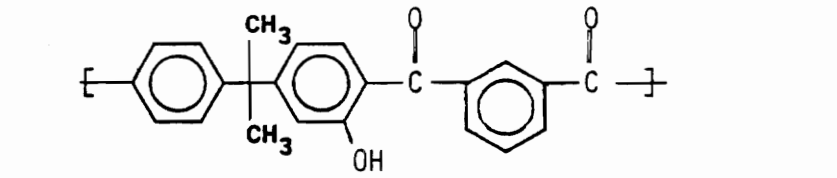


Unsaturation





Rearrangement



SCHEME 9. Side reactions involved in the synthesis of a polyester from a diacid and a diol.

In this reaction an aromatic polyester (in this case, bisphenol-A isophthalate), undergoes a rearrangement to a hydroxybenzophenone structure. The rearrangement takes place when the polymer is exposed to ultraviolet radiation (u.v.) and is termed a Photo-Fries rearrangement.

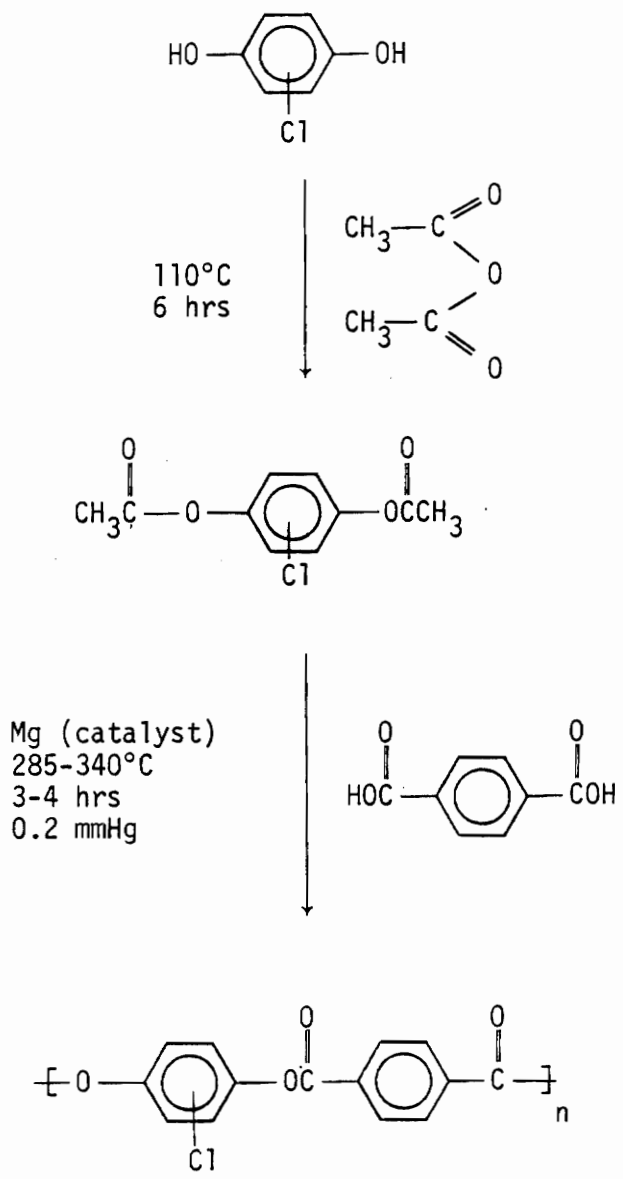
This reaction may be of a beneficial nature in that the ultraviolet radiation energy, which in most polymers leads to chain scission and polymer degradation, [39] leads to a u.v. resistant structure. This phenomenon, in these types of polyesters prepared by solution and interfacial techniques, has been studied and exploited as barrier coatings to u.v.[40,41]

These polyester syntheses are sometimes carried out in the presence of basic catalysts such as calcium acetate, antimony trioxide, and zinc acetate.[36,42] Lewis acids or proton sources can also be used to catalyze the reaction. However, the basic catalysts are generally preferred to minimize the aforementioned side reactions.

Ester interchange reactions are the commercial technique of choice used to produce polyarylates (Bulk Reactions 2 and 3 in Scheme 8). The first of these reactions is sometimes called a melt acidolysis reaction. In a melt acidolysis reaction, the diol is converted into its diacetate derivative. This can be accomplished by the reaction of the diol with acetic anhydride or acetyl chloride. The diacetate is then melt reacted with a dicarboxylic acid to form the polyarylate.[43] Basic catalysts, such as those mentioned above, are added to promote the polymerization. Acetic acid is the by-product of this reaction and is removed by the application of heat

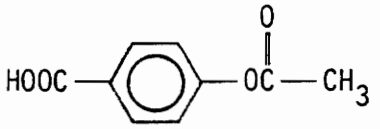
and vacuum to the system. The synthesis of liquid crystal polyesters is commonly accomplished by means of this reaction.[43,44,45] The basic characteristics of a typical reaction are shown in Scheme 10. The salient features of this polymerization are: first, the substituted hydroquinone is converted into its diacetate derivative by refluxing in acetic anhydride. Sodium acetate is sometimes added as a catalyst in this step of the reaction. The substituted hydroquinone diacetate derivative is then isolated and purified to be used in subsequent steps. The reaction between the terephthalic acid and diacetate is a heterogeneous reaction. The temperature of the reaction is initially above the melting point of the diacetate, but the terephthalic acid neither dissolves nor melts in this reaction. Initially the dimers, trimers, and oligomers are molten but as larger oligomers are formed they tend to precipitate from the molten mass. The temperature is thus raised over the course of the reaction to stay above the melting point of the growing polymer. High molecular weight polymer is formed by removing the last traces of acetic acid in the reaction under vacuum.

Many types of aromatic polyesters can be synthesized using the melt acidolysis technique. Hydroquinones with substituents such as Cl, Br and phenyl have been used [46] as well as substituted terephthalic acid (Cl, Br, and phenyl). Other bisphenols besides hydroquinone have also been utilized such as biphenol [45,47] and dihydroxynaphthalene isomers.[46] Various combinations of the bisphenols with the aromatic acids have been used to synthesize polyarylates and liquid crystal polyesters.[48-53] As a final note,

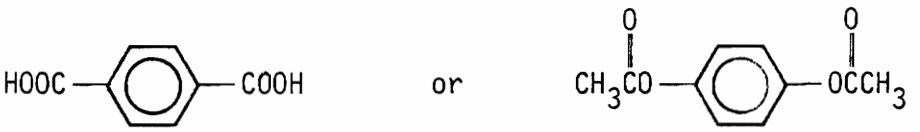


SCHEME 10. Melt acidolysis synthesis of a substituted hydroquinone terephthalate liquid crystalline polyester [42].

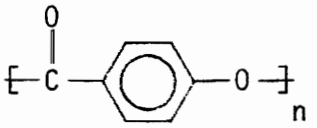
aromatic polyesters can be synthesized from a melt acidolysis technique utilizing only one monomer. The structure of this monomer is such that the acid moiety and acetate moiety are contained within the same molecule. This type of monomer is termed an A-B monomer, where the A represents one type of functionality and B represents another different functional group. Thus, a monomer of this type would be:



This is compared to an A-A or B-B monomer such as:



This particular A-B monomer is called p-acetoxybenzoic acid and yields a polymer of structure:



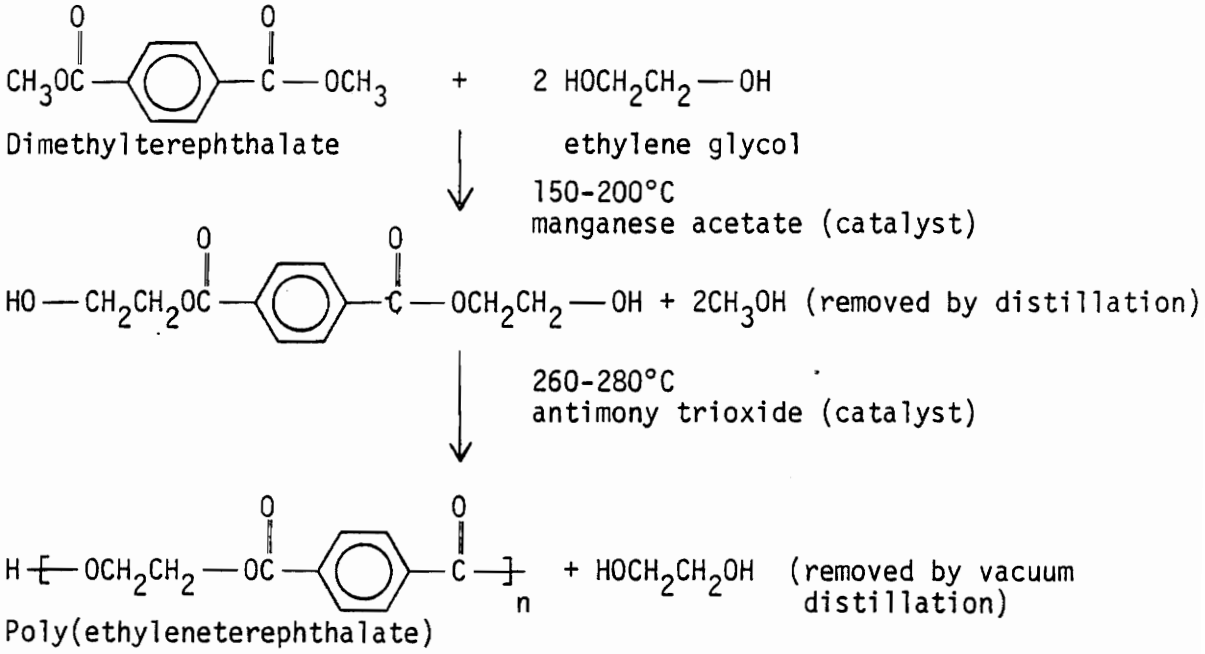
which is liquid crystalline in nature.[36,44]

Other types of ester interchange reactions can also be used to synthesize polyarylate materials. In these types of reactions, the diacid monomer is converted into an ester derivative. An aromatic alcohol (i.e., phenol) or a low molecular weight aliphatic alcohol, such as methanol or ethylene glycol, can be reacted with the diacid to form the ester monomer (Scheme 8, bulk reactions 3 and 4).

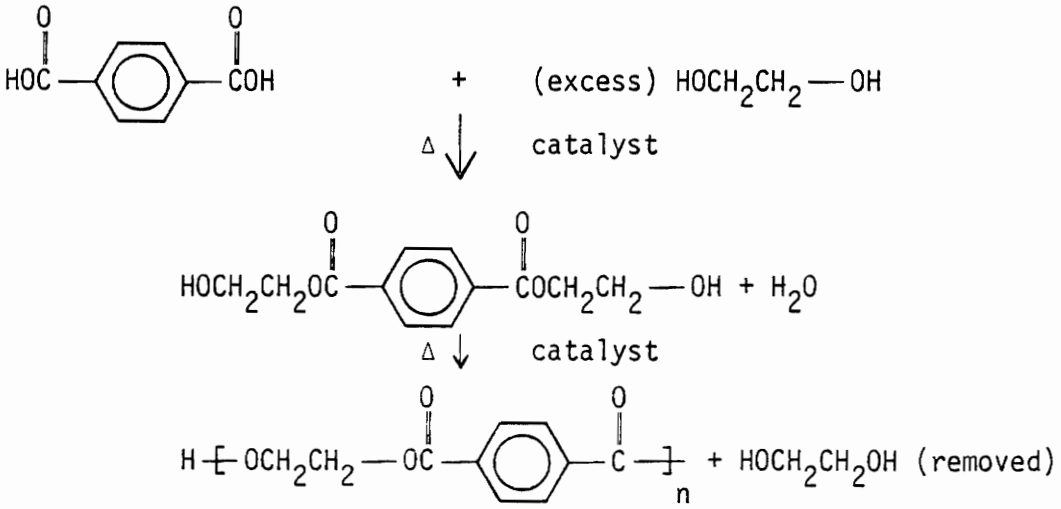
Commercially, polyethylene terephthalate is synthesized by this type of reaction. Scheme 11 illustrates the synthetic steps involved in the production of polyethylene terephthalate by two similar ester interchange techniques. These two techniques are very practical methods of polyester synthesis. In technique 1, dimethyl terephthalate (DMT) is formed from the reaction between methanol and terephthalic acid. This monomer is much easier to purify and react than is terephthalic acid itself (technique 2).

In the first step of the reaction, the dimethyl terephthalate is reacted with ethylene glycol. The methanol ester of terephthalic acid is exchanged for the ethylene glycol ester. This reaction is catalyzed by weak bases such as manganese acetate and is forced to completion by the removal of methanol by distillation. After the first step of the reaction has been completed, the manganese acetate catalyst is deactivated by the addition of some type of phosphorus compound such as phosphoric acid. The second step of the reaction is a true melt polymerization in that the temperature of the reaction is raised above the melting point of the final polymer (258°C), the final temperature being around 290°C. The ester interchange reaction in this step of the reaction is catalyzed by antimony trioxide. The ethylene glycol by-product of the reaction is removed under vacuum, favoring the formation of polymer. This provides another practical point in favor of the ester interchange reaction. The stoichiometry between the DMT and ethylene glycol need not be exactly 1:1 as is the case in most other step-growth reactions. Technique 2 shows that an excess of ethylene glycol can be used to insure the first step in the

Technique 1

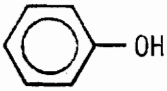


Technique 2

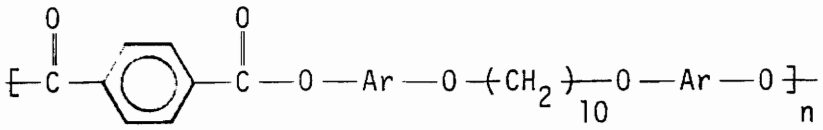


SCHEME 11. Ester interchange reactions used to synthesize polyethylene terephthalate.

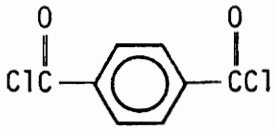
reaction is complete and then the excess removed under vacuum when the polymer is formed. Another favorable aspect of this particular reaction is that the by-products, methanol and ethylene glycol, can be recycled to be used again in the first steps of the two techniques. This negates the need for disposal of by-products. These techniques are further elaborated on by Odian [35] and Flory, [54] and their use in the synthesis of other polyarylates and liquid crystalline polymers has also been discussed.[43,55-59]

The phenyl ester of the diacid (see Scheme 8, bulk reaction 3) has also been used with success in ester interchange reactions.[38,60] However, this technique involves the use of phenol which presents health, environmental, and handling problems. This technique is very similar to that just discussed. A diacid is converted into its phenyl ester derivative by reaction with phenol:  . The phenyl ester is then reacted with an appropriate diol forming a polyester and regenerating phenol.

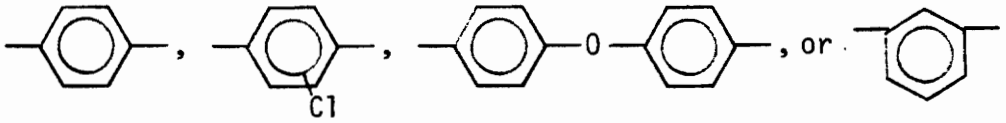
The last bulk technique for the synthesis of polyarylates and liquid crystalline polyesters is more of an academic curiosity at the present time. This reaction (shown schematically as reaction 5 in Scheme 8) takes advantage of the reaction between acid chlorides and alcohols. Lenz, et al.[61,62] have used this reaction to synthesize novel liquid crystal polyesters. Polymers of the general structure:



were synthesized using this method. The polymers were formed from the melt reaction between the acid chloride, terephthaloyl chloride:



and various bisphenols where the aromatic group, Ar, was:



In this reaction, a stoichiometric amount of terephthaloyl chloride was reacted with the bisphenol just above the melting point of the bisphenol. The temperature was then raised as the polymer was formed to stay above the melting point of the polymer. The driving force behind this reaction is the removal of the by-product formed in the reaction. The by-product in this case is hydrogen chloride. Hydrogen chloride, being a gas, was removed first by a stream of nitrogen followed by application of a vacuum. The molecular weight of many of these polymers were increased by heating just below the melting point of the polymers under vacuum in a so called solid state polymerization.[36,62] Two factors will probably keep this reaction from becoming a commercially viable way of synthesizing polyesters. First, the cost of the acid chloride is much more than the cost of the corresponding acid. Second, the reaction liberates the highly corrosive gas hydrogen chloride, which cannot be recycled as was the case with methanol or ethylene glycol. However, on a laboratory

scale, this reaction provides a useful technique for the synthesis of many novel polyarylates and liquid crystal polyesters.

Three different techniques have been discussed as possible methods for the synthesis of polyarylates and liquid crystal polyesters. Each of these methods--solution, interfacial, and bulk--have several variations within the title class. In some cases, the same polyester can be made by all three techniques.[62] However, in many instances the desired polyester can only be synthesized through one technique. The limitation to one technique may be due to solubility, temperature, or reactivity considerations. To a large extent, these considerations are related to the ultimate properties of the polyester.

2.4.2 Properties of Polyarylates and Liquid Crystal Polyesters

As a class, polyesters can assume a whole range of properties. There are totally amorphous as well as highly crystalline polyesters. Thermal properties include polyesters with glass transition temperatures below room temperature to above 200°C. Polyesters with strengths that rival those of metals can also be realized. Limitation will be made to polyarylates and liquid crystalline polyesters "designed" to function as engineering thermoplastics.

Polyethylene terephthalate (PET) is the highest volume polyester manufactured and with good reason. It has been used in fiber or film form for more than 25 years.[63,64]. As a fiber, PET has been extensively used in the textile industry. PET has a melting temperature of 258°C and good mechanical strength up to approximately

175°C. These thermal properties combined with good solvent, abrasion, and crease resistance led to the use of PET as "wash and wear" materials [35] under the tradename of Dacron by the DuPont Company.

Tires which are advertised as having polyester cords usually have PET as those cords. Polyethylene terephthalate was once overwhelmingly used in fiber form, but its use in film or traditional "plastic" form is catching up. As a film, PET has seen applications in photographic and X-ray film and magnetic tape. However, PET's greatest growth has been in the last five years in the food packaging industry.[65,66] Due to its crystallinity, PET serves as a barrier to gases and liquids alike. Foods packaged in PET retain their flavor and freshness because harmful gases, oxygen and carbon dioxide, are kept out while the flavor and aromas are sealed in. More recently, carbonated beverages which were once packaged in aluminum cans and glass bottles are becoming increasingly packaged in PET bottles. This application developed due to the enhanced properties gained by blow molding PET. Blow molding is accomplished by melting PET, or many other polymers, and then forcing air into the molten polymer to mold the polymer into the shape of the surrounding mold. This is analogous to blowing up a balloon inside of a bottle. When PET is blow molded, it is biaxially stretched which induces added crystallinity and order into the film. This added order further enhances the barrier properties and lowers the permeability of the polymer.

Orientation of PET through biaxial deformation of the polymer also enhances the mechanical properties relative to those of the unoriented polymer. Table 2 summarizes some of the mechanical

TABLE 2

SELECTED PROPERTIES OF COMMERCIAL POLYARYLATES AND A LIQUID CRYSTALLINE POLYESTER [66]

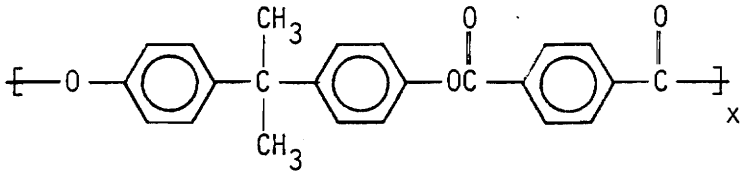
Material	Tensile Strength at Break (psi)(1)	Elongation at Break (%)	Flexural Modulus ($psix10^{-3}$)	Density (g/ml)
PET (unoriented)	8,500-10,500	50-300	350-450	1.34-1.39
PET (oriented)	25,000-36,000	12-130	-	1.45
Bis-A Polyester	8,800- 9,700	50- 65	310-330	1.21
Polycarbonate	9,500	110	340	1.18
Xydar (2) (Liquid Crystal Polyester)	18,200-20,000	4- 5	1,900-2,000	1.35

(1) Pounds per square inch (psi) values may be converted to the SI units, megapascals (MP) by multiplying by 6.89×10^{-3}.

(2) Xydar is manufactured by Dartco Manufacturing Company.

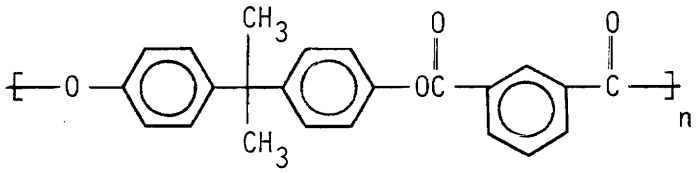
properties of oriented and unoriented polyethylene terephthalate as well as those of selected polyarylates and a liquid crystalline polyester. One notes from Table 2 that the tensile strength is essentially quadrupled (36,000 vs. 10,500 psi) in the oriented PET as compared to the unoriented polymer.

Bisphenol-A based polyarylates have been extensively studied due to the availability of this high volume, highly purified monomer. A wide variety of properties can also be obtained simply by making minor modifications in the structure. The polyarylate synthesized from bisphenol-A and terephthaloyl chloride:



was found to be highly crystalline.[67] On the other hand, if as little as 10 mole percent or more of isophthaloyl chloride was co-reacted with the terephthaloyl chloride, the resulting copolymer was totally amorphous.

The amorphous polyester sold under the tradename Ardel is thought to be synthesized from bisphenol-A and a 50/50 molar mixture of tere- and isophthaloyl chlorides. The polymer composed of bisphenol-A and isophthaloyl chloride:



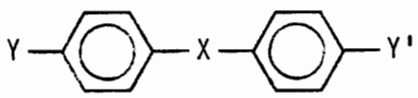
was found to be either semi-crystalline or amorphous depending on the solvent casting conditions. Alteration of the bisphenol monomer also

varies the properties of the polyarylate. For example, if substituents such as Cl, Br, or methyl are present on the bisphenol, the resulting polymers were generally amorphous with higher glass transition temperatures than the polymers derived from the unsubstituted bisphenol.[68,69] The higher glass transition values are due to the substituents restricting the ease of rotation of the phenyl rings. The substituents may also prevent efficient packing of the polymer thus limiting its ability to crystallize. Replacement of the methyl groups in bisphenol-A with ethyl or phenyl groups elicits similar properties from the polyarylate.

Substitution of an all aromatic bisphenol for bisphenol-A, in some cases, produces polyarylates with very unique properties. These unique properties include liquid crystallinity, very high strength, and outstanding thermal properties. Liquid crystals, as alluded to earlier, are structures which flow like a liquid but have order like a crystal. While liquid crystals have been known under other names since 1888, [70] it was not until 1900 that the term "liquid crystal" was coined. Originally, substances which were found to be liquid crystalline were of low molecular weight. The first polymeric liquid crystal studied was the tobacco mosaic virus (TMV).[71] TMV is a protein (essentially a polyamide) of approximately 40,000,000 molecular weight.

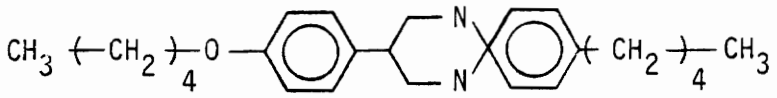
Liquid crystals, whether they are low molecular weight compounds or polymers with molecular weights of millions tend to have several common structural features.[72,73] They tend to have large aspect ratios (e.g., their lengths are much greater than their widths). They

are usually composed of aromatic groups linked by various double bonds (e.g., azo or azoxy) or by rigid bonds (e.g., ester or amide) along their long axis. The rigid bonds do not allow free rotation around the bonds. This second observation leads to the fact that the molecules will have strong dipoles and be relatively "rigid" along the molecular axis. Liquid crystals are sometimes referred to as rigid rodlike molecules. These common structural features tend to define whether a particular molecule can behave as a liquid crystal. A popular analogy is to consider liquid crystals as "logs" on a river. As the logs float down the river, their long axes align parallel to one another but usually without much order in any other direction. Thus, a composite liquid crystal molecule might have a structure as follows:[48]

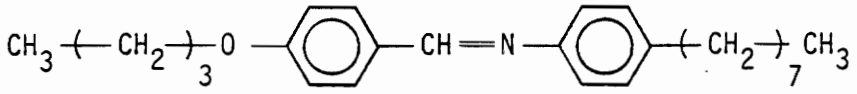


Actual examples of low molecular compounds with this composite structure are given in Scheme 12. Polymeric liquid crystals tend to have the same structural features as the low molecular weight analogs, but these features are repeated throughout the macromolecular chain.

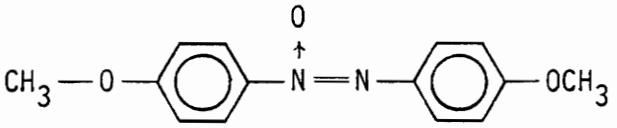
Liquid crystalline materials can be broadly classified into three distinct categories.[74] Nematic liquid crystals are materials which show one-dimensional order. A system which has a helical twist to the nematic state is called a cholesteric liquid crystal. Two-dimensional order within a system is termed smectic liquid crystallinity. Nematic and smectic liquid crystals derive their name from the Greek words



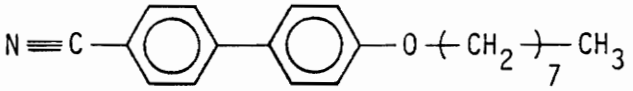
2-(4,n-pentylphenyl)-5-(4-pentyloxyphenyl)pyrimidine



butoxybenzylidine-octylanilene



p-azo-oxyanisole



octyloxycyanobiphenyl

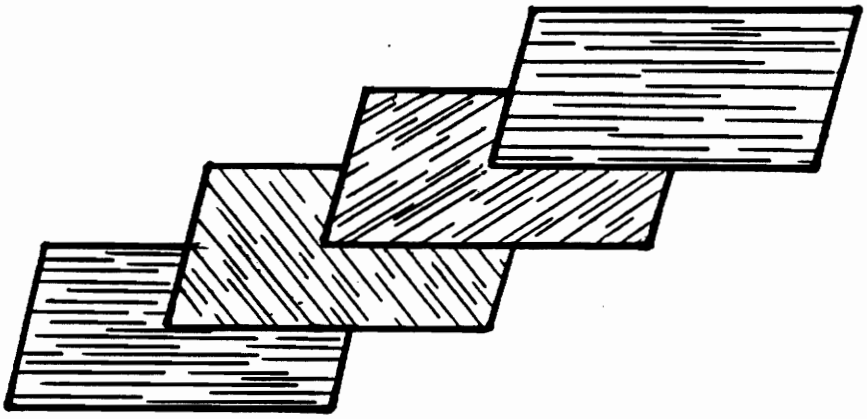
SCHEME 12. Examples of low molecular weight liquid crystals [48].

meaning thread for nematic and soap for smectic systems. Nematic systems display a threadlike morphology under a polarized microscope, while smectic systems have properties of a soap. Cholesteric systems are so named because cholesteryl derivatives were observed to have these structures. These three classes are represented pictorially in Scheme 13. Within the smectic system there are further subdivisions. These subdivisions are termed smectic A, B, C, etc. and arise due to specific tilting of the molecular axes within the lamella or layers of the liquid crystal. The most common polymeric liquid crystal class is the nematic class. This arises due to the fact that a nematic liquid crystal possesses only one-dimensional order which can be obtained by the rigid rodlike portions of polymer chains aligning themselves like logs on a river. In contrast, a smectic liquid crystal would require that the liquid crystalline portion of the polymer chains (termed mesogen) be of approximately equal length so that the mesogens' ends can also align to give two-dimensional order. A cholesteric liquid crystalline polymer would necessarily possess a chiral carbon within the polymer chain to induce the helical twist into the polymer which defines it as a cholesteric liquid crystal.

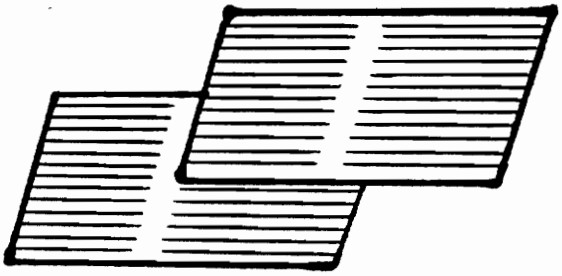
The properties of a liquid crystal are usually only present under certain predefined conditions. Some polymers will only display liquid crystallinity when dissolved in certain solvents at well defined concentrations. A polymer which forms a liquid crystalline structure in solution is termed lyotropic.[44] Kevlar , poly(p-phenylene-terephthalamide), a liquid crystalline polyamide thought to have the structure:

Nematic

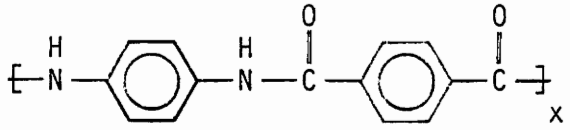
Cholesteric



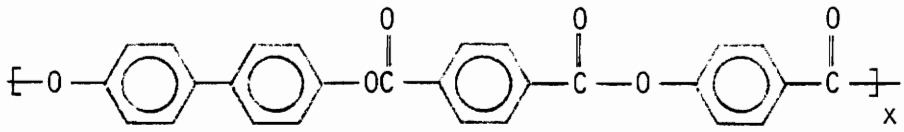
Smectic



SCHEME 13. Pictorial representation of the three classes of liquid crystals.



was developed by the DuPont Company and is one such lyotropic liquid crystalline polymer. The liquid crystallinity in this polymer is obtained by dissolving the polymer in strong solvents such as sulfuric acid which may also contain dissolved lithium chloride salt at a given concentration. This polymer solution can then be forced through a spinneret to afford Kevlar in fiber form. There are many known lyotropic liquid crystalline polymers of the polyamide type as well as of other types. However, the second way of inducing the properties of a liquid crystal is by thermal treatment of a polymer. A polymer which displays liquid crystallinity in the molten phase is termed thermotropic.[44] An example of a thermotropic liquid crystalline polymer is Xydar made by Dartco Manufacturing. Xydar is thought to have the structure:



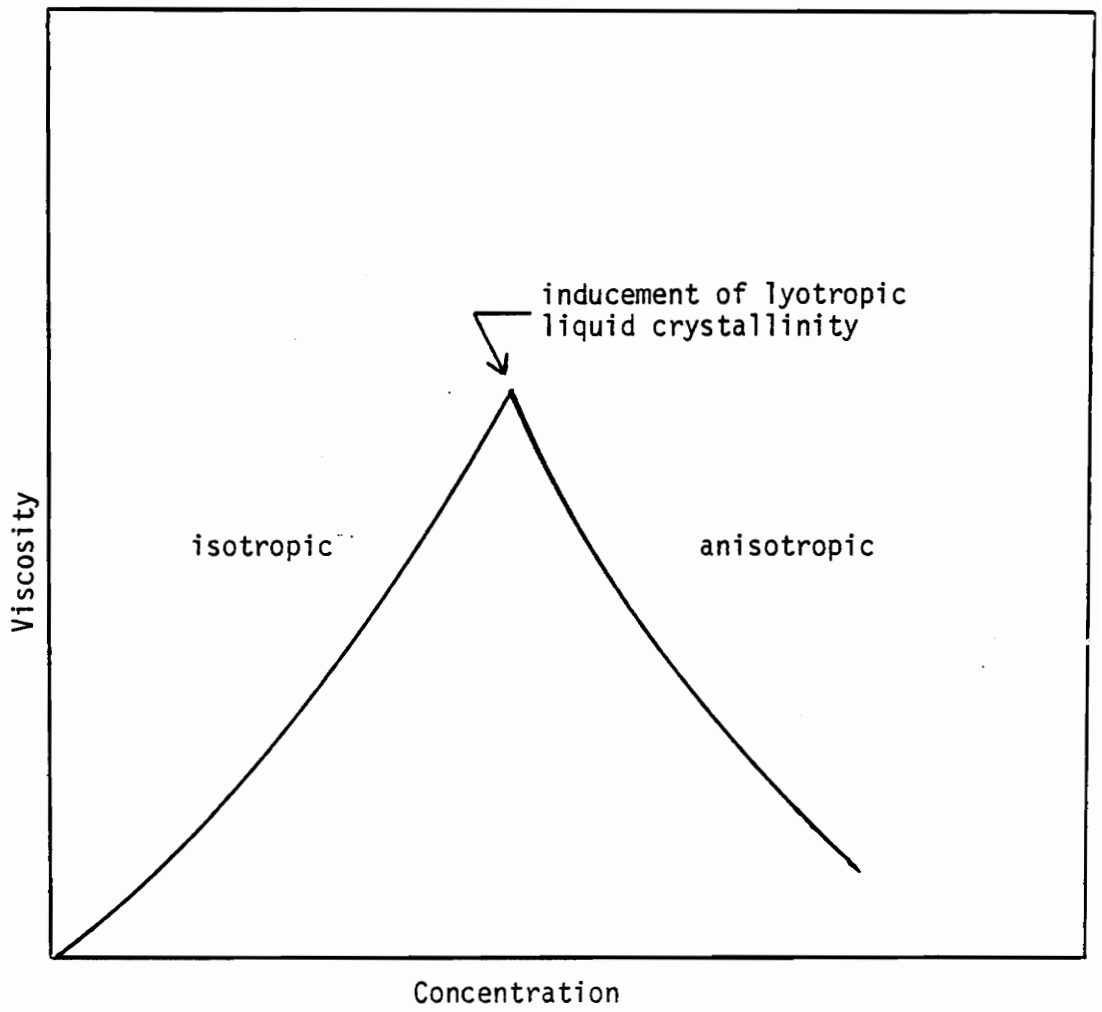
Thermotropic polymeric liquid crystals are currently generating the most interest industrially and academically and have a great potential commercially. This interest is due to the fact that if the liquid crystallinity in a polymer can be induced thermally, the molten polymer can then be molded, extruded, etc. into a variety of shapes directly from the melt. The resulting liquid crystallinity can then

be frozen into place, producing special effects such as high tensile strength in the direction of flow. This eliminates the need for hazardous and/or expensive solvents, i.e., sulfuric acid.

An interesting property of a polymer in its liquid crystalline, anisotropic state (either in solution or in the melt) is the lowering of its viscosity when compared to the same polymer in its isotropic non-liquid crystalline state.[75,76] The viscosity of a potentially liquid crystalline polymer in solution should increase as the concentration of polymer increases; however, when the polymer develops its anisotropic state, the viscosity abruptly decreases (see Scheme 14). A similar sort of phenomenon is observed for thermotropic liquid crystals. Thus, a polymer developing a liquid crystalline melt will show a lower viscosity than the same polymer in its isotropic state. Therefore, a thermotropic liquid crystal polymer can often be processed with a minimal amount of force, and thus energy, due to the relatively low viscosity.

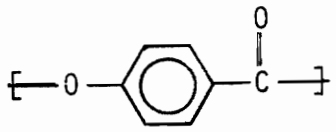
Since a liquid crystal has some residual order in solution or in the melt, other interesting properties have become apparent. For example, a liquid crystal will depolarize plane polarized light which has, in fact, been utilized as one way of characterizing its morphology.[76] However, the greatest interest generated in liquid crystal polymers is due to their outstanding thermal and mechanical properties.

Commercially attractive liquid crystal polymers generally have very high melting points. The liquid crystals based upon the

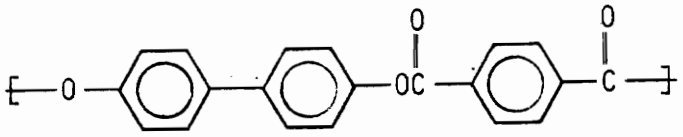


SCHEME 14. The variation of viscosity with increasing polymer concentration for a liquid crystalline polymer [76].

following polymers are reported to have melting points in excess of 500°C.[61,77]



Polyoxybenzoate

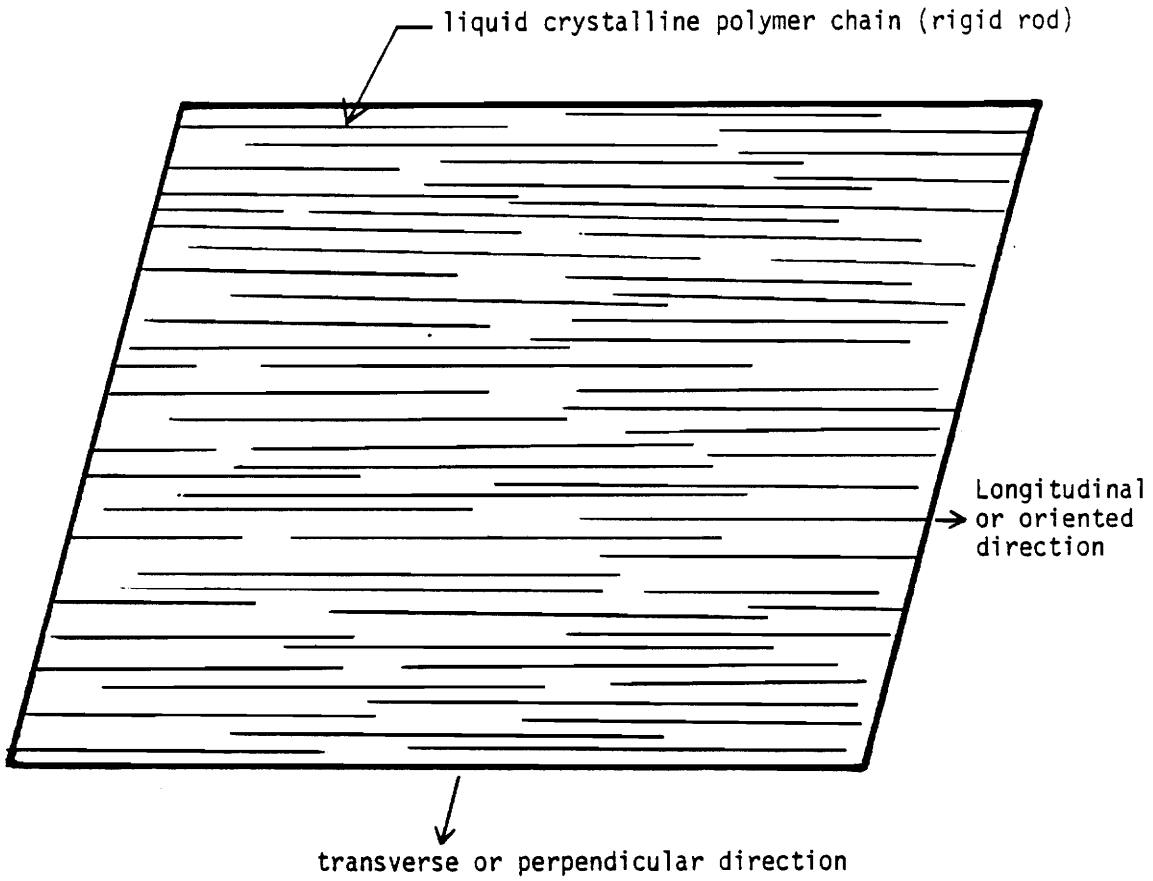


Polybiphenol Terephthalate

The high melting points are a direct result of the nature of the polymer chain. The polymer mesogenic groups have been described as rigid and rodlike in nature. This conformation leads to the high melting points by virtue of the thermodynamic parameters related to melting. The melting of a substance is related to its entropy and heat of fusion in its crystalline and amorphous states. These terms are related in the equation $T_m = \Delta H/\Delta S$ where T_m is the melting point of the polymer, ΔH and ΔS are the change in enthalpy and entropy respectively, upon transition from a crystalline state to an amorphous state. A liquid crystal polymer's melting point is determined to a large extent by the ΔS term since the ΔH term for almost all polymers is comparable. Thus, if ΔS is small then the T_m will be large. This is the case for a liquid crystal since the entropy changes very little when undergoing the transition from the crystalline state to the still somewhat ordered liquid crystalline state. This small entropy change

is due to the fact that a liquid crystalline polymer in its crystalline state is essentially a rigid rod and, when melted, retains this rigid rod conformation over a relatively well defined temperature range.

The high moduli and tensile strengths as well as the low ultimate elongations which characterize liquid crystalline polymers are also related to this rigid rod conformation. In the liquid crystalline state, the molecules are aligned in one- or two-dimensional order along the long axis of the molecule. See Scheme 15. Then, if the mechanical properties are measured along this oriented axis (longitudinal axis), the tensile strength and modulus give very high values while the elongation is correspondingly low. These properties are explained by the fact that the macroscopic stress is more or less directed along the backbone axis of the polymer, where the chain is already extended to nearly its maximum value. Thus, forces could be envisioned molecularly as attempting to deform primary covalent bonds. It has been reported [78] that these mechanical properties could be even higher in a "perfectly" oriented material, where the force is totally directed along a covalently bonded polymer chain backbone. While the mechanical properties in the longitudinal direction are very high, those same properties when measured perpendicular (transverse) to the oriented direction tend to be quite low. These lower mechanical property values are explained by the fact that the force used in the measurement of the properties is now directed, not along the polymer chain, but against secondary bonding between chains (intermolecular bonding). Although this secondary bonding includes

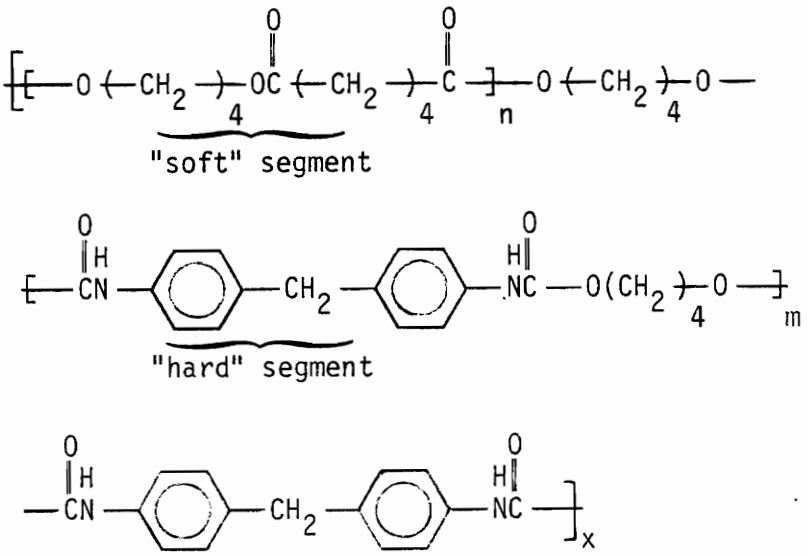


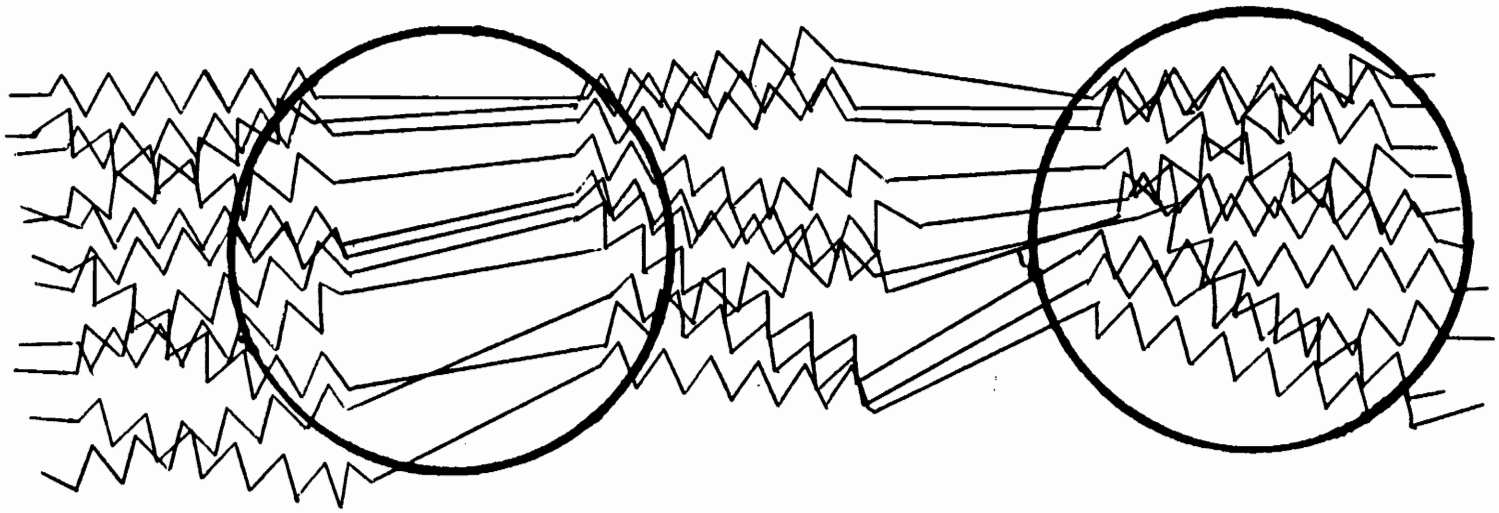
SCHEME 15. Depiction of oriented liquid crystalline polymer.

hydrogen bonding, Van der Waals forces, etc., they do not provide the strength of the oriented primary structures.

2.5 Segmented Copolymers

A segmented copolymer is a variation of a multiblock copolymer as discussed earlier in Chapter 2, Section 1. The "segments" that make up a block copolymer can be of a multitude of architectures and morphologies. The majority of research conducted on segmented copolymers has dealt with "hard and soft" segments within the same polymer chain (see Scheme 16). A "hard" segment is defined as being either glassy or crystalline in nature. A "soft" segment is above its Tg at the test temperature (usually room temperature) and thus is rubbery or elastomeric in nature. An example of a commercially available segmented copolymer is the polyurethane Estane® produced by B. F. Goodrich Corporation. Estane is a thermoplastic elastomer by virtue of its morphology and architecture. Estane is believed to have the following structure[79]





SCHEME 16. Representation of segmented copolymers composed of "hard" and "soft" segments.

The hard segments of Estane are composed of 1,4 butanediol reacted with methylene diisocynate. The soft segment is poly(butylene adipate) of approximately 1000 molecular weight. The thermoplastic elastomer nature of Estane derives from the fact that the hard and soft segments of the polymer chains microphase separate into domains. The hard segments then act as physical crosslinks in the system. The thermoplastic nature of the segmented copolymer results from the fact that the polymer can be heated above the Tg of the hard segments. The polymer will then flow and can be processed and when cooled below the Tg again the domains reform. However, even with the great commercial importance of this segmented polyurethane and other thermoplastic elastomers (i.e., Lycra® and SBS rubber), [10,79,80] research dealing with copolymers composed of two or more hard segments has been sparse. The combinations of morphologies which can be achieved with just two hard segments are:

glass-glass

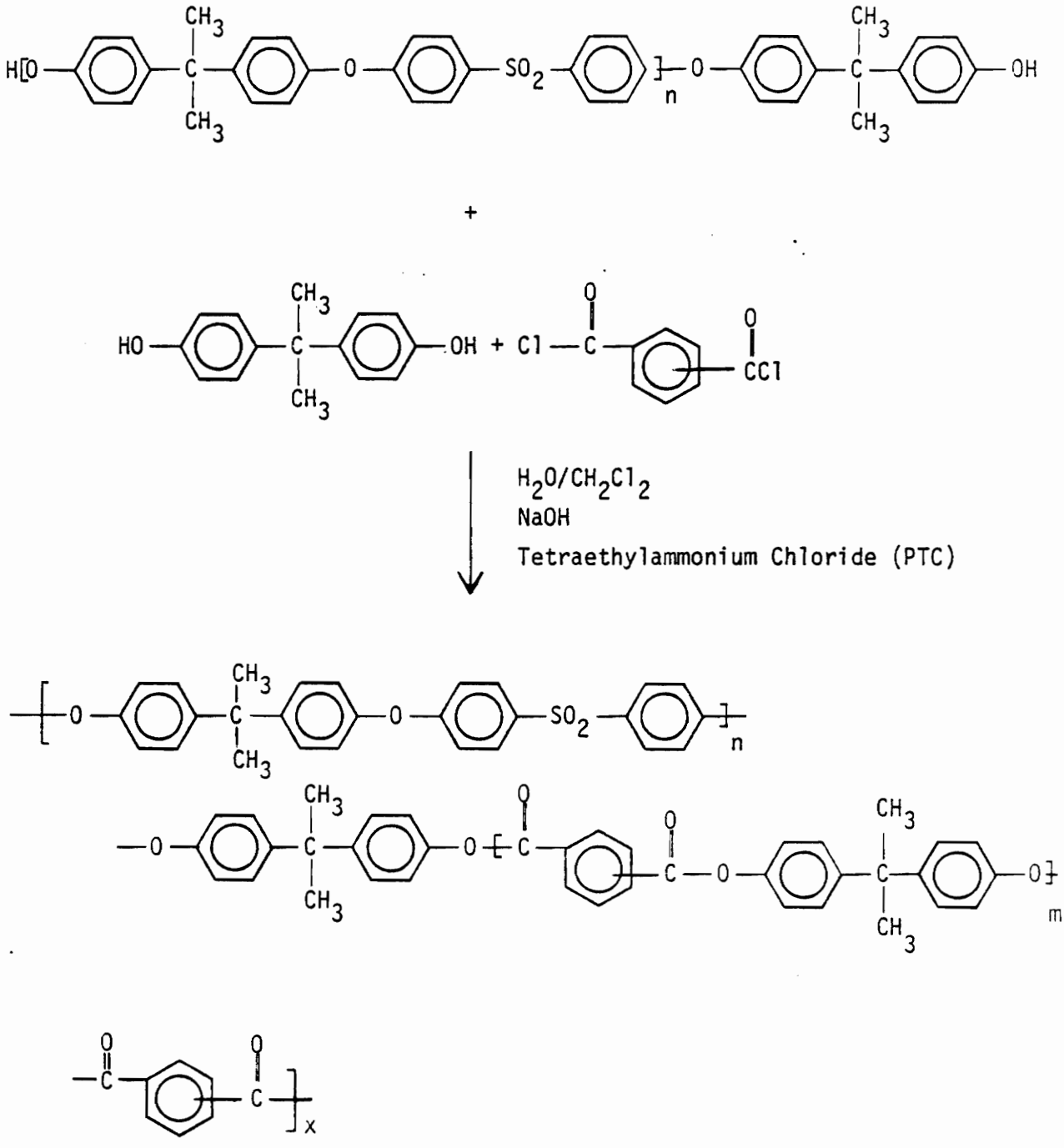
glass-crystalline

crystalline-crystalline.

One study utilizing the glass-glass morphology was based upon segmented copolymers formed from an ester and phosgene forming a carbonate.[81,82] In this study, the segmented copolymers were formed from preformed bisphenol-A-tere/isophthalate oligomers coupled together with phosgene. The glass transitions of the resulting copolymers were found to vary with the relative mole ratios of the ester segment to the carbonate segment. The Tg was observed to be at

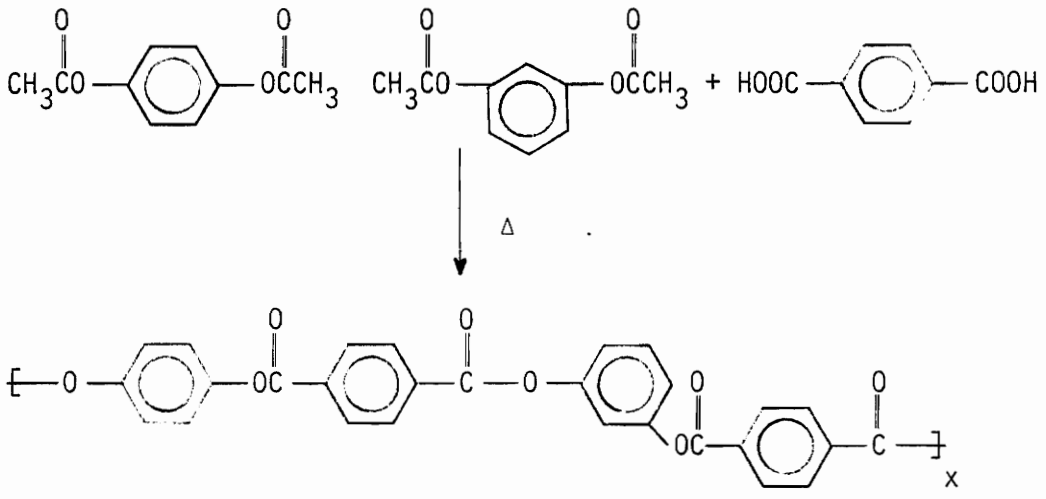
a maximum when the ester to carbonate mole ratio was 6 to 1. This same mole ratio also gave the copolymer with the highest yield stress. When the copolymers contained only the isophthalate unit, the material showed considerable necking when drawn under tension. The terephthalate based copolymers, on the other hand, deformed uniformly when drawn.

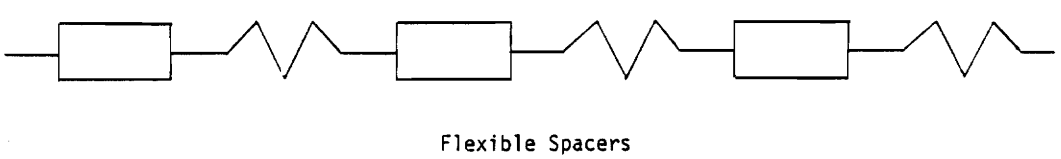
Glass-glass and glass-crystalline morphologies were also obtained by McGrath and coworkers through the synthesis of bisphenol-A-polysulfone-bisphenol-A ester copolymers (see Scheme 17).[83,84,85,86] The segmented copolymers were produced in two different series. In series 1, the composition of the copolymer was held constant at 50% bisphenol-A polysulfone by weight. They were derived from a 6,000 number average molecular weight ($<M_n>$) hydroxyl terminated polysulfone oligomer. This oligomer was reacted interfacially with mixtures of tere/isophthaloyl chlorides and bisphenol-A. The composition of the ester segment was varied from 100% terephthalate to 100% isophthalate. At the extremes in composition in this series, the copolymers were found to show enhanced environmental stress cracking resistance (ESCR). In the second series, the polyester segment composition was held constant at 100% bisphenol-A terephthalate. The overall weight percentage of the 10,000 $<M_n>$ bisphenol-A polysulfone in the copolymer was varied from 50 to 90%. This series yielded two copolymers, the copolymers containing 50 and 60% polysulfone, which showed some evidence of crystallinity. All of the segmented copolymers except the one containing 90% polysulfone showed enhanced solvent resistance,



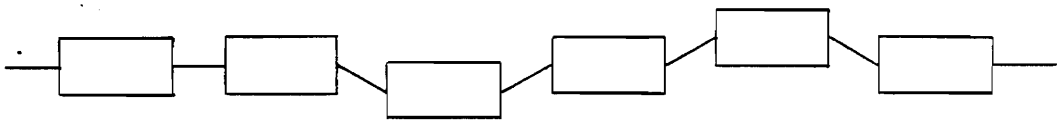
SCHEME 17. Synthetic scheme for the formation of polysulfone-bisphenol-A polyarylate copolymers [85].

As mentioned previously liquid crystalline polymers based on aromatic structures tend to have very high melting points (>500°C). In order to lower these melting points, copolymer technology has been utilized. There have been several avenues of research into what the second component should be in these copolymers. One approach has been to incorporate a flexible rubbery segment into the copolymer along with the mesogenic segment (see Scheme 18).[55,87,88,89] However, from a mechanical property point of view, the desirable properties of high strength, rigidity and low elongation of the liquid crystal is lost due to the rubbery segment. A second approach was to incorporate bends or kinks into the otherwise linear profile of the polymer chain. These kinks can be introduced into the chain via two different approaches. The first way is by using ortho or meta isomers along with the para oriented monomers.[47,90,91] These copolymers were synthesized by a melt acidolysis technique from the diacetates of hydroquinone and resorcinol, and terephthalic acid:

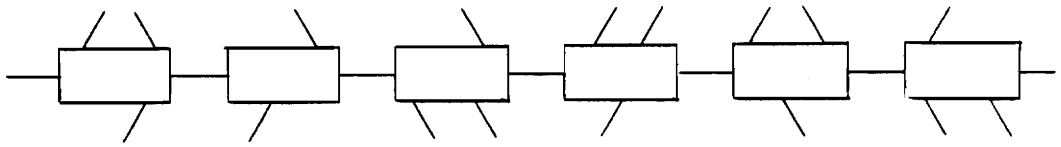




Flexible Spacers

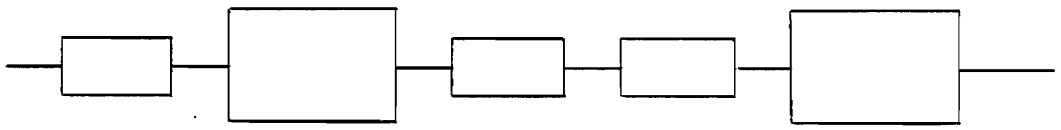


Kinked Links



Substituent

Frustrated Chain Packing



Pseudo-Frustrated Chain Packing

Mesogenic segment

Flexible segment

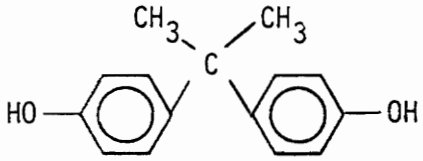
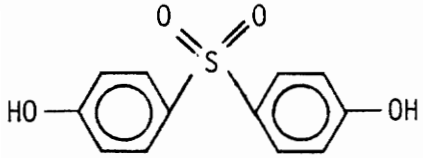
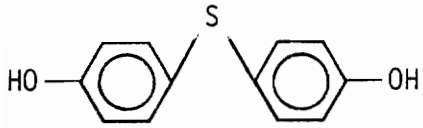
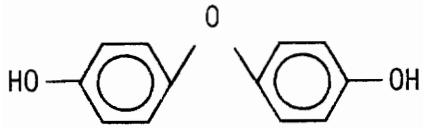
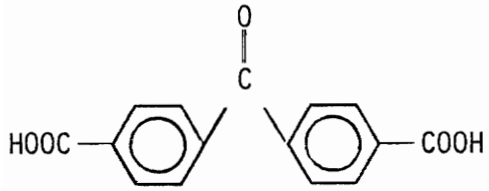
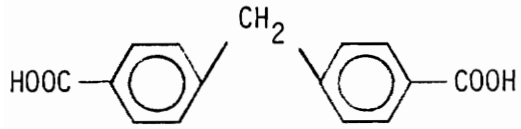
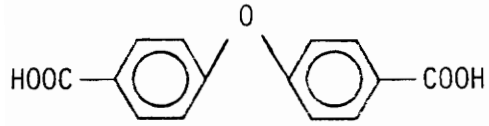
SCHEME 18. Synthetic designs in copolymer technology to lower liquid crystalline polymer melting points.

The resorcinol is meta oriented thus introducing a kink into the polymer chain, but it still is a rigid monomer. This rigidity insures that the mechanical properties are not compromised due to a flexible or rubbery second component. The melting temperatures of the copolymers were seen to decrease as the mole percent of resorcinol increased. However, to lower the melting point below 400°C, the resorcinol content was so high that no liquid crystallinity was detected. Similarly, meta hydroxybenzoic acid: (HO—  —COOH) was copolymerized with hydroquinone and terephthalic acid to produce polymers with reduced melting points. To lower the melting point to under 400°C over 50 mole percent of the m-hydroxybenzoic acid (MHBA) had to be used. This large amount of the meta oriented modifier destroyed the liquid crystallinity in the polymer. The flexural strength, tensile strength, and flexural modulus were increased up to 40 mole percent incorporation of MHBA but were substantially lowered at higher loadings.

Kinks can also be introduced into the polymer chains by using monomers which have aromatic rings linked by one atom. A list of these types of monomers with their structures is given in Table 3.[47,92,93] Knowledge of the valence angles of carbon and oxygen in several of these monomers gives a value of approximately 111° for the angle between the aromatic rings. Since the angle is less than the 180° needed for a linear structure, a kink is introduced into the polymer chain. Use of 30 mole percent of bisphenol-A copolymerized with para-hydroxybenzoic acid and terephthalic acid gave non-liquid crystalline polymers with lowered mechanical properties.

TABLE 3

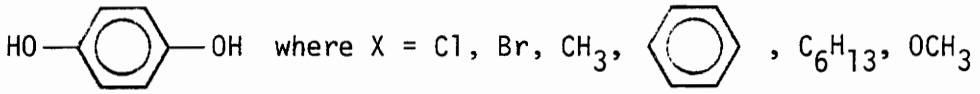
KINKED MODIFIERS USED TO LOWER LIQUID CRYSTALLINE POLYMER Tm's

Structure	Name
	Bisphenol-A
	Dihydroxydiphenylsulfone
	4,4'-Thiodiphenol
	4,4'-Oxydiphenol
	4,4'-Dicarboxybenzophenone
	4,4'-Dicarboxydiphenyl Methane
	4,4'-Dicarboxydiphenyl Ether

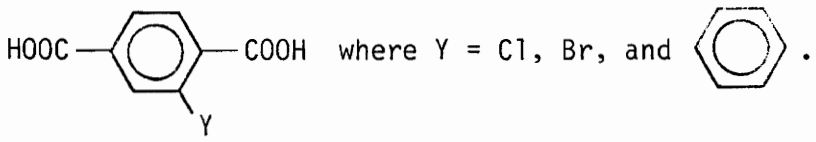
However, replacement of the bisphenol-A with either 4,4'-thiodiphenol or 4,4'-oxydiphenol did give liquid crystalline copolymers. The copolymer with the sulfur linkage gave liquid crystalline melting points low enough to be melt processable at 400°C. The use of kinked modifiers, however, tended to lower the mechanical properties and liquid crystallinity in the copolymers before the melting points could be lowered sufficiently to be melt processable.

The melting points of liquid crystalline polymers are also thought to be lowered if substituents are placed on the aromatic rings of the monomers. This approach is termed frustrated chain packing because the substituents do not allow the polymer's chains to pack into a dense crystalline morphology. This is much like the approach used in the polyolefin industry to lower the density and crystallinity in polyethylene by the use of short chain branching.

Substituted monomers which have been used to make copolymers with lowered melting points are:[45,47,94]



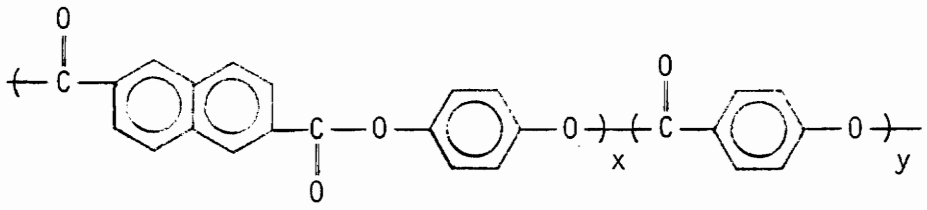
or



The polymers synthesized from terephthalic acid and methyl hydroquinone or chlorohydroquinone diacetates gave melting points above 400°C. The use of phenyl hydroquinone diacetate and

terephthalic acid did give a liquid crystalline polymer with a crystal to nematic transition point of 353°C as polymerized. The elastic modulus was found to increase from the as polymerized value of 440 g/den to 910 g/den (pounds/sq. inch = g/den x density x 12,791) when the polymer is annealed for 60 minutes at 340°C. Placing methyl or chloro substituents in the para position on the phenyl substituent lowered the melting points even further to 314°C and 351°C respectively.[95]

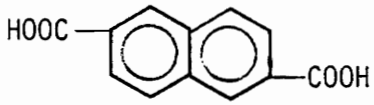
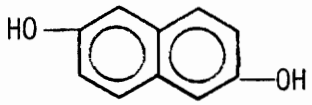
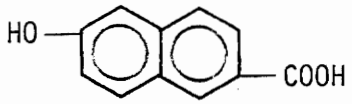
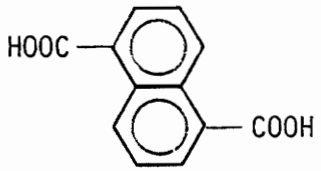
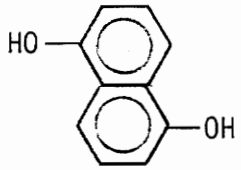
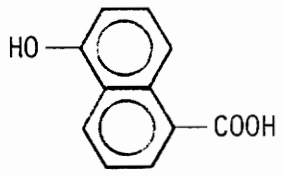
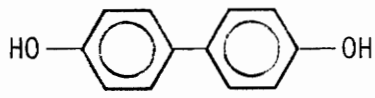
The last approach to lowering the melting points of liquid crystalline polyesters is through pseudo-frustrated chain packing. In this approach, monomers of various sizes are copolymerized to give polymer chains that have varying thickness along the chain. The polymer chains are thus limited in their packing efficiency due to the "bigger" groups in the backbone. Monomers which can be used as the "bigger" groups within the chain are given in Table 4. Copolymers based upon the structure:



gave liquid crystalline polymers with a eutectic melting point of 325°C. The X and Y values corresponding to this eutectic point are 0.25 and 0.75 respectively.[96] Measurements of the mechanical properties of the copolyester with X and Y values of 0.2 and 0.8 gave values of 32,800 lb/in^2 for the tensile strength, 26,000 lb/in^2 for

TABLE 4

MONOMERS USED IN PSEUDO FRUSTRATED CHAIN PACKING APPROACH TO LOWERING MELTING POINTS

Structure	Name
	2,6-Naphthalene Dicarboxylic Acid
	2,6-Dihydroxynaphthalene
	6-Hydroxy-2-Naphthoic Acid
	1,5-Naphthalene Dicarboxylic Acid
	1,5-Dihydroxy Naphthalene
	5-Hydroxynaphthoic Acid
	4,4'-Biphenol

the flexural strength, and a flexural modulus of 1,800,000 lb/in^2. There was also no measurable mold shrinkage of this copolymer. Calundann and coworkers at Celanese also have patents on the copolymers based upon the other derivatives of naphthalene shown in Table 4.[97] Copolymers with structures similar to that shown above but with a mixture of 2,6-naphthalene dicarboxylic acid and terephthalic acid gave liquid crystalline melts with comparable mechanical properties.[98] The eutectic melting point of about 320°C came at a 50 mole percent para hydroxybenzoic acid composition with a 60/40 ratio of the two dicarboxylic acids. The use of biphenol along with hydroquinone and terephthalic acid led to the commercialization of Ekkeel I2000 by the Carborundum Company as well as other products.[99] This copolymer melted at 380°C.

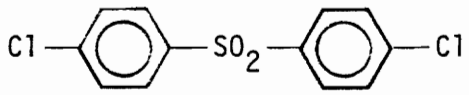
CHAPTER 3

EXPERIMENTAL

3.1 Materials and Their Purification

3.1.1 Monomers

3.1.1.1 Dichlorodiphenylsulfone (DCDPS).

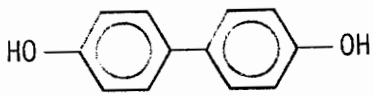


The 4,4'-dichlorodiphenyl sulfone was obtained from the Union Carbide Corporation and was purified by recrystallization. Typically, 150 grams of the DCDPS was dissolved in 1200 ml of toluene while heating on a hotplate. The boiling solution was filtered through a fluted paper filter to remove particulate matter. The filtered solution was reduced in volume, by heating, to 600 ml. The heat was turned off and the solution allowed to cool slowly while being stirred with a magnetic stirrer. After cooling the DCDPS crystals were isolated by suction filtration. The DCDPS was redissolved in 600 ml of clean toluene with heating. This solution was again allowed to cool with stirring and the DCDPS again collected by suction filtration. The solid DCDPS was ground up and placed in a vacuum oven under low heat (70-80°C) for 12 hours. The DCDPS was again ground up and dried an additional 12 hours under vacuum. The yield of the DCDPS was about 125 g in a white crystalline form. The melting point of the recovered monomer was 145-148°C.

3.1.1.2 Hydroquinone (Hq).

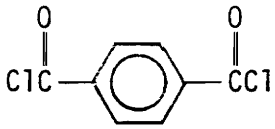
The hydroquinone was obtained from the Tennessee Eastman Company. Approximately 150 grams of the Hq were dissolved in 1000 ml of hot acetone. The acetone was previously brought to a boil with a steady stream of argon bubbled through it. The boiling and purging with argon removed any dissolved oxygen from the acetone. The hot solution was filtered through a fluted paper filter. The volume of the solution was reduced to 500 ml by boiling and then allowed to cool to room temperature with stirring. The Hq was isolated by suction filtration. The white crystals were again dissolved in hot oxygen free acetone and allowed to slowly cool with stirring. The isolated crystals were ground up and dried in a vacuum oven under very low heat (40-50°C) for 24 hours. The purified hydroquinone, with a melting range of 172-174°C was stored in an argon purged dessicator until used.

3.1.1.3 4,4'-Biphenol (Bp).



High purity polymer grade biphenol was obtained from the Buffalo Color Company. This monomer was used without further purification but was dried under vacuum at 50°C for 24 hours before use.

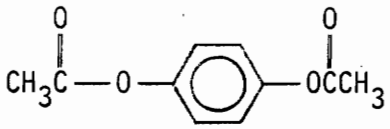
3.1.1.4 Terephthaloyl chloride (TC).



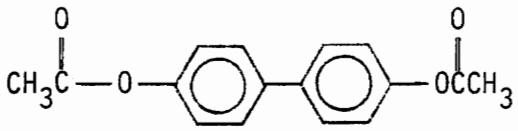
Reagent grade terephthaloyl chloride was obtained from the Aldrich Chemical Company. Purification was accomplished by recrystallization from hexanes. Typically, 150 grams of TC was dissolved in 1 liter of boiling hexanes with stirring.

The solution at this point was hazy white due to the hydrolyzed acidic impurities which are insoluble in the hexanes. The solution was then filtered through a fluted paper filter into another Erlenmeyer flask containing refluxing hexanes. The refluxing hexanes prevent the TC from crystallizing out in the paper filter. The volume of the filtered solution was reduced to 600 ml by distilling off the excess hexanes. The solution was allowed to cool, with stirring, yielding the white crystals of TC. The crystals were isolated by suction filtration and redissolved in hot hexanes. If the solution at this point was not clear with a slight yellow color, it was filtered and then allowed to cool to room temperature. The crystals were isolated, ground up, and then dried under vacuum with no heat for 24 hours. The crystals were crushed again and allowed to dry for an additional 24 hours. The fine white crystals had a melting range from 79-81°C and were kept in a dessicator until used.

3.1.1.5 Bisphenol diacetate synthesis and purification.



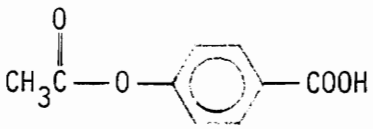
Hydroquinone diacetate



Biphenol diacetate

The bisphenols-hydroquinone and biphenol were derivatized into their respective diacetate forms by one of two methods. Both methods started out by refluxing acetic anhydride with the bisphenol. Typically, 50 grams of the bisphenol was refluxed with a tenfold molar excess of acetic anhydride and about 0.1 grams of sodium acetate, which served as catalyst. The bisphenol would dissolve as the acetic anhydride was heated. The reaction was kept at reflux temperatures for 4 hours. In Method 1, the excess acetic anhydride and acetic acid were removed by distillation. The product was then recrystallized twice from chloroform. In Method 2, the reaction mixture was cooled to room temperature and then poured into a large excess of water. The bisphenol diacetates being insoluble in water would precipitate. The acetic acid, hydrolyzed acetic anhydride, and sodium acetate were soluble in the water thus removing them from the product. The diacetate was then recrystallized twice from chloroform or toluene and dried for 24 hours under vacuum and low heat. The melting point of the 4,4'-biphenol diacetate was 160-163°C, while the melting point of the hydroquinone diacetate was 119-121°C.

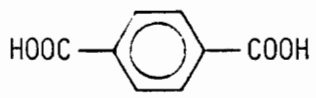
3.1.1.6 Synthesis and purification of p-acetoxybenzoic acid.



The p-acetoxybenzoic acid was prepared from p-hydroxybenzoic acid under Schotten-Baumann conditions. Twenty-five grams of para-hydroxy benzoic acid from the Aldrich Chemical Company was converted into its disodium salt using two equivalents of aqueous sodium hydroxide in a separatory funnel. Acetic anhydride (1.1 equivalents) was then added portionwise to the solution and the separatory funnel shaken vigorously after each addition. This produced a white precipitate. The separatory funnel was shaken an additional 10 minutes after all of the acetic anhydride was added. Dilute HCl was then added until the solution was acidic to pH paper. The white precipitate was then collected by suction filtration. The product was repeatedly washed with distilled water to remove any salts and excess HCl. The product was dissolved in 400 ml of chloroform and filtered through a paper filter. The volume was reduced to 300 ml and then the solution allowed to cool slowly to room temperature.

The fluffy white crystals were collected by suction filtration and dried 24 hours under vacuum and low heat (50-60°C). The melting point of the p-acetoxybenzoic acid was 189-191°C.

3.1.1.7 Terephthalic acid.

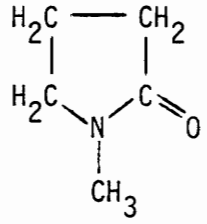


Terephthalic acid from Eastman Kodak Company was converted into its disodium salt using aqueous sodium hydroxide. The solution was filtered once to remove any insoluble material. The solution was then

acidified with HCl to regenerate the terephthalic acid. The white solid was isolated by suction filtration and washed repeatedly with distilled water. The product was dried for 24 hours at 80-90°C under vacuum, crushed, and dried an additional 24 hours.

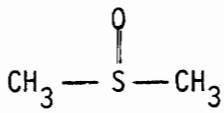
3.1.2 Solvents

3.1.2.1 N-Methyl-2-pyrrolidone (NMP).



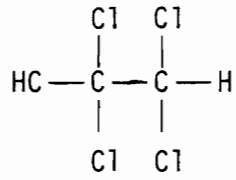
The NMP (Fisher certified grade) was stirred over calcium hydride for a minimum of 24 hours to remove any dissolved water. The NMP was then vacuum distilled from the calcium hydride with collection of the middle fraction boiling over a 3° range (b.p.=202°C at 760 mmHg).

3.1.2.2 Dimethylsulfoxide (DMSO).



Fisher certified grade DMSO was dried and distilled as per the NMP.

3.1.2.3 1,1,2,2-Tetrachloroethane (TCE).



The TCE was purified by vacuum distillation.

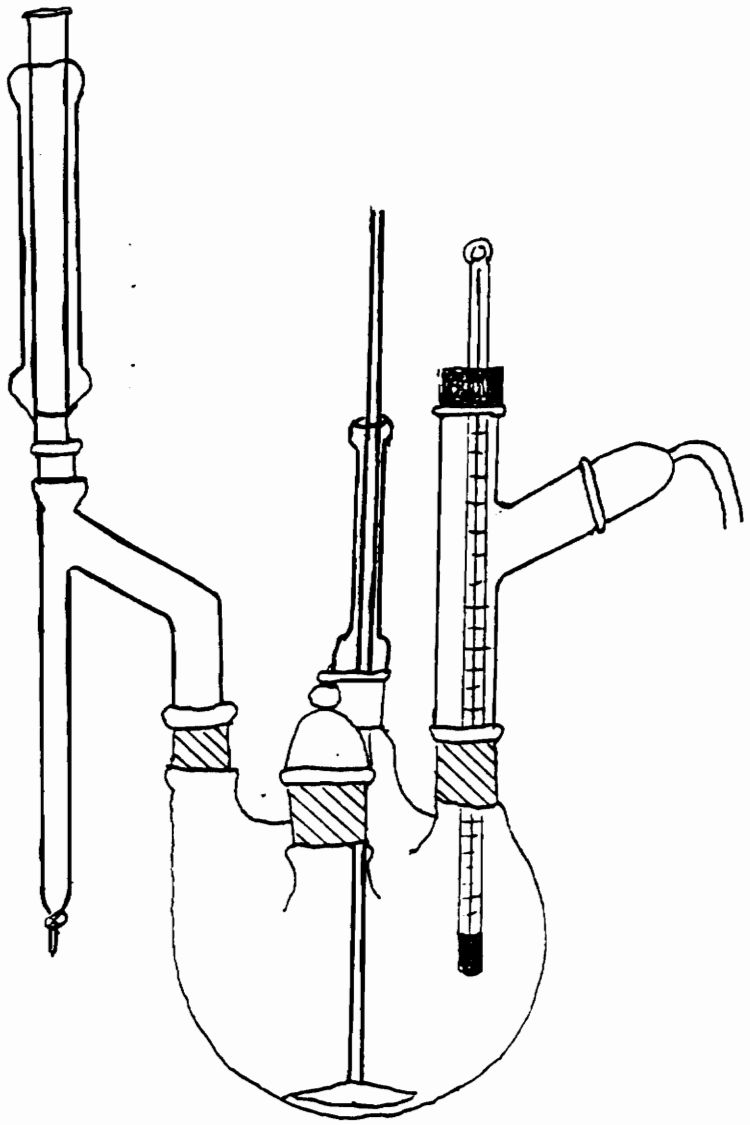
All other solvents were at least certified grade and were used without further purification.

3.1.3 Oligomers and Polymers

3.1.3.1 Hydroxyl terminated hydroquinone/biphenol polysulfones. Typically a hydroxyl terminated hydroquinone/biphenol polysulfone was synthesized in a 500 ml 4-neck round bottom flask. The flask was equipped with 1) an overhead stirrer, (2) a condenser on a Dean Stark trap, 3) a thermometer and gas inlet on a Y-adaptor, and 4) a stopper for addition of reactants. A sketch of the experimental apparatus is shown in Scheme 19. The materials needed for the synthesis of a 6,000 g/mol hydroxyl terminated polysulfone oligomer are:

4,4'dichlorodiphenylsulfone (DCDPS)	40.55 g (0.141 moles)
4,4'-biphenol (Bp)	13.97 g (0.075 moles)
Hydroquinone (Hq)	8.26 g (0.075 moles)
Potassium carbonate (K_2CO_3)	27.00 g (0.196 moles)
N-methyl-2-pyrrolidone (NMP)	200 ml
Toluene	100 ml

The argon purged flask was charged with the DCDPS, followed by the biphenol and hydroquinone. These monomers were weighed on a Teflon coated weighing pan so that they could be washed into the reaction flask with portions of the solvent to insure the desired stoichiometry. The NMP and toluene were then added and the temperature raised by means of a preheated silicon oil bath. Stirring was begun and the contents of the flask heated until a clear amber solution resulted. To this solution was added the potassium carbonate, which changed the color of the solution to a yellow-green.



SCHEME 19. Apparatus used in the synthesis of hydroxyl terminated Hq/Bp polysulfones.

The temperature was allowed to rise until the toluene refluxed and filled the Dean Stark trap. The temperature leveled off at about 140-150°C due to the refluxing toluene. The toluene azeotroped the water produced by the formation of the phenolate anions and was collected in the Dean Stark trap.

The temperature was maintained until all the water produced in the reaction was azeotroped off, which usually took about 3 hours. The temperature was then raised to 180-185°C by removing the water and some of the toluene which collected in the Dean Stark trap. The reaction was allowed to proceed for an additional 14-15 hours. The mixture at this point was almost black, with visible white specks of the potassium carbonate present. The mixture was then cooled to about 100°C and filtered hot through a coarse glass fritted filter. This filtering process removed the unreacted potassium carbonate and other insoluble salts from the mixture. Acetic acid was then added to the cooled solution to neutralize the phenolate end groups. This neutralization process produced a brown solution. The hydroxyl terminated polysulfone oligomer was isolated by addition of small portions of the solution to a tenfold excess of methanol in a rapidly stirred Waring blender. The light brown powdery oligomer was collected by suction filtration and washed repeatedly with water. The oligomer was dried in a vacuum oven at 100°C for 24 hours, crushed up, and dried for an additional 12 hours. The recovered yield for this reaction was nearly quantitative. The actual titrated molecular weight for this oligomer was 5350 g/mole.

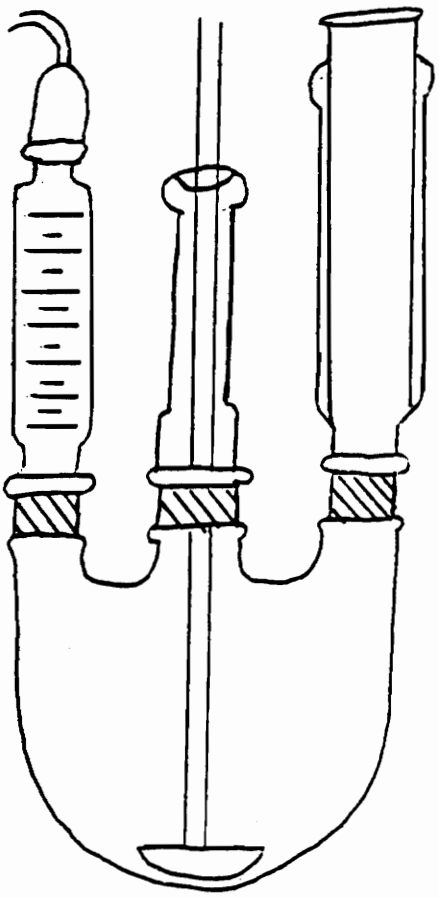
Minor modifications of this technique lead to hydroxyl terminated polysulfones with varying mole ratios of the hydroquinone and biphenol.

3.1.3.2 Poly(arylene ether sulfone)-poly(arlene terephthalate) segmented copolymer.

3.1.3.2.1 Via solution technique. Once the hydroxyl terminated hydroquinone/biphenol polysulfone oligomers were synthesized and characterized as to their number average molecular weight ($<M_n>$), then they were copolymerized to high molecular weight. The solution process employed the following materials:

5350$<M_n>$ hydroxyl terminated Hq/Bp polysulfone	4.000 g (7.5×10^{-4} moles)
4,4'-Biphenol (Bp)	0.014 g (7.5×10^{-5} moles)
Terephthaloyl chloride (TC)	0.167 g (8.25×10^{-4} moles)
Triethylamine (TEA)	0.29 ml (2.09×10^{-3} moles)
Methylene chloride (CH_2Cl_2)	100.0 ml
NMP	< 1 ml

The reaction was carried out in a 250 ml, 3 neck, round bottom flask. The flask was equipped with 1) an overhead stirrer, 2) condenser, and 3) an addition funnel with gas inlet on top. The experimental apparatus is shown in Scheme 20. To the argon purged flask was added the hydroxyl terminated oligomer. This oligomer was dissolved with magnetic stirring using 30 ml of the methylene



SCHEME 20. Apparatus used in the synthesis of polysulfone-polyester segmented copolymers in solution.

chloride. The triethylamine was added to this solution. The triethylamine serves as acid acceptor and catalyst. The biphenol was then added to this solution. The biphenol was not soluble in CH_2Cl_2 so NMP was added dropwise until the biphenol dissolved. Separately, the terephthaloyl chloride was dissolved in 50 ml of CH_2Cl_2 and added dropwise to the solution through the addition funnel. The TC was added over the course of 1 hour. The addition funnel was washed with the remainder of the CH_2Cl_2. The reaction was allowed to proceed for 8 hours after all of the TC was added. The solution was then added incrementally to a tenfold excess of methanol in a stirred blender. The precipitated polymer was an off-white color and fibrous. The polymer was collected by suction filtration and washed several times with water and finally with methanol. The material was dried under vacuum at 100°C for 24 hours. The polymer was obtained in near quantitative yields.

3.1.3.2.2 Via interfacial technique. Another route developed to synthesize the poly(arylene ether sulfone)-poly(arylene terephthalate) segmented copolymers was the interfacial process. Interfacial copolymerizations were carried out in a laboratory Waring blender. A typical reaction was conducted with the following materials:

Hydroxyl terminated 5350$<M_n>$ Hq/Bp polysulfone	3.00 g (5.6×10^{-4} moles)
4,4'-Biphenol	0.01 g (5.6×10^{-5} moles)
Terephthaloyl chloride	0.13 g (6.16×10^{-4} moles)

Sodium hydroxide (NaOH)	0.12 g (3.10×10^{-3} moles)
Tetraethylammonium chloride (TEAC)	0.01 g (5.6×10^{-5} moles)
Methylene chloride	30 ml
Water	20 ml

To the Waring blender was charged the 5350$<M_n>$ hydroxyl terminated Hq/Bp polysulfone oligomer. The oligomer was dissolved using 20 ml of the CH_2Cl_2 with stirring. Separately, the biphenol, NaOH, and TEAC were dissolved in 10 ml of water. The NaOH served to form the disodium salt of the biphenol rendering it soluble in the water. The TEAC functions as the phase transfer catalyst. This aqueous solution was slowly added to the oligomer solution in the blender with no stirring. The vessel was rinsed with 10 ml of water and the wash added to the blender. Finally the terephthaloyl chloride, having been predissolved in 10 ml of the CH_2Cl_2, was added to the blender. The remainder of the CH_2Cl_2 being used to wash the flask containing the terephthaloyl chloride. The reaction mixture was then rapidly stirred for 20 minutes. Periodically the contents of the blender were checked, if the mixture appeared extremely viscous 10 ml aliquots of CH_2Cl_2 were added to lower the viscosity. At the end of the 20-minute time period, the mixture was a white emulsion. The polymer was isolated by adding small portions of the mixture to a tenfold excess of methanol contained in another Waring blender. The polymer was isolated by suction filtration, washed repeatedly with water and finally with methanol. Drying of the polymer was accomplished under vacuum at 100°C for 24 hours.

3.1.3.3 Carboxyl terminated hydroquinone/biphenol polysulfone oligomers. A novel synthesis was developed to produce carboxyl terminated oligomers. A list of materials needed for the synthesis of a 5000 $< M_n >$ oligomer are:

4,4'-Dichlorodiphenylsulfone (DCDPS)	3.5895 g (1.25×10^{-2} moles)
4,4'-Biphenol	1.0825 g (5.81×10^{-3} moles)
Hydroquinone	0.6401 g (5.81×10^{-3} moles)
p-Hydroxybenzoic acid (pHBA)	0.2506 g (1.81×10^{-3} moles)
Potassium carbonate (K_2CO_3)	2.74 g (1.98×10^{-2} moles)
Dimethylsulfoxide (DMSO)	50 ml
Toluene	25 ml

A 250 ml 3-neck round bottom flask was equipped as in Scheme 19, with an overhead stirrer, condenser, Dean Stark trap, gas inlet tube, and thermometer. To this argon purged flask was charged the DCDPS, biphenol, hydroquinone, and p-hydroxybenzoic acid, in that order. The weighing pans were rinsed with small portions of the DMSO to insure proper stoichiometry. The remainder of the DMSO and the toluene were then added to the flask. The contents of the flask dissolved upon heating with a silicon oil bath (150°C) and stirring. Once a homogeneous solution was attained, the potassium carbonate was added producing a reddish-brown mixture. The toluene was allowed to vigorously reflux and azeotrope the water formed in the reaction into the Dean Stark trap. The reaction was allowed to proceed for 4 hours at temperatures between 130-140°C and then the temperature was raised

to about 160°C for an additional 14-15 hours. The contents of the flask were cooled to about 100°C and then filtered through a coarse glass frit to remove the insoluble salts. The potassium carboxylate end groups of the oligomer were converted to their free acid form by neutralizing with aqueous HCl. The carboxyl terminated Hq/Bp polysulfone oligomer was isolated by adding small portions of the solution to a tenfold excess of methanol in a stirred Waring blender.

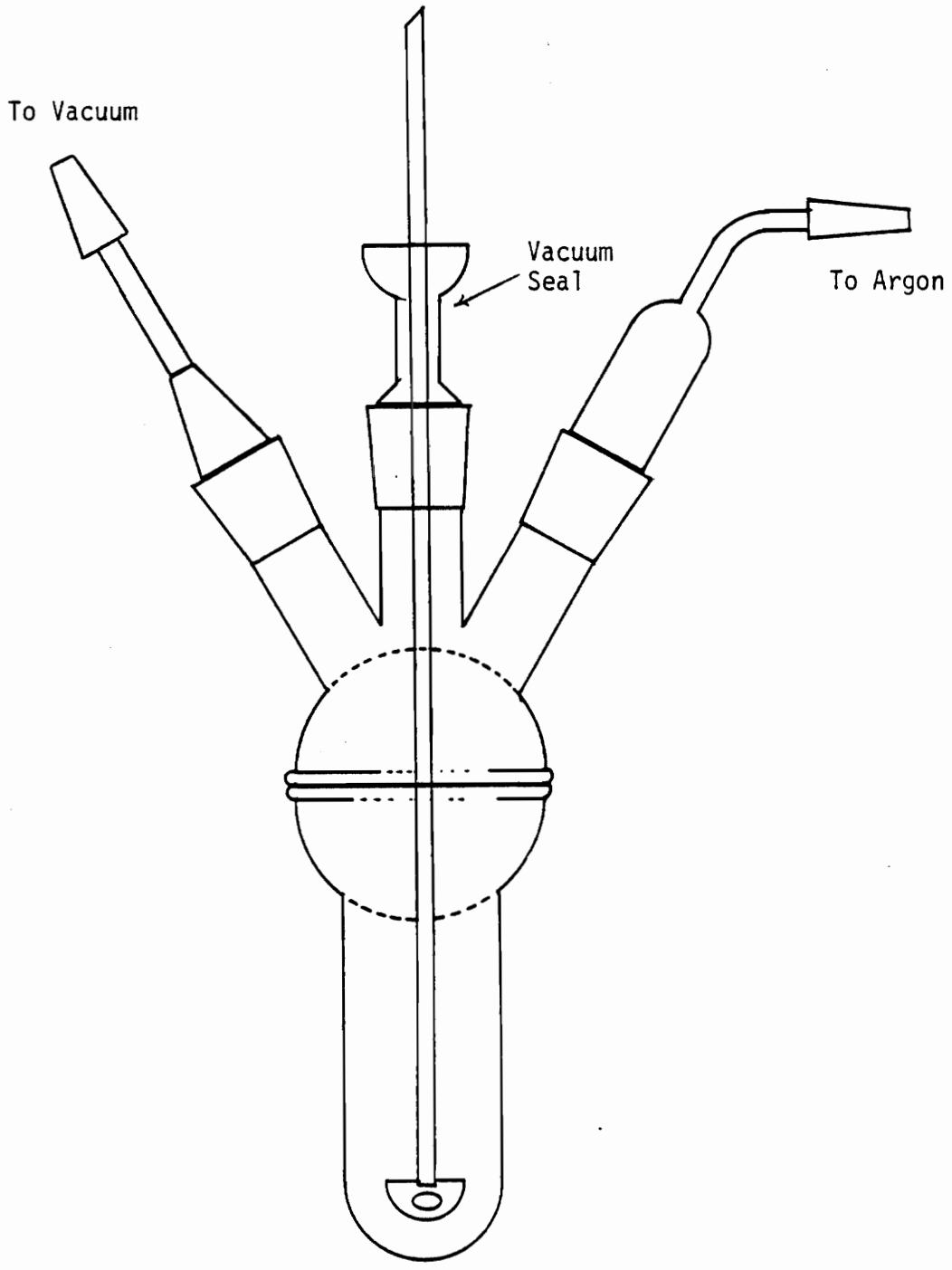
The oligomer was collected by suction filtration and washed repeatedly with water and then methanol. The oligomer was placed in a vacuum oven for 24 hours at 100°C to dry. This reaction was found to be near quantitative upon calculation of the recovered yield. Titration of the carboxyl end groups of the oligomer gave a number average molecular weight of 6200 g/mole.

3.1.3.4 Poly(arylene ether sulfone)-poly(arylate) copolymer from carboxyl terminated oligomer. The carboxyl terminated Hq/Bp polysulfone was chain extended with biphenol diacetate in a melt acidolysis reaction to form high molecular weight polymer. The materials needed for this melt acidolysis reaction were:

Carboxyl terminated 6200 $<M_n>$ Hq/Bp polysulfone oligomer	5.0012 g (8.05×10^{-4} moles)
4,4'-biphenol	0.1499 g (8.05×10^{-4} moles)
Acetic anhydride $(Ac)_2O$	10 ml
Sodium acetate	0.01 g

The reaction was carried out in an in-house made glass apparatus shown in Scheme 21. The carboxyl terminated polysulfone oligomer and biphenol were charged into the reaction vessel. A steady stream of argon was passed into the vessel through the gas inlet tube and out through a condenser which replaces the vacuum adaptor initially in the apparatus. The acetic anhydride and sodium acetate were then added to the reaction vessel. The vessel was heated by a fluidized sand bath until the acetic anhydride began to reflux around 140°C. The biphenol and sodium acetate dissolved in the hot acetic anhydride while the polysulfone oligomer did not. Stirring was accomplished via an overhead mechanical stirrer. The acetic anhydride was allowed to reflux for 4 hours.

The condenser was then replaced with a Dean Stark trap and the flow of argon increased to distill off the excess acetic anhydride and acetic acid. The Dean Stark trap was replaced with the vacuum adaptor and the temperature raised over the course of an hour to 200°C. A slight vacuum (around 5 Torr) was then applied for an additional hour while the temperature was raised to 250°C. The temperature was then raised to 300°C over a period of 1 hour while the pressure was lowered to around 0.5 Torr. The reaction was allowed to proceed for an additional 10 hours. The contents of the reaction vessel were cooled to room temperature, removed from the vessel, and placed in a Soxhlet extractor. The polymer was extracted for 12 hours with acetone. The polymer was then dried under vacuum at 100°C for 12 hours.



SCHEME 21. Apparatus used in the melt acidolysis technique.

3.1.3.5 Synthesis of acetate terminated hydroquinone/biphenol polysulfone. A hydroxyl terminated hydroquinone/biphenol polysulfone was derivatized into a hydroquinone/biphenol polysulfone diacetate oligomer for further reaction in a melt acidolysis process. Typically, the hydroxyl terminated polysulfone was reacted in solution with acetic anhydride to form the desired derivative.

The materials used in this reaction were:

6700 $<M_n>$ Hydroxyl terminated hydroquinone/biphenol polysulfone	20.29g (3.02×10^{-3} moles)
Acetic Anhydride	10 ml (.11 moles)
Sodium acetate	0.1g (1.2×10^{-3} moles)
Chloroform	100 ml

The reaction was run in a 250 ml 4-neck flask equipped with a water cooled condenser, gas inlet, thermometer, and stopper. The hydroxyl terminated hydroquinone/biphenol polysulfone oligomer was weighed into the reaction flask. The polysulfone oligomer was weighed into the reaction flask. The polysulfone oligomer was dissolved in chloroform. After all of the oligomer was dissolved, the acetic anhydride and sodium acetate were added. The reaction flask and contents were heated by means of a silicone oil bath until the chloroform was vigorously refluxing. The reaction was allowed to proceed for 16 hours. The hydroquinone/biphenol polysulfone diacetate oligomer was isolated by precipitation in a tenfold excess of methanol in a blender. The oligomer was isolated by vacuum filtration, washed

with water and finally with methanol. Drying of the oligomer was accomplished in a vacuum oven at 100°C for 24 hours.

3.1.3.6 Synthesis of hydroquinone/biphenol polysulfone-polybiphenol terephthalate 50/50 wt % copolymer via a heat transfer melt acidolysis process. A hydroquinone/biphenol polysulfone diacetate oligomer was copolymerized with biphenol diacetate and terephthalic acid to form a segmented copolymer. The materials needed for this melt acidolysis reaction were:

6700<M_n>hydroquinone/biphenol polysulfone diacetate	2.00g (2.94×10^{-4} moles)
4,4'-Biphenol diacetate (BPD)	5.08g (1.88×10^{-1} moles)
Terephthalic acid (TA)	3.17g (1.91×10^{-2} moles)
Diphenylsulfone (heat transfer medium)	40g

The melt acidolysis reaction vessel in Scheme 21 was used in this reaction. The polysulfone diacetate oligomer, biphenol diacetate, terephthalic acid, and diphenylsulfone were charged into the reaction vessel in that order. The reaction vessel was lowered into a 100°C sandbath and a steady stream of argon passed through the vessel. A drying tube replaced the gas outlet tube in this reaction. The contents of the flask were stirred vigorously while the temperature of the sandbath was raised to 280°C over the course of 1 hour. The diphenyl sulfone heat transfer medium melted around 125°C. After the

diphenyl sulfone melted, the contents of the flask were an opaque white color. The flow of argon was increased to remove the acetic acid formed in the reaction. The reaction was held under these conditions for 12 hours. The temperature was then raised to 300°C for an additional 5 hours. The contents of the vessel were cooled to around 150°C and poured into a tenfold excess of acetone. The product was placed in a Soxhlet extractor and extracted for 16 hours with hot acetone which removes the diphenyl sulfone heat transfer medium. The product was then dried under vacuum at 100°C for 24 hours. A mechanical recovered yield of 71% was realized for this segmented copolymer.

3.1.3.7 Synthesis of hydroquinone/biphenol polysulfone-polyoxybenzoate segmented copolymer via a heat transfer melt acidolysis process. Segmented copolymers containing 50 weight percent of the polyoxybenzoate segment were synthesized in a melt acidolysis process. A heat transfer medium was employed in this process. The reaction was carried out in a similar manner to the polysulfone-poly(biphenol terephthalate) melt acidolysis process. The materials employed in this reaction were:

6700 $<M_n>$ Hydroquinone/biphenol polysulfone diacetate oligomer	3.00g	(4.41×10^{-4} moles)
Terephthalic acid	0.0732g	(4.41×10^{-4} moles)
p-Acetoxybenzoic acid	4.53g	(2.51×10^{-2} moles)
Diphenyl sulfone (heat transfer medium)	30.00g	

The polysulfone diacetate oligomer, terephthalic acid, p-acetoxybenzoic acid and diphenyl sulfone were charged into the reaction flask (see Scheme 21) in that order. The gas outlet tube was replaced with a drying tube. The reaction flask was lowered into a 100°C fluidized sandbath and a steady stream of argon passed through the vessel. Stirring was started as the temperature of the sandbath was rapidly raised to 240°C. The reaction was allowed to proceed for 12 hours at this temperature. The reaction was run an additional 5 hours at 300°C. The contents of the flask were cooled to about 150°C and poured into a tenfold excess of acetone. The isolated polymer was extracted with hot acetone in a Soxhlet extractor for 16 hours to remove the diphenyl sulfone. The product was dried under vacuum for 24 hours at 100°C. A recovered yield of 80% was obtained for this reaction.

3.1.3.8 <u>One pot synthesis of hydroquinone/biphenol polysulfone-poly(biphenol terephthalate) segmented copolymer</u>. The hydroquinone/biphenol polysulfone-poly(biphenol terephthalate) copolymers were also synthesized without the additional steps of isolation of the diacetates of the polysulfone and biphenol. A melt acidolysis process was again used but without the heat transfer medium, diphenyl sulfone. A list of the materials utilized in this reaction follows.

6700 $< M_n >$ Hydroxyl terminated hydroquinone/biphenol polysulfone	5.00g (7.35×10^{-4} moles)
4,4'-biphenol	2.91g (1.56×10^{-2} moles)

Terephthalic acid	2.71g (1.63×10^{-3} moles)
Sodium acetate (catalyst)	0.05g (6.1×10^{-4} moles)
Acetic anhydride	20 ml (0.18 moles)

The preformed hydroxyl terminated hydroquinone/biphenol polysulfone oligomer was charged into the reaction vessel (see Scheme 21). The gas outlet port was replaced with a water cooled condenser in the initial part of the reaction. The biphenol and terephthalic acid were then added to the vessel.

The acetic anhydride and sodium acetate were then added through the gas inlet port in the top of the reaction vessel. The contents of the flask were stirred by means of a high torque overhead stirrer. The temperature was quickly raised to acetic anhydride reflux (~140°C) by means of a heating mantle. The heating mantle was packed with glass wool to insure good heat distribution. The acetic anhydride was allowed to reflux for 4 hours. The excess acetic anhydride and acetic acid were removed by attaching a vacuum adaptor to the reaction vessel. The vacuum was adjusted to 2 to 5 Torr by means of the argon gas flow. The pressure was allowed to return to atmospheric pressure by removing the vacuum source. The temperature of the reaction was raised to 250°C over a period of 1 hour and kept at this temperature for 8 hours. The contents of the flask became very viscous during this time. Vacuum was reapplied and allowed to adjust to 0.5 Torr by stopping the flow of argon. The temperature was raised to 300 ± 10°C

for an additional 4 hours. Finally, the contents of the reaction vessel were cooled to room temperature. The polymer was removed from the reactor by cooling with liquid nitrogen and pulverizing the polymer. The product was placed in a Soxhlet extractor and extracted with hot acetone for 12 hours. The polymer was dried to constant weight in a vacuum oven at 50°C.

3.1.3.9 One pot synthesis of hydroquinone/biphenol polysulfone-polyoxybenzoate segmented copolymers. The hydroquinone/biphenol polysulfone-poly(oxybenzoate) segmented copolymers were synthesized from the following materials.

6700 $\langle M_n \rangle$ Hydroxyl terminated hydroquinone/biphenol polysulfone	3.00g	(4.46×10^{-4} moles)
Terephthalic acid	0.0741g	(4.46×10^{-4} moles)
p-Hydroxybenzoic acid	3.47g	(2.51×10^{-2} moles)
Sodium acetate	0.05g	(6.1×10^{-4} moles)
Acetic anhydride	20 ml	(0.18 moles)

This melt acidolysis reaction was carried out following the same procedure as for synthesizing the polysulfone-poly(biphenol terephthalate) segmented copolymers.

3.1.4 Analysis of Oligomers and Polymers

3.1.4.1 Titration of hydroxyl terminated oligomers. In order to characterize the hydroxyl terminated poly(arylene ether sulfone)

oligomers as to number average molecular weight a potentiometric titration was developed.[85,100] These titrations were carried out using a Fisher Scientific Titrimeter II automatic titrator. A standard calomel electrode was used with a double junction reference. All titrations were performed using a ten millimeter burette filled with a standardized methanol solution of tetramethylammonium hydroxide. The titrator was in the automatic endpoint seeking mode. Previous titrations involving hydroxyl terminated polysulfones were carried out with either dimethylacetamide (DMAc) or dimethylformamide (DMF) as the solvent. However, N-methyl-2-pyrrolidone (NMP) was found to work equally as well as DMAc and DMF and was used as the solvent for the titrations involving hydroxyl terminated hydroquinone/biphenol polysulfone oligomers.

A typical titration of a hydroxyl terminated hydroquinone/biphenol polysulfone oligomer of theoretical 5000 $<M_n>$ was performed as follows. A 0.2524g sample of the polysulfone oligomer was weighed into a 100 ml beaker. The oligomer was dissolved using 40 ml of freshly distilled NMP. The electrodes were lowered into the solution and stirring of the solution was accomplished by a magnetic stir bar. The titration was started after the electrometer stabilized. The titration was continued until a peak was observed on the derivative curve trace recorded on the strip chart recorder. The electrodes were thoroughly rinsed with NMP and then isopropanol and replaced in a buffer solution. In order to calculate the number average molecular weight, a blank titration was first determined. The blank titration was performed as above but with only the same volume

of NMP, no sample was used. The blank volume, if any, was subtracted from the endpoint volume for the sample titration before the number average molecular weight of the oligomer was determined. Generally, a 40 ml volume of NMP produced no peaks whn titrated thus no blank volume correction was needed. The number average molecular weight was calculated within the microprocessor using the formula:

$$\langle M_n \rangle = \frac{(S.W.)(\#E.G.)}{(Conc.)(Vol.)}$$

where S.W. is the sample weight in grams, #E.G. is the number of end groups per molecule, Conc. is the concentration of the tetramethyl ammonium hydroxide titrant in moles/ml, and Vol. is the endpoint volume of titrant in milliliters. Thus for this example, the calculation was:

$$\langle M_n \rangle = \frac{(0.2524g)(2)}{(1.94 \times 10^{-4} \frac{moles}{ml})(0.63\ ml)} = 4130\ gm/mole$$

An average of three titrations was then used as the number average molecular weight of the polymer. In this case, the average value of the oligomer was 4123 $\langle M_n \rangle$.

3.1.4.2 Titration of carboxyl terminated hydroquinone/biphenol polysulfone oligomers. The titration of carboxyl terminated

hydroquinone/biphenol polysulfone oligomers was accomplished in a similar fashion to the titration of hydroxyl terminated polysulfone oligomers. The endpoints for the carboxyl terminated oligomers were found to be more prominent than the hydroxyl terminated endpoints, as one would expect from their relative acidities.

3.1.4.3 Fourier transform infrared spectroscopy. Fourier Transform Infrared (FT-IR) spectra were obtained on the oligomers and polymers using a Nicolet MX-1 spectrometer. The spectra were run in three different ways, as thin cast films on salt plates, as thin films (both cast and compression molded), or as potassium bromide pellets. The thin cast films were made from a 10% solution of the oligomer or polymer in a volatile solvent such as chloroform. The cast films were dried under vacuum under low heat for a minimum of 30 minutes before the spectra were recorded.

3.1.4.4 Intrinsic viscosity determinations. Intrinsic viscosities (IV) of the oligomers and polymers were measured using a Cannon-Ubbelhodhe dilution viscometer. Four concentrations of the polymer in an appropriate solvent were used for the measurements. All the determinations were carried out in a thermostatically controlled water bath at 25°C. Generally, three pure solvent times were determined followed by three measurements of the time a solution of 0.1g in 25 ml of solvent had. Ten ml of this solution were then diluted with 5 ml of the solvent and three more flow times were determined. This new solution was diluted with 5 ml of solvent and

three more flow times measured. Finally, this new solution was diluted with 5 ml of solvent and an average of three measurements were used. The concentrations were converted into grams/deciliter and the times in seconds. The intrinsic viscosity value in deciliters/gram were determined by a computer program which determines the intercept of the specific viscosity versus concentration relationship. The specific viscosity in mathematical terms is:

$$\eta_{sp} = \frac{\eta-\eta_0}{\eta_0} \simeq \frac{t-t_0}{t_0}$$

where η is the viscosity of solution and η_0 is the viscosity of the solvent. The specific viscosity is also approximately equal to the ratio of flow times for the solvent and solution. Thus, the intrinsic viscosity is actually determined to be the intercept of the flow times versus concentration plot. A typical measurement of an intrinsic viscosity of the hydroquinone/biphenol polysulfone-poly(biphenol terephthalate) segmented copolymer with 25 mole % biphenol and 6700 $\langle M_n \rangle$ polysulfone segment was conducted as follows.

The polymer (0.1058g) was weighed into a 25 ml volumetric flask. The polymer was dissolved using chloroform and the volumetric flask filled to the mark with chloroform. The viscometer was filled with 10 ml of pure chloroform and three flow times within one tenth of a second of one another measured. The viscometer was emptied and dried and 10 ml of the polymer solution was filtered through a coarse glass frit into the viscometer. Three flow times were then measured for

this solution. To this solution in the viscometer was added 5 ml of chloroform, the solution thoroughly mixed and three flow times measured. To this new solution was added another 5 ml of chloroform and three more flow times measured. This process was repeated once more to give three flow times for four different concentrations of the solution plus three flow times for the solvent. The data for these measurements are compiled in Table 5. The intrinsic viscosity value $[\eta]^{CHCl_3}_{25°C}$ = 0.78 dl/g for this polymer.

3.1.4.5 Reduced viscosity determination. In some cases, a reduced viscosity value was determined for a polymer. A reduced viscosity value was measured by determining three flow times for the pure solvent and comparing the average time with the average flow time for a 1 wt % polymer solution. The mathematical relationship for a reduced viscosity is:

$$\eta_{red} = \frac{\eta_{sp}}{C} \simeq \frac{(\frac{t-t_0}{t_0})}{C}$$

where η_{sp} is the specific viscosity and C is the concentration of the polymer solution. The specific viscosity value is approximated by the flow times for the pure solvent (t_0) and the polymer solution flow times (5).

A typical reduced viscosity determination was conducted as follows.

TABLE 5

DATA FOR INTRINSIC VISCOSITY MEASUREMENT IN CHLOROFORM AT 25°C ON 6700 $\langle M_n \rangle$ Hq/Bp PSF-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMER CONTAINING 25 MOLE % BIPHENOL

Concentration (g/dl)(1)	Flow Times (sec)			Dilution Factor(2)
	1	2	3	
0 (pure solvent)	85.1	85.1	85.2	0
0.4232	116.0	116.1	116.1	10/10
0.2821	105.5	105.6	105.6	10/15
0.2116	100.1	100.0	100.0	10/20
0.1693	96.8	96.8	96.7	10/25

(1) Original weight of polymer sample = 0.1058g
Intrinsic viscosity $[\eta]$ = 0.7832 dl/g

(2) $\frac{\text{ml of original solution}}{\text{total ml of solution}}$

Three flow times for trifluoromethane sulfonic acid (triflic acid) were determined in a Cannon-Ubbelhodhe dilution viscometer in a water bath at 25°C. The polymer sample (0.2420g of 6700 $< M_n >$ Hq/Bp polysulfone-poly(biphenol terephthalate) with 50 wt % polybiphenol terephthalate) was dissolved in a 25 ml volumetric flask with triflic acid. Immediately after the polymer dissolved three flow times were measured for this solution. The calculations for the reduced viscosity were made as follows:

Average of three solvent flow times (t_0) = 125.63 seconds

Average of three polymer solution flow times (t) = 150.87 seconds

Concentration of solution (C) = $\frac{0.2420g}{0.25\ dl}$ = 0.9680 g/deciliter

$$\eta_{red} = \frac{(\frac{t-t_0}{t_0})}{C} = \frac{(\frac{150.87-125.63}{125.63})}{0.9680\ g/dl} = 0.21\ dl/g$$

3.1.4.6 Gel permeation chromatography. Gel permeation chromatography was used to compare qualitatively the relative molecular weights of the polysulfone oligomers and the polymers made from them. The molecular weight distributions were also compared by this technique. A Waters 244 instrument with Zorbax PSM 1000.Cos columns or microstyrogel columns of 500, 10^3, 10^4, 10^5, and 10^6 angstrom pore size. A differential refractive index detector was used. A 0.25 to 0.30 weight percent solution in chloroform or tetrahydrofuran was used with a flow rate of 0.5 or 1.0 ml/min.

3.1.4.7 Nuclear magnetic resonance spectroscopy. Proton and carbon 13 magnetic resonance spectra were obtained on the oligomers and polymers using two different spectrometers. One instrument was a Varian EM-340 90MHz spectrometer while the other was a 200 MHz IBM FT-NMR with a multinuclear probe, operating at 50.4 MHz for ^{13}C nuclei. Spectra were run on 10 wt% solutions in deuterated chloroform for the proton spectra and 25 wt% solutions in deuterated dimethylsulfoxide or chloroform for the ^{13}C spectra. Tetramethylsilane was used as the lock reference for the 'H spectra while the solvent was used as the lock reference for the ^{13}C spectra.

3.1.4.8 Differential scanning calorimetry. Some of the thermal properties of the polymers and oligomers were determined by differential scanning calorimetry (DSC). The glass transition temperatures (Tg), melting transitions (Tm), and any liquid crystal melting transitions (T_{LQ}) were obtained using a Perkin-Elmer Model DSC-2. The instrument was periodically calibrated using an indium standard for the heat of fusion calibration and high purity solvents and metal standards for the temperature calibrations. The melting and liquid crystal transitions were determined as the highest point of the peaks in the first heating scan. The glass transition temperatures were measured on the second heating scan and were reported as the midpoint of the change in slope of the baseline. Unless otherwise noted, the heating rates were 20 K/min. The samples were tested as cast films, compression molded films, or as polymerized powders.

3.1.4.9 Hot stage optical microscopy. Optical micrographs of the polysulfone oligomers and segmented copolymers synthesized from them were taken using a polarizing microscope equipped with a Mettler hot stage. The samples were either melted between two microscope slides in the hot stage itself or melted with slight pressure in a compression molding machine. The heating rate was 10°C/min from room temperature to 350°C unless otherwise noted.

3.1.4.10 Wide angle X-ray scattering. Wide angle X-ray scattering (WAXS) was performed on selected segmented copolymers. The WAXS patterns were obtained using a table top Philips generator equipped with a Worhus camera. Solution cast as well as compression molded samples of the polymers were examined.

3.1.5 Sample Preparation

For characterization purposes, many of the oligomers and segmented copolymers had to be in film form. The polymer films were also checked for color, optical clarity, and overall mechanical integrity.

3.1.5.1 Solvent casting procedure. Many of the more soluble oligomers and copolymers were dissolved in a suitable solvent and cast into film form. Typically, 1 gram of the oligomer or copolymer was dissolved in 10 ml of chloroform. If the sample was soluble in both chloroform and methylene chloride, chloroform was chosen as the solvent since it evaporates slower giving a more uniform film. The

resulting polymer solution was filtered through glass wool to remove any dust or insoluble material in the solution. The filtered solution was then transferred to a 9 cm diameter petri dish. The petri dish was covered to limit the rate of evaporation of the solvent and to exclude dust from the sample. The film was allowed to air dry for 10-12 hours and then dried under vacuum for an additional 12-15 hours. The film was removed from the petri dish by prying an edge of the film up and allowing air under the film. The films which could not be removed in this manner were soaked in cold water to remove them. The films produced in this manner were of the order of 2 to 4 mils (0.002 to 0.004 inches) thick.

3.1.5.2 Compression molding procedure. Some polymers were made into film form by compression molding of the sample. Typically, the Pasadena compression molding press was heated to 300°C for the known amorphous samples or 400°C for the semicrystalline copolymers. Two 7 in. x 7 in. ferrotype plates (Apollo Metals Company) were washed with acetone and then methylene chloride to remove any grease or oils on the surface of the mirror finish. The ferrotype plates were then sprayed with silicone mold release agent. One to two grams of the polymer sample was then placed in the center of one of the plates. The other plate was used to cover the sample. The two plates with the sample between them was sandwiched between two heavy iron plates. This entire assembly was placed between the preheated platens of the compression molder. The platens were just brought into contact with the assembly with essentially no pressure until the sample came up to

the temperature of the platens. The pressure was then increased quickly to 10,000 psi and then lowered to release any entrapped gas within the polymer sample. This was repeated a minimum of three more times. The pressure was then increased to 20,000 to 40,000 psi depending on the sample and kept there for 30 to 60 seconds. The polymer film was then obtained by either removing the ferrotype plates and immersing them in cold water or by cooling the entire assembly in the compression press. The films were generally between 4 to 10 mils thick depending upon the temperature and pressure used in forming them.

3.1.6 Solubility Characteristics

A qualitative test was used to determine the solubility characteristics of the poly(arlyene ether sulfone)-poly(arylate) segmented copolymers. In this test, a small amount (~0.25 grams) of the polymer sample was placed in each of three different test tubes. To the first test tube was added 10 ml of chloroform, to the second NMP, and to the third triflic acid. The mixtures were allowed to sit with occasional stirring for 30 minutes. The solubility of the polymer sample in each of the solvents were noted at the end of the time period. If the sample did not appear to be soluble in a particular solvent, the mixture was heated by means of a hot air gun. The solubility was again checked after heating. The solubility of each polymer sample was noted as being either soluble or not soluble in the particular solvent and whether the solvent was hot or not.

CHAPTER 4

RESULTS AND DISCUSSION

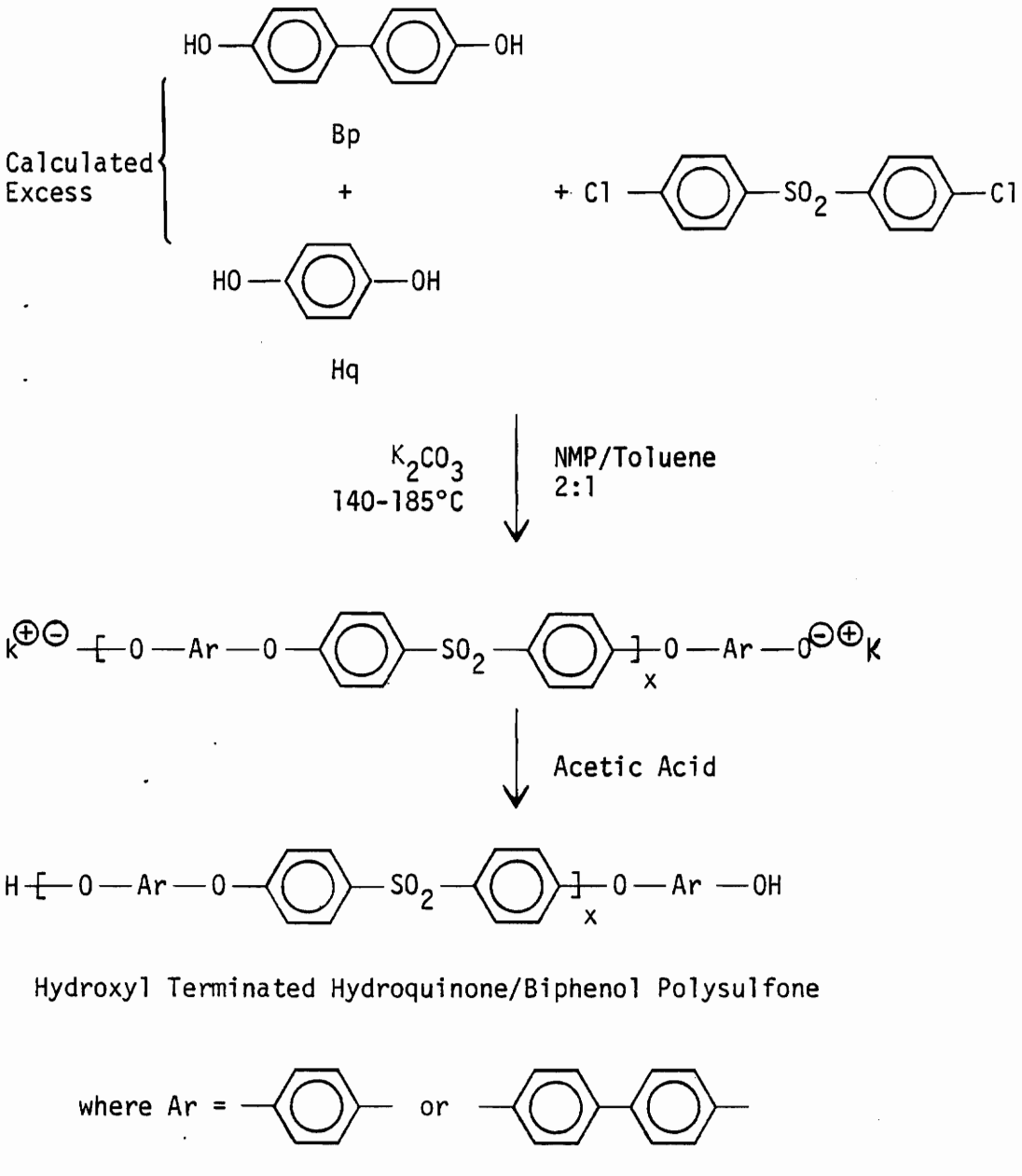
4.1 Introduction

There has been a proliferation of work reported in the literature related to copolymers composed of rubber-glass or rubber-crystalline morphologies. In contrast, there has been very little study of glass-glass or glass-crystalline copolymers. What has been reported indicates that these materials offer many unique and improved properties over existing polymers. The synthesis and properties of copolymers made from two "hard" segments, where one segment is potentially anisotropic, would seem to be an area of great academic as well as industrial importance. The synthesis and characterization of these types of morphologies in segmented copolymers to provide unique and improved properties deserve further investigation.

4.2 Synthesis of Hydroxyl Terminated Poly(Arylene Ether Sulfone) Oligomers

There are basically two methods by which segmented copolymers can be formed. One method is by synthesizing the two segments separately and then linking them together through reactive endgroups or with a coupling agent. The approach to be discussed here is that of synthesizing one of the segments and then polymerizing the second segment in the presence of the first. The first segment is randomly or alternately coupled into the polymer chain through reactive endgroups. In order to synthesize these segmented copolymers, the first segment (in this case, a poly(arylene ether sulfone)) had to be synthesized with functional endgroups and with a controlled molecular weight.

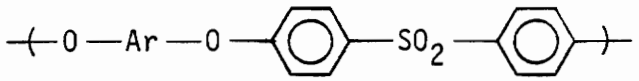
The hydroxyl terminated hydroquinone/biphenol polysulfone oligomers of controlled molecular weight were synthesized by the N-methyl-2-pyrrolidone/potassium carbonate technique.[22,23] The molecular weight as well as the functionality of the hydroquinone/biphenol polysulfone oligomers was controlled by the use of a calculated excess of the bisphenols. The excess of the bisphenols was calculated according to the Carothers equation.[35] The reaction scheme for a hydroxyl terminated hydroquinone/biphenol polysulfone is shown in Scheme 22. Scheme 23 shows the calculations made in order to synthesize a hydroquinone/biphenol polysulfone of 3000 number average molecular weight. From Scheme 23, the moles of hydroquinone and biphenol are greater than the moles of dichlorodiphenylsulfone thus limiting the molecular weight to 3000

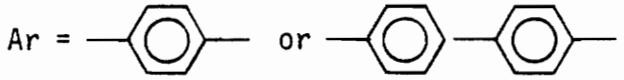


Hydroxyl Terminated Hydroquinone/Biphenol Polysulfone

where Ar = or

SCHEME 22. Reaction scheme for hydroxyl terminated hydroquinone/ biphenol polysulfone.

Repeat Unit 

Ar =  1:1

Target Theoretical Molecular Weight = 3000 g/mole

Repeat Unit Molecular Weight = 362.41 g/mole

Repeat Unit Molecular Weight = MW of DCDPS (287.16 g/mole) added to the average molecular weight of a 50/50 molar mixture of hydroquinone (110.12 g/mole) and biphenol (186.22) minus the MW of two moles of the byproduct HCl (36.46) which in mathematical form is:

$$287.16 + \tfrac{1}{2}(110.12 + 186.22) - 2(36.46) = 362.41 \text{ g/mole.}$$

$$\text{Degree of Polymerization (D.P.)} = \frac{3000 \text{ g/mole}}{362.41 \text{ g/mole}/2} = 16.5558$$

$$\text{D.P.} = 16.5558 = \frac{1+r}{1-r}, \text{ where "r"} = \frac{\text{moles of DCDPS}}{\text{moles of Hq + moles of Bp}}$$

$$r = 0.8861$$

The moles of Hq + Bp were chosen to be 0.15 moles total.

Therefore: moles of DCDPS = 0.8861 (0.15 moles) = 0.1329 moles

Thus:

38.17g (0.1329 moles)	DCDPS
13.97g (0.075 moles)	Bp
8.26g (0.075 moles)	Hq

SCHEME 23. Calculations for a 3000$< M_n >$ hydroxyl terminated hydroquinone/biphenol polysulfone.

g/mole and insuring hydroxyl endgroups. Simple variation of the ratio of hydroquinone to biphenol (see Scheme 22) yielded polysulfones with a range of hydroquinone to biphenol contents. The ratio of hydroquinone to biphenol was varied from 50% Hq/50% Bp to 0% Hq/100% Bp.

After these hydroxyl terminated oligomers were synthesized, they had to be characterized as to number average molecular weight ($<M_n>$). The $<M_n>$ of the poly(arylene ether sulfone) oligomers had to be known accurately so that proper stoichiometry of the subsequent copolymerization could be achieved. The stoichiometry of the reaction to form high molecular weight segmented copolymers is very critical as it is with all step growth reactions. The number average as opposed to the weight average molecular weight was determined since an endgroup analysis was used and it is the end groups which are subsequently reacted. The $<M_n>$ of the oligomers was determined through a potentiometric titration of the hydroxyl endgroups of the poly(arylene ether sulfone) oligomers. The hydroxyl endgroups were titrated with alcoholic tetramethylammonium hydroxide based on the method developed by Wnuk, et al.[100] Past difficulties with this potentiometric titration centered around the quantitative neutralization of the phenate endgroups of the polysulfone oligomers in the last step of their synthesis (see Scheme 22). This problem was alleviated by using an excess of the acetic acid and stirring the polymer solution with the acetic acid for a minimum of 24 hours. Another potential problem was that of a non-prominent endpoint. This problem was addressed by Webster [85] who recommended the use of

N,N-dimethylformamide (DMF) as the titration solvent. However, DMF gave a lower potential "break" in the titration than did N,N-dimethylacetamide (DMAC) which suffered from water absorption. The use of freshly distilled N-methyl-2- pyrrolidone (NMP) was found to alleviate this problem. The use of an automatic titrator was also instrumental in minimizing these problems.

A table of several hydroxyl terminated poly(arylene ether sulfone) oligomers comparing the target theoretical molecular weights and the actual titrated molecular weights is shown in Table 6. This table also contains the recovered percentage yield of the oligomers. As can be seen from the table, there is a good correlation between target and titrated molecular weights as well as high recovered yields. It was observed that at lower target molecular weights, <2000 g/mole, the titrated molecular weight tended to be somewhat higher than the target. This is thought to be due to the nature of the polymerization. At these lower molecular weights, there is a substantial amount of lower molecular weight oligomers (dimers, trimers, etc.) which are lost in the oligomer workup. A step growth polymerization is known to give a distribution of molecular weights including the low molecular weight species. The low molecular weight oligomers are lost due to their solubility and small particle size in the precipitation medium. Thus, the titration is of the higher molecular weight oligomers giving a higher titrated molecular weight than the target value. This same argument is invoked for the lower recovered yields for these oligomers.

TABLE 6

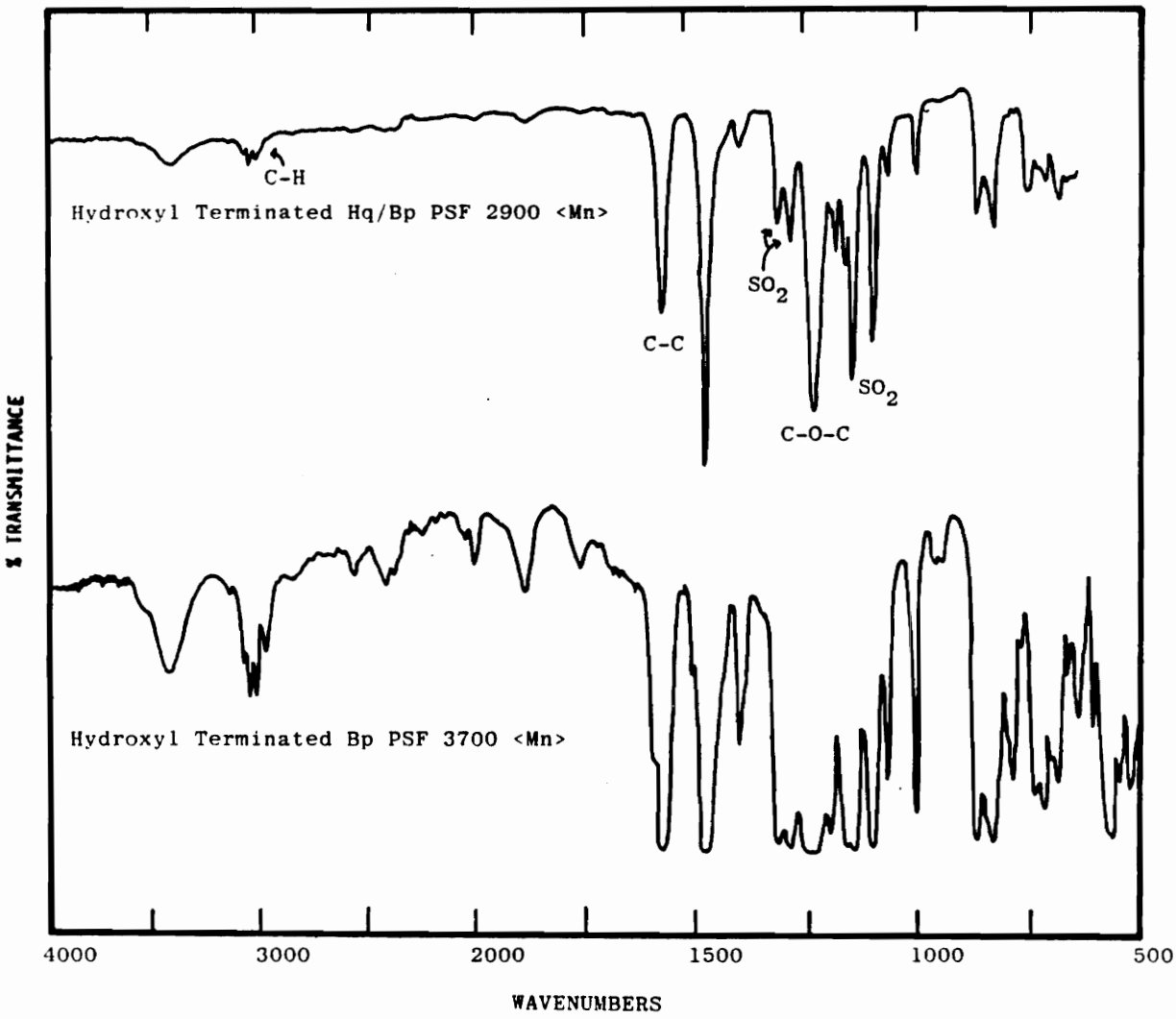
COMPARISON OF TARGET AND TITRATED NUMBER AVERAGE MOLECULAR WEIGHTS FOR SELECTED POLY(ARYLENE ETHER SULFONE) OLIGOMERS

Polysulfone Oligomer	Target $<M_n>$	Titrated $<M_n>$	Recovered % Yield
Hq/Bp 50/50 PSF	1000	1800	82
Hq/Bp 50/50 PSF	2500	2700	61
Hq/Bp 50/50 PSF	6000	5350	88
Hq/Bp 50/50 PSF	10,000	7300	87
Hq/Bp 25/75 PSF	1000	1500	64
Hq/Bp 10/90 PSF	1000	1300	63
Hq/Bp 0/90 PSF	1000	1800	65
Hq/Bp 0/90 PSF	4200	3700	88

4.3 Characterization of Hydroxyl Terminated Poly(Arylene Ether Sulfone) Oligomers

In addition to the potentiometric titration of the hydroxyl terminated poly(arylene ether sulfone) oligomers to determine their molecular weights, other characterization techniques were also used. One such technique was that of Fourier transform infrared spectroscopy (FT-IR). The chemical composition of the polysulfone oligomer could be elucidated from their FT-IR spectra. Especially noteworthy is the presence of the hydroxyl endgroups of the oligomers were confirmed by their characteristic stretching bands. Shown in Scheme 24 are stacked spectra of a 2900 $<M_n>$ hydroquinone/biphenol polysulfone oligomer and of a 3700 $<M_n>$ biphenol polysulfone oligomer. Some of the characteristic FT-IR polysulfone peaks and their assignments are listed in Table 7. In addition to the polysulfone peaks is the very prominent broad peak centered around 3400 cm^{-1} characteristic of the hydroxyl endgroups of the oligomer.

Intrinsic viscosities of selected hydroxyl terminated hydroquinone/biphenol polysulfone oligomers were also determined. The intrinsic viscosity values for these oligomers give a relative indication of the molecular weights of the oligomers. Table 8 is a collection of the intrinsic viscosity values of various molecular weight polysulfone oligomers. These viscosity values were determined in chloroform at 25°C.



SCHEME 24. FT-IR spectra of a 2900 $\langle M_n \rangle$ hydroquinone/biphenol polysulfone oligomer and of a 3700 $\langle M_n \rangle$ biphenol polysulfone oligomer.

TABLE 7

CHARACTERISTIC FT-IR POLYSULFONE PEAK FREQUENCIES AND THEIR ASSIGNMENTS

Frequency (cm^{-1})	Assignments
3100-3000	Aromatic C - H Stretching
1590-1580	Aromatic C - C Stretching
1330-1290	Asymmetric O = S = O Stretching
1250-1240	Asymmetric C - O - C Stretching
1155-1150	Symmetric O = S = O Stretching
1110-1100	Aromatic Ring Vibration

TABLE 8

INTRINSIC VISCOSITY VALUES OF SELECTED HYDROXYL TERMINATED HYDROQUINONE/BIPHENOL POLYSULFONE OLIGOMERS

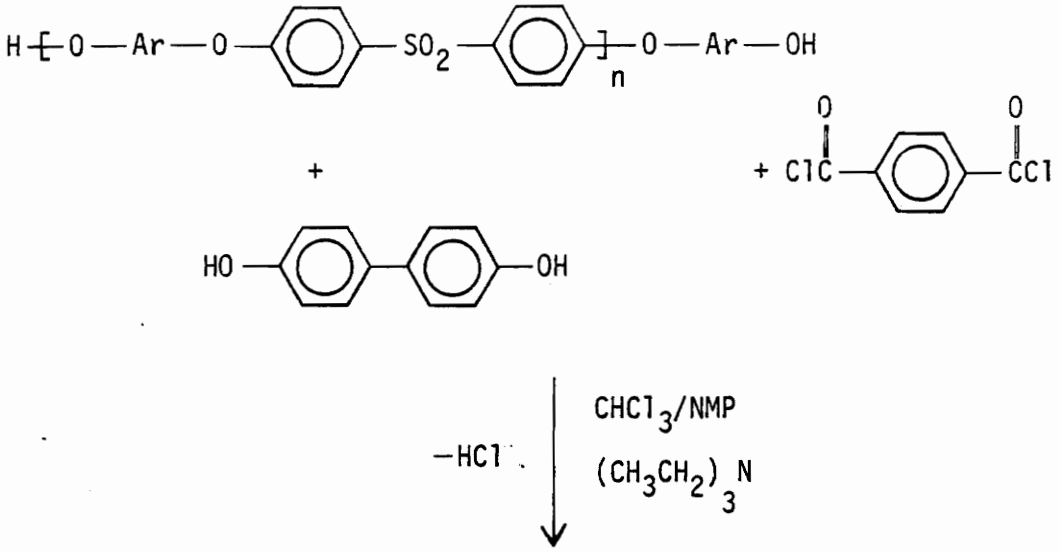
Oligomer	Intrinsic Viscosity Value[1]
2200 $<M_n>$ Hq/Bp 50/50 Polysulfone	0.11 dl/g
2700 $<M_n>$ Hq/Bp 50/50 Polysulfone	0.15 dl/g
7300 $<M_n>$ Hq/Bp 50/50 Polysulfone	0.27 dl/g

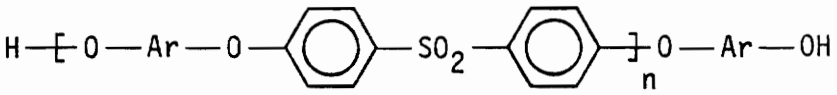
(1) Intrinsic viscosities determined in chloroform at 25°C.

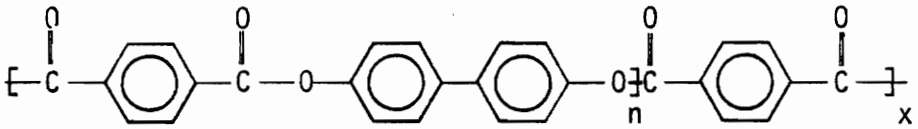
4.4 Synthesis of Poly(Arylene Ether Sulfone)-Poly(Biphenol Terephthalate) Segmented Copolymers Via The Solution Process

A solution process was one method employed in synthesizing segmented copolymers from preformed polysulfone oligomers. Once the hydroxyl terminated poly(arylene ether sulfone) oligomers were characterized as to their number average molecular weights ($<M_n>$), they could be polymerized to high molecular weight polymers by one of several methods. Generally, the polysulfone oligomer was chain extended with terephthaloyl chloride or with terephthaloyl chloride and 4,4'-biphenol. When the polysulfone oligomer was chain extended with just terephthaloyl chloride a fairly simple, perfectly alternating copolymer was formed. If the polysulfone oligomer was reacted with the terephthaloyl chloride and 4,4'-biphenol, a randomly coupled segmented copolymer was obtained. Scheme 25 illustrates the synthesis of a randomly coupled segmented copolymer from a hydroxyl terminated polysulfone oligomer, terephthaloyl chloride, and 4,4'-biphenol. The segmented copolymers represented in Scheme 25 are termed "random" due to the nature of the polymerization. In this reaction sequence, the terephthaloyl chloride can react with either the hydroxyl terminated polysulfone oligomer or with the biphenol. Since the terephthaloyl chloride can react with essentially equal probability with either the polysulfone oligomer or the biphenol, sequences of polysulfone terephthalate and biphenol terephthalate are distributed randomly throughout the polymer chain.

The perfectly alternating copolymers are so termed since only terephthaloyl chloride and the hydroxyl terminated polysulfone

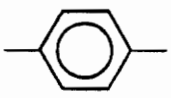
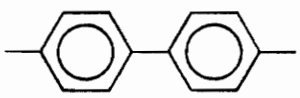






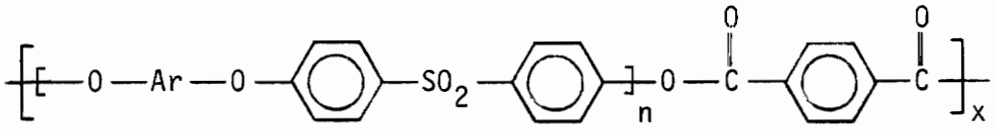
Poly(arylene ether sulfone)-poly(biphenol terephthalate) random segmented copolymer

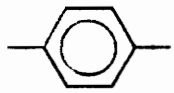
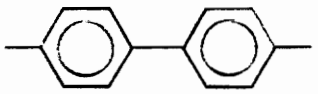
+ $(CH_3CH_2)_3N \cdot HCl_{(solid)}$

Ar =  and 

SCHEME 25. Synthesis of a poly(arylene ether sulfone)-poly(biphenol terephthalate) randomly coupled segmented copolymer via the solution process

oligomers can react. The terephthaloyl chloride can react only with the hydroxyl endgroups of the polysulfone oligomer, thus a terephthalate unit alternates with a polysulfone sequence throughout the polymer chain. The repeat unit for a perfectly alternating segmented copolymer would be represented as below:



Ar =  and 

The triethylamine ($(CH_3CH_2)_3N$) used in the polymer synthesis serves as both catalyst and acid acceptor (refer to Scheme 25). The acidic byproduct, hydrogen chloride, is effectively removed from the reaction by forming triethylamine hydrochloride which is only slightly soluble in the chloroform solvent. A list of the perfectly alternating and randomly coupled segmented poly(arylene ether sulfone)-poly(arylate) copolymers is given in Table 9. The intrinsic viscosity values for the polymers in Table 9 indicate that high molecular weight polymer has been formed. The poly(arlene ether sulfone) segment of the copolymers was also varied in composition. It was observed that the polysulfone oligomers with a mixture of hydroquinone and biphenol tended to be more soluble in the chloroform solvent. The use of all biphenol polysulfone oligomers was severely

TABLE 9

PERFECTLY ALTERNATING AND RANDOMLY COUPLED SEGMENTED[1] POLY(ARYLENE ETHER SULFONE)-POLY(ARYLATE) COPOLYMERS SYNTHESIZED VIA THE SOLUTION PROCESS

Polysulfone Oligomer Used	Oligomer $\langle M_n \rangle$	Amount of Biphenol Added		$[\eta]^{CHCl_3}_{25°}$
		Mole %	Weight %	
Hq/Bp 50/50 PSF	1700	0	0	0.39
Hq/Bp 50/50 PSF	1700	5	0.55	0.59
Hq/Bp 50/50 PSF	5350	0	0	-
Hq/Bp 50/50 PSF	5350	10	1.10	0.87
Hq/Bp 25/75 PSF	1500	0	0	0.63
Hq/Bp 25/75 PSF	1500	5	0.63	0.52

(1) Perfectly alternating copolymers have no added biphenol; randomly coupled segmented copolymers contain the indicated amounts of added biphenol.

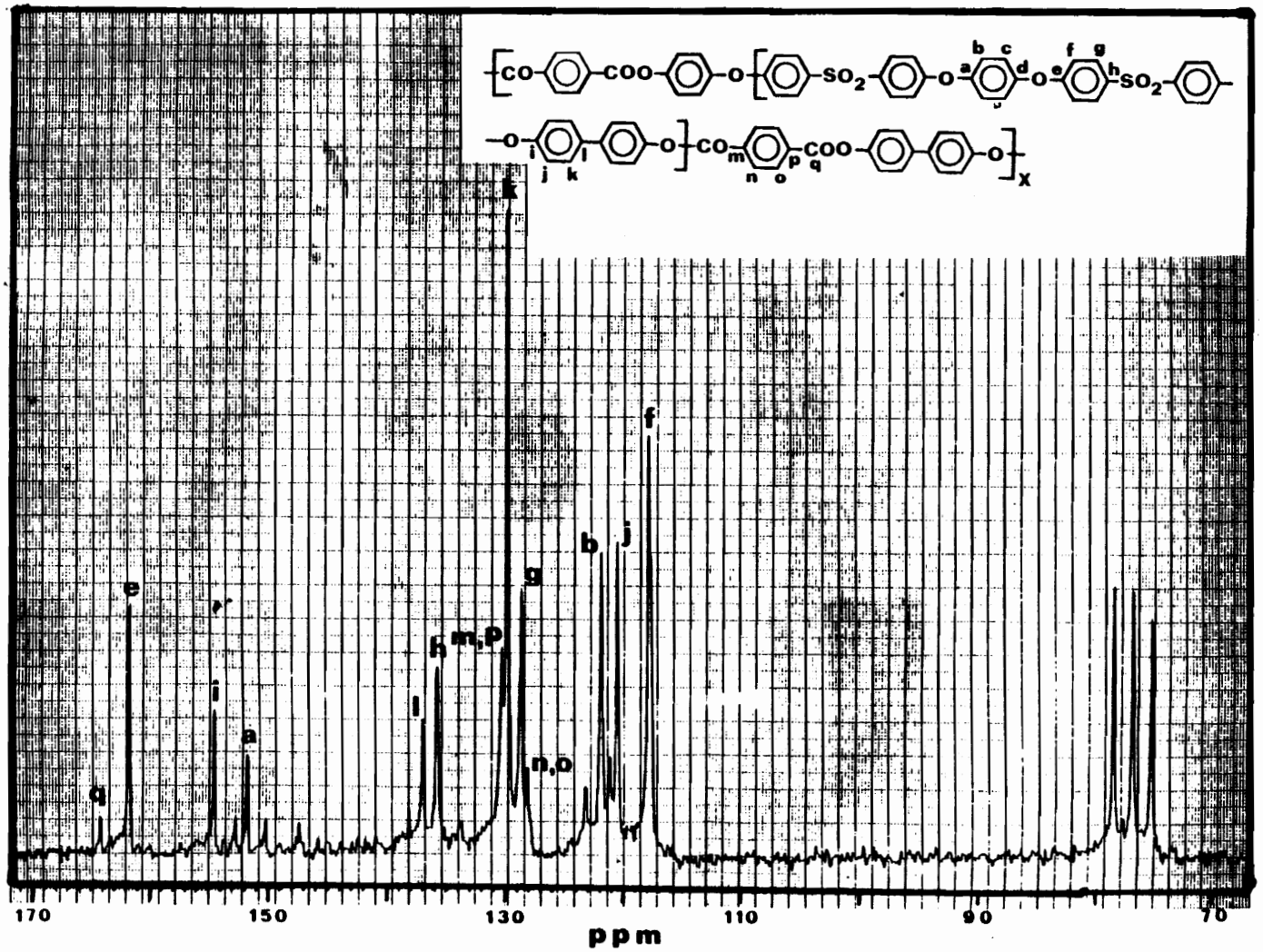
limited due to their solvent induced crystallization and hence limited solubility in the chloroform.

A major limitation of the solution process was the inability to incorporate high amounts of biphenol into the copolymer. Inspection of Table 9 reveals that in no case could more than 10 mole % (1.1 weight %) biphenol be incorporated into the copolymer without inducing premature precipitation. The insolubility of the highly crystalline (and liquid crystalline) biphenol terephthalate segment is the reason for this behavior. This premature precipitation problem necessitated the development of alternate synthetic techniques to overcome the problem, as will be discussed later in this dissertation.

4.5 Characterization of Poly(Arylene Ether Sulfone)-Poly(Biphenol Terephthalate) Segmented Copolymers Synthesized Via The Solution Process

Confirmation of the chemical composition of the poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymers was made by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. A representative ^{13}C NMR spectrum of a hydroquinone/biphenol polysulfone-poly(biphenol terephthalate) segmented copolymer is shown in Scheme 26. The ^{13}C NMR spectrum confirms the structure of the polymer. The peaks arising from the polysulfone segment can be assigned as well as the peaks due to the biphenol terephthalate segment. For example, the peak arising from the ester carbonyl carbon was assigned at 164.2 ppm which correlates with values reported in the literature.[93]

Qualitative solubility testing of the segmented copolymers showed the copolymers to have the same solubility characteristics as the polysulfone oligomers from which they were made. This qualitative test indicates that the low amount of biphenol terephthalate incorporated into the copolymer does not alter the solvent resistance of the copolymer. Differential scanning calorimetry (DSC) also indicated that the biphenol terephthalate content of the copolymer was not high enough to induce any liquid crystallinity or unusual melting behavior. All of the segmented copolymers synthesized via the solution process gave a glass transition in the range of 200° to 220°C.

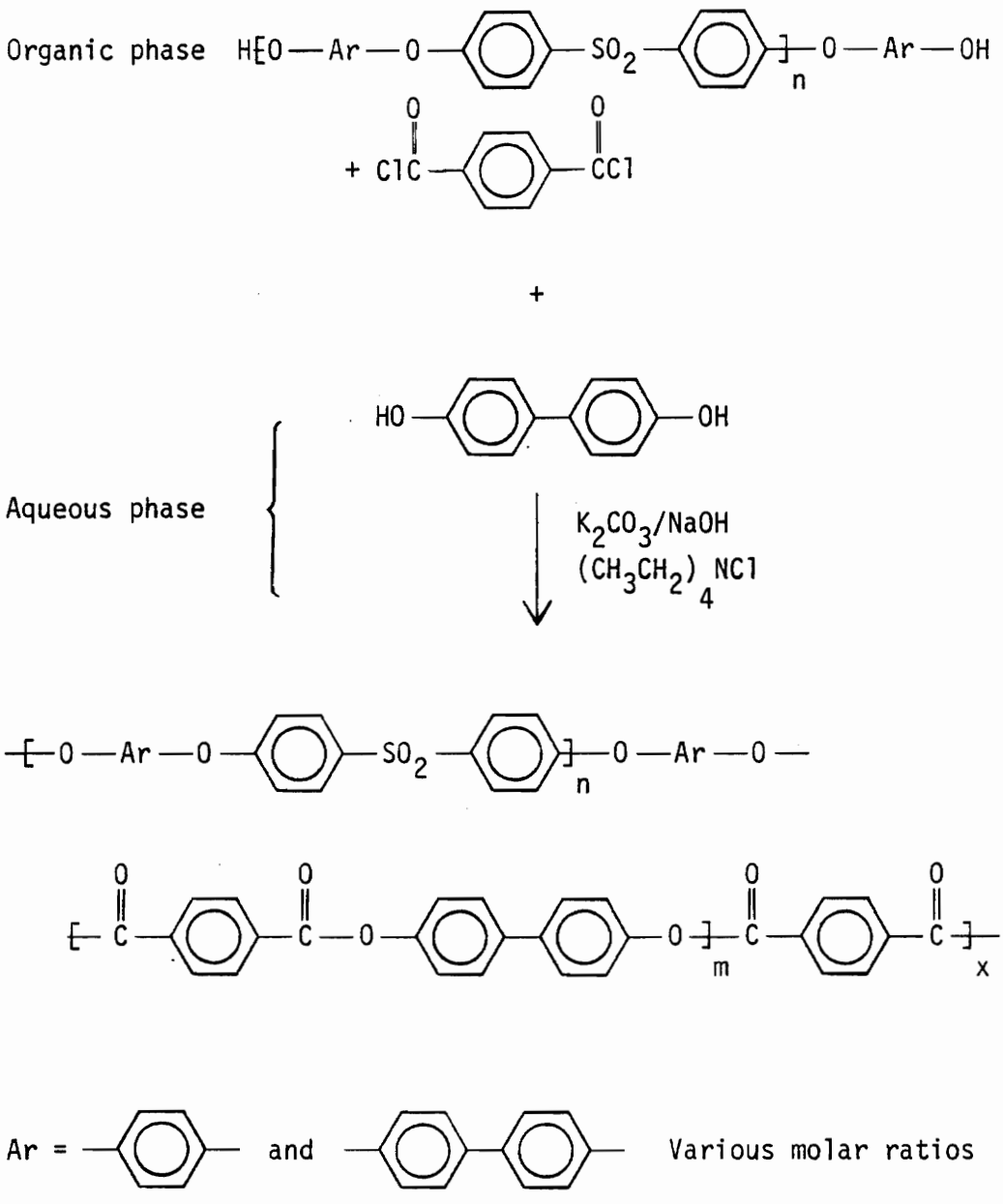


SCHEME 26. ^{13}C NMR spectrum of Hq/Bp 50/50 polysulfone 1700 $\langle M_n \rangle$ -poly(biphenol terephthalate) segmented copolymer containing 5 mole % added biphenol.

4.6 Synthesis of Poly(Arylene Ether Sulfone)-Poly(Biphenol Terephthalate) Segmented Copolymers Via The Interfacial Process

In an effort to overcome the limitations on the amount of added biphenol, and hence the biphenol terephthalate segment molecular weight incorporated into the copolymer, an interfacial process was developed. Interfacial copolymerizations involving hydroxyl terminated bisphenol-A polysulfones and poly(aryl esters) have been investigated previously.[62,76,77] The interfacial technique was found to give high molecular weight polymer with relatively short reaction times (e.g., 15-20 minutes). The nature of the polymerization leads to very clean products since the polymer is soluble in the organic phase only and is therefore separated from the contaminating water soluble inorganic salt byproducts.

The reaction to produce a poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymer is shown in Scheme 27. Chloroform was used as the organic phase solvent in most of the interfacial polymerizations. However, in the case of all biphenol polysulfone based copolymers or copolymers with high contents (>10 mole percent) of biphenol terephthalate, tetrachloroethane was found to be a better solvent. The bases (sodium hydroxide and potassium carbonate) served to solubilize the 4,4'-biphenol by converting it into its phenate form. The tetraethylammonium chloride (TEAC) served as phase transfer catalyst in the reaction. The phase transfer catalyst serves to "transfer" the biphenol from the aqueous phase into the organic phase where it can react. The transfer takes place because the quaternary cation associates with phenate groups of the



SCHEME 27. Interfacial reaction process used to synthesize segmented poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymers.

biphenol in the aqueous phase but, due to the organic nature of the four ethyl groups, the complex is also slightly soluble in the organic phase. Table 10 contains the pertinent information on a series of segmented poly(arylene ether sulfone)-poly(arylate) copolymers synthesized by this interfacial technique.

The percentage of biphenol that can be incorporated into the copolymer was found to be dependent on the molecular weight of the polysulfone segment. It was observed that the greater percentage of biphenol which could be incorporated, the higher was the molecular weight of the polysulfone segment. This observation is explained by the fact that the polysulfone segment helps keep the copolymer in solution since the polysulfone is readily soluble in the solvent.

It is apparent from Table 10 that a greater amount of biphenol can be incorporated into the copolymers by the interfacial technique in comparison to the solution technique. It is theorized that the phenate form of the biphenol is more reactive than the biphenol itself leading to a greater incorporation into the copolymer. While the segmented copolymers may prematurely precipitate from the interfacial reactions, the copolymers are still swollen by the solvent and appear to be still able to react with the phenate form of the biphenol.

Other series of poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymers were synthesized by the interfacial technique. In these series, the molecular weight of the polysulfone segment was varied from 1700 to 7300 $\langle M_n \rangle$ as well as the composition of the polysulfone segment. The polysulfone segment

TABLE 10

SEGMENTED POLY(ARYLENE ETHER SULFONE)-POLY(ARYLATE) COPOLYMERS SYNTHESIZED BY THE INTERFACIAL TECHNIQUE

Polymer(1)	Biphenol Terephthalate Content			$[\eta]_{25°}^{CHCl_3}$
	Mole % Based on Moles of PSF	Mole % Based on Total Moles	Weight %	
1	0	0	0	0.58
2	10	4.5	1.0	0.59
3	20	8.3	2.1	0.68
4	30	11.5	3.0	0.60
5	40	14.3	4.0	0.24 (2)
6	50	16.7	5.0	0.42 (2)
7	60	18.8	5.9	0.41 (2)

(1) All polymers based on 2900 $\langle M_n \rangle$ hydroquinone/biphenol 50/50 polysulfone oligomer.

(2) The intrinsic viscosity solution of these polymers were hazy indicating only partial solubility in chloroform.

composition was varied from a 50/50 molar mixture of hydroquinone/biphenol to a 0/100 hydroquinone/biphenol mixture. The percentage of biphenol was also varied within each of these series.

Those copolymers which contained no added biphenol were synthesized by a pseudo-interfacial technique. The pseudo-interfacial technique was very similar to the interfacial technique but the aqueous phase contained only potassium carbonate. This reaction was termed pseudo-interfacial because no monomer is transferred between phases. The byproduct, hydrogen chloride, was the only material which transferred between the phases.

The segmented copolymers synthesized by the interfacial technique were also found to be limited in the amount of poly(biphenol terephthalate) which could be copolymerized into the polymer. While the amount of biphenol terephthalate which could be incorporated into the copolymers was much higher in the interfacial process than in the solution technique, there was an upper limit on the amount incorporated. The maximum mole percentage (and weight percentage) which could be introduced into the copolymers was found to be dependent on the molecular weight of the polysulfone oligomer. It was found that the higher the molecular weight of the poly(arylene ether sulfone) segment, the greater the amount of biphenol terephthalate which could be copolymerized into the polymer. This is the same finding as for the copolymers made via the solution technique.

4.7 Characterization of Segmented Copolymers Prepared By The Interfacial Technique

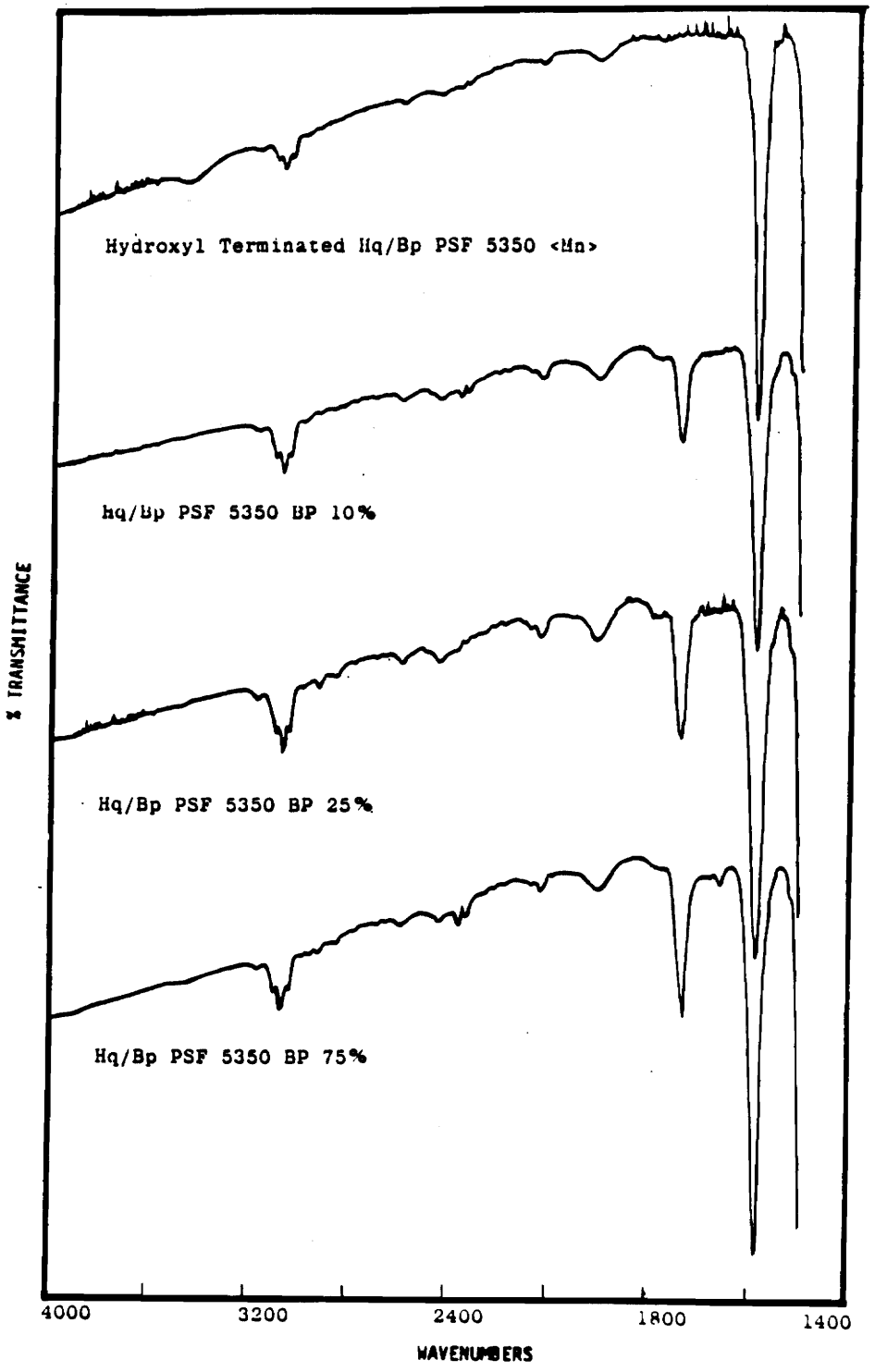
Segmented copolymers synthesized via the interfacial technique were characterized as to their structures and properties by a variety of techniques. The formation of the polyester segment in the presence of the polysulfone oligomer was confirmed by FT-IR. The spectra for a hydroxyl terminated hydroquinone/ biphenol polysulfone of 5350 $<M_n>$ and of the segmented copolymer containing 10 mole percent of biphenol terephthalate and this polysulfone oligomer are shown in Scheme 28. The characteristic polysulfone peaks [refer to Table 7, Section 4.3] as well as the hydroxyl stretch due to the endgroups are evident for the polysulfone oligomer.

The FT-IR spectrum for the segmented copolymer confirms three aspects of the copolymerization. The first aspect considered is the formation of the polyester segment. The spectrum shows a strong absorption centered at 1734 cm^{-1} which is attributed to the ester carbonyl stretching. This peak is not present in the starting polysulfone oligomer (as expected) and is located at a higher wavenumber than the carbonyl due to the terephthaloyl chloride, which would be the only possible contaminant containing a carbonyl group. Secondly, the hydroxyl peak ($\sim$3300 cm^{-1}) due to the polysulfone oligomer has disappeared. The disappearance of the hydroxyl peak is expected if the hydroxyl endgroups of the polysulfone oligomer are reacted and incorporated into an ester linkage. Lastly, the characteristic polysulfone peaks of the hydroquinone/biphenol polysulfone segment are still present. This indicates that the

polysulfone segment is not being degraded when copolymerized with the terephthaloyl chloride and biphenol. FT-IR was also employed to confirm the formation of the poly(biphenol terephthalate) segment. Shown in Scheme 29 is a partial FT-IR of a series of segmented copolymers containing varying amounts of biphenol terephthalate. The mole percentage of biphenol terephthalate was varied from 10 to 75 percent and this increase in the polyester segment is reflected in the size of the ester carbonyl stretch centered around 1734 cm^{-1}. As the amount of polyester is increased the size of the carbonyl stretching peak also increases.

The molecular weights of the poly(arlene ether sulfone)-poly(arylate) segmented copolymers were qualitatively compared by two characterization methods. The first method was by a comparison of the intrinsic viscosity (IV) values of the polysulfone oligomer to the values for the segmented copolymers synthesized from this oligomer. Table 11 is a collection of a series of segmented copolymers and their intrinsic viscosity values. A comparison of the segmented copolymer intrinsic viscosity values to that of the polysulfone oligomer used in synthesizing the polymers shows an increase in the IV value in every case. The IV value for polymer 3 (0.68 dl/g) containing 20 mole percent biphenol terephthalate was found to be approximately four times the value for the polysulfone oligomer (0.18 dl/g).

An interesting observation was made of the intrinsic viscosity solutions for those polymers containing 40 or greater mole percent of the biphenol terephthalate. These solutions were observed to be hazy which is an indication that these polymers were only partially soluble



SCHEME 29. Partial FT-IR spectra of a series of segmented copolymers based upon a 5350 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone (A) and containing 10 (B), 25 (C), and 75 (D) mole % biphenol terephthalate.

TABLE 11

POLY(ARYLENE ETHER SULFONE)-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMERS BASED ON 2900<M_n>Hq/Bp 50/50 POLYSULFONE AND THEIR CORRESPONDING INTRINSIC VISCOSITIES

Polymer	Biphenol Terephthalate Content			$[\eta]^{25°}_{CHCl_3}$ (dl/g)
	Mole % Based on Moles of PSF(2)	Mole % Based on Total Moles	Weight %	
Hq/Bp 50/50 Polysulfone Oligomer	-	-	-	0.18
1(1)	0	0	0	0.58
2	10	4.5	1.0	0.59
3	20	8.3	2.1	0.68
4	30	11.5	3.0	0.60
5	40	14.3	4.0	0.24 (3)
6	50	16.7	5.0	0.42 (3)
7	60	18.8	5.9	0.41 (3)

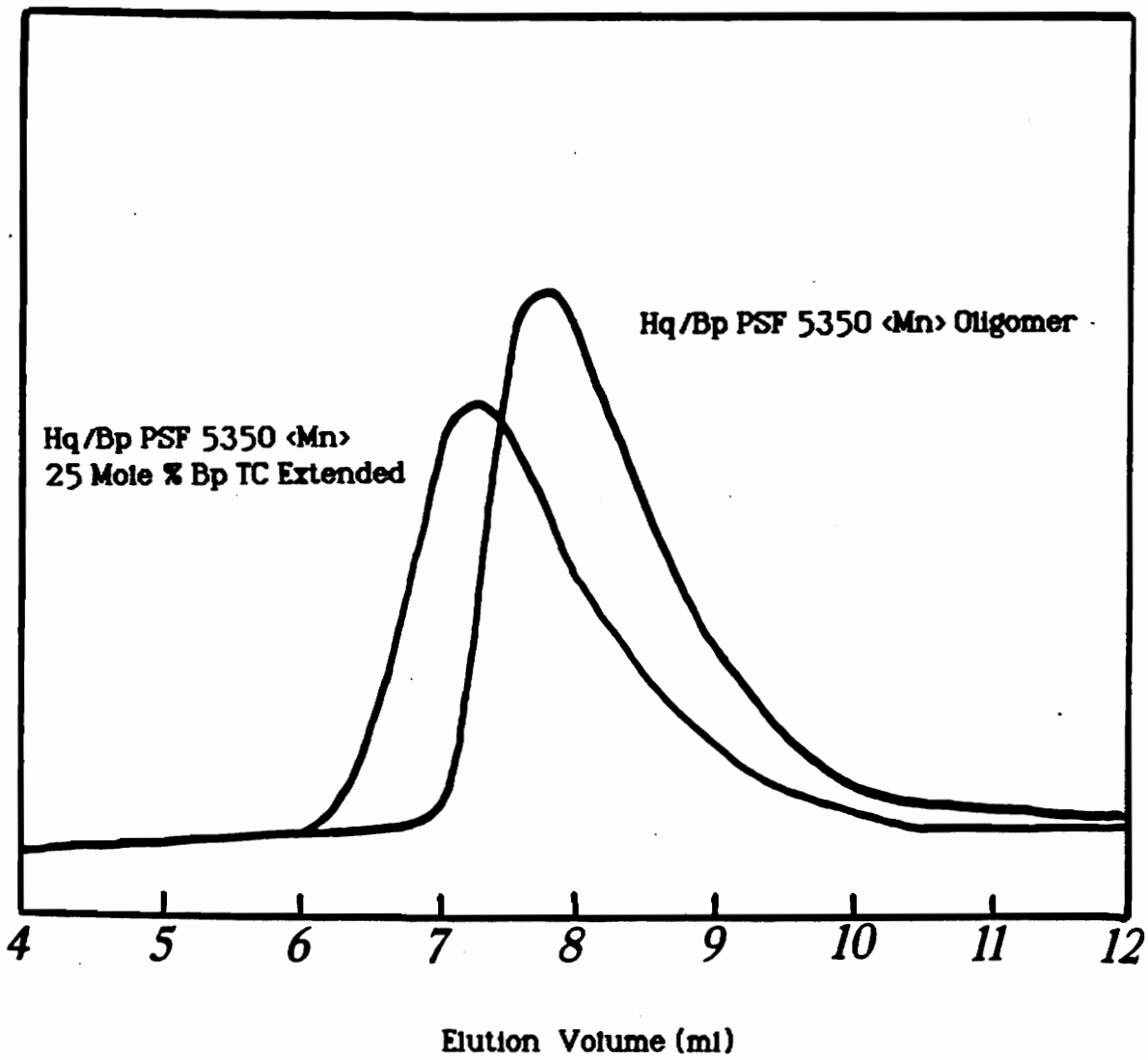
(1) Polysulfone oligomer extended with terephthaloyl chloride; no added biphenol.

(2) PSF is polysulfone oligomer.

(3) The intrinsic viscosity solutions of these polymers were hazy, indicating only partial solubility.

in chloroform. The values quoted should thus be considered only approximate. This indicates that the segmented copolymers are becoming more solvent resistant. These same copolymers were found to be soluble in more polar solvents such as NMP or DMAc. Similar observations were also made for other segmented copolymer series. Gel permeation chromatography (GPC) was also used as a qualitative check on the molecular weights of the segmented copolymers. Absolute molecular weights of the poly(arylene ether sulfone)- poly(arylate) segmented copolymers could not be determined using GPC data. Separation in a GPC column is based on the hydrodynamic volume of the polymer chains. Many polymers having similar conformations in solution are assigned a molecular weight based upon molecular weight standards. The most commonly used standard is polystyrene. However, these segmented copolymers were synthesized with potentially liquid crystalline polyester segments which are known to have extended structures in solution. Thus, a comparison of the molecular weights as obtained from elution volumes of the randomly coiled polystyrene to the extended poly(arylene ether sulfone)- poly(biphenol terephthalates) is not permissable. However, a comparison of the elution volumes of the poly(arylene ether sulfone) oligomers to the segmented copolymers synthesized from them gives a relative indication of molecular weights.

Scheme 30 is an overlay of the gel permeation chromatograms of a 5350 $<M_n>$ hydroquinone/biphenol 50/50 polysulfone and the segmented copolymer synthesized from this oligomer and containing 25 mole percent biphenol terephthalate. The polysulfone oligomer was eluted at 7.9 ml



SCHEME 30. Overlay of gel permeation chromatograms of a 5350 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone oligomer and segmented copolymer synthesized from this oligomer and containing 25 mole % biphenol terephthalate.

while the segmented copolymer eluted at 7.1 ml. The difference in elution volumes plus the fact that the segmented copolymer eluted at a smaller volume than did the polysulfone oligomer (as expected) indicates that the segmented copolymer has a substantially higher molecular weight.

The thermal properties of the segmented copolymers were determined using differential scanning calorimetry (DSC). The glass transition temperatures (Tg) as determined by DSC measurements for a series of segmented copolymers based on a 2900 $<M_n>$ hydroquinone/ biphenol polysulfone are shown in Table 12. It was observed that in all cases the Tg's for the segmented copolymers were of the order of 10 to 15 degrees higher than the Tg for the oligomer. The Tg is expected to increase since it is known that glass transition temperatures are molecular weight dependent up to a critical molecular weight where the Tg levels off. One interesting aspect of this thermal data is that the Tg's did not steadily increase as the polyester content increased, as might be expected. This may be explained by the fact that the segmented copolymers contained a greatly varied poly(biphenol terephthalate) amount on a molar basis (0 to 60 percent) but a very small amount on a weight basis (0 to 6 percent). The Tg of a copolymer is known to be dependent on the weight fraction of the two components making up the copolymer. Thus, these segmented copolymers had very high weight fractions of the polysulfone which would tend to greatly dictate the final Tg of the copolymer. Homopolymer biphenol terephthalate is known to have a very high melting point (>500°C) [61,77] and a very weak if not

TABLE 12

GLASS TRANSITION TEMPERATURES OF A SERIES OF SEGMENTED COPOLYMERS SYNTHESIZED FROM A 2900 $<M_n>$ Hq/Bp 50/50 POLYSULFONE AND CONTAINING VARYING AMOUNTS OF BIPHENOL TEREPHTHALATE

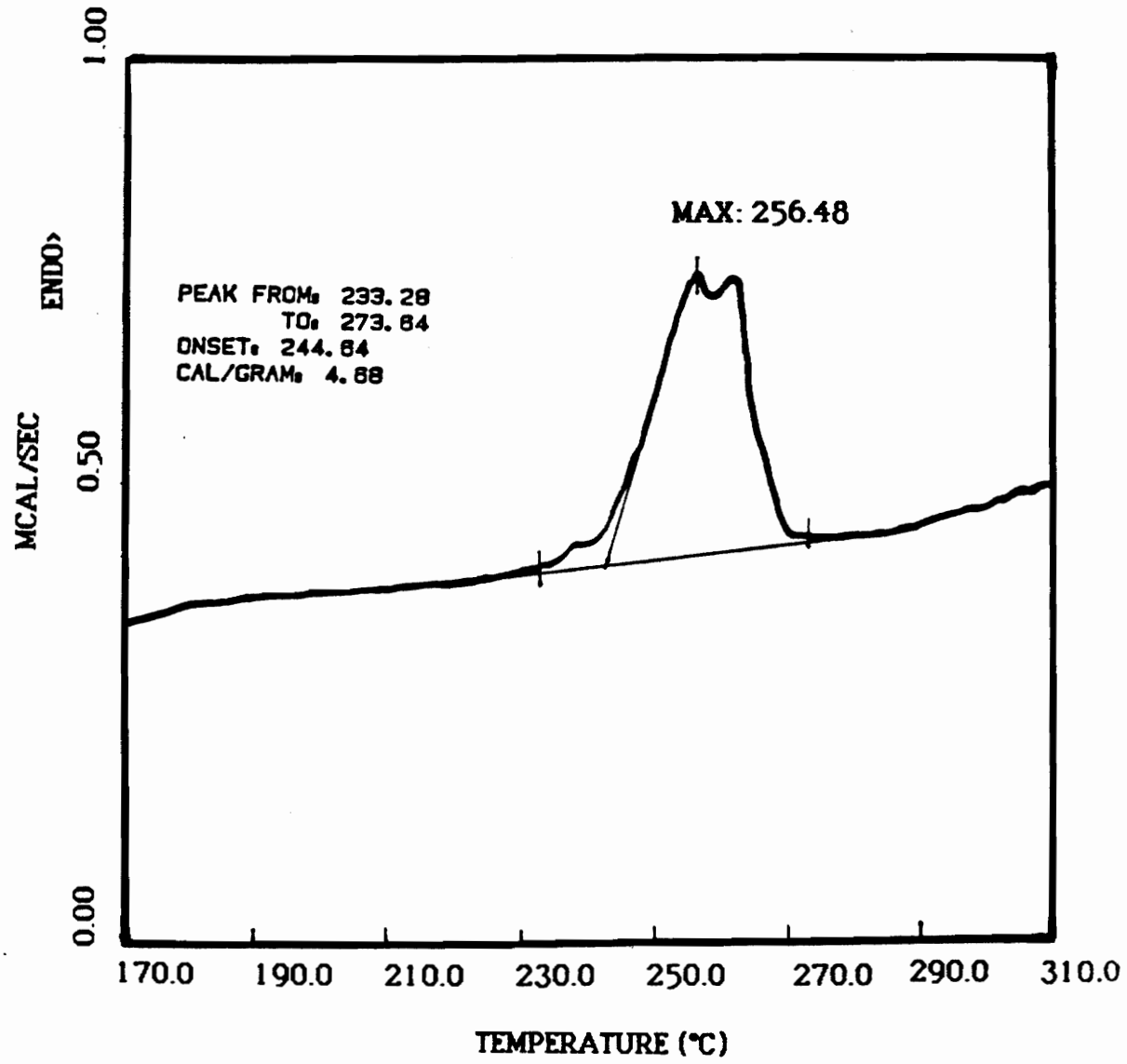
Polymer	Biphenol Terephthalate Content		Tg(°C)[3]
	Mole %[2]	Weight %	
2900 $<M_n>$ Hq/Bp 50/50 PSF Oligomer	-	-	191
1[1]	0	0	212
2	10	1.0	200
3	20	2.1	213
4	30	3.0	208
5	40	4.0	208
6	50	5.0	202
7	60	5.9	206

(1) Polymer 1 is a perfectly alternating segmented copolymer synthesized by chain extending the polysulfone oligomer with terephthaloyl chloride.

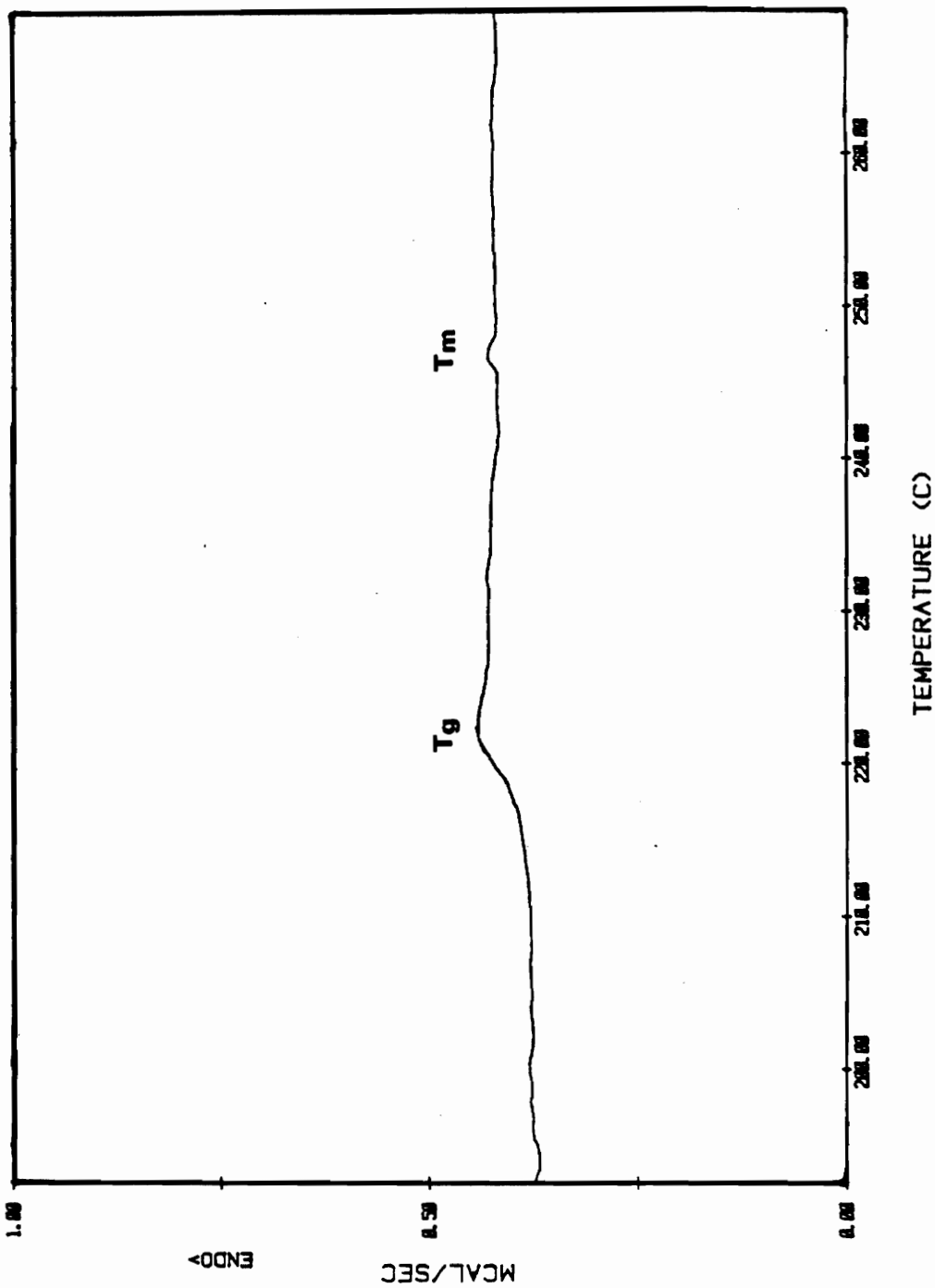
(2) Mole % based on moles of polysulfone oligomer.

(3) The glass transition temperatures were determined on the second heating scan of the sample at 10 K/minute.

imperceptable glass transition temperature. Therefore, the poly(biphenol terephthalate) segment may be microphase separating from the polysulfone segment and the detected Tg may be that of the polysulfone segment. However, no melting point was detected in this series of copolymers which may be due to the small amount of the poly(biphenol terephthalate). A melting endotherm was detected for a 3000< M_n > biphenol polysulfone oligomer chain extended with terephthaloyl chloride, however. Schemes 31 and 32 are the first and third heating scans for this perfectly alternating biphenol polysulfone-terephthalate segmented copolymer. The first heating scan shows a very prominent melting endotherm with the peak maximum at 256°C. Cooling the sample and reheating a second or third time produces the DSC scan shown in Scheme 32. A Tg is evident centered around 218°C and a small but reproducible melting endotherm is evident at 248°C. The small temperature differential between the Tg and Tm (called the Tg-Tm window) almost precludes thermal crystallization. This is the case in known polymer systems such as a bisphenol-A polycarbonate polymer which has a small Tg-Tm window, the glass transition temperature being on the order of 150°C while the Tm is 260°C. The polymer is known to thermally crystallize very slowly. However, casting a film of the biphenol polysulfone-terephthalate segmented copolymer from methylene chloride solvent did induce some crystallinity into the polymer. This solvent effect was also noticed in the hydroquinone/biphenol polysulfone-poly(arylate) copolymer systems containing high weight fractions (~50 percent) of poly(biphenol terephthalate).



SCHEME 31. First heating scan in DSC of 3000 $\langle M_n \rangle$ biphenol polysulfone-terephthalate segmented copolymer.



SCHEME 32. Third heating scan in DSC of 3000 $\langle M_n \rangle$ biphenol polysulfone-terephthalate segmented copolymer.

Analysis of the wide angle X-ray scattering data also confirmed that some of the polymers were crystalline while others were totally amorphous. The same segmented copolymers which showed evidence of crystallinity from DSC scans gave distinct crystalline patterns in WAXS experiments. The segmented copolymer composed of a 5350 $<M_n>$ hydroquinone/biphenol polysulfone extended with 75 mole percent of biphenol was particularly noteworthy. This sample had a WAXS pattern indicative of a semicrystalline polymer when films of the polymer were cast from methylene chloride. When this same sample was heated to 100°C above its crystalline melting point and quenched cooled in liquid nitrogen, the new WAXS pattern indicated semicrystallinity of a different nature. The distinct crystalline lines from the virgin material were lost but faint lines coming at different spacings were evident. These faint lines may be indicative of liquid crystallinity or some type of residual order above the melting point of the virgin material. This residual order was not confirmed by DSC measurements. The low level of this residual order may have precluded its detection by DSC.

4.8 Synthesis of Poly(Arylene Ether Sulfone)-Poly(Biphenol Terephthalate) or Poly(Oxybenzoate) Segmented Copolymers Via The Melt Acidolysis Process

In order to synthesize segmented copolymers with high (> 25 weight percent) polyester contents, a melt acidolysis technique was developed. Even though the interfacial technique was used to produce poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymers with higher biphenol terephthalate contents than the solution technique, polyester contents greater than 25 weight percent were not attainable. As with the solution technique, the segmented copolymers with high biphenol terephthalate contents became insoluble in the reaction medium, thus limiting the total percentage of the polyester which could be incorporated. The limiting factor in these two techniques is the solubility, or the lack thereof, of the polymer in the reaction solvent--the solvent seeming to induce crystallization through the phenomenon of solvent induced crystallization. Three different solvents were used in the interfacial technique: methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and tetrachloroethane ($C_2H_2Cl_4$). The segmented copolymers containing high biphenol terephthalate contents were found to be more soluble in the tetrachloroethane than the chloroform. In turn, the polymers were more soluble in the chloroform than the methylene chloride. However, even in the tetrachloroethane solvent the amount of biphenol terephthalate which could be incorporated into the segmented copolymer was limited to 10 to 15 weight percent.

The development of the melt acidolysis technique circumvented this solubility problem by having the synthesis conducted in the

molten state with no solvent. As with the solution and interfacial techniques, a preformed poly(arylene ether sulfone) oligomer of known molecular weight was reacted in the presence of other monomers to form the final segmented copolymer.

Melt acidolysis techniques have been employed previously to produce liquid crystalline polyesters.[38,44] Liquid crystalline polyesters which have been synthesized utilizing this technique include poly(hydroquinone terephthalate), poly(biphenol terephthalate), poly(oxybenzoate), and a variety of copolymers based upon these polymers.

Two similar melt acidolysis techniques were employed to produce the poly(arylene ether sulfone)-poly(arylate) segmented copolymers. In one technique, a heat transfer medium was used to disperse the heat evenly throughout the system. The other melt acidolysis technique used no heat transfer medium, with the reaction being conducted totally in bulk. This second technique was further subdivided into a two step synthesis and a one pot synthesis both of which will be explained in more detail.

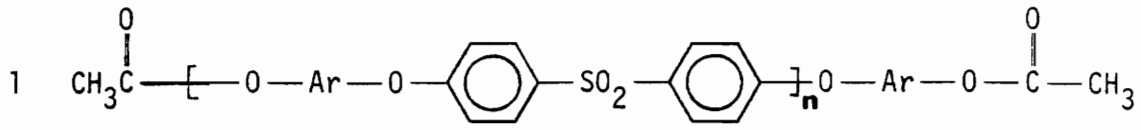
The polyester segment was based on two different aromatic polyesters: poly(biphenol terephthalate) and poly(oxybenzoate). Both of these polyesters are known to form liquid crystalline melts at sufficiently high molecular weights and under certain conditions. [38,44,77]

4.8.1 Heat Transfer Melt Acidolysis Process: Synthesis of Segmented Copolymers Containing Poly(Biphenol Terephthalate)

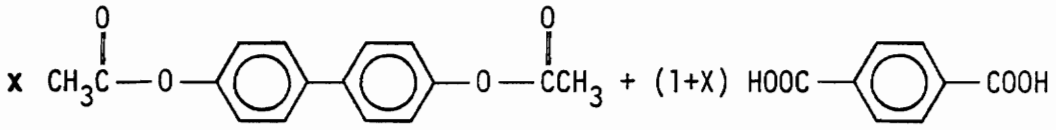
In a melt acidolysis process, the polyester segment is synthesized in the presence of a preformed poly(arylene ether sulfone) oligomer. The synthetic scheme for a melt acidolysis reaction which employs a heat transfer medium is shown in Scheme 33. The heat transfer medium in this case is diphenyl sulfone. Other heat transfer mediums have been employed in the synthesis of liquid crystalline polyesters.[38,44,96] The heat transfer medium in these cases was typically Therminol 66®, which is a mixture of ortho, meta, and para isomers of cyclohexyl biphenyls and dicyclohexyl biphenyls; however, Dowtherm® has also been used.

The diphenyl sulfone is a solid at room temperature but melts at approximately 124°C. Once the diphenyl sulfone melted, the poly(arylene ether sulfone) diacetate oligomer and biphenol diacetate became soluble. The terephthalic acid, however, is not soluble and remains as a finely divided powder in the reaction medium. Thus, this reaction process could also be termed a slurry process. The diphenyl sulfone serves a dual function. One function is to somewhat homogenize the reaction mixture and evenly distribute the heat throughout the system. The second function is that of lowering the viscosity of the system so that good mixing occurs, especially in the latter stages of the polymerization when the viscosity is typically high.

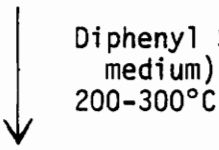
In these reactions, the hydroxyl terminated poly(arylene ether sulfone) oligomer and the 4,4'-biphenol were converted to their

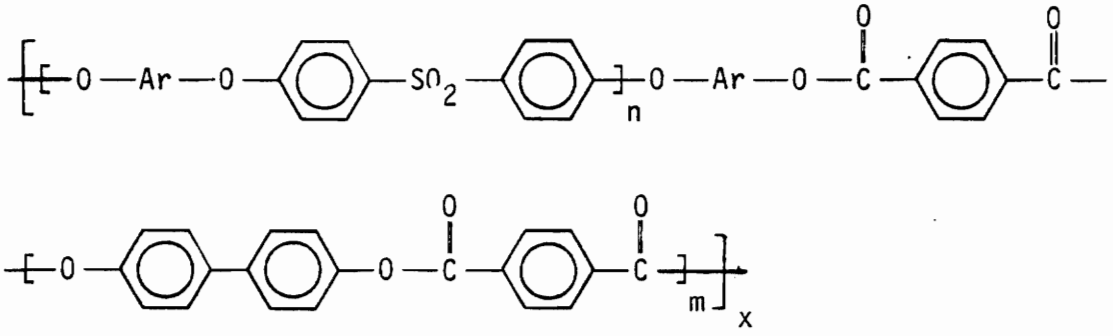


Polysulfone Diacetate Oligomer

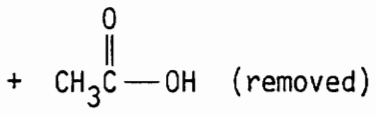


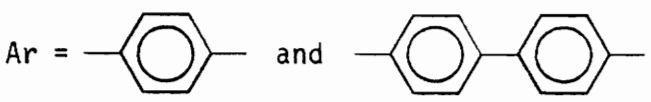
Biphenol Diacetate Terephthalic Acid





Poly(arylene ether sulfone)-Poly(biphenol terephthalate) Copolymer





SCHEME 33. Heat transfer melt acidolysis process used in synthesizing poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymers.

corresponding diacetate derivatives. They were isolated and characterized before being polymerized. All of the reactants were mixed together in the reaction kettle before being heated. The reaction mixture was then heated quickly (~15 minutes) to 200-225°C. This temperature was above the melting points of the diphenyl sulfone and biphenol diacetate. The glass transition temperature of the poly(arylene ether sulfone) oligomer is also typically in this range.

The temperature was kept in this range for approximately 1 hour to incorporate the terephthalic acid into oligomers. The terephthalic acid was incorporated into oligomers to lessen the possibility of sublimation of this monomer at higher temperatures. Sublimation of the terephthalic acid (a major problem) would then result in a stoichiometric imbalance in the reactants and lowering of the final molecular weight of the polymer. The temperature of the reaction mixture was raised stepwise throughout the reaction in an effort to stay above any melting point of the polymers. Staying above the melting point of the polymer enhances the reactivity of the endgroups of the growing chains. The chain ends are much more mobile above the melting point.

The reaction is pushed toward completion by removing the byproduct, acetic acid, from the reaction. The acetic acid is distilled from the reaction at the temperatures (~300°C) employed in the synthesis of the copolymers. A steady stream of argon also enhances the removal of the acetic acid.

The segmented poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymers were isolated from the reaction medium by

pouring the molten mixture into acetone. The diphenyl sulfone was soluble in the acetone and was removed by extracting with acetone. A collection of the segmented copolymers synthesized by this process is shown in Table 13. A much greater percentage of the poly(biphenol terephthalate) was incorporated by this melt acidolysis technique than by the solution or interfacial techniques. Other poly(arylene ether sulfone) oligomers with varying molecular weights (3700-6700 $<M_n>$) as well as varying composition (all biphenol polysulfones) showed similar results.

4.8.2 Heat Transfer Melt Acidolysis Process: Synthesis of Segmented Poly(Arylene Ether Sulfone)-Poly(Oxybenzoate) Copolymers

Poly(arylene ether sulfone)-poly(oxybenzoate) segmented copolymers were also synthesized by a melt acidolysis process employing a heat transfer medium. The synthetic scheme leading to these segmented copolymers is shown in Scheme 34. The overall synthesis is very similar to that of the poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymer synthesis. The diphenyl sulfone is again used as the heat transfer medium.

The major difference between the two synthetic schemes is that the p-acetoxybenzoic acid has a self-limiting (A-B) stoichiometry built into the monomer. Thus, stoichiometry in these reactions is not as critical as for the poly(biphenol terephthalate) containing segmented copolymers.

Another important difference is that control of the polymerization temperature for the poly(oxybenzoate) containing

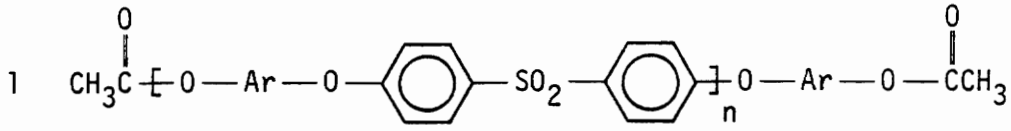
TABLE 13

SERIES OF POLY(ARYLENE ETHER SULFONE)-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMERS SYNTHESIZED VIA THE HEAT TRANSFER MELT ACIDOLYSIS PROCESS

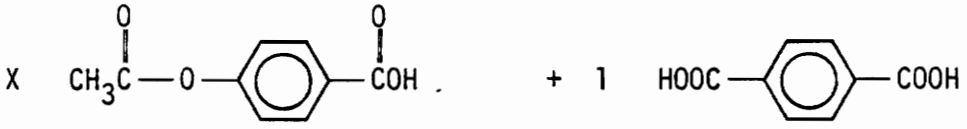
Sample	Polysulfone[1] Segment $\langle M_n \rangle$	Poly(Biphenol Terephthalate) Content[2]	
		Mole %	Weight %
1	3900	11.5	2.3
2	3900	16.7	3.8
3	3900	33.3	13.5
4	3900	42.9	31.9
5	3900	46.2	50.0

(1) The polysulfone was a hydroquinone/biphenol 50/50 polysulfone.

(2) Theoretical or charged amount of poly(biphenol terephthalate).

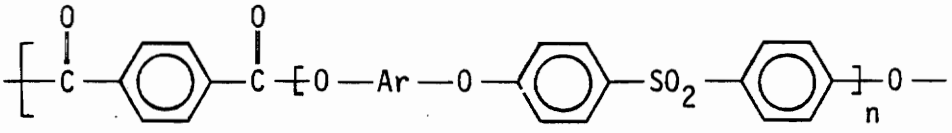


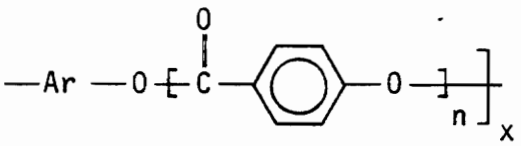
Polysulfone Diacetate Oligomer



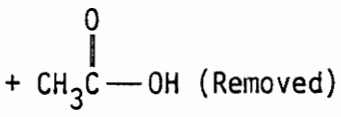
p-Acetoxybenzoic Acid Terephthalic Acid

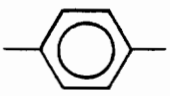
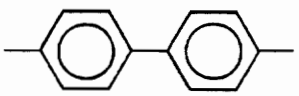
Diphenyl sulfone (heat transfer medium)
200-300°C





Poly(arylene ether sulfone)-Poly(oxybenzoate) Copolymer



Ar =  and 

SCHEME 34. Heat transfer melt acidolysis process for the synthesis of poly(arylene ether sulfone)-poly(oxybenzoate) segmented copolymer.

segmented copolymers is more critical. The p-acetoxybenzoic acid monomer melts at 189-191°C so the initial temperature of the reaction was minimally 200°C. It has also been reported [38,102] that p-acetoxybenzoic acid rapidly polymerizes between 250-280°C. Thus, the temperature of the reaction mixture was adjusted between these limits and kept there for a sufficient time to effect polymerization.

The isolation and workup of the poly(arylene ether sulfone)-poly(oxybenzoate) segmented copolymers were the same as for the poly(biphenol terephthalate) containing copolymers. Table 14 is a collection of two series of poly(arylene ether sulfone)-poly(oxybenzoate) segmented copolymers synthesized via the heat transfer melt acidolysis route.

4.8.3 Two Step Bulk Melt Acidolysis Process

A two step bulk melt acidolysis technique was also developed in order to synthesize the segmented copolymers. The two step technique differs from the heat transfer melt acidolysis process in that no heat transfer medium is used. The elimination of the diphenylsulfone heat transfer medium facilitated the isolation and cleanup of the synthesized copolymers. A source of impurities was also excluded by eliminating the diphenyl sulfone.

The synthetic steps leading to copolymer formation are shown in Scheme 35. The first step of the reaction is the synthesis of the precursor diacetate monomers. Separately, the hydroxyl terminated poly(arylene ether sulfone) oligomer and 4,4'-biphenol were converted into their diacetate derivatives. Both of these diacetates were

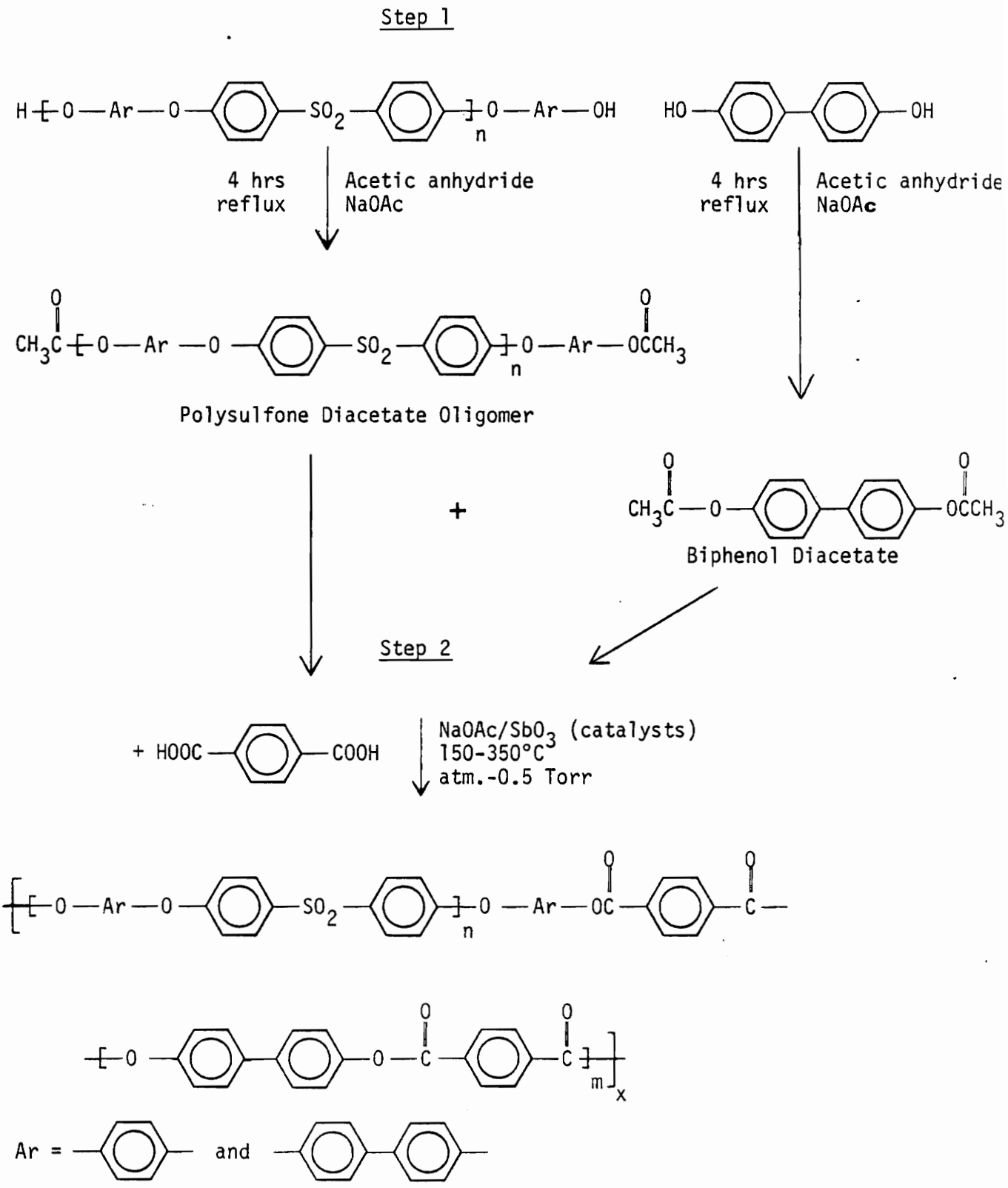
TABLE 14

POLY(ARYLENE ETHER SULFONE)-POLY(OXYBENZOATE) SEGMENTED COPOLYMERS SYNTHESIZED VIA THE HEAT TRANSFER MELT ACIDOLYSIS PROCESS

Sample	Polysulfone[1] Segment $\langle M_n \rangle$	Amount of Poly(Oxybenzoate)[2]	
		Mole %	Weight %
1	3900	66	10
2	3900	89	33
3	6700	97	50
4	6700	99	75

(1) Hydroquinone/biphenol 50/50 polysulfone.

(2) Based on theoretical or charged amount of p-acetoxybenzoic acid.



SCHEME 35. Two step melt acidolysis process used to synthesize poly(arylene ether sulfone)-poly(arylate) segmented copolymers.

isolated and characterized. The reaction quantitatively forms the diacetate endgroups on the polysulfone oligomer and biphenol monomer. In the second step of the melt acidolysis reaction, the two diacetates were reacted with terephthalic acid in the melt.

The temperature of the melt was kept higher than for the heat transfer process due to the higher viscosities encountered. The acetic acid byproduct removal was simplified and made more efficient by applying a vacuum to the system. The vacuum was also used to increase the molecular weight of the copolymers. Once the viscosity of the system became too high to stir, the vacuum was increased to its maximum value (0.5 Torr). This process is termed solid state polymerization and usually takes place below the melting point of the polymer.[56,61] The polymer was isolated by cooling to room temperature and then extracting with acetone in a Soxhlet extractor. Oftentimes when the polymer was cooled, it adhered to the glass reactor and actually removed glass fragments from the walls of the vessel, demonstrating its adhesive properties.

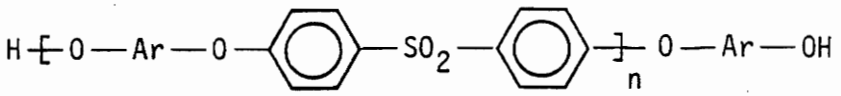
Segmented poly(arylene ether sulfone)-poly(oxybenzoate) copolymers were also synthesized by this two step technique. As with the heat transfer melt acidolysis process, the temperatures were slightly higher for the poly(oxybenzoate) containing copolymers.

4.8.4 One Pot Melt Acidolysis Process

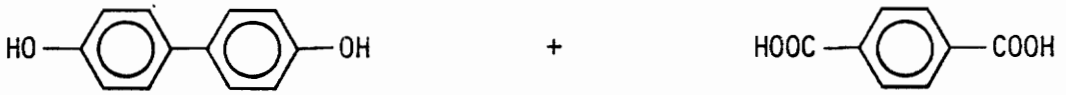
Characterization of the intermediate diacetate products isolated from the two-step melt acidolysis process revealed a quantitative reaction for this step. It was then deduced that isolation of these

intermediate products was not required since no further cleanup of the derivatives is necessary. A one pot or one step process was thus developed to overcome the isolation step of the reaction. Scheme 36 shows the essential features of this one pot melt acidolysis process. In this process, the diacetates of the poly(arylene ether sulfone) oligomer and 4,4'-biphenol are still formed. However, they are formed in the presence of the third monomer, terephthalic acid. The terephthalic acid was not expected nor observed to interfere with the diacetate formation. The diacetates were not isolated or characterized in this process. They were subsequently reacted with the terephthalic acid in the same reaction flask. Before the temperature was raised to the 200°C range to begin the melt acidolysis reaction, the excess acetic anhydride and acetic acid were removed by vacuum distillation. This is much the same process as was used to originally synthesize the diacetates. The catalyst (sodium acetate) used in the acetate formation step is also a catalyst for the melt acidolysic reaction. Thus, the catalyst does not need to be removed or deactivated before the melt acidolysis reaction can take place.

One feature of this one pot melt acidolysis process which required further investigation was the heterogeneous nature of the polysulfone diacetate formation. Previously, when the hydroxyl terminated polysulfone was converted into its diacetate derivative, a solvent was employed. The solvent was usually chloroform, and the poly(arylene ether sulfone) was dissolved in it before being reacted with the acetic anhydride. The poly(arylene ether sulfone) not being soluble in the acetic anhydride alone. In this one pot synthesis, the

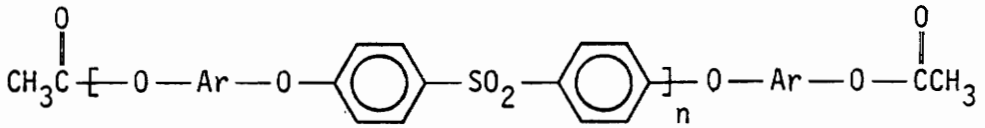


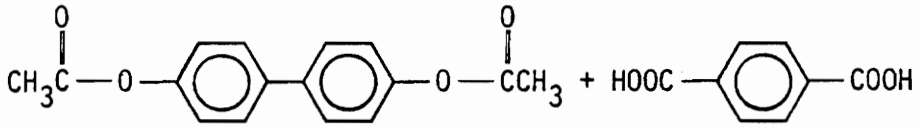
Hydroxyl Terminated Polysulfone Oligomer



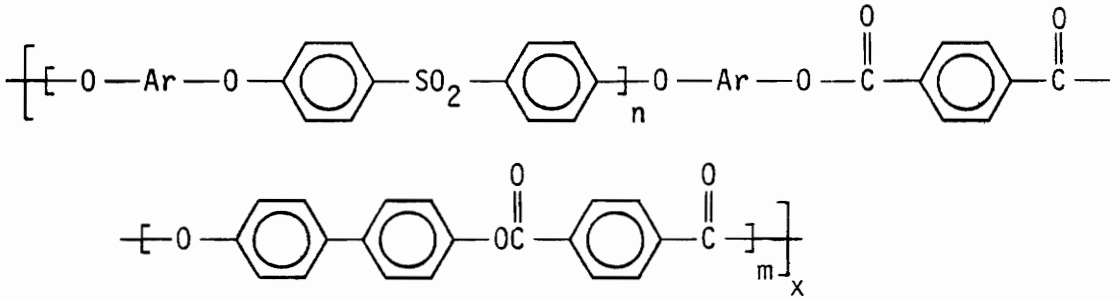
4,4'-Biphenol + Terephthalic Acid

reflux 1-4 hrs. | NaOAc (catalyst) $(Ac)_2O$

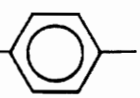
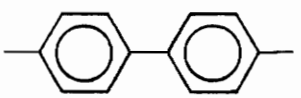




150-350°C
atm-0.5 Torr



Poly(arylene ether sulfone)-Poly(biphenol terephthalate) Copolymer

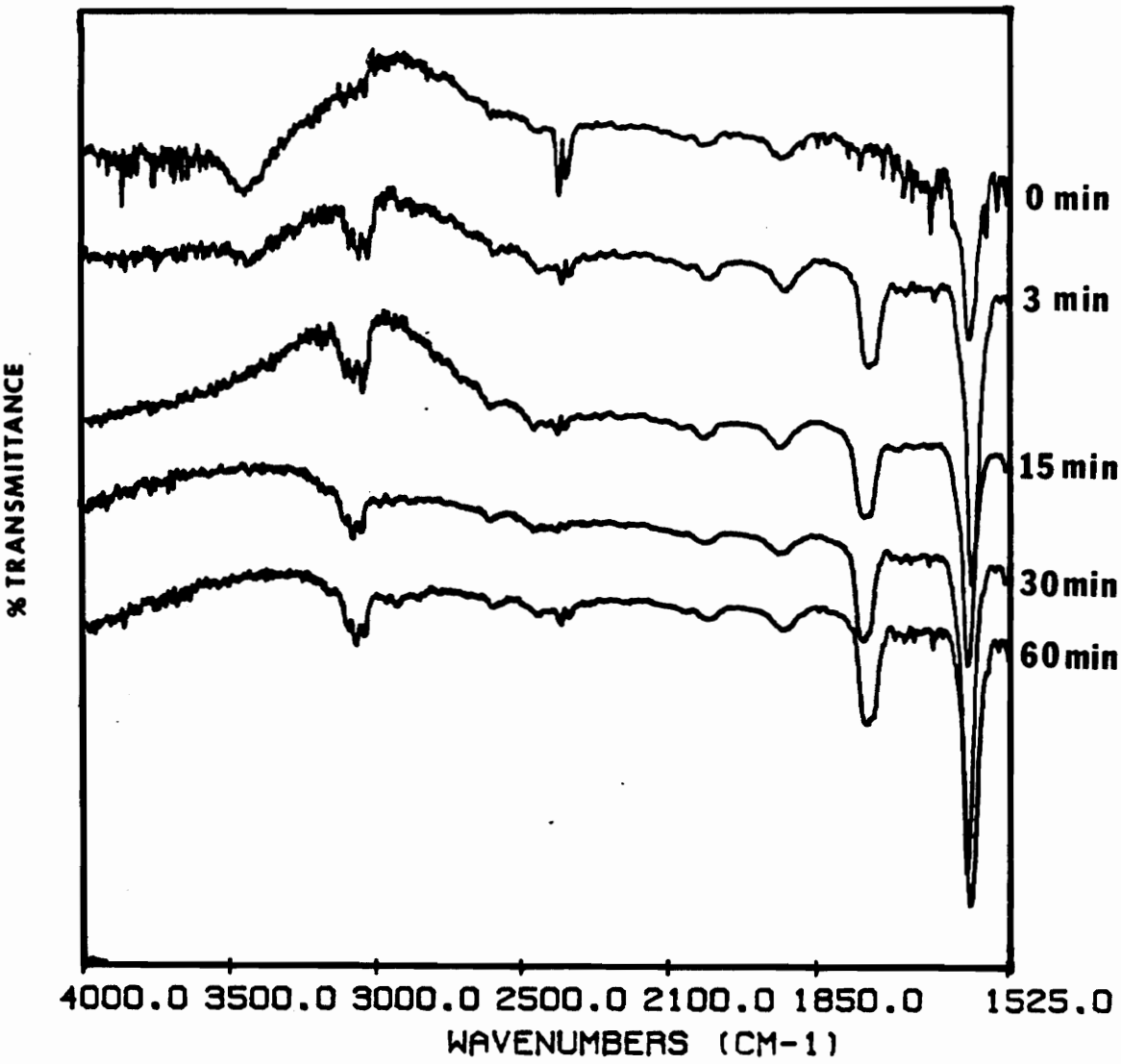
Ar =  and 

SCHEME 36. One pot melt acidolysis process employed in the synthesis of poly(arylene ether sulfone)-poly(arylate) segmented copolymers.

polysulfone was reacted with the acetic anhydride without using a solvent.

In order to confirm the utility of this heterogeneous reaction further investigation was necessary. A model reaction between a hydroxyl terminated hydroquinone/biphenol polysulfone and acetic anhydride with sodium acetate catalyst was studied. Aliquots of the reaction mixture were taken as a function of time, the oligomer isolated, and FT-IR spectra taken of the products. These spectra are overlayed in Scheme 37. In Scheme 37 at time 0, before the reaction was started, one notices a broad hydroxyl stretch centered around 3400 cm^{-1} due to the hydroxyl endgroups of the polysulfone oligomer. Then even in as little reaction time as 3 minutes, the hydroxyl stretch is diminished and a carbonyl stretch appears at 1762 cm^{-1}. The carbonyl stretch appears due to the acetate endgroups being formed. At 15 minutes and greater reaction times, the hydroxyl stretch has completely disappeared and the carbonyl stretch is at its maximum size. The conclusion can thus be drawn that the heterogeneous reaction between a hydroxyl terminated polysulfone and acetic anhydride can be considered quantitative and very fast. Thus, the reaction times employed in this part of the reaction in the one pot synthesis should be many times longer than would appear necessary to completely form the diacetate product.

The melt acidolysis part of the reaction was then conducted in the same manner as for the two step melt acidolysis process. The isolated polymers appeared no different when synthesized using this reaction process in comparison to the other melt acidolysis processes.



SCHEME 37. FT-IR spectra as a function of time for a hydroxyl terminated hydroquinone/biphenol 50/50 polysulfone reacted with acetic anhydride.

A collection of the pertinent data for a series of poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymers is shown in Table 15. This one pot melt acidolysis technique was also used to synthesize poly(arylene ether sulfone)-poly(oxybenzoate) segmented copolymers. Table 16 contains the pertinent information for a series of the poly(oxybenzoate) containing copolymers. Both series of segmented copolymers contain 50 weight percent of the polyester moiety and the poly(arylene ether sulfone) segment molecular weight was varied.

TABLE 15

POLY(ARYLENE ETHER SULFONE)-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMERS SYNTHESIZED VIA THE ONE POT MELT ACIDOLYSIS PROCESS

Sample	Polysulfone Segment $\langle M_n \rangle$	Polysulfone Segment Composition	Poly(Biphenol Terephthalate) Content	
			Mole %	Weight %
1	2900	Hq/Bp 50/50	45.0	50
2	3900	Hq/Bp 50/50	46.2	50
3	4200	Hq/Bp 50/50	46.4	50
4	6700	Hq/Bp 50/50	47.7	50
5	1800	Hq/Bp 0/100	42.9	50
6	3700	Hq/Bp 0/100	46.2	50
7	5500	Hq/Bp 0/100	47.2	50

TABLE 16

POLY(ARYLENE ETHER SULFONE)-POLY(OXYBENZOATE) SEGMENTED COPOLYMERS SYNTHESIZED VIA THE ONE POT MELT ACIDOLYSIS PROCESS

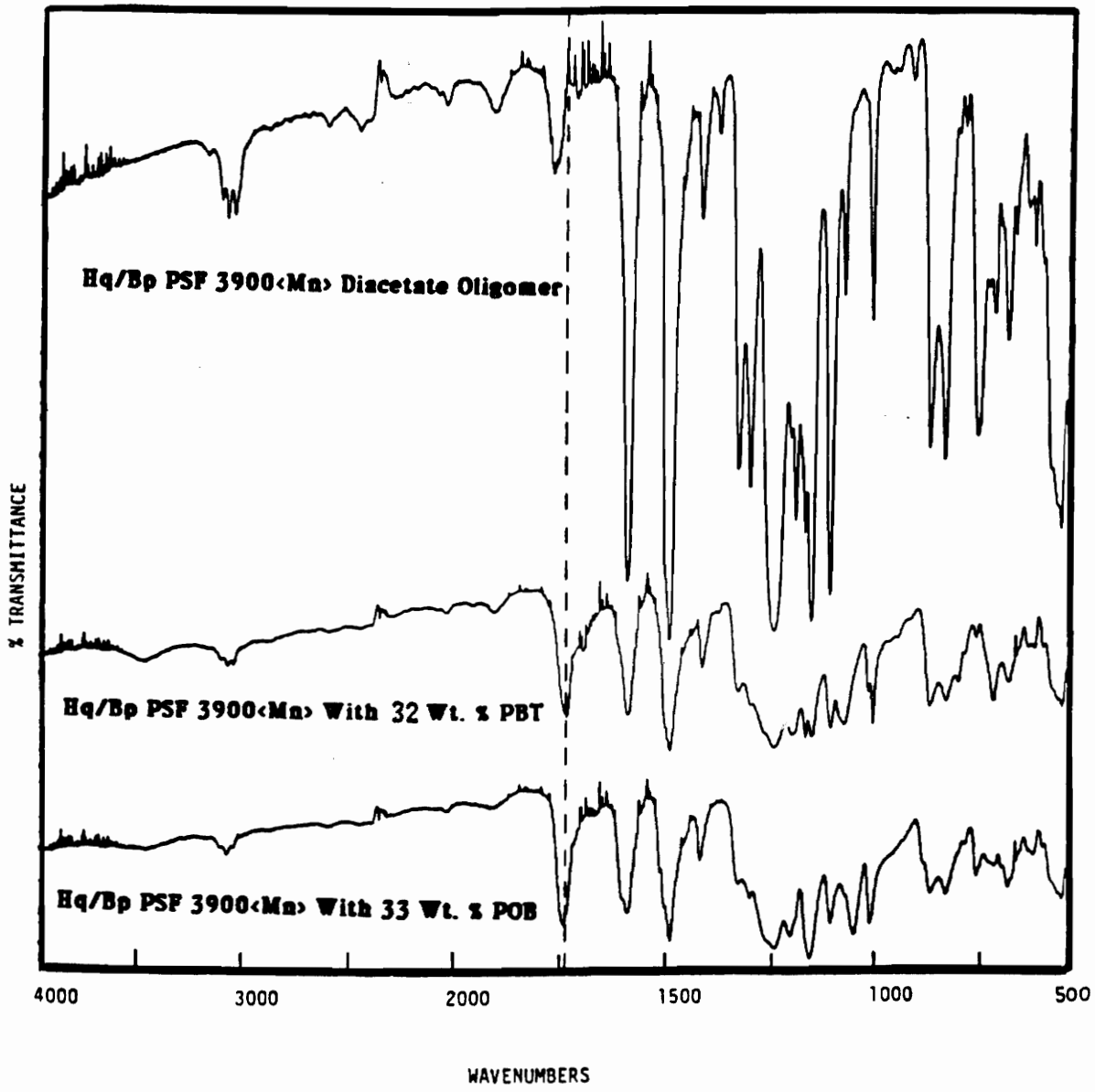
Sample	Polysulfone Segment $\langle M_n \rangle$	Polysulfone Segment Composition	Poly(Oxybenzoate) Content Mole %	Weight %
1	2900	Hq/Bp 50/50	92.6	50
2	3900	Hq/Bp 50/50	94.4	50
3	4200	Hq/Bp 50/50	94.7	50
4	6700	Hq/Bp 50/50	96.6	50
5	1800	Hq/Bp 0/100	88.9	50
6	3700	Hq/Bp 0/100	94.1	50
7	5500	Hq/Bp 0/100	95.8	50

4.9 Characterization of Melt Acidolysis Synthesized Poly(Arylene Ether Sulfone)-Poly(Arylate) Segmented Copolymers

Even though the melt acidolysis technique was subdivided into three different processes, the composition of the segmented copolymers produced were the same. Thus, the same characterization techniques were employed to elucidate the structures and properties of the polymers.

The chemical compositions of the segmented copolymers were confirmed by FT-IR. Scheme 38 is an overlay of FT-IR spectra of a 3900 $\langle M_n \rangle$ hydroquinone/biphenol polysulfone diacetate oligomer and two segmented copolymers made from this oligomer. One of the segmented copolymers contained 32 weight percent poly(biphenol terephthalate) (Sample 4, Table 13). The other copolymer (Sample 2, Table 14) contained 33 weight percent poly(oxybenzoate) segments.

Comparison of the polysulfone diacetate oligomer spectrum with the spectra of the two segmented copolymers confirms the copolymer structure. The poly(arylene ether sulfone) oligomer spectrum shows a carbonyl stretch centered at 1762 cm^{-1} and the characteristic polysulfone peaks (see Section 4.3, Table 7). The carbonyl stretch arises from the acetate endgroups. The spectra for the two segmented copolymers also show a carbonyl stretch. However, the carbonyl stretch for the copolymers comes from the polyester linkages and appears at 1734 cm^{-1}. Thus, comparing the polysulfone oligomer spectrum to the segmented copolymer spectra, the carbonyl stretch of the acetate endgroups of the polysulfone oligomer is lost, as expected, when the copolymers are formed. The carbonyl stretching



SCHEME 38. Overlay of FT-IR spectra of a 3900 $\langle M_n \rangle$ Hq/Bp polysulfone diacetate oligomer and segmented copolymers containing 32 weight % poly(biphenol terephthalate), PBT, and 33 weight % poly(oxybenzoate), POB.

peaks due to the polyester segments are in the region of aromatic carbonyl stretching peaks. The characteristic polysulfone peaks are also evident in the copolymer spectra. This indicates that the poly(arylene ether sulfone) segments are not being degraded when incorporated into the copolymer.

Another salient feature of the FT-IR spectra is the relative intensities of the carbonyl peaks in relation to the polysulfone peaks within the same material. For example, in the polysulfone oligomer spectrum, the carbonyl stretching peak is relatively small in comparison to the polysulfone carbon-oxygen-carbon ether stretch at 1250 cm^{-1}. This is to be expected since there are only two acetate endgroups per oligomer chain, while there are many ether linkages. (See Section 4.8.3, Scheme 35.) Making this same comparison with either of the segmented copolymers gives a different result. The carbonyl peak for the polyester segment is of approximately the same size as the ether stretch of the polysulfone segment. Again this is justified by the fact that the weight percentages of the polyester segments and the polysulfone segments are of the same magnitude. An exact comparison between the relative sizes of the two peaks cannot be made since the two peaks have different extinction coefficients.

Thus, the FT-IR data not only confirms the segmented copolymer structure but also gives some information on the nature of the reaction. It shows that the high temperatures used in this synthesis does not degrade the poly(arylene ether sulfone) nor the poly(arylate) segments. The relative amounts of each segment is also alluded to by FT-IR.

Reduced viscosity values were determined for the poly(arylene ether sulfone)-poly(arylate) segmented copolymers to give a qualitative estimate of the copolymer molecular weights. The reduced viscosity values for a poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymer series are collected in Table 17. The values for this series are all approaching 0.5 deciliters/gram (dl/g). This is an indication that the molecular weights are sufficiently high to display good mechanical and thermal properties. Generally, viscosity values in this range indicate molecular weights on the order of 20,000 to 30,000 g/mole.

Reduced viscosity values were also determined for segmented copolymers based on poly(oxybenzoate). These values are collected in Table 18. The reduced viscosity values for the copolymers with increasing polyester contents are seen to decrease throughout the series. This observation is made in both the poly(biphenol terephthalate) and poly(oxybenzoate) based copolymers. The two most plausible explanations for this observation are directed toward the molecular weights of the copolymers or the nature of viscosity solvent. The lower viscosity values may be due to a lower molecular weight for the poly(arylene ether sulfone)-poly(arylate) copolymers with higher polyester contents. However, other qualitative evidence does not lend credence to this explanation. Extraction of the polymer gave no evidence of an excessive amount of unreacted monomer, which would indicate a lower molecular weight copolymer. FT-IR spectra also indicate no unreacted monomer of any type in the segmented copolymers. Compression molded films of the copolymers, although somewhat brittle,

TABLE 17

REDUCED VISCOSITY VALUES FOR A SERIES OF POLY(ARYLENE ETHER SULFONE)-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMERS

Sample	Polysulfone Segment $\langle M_n \rangle$	Poly(Biphenol Terephthalate) Content		Reduced Viscosity Value(1)
		Mole %	Weight %	
1	3900	16.7	3.8	0.47
2	3900	33.3	13.5	0.37
3	3900	42.9	31.9	0.41
4	3900	46.2	50.0	0.30

(1) The reduced viscosity values were determined in trifluoromethane sulfonic acid (triflic acid) at 25°C. The units of reduced viscosity are deciliters/gram.

TABLE 18

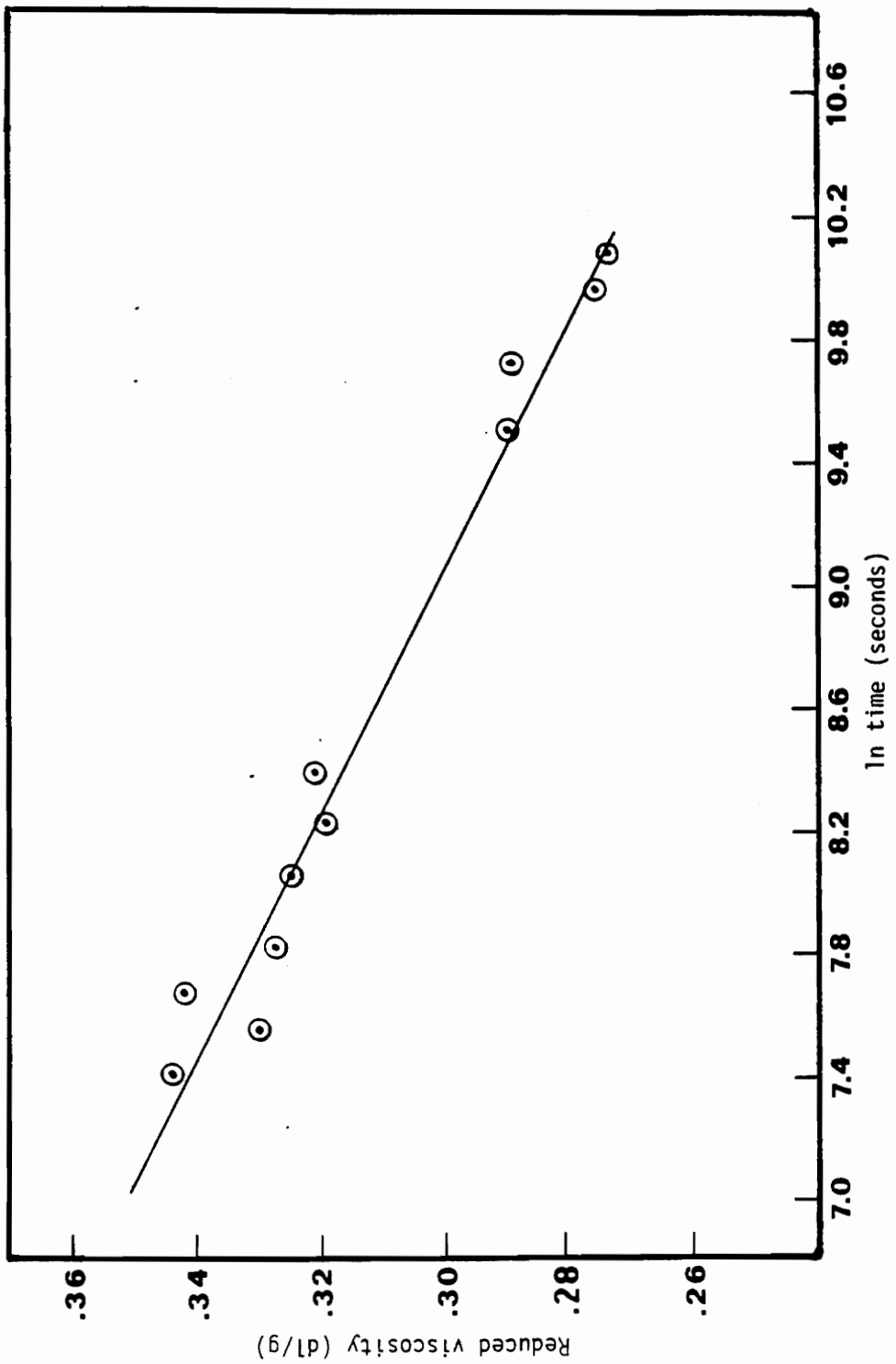
REDUCED VISCOSITY VALUES FOR POLY(ARYLENE ETHER SULFONE)-POLY(OXYBENZOATE) SEGMENTED COPOLYMERS

Sample	Polysulfone Segment $\langle M_n \rangle$	Poly(Oxybenzoate) Content		Reduced Viscosity Values(1)
		Mole %	Weight %	
1	3900	66	10	0.25
2	3900	89	33	0.19
3	6700	97	50	0.23
4	6700	99	75	0.15

(1) Reduced viscosity values determined at 25°C in triflic acid. The units of reduced viscosity are dl/g.

are strong and coherent. A more plausible explanation involves the solvent in which the reduced viscosities were determined. Trifluoromethane sulfonic acid (triflic acid) was used as the solvent since the copolymers with high ester content were insoluble in any common laboratory solvent tested. Triflic acid is one of the strongest acids available. Thus, hydrolysis of the polyester segments of the copolymers is of prime consideration. Since polyesters are susceptible to hydrolysis by acids and bases, it is not surprising that triflic acid would lower the molecular weight of the copolymers.

This theory was tested through a simple experiment. This experiment involved the measurement of the reduced viscosity of a poly(arylene ether sulfone)-poly(oxybenzoate) copolymer (Table 18, Sample 1) as a function of time. The relationship between the reduced viscosity and time is shown in Scheme 39. The reduced viscosity is seen to decrease with ln time almost linearly (correlation coefficient of -0.987). This experiment demonstrates that the triflic acid solvent does lower the molecular weight with time. Thus, the reduced viscosity values given in Tables 17 and 18 are probably low due to this hydrolysis reaction. From Scheme 39, in the limit as ln time goes to zero, the reduced viscosity value is 0.53. This indicates that if the reduced viscosity could be measured before any hydrolysis takes place, the value obtained would be much higher. Another indication that the reduced viscosity values and thus the copolymer molecular weights may be higher than indicated comes from Sample 2 in Table 17. This segmented poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymer has a low enough polyester content (33 mole



SCHEME 39. Relationship between reduced viscosity and time for a poly(arylene ether sulfone)-poly(oxybenzoate) copolymer in triflic acid.

percent) that it is still soluble in N-methyl-2-pyrrolidone (NMP). The reduced viscosity in this non-hydrolyzing solvent was found to be 0.56 dl/g. This value is compared to 0.37 dl/g found when measured in triflic acid. Thus, the segmented copolymer almost certainly has a higher reduced viscosity and resulting higher molecular weight than indicated by the triflic acid determined values.

The solubility of the poly(arylene ether sulfone)-poly(arylate) segmented copolymers in various solvents gave useful information as to their environmental stress crack resistance. The solubility of the segmented copolymers was ranked by visual observation of an approximately 1 percent weight/volume solution of the polymer in various solvents (see Section 3.1.6). The solvents in increasing solvating power were chloroform, NMP, hot NMP, strong acids including triflic acid. Table 19 contains the solubility ranking of a series of poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymers with increasing biphenol terephthalate content. This table shows that as the amount of poly(biphenol terephthalate) content increases, a stronger solvent is required for solubility. Thus, on a qualitative scale, the incorporation of even a small amount, 15 weight percent, of poly(biphenol terephthalate) renders the copolymer more resistant to attack by common organic solvents. Similar results were obtained for the solubility characteristics of the segmented poly(arylene ether sulfone)-poly(oxybenzoate) copolymers.

The thermal properties of the segmented poly(arylene ether sulfone)-poly(arylate) copolymers were also of great interest. The homopolymers, poly(biphenol terephthalate) and poly(oxybenzoate), are

TABLE 19

SOLUBILITY CHARACTERISTICS OF POLY(ARYLENE ETHER SULFONE)-POLY(BIPHENOL TEREPHTHALATE) SEGMENTED COPOLYMERS

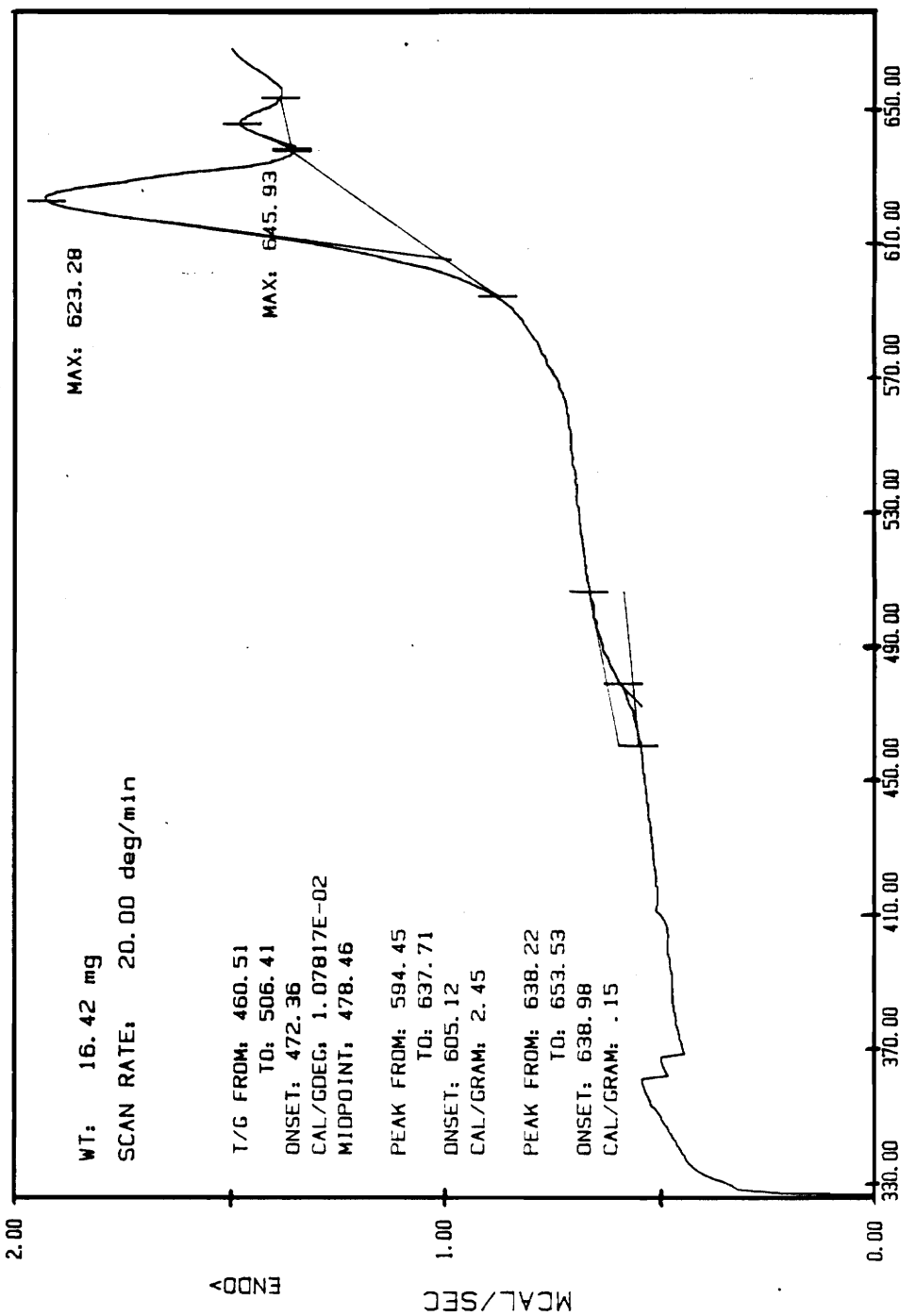
Sample	Polysulfone Segment $\langle M_n \rangle$	Poly(Biphenol Terephthalate) Content		Solubility Solvent[1]
		Mole %	Weight %	
1	3900	11.5	2.3	$CHCl_3$
2	3900	16.7	3.8	NMP
3	3900	33.3	13.5	Hot NMP
4	3900	42.9	31.9	SA[2]
5	3900	46.2	50.0	SA

(1) The solvent listed is the solvent with the lowest solvating power in the series $CHCl_3$ < NMP < Hot NMP < SA in which the polymer was soluble as 1% w/v solutions.

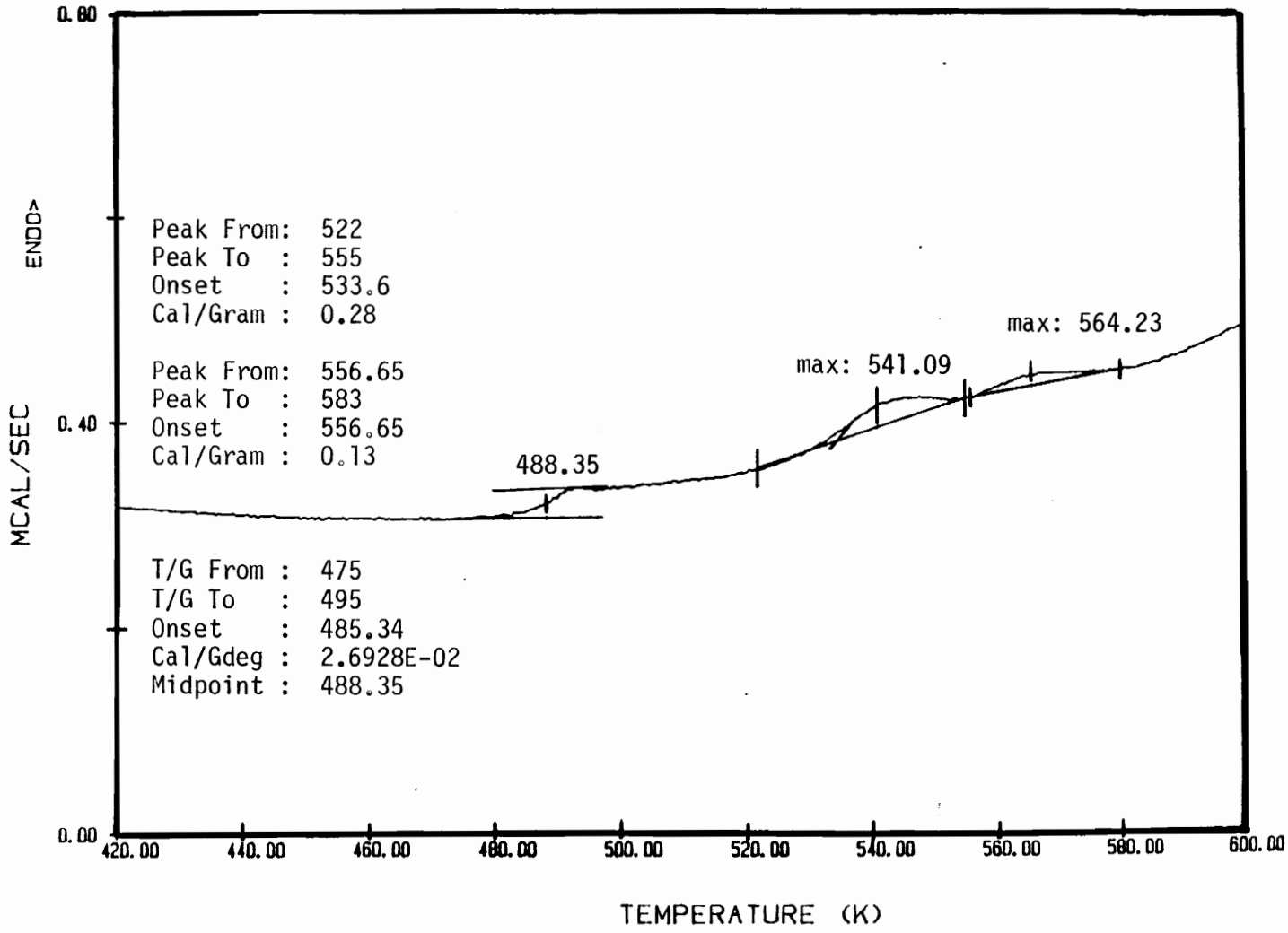
(2) SA is strong acids such as sulfuric acid and triflic acid.

known to be highly crystalline and liquid crystalline.[102,103] The incorporation of segments of these crystalline materials into the amorphous glassy poly(arylene ether sulfone) provided unique thermal properties.

Differential scanning calorimetry (DSC) was used to probe the thermal properties of the poly(arylene ether sulfone)-poly(arylate) segmented copolymers. While most of the segmented copolymers synthesized via the solution or interfacial techniques were totally amorphous, copolymers made by the melt acidolysis technique showed unusual thermal properties. Schemes 40 and 41 are DSC scans of two poly(arylene ether sulfone)-poly(arylate) copolymers. Scheme 40 is a poly(arylene ether sulfone)-poly(biphenol terephthalate) copolymer (Table 15, Sample 3) containing 50 weight percent poly(biphenol terephthalate). Scheme 41 on the other hand, is a poly(arylene ether sulfone)-poly(oxybenzoate) copolymer (Table 16, Sample 4) containing 50 weight percent poly(oxybenzoate). The DSC scans for both segmented copolymers produced a strong glass transition temperature (Tg). The poly(biphenol terephthalate) containing copolymer was based on a 4200 $<M_n>$ hydroquinone/biphenol 50/50 polysulfone and had a measured Tg of 205°C. The poly(oxybenzoate) containing copolymer was based on a 6700 $<M_n>$ hydroquinone/biphenol 50/50 polysulfone and had a Tg of 215°C. As with the solution and interfacially derived segmented copolymers, the glass transition temperatures of these copolymers seemed to be relatively invariant with polyester content. This indicates that the copolymers are microphase separating into polysulfone domains and poly(arylate) domains. The glass transition



SCHEME 40. DSC scan of a 4200 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone-poly(biphenol terephthalate) segmented copolymer containing 50 weight % poly(biphenol terephthalate).



SCHEME 41. DSC scan of a 6700 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone-poly(oxybenzoate) segmented copolymer containing 50 weight % poly(oxybenzoate).

temperatures detected for the segmented copolymers are believed to arise from the polysulfone segments. Further credence to this idea is lent by the glass transition temperature differences between the two samples in Schemes 40 and 41. The poly(arylene ether sulfone) segment of the copolymer containing poly(biphenol terephthalate) had a number average molecular weight of 4200. The poly(oxybenzoate) containing copolymer had a 6700 $<M_n>$ poly(arylene ether sulfone) segment. The Tg for the 6700 $<M_n>$ polysulfone based copolymer was 10°C higher at 215°C than the Tg for the 4200 $<M_n>$ polysulfone based copolymer (Tg = 205°C). Thus, the glass transition temperature increased with an increase in the polysulfone number average molecular weight. The glass transition temperature of a homopolymer is known to be dependent on molecular weight in the same fashion as was observed here.

The DSC scans of these copolymers also revealed multiple endotherms at higher temperatures. Whereas the interfacially prepared copolymers showed one large melting endotherm (see Scheme 31), these copolymers showed one larger endotherm and a smaller endotherm at high temperatures. The poly(biphenol terephthalate) based copolymer showed a large endotherm at 350°C and a smaller endotherm at 373°C. Both of these endotherms were broad but well resolved. The poly(oxybenzoate) based copolymer showed a larger endotherm at 268°C and a 291°C smaller endotherm. These multiple transitions may be due to the crystalline and liquid crystalline nature of the poly(biphenol terephthalate) and poly(oxybenzoate).

The larger of the two endotherms in both cases appear to be true melting endotherms. The smaller second endotherms are theorized to be

liquid crystalline transitions. Support of this theory comes from literature references to thermal properties of liquid crystals. It has been reported [88,104] that liquid crystalline transitions tend to be broad and approximately 10 percent of the area of the crystalline melting endotherm. These two samples showed broad endotherms of approximately a 20°C melting range. The area of the second endotherm of the poly(biphenol terephthalate) based copolymer is approximately 6 percent of the area of the larger endotherm. However, for the poly(oxybenzoate) based copolymer, the smaller of the two endotherms has an area 46 percent of the larger area. Therefore, it is conceivable that the smaller endotherms are liquid crystalline transitions.

DSC scans of other melt acidolysis prepared poly(arylene ether sulfone)-poly(arylate) copolymers also showed glass transition temperatures in the range of 200-220°C. Some of these segmented copolymers also showed multiple melting endotherms. Table 20 is a collection of the glass transition temperatures and large melting endotherm temperatures (Tm) for a variety of melt acidolysis produced poly(arylene ether sulfone)-poly(arylate) copolymers.

The DSC scans for a majority of the melt acidolysis prepared segmented copolymers showed very narrow Tg-Tm "windows." As previously mentioned in this dissertation (Chapter 4, Section 7), the Tg-Tm window determines whether a semicrystalline polymer will thermally crystallize. For these copolymers, the Tg-Tm window was extremely narrow which almost guarantees that thermal recrystallization is prohibited. Repetitive DSC scans of the

TABLE 20

THERMAL PROPERTIES OF POLY(ARYLENE ETHER SULFONE)-POLY(ARYLATE) SEGMENTED COPOLYMERS AS DETERMINED BY DSC

Sample	Polysulfone Segment $\langle M_n \rangle$	Poly(arylate Content) Weight %	Tg(°C)[1]	Tm(°C)(1)
1	3700(2)	7.7 PBT(3)	234	-
2	3900	31.9 PBT	205	355
3	6700	74.7 PBT	214	276
4	3900	10.0 POB(4)	201	-
5	3900	33.0 POB	206	274
6	6700	50.0 POB	215	268
7	6700	75.0 POB	204	336

(1) Tg's and Tm's were measured by the first DSC scan at 20°C/minute.

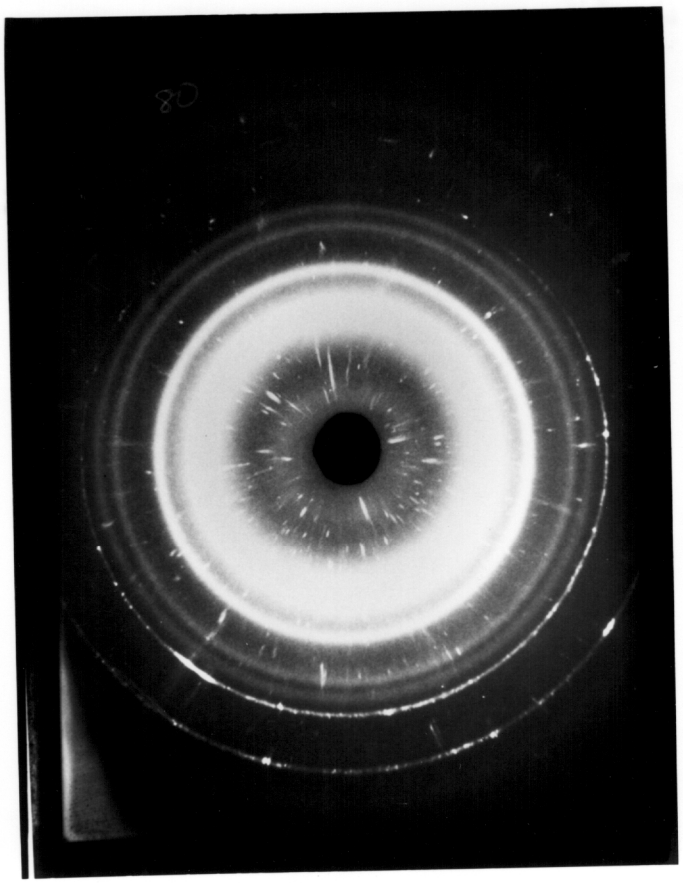
(2) Polysulfone segment is Hq/Bp 0/100 polysulfone; all other polysulfone segments are Hq/Bp 50/50 polysulfones.

(3) PBT designates poly(biphenol terephthalate) based copolymers.

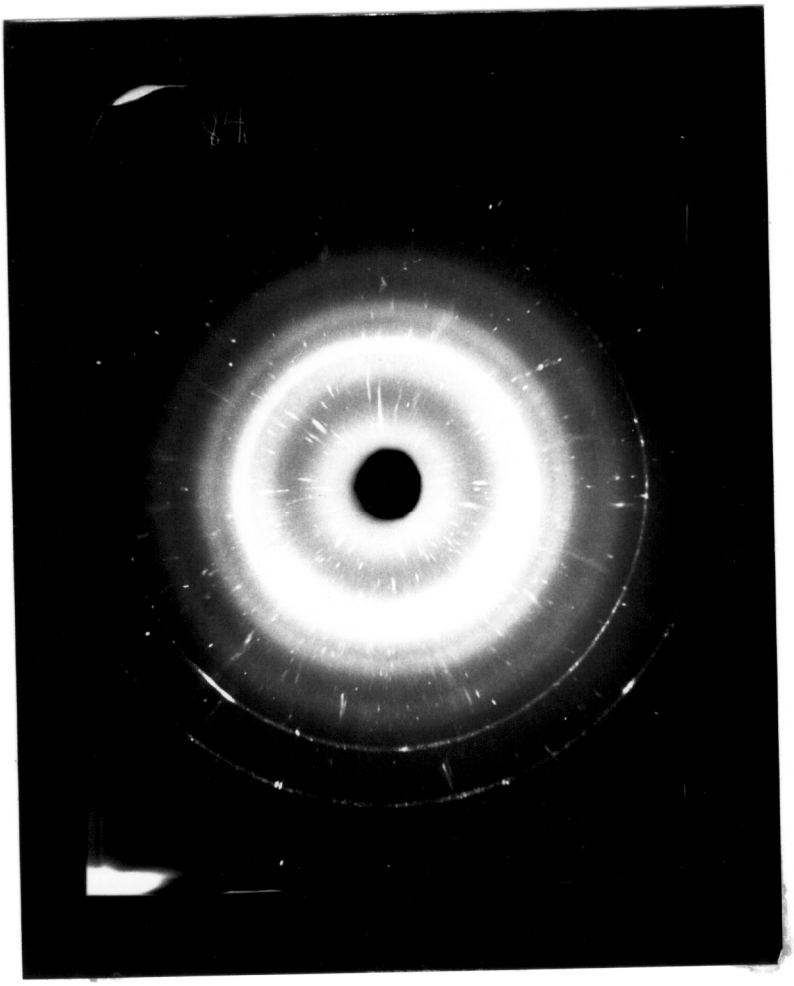
(4) POB designates poly(oxybenzoate) based copolymers.

copolymer samples confirms this statement. Second heating scans show much reduced endotherms for those samples with narrow Tg-Tm windows.

Confirmation of the semicrystalline nature of the copolymers was made by wide angle X-ray scattering (WAXS). Schemes 42 and 43 are WAXS patterns of a poly(arylene ether sulfone)-poly(biphenol terephthalate) (Table 20, Sample 2) and poly(arylene ether sulfone)-poly(oxybenzoate) (Table 20, Sample 5) segmented copolymers respectively. The biphenol terephthalate based copolymer contains 32 weight percent poly(biphenol terephthalate) while the other copolymer contains 33 weight percent poly(oxybenzoate). Both copolymers are based on a 3900 $<M_n>$ hydroquinone/biphenol 50/50 polysulfone. The WAXS patterns for both copolymers show distinct lines indicating crystallinity in the sample. The sharp, bright outer two lines and the bright streaks appear to be anomalous lines not associated with the copolymer. These lines are possibly caused by unextracted diphenyl sulfone used as the heat transfer medium in the reactions. The poly(biphenol terephthalate) based copolymer WAXS pattern shows much sharper lines than does the poly(oxybenzoate) containing copolymer. Both WAXS patterns show the diffuse region associated with the amorphous content of the copolymers. Additionally, a WAXS pattern of an all amorphous copolymer (Table 20, Sample 4) showed no sharp lines, only a diffuse region indicative of the amorphous sample. Thus, WAXS patterns of the poly(arylene ether sulfone)-poly(arylate) copolymers confirms the morphology of the samples as determined through DSC measurements.

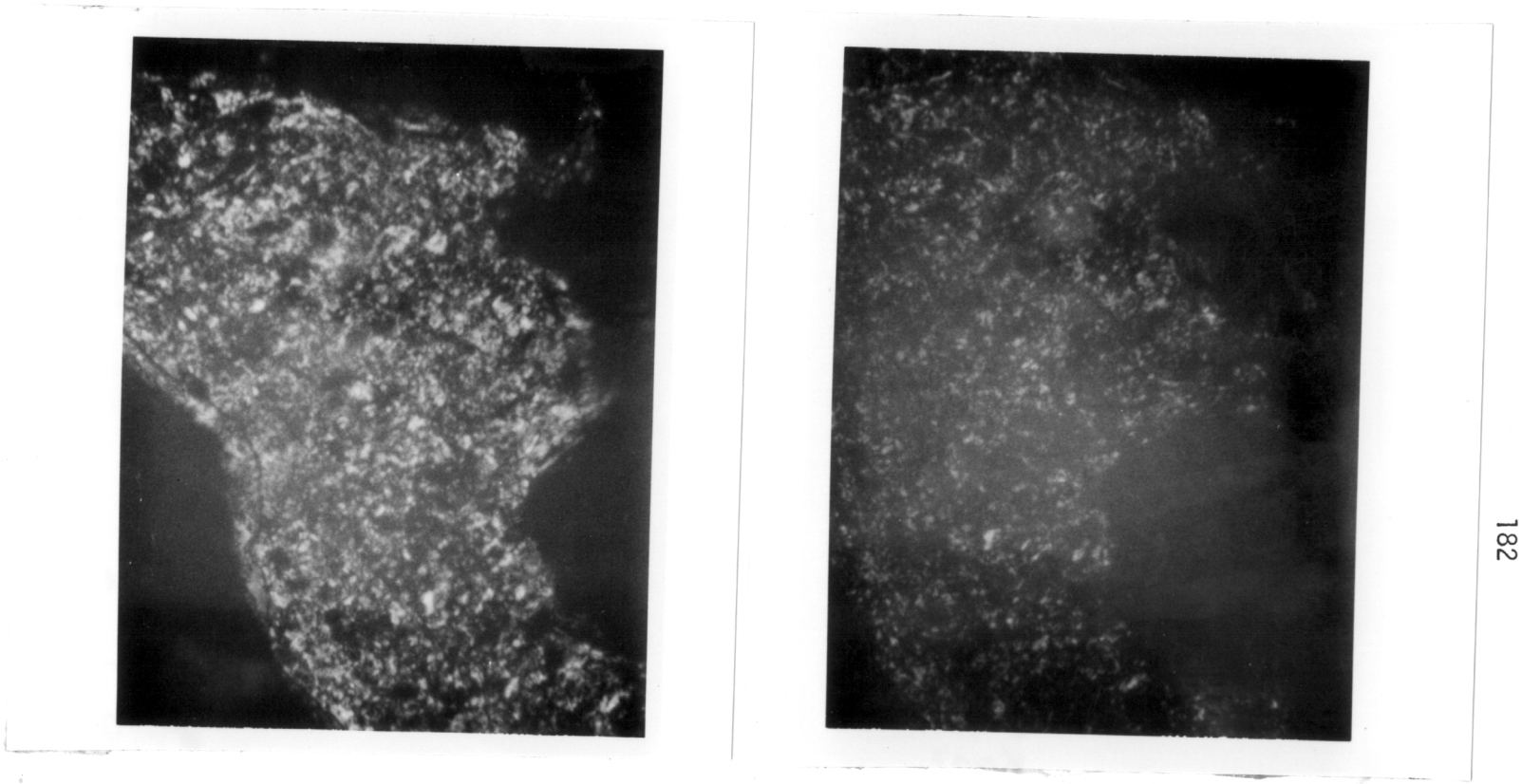


SCHEME 42. Wide angle X-ray scattering pattern of 3900 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone - 32 wt. % poly(biphenol terephthalate) copolymer (Table 20, Sample 2).



SCHEME 43. Wide angle X-ray scattering pattern of 3900 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone - 33 wt. % poly(oxybenzoate) copolymer (Table 20, Sample 5).

To confirm the alluded to liquid crystalline nature of some of the melt acidolysis prepared copolymers, hot stage optical microscopy was performed. Semicrystalline samples when viewed through cross polarizers in an optical microscope will show light and dark regions. The light regions are the result of the crystalline domains depolarizing the polarized light. The dark regions are a result of the amorphous regions of the sample. Scheme 44 shows this type of optical micrograph for a poly(arylene ether sulfone)-poly(oxybenzoate) copolymer containing 33 weight percent of the poly(oxybenzoate). One micrograph was taken at ambient temperature at 400x magnification. The light regions are a result of the depolarization of the polarized light by the crystalline poly(oxybenzoate) domains. The dark regions are a result of the amorphous poly(arylene ether sulfone) domains. Comparison of this optical micrograph with the right one in Scheme 44 gives further evidence of liquid crystallinity in this copolymer. The right optical micrograph in Scheme 44 is of the same copolymer at the same magnification and between cross polarizers but at a temperature of 300°C. Again one sees the light and dark regions associated with crystalline and amorphous regions. However, from DSC data this copolymer has a prominent melting endotherm at 274°C. Thus, even though the sample was heated to above this endothermic transition, there is still some type of residual order in the copolymer. This residual order or liquid crystallinity then depolarizes the polarized light resulting in the light regions in the optical micrograph. One subtle difference which is noted between the two micrographs is the overall amount or brightness of the light regions. The optical



22°C

300°C

SCHEME 44. Optical micrographs of 3900 $\langle M_n \rangle$ Hq/Bp 50/50 polysulfone-33 wt. % poly(oxybenzoate) copolymer (Table 20, Sample 5) viewed between cross polarizers at 22° and 300°C. (400 X magnification)

micrograph taken at 300°C has fewer and less intense light regions. This observation can be explained by the fact that the sample was heated above its first large endotherm. Above this first endotherm a transition takes place from a crystalline phase to a less ordered possibly liquid crystalline phase. Since the sample is changing from containing more ordered crystalline domains to less ordered liquid crystalline domains, the light regions appear less intense. Absolute confirmation of the liquid crystalline nature of these types of samples could not be made. Further heating of the samples should show that the liquid crystalline domains also melt to produce a totally amorphous melt and a uniformly dark optical micrograph. However, the limits of the hot stage of the optical microscope precluded this observation. The copolymer may also decompose before the transition from the liquid crystalline state to the totally amorphous state.[44,47]

Evidence clearly demonstrated the semicrystalline nature of many of the copolymers synthesized by the melt acidolysis technique. However, no single characterization procedure or observation absolutely confirmed or denied the liquid crystalline anisotropic nature of the segmented copolymers. Taken as a whole, however, each characterization technique provided evidence indicating the liquid crystalline nature of the copolymers.

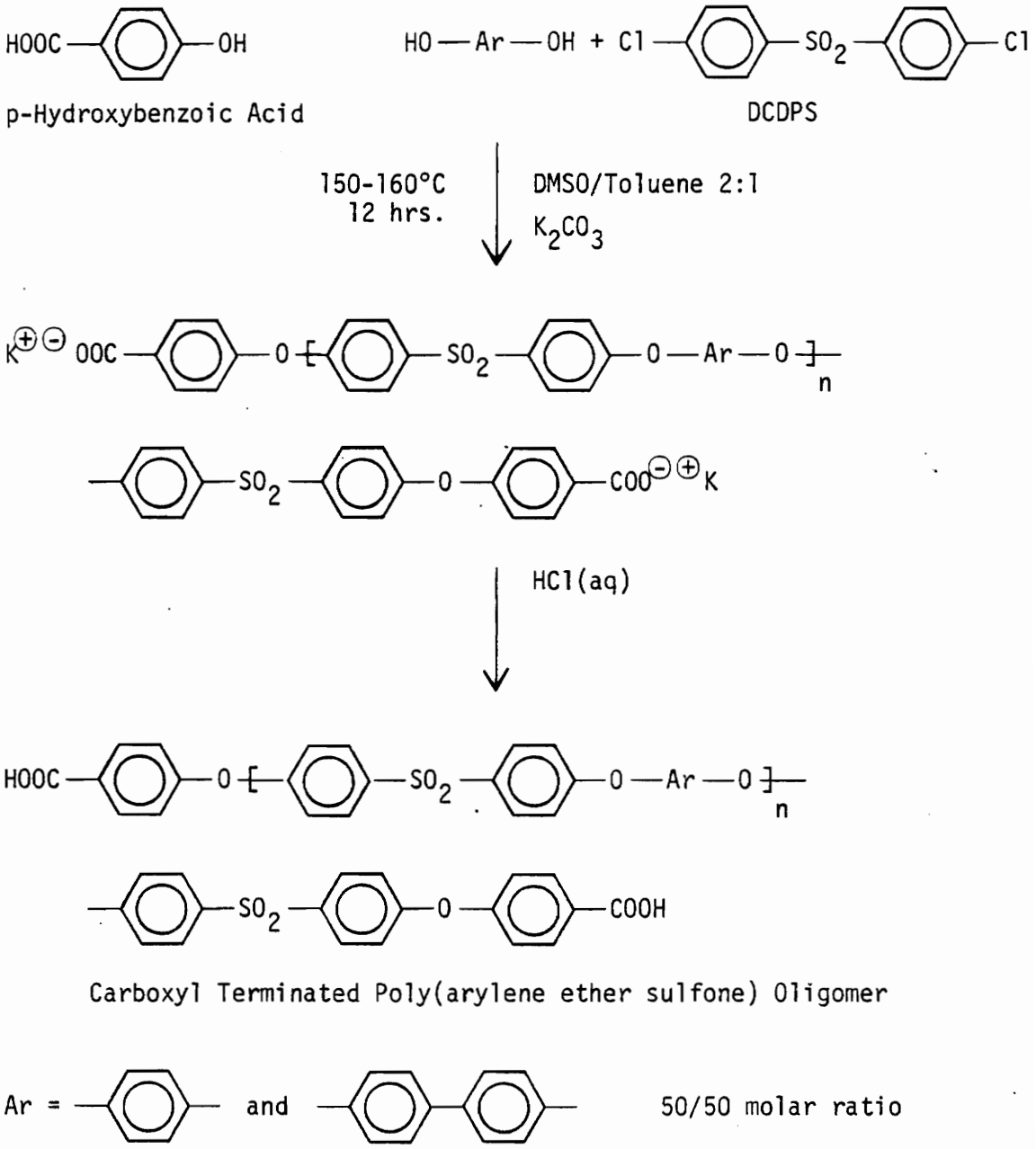
4.10 Synthesis of Carboxyl Terminated Poly(Arylene Ether Sulfone) Oligomers

The major limitation of the melt acidolysis process for synthesizing poly(arylene ether sulfone)-poly(arylate) copolymers was the problem of terephthalic acid sublimation. The terephthalic acid tended to sublime unless it was incorporated into oligomers early in the reaction. If the terephthalic acid sublimed significantly, the stoichiometry of the reaction was upset resulting in lowered molecular weights for the polymers.

Carboxyl terminated poly(arylene ether sulfone) oligomers were synthesized to overcome this limitation. The synthetic scheme leading to a carboxyl terminated polysulfone is shown in Scheme 45. This reaction is very similar to the reaction used to synthesize hydroxyl terminated poly(arylene ether sulfone) oligomers.

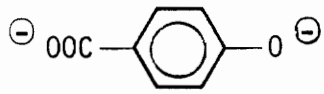
In this nucleophilic displacement reaction the p-hydroxybenzoic acid is monofunctional; that is, the hydroxyl portion of the monomer can displace the chlorine group of the dichlorodiphenyl sulfone (DCDPS) monomer, but the carboxyl group is not a strong enough nucleophile to do this. Thus, the p-hydroxybenzoic acid reacts such that the endgroups of the polysulfone oligomer are carboxyl groups. The molecular weight of the oligomer is controlled by the stoichiometric amount of the monomers used according to the Carothers equation.[35]

The solvent for this reaction was dimethylsulfoxide (DMSO) rather than N-methyl-2-pyrrolidone (NMP) used in the synthesis of hydroxyl



SCHEME 45. Reaction steps leading to the synthesis of carboxyl terminated poly(arylene ether sulfone) oligomers.

terminated polysulfones. It was found that the anions of p-hydroxybenzoic acid:



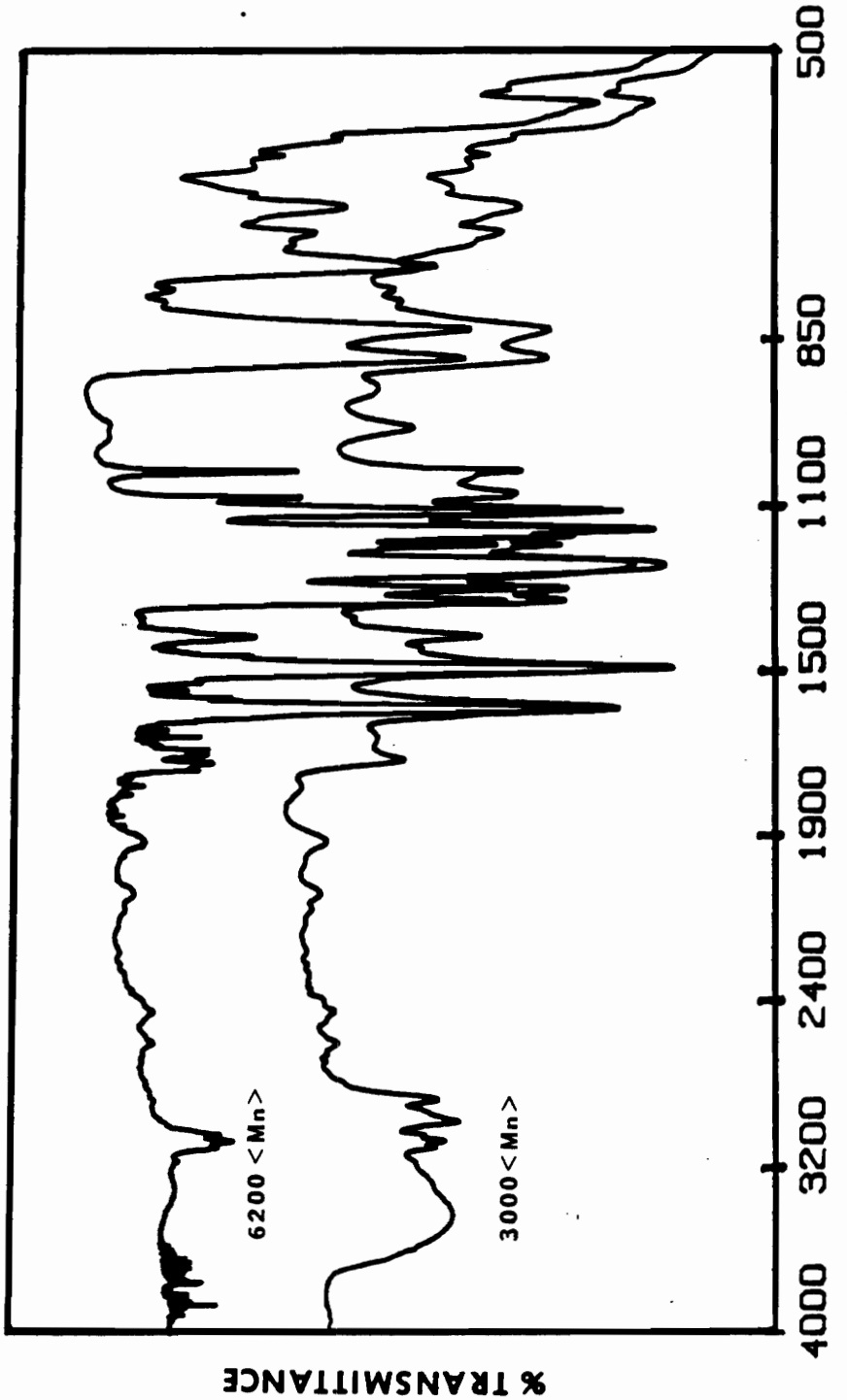
were not soluble in NMP but were soluble in the more polar DMSO solvent.

The carboxyl terminated polysulfone oligomers were isolated and characterized in the same way as the hydroxyl terminated polysulfone oligomers. Their number average molecular weights were determined by potentiometric titration. The endpoints of the titration were found to be sharper and more prominent than those of the hydroxyl termianted oligomers due to the greater acidity of the carboxyl endgroups.

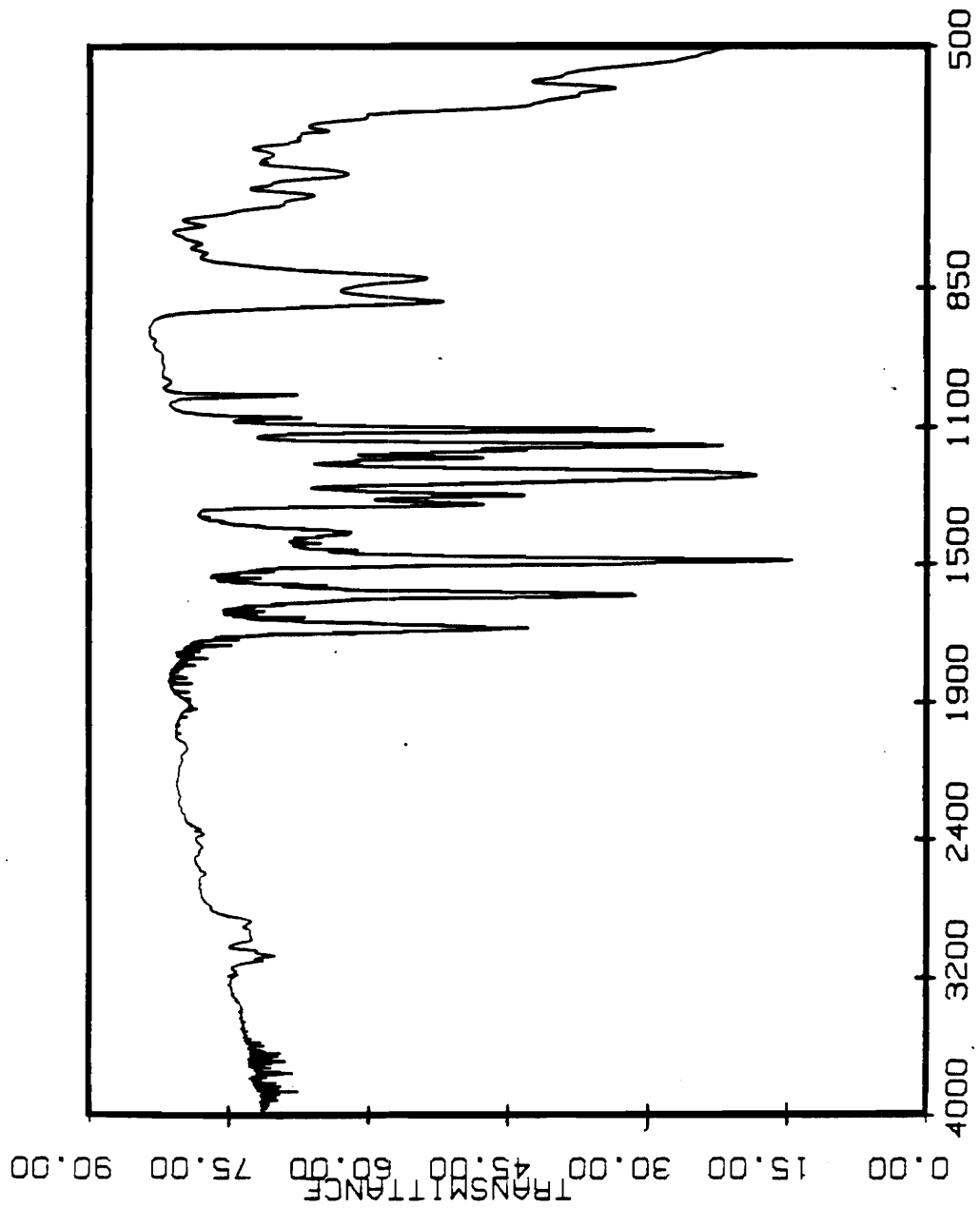
4.11 Characterization of Carboxyl Terminated Poly(Arylene Ether Sulfone) Oligomers)

The composition and nature of the endgroups of the synthesized carboxyl terminated polysulfone oligomers were confirmed by FT-IR and ^{13}C NMR. FT-IR spectra of 6200 $<M_n>$ and 3000 $<M_n>$ carboxyl terminated polysulfones are shown in Scheme 46. From these spectra one of the major peaks of interest occurs at 3400-3500 cm^{-1} which is the hydroxyl stretching of the carboxyl endgroups. At 1722 and 1691 cm^{-1} a doublet attributed to the carbonyl stretching of the carboxyl endgroups occur. The double carbonyl stretching is not fully understood but may arise from hydrogen bonding or association of the carboxyl endgroups of the oligomer.[101] Also at 920 cm^{-1}, an OH out of plane bending occurs. The characteristic polysulfone peaks (see Section 4.3, Table 7) are also in evidence in the spectra.

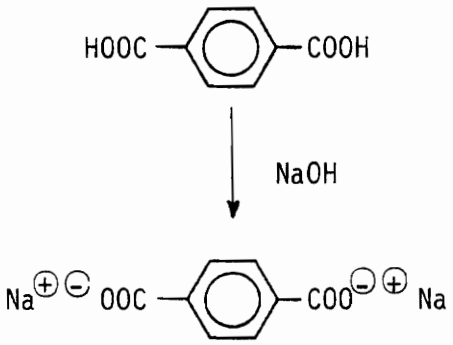
In order to characterize the carboxyl endgroups of the polysulfone oligomer, the endgroups were converted into their sodium salt with sodium hydroxide. The sodium salt of the 6200 $<M_n>$carboxyl terminated poly(arylene ether sulfone) is shown in Scheme 47. The major differences between this spectrum and the free acid form of the same copolymer occurs in the peaks associated with the carboxyl endgroups. First the broad hydroxyl peak from 3400-3500 cm^{-1} disappears, as expected. The OH out of plane bending peak at 920 cm^{-1} also disappears. Both of these peaks were expected to disappear since the hydroxyl portion of the carboxyl endgroups were converted into their anion form:



SCHEME 46. FT-IR spectra of 6200 $\langle M_n \rangle$ and ~3000 $\langle M_n \rangle$ carboxyl terminated poly(arylene ether sulfone) oligomers.



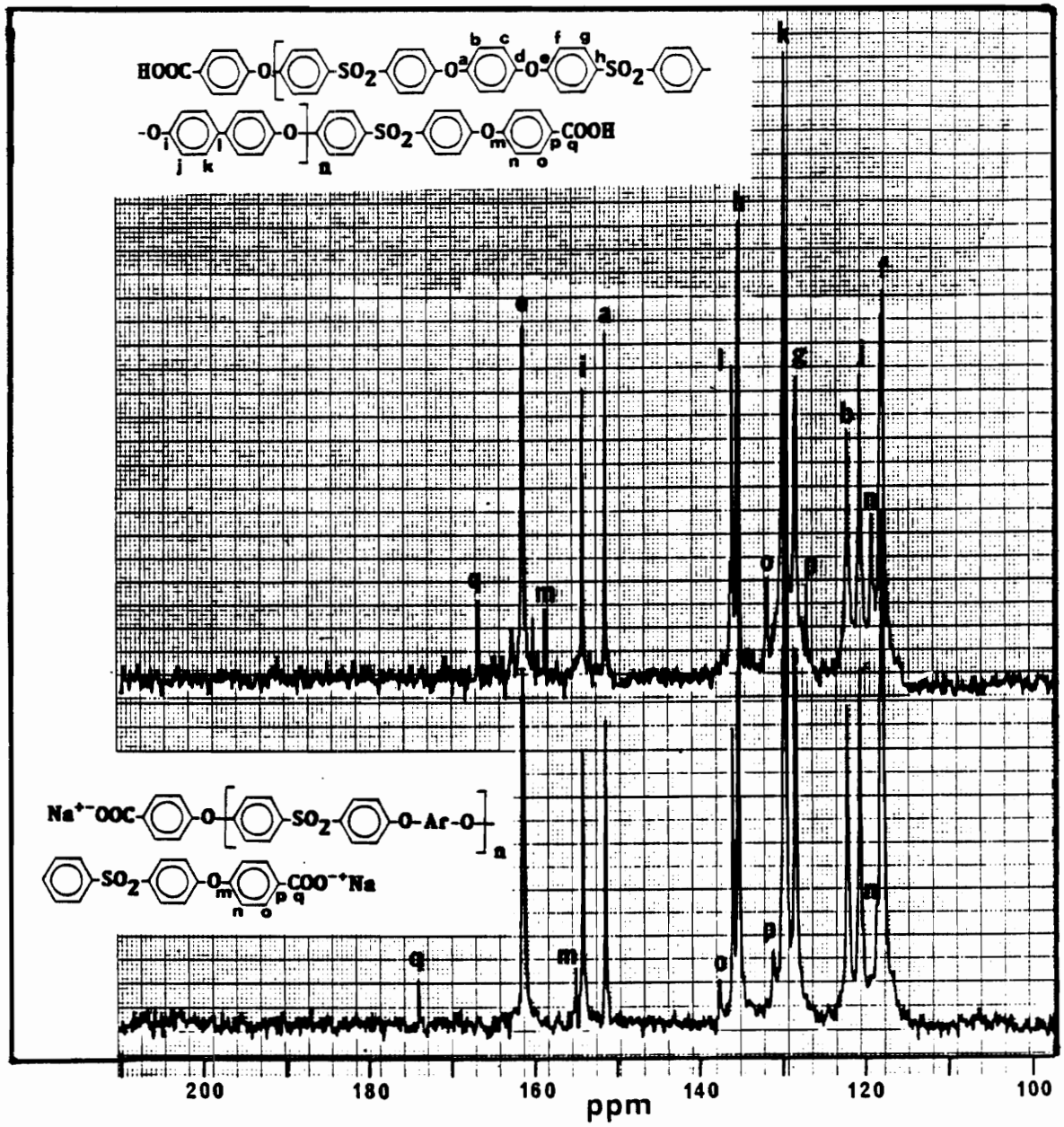
SCHEME 47. FT-IR spectrum of sodium salt of 6200 $\langle M_n \rangle$ carboxyl terminated poly(arylene ether sulfone) oligomer.



The double peak attributed to the carbonyl of the carboxyl group becomes a single peak at 1684 cm^{-1} when the salt forms. The polysulfone peaks remain unchanged when the oligomer is converted into its sodium salt derivative.

A similar sort of characterization procedure was performed using ^{13}C NMR. Scheme 48 is an overlay of the ^{13}C NMR spectra of the 6200 $\langle M_n \rangle$ carboxyl terminated poly(arylene ether sulfone) oligomer (upper spectrum) and the sodium salt of this oligomer (lower spectrum). The peaks of interest are labeled m, n, o, p, and q and are all asscciated with the endgroups of the oligomer. The peak labeled "q" is the carbon of the carbonyl of the carboxyl endgroups and resonates at 169 ppm. Comparison of these same labeled peaks in the sodium salt spectrum shows a dramatic difference. Especially, prominent is the peak labeled "q." This peak has shifted from 169 ppm to 174 ppm due to the greater negative charge associated with this carbon when in the sodium salt form. The other peaks associated with the endgroups are also shifted. Whereas, the peaks associated with the polysulfone repeat units are unaffected by the sodium salt endgroups.

The composition and endgroup nature are thus confirmed by the FT-IR and ^{13}NMR characterization techniques. The reactivity and

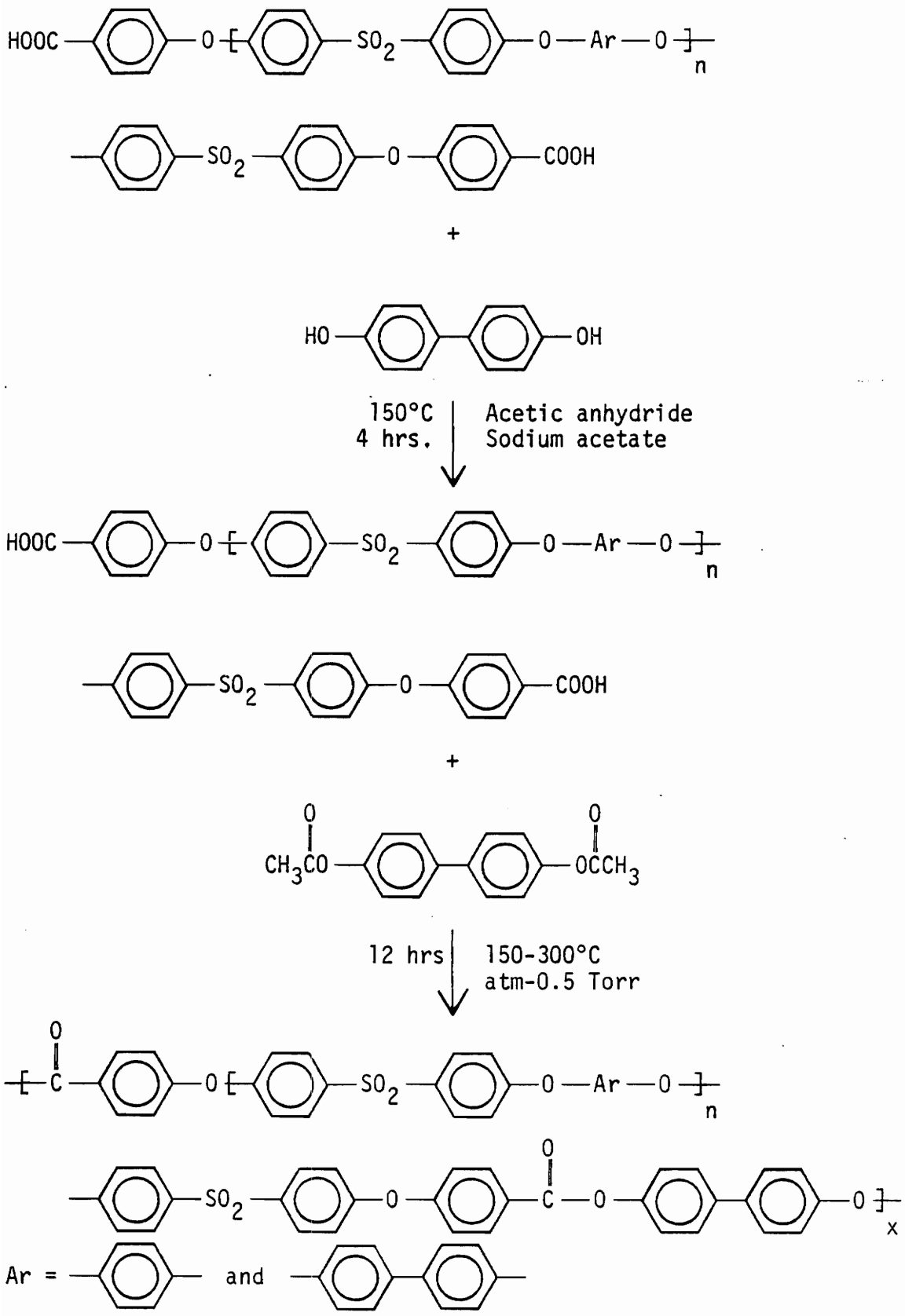


SCHEME 48. ^{13}C NMR spectra overlay of 6200 $\langle M_n \rangle$ carboxyl terminated poly(arylene ether sulfone) oligomer and sodium salt of this oligomer.

stability of the carboxyl terminated poly(arylene ether sulfone) oligomers was evaluated by chain extending these types of oligomers. Biphenol diacetate was used to form high molecular weight polymer in a melt acidolysis reaction.

4.12 Synthesis of Biphenol Diacetate Chain Extended Carboxyl Terminated Poly(Arylene Ether Sulfone) Copolymer

To test the reactivity and stability, as well as the difunctionality of the carboxyl terminated poly(arylene ether sulfone) oligomers, they were chain extended. The chain extender used was biphenol diacetate. The reaction scheme for this chain extension process is shown in Scheme 49. This reaction was carried out in the same manner as for the one pot melt acidolysis process. However, in this reaction, the temperature could be raised much faster and the vacuum applied earlier than in the reactions which used terephthalic acid. In this reaction, there was no problem with sublimation of the monomers as there was for the other reactions.



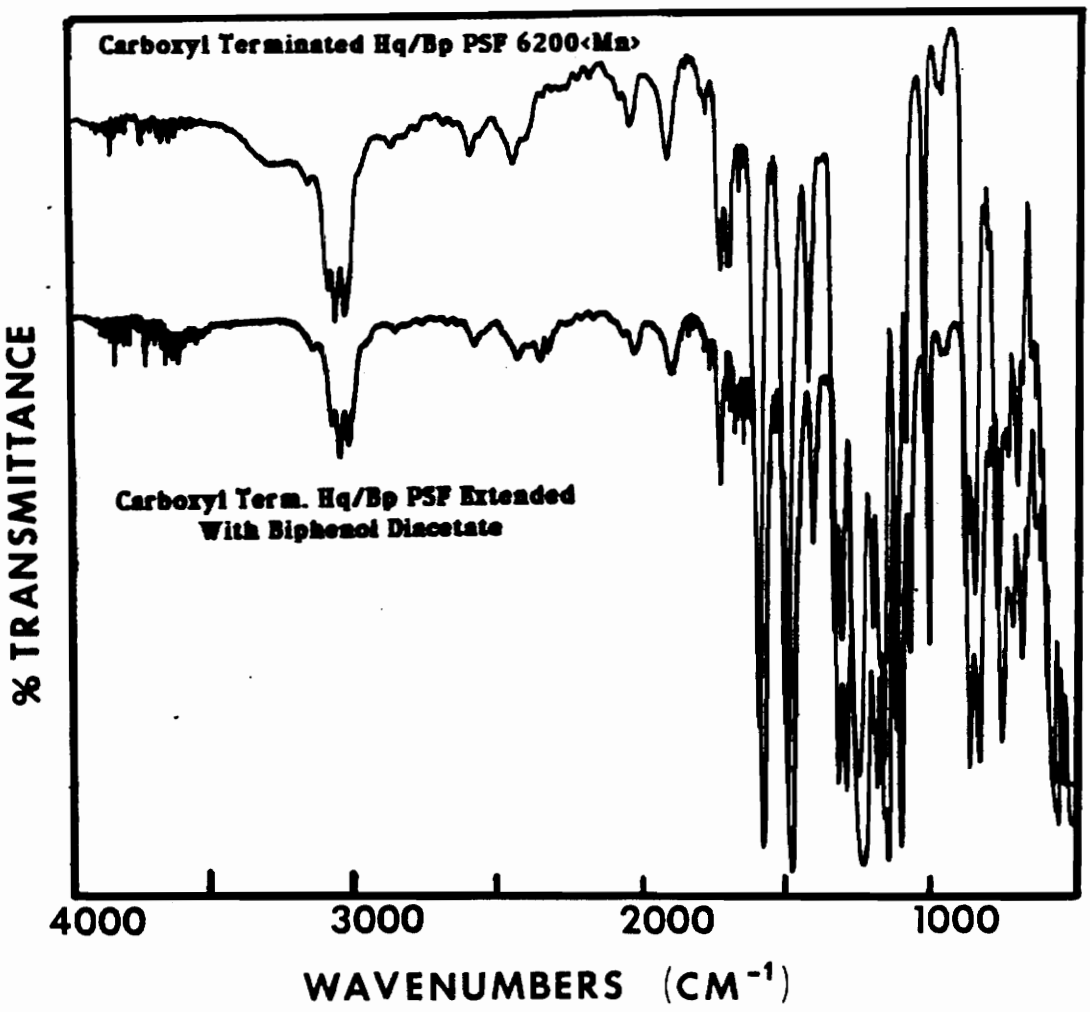
SCHEME 49. Reaction scheme for chain extending a carboxyl terminated poly(arylene ether sulfone) oligomer with biphenol diacetate.

4.13 Characterization of Chain Extended Carboxyl Terminated Poly(Arylene Ether Sulfone) Oligomers

The carboxyl endgroups of the poly(arylene ether sulfone) oligomers were reacted with biphenol diacetate to form a polymer containing ester linkages. Thus, FT-IR was used to confirm the composition of the chain extended polymer by noting the differences between a carboxyl terminated polysulfone and a chain extended polymer. Scheme 50 is an overlay of FT-IR spectra of a 6200 $<M_n>$ carboxyl terminated poly(arylene ether sulfone) oligomer and this same oligomer chain extended with biphenol diacetate.

Two differences are readily apparent by comparison of the spectra. First, the broad peak from 3400-3500 cm^{-1} attributed to the hydroxyl stretching of the carboxyl endgroups disappears from the upper oligomer spectrum. This disappearance is expected since the carboxyl endgroups are reacting with the biphenol diacetate to form ester linkages. These ester linkages are also readily apparent in the lower spectrum. The double peaks attributed to the carbonyl of the carboxyl endgroups appear at 1691 and 1722 cm^{-1} in the upper spectrum of the carboxyl terminated polysulfone oligomer. The spectrum of the chain extended oligomer shows only one carbonyl stretch at 1734 cm^{-1}. This stretching frequency is normal for an aromatic polyester.[101] The characteristic polysulfone peaks are present in both spectra in the same intensities indicating that the polysulfone oligomer is not degrading when it is chain extended.

It appears that the use of carboxyl terminated poly(arylene ether sulfone) oligomers may be an attractive alternative to using



SCHEME 50. Overlay of FT-IR spectra of a 6200 $\langle M_n \rangle$ carboxyl terminated poly(arylene ether sulfone) oligomer and this oligomer chain extended with biphenol diacetate.

terephthalic acid in the melt reactions. It has been shown here that the poly(arylene ether sulfone) oligomers can be made carboxyl terminated. These carboxyl terminated poly(arylene ether sulfone) oligomers can then be chain extended with biphenol diacetate to form copolymers.

CHAPTER 5

CONCLUSIONS

This dissertation has described research, both by myself and other workers, in the area of modification of engineering thermoplastics with potentially anisotropic polyesters. Three different techniques were developed to modify the poly(arylene ether sulfone) engineering thermoplastics. All three techniques produced segmented copolymers, where one segment was a poly(arylene ether sulfone) and the other segment was an aromatic polyester. The aromatic polyesters chosen were potentially anisotropic or liquid crystalline, dependent on the segment lengths and processing conditions.

The first process developed was a solution process. This technique was used to produce poly(arylene ether sulfone)-poly(biphenol terephthalate) segmented copolymers. While this process was very useful in synthesizing perfectly alternating copolymers, it was limited in its ability to produce randomly coupled segmented copolymers with more than 5-10 mole percent poly(biphenol terephthalate). The copolymers with greater than 10-15 mole percent poly(biphenol terephthalate) precipitated prematurely from the solvent, thus limiting their molecular weights. The polymers produced by this technique were shown to be totally amorphous by DSC measurements.

An interfacial process was then developed to overcome the severe limitations of the solution process. This process produced perfectly alternating copolymers as well as randomly coupled segmented copolymers, of poly(arylene ether sulfone)-poly(biphenol terephthalate). This technique allowed an even greater incorporation of the poly(biphenol terephthalate) into the copolymers. Copolymers containing greater than 10 mole percent poly(biphenol terephthalate) were easily produced with some copolymers containing as much as 20 mole percent (6 weight percent). The polymers with the higher percentages of poly(biphenol terephthalate) were shown to be semicrystalline in morphology by DSC and WAXS measurements. These copolymers displayed improved solvent resistance over homopolymer poly(arylene ether sulfone). However, as with the solution technique, the interfacial process was limited in the amount of poly(biphenol terephthalate) which could be incorporated into the copolymers. The copolymers with greater than 25 mole percent poly(biphenol terephthalate) prematurely precipitated from the interfacial solvent limiting their molecular weights.

Finally, a bulk melt acidolysis process was developed and refined to overcome the limitations of both the solution and interfacial techniques. This technique used no solvent and relied on staying above the melting point of the growing polymer to produce high molecular weight polymer. Two types of aromatic polyester segments were synthesized in situ with the poly(arylene ether sulfone) oligomers. One series of segmented copolymers was based on the aromatic polyester, poly(biphenol terephthalate), while the other was

based on poly(oxybenzoate). Both of these polymers were known to be highly crystalline and liquid crystalline. Several variations of the melt acidolysis process were used to synthesize poly(arylene ether sulfone)-poly(arylate) segmented copolymers. Heat transfer, two step, and one pot melt acidolysis processes were all used to produce the segmented copolymers. These techniques allowed the synthesis of segmented poly(arylene ether sulfone)-poly(arylate) copolymers with very high poly(arylate) contents, some as high as 99 mole percent (75 weight percent) of poly(oxybenzoate). The one pot melt acidolysis process provided the easiest route to the copolymer synthesis. The intermediate diacetate oligomers and monomers were made in situ and subsequently reacted without the isolation and characterization step involved in the two step approach. Both of these latter two processes are bulk processes and involved polymer melts with very high viscosities. A solid state polymerization was useful when the molten polymer could no longer be stirred. The heat transfer melt acidolysis process circumvented the high viscosity problems, but created isolation and characterization problems. The solvent resistance of the poly(arylene ether sulfone)-poly(arylate) copolymers was markedly increased as the poly(arylate) content was increased. The solvent resistance was attributed to the semicrystalline nature of the copolymers. DSC, WAXS, and hot stage optical microscope measurements confirmed the glassy-crystalline morphology of the segmented copolymers. Liquid crystallinity in several of the samples was alluded to by multiple melting endotherms in the DSC measurements.

Further evidence of the anisotropic nature of these copolymers was given by hot stage optical microscope observations.

Synthesis and characterization of novel carboxyl terminated poly(arylene ether sulfone) oligomers was accomplished. These carboxyl terminated polysulfones were subsequently chain extended in melt acidolysis reactions to form segmented copolymers. These segmented copolymers were synthesized without the use of the hard to work with terephthalic acid.

CHAPTER 6

FUTURE WORK

The questions answered by this dissertation work lead to many more unanswered questions. As with any scientific study, there were many "what if" questions that could not be investigated in this dissertation work. Many suggestions were made or alluded to throughout the text of this dissertation but reiteration of these and other suggestions will be made here.

The solvent resistance of many of the poly(arylene ether sulfone)-poly(arylate) segmented copolymers was implied by their qualitative insolubility in various solvents. A more quantitative investigation of these segmented copolymers in terms of solvent resistance and environmental stress crack resistance (ESCR) would be useful. Solvent resistant materials are becoming increasingly more important as polymers find newer and more diversified uses.

Liquid crystallinity was inferred from DSC and hot stage optical microscopy but not clearly determined in several of the melt acidolysis prepared segmented copolymers. More detailed DSC measurements involving annealing and quenching studies would prove to be beneficial.

The overall goal of this dissertation study was to synthesize poly(arylene ether sulfone)-poly(arylate) with unusual film properties. These unusual film properties involved liquid

crystallinity or anisotropic properties from the poly(arylate) segments. The poly(arylene ether sulfone) segment was to provide an overall balance of mechanical properties which are not usually found in liquid crystalline polymers. The measurement of the mechanical properties of these poly(arylene ether sulfone)-poly(arylate) copolymers should provide new directions toward fulfilling this goal.

Lastly, the carboxyl terminated poly(arylene ether sulfone) oligomers were chain extended with biphenol diacetate to demonstrate their reactivity and difunctionality. However, no copolymers were synthesized from these carboxyl terminated polysulfones with high poly(arylate) contents. These segmented copolymers should prove to be easier to synthesize and still display any anisotropic properties displayed by the previously produced segmented copolymers.

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