1990

Imide/Arylene Ether Copolymers

Brian J. Jensen

College of Humanities and Sciences
Virginia Commonwealth University

This is to certify that the dissertation prepared by Brian J. Jensen entitled Imide/Arylene Ether Copolymers has been approved by his committee as satisfactory completion of the dissertation requirement for the degree of Doctor of Philosophy in Chemistry.

[redacted]

Dr. R. Gerald Bass, College of Humanities and Sciences,
Director of Dissertation

[redacted]

Dr. Lawrence J. Winters, College of Humanities and Sciences

[redacted]

Dr. Albert T. Sneden, College of Humanities and Sciences

[redacted]

Dr. Vicki H. Wysocki, College of Humanities and Sciences

[redacted]

Dr. Thomas H. Haas, College of Humanities and Sciences

[redacted]

Dr. Lawrence J. Winters, Chairman, Department of Chemistry,
College of Humanities and Sciences

[redacted]

Dr. Elske v.P. Smith, Dean, College of Humanities and Sciences

August 10, 1990
Date

Imide/Arylene Ether Copolymers

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

by

Brian J. Jensen

B.S., Randolph-Macon College, 1980

M.A., The College of William and Mary, 1983

Director: Robert G. Bass

Professor of Chemistry

Virginia Commonwealth University

Richmond, Virginia

August 1990

Acknowledgements

This dissertation is dedicated to my wife Amy, my daughter Chelsea, and my parents Julius and Barbara M. Jensen. Without their inspiration, encouragement and support, this would not have been possible. I would also like to acknowledge the remainder of my family and my wife's family for their encouragement and support.

I would like to express my sincere appreciation and gratitude to:

Dr. R. G. Bass for his guidance and encouragement throughout my graduate career.

The members of my Graduate Committee; Dr. A. T. Sneden, Dr. L. J. Winters, Dr. B. L. Stump, Dr. T. W. Haas and Dr. V. H. Wysocki and the faculty of the Department of Chemistry for their helpful advice.

The graduate students of the Department of Chemistry, particularly Drs. R. O. Waldbauer and S. M. Andrews, for their friendship.

The Polymeric Materials Branch of the NASA Langley Research Center and Dr. Terry L. St. Clair for their support and encouragement.

Mr. Paul M. Hergenrother of the NASA Langley Research Center for his guidance and encouragement throughout this research project.

Drs. Stephen J. Havens and John W. Connell for their helpful discussions, advice and friendship.

The professional and technical staff of the Polymeric Materials Branch of the NASA Langley Research Center for their assistance and support.

Carrington Smith of the Virginia Polytechnic Institute and State University for the amino group titrations.

The author is forever indebted to the people and organizations mentioned above.

TABLE OF CONTENTS

Page

List of Figures iv

List of Tables vi

Abstract ix

Abbreviations xi

Imide/Arylene Ether Copolymers 1

Introduction 2

Research Aim 18

Background 22

Experimental 59

Results and Discussion 92

Conclusion 166

References 167

Appendix 174

Vita 201

LIST OF FIGURES

Figure		Page
1	Comparison of the thermal behavior of amorphous crystalline polymers	7
2	Schematic stress-strain plots: left, a perfectly elastic material; and right, a material that is not perfectly elastic. Area of hysteresis loop represents energy dissipated in the form of heat	10
3	Relationship of molecular weight and mechanical properties	12
4	Structure, designation and thermal transitions of homopolymers	20
5	Typical polyimide synthesis	23
6	Mechanism for polyimide synthesis	25
7	Mechanism for synthesis of aromatic ethers	45
8	Formation of water in nucleophilic substitution using potassium carbonate base	47
9	Synthesis of poly(imide-ether sulfone) copolymer	53
10	Synthesis of copoly(ester imide)s	55
11	Synthesis of imide-aryl ether benzoxazole random copolymers	56
12	Benzylidene containing dianhydride monomers	57
13	Compact tension specimen	62
14	Synthesis of BPA based amine-terminated poly-(arylene ether) oligomers	104

LIST OF FIGURES (CONTINUED)

15 Synthesis of BPF based amine-terminated poly(arylene ether) oligomers 105

16 Calculation of desired monomer stoichiometry 107

17 Synthesis of anhydride-terminated ODA/BTDA oligomers 115

18 Torsional braid analysis of ATPAE (BPA) 6545 + [ODA + BTDA (6545)] segmented copolymer 118

19 Synthesis of anhydride-terminated BABB/BTDA oligomers 123

20 X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer powder 141

21 X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 320°C 142

22 X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 380°C 143

23 DSC curves for ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) solution imidized powder 158

24 DSC curves for ϕ-PI/PAE/PI/PAE/PI-ϕ-(3110) thermally imidized film 159

LIST OF TABLES

Table		Page
1	Characterization of Thermally Staged 6F-BADF Film	28
2	Glass Transition Temperatures of Polyimides	30
3	Glass Transition Temperatures of Polyimides	32
4	Glass Transition Temperatures of Polyimides	33
5	Glass Transition Temperatures of Polyimides	34
6	Glass Transition Temperatures of Polyimides	35
7	Glass Transition and Crystalline Melt Temperatures of Polyimides	37
8	Properties of LARC-CPI	38
9	Synthesis of A-B Systems by Friedel-Crafts Acylation	41
10	Synthesis of A-A, B-B Systems by Friedel-Crafts Acylation	42
11	Synthesis of A-A, B-B Systems by Friedel-Crafts Acylation	43
12	Synthesis of A-B Systems by Nucleophilic Substitution	49
13	Synthesis of A-A, B-B Systems by Nucleophilic Substitution	50
14	Synthesis of A-A, B-B Systems by Nucleophilic Substitution at 155°C Using K_2CO_3 and DMAc/Toluene	51
15	Characterization of Polymers and Blends	95
16	Film Properties of Polymers and Blends	98
17	Fracture Toughness and Energy of Polymers	100
18	Adhesive Properties of Polymers	101

LIST OF TABLES (CONTINUED)

19 Thermogravimetric Analysis of Polymers 103

20 Characterization of BPA Based Oligomers and Polymers 108

21 Characterization of BPF Based Oligomers and Polymers 110

22 Film Properties of BTDA Extended ATPAEs 112

23 Characterization of ATPAE (BPA)//ODA/BTDA Copolymers 113

24 Film Properties of ATPAE (BPA)//ODA/BTDA Copolymers 119

25 Thermogravimetric Analysis of ATPAE (BPA)//ODA/BTDA Copolymers 121

26 Inherent Viscosity of ATPAE (BPA)//BABB/BTDA Copolymers 124

27 Thermal Characterization of ATPAE (BPA)//BABB/BTDA Copolymers 127

28 Film Properties of ATPAE (BPA)//BABB/BTDA Copolymers 130

29 Fracture Toughness and Energy of ATPAE (BPA)//BABB/BTDA Copolymers 132

30 Thermogravimetric Analysis of ATPAE (BPA)//BABB/BTDA Copolymers 134

31 Inherent Viscosity of ATPAE (BPF)//BABB/BTDA Copolymers 136

LIST OF TABLES (CONTINUED)

32 Thermal Characterization of ATPAE (BPF)//BABB/BTDA Copolymers 138

33 Film Properties of ATPAE (BPF)//BABB/BTDA Copolymers 145

34 Fracture Toughness and Energy of ATPAE (BPF)//BABB/BTDA Copolymers 147

35 Thermogravimetric Analysis of ATPAE (BPF)//BABB/BTDA Copolymers 148

36 Controlled Molecular Weight Copolymers 150

37 Fracture Toughness and Energy of Controlled Molecular Weight Copolymers 152

38 Room Temperature Ti/Ti Tensile Shear Strength of Controlled Molecular Weight Copolymers 153

39 Characterization of ϕ-PI/PAE/PI-ϕ (3110) Copolymers...... 155

40 Characterization of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymers 157

41 Adhesive Properties of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymer 161

42 Composite Properties of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymer 164

ABSTRACT

IMIDE/ARYLENE ETHER COPOLYMERS

Brian J. Jensen, Ph.D.
Virginia Commonwealth University
Major Director: Dr. R. G. Bass

Three different series of imide/arylene ether block copolymers were prepared using two different imide blocks and two different arylene ether blocks. Block molecular weights studied were 3110 and 6545 g/mole for each block and all four combinations possible were prepared in each series. Also, several segmented copolymers were prepared by forming the imide segment and the copolymer in the presence of the pre-formed arylene ether block.

Two amine-terminated poly(arylene ether) blocks (ATPAE) were prepared by reacting 1,3-bis(4-fluorobenzoyl)benzene with either 2,2-bis(4-hydroxyphenyl)propane (BPA) or 9,9-bis(4-hydroxyphenyl)fluorene (BPF) and 4-aminophenol. Two anhydride-terminated poly(amic acid) blocks were prepared by reacting 4,4'-oxydianiline (ODA) or 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (BABB) with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The ATPAEs were reacted with the anhydride-terminated poly(amic acids) to provide block copolymers which were either thermally or solution imidized. Thermal imidization was accomplished by heating 1 h each at 100, 200 and 300°C while solution imidization was accomplished by adding toluene to the reaction, heating to 155°C overnight and collecting the toluene/water azeotropic mixture in a Dean-Stark trap.

Some of the block copolymers displayed two Tgs indicating incomptability and phase separation, especially for the higher molecular weight blocks.

The copolymer series preapred by reacting the ATPAE (BPA) blocks with the ODA/BTDA blocks in N,N-dimethylacetamide (DMAc) had inherent viscosities as high as 1.37 dL/g. The copolymer series prepared by reacting ATPAE (BPA) blocks with BABB/BTDA blocks in DMAc or N-methyl-pyrrolidinone (NMP) had inherent viscosities as high as 1.73 dL/g. The copolymer series prepared by reacting ATPAE (BPF) blocks with BABB/BTDA blocks in DMAc, NMP or m-cresol had inherent viscosities as high as 1.08 dL/g. The copolymers were characterized by differential scanning calorimetry (DSC), torsional braid analysis (TBA), thermogravimetric analysis (TGA) and wide angle x-ray diffraction (the BABB/BTDA imide is semi-crystalline). Mechanical properties were measured on copolymer films and fracture energies were measured on moldings. One copolymer was end-capped at a controlled molecular weight to improve processing and evaluated as an adhesive and graphite composite matrix. The chemistry and properties of the copolymers will be discussed and compared to those of the homopolymers.

ABBREVIATIONS

Ad - Adhesive

ASTM - American Society for Testing and Materials

ATPAE - amine-terminated poly(arylene ether)

BABB - 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene

BPA - 2,2-bis(4-hydroxyphenyl)propane

BPF - 9,9-bis(4-hydroxyphenyl)fluorene

BTDA - 3,3',4,4'-benzophenonetetracarboxylic dianhydride

CHP - N-cyclohexyl-2-pyrrolidinone

Coh - cohesive

DABP - diaminobenzophenone

DMA - dynamic mechanical analysis

DMAc - N,N-dimethylacetamide

DMSO - dimethylsulfoxide

D_p - degree of polymerization

DSC - differential scanning calorimetry

DTA - differential thermal analysis

FBB - 1,3-bis(4-fluorobenzoyl)benzene

G_{Ic} - fracture energy

GPC - gel-permeation chromatography

IR - infrared

ITGA - isothermal gravimetric analysis

K_{Ic} - fracture toughness

Ksi - one thousand Psi

LALLS - low angle laser light scattering

LARC-CPI - Langley Research Center-Crystalline Polyimide

ABBREVIATIONS (CONTINUED)

$\overline{M}n$ - number-average molecular weight

$\overline{M}w$ - weight average molecular weight

NMP - N-methylpyrrolidinone

ODA - 4,4'-oxydianiline

PAE - poly(arylene ether)

PI - polyimide

PMDA - pyromellitic dianhydride

Psi - pounds per square inch

RT - room temperature

SI - solution imidized

TBA - torsional braid analysis

Tg - glass transition temperature

Tm - melting temperature

WAXS - wide angle x-ray scattering

IMIDE/ARYLENE ETHER COPOLYMERS

INTRODUCTION

High performance/high temperature polymeric materials are currently used in many applications, such as insulators for microelectronic components, binders in brake systems, coatings on cookware and functional and structural applications on advanced aircraft, space vehicles and missiles. Research on these materials began in the late 1950s, sponsored primarily by the Department of Defense. Since then a great deal of research has been conducted by the military and civilian aerospace organizations concerning thermally stable organic polymers. These materials are finding increasing use in today's marketplace because of advantages in mechanical properties, processability and environmental resistance to corrosion, radiation and temperature extremes (1). Polymeric materials also are used in both functional (sealants, coatings and films) and structural (adhesives, foams and composite matrices) applications.

Early research on heat resistant polymers produced many different thermally stable polymers, as measured by thermogravimetric analyses (TGA), with high glass transition temperatures (Tg). However, most of these new systems were insoluble, intractable and could not be processed into useful components. Because of this, many of the new polymers were referred to as "brick dust" and were soon realized to be of little or no use. The chemical groups and structural features of a polymer that provide optimum heat resistance, such as aromatic or heteroaromatic groups, polar moieties, interchain interactions and crystallinity, almost invariably increase melt viscosity and glass transition temperature and decrease solubility which makes processing these materials into useful components much more difficult. Conversely, the features which increase processability tend to decrease thermal stability and lower the Tg of the polymer. Typically, the thermal stability of the polymer is compromised in an effort to improve its processability. One way to improve processability is to incorporate groups such as oxygen, methylene, carbonyl and sulfonyl or 1,3-phenylene linkages to impart flexibility and solubility to the polymer by disrupting chain symmetry. However, thermal stability is generally reduced when these changes are made. Other methods to improve the processability of a polymer include controlling the molecular weight by offsetting monomer stoichiometry or adding a monofunctional reactant, introducing plasticizers or low molecular weight additives and the use of reactive oligomers. Virtually every thermally stable heterocyclic polymer prepared by the formation of the heterocyclic ring that can be prepared has been reported. Obtaining significant improvement in thermal stability of organic polymers is unlikely (1). As technology demands new materials with tailored properties, improvements in macromolecular design, processability and processing techniques are likely.

When considering a polymer for high temperature applications, the thermal stress in terms of time, temperature and environment must be defined. To be useful for high temperature applications, a polymer must retain usable mechanical properties for tens of thousands of hours at 177°C, thousands of hours at 230°C, hundreds of hours at 300°C, minutes at 540°C and seconds at 700°C or above. Since the type of environment also effects the polymers thermal stability, it must also be thoroughly described (2). Environments with extreme thermal cycling (hot/cold), radiation, chemical attack or physical stress can cause material degradation leading to failure. For most applications, the use temperature of thermoplastics is governed by the glass transition temperature of the polymer. For applications requiring mechanical properties, the polymer Tg should be at least 50°C higher than the use temperature to avoid creep. Creep is the permanent flow-like deformation of a polymer for a given time, temperature, stress environment and is a basic limitation for thermoplastics. On the other hand, thermosetting materials are typically highly crosslinked and resist creep closer to their Tg (if they have a Tg) than thermoplastics.

Heat resistance is the capacity of a material to retain useful properties for a specific period of time at elevated temperature under defined conditions. Both reversible and irreversible changes can occur in polymers. A reversible change, for example, is deformation under load of a polymer as it is heated near the Tg. The deformation occurs without change in chemical structure. Irreversible changes alter the chemical structure, for example, bond breaking by exceeding the thermal stability of a polymer. The chemical factors which influence thermal stability include primary bond strength, secondary bonding forces (van der Waal), hydrogen bonding and resonance stabilization. The physical factors which affect thermal stability include molecular weight and molecular weight distribution, packing (crystallinity), molecular (dipolar) interactions and purity.

Some generalizations can be made concerning thermal stability of organic polymers. Primary bond strength is the single most important influence contributing to heat resistance. Therefore, only groups containing the strongest chemical bonds should be used. The bond dissociation energy (3) of a carbon-carbon single bond is 83.6 kcal/mole and that of a carbon-carbon double bond is 145.8 kcal/mole. In aromatic systems, the latter is even higher. Known as resonance stabilization, this phenomenon adds 39.2 - 68.6 kcal/mole. Therefore, aromatic and heterocyclic rings are commonly used in thermally stable polymers. Polar interactions such as dipole/dipole or hydrogen bonding contribute to heat resistance. Van der Waal forces also play a role in determining the cohesive energy density (σ^2) of a polymer. The σ^2 is defined as the amount of energy needed to vaporize (overcome cohesive forces between molecules) a given volume of the material. Each of these interactions influence the rigidity, Tg and solubility of the polymer. In an effort to increase heat resistance, moieties with low thermooxidative stability such as alicyclic, unsaturated or aliphatic hydrocarbons should be avoided. The structures should be photochemically and hydrolytically inert and should not allow easy pathways for rearrangement or degradation.

Other factors to consider include molecular weight and molecular weight distribution. Lower molecular weight fractions tend to decrease the thermal stability, Tg, and mechanical strength of a polymer. Trace impurities such as metal catalysts, can greatly reduce a polymer's thermal stability by catalyzing degradation reactions, especially at elevated temperatures in the presence of oxygen. Crosslinking, leading to thermosetting polymers, also improves heat resistance since chains cannot be broken by the rupture of a single bond alone. It also increases solvent resistance, modulus and resistance to creep.

Another important factor influencing thermal stability is crystallinity. Crystallinity results from the regular packing of polymer chains, which normally increases density, and crystalline regions serve as physical crosslinks for the amorphous regions. These crystalline regions not only increase thermal stability but also provide stiffness, toughness and solvent resistance to the polymer (4). The amount of crystallinity present in a polymer is called the degree of crystallinity and is given as a percentage. High performance crystalline polymers have degrees of crystallinity typically from ~ 10% - 50% and are therefore semi-crystalline. Higher degrees of crystallinity can be obtained by orienting polymer chains as in fiber spinning.

Two common methods are available to assess the thermal stability of a polymer. They are thermogravimetric analysis (TGA) and isothermo–gravimetric analysis (ITGA). In TGA, the weight loss of a polymer is measured as it is heated at a specific rate in a specific atmosphere. The heating rate and sample form (film versus powder) are important and can have a large effect on the results. TGA gives the temperature at which a certain weight loss (%) occurs. ITGA measures the weight loss of a polymer held at a constant temperature in a specific atmosphere as a function of time. Again, sample form is important and can effect results. Care must be taken when evaluating data from these measurements since no information concerning mechanical properties is obtained. Polymers can display a significant degradation in mechanical properties without exhibiting a significant weight loss. In some rare cases, a polymer can gain weight, most likely by oxidizing, in an air environment. The atmosphere is important since almost all organic polymers display lower thermal stability in air (oxygen) than in an inert atmosphere like nitrogen or argon.

Thermoplastic is a term commonly used to describe a substance that passes through a definite sequence of property changes as its temperature is raised. As shown in Figure 1, amorphous and crystalline materials have different thermoplastic characteristics. Both amorphous and crystalline thermoplastics are glasses at low temperatures and both change to a rubbery elastomer or flexible plastic as the temperature is raised through the Tg. The Tg is a measure of the ease of torsion of the backbone bonds and the beginning of molecular motion (5). Crystalline polymers also have a melting point, Tm, where the flexible thermoplastic becomes a liquid. There are several techniques available for determining the Tg of a polymer such as dilatometry, differential scanning calorimetry (DSC), torsional braid analysis

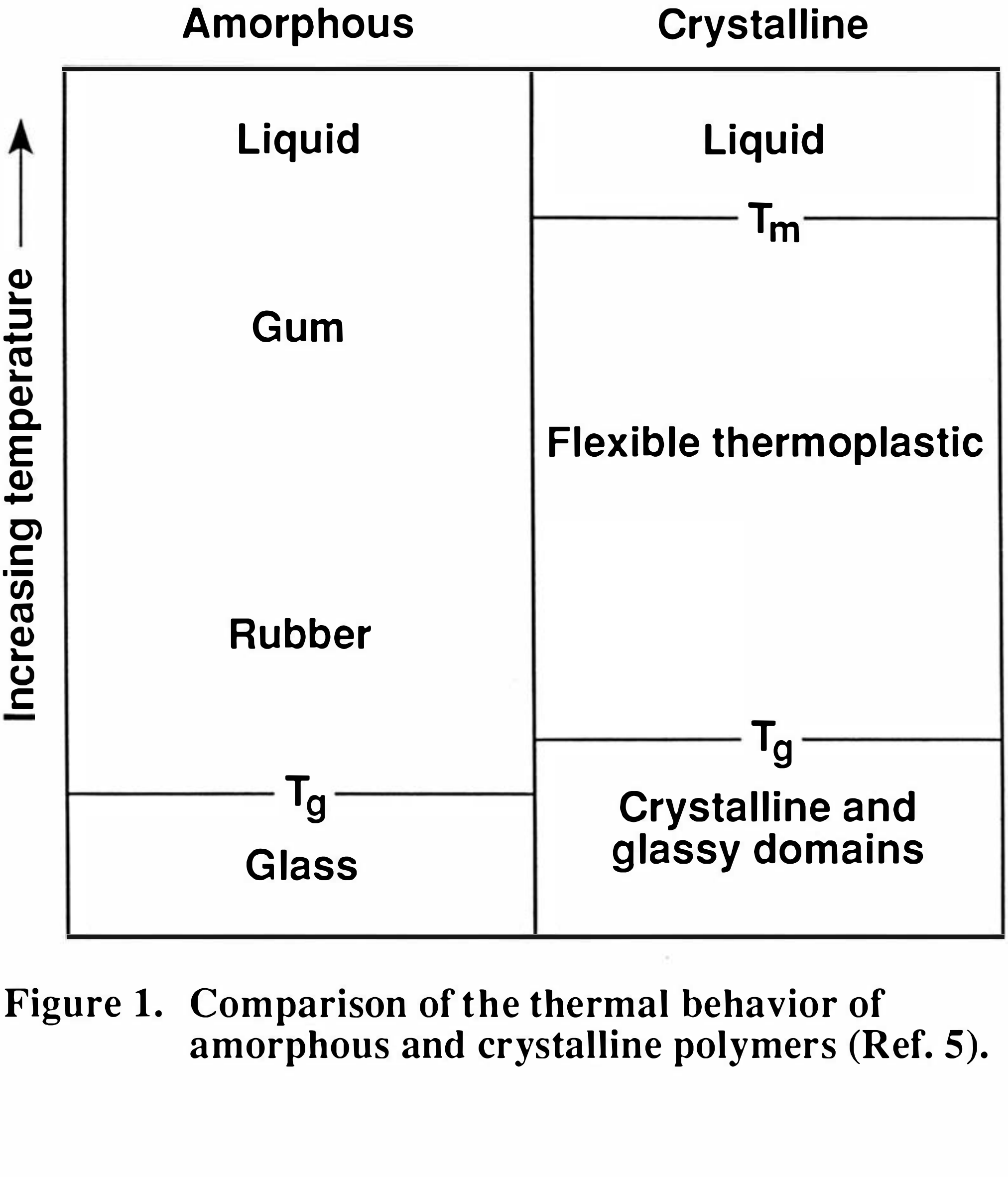


Figure 1. Comparison of the thermal behavior of amorphous and crystalline polymers (Ref. 5).

(TBA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA).

Dilatometry measures the rate of volume expansion of a polymer with temperature, which is dependent on whether the polymer occupies the glassy, rubbery, thermoplastic or liquid state. The change in slope of a volume versus temperature plot can be used to identify the glass transition. DSC operates by separately heating a standard and a sample at the same rate. The temperature of each is monitored by a thermocouple. When a polymer goes through a transition (Tg or Tm), more heat is required to maintain the same temperature as the standard. The change in electrical current, which provides the heat, can be accurately monitored and measured, thus providing an accurate measure of the position and extent of transition. TBA utilizes an inert glass braid which has been impregnated with a polymer solution and dried to remove the solvent. The polymer impregnated braid is suspended in a torsional pendulum device and the period of the pendulum and its damping frequency are measured as a function of temperature. As the polymer is heated through its Tg, a drastic loss in rigidity is detected, accompanied by a sharp maximum in the damping trace. This technique provides a very sensitive measure of the Tg as well as often detecting low temperature secondary transitions. TMA measures Tgs by either elongation of a film sample or penetration of a molded sample. In the film mode, a load is applied to the film and the temperature is increased while measuring elongation. In the penetration mode, a weighted probe (normally with a round tip but sometimes with a flat tip) is placed on the molding and the temperature is increased while measuring penetration. At the Tg, the elongation or penetration increases dramatically and results in a change of slope for the elongation/penetration versus temperature curve. DMA tests materials for elasticity, the ability to store energy, and viscous damping, the ability to dissipate energy as heat. A truly elastic material will recover all of the stored elastic energy, namely the area under the stress-strain curve, once a load is removed as at the left of Figure 2. However, most materials are not truly elastic (anelastic) and will exhibit a hysteresis loop once a load is removed as at the right of Figure 2. The area of the hysteresis loop, which is a measure of the energy dissipated as heat, varies with temperature. Over a broad temperature region in a polymer with multiple transitions, several maxima in area of the hysteresis loops, one for each relaxation process, will be evident. This technique, therefore, provides a measurement of the Tg as well as other relaxations present in a polymer (6).

A knowledge of the molecular weight and molecular weight distribution is vital for even a preliminary understanding of the relationship between structure and properties for polymers. Two fundamentally different approaches are used for measurement of the polymer molecular weight - absolute and secondary. Absolute methods give values that are a direct estimate of molecular weight while secondary methods yield comparisons between molecular weights of different polymers and must be calibrated by an absolute method. Since polymer molecular weights are averages, there are several molecular weights which can be determined. The two most important are number average molecular weight ($\overline{M}$n) and weight average molecular weight ($\overline{M}$w). Some techniques measure $\overline{M}$n (osmometry) while others measure $\overline{M}$w (light scattering). The ratio $\overline{M}$w/$\overline{M}$n is a measure of the polydispersity or molecular weight distribution of the system. $\overline{M}$w is always greater than $\overline{M}$n, except for a monodisperse system, so normally $\overline{M}$w/$\overline{M}$n > 1. The greater the polydispersity, the broader the molecular weight distribution.

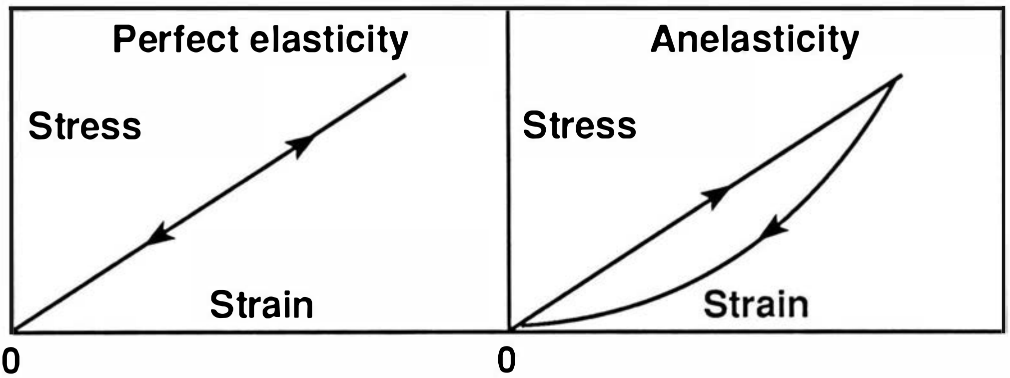


Figure 2. Schematic stress-strain plots: left, a perfectly elastic material; and right, a material that is not perfectly elastic. Area of hysteresis loop represents energy dissipated in the form of heat (Ref. 6).

Polymers must have sufficient molecular weights to exhibit useful mechanical properties. If the molecular weight is too low, there is not enough interchain association or entanglements to provide mechanical strength and the material is brittle. As shown in Figure 3, the molecular weight must reach a certain level before optimum mechanical properties are obtained. Above this minimum molecular weight only a slight increase in mechanical properties is obtained with increasing molecular weight. Furthermore, as molecular weight increases, solution viscosity and melt viscosity, or resistance to melt flow, also increases. Therefore, higher molecular weight polymers are much more difficult to process into useful parts than lower molecular weight polymers. Because of this trade-off, there is a region of optimum combination of mechanical strength and processability at the "knee" in the curve. At this molecular weight the polymer has the highest mechanical strength and best processability.

A variety of screening tests are used to evaluate the performance of a material for a certain application. The polymer forms tested include film, molding, adhesive and composite. They can be tested for ultimate strength, yield strength, modulus, elongation, toughness, resistance to crack propagation and flexure, shear and compression strengths. Many of these tests are performed through a temperature range from cryogenic to over 300°C in a variety of atmospheres (i.e. air, inert gas, vacuum) depending on the proposed application. These tests and measurements are screening devices which give preliminary information to help determine a new materials usefulness. Based on these preliminary results being acceptable , larger components and more involved testing would be required before the material is actually used. Many other factors, including cost, ease of processing, need and competition ultimately determine a material's marketability.

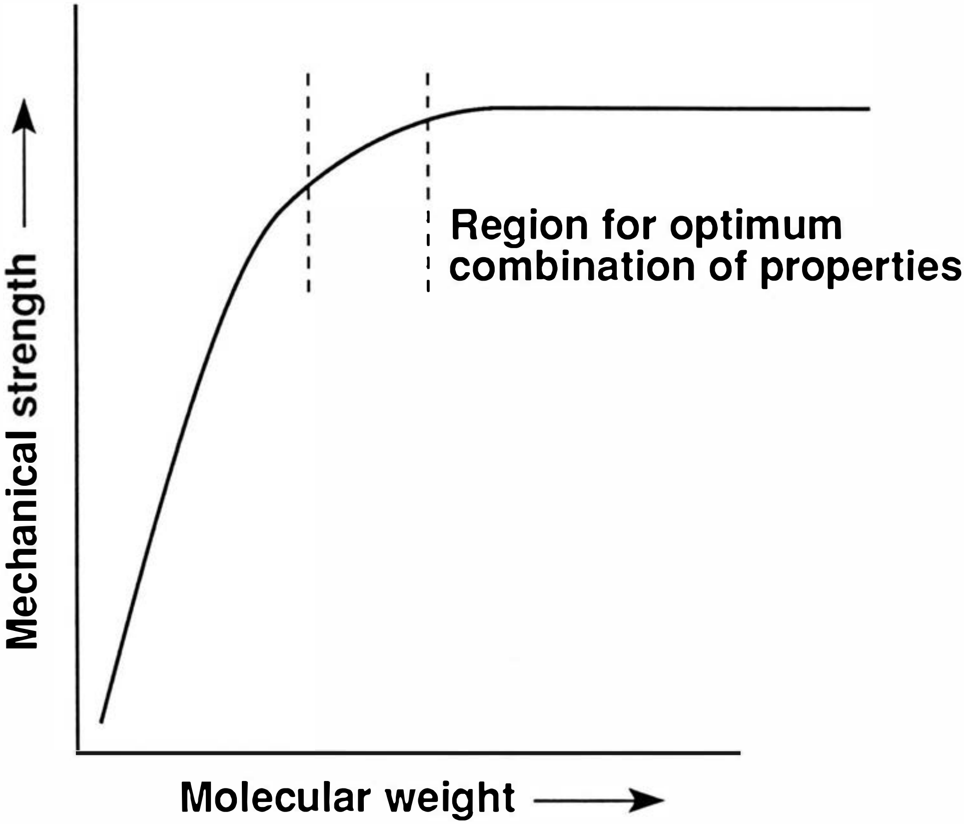


Figure 3. Relationship of molecular weight and mechanical properties.

The type of synthesis used to prepare a polymer is one method used to classify polymers. The three main polymerization reactions are condensation, addition and ring-opening polymerizations. In condensation reactions, monomers react to release a small molecule such as water or alcohol. Addition polymers are formed by the polyaddition reactions of olefins or carbonyl compounds. Ring-opening polymerizations take place by cleavage of a ring with concurrent or subsequent addition of the linear monomer to the end of a growing chain. These polymerization categories reflect different monomer structures and polymerization processes. A related but distinct classification is based on the general mechanistic pathways involved in the polymerization. This classification divides polymerizations into step reactions and chain reactions. Step reactions are those in which the chain growth occurs in a slow, stepwise manner in which monomers react to form dimers, which then react with another monomer or dimer to form a trimer or tetramer, respectively, etc. Therefore, the average molecular weight of the polymer increases slowly over a period of time. Condensation reactions fall into this category. Chain polymerizations, on the other hand, take place by rapid addition of monomers to a growing chain end. Therefore, the system usually contains only unreacted monomer and high molecular weight polymer. Since almost all high performance polymers are prepared by condensation reactions, only stepwise reactions will be discussed further.

Condensation polymerization reactions are used to prepare a wide variety of useful polymers such as polyesters, polycarbonates, polyanhydrides, polyamides, polybenzimidazoles, polyquinoxalines, polyimides and poly(arylene ethers). Since polymer molecular weight increases slowly and high molecular weight is obtained only after the reaction nears completion, stepwise polymerizations have several requirements for high molecular weight. First, only reactions which are near quantitative (> 99% yield) are effective in preparing high molecular polymers. For the degree of reaction to be near quantitative, there must be no interfering side reactions taking place. Typically, demonstration of this for novel systems requires model compound studies. Prior to attempting polymer synthesis on a new reaction, a series of model compounds are prepared from monofunctional reactants of the type to be used in polymerization. Model compound studies have several purposes, the most important of which is to optimize reaction conditions (time, temperature, solvent, etc.) for the highest degree of reaction. If > 99% yield cannot be obtained, high molecular weight polymer will not be prepared. Another requirement to obtain high molecular weight is the use of very pure monomers. Techniques such as differential thermal analysis (DTA), chromatography (liquid and thin layer), visual melting points, and elemental analyses are commonly used to test the purity of monomers. When using difunctional monomers, which is typical in high performance polymer synthesis, the two monomers must be added together in as close to a 1:1 ratio (stoichiometric ratio) as is experimentally feasible. If one or the other monomer exists in excess, the functional group in that monomer will remain unreacted and will terminate polymer chains before the highest molecular weight polymer can be achieved. In fact, offsetting monomer stoichiometry is a common technique used to control the molecular weight of polymers when lower molecular weight is desired. W. H. Carothers (6) was the first to describe mathematically the effect of incomplete reaction on molecular weight. The following equation is a modification of Carothers'

$$Dp = \frac{1 + r}{1 + r - 2rP}$$

early work and takes into account both extent of reaction, P, and offset in monomer stoichiometry, r, when calculating molecular weight. In this equation, DP is the average degree of polymerization and is defined as the average number of structural units per molecule. Note that, for condensation polymers prepared from two reactants, the average number of repeating units per molecule is one-half of the average degree of polymerization. Finally, experimental factors such as weighing and transferring of weighed monomers to the reaction vessels are important, because if the stoichiometry is upset by inaccurate weighing or spillage, high molecular weight polymer will not be obtained.

In an effort to tailor-make polymers with specific properties, copolymers have been developed which contain structural units from two different homopolymers. By varying the amount of one monomer as compared to the other, the properties will normally be more similar to the homopolymer of the major component in the copolymer than to those of the minor component in the copolymer. It should be noted that the sequence of monomer units along a copolymer chain can vary according to the method and mechanism of synthesis. Three different types of sequencing arrangements are commonly found. To describe the differences in these three types of copolymers, copolymer structure will be depicted using monomers A and B. In the first type, random copolymers, no definite sequence of monomer units exists as shown below.

-A-A-B-A-B-B-B-B-A-B-A-A-A-B-

The properties of random copolymers are usually quite different from those of the related homopolymers. The second type, regular copolymers, contain a regular alternating sequence of two monomer units as shown below.

-A-B-A-B-A-B-A-B-A-B-

Again, the properties of the copolymer usually differ markedly from those of the two related homopolymers. The third type, block copolymers, contain a block of one monomer connected to a block of another as shown below.

-A-A-A-A-A-B-B-B-B-B-

Depending upon the mechanism of polymerization, it is possible to control the molecular weight of each block as well as the molecular weight of the entire copolymer. If this is done carefully, various molecular weight blocks can be prepared and studied, which is analogous to different ratios of monomers in the random copolymer example. Unlike the other copolymers, block copolymers retain many of the physical characteristics of the two homopolymers. A segmented copolymer is a type of block copolymer wherein the copolymer and one block is prepared in the presence of the second block. This method of polymerization can produce a copolymer with a broader molecular weight distribution for the block prepared in situ, which may result in different physical properties for the copolymer.

Copolymers and blends of known homopolymers are receiving a tremendous amount of attention in current research. The reason for this is a continually increasing amount of sophisticated applications being developed which demand combinations of properties not attainable with simple homopolymers. The combination of homopolymers, either by blending or copolymerizing, can lead to a variety of results. Almost always, high molecular weight polymer blends are grossly incompatible. The incompatibility of the blend components provides a driving force for each to aggregate in separate phases. This behavior has important ramifications for the physical properties of the resulting blends. In rare cases, compatible blends are formed when the homopolymers are completely soluble in each other. These compatible blends are characterized by single phase morphology, are transparent and exhibit physical properties intermediate to those of the components. When this happens, the blend is said to follow a "rule of mixtures." The two cases discussed above are extremes and a whole range of compatibility exists for different blend systems.

The preparation of block copolymers can produce systems which can fall anywhere on the range from compatible to completely incompatible. Typically, block copolymers exhibit two-phase morphology, but this occurs on a micro-scale rather than the macro-scale dimension of incompatible physical blends. Micro-scale morphology is due to the influence of the intersegment linkages, which restricts the extent to which the phases can separate. The small domain size and excellent interphase adhesion resulting from this microphase morphology can produce a high degree of transparency and a good balance of mechanical properties. The thermal properties of block copolymers display multiple thermal transitions, such as Tgs or Tms, characteristic of each of the components. While crystallinity is possible in block copolymers, it is diminished or eliminated in random systems due to disruption of chain regularity. In order to achieve the ultimate properties in block copolymers, it is important to recognize that a high degree of structural control and integrity is necessary (8).

A more thorough discussion of the subjects addressed in this introduction may be found in references 1-6, 8 and 9.

RESEARCH AIM

Many aromatic polyimides have been reported in the literature (16-37). The original impetus for their synthesis was to obtain higher thermal stability than for previously reported materials. After reaching the goal of high thermal stability, material requirements shifted to preparing more processable polymers which could be manufactured into desired parts. There have been tremendous improvements made in the processability of linear aromatic polyimides by various structural modifications. However, considering their excellent mechanical properties, improvements in processability are still needed before linear polyimides reach their full potential.

Concurrently, a great deal of research has been reported (52-79) concerning poly(arylene ethers). These polymers have very good thermal stability and mechanical properties as well as excellent processability. Many of these polymers exhibit low melt viscosity and are easily processed as thermoplastics. This means that when heated and placed under pressure, poly(arylene ethers) exhibit excellent melt flow to form desired parts.

Therefore, it was postulated that if polyimides and poly(arylene ethers) could be combined properly, the new materials may have the excellent thermal stability and mechanical properties of the polyimides as well as the excellent processability of the poly(arylene ethers). As a rule, polyimides and poly(arylene ethers) are incompatible, so physical blends would produce materials with completely phase separated morphologies. These two-phase morphological systems are coarse dispersions in which the particles are usually large, inhomogeneous and characterized by poor interphase adhesion. The poor interphase adhesion usually results in very poor mechanical properties, presumably related to a high degree of stress concentration in the vicinity of the interphase (8). Therefore, it was postulated that the best approach to combining these two polymer systems was the synthesis of block copolymers. Because of the presence of intersegment chemical linkages which restricts the extent of phase separation, these materials should exhibit two-phase morphology only on a micro-scale rather than the macro-scale dimension of incompatible physical blends.

The preparation of block copolymers using two different polyimide backbones and two different poly(arylene ether) backbones was proposed as shown in Figure 4. Block copolymer combinations to be prepared include ODA/BTDA with FBB/BPA and BABB/BTDA with both FBB/BPA and FBB/BPF. The molecular weight of the blocks to be studied were 3110 and 6545 g/mole for both the polyimide and poly(arylene ether) blocks, for all copolymer combinations studied. These block molecular weights were chosen because they should be high enough to be different from random copolymer but low enough not to cause gross phase separation. A more detailed discussion concerning molecular weight selection is included in the Results and Discussion. Several segmented copolymers also were to be prepared in order to study possible differences in properties for this variation in copolymer structure. For the preparation of adhesives and composites, one block copolymer composition will be prepared with a controlled molecular weight by end-capping with aniline to provide a material with good processability.

Prior to copolymer synthesis, poly(arylene ether) blocks will be prepared and terminated with 4-aminophenol to produce amine-terminated poly(arylene ether) blocks of 3110 and 6545 g/mole. These amine-terminated poly(arylene ether) blocks would then be reacted with anhydride-terminated poly(amic acid) blocks of the desired molecular weights, prepared by offsetting monomer stoichiometry in favor of the dianhydride. Solution

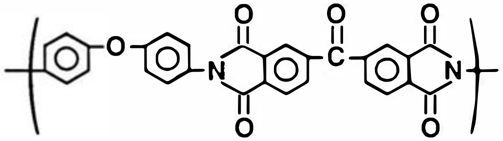
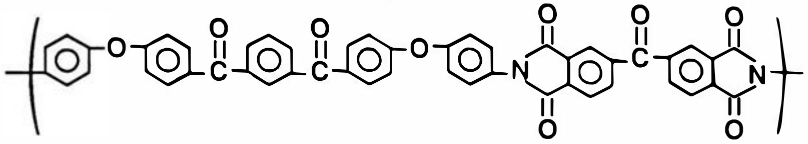
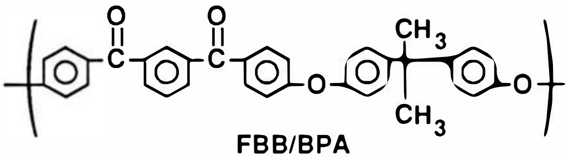
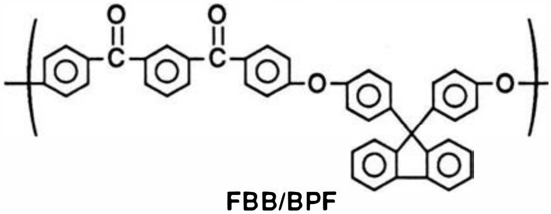
	T_g,°C	T_m,°C
Polyimides		
 **ODA/BTDA**	278	--
 **BABB/BTDA**	222	350
Poly(arylene ethers)		
 **FBB/BPA**	155	--
 **FBB/BPF**	223	--

Figure 4. Structure, designation and thermal transitions of homopolymers.

imidization or thermal imidization of the poly(amic acid) copolymers will be utilized to prepare the imide/arylene ether block copolymers. The resulting block copolymers will be fully characterized and the best candidate will be evaluated as an adhesive and composite matrix.

BACKGROUND

Polyimides are condensation polymers commonly synthesized by the reaction of dianhydrides with diamines. Although polyimides containing aliphatic groups are known (10-16), most of the research reported in the literature has involved aromatic dianhydrides and aromatic diamines. In this reaction, an intermediate poly(amic acid) is formed, which is either thermally or chemically cyclodehydrated (imidized) to form the polyimide as shown in Figure 5. Ar and Ar' are symbolic of aromatic moieties. The preparation of aromatic polyimides by reaction of an aromatic dianhydride with an aromatic diamine, followed by thermal cyclization was first reported by Bower and Frost in 1963 (17). Early U.S. patents were awarded to Edwards (18) and Endrey (19) in 1965 for aromatic polyimides.

A typical synthesis for polyimides is conducted by adding the dianhydride in the form of a fine powder, slurry or solution to a stirred solution or slurry of the diamine in a highly polar solvent at ambient temperature under a nitrogen atmosphere. Some highly polar solvents typically used include N,N-dimethylacetamide (DMAc) and N-methylpyrrolidinone (NMP). The nitrogen atmosphere is necessary to eliminate water from the atmosphere (humidity) from entering the reaction. Typical concentrations measured as solids content (weight to volume) of 15 to 25% are utilized. Bell and coworkers reported (20) the effect of reaction concentration on polymer viscosity in the range from 5% to 25%. They found that reactions at higher concentrations produce polymers with higher viscosities faster than reactions at lower concentrations and, also, these polymers maintained higher viscosities after stirring for long periods (> 200 h) than those made at lower concentrations. High molecular weight poly(amic acids) are readily formed by

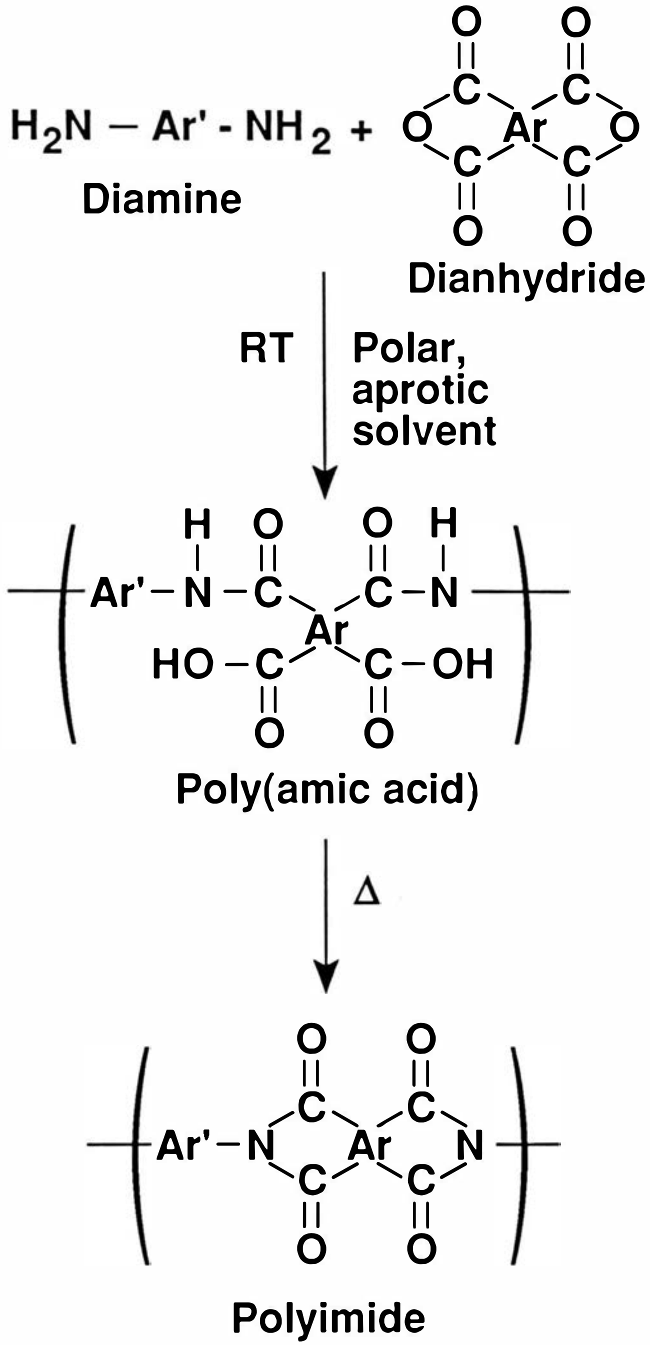
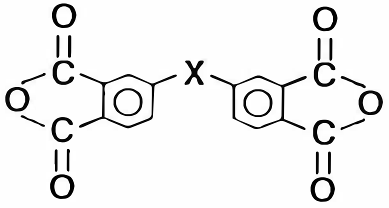
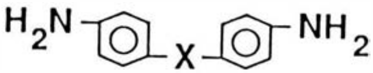


Figure 5. Typical polyimide synthesis.

the nucleophilic attack of an amino group on an anhydride carbonyl group, opening the anhydride ring to form the amic acid. Nucleophilic attack by the amide on the second carbonyl group occurs when the poly(amic acid) is heated, forming the imide ring with the loss of one mole of water. The mechanism is shown in Figure 6. Since the reaction occurs by nucleophilic substitution, the structures of the dianhydride and diamine can have a large effect on reactivity. For the structures shown below, dianhydride (**1**) and diamine (**2**) with connecting group X, the electronic effects of the connecting groups are important. For the dianhydride, electron attracting groups such as carbonyl or sulfonyl increase reactivity by making the carbonyl group more susceptible to nucleophilic attack. Conversely, electron donating groups such as oxygen decrease the reactivity of the dianhydride. For the diamines, electron donating connecting groups increase the reactivity by making the amine group more nucleophilic. These electronic effects are most pronounced when the connecting group is *para* or *ortho*- to the amino group and much less important in *meta*-substituted diamines (20).



1



2

Certain diamines such as 4,4'-diaminodiphenylsulfone or 4,4'-diaminobenzophenone are poor nucleophiles. Therefore, the formation of high molecular weight poly(amic acid) through reaction with a dianhydride, especially a less reactive dianhydride, is often difficult. However, high molecular weight poly(amic acids) have been prepared from the reaction of aromatic dianhydrides with 4,4'-diaminodiphenylsulfone (21) and 4,4'-

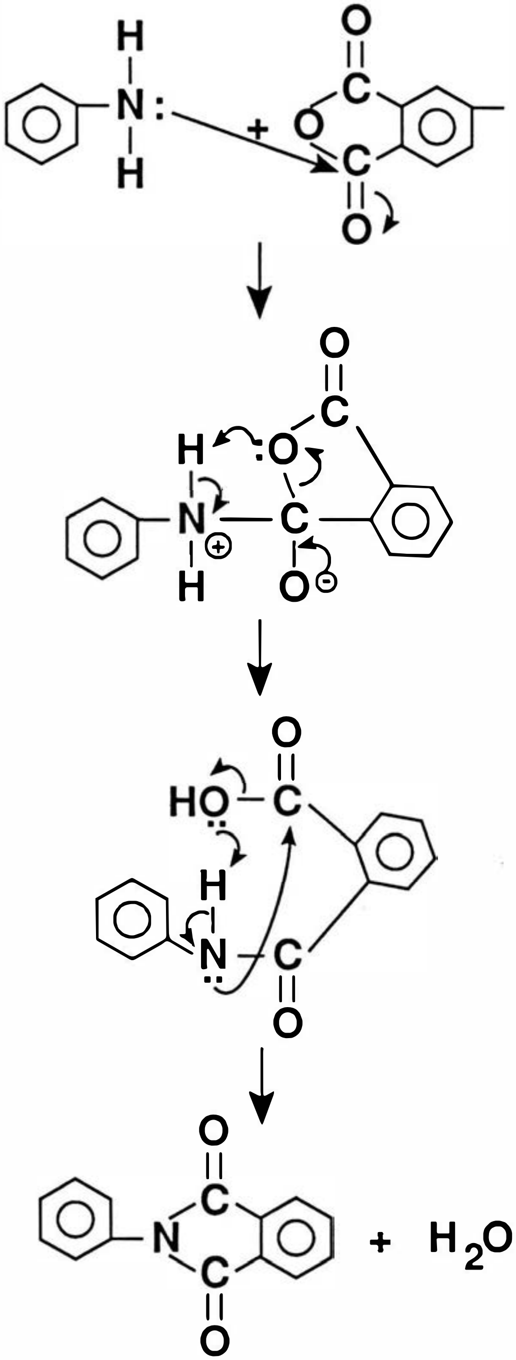


Figure 6. Mechanism for polyimide synthesis.

fig 6

diaminobenzophenone (20). The use of different solvents, in particular those containing ether linkages, has allowed the preparation of high molecular weight poly(amic acids) from monomers which produced only low molecular weight polymer in normal polar aprotic solvents. Two solvents which have received considerable attention are tetrahydrofuran (21,22) and bis(2-methoxyethyl)ether (diglyme) (21,22,23). However, only certain poly(amic acids) can be prepared in high molecular weight in ether solvents whereas most poly(amic acids) can be prepared in high molecular weight in the more universal, highly polar aprotic solvents such as DMAc and NMP. The reactivity of the monomers as well as the solubility of the poly(amic acid) is different in ether solvents than in polar aprotic solvents.

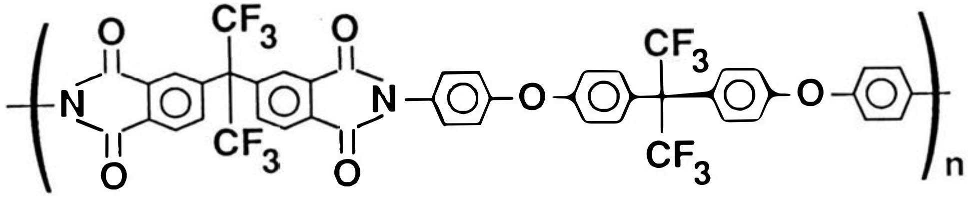
The molecular weight and molecular weight distribution of the poly(amic acid) is influenced by several factors such as solubility of the monomers, reaction time, temperature, solvent, concentration, stirring rate and mode of monomer addition. Reverse addition, that is addition of a diamine to a dianhydride solution is not recommended for the preparation of high molecular weight poly(amic acids). Excess, unreacted anhydride groups are thought to attack the poly(amic acid) causing chain cleavage (17). Thus only dianhydrides that are virtually insoluble in the polymerization solvent will form high molecular weight polymer by the reverse addition. With dianhydrides of this type or when the stirring action is not thorough, there can be interfaces or zones where the polymerization is proceeding independent of the total system. In areas of higher monomer concentration, molecules of significantly different molecular weight, with a preponderance on the high molecular weight end rather than the equilibrium molecular weight will be formed. If the reaction is stirred for longer periods of time, these high molecular weight poly(amic acid) species will undergo molecular weight equilibration (24-26) and chain cleavage (17,27). This instability is important since the properties of the resulting polyimide are directly effected. Since chain cleavage is faster at higher temperatures, poly(amic acid) solutions should be stored cold (0°C) under nitrogen. Ether solvents tend to yield lower molecular weight poly(amic acids) with a broader molecular weight distribution than typical polar solvents, and in some cases ether solvents produce poly(amic acids) with a bimodal molecular weight distribution.

The conversion of poly(amic acid) to polyimide can be accomplished by either thermal or chemical inducement. Thermal cyclodehydration occurs by heating the poly(amic acid) above 250°C. A standard cure for polyimides films is 1 hour each at 100, 200 and 300°C to provide essentially complete imidization. This conversion of poly(amic acid) to polyimide occurs generally with a partially reversible change in molecular weight (27-30). As the poly(amic acid) is heated and converted to polyimide, it undergoes a decrease in molecular weight. The minimum in molecular weight normally occurs between 150 and 200°C, but this may vary with different polymer structures. Continued heating above this point leads to an increase in molecular weight. Table 1 shows the cure temperature, inherent viscosity, number and weight average molecular weight for a particular poly(amic acid) during a cure (30). In this example, even the fully imidized polymer is soluble enough to characterize in solution using gel-permeation chromatography/low angle laser light scattering techniques.

High molecular weight poly(amic acids) free of solvent cannot be isolated from solution in highly polar solvents. Polar, aprotic solvents bind tenaciously to poly(amic acids) and the temperature required to remove these solvents causes imidization. Poly(amic acids) with very low solvent content can be isolated from solutions in ether solvents, particularly

Table 1

Characterization of Thermally Staged 6F-BDAF Film



Sample	[η] (dL/g)	$\bar{M}w$ GPC-LALLS (g/mole)	$\bar{M}n$ GPC-LALLS (g/mole)
40°	0.810	152,000	102,000
75°	0.945	108,000	69,000
100°	0.710	77,000	53,000
125°	0.525	49,000	32,000
150°	0.522	50,000	31,000
175°	0.504	64,000	34,000
200°	0.472	54,000	36,000
225°	0.516	63,000	41,000
250°	0.692	68,000	45,000
275°	0.670	80,000	53,000
300°	0.670	83,000	54,000
325°	0.756	115,000	60,000

Ref. 30

tetrohydrofuran. Polar solvents apparently enhance the cyclodehydration process and serve as a plasticizer, providing flow during processing into a part. If larger, thicker parts are being fabricated, removal of the last traces of solvent can cause the formation of voids, which decreases mechanical properties and thermooxidative stability.

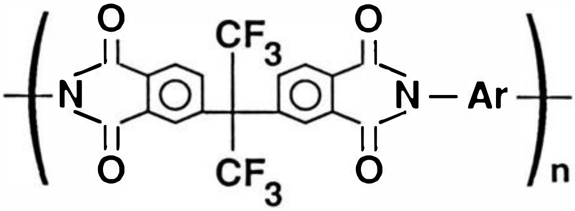
Chemical structure/property relationship studies on polyimides have been extensively conducted. Since the studies were conducted in different laboratories, the method used to determine certain properties may vary. As a result, discretion should be exercised in comparing the properties of a polyimide in one study with one from another study because the method of measurement, thermal history of the polymer, molecular weight of the polymer, etc. may vary.

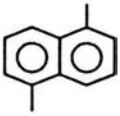
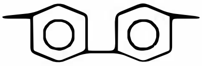
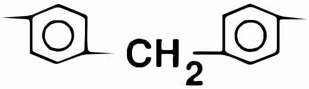
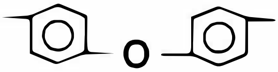
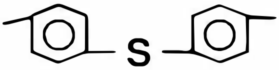
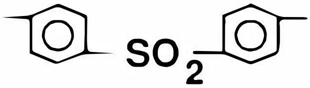
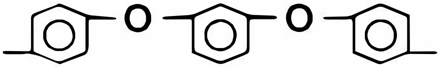
One of the first chemical structure/polymer property relationship studies to be reported for polyimides was by Gibbs and Breder in 1974 (31). These authors prepared a variety of polyimides from a common dianhydride and a series of diamines. The diamines were chosen because of the range from flexible to rigid which they display. Table 2 shows the data for polymer structure, inherent viscosity and Tg for a series of polyimides prepared from 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride. As evident in Table 2, polyimides containing the more rigid moieties [p-phenylene, 1,5-naphthalene and 4,4'-biphenylene] have the highest Tgs while those containing the more flexible moieties [4,4'-diphenyl ether and 1,3-bis(4-phenoxy)benzene] have the lower Tgs. A wide range of Tgs, from 229°C to 365°C, is represented by just varying the diamine used.

Another structure/property relationship study was reported by St. Clair and coworkers in 1984 (32) which utilized three diamines with a variety of dianhydrides. In this case, polyimides were prepared using 1,3-

Table 2

Glass Transition Temperatures of Polyimides



Ar =	Poly (amic acid) η_{inh} , dL/g	T_g , °C
	0.35	326
	0.41	297
	0.64	365
	0.40	337
	0.38	291
	0.46	285
	0.35	283
	0.31	336
	0.35	229

Ref. 31

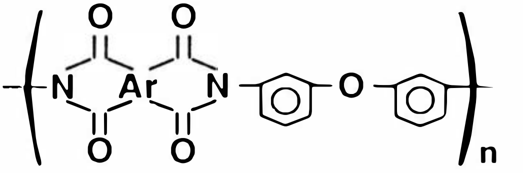
bis(3'-aminophenoxy)benzene, 3,3'-diaminodiphenylsulfone and 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane and results are shown in Tables 3, 4 and 5 respectively. In each case, going from more flexible to more rigid dianhydrides (i.e. proceeding down each of the tables) produced polyimides with higher Tgs. Also, the more flexible diamine, 1,3-bis(3'-aminophenoxy)-benzene, produced polyimides where the whole range of Tgs is lower (167-221°C) than the Tgs of the polyimides from the more rigid diamine, 3,3'-diaminodiphenylsulfone, (213-338°C).

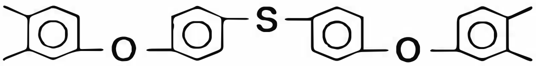
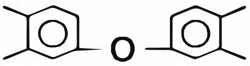
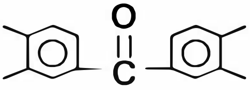
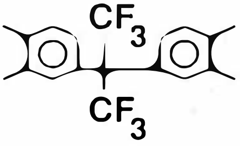
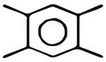
An important structure/property relationship study was reported by Bell and coworkers in 1976 (20). This study investigated the effect of different diamine isomers on polymer Tg. Table 6 summarizes data for polyimides prepared from 4,4'-,3,4'- and 3,3'- isomers of diaminobenzophenone (DABP) and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) or pyromellitic dianhydride (PMDA). These data show a significant decrease in polyimide Tg when a meta- linkage replaces a para- linkage in the diamine. When two meta- linkages replace two para- linkages, the reduction in polyimide Tg is even more dramatic. The magnitude of the reduction in Tg is larger for the less flexible pyromellitic dianhydride series of polyimides than for the series of polyimides based on 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride.

As a class of materials, linear aromatic polyimides are generally considered to be amorphous. However, there are numerous examples of polyimides which display crystallinity (33-37). Kapton® (38), a commercially available polyimide film, has been shown to exhibit molecular aggregation or molecular superstructure (39,40). Kapton® and other reported semi-crystalline polyimides exhibit exceptional thermal stability and resistance to solvents while under stress, but cannot be thermally formed into useful

Table 3

Glass Transition Temperatures of Polyimides

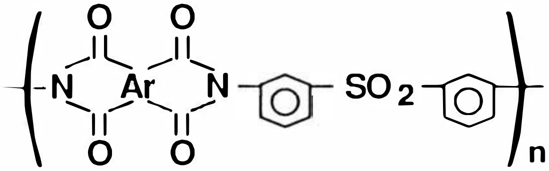


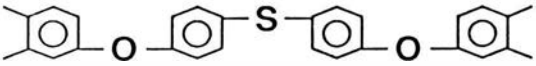
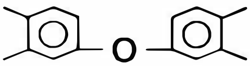
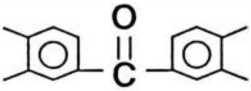
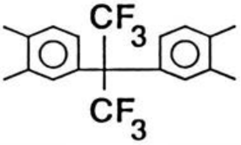
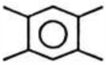
Ar =	Poly (amic acid) η_{inh}, dL/g	T_g, °C
	0.41	167
	0.87	187
	0.80	202
	1.20	206
	0.44	221

Ref. 32

Table 4

Glass Transition Temperatures of Polyimides

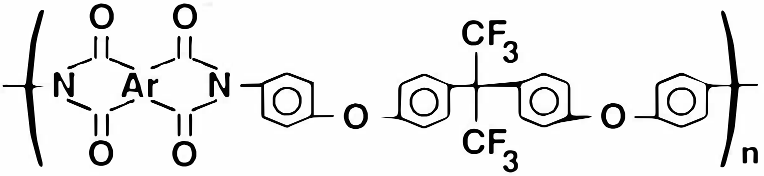


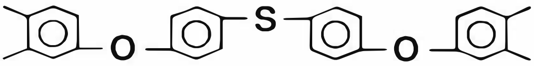
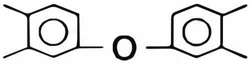
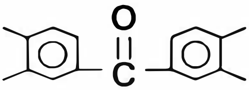
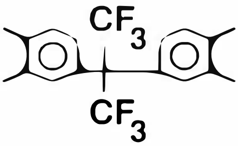
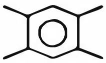
Ar =	Poly (amic acid) η_{inh}, dL/g	T_g, °C
	0.43	213
	0.51	258
	0.42	257
	0.47	279
	0.27	338

Ref. 32

Table 5

Glass Transition Temperatures of Polyimides

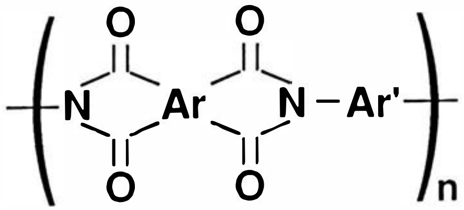


Ar =	Poly (amic acid) η_{inh}, dL/g	T_g, °C
	1.10	210
	1.08	241
	0.94	249
	0.92	263
	0.47	305

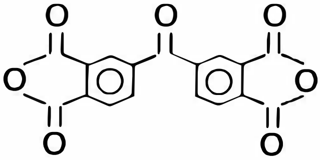
Ref. 32

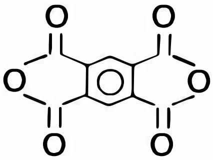
Table 6

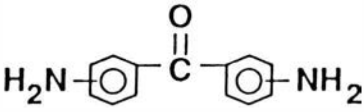
Glass Transition Temperatures of Polyimides



Ar	Ar'	η_{inh} of polyamide acid, dL/g	T_g, °C
BTDA	4,4'-DABP	0.73	295
BTDA	3,4'-DABP	0.64	283
BTDA	3,3'-DABP	0.55	264
PMDA	4,4'-DABP	0.98	380
PMDA	3,4'-DABP	0.84	339
PMDA	3,3'-DABP	0.83	321


BTDA


PMDA



DABP

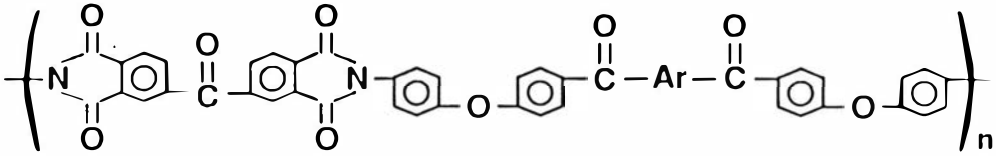
Ref. 20

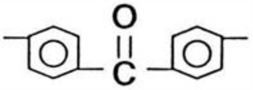
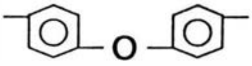
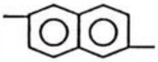
molded objects or composites. The introduction of crystallinity into a polymer has long been recognized as an effective means of improving solvent resistance and increasing modulus. If the proper type and degree of crystallinity is attained, the polymer may also display extremely high toughness. Hergenrother and coworkers have reported (41) a series of polyimides which are semi-crystalline. Crystallinity was introduced into the polyimide by incorporating arylene ether ketone connecting groups into the diamine portion of the polyimide. Table 7 shows data for the different arylene ether ketone containing polyimides. Polymer Tgs range from 215 to 246°C while the melting points (Tms) range from 350 to 427°C. For crystalline polymers, temperatures required to fabricate parts are above the Tm while use temperatures are usually below Tg. Therefore, an ideal crystalline polymer would have a high Tg and a low Tm (high use temperature with a lower processing temperature). The polymer shown at the top of Table 7 has the lowest Tm and has received the most development. That material is called LARC-CPI (for Langley Research Center-Crystalline Polyimide) and has been characterized as a candidate for films, moldings, adhesives and composites Some of the excellent properties determined for LARC-CPI are presented in Table 8 (42). Although this polymer has excellent chemical, physical and mechanical properties, it has relatively high melt viscosity and is somewhat difficult to process into useful parts.

Several polyimides such as Kapton® (38), PI-2080 (43), 5218 (44), Ultem® (45) and LARC-TPI (46) are commercially available and are used as films, moldings, adhesives and composite matrices. Many papers have been published concerning polyimides and numerous reviews on polyimides are available (3, 33, 47-51).

Table 7

Glass Transition and Crystalline Melt Temperatures of Polyimides



Ar =	Poly (amic acid) η_{inh} , dL/g	Polyimide	
		T_g , °C	T_m, °C
	0.81	222	350
	0.62	233	427
	0.57	233	422
	0.52	215	418
	0.42	246	424

Ref. 41

Table 8

Properties of LARC-CPI

Glass transition temperature: 222°C
Crystalline melt temperature: 350°C
Melt viscosity at 395°C at angular frequency of 0.1 rad/sec: 10^5 Pa·sec
Equilibrium moisture pickup: < 1%
Dielectric constant at 1 MHz: 3.1
Solvent Resistance: Excellent
Fracture Energy (G_{Ic}): 6650 J/M^2 (38 in lb/in^2)

Unoriented Thin Film Tensile Properties (Through 1 hr @ 300°C)

Test Condition	Strength, MPa (Ksi)	Modulus, GPa (Ksi)	Elongation, %
25°C	151.7 (22.0)	4.34 (630)	8.3
25°C after 100 hr soak in 30%aq. NaOH	139.9 (20.3)	4.07 (590)	5.0
177°C	104.8 (15.2)	3.72 (540)	21.1
232°C	35.8 (5.2)	1.69 (245)	76.1
232°C after 100 hr @ 316°C in air	57.9 (8.4)	2.35 (341)	9.6

Ti/Ti Adhesive Properties [RT → 400°C under 6.9 MPa (1000 psi), hold 15 min @ 400°C]

Test Condition	Tensile Shear Strength, MPa (psi)
25°C	43.1 (6250)
25°C after 1000 hr @ 232°C	49.1 (7120)
177°C	31.1 (4510)
232°C	4.1 (590)
232°C after 1000 hr @ 232°C	18.9 (2740)
232°C after 100 hr @ 316°C in air	25.3 (3670)

Ref. 42

One family of polymers that has good mechanical properties as well as relatively low melt viscosity and good processability is the poly(arylene ethers). The synthesis of poly(arylene ethers) involves the nucleophilic displacement of activated aromatic halides in polar solvents by alkali metal phenolates or Friedel-Crafts processes. Nucleophilic displacement and Friedel-Crafts reactions leading to high molecular weight poly(arylene ethers) were initially reported in the late 1950s (52) and early 1960s (53), respectively.

The large family of poly(arylene ethers) can be divided into poly(aromatic ketones) and poly(aromatic sulfones). Unlike poly(aryl sulfones) which are typically amorphous, most poly(aryl ketones) exhibit partial crystallinity, usually with melting points above 300°C. The synthetic routes to these materials have much in common. In fact polymerization reactions suitable for preparing poly(aryl sulfones) can be used to prepare amorphous poly(aryl ketones) without any modification. However, to prepare crystalline poly(aryl ketones), which precipitate prematurely from solution due to limited solubility in most organic solvents, modifications to typical Friedel Crafts and nucleophilic displacement reactions have been made.

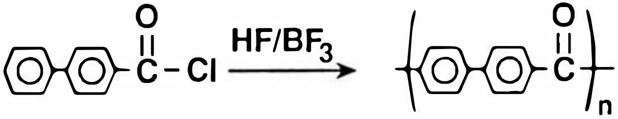
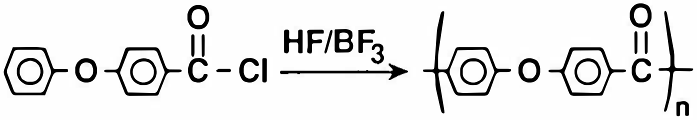
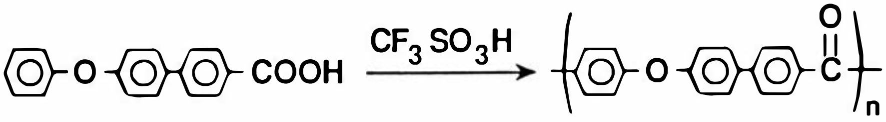
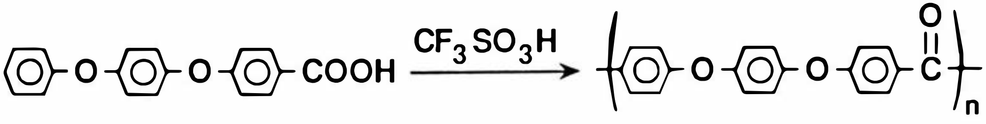
Polymerization by Friedel-Crafts acylation has been studied intensely in the last two decades. Both A-B (one component) and A-A, B-B (two component) systems have been successfully polymerized to high molecular weight polymers. Regardless of the monomer system, the formation of useful polymers depends on the solubility of the polymer in the reaction mixture and the quantitative acylation of either a phenoxy or a biphenyl group regiospecifically at the para position. For A-B systems, Marks (54) was successful at preparing high molecular weight crystalline poly(aryl ketones) by utilizing the unique combination of anhydrous hydrogen fluoride/boron trifluoride as a catalyst and solvent system as shown in Table 9. Colquhoun and Lewis (55) also prepared high molecular weight poly(aryl ketones) from A-B systems but they utilized trifluoromethanesulfonic acid, a strong acid capable of protonating the polyketones, as solvent. Several of their polymers are also shown in Table 9.

While one component A-B systems have received some attention, the majority of research has focused on two component A-A, B-B systems. Utilizing anhydrous hydrogen fluoride/boron trifluoride as Marks had done, Janson (56) was successful preparing high molecular weight polymer from two component systems as shown in Table 10 using terephthalic acid. Also shown in Table 10, Dahl (57) used the same solvent/catalyst to prepare high molecular weight poly(aryl ketone) from terephthaloyl chloride. Using a different solvent, trifluoromethanesulfonic acid, Jansons (56) prepared high molecular weight polymer from isophthaloyl chloride and diphenyl ether.

Until 1984, hydrogen fluoride/boron trifluoride and trifluoromethanesulfonic acid were the only solvent-catalyst systems useful for preparation of high molecular weight PAEs. These methods are not ideal for industrial practice due to their cost and handling problems. Aluminum chloride, used originally, has received renewed interest. Jansons (58) reported numerous examples in which $AlCl_3$ in methylene chloride (and other chlorinated solvents) in conjunction with a Lewis base proved to be effective in giving high molecular weight polymers. The preferred Lewis bases are dimethylformamide, lithium chloride and ammonium chlorides. It was claimed that the complex formed from $AlCl_3$ and a Lewis base could either act as a solvent or as a swelling medium for the polymer. Structures and limited data for two early poly(aryl ketones) synthesized by Effenberger and Epple (59) and Goodman and coworkers (60) using $AlCl_3$ are shown in Table 11.

Table 9

Synthesis of A-B Systems by Friedel-Crafts Acylation

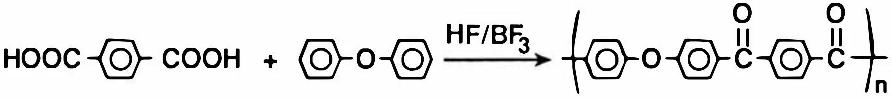
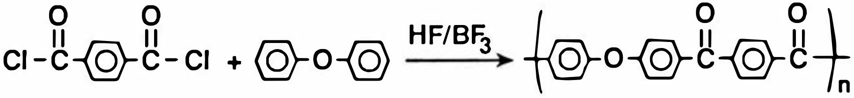
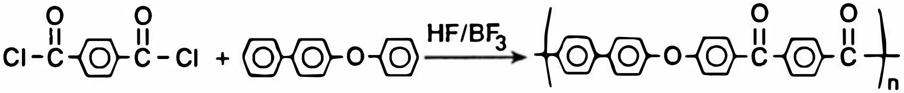
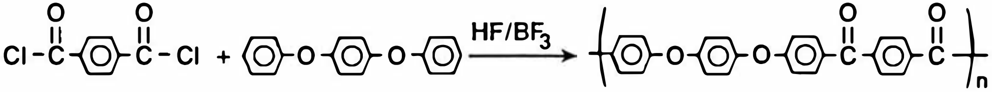
	η_{inh} (dL/g)	T_g (°C)	T_m (°C)
	1.7[a]	--	--
	1.33[a]	163	361
	1.88[b]	216	486
	1.19[b]	152	330

a) 0.5 g/dL in H_2SO_4 at 30°C
Ref. 54

b) 1.0 g/dL in CF_3SO_3H at 30°C
Ref. 55

Table 10

Synthesis of A-A, B-B Systems by Friedel-Crafts Acylation

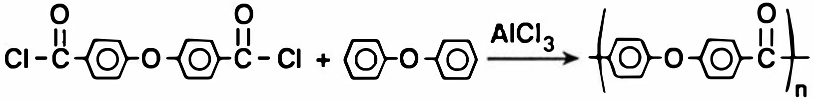
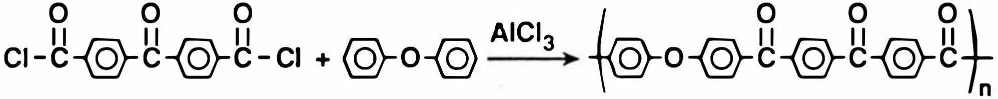
	η_{inh} (dL/g)	T_g (°C)	T_m (°C)
	1.16[a]	--	--
 Ref. 56	0.95[b]	175	280
	0.43[a]	--	402
 Ref. 57	0.90[a]	--	360

a) 0.1 g/dL in H_2SO_4 at 30° C

b) 0.125 g/dL in H_2SO_4 at 30°C

Table 11

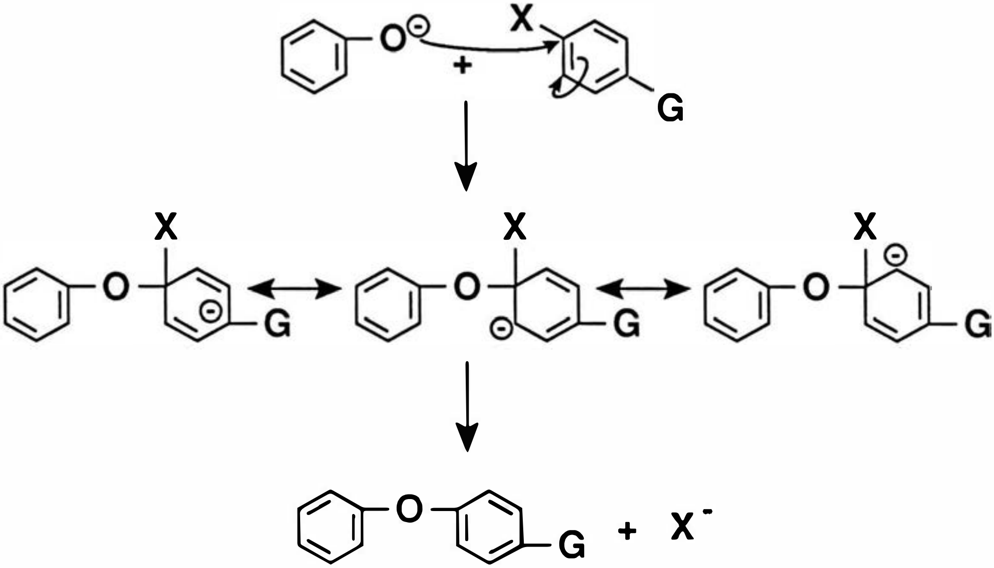
Synthesis of A-A, B-B Systems by Friedel-Crafts Acylation

	η_{inh} (dL/g)	T_g (°C)	T_m (°C)
 Ref. 59	1.03[a]	--	--
 Ref. 60	--	--	370-380

a) 0.1 g/dL in H_2SO_4 at 30° C

Nucleophilic substitution, the second method used to prepare poly(arylene ethers), involves the reaction of an alkali metal phenoxide with activated aromatic halides to give a high yield of the corresponding ethers. As shown in Figure 7, the mechanism proceeds through an anionic intermediate, sometimes called a Meisenheimer complex, several of which have been isolated (61). The leaving groups typically utilized are halogens and the order of reactivity is F > Cl > Br > I. Furthermore, activating groups are required in the ortho or para positions to the leaving group to allow the formation of higher yields of the desired product. The activating groups are electron withdrawing thereby stabilizing the intermediate both by induction and by delocalization of the negative charge. Electron withdrawing groups in the meta position have very little activating effect. To prepare polymers, the dihalide must be sufficiently activated as well as have a good leaving group (F or Cl). Furthermore, the bisphenol must be a good nucleophile and attack the dihalide at the electron difficient aromatic carbon.

The initial development of poly(arylene ethers) by nucleophilic displacement took place concurrently in two research groups. Rose and coworkers reported (62,63) low molecular weight polymer by reacting the disodium salt of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) with 4,4'-dichlorobenzophenone in dimethylsulfoxide (DMSO) containing a catalytic amount of copper oxide. Johnson and coworkers, using the fluoro analog (4,4'-difluorobenzophenone) reported (64-66) a high molecular weight poly(arylene ether) after only 0.5 h of reaction time at 135°C in DMSO. Besides chemical reactivity, two factors essential for the formation of high molecular weight are: 1) a suitable solvent and 2) exclusion of air and water. Solvents are chosen because of their ability to dissolve the alkali bisphenoxide as well as the growing polymer chains under anhydrous



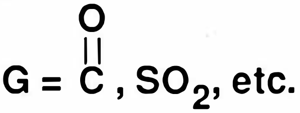
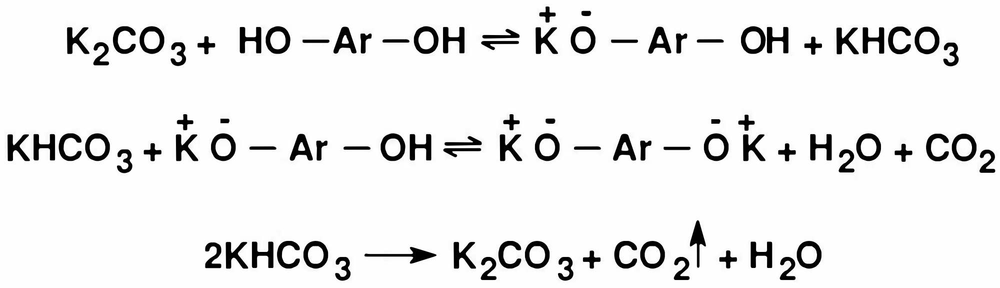

$$G = \overset{\overset{\displaystyle O}{\|}}{C}\,,\ SO_2,\ \text{etc.}$$

Figure 7. Mechanism for synthesis of aromatic ethers.

conditions. The presence of water causes hydrolysis of the activated aromatic halides and, to a small extent, chain scissions via the attack of sodium hydroxide on the polymer chains. The exclusion of atmospheric oxygen is necessary due to the ease with which phenoxides are oxidized at elevated temperature.

There are several undesirable features associated with the above reaction conditions. An exact stoichiometry in base is required since excess sodium hydroxide will degrade the dihalide and the polymer. On the other hand, a deficiency of base will obviously give incomplete reaction. An improved procedure using anhydrous potassium carbonate in a polar aprotic solvent first appeared in the patent literature in the late 1970s (67,68). More recent work has reported the use of anhydrous potassium carbonate and toluene with N,N'-dimethylacetamide (69) or N-methylpyrrolidinone (70). Potassium carbonate is a sufficiently strong base to react with phenols at elevated temperatures and is only sparingly soluble in organic solvents. Therefore, the potassium bisphenoxide and water is generated gradually during the reaction. Because of its limited solubility, potassium carbonate can be used in excess without hindering the production of high molecular weight polymer. The formation of water under these reaction conditions is shown in Figure 8 (69). To maintain the necessary anhydrous conditions, toluene is added to the reaction. When heated, toluene forms an azeotropic mixture with water present in or formed by the reaction, which is removed by distillation into a Dean-Stark trap.

Compared to the dimethylsulfoxide/aqueous sodium hydroxide system, this alternate route appears to be nearly 10 times slower. The slower reaction rates may be due to hydrogen bonding between the phenoxide and unreacted phenols, the lower dielectric constant of the reaction medium due



$$\mathrm{K_2CO_3 + HO-Ar-OH \rightleftharpoons \overset{+}{K}\,\overset{-}{O}-Ar-OH + KHCO_3}$$

$$\mathrm{KHCO_3 + \overset{+}{K}\,\overset{-}{O}-Ar-OH \rightleftharpoons \overset{+}{K}\,\overset{-}{O}-Ar-\overset{-}{O}\,\overset{+}{K} + H_2O + CO_2}$$

$$\mathrm{2KHCO_3 \longrightarrow K_2CO_3 + CO_2\uparrow + H_2O}$$

Figure 8. Formation of water in nucleophilic substitution using potassium carbonate base.

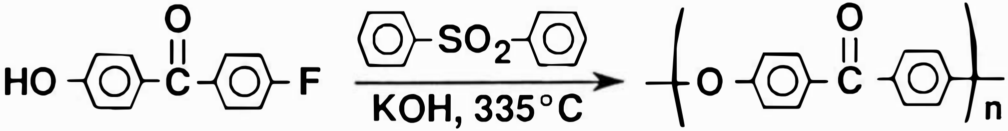
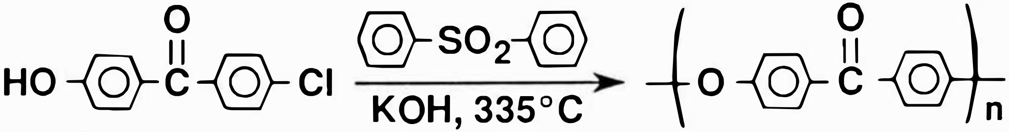
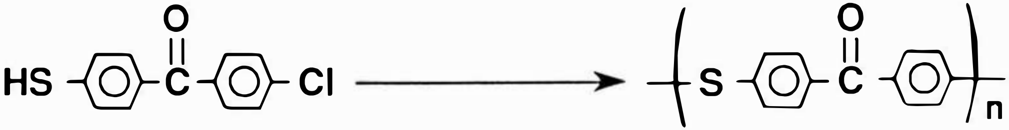
to the presence of toluene or possibly the initial heterogeneous nature of the potassium carbonate. Therefore, higher temperatures are required to produce high molecular weight polymers. Viswanathan and coworkers reported (69) that at the end of 10 h under the above conditions, the reaction carried out at 157°C produced high molecular weight polymer while the one at 140°C yielded only trimers and oligomers. Hergenrother and coworkers have reported (71-73) many additional high molecular weight poly(arylene ethers) synthesized by this alternate process.

To prepare high molecular weight crystalline poly(arylene ethers), modifications to the above procedure are necessary. The main problem in the preparation of crystalline polymers is the insolubility with increasing molecular weight. In the procedure discussed above, crystalline poly(arylene ethers) precipitate from solution before high molecular weight is achieved (64). However, Rose and coworkers (74-76) discovered that high molecular weight crystalline polymers could be prepared in diphenylsulfone. The reaction simply involved mixing the appropriate amounts of monomers in diphenylsulfone and heating the mixture to 335°C for 2-3 h. On cooling, the viscous melt set to a hard solid which was ground to a powder then extracted with water and methanol. The structures, inherent viscosities and thermal transition temperatures for several of these poly(arylene ethers) are listed in Tables 12, 13 and 14.

Several thermoplastic poly(arylene ethers) such as Udel® (polysulfone) (80), Kadel® (polyketone) (80), PEEK® [poly(ether ether ketone)] (81), and Victrex® PES (polyethersulfone) (81) are commercially available. These materials are excellent high performance engineering thermoplastics and are used in a variety of applications such as coatings, adhesives composites, molded components, toughening agents and

Table 12

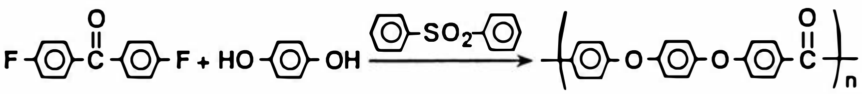
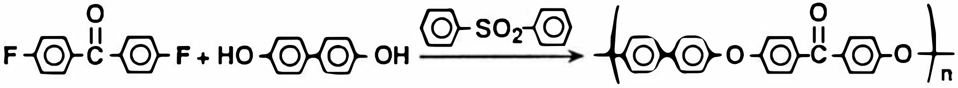
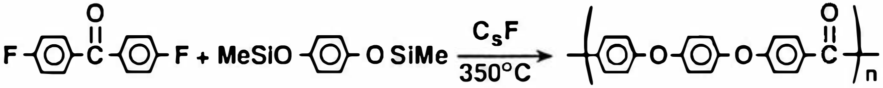
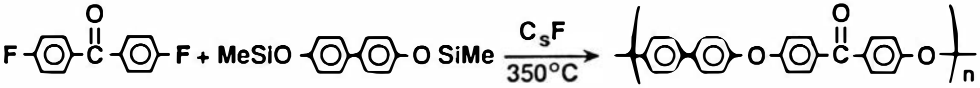
Synthesis of A-B Systems by Nucleophilic Substitution

	η_{inh}[a] (dL/g)	T_g (°C)	T_m (°C)
 Ref. 74	1.15	154	367
 Ref. 75	0.79	--	--
 Ref. 77	0.73	--	352

a) 0.1 g/dL in H_2SO_4

Table 13

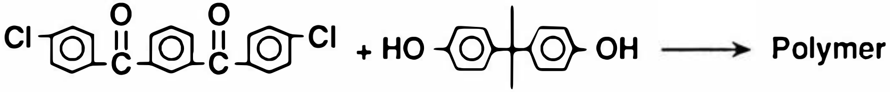
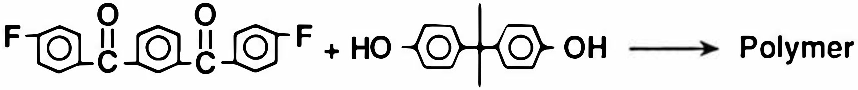
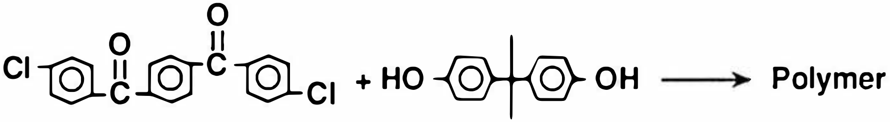
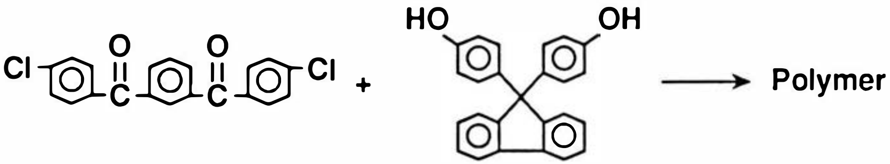
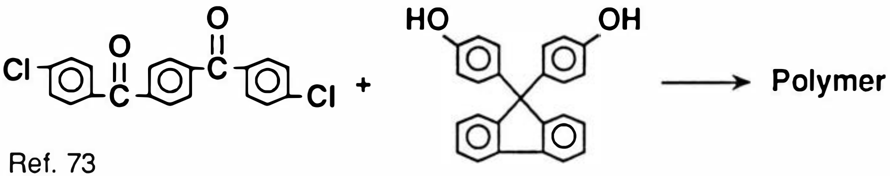
Synthesis of A-A, B-B Systems by Nucleophilic Substitution

	$\eta_{inh}{}^{a}$ (dL/g)	T_g (°C)	T_m (°C)
	1.27	144	335
	--	167	416
Ref. 78			
	0.79	--	344
	0.62	--	421
Ref. 79			

a) 0.1 g/dL in H_2SO_4

Table 14

Synthesis of A-A, B-B Systems by Nucleophilic Substitution at 155°C Using K_2CO_3 and DMAc/Toluene

	$\eta_{inh}{}^{a}$ (dL/g)	T_g (°C)	T_m (°C)
	0.57	152	--
	1.23	155	--
	0.68	166	--
	0.95	223	--
	1.27	243	--

Ref. 73

a) 0.5% in $CHCl_3$ at 25°C

ultrafiltration membranes. Many excellent references (82,83) are available on poly(arylene ethers) which discuss the synthesis, characterization and chemical and physical properties of these high performance polymers.

Both polyimides and poly(arylene ethers) are engineering materials with many attractive properties for a variety of applications. Polyimides are known for their excellent thermal stability, chemical resistance and mechanical properties but are somewhat difficult to process into useful composites, adhesives or moldings. Poly(arylene ethers) are known for their good mechanical properties, thermal stability and ease of processing into useful parts. In an effort to improve the processability of polyimides, a variety of copolymers containing the imide unit as well as other more flexible repeat units have been prepared. Copolyimides containing other flexible units have been synthesized as random, block and graft copolymer systems. In some early work, researchers incorporated organosiloxane units or blocks into the polyimide (84-87). These materials were useful as films, adhesives and coatings. More recently, polysiloxane-containing polyimides have been prepared and reported (88-91) which exhibit high glass transition temperatures, good ductility, excellent thermal stability and low dielectric constants. These copolymers are based on aminopropyl-terminated polydimethylsiloxane oligomers which were incorporated into the polyimide backbone. In 1984, Johnson et. al. reported (92) the incorporation of imide units into a polysulfone polymer. As shown in Figure 9, a bisphenol prepared from p-aminophenol and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride containing the imide moiety was then polymerized to a poly(imide-ether sulfone) copolymer. For these random copolymers, made by varying the ratio of one bisphenol to the other, properties corresponded

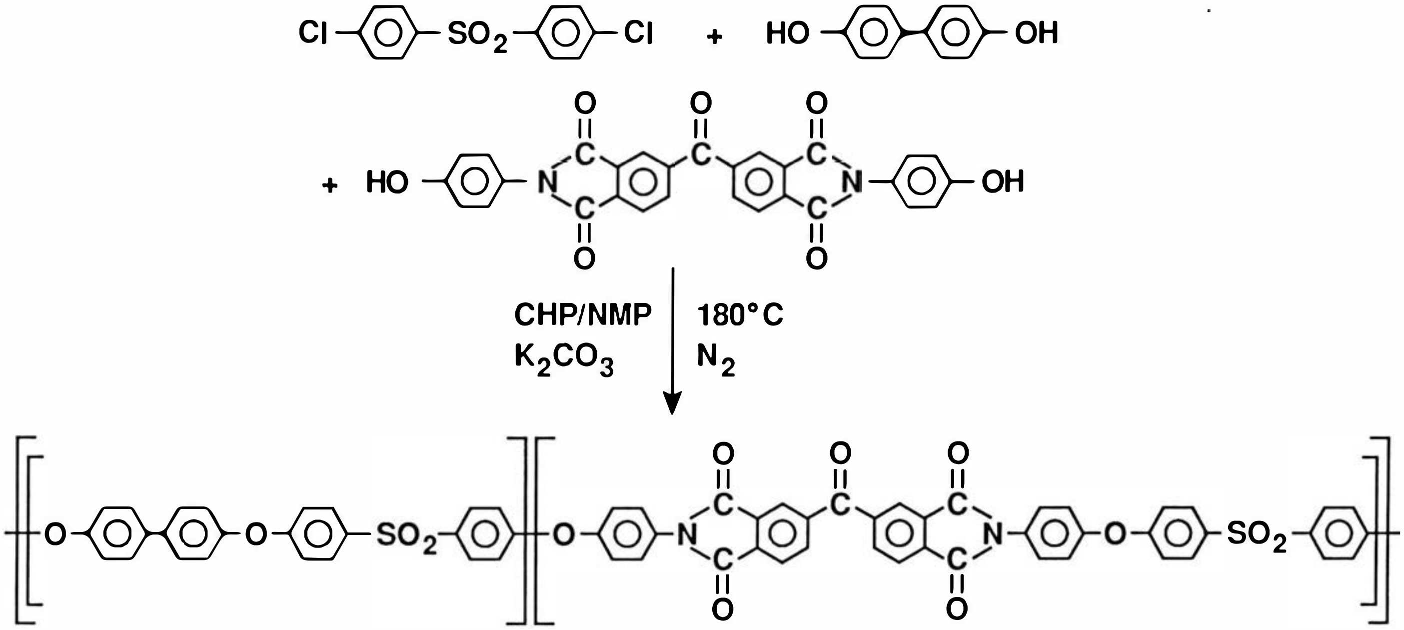
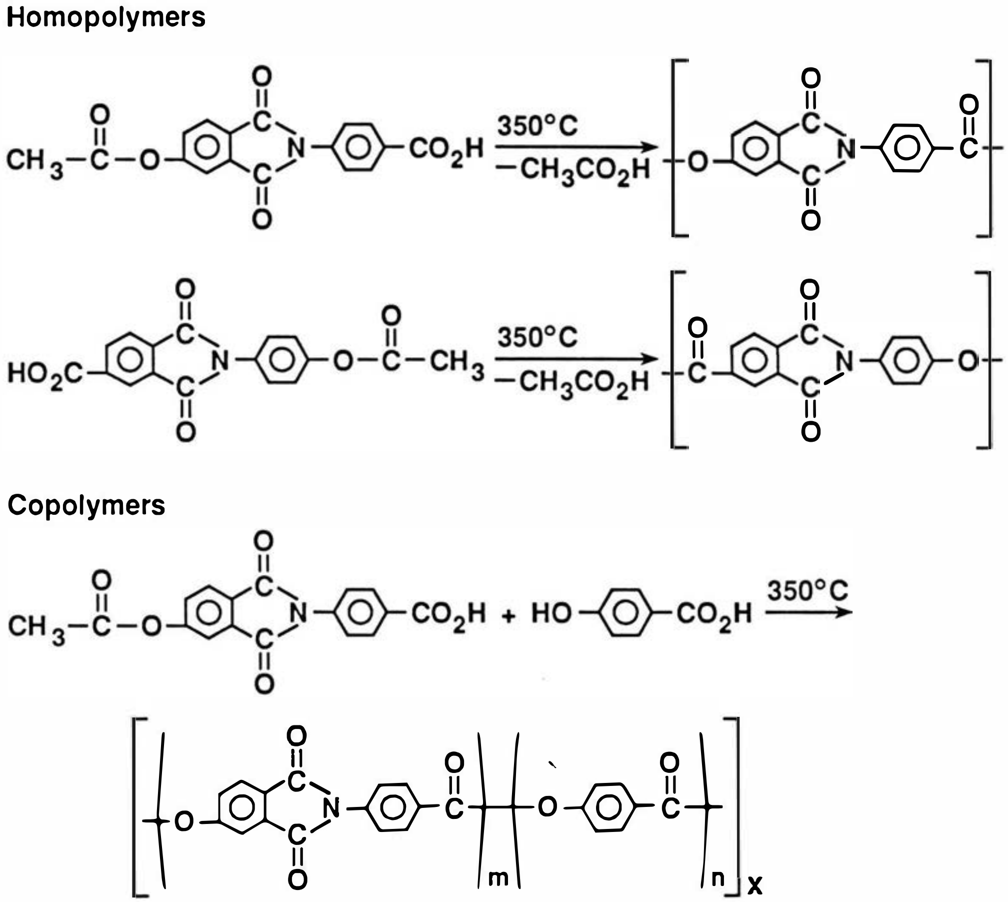


Figure 9. Synthesis of poly(imide-ether sulfone) copolymer.

directly to the content of each monomer present. Copolymers with higher imide content had higher strength and modulus, as expected.

In 1988, Kricheldorf et. al. reported (93) copoly(ester imide)s of 4-hydroxybenzoic acid and N-(4-carboxyphenyl)-4-hydroxyphthalimide. Synthesis of homopolymers shown in Figure 10 was accomplished in the melt at temperatures between 250-350°C or in an inert reaction medium at 350°C. Also shown are copolymers prepared by varying the ratio of monomers to provide higher or lower imide content. These copolymers are semi-crystalline with Tms ranging from 390 to 340°C, corresponding to decreasing imide content. The synthesis of imide-aryl ether benzoxazole random copolymers was recently reported (94) by Hedrick et. al. As shown in Figure 11, a benzoxazole containing diamine, along with oxydianiline, was reacted with pyromellitic dianhydride to form the copolymers. Cassidy et. al. have recently reported (95) copoly(imidine-imides) which were prepared by incorporating pendent benzylidene groups on the dianhydride monomers as shown in Figure 12. Reaction of these dianhydrides and other dianhydrides with diamines led to the copoly(imidine-imides). The new copolymers have greatly enhanced solubility and form tough, transparent films from N-methylpyrrolidinone.

Grade and Verbicky have recently reported (96) polyimide-polyformal block copolymers in an effort to prepare a more flexible polymer possessing the excellent thermooxidative stability of polyimides. Aromatic polyformals exhibit exceptional thermooxidative stability while having a significantly lower Tg and modulus than most polyimides (97-101). Therefore, amine-terminated polyformal oligomers were reacted with anhydride-terminated polyimide oligomers to form the copolymers. The thermal properties and thermal stability were evaluated for these copolymers and found to be excellent.



Ratio of m:n varied from 4:1 to 1:9

Figure 10. Synthesis of copoly(ester imide)s.

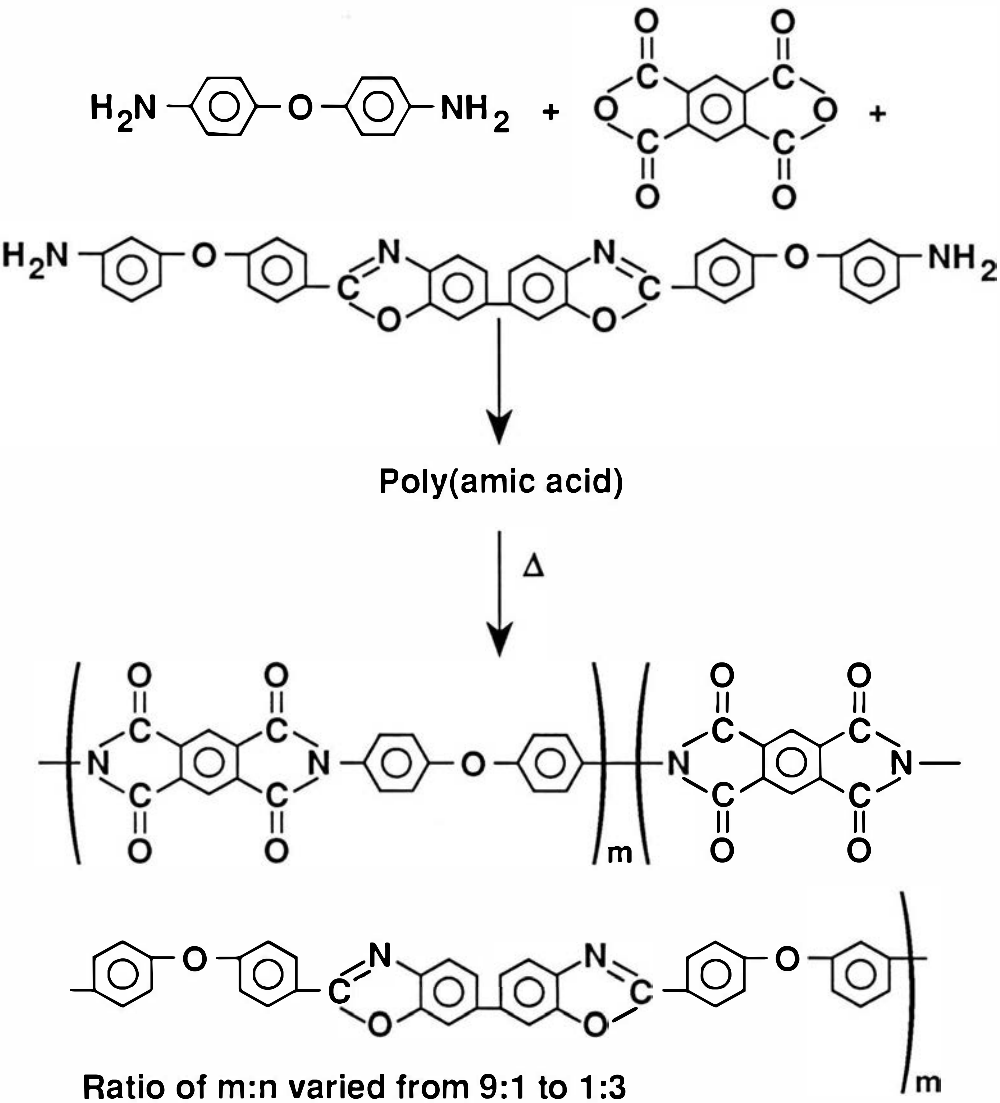


Figure 11. Synthesis of imide-aryl ether benzoxazole random copolymers.

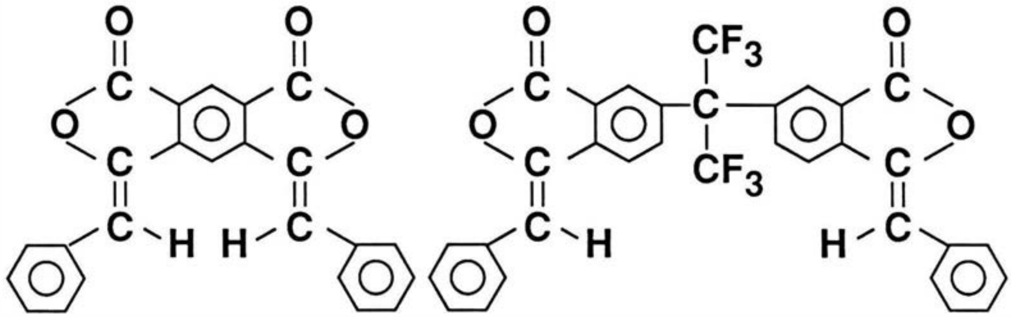


Figure 12. Benzylidene containing dianhydride monomers.

Imide homo and copolymers containing carbonyl and ether connecting groups have been reported recently by Hergenrother and Havens (102) and were found to have an attractive combination of properties. Depending on the chemical structure, Tgs ranged from 172 to 258°C and several of these polymers were crystalline.

Because of the excellent properties associated with polyimides and poly(arylene ethers), it was envisaged that block copolymers containing each of the above moieties may have an excellent overall combination of properties. The imide portion should impart high mechanical properties and thermal stability and the arylene ether portion should impart good processability and high toughness into the proposed block copolymers.

EXPERIMENTAL

General

Melting points were determined using a Thomas Hoover melting point apparatus or a DuPont Model 990 Differential Thermal Analyzer (DTA) at a heating rate of 10°C/min. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Inherent viscosities (η_{inh}) were obtained using a Cannon-Ubbelohde viscometer on 0.5% solutions in chloroform ($CHCl_3$), DMAc, NMP or m-cresol at 25°C. Infrared (IR) spectra were obtained on a Nicolet 60SX Fourier Transform Infrared Spectrometer System equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. A Harrick Diffuse Reflectance Attachment (DRA-Praying Mantis Model, Harrick Scientific Corporation) was used for all reflectance measurements. Proton nuclear magnetic resonance ('H-NMR) spectra were taken on a Varian EM 360A spectrometer with tetramethylsilane as internal standard. Gel-permeation chromatography (GPC) was performed on a Waters Associates chromatograph using chloroform as the mobile phase at a flow rate of 1 mL/min., an ultra-Styragel column bank (10^6, 10^5, 10^4, 10^3 Å) and UV detector at 254 nm wavelength. Differential scanning calorimetry (DSC) was performed on a DuPont Model 990 Thermal Analyzer in combination with a standard DuPont DSC cell at a heating rate of 20°C/min. The apparent glass transition temperature (Tg) was taken at the inflection point of the ΔT versus temperature curve. Torsional braid analyses (TBA) were conducted at a heating rate of 3°C/min in a nitrogen atmosphere over the temperature range -100 to 400°C on solution coated braids which were cured 1 h each at 100, 200 and 300°C. The Tg values were taken at the peak of the damping curves. Thermogravimetric analyses (TGA) were performed on film samples using a Perkin-Elmer program temperature controller model UV-1 in combination with a heater controller and an autobalance model AR-2 at a heating rate of 2.5°C/min in both air and nitrogen flowing at a rate of 15 ml/min. Polymer melt viscosity was measured using a Rheometrics System IV rheometer with a parallel plate configuration with the top plate operating in an oscillating mode at different frequencies (0.1 to 100 radians/sec). Wide angle x-ray scattering (WAXS) data was obtained on powder or thin film specimens using a Phillips XRG 3600 x-ray diffractometer. With the x-ray diffractometer operated at 45 kV and 40 mA, using copper radiation with a flat sample holder and a graphite monochromator, the intensity of one second counts taken every 0.01 degrees (2θ) were recorded on hard disc for the angular range: 10 - 40° (2θ). An external α-quartz standard was used in goniometer alignment. TBA, TGA, melt viscosity and WAXS analyses were performed by the technical staff of NASA-Langley. The number average molecular weight was determined at Virginia Polytechnic Institute and State University for the amine terminated poly(arylene ethers) (ATPAE) by amine group titration using a MCI Model GT-05 Autotitrator with 0.02 M HBr in glacial acetic acid as the titrant. The ATPAEs were dissolved in a 2:1 mixture of chlorobenzene and acetic acid.

Films

DMAc, NMP or m-cresol solutions (15% solids) of the various polymers were centrifuged, the decantate doctored onto plate glass and dried at 25°C to a tack-free form in a dust proof chamber. The films on glass were cured 1 h each at 100, 200 and 300°C. Mechanical tests were performed according to ASTM D882 on four specimens per test condition.

Moldings

The polymers were compression molded in a stainless steel mold using a hydraulic press equipped with electrically heated platens. The temperature and pressure used depended on the particular sample and varied accordingly. Four compact tension specimens (see Figure 13), approximately 0.62 x 0.62 x 0.32 in thick, were cut from the 1.25 in square moldings and tested by a known procedure (103).

Adhesive Specimens

The as prepared poly(amic acid) solutions were used to brush coat 112 E-glass, with an A-1100 finish, secured on a frame. Each coat was dried in an air circulating oven for ~ 1 h each at 100 and 200°C which converted most of the poly(amic acid) to polyimide. Generally, ten coats were required to provide a 12 mil thick boardy tape. Titanium (Ti, 6Al-4V) to titanium tensile shear specimens with a Pasa-Jell 107 surface treatment were fabricated by placing in a preheated hydraulic press, heating rapidly to temperature, applying pressure and holding from 15 - 30 min. Four specimens were tested for each condition according to ASTM D1002.

Composites

Prepreg was prepared using a Research Tool Corporation Model 30 drum winder with the drum speed set at 3 rpm, the fiber tension at 0.1% and the transverse rate at 42%. Using a die with a 0.02 in. wide x 0.22 in. long gap and a guide roller of 0.22 in. (which determines the width of a tow as it is placed on the drum), NMP solutions (25% solids content) of the end-capped polymers were coated onto Hercules AS-4 graphite fiber (12K tow, unsized). Prepregs 76 in. long and up to 12 in. wide were prepared on this drum

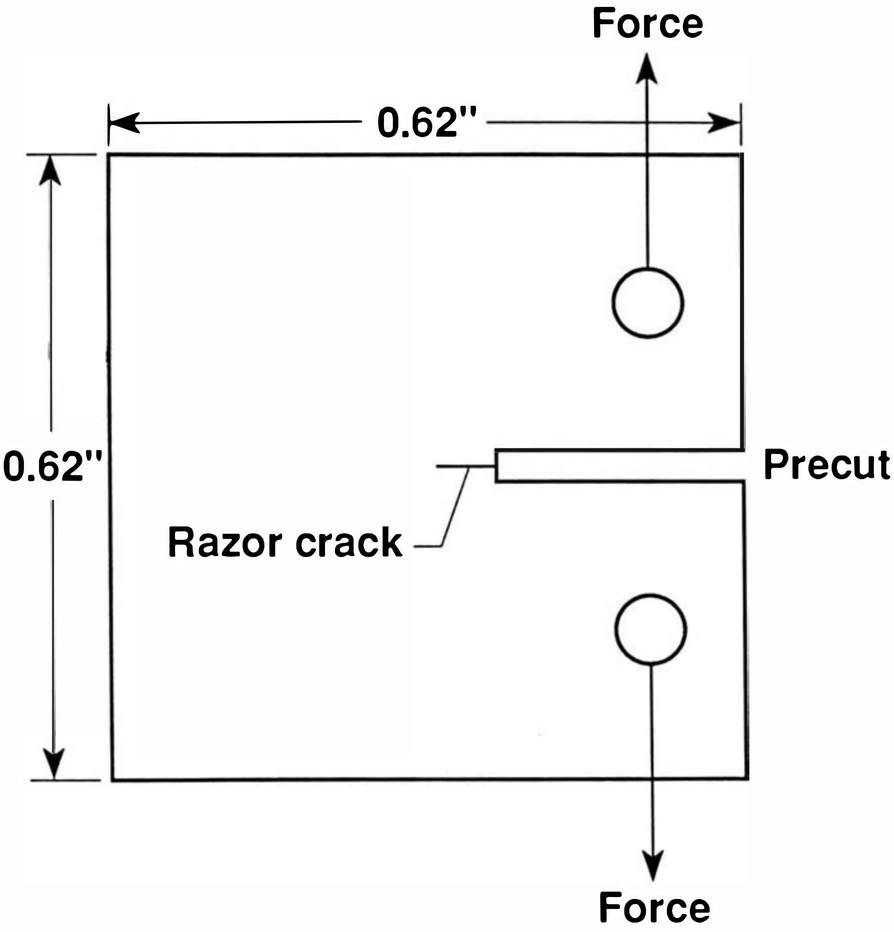


Figure 13. Compact tension specimen.

winder. The prepregs were air dried on the drum for 16 h followed by drying in an oven by slowly heating (4°C/min) to 200°C and holding for 1 h. Unidirectional composites were prepared by stacking prepreg (10 layers for flexure specimen and 18 layers for short beam shear specimen) in a 3 in. x 3 in. stainless steel mold. The mold was then introduced to a hydraulic press with electrically heated platens preheated to 400°C. The mold was heated rapidly (during ~ 45 min.) to 380°C where a pressure of 300 psi was applied. The mold was held at 380°C under 300 psi for 15 min. then allowed to cool to room temperature while pressure was maintained. The 10 ply panels were cut into flexural specimens (3 in. x 0.5 in.) and tested according to ASTM D790-86. The 18 ply panels were cut into short beam shear specimens (0.75 in. x 0.25 in.) and tested according to ASTM D2344-84.

Starting Materials and Reagents

N,N-Dimethylacetamide (DMAc) was obtained commercially (Fluka Chemical Co.) and was used as received. N-Methyl-2-pyrrolidinone (NMP) was obtained commercially (Aldrich Chemical Co.) and was used as received. m-Cresol was obtained commercially (Aldrich Chemical Co.) and was used as received. Toluene was obtained commercially (Fisher Scientific) and was used as received. Chloroform ($CHCl_3$) was obtained commercially and was used as received. 4-Aminophenol was obtained commercially and was sublimed under vacuum at 170 - 175°C, m.p. 188 - 190°C.

Monomers

1,3-Bis(4-fluorobenzoyl)benzene (FBB)

Anhydrous powdered aluminum chloride (164.7 g, 1.240 mol) was added during ~ 5 min to a stirred solution of isophthaloyl chloride (101.5 g, 0.500 mol) in fluorobenzene (480.5 g, 5.000 mol). The reaction became exothermic, with the temperature increasing to ~ 60°C. After the exotherm subsided, the reaction was maintained at ~ 75°C for 4 h and then poured into cold, aqueous hydrochloric acid. The suspension was distilled to remove excess fluorobenzene and the residual solid was collected by filtration. The crude product was recrystallized from toluene to afford 1,3-bis(4-fluorobenzoyl)benzene as white crystals (130.5 g, 81% yield), m.p. 178 - 179°C. Anal. Calcd. for $C_{20}H_{12}F_2O_2$: C, 74.53%; H, 3.75%; F, 11.79%. Found: C, 74.33%; H, 3.59%; F, 11.42%.

9,9-Bis(4-hydroxyphenyl)fluorene (BPF)

9-Fluorenone (135.15 g, 0.7500 mol) was reacted with phenol (282.34 g, 3.000 mol) in the presence of 3-mercaptopropionic acid (~ 2 g) at ~ 50°C with stirring while hydrogen chloride gas was bubbled into the mixture. After 4 h at ~ 50°C, the reaction mixture became light amber and viscous. The reaction was terminated when a light green solid formed and the mixture became too viscous to stir. The crude product was steam distilled to remove phenol, air dried at ~ 100°C, and was recrystallized twice from toluene to afford 9,9-bis(4-hydroxyphenyl)fluorene as an off-white solid (105 g, ~ 40% yield), m.p. 222 - 223.5°C [Lit. (104) m.p. 223 - 224°C].

2,2-Bis(4-hydroxyphenyl)propane (BPA)

This monomer was obtained commercially (Aldrich Chemical Co.) and was recrystallized from toluene to yield a white crystalline solid, m.p. 156 - 157°C.

1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene (BABB)

4-Aminophenol (10.91 g, 0.100 mol) was dissolved in a solution of DMAc (75 ml) and toluene (75 ml) in a three-necked flask equipped with a Dean-Stark trap. Powdered anhydrous potassium carbonate (17.28 g, 0.125 mol) was added and water was removed by azeotropic distillation with toluene. Toluene was removed until the temperature reached 130 - 140°C. Then 1,3-bis(4-fluorobenzoyl)benzene (16.12 g, 0.050 mol) was added and the reaction mixture stirred at 130 - 140°C overnight under a nitrogen atmosphere. The mixture was allowed to cool and subsequently added to water to precipitate a solid which was collected by filtration and dried. Two recrystallizations from 1:1 toluene-ethanol afforded 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene as a tan solid (14.5 g, 58% yield), m.p. 161.5 - 164°C; IR (KBr) 3445, 3379 cm^{-1} (s, NH_2), 1639 cm-1 (vs, sharp, C=0); 'HNMR ($CDCl_3$) δ 3.60 (s, 4H, NH_2), 6.3 - 8.3 (m, 20H, aromatic). Anal. Calcd. for $C_{32}H_{24}N_2O_4$: C, 76.79%; H, 4.83%; N, 5.60%. Found: C, 76.62%; H, 5.11%; N, 5.28%.

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA)

This monomer was obtained commercially (Allco Chemical Co.) and was sublimed at 210°C under vacuum to yield a white crystalline solid, m.p. 224 - 226°C.

4,4'-Oxydianiline (ODA)

This monomer was obtained commercially (Aldrich Chemical Co.) and was sublimed at 175°C under vacuum to yield an off white solid, m.p. 190 - 192°C.

Polymers

The poly(arylene ethers) were prepared by nucleophilic aromatic substitution using a non-stoichiometric ratio of monomers, a slight excess of potassium carbonate and DMAc as solvent at 20 - 25% solids content. Water was removed by azeotropic distillation with toluene into a Dean-Stark trap, and the reaction was stirred at ~ 155°C overnight under a nitrogen atmosphere. Polymers are represented using the abbreviations of the monomers used in polymer preparation.

FBB/BPA

1,3-Bis(4-fluorobenzoyl)benzene (80.579 g, 0.2500 mol), 2,2-bis(4-hydroxyphenyl)propane (55.932 g, 0.2450 mol), and potassium carbonate (76 g, 0.55 mol) in DMAc (500 ml) and toluene (70 ml) were stirred in a nitrogen atmosphere. Water was removed by azeotropic distillation with toluene into a Dean-Stark trap. The reaction was heated to ~ 155°C during ~ 3 h and held at ~ 155°C for 16 h. The reaction was allowed to cool to ~ 80°C, filtered through a sintered glass funnel and neutralized with a 50:50 mixture of acetic acid/DMAc. The polymer solution was poured into water in a blender to precipitate the polymer which was washed successively with water and methanol and subsequently stirred in boiling methanol. Drying in air at 100°C for 4 h afforded an off-white polymer in > 95% yield (η_{inh} = 0.87 dL/g, $CHCl_3$ at 25°C; Tg = 156°C, DSC at 20°C/min).

FBB/BPF

1,3-Bis(4-fluorobenzoyl)benzene (209.51 g, 0.6500 mol), 9,9-bis(4-hydroxyphenyl)fluorene (222.99 g, 0.6363 mol), and potassium carbonate (191.6 g, 1.386 mol) in DMAc (1300 ml) and toluene (250 ml) were stirred under a Dean-Stark trap in a nitrogen atmosphere. Water was removed by azeotropic distillation with toluene into a Dean-Stark trap. The reaction was heated to ~ 155°C during ~ 3 h and held at ~ 155°C for 16 h. The reaction was allowed to cool to ~ 80°C, filtered through a sintered glass funnel and neutralized with a 50:50 mixture of acetic acid/DMAc. The polymer solution was poured into water in a blender to precipitate the polymer which was washed successively with water and methanol and subsequently stirred in boiling methanol. Drying in air at 100°C for 4 h afforded an off-white polymer in > 95% yield (η_{inh} = 0.68 dL/g, $CHCl_3$ at 25°C; Tg = 223°C, DSC at 20°C/min).

The poly(amic acids) were prepared at a concentration of 15% solids (w/w) by the slow addition of a stoichiometric amount of the dianhydride to a mechanically stirred solution of the diamine in DMAc under a nitrogen atmosphere at room temperature. Polymerization solutions were stirred overnight and inherent viscosities were subsequently determined. Polymers are represented using the abbreviations of the monomers used in polymer preparation.

ODA/BTDA

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (3.2223 g, 0.0100 mol) was added to a mechanically stirred solution of 4,4'-oxydianiline (2.0024 g, 0.0100 mol) in DMAc (32.8 g) under nitrogen. The reaction was stirred at room temperature (RT) overnight and the inherent viscosity subsequently determined (η_{inh} = 1.59 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 278°C, DSC at 20°C/min).

BABB/BTDA

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (1.6112 g, 0.0050 mol) was added to a mechanically stirred solution of 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (2.5028 g, 0.0050 mol) in DMAc (23.2 g) under nitrogen. The reaction, which became very viscous in < 10 min, was stirred overnight at RT and the inherent viscosity subsequently determined (η_{inh} = 1.32 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 222°C, Tm = 350°C, DSC at 20°C/min).

Blends

FBB/BPA//ODA/BTDA

A blend of high molecular weight polymers was prepared by dissolving 1.13 g of FBB/BPA (Tg = 156°C, η_{inh} = 0.87 dL/g, $CHCl_3$ at 25°C) in DMAc (7.4 g). A solution of 1.13 g of ODA/BTDA poly(amic acid) (η_{inh} = 1.59 dL/g, DMAc at 25°C) in DMAc (7.4 g) was then added to the previous solution with stirring at RT. The solution became cloudy immediately and was stirred overnight. A film was cast from a thoroughly mixed solution and cured 1 h each at 100, 200 and 300°C. The film displayed two distinct phases, an essentially clear non-continuous phase and a yellow continuous phase. The cured blend Tg was determined on a sample representative of both phases of the film (Tg = 155 and 278°C, DSC at 20°C/min).

FBB/BPA//BABB/BTDA

A blend of high molecular weight polymers was prepared by dissolving 1.3 g of FBB/BPA (Tg = 156°C, η_{inh} = 0.75 dL/g, $CHCl_3$ at 25°C) in DMAc (10.5 g). A solution of 1.3 g BABB/BTDA poly(amic acid) (η_{inh} = 0.69

dL/g, DMAc at 25°C) in DMAc (3.7 g) was then added to the previous solution with stirring at RT. Almost immediately a precipitate appeared which was later identified as the FBB/BPA polymer. A film was cast from a thoroughly mixed solution and cured 1 h each at 100, 200 and 300°C. The film displayed two distinct phases, one essentially clear non-continuous phase and the other an orange-yellow continuous phase. The cured blend Tg and Tm were determined on a sample representative of both phases of the film. (Tg = 155 and 220°C, Tm = 361°C, DSC at 20°C/min).

FBB/BPF//BABB/BTDA

A blend of high molecular weight polymers was prepared by dissolving 1.3 g of FBB/BPF (Tg = 223°C, η_{inh} = 0.95 dL/g, CHCl3 at 25°C) in DMAc (10.5 g). A solution of 1.3 g BABB/BTDA poly(amic acid) (η_{in}h = 0.69 dL/g, DMAc at 25°C) in DMAc (3.7 g) was then added to the previous solution with stirring at RT. A film was cast and cured 1 h each at 100, 200 and 300°C which displayed two distinct phases, one essentially clear non-continuous phase and the other an orange-yellow continuous phase. The cured blend Tg and Tm were determined (Tg = 223°C, Tm = 362°C, DSC at 20°C/min). If the polymer solution was left standing longer than ~ 1 week, a precipitate appeared which was later identified as the FBB/BPF polymer.

Oligomers

ATPAE (BPA) 3110

1,3-Bis(4-fluorobenzoyl)benzene (22.562 g, 0.0700 mol), 2,2-bis (4-hydroxyphenyl)propane (13.583 g, 0.0595 mol), 4-aminophenol (2.292 g, 0.0210 mol) and pulverized potassium carbonate (21.28 g, 0.154 mol) were dissolved in DMAc (115 ml) and toluene (40 ml) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer and a Dean-Stark trap. The reaction was heated to ~ 150°C during ~ 3 h and held at 150°C for 16 h. The reaction was allowed to cool to < 60°C and poured into water in a blender to form a tan precipitate. The precipitate was subsequently washed in water and washed in boiling water. Drying in air at 100°C afforded a light tan polymer in > 95% yield (η_{inh} = 0.16 dL/g, $CHCl_3$ at 25°C; Tg = 133°C, DSC at 20°C/min).

ATPAE (BPA) 6545

1,3-Bis(4-fluorobenzoyl)benzene (32.232 g, 0.1000 mol), 2,2-bis(4-hydroxyphenyl)propane (21.117 g, 0.0925 mol), 4-aminophenol (1.637 g, 0.0150 mol) and pulverized potassium carbonate (30.4 g, 0.22 mol) were dissolved in DMAc (150 ml) and toluene (40 ml) in a three-necked round bottom flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer and a Dean-Stark trap. The reaction was heated to ~ 155°C during ~ 3 h and held at 155°C for 16 h. The reaction was allowed to cool to < 60°C and poured into water in a blender to form a light tan precipitate. The precipitate was subsequently washed in water and washed in boiling water. Drying in air at 100°C afforded a light tan polymer in > 95% yield (η_{inh} = 0.29 dL/g, $CHCl_3$ at 25°C; Tg = 146°C, DSC at 20°C/min).

ATPAE (BPF) 3110

1,3-Bis(4-fluorobenzoyl)benzene (25.785 g, 0.0800 mol), 9,9-bis(4-hydroxyphenyl)fluorene (22.867 g, 0.06526 mol), 4-aminophenol (3.218 g, 0.02949 mol) and pulverized potassium carbonate (24.0 g, 0.176 mol) were dissolved in DMAc (150 ml) and toluene (40 ml) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer and a Dean-Stark trap. The reaction was heated to ~ 155°C during ~ 3 h and held at 155°C for 16 h. The reaction was poured into water in a blender to form a light tan precipitate. The precipitate was subsequently washed in water and washed in boiling water. Drying in air at 100°C afforded a light tan polymer in > 95% yield (η_{inh} = 0.16 dL/g, $CHCl_3$ at 25°C; η_{inh} = 0.18 dL/g, DMAc at 25°C; Tg = 193°C, DSC at 20°C/min).

ATPAE (BPF) 6545

1,3-Bis(4-fluorobenzoyl)benzene (25.785 g, 0.0800 mol), 9,9-bis(4-hydroxyphenyl)fluorene (25.244 g, 0.07206 mol), 4-aminophenol (1.7325 g, 0.01588 mol) and pulverized potassium carbonate (24.0 g, 0.176 mol) were dissolved in DMAc (150 ml) and toluene (45 ml) in a three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer and a Dean-Stark trap. The reaction was heated to ~ 155°C during ~ 3 h and held at 155°C for 16 h. The reaction was poured into water in a blender to form a light tan precipitate. The precipitate was subsequently washed in water and washed in boiling water. Drying in air at 100°C afforded a light tan polymer in > 95% yield (η_{inh} = 0.29 dL/g, $CHCl_3$ at 25°C; η_{inh} = 0.30 dL/g, DMAc at 25°C; Tg = 207°C, DSC at 25°C).

Polymerizations of ATPAE Oligomers

Amine-terminated poly(arylene ethers) were prepared at calculated number average molecular weights ($\overline{M}$ns) of 3110 and 6545 g/mole. As a verification that the actual $\overline{M}$n is essentially the same as the calculated $\overline{M}$n, the ATPAEs were reacted with a stoichiometric amount of BTDA, based on calculated $\overline{M}$ns. A significant increase in η_{inh} and Tg is an indication that the calculated $\overline{M}$ns are essentially correct.

ATPAE (BPA) 3110/BTDA

ATPAE (BPA) 3110 (6.220 g, 0.00200 mol) was dissolved in DMAc (28 g) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a nitrogen outlet. BTDA (0.6445 g, 0.00200 mol) was added all at once and the reaction was stirred for 6 h at RT to produce a clear, viscous, reddish-orange solution (η_{inh} = 0.79 dL/g DMAc at 20°C/min). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 165°C, DSC at 20°C/min).

ATPAE (BPA) 6545/BTDA

ATPAE (BPA) 6545 (6.5450 g, 0.00100 mol) was dissolved in DMAc (34 g) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a nitrogen outlet. BTDA (0.322 g, 0.00100 mol) was added all at once and the reaction was stirred for 6 h at RT to produce a clear, viscous, reddish-orange solution (η_{inh} = 1.10 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 162°C, DSC at 20°C/min).

ATPAE (BPF) 3110/BTDA

ATPAE (BPF) 3110 (3.110 g, 0.00100 mol) was dissolved in DMAc (22.8 g) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a nitrogen outlet. BTDA (0.3222 g, 0.00100 mol) was added all at once and the reaction gelled within ~ 5 min. After stirring overnight at RT and diluting with DMAc (3 g), the gell dissipated to form a clear, viscous, reddish-orange solution (η_{inh} = 1.16 dL/g, DMAc @ 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 226°C, DSC at 20°C/min).

ATPAE (BPF) 6545/BTDA

ATPAE (BPF) 6545 (3.2725 g, 0.00050 mol) was dissolved in DMAc (22.4 g) in a three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a nitrogen outlet. BTDA (0.1611 g, 0.00050 mol) was added all at once and the reaction was stirred for 6 h at RT to produce a clear, viscous, reddish-orange solution (η_{inh} = 1.40 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 227°C, DSC at 20°C/min).

Block Copolymers

Anhydride terminated polyamic acids were prepared at 15% solids in DMAc, NMP or m-cresol by adding BTDA to the amine solution stirred under nitrogen. Molecular weight was controlled by offsetting monomer stoichiometry in favor of the dianhydride. These reactions were stirred for 3 h to form clear, moderately viscous solutions. A solution of the appropriate ATPAE in the same solvent as the poly(amic) acid was then added and stirring under nitrogen was continued for 3 - 24 h depending on whether or not the polymer had gelled. On rare occasions, heating to ~ 70°C was required to dissipate this gel.

ATPAE (BPA) 3110//ODA/BTDA 3110

BTDA (2.2556 g, 0.00700 mol) was added to a solution of ODA (1.1844 g, 0.005915 mol) in DMAc (17.2 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 3110 (3.3744 g, 0.00109 mol) in DMAc (17.2 g) was added to the polyamic acid solution prepared above to form a cloudy, viscous solution which was stirred for 4 h at RT. Dilution with DMAc to 0.5% concentration produced a clear solution (η_{inh} = 0.46 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 168°C, DSC at 20°C/min).

ATPAE (BPA) 3110//ODA/BTDA 6545

BTDA (3.2223 g, 0.0100 mol) was added to a solution of ODA (1.8490 g, 0.009234 mol) in DMAc (25.4 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 3110 (2.3823 g, 0.000766 mol) in DMAc (11.9 g) was added to the polyamic acid solution prepared above to form a cloudy, viscous solution which was stirred for 4 h at RT. Dilution with DMAc to 0.5% concentration produced a clear solution (η_{inh} = 0.50 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 167 and 265°C, DSC at 20°C/min).

ATPAE (BPA) 6545//ODA/BTDA 3110

BTDA (1.6112 g, 0.00500 mol) was added to a solution of ODA (0.8460 g, 0.004225 mol) in DMAc (13.9 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 6545 (5.0724 g, 0.000775 mol) in DMAc (28.7 g) was added to the polyamic acid solution prepared above to form a cloudy, moderately viscous solution which was stirred for 4 h at RT. Dilution with DMAc to 0.5% concentration produced a clear solution (η_{inh} = 0.38 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 164°C, DSC at 20°C/min).

ATPAE (BPA) 6545//ODA/BTDA 6545

BTDA (2.2556 g, 0.00700 mol) was added to a solution of ODA (1.2943 g, 0.006464 mol) in DMAc (17.7 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 6545 (3.5094 g, 0.000536 mol) in DMAc (17.5 g) was added to the polyamic acid solution prepared above to form a cloudy, moderately viscous solution which was stirred for 4 h at RT. Dilution with DMAc to 0.5% concentration produced a clear solution (0.37 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 171 and 265°C, DSC at 20°C/min).

ATPAE (BPA) 6545//ODA/BTDA 6545

BTDA (2.2556 g, 0.00700 mol) was added to a solution of ODA (1.2943 g, 0.006464 mol) in DMAc (17.7 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 6545 (3.5499 g, 0.000542 mol) in DMAc (17.7 g) was added to the polyamic acid solution prepared above to form a cloudy, very viscous solution which was stirred for 4 h at RT. Dilution with DMAc to 0.5% concentration produced a clear solution (η_{inh} = 1.37 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 171 and 265°C, DSC at 20°C/min).

ATPAE (BPA) 6545 + [ODA + BTDA (6545)] segmented

BTDA (0.9667 g, 0.00300 mol) was added to a solution of ATPAE (BPA) 6545 (1.5214 g, 0.0002325 mol) and ODA (0.5547 g, 0.00277 mol) in DMAc (17.2 g). The mixture was stirred at RT under N_2 for 2 h to form a cloudy, viscous solution. Dilution with DMAc to 0.5% concentration produced a clear solution (0.97 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg was determined (Tg = 168 and 265°C, DSC at 20°C/min).

ATPAE (BPA) 3110//BABB/BTDA 3110

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.3315 g, 0.00266 mol) in DMAc (13.9 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPA) 3110 (2.4593 g, 0.000791 mol) in DMAc (13.9 g) was added to the polyamic acid solution prepared above and the reaction was stirred for 16 h at RT to produce a clear, reddish-orange solution (η_{inh} = 0.63 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 175°C, Tm = 354°C, DSC at 20°C/min).

ATPAE (BPA) 3110//BABB/BTDA 3110 (NMP)

BTDA (0.8700 g, 0.002700 mol) was added to a solution of BABB (1.0272 g, 0.002052 mol) in NMP (10.8 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 3110 (1.8972 g, 0.000610 mol) in NMP (10.8 g) was added to the polyamic acid solution prepared above and the reaction was stirred for 4 h at RT to produce a clear, reddish-orange solution (η_{inh} = 0.90 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 175°C, Tm = 338 and 352°C, DSC at 20°C/min).

ATPAE (BPA) 3110//BABB/BTDA 3110 (m-cresol)

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.3315 g, 0.00266 mol) in m-cresol (13.9 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPA) 3110 (2.4593 g, 0.000791 mol) in m-cresol was added to the polyamic acid solution prepared above and the reaction was stirred for 4 h at RT to produce a clear reddish solution (η_{inh} = 0.54 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 178°C, Tm = 335 and 352°C, DSC at 20°C/min).

ATPAE (BPA) 3110//BABB/BTDA 6545

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in DMAc (13.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 3110 (1.0887 g, 0.0003501 mol) in DMAc (6.2 g) was added to the polyamic acid solution prepared above and the reaction was stirred for 4 h at RT to produce a clear, reddish-orange solution (η_{inh} = 0.87 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 170°C, Tm = 354°C, DSC at 20°C/min).

ATPAE (BPA) 3110//BABB/BTDA 6545 (NMP)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in NMP (13.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 3110 (1.0887 g, 0.0003501 mol) in NMP (6.2 g) was added to the polyamic acid solution prepared above and the reaction was stirred for 4 h at RT to produce a very viscous, gel-like solution. Stirring an additional 20 h produced a viscous, clear, reddish-orange solution (η_{inh} = 1.73 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tm was determined (Tg = not detected, Tm = 358°C, DSC at 20°C/min).

ATPAE (BPA) 6545//BABB/BTDA 3110

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.3315 g, 0.00266 mol) in DMAc (13.9 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 6545 (5.1756 g, 0.000791 mol) in DMAc (29.3 g) was added to the polyamic acid solution prepared above and the reaction was stirred 4 h at RT to produce a cloudy, viscous solution. Dilution with DMAc to 0.5% concentration produced a clear solution (η_{inh} = 0.81 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 168°C, Tm = 353°C, DSC at 20°C/min).

ATPAE (BPA) 6545//BABB/BTDA 3110 (NMP)

BTDA (0.6445 g, 0.00200 mol) was added to a solution of BABB (0.7609 g, 0.00152 mol) in NMP (8.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 6545 (2.9577 g, 0.000452 mol) in NMP (16.8 g) was added to the poly(amic acid) solution prepared above and the reaction was stirred 4 h at RT to produce a clear, viscous solution (η_{inh} = 1.0 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 168°C, Tm = 335 and 352°C, DSC at 20°C/min).

ATPAE (BPA) 6545//BABB/BTDA 6545

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.5452 g, 0.003087 mol) in DMAc (15.2 g). The mixture was stirred at RT under N_2 for 2 h to form a clear solution. A solution of ATPAE (BPA) 6545 (2.6730 g, 0.0004084 mol) in DMAc (15.2 g) was added to the polyamic acid solution prepared above and the reaction formed a transparent gel within ~ 10 min. Stirring 16 h at RT produced a clear orange solution (η_{inh} = 0.89 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 165°C, Tm = 335 and 350°C, DSC at 20°C/min).

ATPAE (BPA) 6545//BABB/BTDA 6545 (NMP)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in NMP (13.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPA) 6545 (2.2912 g, 0.000350 mol) in NMP (13.0 g) was added to the polyamic acid solution prepared above and the reaction was stirred 4 h at RT to produce a clear orange, viscous solution (η_{inh} = 1.03 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 164 and 220°C, Tm = 343 and 355°C, DSC at 20°C/min).

ATPAE (BPA) 6545//BABB/BTDA 6545 (m-cresol)

BTDA (0.0667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in m-cresol (13.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPA) 6545 (2.2912 g, 0.000350 mol) in m-cresol (13.0 g) was added to the polyamic acid solution prepared above and the reaction was stirred 4 h at RT to form a clear reddish solution (η_{inh} = 0.63 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 168°C, Tm = 343 and 357°C, DSC at 25°C/min).

ATPAE (BPF) 3110//BABB/BTDA 3110

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.3315 g, 0.002660 mol) in DMAc (13.9 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (2.4593 g, 0.000791 mol) in DMAc (13.9 g) was added to the polyamic acid solution prepared above and the reaction was stirred 4 h at RT to form a clear reddish-orange solution (η_{inh} = 1.02 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 335 and 352°C, DSC at 20°C/min).

ATPAE (BPF) 3110//BABB/BTDA 3110 (NMP)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.1413 g, 0.002280 m) in NMP (12.0 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (2.108 g, 0.000678 mol) in NMP (12.0 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring 16 h at RT produced a clear orange solution (η_{inh} 0.82 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 227°C, Tm = 331 and 350°C, DSC at 20°C/min).

ATPAE (BPF) 3110//BABB/BTDA 3110 (m-cresol)

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.3315 g, 0.002660 mol) in m-cresol (13.9 g). The mixture was stirred at RT under N_2 for 5 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (2.4593, 0.00791 mol) in m-cresol (13.9 g) was added to the polyamic acid solution prepared above and the reaction was stirred 16 h at RT to form a clear reddish solution (η_{inh} = 0.61 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 332 and 360°C, DSC at 20°C/min).

ATPAE (BPF) 3110//BABB/BTDA 6545

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.5452 g, 0.003087 mol) in DMAc (15.2 g). The mixture was stirred at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (1.2701 g, 0.0004084 mol) in DMAc (7.2 g) was added to the polyamic acid solution prepared above and the reaction became cloudy immediately. Stirring 16 h at RT produced an essentially clear, viscous reddish-orange solution (η_{inh} = 1.08 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 337 and 352°C, DSC at 20°C/min).

ATPAE (BPF) 3110//BABB/BTDA 6545 (NMP)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in NMP (13.0 g). The mixture was stirred for at RT under N_2 for 2 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (1.0887 g, 0.0003501 mol) in NMP (6.2 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min.

Stirring at RT for 84 h produced a clear, viscous, reddish orange solution (η_{inh} = 0.75 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 227°C, Tm = 332 and 352°C, DSC at 20°C/min).

ATPAE (BPF) 3110//BABB/BTDA 6545 (m-cresol)

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.5453 g, 0.003087 mol) in m-cresol (15.2 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 3110 (1.2701 g, 0.0004084 mol) in m-cresol (7.2 g) was added to the polyamic acid solution prepared above and the reaction was stirred at RT to 18 h to produce a clear, viscous, reddish-orange solution (η_{inh} = 0.56 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 225°C, Tm = 330 and 350°C, DSC at 20°C/min).

ATPAE (BPF) 6545//BABB/BTDA 3110

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.1413 g, 0.00228 mol) in DMAc (12.0 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (4.4363 g, 0.0006778 mol) in DMAc (25.1 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring at 80°C for 6 h periods on consecutive days produced a clear reddish orange solution (η_{inh} = 0.47 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 227°C, Tm = 345°C, DSC at 20°C/min).

ATPAE (BPF) 6545//BABB/BTDA 3110 (NMP)

BTDA (0.6445 g, 0.00200 mol) was added to a solution of BABB (0.7608 g, 0.00152 mol) in NMP (7.7 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (2.9575 g, 0.000452 mol) in NMP (16.8 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring at RT for ~ 72 h produced a clear, viscous, reddish-orange solution (η_{inh} = 1.04 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 340 and 352°C, DSC at 20°C/min).

ATPAE (BPF) 6545//BABB/BTDA 3110 (m-cresol)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.1413 g, 0.00228 mol) in m-cresol (12.0 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (4.4363 g, 0.0006778 mol) in m-cresol (25.1 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring at 50°C for 0.5 h produced a clear, reddish-orange solution (η_{inh} = 0.61 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228, Tm = 338 and 370°C, DSC at 20°C min).

ATPAE (BPF) 6545//BABB/BTDA 6545

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in DMAc (13.0 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (2.2912 g, 0.000350 mol) in DMAc (13.0 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring at 105°C for 2 h produced a clear reddish-orange solution (η_{inh} = 0.35 dL/g, DMAc at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 353°C, DSC at 20°C/min).

ATPAE (BPF) 6545//BABB/BTDA 6545 (NMP)

BTDA (0.9667 g, 0.00300 mol) was added to a solution of BABB (1.3245 g, 0.002646 mol) in DMAc (13.0 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (2.2912 g, 0.000350 mol) in DMAc (13.0 g) was added to the polyamic acid solution prepared above and the reaction formed a gel within ~ 10 min. Stirring at 100°C for 4 h produced a clear, reddish-orange solution (η_{inh} = 0.96 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 228°C, Tm = 347 and 357°C, DSC at 20°C/min).

ATPAE (BPF) 6545//BABB/BTDA 6545 (m-cresol)

BTDA (1.1278 g, 0.003500 mol) was added to a solution of BABB (1.5452 g, 0.003087 mol) in m-cresol (15.2 g). The mixture was stirred at RT under N_2 for 3 h to form a clear orange solution. A solution of ATPAE (BPF) 6545 (2.6730 g, 0.000410 mol) in m-cresol (15.2 g) was added to the polyamic acid solution prepared above and the reaction was stirred at RT for 48 h to produce a clear, viscous, reddish-orange solution (η_{inh} = 0.72 dL/g, m-cresol at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C and the polyimide Tg and Tm were determined (Tg = 232°C, Tm =355°C, DSC at 20°C/min).

Controlled Molecular Weight Copolymers

PI/PAE/PI (3110)

A copolymer was prepared with the $\overline{M}n$ controlled to ~ 9300 g/mole by reacting a 2:1 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI block copolymer. Thus, BTDA (5.1557 g, 0.01600 mol) was added to a solution of BABB (6.0868 g, 0.01216 mol) in NMP (45.0 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPF) 3110 (5.6213 g, 0.00181 mol) in NMP (22.5 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2 h at RT (η_{inh} = 0.46 dL/g, NMP at 25°C). This solution was used to prepare scrim cloth for adhesive samples.

PI/PAE/PI (3110) SI

A copolymer was prepared with the $\overline{M}n$ controlled to ~ 9300 g/mole as before to produce a PI/PAE/PI block copolymer which was solution imidized (SI). Thus BTDA (5.1557 g, 0.01600 mol) was added to a solution of BABB (6.0868 g, 0.01216 mol) in DMAc (63.7 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPF) 3110 (5.6213 g, 0.001810 mol) in DMAc (31.9 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2 h at RT. The copolymer was then solution imidized by adding toluene (40 ml) then distilling a water/toluene azeotropic mixture from the reaction while heating to 155°C and holding at temperature for 16 h. The yellow precipitate which formed was washed with water, methanol and boiling methanol followed by drying in air at 100°C overnight. The copolymer Tg and Tm were determined on the powder (Tg = 220°C, Tm = 363°C, DSC at 20°C/min). This powder was used to make a molding to measure fracture toughness of the copolymer.

PAE/PI/PAE (3110)

A copolymer was prepared with the $\overline{M}n$ controlled to ~ 9300 g/mole by reacting a 2:1 ratio of ATPAE (BPF) 3110 with BABB/BTDA (3110) to produce a PAE/PI/PAE block copolymer. Thus, BTDA (2.5779 g, 0.00800 mol) was added to a solution of BABB (3.0434 g, 0.00608 mol) in NMP (22.5 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPF) 3110 (11.2426 g, 0.00362 mol) in NMP (45.0 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 3 h at RT (η_{inh} = 0.45 dL/g, NMP at 25°C). This solution was used to prepare scrim cloth for adhesive samples.

PAE/PI/PAE (3110) SI

A copolymer was prepared with the $\overline{M}n$ controlled to ~ 9300 g/mole as before to produce a PAE/PI/PAE block copolymer which was solution imidized (SI). Thus BTDA (2.5779 g, 0.00800 mol) was added to a solution of BABB (3.0434 g, 0.00608 mol) in NMP (31.9 g). The mixture was stirred at RT under N_2 for 3 h to form a clear solution. A solution of ATPAE (BPF) 3110 (11.2426 g, 0.00362 mol) in NMP (63.7 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2 h at RT. The copolymer was then solution imidized by adding toluene (35 ml) then distilling a water/toluene azeotropic mixture from the reaction while heating to 155°C and holding at temperature for 16 h. The yellow gelled copolymer was transferred to water in a blender to form a yellow solid. The yellow powder was washed in methanol and boiling methanol followed by drying in air at 100°C overnight. The copolymer Tg and Tm were determined on the powder (Tg = 225°C, Tm = 342°C, DSC at 20°C/min). This powder was used to make a molding to measure fracture toughness of the copolymer.

End-Capped Copolymers

ϕ-PI/PAE/PI-ϕ (3110) SI

A copolymer was prepared with the $\overline{M}$n controlled to ~ 9300 g/mole by reacting a 2:1 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI block copolymer which was then end-capped with aniline. Thus, BTDA (3.8668 g, 0.01200 mol) was added to a solution of BABB (4.5651, 0.009120 mol) in NMP (33.7 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (4.2160 g, 0.001356 m) in NMP (16.9 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.2525 g, 0.002711 mol) in NMP (1.01 g) was added and stirring continued for 2 h. The end-capped copolymer was then solution imidized by adding toluene (35 ml) then distilling a water/toluene azeotropic mixture from the reaction while heating to 155°C and holding at temperature for 16 h. The yellow precipitate which formed was washed in water, methanol and boiling methanol followed by drying in air at 100°C overnight. The Tg and Tm were determine on the powder (Tg = 227°C, Tm = 382°C, DSC at 20°C/min).

ϕ-PI/PAE/PI-ϕ (3110)

A copolymer was prepared with the $\overline{M}$n controlled to ~ 9300 g/mole by reacting a 2:1 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI block copolymer which was end-capped with aniline. Thus, BTDA (3.8668 g, 0.01200 mol) was added to a solution of BABB (4.5651 g, 0.009120 mol) in NMP (33.7 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (4.2160 g, 0.001356 mol) in NMP (16.9 g) was added to the poly(amic acid) prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.2525 g, 0.002711 mol) in NMP (1.01 g) was added an stirring continued for 2 h to form a clear reddish-orange solution (η_{inh} = 0.47 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C. The resulting film was brittle and cracked upon removal from the glass plate. The polymer Tg and Tm were determined on the film sample (Tg = 227°C, Tm = 382°C, DSC at 20°C/min).

ϕ-PI/PAE/PI/PAE/PI-ϕ (3110)

A copolymer was prepared with $\overline{M}n$ controlled to ~ 15,500 g/mole by reacting a 3:2 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI/PAE/PI block copolymer which was then end-capped with aniline. Thus, BTDA (3.2223 g, 0.0100 mol) was added to a solution of BABB (3.8042 g, 0.00760 mol) in NMP (28.1 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (4.6843 g, 0.001506 mol) in NMP (18.7 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.1402 g, 0.001506 mol) in NMP (0.56 g) was added and stirring continued for 2 h to form a clear reddish-orange solution (η_{inh} = 0.54 dL/g, NMP at 25°C). A polymer film was cast and cured 1 h each at 100, 200 and 300°C. The resulting film was brittle and the polymer Tg and Tm were determined (Tg = 223°C, Tm = 370°C, DSC at 20°C/min).

ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) SI

A copolymer was prepared with $\overline{M}n$ controlled to ~ 15,500 g/mole by reacting a 3:2 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI/PAE/PI block copolymer which was then end-capped with aniline.

Thus, BTDA (3.2223 g, 0.0100 mol) was added to a solution of BABB (3.8042 g, 0.00760 mol) in NMP (28.1 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (4.6843 g, 0.001506 mol) in NMP (18.7 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.1402 g, 0.001506 mol) in NMP (0.56 g) was added and stirring continued for 2h. The end-capped copolymer was then solution imidized by adding toluene (40 ml) then distilling a water/toluene azeotropic mixture from the reaction while heating to 155°C and holding at temperature for 16 h. The yellow precipitate which formed was washed in water, methanol and boiling methanol followed by drying in air at 100°C overnight. The polymer Tg and Tm were determined on the powder (Tg = 225°C, Tm = 377°C, DSC at 20°C/min). This powder was used to make a molding to measure fracture toughness of the copolymer.

ϕ-PI/PAE/PI/PAE/PI-ϕ (3110)

A copolymer was prepared with $\overline{M}n$ controlled to ~ 15,500 g/mole by reacting a 3:2 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI/PAE/PI block copolymer which was then end-capped with aniline. Thus, BTDA (9.6669 g, 0.0300 mol) was added to a solution of BABB (11.4127 g, 0.0228 mol) in NMP (84.3 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (14.0529 g, 0.004519 mol) in NMP (56.1 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.4208 g, 0.004519 mol) in NMP (1.7 g) was added and stirring continued for 2 h to form a clear reddish-orange solution (η_{inh} = 0.58 dL/g, NMP at 25°C). This solution was used to prepare graphite prepreg.

ϕ-PI/PAE/PI/PAE/PI-ϕ (3110)

Another batch of the previous copolymer was prepared with $\overline{M}n$ controlled to ~ 15,500 g/mole by reacting a 3:2 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI/PAE/PI block copolymer which was then end-capped with aniline. Thus, BTDA (12.889 g, 0.0400 mol) was added to a solution of BABB (15.217 g, 0.0304 mol) in NMP (112.4 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (18.7373 g, 0.006025 mol) in NMP (75.0 g) was added to the poly(amic acid) prepared above to form a clear solution which was stirred for 2.5 h at RT. Afterwards, aniline (0.5611 g, 0.006025 mol) in NMP (2.25 g) was added and stirring continued for 2 h to form a clear reddish-orange solution (η_{inh} = 0.56 dL/g, NMP at 25°C).

ϕ-PI/PAE/PI/PAE/PI-ϕ (3110)

Another batch of the previous copolymer was prepared at a higher concentration (30% solids vs 20% solids) with $\overline{M}n$ controlled to ~ 15,500 g/mole by reacting a 3:2 ratio of BABB/BTDA (3110) with ATPAE (BPF) 3110 to produce a PI/PAE/PI/PAE/PI block copolymer which was then end-capped with aniline. Thus, BTDA (12.8894 g, 0.0400 mol) was added to a solution of BABB (15.217 g, 0.0304 mol) in NMP (65.6 g). The mixture was stirred at RT under N_2 for 2.5 h to form a clear solution. A solution of ATPAE (BPF) 3110 (18.7373 g, 0.006025 mol) in NMP (43.7 g) was added to the poly(amic acid) solution prepared above to form a clear solution which was stirred for 2.5 at RT. Afterwards, aniline (0.5611 g, 0.006025 mol) in NMP (1.3 g) was added and stirring continued for 2 h to form a clear reddish-orange solution. Solution viscosity (NMP at 25°C) was measured on four consecutive days of continued stirring and was found to be 0.87 dL/g, 0.77 dLg, 0.68 dL/g and 0.66 dL/g, respectively.

Combined Solution

Due to previous results from prepreg preparation, it was determined that a prepreg solution of 25% solids content would provide the required amount of resin (~ 38% by weight) on subsequent prepreg following experimental conditions used previously. Therefore, the two solutions discussed above (one at 20% solids content and the other at 30% solids content) were combined to form the solution used to prepare the necessary prepreg for composite preparation.

RESULTS AND DISCUSSION

Imide/arylene ether block copolymers were prepared and characterized. The molecular weight of the blocks studied were 3110 and 6545 g/mole for both the polyimide and poly(arylene ether) blocks. In order to prepare these block copolymers, several monomers were synthesized and purified. Afterward, homopolymers were prepared which were high molecular weight polymers of the same structure as the lower molecular weight blocks used for copolymer synthesis. Two structurally different amine-terminated poly(arylene ethers) (ATPAE) were prepared at two different molecular weights to provide four different ATPAEs. Three different copolymer combinations were studied. The first combination studied was an ODA/BTDA polyimide block and a FBB/BPA poly(arylene ether) block. The second combination studied was a BABB/BTDA polyimide block and a FBB/BPA poly(arylene ether) block. The third combination studied was a BABB/BTDA polyimide block and a FBB/BPF poly(arylene ether) block. The structures for these polymers are shown in Figure 4. The following discussion will be organized such that the monomers, homopolymers and ATPAEs will be discussed first. Then the block copolymer combinations will be addressed in the order listed above. Therefore, the discussion will contain the synthesis, characterization and properties for the first block copolymer combination before the next copolymer combination is addressed, and so forth. Finally, one block copolymer was end-capped at a controlled molecular weight to enhance processability. A significant quantity of this material was prepared, characterized and used to prepare adhesives and composites for mechanical testing. A discussion of this work will follow the previous sections.

Monomers

Synthesis of the 1,3-bis(4-fluorobenzoyl)benzene was accomplished by a typical Friedel-Crafts acylation reaction. The reaction proceeded smoothly and in very high yields, with a crude product yield > 90%. One recrystallization from toluene provided polymer grade monomer. Synthesis of the 9,9-bis(4-hydroxyphenyl)fluorene was more difficult and time consuming. The reaction mixture became very viscous and difficult to stir, which interfered with the bubbling of the hydrogen chloride gas. Steam distillation required several days to remove all residual fluorobenzene and the crude product yield was ~ 60%. Two recrystallizations from toluene were required to provide polymer grade monomer. Synthesis of 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene was accomplished by first preparing the potassium salt of 4-aminophenol, which was then reacted with 1,3-bis(4-fluorobenzoyl)benzene. The reaction was maintained at 130-140°C overnight under a nitrogen atmosphere to provide a high yield (> 95%) of crude product. However, two recrystallizations from 1:1 toluene-ethanol, which reduced the yield significantly, were necessary to provide polymer grade monomers. The remaining monomers were obtained commercially and either recrystallized or sublimed to provide polymer grade monomers.

Polymers and Blends

The poly(arylene ether) (PAE) homopolymers were prepared by nucleophilic aromatic substitution using a slight offset in stoichiometry favoring the activated difluoro compound, a slight excess of potassium carbonate and DMAc as solvent at 20-25% solids content. The offset in stoichiometry leads to fluoro-terminated polymers, which are more thermally stable than hydroxy-terminated PAEs. Completely anhydrous conditions are necessary to produce high molecular weight polymer so toluene is used to form an azeotropic mixture to remove any water present. Using the conditions described previously, high molecular weight PAEs were readily prepared in excellent yield.

The poly(amic acid) homopolymers were prepared by nucleophilic aromatic substitution using a stoichiometric ratio of monomers at 15% solids (w/w) under a nitrogen atmosphere. The dianhydride solid was added to a mechanically stirred solution of the diamine in DMAc. Reaction mixtures were stirred overnight and inherent viscosities were subsequently determined. The poly(amic acids) were thermally imidized to polyimides (PI) by casting a solution on glass, drying to a tack free form in a dust proof chamber and curing 1 h each at 100, 200 and 300°C in a circulating air oven. This is a standard cure used by many to produce films which are considered fully imidized.

Properties for the homopolymers are shown in Table 15. Inherent viscosities of the PAEs were high, but viscosities over 1.0 dL/g can be reached when a stoichiometric ratio of monomers is used. The poly(amic acids) had very high viscosities indicating very high molecular weight. For preparing films, very high viscosities are not a disadvantage, as would be the case in the preparation of test specimens for moldings or adhesives. However, once a certain molecular weight and therefore viscosity is reached, film properties remain relatively constant. The viscosity at which film properties become constant is probably between 0.6 and 0.8 dL/g for these homopolymers. If the films are to be oriented, higher viscosities are desirable. The FBB/BPA polymer has the lowest Tg of 156°C and is therefore the most flexible. The FBB/BPF and the BABB/BTDA polymers have essentially the same Tg (222-223°C) but the latter polymer is semi-crystalline with a Tm of

Table 15

Characterization of Polymers and Blends

Polymer or Blend	η_{inh}, (dL/g)	T_g,[a] (°C)	T_m,[a] (°C)
FBB/BPA	0.87[b]	156	--
FBB/BPF	0.68[b]	223	--
ODA/BTDA	1.59[c]	278	--
BABB/BTDA	1.32[c]	222	350
FBB/BPA//ODA/BTDA 1:1 Blend	—	155, 273	--
FBB/BPA//BABB/BTDA 1:1 Blend	—	155, 223	361
FBB/BPF//BABB/BTDA 1:1 Blend	—	223	362

a) Measured by DSC at a heating rate of 20°C/min

b) Measured in $CHCl_3$ at 25°C and 0.5% concentration

c) Measured in DMAc at 25°C and 0.5% concentration

350°C. The ODA/BTDA has the highest Tg (278°C) and is amorphous like the PAEs.

Polymer blends were prepared by mixing equal amounts and concentrations of poly(amic acid) solutions with PAE solutions. No inherent viscosities for these blends are shown in Table 15 because the solutions became cloudy due to the incompatibility of the polymers. Measuring the solution viscosities was attempted but results were inconsistent and erratic and, therefore, are not reported. A 1:1 blend of FBB/BPA//BABB/BTDA displayed two Tgs corresponding to the Tgs of the homopolymers, with only a 5°C reduction in the Tg of the polyimide and no change in the Tg of the PAE. The presence of two Tgs at essentially the same temperatures as the homopolymers indicates a high degree of incompatibility. Completely compatible blends are rare but do display single phase morphology with properties representing a weighted average of the two homopolymers. Therefore, a 1:1 completely compatible blend would display a Tg at the average of the two homopolymer Tgs. The FBB/BPA//BABB/BTDA blend also displays two Tgs, as well as a Tm, indicating that these polymers are also incompatible in the solid state. The final blend in Table 15 displays only one Tg but this should not be taken to mean that the FBB/BPF and the BABB/BTDA are compatible. These homopolymers have essentially equivalent Tgs (222 and 223°C) so conclusions concerning compatibility should not be drawn from this data alone. Examination of a film prepared from this blend shows the presence of two phase morphology, indicating that these polymers also are incompatible. This blend also is semi-crystalline with a Tm of 362°C.

Film properties for the polymers and blends are shown in Table 16. Films were tested for tensile strength, tensile modulus and elongation at room temperature, 93°C and 177°C. The two elevated temperatures were chosen due to requirements for potential applications. The 93°C test, which is 200°F, is performed because this is the upper use temperature for commercial aircraft structural applications such as wings, rudders, fuselage and surface skins. The 177°C test, which is 350°F, is performed because this is the upper use temperature for some military aircraft structural applications.

Properties of the PAEs are shown in the first two rows of Table 16. The FBB/BPA polymer was not tested at 177°C since this is above the polymer Tg (156°C). Both PAEs have RT tensile strength of ~ 13 Ksi and modulus of ~ 380 Ksi. However, the FBB/BPA polymer has an extremely high elongation while the FBB/BPF polymer has relatively low elongation. One must realize that elongation is more sensitive to flaws in the film, such as dust or edge effects, than strength or modulus. Subsequent tests on different films of FBB/BPF gave similar results. At 93°C, the PAEs retained 60% and 75% of their strength and over 90% of their modulus. The FBB/BPF polymer retained only 40% of its strength but 80% of its modulus at 177°C. The PIs have excellent tensile strength and modulus with the BABB/BTDA being significantly better than the PAEs. The BABB/BTDA was not tested at 93°C but expected to have a very high retention of properties at that temperature. This polymer retains 70% of its strength and 86% of its modulus at 177°C, which is excellent for a linear polymer. At least some of this excellent retention of properties can be attributed to the crystallinity present in the polymer. The ODA/BTDA which is amorphous but has a higher Tg (278°C vs 223°C) retains only 49% and 55% of its strength and modulus, respectively, at 177°C. Film properties for two of the polymer blends are shown in Table 16. Each of these films had a textured, orange peel surface due to the phase separation that occurred but the films were tested anyway. The third blend

Table 16

Film Properties of Polymers and Blends

Polymer or Blend	Tensile Strength, Ksi (Modulus, Ksi) [Elongation, %] RT	93°C	177°C
FBB/BPA	12.7 (381) [136]	7.6 (340) [124]	—
FBB/BPF	13.5 (378) [4.6]	10.0 (349) [3.5]	5.5 (304) [2.5]
ODA/BTDA	19.5 (526) [14.6]	15.7 (393) [24.4]	9.6 (290) [18.2]
BABB/BTDA	22.0 (630) [8.3]	—	15.2 (540) [21]
FBB/BPA//ODA/BTDA[a] 1:1 Blend	9.1 (289) [0.5]	5.9 (200) [9.0]	—
FBB/BPA//BABB/BTDA[b] 1:1 Blend	--	—	—
FBB/BPF//BABB/BTDA[a] 1:1 Blend	9.4 (203) [7.0]	7.6 (275) [9.5]	4.2 (259) [29.9]

a) Textured, orange peel surface, two phase morphology

b) Gross phase separation, discontinuous phase thicker produced a film with gross phase separation, with the discontinuous phase significantly thicker than the continuous phase. Because of this morphology and the difficulties associated with measuring film thickness, which is necessary to calculate film properties, this blend was not tested. Due to the two phase morphology, which probably has poor interphase adhesion, the film properties for these blends were poor. This result is expected for blends of incompatible polymers.

The fracture toughness, K_{Ic}, of three of the homopolymers was measured and is shown in Table 17. The ODA/BTDA polymer, which is difficult to process into a molding, was not tested. However, the fracture toughness of this polymer is expected to be low (< 500 Psi $\cdot\sqrt{\text{in}}$, based on other amorphous, linear polyimides). Also shown in Table 17 is fracture energy, G_{Ic}, which is calculated using K_{Ic} and modulus by the equation given under Table 17. The FBB/BTDA polymer is extremely tough with a G_{Ic} of 67 in-lbs/in^2. The fracture energy of FBB/BPF (15 in-lbs/in^2) is more typical of commercial amorphous PAEs which normally have fracture energies between 10 and 20 in-lbs/in^2. The BABB/BTDA polyimide is also an extremely tough polymer displaying one of the highest reported fracture energies, 38 in-lbs/in^2, for polyimides. The failed fracture surfaces of the compact tension specimen for both the FBB/BPA and BABB/BTDA polymers were very rough and highly crazed, indicative of a fracture mechanism that absorbs energy by distributing it over a large surface area with yielding in contrast to stable crack growth characteristic of brittle materials.

Adhesive properties on titanium to titanium (Ti/Ti) tensile shear specimens are shown in Table 18. Once again the ODA/BTDA polymer was not tested since fabrication into good samples is difficult. The PAEs were not tested at the higher temperatures due to their lower Tgs. The BABB/BTDA

Table 17

Fracture Toughness and Energy of Polymers

Polymer	Fracture Toughness K_{Ic}, psi · $\sqrt{in}$	Fracture Energy G_{Ic}, in-lbs/in^2
FBB/BPA	5070	67
FBB/BPF	2400	15
ODA/BTDA	a	a
BABB/BTDA	4890	38

a) Not measured

$$G_{Ic} = \frac{(K_{Ic})^2}{\text{Modulus}}$$

Table 18

Adhesive Properties of Polymers[a]

Polymer	Tensile Shear Strength, Psi (Failure Mode[b])				
	RT	93°C	150°C	177°C	232°C
FBB/BPA	5300 (Coh)	3900 (Coh)	—	—	—
FBB/BPF	5450 (Coh)	4550 (Coh)	3500 (Coh)	—	—
ODA/BTDA[c]	—	—	—	—	—
BABB/BTDA	6250 (Coh)	—	—	4510 (Coh)	590 (Ad) [3670 (Coh)][d]

a) Ti/Ti tensile shear strength

b) Coh = cohesive failure, Ad = adhesive failure

c) Difficult to process, not tested

d) After annealing 100 hr at 316°C

had excellent RT tensile shear strength of 6250 psi while both the PAEs were very good (> 5000 psi). The FBB/BPF polymer maintains very good strength up to 150°C while the BABB/BTDA polyimide has excellent strength up to 232°C after annealing 100 h at 316°C. These properties will be used for comparison with similar properties for the block copolymers discussed later.

The homopolymers were subjected to thermogravimetric analysis (TGA) at 2.5°C/min in both air and nitrogen flowing at 15 ml/min. The temperature at 5% weight loss in air and nitrogen for both polyimides was 490°C and ~ 520°C, respectively as shown in Table 19. The temperatures at 5% weight loss in air for the FBB/BPA and FBB/BPF were 475°C and 480°C, respectively while the same data for nitrogen atmosphere was 475°C and 525°C. Each of these materials has sufficient thermal stability for long term use at 177°C and for shorter periods at 232°C.

Amine Terminated Poly(Arylene Ethers)

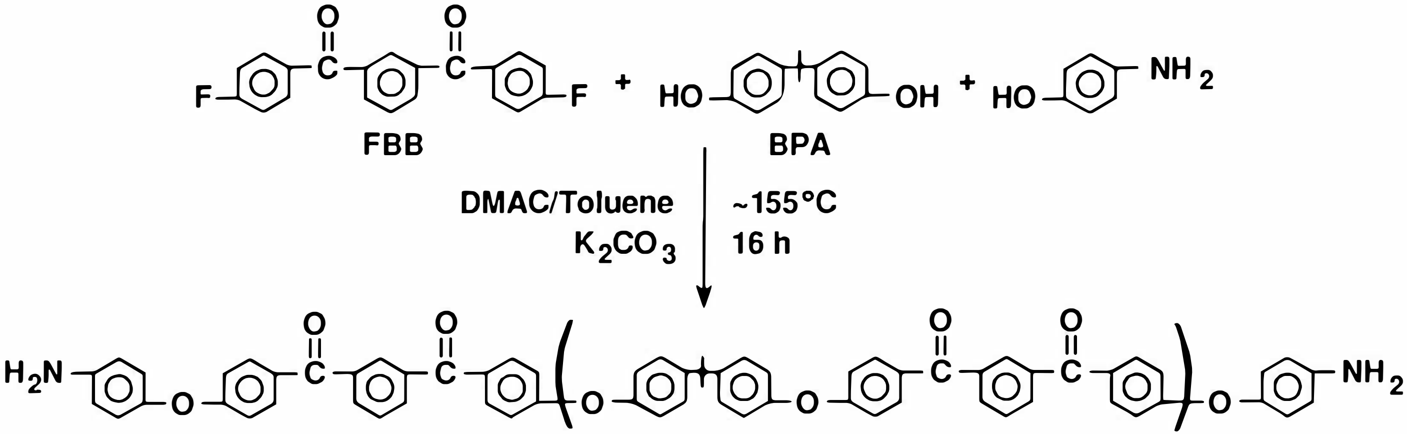
The amine-terminated poly(arylene ethers) (ATPAE) were prepared by adding FBB, the appropriate bisphenol, 4-aminophenol, potassium carbonate, toluene and DMAc to a three-neck flask equipped with a thermometer, nitrogen inlet, Dean-Stark trap and a condenser and heating to 155°C and holding 16 h. Precipitation in a blender followed by washing to remove salts and solvent provided the ATPAEs as light tan solids. The ATPAEs, prepared with either BPA or BPF, where synthesized with calculated number average molecular weights ($\overline{M}n$) of 3110 and 6545 g/mole as shown in Figures 14 and 15. Assuming the extent of reaction, P, is 1 or complete reaction is achieved, the modified Carothers equation discussed earlier reduces to $Dp = 1 + r/1 - r$, where Dp is degree of polymerization and r is monomer ratio. To find the desired Dp, the desired $\overline{M}n$ is divided by one-half

Table 19

Thermogravimetric Analysis of Polymers

Polymer	Temperature,[a] °C at 5% Weight Loss Air	N$_2$
FBB/BPA	475	475
FBB/BPF	480	535
ODA/BTDA	490	520
BABB/BTDA	490	525

[a] Heating rate of 2.5°C/min



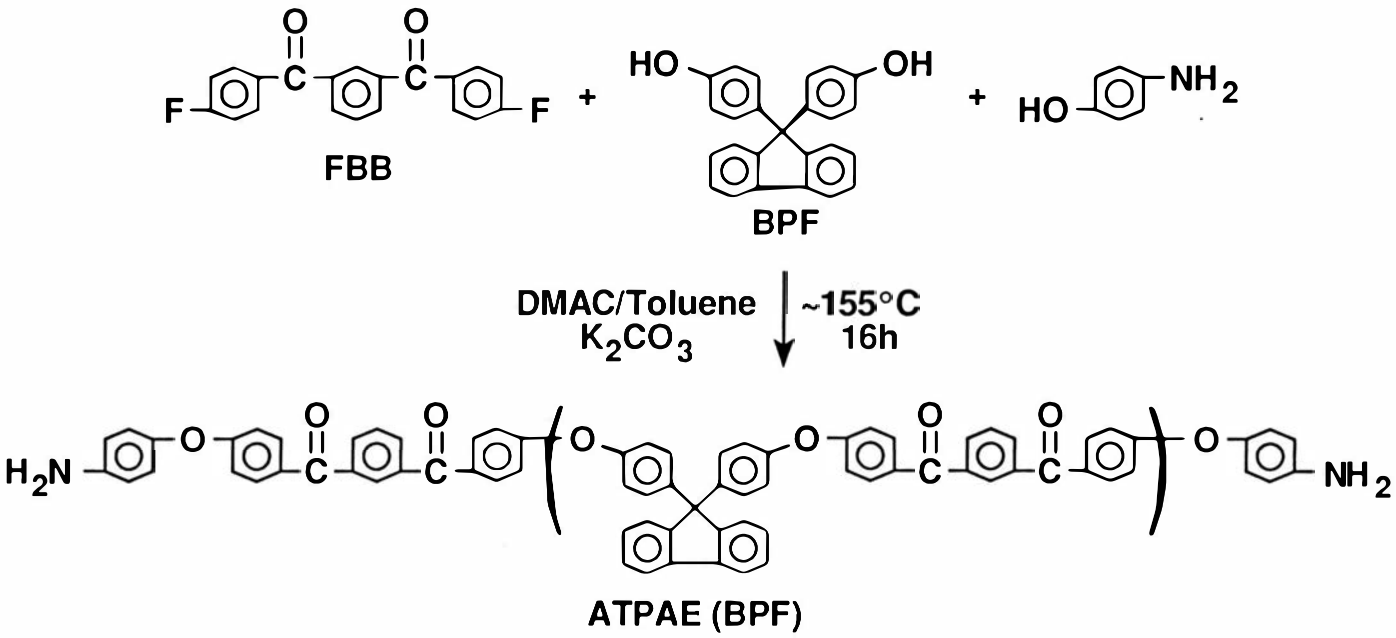
ATPAE (BPA)

$\overline{M}_n$ = 3110 g/mole and $\overline{M}_n$ = 6545 g/mole

r = 0.850 r = 0.925

r = ratio of BPA to FBB

Figure 14. Synthesis of BPA based amine-terminated poly (arylene ether) oligomers.



$\overline{M}_n$ = 3110 g/mole and $\overline{M}_n$ = 6545 g/mole
r = 0.816 r = 0.908
r = ratio of BPF to FBB

Figure 15. Synthesis of BPF based amine-terminated poly (arylene ether) oligomers.

of the repeat unit molecular weight. For the BPA based polymer, the repeat unit molecular weight is 510 g/mole, so 255 is used in the calculation. For the BPF based polymer, the repeat unit molecular weight is 632 g/mole, so 316 is used in the calculation. Two examples of calculating the r values used to prepare desired molecular weights as well as the other r values used to prepare the ATPAEs are shown in Figure 16. The molecular weights used were selected somewhat arbitrarily but several considerations were made. Since the homopolymers were known to be incompatible, block length too long would produce copolymers that "act like" blends. However, since the repeat unit molecular weights for these polymers is rather high (510 and 632 g/mole), block lengths must be large enough that the copolymers don't "act like" random copolymers. Following this line of reasoning, 3110 g/mole was selected to give blocks of ~ 5-6 repeat units and 6545 was selected to give blocks of ~ 10-12 repeat units on average. It was believed that these block lengths would be long enough to display properties different from either high molecular weight blends or random copolymers.

Data for BPA based ATPAEs are shown in Table 20. As expected, the lower molecular weight oligomer had lower viscosity as well as a lower Tg. Viscosities were measured in $CHCl_3$ and Tgs were measured by DSC at 20°C/min. The last column shows experimental $\overline{M}n$ measured by potentiometric titration of the aromatic amine with 0.02 M HBr in glacial acetic acid. The equation used to calculate $\overline{M}n$ is shown below

$$\overline{M}n = \frac{\text{weight polymer (g)}}{\text{molarity HBr (mol/L) x amount titrant (L) X 2 NH}_2\text{/chain}}$$

To prepare ATPAE (BPA) 3110,

$D_p = 3110 \div 255 = 12.19$

$D_p = \frac{1+r}{1-r} \quad 12.19 = \frac{1+r}{1-r} \quad \therefore r = 0.848$

To prepare ATPAE (BPA) 6545, r = 0.925
To prepare ATPAE (BPF) 3110,

$D_p = 3110 \div 316 = 9.84$

$D_p = \frac{1+r}{1-r} \quad 9.84 = \frac{1+r}{1-r} \quad \therefore r = 0.816$

To prepare ATPAE (BPA) 6545, r = 0.908

Figure 16. Calculation of desired monomer stoichiometry.

Table 20

Characterization of BPA Based Oligomers and Polymers

Oligomer or Polymer	η_{inh}, dL/g	DSC T_g, °C[c]	$\overline{M}_n$, g/mole
ATPAE (BPA) 3110	0.16[a]	133	3600
ATPAE (BPA) 6545	0.29[a]	146	7300
ATPAE (BPA) 3110 + BTDA	0.79[b]	165	--
ATPAE (BPA) 6545 + BTDA	1.1[b]	162	--

a) Measured in $CHCl_3$ at 25°C and 0.5% concentration

b) Measured in DMAc at 25°C and 0.5% concentration

c) Measured a a heating rate of 20°C/min after heating to 300°C

The experimental $\overline{M}$ns are 10-15% higher than the calculated $\overline{M}$ns. As a method used to confirm calculated molecular weights, the ATPAEs were reacted with a stoichiometric amount of BTDA, based on the calculated $\overline{M}$ns of the ATPAEs. The inherent viscosities shown in the table are high, confirming that the calculated $\overline{M}$ns are essentially correct. Since the experimental $\overline{M}$ns were determined late in the study and the calculated $\overline{M}$ns were providing good results, the calculated $\overline{M}$ns were used for stoichiometry calculations in all the reactions in the project. As a test of the experimental $\overline{M}$n, a reaction of ATPAE (BPA) 3110 and BTDA was done where the stoichiometry was based on a $\overline{M}$n of 3600 g/mole. This reaction provided a polymer with η_{inh} = 1.1 dL/g (an increase from 0.79 dL/g), indicating that the experimental $\overline{M}$n for the ATPAE is more correct than the calculated $\overline{M}$n. This difference, however, would probably not significantly change polymer properties, such as tensile strength, modulus and elongation.

Data for ATPAE (BPF) oligomers are shown in Table 21. As expected, the lower molecular weight oligomer had lower viscosity as well as a lower Tg. The viscosities were measured in DMAc and Tgs were measured by DSC at 20°C/min. The last column shows experimental $\overline{M}$n measured by potentiometric titration of the aromatic amine as previously discussed. These experimental $\overline{M}$ns are 15% and 3% higher than the calculated $\overline{M}$n for the 3110 and 6545 ATPAE oligomers, respectively. As a method used to confirm calculated molecular weights, the ATPAEs were reacted with a stoichiometric amount of BTDA, based on the calculated $\overline{M}$ns of the ATPAEs. As shown in Table 21, very high viscosities were obtained, confirming that the calculated $\overline{M}$ns are essentially correct. Since experimental $\overline{M}$ns were determined late in the study and the calculated $\overline{M}$ns were providing good results, the calculated $\overline{M}$ns were used for stoichiometry calculations in all the reactions in the project.

Table 21

Characterization of BPF Based Oligomers and Polymers

Oligomer or Polymer	η_{inh}, dL/g[a]	DSC T_g, °C[b]	$\overline{M}_n$, g/mole
ATPAE (BPF) 3110	0.18	193	3500
ATPAE (BPF) 6545	0.30	207	6700
ATPAE (BPF) 3110 + BTDA	1.16	226	--
ATPAE (BPF) 6545 + BTDA	1.40	227	--

a) Measured in DMAc at 25°C and 0.5% concentration

b) Measured at a heating rate of 20°C/min after heating to 300°C

The Tgs are shown for these two polymers and are essentially the same (226-227°C). This Tg is slightly higher than for the PAE homopolymer which has a Tg of 223°C. This slight increase in Tg is probably due to the small amount of imide present in these two polymers.

Films were prepared and properties were measured at RT, 93°C and 177°C for the ATPAEs polymerized with BTDA. Data for tensile strength, modulus and elongation are shown in Table 22. The first two polymers listed in the table are based on BPA and have essentially identical properties at RT and 93°C. However, the ATPAE (BPA) 6545/BTDA polymer has very high elongation with no strength or modulus at 177°C. The ATPAE (BPA) 3110/BTDA, which has a higher imide content, has low but measurable strength and modulus and an elongation of 80%. Data for the BPF based polymers are shown in the last two rows of the table. There are slight differences in properties between the two BPF based polymers but the most important data in Table 22 is the retention of properties at 177°C for BPF based polymers. These polymers retain over 50% of their strength and 80% of their modulus because of their higher Tgs (226°C vs 165°C) than the BPA based polymers.

Block Copolymers

ATPAE (BPA)//ODA/BTDA Copolymers

Four different block copolymers were prepared using ATPAE based on BPA and ODA/BTDA each with blocks of 3110 and 6545 g/mole for calculated $\overline{M}$ns. As shown in Table 23, the copolymers were prepared with the same molecular weight blocks as well as with different molecular weight blocks. The first and last copolymers listed in the table have equal length blocks and therefore have an equal amount of imide and arylene ether

Table 22

Film Properties of BTDA Extended ATPAEs

Polymer	Tensile Strength, Ksi (Modulus, Ksi) [Elongation, %]		
	RT	93°C	177°C
ATPAE (BPA) 3110/BTDA	10.9 (367) [4.0]	9.1 (333) [3.3]	1.2 (124) [80]
ATPAE (BPA) 6545/BTDA	11.1 (367) [5.7]	8.5 (329) [5.2]	– — [> 100]
ATPAE (BPF) 3110/BTDA	10.3 (413) [3.3]	10.2 (352) [3.5]	6.8 (374) [3.0]
ATPAE (BPF) 6545/BTDA	11.9 (400) [3.8]	11.2 (378) [3.7]	6.2 (321) [3.4]

Table 23

Characterization of ATPAE (BPA)//ODA/BTDA Copolymers

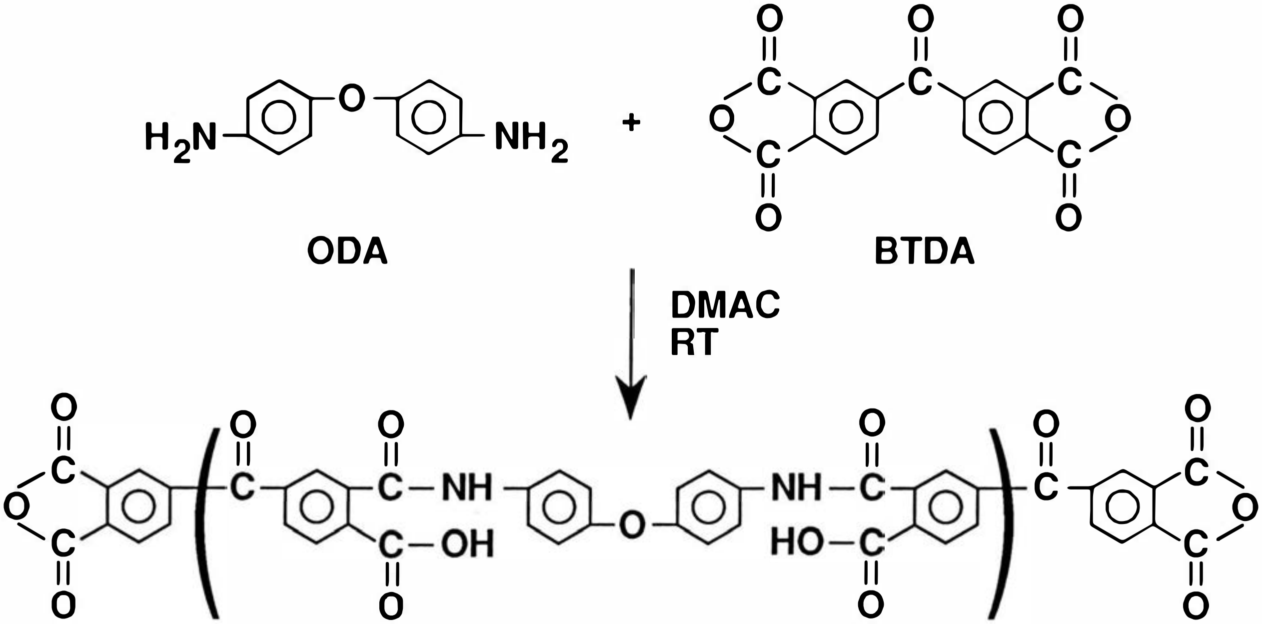
Copolymer	η_{inh},[a] dL/g (Polyamic Acid)	T_g, °C (Polyimide)	
		DSC[b]	TBA[c]
ATPAE (BPA) 3110//ODA/BTDA 3110	0.46	168	216
ATPAE (BPA) 3110//ODA/BTDA 6545	0.50	167, 265	267
ATPAE (BPA) 6545//ODA/BTDA 3110	0.38	164	176
ATPAE (BPA) 6545//ODA/BTDA 6545	0.37 (1.37)	171, 265	214
ATPAE (BPA) 6545 + [ODA + BTDA (6545)] Segmented	0.97	168, 265	172, 270

a) Measured in DMAc at 25°C and 0.5% concentration

b) Measured by DSC at 20°C/min after curing 1 h at 300°C

c) Measured by TBA at 3°C/min after curing 1 h at 300°C present. The other two copolymers have different length blocks and, therefore, twice as much of one polymer repeat unit as the other polymer repeat unit present. The ATPAE (BPA) 6545//ODA/BTDA 6545 was originally prepared at a stoichiometric ratio of oligomers to produce a highly viscous solution with inherent viscosity of 1.37 dL/g, shown in parenthesis. This very high viscosity was encouraging since it indicated that the calculated molecular weights were essentially correct, but polymers with viscosity, and therefore molecular weight, this high are very difficult to process. So these copolymers were prepared with a 1.5% offset in stoichiometry favoring the ODA/BTDA oligomer. The viscosities reported in the first column in Table 23 are for the copolymers prepared using this slight offset in stoichiometry. The decrease in viscosity due to this stoichiometry offset was much greater than expected but the copolymers with low inherent viscosities still produced tough, creasable films upon curing to 300°C.

The copolymers are prepared by first preparing the anhydride terminated ODA/BTDA blocks at 3110 or 6545 g/mole in DMAc. This is accomplished by offsetting the ODA to BTDA monomer ratio to 0.845 and 0.923 to provide $\overline{M}n$ of 3110 and 6545 g/mole, respectively, as shown in Figure 17. After stirring for ~ 3 h a solution of the ATPAE in DMAc was added to the poly(amic acid) solution and stirring continued for ~ 4 h. Individually, each solution was clear but colored (yellow for the ODA/BTDA and dark orange for the ATPAE) however, upon mixing the resulting solution was cloudy and no longer transparent. Small amounts of other solvents were added (e.g. dioxane) and the solutions were warmed (~ 60°C) or cooled (~ 0°C) but the solutions never became clear. Upon standing for long periods, the cloudy solution formed two distinct layers. Samples of each layer were dryed on glass up to 300°C to form films which were analyzed by DSC. The



ODA/BTDA

$\overline{M}_n$ = 3110 g/mole and $\overline{M}_n$ = 6545 g/mole
r = 0.845 r = 0.923
r = ratio of ODA to BTDA

Figure 17. Synthesis of anhydride-terminated ODA/BTDA oligomers.

film from the top layer had a Tg essentially equivalent to the ODA/BTDA (~ 280°C) and the film from the bottom layer had a Tg essentially equivalent to the PAE (~ 160°C). This information indicates that the different blocks are incompatible in DMAc and depolymerization occurs after the solution stands for long periods resulting in a complete phase separation of two layers. Solution inherent viscosities were measured immediately after polymerization on 0.5% solutions which became clear when diluted to this concentration. Films were prepared from thoroughly mixed solutions of the copolymers shortly after polymerization. When cured to 300°C, the cloudy solutions produced either hazy, yellow-orange films or textured films with indications of phase separation occurring. The last copolymer shown in Table 23 is a segmented copolymer prepared by synthesizing one block and the copolymer in the presence of one preformed block. This synthetic technique allows for the preparation of a copolymer where one block can have a more random molecular weight distribution while the preformed block is unaffected. Systems prepared in which the monomers and oligomers have very different reaction rates can display different properties from copolymers prepared from two preformed blocks. Preparation of this segmented copolymer at a stoichiometric ratio provided high inherent viscosity.

The last two columns in Table 23 show polymer Tgs measured by DSC and TBA. Copolymers with longer polyimide blocks show two Tgs, while those with shorter polyimide blocks display only the lower PAE Tg. The DSC data for the segmented copolymer is very similar to the DSC data for the block copolymer of the same composition indicating a similarity in copolymer structure by either synthetic technique. The presence of the two Tgs is further evidence of incompatibility and phase separation. For the block copolymers, the TBA curves display only one peak in the damping curve, however, the peaks are broader than for normal homopolymers and several have a shoulder present. For copolymers with equal length blocks, the Tgs by TBA are approximately the average of the two homopolymer Tgs, since the blocks are present in equal amounts. These peaks are broader than normal. The ATPAE (BPA) 3110/ODA/BTDA 6545 has a Tg at 267°C while the ATPAE (BPA) 6545//ODA/BTDA 3110 has a Tg at 176°C, which reflects the polymer present in the greatest amount. Both of these curves have a shoulder present in the area of the minor component Tg but temperatures are not given since a definite peak is not present. The TBA instrument measures the softening of a polymer by a mechanical technique where DSC measures only change in temperature of the polymer versus a standard. Therefore, Tgs by the two techniques often give different results on complicated block copolymers or blends and interpretation of the data is necessary. The TBA curve for the segmented copolymer is shown in Figure 18. There is an obvious peak at 172°C but also a less obvious peak or shoulder at 270°C in the damping (lower) curve. The rigidity curve (upper) shows a sharp decrease at the first damping peak and continues to decrease slowly until after the 270°C peak. Between the two peaks, the PAE block is flexible but the imide block is still rigid. The rigidity curve then levels off after heating above 270°C where both blocks are flexible. The interpretation of TBA data for these systems is involved but results can be explained by the presence of two different blocks. TBAs for the other copolymers shown in the table are included in the Appendix for reference.

Film properties were measured for the copolymers and resulting data are presented in Table 24. Two of the block copolymers, which contain the long PAE block, had textured surfaces that resembled the surface of an orange. The properties of both of these films were low, most likely due to

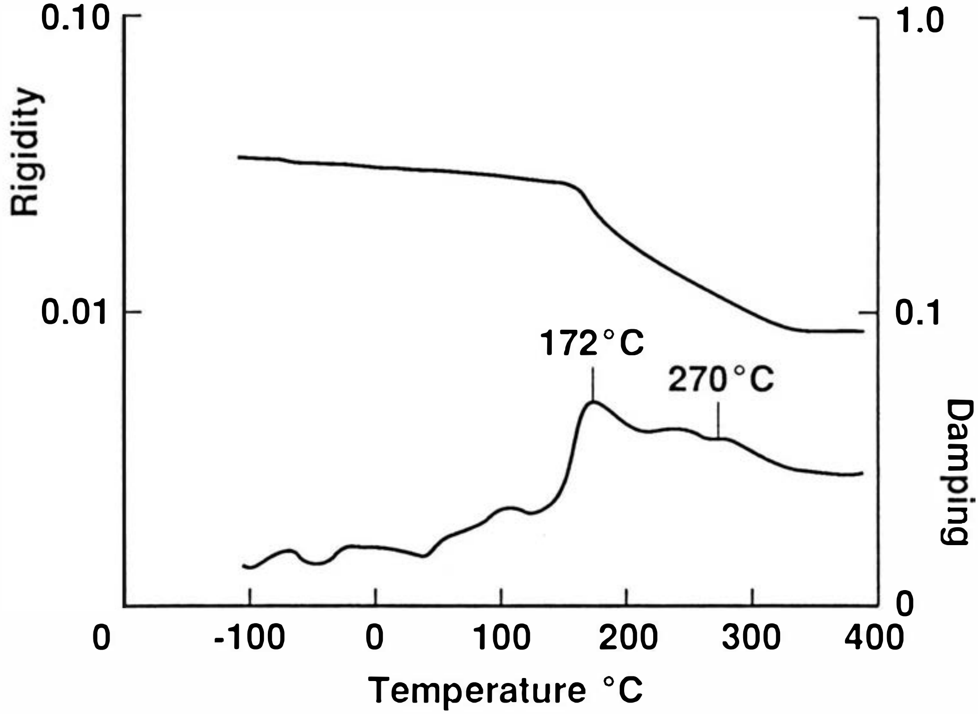


Figure 18. Torsional braid analysis of ATPAE (BPA) 6545 + [ODA + BTDA (6545)] segmented copolymer.

Table 24

Film Properties of ATPAE (BPA)//ODA/BTDA Copolymers

	Tensile Strength, Ksi (Modulus, Ksi) [Elongation, %]		
Polymer	RT	93°C	177°C
ATPAE (BPA) 3110/ODA/BTDA 3110	14.1 (415) [4.9]	11.7 (400) [4.9]	3.8 (156) [10.3]
ATPAE (BPA) 3110//ODA/BTDA 6545	16.2 (431) [5.7]	13.0 (389) [5.3]	6.2 (50) [19.1]
ATPAE (BPA) 6545//ODA/BTDA 3110a	5.8 (321) [1.9]	4.2 (268) [1.9]	— (—) [—]
ATPAE (BPA) 6545//ODA/BTDA 6545a	11.2 (324) [4.6]	9.4 (299) [4.6]	3.9 (60) [17.7]
ATPAE (BPA) 6545 + [ODA + BTDA (6545)] Segmented	15.4 (358) [23.2]	11.5 (363) [> 50]	4.5 (102) [> 50]

a) Textured, orange peel surface

texture caused by incompatibility. Also, ATPAE (BPA) 6545//ODA/BTDA 3110 had essentially no strength or modulus at 177°C since the major component in this copolymer has a Tg of 155°C. The properties of these copolymers follow a "rule of mixtures" meaning the values fall between those of the homopolymers and when not present in equal amounts, closer to those of the major component. For example, the ATPAE (BPA) 3110//ODA/BTDA 6545, which has imide as the major component, has the highest strength at each temperature tested and the highest modulus at RT. It was surprising that this copolymer did not have the highest modulus at 93°C and 177°C as well. The segmented copolymer listed at the bottom of Table 24 did not produce a film with a textured surface and had good properties at each temperature. For all of the copolymers listed, there is a significant decrease in properties at 177°C due to the presence of the low Tg PAE block.

The copolymers were subjected to thermogravimetric analysis at 2.5°C/min in both flowing air and nitrogen (15 ml/min) and results are shown in Table 25. The temperatures at 5% weight loss are in the range of 420-445°C in air and 465-500°C in nitrogen. Therefore, the copolymers are a little less stable in air than the homopolymers but have thermal stabilities similar to the homopolymers in a nitrogen atmosphere. In either case the thermal stabilities are very good for the use temperatures considered.

The results from this phase of the work were very encouraging. It was shown that the copolymers could be prepared in high molecular weight and that the calculated molecular weights were essentially correct. Using these calculated molecular weights, appropriate stoichiometries were determined. The properties measured for the copolymers gave mixed results. Film properties for block copolymers containing short PAE blocks were as expected, i.e. a weighted average of the homopolymer properties, while

Table 25

Thermogravimetric Analysis of ATPAE (BPA)//ODA/BTDA Copolymers

Copolymer	Temperature,[a] °C at 5% Weight Loss	
	Air	N_2
ATPAE (BPA) 3110/ODA/BTDA 3110	420	465
ATPAE (BPA) 3110//ODA/BTDA 6545	445	480
ATPAE (BPA) 6545//ODA/BTDA 3110	440	500
ATPAE (BPA) 6545//ODA/BTDA 6545	420	470
ATPAE (BPA) 6545 + [ODA + BTDA (6545)] Segmented	440	485

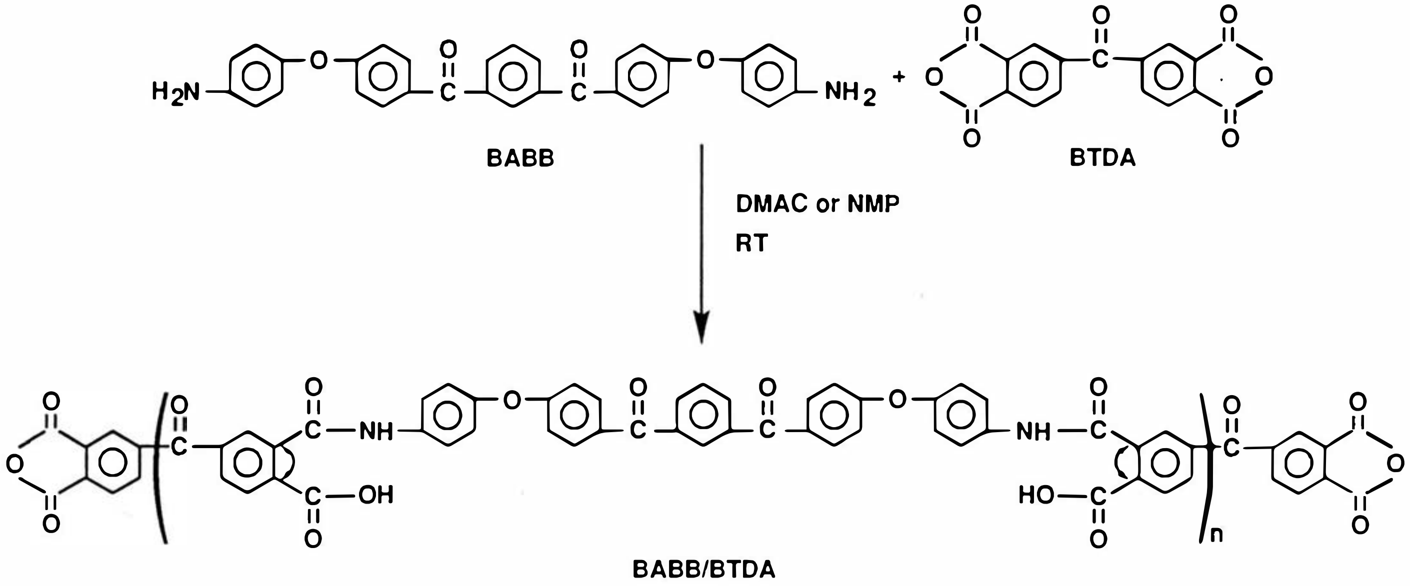
[a] Heating rate of 2.5°C/min in atmosphere flowing at 15 ml/min

properties for the block copolymers containing long PAE blocks were poor due to incompatibility. The choice of block molecular weights proved to be prophetic since a range of miscibility was studied. Copolymers with shorter block lengths display much better miscibility than copolymers with longer block lengths.

ATPAE (BPA)//BABB/BTDA Copolymers

In the next phase of the research, the PAE block remained the same but the structure of the PI block changed. A new crystalline polyimide has been developed, LARC-CPI, which has excellent properties but is difficult to process. The diamine (BABB) used to prepare LARC-CPI was prepared by reacting the FBB, which is one of the monomers used to prepare the PAE, with 4-aminophenol. Therefore, the PAE and LARC-CPI contain the same arylene ether ketone segment in the polymer backbone. The presence of this unit in both polymers should make the copolymer more compatible and could posssibly eliminate the textured surface on films of the longer block copolymers. Since the PAE has lower melt viscosity compared to LARC-CPI, an improvement in processability was expected.

Four different block copolymers were prepared using ATPAE based on BPA and BABB/BTDA (the monomers used to prepare LARC-CPI) each with blocks of 3110 and 6545 g/mole for calculated $\overline{M}$ns as shown in Figure 19. As shown in Table 26, the copolymers were prepared with the same molecular weight blocks as well as with different molecular weight blocks as in the previous section. Each of these copolymers was prepared using a stoichiometric ratio of oligomers to produce highly viscous solutions. The last copolymer listed in the table is a segmented copolymer of the same composition as the ATPAE (BPA) 6545//BABB/BTDA 6545 block copolymer



$\overline{M}_n$ = 3110 g/mole and $\overline{M}_n$ = 6545 g/mole

r = 0.76 r = 0.88

r = ratio of BABB to BTDA

Figure 19. Synthesis of anhydride-terminated BABB/BTDA oligomers.

Table 26

Inherent Viscosity of ATPAE (BPA)//BABB/BTDA Copolymers

	Polyamic Acid η_{inh}, dL/g*		
Copolymer	DMAc	NMP	m-Cresol
ATPAE (BPA) 3110//BABB/BTDA 3110	0.63	0.90	0.54
ATPAE (BPA) 3110//BABB/BTDA 6545	0.87	1.73	--
ATPAE (BPA) 6545//BABB/BTDA 3110	0.81	1.00	--
ATPAE (BPA) 6545//BABB/BTDA 6545	0.89	1.03	0.64
ATPAE (BPA) 6545 + [BABB + BTDA (6545)] Segmented	1.15	--	--

*Measured at 25°C and 0.5% concentration but prepared differently. All the block copolymers were synthesized in both DMAc and NMP and two were also synthesized in m-cresol. The resulting inherent viscosities, which are shown in Table 26 range from 0.63 to 0.89 dL/g in DMAc, from 0.90 to 1.73 dL/g in NMP and from 0.54 to 0.64 in m-cresol. On occasion, some reactions in DMAc became very viscous and formed a gel within 15 min, but stirring overnight provided a clear viscous solution. This gelation did not occur for all reactions in DMAc or even on all repetitions of the same reaction. The mechanism of gelation is not fully understood but is believed to be caused by the presence of some very high molecular weight polymer causing many chain entanglements. Upon stirring, an equilibration takes place, decreasing the molecular weight of these very long polymer chains as well as decreasing the polydispersity of the whole polymer. Since oligomers of significant molecular weight are reacting, it is obvious that only a few reactions are necessary to produce relatively high molecular weight polymer. Gelation did not occur in NMP or m-cresol with any of the block copolymers. Since these solvents are considered poorer solvents for the formation of poly(amic acids), the DMAc solvent was expected to produce the higher molecular weight polymer originally. The inherent viscosities shown in Table 26 are for reactions after equilibration. Apparently the DMAc prepared polymers equilibrate to a lower viscosity than the NMP prepared polymers. Viscosities over 1.0 dL/g are considered high and a viscosity of 1.73 dL/g for the ATPAE (BPA) 3110//BABB/BTDA 6545 is very high. Polymerizations in m-cresol gave the lowest viscosities for any of the solvents used. The segmented copolymer at the bottom of the table was prepared only in DMAc. After gelling within 15 min followed by stirring 48 h to produce a solution, its η_{inh} was 1.15 dL/g.

Results from thermal characterization of the copolymers are shown in Table 27. The Tgs and Tms (in parentheses) are listed in columns below the solvent in which the polymers were prepared. The solvent used for synthesis does not appear to have a large effect on resulting polymer Tg, as expected. However, the Tgs are slightly higher for shorter PAE block copolymers (170 to 178°C) compared to those with longer PAE blocks (164 to 168°C). As compatibility increases and phase separation decreases, the copolymer Tg should approach the average of the two homopolymer Tgs. Therefore, a random or completely compatible block copolymer should have a Tg of 189°C. Since the polyimide portion of the molecule is crystalline, the Tgs in Table 27 probably represent the PAE portion of the copolymer. Since the lower molecular weight blocks are more compatible, there is a larger increase in Tg for the shorter block copolymers (155 to 175°C) than for the longer block copolymers (155 to 165°C). For the ATPAE (BPA) 6545//BABB/BTDA 6545 synthesized in NMP, an obvious change in slope at 220°C occurred in the DSC trace. This is most likely due to the polyimide Tg. A similar DSC trace was obtained from the ATPAE (BPA) 6545//BABB/BTDA 6545 segmented copolymer which also showed a Tg of 164°C and an obvious change in slope at 220°C. The melting points for the copolymers are shown in parentheses. Some copolymers had two melting peaks so two numbers are reported. However, all melting peaks were broad, some containing shoulders but not definite peaks at the lower melting points (335 to 343°C) for those reported. Although different Tms are given for copolymers from different solvents, it appears that there is no definite trend developing and, for a given copolymer, the Tm is essentially the same for either solvent. Only slight differences in position and intensity are noted for the melting peaks.

Table 27

Thermal Characterization of ATPAE (BPA)//BABB/BTDA Copolymers

	DSC Tg (Tm), °C^a				TBA Tg, °C^b
Copolymer	DMAc	NMP	m-Cresol	DMAc^c	DMAc
ATPAE (BPA) 3110//BABB/BTDA 3110	175 (354)	175 (338,352)	178 (335,352)	175 (363)	193
ATPAE (BPA) 3110//BABB/BTDA 6545	170 (354)	— (358)	—	182 (370)	249
ATPAE (BPA) 6545//BABB/BTDA 3110	168 (353)	168 (335, 352)	—	165 (368)	185
ATPAE (BPA) 6545//BABB/BTDA 6545	165 (335, 350)	164, 220 (343, 355)	168 (343, 357)	165, 230 (370)	168, 205
ATPAE (BPA) 6545 + [BABB + BTDA (6545)] Segmented	164, 220 (338, 353)	—	—	170 (367)	200

[a] Measured at a heating rate of 20°C/min after curing 1 h at 300°C

[b] Measured at a heating rate of 3°C/min after curing 1 h at 300°C

[c] Solution imidized, toluene azeotrope at 155°C for 16 h

The last column in Table 27 under DSC Tg (Tm) gives data for polymers synthesized in DMAc which were solution imidized by adding toluene to the reaction and heating to 155°C while collecting the toluene/water azeotropic mixture instead of thermally imidized to 300°C. Holding for 16 h at 155°C provided yellow insoluble powders. The most important information in this column is the higher Tms for solution imidized copolymers. In polymers, higher melting points may indicate a slightly higher degree and/or more perfect crystallinity. Although not conclusive, this data indicates that solution imidization allows for better alignment of polymer chains resulting in a higher degree of crystallinity. Others also have observed that solution imidization produces a higher degree and/or more perfect crystallinity than thermal imidization in PIs (105).

The last column in Table 27 gives Tgs as measured by TBA only on copolymers prepared in DMAc. This mechanical measure of Tg gives different results from DSC and a wide range of temperatures (168 to 249°C). The ATPAE (BPA) 3110//BABB/BTDA 3110 gives one peak in the damping curve indicating a transition at 193°C which was approximately the average transition for the homopolymers. The ATPAE (BPA) 3110//BABB/BTDA 6545 displayed a transition at 249°C, higher than either homopolymer Tg. This transition must be influenced by the rigidity in the crystalline regions of the PI, which is present in twice the amount as the PAE. The ATPAE (BPA) 6545//BABB/BTDA 3110 had a transition at 185°C, slightly higher than the calculated Tg from the rule of mixtures (177.4°C). The ATPAE (BPA) 6545//BABB/BTDA 6545 displayed two peaks in the damping curve at 168 and 205°C. These transitions are approximately 15°C above and below the Tgs of the PAE and PI, respectively indicating some incompatibility between the blocks at this molecular weight level. The segmented copolymer displayed a broad peak with a maximum at 200°C. Although the block copolymer of the same composition displayed two peak maxima, the breadth of the peaks are similar. The absence of the two peaks may indicate that the segmented copolymer is slightly more compatible than the block copolymer of the same composition. The TBA curves for the copolymers shown in Table 27 are included in the Appendix for reference.

To study crystallinity, wide angle x-ray scattering analysis was performed on cured films of copolymers synthesized in DMAc. Resulting data indicated that the block and segmented copolymer films cured up to 300°C for 1 h were crystalline. Judging by peak intensity and sharpness, the ATPAE (BPA) 3110//BABB/ BTDA 6545 had the highest degree of crystallinity as expected due to its high imide content. The ATPAE (BPA) 3110//BABB/BTDA 3110 had the second highest degree of crystallinity. The ATPAE (BPA) 6545//BABB/BTDA 6545 and the segmented copolymer of the same composition appeared to have similar amounts of crystallinity but less than the previous two copolymers. As expected, ATPAE (BPA) 6545//BABB/BTDA 3110 has the least amount of crystallinity since it has the least amount of imide present. Wide angle x-ray data was also taken on the ATPAE (BPA) 6545//BABB/BTDA 6545 powder which was solution imidized. Comparing this to the data from the thermally imidized film of the same composition, its apparent that solution imidization produced the higher degree of crystallinity, supporting the DSC interpretation. All x-ray diffraction patterns are included in the Appendix for reference.

Tensile properties for the ATPAE (BPA)//BABB/BTDA copolymers are shown in Table 28. The properties are dependent on the relative amounts of PAE and PI present in the copolymer. That is, film properties follow a rule of mixtures. Higher imide content leads to higher strength and modulus while

Table 28

Film Properties of ATPAE (BPA)//BABB/BTDA Copolymers

Polymer	Tensile Strength, Ksi (Modulus, Ksi) [Elongation, %]		
	RT	93°C	177°C
ATPAE (BPA) 3110//BABB/BTDA 3110	15.0 (514) [3.5]	12.7 (449) [3.2]	3.4 (135) [38]
ATPAE (BPA) 3110//BABB/BTDA 6545	16.2 (535) [3.8]	14.5 (516) [3.7]	5.9 (304) [30]
ATPAE (BPA) 6545//BABB/BTDA 3110	13.2 (435) [8.1]	10.5 (433) [16.1]	1.4 (36) [74]
ATPAE (BPA) 6545//BABB/BTDA 6545	14.2 (519) [4.3]	10.9 (437) [3.2]	2.7 (114) [49]
ATPAE (BPA) 6545 + [BABB + BTDA (6545)] Segmented	16.0 (457) [6.1]	12.7 (443) [3.8]	2.2 (85) [53]

higher arylene ether content gives lower strength and modulus but higher elongation. For example, the ATPAE (BPA) 3110//BABB/BTDA 6545 had the highest strength and modulus at each temperature tested, maintaining 90% and 96% of its strength and modulus, respectively at 93°C and 36% and 57% of its strength and modulus at 177°C. In contrast, the ATPAE (BPA) 6545//BABB/BTDA 3110 had the lowest strength and modulus at all temperatures tested, retaining only 11% and 8% of its strength and modulus, respectively at 177°C, but the highest elongation of the block copolymers. The other copolymers, which had equal amounts of imide and arylene ether, displayed properties intermediate to these extremes. Overall the copolymers had very good properties at 93°C but poor properties at 177°C.

Fracture toughness and energy were measured for the ATPAE (BPA)//BABB/BTDA copolymers and results are reported in Table 29. The moldings were prepared by placing solution imidized powders in a stainless steel mold and heating in a hydraulic press with electrically heated platens. The high molecular weight copolymers were molded at 380-390°C under 300-500 psi during ~ 0.5 h. These unoptimized conditions were sufficient, and possibly excessive, to produce void free moldings for measurement. The processing conditions were not optimized since the molecular weight of the copolymers was not controlled, and obtaining fracture toughness data was the major purpose here. Data from the table shows that the copolymers were very tough, with fracture energies ranging from 22-44 in-lbs/in^2. As previously shown this value is calculated by squaring the fracture toughness and dividing by modulus, in this case obtained on film samples. Since the moduli for the copolymers are different, there is not a direct correlation between fracture toughness and fracture energy. However, a trend is obvious in the data, especially for the fracture energy of the block copolymers. The trend is

Table 29

Fracture Toughness and Energy of ATPAE (BPA)//BABB/BTDA Copolymers

Copolymer	Fracture Toughness K_{Ic}, psi $\cdot \sqrt{\text{in.}}$	Fracture Energy G_{Ic}, in.-lbs/in.^{2}
ATPAE (BPA) 3110//1,3-BABB/BTDA 3110	3370	22
ATPAE (BPA) 3110//1,3-BABB/BTDA 6545	3900	28
ATPAE (BPA) 6545//1,3-BABB/BTDA 3110	3930	36
ATPAE (BPA) 6545//1,3-BABB/BTDA 6545	4760	44
ATPAE (BPA) 6545 + [1,3-BABB + BTDA (6545)] Segmented	3350	25

for increasing fracture energy (and fracture toughness) with increasing block length. The copolymer with two long blocks has twice the fracture energy (44 in-lbs/in^2) as the copolymer with two short blocks (22 in-lbs/in^2). The copolymers with one long and one short block have intermediate values. The low values of the segmented copolymer compared to the ATPAE (BPA) 6545//BABB/BTDA (6545) block copolymer were unexpected and the reasons are not fully understood. When comparing toughness data from the copolymers to the homopolymers, its obvious that a "rule of mixtures" calculation predicts numbers that are higher than experimental data. The only copolymer with toughness intermediate to that of the homopolymers is the ATPAE (BPA) 6545//BABB/BTDA 6545. In any case, the fracture toughness and energy for the copolymers are very high. Examination of the fracture surfaces of the compact tension specimen revealed a rough and highly crazed surface. This surface is indicative of a failure mechanism that absorbs energy by distributing it over a large surface area with yielding in contrast to stable crack growth characteristic of brittle materials.

The copolymers were subjected to thermogravimetric analysis at 2.5°C/min in both flowing air and nitrogen (15 ml/min) and results are shown in Table 30. The temperatures at 5% weight loss are in the range of 420-450°C in air and 440-490°C in nitrogen. Therefore, the copolymers are a little less stable in both air and nitrogen than the homopolymers. However, in both air and nitrogen the thermal stabilities are very good.

The results of this phase of the work were also very encouraging. An amorphous PAE and a semi-crystalline PI were used to prepare block copolymers which were semi-crystalline. The PAE and PI blocks were compatible enough to produce good, clear films with no surface irregularities. The copolymers had very good mechanical properties at RT and 93°C,

Table 30

Thermogravimetric Analysis of ATPAE (BPA)//BABB/BTDA Copolymers

Copolymer	Temperature,[a] °C at 5% Weight Loss Air	Temperature,[a] °C at 5% Weight Loss N_2
ATPAE (BPA) 3110/BABB/BTDA 3110	420	440
ATPAE (BPA) 3110//BABB/BTDA 6545	420	450
ATPAE (BPA) 6545//BABB/BTDA 3110	425	470
ATPAE (BPA) 6545//BABB/BTDA 6545	440	480
ATPAE (BPA) 6545 + [BABB + BTDA (6545)] Segmented	450	490

[a] Heating rate of 2.5°C/min

however properties at 177°C were poor. The copolymers could be compression molded at high temperature and pressure and polymer toughness proved to be excellent.

ATPAE (BPF)//BABB/BTDA Copolymers

In an effort to increase the high temperature mechanical properties of the block copolymers, the next phase of the work used the same PI block but replaced the PAE block with another PAE that had a higher Tg. The Tg of the previous PAE (155°C), limited high temperature mechanical properties well below the capability of the PI block. The new PAE block has the same Tg (223°C) as the PI and therefore should allow the maintenance of properties close to the capability of the PI.

Four different block copolymers were prepared using ATPAE based on BPF and BABB/BTDA each with blocks of 3110 and 6545 g/mole for calculated $\overline{M}$ns. As shown in Table 31, the copolymers were prepared with the same molecular weight blocks as well as with different molecular weight blocks as before. Each of these copolymers was prepared using a stoichiometric ratio of oligomers to produce highly viscous solutions. The last two copolymers listed in the table are segmented copolymers of the same composition as the two block copolymers with equal molecular weight blocks. All the block copolymers were synthesized in DMAc, NMP and m-cresol. The resulting inherent viscosities range from 0.35 to 1.08 dL/g in DMAc, from 0.75 to 1.04 dL/g in NMP and from 0.61 to 0.72 dL/g in m-cresol. Several polymerizations, as noted in Table 31, became very viscous and formed a gel within 15 min which dissipated upon heating to 60-80°C. This gelation occurred in each of the three solvents but not in the same reaction or even in all repetitions of the same reaction. The mechanism of gel formation is not

Table 31

Inherent Viscosity of ATPAE (BPF)//BABB/BTDA Copolymers

	Polyamic Acid η_{inh}, dL/g[a]		
Copolymer	DMAc	NMP	m-Cresol
ATPAE (BPF) 3110//BABB/BTDA 3110	1.02	0.82	0.61
ATPAE (BPF) 3110//BABB/BTDA 6545	1.08	0.75	0.64
ATPAE (BPF) 6545//BABB/BTDA 3110	0.47[b]	1.04	0.61[b]
ATPAE (BPF) 6545//BABB/BTDA 6545	0.35[b]	0.96	0.72
ATPAE (BPF) 3110 + [BABB + BTDA (3110)] Segmented	----	1.00[b]	----
ATPAE (BPF) 6545 + [BABB + BTDA (6545)] Segmented	----	0.89[b]	----

[a] Measured at 25°C and 0.5% concentration

[b] Formed a gel which dissipated upon heating to 60-80°C

fully understood but a possible explanation was discussed previously. The inherent viscosities shown in Table 31 are for reactions after heating to dissipate the gel. This heating process appears to have a significant effect on DMAc viscosities, resulting in the low viscosities of 0.35 and 0.47 dL/g, but a less important effect on viscosities of copolymers made in either NMP or m-cresol. With this in mind, the DMAc appeared to produce the highest inherent viscosities, closely followed by NMP while m-cresol gave the lowest viscosity copolymers. However, upon curing 1 h at 300°C all copolymers produced tough, creasable films. The segmented copolymers were prepared in only NMP but gave high viscosities even after warming to dissipate the gel.

Thermal characterization of the copolymers are shown in Table 32. The DSC Tgs and Tms (in parentheses) are listed in columns below the solvent in which they were prepared. As expected, the solvent does not appear to have a large effect on resulting polymer Tg since high molecular weight copolymer is formed in each of the solvents used. Each copolymer displayed only one Tg since the Tgs of the homopolymers were essentially the same (222°C for the PI and 223°C for the PAE) but it occurred at a slightly higher temperature for the copolymers than for either homopolymer. The increase in Tg of ~ 5°C was unexpected but may occur from some chain to chain interaction of PAE and PI blocks since curing cycles and times remained constant. Each of these DSC samples were films that had been cured 1 h each at 100, 200 and 300°C which was the same cure cycle used for the homopolymers. The last column under DSC shows results of measurements on powder samples which were solution imidized by collecting a toluene/water azeotropic mixture from a copolymer solution in DMAc held at 155°C for 16 h. Except for a slight increase in Tg for the copolymers with different length blocks, this imidization technique produced

Table 32

Thermal Characterization of ATPAE (BPF)//BABB/BTDA Copolymers

	DSC Tg (Tm), °C[a]				TBA Tg, °C[b]
Copolymer	DMAc	NMP	m-Cresol	DMAc[c]	NMP
ATPAE (BPF) 3110//BABB/BTDA 3110	228 (335,352)	227 (331,350)	228 (332,360)	223 (365)	233
ATPAE (BPF) 3110//BABB/BTDA 6545	228 (337,352)	227 (332,352)	225 (330,350)	225 (372)	239
ATPAE (BPF) 6545//BABB/BTDA 3110	227 (345)	228 (340,352)	228 (338)	227 (----)	229
ATPAE (BPF) 6545//BABB/BTDA 6545	228 (353)	228 (347,357)	232 (355)	223 (372)	240
ATPAE (BPF) 3110 + [BABB + BTDA (6545)] Segmented	----	227 (332,350)	----	----	
ATPAE (BPF) 6545 + [BABB + BTDA (6545)] Segmented	----	231 (350)	----	----	

[a] Measured at a heating rate of 20°C/min after curing 1 h at 300°C
[b] Measured at a heating rate of 3°C/min after curing 1 h at 300°C
[c] Solution imidized, toluene azeotrope at 155°C for 16 h

copolymers with the same Tg as the homopolymers. While this data is interesting, more important differences appear in the melting points of the thermally imidized copolymers from different solvents. Some copolymers display two melting endotherms while others display only one. However, all melting peaks were broad, some containing shoulders but not definite peaks in the unrepresented temperature range. The melting peak position and intensity for polymers can be affected by many variables such as molecular weight, residual solvent, thermal history, etc. and it would not be justifiable to conclude that the different solvents were responsible for the differences in Tms discussed here. The solution imidization technique, however, produced only single Tms and at temperatures higher than the thermal imidization technique. The DSC trace of ATPAE (BPF) 6545//BABB/BTDA 3110 did not have a melting peak present but there was an obvious change in slope in the 365 to 375°C range. Possibly, since the polyimide component was the minor component in the system, this technique was not sensitive enough to show a melting peak but did show the presence of a melt by the change in slope. The discussion concerning crystallinity in the ATPAE (BPA)//BABB/BTDA block copolymers is valid for these block copolymers since the crystalline PI block is the same.

The last column in Table 32 gives copolymer Tgs as measured by TBA only on copolymers prepared in NMP. This mechanical measure gives different results from DSC and a relatively wide range of temperatures (229-240°C). The lowest Tg was for the ATPAE (BPF) 6545//BABB/BTDA 3110 in which the major component is the amorphous PAE. The next lowest Tg was for the copolymer containing both blocks of 3110 g/mole. The other two block copolymers, which contain the long PI block, had Tgs 16-17°C above the Tg of the homopolymers. Apparently the crystalline regions in the polyimide blocks significantly increase the TBA Tg for copolymers with long PI blocks while causing only a modest increase for copolymers with shorter PI blocks. The TBA Tg of the ATPAE (BPF) 3110 + [BABB + BTDA (3110)] segmented copolymer was 232°C, essentially equivalent to the Tg of the corresponding block copolymer. The Tg by TBA of the ATPAE (BPF) 6545 + [BABB + BTDA (6545)] segmented copolymer was 233°C or 7°C below the Tg for the corresponding block copolymer. This difference may be due to structural variations due to the differences in synthesis providing less crystallinity in the segmented version (lower Tg by TBA) than the block copolymer. TBA curves for all copolymers shown in the table are included in the Appendix for reference.

Wide angle x-ray scattering analysis was performed on each of the copolymers and diffraction patterns are included in the Appendix for reference. Judging by the peak intensities, the copolymers with longer imide blocks were more crystalline than those with shorter imide blocks, as expected. Also, the segmented copolymers appeared to be less crystalline than the block copolymers of the same composition. This evidence supports the previous discussion in that the block copolymer had a higher Tg by TBA than the segmented copolymer of the same composition. DSC data indicates that the copolymers do not recrystallize after heating above the Tm. To prepare moldings, the copolymers must be heated above Tm for complete consolidation. Therefore, x-ray diffraction was performed on copolymers that were molded at several different temperatures. Figure 20 shows the x-ray diffraction pattern for the solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer powder indicating a high degree of crystallinity. Figures 21 and 22 are for the same copolymer molded 0.5 h at 320°C and 380°C, respectively. Molding at 320°C maintains crystallinity but does not produce

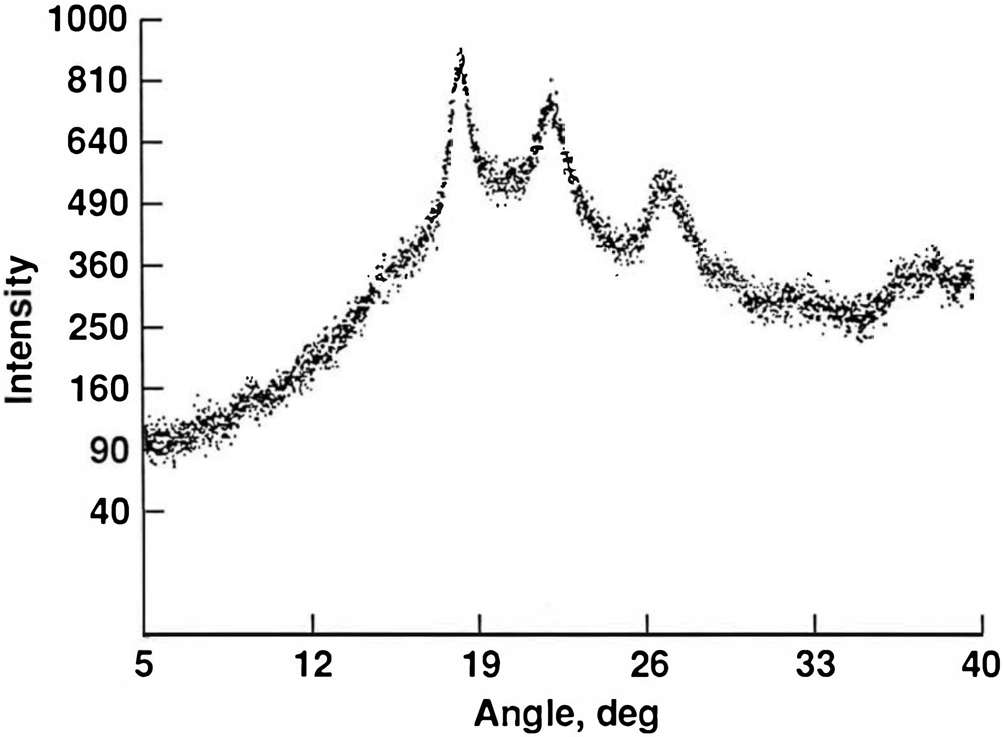


Figure 20. X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer powder.

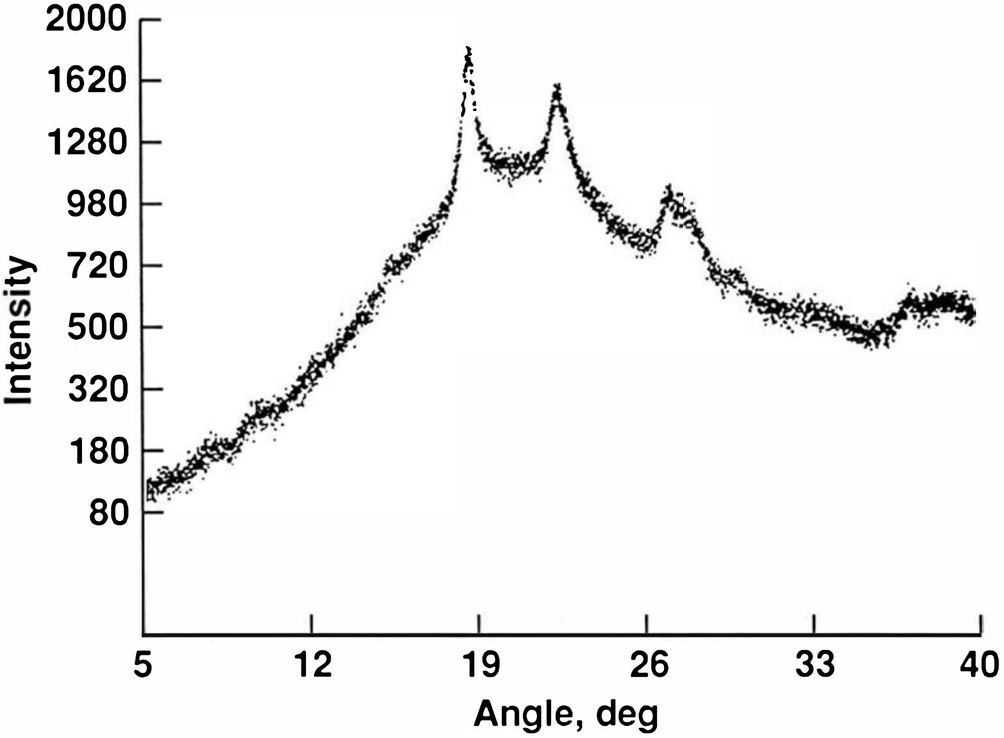


Figure 21. X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 320°C.

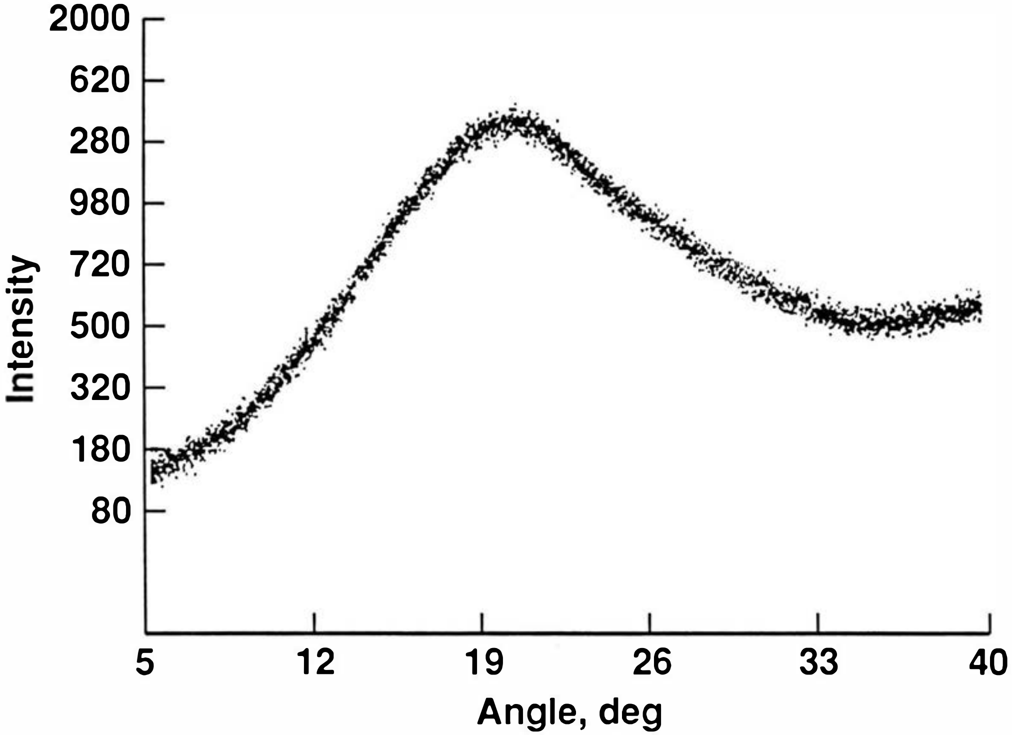


Figure 22. X-ray diffraction pattern for solution imidized ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer molded 0.5 h at 380°C.

consolidated moldings while molding at 380°C eliminates crystallinity but produces consolidated moldings. Again, the crystallinity is not recoverable after annealing 2 h at 310°C.

Tensile properties for the ATPAE (BPF)//BABB/BTDA copolymers are shown in Table 33. The RT tensile strengths for the block copolymers range from 13.0 to 15.9 Ksi while the tensile moduli range from 408 to 489 Ksi. The ATPAE (BPF) 3110//BABB/BTDA 3110 has the lowest strength but the highest modulus while ATPAE (BPF) 6545//BABB/BTDA 6545 has the highest strength and the lowest modulus at RT. The elevated temperature properties continue this trend for modulus, with ATPAE (BPF) 3110//BABB/BTDA 3110 maintaining the highest modulus and the ATPAE (BPF) 6545//BABB/BTDA 6545 having the lowest modulus. However, unexpectedly the copolymer with the highest RT strength has the lowest strength at both 93 and 177°C. Unlike the previous copolymers, the tensile properties of the copolymers discussed here do not follow a rule of mixtures. That is, the copolymer with the highest imide content does not have the highest strength and modulus and the copolymer with the highest arylene ether content does not have the highest elongation for unknown reasons. The most important information from the table is the excellent retention of properties at 177°C. The first three block copolymers listed in Table 33 retained almost 60% of their tensile strength and 90% of their modulus when tested at 177°C. As expected, this retention of properties at 177°C is much better than for the previous copolymers which contained a PAE block with a significantly lower Tg. The segmented copolymers had tensile properties slightly poorer than the corresponding block copolymers. There appears to be a slight penalty in mechanical performance for the segmented versus block copolymer architecture.

Table 33

Film Properties of ATPAE (BPF)//BABB/BTDA Copolymers

Polymer	Tensile Strength, Ksi (Modulus, Ksi) [Elongation, %]		
	RT	93°C	177°C
ATPAE (BPF) 3110//1,3-BABB/BTDA 3110	13.0 (489) [3.3]	13.0 (452) [3.6]	7.6 (442) [2.5]
ATPAE (BPF) 3110//1,3-BABB/BTDA 6545	15.0 (480) [4.1]	13.3 (428) [4.5]	8.6 (435) [5.9]
ATPAE (BPF) 6545//1,3-BABB/BTDA 3110	14.7 (425) [5.0]	12.8 (415) [4.6]	8.2 (379) [3.2]
ATPAE (BPF) 6545//1,3-BABB/BTDA 6545	15.9 (408) [6.0]	11.6 (354) [4.8]	7.3 (331) [3.0]
ATPAE (BPF) 3110 + [1,3-BABB + BTDA (3110)] Segmented	13.2 (427) [3.7]	11.5 (406) [9.2]	6.2 (367) [7.1]
ATPAE (BPF) 6545 + [1,3-BABB + BTDA (6545)] Segmented	12.8 (409) [4.8]	11.5 (355) [8.1]	7.5 (357) [2.9]

Fracture toughness and energy were measured for the ATPAE (BPF)//BABB/BTDA block copolymers and results are reported in Table 34. The moldings were prepared by heating solution imidized powder in a mold at 380-390°C under 300 to 500 Psi during ~ 0.5 h. The molding conditions were again not optimized since the molecular weight of the copolymers was not controlled. However, void free moldings were produced and tested to obtain fracture toughness data. The four block copolymers shown in Table 34 were tough with fracture toughness ranging from 1670 to 1950 Psi $\cdot \sqrt{in}$ and fracture energy ranging from 5.7 to 8.8 in · lbs/in^2. The ATPAE (BPF) 3110//BABB/BTDA 3110 had the lowest fracture toughness and fracture energy while the other three were comparable. These values are well below a rule of mixtures calculation using the data for homopolymers (BABB/BTDA K_{Ic} = 4890 Psi $\cdot \sqrt{in}$ and FBB/BPF K_{Ic}= 2400 Psi $\cdot \sqrt{in}$) but are still relatively good since the homopolymers are so tough originally. Examination of the fracture surfaces of the compact tension specimen revealed a relatively smooth surface with no indication of crazing as in the previous block copolymers. It is obvious from the examination that these block copolymers are not as tough as the copolymers discussed previously.

The copolymers were also analyzed by thermogravimetric analysis at 2.5°C/min in both flowing air and nitrogen (15 ml/min) and results are shown in Table 35. The temperatures at 5% weight loss are in the range of 410 to 490°C in air and 425 to 495°C in nitrogen. The thermal stability of the copolymers is very good for proposed use temperatures but lower than the homopolymers.

The results of this phase of the work were again encouraging. A new series of block copolymers were prepared in which the amorphous PAE block had a high Tg (223°C, equivalent to that of the PI) and the PI block was semi-

Table 34

Fracture Toughness and Energy of ATPAE (BPF)//BABB/BTDA Copolymers

Polymer	Fracture Toughness K_{Ic}, psi $\cdot \sqrt{in.}$	Fracture Energy G_{Ic}, in.-lbs/in.^{2}
ATPAE (BPF) 3110//1,3-BABB/BTDA 3110	1670	5.7
ATPAE (BPF) 3110//1,3-BABB/BTDA 6545	1950	7.9
ATPAE (BPF) 6545//1,3-BABB/BTDA 3110	1940	8.8
ATPAE (BPF) 6545//1,3-BABB/BTDA 6545	1860	8.5

Table 35

Thermogravimetric Analysis of ATPAE (BPF)//BABB/BTDA Copolymers

Copolymer	Temperature,[a] °C at 5% Weight Loss Air	Temperature,[a] °C at 5% Weight Loss N_2
ATPAE (BPF) 3110//BABB/BTDA 3110	440	495
ATPAE (BPF) 3110//BABB/BTDA 6545	480	525
ATPAE (BPF) 6545//BABB/BTDA 3110	400	445
ATPAE (BPF) 6545//BABB/BTDA 6545	440	475
ATPAE (BPF) 3110 + [BABB + BTDA (3110)] Segmented	460	500
ATPAE (BPF) 6545 + [BABB + BTDA (6545)] Segmented	410	475

[a] Heating rate of 2.5°C/min in atmosphere flowing at 15 ml/min

crystalline. The copolymers had very good mechanical properties at RT and 93°C and most had excellent retention of properties at 177°C. The thermal stability is very good for the proposed use temperature and toughness is good for translation into composites. One block copolymer, ATPAE (BPF) 3110//BABB/BTDA 3110, was selected for controlled molecular weight and end-capping studies due to an overall attractive combination of properties. One important reason for selecting this copolymer for additional work was the excellent modulus at both RT (489 Ksi) and 177°C (442 Ksi). The resin modulus is critical in obtaining good composite properties because the composite matrix must support the fibers and transfer loads from one fiber to the next (106). Also, this particular block copolymer is 50% PAE and 50% PI, so possibly the more easily processed PAE segment will provide a copolymer that is more easily processed than the BABB/BTDA polyimide.

Controlled Molecular Weight Copolymers

In an effort to make ATPAE (BPF) 3110//BABB/BTDA 3110 with improved processability, the copolymer was synthesized at a controlled molecular weight by offsetting oligomer stoichiometry. By using a 2:1 ratio of BABB/BTDA 3110 to ATPAE (BPF) 3110, a block copolymer of ~ 9300 g/mole was prepared and designated PI/PAE/PI (3110) identifying the average chain composition. When a 2:1 ratio of ATPAE (BPF) 3110 to BABB/BTDA 3110 was used, a block copolymer of ~ 9300 g/mole was prepared and designated PAE/PI/PAE (3110) again identifying the average chain composition. Table 36 shows data for the two copolymers as well as solution imidized (SI after designation) powders of the two copolymers. Inherent viscosities are essentially equivalent as expected and Tgs are similar except for the PAE/PI/PAE (3110) SI which has a slightly higher Tg of 225°C. Tgs by TBA

Table 36

Controlled Molecular Weight Copolymers

Copolymer	η_{inh}, dL/g[a]	DSC Tg (Tm), °C[b]	TBA Tg, °C[a]
PI/PAE/PI (3110)	0.46	218 (362)[d]	228
PI/PAE/PI (3110) SI	—	217 (363)[e]	—
PAE/PI/PAE (3110)	0.45	217 (377)[d]	233
PAE/PI/PAE (3110) SI	—	225 (342)[e]	—

[a] Measured in NMP at 25°C and 0.5% concentration
[b] Measured at a heating rate of 20°C/min
[c] Measured data heating rate of 3°C/min after curing 1 h at 300°C
[d] Film cured to 300°C
[e] Solution imidized, toluene azeotrope at 155°C for 16 h

are slightly higher than DSC Tgs, which also occurred for the high molecular weight versions. Moldings were prepared at 380°C under 500 psi and fracture toughness and energy were measured as shown in Table 37. The block copolymer with higher imide content had both higher fracture toughness and energy than the copolymer with higher arylene ether content. The modulus used in the calculation was from film testing of the high molecular weight version of the same system. Table 38 shows room temperature Ti/Ti tensile shear strength data. When processed at 380°C under 300 psi, the PI/PAE/PI (3110) had fair strength while the PAE/PI/PAE (3110) strength was very low and polymer flow was very poor. Higher temperatures and pressures produced better strengths but still unacceptable failure modes. Since the copolymers were not giving good values and high pressures were required, it was believed that reactions either increasing molecular weight or crosslinking were occurring. Measurement of the melt viscosity at 400°C for the two block copolymers was attempted but proved unsuccessful. The viscosities never stabilized but kept increasing with time indicating that reactions leading to chain extension or crosslinking were occurring. Therefore, it was decided that the copolymers must be end-capped to produce melt stable materials.

End-Capped Copolymers

Due to the higher fracture toughness of the PI/PAE/PI (3110) copolymer, this composition was selected for further end-capping studies. This material was prepared as before but a final step of addition of a specific amount of aniline produced phenyl terminated copolymers from the previously anhydride terminated copolymers. End-capping with phenyl groups provided unreactive terminal groups and, therefore melt stable

Table 37

Fracture Toughness and Energy of Controlled Molecular Weight Copolymers

Polymer	Fracture Toughness K_{Ic}, psi$\cdot\sqrt{\text{in.}}$	Fracture Energy G_{Ic}, in.-lbs/in.^{2}
PI/PAE/PI (3110)	2080	8.9
PAE/PI/PAE (3110)	1720	6.1

Table 38

Room Temperature Ti/Ti Tensile Shear Strength of Controlled Molecular Weight Copolymers

	Bonding Conditions		
Copolymer	300 Psi at 380°C	500 Psi at 400°C	2000 Psi at 385°C
PI/PAE/PI (3110)	2465 (50%)	----	----
PAE/PI/PAE (3110)	830 (0%)	1350 (0%)	2380 (90%)

copolymers. The copolymer was prepared twice, first in the powder form by solution imidizing and designated ϕ-PI/PAE/PI-ϕ (3110) SI and second as a poly(amic acid) solution and designated ϕ-PI/PAE/PI-ϕ (3110) for film casting. Characterization data of the copolymers is shown in Table 39. The inherent viscosity of 0.47 dL/g is essentially equivalent to that of the molecular weight controlled copolymer lacking end-caps described previously. The copolymers had the same Tg at 212°C but different Tms. The ϕ-PI/PAE/PI-ϕ (3110) SI melting point was 382°C, which is 12°C higher than for the thermally imidized copolymer. Similar results were seen for the high molecular weight material. The next column in Table 39 gives the recrystallization peak temperature which occurred on the second DSC scan after quenching the copolymer samples from 400°C on a RT metal surface. This is the first example of any copolymers studied which would recrystallize after heating above the original melting point. The recrystallization peak maxima were at 300°C for the solution imidized copolymer and at 310°C for the thermally imidized copolymer. Both peaks were very sharp, indicating a rapid recrystallization process. The ability to recrystallize is important since processing must occur above the original Tm, producing an amorphous material which can be annealed to recrystallize, thereby increasing selected properties. The thermal stability in both air and nitrogen is very good for both copolymers.

The ϕ-PI/PAE/PI-ϕ (3110) SI powder was placed in a small mold and heated to 380°C under 100 psi for 15 min. The molding produced was fully consolidated and a significant amount of molding flash was produced. This information was encouraging since the copolymer flowed so well at this low pressure (previous moldings were prepared at 500 psi) indicating that they could probably be processed at even lower pressure. However, the molding

Table 39

Characterization of ϕ-PI/PAE/PI-ϕ (3110) Copolymers

Copolymer	η_{inh}, dL/g^{a}	DSC Tg (Tm), °C^{b}	DSC Recrystallization, °C^{b}	TGA, Temperature at 5% Weight Loss, °C^{c} Air	N$_2$
ϕ-PI/PAE/PI-ϕ (3110) SI	—	212 (382)	300	450	505
ϕ-PI/PAE/PI-ϕ (3110)	0.47	212 (370)^{d}	310^{d}	455	510

^{a}Measured in NMP at 25°C and 0.5% concentration
^{b}Measured at a heating rate of 20°C/min
^{c}Heating rate of 2.5°C/min in atmosphere flowing at 15 ml/min
^{d}Film cured 1 h each at 100, 200 and 300°C

was extremely brittle and fractured under very little stress. The fracture toughness was not measured but would have been extremely low due to the low molecular weight. The previous copolymers prepared at the same molecular weight but not end-capped were tough (G_{Ic} = 6-9 in-lbs/in^2) but the toughness must be attributed to an increase in molecular weight during the molding process. Because of the brittleness in the ~ 9300 g/mole end-capped copolymers, it was decided that a higher molecular weight version would have a better balance of properties.

The next logical increase in molecular weight is to the copolymer containing five blocks of 3110 g/mole to give a $\overline{M}n \approx$ 15,550 g/mole. Synthesis of this copolymer is accomplished by using a 3:2 ratio of BABB/BTDA (3110) to ATPAE (BPF) 3110 followed by addition of an appropriate amount of aniline to end-cap, producing a copolymer designated ϕ-PI/PAE/PI/PAE/PI-ϕ (3110). As before, the same copolymer solution imidized is designated the same as above followed by SI.

Characterization of this end-capped copolymer is presented in Table 40. Several copolymer batches were prepared at 20% solids content and inherent viscosity ranged from 0.54 to 0.58 dL/g. This is higher than the viscosity of the previous copolymer (0.47 dL/g) as expected. Results from DSC are listed in Table 40 and actual DSC curves are shown in Figures 23 and 24 for the solution imidized and the thermally imidized copolymers, respectively. It is seen from the table that the Tgs are essentially the same while melting and recrystallization peak positions are different. The solution imidized copolymer melts 7°C higher (as expected) and recrystallizes 15°C lower than the thermally imidized copolymer. Examination of the figures reveals differences other than just the peak positions shown in Table 40. Each figure has two curves, the top curve is the 1st scan to 400°C followed by

Table 40

Characterization of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymers

				TGA, Temperature at 5% Weight Loss, °C[c]	
Copolymer	η_{inh}, dL/g[a]	DSC Tg (Tm), °C[b]	DSC Recrystallization, °C[b]	Air	N_2
ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) SI	—	225 (377)	305	475	515
ϕ-PI/PAE/PI/PAE/PI-ϕ (3110)	0.54-0.58[d]	223 (370)[e]	320[e]	480	520

[a] Measured in NMP at 25°C and 0.5% concentration
[b] Measured at a heating rate of 20°C/min
[c] Heating rate of 2.5°C/min in atmosphere flowing at 15 ml/min
[d] Range of viscosity for different batches
[e] Film cured 1 h each at 100, 200 and 300°C

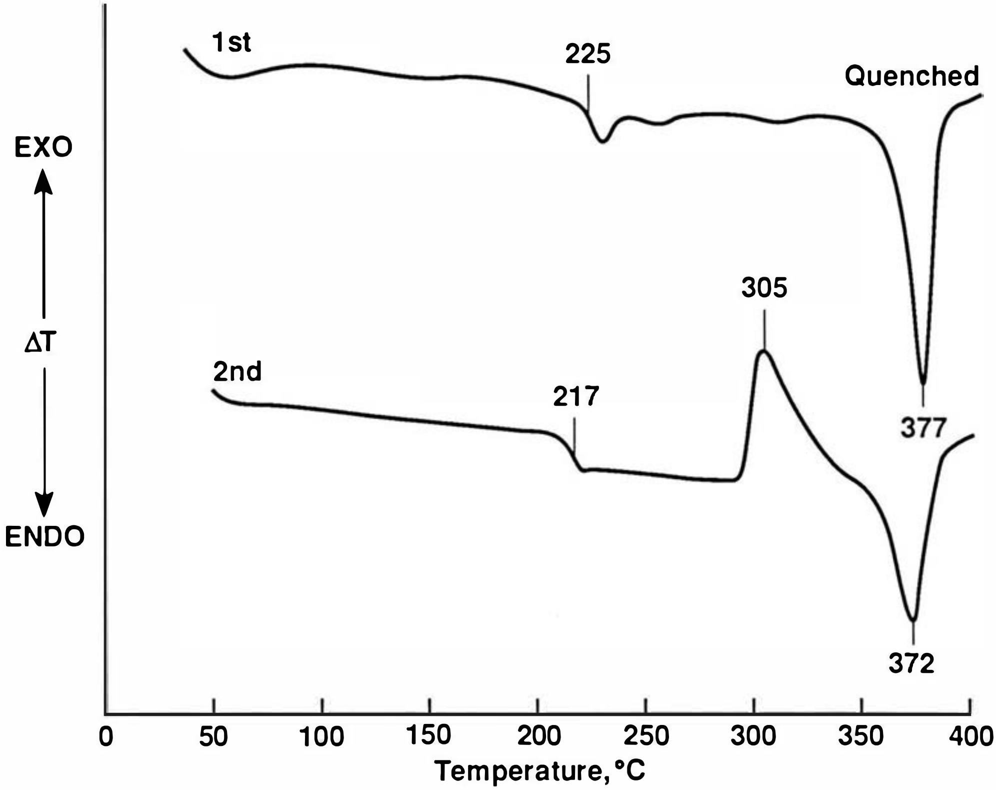


Figure 23. DSC curves for ϕ-PI/PAE/PI/PAE/PI-ϕ(3110) solution imidized powder.

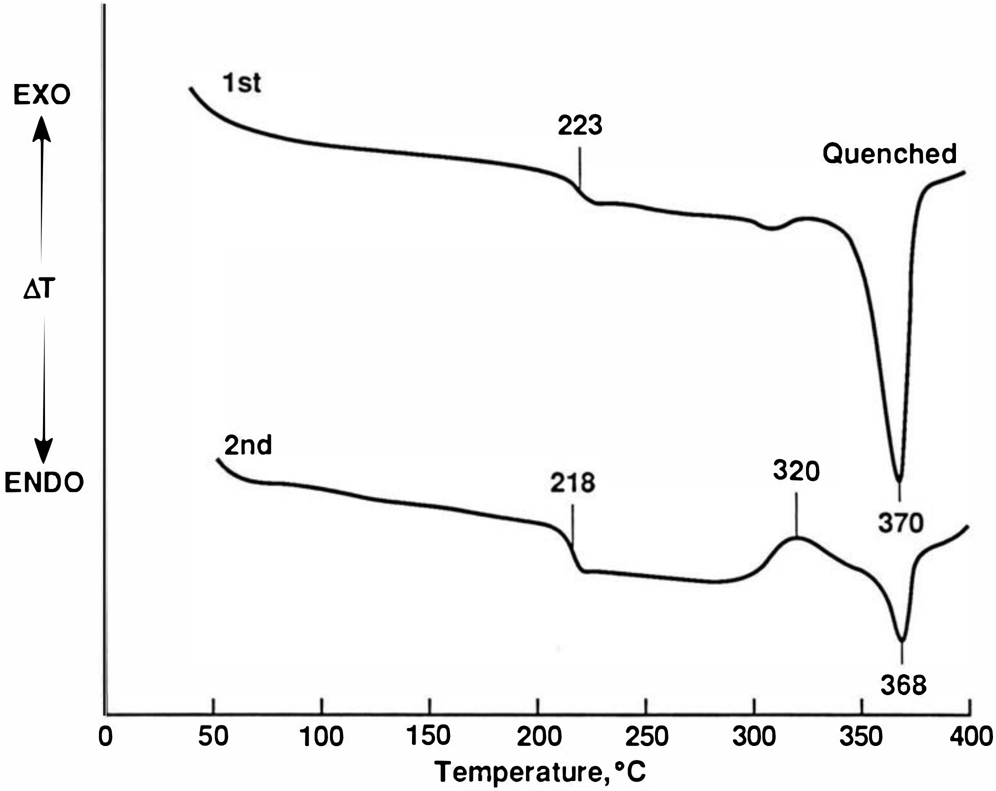


Figure 24. DSC curves for ϕ -PI/PAE/PI/PAE/PI- ϕ(3110) thermally imidized film.

quenching and the bottom curve is the same sample rerun after quenching. The solution imidized powder was run after drying in air at 110°C and the thermally imidized sample was from a film cured 1 h each at 100, 200 and 300°C. The Tgs have shifted 5-8°C lower on the second run, which is when the copolymer is completely amorphous. Also, the recrystallization peak for the solution imidized copolymer is larger and sharper than for the thermally imidized copolymer. Furthermore, the subsequent melting peak is more intense indicating a higher amount of crystallinity in the solution imidized copolymer as expected from previous data on high molecular weight copolymers. DSC instrument settings are the same in both figures and sample size is larger (12.4 mg vs 9.9 mg) for the thermally imidized copolymer. The last column in Table 40 shows that TGA data and thermal stabilities are again very good.

Molding the copolymer at 380°C and 100 psi for 15 min produced a good, consolidated molding with a small amount of molding flash, indicating that the processing conditions were adequate but not excessive. Compact tension specimens were cut from this molding and tested for fracture toughness and energy. The resulting fracture toughness (K_{Ic}) was 455 psi $\sqrt{\text{in}}$ and fracture energy (G_{Ic}) was 0.42 in · lbs/in^2. These values were lower than desired but increasing toughness by increasing molecular weight would compromise processability. Therefore, a decision was made to continue work with this system.

Ti/Ti tensile shear strength was measured for the ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) copolymer with results listed in Table 41. The glass scrim cloth was coated with a 20% solids solution of the copolymer in NMP and dried 1 h each at 100 and 200°C to convert most of the poly(amic) acid to polyimide and to remove the solvent. Approximately 10 coats were required to produce

Table 41

Adhesive Properties of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymer

Test Temperature	Ti/Ti Tensile Shear Strength,[a] Psi			
	200 Psi	200 Psi, Then Annealed 16 h at 310°C	200 Psi, Then Aged 100 h at 316°C	100 Psi
RT	5050 (Coh)	4950 (Coh)	4200 (Coh)	5050 (Coh)
93°C	4950 (Coh)	4850 (Coh)	——	4850 (Coh)
177°C	3350 (Coh)	4250 (Coh)	3700 (Coh)	3550 (Coh)
232°C	300 (Ad)	1100 (Ad)	1250 (Ad)	——

[a] All samples bonded at 380°C for 20 min under listed pressure

[b] (Coh) = cohesive failure, (Ad) = adhesive failure

a 12 mil thick boardy tape. All samples listed in the table were heated to 380°C under the pressure listed and held at 380°C for 20 min. The first column shows the as prepared 200 psi data which was excellent from RT to 177°C and poor at 232°C. In an effort to increase the adhesive properties at 232°C, samples were annealed for 16 h at 310°C to induce crystallinity. The second column shows that annealing under these conditions increases tensile shear strength at both 177 and 232°C while maintaining excellent values at RT and 93°C. To gain information on thermal stability of the adhesive, samples were aged 100 h at 316°C. This aging produces a slight decrease in RT properties but an increase in 177 and 232°C strength when compared to the as prepared samples. Aging produces higher amounts of crystallinity, increasing high temperature properties, but most likely reduces toughness resulting in slightly lower RT strength. Overall these results are excellent and the 232°C values of over 1000 psi were impressive considering the copolymer Tg was ~ 220°C. Examination of the adhesive samples showed the adhesive had flowed very well and the pressure applied during bonding may have been excessive. Therefore, additional adhesive samples were prepared under the same conditions except the pressure was reduced from 200 psi to 100 psi. The last column in Table 41 gives these results indicating that 200 psi is not necessary to produce excellent strength in Ti/Ti tensile shear specimens. To study the effect of processing temperature on adhesive strengths, samples were prepared at 340 and 360°C under 100 psi for 20 min. Resulting tensile shear strengths were 450 and 1850 psi, respectively. As expected, to obtain good adhesive values, temperatures above the melting point of the copolymer (~ 375°C) were required.

Unidirectional composites using Hercules AS-4 graphite fiber and ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) were prepared. Prepreg was first prepared by coating the fiber with a 20% solids copolymer solution in NMP but the amount of resin on the fiber was low at 31.7%. Desirable resin content of prepregs is 36-38% which typically produce composites with the desired 32-34% resin content. There are several methods to increase the amount of resin applied to the fiber such as increasing the die size and increasing the concentration of the polymer solution. The next die size available was much larger than necessary, so the solution concentration was changed. A large amount of 20% solids solution had been prepared and a 25% solution was needed, so an equal amount of 30% solids copolymer in NMP was prepared and combined with the 20% solution. The resulting 25% solids solution produced prepreg with 36.3% and 37.7% resin on consecutive runs, within the range desired, under the conditions discussed in the experimental. Unidirectional composites were prepared in a 3 in. x 3 in. stainless steel mold by heating to 380°C under 300 psi and holding at temperature and pressure for 15 min. Ten ply composite panels were prepared for flexural specimen (~ 0.075 in. thick) and 18 ply composite panels were prepared for short beam shear specimen (~ 0.125 in. thick). Results from flexural and short beam shear tests are shown in Table 42. The flexural properties were measured at RT, 93°C and 177°C while short beam shear strength was also tested at 232°C. The flexural strength of 216,000 psi is very good for a thermoplastic matrix composite and retention of flexural strength at elevated temperature is excellent (> 77% strength retention of 177°C). The flexural modulus is also very good at RT and retention of modulus at elevated temperature is excellent. The short beam shear strengths were measured on the as prepared composite and on composite which had been annealed for 16 h at 310°C. The properties from the as prepared composite are very good at RT and 93°C but decrease rapidly from 177°C and higher. Samples annealed to

Table 42

Composite Properties of ϕ-PI/PAE/PI/PAE/PI-ϕ (3110) Copolymer

Test Temperature	Flexural Strength, Psi	Flexural Modulus, Psi	Short Beam Shear Strength, Psi	
			As Prepared	Annealed 16 h at 310°C
RT	216,000	17.0×10^6	10,700	10,100
93°C	198,000	16.4×10^6	9,400	9,300
177°C	167,000	16.5×10^6	6,700	8,300
232°C	——	——	1,400	5,600

induce crystallinity had similar properties to the unannealed samples at RT and 93°C, but much better short beam shear strengths at 177°C and 232°C than the as prepared sample.

CONCLUSIONS

A series of novel polyimide/poly(arylene ether) copolymers have been prepared. Two different polyimides and two different poly(arylene ethers), with block molecular weights of 3110 and 6545 g/mole, were used to prepare the block and segmented copolymers. One polyimide was semi-crystalline which led to semi-crystalline copolymers. Copolymers displayed very good mechanical properties, excellent fracture toughness and very good thermal stability. One block copolymer was selected, because of an overall excellent combination of properties, for end-capping molecular weight control studies and evaluation as an adhesive and graphite composite matrix. The processability of the end-capped copolymer was good, showing an improvement over the polyimide homopolymer, and adhesive and composite properties were very good.

REFERENCES

(1) P. M. Hergenrother, "Heat-Resistant Polymers," *Encyclopedia of Polymer Science and Engineering*, 2nd ed., vol. 7, pp. 639-665 (1987).

(2) P. E. Cassidy, *Thermally Stable Polymers*, Dekker, New York, 2, 1980.

(3) T. L. Cottrell, *The Strength of Chemical Bonds*, 2nd ed., Butterworths, London, 1958.

(4) F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Wiley and Sons, New York, 1971.

(5) H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, Ch. 1, 1981.

(6) R. F. Boyer, "Automated Dynamic Mechanical Testing," "Polymer Characterization" in Advances in Chemistry Series of ACS, C. D. Carver, Ed., Washington, DC, 1983.

(7) W. H. Carothers, *Trans. Faraday Soc.*, *32*, 39 (1936).

(8) A. Noshay and J. E. McGrath, *Block Copolymers: Overview and Critical Survey*, Academic Press, New York, 1977.

(9) F. A. Bovey and F. H. Winslow, Eds., *Macromolecules: An Introduction to Polymer Science*, Academic Press, New York, 1979.

(10) W. M. Edwards and I. M. Robinson, U.S. Patent 2,710,853 (June 1955).

(11) W. A. Feld, B. Ramalingam and F. W. Harris, *J. Polym. Sci., Polym. Chem. Ed.*, *21*, 319 (1983).

(12) F. W. Harris, M. W. Beltz, S. Das and R. K. Gupta, *Polym. Prepr.*, *25*(1), 160 (1984).

(13) F. W. Harris, A. J. Karnavas, C. N. Cucuras and S. Das, Polym. Prepr., 26(2), 287 (1985).

(14) F. W. Harris, A. J. Karnavas, S. Das, C. N. Cucuras and P. M. Hergenerother, Polym. Matl. Sci. Eng. Proceedings, 54, 89 (1986).

(15) F. W. Harris, M. W. Beltz and P. M. Hergenrother, SAMPE J., 23(1), 6 (1987).

(16) B. J. Jensen and P. R. Young, Polyimides, K. L. Mittal, Ed., Plenum Pub. Co., New York, vol. 1, 417 (1984).

(17) G. M. Bower and L. W. Frost, J. Polym. Sci., A1, 3135 (1963).

(18) W. M. Edwards, U.S. Patents 3,179,164 and 3,179,634 (April 1965 to DuPont).

614

(19) A. L. Endrey, U.S. Patents 3,179,631 and 3,179,633 (April 1965 to DuPont).

(20) V. L. Bell, B. L. Stump and H. Gager, J. Polym. Sci., Polym. Chem. Ed. 14, 2275 (1976).

(21) A. H. Egli and T. L. St. Clair in Recent Advances in Polyimide Science and Technology, W. D. Weber and M. R. Gupta, Eds., Society of Plastics Engineers, Inc., Poughkeepsie, New York, 57 (1987).

(22) R. A. Orwoll, T. L. St. Clair and K. D. Dobbs, J. Polym. Sci., Polym. Phys. Ed., 19, 1385 (1981).

(23) T. L. St. Clair and D. J. Progar in Adhesion Sci. Tech., L. H. Lee, Ed. Plenum Press, New York, 187 (1975).

(24) W. Volksen and P. M. Cotts in Polyimides, K. L. Mittal, Ed., Plenum Press, New York, vol. 1, 1984, p. 163.

(25) P. Cotts and W. Volksen, ACS Symp. Ser. 242, 227 (1984).

(26) C. C. Walker, J. Polym. Sci.: Pt. A. Polym. Chem. 26, 1649 (1988).

(27) R. A. Dine-Hart and W. W. Wright, J. Appl. Polym. Sci. 11, 609 (1967).

(28) V. Y. Smirnova, L. A. Laius, M. I. Bessonov, S. V. Bushin, T. I. Garmonova, M. M. Koton, V. S. Skazka and L. M. Shcherbakova, Polym. Sci. USSR 17(10), 2549 (1975).

(29) P. R. Young and A. C. Chang, Soc. Adv. Matl. Proc. Eng. Series 32, 1051 (1987).

(30) P. R. Young, J. R. J. Davis and A. C. Chang, Sci. Adv. Matl. Proc. Eng. Series 34, 1450 (1989).

(31) H. H. Gibbs and C. V. Breder, Polym. Prepr. 15(1), 775 (1974).

(32) A. K. St. Clair, T. L. St. Clair and K. T. Shevket, Polym. Matl. Sci. Eng. Prepr. 51, 62 (1984).

(33) C. E. Sroog, "Polyimides" in Encyclopedia of Polymer Science and Technology, H. F. Mark, N. G. Gaylord and N. M. Bikales, Eds., Interscience, New York, 1969, vol. 11, p. 247.

(34) C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards and K. L. Oliver, J. Polym. Sci. A, 3, 1373 (1965).

(35) R. M. Ikeda, J. Polym. Sci. B, 4, 353 (1966).

(36) N. A. Adrova , M. I. Bessonov, L. A. Laius and A. P. Rudakov, Polyimides, Technomic Publishing Co., Inc., Stamford, CT, 1970.

(37) T. L. St. Clair and A. K. St. Clair, J. Polym. Sci., Polym. Chem. Ed., 15, 1529 (1977).

(38) E. I. DuPont Co., Wilmington, DE 19898.

(39) S. Isoda, H. Shimoda, M.Kochi and H. Kambe, J. Polym. Sci., Polym. Phys. Ed., 19, 1293 (1981).

(40) S. Isoda, M.Kochi and H. Kambe, J. Polym. Sci., Polym. Phys. Ed., 20, 837 (1982).

(41) P. M. Hergenrother, N. T. Wakelyn and S. J. Havens, J. Polym. Sci.: Pt. A: Polym. Chem. 25, 1093 (1987).

(42) P. M. Hergenrother and S. J. Havens, SAMPE J. 24(4), 13 (1988).

(43) Lenzing Aktiengesellschaft, A-4860 Lenzing, Austria.

(44) Ciba-Geigy Corp., Hawthorne, NY 10532.

(45) General Electric Co. Pittsfield, MA 01202.

(46) Mitsui-Toatsu Chemicals, Inc., 140 E. 45th St., New York, NY 10017.

(47) M. I. Bessonov, M. M.Koton, V. V. Kudryavtsev and L. A. Laius, Polyimides, Plenum Publishing Co., New York, 1987.

(48) J. P. Critchley, G. J. Knight and W. W. Wright, Heat Resistant Polymers, Plenum Press, New York, 1983.

(49) Polyimides, K. L. Mittal, Ed., Plenum Press, New York, vols. 1 and 2, 1984.

(50) "Recent Advances in Polyimide Science and Technology," W. D. Weber and M. R. Gupta, Eds., Society of Plastics Engineers, Inc., Poughkeepsie, New York, 1987.

(51) P. M. Hergenrother, "Heat Resistant Polymers" in Encyclopedia of Polymer Science and Engineering, 2nd ed., vol. 7, pp. 639-665 (1987).

(52) A. Kreuchumas, U.S. Patent 2,822,351 (1958).

(53) W. H. Bonner, U.S. Patent 3,065,205 (1962) (to DuPont)

(54) B. M. Marks, U.S. Patent 3,441,538 (1969)

(55) H. W. Colquhoun and D. F. Lewis, British Patent 2,116,990 (1983).

(56) V. Jansons, U.S. Patent 4,361,693 (1982).

(57) K. J. Dahl, U.S. Patent 3,956,240 (1976).

(58) V. Jansons and H. C. Gors, WO 84 03, 892 (1984).

(59) F. Effenberger and G. Epple, Angew. Chem. Int. Ed., 11, 299 (1972).

(60) I. Goodman, J. E. McIntyre and W. Russell, British Patent 971,227 (1964).

(61) N. L. Allinger, M. P. Cava, D. C. DeJongh, C. R. Johnson, N. A. Lebel and C. L. Stevens, Organic Chemistry, 2nd ed., Worth Publishers, Inc., New York, 1976.

(62) B. E. Jennings, M. E. B. Jones and J. B. Rose, J. Polym. Sci. Part C, 715 (1967).

(63) J. B. Rose, Chem. Ind. (London), 461 (1968).

(64) R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam, J. Polym. Sci. Part A-1, 5, 2375 (1967).

(65) R. N. Johnson and A. G. Farnham, British Patent 1,078,234 (1967).

(66) R. N. Johnson and A. G. Farnham, U.S. Patent 4,108,837 (1978).

(67) I. C. Taylor, German Patent 2,635,101 (1977).

(68) B. Gerd and C. Claus, German Patent 2,749,645 (1978).

(69) R. Viswanathan, B. C. Johnson and J. E. McGrath, Polymer 25, 1827 (1984).

(70) D. K. Mohanty, Y. Sachdeva, J. L. Hedrick, J. F. Wolfe and J. E. McGrath, Polym. Prepr., 25(2), 19 (1984).

(71) B. J. Jensen, P. M. Hergenrother and S. J. Havens, Polym. Prepr. 26(2), 174 (1985).

(72) P. M. Hergenrother, S. J. Havens and B. J. Jensen, Intl. SAMPE Tech. Conf. Series, 18, 454 (1986).

(73) P. M. Hergenrother, B. J. Jensen and S. J. Havens, Polymer 29, 358 (1988).

(74) T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose and P. A. Staniland, Polymer, 22, 1096 (1981).

(75) J. B. Rose, British Patent 1,414,424 (1975).

(76) J. B. Rose, U.S. Patent 4,010,147 (1977).

(77) T. E. Attwood, A. B. Newton and J. B. Rose, Br. Polym. J., 4, 391 (1972).

(78) T. E. Attwood, T. King, I. D. McKenzie and J. B. Rose, Polymer, 18, 365 (1977).

(79) P. A. Staniland, U.S. Patent 4,331,798 (1982).

(80) Amoco Performance Products Inc., Bound Brook, NJ 08805

(81) ICI Americas Inc., Wilmington, DE 19897

(82) M. J. Mullins and E. P. Woo, J. Macromol. Sci. Revs. Macromol. Chem. Phys. C27(2), 313 (1987).

(83) J. B. Rose, Polymer, 15, 456 (1974).

(84) F. F. Holub, U.S. Patent 3,325,450 (1967).

(85) F. F. Holub, U.S. Patent 3,598,784 (1971).

(86) W. A. Fessler, U.S. Patent 3,736,290 (1973).

(87) J. T. Hoback and F. F. Holub, U.S. Patent 3,740,305 (1973).

(88) J. E. McGrath, P. M. Sormani, C. S. Elsbernd and S. Kilic, Makromol. Chem., Macromol. Symp., 6, 67 (1986).

(89) J. D. Summers, C. A. Arnold, R. H. Bott, L. T. Taylor, T. C. Ward and J. E. McGrath, Polym. Prepr., 27(2), 403 (1986).

(90) C. A. Arnold, J. D. Summers, R. H. Bott, L. T. Taylor, T. C. Ward and J. E. McGrath, SAMPE Symposium No. 32, 586 (1987).

(91) C. A. Arnold, J. D. Summers, D. Chen, Y. P. Chen and J. E. McGrath, Polym. Prepr., 29(1), 349 (1988).

(92) B. C. Johnson, J. L. Hedrick, F. Campbell and J. E. McGrath, SAMPE Symp. Series, 29, 447 (1984).

(93) H. R. Kricheldorf, G. Schwarz and W. Nowatzky, Polymer, 30, 936 (1988).

(94) J. L. Hedrick, J. G. Hilborn and J. W. Labadie, Polym. Prepr., 30(1), 265 (1989).

(95) P. E. Cassidy, M. Arai, J. M. Farley and M. Mores, Polym. Matl. Sci. Eng., 60, 304 (1989).

(96) M. M. Grade and J. W. Verbicky, Jr., J. Polym. Sci., Polym. Chem. Ed., 27, 1467 (1989).

(97) R. Barclay, Jr., U.S. Patent 3,069,386 (1962).

(98) A. S. Hay, German Patent 2,738,962 (1978).

(99) A. S. Hay, German Patent 2,819,582 (1979).

(100) G. R. Loucks and F. J. Williams U.S. Patent 4,136,087 (1979).

(101) A. S. Hay, F. J. Williams, H. M. Relles, B. M. Boulette, P. E. Donahue and D. S. Johnson, J. Polym. Sci., Polym. Lett. Ed., 21(6), 449 (1983).

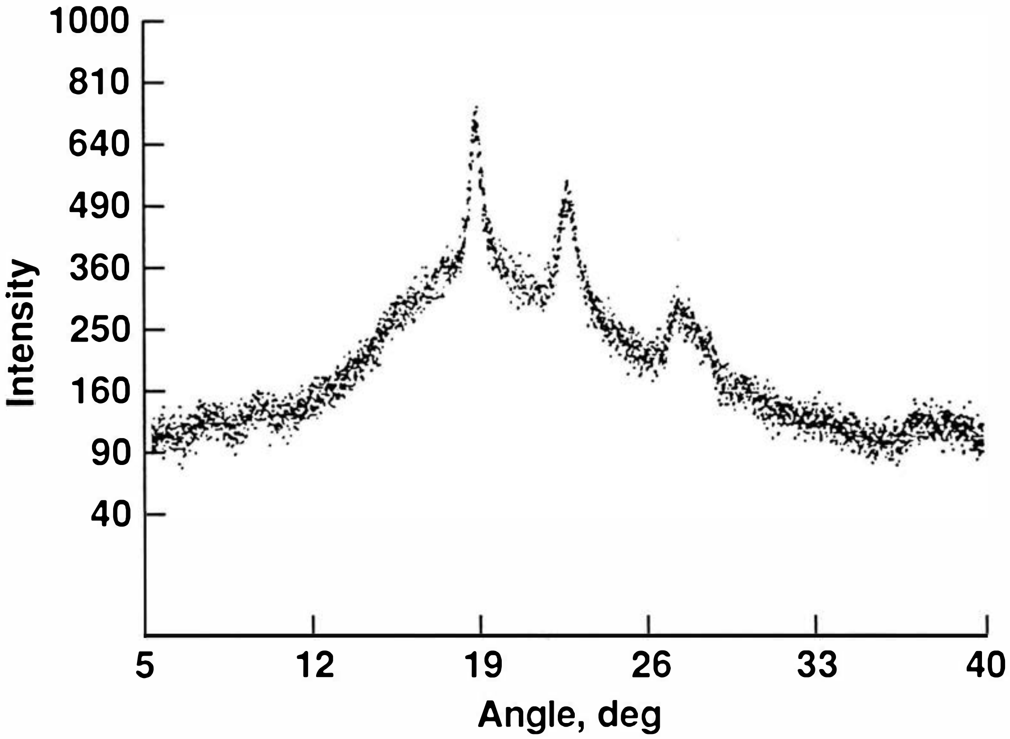
(102) P. M. Hergenrother and S. J. Havens, Polyimides: Materials, Chemistry and Characterization, C. Feger, M. M. Khojasteh and J. E. McGrath, Eds., Elsevier, Amsterdam, 453 (1989).

(103) J. A. Hinkley, J. Appl. Polym. Sci., 32, 5653 (1986).

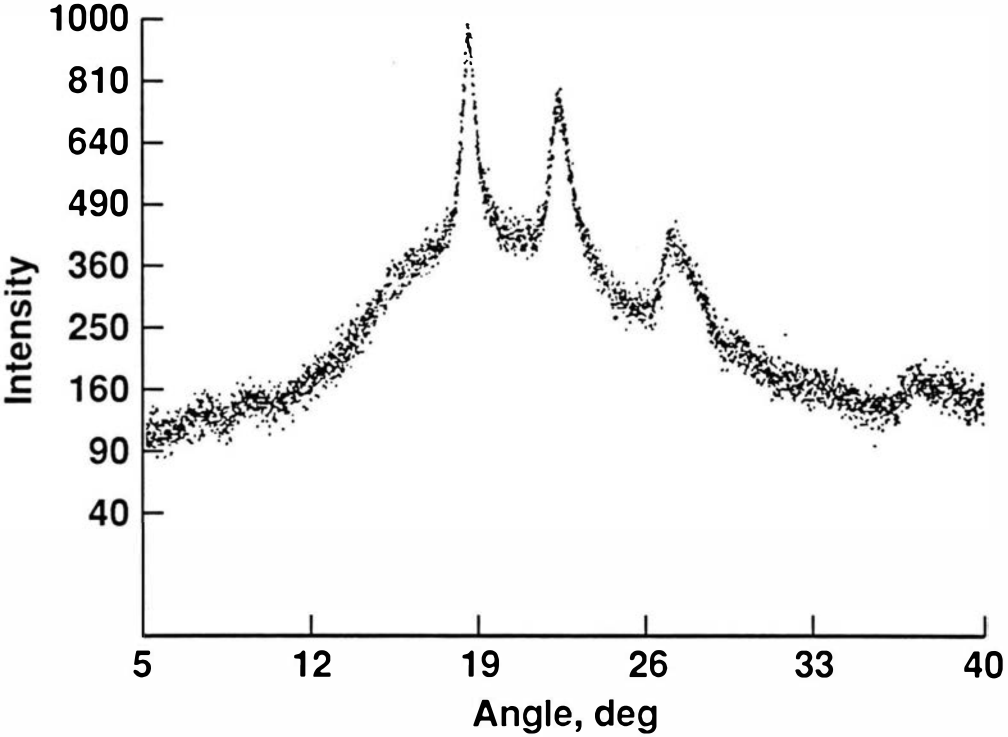
(104) I. Smedley, J. Chem. Soc., 87, 1249 (1905).

(105) U.S. Patent Application, Serial Number 07/035, 430, Filed April 7, 1987 (Terry L. St. Clair).

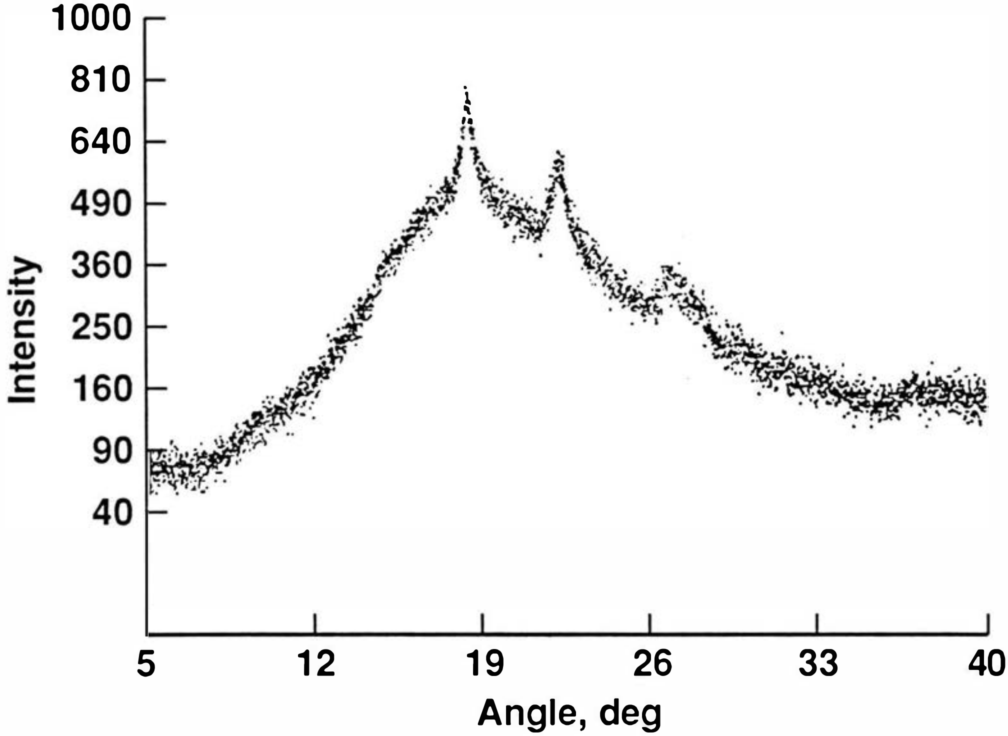
(106) P. M. Hergenrother and N. J. Johnston, Polym. Matl. Sci. Eng., 59, 697 (1988).



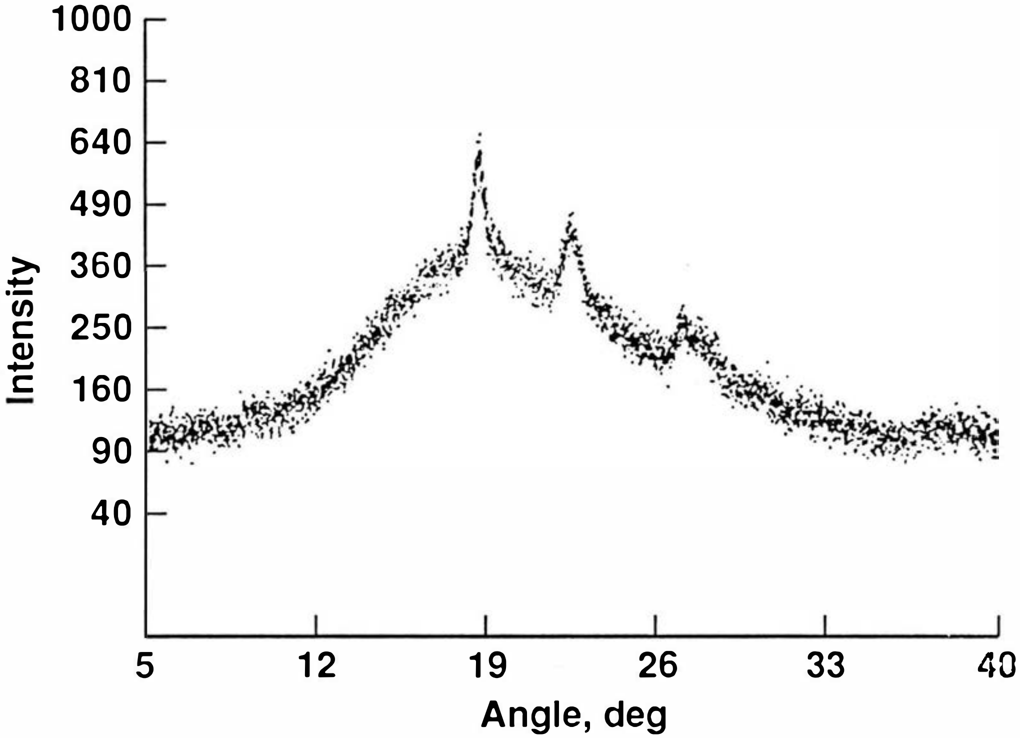
X-ray diffraction pattern for ATPAE (BPA) 3110// BABB/BTDA 3110 copolymer film.



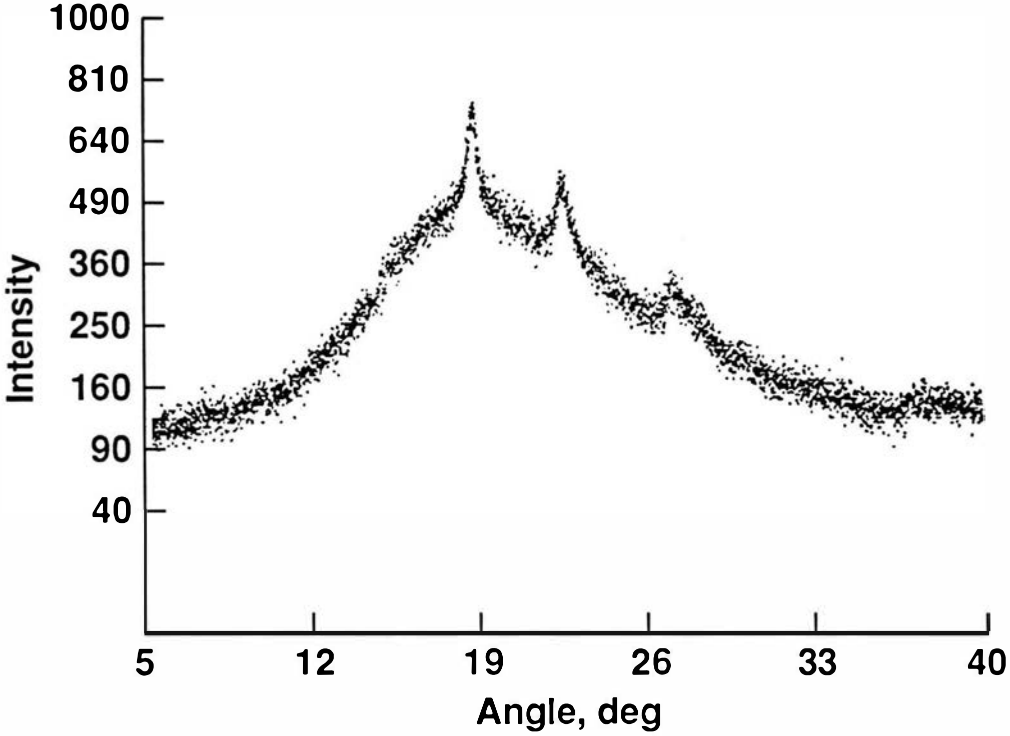
X-ray diffraction pattern for ATPAE (BPA) 3110// BABB/BTDA 6545 copolymer film.



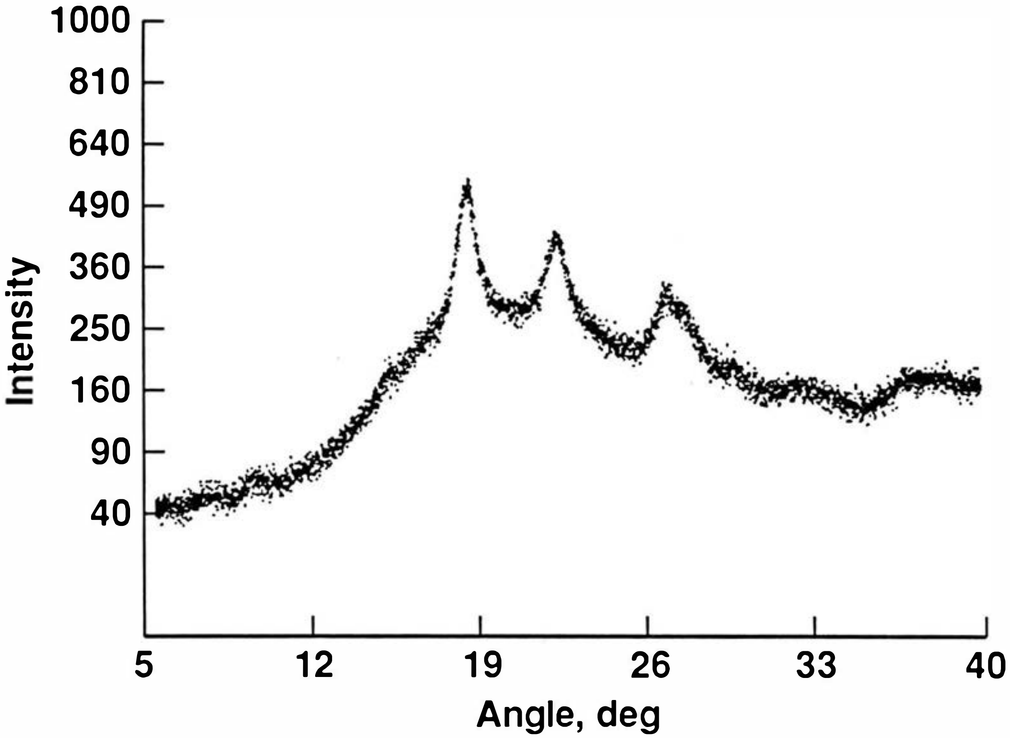
X-ray diffraction pattern for ATPAE (BPA) 6545// BABB/BTDA 3110 copolymer film.



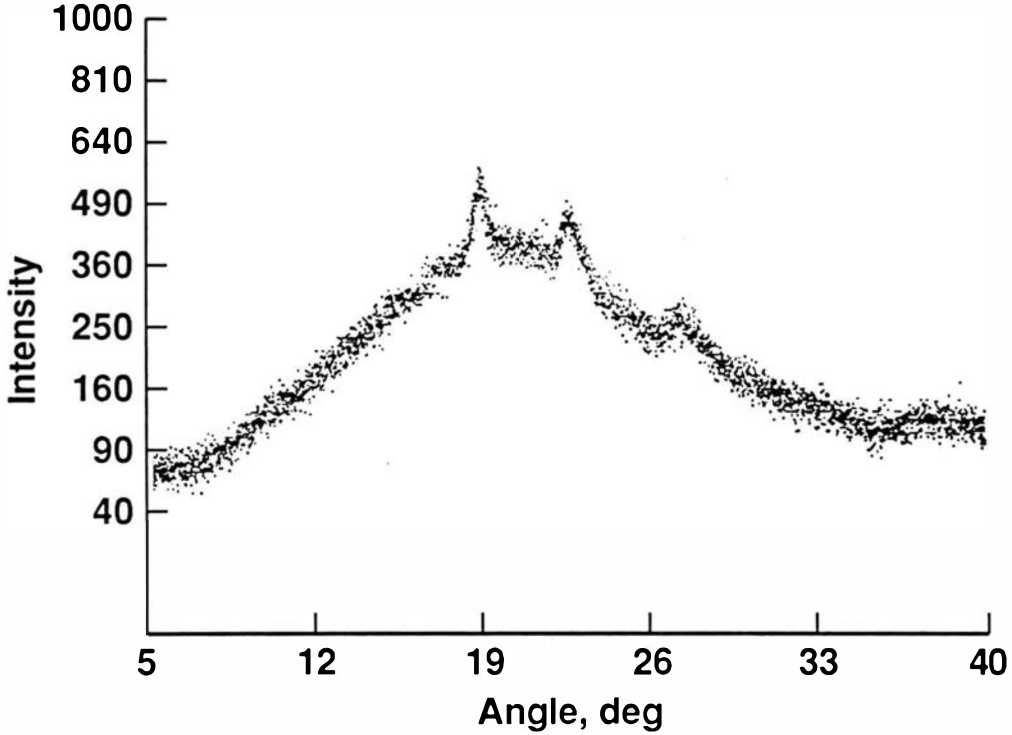
X-ray diffraction pattern for ATPAE (BPA) 6545// BABB/BTDA 6545 copolymer film.



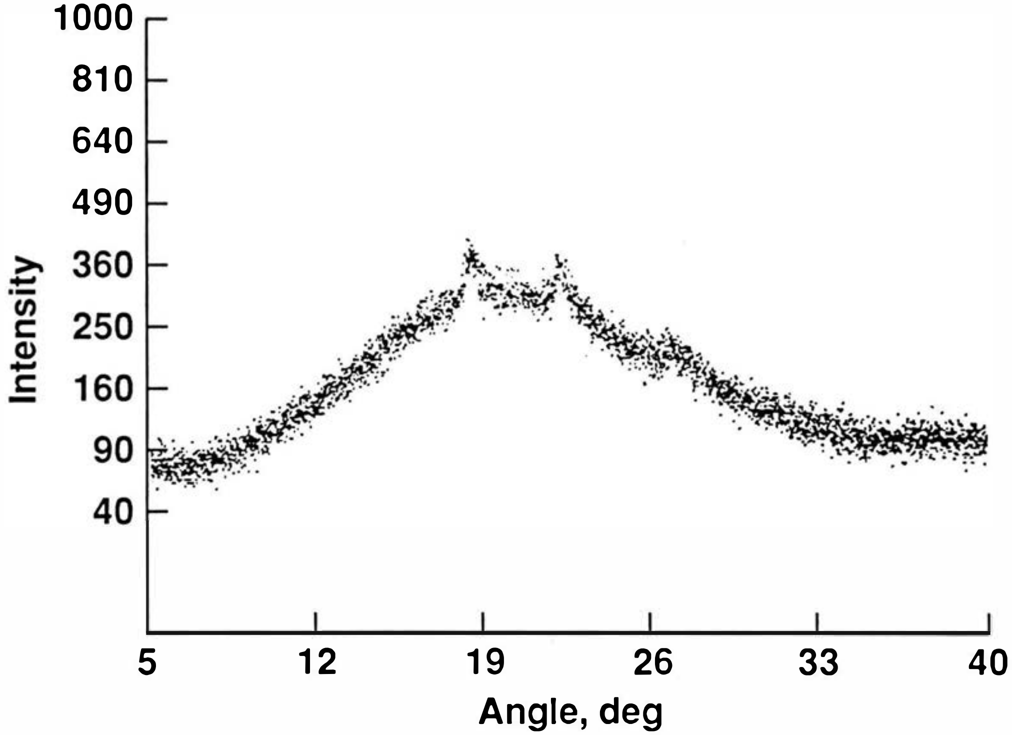
X-ray diffraction pattern for ATPAE (BPA) 6545 + [BABB + BTDA (6545)] segmented copolymer film.



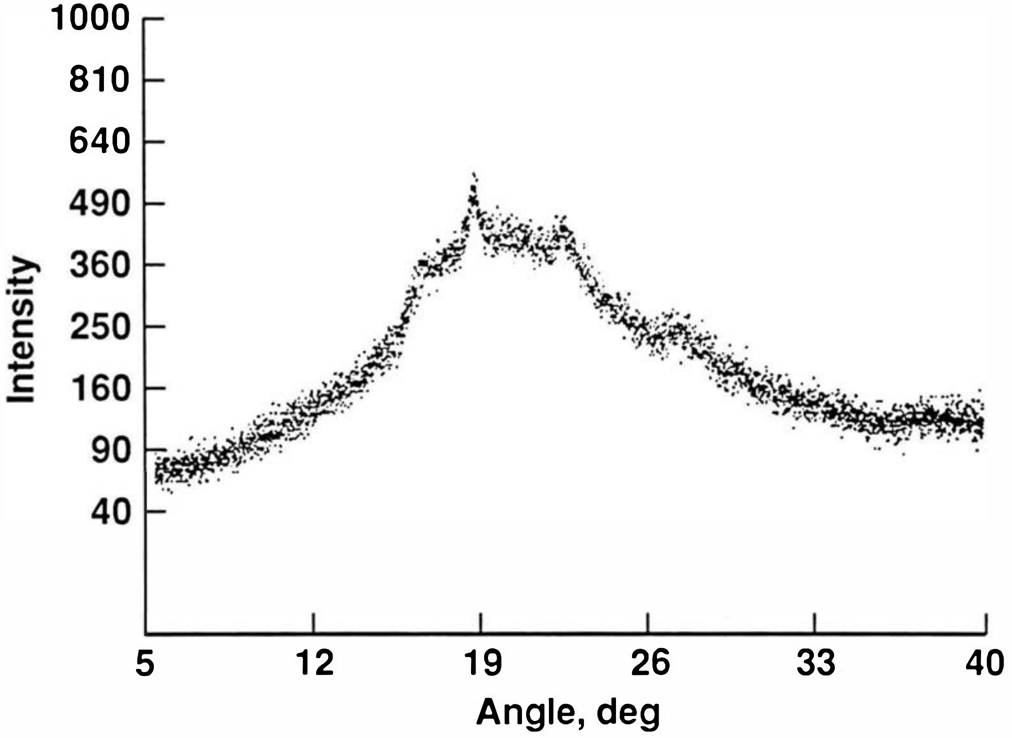
X-ray diffraction pattern for ATPAE (BPA) 6545// BABB/BTDA 6545 solution imidized copolymer powder.



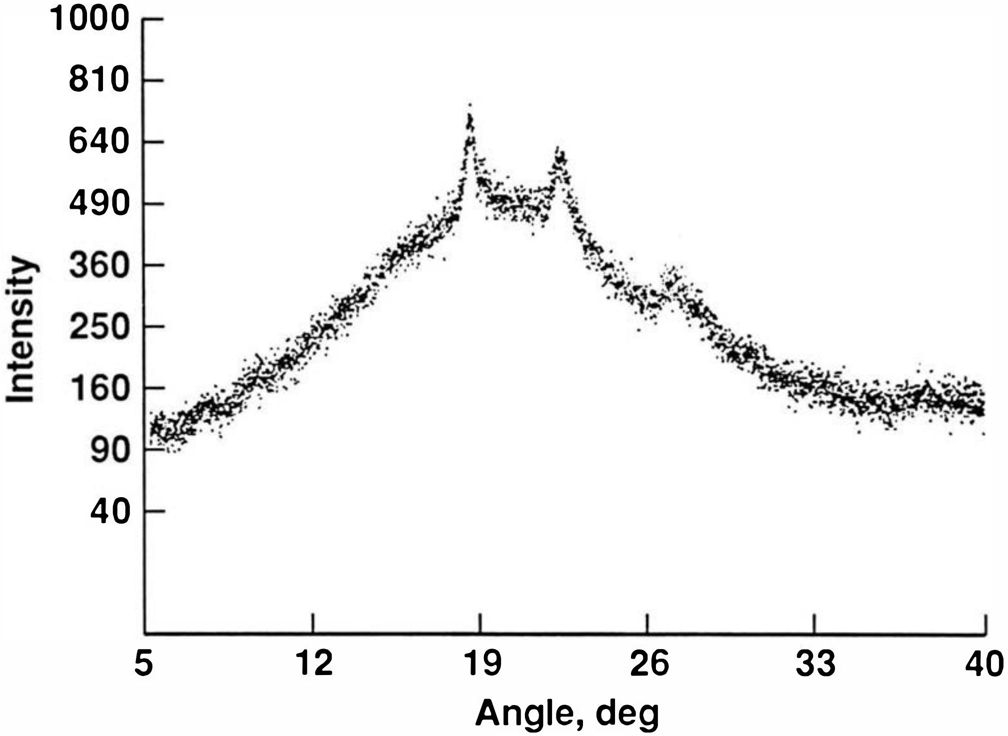
X-ray diffraction pattern for ATPAE (BPF) 3110// BABB/BTDA 3110 copolymer film.



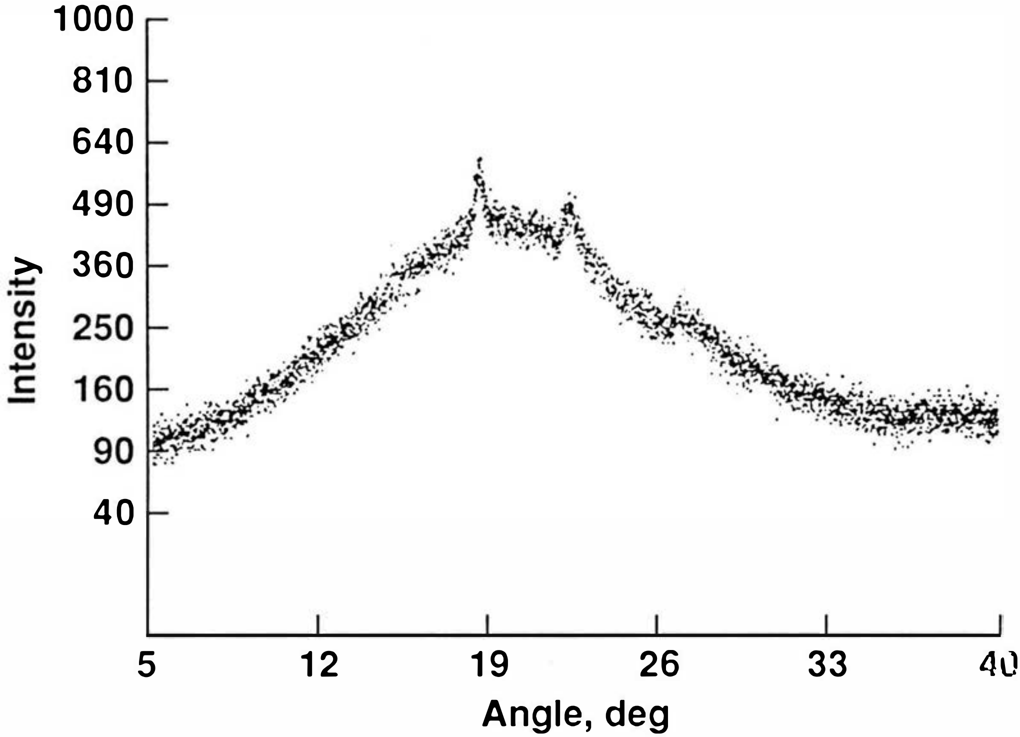
X-ray diffraction pattern for ATPAE (BPF) 3110//BABB/BTDA 6545 copolymer film.



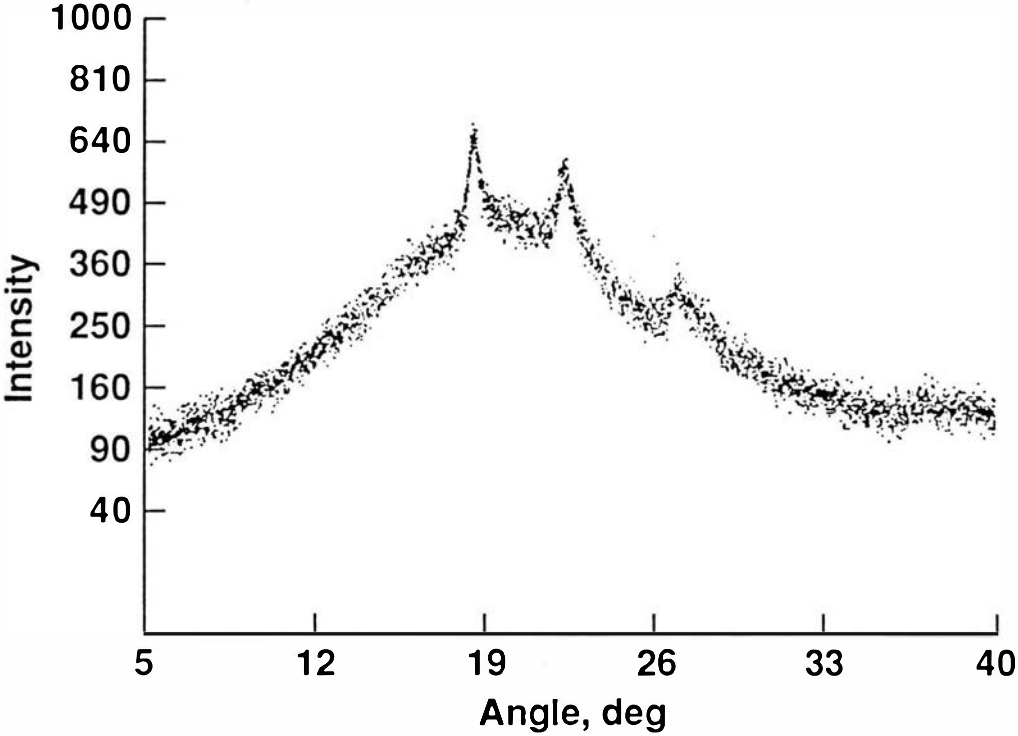
X-ray diffraction pattern for ATPAE (BPF) 6545// BABB/BTDA 3110 copolymer film.



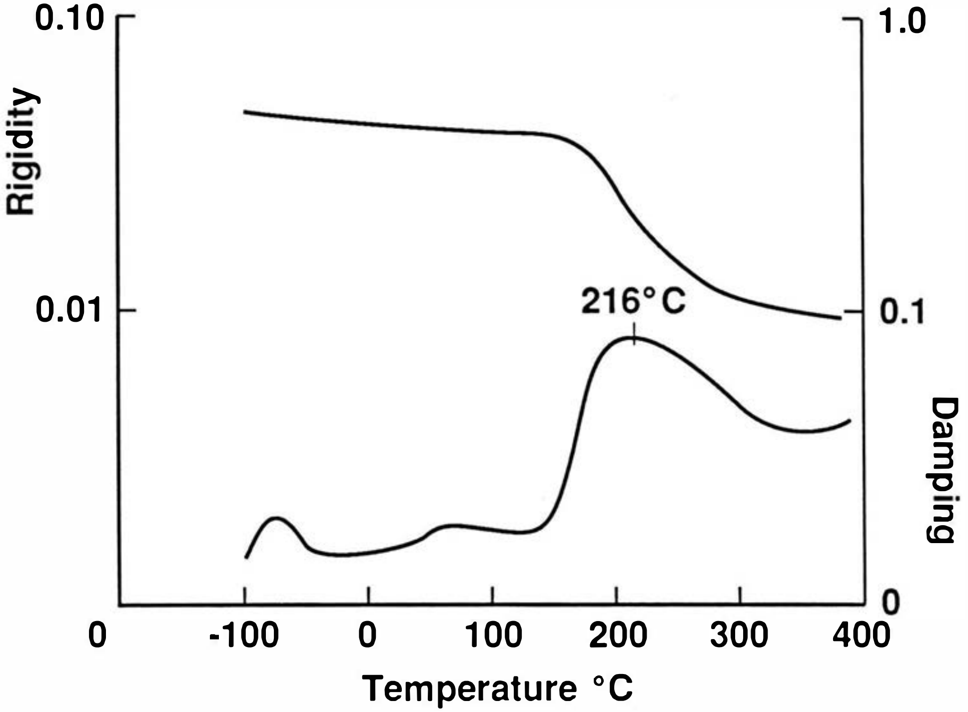
X-ray diffraction pattern for ATPAE (BPF) 6545// BABB/BTDA 6545 copolymer film.



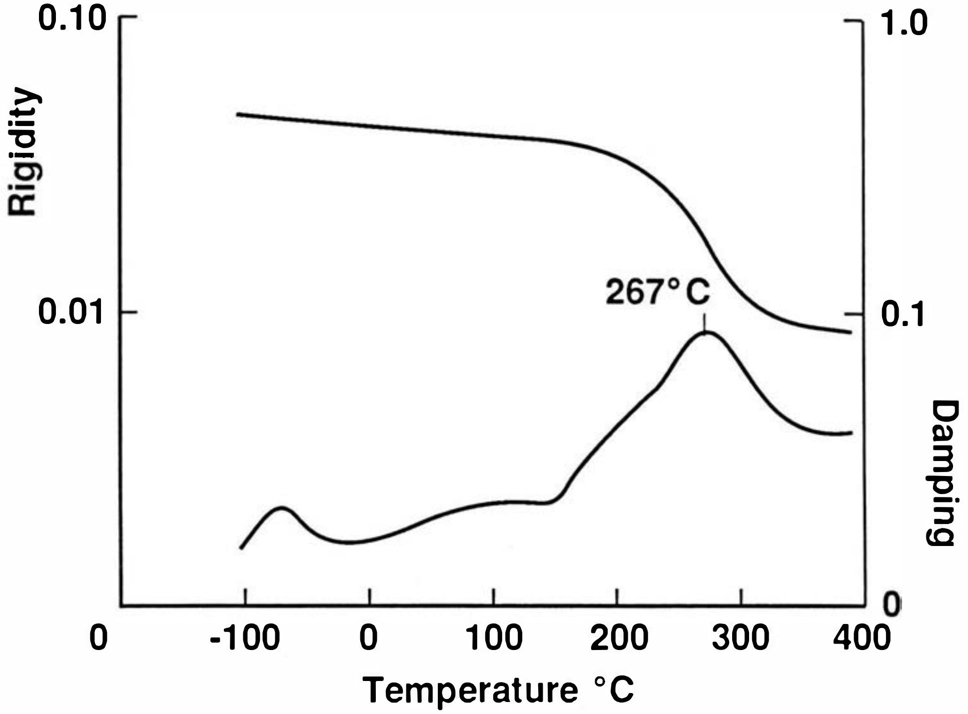
X-ray diffraction pattern for ATPAE (BPF) 3110 + [BABB +BTDA (3110)] segmented copolymer film.



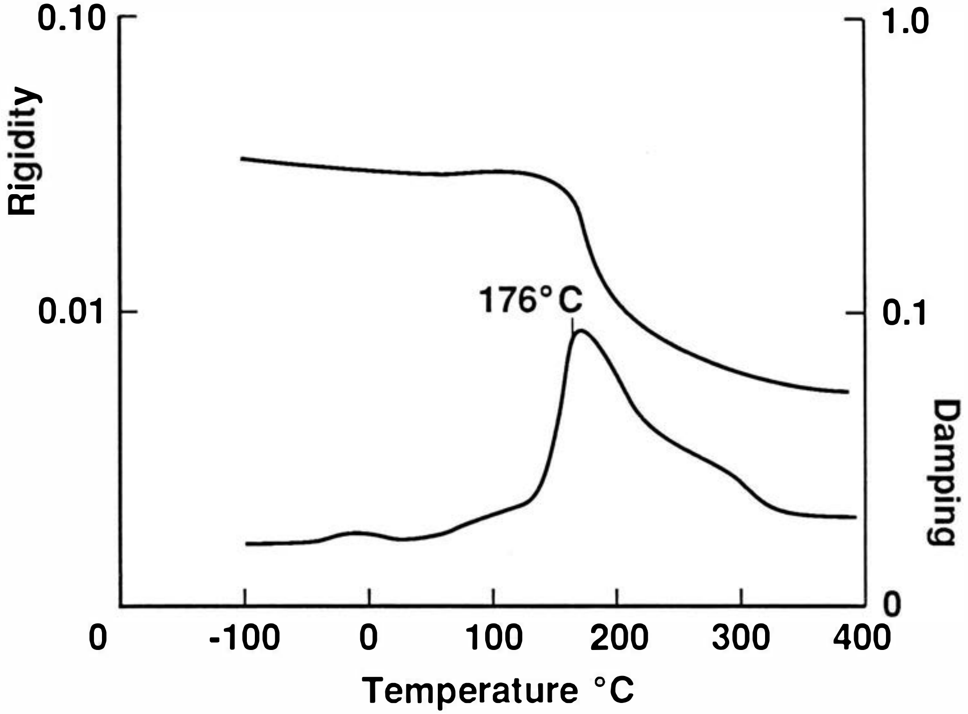
X-ray diffraction pattern for ATPAE (BPF) 6545 + [BABB + BTDA (6545)] segmented copolymer film.



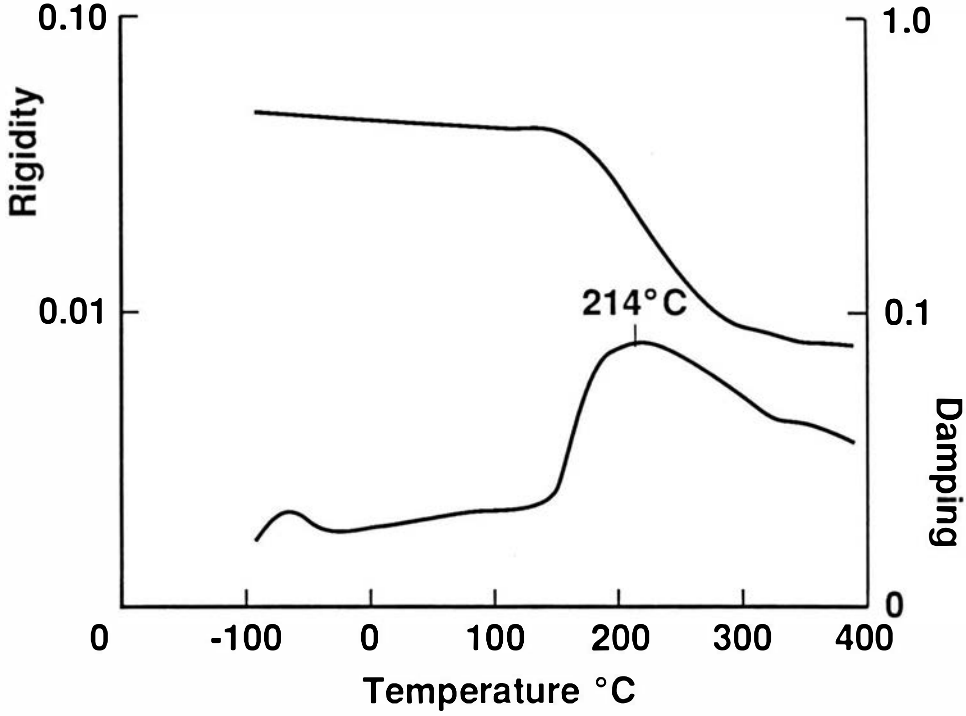
TBA of ATPAE (BPA) 3110//ODA/BTDA 3110 copolymer.



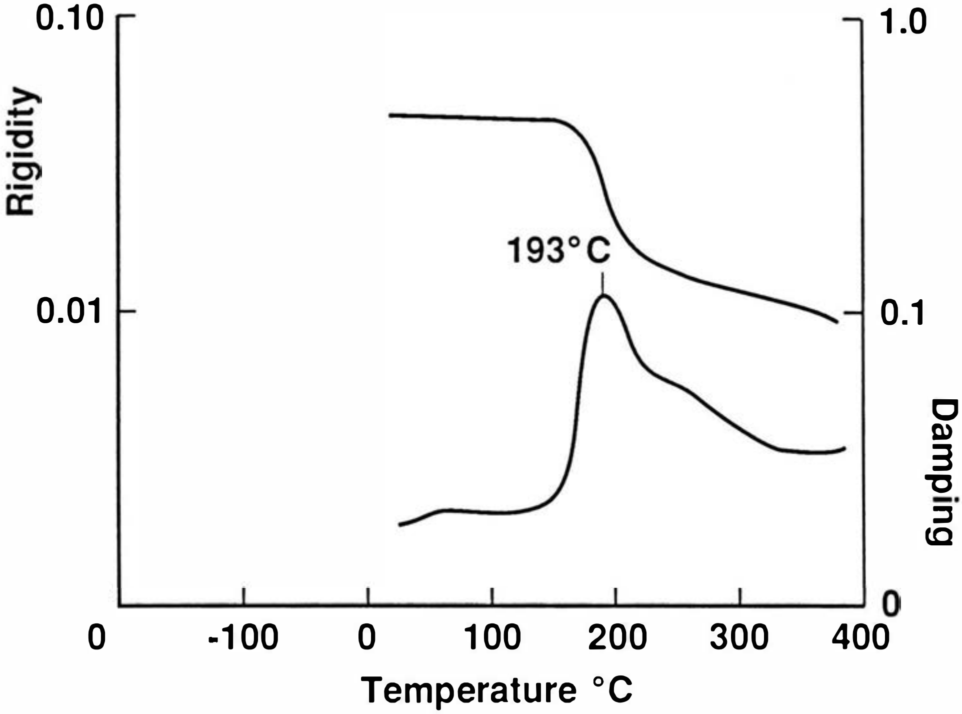
TBA of ATPAE (BPA) 3110//ODA/BTDA 6545 copolymer.



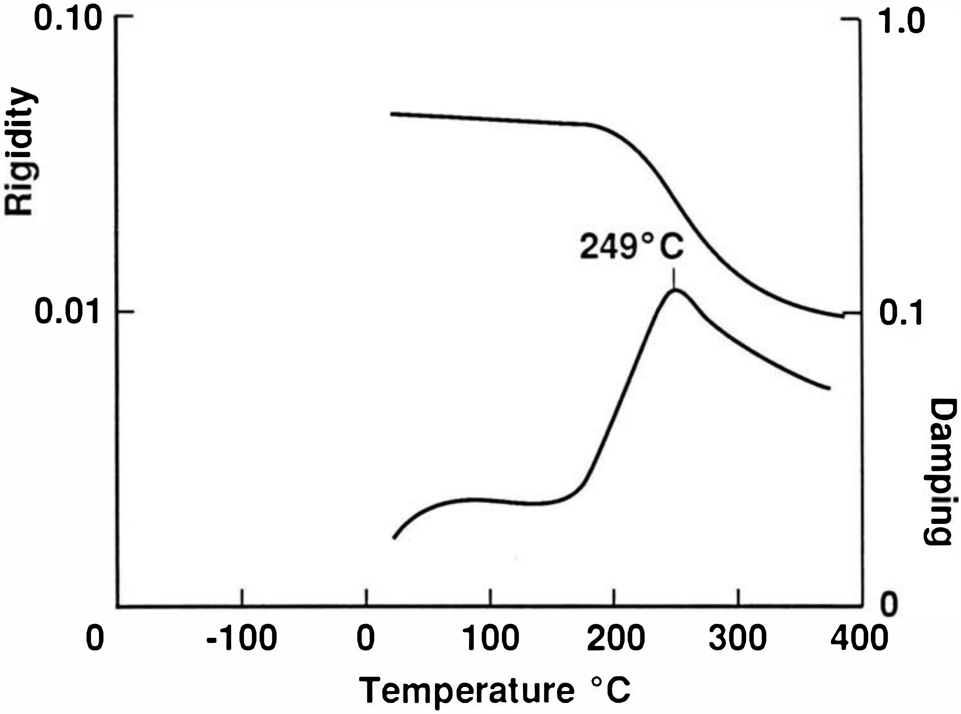
TBA of ATPAE (BPA) 6545//ODA/BTDA 3110 copolymer.



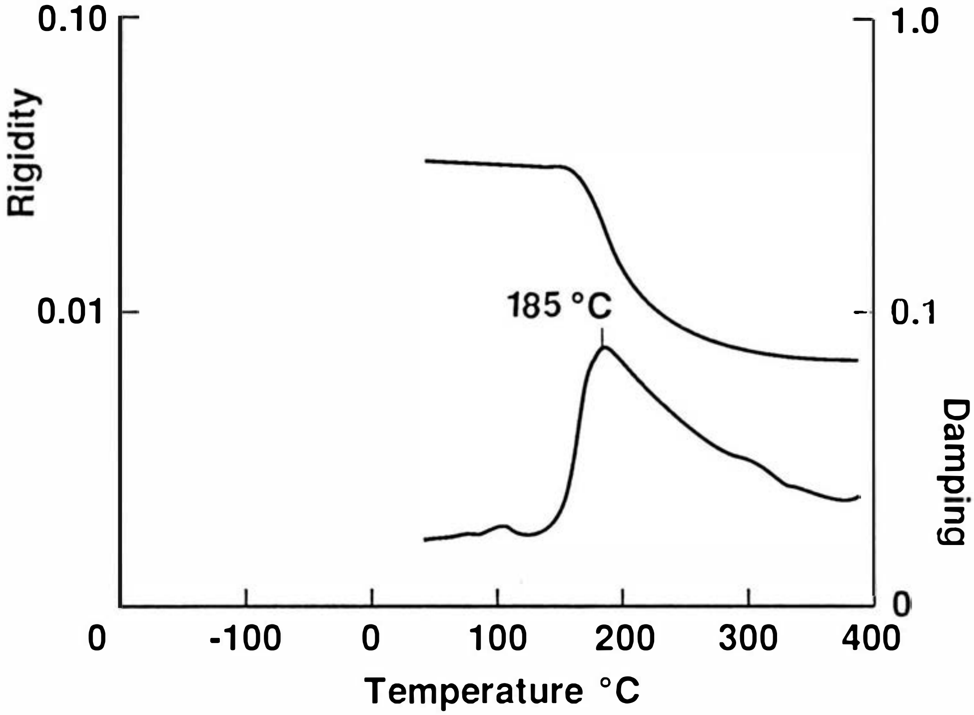
TBA of ATPAE (BPA) 6545//ODA/BTDA 6545 copolymer.



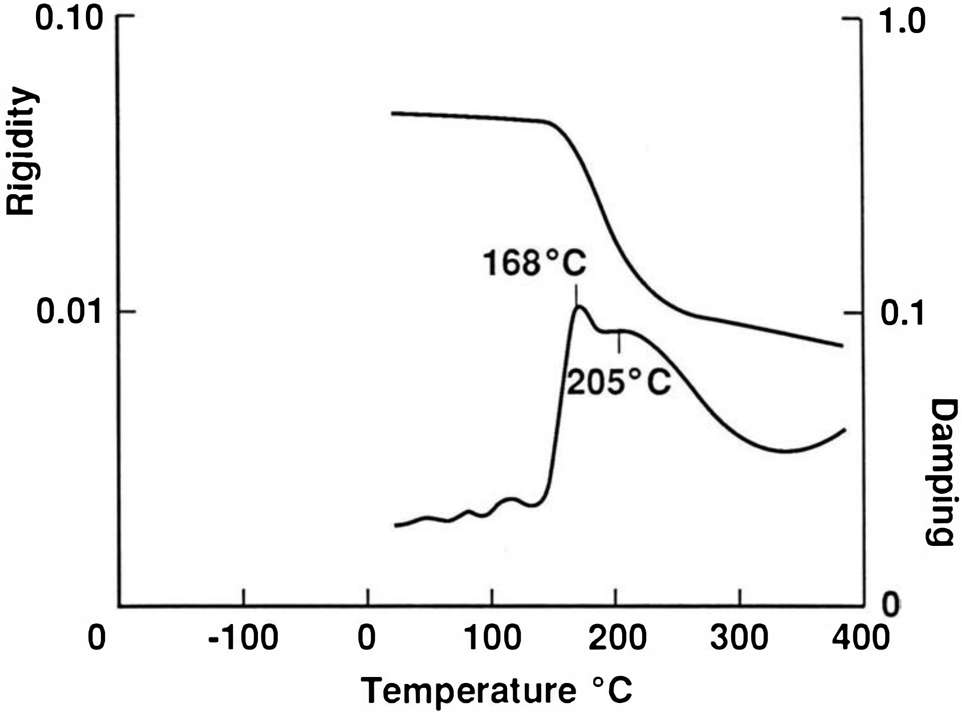
TBA of ATPAE (BPA) 3110//BABB/BTDA 3110 copolymer.



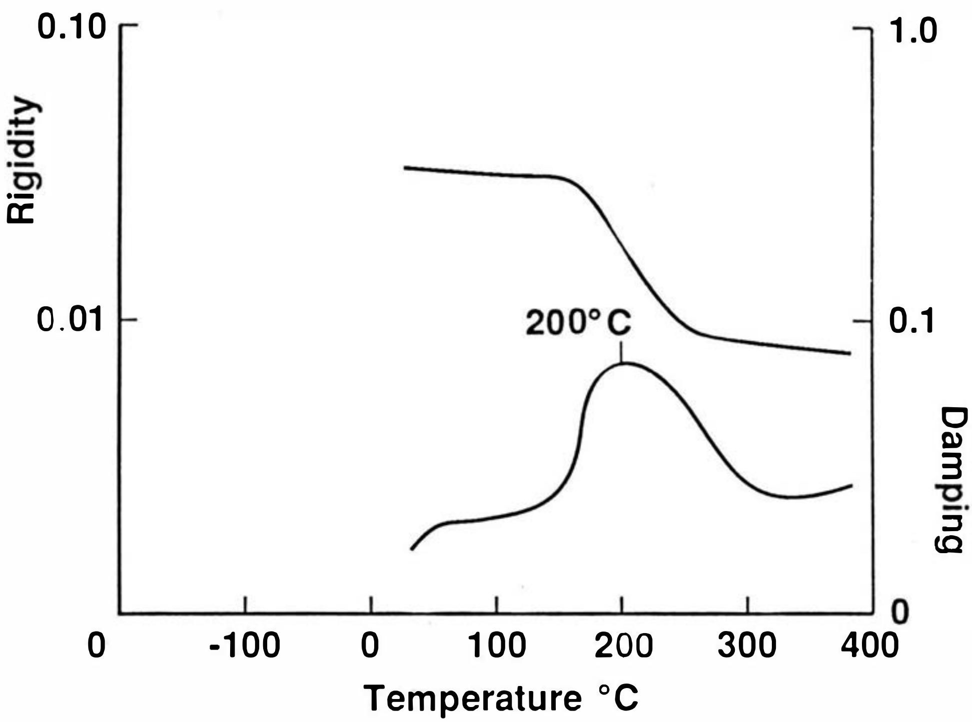
TBA of ATPAE (BPA) 3110//BABB/BTDA 6545 copolymer.



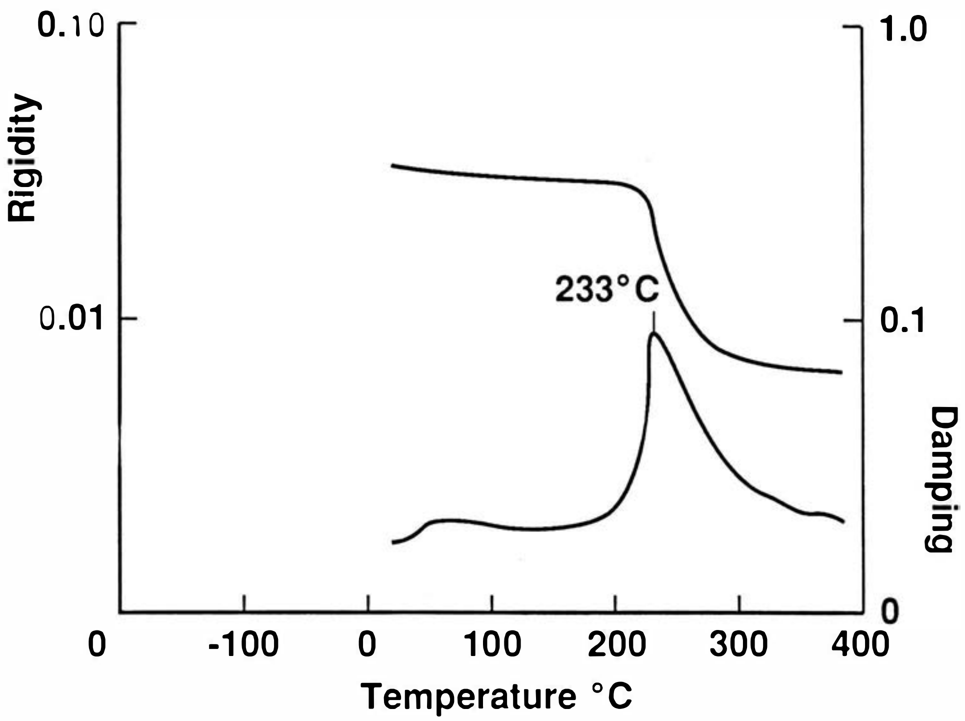
TBA of ATPAE (BPA) 6545//BABB/BTDA 3110 copolymer.



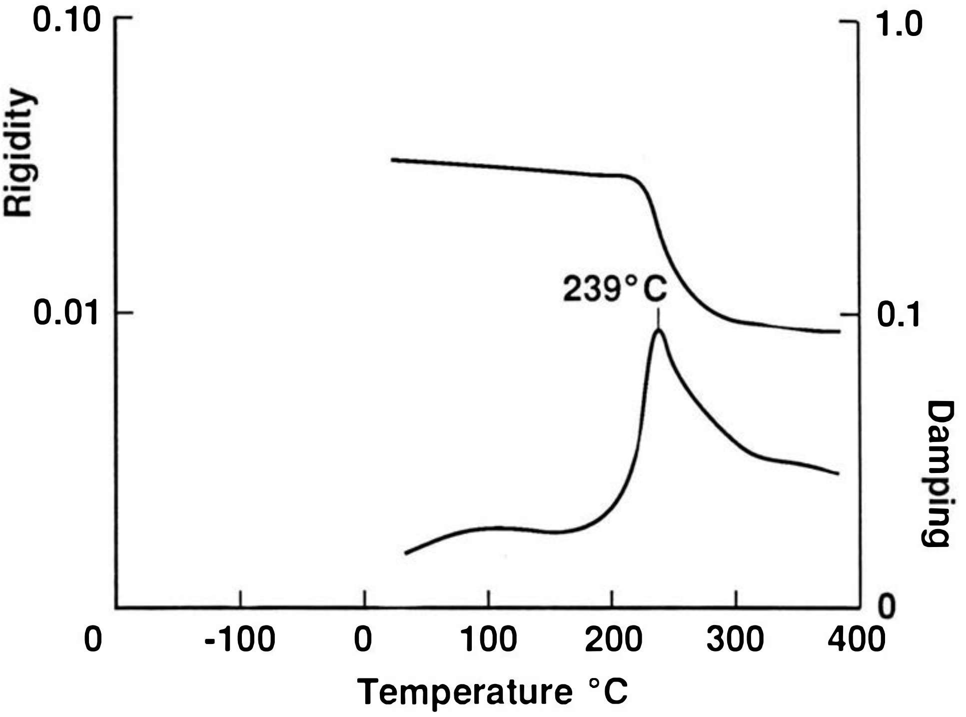
TBA of ATPAE (BPA) 6545//BABB/BTDA 6545 copolymer.



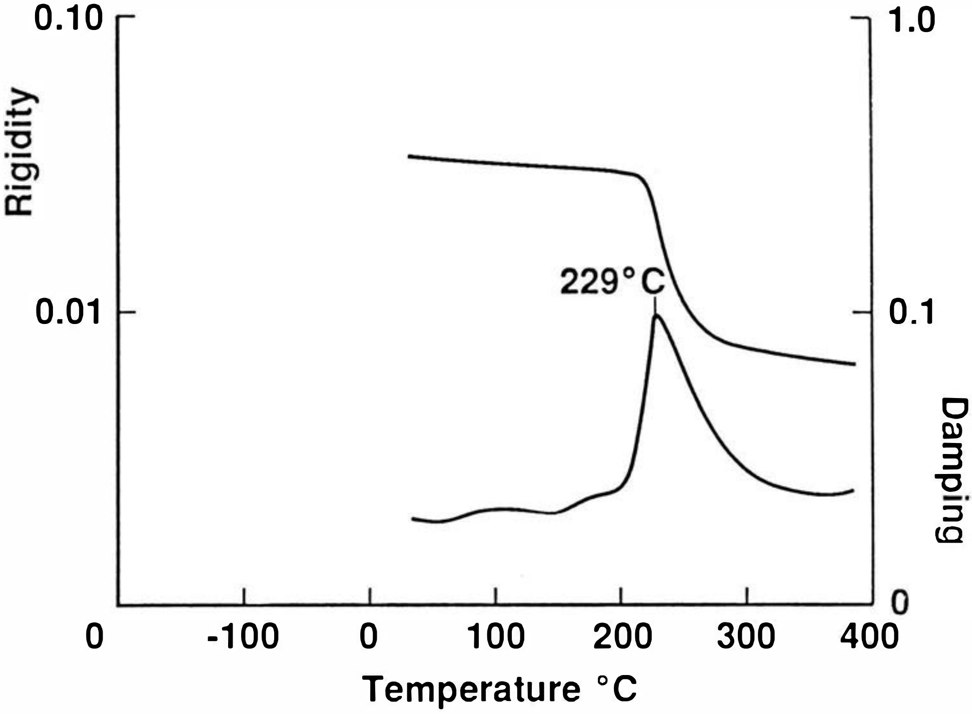
TBA for ATPAE (BPA) 6545 + [BABB + BTDA (6545)] segmented copolymer.



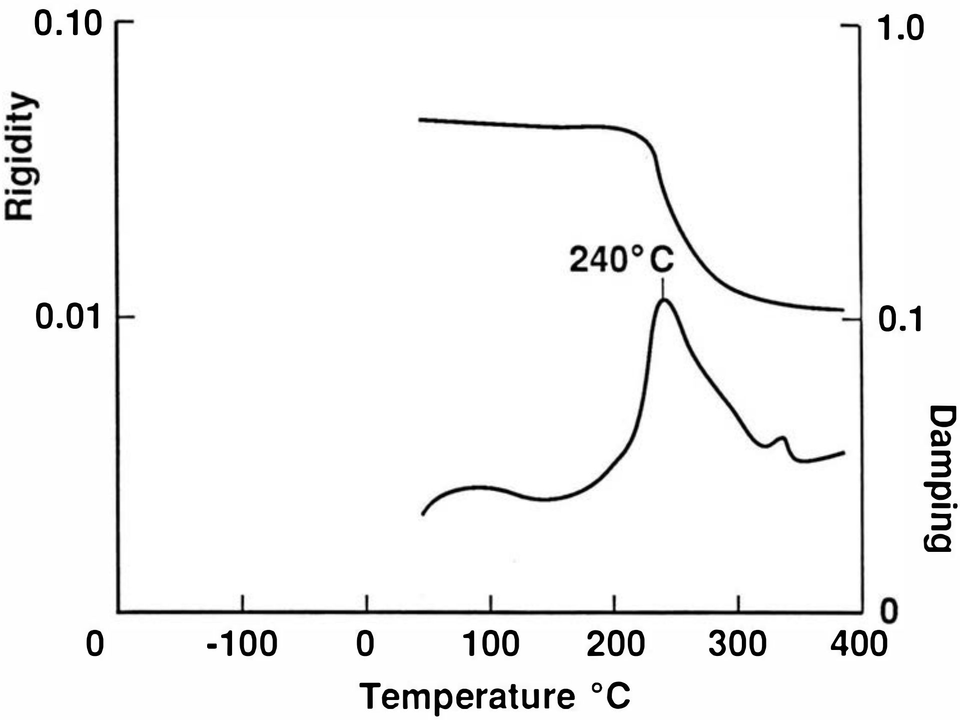
TBA for ATPAE (BPF) 3110//BABB/BTDA 3110 copolymer.



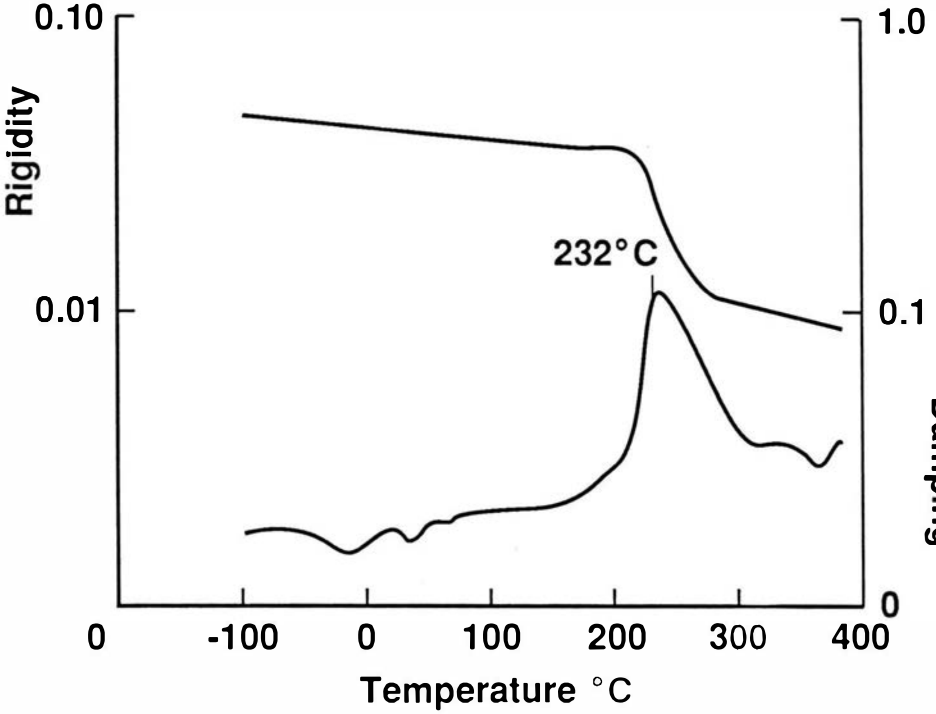
TBA for ATPAE (BPF) 3110//BABB/BTDA 6545 copolymer.



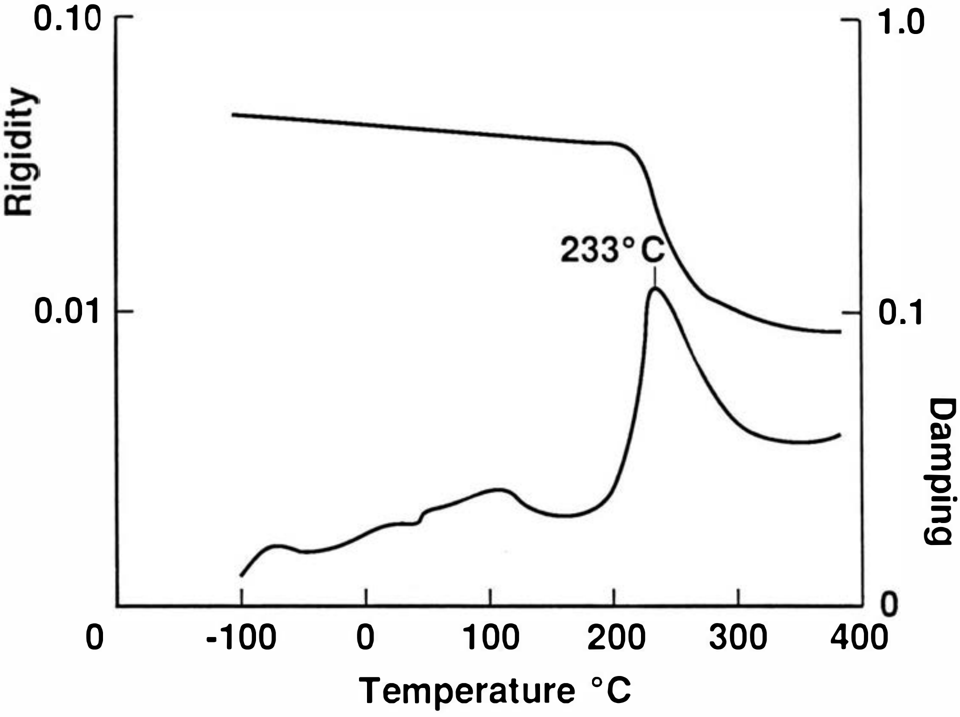
TBA for ATPAE (BPF) 6545//BABB/BTDA 3110 copolymer.



TBA for ATPAE (BPF) 6545//BABB/BTDA 6545 copolymer.



TBA for ATPAE (BPF) 3110 + [BABB + BTDA (3110)] segmented copolymer.



TBA for ATPAE (BPF) 6545 + [BABB + BTDA (6545)] segmented copolymer.

VITA

[redacted]

[redacted]

[redacted]