

Chemical Modification of 3,3',4,4'-Biphenyltetracarboxylic Dianhydride Polyimides by a Catechol-Derived Bis(ether amine)

CHIN-PING YANG, SHENG-HUEI HSIAO, RUEI-SHIN CHEN, CHI-SHU WEI

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, Republic of China

Received 9 April 2001; accepted 31 July 2001

ABSTRACT: Having previously demonstrated that the polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 1,2-bis(4-aminophenoxy)benzene [termed triphenyl ether catechol diamine (TPEC)] exhibited superior tensile properties in addition to good thermal properties, we now provide a preliminary assessment of the properties of the copolyimides prepared from BPDA, TPEC, and another aromatic diamine. The homopolyimides derived from BPDA and many aromatic diamines generally possessed good mechanical properties and thermal properties; however, they were insoluble in available organic solvents. In several cases, organosoluble BPDA copolyimides could be prepared from BPDA and equimolar mixtures of TPEC and another aromatic diamine. All the copolyimides could be formed into tough films with high moduli and strengths and, in most cases, high extensions to break. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 351–358, 2002; DOI 10.1002/app.10342

Key words: superior tensile properties; 3,3',4,4'-biphenyltetracarboxylic dianhydride; 1,2-bis(4-aminophenoxy)benzene [triphenyl ether catechol diamine (TPEC)]; polyimides; mechanical properties; toughness

INTRODUCTION

Aromatic polyimides have attracted much attention on account of their excellent thermal stability and electrical properties.^{1,2} Some of them are widely used in industry as structural materials and electrically insulating materials. However, the fabrication and processing of imide polymers have been limited because fully cured imide polymers are generally infusible and insoluble in most solvents. A number of methods have been used to overcome intractability but maintain reasonably

high-temperature characteristics. For tractability, polyimides have been modified either through the attachment of a bulky pendant group or through the introduction of flexible, nonsymmetrical, and thermally stable linkages to the backbone. Among these modifications, the introduction of flexible groups, such as ether, methylene, carbonyl, sulfide, sulfone, isopropylidene, or hexafluoroisopropylidene groups, into polymeric main chains via diamine or dianhydride monomers has been found to be effective and successful,^{3–9} the introduction of asymmetric structures (e.g., meta-linked or ortho-linked) into main chains has also met with success.^{10–16}

Polyimides synthesized from ether diamines generally possess increased flexibility, elongation, and toughness while retaining excellent

Correspondence to: C.-P. Yang (cpyang@ttu.edu.tw).

Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC 89-2218-E-036-014.

Journal of Applied Polymer Science, Vol. 84, 351–358 (2002)
© 2002 John Wiley & Sons, Inc.

thermal stability. Among the diamines composed of two phenylene rings connected by one ether linkage, commercial products include 4,4'-oxydianiline and 3,4'-oxydianiline; among the three-ringed diamines with two oxy bridges, only 1,4-bis(4-aminophenoxy)benzene [termed triphenyl ether hydroquinone diamine (TPEQ)] and 1,3-bis(4-aminophenoxy)benzene [termed triphenyl ether resorcinol diamine (TPER)], not 1,2-bis(4-aminophenoxy)benzene [termed triphenyl ether catechol diamine (TPEC)], are available. In fact, detailed scholarly reports on polyimides of TPEC or their copolyimides are rarely found.^{17,18}

Previously, we reported that the nucleophilic chlorodisplacement reaction between *p*-chloronitrobenzene with ortho-substituted aromatic diols such as catechol and 2,3-dihydroxynaphthalene could successfully proceed to form ortho-linked dinitro compounds, which could be readily reduced to ortho-linked diamines used in the synthesis of polyamides and polyimides.^{14–16} Recently, we studied polyimides derived from TPEC with commercial dianhydrides in an effort to enhance the solubility.¹⁷ However, unless 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride was incorporated, these polyimides were not organosoluble. We also found that the polyimide derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and TPEC possessed superior tensile properties; it exhibited a high extension to break, up to 112%, in addition to a high ultimate tensile strength and a high modulus. In this article, we report on the properties of a series of copolyimides based on BPDA and equimolar mixtures of TPEC and another diamine. All copolyimides were characterized with regard to their solubility behavior, tensile properties, and thermal properties. These polymers may provide an alternative series of relatively inexpensive, processable polyimides. The differences in properties between the copolyimides and the homopolyimides based on BPDA were also compared.

EXPERIMENTAL

Materials

BPDA (**I_B**; Chriskev, Leawood, KS) and other dianhydrides, including pyromellitic dianhydride (**I_A**; Lancaster, Tokyo, Japan), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**I_C**; Acros, Pittsburgh, PA), 3,3',4,4'-diphenylsulfonetetra-

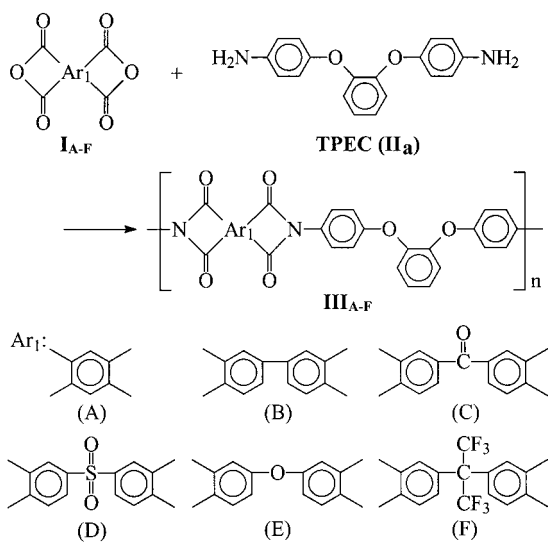
carboxylic anhydride (**I_D**; New Japan Chemical Co., Osaka, Japan), 4,4'-oxydiphthalic anhydride (**I_E**; Chriskev), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**I_F**; Chriskev), were recrystallized from acetic anhydride before use. TPEC (**II_a**) was synthesized as reported.¹⁶ *p*-Phenylenediamine (**II_f**; Wako, Osaka, Japan) and *m*-phenylenediamine (**II_g**; TCI, Tokyo, Japan) were vacuum-distilled. 1,4-Bis(4-aminophenoxy)-2-methylbenzene (**II_d**), 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**II_e**), and 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (**II_i**) were synthesized by the aromatic nucleophilic substitution reaction of the corresponding aromatic diols with *p*-chloronitrobenzene in the presence of potassium carbonate (K₂CO₃) followed by the subsequent reduction of the intermediate bis(4-nitrophenoxy) compounds with hydrazine and Pd/C. Other diamines, including TPER (**II_b**), TPEQ (**II_c**), 4,4'-oxydianiline (**II_h**), 3,4'-oxydianiline (**II_j**), 4,4'-methylenedianiline (**II_k**), and 4,4'-bis(4-aminophenoxy)biphenyl (**II_k**) were all purchased from TCI and used as received. *N,N*-Dimethylacetamide (DMAc; Fluka, Tokyo, Japan) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Polymer Synthesis

The homopolyimides of the TPEC series (**III_{A–F}**) and BPDA series (**IV_{a–1}**) and the copolyimides of the BPDA–TPEC series (**V_{a–1}**) were synthesized according to a general procedure described here for copolyimide **V_b**. Both TPEC (0.292 g, 1.0 mmol) and **II_b** (0.292 g, 1.0 mmol) were dissolved in 9 mL of DMAc, and then the dianhydride BPDA (0.588 g, 2.0 mmol) was added portionwise within 30 min. After the mixture was completely dissolved, it was stirred at room temperature for another hour. The obtained copoly(amic acid) solution was spread on a glass plate, which was placed in an 80°C oven for 1 h to remove the solvent. The semidried poly(amic acid) film was further dried and imidized by sequential heating at 120, 150, 180, and 210°C separately for 10 min and 250°C for 30 min. The inherent viscosity of the copolyimide (**V_b**) was 2.16 dL g⁻¹, as measured at a concentration of 0.5 g dL⁻¹ in *N*-methyl-2-pyrrolidone (NMP) at 30°C.

Measurements

The inherent viscosities were determined with a Cannon-Fenske viscometer at 30°C. Differential



scanning calorimetry (DSC) traces were obtained on a TA Instruments (New Castle, DE) DSC 2010 in flowing nitrogen ($40 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $15^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050, and experiments were carried out on samples ($10 \pm 2 \text{ mg}$) heated in flowing nitrogen ($100 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $20^\circ\text{C min}^{-1}$. Tensile properties were measured on an Instron (Canton, MA) model 1130 universal tester with a load cell of 5 kg. A gauge length of 2 cm and a crosshead speed of 5 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens 0.5 cm wide, 6 cm long, and about 0.05 mm thick. Reported data are averages of at least three replica tests.

RESULTS AND DISCUSSION

Polymer Synthesis

TPEC was synthesized by the reaction of catechol with *p*-chloronitrobenzene in the presence of K_2CO_3 to form a dinitro compound followed by Pd/C catalytic hydrazine reduction.¹⁶ Polyimides **III**_{A-F} were prepared by the classical two-step procedure from diamine TPEC with six commercially available dianhydrides (**I**_{A-F}) via poly(amic acid)s followed by thermal imidization (Scheme 1). The procedure for preparing polymers was as follows. A solid dianhydride was added to the diamine solution in dry DMAc to form the poly(amic acid). The poly(amic acid) solution was

coated uniformly on a glass plate, which was heated slowly to evaporate the solvent, and it was heated gradually to 250°C to form the polyimide through cyclodehydration. Therefore, the polyimides obtained were all in the form of a thin film. As shown in Table I, the inherent viscosities of the intermediate poly(amic acid)s ranged from 0.82 to 1.86 dL g^{-1} , indicating the formation of high molecular weights. The casting film of polyimide **III**_A, which was derived from **I**_A, cracked upon creasing, possibly because of the backbone rigidity. The other TPEC-based polyimides (**II**_{B-F}) afforded good-quality, creasable films.

For a comparison of the properties of the polyimides based on BPDA, BPDA was polymerized with 12 different diamines to form a series of BPDA polyimides (**IV**_{a-1}), as depicted in Scheme 2. The intermediate poly(amic acid)s had high inherent viscosities ranging from 1.05 to 2.50 dL g^{-1} (as shown in Table I), and all the thermally converted polyimide films were flexible and creasable without cracking, indicating that high molecular weight polymers had been obtained. Except for the polyimide (**IV**_b) obtained from BPDA and TPER, all the films of the **IV** BPDA homopolyimides were transparent and pale yellow. The film made from **IV**_b was slightly opaque, possibly because of its semicrystalline nature.¹⁹⁻²¹

A series of random copolyimides (**V**_{b-1}) were prepared from BPDA with an equimolar mixture of TPEC and another diamine comonomer. The resulting copolymers with high molecular weights showed inherent viscosities of $1.22\text{--}2.86 \text{ dL g}^{-1}$, as tabulated in Table I. Except for **V**_f and **V**_g, which contained more rigid diamine components such as **II**_f and **II**_g, the copolyimides were soluble in organic solvents such as NMP and *m*-cresol. Therefore, the characterization of the inherent viscosity of most of the copolyimides was carried out without any difficulty in organic solvents. This result also revealed that the solubilities of the BPDA–TPEC copolyimides were better than those of the corresponding homopolyimides. The insoluble copolyimides **V**_f and **V**_g had inherent viscosities of 1.22 and 1.29 dL g^{-1} , respectively, with concentrated sulfuric acid as the solvent. This indicated that these polymers, including homopolyimides and copolyimides based on BPDA, had good acid resistance, as mentioned in our previous report.¹⁷ Moreover, the casting films of all the copolyimides possessed good transparency and high toughness, indicating good characteristics of the films.

Table I Inherent Viscosities (η_{inh}) and Tensile Properties of Polyimides and Copolyimides

Polymer Code	η_{inh} (dL/g) ^a	Tensile Properties			
		Strength at Yield (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
III _A	1.63	—	74	6	2.1
III _B	1.86	116	100	112	2.3
III _C	1.08	—	108	7	2.4
III _D	0.82	—	111	9	2.5
III _E	0.98	—	113	19	2.3
III _F	0.93	—	104	8	2.4
IV _a (= III _B)	1.86	116	100	112	2.3
IV _b	2.46	137	136	96	2.7
IV _c	2.50	—	158	93	2.9
IV _d	2.41	—	107	22	2.3
IV _e	1.12	—	116	39	2.6
IV _f	1.99	—	246	15	5.2
IV _g	1.05	169	168	16	3.2
IV _h	1.92	—	164	80	2.5
IV _i	1.13	147	146	95	2.6
IV _j	1.25	111	111	37	2.3
IV _k	1.25	135	127	47	2.7
IV _l	2.43	116	116	23	2.1
V _a (= III _B = IV _a)	1.86	116	100	112	2.3
V _b	2.16	122	112	93	2.6
V _c	2.61 ^b	122	122	42	2.6
V _d	2.86 ^b	139	138	58	2.5
V _e	1.42	113	109	35	2.2
V _f	1.22 ^c	149	136	60	3.5
V _g	1.29 ^c	143	134	63	2.9
V _h	2.42 ^b	137	137	73	2.5
V _i	1.69	128	127	98	2.4
V _j	1.27	107	103	36	2.2
V _k	1.28	116	109	31	2.3
V _l	1.68	124	122	54	2.2

^a Measured for the poly(amic acid) precursors of polyimides III_{A-F} and IV_{a-l} at a concentration of 0.5 g/dL in DMAc at 30°C. Copolyimides V_{a-l} were measured in NMP.

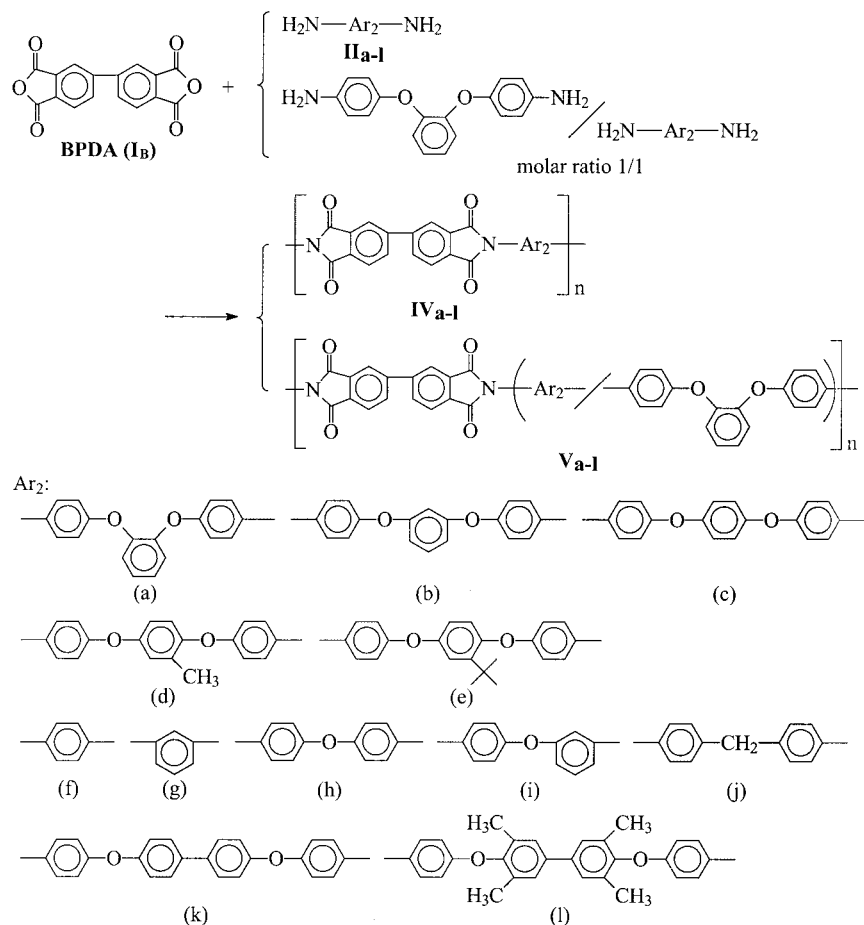
^b Measured at a concentration of 0.5 g/dL in *m*-cresol at 30°C.

^c Measured at a concentration of 0.5 g/dL in concentrated H₂SO₄ at 30°C.

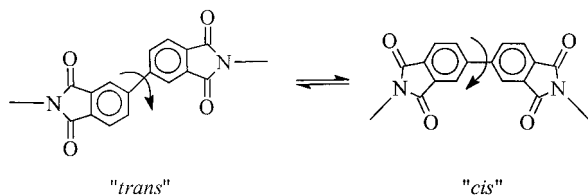
Properties of the Polymers

The cast films of all the homopolyimides and copolyimides were subjected to tensile testing, and the results are summarized in Table I. Among the TPEC-based polyimides (III_{A-F}), the BPDA/TPEC polyimide (III_B) possessed superior tensile properties; it exhibited a high extension to break, up to 112%, in addition to a high ultimate tensile strength and a high modulus of 100 MPa and 2.3 GPa, respectively. From the results of the BPDA homopolyimides IV_{a-l}, it was found that all the IV polymers possessed excellent tensile proper-

ties. The values were high, with moduli ranging from 2.1 to 5.2 GPa and tensile strengths between 100 and 246 MPa. Most of them necked during the tensile test and showed a relatively higher extension to break, thereby behaving as tough materials. It is postulated that the high toughness resulted in part from the unique structure of the BPDA unit. This monomer is fairly rigid but can undergo rotation about the central biphenyl single bond. It can assume a range of conformations between the extremes of trans to cis, as shown for the imide segment:



Scheme 2



The *trans* structure has an extended or crankshaft geometry, with imide links that are parallel but not collinear. This conformation would provide a rodlike structure and, therefore, a high modulus. The *cis* (kinked) structure has an angle of about 150° between imide bonds, which should give rise to a more coiled polymer chain but still provide a fairly stiff structure. Because the rings of biphenyl units are generally not coplanar, however, intermediate conformations are likely to be more favorable than either of these two extremes (according to semiempirical molecular orbital calculations, the BPDA unit has a dihedral angle at the biphenyl bonds of about $40\text{--}140^\circ$).²² The ca-

pability of this monomer unit to assume a range of conformations while retaining considerable rigidity and rodlike character may be responsible for the combination of high elongation with high modulus and high strength displayed in the BPDA-based polyimides.

The change in the tensile properties also depended on the structure of the diamine component. If one compares BPDA/*p*-phenylenediamine (IV_f) and BPDA/*m*-phenylenediamine (IV_g), which are structural isomers of one another, the difference in the mechanical properties is strikingly clear. IV_f exhibits the high modulus of a highly rodlike material, but IV_g has the more moderate modulus of a more flexible backbone. Moreover, the tensile strength of the IV_f film was substantially higher than the strengths of IV_g and the other IV polyimides. However, the IV_g film exhibited a similar elongation in comparison with IV_f, despite the less stiff backbone. The incorporation of flexible ether linkages into the polyimide backbone, such as IV_h

and **IV_i**, generally resulted in an increase in elongation but a decrease in strength and modulus. It is interesting to compare the tensile properties of the BPDA/TPEC (**IV_a**) film with those of the BPDA/TPER (**IV_b**) and BPDA/TPEQ (**IV_c**) polyimides, which had isomeric repeat units. Although **IV_a** (i.e., **III_B**) contained TPEC with the ortho-linked phenylene unit, its tensile property was good enough to make it a useful material, especially for its high extension. Moreover, the introduction of the pendant methyl or *tert*-butyl group seemed to cause a decrease in both strength and toughness in a comparison of **IV_d**, **IV_e**, and **IV_l** with **IV_c** and **IV_k**. This may be because the pendant groups increased the separation between chains and decreased the intermolecular interactions.

For the preparation of high-performance polymers with balanced tensile properties and solubility, copolyimides (**V_{b-1}**) based on BPDA and mixtures of aromatic diamines were also synthesized. These copolymers showed a clear yield point in their stress-strain curves and high toughness; their tensile strengths, elongations to break, and initial moduli were recorded as 103–138 MPa, 31–98%, and 2.2–3.5 GPa, respectively. In a comparison of **V_f** and **V_g** with **IV_f** and **IV_g**, the effect of incorporating the TPEC component into the polymer backbone was definite; the elongations at break of **V_f** and **V_g** were remarkably enhanced by up to 60 and 63%, respectively. This effect could also be found in polymers **V_d** and **V_l** with pendant methyl groups. According to the data, although the tensile strengths and initial moduli of these copolyimides decreased, their strengths were all higher than 100 MPa, revealing that this series of copolyimides possessed outstanding tensile properties.

The solubility of these polyimides was tested semiquantitatively, and the results are summarized in Table II. Among the TPEC-based polyimides (**III_{A-F}**), only **III_F**, containing a bulky hexafluoroisopropylidene linkage in the dianhydride segment, was soluble.¹⁷ Although **III_B** was slightly soluble (just about 0.5 wt %) in NMP, it was noted for its excellent extension, as mentioned previously; therefore, the serial BPDA polyimides (**IV_{a-1}**) were synthesized. However, although these BPDA polyimide films exhibited excellent tensile properties, they showed poor solubility. Only **IV_a** (or **III_B**) and **IV_l**, which contained ortho-substituted phenylene units and tetramethyl substituents, respectively, in the diamine moiety, were slightly soluble in NMP (<1 wt %),

Table II Solubility Behavior^a of Polyimides and Copolyimides

Polymer Code	Solvents			
	NMP	DMAc	DMF	<i>m</i> -Cresol
IV_a	+	–	–	+
IV_b	–	–	–	±
IV_c	–	–	–	–
IV_d	–	–	–	–
IV_e	–	–	–	–
IV_f	–	–	–	–
IV_g	–	–	–	–
IV_h	–	–	–	–
IV_i	–	–	–	+
IV_j	–	–	–	–
IV_k	–	–	–	–
IV_l	+	–	–	+
V_a (= IV_a)	+	–	–	+
V_b	++	–	–	++
V_c	–	–	–	+
V_d	±	–	–	++
V_e	++	±	±	++
V_f	–	–	–	–
V_g	–	–	–	S
V_h	–	–	–	+
V_i	++	–	–	++
V_j	+	–	–	+
V_k	+	–	–	+
V_l	++	S	S	++

^a Solubility was measured at a polymer concentration (*C*); ++ = soluble on heating at *C* > 5 wt %; + = soluble on heating at *C* = 0.5 wt %; ± = partially soluble at *C* = 0.5 wt %; S = swelling at *C* = 0.5 wt %; – = insoluble at *C* = 0.5 wt %.

and the rest of the **IV** polymers were insoluble, as shown in Table II.

One successful approach to increasing the solubility of polymers is the synthesis of copolymers. On the basis of the aforementioned results, TPEC was chosen to modify the properties of BPDA polyimides. In most cases, copolyimides of the **V** series showed a substantially increased solubility in comparison with the solubility of the corresponding homopolyimides. Among the four kinds of tested solvents, the **V** polymers showed better solubility in *m*-cresol and NMP, and they were hardly soluble in DMAc and *N,N*-dimethylformamide (DMF).

The thermal properties of all the BPDA homopolyimides and copolyimides were evaluated by TGA and DSC. The results are summarized in Table III. DSC measurements were conducted at a heating rate of 15°C min^{–1} in nitrogen. Quench-

Table III Thermal Properties of Polyimides and Copolyimides

Polymer Code	DSC	TGA	
	T_g^a (°C)	Decomposition Temperature in Nitrogen (°C) ^b	Residue at 800°C in Nitrogen (wt %)
IV _a	250	599	60
IV _b	236	594	63
IV _c	265	604	61
IV _d	265	526	61
IV _e	268	545	52
IV _f	—	638	65
IV _g	336	613	64
IV _h	—	610	64
IV _i	274	604	64
IV _j	312	596	70
IV _k	—	603	65
IV _l	339	523	56
V _a (= IV _a)	250	599	60
V _b	242	598	63
V _c	257	600	63
V _d	255	557	60
V _e	259	553	56
V _f	—	607	63
V _g	285	605	63
V _h	270	596	63
V _i	261	603	62
V _j	274	578	64
V _k	257	597	64
V _l	297	540	64

^a Midpoint of baseline shift in the second heating DSC trace with a heating rate of 15°C/min under a nitrogen atmosphere.

^b Temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20°C/min.

ing from an elevated temperature of about 400°C to room temperature in air gave predominantly amorphous samples so that the glass-transition temperatures (T_g 's) of most polymers could be easily measured in the second DSC heating traces. However, in some cases, such as **IV_f**, **IV_h**, and **IV_k**, no discernible glass transition was observed because of the rigid backbones. As shown in Table III, seven of the **IV** polyimides revealed a well-defined T_g between 250 and 339°C by DSC. **IV_a** exhibited a relatively lower T_g in the **IV** series, so the introduction of the ortho-substituted aromatic rings into the macromolecular backbones would be expected to modestly decrease the T_g values of the BPDA polyimides.

The BPDA-TPEC copolymers (**V**) containing *o*-phenylene units were prepared to have lower T_g

values with improved solubility with respect to BPDA homopolyimides. No discernible T_g was observed for copolyimide **V_f** by DSC. The other copolyimides of the **V** series showed clear glass transitions between 242 and 297°C, following the decreasing order of chain flexibility and steric hindrance of the polymer backbones. In general, the incorporation of asymmetric *m*-phenylene units or flexible ether linkages led to a decrease in T_g . For example, polymers **V_c**, **V_f**, and **V_h**, which contained all para-substituted phenylene rings in the —Ar₂— segment, had higher T_g values than the analogous polymers **V_b**, **V_g**, and **V_i**, which contained some meta-substituted phenylene units in the —Ar₂— segment. **V_l** displayed a higher T_g than **V_k** because of the hindrance effect of the chain rotation in the tetramethyl-substituted diamine moiety.

The thermal stability of the polymers was characterized by TGA conducted at a heating rate of 20°C min⁻¹. The temperatures at 10% weight loss (T_{10}) and char yields at 800°C in a nitrogen atmosphere were determined from the original thermograms and also are tabulated in Table III. The T_{10} values of these polymers stayed within 523–638°C, and the amount of carbonized residue was more than 52%. The polymers **IV_{c,k}** and **V_{c,k}** without pendant groups showed higher T_{10} values than the polymers **IV_{d,e,l}** and **V_{d,e,l}** with less stable alkyl substituents, and the differences in the T_{10} values were within 40–60°C. According to the data, these polymers showed outstanding thermal stability, and there was no significant difference between the homopolyimides and copolyimides. Therefore, using TPEC to produce copolyimides could not only decrease their T_g values but also retain their excellent thermal stability, so the BPDA-TPEC copolyimides possessed good thermal properties and processability.

CONCLUSIONS

TPEC was successfully used to modify the properties of BPDA polyimides. The copolyimides based on BPDA and equimolar mixtures of TPEC and another aromatic diamine showed good tensile properties and high thermal stability. Several modified BPDA copolyimides were organosoluble and had modest T_g values. Therefore, this series of BPDA/TPEC-based copolyimides demonstrated a good combination of properties and processability.

REFERENCES

1. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Chapman & Hall: New York, 1990.
2. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
3. Bell, V. L.; Stump, B. L.; Gager, H. J. *J Polym Sci Polym Chem Ed* 1976, 14, 2275.
4. Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanocoski, J. E.; Manello, J. S.; Webber, M. T. *J Polym Sci Polym Chem Ed* 1980, 18, 3069.
5. Fled, W. A.; Ramalingam, B.; Harris, F. W. *J Polym Sci Polym Chem Ed* 1983, 21, 319.
6. Ghatge, N. D.; Shinde, B. M.; Mulik, U. P. *J Polym Sci Polym Chem Ed* 1984, 22, 3359.
7. Imai, Y.; Malder, N. N.; Kakimoto, M. *J Polym Sci Part A: Polym Chem* 1989, 22, 2189.
8. Yamada, M.; Kusama, M.; Matsumoto, T.; Kurosaki, T. *J Polym Sci Part A: Polym Chem* 1997, 35, 1027.
9. Eastmond, G. C.; Paprotny, J. *Polymer* 1994, 35, 5148.
10. Eastmond, G. C.; Paprotny, J. *Macromolecules* 1995, 28, 2140.
11. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. *Macromolecules* 1996, 29, 1382.
12. Akutsu, F.; Inoki, M.; Sawano, M.; Kasashima, Y.; Naruchi, K.; Miura, M. *Polymer* 1998, 39, 6093.
13. Hsiao, S. H.; Yang, C. P.; Chu, K. Y. *Macromolecules* 1997, 30, 165.
14. Yang, C. P.; Chen, W. T. *Macromolecules* 1993, 26, 4865.
15. Yang, C. P.; Chen, W. T. *Makromol Chem* 1993, 194, 1595.
16. Yang, C. P.; Cherng, J. J. *J Polym Sci Part A: Polym Chem* 1995, 33, 2209.
17. Hsiao, S. H.; Yang, C. P.; Chen, S. H. *J Polym Sci Part A: Polym Chem* 2000, 38, 1551.
18. Eastmond, G. C.; Paprotny, J. *Synthesis* 1998, 894.
19. Kreuz, J. A.; Hsiao, B. S.; Renner, C. A.; Goff, D. L. *Macromolecules* 1995, 28, 6926.
20. Hsiao, B. S.; Kreuz, J. A.; Cheng, S. Z. D. *Macromolecules* 1996, 29, 135.
21. Srinivas, S.; Caputo, F. E.; Graham, M.; Gardner, S.; Davis, R. M.; McGrath, J. E.; Wilkes, G. L. *Macromolecules* 1997, 30, 1012.
22. Hasegawa, M.; Sensui, N.; Shindo, Y.; Yokota, R. *Macromolecules* 1999, 32, 387.