

Synthesis and Properties of Aromatic Polyimides Based on Ether-Sulfone-Diamines

Sheng-Huei Hsiao*, Chin-Ping Yang and Ting-Kuo Lo

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., Sec. 3, Taipei 10451, Taiwan, ROC

Abstract: Two diamine monomers, 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (**III_a**) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline (**III_b**), were prepared by an aromatic nucleophilic substitution of 4,4'-sulfonyldiphenol (**I_a**) and 4,4'-sulfonylbis(2,6-dimethylphenol) (**I_b**) with *p*-chloronitrobenzene in the presence of potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compounds. The diamines **III_a** and **III_b** were used as monomers with various aromatic tetracarboxylic dianhydrides (**IV_{a-f}**) to synthesize polyimides. The polymerization was conducted in two steps via the formation of a poly(amic acid) precursor followed by thermal cyclodehydration. The poly(amic acid)s had inherent viscosities above 0.87 and up to 2.56 dL/g. Most poly(amic acid)s could be coated and thermodehydrated into flexible and transparent polyimide films. The polyimides derived from the dianhydrides containing -O- and -SO₂- or -C(CF₃)₂- bridging groups between the phthalic anhydride units were soluble in some organic solvents such as *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF). The glass transition temperatures (*T_g*) of the polyimides were in the range from 254 to 300 °C. The methyl-substituted polyimides exhibited slightly higher solubility and higher *T_g* compared to the corresponding unsubstituted polyimides. Thermogravimetric analysis (TG) showed that the polyimides containing methyl substituents started to lose weight around 450 °C and the unsubstituted ones started to lose weight around 550 °C.

Keywords: Polyimides, Ether-sulfone-diamines.

Introduction

Polyimides have earned a reputation as high performance materials because of their excellent thermal and mechanical properties and chemical resistance [1,2]. These properties have been exploited for a wide variety of applications that include polymer matrices for advanced composites, semipermeable membranes for gas separation, semiconductor materials for electronic applications, high temperature adhesives, and coatings. However, aromatic polyimides are basically intractable or only processable under extreme conditions, due to strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution or melting. The most common technique for the preparation of polyimides is a two-step polymerization process which allows the use of a soluble precursor, poly(amic acid), to deposit thin films, followed by thermal cure to polyimide. There are,

however, certain limitations connected with the instability of poly(amic acid) solutions, such as completeness of imidization, elimination of released water and the formation of microvoids in the final bulk materials. To overcome these problems, several structural modifications of the polymer backbone [3-7] have been utilized to modify the polymer properties, either by lowering the interchain interactions or reducing the stiffness of the polymer chain.

Incorporation of flexible linkages such as ether and isopropylidene in the polyimide backbone leads to a decreased glass transition and an enhanced moldability. An important example is the Ultem[®] resin developed by General Electric Co. [8]. However, the loss of thermal stability and significant decrease in mechanical strength on heating are almost always a consequence of the reduced chain stiffness. The insertion of sulfone groups into the macromolecular chain generally results in an improved solubility, together with interesting proper-

*To whom all correspondence should be addressed.

Tel: 886-2-25925252-2977; Fax: 886-2-25861939; E-mail: shhsiao@che.ttit.edu.tw

ties such as increased T_g and high thermo-oxidative stability [9-13]. Hence, the goal of better thermal stability together with good processability may be achieved in preparing polyimides bearing both sulfone and flexibilizing links such as ether.

The presence of methyl substituents on a ring unit at *ortho* positions to the ether linkage generally increased the T_g of the polymers, due to the hindrance effect of the chain rotation [14,15]. Furthermore, the methyl-substituted aromatic poly(ether ketone)s were found to crosslink by radiation of ultraviolet light due to the presence of a sensitizing benzophenone structure [14,15]. In addition, some methyl-substituted polysulfones were found to exhibit more favorable gas separation properties when compared to their unsubstituted counterparts [16-18].

Thus, the present work focuses on the preparation and characterization of polyimides having ether and sulfone in the main chain, together with methyl substituents on the aromatic units. The combination was considered potentially attractive because the anticipated polymers were expected to exhibit a favourable balance of properties. For comparison, related polyimides without methyl substitution were also prepared and characterized.

Experimental

1. Materials

The ether-sulfone-diamine monomers, 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (**III_a**) (mp. 188~189 °C) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline (**III_b**) (mp. 186~188 °C), were prepared by aromatic nucleophilic chloro substitution reaction of the bisphenols, 4,4'-sulfonyldiphenol (Sigma) and 4,4'-sulfonylbis(2,6-dimethylphenol) (Aldrich), and *p*-chloronitrobenzene in the presence of potassium carbonate, followed by palladium-catalyzed hydrazine reduction of the intermediate dinitro compounds. Details of the synthesis and characterization data of diamines **III_a** and **III_b** have been described in the preceding paper [19].

Pyromellitic dianhydride (PMDA; **IV_a**, from Aldrich) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA; **IV_c**, from Aldrich) were recrystallized from acetic dianhydride prior to use. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA; **IV_b**, from Oxychem), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA; **IV_d**, from New Japan Chemical Co.), 4,4'-oxydiphthalic anhydride (ODPA; **IV_e**, Oxychem), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **IV_f**, from Hoechst Celanese) were used with-

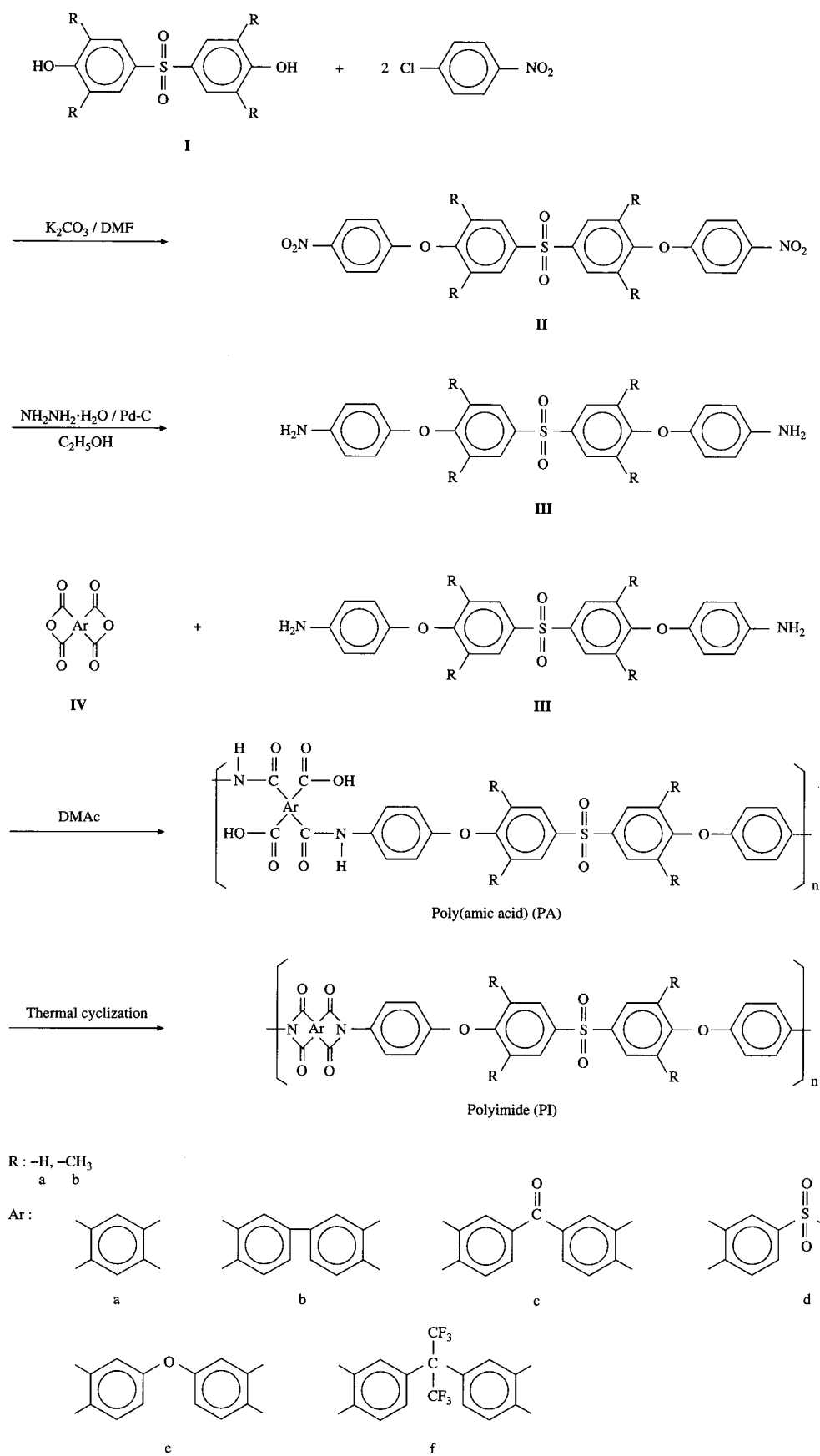
out further purification. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2. General polymerization procedure

A calculated quantity of diamine **III_a** or **III_b** was dissolved in 9.5 mL of dried DMAc in a 50 mL flask. After the diamine was dissolved completely, an equal molar quantity of a dianhydride was added portionwise over about 30 min. The mixture was stirred at room temperature for 3 hrs to afford a viscous poly(amic acid) solution. The total amount of the diamine and the dianhydride used was 1.0 g, and thus the resulting polymer solution had a concentration of about 10% by weight. The inherent viscosity of the resulting poly(amic acid) was measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The polymer solution was poured into a 9 cm glass culture dish, which was placed in a 80 °C oven overnight to remove the solvent. The semi-dried poly(amic acid) film was further dried and transformed into polyimide by sequential heating at 120 °C for 10 min, 180 °C for 10 min, 200 °C for 10 min, 250 °C for 30 min. After being soaked in hot water, a flexible polyimide film was lifted off the glass surface.

3. Measurements

The inherent viscosities of polymers were determined for a solution of 0.5 g/100 mL in DMAc at 30 °C using an Ubbelohde suspended level viscometer. Wide-angle X-ray diffraction patterns were obtained for film specimens of about 0.1 mm thick on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered Cu K_{α} radiation (1.5418 Å). A Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. The scan rate was 20 °C/min. The glass transition temperatures (T_g s) were read at the middle of the change in the heat capacity, and were taken from the second heating scan after quick cooling from approximately 430 °C. Thermogravimetric (TG) data were obtained on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 1 mg samples heated in flowing nitrogen or air (50 cm³/min) at a scan rate of 20 °C/min. The measurements were taken after an initial 250 °C/5 min drying step. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the samples. A crosshead gauge of 2 cm and a strain rate of 5 cm/min were used. Measurements were performed with film specimens (0.5 cm wide, 6 cm long, and



Scheme I

Table I. Inherent viscosities of poly(amic acid)s and film properties of polyimides.

Monomers		Poly(amic acid)s		Polyimide	
tetracarboxylic dianhydride	diamine	code	$\eta_{inh}^{(a)}$ (dL/g)	code	film quality
IV _a	III _a	PA _a	1.18	PI _a	Flexible
IV _b	III _a	PA _b	0.96	PI _b	Flexible
IV _c	III _a	PA _c	0.91	PI _c	Flexible
IV _d	III _a	PA _d	0.99	PI _d	Flexible
IV _e	III _a	PA _e	1.13	PI _e	Flexible
IV _f	III _a	PA _f	0.87	PI _f	Flexible
IV _a	III _b	Me-PA _a	2.05	Me-PI _a	Brittle
IV _b	III _b	Me-PA _b	2.28	Me-PI _b	Flexible
IV _c	III _b	Me-PA _c	1.08	Me-PI _c	Flexible
IV _d	III _b	Me-PA _d	0.97	Me-PI _d	Flexible
IV _e	III _b	Me-PA _e	1.08	Me-PI _e	Flexible
IV _f	III _b	Me-PA _f	2.56	Me-PI _f	Brittle

(a) Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

about 0.1 mm thick) and an average of at least five individual determinations was used.

Results and Discussion

1. Polymer synthesis

Polyimides were prepared by the standard room temperature synthesis of the poly(amic acid) from diamine and dianhydride monomer with subsequent coating and thermal cure to polyimide. The synthetic route and the structures of the polymers are illustrated in Scheme I. The ring-opening polyaddition of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]-dianiline (**III_a**) or 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline (**III_b**) with different aromatic tetracarboxylic dianhydrides in DMAc at room temperature formed poly(amic acid)s with inherent viscosities greater than 0.87 dL/g and up to 2.56 dL/g. The inherent viscosities and codes of the prepared polymers are summarized in Table I. In most cases, the poly(amic acid)s derived from diamine **III_b** were obtained with higher viscosities compared to those from diamine **III_a**. This may be attributed to the higher basicity of diamine **III_b** due to the presence of methyl substituents. On the other hand, the presence of methyl substituents on the phenylene unit at *ortho* positions to the ether linking group increased the stiffness of the polymers due to the hindrance effect of the chain rotation, thus leading to increased viscosities of the polymer solutions. Nevertheless, the molecular weights of all the poly(amic acid)s were high enough to permit the casting of flexible, tough, and transparent films. The poly(amic acid) films were thermally dehydrated at temperatures up to 250 °C, producing polyimide films. Except for **Me-PA_a** and **Me-PA_f**, all poly(amic acid)s gave good-quality, creasable films

when thermally converted to polyimides. The brittle nature of the **Me-PA_a** film may be due to the structural rigidity of its polymer chains. The reason why the **Me-PA_f** film embrittled is not very clear.

2. Properties of polymers

The results of qualitative solubility tests of all the polyimides are given in Table II. The polyimides having flexible linkers to the dianhydride moieties showed better solubility as in the case DSDA-, ODPD-, and 6FDA-derived polymers. They were soluble in cold or hot DMAc, DMF, and *m*-cresol. The polyimides with 6FDA moiety showed the best solubility characteristics, e.g., **PI_f** and **Me-PI_f** were readily soluble in less polar chloroform. This is probably because the hexafluoroisopropylidene groups bonded to the main chain make the chain packing loose. In the cases of BPDA- and 6FDA-based polyimides, the methyl-substituted polymers were more soluble than the unsubstituted counterparts in a number of solvents.

The crystallinity of the prepared polyimides was evaluated by wide-angle X-ray diffraction measurements. None of the polymers showed any strong reflection peaks over the 2 θ range of 5~40°, indicating an amorphous nature. Most of the polyimides afforded flexible and creasable films. These films were subjected to a tensile test, and their tensile properties are summarized in Table III. They showed a tensile strength of 72~92 MPa, an elongation at break of 7~12%, and an initial modulus of 1.37~1.67 GPa.

The thermal properties of these polyimides were determined by means of dynamic thermogravimetry (TG) and differential scanning calorimetry (DSC). Some thermal behavior data are presented in Table IV. As a representative example, the TG thermograms of polyimides **PI_a** and **Me-PI_a** are reproduced

Table II. Solubility behavior of polyimides.^(a)

Polymer	Solvent ^(b)							
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	dioxane	chloroform
PI _a	-	-	-	-	-	-	-	-
PI _b	-	-	-	-	+h	-	-	-
PI _c	-	-	-	-	-	-	-	-
PI _d	-	+	+	-	+h	-	-	-
PI _e	-	+	+	-	+h	-	-	-
PI _f	-	+	+	-	-	-	-	+
Me-PI _a	-	-	-	-	-	-	-	-
Me-PI _b	+	+	+h	-	+	-	+h	+
Me-PI _c	-	-	-	-	-	-	-	-
Me-PI _d	-	+h	+	+	+h	-	-	-
Me-PI _e	-	+h	+	+h	+h	-	-	-
Me-PI _f	+h	+	+	+	+	+	+h	+

(a) Measured at 1.0% (w/v). +: soluble at room temperature; +h: soluble on heating; -: insoluble even on heating.

(b) NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Table III. Tensile properties of polyimide films.

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
PI _a	72	12	1.51
PI _b	86	10	1.49
PI _c	92	8	1.66
PI _d	88	11	1.60
PI _e	84	9	1.67
PI _f	92	10	1.37
Me-PI _b	77	8	1.54
Me-PI _c	81	8	1.43
Me-PI _d	79	7	1.41
Me-PI _e	78	8	1.38

Table IV. Thermal properties of polyimides.

Polymer	T _g ^(a) (°C)	T _i ^(b) (°C)		T ₁₀ ^(c) (°C)		Char yield ^(d) (%)
		in N ₂	in air	in N ₂	in air	
PI _a	— ^(e)	546	536	558	559	55.9
PI _b	285	527	536	555	569	61.0
PI _c	275	546	541	566	567	59.8
PI _d	287	520	518	530	552	53.2
PI _e	254	529	534	551	562	53.5
PI _f	287	534	529	553	540	54.0
Me-PI _a	—	443	432	454	456	49.5
Me-PI _b	295	427	418	440	462	51.8
Me-PI _c	284	430	424	448	465	51.3
Me-PI _d	290	432	421	438	438	43.9
Me-PI _e	257	421	416	440	459	54.3
Me-PI _f	300	425	415	453	482	48.8

(a) From the second heating traces of DSC measurement conducted with a heating rate of 20 °C/min in nitrogen.

(b) Initial decomposition temperature determined by TG with a heating rate of 20 °C/min.

(c) Temperatures at which 10% weight loss was recorded by TG.

(d) Char yield at 800 °C in nitrogen.

(e) No discernible transition was observed in DSC trace.

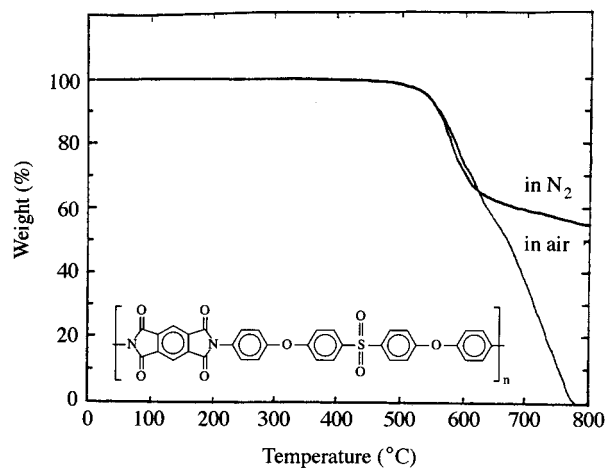


Figure 1. TG thermograms of polyimide PI_a, with a heating rate of 20 °C/min.

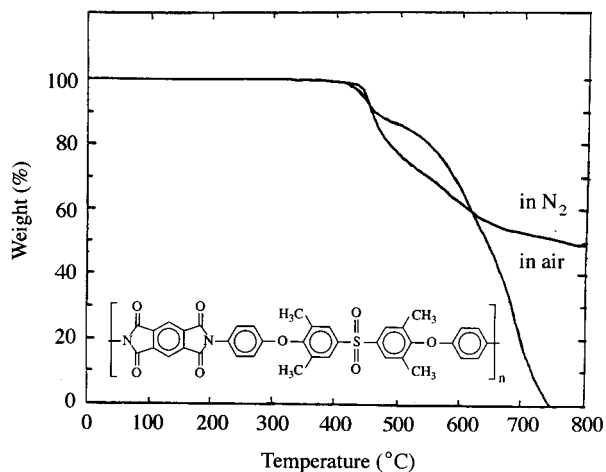


Figure 2. TG thermograms of polyimide Me-PI_a, with a heating rate of 20 °C/min.

in Figures 1 and 2, respectively. As shown in Figure 1, polymer **PI_a** showed a very similar TG behavior in nitrogen and air atmospheres below 600 °C, but when the temperature was increased above 600 °C, the polymer showed a rapid weight loss due to oxidative degradation and decomposed nearly completely at 790 °C. As can be seen from Figure 2, the presence of methyl substituents on the aromatic rings led to an earlier decomposition, due to the less thermally stable nature of aliphatic groups. Moreover, it also can be seen from the TG thermograms of polymer **Me-PI_a** that the rate of decomposition in air is slower than in nitrogen in the temperature range of 450~600 °C. This may be attributed to some possible oxidative interchain crosslinking between aliphatic segments of the polymer chain when thermally degraded in air. All the other polyimides showed similar thermal behavior, and some of their TG data are summarized in Table IV. The polyimides without methyl substituents lost 10% weight at temperatures in the range of 530~569 °C, and the methyl-substituted polyimides lost 10% weight in the range of 438~465 °C.

DSC measurements were carried out at a scan rate of 20 °C/min in flowing nitrogen. Rapid cooling from an elevated temperature (approximately 430 °C) to room temperature yielded predominantly amorphous samples so that in most cases distinct baseline shifts could be observed in the subsequent second heating DSC traces. The T_g of the polymer is defined as the midpoint temperature of the baseline shift. As listed in Table IV, the T_g values of the methyl-substituted polyimides stayed in the 284~300 °C range, and those of the unsubstituted polyimides were in the range of 254~287 °C. The difference in T_g values between the methyl-substituted polyimides and the corresponding unsubstituted analogues are attributed to the hindrance effect of the chain rotation in the methyl-substituted polymers. Comparisons of T_g s of the polyimides obtained from different dianhydrides showed that the polyimides derived from ODPDA showed the lowest T_g s because of the presence of a flexible ether bridge between the phthalimide units.

Conclusions

Two series of aromatic polyimides having moderate to high molar masses were synthesized via a classical two-stage polymerization method from aromatic dianhydrides with ether-sulfone-diamines based on 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol). The polyimides obtained

from the dianhydrides containing ether, sulfonyl, or a hexafluoroisopropylidene connector revealed higher solubility in organic solvents. The methyl-substituted polyimides showed a higher T_g but a lower initial decomposition temperature than the corresponding unsubstituted polymers.

Acknowledgement

Financial support of this research by the National Science Council of the Republic of China, under the Grant No. NSC 86-2216-E036-004, is gratefully acknowledged.

References

1. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, Eds., *Polyimides*, Chapman and Hall, N. Y., 1990.
2. M. K. Ghosh and K. L. Mittal, Eds., *Polyimides: Fundamentals and Applications*, Marcel Dekker, N. Y., 1996.
3. C.-P. Yang and W.-T. Chen, *Macromolecules*, **26**, 4865 (1993).
4. C.-P. Yang and J.-H. Lin, *J. Polym. Sci., Polym. Chem.*, **32**, 423 (1994).
5. J. R. Sasthav and F. W. Harris, *Polymer*, **36**, 4911 (1996).
6. F. W. Harris, S.-H. Lin, F.-M. Li and S. Z.-D. Cheng, *Polymer*, **37**, 5049 (1996).
7. S. Tamai, A. Yamaguchi and M. Ohta, *Polymer*, **37**, 3683 (1996).
8. J. G. Wirth, *High Performance Polymers: Their Origin and Development*, R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier, Amsterdam, 1986.
9. G. L. Brode, J. H. Kawakami, G. T. Kwiatkowski and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 575 (1974).
10. G. T. Kwiatkowski, G. L. Brode, J. H. Kawakami and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 589 (1974).
11. C. Chiriac and J. K. Stille, *Macromolecules*, **10**, 712 (1974).
12. J. Adduci, L. L. Chapoy, G. Jonsson, J. Kops and B. M. Shinde, *J. Appl. Polym. Sci.*, **28**, 2069 (1983).
13. S. B. Idage, B. B. Idage, B. M. Shinde and S. P. Vernekar, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 583 (1989).
14. Y. Delaviz, A. Gungor, J. E. McGrath and H. W. Gibson, *Polymer*, **34**, 210 (1993).
15. F. Keitou, M. Kakimoto and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 317 (1994).
16. J. S. McHattie, W. J. Koros and D. R. Paul, *Polymer*, **32**, 840 (1991).
17. J. S. McHattie, W. J. Koros and D. R. Paul, *Polymer*, **33**, 1701 (1992).
18. C. L. Aitken, W. J. Koros and D. R. Paul, *Macromolecules*, **25**, 3651 (1992).
19. S.-H. Hsiao and P.-C. Huang, *Macromol. Chem. Phys.*, **198**, 4001 (1997).