

Structure–property study of polyimides derived from PMDA and BPDA dianhydrides with structurally different diamines

Sheng-Huei Hsiao^{*}, Yu-Jen Chen

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Sec., Taipei 10451, Taiwan, ROC

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Abstract

A series of aromatic diamines were polymerized with two aromatic dianhydrides, pyromellitic dianhydride and 3,3',4,4'-biphenyltetracarboxylic dianhydride, and the resulting poly(amic acid)s were thermally cyclodehydrated to aromatic polyimides. The polyimides were characterized by determining the glass transition temperatures (T_g), thermal stability, coefficients of thermal expansion, and wide-angle X-ray diffraction. Structure–property relationships are elucidated and discussed in terms of the structural fragments in the polymer chain. The PMDA-based polyimides generally revealed a higher T_g than the corresponding BPDA-based analogues. Generally, the dilution of the imide content by the insertion of oxyphenylene segments into the diamines significantly reduced the T_g . The introduction of *m*- or *o*-phenylene units into the polymer backbone usually resulted in a decrease in T_g . The attachment of pendant groups on the backbone may lead to decreased or increased T_g s, depending on the structure of pendant groups. As evidenced by X-ray diffraction, the polyimides derived from rigid, rod-like diamines or the diamines having two or three *p*-oxyphenylene showed a higher crystalline tendency. The presence of aliphatic pendant groups slightly reduced the thermal stability of the polyimides. The other structural changes did not show a dramatic influence on the thermal stability. Some polyimides obtained from *p*- or *m*-phenylenediamine had low thermal expansion coefficients below $2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimides; Structure–property relationships; Pyromellitic dianhydride; 3,3',4,4'-Biphenyltetracarboxylic dianhydride

1. Introduction

Aromatic polyimides exhibit many useful properties such as high transition temperatures, excellent dimensional stability, low dielectric constants, and outstanding thermal and thermo-oxidative stability [1,2]. Therefore, some of these materials are being used in such applications as high performance structural materials and packaging in printed electronic circuitry. Polyimides are primarily used in the aerospace and microelectronics industries in the forms of films, moldings, and foams.

Films of aromatic polyimides represent the largest end-use area for the polyimides. Typical examples are Du Pont's Kapton type polyimide, derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), and Ube's Upilex type polyimides, i.e., Upilex R from 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) and ODA and Upilex S from BPDA and *p*-phenylenediamine. Since the Kapton polyimide was commercialized in early 1960s, a number of polyimides have been reported [3–6], and their structure–property relationships also have been extensively investigated for practical applications [7–13]. Here, “structure” means in general the chemical structure of the polyimide backbone. Numeral systematic studies revealed that the chain stiffness is the most important factor affecting directly their physical properties. In order to make an effort to

^{*} Corresponding author. Tel.: +886-2-25925252; fax: +886-2-25861939.

E-mail address: shhsiao@ttu.edu.tw (S.-H. Hsiao).

understand the structure–property relationships in the polyimide system, the present study describes the properties of serial systematically varied polyimides derived from PMDA and BPDA with various structurally different aromatic diamines and focuses on the study of the effect of structural changes on the glass transition temperature, crystallinity, and thermal expansion coefficient of the polyimides.

2. Experimental

2.1. Materials

p-Phenylenediamine (**Ia**) was purified by vacuum sublimation. *m*-phenylenediamine (**Ib**) was purified by vacuum distillation. ODA (**Ic**) (TCI), 3,4'-oxydianiline (**Id**) (Mitsui Petrochemical Ind.), 1,4-bis(4-aminophenoxy)benzene (**Ie**) (TCI), and 1,3-bis(4-aminophenoxy)benzene (**If**) (TCI) were used as received. According to a well-established method [7], 1,2-bis(4-aminophenoxy)benzene (**Ig**) (mp 137–138 °C), 2,5-bis(4-aminophenoxy)toluene (**Ih**) (mp 99–100 °C), 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene (**Ii**) (mp 128–129 °C), 2,5-bis(4-aminophenoxy)biphenyl (**Ij**) (mp 45–46 °C), 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**Ik**) (mp 129–131 °C), and bis[4-(4-aminophenoxy)phenyl] ether (**Il**) (mp 126–127 °C) were prepared by the aromatic nucleophilic substitution reaction of 4-chloronitrobenzene with the corresponding bisphenols in the presence of potassium carbonate, and subsequent reduction of the intermediate dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. PMDA (Aldrich) was recrystallized from acetic anhydride prior to use. BPDA (Oxychem) was purified by vacuum sublimation. *N,N*-dimethylacetamide (DMAc) was stirred over powdered calcium hydride overnight, and then distilled under reduced pressure and stored over 4 Å molecular sieves.

2.2. Polymer synthesis

A typical example of polymerization is as follows. To a stirred solution of 0.2688 g (2.48 mmol) of diamine **Ia** in 9.5 ml of dried DMAc in a 50 ml flask was added 0.7321 g (2.48 mmol) of sublimed BPDA in one portion. Thus, the solid content of the solution is approximately 10 wt.%. The mixture was stirred at room temperature for 2 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 2.25 dl g⁻¹, as measured in DMAc at a concentration of 0.5 g dl⁻¹ at 30 °C. The polymer solution was diluted with 10 ml of DMAc and then spread on a 9 cm glass culture dish, which was placed overnight in an 80 °C oven to remove most of the solvent. The semi-

dried poly(amic acid) film was further dried and transformed into polyimide **IIIa** by the following heating program: 150 °C/30 min, 200 °C/30 min, 250 °C/30 min, and 300 °C/1 h.

All other polyimides were synthesized by using the similar procedure as above.

2.3. Measurements

The inherent viscosities of the poly(amic acid)s were measured with an Ubbelohde viscometer at 30 °C. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer differential scanning calorimeter DSC 7 or Pyris 1 DSC at a scan rate of 20 °C min⁻¹ in flowing nitrogen (30 cm³ min⁻¹). Glass transition temperatures (*T*_gs) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling. Thermomechanical analysis (TMA) was conducted with a Perkin–Elmer TMA 7 instrument. For the determination of *T*_g, the TMA experiments were conducted from 40 to 300 °C or 500 °C at a scan rate of 10 °C min⁻¹ using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Apparent *T*_g's were taken as the onset temperature of probe displacement on the TMA traces. For the determination of the coefficient of thermal expansion (CTE), the TMA experiments were conducted from 40 to 300 °C at a scan rate 10 °C min⁻¹ using an expansion probe under an applied constant load of 50 mN. The CTE values were determined from the dimension change in the 100–200 °C range on the TMA traces. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 20 mA). The scanning rate was 2° min⁻¹ over a range of $2\theta = 5\text{--}45^\circ$. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Experiments were carried out on approximately 10 mg of samples in flowing nitrogen (flow rate 100 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹.

3. Results and discussion

3.1. Polymer synthesis

Two series of aromatic polyimides, **IIa–I** and **IIIa–I**, were prepared by the classical two-step procedure from diamines **Ia–I** listed in Fig. 1 with dianhydrides PMDA and BPDA via poly(amic acid)s followed by thermal imidization. Polymer preparation involved adding a solid dianhydride to the diamine solution in dry DMAc

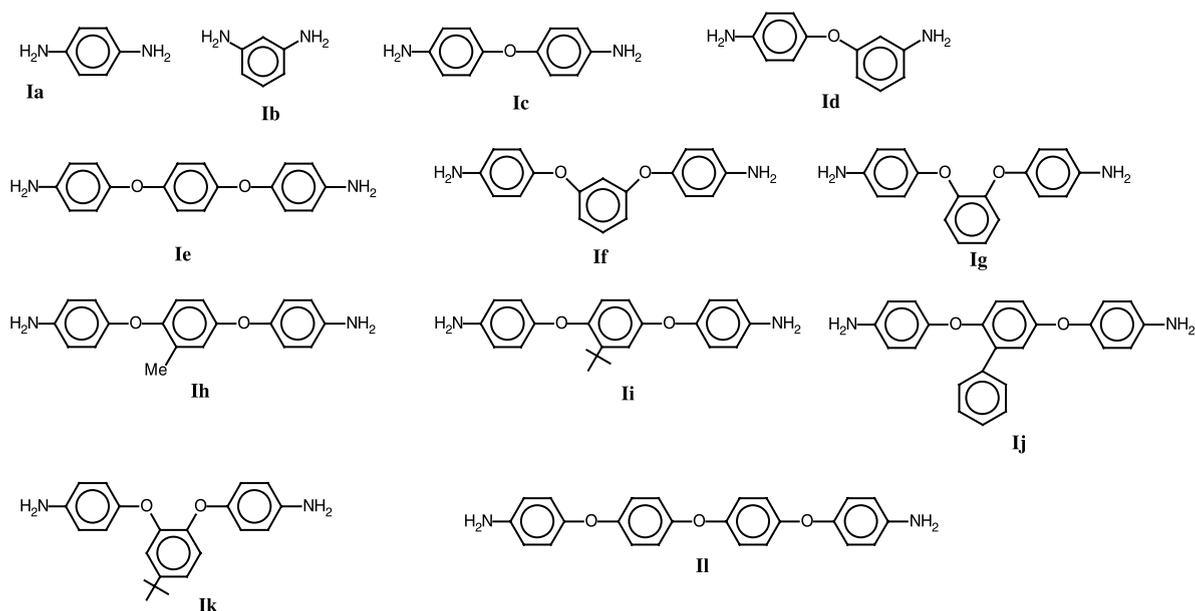


Fig. 1. Diamines used for polyimide synthesis.

to form the soluble poly(amic acid), pouring the poly(amic acid) solution onto a glass substrate, slowly evaporating the solvent, and finally thermally dehydrating to form the polyimide. Thus, all the polyimides were obtained in the form of films. As shown in Tables 1–3, the inherent viscosities of the intermediate poly(amic acid)s are in the range of 0.88–2.64 dl g⁻¹, indicating the formation of high molecular weight. Except for those derived from rigid diamines such as **IIa**, **IIb**, and **IIIb**, all the polyimides afforded tough and flexible films. Polyimide **IIa** yielded an extremely brittle film, due to a high degree of crystallinity as evidenced by the wide-angle X-ray diffraction. Possibly due to the structural rigidity, the films of polyimides **IIb** and **IIIb** also embrittled during thermal imidization. Key structural features of the polyimides were verified by FTIR spectroscopy. The characteristic absorption bands of the imide ring were observed near 1780 (asym. C=O str.), 1720 (sym. C=O str.), 1380 (C–N str.), 1120 and 740 cm⁻¹ (imide ring deformation). The aryl ether stretching absorbed near 1240 cm⁻¹. The disappearance of amide and carboxyl absorptions indicates a virtually complete conversion of the poly(amic acid) precursor into the polyimide.

3.2. Properties of polyimides

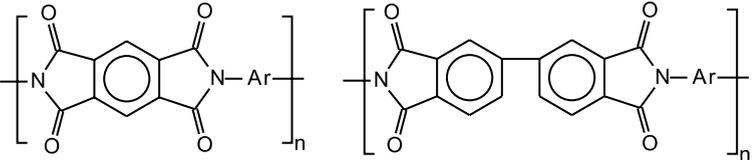
3.2.1. Ether diamines with different chain length

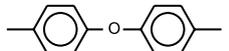
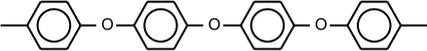
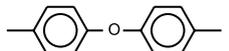
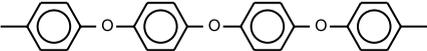
The effects of chain length of diamines on the properties of polyimides were studied by using polyimides synthesized from ether diamines having a different number of *p*-oxyphenylene units and PMDA or BPDA,

and the results are summarized in Table 1 and Fig. 2. The casting films of polyimide **IIa** obtained from PMDA and *p*-phenylenediamine embrittled during the thermal imidization process, probably caused by the structural rigidity and high level of crystallinity. Incorporation of flexible ether linkages into the backbone significantly enhanced the toughness of the polyimide films. Because of higher conformational flexibility of the BPDA moiety, even the polyimide (**IIIa**) from BPDA and rigid, rod-like *p*-phenylenediamine still could be fabricated into flexible, creasable and tough films. As can be seen from Fig. 2, polyimide **IIa** showed a strong, sharp reflection around $2\theta = 20^\circ$, indicating a high level of crystallinity. However, the BPDA polyimide **IIIa** seemed to have a decreased extent of crystallinity as shown by its X-ray diffraction pattern. These results are in good agreement with their film properties. By contrast to them, polyimides **IIc** and **IIIc** derived from ODA (**Ic**) seemed to exhibit almost completely amorphous patterns. It is interesting to note that the polyimides derived from the diamines having three aromatic rings bridged with two ether linkages (**Ie**) and that having four aromatic rings bridged with three ether linkages (**II**), such as **IIe**, **III**, **IIIe** and **IIII**, showed a slightly enhanced crystallinity compared to the corresponding polyimides **IIc** and **IIIc**. This may be attributable to the fact that the more flexible diamine segments in the former polyimides might allow the better packing of the polymer chains during thermal imidization at elevated temperatures.

The thermal transitions of this category of polyimides were first investigated by DSC measurements. However, in most cases, DSC detected no melting transitions and

Table 1
Properties of polyimides based on ether diamines having different chain length



Polyimide code	Dianhydride	Diamine	Ar	η_{inh}^a (dl g ⁻¹)	Film quality ^b	T_g^c (°C)	T_d^d (°C)	Char yield ^e (%)	CTE (ppm °C ⁻¹) ^f
IIa	PMDA	Ia		2.64	Brittle	>500	632	59	20
IIc	PMDA	Ic		2.44	Flexible	352	614	58	50
IIe	PMDA	Ie		2.51	Flexible	312	604	57	44
III	PMDA	II		2.54	Flexible	295	588	56	20
IIIa	BPDA	Ia		2.25	Flexible	305	640	65	13
IIIc	BPDA	Ic		2.02	Flexible	270	612	64	28
IIIe	BPDA	Ie		2.15	Flexible	265 (265) ^g	601	61	37
IIII	BPDA	II		1.21	Flexible	222 (235) ^g	589	58	13

^a Inherent viscosity of the poly(amic acid) precursor determined on 0.5 g dl⁻¹ solution in DMAc at 30 °C.

^b Polyimide films obtained by sequential heating of the poly(amic acid) films at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 30 min.

^c Measured by TMA (penetration method) with a penetration probe of 1.0 mm diameter and an applied constant load of 10 mN, at a heating rate of 10 °C min⁻¹.

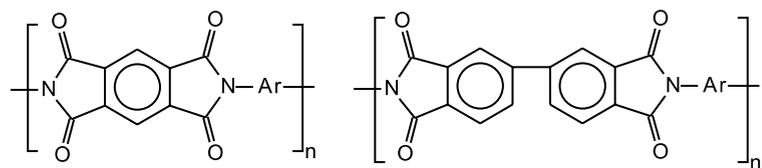
^d Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹ in nitrogen.

^e Residual weight % when heated to 800 °C in nitrogen.

^f CTE between 100 and 200 °C by TMA (expansion method) at a heating rate of 10 °C min⁻¹.

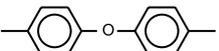
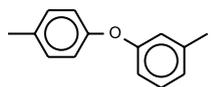
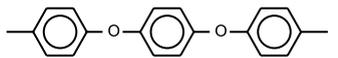
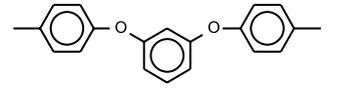
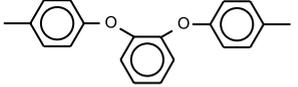
^g Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 400 °C.

Table 2
Effect of catenation of the phenylene unit in diamine on property of polyimide



Polyimide code	Dianhydride	Diamine	Ar	η_{inh}^a (dl g ⁻¹)	Film quality ^b	T_g^c (°C)	T_d^d (°C)	Char yield ^e (%)	CTE (ppm °C ⁻¹) ^f
IIa	PMDA	Ia		2.64	Brittle	>500	632	59	20
IIb	PMDA	Ib		1.71	Brittle	418	627	57	24
IIc	PMDA	Ic		2.44	Flexible	352	614	58	50
II d	PMDA	Id		1.75	Flexible	319	607	59	96
IIe	PMDA	Ie		2.51	Flexible	312	604	57	44
II f	PMDA	If		2.35	Flexible	326	608	53	34
II g	PMDA	Ig		1.32	Flexible	313	586	57	26
IIIa	BPDA	Ia		2.25	Flexible	305	640	65	13
IIIb	BPDA	Ib		1.34	Brittle	316 (330) ^g	618	64	6

Table 2 (continued)

Polyimide code	Dianhydride	Diamine	Ar	η_{inh}^a (dl g ⁻¹)	Film quality ^b	T_g^c (°C)	T_d^d (°C)	Char yield ^e (%)	CTE (ppm °C ⁻¹) ^f
IIIc	BPDA	Ic		2.02	Flexible	270	612	64	28
IIIId	BPDA	Id		1.56	Flexible	259 (271)	604	64	31
IIIe	BPDA	Ie		2.15	Flexible	265 (265)	601	61	37
IIIIf	BPDA	If		1.67	Flexible	232 (236)	608	63	57
IIIg	BPDA	Ig		1.19	Flexible	235 (247)	614	63	43

^a Inherent viscosity of the poly(amic acid) precursor determined on 0.5 g dl⁻¹ solution in DMAc at 30 °C.

^b Polyimide films obtained by sequential heating of the poly(amic acid) films at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 30 min.

^c Measured by TMA (penetration method) with a penetration probe of 1.0 mm diameter and an applied constant load of 10 mN, at a heating rate of 10 °C min⁻¹.

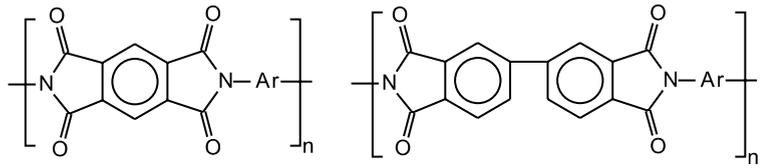
^d Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹.

^e Residual weight % when heated to 800 °C in nitrogen.

^f CTE between 100 and 200 °C by TMA (expansion method) at a heating rate of 10 °C min⁻¹.

^g Values in the parentheses are the T_g determined by DSC; midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 400 °C.

Table 3
Effect of pendant group in ether diamines having three benzene rings on property of polyimide



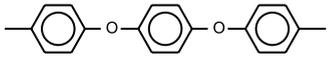
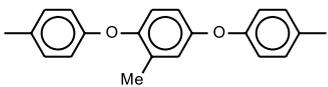
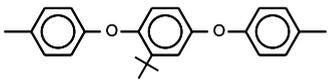
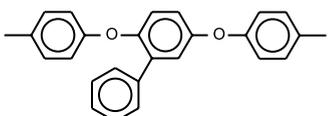
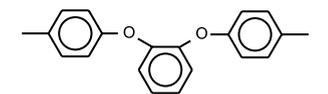
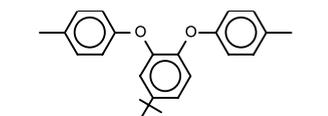
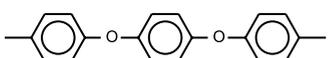
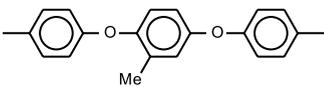
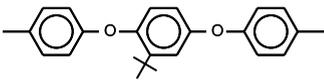
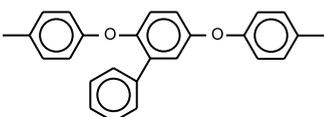
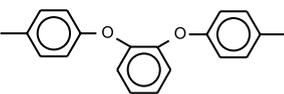
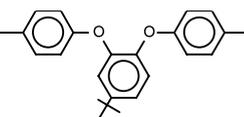
Polyimide code	Dianhydride	Diamine	Ar	η_{inh}^a (dl g ⁻¹)	Film quality ^b	T_g (°C)		T_d^c (°C)	Char yield (%) ^d	CTE (ppm °C ⁻¹) ^e
						DSC ^f	TMA ^g			
IIe	PMDA	Ie		2.51	Flexible	– ^h	312	604	57	44
IIh	PMDA	Ih		1.67	Flexible	–	310	522	58	20
IIi	PMDA	Ii		1.62	Flexible	–	314	538	47	62
IIj	PMDA	Ij		1.12	Flexible	276	266	586	60	67
IIg	PMDA	Ig		1.32	Flexible	–	313	586	57	26
IIk	PMDA	Ik		2.21	Brittle	–	321	551	53	27
IIIe	BPDA	Ie		2.15	Flexible	265	265	601	61	37

Table 3 (continued)

Polyimide code	Dianhydride	Diamine	Ar	η_{inh}^a (dl g ⁻¹)	Film quality ^b	T_g (°C)		T_d^c (°C)	Char yield (%) ^d	CTE (ppm °C ⁻¹) ^e
						DSC ^f	TMA ^g			
IIIh	BPDA	Ih		1.58	Flexible	276	254	522	61	53
IIIi	BPDA	Ii		1.36	Flexible	278	270	543	48	96
IIIj	BPDA	Ij		0.88	Flexible	251	243	596	65	83
IIIg	BPDA	Ig		1.19	Flexible	247	235	614	63	43
IIIk	BPDA	Ik		1.35	Flexible	258	256	556	58	72

^a Inherent viscosity of the poly(amic acid) precursor determined on 0.5 g dl⁻¹ solution in DMAc at 30 °C.

^b Polyimide films obtained by sequential heating of the poly(amic acid) films at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 30 min.

^c Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹.

^d Residual weight % at 800 °C in nitrogen.

^e CTE between 100 and 200 °C by TMA (expansion method) at a heating rate of 10 °C min⁻¹.

^f The sample were heated to 400 °C with a heating rate of 20 °C min⁻¹ and rapidly cooled to 30 °C at -200 °C min⁻¹. The midpoint of baseline shift on the subsequent second DSC trace was defined as T_g .

^g The onset temperature of the probe displacement on the TMA traces. A penetration probe of 1.0 mm diameter and an applied constant load of 10 mN were employed.

^h No discernible transitions was observed.

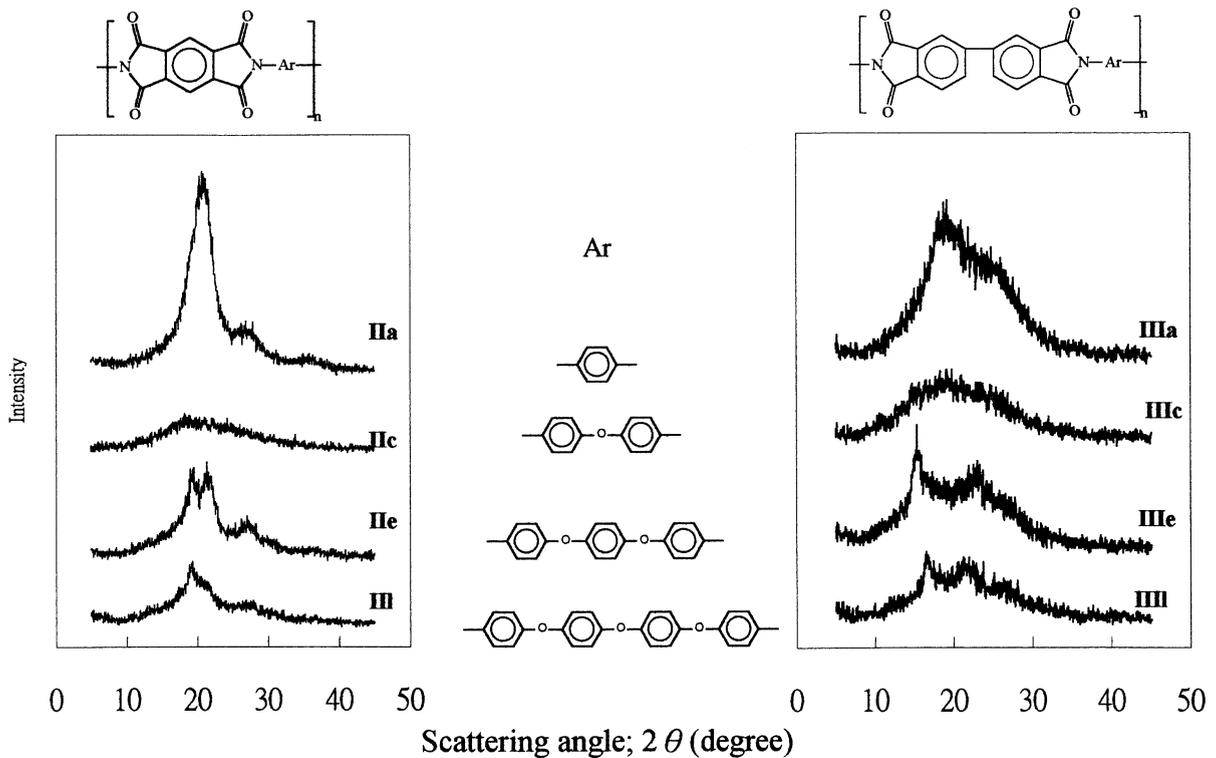


Fig. 2. Wide-angle X-ray diffraction patterns of polyimides based on diamines with different numbers of *p*-oxyphenylene groups.

discernible glass transitions up to 500 °C, possible due to high melting points of these polyimides. Only two BPDA polyimides (**IIIe** and **IIII**) of this category exhibited melting endotherms in the first DSC heating traces before 500 °C. As shown in Fig. 3, the first DSC heating traces of polyimides **IIIe** and **IIII** that showed clear melting endothermic peaks around 467 and 386 °C, respectively. Rapid cooling (rate = 200 °C min⁻¹) and reheating showed strong *T_g*s at 265 and 235 °C, respectively, and disappearance of the melting transitions. The DSC thermal behavior of polyimide **IIII** is similar to that of AurumTM (*T_g* = 250 °C, *T_m* = 388 °C), a melt-processable semi-crystalline polyimide developed by Mitsui Chemicals, Inc. [14].

The apparent *T_g* data in Table 1 were generated on films by the TMA method using a penetration probe. The *T_g* values generally decreased with increased chain flexibility. The rigid, rod-like polyimide **IIa** did not show *T_g* transition up to 500 °C. All the PMDA polyimides revealed a higher *T_g* in comparison to that of the corresponding BPDA ones because of a higher rigidity of the polymer chain. The thermal stability of polymers was ascertained by TGA. The decomposition temperatures (*T_d*) at 10% weight loss and the anaerobic char yield at 800 °C in nitrogen for the polyimides are also summarized in Table 1. The polyimides without ether

linkages were more thermally stable than the corresponding ones with ether linkages. It seems that when the length of the oxyphenylene unit increased, the thermal stability of the polymers was reduced slightly.

One of the most important considerations for a package design that increases lifetime of the device is the minimization of stress [15]. It arises nearly exclusively because the package is a composite material with different CTE and moduli. The CTEs of conductor metal, chip, and substrate are usually low (between 2 and 20 ppm). Thus, a dielectric with low CTE is desirable. Here, the effects of linearity and rigidity of molecular chains on the CTEs of polyimide films was investigated. As shown in Table 1, the polyimides **IIa** and **IIIa** obtained from rigid, rod-like *p*-phenylenediamine had low CTEs of 20 and 13 ppm °C⁻¹, respectively. But the polyimides obtained from the diamines had a flexible ether linkage, such as diamines **Ic** and **Ie**, had increased CTEs. However, it is worth mentioning that the polyimides derived from the flexible diamine **II** also showed a relatively lower CTEs, the same with those of the polyimides derived from rigid *p*-phenylenediamine. It was recognized that the low CTEs related to the linearity in the polymer molecular skeletons [16,17]. Therefore, the low CTEs associated with polyimides **III** and **IIII** imply that the flexible segment of diamine **II** may help the molecular

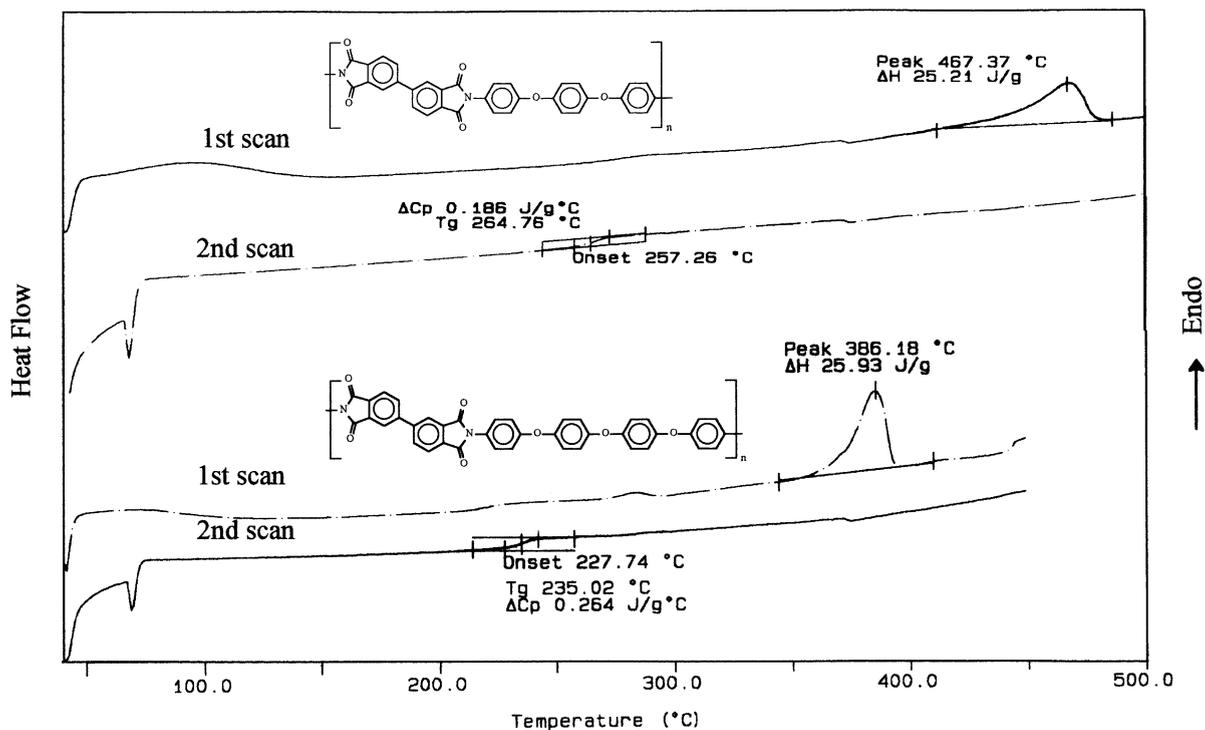
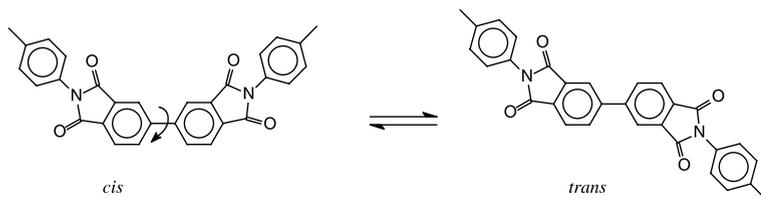


Fig. 3. DSC thermograms of polyimides **IIIe** (top) and **IIII** (bottom) at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen.

skeletons to a linear arrangement. Moreover, although there was a less rigid structure due to the biphenyl skeleton of BPDA, all the BPDA-based polyimides in this category showed a lower CTE than the corresponding PMDA-based ones. This may be attributable to the fact that the kinked (*cis*) conformation of BPDA could be transformed into the extended (*trans*) conformation by rotation around the central single bond during the thermal imidization process at elevated temperature [18], thus leading to a linear arrangement of polymer chains and low CTEs (see the following scheme).



3.2.2. Diamines with different catenated positions on the benzene ring

The effect of catenation of the phenylene unit on the properties of obtained polyimides was studied by using some isomeric diamines. Properties of polyimides syn-

thesized from PMDA and BPDA with various diamine isomers having one to three benzene rings are listed in Table 2. As mentioned above, the casting films of polyimides **IIa**, **IIb**, and **IIb** are noncreasable due to high crystallinity or structural rigidity. All other polyimides shown in Table 2 gave good quality, creasable films.

In most cases, the tendency is for T_g to decrease as the polymer goes from all *para* catenation to all *meta* or partially *meta* or *ortho*. The explanation is that an overall decrease in T_g correlates with backbone flexibility. It was also found that all the PMDA-derived

polyimides showed a higher T_g than the corresponding BPDA-derived polyimides. Furthermore, the T_g s of most BPDA-based polyimides listed in Table 2 also could be easily detected by DSC experiments. The T_g values generated by DSC are slightly different from those de-

tected by TMA, possibly due to the different thermal history and the different nature of the testing techniques. As listed in Table 2, the TGA and CTE data of these polyimides show no significant dependence on the isomeric attachment of the diamine.

The effect of catenation of the phenylene unit in diamine on the crystallinity of polyimides is shown in Fig. 4. It is evident that changing the *p*-phenylenediamine moiety into *m*-phenylenediamine reduced the polymer crystallinity drastically. Fig. 4 also shows that the polyimides derived from the bisaminophenoxybenzenes with the *meta* or *ortho* catenation on the central ring revealed a decreased crystallinity than the corresponding polyimides with *para* catenation on the central ring. This is most apparent with *ortho* catenation and to a lesser extent with *meta* catenation. For example, polyimide **III**f still exhibited some levels of crystallinity, whereas polyimide **III**g almost showed no crystallinity. Film of the former was semi-transparent, while the latter transparent. As illustrated in Fig. 5, the DSC scan of the as-prepared sample of polyimide **III**f showed a medium endothermic peak at 385 °C due to melting of the crystalline regions in **III**f and a smaller peak at 305 °C possibly due to the imperfect and thinner crystals. After annealing at 300–390 °C for 10 min, the small low-temperature endotherm is observed at temperatures of about annealing temperature (T_a) + 10 °C. These results

are similar to those reported earlier by Srinivas et al. [19]. The main endotherm is essentially independent of annealing temperature except for the case at $T_a = 380$ °C. The two endothermic peaks merges together at a higher temperature of 393 °C when a T_a of 380 °C is applied. Another intermediate endotherm described by Hsiao et al. [20] and Srinivas et al. [19] was not observed, possibly due to a higher heating rate (20 °C min⁻¹) employed in this study.

3.2.3. Ether diamines having pendant substituents

In order to study the effect of pendant groups on the properties of polyimides, the polyimides were synthesized from 1,4-bis(4-aminophenoxy)benzenes bearing methyl (**II**h), *t*-butyl (**II**i) and phenyl (**II**j) substituents in the central benzene ring and 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**II**k) with PMDA and BPDA. Properties of the obtained polyimides are summarized in Table 3. Except for polyimide **III**k, all the polyimides afforded flexible and tough films. The casting film of polyimide **III**k embrittled during the thermal imidization process, possibly because of the rigid nature of this polyimide. As can be seen in Table 3, the introduction of pendant *t*-butyl groups causes a slight increase in the T_g of the polyimides. However, the attachment of pendant phenyl groups leads to a slight decrease in T_g . There may

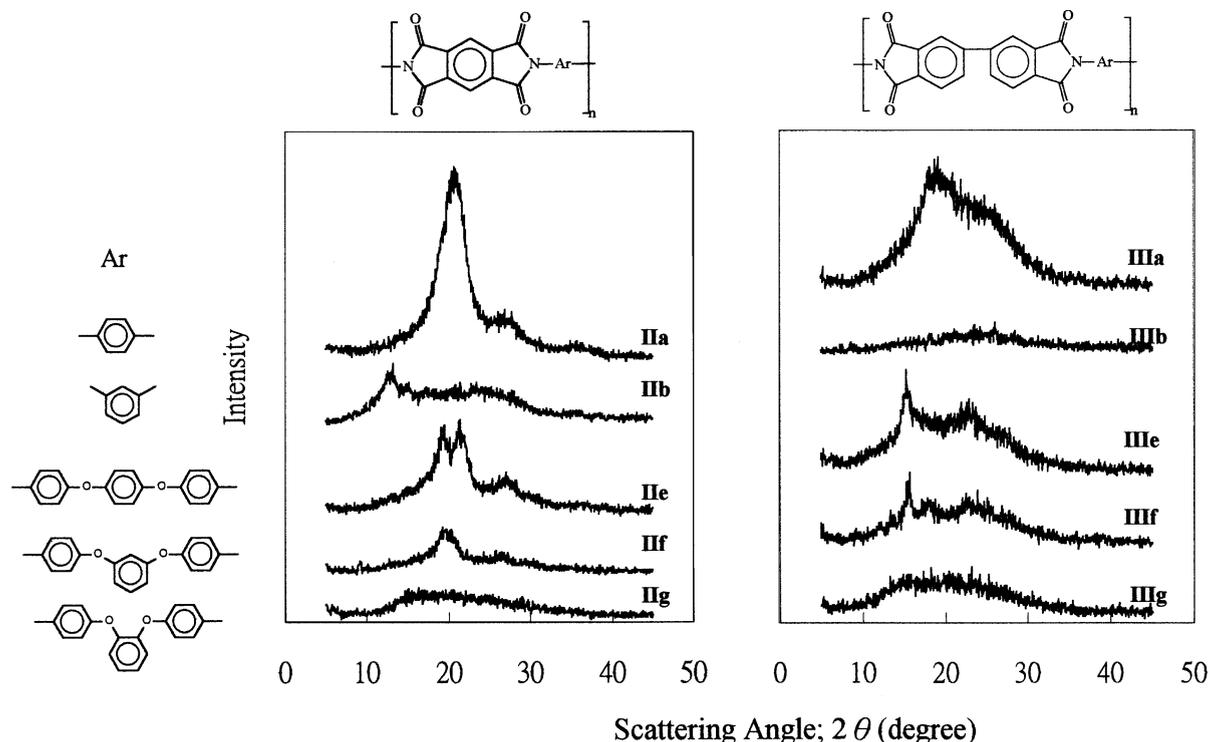


Fig. 4. Effect of catenation of the phenylene unit in diamine on the crystallinity of polyimides.

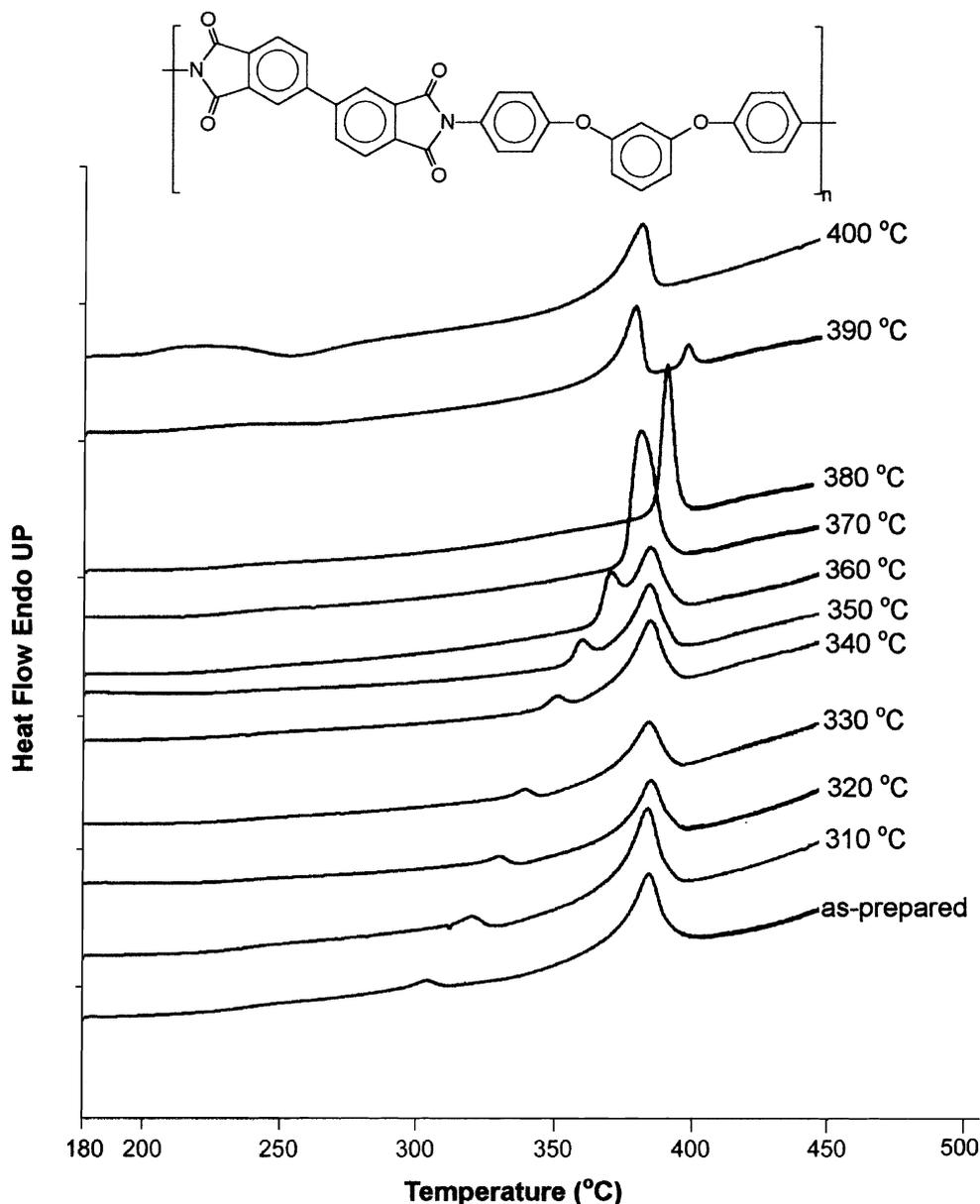


Fig. 5. DSC heating scans ($20\text{ }^{\circ}\text{C min}^{-1}$) for polyimide **III**f sample isothermally annealed at various temperatures, each for 10 min.

be two phenomena working in opposite directions: increased steric hindrance causing a T_g increasing, and increased fractional free volume causing a T_g lowering. The former phenomenon seemed to be the primary operator in the polyimides with pendant *t*-butyl groups, and the latter phenomenon seemed to play a more important role in the polyimides with pendant phenyl groups. For the substituted polyimides based on PMDA, only the phenyl-pendant **II**j had clear T_g as measured by both DSC and TMA. The other substituted PMDA polyimides did not show well-defined T_g by

DSC. However, the T_g values of all BPDA polyimides with pendant group could be detected by both calorimetric and mechanical techniques. The T_g values measured by the DSC method was usually slightly higher than that detected by the TMA method.

The introduction of methyl and *t*-butyl groups lowered the decomposition temperatures of polymers, while the effects of the phenyl group did not seem significant. In most cases, the incorporation of bulky pendant groups such as *t*-butyl and phenyl groups causes an increased CTE because of increased free volume. The ef-

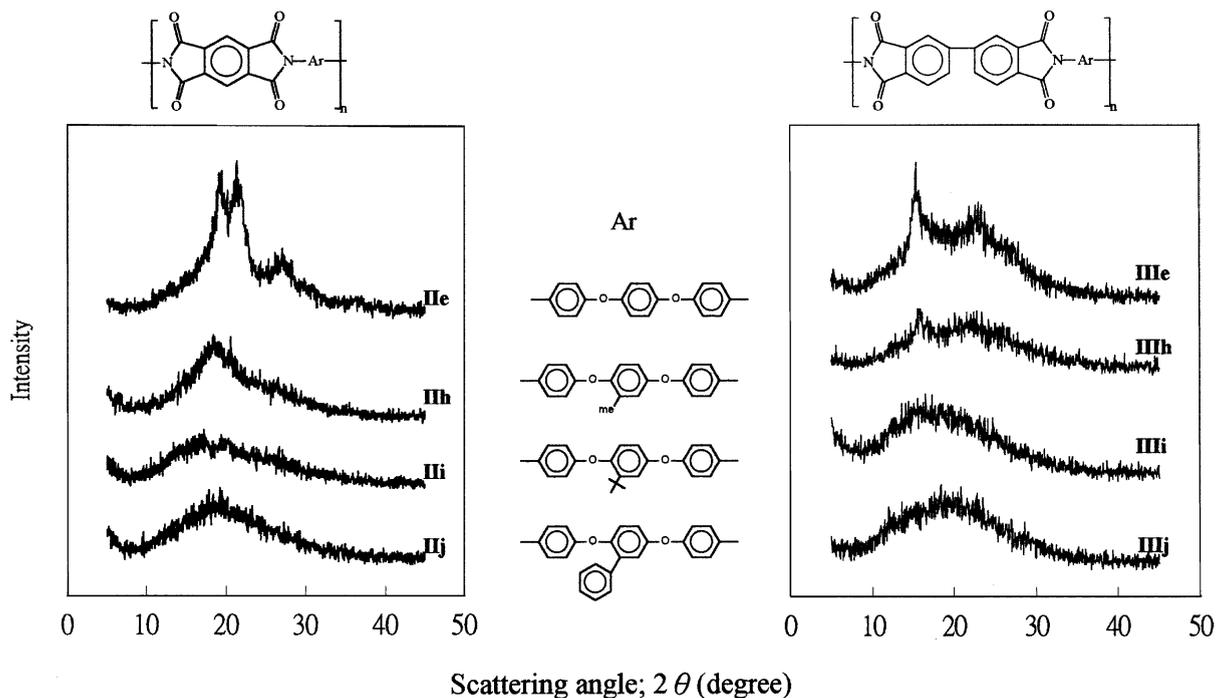


Fig. 6. Effect of the pendant group on the crystallinity of polyimides.

fect of introducing pendant groups on the polymer crystallinity can be evidently seen from Fig. 6. The introduction of methyl substituents slightly lowered the crystallinity of polymers. However, the attachment of bulky *t*-butyl or phenyl group causes a significant decrease in crystallinity.

4. Conclusions

Several systematically varied aromatic polyimides having high molecular weights were prepared by the classic two-step procedure from dianhydrides PMDA and BPDA with various structurally different diamines, and almost all the polymers afforded flexible and tough films by successive heating the poly(amic acid) films to elevated temperatures. In general, the T_g of polyimides decreased with increasing backbone flexibility. The PMDA-derived polyimides generally exhibited a higher T_g than the corresponding BPDA-derived polyimides. The incorporation of ether linkages and *m*- or *o*-phenylene units into the polymer main chain generally led to a decrease in T_g . The introduction of pendant *t*-butyl groups resulted in an enhanced T_g due to increased rotational barriers; however, the attachment of pendant phenyl groups caused a lowered T_g because of increased free-volume fractions. As evidenced by X-ray diffraction analysis, the PMDA polyimides derived from rigid di-

amines, such as *p*-phenylenediamine, and ether diamines having three or four benzene rings bridged with two or three ether groups, such as diamines **Ie**, **If**, and **II**, showed moderate to high levels of crystallinity. In the case of BPDA polyimides, only those derived from multiring ether diamines such as **Ie**, **If**, and **II** showed a moderate level of crystallinity. The insertion of less symmetric structures such as *m*- or *o*-phenylene and the attachment of bulky pendant groups reduced the polymer crystallinity. Most polyimides exhibited high thermal stability, and it was found that the chain length of ether diamines, the catenation position of the phenylene unit, and the aromatic pendant groups had not a significant influence on the thermal stability of the polyimides. The polyimides obtained from PMDA or BPDA and *p*- or *m*-phenylenediamines had low thermal expansion coefficients. Some polyimides obtained from the diamines which have flexible ether linkage also showed low thermal expansion coefficients. It was proposed that the low thermal expansion coefficient appeared when the conformation of the molecular chain became linear.

Acknowledgements

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