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Polymer 40 (1999) 1603–1610

polymer

Structure and properties of rodlike poly(*p*-phenylene pyromellitimide)s containing short side groups

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Received 14 January 1998; revised 6 April 1998; accepted 11 May 1998

Abstract

Fully rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA) exhibits a high modulus but is considered a useless polymer because of its high brittleness. In this study, the high brittleness was successfully healed with only a minor effect on the high modulus by incorporating short side groups, such as methyl, methoxy and trifluoromethyl, into the PDA unit of the polymer backbone. Furthermore, refractive indices, dielectric constants, and their anisotropies were all reduced by the incorporation of side groups. However, both in-plane thermal expansivity and thermal stability were relatively degraded by the incorporation of side groups. The polyimides exhibited relatively low packing coefficients because of the limited bulkiness of the side groups. They exhibited glass transition temperatures which are not expected for PMDA-PDA polyimide, indicating that the chain mobility was improved by incorporating side groups. With the improved chain mobility, molecular ordering was slightly improved, showing a bundle-like ordering without regular packing.

Keywords: Rodlike polyimide; Short side group; Structure

1. Introduction

Since poly(4,4′-oxydiphenylene pyromellitimide) was introduced in the early 1960s [1,2], aromatic polyimides have been extensively used in the microelectronics industry as interdielectric layers, passivation layers and alpha-particle barriers owing to their excellent chemical and physical properties [3–10]. In particular, fully rodlike polyimides have gained great attention from both industry and academia because they can potentially provide a high modulus and high strength as well as high dimensional stability. A representative rodlike polyimide is poly(*p*-phenylene pyromellitimide) (PMDA-PDA). The PMDA-PDA polyimide is thermally stable up to about 600°C, showing no glass transition below its decomposition temperature. However, this polyimide is very brittle so that its mechanical properties could not always be easily measured.

In this study, we have attempted to improve its mechanical properties without degrading the advantageous properties by incorporating short side groups into the polymer backbone. PMDA-PDA polyimides with various side chains were synthesized from pyromellitic dianhydride with *p*-phenylene diamines containing methyl, methoxy, and trifluoromethyl groups, as shown in Fig. 1, and their mechanical properties were investigated. In addition, structures and other properties were measured by wide angle X-ray diffraction, prism coupling, density measurement, thermogravimetry, dynamic mechanical thermal analysis, and thermomechanical analysis.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA) and 2,5-diaminobenzotrifluoride (CF3PDA) were supplied from Chriskev (Kansas, USA) and Marshallton (Virginia, USA), respectively. All the other chemicals used in this study were purchased from Aldrich. PMDA was purified by drying at 120°C for 1 day in vacuum prior to use. CF3PDA and *p*-phenylene diamine (PDA) were sublimed under reduced pressure, respectively. 2,5-Diaminoanisole sulfate hydrate and 2,5-diaminotoluene sulfate were converted to 2,5-diaminoanisole (MEOPDA) and 2,5-diaminotoluene (MEPDA), respectively, by neutralization with sodium hydroxide and subsequent extraction with chloroform. These diamines were further purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure.

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PII: S0032-3861(98)00375-9

2.2. Synthesis of poly(amic acid)s

PMDA-PDA poly(amic acid) (PAA) was synthesized by slowly adding the equivalent mole of the sublimed PMDA to the purified PDA in dry NMP in a glove box filled with dry nitrogen gas. Once the dianhydride addition was completed, the reaction flask was capped tightly and stirring was continued for 2 days to make the polymerization mixture completely homogeneous. The other three poly(amic acid)s were prepared in the same manner as the PMDA-PDA PAA was synthesized: PMDA-MEPDA, PMDA-CF3PDA, and PMDA-MEOPDA PAAs. The solid contents of the precursor solutions were 10–15 wt%. The precursor solutions were filtered with silver metal membranes of 1.0 μm pore size, tightly sealed, and stored in a refrigerator before use.

For the poly(amic acid)s, intrinsic viscosity $[\eta]$ measurements were carried out in NMP at 25.0°C using a Ubbelohde suspended level capillary viscometer as described in the literature [11–13]. In order to minimize the polyelectrolyte effect in the viscosity measurement, NMP was purified by distillation over phosphorus pentoxide (P_2O_5) under reduced pressure and further treated with 0.02 M P_2O_5, followed by filtration before use [11–13]. All the solutions were filtered through 0.5-μm Fluoropore filters (Millipore) before measurement. For a given poly(amic acid), the relative and specific viscosities were measured at four different concentrations over the range of 0.10–0.60 g/dl, and the $[\eta]$ value was determined by extrapolation of the reduced and inherent viscosities to infinite dilution. The $[\eta]$ was determined to be 0.538 dl/g for PMDA-PDA PAA, 0.868 dl/g for PMDA-MEPDA PAA, 0.213 dl/g for PMDA-CF3PDA PAA, and 0.579 dl/g for PMDA-MEOPDA PAA.

2.3. Preparation of polyimide films

All the precursor solutions were spin-coated on glass substrates, followed by soft-baking on a hotplate at 80°C for 1 h. The soft-baked precursor films were thermally imidized in an oven with dried N_2 gas flow by a three-step imidization process: 150°C/30 min, 230°C/30 min, and 380°C/60 min with a ramping rate of 2.0 K/min. After the thermal imidization, the samples were cooled to room temperature with a rate of 10 K/min. The thickness of the imidized films was 10–11 μm. The films were taken off from the glass substrates with the aid of deionized water, followed by drying for 1 day at 100°C in a vacuum oven. For measurements of structures and properties, films were cut into appropriate sizes.

2.4. Characterization

Wide angle X-ray diffraction (WAXD) measurements were performed at room temperature in both reflection and transmission goniometry, using a Rigaku vertical diffractometer (Model RINT-2500) with a rotating anode X-ray generator. The Cu K_α radiation source was operated at 40 kV and 60 mA. A divergence slit of one degree was employed together with two receiving slits of 0.5°. All the measurements were carried in $\theta/2\theta$ mode. The 2θ scan data were collected at 0.01° interval over the range of 4–70° and the scan speed was 0.1°(2θ)/min. The measured WAXD patterns were corrected to the background runs. The WAXD patterns were deconvoluted in the following manner. An interactive curve-fitting technique based on a non-linear-least-squares estimation algorithm was used to fit a collection of pseudo-Voight functions and one linear baseline to the WAXD profile [14,15]. For each deconvoluted peak, coherence length (L_C) was estimated from its full width at half-maximum with an instrumental broadening of 0.15° using the Scherrer equation [16,17].

Densities of polyimide films were measured at 30°C using a calibrated density gradient column filled with carbon tetrachloride/cyclohexane mixtures. Packing coefficients (Ks) of films were estimated from the measured densities in accordance with the following equation proposed by Slonimskii et al. [18]:

$$K = \frac{V_{\text{int}}}{V_{\text{true}}} \tag{1}$$

$$= \frac{N_A \sum \Delta V_i}{M/d} \tag{2}$$

Here, V_{int} is the total intrinsic volume of the atoms consisting of the repeating unit, V_{true} is the molar volume calculated from the density d, ΔV_i is the volumetric increment of atoms, M is the molecular weight of the repeating unit, and N_A is Avogadro's number.

Refractive indices were measured at room temperature using a prism coupler equipped with a He–Ne laser light source of 632.8 nm wavelength (that is, 474.08 THz in optical frequency) and controlled by a personal computer [17,19]. The refractive index in the film plane (n_{xy}) was measured in the transverse electric mode, whereas the refractive index in the out-of-plane (n_z) was obtained in the transverse magnetic mode. All measurements were performed using a cubic zirconia prism of $n = 2.1677$ at a wavelength of 632.8 nm.

In-plane thermal expansion coefficients (TECs) were measured with a load of 5 g at a ramping rate of 5.0 K/min over the range of 50–250°C under a N_2 gas flow using a Seiko thermomechanical analyzer (TMA, Model-120 CU) with a tension probe. Before the measurement, the film specimens were heated to 250°C with a ramping rate of 10.0 K/min, soaked for 20 min at that temperature and then cooled down to 30°C with a cooling rate of 10.0 K/min, in order to remove residual stress in the films. TEC was averaged over the range of 100–200°C. The gauge length was 20.0 mm and the width of film strips was 2 mm. Glass transition temperatures (T_gs) were measured in tension mode using a Polymer Laboratory dynamic mechanical thermal analyzer (DMTA, Model MK-11DM). The gauge length was 5–6 mm and the width of film strips was 6.35 mm. Measurements were carried out over the range of 25–450°C at a frequency of 1 Hz and a ramping rate of 3.0 K/min. T_g was taken as the onset temperature of glass transition in the storage modulus versus temperature curve. Thermal stabilities were measured over 50–800°C using a Perkin–Elmer thermogravimetric analyzer (TGA, Model TGA7). During the measurement, dry nitrogen gas was purged at a flow rate of 100 ml/min and a ramping rate of 5.0 K/min was employed.

Mechanical properties of the films were measured at room temperature using an Instron mechanical tester (Model 4052). Polyimide films removed from the substrates were manually diced into film strips with a width of 2.5 mm. The gauge length and crosshead speed were 25 mm and 2.0 mm/min, respectively.

3. Results and discussion

3.1. Structure

X-Ray diffraction patterns of polyimide films are shown in Fig. 2. For rodlike PMDA-PDA, the reflection pattern had only two peaks, one large, broad peak at 20.7° (2θ) and another weak, broad peak at about 25.6°, consequently showing no regularly ordered structure. The peak at 20.7° is the amorphous halo, giving a *d*-spacing of 4.3 Å which corresponds to the average intermolecular distance in the direction of film thickness. For the amorphous halo, a coherence length (L_C) was estimated to be 27.2 Å. On the other hand, the transmission pattern exhibited an amorphous halo peak as well as multiple (00*l*) peaks. The amorphous halo peak at 18.8° gives a *d*-spacing of 4.7 Å which corresponds to the average intermolecular distance in the film plane. This mean intermolecular distance is larger than that in the direction of film thickness, indicating that the rodlike polymer chains in the thin film are packed more densely in the direction of film thickness than the film plane. Its L_C was estimated to be 32.3 Å.

The multiple (00*l*) peaks are (001) peak at 7.26° (12.2 Å), (002) peak at 14.6° (6.1 Å), (003) peak at 21.6° (4.1 Å), (004) peak at 29.1° (3.1 Å), (005) peak at 36.6° (2.5 Å), and (006) peak at 44.4° (2.0 Å). From the (00*l*) peaks, we can get at least three pieces of structural information as follows: First, the length of the repeating unit projected along the chain axis is estimated to be 12.2 Å. Second, the appearance of (00*l*) peaks might result from the polymer chains ordered in bundles without any regularly lateral ordering. For some of the (00*l*) peaks, L_Cs were estimated: 104.4 Å for the (001) peak, 95.1 Å for the (002), 80.0 Å for the (003), and 81.2 Å for the (004). Third, the (00*l*) peaks appeared only in the transmission pattern, indicating that the polymer chains are preferentially oriented in the film plane.

Therefore, from the X-ray diffraction results it is speculated that the bundle-like ordered phase has a dimension of 95.1 Å length (which is equivalent to 7–8 repeating units), 32.3 Å width (which corresponds to 6–7 polymer chains) in the film plane and 27.2 Å width (which corresponds to 6–7 polymer chains) in the direction of film thickness: here, there are adapted the L_Cs of the (002) peak and the amorphous halos in the transmission and reflection patterns as the representative size parameters for the ordered phase.

Similar WAXD patterns were observed for PMDA-MEPDA, PMDA-CF3PDA and PMDA-MEOPDA polyimide films. All the polymer chains were favorably aligned in the film plane, regardless of incorporating side groups. However, all diffraction peaks were broadened and weakened and the mean intermolecular distances were increased, depending on the side groups. For PMDA-MEPDA, the L_C was 75.4 Å for the (002) peak, 64.5 Å for the (003), 58.2 Å for the (004), 14.6 Å for the amorphous halo in the transmission pattern, and 17.3 Å for the amorphous halo in the reflection, whereas the mean intermolecular distance was 4.9 Å in the direction of film thickness and 5.2 Å in the film plane. For PMDA-MEOPDA, the L_C was 72.7 Å for the (002) peak, 54.1 Å for the (003), 52.2 Å for the (004), 11.4 Å for the amorphous halo in the transmission pattern, and 14.1 Å for the amorphous halo in the reflection, whereas the mean intermolecular distance was 5.2 Å both in the direction of film thickness and in the film plane. For PMDA-CF3PDA, the L_C was 61.7 Å for the (002) peak, 54.7 Å for the (004), 13.4 Å for the amorphous halo in the transmission pattern, and 16.1 Å for the amorphous halo in the reflection, whereas the mean intermolecular distance was 5.0 Å in the direction of film thickness and 5.4 Å in the film plane. Unlike the other polyimides, PMDA-MEOPDA exhibited the same mean intermolecular distance in the film plane and in the direction

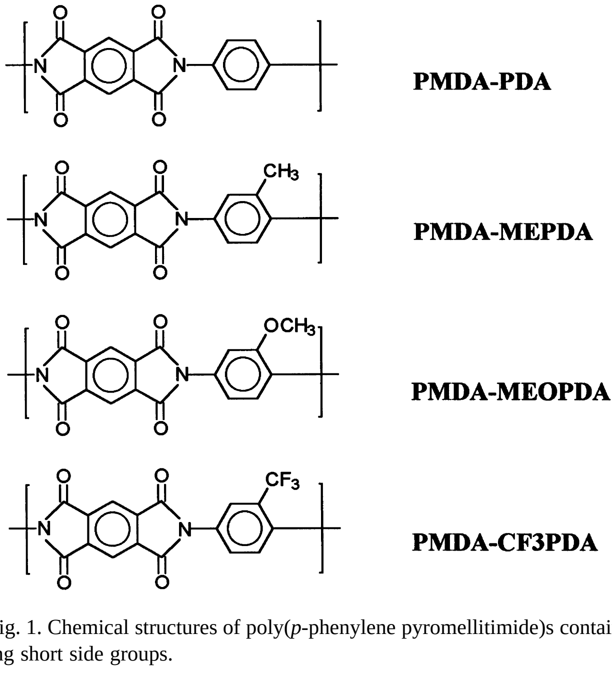

Fig. 1. Chemical structures of poly(*p*-phenylene pyromellitimide)s containing short side groups.

of film thickness. This might be attributed to the relatively bulky methoxy side group on the backbone.

As considered above, all the polymers seem to be in a biphasic state, more-ordered and less-ordered phases. However, the polymer chains even in the more-ordered phase like bundle are not laterally packed in a regular way. The bundle-like interchain ordering was decreased in size by the incorporation of side groups. The effect of side group on the interchain ordering is in increasing order PMDA-PDA < PMDA-MEPDA < PMDA-MEOPDA < PMDA-CF3PDA. In addition, the mean intermolecular distance was increased as the bulkiness of the side group increased, resulting in a decrease in the chain packing density.

Besides the diffraction peaks described above, it is worthy to pay attention to the shoulder diffraction peak around 25.5–26.5° in the reflection pattern. This peak is considered to be related to the intermolecular packing order, along with the diffraction peak around 17.2–20.7°. The peak is very weak, and broad for the PMDA-PDA polyimide. However, the peak is enhanced in intensity by incorporating side groups. The intensity enhancement is in increasing order: PMDA-PDA < PMDA-MEPDA < PMDA-MEOPDA < PMDA-CF3PDA. From this fact it is speculated that the degree of regular interchain ordering is increased by incorporating side groups. This may originate from the chain mobility improved by rotational freedom due to the side groups as well as the intermolecular interaction via the side groups.

3.2. Optical and dielectric properties

In-plane and out-of plane refractive indices (n_{xy} and n_z) measured at 632.8 nm are summarized in Table 1. All the polyimides in thin films showed n_{xy}s larger than n_zs, regardless of the side groups. In comparison, n_{xy} is, in increasing order, PMDA-CF3PDA < PMDA-MEOPDA < PMDA-MEPDA < PMDA-PDA, whereas n_z also increases in the order PMDA-CF3PDA < PMDA-PDA < PMDA-MEOPDA < PMDA-MEPDA. For all the polyimides, n_{xy} is always higher than n_z. This indicates two things: first, these polyimides are positively birefringent polymers; that is, the polarizability along the chain axis is higher than that normal to the chain axis. Birefringence (Δ) in the thin film is, in increasing order, PMDA-CF3PDA < PMDA-MEOPDA < PMDA-MEPDA < PMDA-PDA. Second, all the polyimide chains are preferentially aligned in the film plane. These are consistent with the results observed in the X-ray diffraction study as described above.

The average refractive index [$n_{av} = (2n_{xy} + n_z)/3$] is, in increasing order, PMDA-CF3PDA < PMDA-MEOPDA < PMDA-MEPDA < PMDA-PDA. These refractive indices are attributed to the polarizabilities of atoms consisting of polymer backbones and their chemical bonds. In general, higher polarizability causes a higher dipole moment under electromagnetic field, providing a higher refractive index. The fluorine atom exhibits a relatively low polarizability because of its high electronegativity and small volume, whereas the carbon atom presents high polarizability [20]. Both oxygen and hydrogen have intermediate polarizabilities [20]. When these atoms are involved in the formation of chemical bonds, the polarizabilities of the chemical bonds also contribute to the refractive index. Therefore, the incorporation of low polarizable atoms, as well as low polarizable chemical bonds into the polymer chain can reduce the refractive index. PMDA-CF3PDA has the lowest refractive index, which is contributed from the trifluoromethyl side group. In fact, for this polymer, the fluorine atoms contribute positively to the reduction of refractive index and, however, their chemical bonds to the carbon atom contribute negatively because of the relatively high polarizabilities caused by the large difference between the electronegativities of fluorine and carbon atoms. However, from the result it is evident that in the reduction of refractive index the former contribution is higher than the latter one. Overall, the relatively low refractive indices of the PMDA-PDAs containing side groups are attributed to the incorporation of side groups containing fluorine, oxygen and hydrogen atoms which have relatively lower polarizabilities than that of carbon atom. In comparison, the contribution in the reduction of refractive index is high for the trifluoromethyl group, intermediate for the methoxy group and low for the methyl group. In addition, the reduction of refractive index due to the incorporation of side groups is also contributed in part from an increase in the free volume of the polymer caused by the steric bulkiness of side group. That is, the side group with a steric bulkiness leads to a less efficient packing of the polymer chains, resulting in an increase of free volume in the polymer film.

Table 1
Optical and dielectric properties of poly(*p*-phenylene pyromellitimide)s containing short side groups

Polyimide	Film thickness (μm)	Optical properties[a]				Dielectric properties[b]			
		n_{xy}	n_z	n_{av}	Δ	ε_{xy}	ε_z	ε_{av}	$\Delta\varepsilon$
PMDA-PDA	10.0	1.823	1.582	1.743	0.241	3.323	2.503	3.038	0.820
PMDA-MEPDA	10.5	1.751	1.595	1.699	0.156	3.066	2.544	2.887	0.522
PMDA-MEOPDA	11.0	1.743	1.589	1.692	0.154	3.038	2.525	2.863	0.513
PMDA-CF3PDA	11.5	1.678	1.556	1.637	0.122	2.816	2.421	2.680	0.395

[a] Measured at 632.8 nm (474.08 THz).

[b] Estimated from refractive indices using Maxwell's equation ($\varepsilon = n^2$).

Dielectric constants of the polyimides were estimated from the measured refractive indices using Maxwell's equation ($\varepsilon = n^2$) [21]. The results are illustrated in Table 1. PMDA-PDA exhibited the highest in-plane and average dielectric constant (ε_{xy} and ε_{av}), whereas PMDA-MEPDA had the highest out-of-plane dielectric constant (ε_z). In contrast, PMDA-CF3PDA exhibited the lowest ε_{xy}, ε_z, and ε_{av}. In addition, this polyimide had the lowest anisotropy in the dielectric constant. Large anisotropy in the dielectric constant often causes near-coupled-noise due to crosstalk in the performance of microelectronic devices [10]. Therefore, PMDA-CF3PDA may be suitable for applications in microelectronic devices because of its low dielectric constant and anisotropy.

3.3. Density and packing coefficient

The densities of the polyimides were measured. As listed in Table 2, density is, in increasing order, PMDA-MEPDA $<$ PMDA-MEOPDA $<$ PMDA-PDA $<$ PMDA-CF3PDA. In particular, PMDA-CF3PDA exhibits the highest density, which results from the heavy fluorine atoms of the side group despite its bulkiness. In contrast, PMDA-MEPDA has the lowest density, which is contributed by the light hydrogen atoms of the side group in spite of its relatively low bulkiness.

Molecular packing coefficients were estimated from the measured densities using Eq. (2). The results are listed in Table 2. Molecular packing coefficient (K) is, in increasing order, PMDA-CF3PDA $<$ PMDA-MEOPDA $<$ PMDA-EPDA $<$ PMDA-PDA. That is, the incorporation of side group disturbs the packing of polymer chains. The disturbance of molecular packing increases significantly as the bulkiness of the side group increases. Consequently, the bulkiness of side group is in decreasing order trifluoro $>$ methoxy $>$ methyl $>$ hydrogen.

3.4. In-plane thermal expansion and glass transition

In-plane thermal expansion coefficients (TECs) were measured and averaged over the range of 100–200°C. The results are presented in Table 2. The TEC of PMDA-PDA film could not be measured because of its brittleness. PMDA-PDA in thin films was previously reported to have a TEC of 2.0 ppm/°C [17]. However, in this study PMDA-MEPDA was found to exhibit a TEC of -1.6 ppm/°C. In fact, in the previous measurement [17], a TMA analyzer (Model 943) of TA Instruments with a gauge length of ca. 6 mm was employed, whereas in the present study a new TMA system from Seiko Instruments with a gauge length of 20 mm was used. The differences in the instruments and the gauge lengths might cause a difference in the measured TEC. For this reason, we speculate that in the present study the PMDA-PDA film has a TEC similar to that of the PMDA-MEPDA film. In comparison, in-plane TEC is, in increasing order, PMDA-MEPDA ($\approx$ PMDA-PDA) $<$ PMDA-MEOPDA $<$ PMDA-CF3PDA. That is, the larger bulkiness of side group causes higher TEC in the polymer film.

In particular, PMDA-MEPDA showed a negative TEC. That is, this polyimide film shrank rather than expanded as the temperature increased. This TEC behavior might be related to the characteristic of the film formation process. The polyimide film was spin-coated on substrates, followed by soft-baking and imidization. Through the film formation process, the shrinkage takes place in the direction of film thickness and, however, is constrained in the film plane because of the interfacial adhesion between the film and the substrate. The shrinkage in the direction of film thickness causes polymer chains packed densely in the shrinking direction and also promotes polymer chains aligned in the film plane rather than at random. These are evident in the X-ray diffraction pattern (Fig. 2). On the other hand, the polymer chains in the plane of the film adhering to the substrate experience a force driven by the constrained shrinkage, but the chain movements might be restricted very much. This circumstance may lead the polymer chains to be laid in an orientation which is stretched by a certain degree in the radial direction in the film plane, finally resulting in a relatively poor molecular packing in the film plane: the poor molecular packing is detected on the X-ray diffraction pattern. At the same time, a residual stress is also built up in the film. These factors may cooperatively play the main role in driving thermal shrinkage enough to overcome thermal expansion, resulting in a negative TEC. In fact, the residual stress was attempted to be removed by preheating of the film at 250°C before the TEC measurement. However, the residual stress may not be completely removed due to the rigid rodlike characteristic and high T_g of the polyimide.

Thermal expansion behaviors of numerous aromatic polyimides were previously investigated by Numata and

Table 2
Densities, packing coefficients and thermal properties of poly(*p*-phenylene pyromellitimide)s containing short side groups

Polyimide	Film thickness (μm)	Density (g/cm^3)	Packing coefficient, K	In-plane TEC (ppm/°C)	T_g^a (°C)	T_d^b (°C)
PMDA-PDA	10.0	1.500	0.715	—	—	570
PMDA-MEPDA	10.5	1.427	0.697	−1.6	368	450
PMDA-MEOPDA	11.0	1.438	0.692	0.4	365	430
PMDA-CF3PDA	11.5	1.518	0.661	5.3	412	510

[a] Glass transition temperature.
[b] Degradation temperature.

coworkers [22,23]. They found negative TECs for slightly stretched films of poly(*p*-phenylene biphenyltetracarboximide) which has a high rigidity and linearity. Negative TECs were also reported for oriented liquid crystalline polymers with high molecular linearity and rigidity [24]. They have concluded that a polyimide having a high molecular linearity with a high chain rigidity has an intrinsic tendency to reveal a slightly negative TEC in stretched films and, however, a low TEC even in unstretched films. This helps us to understand a negative TEC behavior in the PMDA-MEPDA film prepared on substrates.

PMDA-MEPDA is expected to have an intrinsically low TEC because of its fully rodlike, linear chain characteristic with an extremely high chain rigidity. Thus, if this polyimide film is prepared free-standing rather than on the substrate, it may exhibit a positively small TEC. That was evident in the TEC measurements previously made by Numata et al. [23]: the free-standing film exhibited an in-plane TEC of 1.65 ppm/°C.

Similar negative TEC behavior, as observed for the PMDA-MEPDA film, is expected for the other polyimides because of the fully rodlike, linear chain characteristic, but did not show up. This indicates that their thermal expansions are relatively high enough to overcome such thermal shrinkage, consequently resulting in positive TECs.

The T_g of PMDA-PDA polyimide also could not be measured in the DMTA measurement because of its brittleness. However, T_gs of the other polyimides were determined. Here, T_g of each polyimide was taken as the onset point of glass transition in the storage modulus versus temperature curve. The results are presented in Table 2. T_g was determined to be 368°C for PMDA-MEPDA, 365°C for PMDA-MEOPDA, and 412°C for PMDA-CF3PDA. The results indicate that rodlike PMDA-PDA polyimide overall becomes flexible via incorporating short side groups into the backbone. In addition, it is noted that the β transition [25–27] related to the rotation along the C–N bond in the backbone was clearly detected to be below 300°C for all the PMDA-PDAs containing side groups.

3.5. Thermal stability

Fig. 3 shows thermograms of PMDA-PDAs with side groups. Thermal degradation starts over the range of 430–570°C, depending upon the side groups. Degradation temperature (T_d) is, in decreasing order, PMDA-PDA > PMDA-CF3PDA > PMDA-MEPDA > PMDA-MEOPDA.

As observed for PMDA-PDA, both PMDA-MEPDA and PMDA-CF3PDA showed one-step weight loss behaviors in the thermograms. This indicates that for these polyimides the side groups are thermally degraded together with the main chain parts. However, PMDA-MEOPDA polyimide exhibited a two-step weight loss behavior. The weigh loss in the first step is almost equivalent to the weight percentage of the methoxy side group to the total weight of the polymer. Thus, it is believed that this weight loss is attributed to the thermal degradation of the methoxy side group. Then, the main chain part of the polymer is degraded in the second step in the high temperature region.

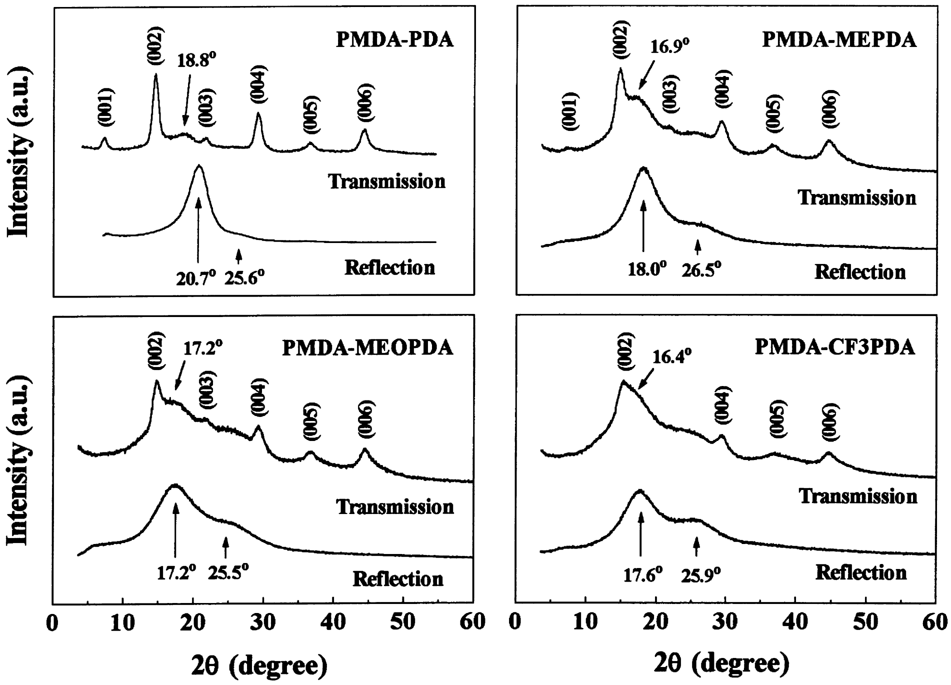

Fig. 2. Reflection and transmission X-ray diffraction patterns of polyimides in thin films. The Cu K_α radiation source was used.

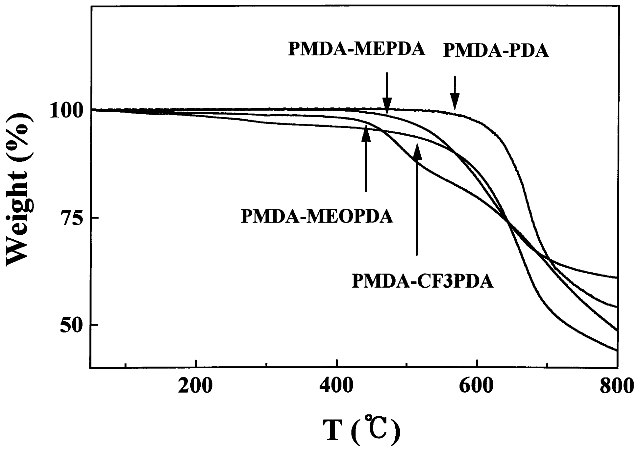

Fig. 3. Thermogravimetric diagrams of poly(*p*-phenylene pyromellitimide)s containing methyl, methoxy, and trifluoromethyl side groups.

3.6. Mechanical properties

The mechanical property of PMDA-PDA also could not be obtained due to its high brittleness. However, in-plane mechanical properties of the other polyimides have been measured at room temperature, indicating that the brittleness of PMDA-PDA was healed by incorporating short side groups into the polymer backbone. The results are summarized in Table 3. Young's modulus, which is the parameter of mechanical hardness, is, in decreasing order, PMDA-MEPDA $>$ PMDA-MEOPDA $>$ PMDA-CF3PDA. These moduli are correlated to the molecular packing coefficients in Fig. 4. The modulus increases linearly with the molecular packing coefficient. From this relationship, the modulus of PMDA-PDA can be estimated to be 12.2 GPa. The estimated value is in good agreement with the modulus (12.2 GPa) reported previously [17]. Conclusively, a highly well packed polyimide exhibits a high modulus. This is consistent with statements reported previously by Numata et al. [23] and Yamada et al. [28]. The modulus of PMDA-PDA was reduced by incorporating short side groups into the backbone. However, the reduction of modulus due to the side groups is relatively small. This means that the high modulus nature, which is the most advantageous property of fully rodlike PMDA-PDA polyimide, can be retained through incorporation of such short side groups into the polymer backbone.

For these polyimides, stresses at break were in the range of 197–262 MPa, depending on the side groups, whereas strains at break were 2.2–3.9%. These strains, which are an indicator of chain flexibility and toughness, are surprisingly lower than what ($>$ 5%) we have expected, because PMDA-PDA was previously reported to reveal a 5% strain at break [17]. In fact, both stress and strain at break are very sensitive to the quality of specimens including length-to-width ratio and defect level in the specimen and its edges. In our study, the polyimide films were prepared in a limited size, so that the length-to-width ratio of film strips was not high enough: only 25 mm length and 2.5 mm width. Also, the films, which were removed from the substrates, were diced into film strips by hand using blades and thus the film strips might have lots of crack-tips on their side edges. These might cause the relatively low strains at break.

4. Conclusions

In this study, we have attempted to improve the brittleness of fully rodlike PMDA-PDA polyimide while keeping its advantageous properties by incorporating short side groups into the polymer backbone. For this, PMDA-PDA polyimides containing side groups, such as methyl, methoxy and trifluoromethyl, were synthesized in thin films. Their structures and properties were determined and then compared to those of PMDA-PDA polyimide itself while considering the role of side groups.

The PMDA-PDAs with side groups exhibited relatively

Table 3
Mechanical properties of poly(*p*-phenylene pyromellitimide)s containing short side groups

Polyimide	Film thickness (μm)	Young's modulus (GPa)	Stress at break (MPa)	Strain at break (%)
PMDA-PDA	10.0	12.2[a]	—	—
PMDA-MEPDA	10.5	11.4 (1.0)[b]	262 (26)	3.9 (0.8)
PMDA-MEOPDA	11.0	11.2 (0.3)	197 (12)	2.2 (0.6)
PMDA-CF3PDA	11.5	10.1 (1.5)	223 (10)	3.1 (0.4)

[a] The modulus was estimated from the Young's modulus versus packing coefficient plot in Fig. 4.

[b] The numbers in parentheses indicate 1 standard deviation.

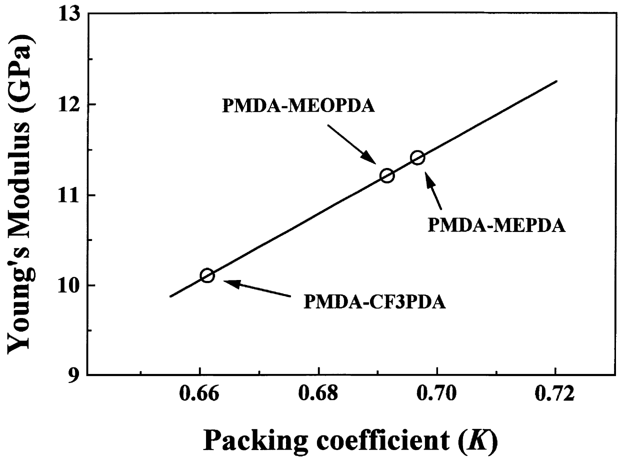

Fig. 4. Correlations between molecular packing coefficient and Young's modulus of poly(p-phenylene pyromellitimide)s containing methyl, methoxy, and trifluoromethyl side groups.

low packing coefficients because of the limited bulkiness of the side groups. They exhibited T_gs which are not expected for PMDA-PDA polyimide, reflecting that its chain mobility was improved by incorporating side groups. With this sense, we have expected that the side group containing polyimides are regularly ordered in the solid state. However, it is only evident in the X-ray diffraction patterns that the molecular orderings were slightly improved, showing a bundle-like ordering without regular packing.

These structural changes were reflected directly on the properties. By incorporating short side groups, the brittleness of PMDA-PDA was successfully healed with only a minor effect on the Young's modulus. Refractive indices, dielectric constants, and their anisotropies were reduced, depending on the side groups. However, both in-plane thermal expansivity and thermal stability were relatively degraded by the incorporation of side groups.

Acknowledgements

This study was supported in part by the New Materials Research Fund in 1997 and the Basic Science Research Institute Program (Contract No. BSRI-97-3438) from the Ministry of Education Korea and by the Korea Science and Engineering Foundation (KOSEF) (Contract Nos. 95-0501-08-01-3 and 961-0301-006-2).

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