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Structure–property relationships for partially aliphatic polyimides

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Abstract The structure–property relationship was studied for partially aliphatic polyimides containing alicyclic dianhydride and aromatic diamine unit. Rel-[1S,5R,6R]-3-oxabicyclo[3,2,1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione) (DAn) was used as an unsymmetrical spiro dianhydride, and 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) were used as symmetrical non-spiro dianhydrides. The dianhydrides were polymerized with two aromatic diamines, 4,4'-oxydianiline (ODA) and 4,4'-(hexafluoroisopropylidene)dianiline (FDA), using a conventional two-step chemical imidization method. Structures of the PAI-PIs prepared were confirmed by $^1\text{H-NMR}$ and FT-IR spectroscopy. Solubility of the polyimides was tested in various organic solvents. Thermal properties of the PAI-PIs were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). UV-visible spectroscopy was performed to evaluate the optical transparency of the polyimides. The effect of monomer structure on the properties was studied. The PAI-PIs prepared from DAn showed improved solubility, thermal properties, and transparency when compared with PAI-PIs derived from CPDA and BOCA. It is considered that the rigid, unsymmetrical spiro structure of DAn leads to rigidity, bulkiness, irregularity,

and non-linearity of the polyimide chains, resulting in the enhanced properties of DAn polyimides. The molecular arrangement in the polyimides has also been studied by wide-angle X-ray diffraction (WAXD) and was correlated with the properties.

Keywords Unsymmetrical spiro dianhydride · Partially aliphatic polyimide · Structure–property relationship · WAXD

Introduction

Aromatic polyimides possess excellent thermal properties, mechanical strength, chemical resistance, and durability that are rarely available from other organic polymers. However, they have poor processability including limited solubility in organic solvents which is caused by rigid polymer backbone and strong interchain interaction [1]. In addition, the polyimides have strong absorption in UV and visible region, so their colors are yellow to brown. It is well known that the formation of intermolecular charge-transfer complex (CTC) is the main reason for the optical property. These shortcomings could narrow down the industrial application of the polyimides.

To overcome the drawbacks described above, polyimide structure modifications have been made extensively. The incorporation of aliphatic moiety is one of the effective ways to achieve increased solubility, enhanced transparency and decrease in dielectric constant [2–5]. Thus, aliphatic polyimides have attracted much attention in recent years for such potential applications as liquid crystal orientation layers, nonlinear optical buffer layers, and low dielectric materials [6–8]. The enhanced properties of aliphatic polyimides arise from reduced intermolecular interactions

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[9–14]. However, such a weakened interaction makes aliphatic polyimides have glass transition temperatures (T_g s) lower than those of aromatic ones, and this is a major drawback of aliphatic polyimides in further applications. One approach to improving thermal stability of an aliphatic polyimide while maintaining its solubility and transparency involves the development of partially aliphatic polyimides (PAI-PIs). As a part of systematic approach to the development, this paper attempts to establish the structure–property relationships for PAI-PIs.

To the best of our knowledge, there has been no report of structure–property relationship for PAI-PIs containing different types of alicyclic dianhydrides. In this work we have focused on the effect of symmetrical spiro structure of alicyclic dianhydride on polyimide properties. Rel-[1S,5R,6R]-3-oxabicyclo[3,2,1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione) (DAn) was used as an unsymmetrical spiro dianhydride, and 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) were used as symmetrical non-spiro dianhydrides. The dianhydrides were polymerized with aromatic diamines. The properties of the PAI-PIs have been studied including solubility, thermal properties, and optical transparency. The effect of monomer structure on the properties was studied. The molecular arrangement in the polyimides has also been studied by wide-angle X-ray diffraction (WAXD) and was correlated with the properties.

Experimental

Materials

DAn was prepared according to a previously reported procedure [15] and was recrystallized using toluene and acetic anhydride before use. CPDA and FDA were purchased from Tokyo Chemicals, and used as received. BOCA, ODA, and PMDA were purchased from Aldrich Chemical Co. and used without purification. Solvents of commercial grades were purified according to standard methods and stored under nitrogen atmosphere.

Characterization

^1H -NMR spectra were recorded on a Bruker 400-MHz spectrometer in $\text{DMSO}-d_6$ with tetramethylsilane (TMS) as an internal standard. IR spectra were taken on Genesis Fourier transform infrared (FT-IR) spectrophotometer. Thin films for UV-visible spectroscopy were prepared by dissolving 10–15% PAI-PIs in DMF followed by filtration with a membrane filter of 0.2- μm pore size. The solution

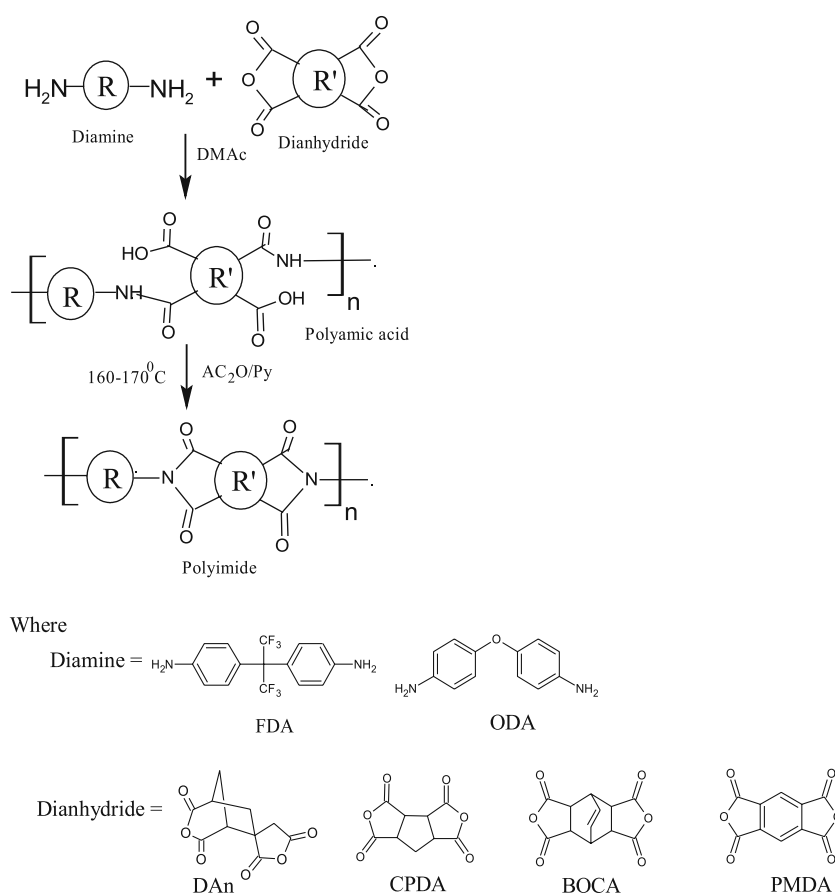
was applied onto clean quartz plates by spin coating with a Hana 150-A spin coater, and the resultant films were heated at 150 °C for 3 h on a hot plate to remove the solvent. UV-visible spectra of the films were recorded on a Perkin Elmer Lambda 25 UV/Vis Spectrometer. Inherent viscosities were determined using a Cannon-Fenske viscometer at a concentration of 0.5 g/dL in *N*-methylpyrrolidone (NMP) at 30 °C. Thermal analyses were carried out on a Shimadzu DSC-60 and TGA-50. The differential scanning calorimetry (DSC) was conducted under a nitrogen (or air) stream at a flow rate of 50 mL/min and a heating rate of 30 °C/min. Thermogravimetric analyses (TGA) were carried out under air or nitrogen flow of 50 mL/min with a heating rate of 10 °C/min. For the first run in DSC and in TGA, the samples were heated to 300 °C. After cooling to room temperature, a second run was performed in order to measure T_g s and other thermal properties. Wide-angle X-ray diffraction (WAXD) measurements of the samples were conducted at room temperature in the reflection mode using a Bruker-D2 Phaser. The $\text{Cu K}\alpha$ radiation ($\lambda=1.54\text{\AA}$) source was operated at 50 kV and 40 mA. The 2θ scan data were collected at 0.02 intervals over the range 5–35° and at a scan speed of 0.2 (2 h)/min.

Polyimide synthesis

General method of the polyimide synthesis is shown in Scheme 1. A representative example for the synthesis is as follows. FDA (0.840 g, 2.50 mmol) in *N,N*-dimethylacetamide (DMAc; 3 mL) was taken in a flame-dried 50-mL two-neck round-bottomed flask fitted with a condenser and a nitrogen inlet. After complete dissolution of the diamine, the flask was cooled to 5 °C in an ice bath. To this solution was added DAn (0.560 g, 2.50 mmol) in DMAc (3 mL), and the resultant solution was stirred until a homogeneous solution formed and its temperature was allowed to return to room temperature. The solution was further stirred under nitrogen atmosphere for 6 h at room temperature, and then temperature was slowly raised to 60 °C and maintained at this temperature for overnight. Chemical imidization was carried out by addition of acetic anhydride and pyridine to the solution and subsequent heating at 170 °C for 5 h. After cooling to room temperature the solution was poured into distilled water (500 mL). A precipitate formed, which was collected by filtration. Washing with water (100 mL) and methanol (100 mL) followed by drying in vacuum afforded a white powder of DAn/FDA.

Results and discussion

An unsymmetrical spiro alicyclic dianhydride (DAn) and symmetrical non-spiro aliphatic dianhydrides (CPDA and

Scheme 1 General method of polyimide synthesis

BOCA) were polymerized with aromatic diamines (FDA and ODA) to prepare PAI-PIs. For comparison fully aromatic polyimides were prepared using PMDA. As illustrated in Scheme 1, the polyimides were prepared by a two-step procedure; a poly(amic acid) (PAA) was synthesized by reacting a diamine with equimolar amount of a dianhydride, and then polyimide were obtained by subsequent chemical imidization of the PAA at 160–170 °C in the presence of acetic anhydride and pyridine. Inherent viscosities of all the PAI-PIs prepared were measured at

30 °C in NMP and in range of 0.26–0.48 g/dL (Table 1). The lower viscosities of FDA-based PAI-PIs than those of ODA-based ones can be attributed to the lower basicity of FDA. The presence of highly electron-withdrawing fluorine on FDA decreases the reactivity of amino group and leads to the formation of the low molecular weight PAI-PIs.

The formation of polyimides was confirmed by FT-IR and ¹H-NMR spectroscopy. In the FT-IR spectra (Fig. 1), the characteristic absorption bands of the five-membered imide ring at 1,782 and 1,722 cm^{−1} (imide carbonyl

Table 1 Viscosities, degrees of imidization, and XRD data of polyimides

Dianhydride	Diamine	Polyimide code	Inherent viscosity (dL/g) ^a	Degree of imidization ^b	FWHM ^c	Bragg's angle(2θ)	d- Spacing (Å)
DAn	FDA	DAn/FDA	0.31	94	4.24	14.64	5.93
CPDA	FDA	CPDA/FDA	0.28	97	3.59	15.17	5.84
BOCA	FDA	BOCA/FDA	0.26	96	3.70	15.84	5.67
DAn	ODA	DAn/ODA	0.48	93	5.52	15.72	5.58
CPDA	ODA	CPDA/ODA	0.41	96	5.27	15.66	5.72
PMDA	ODA	PMDA/ODA	–	–	1.93	14.07, 19.03 22.40, 26.50	–

^a Measured at a concentration of 0.5 g/dL in NMP at 30 °C

^b Calculated from ¹H-NMR spectra (DMSO-d₆)

^c FWHM Full width at half maximum calculated from XRD graph

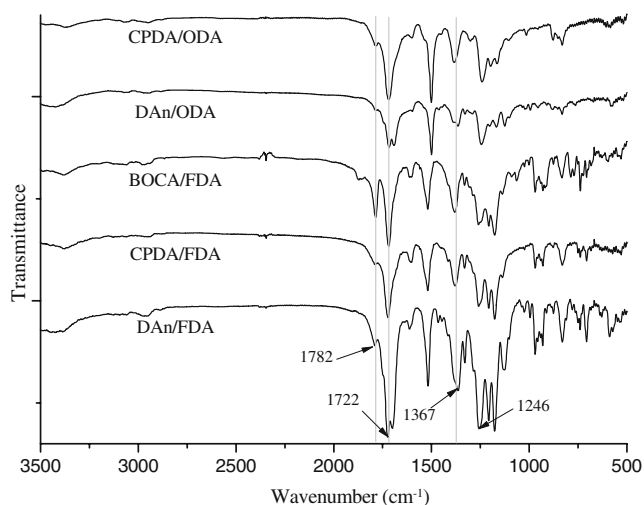


Fig. 1 FT-IR spectra of partially aliphatic polyimides

asymmetric and symmetric stretching, respectively) and $1,367\text{ cm}^{-1}$ (C-N stretching) together with a strong absorption band at $1,246\text{ cm}^{-1}$ due to the C-O stretching were observed. Further, in their $^1\text{H-NMR}$ spectra (Fig. 2), all the PAI-PIs showed complicated multiplet peaks between 1.8 and 3.9 ppm, and between 6.9 and 7.8 ppm due to the aliphatic and aromatic protons, respectively. Appearance of a small peak at around 10.2 ppm due to the amide protons was observed, indicating the presence of trace amount of uncyclized amic acid groups. Thus, the degree of chemical imidization was calculated by comparing the integrations of residual amide protons with those of aromatic protons according to the reported method [16, 17]. The degrees of chemical imidization for the PAI-PIs are given in Table 1. The slightly lower degrees of imidization of DAn-containing polyimides are probably due to its unsymmetrical structure and the presence of seven-membered ring.

The solubility behavior of the resulting polyimides was investigated in various kinds of solvents by dissolving 10 mg of powdery polymer samples in 1 mL of the solvent either at room temperature or at elevated temperature, and

the results are summarized in Table 2. As expected, PMDA-based polyimides showed limited solubility in the organic solvents because of the strong intermolecular forces between the polyimide chains. However, it was observed that all the PAI-PIs examined here exhibited good solubility in polar organic solvents such as NMP, DMAc, DMF and DMSO even at room temperature. This can be attributed to the reduced intermolecular interaction between the polymer chains by the introduction of the alicyclic dianhydrides.

DAn-containing polyimides showed higher solubility than the rest of the polyimides. This can be explained by the unsymmetrical spiro structure of DAn. The incorporation of DAn into a PAI-PI leads to irregularity, bulkiness, and non-linearity of the polyimide chains (Detailed explanations are given below), resulting in disturbance of the chain packing and decreased intermolecular interaction. Consequently, solvent molecules can easily penetrate into the polyimide matrix to solubilize the chains [18]. The other alicyclic dianhydrides (CPDA and BOCA) have symmetrical non-spiro structure, so their polyimides do not have such effects, showing lower solubility than DAn-based polyimides.

On the other hand, FDA-based PAI-PIs showed higher solubility than ODA-based ones: FDA-containing PAI-PIs are soluble at room temperature not only in the polar solvents but also in such moderately polar solvents as THF and 1,4-dioxane. It was considered that the bulky trifluoromethyl pendant groups enlarge free volume in the polyimide matrix [18]. This effect, coupled with the low polarizability of C-F bond, make the FDA polymers more soluble than ODA ones. BOCA/FDA was insoluble in low boiling solvents; this maybe due to π - π interaction between aromatic moiety in diamine unit and the C = C bond in BOCA unit.

Wide-angle X-ray diffraction (WAXD) measurements were conducted to study the molecular arrangement of the polyimides (Fig. 3 and Table 1). The fully aromatic polyimide, PMDA/ODA, presented a peak pattern in the region $2\theta < 30^\circ$ that is quite different from those of PAI-PIs. The peaks ($2\theta = 14.07, 19.03, 22.40$ and 26.50°) for PMDA/

Fig. 2 $^1\text{H-NMR}$ spectrum of DAn/FDA

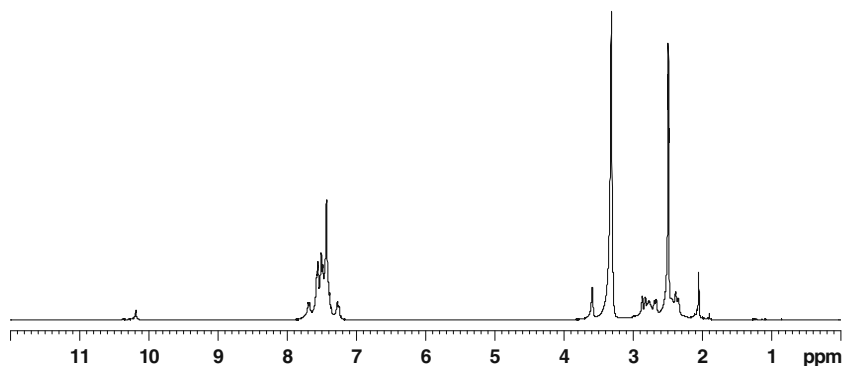


Table 2 Solubility of polyimides^a

Polyimide	Solvent ^b										
	H ₂ SO ₄	DMSO	DMAc	DMF	NMP	THF	Dioxane	Py	CHCl ₃	Acetone	MeOH
DAn/FDA	++	++	++	++	++	++	++	++	+-	++	-
CPDA/FDA	++	++	++	++	++	++	+-	++	-	-	-
BOCA/FDA	++	++	++	+	+	-	+-	+-	-	-	-
DAn/ODA	++	++	++	++	++	+-	+	++	-	-	-
CPDA/ODA	++	++	++	++	++	-	-	+-	-	-	-
PMDA/ODA	++	-	-	-	-	-	-	-	-	-	-

^a Solubility: ++: soluble at room temperature; +: soluble upon heating; +-: partially soluble; -:insoluble

^b H₂SO₄ sulfuric acid; DMSO dimethyl sulfoxide; DMF dimethylformamide; NMP *N*-vinylpyrrolidone; THF tetrahydrofuran; Py pyridine; CHCl₃ chloroform; MeOH methanol

ODA are sharp and strong, suggesting high crystallinity of the polyimide. Thus, PMDA/ODA showed the limited solubility in organic solvents. Whereas in the case of PAI-PIs, only broad, low intensity peaks around $2\theta=14\text{--}16^\circ$ were observed. The broad peaks are due to the diffraction

of intermolecular packing having some regularity, combined with amorphous halo [19]. This indicates that the PAI-PI solids are non-crystalline. The introduction of alicyclic dianhydride units in the polyimide backbone disrupts the internal order in the polyimide matrices, which is responsible for increased solubility of PAI-PIs in polar organic solvents.

Because the molecular arrangement in PAI-PIs is found to be regular to some extent, we can evaluate the regularity in intermolecular packing using the X-ray peaks [20]. It is generally accepted that the increasing full width at half maximum (FWHM) is attributable to a decreasing thickness of the periodicity in intermolecular packing which can be referred to crystallinity [20]. FWHM values of CPDA/FDA and BOCA/FDA were 3.59° and 3.70° , respectively, which are lower than that of DAn/FDA (4.24°). These results indicate that DAn/FDA has lower internal order when compared with CPDA/FDA and BOCA/FDA. The same tendency was observed in ODA-based PAI-PIs. This can be explained based on the unique unsymmetrical spiro structure of DAn. First, the unsymmetry would result in some different bonding sequences in the main chain [21]. Second, because of the spiro structure, the two pairs of anhydride carbonyl groups are twisted [22], hence the polyimide chains bearing DAn unit should be highly twisted. These combined effects lead to irregularity, bulkiness, and non-linearity of the polymer chains, resulting in disturbance of the chain packing. The PAI-PIs obtained from CPDA and BOCA have symmetrical non-spiro structure, which facilitates the regular arrangement of the polymer chains, leading to lower FWHM values than those of DAn-based polyimides. The higher solubility of DAn-containing polyimides is partly attributable to their lower intermolecular order and decreased intermolecular interaction.

ODA-containing polyimides showed increased FWHM (i.e., lower internal order) than FDA-based polyimides due

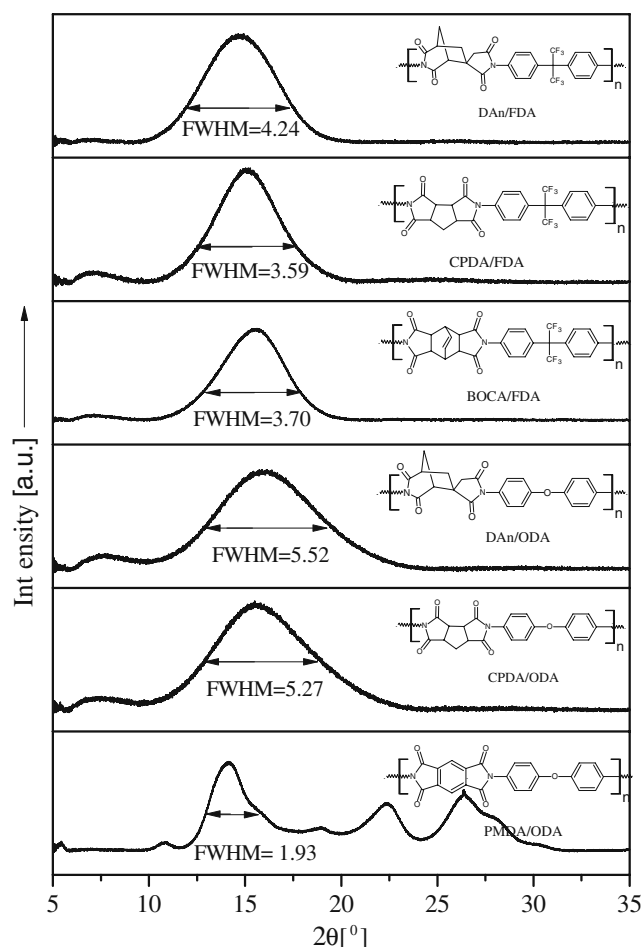
**Fig. 3** WAXD curves for the polyimides

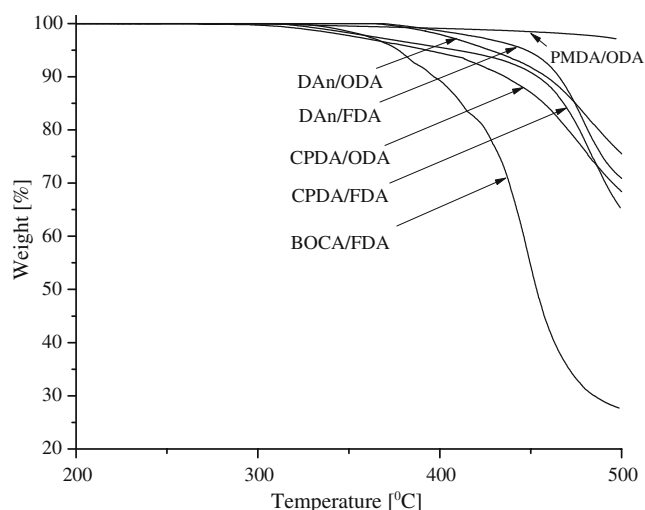
Table 3 Thermal properties of polyimides

Polyimide	T_g (°C) ^a	T_d (°C) ^b		Char yield ^c (%)
		In air	In N ₂	
DAn/FDA	278	436	467	71
CPDA/FDA	255	427	453	68
BOCA/FDA	240	398	410	27
DAn/ODA	266	421	456	75
CPDA/ODA	245	414	438	70
PMDA/ODA	—	—	—	93

^a Measured under air atmosphere^b Temperature at which 10 wt% weight loss was recorded by TGA^c Residual wt% at 500 °C under nitrogen atmosphere

to the presence of the bridging oxygen atom in ODA monomer, which imparts more flexibility, leading to decrease in the regularity of chain packing. On the other hand, FDA-containing polyimides have a tendency to show greater d-spacing than ODA ones. The larger d-spacing indicates the less close chain packing in FDA polyimides, which can be explained by bulky trifluoromethyl groups in FDA. It was considered that the higher solubility of FDA polyimides than that of ODA ones is attributable to the less close packing and low polarizability of C-F bond of PDA polyimides compared with ODA ones.

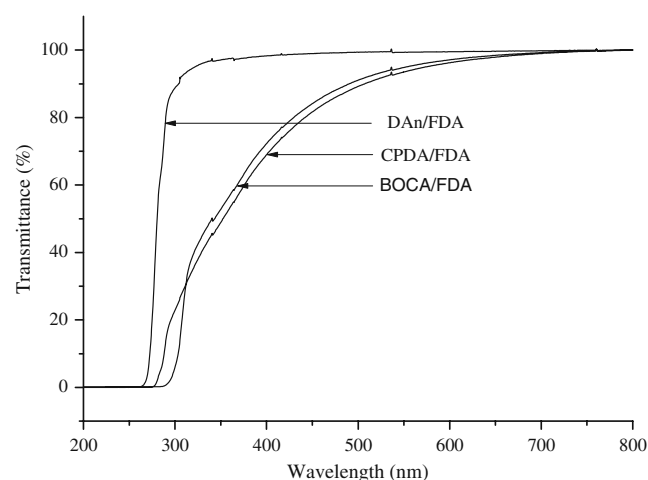
DSC and TGA were employed to investigate thermal properties of the polyimides. The thermal analysis data for the polyimides are summarized in Table 3, and TGA thermograms are shown in Fig. 4. T_g s of PAI-PIs measured by DSC were recorded in the range of 240–278 °C. As expected, T_g s of these polyimides depended on the structure of the dianhydride unit. DAn-containing PAI-PIs have higher T_g s than the other PAI-PIs. This can be

**Fig. 4** TGA thermograms of the polyimides

explained by the structure of DAn: high rotational energy barrier and backbone rigidity would arise from the bulkiness and rigidity of DAn unit, respectively. On the other hand, T_g s of ODA-containing PAI-PIs are lower than those of FDA-containing ones probably because of facilitated bond rotation due to the presence of bridging oxygen between two phenyl rings in ODA, which results in the chain flexibility.

Thermal decomposition of the polymers was studied by TGA under air or nitrogen atmosphere at a heating rate of 10 °C/min, and the results are presented in Table 3. Except BOCA/FDA, the PAI-PIs showed 10% weight loss in the range of 414–436 °C under air, and 438–467 °C under nitrogen atmosphere, and char yields above 68% at 500 °C under nitrogen atmosphere. DAn-containing polyimides showed exceptionally higher thermal stability than the other PAI-PIs: 10% weight loss temperatures were over 456 °C and char yields at 500 °C were more than 71% under nitrogen atmosphere. BOCA/FDA showed the lowest thermal stability compared to the other polyimides. The degradation of BOCA/FDA starts at around 360 °C under nitrogen atmosphere to yield a very low char yield of 27% at 500 °C. This is partly attributable to the decomposition of the polyimide through retro-Diels Alder reaction, which leads to rapid degradation and weight loss of the polyimide [23, 24].

Transmission UV-visible spectra of PAI-PIs were recorded using thin films spin-coated on quartz plates (Fig. 5). As expected, all PAI-PIs exhibit cutoff wavelengths in UV region shorter than 300 nm, indicating that the PAI-PIs are highly transparent in visible region. The cutoff wavelength was taken where transmittance becomes less than 1%. It can be seen that the DAn/FDA polyimide shows over 90% transparency at longer wavelength than 300 nm and cutoff wavelength is shorter than those of

**Fig. 5** The transmission UV-visible spectra of PAI-PIs

CPDA/FDA and BOCA/FDA polyimides. The higher transparency and shorter cutoff wavelength of DAn-based polyimides can be attributed for the less chain packing and less intermolecular interaction of the polyimide chains compared to the other dianhydride-based PAI-PIs.

Conclusion

PAI-PIs were prepared using alicyclic dianhydrides and aromatic diamines, and the effect of monomer structure on the properties of the polyimides was studied. The experimental results indicate that the PAI-PIs based on the unsymmetrical spiro dianhydride (DAn) have shown higher thermal properties, higher transparency and better solubility when compared with the PAI-PIs containing symmetrical non-spiro dianhydride (CPDA and BOCA) units. This can be attributed to rigidity, bulkiness, irregularity, and non-linearity of the polyimide chains containing DAn unit. It was also confirmed by WAXD study that the DAn-based PAI-PIs have lower internal order than the PAI-PIs containing CPDA or BOCA unit.

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