

Organosoluble and Light-Colored Fluorinated Semialicyclic Polyimide Derived from 1,2,3,4-Cyclobutanetetracarboxylic Dianhydride

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ABSTRACT: In this study, the alicyclic dianhydrides 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) was polymerized with seven kinds of fluorinated aromatic diamines, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (1), 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (2), 1,4-bis(4-amino-2-trifluoromethylphenoxy)diphenyl (3), 1,4-bis(4-amino-2-trifluoromethylphenoxy) diphenyl ether (4), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (5), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl sulfone (6), and 2,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (7), via a two-step polycondensation procedure to prepare seven kinds of fluorinated semialicyclic polyimides (PI) PI-1 ~ PI-7. The structures of these polyimides were confirmed by infrared spectroscopy (IR). Solubility of the polyimides was tested in various organic solvents and their thermal properties were investigated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). Ultraviolet-visible spectra (UV-vis) and near infrared

absorption spectra (NIR) were obtained to evaluate the optical properties of these polyimides. The obtained polyimides PI-1 ~ PI-7 displayed excellent solubility in a variety of organic solvents; they were readily soluble in amide-type polar solvent. These polyimide films exhibited good optical transparency in the visible light region (400–700 nm) with the transmittance higher than 80% at 450 nm, and these polyimide films showed little absorption at the optocommunication wavelengths of 1.30 and 1.55 μm . These polyimides showed good thermal stability with the 10% thermal decomposing temperatures higher than 443°C in nitrogen and the glass transition temperatures higher than 265°C. In addition, the effect of the structure of fluorinated diamines on the properties of polyimide films was also compared. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1371–1376, 2012

Key words: polyimides; fluorinated diamines; alicyclic dianhydrides; transparency; solubility

INTRODUCTION

Wholly aromatic polyimides (PIs) exhibit excellent thermal stability, good mechanical properties and electrical properties and then have been widely used in a variety of fields such as aerospace and microelectronics. However, most of the aromatic polyimides possess poor processability due to high glass transition temperature and low solubility in organic solvents. Recently, much research effort has been devoted to developing high performance polyimide materials with good solubility and high optical transparency.^{1–5} The optical transparency of polyimide films is of special importance in some applications, such as flexible solar radiation protectors, orientation films in liquid crystal display devices, and

optical half-wave plates for planar light-wave circuits. However, aromatic polyimides that are from aromatic tetracarboxylic anhydride and aromatic amine between the UV and the visible area have strong absorption, rendering their color close to yellow or brown and poor percent transmission of light because of their highly conjugated aromatic structures and the intermolecular charge transfer complex (CTC) formation between the aromatic moieties in these polymers.⁶ Because these problems restrict further applications of these polyimides, considerable efforts have been made to improve their properties by structural modification. One of the successful approaches to prepare colorless, transparent, and soluble polyimides maintaining their high thermal stability is the introduction of alicyclic structures into the polyimide backbones. Some alicyclic-aromatic polyimides have been prepared from alicyclic dianhydride or alicyclic diamines. These polyimides were found to possess colorless, high transparency, better solubility as well as high thermal stability.^{7,8} 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) is one of the promising monomers for the synthesis of alicyclic polyimides having these properties described above, since

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the four element alicyclic ring and nonplanar structure monomer effectively decrease the intermolecular interaction between polyimide chains, compared to an aromatic monomer. Some papers have reported that polyimide resins manufactured from CBDA and aromatic diamines were transparent and uncolored and exhibited excellent heat resistance. Furthermore, transparent and light-colored polyimides have been prepared using dianhydride and diamine monomers substituted with fluorine moieties in the side groups.^{9–13} Moreover, these polyimides were shown to have superior solubility, thermal stability, and optical transparency characteristics compared with other commercialized polyimides. However, only a few papers include the discussion on effects of internal linkage groups of fluorinated diamine on the optical and thermal properties of polyimide thin films. Therefore, in our studies, seven kinds of fluorinated diamines were bought or synthesized, and subsequently polycondensed with the alicyclic dianhydride CBDA to produce the fluorinated polyimides PI-1 ~ PI-7. These fluorinated polyimides were characterized with regard to solubility, thermal and optical properties. Furthermore, the effect of internal linkage group of fluorinated diamine monomers on the properties of polyimide was investigated. Although the effects of internal linkage groups of fluorinated diamine on the optical properties of polyimide thin film were reported by Wonbong Jang et al., and their results were different from ours, and they studied only the effects of diamine with fluorinated groups on the properties of polyimide derived from three kinds of aromatic dianhydrides such as 4,4-hexafluoroisopropylidenediphthalic anhydride (6FDA), 3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA), and 4,4-oxydiphthalic anhydride (ODPA).¹¹ They failed to investigate the difference of diamines affecting the properties of polyimide derived from alicyclic dianhydride.

EXPERIMENTAL

Materials

1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) were friendly provided by Huahui opto-electronic materials Sci-Tech Co., Ltd. (China anshan) and recrystallized from acetic anhydride before use. The fluorinated diamines, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (1), 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (2), and 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (3) were purchased from POME Sci-Tech Co., Ltd., Beijing, and were used as received. 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl ether(4), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (5), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenyl sulfone (6),

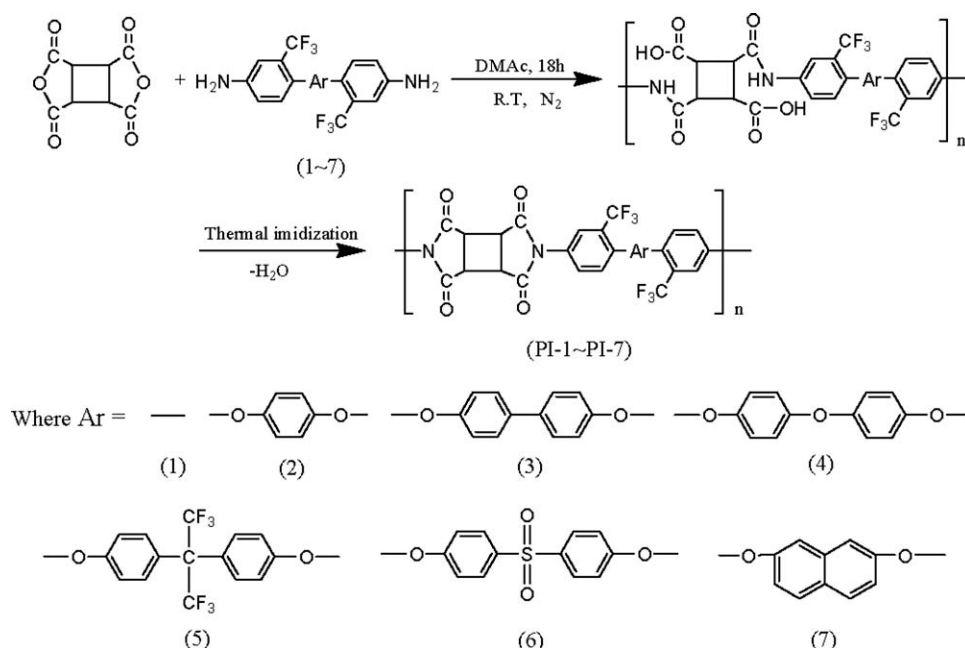
and 2,7-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (7) were synthesized according to the literature.^{11–14} *N,N*-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored by molecular sieves.

Polyimide synthesis

The polyimides were synthesized from CBDA dianhydrides and various diamines via a two-step method. The synthesis of polyimide PI-1 is used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 3.2023 g (0.01 mol) of 1 in 31.10 mL of DMAc in a 100-mL flask, 1.9611 g (0.01 mol) of dianhydride CBDA was added in one portion. Therefore, the solid content of the solution was approximately 15 wt %. The mixture was stirred at room temperature overnight (for 18 h) to afford a highly viscous poly(amic acid) (PAA) solution. The inherent viscosity of the intermediate poly(amic acid) was 0.98 dL/g, measured in DMAc at a concentration of 0.5g/dL at 30°C. The PAA was subsequently converted into polyimide by the thermal imidization process. For the process, the obtained poly(amic acid) solution was poured onto a clean glass substrate, which was placed in a 80°C oven overnight to the slow release of the casting solvent. The semidried PAA film was further dried and transformed into PI-1 film by sequential heating at 120°C for 60 min, 150°C for 60 min, 200°C for 60 min, 250°C for 60 min and 300°C for 30 min. The polyimide film was stripped from the glass substrate by being soaked in water. Finally, the obtained PI-1 film was dried in oven at 100°C for 120 min before being measured. Other polyimide films PI-2 ~ PI-7 were prepared according to the above method.

Measurements

The inherent viscosities of PAA samples were measured at 30°C with an Ubbelohde viscometer using DMAc as a solvent. Infrared spectra (IR) of the polyimides were obtained with an instrument (Beijing Second Optical Instrument Industry) from 500 to 4000 cm^{-1} . Dynamic mechanical thermal analyses (Rheometric Scientific DMTA IV) were performed on polyimide films at a heating rate of 5°C/min in the range of 30–310°C with a load frequency of 1 Hz under nitrogen atmosphere. The glass-transition temperature (T_g) values were determined as the highest peak temperature of the $\tan \delta$ plot. Ultraviolet-visible (UV-vis) spectra and near-infrared (NIR) spectra of the polyimide films were recorded on an Agilent UV/vis/NIR spectroscopy. Thermogravimetric analysis was done with a thermogravimetric analyzer (TGA, PE Instruments Co.) from 25 to 1000°C



Scheme 1 Synthesis of fluorinated polyimides PI-1 ~ PI-7.

at a heating rate of 10°C/min in nitrogen atmosphere. The 5 wt % and 10 wt % degradation temperature ($T_{5\%}$ and $T_{10\%}$) and the residues at 550°C (R_{w550}) were obtained.

RESULTS AND DISCUSSION

Polyimide synthesis

The polyimides PI-1 ~ PI-7 were prepared from dianhydride CBDA and seven kinds of fluorinated diamines by a conventional two-step synthetic method shown in Scheme 1. Despite the presence of electron-withdrawing CF_3 substituents, CBDA was still sufficiently reactive to give high molecular weight PAA when allowed to polymerize for a long time. As shown in Table I, the inherent viscosities of the intermediate PAA ranged from 0.78 to 0.98 dL/g. Except for PI-1, the molecular weights of the other

PAA were sufficiently high to permit the casting of flexible and tough PAA films, which were subsequently converted into tough polyimide films by extended heating at elevated temperatures. The formation of polyimides was confirmed with IR. Figure 1 demonstrates the IR spectra of PI-1 ~ PI-7. All the polyimides exhibited characteristic imide group absorptions around 1780 and 1720 cm^{-1} (typical of asymmetrical and symmetrical imide carbonyl stretch), 1370 cm^{-1} (C–N stretch), and 1060 and 785 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C–O and C–F stretch. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the poly(amic acid) precursor into polyimide.

TABLE I
Optical Properties of Fluorinated Polyimides PI-1 ~ PI-7

Polyimides	$[\eta]_{\text{inh}}$ (dL/g) ^a	Film thickness (μm)	λ_o (nm) ^b	$T_{450\text{nm}}$ (%) ^b
PI-1	0.98	59	385	82.6
PI-2	0.89	45	313	81.5
PI-3	0.93	51	311	80.0
PI-4	0.86	47	320	81.5
PI-5	0.88	50	307	84.6
PI-6	0.80	52	315	82.0
PI-7	0.78	52	366	70.1

^a Inherent viscosities measured with PAA at a concentration of 0.5g/dL in DMAc at 30°C.

^b λ_{cutoff} : UV cutoff wavelength; $T_{450\text{nm}}$: transmittance at 450 nm.

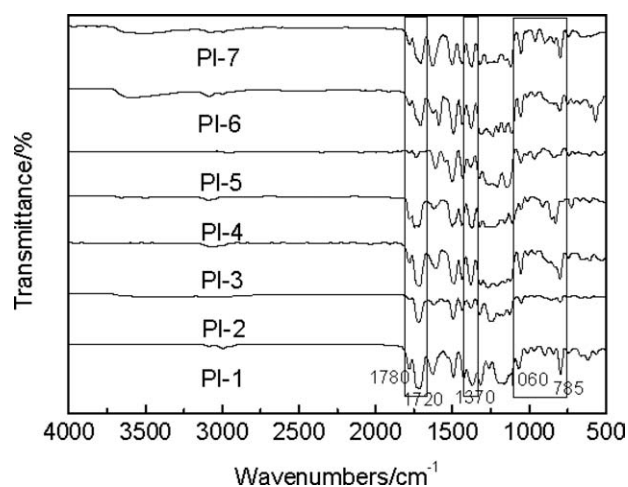


Figure 1 IR spectra of fluorinated polyimides PI-1 ~ PI-7.

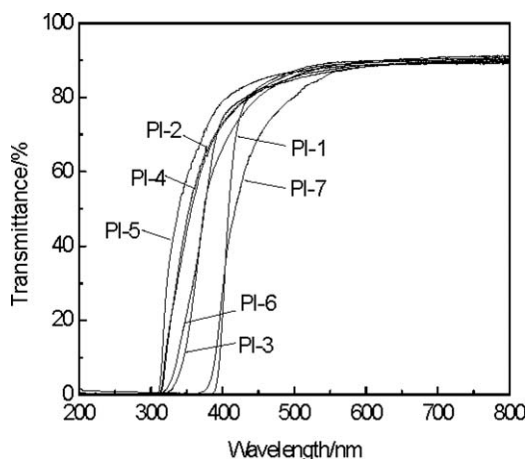


Figure 2 UV-visible spectra of fluorinated polyimides PI-1 ~ PI-7.

Optical transparency

Polyimide thin films were measured for optical transparency with UV-vis spectroscopy. Figure 2 depicts the UV-vis spectra of the obtained polyimide films, and the cutoff wavelengths (λ_0) from the UV-vis spectra are listed in Table I. Except for PI-7, other polyimide films exhibit high optical transparency exceeding 80% at 450 nm. As a result, all the fluorinated polyimides derived from CBDA with flexible groups like ether linkage or bulky CF_3 group in the diamine were light-colored and transparent. These results are attributed to the reduction of the intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The CBDA is the most simple alicyclic dianhydride monomer. The introduction of alicyclic structure into the polyimide main chain is helpful to reduce the conjugated aromatic structures and the intermolecular charge transfer complex (CTC) formation. The good optical transparency and lighter color of PI-2 ~ PI-6 polyimide films result from the aromatic ether and bulky $-\text{C}(\text{CF}_3)_2-$ as well as $\text{O}=\text{S}=\text{O}$. The flexible linkage of fluorinated diamine could inhibit the formation of the CTC, which was sufficiently effective. The light color of the polyimides with the CF_3 groups in their diamine moieties could be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing CF_3 group was effective in reducing the CTC formation between polyimide chains through the steric hindrance and the inductive effect by decreasing the electron-donating property of the diamine moieties. Moreover, the CF_3 group might weaken chain-to-chain cohesive force due to lower polarizability of the C—F bond. Due to the rigid linkage of diamine 1, UV cutoff wavelength of PI-1 polyimide film was 386 nm, while the optical transparency of PI-1 was higher with 82.6% at 450 nm. For PI-7, the slightly poor

transparency and color of polyimide film could be explained from the rigid bulky naphthalene linkage.

Polymer materials, such as acrylic, epoxy, silicone, and polyimide are used to fabricate planar light-wave circuit (PLC) devices. Whereas the electronic transition causes the absorption in the UV and visible regions, the harmonics and their coupling of the stretching vibration of chemical bonds cause the absorption in the near-infrared region. Carbon—hydrogen (C—H) and oxygen—hydrogen (O—H) bond are reported to strongly affect the absorption in both 1.30 and 1.55 μm wavelengths, which are used in optical communications, is an important consideration in using these polymer for optical devices. There are three major absorption bands shown in the spectra (Fig. 3): the first overtone of the C—H stretching vibration band (1600–1700 nm), the combination of the C—H stretching and bending bands (1350–1450 nm), and the second overtone of the C—H stretching band (1100–1160 nm). These absorption bands are similar to those reported in the literature.¹⁵ The intrinsic optical loss of the prepared polyimide based waveguides at 1310 nm is primarily contributed from the combination band of C—H stretching and bending bands, and the second overtone of C—H stretching vibration. To reduce these absorptions, the polymers have been modified in such ways as deuterization and fluorination to reduce the C—H bond. It is reported that the absorption due to C—H bonds can be reduced by the replacement of hydrogen in C—H bonds to heavier atoms such as fluorine (F), chlorine (Cl), and deuterium (D). Therefore, the absorption in the near-infrared region is strongly related to the number of C—H bonds in the polymer. The smaller the number of C—H bond in the polymer, the lower the absorption in the near-infrared region.¹⁶ As shown in Figure 3, fluorinated PI-1 has very low absorption at the telecommunication lengths of 1.30 and 1.55 μm . Other fluorinated

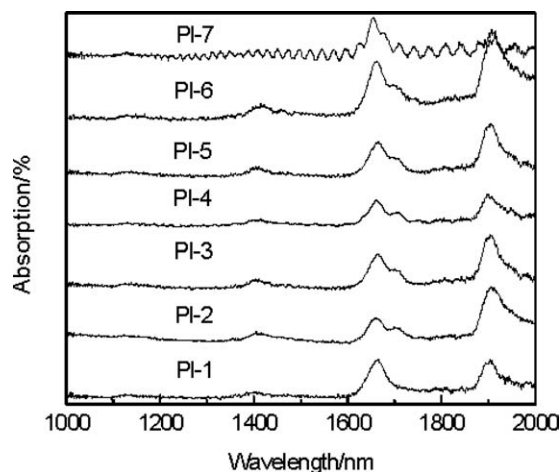


Figure 3 NIR spectra of fluorinated polyimides PI-1 ~ PI-7

TABLE II
Solubility of Fluorinated Polyimides PI-1 ~ PI-7

PIs	Solvents ^a							
	NMP	DMF	DMAc	DMSO	THF	Acetone	Chloroform	MC
PI-1	+++	+++	+++	+++	++	++	+	+
PI-2	+++	+++	+++	+++	+++	+++	++	++
PI-3	+++	+++	+++	+++	+++	+++	++	++
PI-4	+++	+++	+++	+++	+++	+++	++	++
PI-5	+++	+++	+++	+++	+++	+++	++	++
PI-6	+++	+++	+++	+++	+++	+++	++	++
PI-7	+++	+++	+++	+++	+++	++	++	++

Qualitative solubility was determined as 10 mg of polymer in 1 mL of solvent. +++: soluble at room temperature; ++: soluble on heating at 100°C or the boiling point of the solvent; +: partial soluble on heating; -: insoluble on heating.

^a NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; MC, methylene chloride.

polyimides PI-2 ~ PI-7 also exhibit a similar absorption behavior. These fluorinated polyimides exhibit good transparency in the 1.30 and 1.55- μm band. Because PI-1 is brittle, other fluorinated polyimides derived from CBDA are flexible, which are expected to be applicable to optical waveguide applications.

Organosolubility

The solubilization of rigid-chain polyimides has been made through the synthetic modification of the flexibilizing linkages or by introducing bulky side group or molecular asymmetry into the backbone. The main concepts of these approaches are to decrease the polymer chain-chain interactions, chain packing, and charge-transfer electronic polarization interactions.

In this article, the solubility of polyimides was tested qualitatively in various organic solvents and the results are summarized in Table II. All the obtained fluorinated polyimides exhibited good solubility, presumably because of the bulky pendant CF_3 group, $-\text{C}(\text{CF}_3)_2-$, 2,7-naphthalene and flexible aromatic ether linkage group of diamines. The solubility behavior of the polyimides depends on their chain packing density and intermolecular interactions.

TABLE III
Thermal Properties of Fluorinated Polyimides PI-1 ~ PI-7

Polyimides	T_g (°C) ^a	$T_{5\%}$ (°C) ^a	$T_{10\%}$ (°C) ^a	R_{w550} (%) ^a
PI-1	—	432	460	66.9
PI-2	291	433	459	68.0
PI-3	292	452	471	74.7
PI-4	265	421	443	68.9
PI-5	295	440	464	75.1
PI-6	294	446	462	67.2
PI-7	270	445	466	75.5

^a T_g : glass transition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively; R_{w550} : residual weight ratio at 550°C in nitrogen.

Thus, the PI-2 ~ PI-7 fluorinated polyimides derived from more flexible diamines displayed excellent solubility. In aprotic polar solvents, such as NMP (*N*-methyl-2-pyrrolidone), DMAc (*N,N*-dimethylacetamide), DMF (*N,N*-dimethylformamide), and DMSO (dimethyl sulfoxide), they showed excellent solubility and even in less polar solvents, for instance, THF (tetrahydrofuran), acetone, chloroform, and MC (methylene chloride), they were soluble. This might be due to the presence of the flexible ether structure and the bulky CF_3 substitutes in the fluorinated diamine, as well as alicyclic structure in the CBDA dianhydrides, which further hindered dense chain packing and reduced chain-chain interactions. Due to the rigid linkage of diamine 1, PI-1 can be soluble or partially soluble in less polar solvents on heating at 100°C or the boiling point of the solvent.

Thermal properties

DMA and TGA were used to evaluate the thermal properties of the polyimide films. The thermal

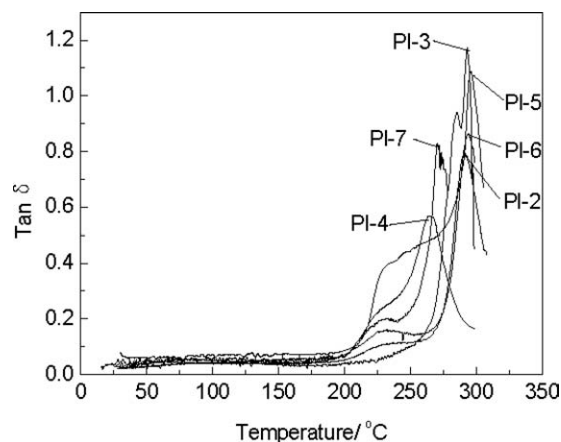


Figure 4 Tan δ - T curves of fluorinated polyimides PI-2 ~ PI-7.

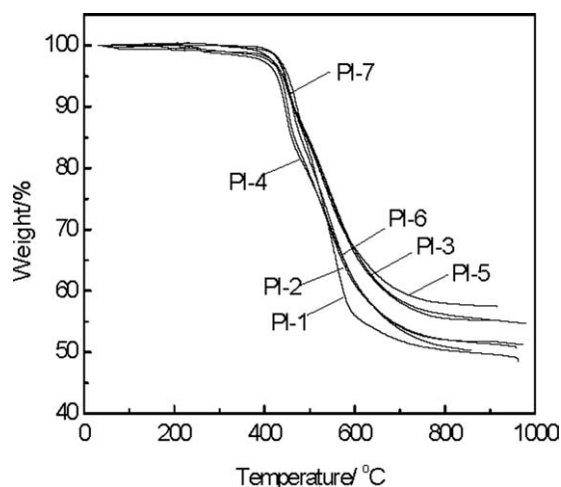


Figure 5 TGA curves of fluorinated polyimides PI-1 ~ PI-7.

behavior data of all the fluorinated polyimides derived from CBDA are listed in Table III. The glass-transition temperature (T_g) values of the fluorinated polyimides were obtained from DMA measurements (Fig. 4). The T_g value of PI-1 film was not obtained by DMA because the PI-1 film was brittle. Other fluorinated polyimides PI-2 ~ PI-7 showed T_g values in the range of 265–295°C. This might be a result of lower free volume and increase the interchain interactions, which should increase T_g . Therefore, on the basis of the same rigid alicyclic dianhydride component CBDA, all these fluorinated polyimides exhibited a higher T_g values above 265°C.

The thermal stabilities of these fluorinated polyimides were evaluated by TGA under nitrogen with a 5% weight-loss temperature ($T_{5\%}$) and 10% weight-loss temperature ($T_{10\%}$) for comparison (Fig. 5). These are summarized in Table III. The decomposition temperatures at a 10% weight loss of these fluorinated polyimides were recorded in the range of 443–471°C in nitrogen. This may be a result of relatively higher rigidity of the polyimide molecular chains. All the fluorinated polyimides left more than 66.9% char yields at 550°C in nitrogen. The TGA results showed these polyimides exhibited an excellent thermal stability, and they also showed high solubility and optical transparency. However, the thermal decomposition temperature of these fluorinated polyimides is lower than the wholly aromatic polyimides because of the poor thermal stability of four-membered alicyclic structure.

CONCLUSIONS

Seven kinds of organosoluble and light-colored polyimides PI-1 ~ PI-7 were obtained successfully from alicyclic dianhydride CBDA with various fluorinated diamines 1 ~ 7 by the two-step thermal imidization methods. The final polyimides displayed good film-forming capability, high solubility, fantastic optical properties, and excellent thermal properties. These polyimides displayed excellent solubility in aprotic polar solvents, even in less polar solvent, they were soluble. These polyimide films exhibited good optical transparency in the visible light region (400–700 nm) with the transmittance higher than 80% at 450 nm, and these polyimides showed little absorption at the optocommunication wavelengths of 1.30 and 1.55 μm . The fluorinated polyimides with CBDA exhibited high T_g above 265°C and 10% thermal decomposition temperature above 443°C.

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