

Quaternary Copolyimides with Various Monomer Contents: Thermal Property and Optical Transparency

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Abstract: Several quaternary copolyimides (Co-PIs) were prepared using various molar ratios of two dianhydrides and two diamines: 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) (PMDA), 2,2'-bis(trifluoromethyl)benzidine (TFB), and *trans*-1,4-cyclohexanediamine (CHDA). Copolymerization of the monomers afforded poly(amic acid)s (PAA), which were solution-cast onto glass plates and subjected to thermal imidization to yield the Co-PI films. These Co-PI films showed no significant decomposition below 500 °C in a N₂ atmosphere. Finally, the films were colorless and exhibited high optical transparencies, with UV-vis. absorption edges of 342-367 nm and low yellow index (YI) values of 1.72-5.09.

Keywords: quaternary copolyimide, transparent and colorless polyimide, thermal property, optical transparency.

Introduction

Aromatic polyimides (PIs) are well known as high-performance polymers, but are difficult to process in fully imidized form because of their high softening temperatures and limited organic solubility.¹⁻⁶ In addition, strong absorption in the visible region of the UV-vis. spectrum-which is due to the highly conjugated aromatic structures and the formation of intermolecular charge-transfer complexes (CT complexes)-induces pale yellow or deep reddish yellow coloration in PIs.⁷⁻¹⁰

Recently, substantial research effort has been devoted to the development of high-performance PI materials with excellent thermomechanical and optical properties and good solubility. In particular, colorless and transparent PIs have been prepared using dianhydride and diamine monomers substituted with fluorinated side groups.¹¹⁻¹⁴ Moreover, these PIs have superior solubility, thermal stability, and optical transparency as compared to other commercialized PIs. In addition, optically colorless and transparent PI films have many potential uses in electro-optical devices, flexible display substrates, and semiconductor applications.^{15,16}

Several approaches have been used to prepare colorless and transparent PIs, including incorporation of kink linkages in the main chain to reduce linearity,^{17,18} introduction of pendant groups in the main chain to reduce molecular packing, and introduction of strong electron-withdrawing side groups such as fluorinated groups.¹⁷⁻²² In general, the low cutoff wavelength (λ_0) and colorless nature of PI films can be attributed

to the CF₃ substituents in the monomers, which inhibit CT-complex formation and decrease intermolecular interactions. However, research into the preparation of colorless and transparent PIs largely relies on the design and synthesis of new PI monomers.

Another approach to obtain PI films with the desired properties is based on copolymerization. A copolyimide (Co-PI) typically possesses much lower molecular regularity than does the corresponding homopolyimide. This decreased regularity can lead to a reduction in intermolecular interactions, which in turn, results in new features such as modified thermomechanical, gas permeation, and solubility properties.²³⁻²⁸ Furthermore, the properties of Co-PIs can be adjusted by varying the comonomer ratio, that is, by selecting the appropriate ratio of the dianhydride and diamine components.

In our previous paper, we reported the preparation of a colorless PI by thermal imidization of an aromatic precursor polymer based on the reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)benzidine (TFB).²⁹⁻³¹ In this paper, we describe a method for preparing colorless and transparent PI films by thermal imidization and discuss the thermal properties, morphologies, and optical transparencies of the products.

Our main objective was to investigate the effects of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) (PMDA) and *trans*-1,4-cyclohexanediamine (CHDA) contents on the thermal properties and optical transparency of the homopolyimide composed of 6FDA and TFB. Quaternary Co-PIs with PMDA and CHDA monomers incorporated into the 6FDA/TFB system could potentially exhibit new properties

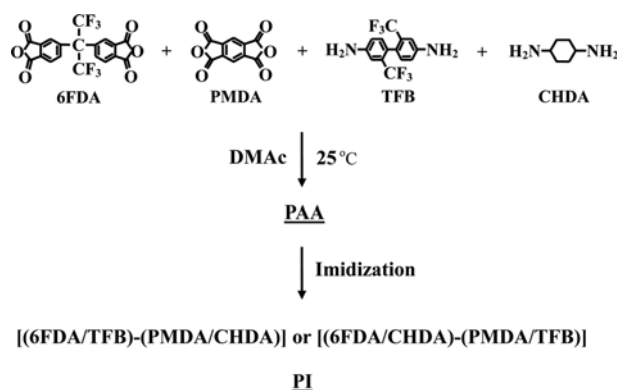
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that are not obtainable with the 6FDA/TFB homopolyimide. The introduction of PMDA and CHDA into Co-PIs having linear, flexible structures modifies their thermal properties and optical transparency because of the effect on CT complex formation.

Experimental

Materials. Monomers were purchased from TCI (Tokyo, Japan) and Aldrich Chemical Co. (Yongin, Korea) and used as received. *N,N*-Dimethylacetamide (DMAc) was dried over molecular sieves before use. All the other reagents were used without further purification.

Preparation of Co-PI Films. Scheme I depicts the relevant chemical structures for the polymerization route, and Table I shows the monomer content ratios of the Co-PIs I-V prepared in this study. All the samples were prepared as solutions. A representative procedure for the preparation of sample II (mole ratio 6FDA:PMDA:TFB:CHDA=0.9:0.1:0.9:0.1) is as follows. 6FDA (11.1 g, 2.47×10^{-2} mol) and PMDA (0.6 g, 2.74×10^{-3} mol) were added to 30 mL DMAc at 0 °C, and the mixture was stirred to afford a homogeneous solution. In a separate beaker, TFB (8.0 g, 2.47×10^{-2} mol) and CHDA (0.3 g, 2.74×10^{-3} mol) were dissolved in 30 mL DMAc. The resulting solution was added dropwise to the 6FDA/PMDA/DMAc system over 30 min with vigorous stirring to obtain a homogeneously dispersed mixture of poly(amic acid) (PAA) in



Scheme I. Synthetic route of Co-PI.

Table I. Monomer Compositions in Co-PI Films Containing Four Monomer Components

Co-PI	6FDA (mol) ^a	PMDA (mol)	TFB (mol)	CHDA (mol)
I	1.0	0.0	1.0	0.0
II	0.9	0.1	0.9	0.1
III	0.8	0.2	0.8	0.2
IV	0.7	0.3	0.7	0.3
V	0.6	0.4	0.6	0.4

^aMolecular weights of 6FDA, PMDA, TFB, and CHDA are 444.25, 218.12, 320.23, and 224.17 g/mol, respectively.

Table II. Heat-Treatment Conditions for Co-PI Films Containing Four Monomer Components

Samples	Temperature (°C)/Time (h)/Pressure (Torr)
PAA	0/1/760 → 25/14/760 → 50/1/760 → 80/1/1
PI	110/0.5/1 → 140/0.5/1 → 170/0.5/1 → 200/0.5/760 → 230/0.5/760 → 250/0.5/760

Table III. Thermal Properties of Co-PI Films Containing Four Monomer Components

Co-PI	I.V. ^a	T_g (°C)	$T_D^{i,b}$ (°C)	$W_R^{600,c}$ (%)	CTE ^d (ppm/°C)
I	0.64	289	503	76	57.1
II	0.68	320	522	80	45.9
III	0.65	321	523	85	39.6
IV	0.67	346	525	88	32.6
V	0.63	348	528	89	26.5

^aInherent viscosities were measured at 30 °C using 0.1 g/100 mL solutions in *N,N*-dimethylacetamide. ^bAt a 2% initial weight-loss temperature. ^cWeight percent of residue at 600 °C. ^dCoefficient of thermal expansion (temperature range for CTE is 50–170 °C).

DMAc with 15 wt% solid content. This mixture was stirred vigorously at 0 °C for 1 h and then at 25 °C for 14 h. The solution was cast onto glass plates, and the solvent was evaporated at 50 °C for 1 h and at 80 °C for 1 h under vacuum. The PAA film was imidized on the glass plate by sequential heating at 110, 140, 170, 200, 230, and 250 °C for 30 min each under different pressure conditions. Table II lists the conditions employed for drying the PAA films and the subsequent imidization reactions. The PI films obtained in this study were soluble in organic solvents such as *N*-methylpyrrolidine (NMP), dimethyl sulfoxide (DMSO), and DMAc. Hence, the inherent viscosities of the resulting Co-PI films in DMAc were measured at a concentration of 0.1 g/dL at 30 °C and found to range from 0.63 to 0.68 (see Table III).

No fixing tools were used to orient the glass plate during the heat treatment because orientation is known to influence some characteristics of the film, such as thermo-optical properties.

Characterizations. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 360 IR spectrometer. Differential scanning calorimetry (DSC 200F3) was performed using a NETZSCH instrument, and thermogravimetric analysis (Auto TGA 1000) was carried out with a TA instrument at a heating rate of 20 °C/min under N₂ flow. The coefficients of thermal expansion (CTE) of the samples were measured with a macroexpansion probe (TMA-2940), which was used to apply an expansion force of 0.1 N to the films at a heating rate of 5 °C/min in the temperature range 40–170 °C.

The color intensity of the polymer films was evaluated using a Minolta spectrophotometer (Model CM-3500d). Measure-

ments were performed using 66-69 mm-thick films with an observational angle of 10° and a CIE-D illuminant. A CIE LAB color difference equation was used. UV-vis. spectra of the polymer films were recorded using a Shimadzu UV-1601 spectrophotometer.

Results and Discussion

FTIR Analysis. The formation of the PAAs and the completion of imidation were confirmed by examining FTIR spectra (Figure 1). A representative IR result for sample II is discussed here. The C=O stretching peaks at 1710 and 1602 cm^{-1} , which are due to the acid and amide groups of PAA, respectively, shift to higher frequencies in the imides, to approximately 1784 and 1712 cm^{-1} (C=O, stretch). In addition, the presence of a feature at 1378 cm^{-1} , corresponding to C-N-C stretching, confirms the formation of imides.³²

Thermal Properties of the Co-PI Films. All the Co-PIs prepared in this study were assumed to be random PIs, on the basis of the single glass transition temperature (T_g) in the DSC trace of each sample (Table III). As shown in Table III, T_g increases gradually from 289 to 348 $^\circ\text{C}$ when the PMDA and CHDA monomer contents are increased up to a mole ratio of 0.4 . The presence of the 6FDA and TFB monomers in the Co-PIs might result in more fractional free volume than in the PMDA and CHDA monomer structures due to the bent structure of the bulky CF_3 groups, which enables a greater degree of phenyl ring rotation and results in a decrease in chain stiffness.^{33,34}

The initial thermal decomposition temperatures (T_D^i) of the Co-PIs for 2% weight loss in a N_2 atmosphere are also listed in Table III. The PIs undergo a single decomposition starting at a temperature above 500 $^\circ\text{C}$, and their T_D^i values increase linearly with the PMDA and CHDA contents (see Figure 2). Comparison of compositionally different PI backbones shows that the PI with the highest number of CF_3 groups directly connected to the main-chain phenyl rings (sample I) has the

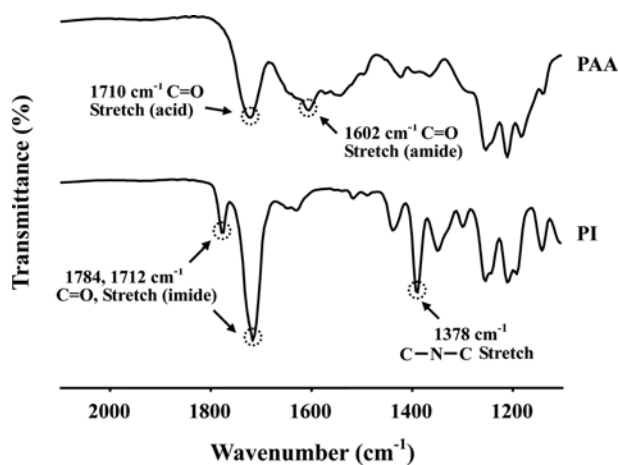


Figure 1. FTIR spectra of PAA-II and PI-II.

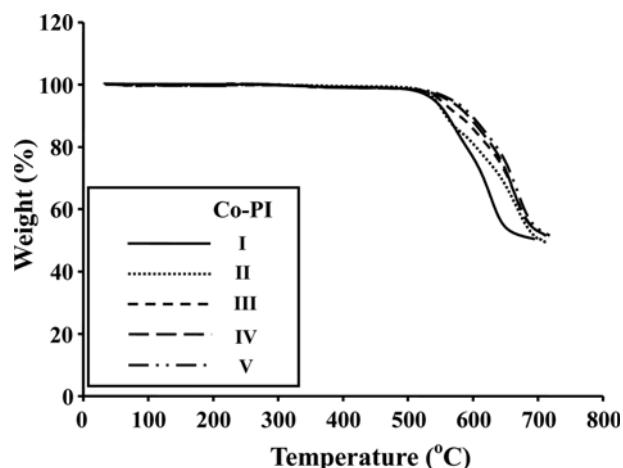


Figure 2. TGA thermograms of Co-PI films with various monomer mole ratios.

lowest thermal stability. With a higher TFB ratio, conformational freedom is restricted because the bulky CF_3 groups hinder free rotation even along the main-chain axis; this gives rise to high torsional strain and steric hindrance and thus aids easy dissociation of the CF_3 radicals.³³ Hence, PIs with a greater number of CF_3 groups exhibit lower thermal stability. This conclusion is supported by the weight residue at 600 $^\circ\text{C}$ (wt_R^{600}): the Co-PI with the highest 6FDA and TFB contents has the lowest wt_R^{600} . For example, in the Co-PI series, both T_D^i and wt_R^{600} increase linearly from 503 to 528 $^\circ\text{C}$ and from 76% to 89% , respectively, when the PMDA and CHDA contents are increased up to a mole ratio of 0.4 (see Table III).

The CTE is a function of molecular orientation. A high degree of molecular orientation gives rise to a low CTE, and hence, the residual stress is low. In samples I-V, the presence of bulky groups in the polymer chains causes a large reduction in the PI orientation, and this results in high CTE values. The CTE values of the Co-PI films with various monomer ratios (Table III) fall in the range 26.5 - 57.1 $\text{ppm}/^\circ\text{C}$. The Co-PI containing PMDA and CHDA (sample V) shows the lowest CTE, 26.5 $\text{ppm}/^\circ\text{C}$; this may be attributed to the presence of a *para*-linkage unit, which induces close packing and chain-chain interactions, thereby lowering the CTE. However, the Co-PI obtained from 6FDA and TFB (sample I) shows the highest CTE, 57.1 $\text{ppm}/^\circ\text{C}$, because of the bulky CF_3 groups and *meta*-linkage unit in 6FDA and TFB, which reduces the extent of close packing. This may also mean that the *meta*-linkage monomer units arising from 6FDA are unexpectedly bent, in contrast to the phthalimide units from PMDA.

It is most likely that incorporation of relatively bulky substituents in the PI backbone and *meta*-linkage units weakens the intermolecular interactions between the PI chains; consequently, molecular motion in these PIs is more facile than that in rigid-rod type PIs (no substituents and *para*-linkage units).³⁵ These results are also supported by the T_g data discussed above (Table III). The CTE results for the PI films

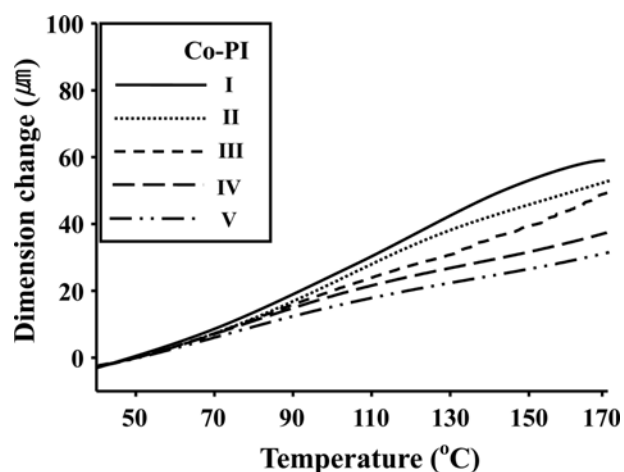


Figure 3. TMA thermograms of Co-PI films with various monomer mole ratios.

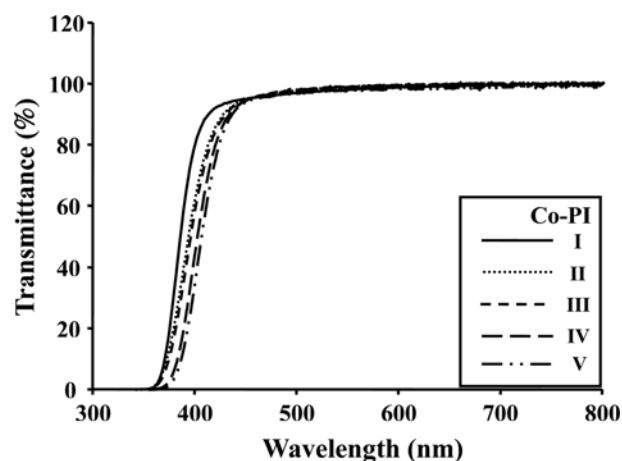


Figure 4. UV-Vis transmittance of Co-PI films with various monomer mole ratios.

with various monomer ratios are shown in Figure 3.

Optical Properties. Typical UV-vis. spectra measured for all the Co-PI thin films with various monomer ratios are shown in Figure 4. The optical properties of the Co-PIs could be elucidated from λ_0 which is the range of wavelength at which the energy flowing through the system begins to reduce or attenuated, the transmittance at 450 nm, and the yellow index (YI) in Table IV. All the PI films exhibited λ_0 values smaller than 370 nm. Sample I had the lowest λ_0 (342 nm) because the steric hindrance resulting from the relatively large number of CF_3 groups in this PI reduced chain-chain interactions and thereby enhanced the free volume.^{33,34}

The transmittance at 450 nm for this PI film containing only 6FDA/TFB was 97%, and sample I showed the lowest YI, 1.72 (Table IV). This might be due to the effect of the CF_3 group: PIs containing CF_3 groups had a lower YI than did their respective CF_3 -free counterparts. The bulky electron-withdrawing CF_3 groups in the monomer moieties were pre-

Table IV. Optical Properties of Co-PI Films Containing Four Monomer Components

Co-PI	Film Thickness (μm)	λ_0^a (nm)	450 nm ^{trans} (%)	Y.I. ^b
I	66	342	97	1.72
II	69	343	95	2.06
III	68	344	95	3.73
IV	67	354	94	3.95
V	68	367	92	5.09

^aCutoff wavelength. ^bYellow index.

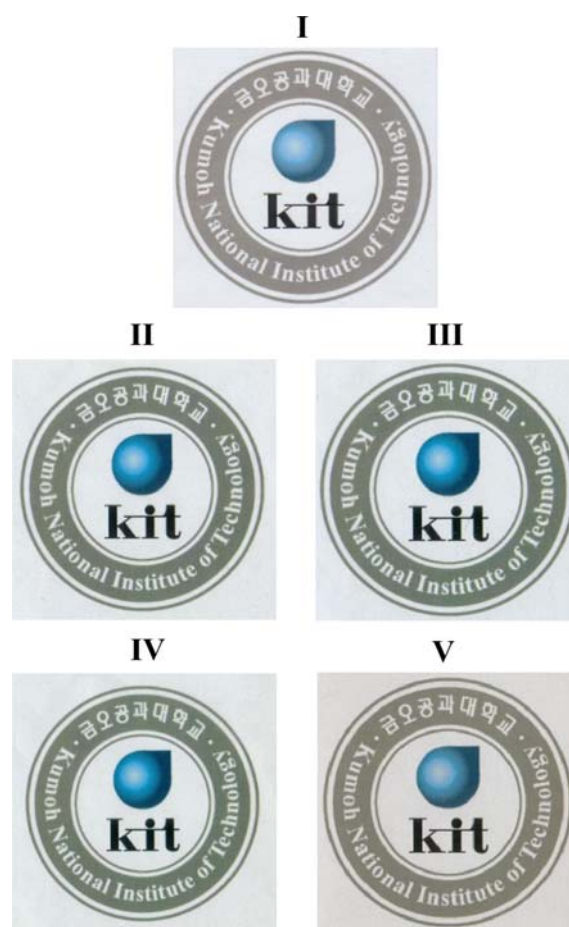


Figure 5. Photographs of Co-PI films with various monomer mole ratios.

sumably effective in preventing CT complex formation between the polymer chains through steric hindrance and inductive effects (by degrading the electron-withdrawing properties of the dianhydride moieties).^{36,37} For comparison, the optical properties of the sample V film are also given in Table IV. This film showed relatively high λ_0 and YI values of 367 nm and 5.09, respectively, and the lowest optical transmittance of 92% at 450 nm. The results revealed that this Co-PI sys-

tem, which has a linear and stiff backbone, has poor optical characteristics because of the facile electron conjugation along its backbone and molecular packing of the polymer chains.

The solvent-cast films of the Co-PIs in samples I and II are almost colorless and transparent, as shown in Figure 5 (I and II). The films of samples III-V appeared to be slightly yellow, but the film was sufficiently transparent to allow for easy visualization of letters through it.

Conclusions

A series of quaternary Co-PIs were synthesized from two dianhydride (6FDA and PMDA) and two diamine monomers (TFB and CHDA). Of these, 6FDA and TFB are commonly used in colorless and transparent PIs. The Co-PI films based on 6FDA and TFB with various PMDA and CHDA monomer mole ratios were investigated systematically. The thermal properties (T_g , T_D^i , w_R^{600} , and CTE) of the Co-PI films were found to improve with increasing PMDA and CHDA contents. However, the optical transparency of the Co-PI films deteriorated with an increase in the PMDA and CHDA contents. The variations in these properties might be related to the chemical structures of PMDA and CHDA in the Co-PI main chain.

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