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Preparation of Robust, Flexible, Transparent Films from Partially Aliphatic Copolyimides

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Abstract: Robust, flexible, and transparent films have been prepared from partially aliphatic copolyimides, and their structure-property relationship was systematically studied. Spiro-type rel-(1'R,3S,5'S)-spiro[furan-3(2H),6'-[3]oxabicyclo[3.2.1]octane]-2,2',4',5(4H)-tetrone (DAn) and ladder-type 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) were used as cycloaliphatic dianhydride. Each dianhydride and an aromatic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), were polymerized with an aromatic diamine, 4,4'-oxydianiline (ODA). Molar feed ratio of the aliphatic and aromatic dianhydrides was varied, and the molar ratios of dianhydride units in the obtained poly(amic acid)s were in good agreement with the molar feed ratios. Highly flexible and transparent films were obtained from the copolyimides. The relationship between structure and properties such as film flexibility, solubility, optical transparency, and thermal stability is explained by intermolecular interactions, degree of intramolecular conjugation, intermolecular charge transfer complex formation and backbone flexibility including the measurement of *d*-spacing values by wide-angle X-ray diffraction (WAXD) analysis. The polyimide prepared with the molar feed ratio of DAn:BTDA:ODA of 0.9:0.1:1 gave thin films having high flexibility, transparency, and colorlessness coupled with good solubility, thermal stability, and mechanical properties.

Keywords: partially aliphatic copolyimide, flexible and transparent film, structure-property relationship.

Introduction

Recently, the development of flexible, transparent plastic substrates has attracted much attention because of their potential applications in roll-up displays, conformable displays, and portable devices. Polyimides are considered a good candidate for the substrate material because of their good thermal, mechanical, electrical, and chemical properties.[1] However, most aromatic polyimides have poor processability including limited solubility in organic solvents. They also have strong absorption in the visible region, rendering their color to yellow or brown.[2] The aromatic polyimides contain both electron donor (aromatic diamine unit) and acceptor moieties (aromatic dianhydride unit) within a repeating unit, which form intra- and intermolecular charge transfer (CT) complex. The poor processability and coloration of the aromatic polyimides are mainly due to the formation of CT complex.[3] Especially the CT complex holds polyimide chains together very tightly. To overcome the drawbacks, structural modification of polyimide has been extensively studied. The incorporation of aliphatic moiety in polyimide backbone suppresses the CT interactions and, as a result, enhanced solubility and transparency can be achieved.[3-7] Fully aliphatic polyimides, however, do not have enough film flexibility due to weakened intermolecular interactions.[8-10] Therefore one approach to improving flexibility while maintaining transparency and solubility involves the development of partially aliphatic polyimides.[10-14] The other approaches to flexible, transparent polyimide film have been developed, including the incorporation of fluorine-containing moieties into polyimide backbone[15,16] and the preparation of polyimide-inorganic nanocomposite films.[17,18]

In this work we have attempted to prepare polyimide films having good flexibility, transparency, colorlessness, solubility, thermal stability and mechanical properties from partially aliphatic polyimides. To the best of our knowledge, the report on polyimide film that provides all the evidence of the above-mentioned properties has been very rare.[10] In order to achieve the properties, we thought it is necessary to precisely control the ratio of rigid/flexible moieties as well as the ratio of aliphatic/aromatic moieties in polyimide backbone. In the present study, two cycloaliphatic dianhydrides having structural rigidity, rel-(1'R,3S,5'S)-spiro[furan-3(2H),6'-[3]oxabicyclo[3.2.1]-octane]-2,2',4',5(4H)-tetrone (DAn) and 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA), were chosen because the incorporation of them into polyimide backbone could effectively enhance the solubility, transparency, and thermal stability of

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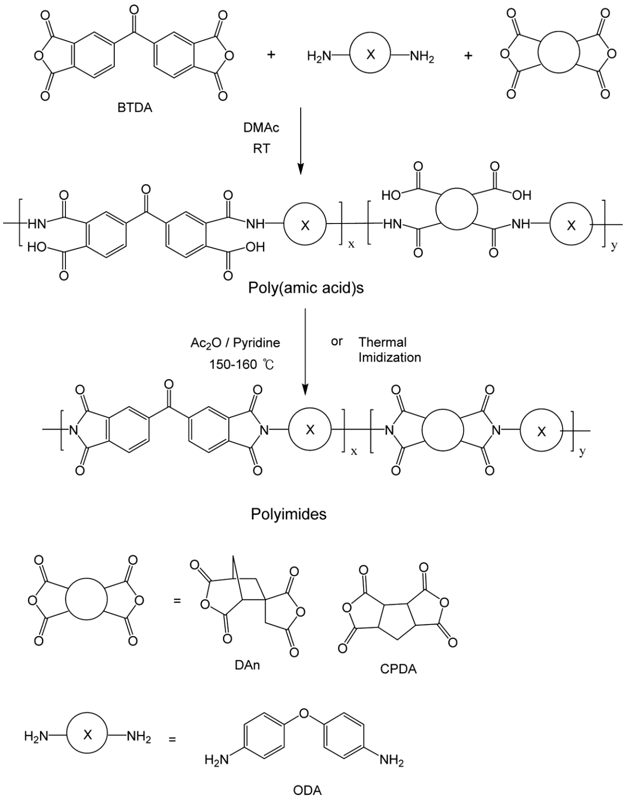
*Corresponding Author. E-mail: cmchung@yonsei.ac.kr the polyimides.[19] Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) was employed as a flexible aromatic dianhydride comonomer to increase the degree of aromaticity and flexibility of polyimide backbone. The cycloaliphatic dianhydride (DAn or CPDA) and BTDA were polymerized with a flexible aromatic diamine, 4,4'-oxydianiline (ODA), to obtain partially aliphatic copolyimides. Molar feed ratio of the aliphatic and aromatic dianhydrides was varied and the structure-property relationship of the copolyimides was studied.

Experimental

Materials. Rel-(1'R,3S,5'S)-spiro[furan-3(2H),6'-[3]oxabicyclo[3.2.1]-octane]-2,2',4',5(4H)-tetrone (DAn) was prepared according to a previously reported procedure[20] and was recrystallized using toluene and acetic anhydride before use. 1,2,3,4-Cyclopentanetetracarboxylic dianhydride (CPDA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), and 4,4'-oxydianiline (ODA) were purchased from Tokyo chemicals, Japan. All the other materials were commercially available unless otherwise noted. Solvents are of commercial grade and were purified by the standard methods and stored under a nitrogen atmosphere.

Characterization. ^{1}H NMR spectra were taken on a Bruker 400-MHz spectrometer in DMSO-d_6. IR spectra were taken on a Perkin Elmer Spectrum One B FTIR spectrometer. UV/visible spectra were recorded on a Perkin Elmer Lambda 25 UV/Vis spectrometer. The solubility behavior of the 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 temperatures. Inherent viscosities were determined using a Cannon-Fenske viscometer at a concentration of 0.50 g/dL in *N,N*-dimethylacetamide (DMAc) at 30 °C. Thermal analyses were carried out on a Shimadzu DSC-60 and TGA-50 at a heating rate of 20 and 10 °C/min, respectively, under air or nitrogen (50 mL/min). Spin coating was performed using a Hana 150-A spin coater. Film casting was performed using a Neurtek instrument 1117 micrometer adjustable film applicator. Calculation of electron affinities was carried out at the B3LYP/6-31G(d,p) level with the Gaussian 03 program package.[21-24] 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 CuK$_\alpha$ radiation (λ=1.54 Å) source was operated at 50 kV and 40 mA. The 2θ scan data were collected at 0.02° intervals over the range 5-30° and at a scan speed of 0.2°/min. The *d*-spacing in the polyimide films was calculated from the scattering angle (2θ) according to the Bragg's equation ($n\lambda=2d\sin\theta$). Tensile strength and elongation tests were carried out using a universal testing machine (EZ-test; Shimadzu) at room temperature. The grip distance was 10 mm and the tensile strength test speed rate was 5 mm/min. An average value was taken from the five sample measurements under the same conditions for each specimen.



Scheme I. Synthesis of polyimides.

Polyimide Synthesis. A general method of polyimide synthesis is shown in Scheme I. All the polyimides were synthesized in a similar manner, as exemplified by the preparation of PAA-DAn-50 and PI-DAn-50. ODA (1.00 g, 5.0 mmol) in DMAc (9 mL) was taken in a flame-dried 50-mL two-neck round-bottomed flask fitted with a condenser and a nitrogen inlet. To this solution, BTDA (0.81 g, 2.5 mmol) and DAn (0.56 g, 2.5 mmol) were added in one portion, and the resultant solution was allowed to be stirred at room temperature for 24 h. A clear viscous solution of PAA-DAn-50 was obtained. The PAA solution was divided into two portions, and the one portion is chemically imidized by addition of acetic anhydride and pyridine and subsequent heating at 150-160 °C for 5 h. After cooling to room temperature the polyimide-containing solution was poured into distilled water (500 mL). A precipitate formed and it was collected by filtration. Washing with water (100 mL) and methanol (100 mL) followed by drying in vacuum afforded a brown, powdery PI-DAn-50. Another portion was used for the film preparation by thermal imidization (see below).

Film Preparation. Each polyimide film was prepared by casting a viscous PAA solution on a clean glass plate using a doctor blade. Thermal imidization was performed by stepwise heating the PAA films in an oven. First, the films were kept at 50 °C overnight under vacuum to remove the solvent, then temperature was stepwise increased to 80, 120, and 220 °C.

The samples were allowed to stand at each temperature for an hour. Finally the imidization was completed by heating at 250 ºC for 6 h to give polyimide films. The imidized films were cooled to room temperature and immersed in a water bath for 1 h and then the films were slowly peeled off from glass plates and further dried at 100 ºC for 3 h in an oven.

Results and Discussion

DAn and CPDA are spiro- and ladder-type cycloaliphatic dianhydrides, respectively, which are known to be very rigid structures (Scheme I).[13,20,25] The aromatic monomers (BTDA and ODA) are known to be relatively flexible because of the carbonyl and ether linkage, respectively.[26,27] The cycloaliphatic dianhydride (DAn or CPDA) and BTDA were polymerized with ODA to obtain partially aliphatic copolyimides. Molar feed ratio of the aliphatic and aromatic dianhydrides was varied to control the balance between aliphaticity and aromaticity and between flexibility and rigidity of the copolyimides as summarized in Table I.

The copolyimides were prepared by means of a conventional two-step procedure as illustrated in Scheme I. First, the mixed dianhydrides (a cycloaliphatic dianhydride + BTDA) and ODA were reacted to give poly(amic acid)s (PAAs). In the second step, the PAAs were converted to copolyimides by chemical or thermal imidization. The mechanism of PAA formation involves a nucleophilic substitution reaction at the carbonyl carbon atom of the dianhydride by a diamine. Hence the polymerization reactivity of the monomers is expected to depend upon the electrophilicity of the carbonyl groups of the dianhydrides and the nucleophilicity of the amino nitrogen atom of the diamine. Electrophilicity of the dianhydrides is usually gauged in terms of electron affinity (Ea) of the molecules.[28] In this study Ea values of BTDA, DAn and CPDA were determined to be 2.80, 1.12, and 0.77, respectively, by a molecular simulation. The aliphatic dianhydrides (DAn and CPDA) showed much lower Ea values compared to BTDA. It is considered that the high Ea value of BTDA is due to that BTDA is bridged by electron withdrawing carbonyl group. Because BTDA has the higher Ea value compared to DAn and CPDA, it would have higher reactivity than the other dianhydrides when they react with ODA.

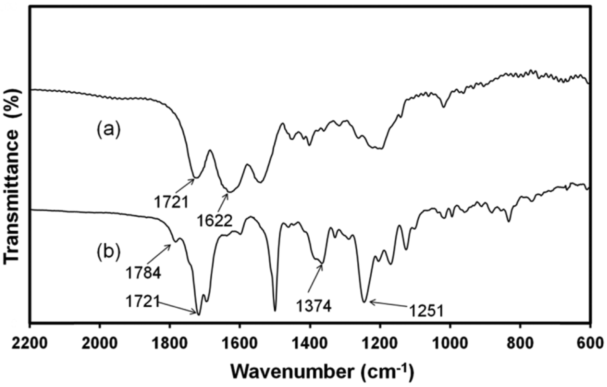


Figure 1. IR spectra of (a) PAA-DAn-90 and (b) PI-DAn-90.

The formation of the copolyimides was confirmed by FTIR spectroscopy, as exemplified by the formation of PI-DAn-90 (Figure 1). In the FTIR spectrum of the first step product (Figure 1(a)), absorption bands at 1721 cm^{-1} (C=O, carboxyl) and 1622 cm^{-1} (C=O, amide) were observed, indicating the formation of PAA-DAn-90. The FTIR spectrum of the second step product (Figure 1(b)) showed the characteristic absorption bands of the five-membered imide ring at 1784 and 1721 cm^{-1} (due to imide carbonyl asymmetric and symmetric stretching, respectively) and at 1374 cm^{-1} (due to C-N stretching) together with a strong absorption band at 1251 cm^{-1} due to the C-O stretching, indicating the formation of PI-DAn-90.

The composition of PAAs was investigated by ^{1}H NMR spectroscopy using two peaks observed at 10.6 ppm due to amide N-H connected to the aromatic dianhydride unit and

Table I. Molar Feed Ratio Used in the Polyimide Synthesis and Film Quality of Polyimides Prepared by Thermal Imidization

Polyimide	DAn (mmol)	CPDA (mmol)	BTDA (mmol)	ODA (mmol)	Molar Feed Ratio[a]	Film Quality
PI-BTDA-100	0	0	5.0	5.0	0:1:1	Flexible
PI-DAn-10	0.5	0	4.5	5.0	0.1:0.9:1	Flexible
PI-DAn-30	1.5	0	3.5	5.0	0.3:0.7:1	Flexible
PI-DAn-50	2.5	0	2.5	5.0	0.5:0.5:1	Flexible
PI-DAn-70	3.5	0	1.5	5.0	0.7:0.3:1	Flexible
PI-DAn-90	4.5	0	0.5	5.0	0.9:0.1:1	Flexible
PI-DAn-100	5.0	0	0	5.0	1:0:1	Brittle
PI-CPDA-30	0	1.5	3.5	5.0	0.3:0.7:1	Flexible
PI-CPDA-50	0	2.5	2.5	5.0	0.5:0.5:1	Flexible
PI-CPDA-70	0	3.5	1.5	5.0	0.7:0.3:1	Flexible
PI-CPDA-100	0	5.0	0	5.0	1:0:1	Brittle

[a] Molar ratio of DAn:BTDA:ODA or CPDA:BTDA:ODA.

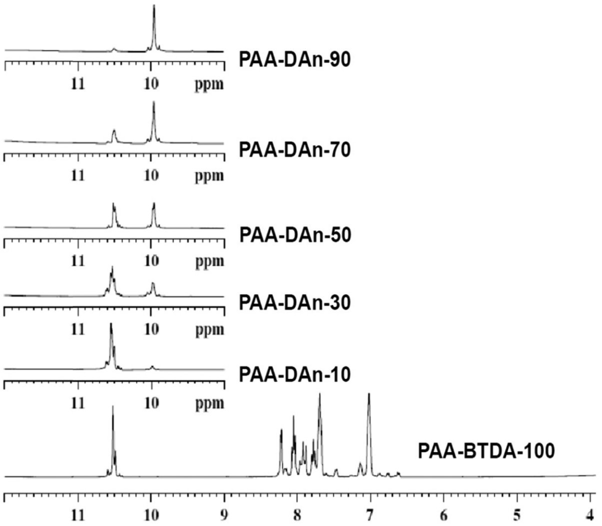


Figure 2. ^{1}H NMR spectra of PAA-DAn copolymers and PAA-BTDA-100.

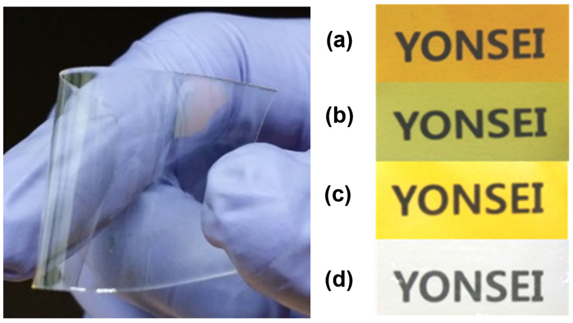


Figure 3. A photograph of a film of PI-DAn-90 (left) and photographs of polyimide films with various DAn contents: (a) PI-BTDA-100; (b) PI-DAn-50; (c) PI-DAn-70; (d) PI-DAn-90. Film thickness is in the range of 22-30 μm.

at 9.9 ppm due to amide N-H connected to the aliphatic dianhydride unit (Scheme I and Figure 2). The ratios of integration values of the peaks were measured to determine molar ratios of aliphatic dianhydride:BTDA unit in PAAs. The molar ratios of the dianhydrides in PAAs were found to be in good agreement with those in the feeds (Table II).

The viscosity of DAn-based PAAs (PAA-DAn) was in the range of 0.33~0.41 dL/g and that of CPDA-based PAAs (PAA-CPDA), 0.22~0.34 dL/g (Table II). PAAs having molecular weights enough to prepare good free-standing films could be obtained despite of relatively big difference between Ea values of BTDA and the cycloaliphatic dianhydrides. This is due to the high basicity of the amino groups in ODA.[28] Powdery polyimides were prepared by chemical imidization of PAAs in solution state in the presence of acetic anhydride and pyridine. Polyimide thin films were prepared by means of casting of the PAA solutions on glass substrates and subsequent thermal imidization of PAAs in the film state.

Highly flexible films were obtained with the molar feed ratios of DAn:BTDA of 0:1~0.9:0.1 (Table I). As a representative example, a photograph of a PI-DAn-90 film is shown in Figure 3 (left). In the case of CPDA-based polyimides, flexible films were obtained with the molar feed ratios of CPDA:BTDA of 0:1~0.7:0.3. Films of PI-DAn-100 and PI-CPDA-100 were brittle despite the fact that they contain flexible ODA units. It is considered that the incorporation of the flexible aromatic dianhydride (BTDA) would lead to the further increased chain flexibility and the formation of interchain CT interaction, which

Table II. Inherent Viscosity and Composition of PAA Samples

Poly(amic acid)	Molar Feed Ratio[a]	Inherent Viscosity (dL/g)[b]	Integration Value from ^{1}H NMR[c]		Molar Ratio of DAn (or CPDA): BTDA in PAAs[d]
			I_{AL}	I_{AR}	
PAA-BTDA-100	0:1:1	0.42	--	--	--
PAA-DAn-10	0.1:0.9:1	0.38	0.05	1.00	0.05:0.95
PAA-DAn-30	0.3:0.7:1	0.33	0.43	1.00	0.30:0.70
PAA-DAn-50	0.5:0.5:1	0.37	0.92	1.00	0.48:0.52
PAA-DAn-70	0.7:0.3:1	0.40	2.38	1.00	0.70:0.30
PAA-DAn-90	0.9:0.1:1	0.41	10.09	1.00	0.92:0.08
PAA-DAn-100	1:0:1	0.36	--	--	--
PAA-CPDA-30	0.3:0.7:1	0.34	0.41	1.00	0.29:0.71
PAA-CPDA-50	0.5:0.5:1	0.31	0.96	1.00	0.49:0.51
PAA-CPDA-70	0.7:0.3:1	0.30	2.4	1.00	0.72:0.28
PAA-CPDA-100	1:0:1	0.22	--	--	--

[a]Molar feed ratio of DAn:BTDA:ODA or CPDA:BTDA:ODA. [b]Measured at a concentration of 0.5 g/dL in DMAc at 30 °C. [c]I_{AL}: integration value of amide N-H connected to the aliphatic dianhydride unit; I_{AR}: integration value of amide N-H connected to the aromatic dianhydride unit. [d]Determined with the integration values.

Table III. Solubility of Polyimides[a]

Polyimide[b]	Solvent[c]										
	H_2SO_4	DMSO	DMAc	DMF	NMP	THF	Dioxane	Py	$CHCl_3$	Acetone	MeOH
PI-BTDA-100	++	--	--	--	--	--	--	--	--	--	--
PI-DAn-10	++	--	--	--	--	--	--	--	--	--	--
PI-DAn-30	++	--	--	--	--	--	--	--	--	--	--
PI-DAn-50	++	S	S	S	S	--	--	--	--	--	--
PI-DAn-70	++	+-	+-	++	+-	--	--	--	--	--	--
PI-DAn-90	++	++	++	++	++	--	--	--	--	--	--
PI-DAn-100	++	++	++	++	++	+-	+	++	--	--	--
PI-CPDA-30	++	--	--	--	--	--	--	--	--	--	--
PI-CPDA-50	++	--	--	--	--	--	--	--	--	--	--
PI-CPDA-70	++	S	S	S	S	--	--	--	--	--	--
PI-CPDA-100	++	++	++	++	++	--	--	+-	--	--	--

[a]Solubility: ++: soluble at room temperature; +: soluble upon heating; +-: partially soluble; --:insoluble; S: swollen. [b]Chemically imidized polyimides from PAAs in DMAc using pyridine and acetic anhydride at 160 °C for 5 h. [c]H_2SO_4: sulfuric acid; DMSO: dimethylsulfoxide; DMF: dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran; Py: pyridine; $CHCl_3$: chloroform; MeOH: methanol.

results in flexible film formation.

A PI-BTDA-100 film was dark-brown (Figure 3(a)) and as the content of DAn increased the film color became pale (Figure 3(b) and (c)). The film of PI-DAn-90 was almost colorless as shown in Figure 3(d). The reason for the colorlessness of the PI-DAn-90 film is explained below based on wide-angle X-ray diffraction (WAXD) analysis.

The solubility behavior of the resulting polyimides was investigated with various kinds of solvents by dissolving 10 mg of powdery polyimide samples in 1 mL of the solvents either at room temperature or at elevated temperatures, and the results are summarized in Table III. All the polyimides tested were soluble in sulfuric acid. As expected, the fully aromatic polyimide, PI-BTDA-100, was not soluble in the organic solvents. While PI-DAn-10, PI-DAn-30, and PI-DAn-50 were insoluble or swollen in the solvents, PI-DAn-90 and PI-DAn-100 showed good solubility in high-boiling solvents such as NMP, DMAc, DMF and DMSO even at room temperature. In the case of CPDA-based polyimides only PI-CPDA-100 was soluble in the high-boiling solvents and the rest of the CPDA polyimides were insoluble or swollen.

It is known that polymer solubility is influenced by two main factors, flexibility of backbone and intermolecular interactions.[29] Generally, as the degree of backbone flexibility increases and/or as the degree of intermolecular interactions decreases the polymer solubility increases. Because DAn and CPDA are rigid while BTDA is relatively flexible, the degree of backbone flexibility of the polyimides would decrease with increasing content of DAn or CPDA unit. On the other hand, the degree of intermolecular interactions would decrease as the content of the alicyclic dianhydride unit increases. In this work, it was thought that the intermolecular interactions would be the dominant factor in polyimide solubility because the polyimides showed increased solubility with increasing cycloaliphatic content (Table III). On the other hand, DAn-based polyimides showed higher solubility than CPDA ones. This might be attributable to the unsymmetrical spiro structure of DAn: the incorporation of DAn into polyimide leads to irregularity, bulkiness, and non-linearity of the polyimide chains, resulting in effective disturbance of the chain packing and decreased intermolecular interactions.[19]

The structure-solubility relationship of the polyimides is further explained based on WAXD analysis. The *d*-spacing values of PI-DAn-90 and PI-DAn-100 were much higher than those of the other DAn polyimides (Table IV). CPDA polyim-

Table IV. WAXD Data of Polyimides

Polyimide	Bragg's Angle (2*θ*)	*d*-Spacing (Å)
PI-BTDA-100	18.41	4.81
PI-DAn-10	18.38	4.82
PI-DAn-30	18.37	4.82
PI-DAn-50	18.39	4.82
PI-DAn-70	18.22	4.86
PI-DAn-90	16.30	5.43
PI-DAn-100	15.72	5.63
PI-CPDA-30	18.48	4.80
PI-CPDA-50	18.45	4.80
PI-CPDA-70	18.36	4.83
PI-CPDA-100	15.52	5.70

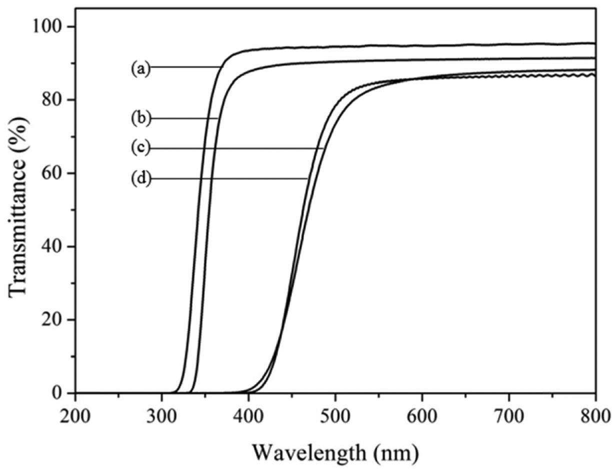


Figure 4. UV-visible spectra of polyimide films: (a) PI-DAn-90 (spin coated, 2 μm thick); (b) PI-DAn-90 (cast, 25 μm thick); (c) PI-CPDA-70 (cast, 29 μm thick); (d) PI-BTDA-100 (cast, 25 μm thick).

ides showed a similar tendency. The *d*-spacing value is often referred to the average intersegmental distance in linear polymers, so a larger *d*-spacing value indicates less close chain packing.[30-32] The less close chain packing probably resulted in decreased intermolecular interactions, leading to decreased cohesive force. This may help solvent molecules easily penetrate into the polyimide matrix to solubilize the chains.

Transmission UV-visible spectra were recorded using the polyimide films prepared by thermal imidization (Figure 4 and Table V). The film thickness ranged from 22 to 30 μm. It was difficult to obtain good films for UV-visible spectroscopy from PI-DAn-100 and PI-CPDA-100 because of their brittleness, so these polyimides were not used. It can be seen that the polyimide films tested in this work showed up to 88% transmittance in the visible region. A spin-coated film (thickness =2 μm) of PI-DAn-90 showed up to 94% transmittance in the visible region.

Cutoff wavelength of a polyimide film is another measure of optical transparency of the film. The cutoff wavelength was taken where transmittance becomes less than 1 percent. As the content of the aliphatic unit increased, the cutoff wavelength gradually decreased (Table V). It should be noted that PI-DAn-90 showed a significantly lower cutoff wavelength (336 nm) and quite higher transmittance (87%) at 400 nm compared to the other DAn- or CPDA-based polyimides. The spin-coated film (thickness=2 μm) of PI-DAn-90 showed 93% transmittance at 400 nm. In addition PI-DAn-90 afforded the only colorless film as mentioned above (Figure 3).

Table V. Optical Properties of Polyimide Films Prepared by Casting

Polyimide	Film Thickness (μm)	Cutoff Wavelength (nm)	400 nm_{trans}[a] (%)
PI-BTDA-100	25	412	0
PI-DAn-10	27	402	0
PI-DAn-30	25	390	2
PI-DAn-50	22	387	1
PI-DAn-70	24	383	4
PI-DAn-90	25	336	87
PI-CPDA-70	29	401	1
PI-DAn-90[b]	2	318	93

[a]Percent transmittance at 400 nm. [b]Prepared by spin coating.

Optical transparency and colorlessness of the polyimides are influenced by intramolecular conjugation and intermolecular CT complex formation.[2,33-35] It is expected that the incorporation of aliphatic unit in polyimide backbone results in reduced conjugation and CT complex formation. The high transparency and colorlessness of PI-DAn-90 can be explained by the highest content of aliphatic unit among the DAn-based copolyimides. This is supported by the *d*-spacing values of the polyimides (Table IV): the highest *d*-spacing value of PI-DAn-90 among the DAn- or CPDA-based copolyimides might indicate the lowest degree of intermolecular CTC formation. This, together with the lowest degree of conjugation, leaded to highest transparency and colorlessness of PI-DAn-90.

Differential scanning calorimetry (DSC) was employed to investigate glass transition temperature (T_g) of the polyimides, and the results are shown in Figure 5 and Table VI. T_gs of the polyimides were recorded in the range of 260-279 °C. Interestingly, T_g increases and then decreases as the aliphatic content increases. This could be explained by backbone rigidity and intermolecular interactions. It is known that T_g increases with increasing degree of backbone rigidity and intermolecular inter-

Table VI. Thermal Properties of Polyimides

Polyimide[a]	T_g (°C)[b]	T_d (°C)[c]			
		In Air		In N_2	
		T_5	T_{10}	T_5	T_{10}
PI-BTDA-100	264	-	-	-	-
PI-DAn-10	266	496	-	-	-
PI-DAn-30	270	443	499	483	-
PI-DAn-50	279	424	462	462	488
PI-DAn-70	268	412	439	453	481
PI-DAn-90	260	410	437	460	475
PI-DAn-100	-	387	410	430	457
PI-CPDA-30	267	445	-	-	-
PI-CPDA-50	272	421	459	449	498
PI-CPDA-70	260	412	438	445	469
PI-CPDA-100	-	391	413	422	459

[a]Thermally imidized films. [b]Measured under air atmosphere. [c]T_5 and T_{10} are temperatures at which specimens show 5 and 10 wt% decomposition, respectively.

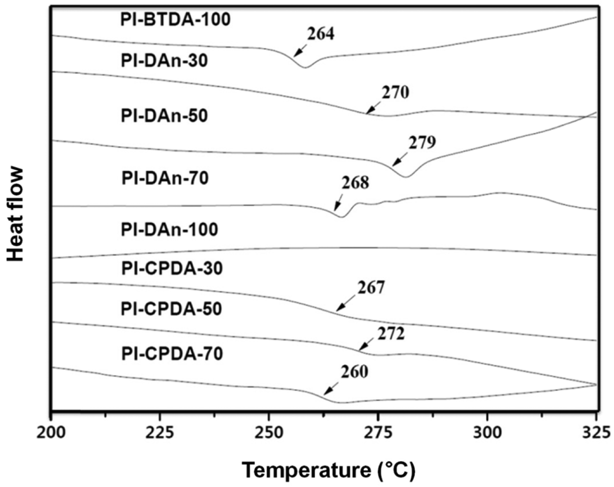


Figure 5. DSC thermograms of polyimides.

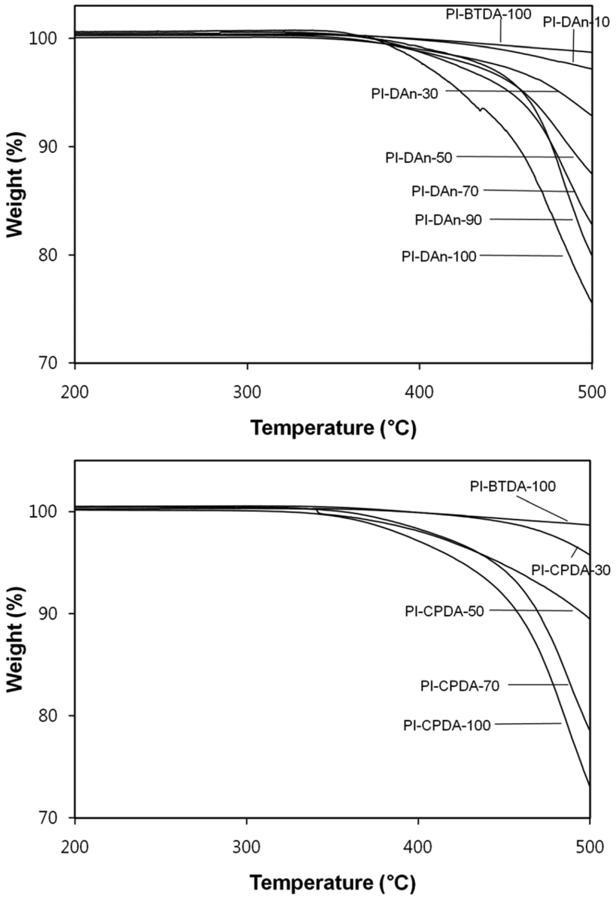


Figure 6. TGA thermograms of polyimides.

Table VII. Mechanical Properties of Polyimides

Polyimide	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
PI-BTDA-100	110.3	11.8	2.1
PI-DAn-10	105.1	9.2	1.9
PI-DAn-30	103.2	9.0	1.6
PI-DAn-50	96.7	7.2	1.9
PI-DAn-70	90.3	8.0	1.7
PI-DAn-90	86.5	7.5	1.9
PI-DAn-100[a]	-	-	-
PI-CPDA-30	81.0	7.3	2.0
PI-CPDA-50	84.1	6.5	1.9
PI-CPDA-70	71.5	5.3	2.0
PI-CPDA-100[a]	-	-	-

[a] Polymer films were too brittle to be measured.

actions. As the cycloaliphatic content increases, backbone rigidity increases but intermolecular interactions become weaker as mentioned above. In the range of molar feed ratio of DAn:BTDA (or CPDA:BTDA) from 0:1 to 0.5:0.5, backbone rigidity would mainly affect polyimide T_g, hence T_g increases. However, the incorporation of higher content of aliphatic unit resulted in decrease in T_g, and this may be attributed to predominant influence of reduced intermolecular interaction rather than increased backbone rigidity.

Thermal decomposition of the polymers was studied by thermogravimetric analysis (TGA) under air or nitrogen atmosphere at a heating rate of 10 °C/min, and the results are presented in Table VI and Figure 6. As expected, decomposition temperature (T_d) decreased as the aliphatic content increased. As a representative example, PI-DAn-90 showed 10% weight loss at 437 °C under air, and at 475 °C under nitrogen atmosphere. PI-CPDA-70 showed 10% weight loss at 438 °C under air, and at 469 °C under nitrogen atmosphere.

Mechanical properties of the polyimide films were investigated using their stress-strain curves obtained with a UTM and the results are listed in Table VII. These polyimide films possess tensile modulus of 1.6-2.1 GPa, tensile strength of 71.5-110.3 MPa, and elongation at break around 5.3-11.8%. The UTM traces for highly rigid polyimides (PI-DAn-100, PI-CPDA-100) were not measured because the films were brittle. The obtained flexible films exhibited appreciable tensile strength, indicating that they are mechanically robust. Tensile strength of the flexible films decreased as the content of cycloaliphatic monomer unit, but still they have enough strength for industrial applications.

Conclusions

Two rigid cycloaliphatic dianhydrides, DAn and CPDA, were polymerized with a relatively flexible aromatic dianhydride (BTDA) and diamine (ODA) to obtain partially aliphatic copolyimides. Film flexibility, solubility in organic solvents, optical transparency, color, thermal properties, and mechanical properties of the polyimides were greatly influenced by the molar feed ratio of DAn (or CPDA):BTDA. The polyimide properties are explained by intermolecular interactions, degree of intramolecular conjugation, intermolecular CTC formation, backbone flexibility and *d*-spacing values. PI-DAn-90 gave thin films having high flexibility, transparency, and colorlessness coupled with good solubility, thermal stability, and mechanical properties.

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