

Fully Aliphatic Polyimides from Adamantane-Based Diamines for Enhanced Thermal Stability, Solubility, Transparency, and Low Dielectric Constant

Anu Stella Mathews, Il Kim, Chang-Sik Ha

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

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ABSTRACT: We have synthesized a series of fully aliphatic polyimides (APIs) from bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) and various aliphatic diamines, including linear aliphatic, flexible alicyclic, and rigid adamantyl diamines. We performed the polymerization reactions using one-step syntheses in *m*-cresol at elevated temperatures without the isolation of poly(amic) acid. The chemical composition and structure of the polymers were characterized by nuclear magnetic resonance (NMR) and infrared (IR) spectrometry. The characterization data are reported from analyses using gel permeation chromatography (GPC), thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), and wide-angle X-ray diffraction (WXAD) measurements. The polyimides are also subjected to solubility, solution viscosity, tensile strength, transparency, and dielectric constant measure-

ments. The resultant polyimides possess well-controlled molecular weight, reasonable intrinsic viscosity, good transparency, enhanced solubility, low dielectric constants, and high glass transition temperature, together with marginal thermal and mechanical stability. These properties were enhanced in copolyimides containing equimolar amounts of rigid and flexible moieties. These rigid-rod APIs derived from the alicyclic dianhydride and aliphatic diamines are promising candidates as advanced materials for future applications in micro- and photoelectronic devices. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3316–3326, 2006

Key words: aliphatic polyimides; adamantane; mechanical properties; low dielectric constant; glass transition enhancement

INTRODUCTION

Polyimides are one of the most important classes of polymers used in the microelectronics and photoelectronics industries. Because of their high thermal stability, chemical resistance, and good mechanical and electric properties, polyimides are often applied in photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays.¹ Most of the investigations into polyimides have concentrated on wholly or partially aromatic systems. Although aromatic polyimides possess excellent thermal stability, chemical resistance, and mechanical properties, there are a number of obstacles that hinder extending their applications in optoelec-

tric materials and high-speed multilayer printed wiring boards—their insolubility in common solvents in the fully imidized form, the light or dark-yellow color of their films caused by intra- and intermolecular charge transfer (CT) interactions, and their high dielectric constants. As a result, fully aliphatic and alicyclic polyimides (API) are currently being considered for their applications in optoelectronics and interlayer dielectric materials because of their higher transparencies and lower dielectric constants,^{2–4} which result from their low molecular density and polarity and low probability of undergoing inter- or intramolecular CT. Nevertheless, polyimides derived from aliphatic monomers are most suited for applications that have less-stringent thermal requirements.⁵

It is well known that rigid-rod structures reduce the coefficient of thermal expansion (CTE) of polyimides.⁶ Adamantane (tricyclo[3.3.3.1.1.^{3,7}]decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations,⁷ is the most salutary alicyclic candidate for incorporation into aliphatic polyimides (APIs), to enhance their thermal stability without sacrificing their high transparency, solubility and low dielectric constants.⁸ Adamantane's diamond-like cage structure is relatively in-

Correspondence to: C.-S. Ha (cscha@pusan.ac.kr).

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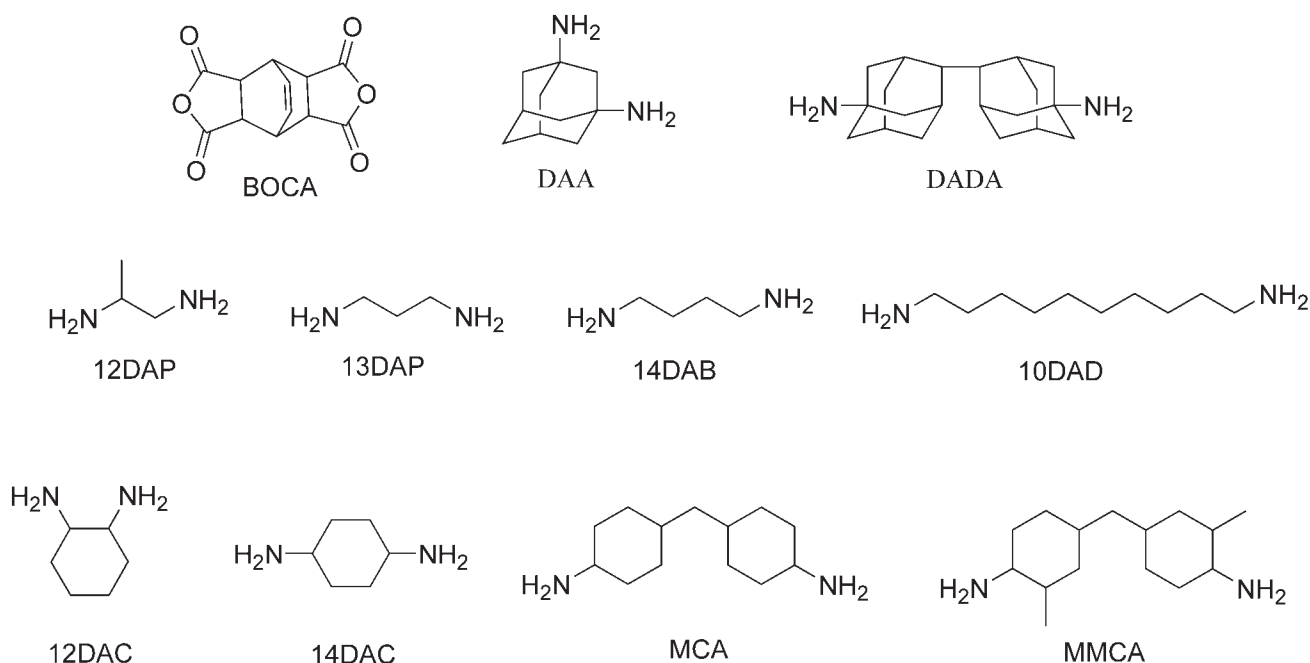


Figure 1 Structures of the monomers selected for the synthesis of fully aliphatic polyimides.

sensitive to degradation reactions caused by nucleophilic, electrophilic, or elimination reactions. The presence of pendent adamantane groups often causes dramatic increases in the glass transition temperatures and solubility of polymers without sacrificing their thermal stability. The bulkiness of the adamantane units tends to inhibit the packing of polymer chains; this process ultimately decreases their crystallinity and increases their solubility.⁹ Therefore, we became interested in synthesizing and characterizing polyimides that incorporate adamantane units.

In this article, we report the synthesis and characterization of a series of fully APIs that can be broadly classified into homopolyimides with rigid adamantyl or flexible aliphatic units and copolymers containing rigid adamantane and flexible moieties together with alicyclic dianhydride residues. For that purpose, we synthesized the monomers 1,3-diaminoadamantane and 3,3'-diamino-1,1'-diadamantane. Our present investigation focused mainly on studying the solubility, crystallinity, and thermal, dielectric, and optical properties of all of the synthesized APIs and the effects that the incorporation of adamantane units had on the basic behavior of the flexible aliphatic/alicyclic polyimides.

EXPERIMENTAL

Materials

All reagents and chemicals were purchased from Aldrich Chemical (Fig. 1). Bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) was recryst-

allized from acetic anhydride and dried at 150°C under vacuum before use. The alicyclic diamines 1,2-diaminocyclohexane (12DAC), 1,4-diaminocyclohexane (14DAC), and 4,4'-methylene bis(cyclohexylamine) (MCA) were distilled under reduced pressure and were stored in the dark prior to use. 4,4'-Methylene bis(2-methylcyclohexylamine) (MMCA) was recrystallized from hexane and dried at 50°C. The aliphatic diamines, 1,2-diaminopropane (12DAP), 1,3-diaminopropane (13DAP), 1,4-diaminobutane (14DAB), and 1,10-diaminodecane (10DAD) were used as received. The solvent *m*-cresol was dried over CaCl₂, then over molecular sieves, distilled under reduced pressure, and stored under nitrogen in the dark.

Monomer synthesis

1,3-Diaminoadamantane (DAA) and 3,3'-diamino-1,1'-diadamantane (DADA) were synthesized according to procedures in the literature¹⁰⁻¹² and were purified through vacuum sublimation. When the solid 1,3-diaminoadamantane was exposed to air, it rapidly transformed into a colorless liquid and then reformed into a white solid. The IR spectra of this compound did not agree with its proposed structure, because of its instability and moisture sensitivity.

1,3-Diaminoadamantane

¹H NMR (300 MHz, benzene-d₆) δ (ppm) 1.23 (2H, s, H-2), 1.32 (10H, m, H-4, H-6, H-8, H-9, H-10), 1.44 (4H, NH₂), 1.95 (2H, m, H-5, H-7); ¹³C NMR (75.45

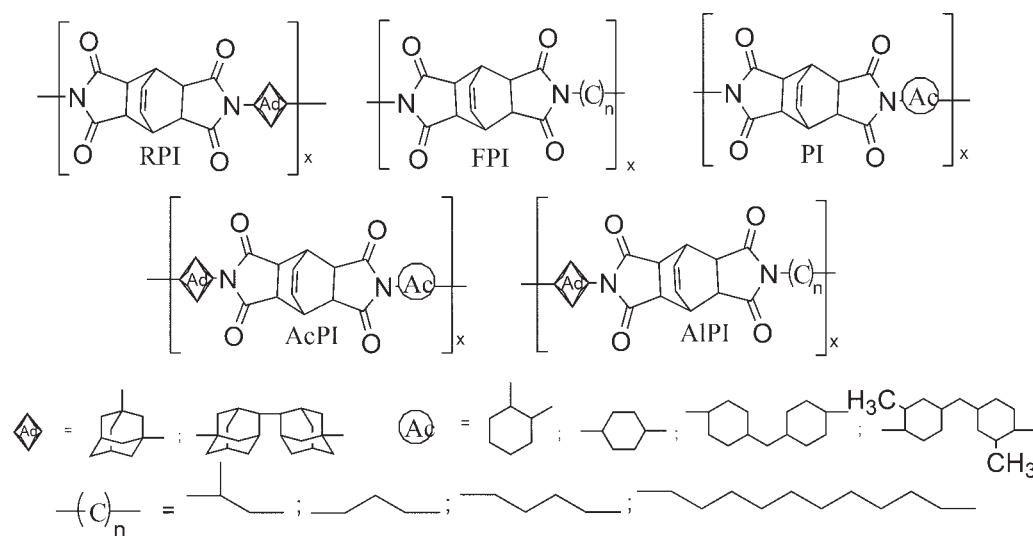


Figure 2 Structures of the aliphatic polyimides sorted into five categories, according to their constituents and chemical structures.

MHz, benzene- d_6) δ (ppm) 31 (C-5, C-7), 35.38 (C-6), 45.3 (C-4, C-8, C-9, C-10), 49.22 (C-1, C-3), 54.7 (C-2).

3,3'-Diamino-1,1'-diadamantane

IR (KBr) ν 3425 (NH₂), 3005, 2900, 1680, 1382–1270, 1206, 1110, 820, 760 cm^{-1} . ¹H NMR (300 MHz, DMSO- d_6) δ (ppm) 1.29 (4H, m, H-5, H-7), 1.33–1.45 (24H, m, H-2, H-4, H-6, H-8, H-9, H-10), 2.01 (4H, s, NH₂). ¹³C NMR (75.45 MHz, DMSO- d_6) δ (ppm) 29 (C-5, C-7), 33.5 (C-8, C-9), 35.3 (C-6), 39.22 (C-1), 44.7 (C-2), 45.3 (C-4, C-10), 47.2 (C-3).

Preparation of fully aliphatic polyimides through one-step polymerizations

Polyimides that are soluble in organic solvents can be synthesized through a one-step method.¹³ We synthesized APIs that can be classified into five distinct categories according to their constituents and chemical structures (Fig. 2). The first category (RPI) is composed of rigid APIs formed from BOCA and adamantyl diamines. The flexible polyimides derived from BOCA and linear aliphatic diamines and the homopolymers of BOCA and alicyclic diamines constitute the second (FPI) and third (PI) classes, respectively. The fourth group (AlPI) includes APIs containing BOCA and a 1 : 1M ratio of rigid adamantyl and flexible linear aliphatic diamines. The polycondensation products of BOCA and equimolar amounts of adamantyl and alicyclic diamines constitute the fifth group (AcPI).

Homopolyimide synthesis

Equimolar amounts of the dianhydride and diamine (i.e., 0.25 g, 1 mmol BOCA, and 0.21 g, 1 mmol MCA) in *m*-cresol (3 mL) were placed in a three-

neck flask equipped with a mechanical agitator, nitrogen inlet tube, and thermometer. The flask was then warmed in an oil bath at 60°C for 30 min and was heated to 130°C to prepare a homogeneous solution that was maintained at that temperature for 2 h. The bath was then heated up to 200°C under a flow of nitrogen and maintained under these conditions until no further rise in viscosity was observed. On completion of the reaction, the viscous polymer solution was cooled under nitrogen and poured into a large quantity of methanol (40 mL) to precipitate the APIs, which were filtered off, washed repeatedly with methanol to remove any remaining *m*-cresol, and was dried under vacuum at 70°C for 8 h. For polymerizations involving DAA, the steps prior to the initial heating were performed in a nitrogen glove box because of the air sensitivity of the monomer.

Copolyimide synthesis

Equimolar amounts of the dianhydride and diamine (e.g., 0.5 g, 2 mmol BOCA, 0.21 g, 1 mmol MCA, and 0.17 g, 1 mmol DAA) were dissolved in *m*-cresol (5 mL) and were charged into the experimental setup described earlier. A 1 : 1M ratio of the adamantane-containing and aliphatic diamines was used to form the copolyimides. The reaction mixture was treated in the same manner as described earlier. After the completion of one step polymerization, the APIs formed were precipitated in excess amount of methanol (50 mL) and were washed thoroughly and dried in vacuum at 70°C for 8 h.

Film casting

A solution of the white powdered APIs dissolved in DMF was poured into a Petri dish and heated under

a nitrogen atmosphere in the following increments: 60°C for 2 h, 80°C for 2 h, 150°C for 2 h, 200°C for 1 h, and 250°C for 1 h. To perform the dielectric constant and transparency measurements, the solutions of APIs obtained prior to precipitation were spin-coated onto clean ITO glass and quartz plates, respectively, and then subjected to the heating cycle described above.

Characterization

^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus-300 (300 MHz) NMR spectrometer. Infrared spectra (KBr disks) were recorded on a Shimadzu IR Prestige-21 spm using a Ge-KBr beam splitter. Viscosity measurements were performed using an Ubbelohde viscometer at 30°C after dissolving the APIs in H_2SO_4 . Average molecular weight (M_n) and PDI of the soluble APIs were estimated by gel permeation chromatograph (GPC) using a Waters 515 differential refractometer with Waters 410 HPLC Pump and two Styrogel HR 5E columns in DMF (0.1 mg/L) solvent at 42°C, calibrated with polystyrene standards. The solubility test was performed using equal amounts of APIs in matched quantities of commonly used solvents. To investigate the thermal stability of the APIs, thermogravimetric analyses were performed under nitrogen using a TGA Q50 Q Series thermal analyzer at a heating rate of 10°C/min from room temperature to 600°C. Measurements of glass transition temperature were performed using a DSC Q 100 TA instrument at a heating rate of 10°C/min under a nitrogen atmosphere. The transparencies of the polyimide films were measured from ultraviolet-visible spectra recorded from one accumulation on a SHIMADZU UV-1650 PC spectrometer optimized with a spectral width of 200–800 nm, a resolution of 0.5 nm, and a scanning rate of 200 nm/min; the thickness of each film was $\sim 1 \mu\text{m}$. Wide-angle X-ray diffraction (WXAD) measurements of the pulverized samples were conducted at room temperature in the reflection mode using a Rigaku diffractometer (Model Rigaku Miniflex). 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 0.01° intervals over the range $1.5\text{--}70^\circ$ and at a scan speed of $0.5^\circ(2\theta)/\text{min}$. Tensile properties were determined from stress–strain curves obtained with Kyungsang Universal Testing Measurement (UTM) Materials Testing System (Model KSU-05) at a strain rate of 10 mm/min at room temperature. Measurements were performed with film specimens (50 mm in gauge length, 10 mm wide, and 0.1 mm thick). The dielectric constant was obtained at 1 MHz using an impedance-gain phase analyzer (HP4194A) and the formula $K = C d/A\epsilon_0$, where C is the observed capacitance, d is the film thickness, A is the area,

and ϵ_0 is the free permittivity. The thickness of each film was $1.0 \pm 0.05 \mu\text{m}$.

RESULTS

Monomer selection

For the synthesis of the APIs, we selected bicyclo [2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) as the rigid alicyclic dianhydride; it has been proved to impart excellent thermal and optical properties to polyimides.¹⁴ Two diamines possessing adamantyl moieties, 1,3-diaminoadamantane (DAA) and 3,3'-diamino-1,1'-diadamantane (DADA), were selected to provide APIs with low dielectric constants and high thermal and dimensional stabilities. Unfortunately, matching the coefficient of thermal expansion (CTE) of APIs that incorporate rigid alicyclic backbones with that of the substrate is difficult and the resultant polyimide films are very brittle. A number of approaches have been reported to rectify this problem, such as utilizing a combination of rigid and flexible alicyclic monomers.^{10,15} Copolymerization of rigid monomers with flexible ones has been used to control the thermal and mechanical properties of polyimides to meet specific processing and property requirements. Therefore, we decided to prepare and compare the properties of homo- and copolyimides derived from rigid adamantyl and flexible linear and alicyclic monomers. We chose to use 1,2-diaminopropane (12DAP), 1,3-diaminopropane (13DAP), 1,4-diaminobutane (14DAB), and 1,10-diaminodecane (10DAD) as flexible linear aliphatic diamines with the intention of studying the impact that increasing chain length and flexibility has upon the inherent characteristics of the APIs. The alicyclic monomers 1,2-diaminocyclohexane (12DAC), 1,4-diaminocyclohexane (14DAC), 4,4'-methylene bis(cyclohexylamine) (MCA), and 4,4'-methylene bis(2-methyl cyclohexylamine) (MMCA) were selected with the objective to study how the basic traits of the polyimides vary with respect to the effects of the constitutional isomerism, methyl substituents, and steric hindrance of their diamine subunits.

Polymerization

Carboxylic acid salts generally result from the reactions of dianhydrides with highly basic diamines, such as aliphatic and alicyclic diamines, together with polyamic acids. This salt formation prevents the isolation of high molecular-weight polyamic acids. One-pot polyimide syntheses performed at a high temperature and without isolating any polyamic acid seemed to be a useful method for preparing high-molecular-weight polyimides, because the

TABLE I
GPC Molecular Weights, Viscometric and Thermal Properties of Fully Aliphatic Polyimides

Polyimide (API)	Adamantyl diamine	Aliphatic diamine	η (dL/g)	GPC molar mass		T_g ($^{\circ}$ C)	T_d ($^{\circ}$ C)	
				$10^4 M_n$	PDI		5%	10%
RPI ₁	DAA		0.32	a	a	–	325	353
RPI ₂	DADA		0.36	a	a	–	328	365
FPI ₁		12DAP	0.16	0.24	1.6	212	264	304
FPI ₂		13DAP	0.19	0.36	1.8	210	270	323
FPI ₃		14DAB	0.21	0.69	1.9	211	259	320
FPI ₄		10DAD	0.23	a	a	219	242	313
AlPI ₁	DAA	12DAP	0.18	0.52	1.4	222	285	310
AlPI ₂	DAA	13DAP	0.21	0.58	1.6	220	309	340
AlPI ₃	DAA	14DAB	0.22	0.95	1.8	221	308	334
AlPI ₄	DAA	10DAD	0.25	1.07	1.5	221	300	323
AlPI ₅	DADA	12DAP	0.2	0.92	1.3	223	320	385
AlPI ₆	DADA	13DAP	0.23	0.93	1.5	223	327	409
AlPI ₇	DADA	14DAB	0.24	1.46	1.2	224	324	407
AlPI ₈	DADA	10DAD	0.27	1.29	1.6	225	314	396
PI ₁		12DAC	b	a	a	–	343	378
PI ₂		14DAC	b	a	a	–	347	367
PI ₃		MCA	0.56	4.52	2.4	239	358	385
PI ₄		MMCA	0.5	4.35	2.4	241	326	364
AcPI ₁	DAA	12DAC	0.39	a	a	–	330	420
AcPI ₂	DAA	14DAC	0.41	1.63	1.1	–	334	422
AcPI ₃	DAA	MCA	0.47	4.05	2.1	250	420	436
AcPI ₄	DAA	MMCA	0.43	3.37	2	251	341	429
AcPI ₅	DADA	12DAC	0.4	a	a	–	410	429
AcPI ₆	DADA	14DAC	0.41	a	a	–	413	430
AcPI ₇	DADA	MCA	0.52	3.47	2.3	248	425	448
AcPI ₈	DADA	MMCA	0.48	3.28	2.2	249	419	433

^a Polymers cannot be dissolved in DMF.

^b Polymers precipitated during polycondensation reaction.

amines used for the salt formation can be regenerated during thermal cyclization. Therefore, we prepared our APIs of interest at 60–200 $^{\circ}$ C in *m*-cresol under a nitrogen atmosphere without isolating any polyamic acids. These polymerizations proceeded in the homogeneous state to produce APIs quantitatively. Table I summarizes the results of these polymerizations.

The polymer precipitation occurred when we used the rigid diamines 12DAC and 14DAC, which limited the molecular weights of their corresponding homopolyimides. We found that the viscosity of the linear APIs increased upon incorporating adamantyl groups, presumably because of their bulkiness. In contrast, the viscosity of the alicyclic polyimides decreased upon incorporation of bulky adamantane moieties, because they sterically hindered the polymerization reaction. According to GPC data, M_n and PDI of the polyimides ranged from 2400 to 45,200, and 1.1 to 2.4 respectively. Unfortunately the values of very rigid backboned API cannot be obtained because of their low solubilities. The lower M_w/M_n values comparative to those of conventional PIs may be due to the somewhat low reactivity of monomers containing the rigid and bulky groups.¹⁶ Representative GPC traces are shown in Figure 3.

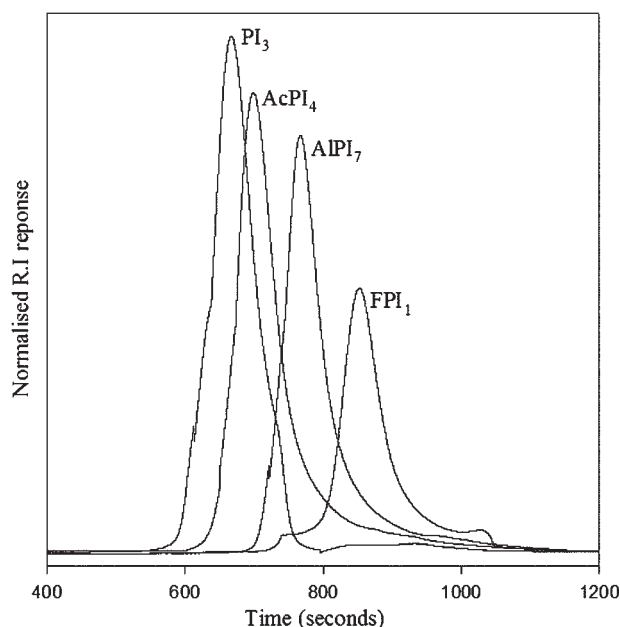


Figure 3 GPC traces of fully aliphatic polyimides, PI₄, AcPI₄, AcPI₈, and FPI₁.

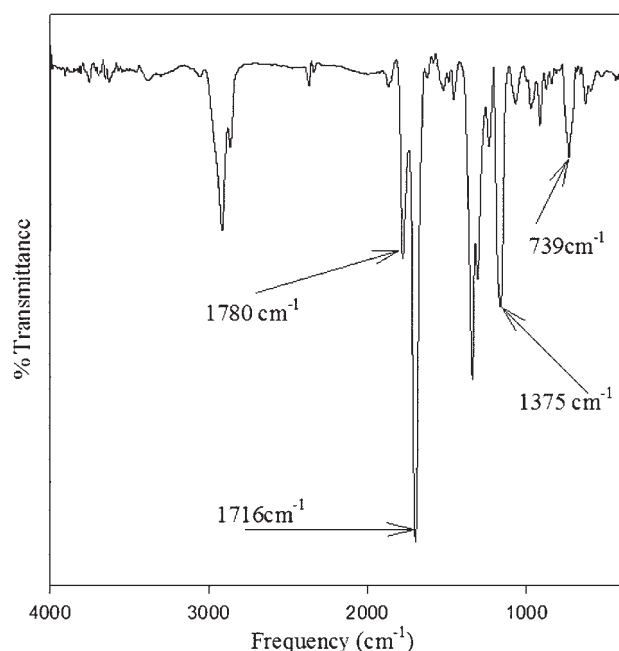


Figure 4 IR spectrum of a representative fully aliphatic polyimide, RPI₁.

Characterization of APIs

Figure 4 presents a representative FTIR spectrum of a polyimide containing adamantyl moieties. We observe a number of typically characteristic peaks at 1780 (C=O symmetric stretching), 1716 (C=O asymmetric stretching), 1375 (C–N–C stretching), 739 (imide ring deformation), 2800–2900 (aliphatic C–H stretching), 1465 (CH₂ bending), and 1450 and 1395 cm⁻¹ (CH₃ bending).¹⁷ The slight shifts of the absorption peaks from the usual wavenumber values can be attributed to the nonconjugation due to the absence of aromatic ring.¹⁸ The characteristic imide group bands at 1780 and 1716 cm⁻¹ support the formation of a fully imidized structure.

In addition, as Figure 5 indicates, NMR spectra confirmed the APIs. All showed the characteristic peaks together with the C=C peak (around 6 ppm and 176 ppm in ¹H and ¹³C NMR spectra respectively). This rules out the possibility of the double bond of the dianhydride to rupture and react at elevated temperatures of polymerization. The *c* and *d* proton signals were broadened through the interaction with the nearby C=C groups. The copolymers showed the characteristic peaks of both the diamine residues, confirming the expected structures. In ¹³C spectra, the splitting of carbon peak of C=O occurs in copolyimides, proving the presence of different moieties in the two sides of the imide ring.

Solubility

We determined the solubility of the polyimides in various kinds of organic solvents using powdery

samples; Table II lists the results. The homopolyimides obtained from 12DAC, 14DAC, DAA, and DADA were soluble only in *m*-cresol and sulfuric acid because of the rigidity of their backbones. Copolymerization of both rigid and flexible diamines with BOCA produced APIs that had improved solubility relative to those of the corresponding single-diamine polyimides. Enhanced solubility in polyimides is generally governed by the presence of flexible backbones, bulky noncoplanar groups, and kink

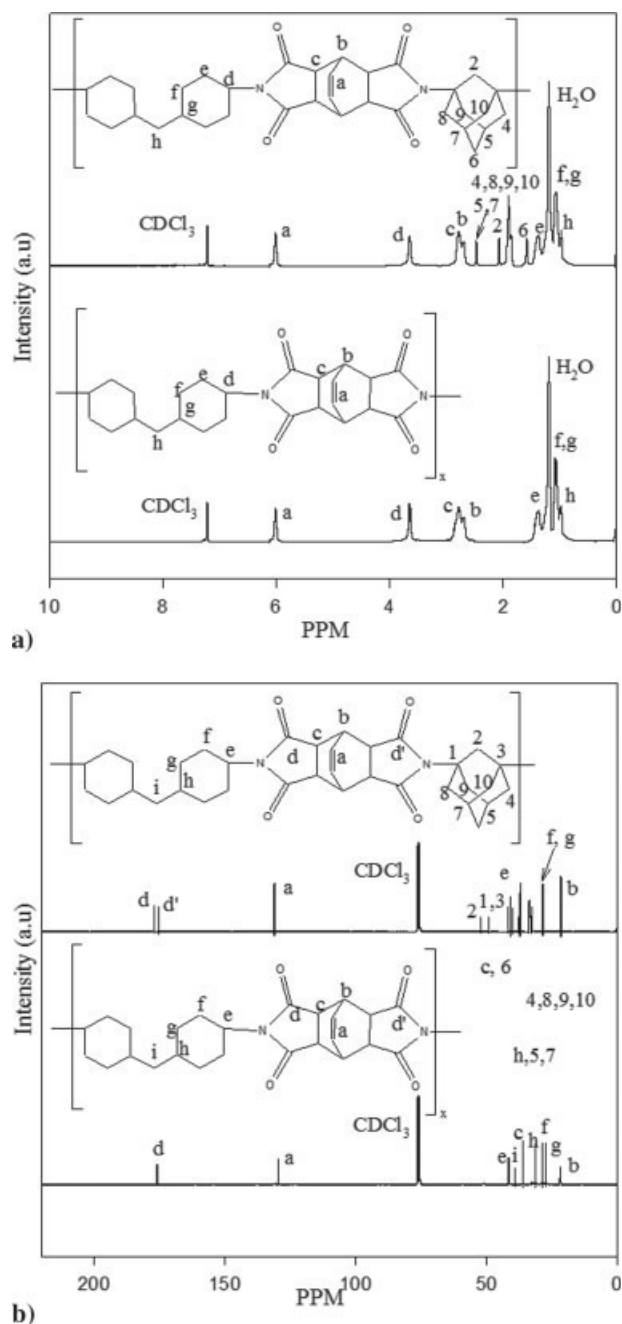


Figure 5 (a) ¹H NMR spectra of fully aliphatic polyimides, PI₃ and AcPI₃. (b) ¹³C NMR spectra of fully aliphatic polyimides, PI₃ and AcPI₃.

TABLE II
Solubility of Synthesized Aliphatic Polyimides

API	Solvents ^a									
	NMP	DMAc	DMF	DMSO	THF	CH ₃ OH	m-Cresol	CHCl ₃	Pyridine	H ₂ SO ₄
RPI ₁	±	±	±	±	±	-	++	±	±	++
RPI ₂	+	-	+	-	-	-	++	+	±	++
FPI ₁	++	+	++	+	+	-	++	++	+	++
FPI ₂	+	+	+	+	+	-	++	++	+	++
FP ₃	+	+	+	+	+	-	++	+	+	++
FPI ₄	±	±	±	±	±	-	++	+	±	++
AlPI ₁	++	++	++	++	++	-	++	++	+	++
AlPI ₂	++	++	++	++	++	-	++	++	+	++
AlPI ₃	++	±	++	+	+	-	++	++	+	++
AlPI ₄	±	+	+	±	±	-	++	++	±	++
AlPI ₅	++	++	++	+	+	-	++	++	++	++
AlPI ₆	++	+	++	+	±	-	++	++	±	++
AlPI ₇	+	+	++	+	±	-	++	+	±	++
AlPI ₈	+	+	+	+	±	-	++	+	±	++
PI ₁	±	-	±	-	-	-	++	-	-	++
PI ₂	±	±	±	±	±	-	++	±	+	++
PI ₃	+	+	+	+	+	-	++	+	+	++
PI ₄	+	+	+	+	+	-	++	+	±	++
AcPI ₁	±	±	+	±	±	-	++	±	±	++
AcPI ₂	+	±	+	±	±	-	++	+	±	++
AcPI ₃	++	+	+	+	±	-	++	++	±	++
AcPI ₄	++	+	++	+	+	-	++	++	±	++
AcPI ₅	+	+	+	+	+	-	++	±	±	++
AcPI ₆	++	+	++	±	±	-	++	+	+	++
AcPI ₇	+	±	++	±	±	-	++	++	+	++
AcPI ₈	+	+	++	+	+	-	++	++	+	++

^a Solubility: (++) soluble at room temperature; (+) soluble upon heating; (±) partially soluble or swells; (-) insoluble.

linkages; all of these factors reduce the degree of polymer chain interaction and their rigidity.^{19,20} In our case, the improved solubility of the copolyimides clearly arose from the presence of a flexible aliphatic backbone together with the bulky adamantyl moieties, which create steric hindrance and curtail both interchain interactions and chain packing.

Thermal stability and phase transitions

We used DSC and TGA to evaluate the thermal behavior of the polyimides. The polymers underwent their 5% weight losses within the temperature range from 242 to 421°C. The temperatures for 10% gravimetric loss (T_{10}), which is an important criterion for evaluating thermal stability, were in the range 304–440°C. Figure 6 displays representative TGA curves; Table I summarizes the results. Although they have rigid backbones, the thermal stabilities of the homopolyimides derived from the diamines DAA and DADA were low. This situation may be due to the low degree of intermolecular interactions because of the steric hindrance provided by the bulky adamantyl groups. The polyimides containing linear aliphatic chains on their backbones were the least resistant to temperature; their stability decreased upon increasing the length of

their thermally fragile alkyl chains. The APIs containing 12DAP residues were less thermally stable than those containing 13DAP backbones. This can be attributed to two reasons: first one being the larger

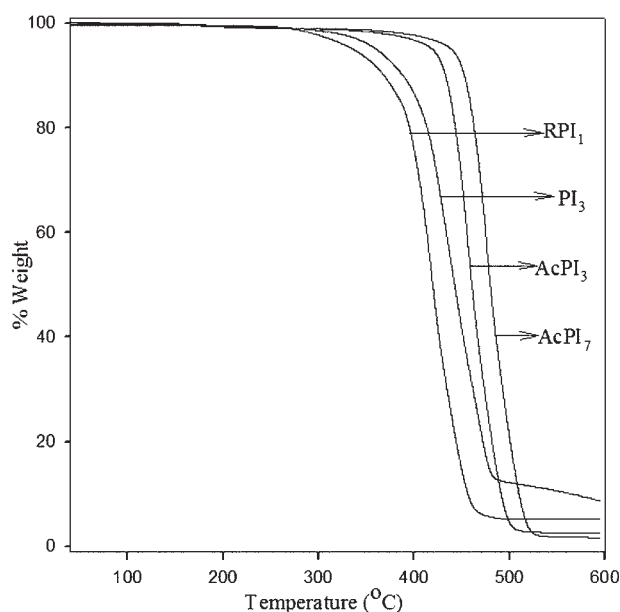


Figure 6 TG curves of RPI₂, PI₄, AcPI₄, and AcPI₈ displaying the enhancement of thermal resistance upon incorporation of adamantane moieties.

separation between imide chains due to methyl unit in the side chain of each 12DAP moiety, which is evidenced by the splitting of WAXD peaks upon the change of 12DAP residue to 13DAP showing enhanced internal order; the second reason can be related to the small structural difference between the monomers, such as the presence of a tertiary carbon atom in 12DAP containing APIs. Among the alicyclic polyimides derived from 12DAC and 14DAC, we found that the former API had the lower thermal stability due to the structural difference arising from their ortho linkage to imide moieties as well as weak interchain interactions. Similarly, the APIs based on the MMCA diamine exhibited lower thermal stabilities than did those of the MCA-based APIs due to the presence of tertiary carbon atom together with the difference in interchain interactions. Our study suggests that the structural difference of the monomers used also played a significant role in the thermal stability of the final APIs together with the rigidity and interchain interaction factors.

The glass transition temperatures of the polyimides were in the range 210–251°C (Table I), with the exception that we did not detect values of T_g for the most rigid homo-APIs, i.e., those derived from DAA, DADA, 12DAC, and 14DAC. The polyimides containing the linear aliphatic residues 12DAP, 13DAP, 14DAB, and 10DAD possessed melting temperatures of ~ 320 – 380°C and values of T_g in the range 210–225°C, which reappeared upon performing repeated scans. This finding suggests that each of these polyimides has a semicrystalline nature, which we confirmed through wide-angle X-ray diffraction (WAXD). We also used WAXD to confirm that all of the other APIs had semicrystalline properties, even though we did not observe any melting transitions in the range 70–400 °C, either because they have values of T_m above 400°C or because they decomposed before they melted. The values of T_g of the copolyimides shifted to higher temperatures. The T_g of polyimides can be mainly explained in terms of chain rigidity without considering specific intermolecular interactions.²¹ Thus, in the present study, the bulky adamantane groups inhibited chain mobility and generated extra chain rigidity. The higher values of T_g of the polyimides based on 12DAP, relative to those based on its isomer 13DAP, and the enhanced values of T_g of the APIs possessing MMCA backbones, relative to those possessing MCA units, suggest that the glass transition temperatures of these types of APIs increase gradually upon increasing the chain rigidity induced by the methyl substitution. Figure 7 presents typical DSC curves. In general, the increased chain rigidity due to the pendent cardo groups restricted the free rotation about the poly-

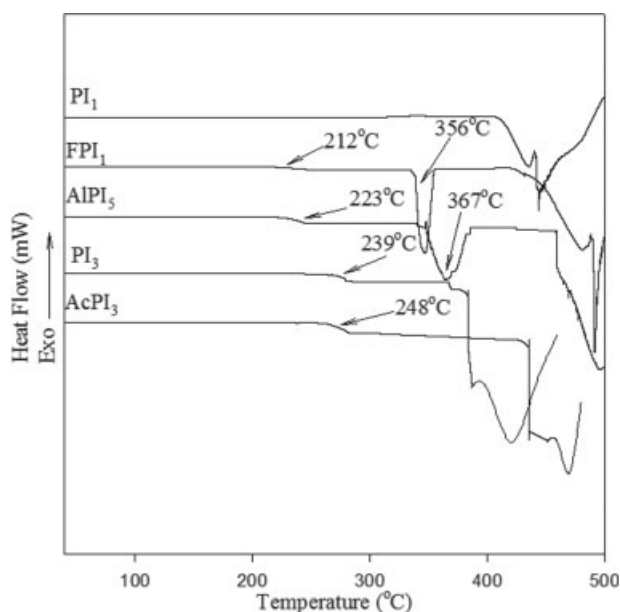


Figure 7 DSC traces of the fully aliphatic polyimides FPI₁, AIPi₅, PI₁, PI₃, and AcPI₃.

mer backbone to yield polyimides with high glass transition temperatures.

Optical properties

Fully APIs exhibit high transparency because of their low molecular density, polarity, and probabilities of mediating inter- and intramolecular CT. Though semicrystalline polymers frequently exhibit light scattering that deteriorate optical transparency, we expect that the factors mentioned above predominate over the semicrystallinity of the APIs, yielding APIs having transparencies above 80%. For homo polyimides based on aliphatic chains the transparency decreased (80–82%), which could be explained on the basis of enhanced crystallinity. The lowest transparency, 80%, was observed for the 10DAD based API, which showed the splitting of WAXD peaks below $2\theta = 20^\circ$ due to interchain interaction. For alicyclic diamine based APIs the transparency was higher (around 85%) due to the reduced crystallinity. Indeed, further enhancement in transparency to $\sim 95\%$ resulted from the incorporation of the adamantyl groups; we attribute this finding to the loosening of the intermolecular packing that results from the low polarizability and bulk of these pendent groups. The WAXD patterns of APIs containing adamantane did not show any peaks except the amorphous halo around $2\theta = 16^\circ$. This amorphous nature can also be attributed to the enhanced transparency of APIs with adamantane units in its backbone. This trend is demonstrated in Figure 8, which presents the UV-vis spectra of $\sim 1\text{-}\mu\text{m}$ -thick polyimide films

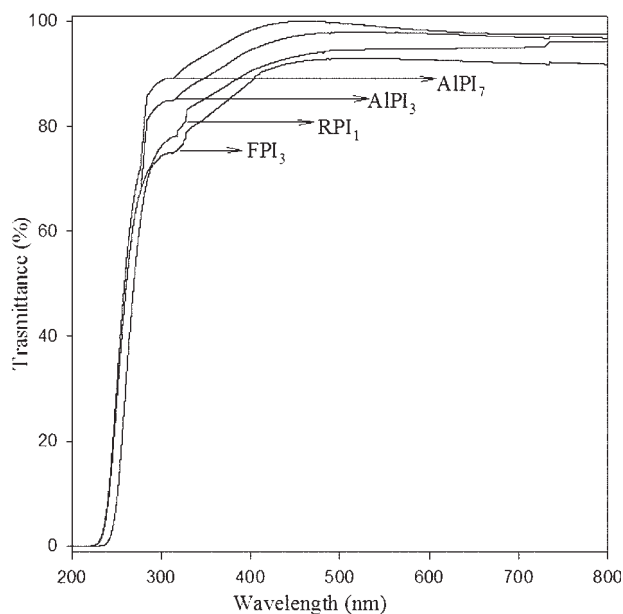


Figure 8 UV-vis spectra of polyimides displaying the dramatic escalation of transparency upon the incorporation of adamantane units.

based on DAA, 14DAB, 14DAB, and DAA (1 : 1), and 14DAB and DADA (1 : 1).

Crystallinity

We performed WAXD experiments in an attempt to evaluate the crystallinities of our synthesized polyimides; Figure 9 displays representative WAXD results. All of the APIs exhibited peaks in the region $2\theta < 20^\circ$, which indicates that they possess crystalline structures as well as intermolecular regularity. The linear aliphatic diamine-based APIs presented patterns in the region $2\theta < 20^\circ$ that are different from those of the alicyclic APIs. The broad peak centered at $2\theta = 16.02^\circ$ (d -space = 5.5 Å) shifted to a lower position and split into several smaller peaks when we changed the diamine from 12DAP to 13DAP. In addition, the peak intensity increased as the chain length of the polyimide backbone increased; this finding suggests a high degree of internal order. Alicyclic APIs exhibited a peak at $2\theta = 16.54^\circ$, which corresponds to a d -spacing of 5.3 Å.

Incorporation of adamantyl moieties into the alicyclic and APIs resulted in a lowering of the peak intensity and broadening of the peaks at $2\theta < 20^\circ$. The decreased scattering intensity suggests a disruption of the internal order; the broadening of the peaks arises from the lattice strain²² that result from the presence of the bulky and rigid pendent adamantane groups. The broad peak is due to the diffraction of a poor intermolecular packing combined with amorphous halo.²³ We observed a lower crystallinity for the copolyimides containing 1,3-diaminoadamantane

and 3,3'-diamino-1,1'-diadamantane residues, presumably because of the low degree of dipolar inter-chain interactions between the bulky moieties; this result is consistent with their higher solubility.

Mechanical properties

The mechanical properties of the fully APIs were investigated using the stress-strain curves obtained from UTM and the results are listed in Table III.

These API films possess a tensile modulus of 1.3–2.5 GPa, tensile strength in the range of 78.7–118 MPa, and elongation at break around 3.4%–15%. Most of the polyimides exhibited appreciable tensile strength, indicating that they are mechanically stringent.

The UTM traces for highly rigid APIs (RPI1, RPI2, PI1, PI2, AcPI1, AcPI2 and AcPI5) were not measured because the films were too brittle. The flexible films obtained showed strong and tough nature. Tensile strength of the flexible APIs was enhanced as a result of the incorporation of adamantane moieties which improve the rigidity of the polymer chain.

Dielectric constant

We observed appreciably low dielectric constants for all the APIs (Table III). The homopolyimides derived from aliphatic linear diamines had comparatively high ϵ values because of their higher degree of close chain packing; the values decreased proportionally with respect to the alkyl chain length as a result of

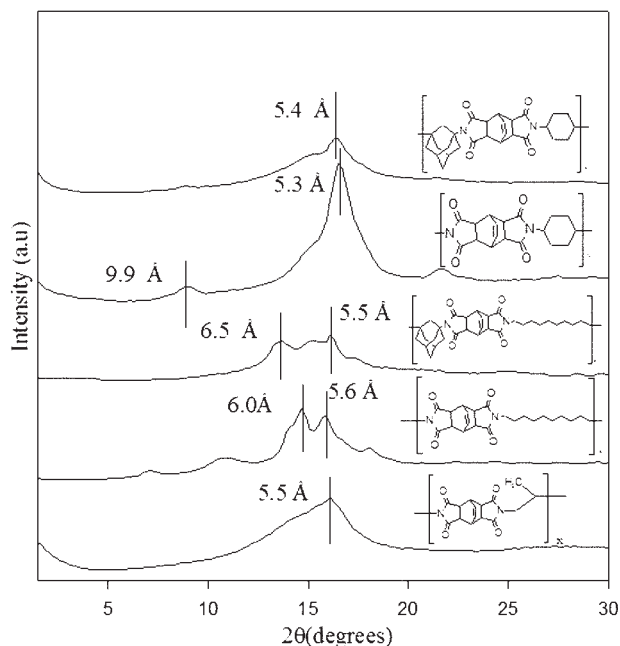


Figure 9 X-ray diffractograms of FPI₂, FPI₄, AIPI₄, PI₂, and AcPI₂. The structures of the polyimides are presented above the corresponding curves.

TABLE III
Physical Properties of Fully Aliphatic Polyimide Films

Polyimide (API)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	Dielectric constant ϵ
RPI ₁	a	a	a	2.52
RPI ₂	a	a	a	2.63
FPI ₁	a	a	a	2.89
FPI ₂	a	a	a	2.92
FP ₃	a	a	a	2.86
FPI ₄	84	4	2.1	2.74
API ₁	79	3.4	1.6	2.59
API ₂	78.7	3.8	1.6	2.62
API ₃	80	4.4	1.6	2.56
API ₄	88.2	5.2	1.9	2.44
API ₅	81	3.7	1.65	2.84
API ₆	81	4.1	1.63	2.83
API ₇	81.8	4.8	1.7	2.79
API ₈	89.6	5.6	1.93	2.61
PI ₁	a	a	a	2.62
PI ₂	a	a	a	2.64
PI ₃	99.8	15	2.5	2.58
PI ₄	99	14.5	2.4	2.57
AcPI ₁	a	a	a	2.34
AcPI ₂	a	a	a	2.36
AcPI ₃	113.5	11.5	1.9	2.49
AcPI ₄	104.9	11.2	1.9	2.44
AcPI ₅	a	a	a	2.55
AcPI ₆	100.8	10	1.3	2.56
AcPI ₇	118	13.8	2.1	2.5
AcPI ₈	118	13.6	2.0	2.48

^a Polymers were too brittle to be measured.

diminution in the degrees of chain packing and interchain interactions. Inefficient chain packing, which induces free volume, may be the reason for the lower values of ϵ of the alicyclic polyimides.¹⁷ Among the constitutional isomers of diaminocyclohexane, the API derived from the 1,2-isomer possessed the lower value of ϵ , possibly because of its higher free volume. The dielectric constants decreased further for the APIs based on MCA and MMCA; of these systems, the presence of the methyl-substituted bicyclohexane moiety led to a much lower value of ϵ as a result of its greater free volume. In particular, AcPI₁ and AcPI₂ possessed the lowest values of ϵ ; we attribute this finding to the presence of the highly rigid and bulky alicyclic moieties, which sterically hinder the packing and enlarge the free volume in the polyimides. The copolyimides containing adamantyl moieties also possess large free volumes because of their bulky pendent groups, as is evident from their low values of ϵ . Unexpectedly, we found that the values of ϵ of the APIs containing diadamantyl groups were higher than those of the APIs containing adamantyl groups, regardless of the increased dilution of the polar imide groups that is caused by the more-bulky diadamantyl moieties. We explain this finding on the basis of the linear structures of the diadamantane-containing APIs relative to those of the noncoplanar adamantane-containing APIs; i.e., the former species have smaller molar

volumes.¹² In general, an increased free volume correlates with a decreased dielectric constant for these APIs, except for the rigid adamantane-based homopolyimides.

DISCUSSION

This study about fully APIs reveals a number of interesting facts. In comparison with commercially available polyimides (Ultem 1000; $T_g = 215^\circ\text{C}$, tensile strength = 105 MPa), we observed that the adamantyl units can effectively enhance the glass transition temperatures and tensile strength of the polyimides. The highest values of glass transition temperature and tensile strength was found for copolyimides containing adamantyl and dicyclohexyl units presumably because of a balance between stiffness, polarity, and free volume of their backbone units. Without having to incorporate expensive fluorine or silicon compounds into their structures, the copolyimides of alicyclic and adamantyl diamines with BOCA (AcPI) exhibited dielectric constants as low as 2.34 ~ 2.56, while possessing enhanced solubilities and transparencies. Even the commercial polyimide, Kapton[®], has ϵ value around 3, together with the demerits that they are insoluble in organic solvents and are highly colored. On the other hand, our copolyimides, AcPI₃, AcPI₄, AcPI₇, AcPI₈, shows

superior properties like low dielectric constant (2.44–2.5) together with excellent solubility in common organic solvents and high transparency $\sim 90\%$. Transparent polyimide films of the AcPIs have appreciable thermal stability and seem suited for application to the construction of optical devices, rather than using aromatic polyimides possessing aliphatic, alicyclic, or alkynyl side chains. Because of the low hydrophobicity and polarity of the rigid and bulky adamantane units, together with the flexibility of the alicyclic chains, the copolyimides are quite soluble in common organic solvents and, therefore, they can be processed directly. The adamantane-based APIs rank superior to the bisadamantane-based polyimides because of their higher solubilities, values of T_g , and transparencies and their lower dielectric constants, but their thermal and mechanical stabilities were lower because of weak interchain interactions. Worldwide research is progressing for a practically applicable polyimide candidate devoid of demerits; despite the bewildering number of candidate materials under investigation, a clear winner has yet to emerge. Nevertheless, our present study suggests that fully APIs and, especially, copolyimides-based on adamantane/bisadamantane units and bis(cyclohexylamine) residues (AcPI₇, AcPI₈) possess high transparency ($\sim 95\%$), high values of T_g (240–251°C), enhanced solubility, and low dielectric constants (2.44–2.5), together with marginal thermal stability ($T_{d(10\%)} = 429\text{--}440^\circ\text{C}$) and tensile strength (104–118 MPa); these properties suggest that they may find an immense range of applications in flexible PLED substrates, soft-printed circuit boards, inter-level dielectric insulators, high-speed passivation or dielectric films, and alignment films.

CONCLUSIONS

We synthesized a series of fully APIs based on BOCA and aliphatic, alicyclic, and/or adamantyl diamines through polyaddition/polycondensation reactions. These APIs possessed inherent viscosities of 0.16–0.56 dL/g. The optically clear organic-soluble APIs that we prepared exhibited low dielectric constants and high thermal stabilities. Our study reveals that copolyimides containing adamantyl moieties

together with flexible aliphatic groups display improved thermal and mechanical stabilities, solubility, and transparency and lower dielectric constant. Thus, the APIs have potential for applications within micro- and optoelectronic devices. The utility of many polymers in optoelectronic and electronic applications would be also governed by thermo-oxidative stability, which was not evaluated in this work. Therefore, further studies to evaluate the thermo-oxidative stability of the fully APIs and the influence of adamantane moieties are now underway and will be reported elsewhere.

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