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Fully Aliphatic Polyimides – Influence of Adamantane and Siloxane Moieties

*Anu Stella Mathews, Il Kim, Chang-Sik Ha**

Summary: Series of fully aliphatic polyimides were prepared from cyclobutane-1,2,3,4-tetracarboxylic dianhydride and aliphatic diamines. The variations of the basic properties of these polyimides as a result of the incorporation of adamantyl and siloxane moieties are examined. The structure of the polyimides where confirmed by FT-IR spectroscopy. It was found that polyimides with appropriate ratio of adamantane and siloxane groups showed excellent solubility, good thermal stability, high glass transition temperature, low dielectric constant and beneficial transparencies.

Keywords: adamantane; aliphatic polyimides; siloxane; thermal stability; transparency

Introduction

Polyimides (PI) possess excellent thermal, mechanical and electrical properties and thus have found immense applications in technologies ranging from microelectronics to high temperature matrices and adhesives to gas separation membranes.[1,2] Fully aliphatic and alicyclic polyimides (API) are currently being considered for their applications in optoelectronics and inter-layer dielectric materials due to their higher transparencies and lower dielectric constants, compared to aromatic polyimides.[3] Nevertheless, polyimides derived from aliphatic monomers are most suited for applications that have less-stringent thermal requirements. Previous studies revealed that adamantane (tricycle [3.3.3.1.1.[3,7]] decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations,[4] is the most salutary alicyclic candidate for incorporation into aliphatic polyimides to enhance thermal stability without sacrificing their high transparency, solubility and low dielectric constants. On the other hand, increasing importance of polyimides for gas-separation, microelectronics and optoelectronics applications have paved the way for the introduction of silicon moieties into the backbone of PIs promoting significant increase in permeability, permselectivity and adhesive ability and silicon containing aromatic polymers has attracted much scientific and technological interest due to their superior permeability and adhesive ability between substrates and polyimides together with low dielectric constant.[5] In this work, we wish to discuss how adamantyl group and siloxane moieties influence the basic properties of aliphatic polyimides. For this purpose we adopt a one step imidization approach to directly synthesize a series of aliphatic polyimides (API) and polyimide-siloxanes (APISiO) by the copolymerization of aliphatic diamines and adamantyl diamine or siloxane diamine and dianhydride monomer.

Experimental Part

Materials

Cyclobutane-1,2,3,4-tetracarboxylic dianhydrides (CBDA) were recrystallized from acetic anhydride and dried at 150 °C under vacuum before use. 1,3-bis (3-amino propyl)-tetra methyl disiloxane (APTMS) obtained from Gelest – AZmax Co., Ltd (Chiba, Japan) and 1,4-diaminobutane (14DAB)

Department of Polymer Science and Engineering,
Pusan National University, Busan, Korea
Fax: (+82)51-514-4331
E-mail: csha@pusan.ac.kr

were used as received. The alicyclic diamines 1,4-diaminocyclohexane (14DAC) was distilled under reduced pressure and stored in the dark prior to use. The solvent m-cresol was dried over $CaCl_2$, then over 4 Å Linde type 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, as shown in Scheme 1 according to the previous litereture[6] starting from 1-bromoadamantane and 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. Because of its instability and moisture sensitivity, the IR spectra of this compound did not agree with its proposed structure.

1,3-Diaminoadamantane

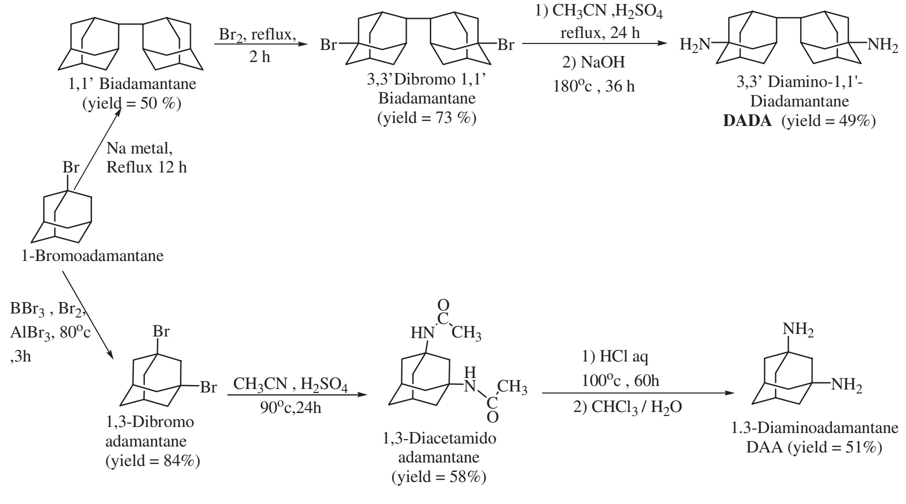
^1H NMR (300 MHz, benzene-d_6): δ (ppm) = 1.23 (2H, s, H-2), 1.32 (10H, m, H-4, H-6, H-8, H-9, H-10), 1.44 (4H, NH_2), 1.95 (2H, m, H-5, H-7); ^{13}C NMR (75.45 MHz, benzene-d_6): δ (ppm) = 31 (C-5, C-7), 35.4 (C-6), 45.3 (C-4, C-8, C-9, C-10), 49.22 (C-1, C-3), 54.7 (C-2). *3,3′-Diamino-1,1′-diadamantane:* IR (KBr): ν (cm^{-1}) = 3425 (NH_2), 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, NH_2). ^{13}C NMR (75.45 MHz, DMSO-d_6): δ (ppm) = 29 (C-5, C-7), 33.5 (C-8, C-9), 35.3 (C-6), 39.2 (C-1), 44.7 (C-2), 45.3 (C-4, C-10), 47.2 (C-3).

Preparation of APIs and APISiOs through One-Step Polymerizations

Equimolar amount of the dianhydride was added slowly to diamine in m-cresol preheated to 60 °C. The solution is then heated to 100 °C for 12 hours followed by 150 °C for 4 hours and 200 °C for 48 hours and was precipitated in methanol and dried at 60 °C. For co-polyimides containing 1:1 ratio of aliphatic diamines and/or adamantyl diamines and/or APTMS, all the reactions were conducted in nitrogen atmosphere. The structures of the synthesised polyimides are given in Figure 1.

Film Casting

A 5–7 wt% solution of polymer in chloroform was prepared and was poured into a Petri dish. The casting films were dried in an oven at 40 °C for 6 hours without vacuum



Scheme 1.
Synthesis route of DAA and DADA.

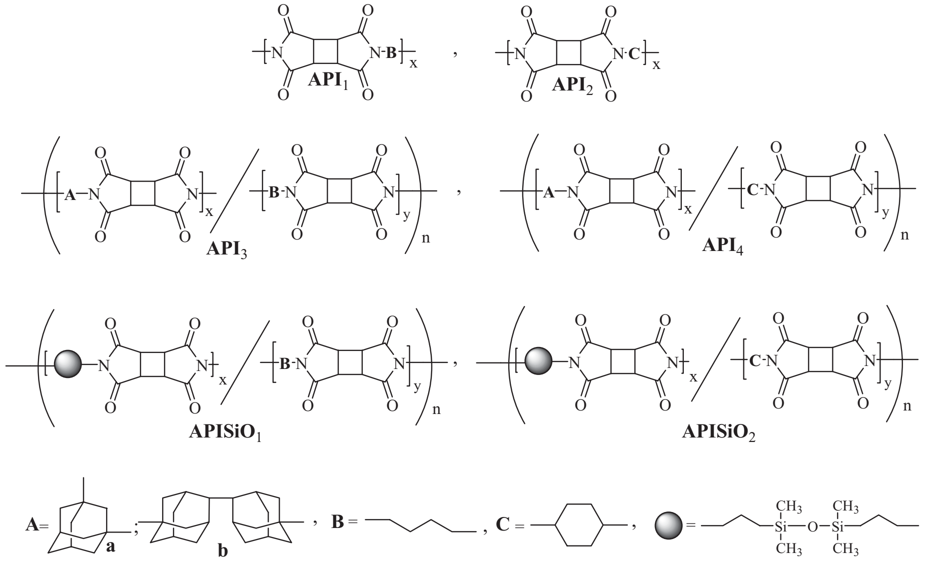


Figure 1.
Structures of the synthesized polymers.

and for another 6 hours with vacuum, and the resulting film samples were dried at 80 °C for 6 hours and then at 100 °C for 10 hours. To perform the dielectric constant and transparency measurements, the solutions of polymers were spin-coated onto clean ITO glass and quartz plates, respectively, and then subjected to the heating cycle.

Measurements

Infrared spectra (KBr disks) were recorded on a Shimadzu IR Prestige-21 spm using a Ge-KBr beam splitter. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Plus-300 (300 MHz) NMR spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on TGA Q50 Q Series thermal analyzer. The sample was heated using a 10 °C/min heating rate from 50 to 600 °C. Differential scanning calorimetry (DSC) was conducted under nitrogen with TA instruments Q 100 differential scanning calorimeter. The sample was heated at 20 °C/min from 50 °C to 500 °C. 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 ca. 1 μm. The dielectric constant was obtained at 1 MHz using an impedance-gain phase analyzer (HP4194A) and the formula $K = C \cdot d/A\varepsilon_o$, where C is the observed capacitance, d is the film thickness, A is the area, and ε_o is the free permittivity. The thickness of each film was 1.0 ± 0.05 μm. Viscosity measurements were performed using an Ubbelohde viscometer at 30 °C after dissolving the APIs in H_2SO_4. Molecular weight of polyimides were measured using gel permeation chromatography (GPC) with 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 polymer in matched quantities of commonly used solvents.

Results and Discussion

Structural characteristics of the polymers obtained by IR analysis confirms the earmark absorption bands of imide group around 1780 (C=O symmetric stretching), 1720 (C=O asymmetric stretching), 1380 and 730 cm^{-1} (C–N–C bond and the imide ring deformation) for all samples. The major difference between the pure APIs and silicon containing APISiOs is the bands of Si domain stretching between $1000 \sim 1180$ cm^{-1} and around 850 cm^{-1} (Si–O–Si asymmetric stretching), around 1400 cm^{-1} ($Si–CH_3$) and at 787 cm^{-1} (Si–C) as shown in Figure 2.

In addition, structural confirmation was also done using both ^1H and ^{13}C NMR spectroscopies. The homopolymers API_1 and API_2 showed all the butylene and cyclohexane peaks respectively together with the dianhydride peaks, while the copolyimides showed the characteristic peaks of both the diamine residues in both ^1H and ^{13}C NMR spectra. The siloxane groups gave peaks at 0.41 ppm ($Si–CH_3$), $1.65 - 1.5$ ppm (CH_2), and 3.48 ppm ($N–CH_3$) together with the peaks of the other diamine group. In ^{13}C NMR spectra the splitting of the C=O peak around 178 ppm also confirmed the formation of copolyimides.

The physical properties of the synthesized polymers are tabulated in Table 1. The polyimides which contained only aliphatic units had thermal properties inferior to other ones due to the highly flexible backbone. API_1 was found to be less thermally stable due to the fragile butylene chain in its backbone, while the dielectric constant was higher than other APIs and transparency was lower than that of others. This can be attributed to the low free volume between the polyimide chains. Addition of adamantane improved those properties. The increase of free volume

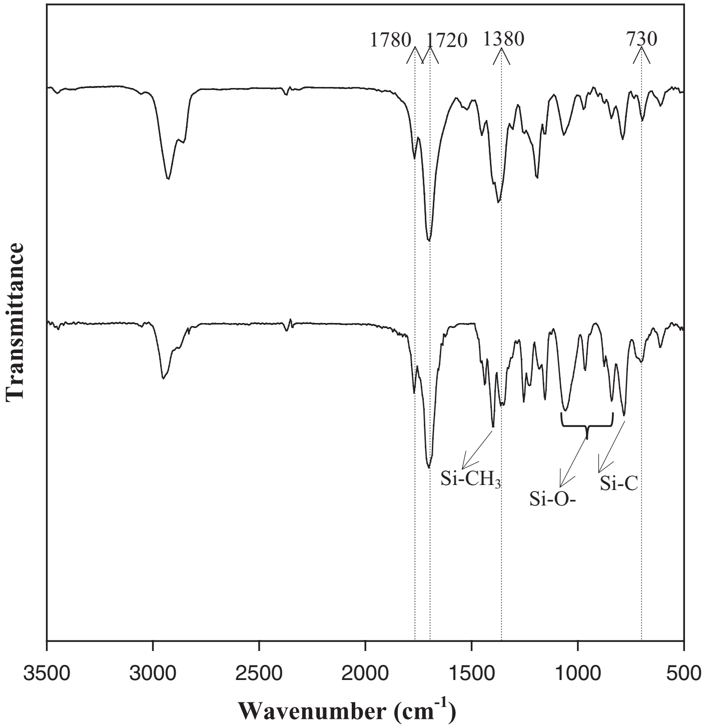


Figure 2.
FT-IR spectra of representative API_2 and $APISiO_2$.

Table 1.
Properties of Synthesized APIs and APISiOs.

Structure	η (dL/g)	10^4Mn	PDI	Td 10% (°C)	Tg (°C)	T %[d)]	ε
API_1	0.20	0.63	1.8	325	211	85	2.83
API_2	a)	b)	b)	370	c)	89	2.6
API_{3a}	0.23	0.90	1.6	350	227	88	2.52
API_{3b}	a)	b)	b)	435	c)	92	2.49
API_{4a}	0.24	1.43	1.3	417	230	86	2.79
API_{4b}	0.41	b)	b)	436	c)	90	2.56
$APISiO_1$	0.36	2.6	1.7	400	213	83	2.50
$APISiO_2$	0.45	3.3	2	440	c)	84	2.46

a) polymers precipitated during polycondensation reaction;
b) polymers were insoluble in DMF;
c) no transition was noted due to the high rigidity of polymers;
d) T is the transparency measured using UV-Vis spectroscopy.

by the incorporation of bulky adamantyl groups increased the transparency and lowered the ε values and the rigidity of the pendant group improved the thermal stability of API_1. For API_2, DSC curves did not show any significant glass transition in the range 40–500 °C due to the high rigidity of the backbone. The copolyimides of alicyclic and adamantyl diamines exhibited dielectric constants as low as $2.49 \sim 2.83$, while possessing enhanced solubilities and transparencies together with the increase of thermal stability. The synthesized APISiOs possess high T_g, 10% weight decomposition (Td 10%) ranging from 400–440 °C and low ε values 2.46–2.50.

Upon comparing the API based on DAA and DADA it was seen that those based on DADA excelled others in thermal stability and glass transition temperature. This can be explained by taking the rigidity factor into account. DADA having two bulky adamantane moieties should have higher rigidity than those with DAA in backbone and APIs based on DAA have low degree of intermolecular interactions because of the steric hindrance arising from the nonlinear orientation of DAA groups. Thermal stability was further improved when silica was introduced. The increase in the thermal stability may be resulted from high thermal stability of silica and the pseudo-crosslinking nature of silicon particles.[7] We observed appreciably low dielectric constants for all the APIs. The homopolyimides derived from aliphatic linear diamines had comparatively high ε values because of their higher degree of close chain packing. Inefficient chain packing, which induces free volume, may be the reason for the lower values of ε of the alicyclic polyimides.[8] The copolyimides containing adamantyl moieties also possess large free volumes because of their bulky pendant groups, as is evident from their low values of ε. Unexpectedly, we found that the values of ε of the APIs containing DADA 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 biadamantyl moieties. We explain this finding on the basis of the linear structures of the biadamantane-containing APIs relative to those of the non-coplanar adamantane-containing APIs; i.e., the former species have smaller molar volumes.[9] As a result of incorporation of APTMS in polymer chain the dielectric constant was found to decrease. This can be explained in terms of an overall enhancement of small scale molecular mobility by the incorporation of silica domains in the polyimidosiloxane backbone, arising from loosened molecular packing of APISiO chains as compared to API chains.[10] Solubility data of synthesized APIs and APISiOs are tabulated in Table 2. Incorporation of adamantane and siloxane moieties enhanced the solubility due to the decrease of interchain interactions.

Fully aliphatic polyimides exhibit high transparency because of their low molecular density, polarity, and probabilities of

Table 2.
Solubility of Synthesized APIs and APISiOs.

Structure	Solvents[a]							
	NMP	DMAc	DMF	THF	DMSO	m-Cresol	$CHCl_3$	H_2SO_4
API_1	+	+	+	+	+	++	+	++
API_2	–	–	–	–	–	++	–	++
API_{3a}	++	+	+	+	+	++	+	++
API_{3b}	++	+	++	++	+	++	+	++
API_{4a}	±	±	±	±	±	++	±	++
API_{4b}	++	+	++	++	+	++	+	++
$APISiO_1$	++	++	++	++	++	++	++	++
$APISiO_2$	++	++	++	++	++	++	++	++

[a] Solubility: (++) soluble at room temperature; (+) soluble upon heating; (±) partially solubleor swells; (–) insoluble.

mediating inter- and intra-molecular charge transfer. We expected that these combined factors would result in all of our synthesized APIs having transparencies above 80%, especially those based on DAA and DADA ca. 90%. This enhanced transparency as a result of the incorporation of the adamantyl groups is designated to the loosening of the intermolecular packing that results from the low polarizability and bulkiness of these pendant groups. Unfortunately Si content adversely affected the transparency of the polymers due to the interchain crosslinking nature of siloxane in the APISiO backbones.

Conclusions

We synthesized a series of fully aliphatic polyimides through polyaddition/polycondensation reactions. The organic-soluble APIs and APISiOs that we prepared exhibited low dielectric constants and appropriate thermal stability. Incorporation of adamantyl and siloxane moieties enhanced the thermal and dielectric properties of the polymers. Loss of transperency was the only demerit as a result of incorporation of siloxanes though the transperency was still above 80%. Si and adamantane moieties attributed shoulder to shoulder for the lower dielectric constants of adamantyl based APISiOs which makes them a strong competent among technologically significant materials. Thus they have potential for applications in micro- and optoelectronic devices.

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