Synthesis and Properties of Organosoluble Polyimides Derived from Bis(4-amino-3, 5-dimethyl phenyl) Halo Phenyl Methane and Various Dianhydrides

R. Hariharan, M. Sarojadevi

Department of Chemistry, Anna University, Chennai 600025, India

Received 20 April 2005; accepted 7 December 2005
DOI 10.1002/app.24152

ABSTRACT: A series of organosoluble polyimides with various aromatic tetracarboxylic acid dianhydrides was prepared from diamine monomers using one- and two-step methods. All the polyimides were soluble in aprotic solvents such as NMP, DMF, DMAc, and DMSO. The polyimides showed excellent thermal stability and good mechanical properties. The glass-transition temperature of the prepared polyimides ranged from 210°C to 325°C. All the polyimides formed tough transparent films, with tensile strength of 84–118 MPa, 8%–12% elongation, and 1.5–2.3 GPa modulus. These polyimide films were found to have a dielectric constant in the range of 3.29–3.80 at 1 kHz and 3.14–3.76 at 10 kHz and low moisture uptake, 0.52%–1.10%. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4127–4135, 2006

Key words: polyimides; high performance polymers; UV-vis spectroscopy; dielectric properties and mechanical properties

INTRODUCTION

Aromatic polyimides have been widely used in microelectronics, aerospace, and other engineering industries in the form of films and moldings because of their unique properties such as high glass-transition temperature, excellent thermal stability, low dielectric constant, and good dimensional stability.[1–4] They have wide applications in the electronics industry as flexible circuitry substrates, stress buffers, interlayer dielectrics, and passivation layers. Optically transparent polyimide films have been used in solar radiation protectors, as orientation films in liquid crystal display devices, as optical wave guides for communication interconnects, and as optical half-wave plates for planar light-wave circuits. However, most polyimides are difficult to process because of their limited solubility in commercial solvents and high softening temperature.[5,6] They are processable only under extreme conditions because of their strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution, or melting.[7] To increase the utility of these high-performance materials, extensive research is going on all over the world about how to synthesize organosoluble polyimides without loss of their thermal properties.

Several modifications of the chemical structure have been made to improve the solubility and processability of polyimides with reasonable thermal stability. Incorporation of flexible segments, bulky pendant groups, introduction of noncoplanar moieties and/or unsymmetrical moieties into the rigid polyimide backbone are some of the methods that have been successful in decreasing crystallinity and intermolecular interactions in order to increase solubility and tractability.[8–16] Solubility of polyimides can also be improved by incorporation of less symmetric structures such as ortho- and meta-catenated aromatic units in the main chain.[17–20]

The solubility of the polyimides is expected to be enhanced by the halogen atoms in the polymer because of polar interaction and also a unsymmetrical structure when they are in the meta/para positions. Hence, in this study, a new type of diamine containing different substituents (Cl, Br, $OCH_2C_6H_5$) at the meta/para positions in the phenyl ring was synthesized and subsequently polycondensed with aromatic dianhydrides to produce a series of polyimides. The polymers were analyzed for solubility, moisture absorption, thermal properties and dielectric properties.

EXPERIMENTAL

Materials

m-Bromo benzaldehyde, *p*-chloro benzaldehyde, *p*-fluoro benzaldehyde, *m*-benzyloxy benzaldehyde, and *m*-chloro benzaldehyde were purchased from E-Merk (Mumbai, India) and used without any purification; 2,6-dimethyl aniline (Aldrich, Mumbai, India) and hydrochloric acid (HCl; Spectrochem) were used as

---

Correspondence to: M. Sarojadevi (msrde2000@yahoo.com).

Journal of Applied Polymer Science, Vol. 102, 4127–4135 (2006)

received; pyromellitic dianhydride (PMDA; E-Merk, purified by sublimation), 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BPTDA; Sigma), and oxydiphathalic anhydride (ODPA; E-Merk) were recrystallised from acetic anhydride. *N*-methyl-2 pyrrolidone (Aldrich) and *N,N*-dimethylformamide (DMF; E-Merk) were purified by refluxing with calcium hydride, distilled under reduced pressure, and stored over 4-Å molecular sieves.

Monomer synthesis

The diamine monomers—various bis(4-amino-3,5-dimethyl phenyl)-substituted (*X*′)phenyl methanes (where *X*′ is 3′-chloro, 3′-bromo, 3′-benzyloxy, 4′-chloro, or 4′-fluoro)—were synthesized according to a procedure reported previously.[21]

Polymer synthesis

One-step method

PMDA (0.01*M*, 2.18 g) was added immediately to a solution of diamine BADCM (0.01*M*, 3.64 g) in 15 mL of *m*-cresol and stirred at room temperature for 2 h. Then 1 mL of isoquinoline (catalyst) and 20 mL of toluene were added and refluxed at 180°C for 5 h while the water formed was azeotropically removed. The reaction mixture was cooled and poured into methanol, and the polymer was collected, washed in hot methanol, and dried in vacuum at 140°C for 12 h. All other polyimides were synthesized by the same procedure using different diamines and dianhydrides.

Two-step method

Chemical imidization. PMDA (0.01 mol, 2.18g) was added to a solution (0.01 mol, 3.64 g) of BADCM in 12 mL of DMF and then stirred at room temperature for 12 h. Then 8 mL of acetic anhydride and 5 mL of pyridine were added, stirred for 3 h at 100°C and the polymer precipitated in methanol and dried in vacuum at 100 °C for 12 h.

Thermal imidization (film casting). Polyimide films were prepared by spreading poly(amic acid) (prepared by stirring diamine and dianhydride in DMAc solution at room temperature for 18 h) on a 9-cm glass culture dish and then heating at 80°C overnight. The semidried film was further dried and transformed into polyimide film by heating at 120°C for 45 min, 150°C for 30 min, 180°C for 30 min, 250°C for 30 min, and 300°C for 60 min.

Measurements

Elemental analysis was performed on a Carlo Erba EA 1108 microanalyzer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet spectrometer using a KBr pellet of the polymer. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Jeol-Ex-200 spectrometer with $CDCl_3$ as the solvent, and the chemical shifts were calibrated by using 1% TMS as a reference. Differential scanning calorimetric (DSC) analysis was performed on a Perkin–Elmer differential scanning calorimeter DSC 7 at a scan rate of 10°C/min in flowing nitrogen. Thermogravimetric analysis (TGA) was conducted with a TGA 2050, a thermal analyzer instrument. Experiments were carried out with approximately 10 mg of the sample in flowing nitrogen at a heating rate of 10°C/min. The inherent viscosity of the prepared polyimides was measured with an Ubbelohde viscometer using a 0.5 g/dL solution in NMP at 30°C. Solubility was noted visually by mixing 0.05 g of the polyimide sample [in both the one- and two-step (thermal imidization) methods] with 8 mL of the solvent at room temperature. Polyimides prepared as described above were used for FTIR, ^{1}H-NMR, DSC, TGA, elemental analysis, inherent viscosity, and solubility measurements. Polyimide films prepared according to the procedure described above were used for studying the mechanical and electrical properties. The mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5-kg load cell at a crosshead speed of 5 cm/min on strips with a thickness of approximately 0.15–0.20 mm, a width of 0.5 cm, and a gauge length of 2 cm. Dielectric properties were studied on polymer films by the parallel plate capacitor method using an HP-4194A Impedance/Gain phase analyzer at frequencies of 1 and 10 kHz. Gold electrodes were vacuum-deposited on both surfaces of the dried films (5 cm × 0.5 cm × 0.15–0.20 mm). Moisture absorption was measured by immersing the specimens in water at room temperature for 3 days, and the weight difference was determined. The UV–vis spectra of the polymer were recorded on a Shimadzu UV–visible spectrophotometer.

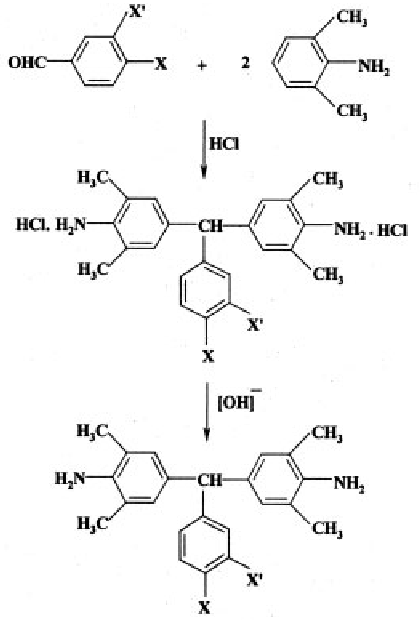
RESULTS AND DISCUSSION

Monomer synthesis

Various bis(4-amino-3,5-dimethyl phenyl)-substituted (*X*′)phenyl methanes (where *X* is 3-chloro, 3-bromo, 4-fluoro, 4-chloro, or 3-benzyloxy) were prepared from a variety of substituted benzaldehydes and 2,6-dimethyl aniline (Scheme 1). Their structures were confirmed by elemental analysis, FTIR, ^{1}H-NMR and ^{13}C-NMR spectra.

Polymer synthesis

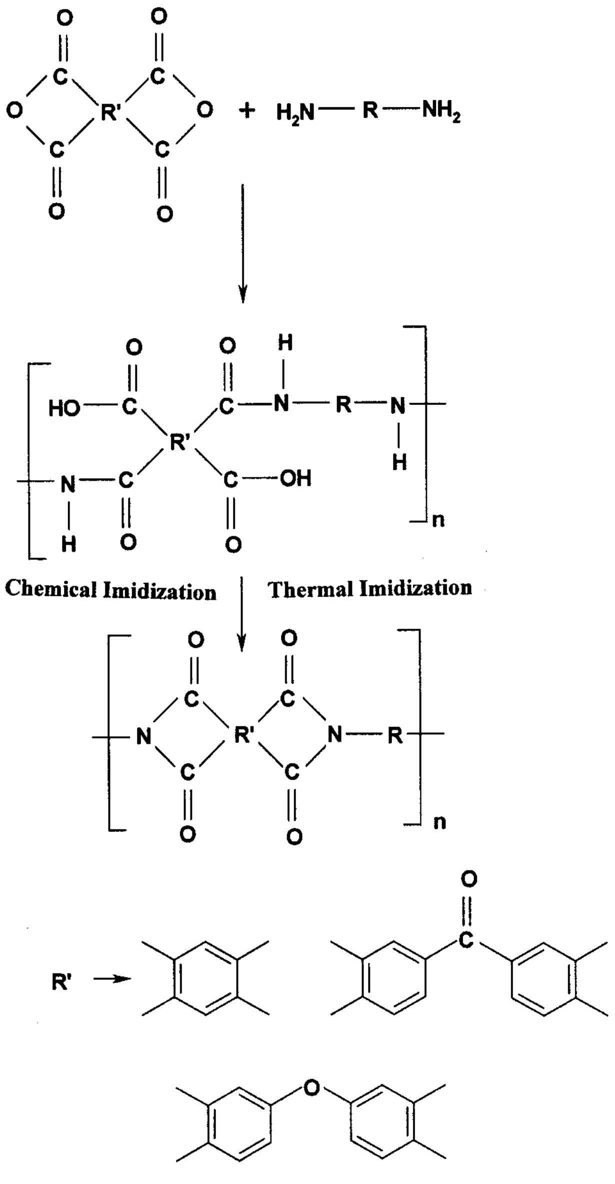
Polyimides are generally prepared by one-step and/or two-step solution polycondensation methods (Scheme 2). In the present study, polyimides were



X'	Cl	Br	H	H	OCH₂C₆H₅
X	H	H	F	Cl	H
MONOMER	BACM	BABM	BAPFM	BAPCM	BABOM

Scheme 1 Preparation of diamines.

synthesized according to both methods for the sake of comparison. The one-step method is very useful in the polymerization of unreactive dianhydrides and diamines. Using this procedure in the present study, the diamine and dianhydride were reacted in an N_2 atmosphere at elevated temperature (180°C) in *m*-cresol, using isoquinoline as the catalyst. Sterically hindered monomers react rapidly at elevated temperatures to give high-molecular-weight polyimides because the excellent solvation of a polymer at high temperature may allow it to have a desired conformation for close packing. All polymers obtained by this method had a good yield. The one-step method does not have an intermediate poly(amic acid) stage, and so chain growth and imidization occur simultaneously at elevated temperature. All the monomers were sufficiently reactive to produce polyimides of high molecular weight, as evident from their inherent viscosity values. The monomer BAPFM, which is less basic than normal aromatic amines because of inductive deactivation of the fluoro group, was still sufficiently reactive to produce high-molecular-weight polyimides. All the polyimides afforded good quality and creasable films. The spectroscopic data of the polyimide samples prepared by the two-step method (thermal and chemical imidization) were identical to those derived by the one-step method, so the data are not presented separately. The polyimides were characterized by elemental analysis, FTIR, and ^{1}H-NMR. The elemental analysis data (Table I) of all the polyimides were in good agreement with their calculated values. Figure 1 shows the FTIR spectrum of a representative polyimide (BACM-PMDA). The absorption around 1778 and 1728 cm^{-1} was a result of asymmetric and symmetric stretching of the C=O group of the imide. The strong bands at 2960 and 2924 cm^{-1} were a result of C—H stretching of the CH_3 group, an intense band at 1364 cm^{-1} was from C—N—C stretching of the imide ring, and the band at 1114 cm^{-1} was from imide ring deformation. The ^{1}H-NMR spectrum of the representative polyimide (PI_{1a}) is shown in Figure 2. All the polyimides showed a signal around 2.17 δ for 12 methyl protons and in the range 6.96–8.50 δ



R → BACM, BABM, BAPCM, BAPFM, BABOM

Scheme 2 Preparation of polyimides.

TABLE I
Elemental Analysis Data of Polyimides

Code	Polyimide	Molecular formula	Yield (%)	Elemental analysis (wt %)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
PI_{1a}	BACM + PMDA	$C_{33}H_{23}N_2O_4Cl$	89	72.46	71.4	4.23	3.99	5.12	5.31
PI_{1b}	BACM + BTDA	$C_{40}H_{27}N_2O_5Cl$	91	73.79	73.18	4.18	4.40	4.30	4.21
PI_{1c}	BACM + ODPA	$C_{39}H_{27}N_2O_5Cl$	89	73.29	72.13	4.26	4.13	4.38	4.41
PI_{2a}	BABM + PMDA	$C_{33}H_{23}N_2O_4Br$	90	67.02	66.01	3.92	3.68	4.74	4.93
PI_{2b}	BABM + BTDA	$C_{40}H_{27}N_2O_5Br$	91	69.98	69.37	3.79	3.69	3.90	3.84
PI_{2c}	BABM + ODPA	$C_{39}H_{27}N_2O_5Br$	90	69.07	68.31	3.91	3.80	4.03	4.05
PI_{3a}	BAPFM + PMDA	$C_{33}H_{23}N_2O_4F$	87	74.71	74.20	4.36	4.23	5.28	5.40
PI_{3b}	BAPFM + BTDA	$C_{40}H_{27}N_2O_5F$	92	75.70	75.6	4.28	4.34	4.41	4.38
PI_{3c}	BAPFM + ODPA	$C_{39}H_{27}N_2O_5F$	88	75.23	74.64	4.37	4.50	4.50	4.58
PI_{4a}	BAPCM + PMDA	$C_{33}H_{23}N_2O_4Cl$	90	72.46	72.10	4.20	4.17	5.12	5.11
PI_{4b}	BAPCM + BTDA	$C_{40}H_{27}N_2O_5Cl$	92	73.79	73.49	4.18	4.14	4.30	4.28
PI_{4c}	BAPCM + ODPA	$C_{39}H_{27}N_2O_5Cl$	90	73.29	72.93	4.26	4.17	4.38	4.28
PI_{5a}	BABOM + PMDA	$C_{40}H_{30}N_2O_5$	91	77.65	77.39	4.88	4.56	4.52	4.66
PI_{5b}	BABOM + BTDA	$C_{47}H_{34}N_2O_5$	91	78.10	77.96	4.74	4.27	3.87	3.88
PI_{5c}	BABOM + ODPA	$C_{46}H_{34}N_2O_5$	89	77.73	77.62	4.82	4.74	3.94	3.90

for aromatic protons. The spectroscopic data of all the polyimides agreed well with the proposed structure.

Solubility of polyimides

Most of the polyimides obtained via both the one-step and two-step (chemical imidization) methods were soluble in polar aprotic solvents such as NMP, DMF, and DMAc. (Table II). They were soluble even in solvents that had low boiling points, such as chloroform and THF. Polyimides obtained by chemical imidization exhibited solubility that was similar to that of the polyimides prepared by the one-step method, so separate data are not given. The excellent solubility may be a result of the presence of a bulky pendant-substituted phenyl group, which decreased the polymer's inter- and intrachain interactions and disturbed the coplanarity of the aromatic units to reduce the packing efficiency and crystallinity.[22] Even those polyimides with a rigid pyromellitic unit showed good solubility in the test solvents, indicating that incorporation of a bulky pendant group is one of the best methods of improving solubility. A halo substitution in the pendant phenyl group also enhanced solubility by polar interactions with the solvents. The polyimides prepared from thermal imidization (two-step method) exhibited very poor solubility (especially PMDA-derived polyimides), which may have been a result of partial crosslinking of polyimide during imidization.[23]

Inherent viscosity

The inherent viscosity of the polyimides measured in NMP (Table III) varied according to the type of bridging between the phthalimide groups in the dianhydride part of the polyimide and the stiffness of the polymer chain. Viscosity also varied with the extent of polymer chain mobility. The presence of a methyl substituent on the benzene ring increased the segmental rigidity of the polymer backbone (PI_{1a}–PI_{5c}), resulting in increased solution viscosity. The inherent viscosity of the polyimides containing PMDA was higher than that of the BTDA- and ODPA-based polyimides. The inherent viscosity of all the polyimides was sufficiently high to permit the casting of flexible and tough films. The inherent viscosity values of the polyimides prepared by thermal imidization (two-step method; 0.54–0.68 dL/g) were in fact lower than those of the polyimides prepared by the one-step method (1.09–1.33 dL/g) and by chemical imidization (0.89–1.33 dL/g), possibly because of the molecular weight of the poly(amic acid) drops during the thermal cure of the polyimide as a result of a reverse propagation reaction.[24] A reverse propagation reaction does not occur during chemical imidization; hence, the decrease in molecular weight that occurred in thermal imidization does not occur in

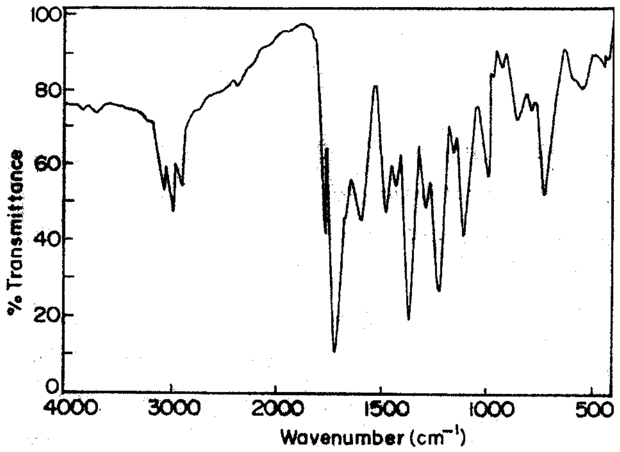


Figure 1 FTIR spectrum of polyimide PI_{1a}.

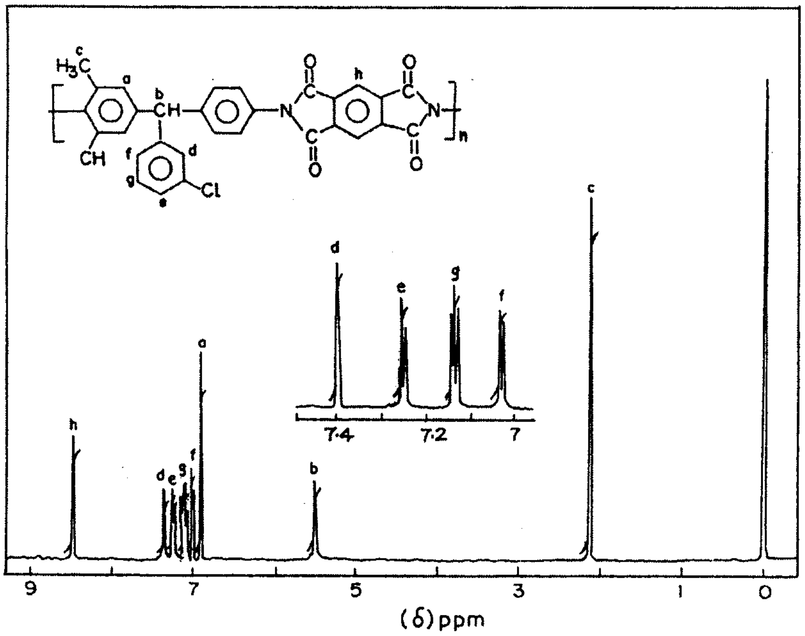


Figure 2 ^{1}H-NMR spectrum of polyimide PI_{1a}.

chemical imidization. The inherent viscosity values of polyimides prepared by the one-step method were generally higher than those of the polyimides prepared by the two-step method. This is because in the one-step method, the excellent solvation of the polymer at high temperature provides enough energy (even for sterically hindered monomers) to obtain a more favorable conformation for packing,[2] which resulted in higher viscosity than in chemical imidization.

Optical properties

Wholly aromatic polyimides strongly absorb visible light because of their aromatic conjugated structures, and the intermolecular or intramolecular charge-transfer complexes formed between or within the polymer chains usually produce polymers that are pale yellow to deep brown. The coloration of polyimides always hinders their widespread use in applications for which colorlessness and transparency are big concerns. The color intensity of the dianhydride moieties of the polyimides from deep to pale was in the order deep PMDA > BTDA > pale ODPA, when the diamine structure was fixed. The color intensity of the polyimides could also be elucidated from the cutoff wavelength (λo) observed in the UV–vis absorption spectra.

The UV–vis spectra of polyimides obtained from various diamines and dianhydrides at a concentra-

TABLE II
Solubility Behavior of Polyimides Prepared by One-Step and Two-Step (Thermal Imidization) Methods

Code	Polyimide	NMP	DMF	DMSO	DMAc	THF	$CHCl_3$
PI_{1a}	BACM + PMDA	++ (±)	++ (±)	++ (−)	++ (±)	± (−)	++ (−)
PI_{1b}	BACM + BTDA	++ (++)	++ (++)	++ (±)	++ (++)	++ (±)	++ (±)
PI_{1c}	BACM + ODPA	++ (++)	++ (++)	++ (+)	++ (++)	++ (+)	++ (+)
PI_{2a}	BABM + PMDA	++ (±)	++ (±)	++ (−)	++ (±)	± (−)	++ (−)
PI_{2b}	BABM + BTDA	++ (++)	++ (++)	++ (±)	++ (++)	± (−)	++ (−)
PI_{2c}	BABM + ODPA	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	++ (+)
PI_{3a}	BAPFM + PMDA	++ (±)	++ (±)	++ (−)	++ (±)	++ (−)	++ (−)
PI_{3b}	BAPFM + BTDA	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)
PI_{3c}	BAPFM + ODPA	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)
PI_{4a}	BAPCM + PMDA	++ (±)	++ (±)	++ (−)	++ (±)	± (−)	++ (−)
PI_{4b}	BAPCM + BTDA	++ (++)	++ (++)	++ (±)	++ (++)	++ (±)	++ (±)
PI_{4c}	BAPCM + ODPA	++ (++)	++ (++)	++ (+)	++ (++)	++ (+)	++ (+)
PI_{5a}	BABOM + PMDA	++ (±)	++ (±)	± (−)	++ (±)	++ (−)	++ (−)
PI_{5b}	BABOM + BTDA	++ (++)	++ (++)	± (++)	++ (++)	++ (+)	++ (+)
PI_{5c}	BABOM + ODPA	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)	++ (++)

Data in parentheses are for polyimides prepared by the two-step method (thermal imidization): ++, completely soluble; +, soluble on heating; ±, sparingly soluble on heating; −, insoluble.

TABLE III
Inherent Viscosity and Optical Properties of Polyimides

Code	Polyimides	η (dL/g)				
		One step	Thermal imidization	Chemical imidization	λo	% Transmittance
PI$_{1a}$	BACM + PMDA	1.33	—	1.02	361.3	83.7
PI$_{1b}$	BACM + BTDA	1.27	0.65	0.94	338.0	85.4
PI$_{1c}$	BACM + ODPA	1.22	0.60	0.90	312.0	92.0
PI$_{2a}$	BABM + PMDA	1.28	—	1.05	358.8	71.4
PI$_{2b}$	BABM + BTDA	1.19	0.68	0.97	338.2	78.5
PI$_{2c}$	BABM + ODPA	1.10	0.64	0.94	322.0	81.2
PI$_{3a}$	BAPFM + PMDA	1.24	—	0.99	341.7	83.3
PI$_{3b}$	BAPFM + BTDA	1.20	0.68	0.92	335.2	88.7
PI$_{3c}$	BAPFM + ODPA	1.09	0.54	0.90	302.8	92.6
PI$_{4a}$	BAPCM + PMDA	1.33	—	1.01	347.0	83.3
PI$_{4b}$	BAPCM + BTDA	1.27	0.67	0.94	329.4	88.7
PI$_{4c}$	BAPCM + ODPA	1.21	0.62	0.91	319.0	92.6
PI$_{5a}$	BABOM + PMDA	1.31	—	0.97	329.4	89.2
PI$_{5b}$	BABOM + BTDA	1.25	0.62	0.92	318.6	90.0
PI$_{5c}$	BABOM + ODPA	1.15	0.58	0.89	302.6	95.2

tion of 5×10^{-3} mol/L in NMP solution and the cutoff wavelength and percentage transmittance at 500 nm from the spectra are given in Table III. All the polyimides had a λo of less than 400 nm, and all the polyimides exhibited high optical transparency (71%–95% transmittance). The ODPA-based polyimide formed fairly transparent films in contrast to the other dianhydride-based polyimides. These results were attributed to the reduced intermolecular charge-transfer complex (CTC) formation between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties.

The light color of the PIs (with high transmittance) can be explained by the decreased intermolecular interactions. The bulky phenyl group and halo substitution were effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (F > Cl > Br; by decreasing the electron-donating property of the diamine moieties). The decrease in intermolecular CTC formation may also have been a result of changes in the structure of the respective diamine. Among the polyimides, those containing benzyloxy units exhibited a higher percentage of transmittance because of their efficiency in increasing free volume by steric hindrance.[25] Polyimides derived from PMDA showed strong absorption with a high cutoff wavelength because of the electronic conjugation in the structure.

Moisture absorption and dielectric properties

Measurement of the dielectric constants was performed between gold layers. This procedure excluded any contact problems. The dielectric constants of all the polyimides were lower (Table IV) than those of the

TABLE IV
Electrical and Mechanical Properties of Polyimides

Polymer code	Polymer	Dielectric constant		Moisture absorption (%)	Tensile strength (MPa)	% Elongation	Tensile modulus (GPa)
		1 KHz	10 KHz				
PI$_{1a}$	BACM + PMDA	3.51	3.48	0.84	99	9	2.1
PI$_{1b}$	BACM + BTDA	3.49	3.47	1.00	94	10	1.8
PI$_{1c}$	BACM + ODPA	3.67	3.54	0.86	92	11	1.5
PI$_{2a}$	BABM + PMDA	3.61	3.59	0.74	118	8	2.2
PI$_{2b}$	BABM + BTDA	3.62	3.60	1.10	95	9	2.1
PI$_{2c}$	BABM + ODPA	3.70	3.69	0.78	92	9	2.0
PI$_{3a}$	BAPFM + PMDA	3.31	3.16	0.56	111	8	2.3
PI$_{3b}$	BAPFM + BTDA	3.29	3.14	0.70	97	9	2.2
PI$_{3c}$	BAPFM + ODPA	3.42	3.29	0.52	95	12	2.1
PI$_{4a}$	BAPCM + PMDA	3.52	3.48	0.70	101	9	2.1
PI$_{4b}$	BAPCM + BTDA	3.46	3.44	1.00	96	11	1.9
PI$_{4c}$	BAPCM + ODPA	3.66	3.53	0.70	94	12	1.6
PI$_{5a}$	BABOM + PMDA	3.72	3.65	0.98	102	12	2.0
PI$_{5b}$	BABOM + BTDA	3.68	3.64	1.10	94	11	1.7
PI$_{5c}$	BABOM + ODPA	3.80	3.76	1.00	84	10	2.7

commercial polyimides such as Kapton films (3.94 at 10 kHz). Polyimide films with a thickness of 0.15–0.20 mm were used in this study. The decreased dielectric constant may be attributed to the pendant group and the halo substituent present in it, which resulted in less efficient chain packing and increased free volume.

The presence of fluorine substitution in polyimides PI_{3a}–PI_{3c} decreased the dielectric constant further. This may have been because the strong electronegativity of the fluorine may have resulted in very low polarizability of the C—F bonds, thereby decreasing the dielectric constant.[23] The dielectric constant varied with respect to the dianhydride in the order ODPA-PI > PMDA-PI > BTDA-PI. The lowest dielectric constant for BTDA-PI may be attributed to the presence of a carbonyl group with a high-electron-withdrawing nature decreasing electron polarizability and hindering electronic interaction and hence reducing the dielectric constant.[27] On the other hand, the strong electron-attracting property resulting from the high electronegativity of halogen atoms (F > Cl > Br) could have induced an additional permanent dipole in the benzene ring connected to it. These dipoles may increase polarization and hence the dielectric constant. The experimental data indicate that the effects of these additional permanent dipoles were smaller than the other effects (i.e., chain–chain interaction, free volume, and electronic polarization in the polyimides).[28]

Polyimide materials usually show higher moisture uptake than hydrocarbon polymers because of the presence of a polar imide group. The equilibrium moisture absorption of the polyimide films was determined by immersing the specimens at 25°C in deionized water for 3 days and then measuring the difference in weight of the film before and after immersion. Absorption of moisture in aromatic polyimides can be as high as 3.0%–3.5%, depending on the chemical structure of the polymer and the relative humidity of the surrounding environment, which have a significant influence on the dielectric properties of the polymer.[27] Several factors may explain moisture absorption by polyimides, including chemical structure, introduction of halo groups and other functional groups, and geometrical packing of the polymer chain, as well as film-processing parameters. The presence of bulky groups could loosen the packing of the polyimide backbone chains, resulting in increased free volume of the polymers, which would make them entrap a lot of water molecules. The presence of a fluoro group introduced hydrophobic features, which inhibited the absorption of water molecules on the surface of the fluorinated polymers. The former effect was predominate in the polyimides with Cl, Br, and benzyloxy substituents, as was evident from the results obtained. However, in fluoro-substituted polyimides the latter effect was more predominant, resulting in lower moisture absorption than in the other halo-substituted (Cl, Br) polyimides. Though substitution of Cl and/or Br in the polyimide was expected to reduce moisture absorption and the dielectric constant because of electron polarizability, it was not sufficient (electronegative enough) to do so. In addition, other functional groups in the polymer chain also might affect moisture uptake. It seems that ether-bridged polyimides showed lower moisture absorption than those linked with carbonyl groups, probably a C=O group, which would play a major role in increasing moisture absorption by forming hydrogen bonds with water molecules. Similar observations were reported previously.[29,30] Absorption by the different polyimides was found to be in the order BTDA-PI > ODPA-PI > PMDA-PI.

Mechanical properties

Tensile strength of the polyimide films was measured with an Instron UTM (Table IV). All the polyimides exhibited good tensile strength (84–118 MPa), percent elongation (8%–12%), and modulus (1.5–2.3 GPa), enhancing their utility in semiconductor applications. All the polyimides exhibited a distinct yield point in their stress–strain curves and moderate elongation at break, indicating high toughness. The BTDA- and ODPA-based polyimides exhibited lower modulus than that of the PMDA-based polyimides because of the inherent rigidity of the pyromellitic unit. In general, the modulus, which is the parameter of mechanical hardness, decreased in the order PMDA-PI > BTDA-PI > ODPA-PI. Percent elongation, which is a measure of flexibility and toughness, decreased in the order ODPA-PI > BTDA-PI > PMDA-PI. In contrast to the modulus behaviour, elongation at break for BTDA-PI was almost comparable to that of ODPA-PI, which

TABLE V
Thermal Properties of Polyimides

Code	Polyimide	T_g	T_{10}	Char yield (%)
PI_{1a}	BACM + PMDA	324	532	42.95
PI_{1b}	BACM + BTDA	322	528	45.85
PI_{1c}	BACM + ODPA	305	510	40.36
PI_{2a}	BABM + PMDA	325	491	57.98
PI_{2b}	BABM + BTDA	320	484	59.26
PI_{2c}	BABM + ODPA	310	452	53.16
PI_{3a}	BAPFM + PMDA	250	537	46.95
PI_{3b}	BAPFM + BTDA	248	532	52.80
PI_{3c}	BAPFM + ODPA	236	505	42.26
PI_{4a}	BAPCM + PMDA	321	469	43.59
PI_{4b}	BAPCM + BTDA	319	458	48.85
PI_{4c}	BAPCM + ODPA	302	434	42.36
PI_{5a}	BABOM + PMDA	238	453	54.93
PI_{5b}	BABOM + BTDA	225	440	53.08
PI_{5c}	BABOM + ODPA	210	405	50.26

T_{10}, temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min.

Char yield, residual weight (%) at 800°C in nitrogen.

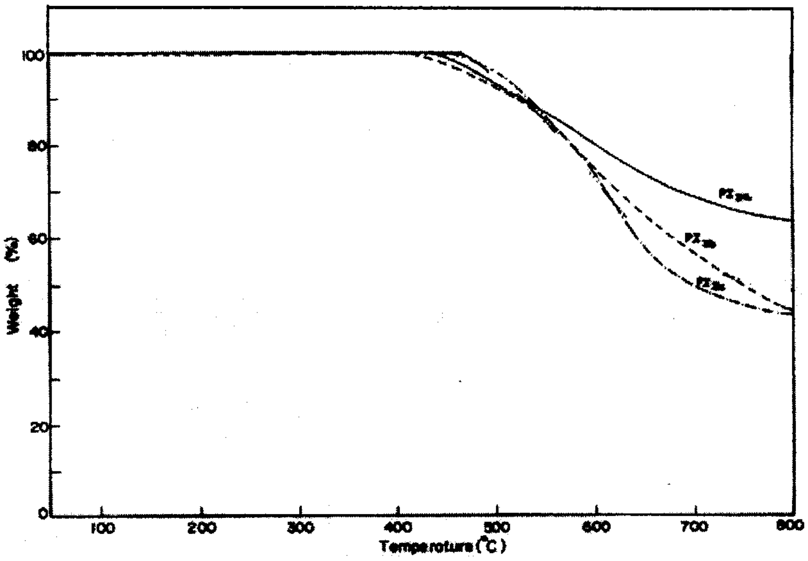


Figure 3 TGA curves of polyimides PI_{3a}, PI_{3b}, and PI_{3c}.

exhibited high chain ordering. In addition, ether-linked ODPA-PI with irregular chain–chain ordering had a strain at break comparable to that of BTDA-PI. This result indicates that both the high chain ordering and the limited chain flexibility are directly reflecting the mechanical properties.[31]

Thermal properties

The thermal properties of the polyimides were evaluated by DSC and TGA and the data are presented in Table V. The thermograms of the representative polyimides are given in Figure 3. Polymer series 1–4 underwent single-stage decomposition. All the polymers were stable up to 400°C. The methyl substituent was expected to degrade at a lower temperature and the backbone at a higher temperature. However, this did not occur; the decomposition of the methyl groups occurred along with the main chain at about 400°C.[25] The temperature at which 10% weight loss of the polymer occurred (T_{10}) was very high, indicating high thermal stability of the polymers. The thermal stability of the polyimides with various dianhydrides decreased in the order PMDA-PI > BTDA-PI > ODPA-PI. The PMDA-based polyimides exhibited higher thermal stability than the BTDA- and ODPA-based polyimides because of the inherent rigidity of the PMDA unit. The presence of flexible linkages like —O— and C=O contributed to the decrease in thermal stability. Polyimides $5_{a–c}$

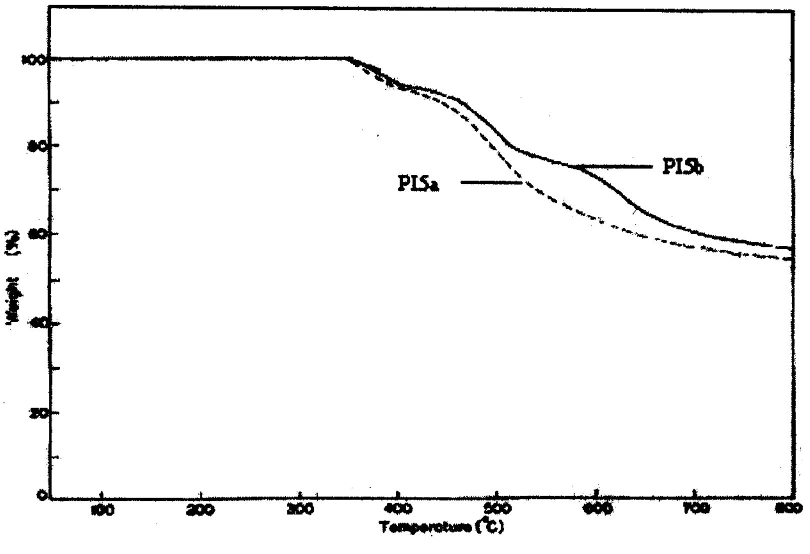


Figure 4 TGA curves of polyimides PI_{5a} and PI_{5b}.

showed two-stage decomposition. The representative TGA curves of these polyimides showing double-stage decomposition are given in Figure 4. The first stage occurred around 340°C. The char yield of the polyimides, which correlates to the ability to sustain combustion, was high (40%–59.2%) at 800°C. The T_g values of the polyimides were in the range of 210°C–325°C (Table V). This can be correlated to the structure of the amine component and the stiffness of the polymer backbone. The presence of a methyl substituent ortho to the imide ring enhanced the segmental rigidity of the polymer, thereby enhancing the T_g. The PMDA-based polyimides exhibited higher T_g values than the BTDA- and ODPA-based polyimides, because the presence of a rigid pyromellitic unit enhanced the rigidity of the polymer chain and hence the T_g. Except for PI_{5c}, all the polyimides prepared in the present study exhibited higher T_g values than the commercial polyimide, namely, Ultem 1000 (T_g 215°C).

CONCLUSIONS

A number of polyimides were prepared from diamines containing halo/benzyloxy substituents with various aromatic tetracarboxylic acid dianhydrides. The polyimides obtained were soluble in polar aprotic solvents such as NMP, DMF, and DMAc and in low-boiling-point solvents such as chloroform and THF. The fluoro-substituted polyimides had less moisture absorption and a lower dielectric constant than the other halo- (Cl, Br) and benzyloxy-substituted polyimides. Polyimides containing benzyloxy units were found to have maximum clarity, and those containing PMDA were strongly colored. All the polyimide films exhibited good tensile strength (84–118 MPa), percent elongation (8%–12%), modulus (1.5–2.3 GPa), and toughness, enhancing their utility in semiconductor applications. The T_g values of the polyimides were in the range of 210°C–325°C. The temperature at which 10% weight loss of the polymer occurred (T_{10}) was very high, indicating high thermal stability of polymers. The char yield of the polyimides, which correlates with the ability to sustain combustion, was high.

References

1. Ghost, M. K.; Mittal, K. L., Eds. Polyimide: Fundamental and Applications; Marcel Dekker: New York; 1996; p 1.
2. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds. Polyimides, Chapman & Hall: New York, 1990; p 1.
3. Feger, C.; Khojasteh, M. M.; McGrath, J. E., Eds. Polyimides: Materials, Chemistry and Characterization; Elsevier: Amsterdam; 1989; p 1.
4. Mittal, K. L., Ed. Polyimides: Synthesis Characterization and Applications; Plenum: New York; 1986; p 1.
5. Eichstadt, E. A.; Ward, T. C.; Bagwell, M. D.; Farr, I. V.; Dunson, D. L.; McGrath, J. E. Macromolecules 2002, 35, 7561.
6. Ahn, S.-K.; Kim, Y.-H.; Shin, D.-C.; Kwon, S.-K. Bull Korean Chem Soc 2000, 21, 377.
7. Hsiao, S.-H.; Huang, P.-C. J Polym Sci, Part A: Polym Chem 1996, 36, 1649.
8. Yamaguchi, A.; Tamai, S.; Otho, M. Polymer 1996, 37, 3683.
9. Yagci, H.; Ostrowski, C.; Mathias, L. J. J Polym Sci, Part A: Polym Chem 1999, 37, 1189.
10. Hsiao, S. H.; Dai, L. R. J Polym Sci, Part A: Polym Chem 1999, 37, 665.
11. Ayala, D.; Lozano, A. E.; de Adajo, J.; De le Campa, J. G. J Polym Sci, Part A: Polym Chem 1999, 37, 805.
12. Liou, G. S.; Maruyama, M.; Kakimoto, M.; Imai, Y. J Polym Sci, Part A: Poly Chem 1993, 31, 2499.
13. Hsiao, S. H.; Li, C. T. Macromolecules 1998, 31, 7213.
14. Grubb, T. L; Ulery, V. L; Smith, T. J.; Tullos, G. L.; Yagci, H.; Mathias, L. J.; Langsam, M. Polymer 1999, 40, 42.
15. Li, F.; Fang, S.; Ge, J. J.; Honigfort, P. S; Chen, J. C.; Farris, F. W.; Chen, S. I. D. Polymer 1999, 40, 4517.
16. Li, F.; Ge, J. J.; Honigfort, P. S.; Fang, S.; Chen, J. C.; Farris, F. W.; Cheng, S. I. D. Polymer 1999, 40, 4987.
17. Eastmond, G. C.; Paprotny, J. Macromolecules 1995, 28, 2140.
18. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. Macromolecules 1996, 29, 1382.
19. Akutsu, F.; Inoki, M.; Sawano, M.; Kasashima, Y.; Naruchi, K.; Miure, M. Polymer 1998, 39, 6093.
20. Hsiao, S. H.; Yang, C. P.; Chu, K. Y. Macromolecules 1997, 30, 165.
21. Hariharan, R.; Bhuvana, S.; Anuradha G.; Sarojadevi, M. Polym Int 2004, 53, 1442.
22. Yang, C. P.; Hsiao, S. H.; Yang, H. W. Macromol Chem Phys 2000, 20, 409.
23. Yang, C. P.; Hsiao, S. H.; Chen, K. H. Polymer 2002, 43, 5095.
24. Yang, C. P.; Hsiao, S. H.; Hsu, J. J Polym Sci, Part A: Polym Chem 2002, 40, 524.
25. Qian, Z. G.; Ge, Z. Y.; Li, Z. X.; He, M. H.; Li, J. G.; Pang, Z. Z.; Fan, L.; Yang, S. Y. Polymer 2002, 43, 6057.
26. Wang, C. S.; Leu, T. S. Polymer 2000, 41, 3581.
27. Wang, C. S.; Yang, R. W. J Appl Polym Sci 1997, 66, 609.
28. Xie, K.; Liu, J. G.; Zhou, H. W.; Zhang, S. Y.; He, M. H.; Yang, S. Y. Polymer 2001, 42, 7267.
29. Yang, C. P.; Su, Y. Y. J Polym Sci, Part A: Polym Chem 2004, 42, 222.
30. Yang, C. P.; Chen, T. W. Macromolecules 1993, 26, 4865.
31. Ree, M.; Shin, T. J.; Lee, S. W. Korean Polym J 2001, 9, 1.