

Kinetic Study of Low-Temperature Imidization of Poly(amic acid)s and Preparation of Colorless, Transparent Polyimide Films

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ABSTRACT: Conventional synthesis of polyimides includes high-temperature (160–350 °C) imidization of poly(amic acid)s. In the present work, imidization has been carried out at much lower temperatures (40–160 °C). 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) or pyromellitic dianhydride (PMDA) was polymerized with an aromatic diamine, 4,4'-diaminodiphenylmethane (DDPM), to give poly(amic acid)s, which were then imidized chemically. Imidization was more than 90% complete even at the very low imidization temperature of 40 °C. It was found that the imidization occurs in two steps: an initial rapid cyclization and a subsequent slower cyclization. The activation energy for the rapid process was determined to be 4.3 kJ/mol, and that of the slower process, 4.8 kJ/mol. As the imidization

temperature decreases, the transmittance of the resulting polyimides tends to gradually increase, the cutoff wavelength decreases and the color becomes pale. A partially aliphatic polyimide based on HPMDA and DDPM prepared at 40 °C yielded thin films that were highly transparent and colorless, and had good flexibility, solubility and thermal stability. The polyimide films prepared in this study may be good candidates for flexible, transparent plastic substrates in the display industry. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 1593–1602

KEYWORDS: flexible film; kinetics; low-temperature chemical imidization; partially aliphatic polyimide; transparent

INTRODUCTION Polyimides are well known as high-performance materials because of their good chemical resistance, high mechanical strength, low dielectric permittivity, and excellent thermal stability.^{1–3}

In recent years, polymer researchers have been interested in the development of flexible and transparent plastic substrates because of their potential applications in folding displays, roll-up displays, conformable displays and portable devices. Polyimides are regarded a suitable candidate for substrate materials because of the desirable properties mentioned above.^{4–7} However, aromatic polyimides have strong intermolecular interactions due to the formation of charge-transfer complexes (CTCs), and thus usually have poor processability, including limited solubility in organic solvents. Aromatic polyimides also show strong absorption in the visible region, making them yellow or brown.⁸ To overcome these drawbacks, structural modifications to polyimides have been comprehensively studied. One efficient method is the incorporation of an aliphatic moiety to improve solubility and transparency.^{8–17} Other approaches that have been developed for fabricating flexible, transparent polyimide films

include the incorporation of fluorine-containing moieties into the polyimide backbone and the preparation of polyimide–inorganic nanocomposite films.^{18–21} However, there has been no report on the preparation of transparent polyimide films by means of controlling the imidization temperature.

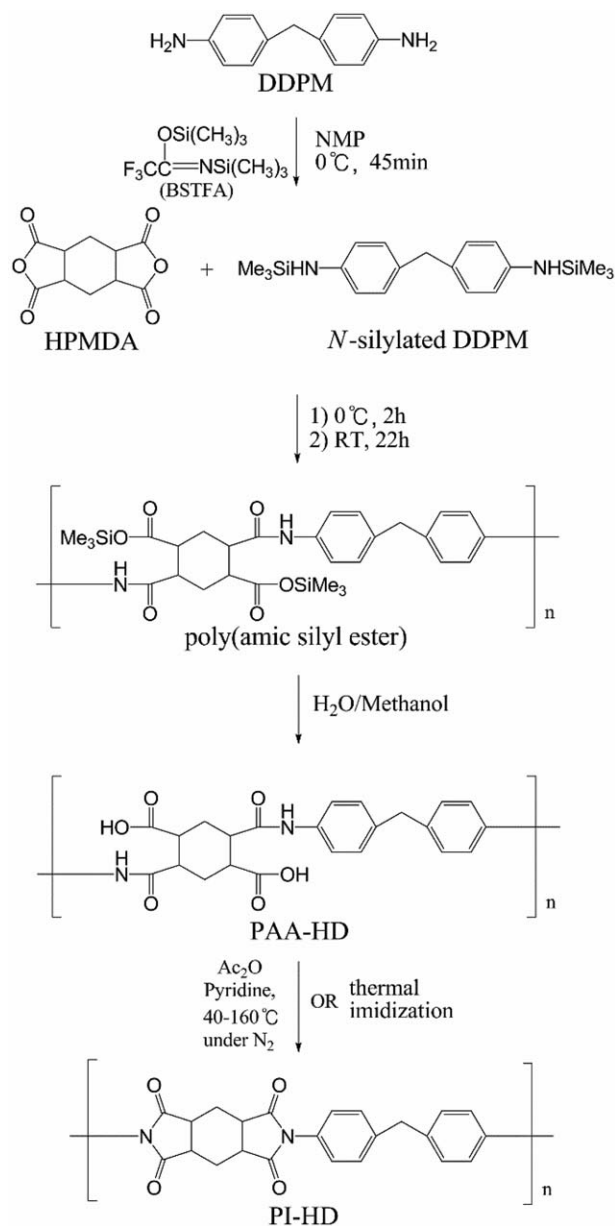
Conventional chemical imidization has been conducted at around 160 °C, and thermal imidization, at higher temperatures up to 350 °C.^{3,22–26} Imidization under high temperatures usually yields brown polyimides. For example, yellow or brown powders are obtained from even fully aliphatic or fluorine-containing polyimides when the imidization is performed under the conventional high-temperature conditions. To overcome these drawbacks, we have attempted to conduct imidization at lower temperatures of 40–160 °C. This approach has the advantages of easy process control and hence easy industrial application. In addition, the low-temperature imidization method is inexpensive and environmentally friendly.

There have been a few reports on low-temperature imidization, but they have mainly focused on the imidization kinetics of fully aromatic poly(amic acid)s.^{27,28} In the present work, we prepared transparent polyimide films from partially aliphatic

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poly(amic acid)s by means of low-temperature imidization and also studied the imidization kinetics.

In the present study, 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) was chosen as an aliphatic dianhydride monomer to decrease CTC effects. Pyromellitic dianhydride (PMDA) was employed as a comparison aromatic dianhydride monomer. HPMDA and PMDA were polymerized with an aromatic diamine, 4,4'-diaminodiphenylmethane (DDPM), to obtain partially aliphatic and fully aromatic poly(amic acid)s (Schemes 1 and 2, respectively). The kinetics of their chemical imidization at the temperatures of 40–160 °C and the effect of imidization temperature on polyimide properties such as optical transparency were studied.

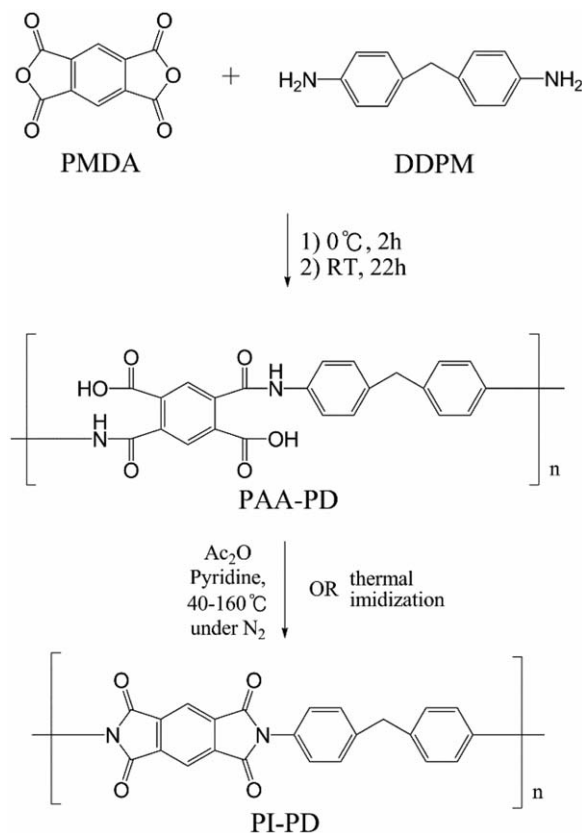
EXPERIMENTAL

Materials

HPMDA, PMDA, and DDPM were purchased from Tokyo Chemicals and used as received. *N,O*-Bis(trimethylsilyl)tri-fluoroacetamide (BSTFA), 4,4'-oxydianiline (ODA), acetic anhydride (Ac₂O) and pyridine (Py) were purchased from Aldrich Chemical Co. and used without purification. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Duksan Co., distilled under reduced pressure and stored under a nitrogen atmosphere before use.

Characterization

¹H NMR spectra of samples dissolved in DMSO-d₆ were acquired using a Bruker Avance II 400-MHz spectrometer. IR spectra were acquired using a PerkinElmer Spectrum One B FT-IR spectrometer. UV/visible spectra were acquired using a PerkinElmer Lambda 25 UV/Vis spectrometer. The solubility behaviors of polyimides in various kinds of solvents were investigated by dissolving 10 mg of powdery polymer samples in 1 mL of solvent, either at room temperature or at elevated temperatures. Inherent viscosities were determined at 30 °C using a Cannon-Fenske viscometer; samples of concentration 0.50 g/dL in NMP were used. Thermal analyses were carried out using a Shimadzu TGA-50 and DSC-60, using a heating rate of 10 °C/min under a nitrogen flow (50 mL/min). Gel permeation chromatography (GPC) analysis was carried out using a doubly connected Showa Denko



Shodex KF-806L column at 100 °C and an eluent of 0.05 mol/L LiBr in NMP applied at the flow rate of 1.0 mL/min; the results were calibrated with respect to polystyrene standards. Film casting was performed using a Neurtek Instruments 1117 micrometer adjustable film applicator. The thickness of the thin film was measured using a Mitutoyo Company 293-348 IP65 digimatic outside micrometer.

Synthesis of PI-HD

DDPM (20.23 g, 0.10 mol) was dissolved in NMP (385 mL) in a flame-dried 500-mL three-neck round-bottom flask under nitrogen. BSTFA (5.15 g, 0.20 mol) was added to this solution with stirring; digital mixer equipment (EYELA NZ-1000) was used for stirring. The solution was stirred at 0 °C for 45 min, and then HPMDA (22.64 g, 0.10 mol) was added to the solution. The resultant solution was stirred at 0 °C for 2 h and then at room temperature for 22 h, yielding a clear and viscous poly(amic acid silyl ester) (PASE) solution. The PASE solution was poured into a mixture of distilled water and methanol, forming a precipitate that was collected by filtration. Washing with water (100 mL) and methanol (100 mL) followed by drying in vacuum afforded PAA-HD as a white powder. The yield was 44.98 g (99%). The PAA-HD powder was dissolved in NMP and then chemically imidized by addition of acetic anhydride and pyridine and subsequent heating at 40 °C for 24 h. The polyimide-containing mixture was cooled to room temperature and then poured into distilled water (500 mL), forming a precipitate that was collected by filtration. Washing with water (100 mL) and methanol (100 mL) followed by drying in vacuum afforded PI-HD as a powder. Other chemical imidizations were carried out in the same manner as above, but using the imidization temperatures of 60, 80, 100, 120, 140, or 160 °C (Scheme 1). PI-HD was also prepared by thermal imidization of PAA-HD, by increasing the temperature stepwise to 80, 120, 220, and 300 °C; the samples were allowed to stand at each temperature for 1 h and at 300 °C for 2 h, thus yielding a powder. FT-IR spectra of PAA-HD and PI-HD are presented in Figure S1 in the Supporting Information. FT-IR (KBr, cm^{-1}): 2929 (aliphatic C–H stretch), 1778 (imide C=O asymmetric stretch), 1712 (imide C=O symmetric stretch), 1513 (aromatic C=C stretch), 1381 (imide C–N–C stretch). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 1.92–1.95 (m, 2H), 2.24–2.27 (m, 2H), 3.19 (s, 4H), 4.05 (s, 2H), 7.10–7.22 (m, ArH, 4H), 7.24–7.37 (m, ArH, 4H).

Synthesis of PI-PD

PMDA (22.26 g, 0.10 mol) and DDPM (20.23 g, 0.10 mol) in NMP (382 mL) were added to a flame-dried 500-mL three-neck round-bottom flask under nitrogen. The resultant solution was stirred at 0 °C for 2 h and then at room temperature for 22 h, yielding a clear and viscous solution of poly(amic acid) (PAA-PD). The PAA-PD was chemically imidized by addition of acetic anhydride and pyridine and subsequent heating at 40 °C for 24 h. The polyimide-containing mixture was cooled to room temperature and then poured into distilled water (500 mL), forming a precipitate that was collected by filtration. Washing with water (100 mL) and methanol (100 mL) followed by

drying in vacuum afforded PI-PD as a powder. Other chemical imidizations were carried out in the same manner as above, but using the imidization temperatures of 60, 80, 100, 120, 140, or 160 °C (Scheme 2). PI-PD was also prepared by thermal imidization of PAA-PD, by increasing the temperature stepwise to 80, 120, 220, and 300 °C; the samples were allowed to stand at each temperature for 1 h and at 300 °C for 2 h, thus yielding a powder. FT-IR spectra of PAA-PD and PI-PD are presented in Figure S2 in the Supporting Information. FT-IR (KBr, cm^{-1}): 1777 (imide C=O asymmetric stretch), 1722 (imide C=O symmetric stretch), 1512 (aromatic C=C stretch), and 1366 (imide C–N–C stretch).

Film Preparation

PI-HD powder was dissolved in NMP at a concentration of 10 wt %. Polyimide films were prepared by casting the polyimide solution onto clean glass plates using a doctor blade. The films were kept at 50 °C overnight under vacuum, and then temperature was increased stepwise to 80, 120, and 150 °C to remove the solvent; the samples were allowed to stand at each temperature for 1 h. This yielded polyimide films, which were then cooled to room temperature and immersed in a water bath for 1 h. The films were then slowly peeled away from the glass plates and further dried at 100 °C for 3 h in an oven.

RESULTS AND DISCUSSION

Synthesis of Poly(amic acid)

The poly(amic acid)s (PAA-HD and PAA-PD) were first prepared by a conventional method from the corresponding dianhydrides and DDPM (Schemes 1 and 2), and their number average molecular weights (\bar{M}_n) were measured to be 0.37×10^5 and 1.15×10^5 g/mol, respectively (Table 1). However, the PAA-HD \bar{M}_n was considered too low for it to be used for kinetic study or film preparation. This is attributable to the low electrophilicity of the HPMDA carbonyl groups and the low nucleophilicity of the DDPM amino groups. Electrophilicity of a dianhydride is usually gauged in terms of its electron affinity (EA).³ In this study, the EA values of PMDA and HPMDA were determined to be 2.92 and 0.75, respectively, by molecular simulation.²⁹ These results indicate that HPMDA is less electrophilic than PMDA. Furthermore, aromatic diamines are generally less basic and less nucleophilic than aliphatic diamines; therefore, the reactivity of DDPM is relatively low.³⁰ To increase the nucleophilicity of DDPM, the amino groups were activated by *in situ* silylation using BSTFA as a silylation agent (Scheme 1).³¹

Table 1 lists molecular weights and inherent viscosities of the poly(amic acid)s; the use of the silylated DDPM significantly increased the \bar{M}_n of PAA-HD (0.97×10^5 g/mol).

Synthesis of Polyimides

Polyimides were synthesized from the poly(amic acid)s by means of the chemical or thermal imidization method; Table 2 lists the chemical imidization reaction conditions used for

TABLE 1 Molecular Weight^a and Inherent Viscosity of Poly(amic acid)s

Poly(amic acid)	\bar{M}_n ($\times 10^5$ g/mol)	\bar{M}_w ($\times 10^5$ g/mol)	PDI ^d	Inherent Viscosity (dL/g) ^e
PAA-HD ^b	0.37	0.96	2.6	0.23
PAA-HD ^c	0.97	1.68	1.7	0.33
PAA-PD ^b	1.15	1.94	1.7	0.45

^a Measured in NMP by means of GPC; polystyrene was used as a standard.

^b Prepared using unsilylated DDPM.

^c Prepared by an *in situ* silylation method.

^d Polydispersity index.

^e Measured at a concentration of 0.5 g/dL in NMP at 30 °C.

various samples. Notably, whereas the reaction temperatures of conventional chemical imidization methods are 150–160 °C, the imidization in this study was conducted at 40, 60, 80, 100, 120, 140, or 160 °C. Increased amounts of acetic anhydride and pyridine were needed to achieve high degree of imidization (>90%) compared to the conventional imidization, so the molar feed ratio of poly(amic acid) repeating unit:acetic anhydride:pyridine was 1:5:5, 1:10:10, or 1:20:20. For comparison, thermal imidization was performed by step-wise heating of poly(amic acid) powders at 80, 120, 220, and 300 °C.

Photographs of the polyimide powders obtained in this study are shown in Figure 1. Whereas white powders of PI-HD were obtained at 40, 60, and 80 °C, gray PI-HD powders were obtained at higher temperatures. Especially, the color of PI-HD-140-10 and PI-HD-160-10 powders was dark gray. The PI-HD-thermal powder obtained by thermal imidization was almost brown [Fig. 1(b)].

Structural Confirmation of Polyimide

PAA-HD and PI-HD were characterized by ¹H NMR spectroscopy (Fig. 2). Both PAA-HD and PI-HD showed complicated multiplet peaks between 1.9 and 4.0 ppm, and between 6.7 and 7.6 ppm, attributed to the aliphatic and aromatic protons, respectively. In the case of PAA-HD, two peaks were observed at 9.44 ppm, attributed to amide N–H protons, and at 11.85 ppm, attributed to carboxyl O–H protons (Fig. 2,

top). In the spectrum of PI-HD, these two peaks disappeared, indicating that PAA-HD was converted into PI-HD (Fig. 2, bottom).

Degree of Imidization of Polyimides According to Temperature

The degree of imidization of the polyimides was analyzed by means of FT-IR spectroscopy. The chemical imidization was conducted for 24 h. The absorbance of the band attributed to imide C–N–C (1381 or 1366 cm^{−1}) was compared with an internal standard band attributed to C=C aromatic stretch (1513 or 1512 cm^{−1}). The ratio of these absorbances was compared with that of a reference polyimide prepared by means of thermal imidization. The degree of chemical imidization of the polyimide was calculated by using the following equation:

$$\text{degree of imidization (\%)} = \frac{A_S(1381 \text{ or } 1366 \text{ cm}^{-1})/A_S(1513 \text{ or } 1512 \text{ cm}^{-1})}{A_R(1381 \text{ or } 1366 \text{ cm}^{-1})/A_R(1513 \text{ or } 1512 \text{ cm}^{-1})} \times 100$$

where A_S is the absorbance of the sample and A_R is the absorbance of the reference. Table 3 presents the degrees of imidization of PI-HD and PI-PD samples imidized at various temperatures. More than 90% imidization was achieved even at the very low imidization temperature of 40 °C, and the degree of imidization increased with increasing temperature. The degree of imidization of PI-HD-40-10 is greater than

TABLE 2 Chemical Imidization Conditions

Polyimide ^a	Temperature (°C)	Molar feed Ratio ^b	Polyimide ^a	Temperature (°C)	Molar feed Ratio ^b
PI-HD-40-5	40	1:5:5	PI-PD-40-10	40	1:10:10
PI-HD-40-10	40	1:10:10	PI-PD-60-10	60	1:10:10
PI-HD-40-20	40	1:20:20	PI-PD-80-10	80	1:10:10
PI-HD-60-10	60	1:10:10	PI-PD-100-10	100	1:10:10
PI-HD-80-10	80	1:10:10	PI-PD-120-10	120	1:10:10
PI-HD-100-10	100	1:10:10	PI-PD-140-10	140	1:10:10
PI-HD-120-10	120	1:10:10	PI-PD-160-10	160	1:10:10
PI-HD-140-10	140	1:10:10			
PI-HD-160-10	160	1:10:10			

^a PI-HD: polyimide of HPMDA and DDPM; PI-PD: polyimide of PMDA and DDPM.

^b Molar ratio of poly(amic acid) repeating unit:acetic anhydride:pyridine.

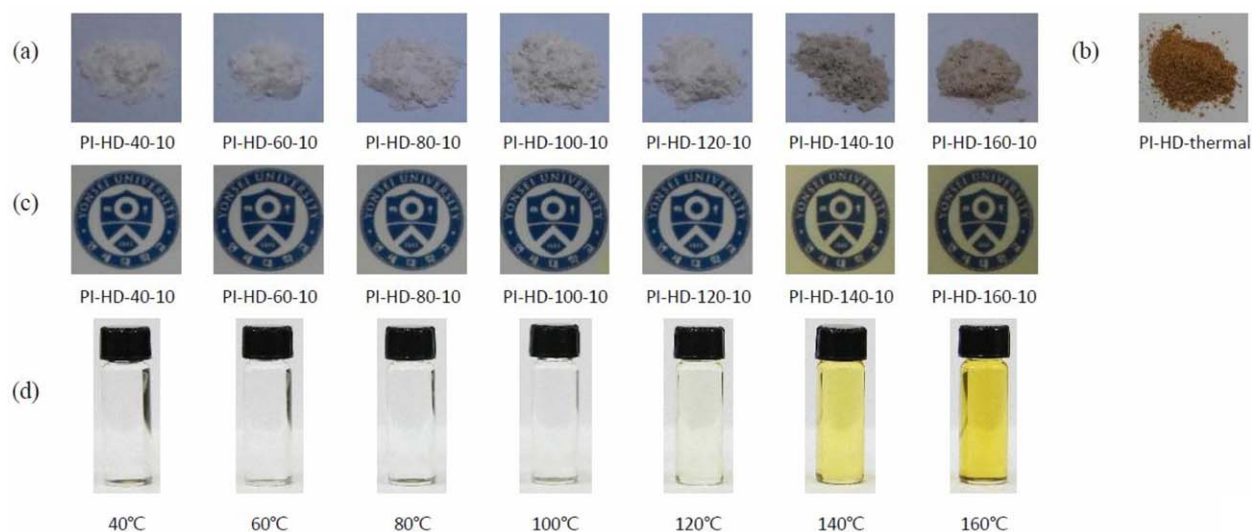


FIGURE 1 Photographs of polyimide powders, films and reaction solvent: (a) PI-HD powders obtained by chemical imidization. (b) PI-HD powder obtained by thermal imidization. (c) PI-HD films covering a printed mark. (d) Coloration of NMP at various temperatures equal to the chemical imidization temperatures used. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that of PI-HD-40-5, and same as that of PI-HD-40-20, so the molar feed ratio of 1:10:10 was used in the other imidizations at different temperatures.

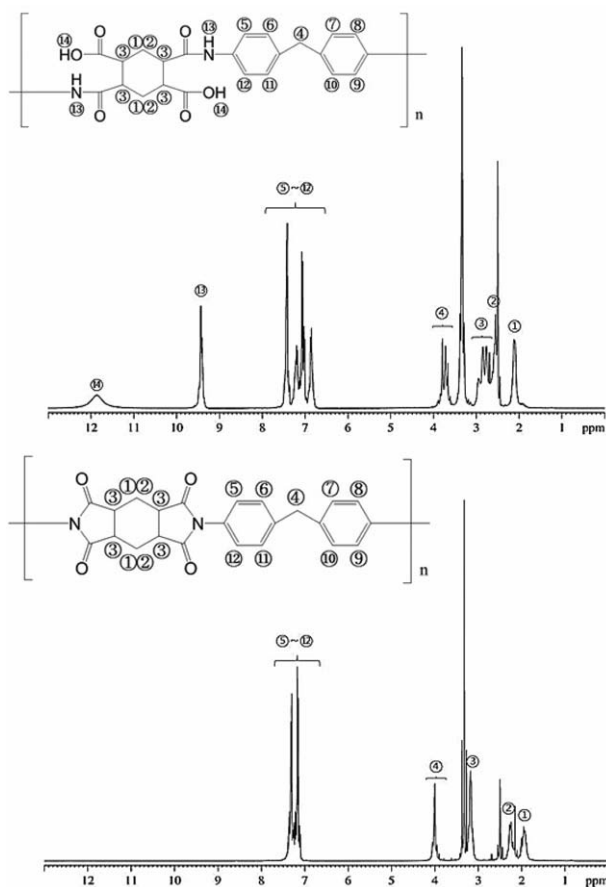


FIGURE 2 ^1H NMR spectra of PAA-HD and chemically imidized PI-HD.

Determination of Activation Energy of Chemical Imidization

Because of easier sample preparation, NMR spectroscopy was used for kinetic study of imidization instead of FT-IR spectroscopy. The degree of imidization of PI-HD prepared at

TABLE 3 Degree of Imidization and Thermal Properties of Polyimides

Polyimide ^a	Degree of Imidization (%)	T_d^5 (°C) ^b	T_g (°C) ^c
PI-HD-40-5	91	415	291
PI-HD-40-10	94	436	309
PI-HD-40-20	94	451	308
PI-HD-60-10	94	453	305
PI-HD-80-10	94	460	307
PI-HD-100-10	96	466	301
PI-HD-120-10	99	471	302
PI-HD-140-10	99	475	307
PI-HD-160-10	100	494	309
PI-PD-40-10	91	481	360
PI-PD-60-10	93	489	369
PI-PD-80-10	94	493	372
PI-PD-100-10	94	494	373
PI-PD-120-10	96	499	374
PI-PD-140-10	98	>500 ^d	374
PI-PD-160-10	100	>500 ^d	379

^a Chemically imidized polyimides from PAA at 40, 60, 80, 100, 120, 140, or 160 °C for 24 h.

^b T_d^5 are temperatures at which specimens show 5 wt % decomposition under N_2 .

^c T_g measured at a heating rate 10 °C/min under N_2 .

^d The expression ">500" represents that T_d^5 was not observed up to 500 °C.

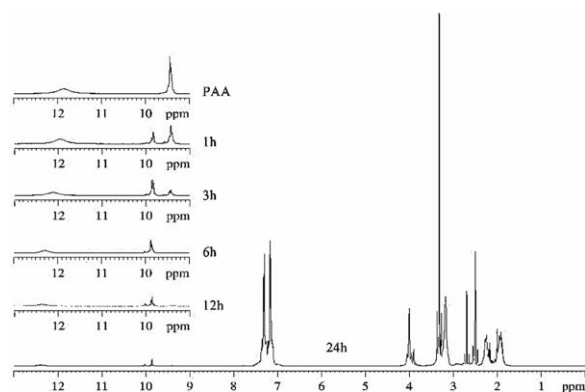


FIGURE 3 ^1H NMR spectra of PI-HD-40-10.

various imidization temperatures as a function of time was investigated by ^1H NMR spectroscopy. As a representative example, the 9.44 ppm peaks attributed to amide N-H protons in PAA-HD-40-10 gradually disappeared as the imidization proceeded (Fig. 3). A relatively small peak around 9.9 ppm attributed to the isoimide structure appeared and then disappeared during the imidization. The integration values of the 9.44 ppm peaks were compared to those of the 7.1–7.4 ppm peaks attributed to aromatic protons to determine the degree of imidization. The degree of imidization of the other polyimides was determined in a similar fashion. ^1H NMR spectra of the polyimides are shown in Figures S3–S10 in the Supporting Information.

The imidization rate increases with increasing temperature and the imidization is characterized by an initial rapid cyclization and a subsequent slower cyclization process (see Fig. S11 in the Supporting Information).³² This trend is attributed to the reduced entropy of poly(amic acid) with imidization.^{32,33} Although the data do not support an unequivocal determination of the reaction order, it seems that the poly(amic acid) underwent a first-order imidization reaction, so the data on imide formation were fitted into the first-order rate expression³²:

$$\ln\left(\frac{1}{1-p}\right) = kt + \text{constant} \quad (1)$$

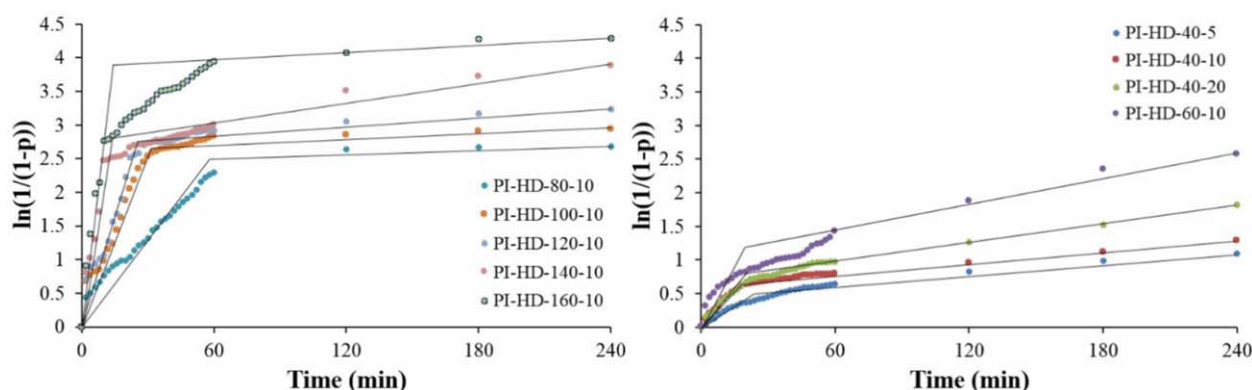


FIGURE 4 Degree of imidization versus time at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where p is degree of imidization ($\times 1/100$) and k , rate constant. A plot of $\ln(1/(1-p))$ versus time at various temperatures is shown in Figure 4.

Though arbitrary fittings were applied, they show that the two-step process correlates well with the imidization process. The rate constants of the imidization (k_1 for initial rapid cyclization and k_2 for subsequent slower cyclization) were determined from the slopes of the corresponding graphs in Figure 4. The rate constant increased with increasing amounts of dehydrating agent and amine used, and also with increasing temperature.

By using the Arrhenius equation and the rate constants k_1 and k_2 , the activation energies (E_a) can be obtained from plots of $\ln k$ versus $1/T$. k is related to E_a for imidization and the frequency factor, A , as shown in eq 2:

$$k = A \exp\left[-\left(\frac{E_a}{RT}\right)\right] \quad (2)$$

The natural logarithm of eq 2 gives eq 3.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

Through the above equation, a plot of $\ln k$ versus $1/T$ gives $\ln A$ as the intercept and $-E_a/R$ as the slope (Fig. 5).

E_a for the initial rapid process was determined to be 4.3 kJ/mol, whereas E_a for the latter slower process was 4.8 kJ/mol. It has been reported that E_a for thermal imidization of a poly(ester amic acid) is about 20 kJ/mol.³² In another report, E_a for chemical imidization of a poly(amic acid) of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and 1,5-diaminonaphthalene was presented to be 12.3 kJ/mol when an approximately 13:1 molar ratio of amine catalyst to PAA repeating unit was used.²⁸

Solubility and Thermal Properties of Polyimides

The solubility behavior of the synthesized polyimides in various solvents was investigated by dissolving 10 mg of polyimide powder samples in 1 mL of the solvents either at room

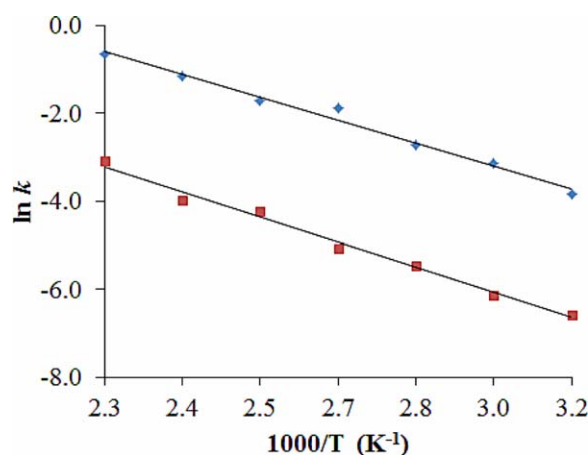


FIGURE 5 Arrhenius plot of $\ln k_1$ (upper line) and $\ln k_2$ (lower line) versus $1000/T$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature or at elevated temperatures; Table 4 summarizes the results. It was observed that PI-HD exhibited good solubility in polar organic solvents such as DMSO, DMAc, DMF, and NMP, even at room temperature. In contrast, PI-PD samples were partially soluble in those solvents. This was attributed to weaker intermolecular interactions between the partially aliphatic PI-HD chains compared to the fully aromatic PI-PD. On the other hand, the chemically imidized polyimides showed greater solubility than thermally imidized

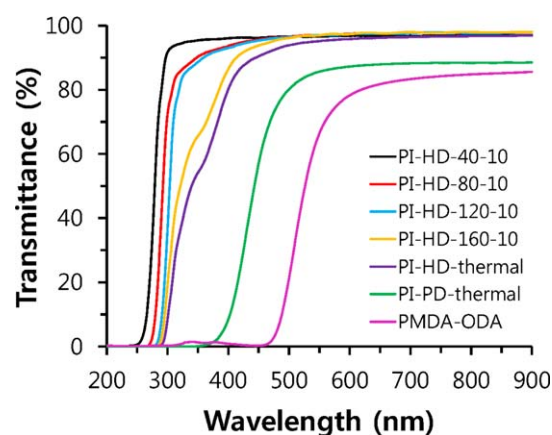


FIGURE 6 UV-visible spectra of polyimide films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyimides. This was considered to occur because the chemical imidization process would yield loosely packed solid polyimide, which would be more soluble than that prepared by thermal imidization. Thermal imidization usually produces a compactly aggregated polymer material, which results in a diffusion limitation of the solvent.³⁴

Thermal decomposition of the polyimides was studied by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C/min; Table 3 presents the

TABLE 4 Solubility of Polyimides^a

Polyimide ^b	Solvent									
	DMF	DMAc	NMP	DMSO	Py	Dioxane	THF	CHCl ₃	Acetone	MeOH
PI-HD-40-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-60-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-80-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-100-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-120-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-140-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-160-10	++	++	++	++	++	+-	+-	+-	-	-
PI-HD-thermal ^c	+-	+-	+-	+-	+-	-	-	-	-	-
PI-PD-40-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-60-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-80-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-100-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-120-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-140-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-160-10	+-	+-	+-	+-	-	-	-	-	-	-
PI-PD-thermal ^c	-	-	-	-	-	-	-	-	-	-

^a Solubility: ++: soluble at room temperature; +-: partially soluble; -: insoluble.

^b Chemically imidized polyimides from PAAs in NMP using pyridine and acetic anhydride at 40, 60, 80, 100, 120, 140, or 160 °C for 24 h.

^c Polyimide powder prepared by thermal imidization.

Abbreviations: DMF: dimethylformamide; DMAc: dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran; CHCl₃: chloroform; MeOH: methanol.

TABLE 5 Transmittances and Cutoff Wavelengths of Polyimide Films

Polyimide ^a	Film Thickness (μm)	400 nm _{trans} ^b (%)	550 nm _{trans} ^c (%)	Cutoff Wavelength (nm)
PI-HD-40-10	28	96	97	253
PI-HD-60-10	29	94	95	262
PI-HD-80-10	27	94	97	272
PI-HD-100-10	28	92	96	279
PI-HD-120-10	29	93	97	283
PI-HD-140-10	30	89	98	287
PI-HD-160-10	29	86	97	288
PI-HD-thermal ^d	28	80	95	292
PI-PD-thermal ^d	33	8	86	371
PMDA-ODA ^d	31	0	66	466

^a Polyimide films prepared by doctor blading. No films of the chemically imidized PI-PDs could be prepared because of their poor solubility.

^b Percent transmittance at 400 nm.

^c Percent transmittance at 550 nm.

^d Polyimide films prepared by thermal imidization.

results. Decomposition temperature (T_d^5) decreased as the imidization temperature decreased. On the other hand, the fully aromatic polyimides (PI-PD) showed higher T_d^5 than partially aliphatic polyimides (PI-HD). Although PI-HD-40-10 showed the lowest T_d^5 of 436 °C, this is high enough for industrial use.

The TGA curves of the polyimides are shown in Figures S13 and S14 in the Supporting Information. Glass transition temperatures (T_g s) of the polyimides are higher than 300 °C except PI-HD-40-5.

Optical Properties of Polyimides

Transmission UV-visible spectra were acquired from PI-HD films prepared by chemical or thermal imidization (Fig. 6, Table 5, and Fig. S12 in the Supporting Information). UV-visible spectroscopy of thermally imidized PI-PD and PMDA-ODA films was also conducted for comparison. Films of the chemically imidized PI-PDs could not be prepared because of their low solubility. The film thickness ranged from 27 to 33 μm. As the chemical imidization temperature of PI-HD decreased, the transmittance at 400 nm tended to gradually

increase. In addition, the PI-HD film prepared by thermal imidization showed lower transmittance at 400 nm (80%) than chemically imidized polyimides (86–96%). At 550 nm, the chemically and thermally imidized PI-HDs exhibited similar transmittance (95–98%). The fully aromatic polyimides, PI-PD and PMDA-ODA, showed considerably lower transmittance (<10%) at 400 nm compared to the partially aliphatic PI-HD polyimides. The PI-HD-40-10 film showed the greatest transmittance of 96 and 97% at 400 and 550 nm, respectively. Cutoff wavelength of a polyimide film is another measure of its optical transparency; herein the cutoff was considered to be the wavelength at which the transmittance becomes less than 1%. As the chemical imidization temperature of PI-HD decreased, the cutoff wavelength shortened (Table 5). In addition, the PI-HD film prepared by thermal imidization had longer cutoff wavelengths (292 nm) than films of chemically imidized polyimides (253–288 nm). The fully aromatic polyimides, PI-PD and PMDA-ODA, had considerably longer cutoff wavelengths than partially aliphatic PI-HD polyimides. Notably, the PI-HD-40-10 film had a

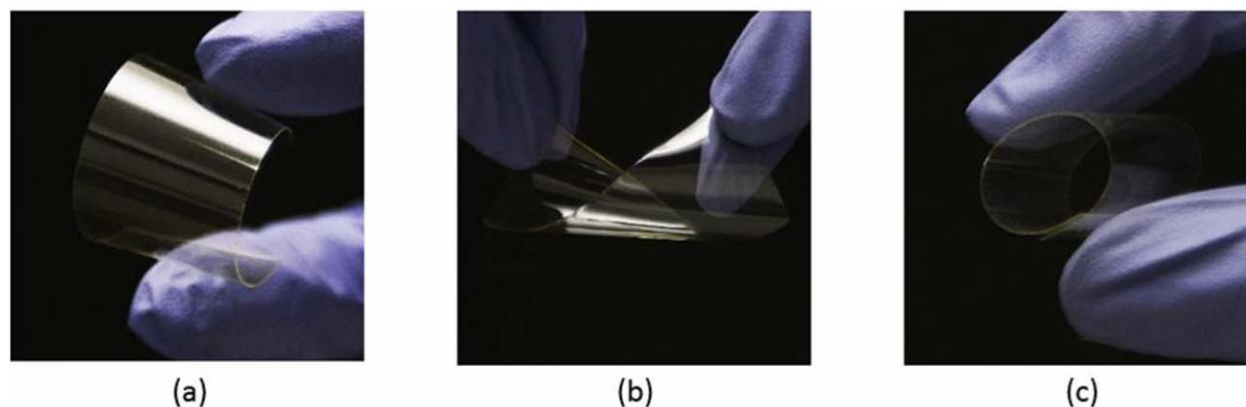


FIGURE 7 Photographs of a film of PI-HD-40-10 under (a) bending, (b) twisting and (c) rolling. Film thickness is 28 μm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

considerably shorter cutoff wavelength (253 nm) than the other PI-HD-based polyimides.

It was also observed that the imidization temperature influences the color of polyimide films. As the imidization temperature of PI-HD was decreased, the color of the resulting PI-HD films gradually became pale; the PI-HD-40-10 film was almost colorless [Fig. 1(c)]. Films of PI-HD-140-10 and PI-HD-160-10 were yellow.

In this study, the transparency and color of polyimide film were considered to be affected by the chemical structure of the polyimide and by the imidization temperature. It is well known that the opacity and color of polyimide films is attributable to intramolecular conjugation and intra- and intermolecular CTC formation.^{3,35–37}

Because PI-HD polymers are partially aliphatic, the PI-HDs have reduced or no conjugation and CTC effects, and thus show higher transparency and less color than fully aromatic PI-PDs.

As described above, as imidization temperature is increased, the transparency of the resulting polyimide films decreases and they become yellow. One reason for the low transparency and yellow color of PI-HD-140 and PI-HD-160 films could be a certain chemical change to the polyimides at higher temperatures (140 and 160 °C) that cannot be detected by IR or NMR spectroscopy. Another reason could be that the decreased transparency and yellowing of the polyimide films is caused by remaining solvent in the films. It has been shown that polyimide films contain small amounts of residual solvent.^{38–40} In this study, the imidization solvent, NMP, became yellow under the reaction conditions [Fig. 1(d)]. It was assumed that the yellowed residual solvent was partially responsible for making the films yellow.

Highly flexible films were obtained from most of the polyimides prepared in this work. A representative example was the highly flexible PI-HD-40-10 film (Fig. 7). There was no significant change to the films' appearance when they were bent, twisted and rolled up many times.

CONCLUSIONS

HPMDA or PMDA was polymerized with an aromatic diamine, DDPM, to give poly(amic acid)s. Chemical imidization of the poly(amic acid)s was attempted at the low temperatures of 40–160 °C. More than 90% imidization was achieved, even at very low imidization temperature of 40 °C. The degree of imidization increased with increasing imidization temperature.

The imidization rate increases with temperature and the imidization occurs in two steps: an initial rapid cyclization and a subsequent slower cyclization process. Assuming that the imidization was a first-order reaction, the activation energy for the initial rapid process was determined to be 4.3 kJ/mol, whereas the activation energy for the slower process was determined to be 4.8 kJ/mol.

As the chemical imidization temperature of PI-HD is decreased, its transmittance at 400 nm tends to gradually increase, its cutoff wavelength decreases, and it becomes paler. A film of PI-HD-40-10 showed up to 97% transmittance in the visible region, a considerably low cutoff wavelength (253 nm), and colorlessness. This was probably due to reduced or absent conjugation and CTC formation, in conjunction with a lack of yellowing at the low imidization temperature used. In addition, PI-HD-40-10 had good solubility and thermal stability, and yielded thin films that were highly flexible.

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