Chemical Imidization Study by Spectroscopic Techniques. 2. Polyamic Acids

Mohammed H. Kailani and Chong Sook Paik Sung*

Polymer Program, Institute of Material Science, Department of Chemistry, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269-3136

Received January 23, 1998; Revised Manuscript Received June 5, 1998

ABSTRACT: Chemical imidization of polyamic acid based on 1,5-diaminonaphthalene and a dianhydride was studied by UV−visible and FT-IR ATR techniques under various reaction conditions, such as polyamic acid concentration, solvent condition (dry vs humidity-exposed NMP), catalysts of tertiary amines with different degrees of steric crowding and base strength, and the concentration of the acetic anhydride and pyridine. With acetic anhydride and pyridine, the reaction was very similar to that of the model amic acids, with the simultaneous formation of bisimide groups and bisisoimide groups, followed by isomerization of bisisoimde groups to bisimide groups, which is very sensitive to the dryness of the solvent. The reaction with polymer films supported a similar trend. Chemical imidization seems to proceed by nucleophilic catalysis by tertiary amines, depending on the steric crowding as well as the base strength. Reducing steric crowding in the catalyst facilitates the formation of an acylammonium (or pyridinium) cation. The adjacent positive charge on the nitrogen makes the acyl group more electrophilic, making it easier for the amic acid anion to attack and form the mixed anhydride intermediate. The catalyst can further accelerate the reaction by deprotonating the mixed anhydride if the tertiary amine is not sterically crowded. The anionic mixed anhydride quickly cyclizes to give an imide group and an isoimide group. *N*-Methylpyrrolidine and triethylenediamine were found to make the reaction at least 50 times faster than pyridine, which is the most commonly used industrial catalyst, without changing the molecular weight and its distribution. This investigation shows that the acidity of the original amic acid and the acid produced during the reaction have a profound impact on the products and their ratio, which can be understood based on the mechanistic scheme proposed for the model amic acid. It is suggested that a careful choice of polyamic acid concentration, dehydrating agent, and catalyst may lead to greater control over the reaction and the polymer properties.

Introduction

In the preceding paper, we described the chemical imidization study of the low molecular weight model amic acid and bisamic acid by UV−visible spectroscopy and H NMR spectroscopy. The dehydrating mixture used was acetic anhydride and pyridine. We were able to elucidate the kinetics and the mechanisms with these model amic acids as a function of the concentration, the temperature, and the dryness of the solvent (NMP) used for chemical imidization.

We extend the chemical imidization studies to polyamic acid made from 1,5-diaminonaphthalene (DAN) and a partially fluorinated dianhydride, as a function of the polymer concentration, the dryness of NMP, and the concentrations of the acetic anhydride and pyridine. Also, to find the optimum conditions for chemical imidization, different catalysts were evaluated. Since previous literature[1] reported that the molecular weight of the resulting polyimide depended on the ratio of acetic anhydride and pyridine to the amic acid in the starting polymer, size exclusion chromatography was also used to evaluate molecular weight changes. Previous study[2] on polyamic acid film required a delay between sample removal from the reaction mixture and IR measurement, which could introduce uncertainties in the analysis and the interpretation of the results. FT-IR in the attenuated total reflection mode was used to explore how polyamic acid films are affected by chemical imidization as opposed to the solution studies, by developing in situ monitoring technique.

As mentioned in our earlier study,[3] we chose DAN as a model diamine due to its potential as an extrinsic sensor to monitor cure for in situ processing since its reactivity can be correlated to other aromatic diamines. A partially fluorinated dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was also chosen as a dianhydride because it improves the solubility of the resulting polyimide and its lack of conjugation simplifies the UV−visible spectra for the polymer.

Experimental Section

Synthesis of Polyamic Acid. Two concentrations (4 and 19 wt %) of polyamic acid solutions were prepared. The first solution was used as a stock solution for kinetic studies, while the latter was used to cast polyamic acid films for FT-IR film studies.

4 wt % Solution. 2.58 g (16.3 mmol) of crystallized and sublimed DAN in 100 mL distilled NMP was reacted with 7.24 g (16.3 mmol) of 6FDA in 250 mL 1-methyl-2-pyrrolidinone, (NMP), by agitation in the dark cabinet overnight. This solution, stored in a refrigerator, was diluted to various concentrations for kinetic studies.

19 wt % Solution. This solution was prepared first by dissolving 1.27 g (8.02 mmol) of recrystallized and sublimed DAN in 10 mL of distilled NMP in a 30 mL brown glass bottle by immersion in an ultrasonic bath. After dissolution, 3.56 g (8.02 mmol) of 6FDA in 10 mL of distilled NMP was added to react for 22 h in the dark, and the reaction was stored in the refrigerator after tightly wrapping the bottle with Parafilm. When the bottle was opened, it was warmed to room temperature and purged with dry argon.

Chemical Imidization Procedure. The dehydrating mixture was prepared in a dry 5.0 mL volumetric flask under dry nitrogen, using two Hamilton Gastight 900 series 250 μL syringes. Reference 4 contains information on the amount of

S0024-9297(98)00096-5 CCC: $15.00

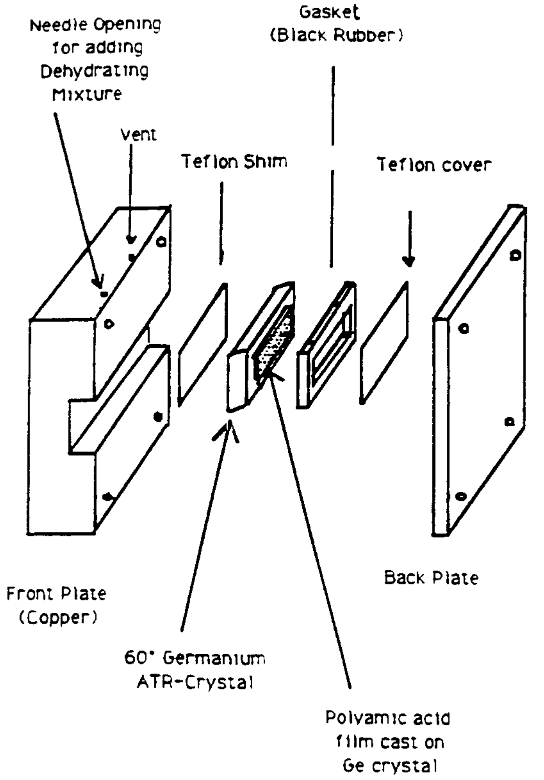

Figure 1. Diagram of the IR−ATR holder showing the details of the chamber in which dehydrating mixture was injected on one side of the ATR element.

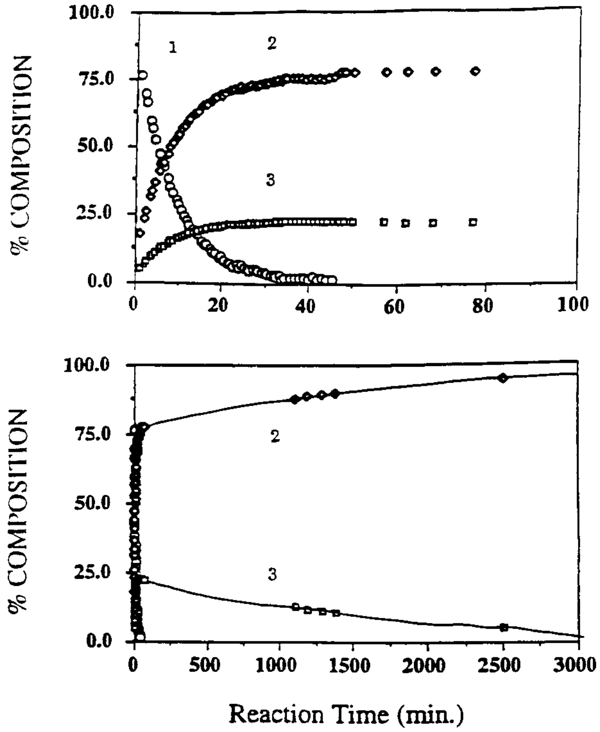

Figure 2. Composition profiles as a function of chemical imidization time for the reaction of polyamic acid corresponding to 8.0×10^{-5} M amic acid unit concentration performed at 38 °C in humidity-exposed NMP: (1) bisamic acid group; (2) bisimide group; (3) bisisoimide group.

the reagents used to make 5.0 mL NMP solutions of the dehydrating mixtures. The polyamic acid solution was diluted to twice the reaction concentration from 4 wt % stock solution under dry argon. 1.0 mL of the polyamic acid solution and 1.0 mL of the dehydrating mixture were added to start the reaction in a small glass vial. After a certain reaction time, 4 μL aliquots were diluted in a cuvette placed in the UV−visible instrument (Perkin-Elmer diode array 3840 instrument) containing 1.8 mL of NMP. After the solution was stirred in the cuvette for 30 s, UV−visible spectra were taken. It took 1 min for spectral acquisition to be performed after the sample was withdrawn from the reaction mixture. Other details of the procedure for wet vs dry NMP can be found in the preceding paper[6] as well as in the ref 4.

Size Exclusion Chromatography (SEC). This was run after a 2-fold dilution of the reaction mixture with filtered tetrahydrofuron (THF), at 30 °C at a rate of 1.0 mL/min, using both refractive index and tunable UV−visible detectors, which was set at 315 and 280 nm for polyamic acid and polyimide, respectively.

FT-IR Spectroscopy. To study chemical imidization of polyamic acid films in situ, attenuated total reflection (ATR) method was used by casting polyamic acid film from a 19 wt % polyamic acid solution in NMP on one side of the ATR element (a germanium parallelogram with a dimension of 50 mm × 10 mm × 2 mm with a 60° entrance angle). After the film was dried under vacuum for 21 h, the film, whose thickness was about 7 μm was placed in a special holder shown in Figure 1. This holder has a chamber where the dehydrating mixture is injected to be in contact with the polyamic acid film and then, diffused into the film, thus initiating the chemical imidization. The dehydrating mixture is on one side of the film, while the ATR element is on the other. A black rubber gasket makes a seal around the dehydrating solution, keeping it in contact with the polyamic acid film. The dehydrating mixture for this experiment was prepared in cyclohexane, a nonsolvent for both the polyamic acid and its dehydration products. Cyclohexane does not have IR bands that strongly overlap with the monitored peaks, such as imide, amic acid, and isoimide. The dehydrating mixture was prepared in a 5 mL volumetric flask by mixing 400 μL of acetic anhydride with 300 μL of pyridine in dry cyclohexane, giving a concentration of 0.848 M in acetic anhydride and 0.742 M in pyridine. This concentration is close to those normally used in the reactions on films. The reaction was run at room temperature using a Nicolet FT-IR instrument. The details of the experiment are described in the ref 4. The penetration depth of the sampling IR beam using this Ge ATR element is estimated to be about 0.2 to 0.3 μm.[5]

Results and Discussion

1. Effect of Polyamic Acid Concentration. In this study, acetic anhydride and pyridine were used as dehydrating mixture. The molar ratio of both acetic anhydride and pyridine to amic acid was greater than 10 for these reactions, to simplify the kinetics as pseudo first order.

a. Humidity-Exposed Solvent (NMP). UV−visible spectral changes during the chemical imidization corresponding to 8.0×10^{-5}M amic acid unit concentration in polyamic acid solution show both an increase in absorption at 380 nm due to the formation of bisisoimide group and a simultaneous shift of the bisamic acid group absorption at 315 nm to the bisimide group peak at 290 nm. Deconvolution of the UV−visible spectra based on the spectra of the bisamic acid group, the bisisoimide group, and the bisimide group provides the percent composition as a function of reaction time as shown in Figure 2. The first stage of the reaction was found to follow parallel pseudo-first-order kinetics, while the second stage of the reaction where the bisisoimide group is converted to the bisimide group was found to be much slower even though it follows first-order kinetics. The reaction mechanism can be described as in Scheme 1. The rate constants for such a scheme are listed in Table 1. The rate constants, k_1 and k_2, are similar to the case

Scheme 1. Simplified Mechanism Describing Polyamic Acid Reaction to Polyimide (PI) (PAA) and Polyisoimide (PIso), When Acetic Anhydride/Pyridine Is Used To Carry Out the Chemical Imidization Using NMP as a Solvent

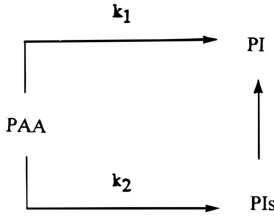

Table 1. Apparent Rate Constants and the Times to Reach the Maximum Concentration of Bisisoimide Group for Chemical Imidization of Polyamic Acid in Both Humidity Exposed and Dry NMP[a]

polyamic acid concentration[b] ($\times 10^{-5}$M)	time for max bisisomide (min)	apparent rate constant $k_1 + k_2$ (min^{-1})	apparent rate constant k_3[c] (min^{-1})
	Air Exposed Solvent		
8	≈75	0.12	9×10^{-4}
3000 (1.0 wt %)	≈55	–	1×10^{-3}
	Dry Solvent		
8	1	–	0.76
300 (0.1 wt %)	10	–	≈ 0.4
900 (0.3 wt %)	29	–	≈ 0.3
1500 (0.5 wt %)	34	–	≈ 0.3

[a] Concentrations of acetic anhydride and pyridine for all reactions are 0.212 and 0.185 M, respectively. All reactions were performed at 38 °C. [b] Amic acid unit concentration. [c] Definitions of k_1, k_2, and k_3 are shown in Scheme 1.

of the monoamic acid or bisamic acid model compound in humidity-exposed NMP, as described in the preceding paper.[6] While k_3 was measurable with polyamic acid, the isomerization was too slow with the bisamic acid model compound.

As described in the preceding paper, the isomerization is strongly influenced by the amount of moisture since it hydrates acetate ion which catalyzes the reaction.[6] The reason that model acids did not show isomerization might be explained based on the reduced amount of moisture in the polymer reaction, since the polyamic acid was not exposed to atmospheric humidity after synthesis in solution.

The reaction in a higher polyamic acid concentration, 3.0×10^{-2} M corresponding to 1.0 wt % has been already described.[3] The reaction scheme is analogous to Scheme 1. Since the first stage of the reaction did not fit the parellel pseudo-first-order kinetics, the time to reach the maximum amount of bisisoimide groups is listed in Table 1. During the reaction in a higher concentration of monoamic acid, a high concentration of the mixed anhydride intermediate was observed.[6] Since a mixed anhydride is included in the concentration of the amic acid due to its similarity to the latter in UV–visible spectra, a high concentration of the mixed anhydride results in inaccurate values of the amic acid composition, resulting in a deviation in the kinetic plot. In low concentration reactions, it is not a problem, as described in the preceding paper[6] based on a proposed reaction mechanism which involves many equilibria.

b. Dry Solvent (NMP). When the solvent was kept dry by using very stringent procedures to prevent air from coming in contact with the solvent, the second stage of the reaction became extremely fast. Figure 3 illustrates the compositions, after reaction in 0.5 wt % polyamic acid in dry solvent, showing a fast isomerization of bisisoimide groups to bisimide groups. When the dryness of the solvent is changed, the isomerization is strongly influenced while the first stage reaction is independent. Another important observation was that the isomerization takes place only after polyamic acid has been consumed. This trend is the same as observed in model amic acids[6] and was explained based on the acetate ion needed to catalyze the isomerization. When the starting amic acid or polyamic acid is present due to its stronger acidity in comparison to acetic acid byproduct, the acetate ion is mostly in the acid form and thus is unable to catalyze the isomerization.

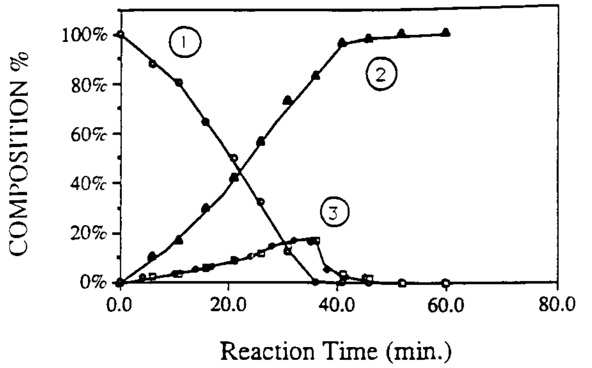

Figure 3. Composition profiles as a function of chemical imidization time for 0.5 wt % polymer in dry NMP: (1) bisamic acid group; (2) bisimide group; (3) bisisoimide group.

Table 2. Kinetic Parameters Obtained for Chemical Imidization of 0.5 wt % Polyamic Acid (1.5×10^{-2} M Amic Acid Unit Concentration) in Dry NMP[a]

temp (°C)	k_1 ($\text{min}^{-1} \times 10^2$)[b]	k_2 ($\text{min}^{-1} \times 10^2$)[b]	k_3 ($\text{min}^{-1} \times 10^2$)[b]
38	5.30	1.73	8.52
45	8.06	2.62	9.27
52	12.6	4.11	12.1
E_a	12.3	12.3	13.2

[a] Concentrations of acetic anhydride and pyridine for all reactions are 0.212 and 0.185 M, respectively. [b] Definitions of k_1, k_2, and k_3 are shown in Scheme 1.

Once the polyamic acid is consumed, the acetate ion can catalyze the reaction since the water molecule does not hydrate the acetate ion in dry solvent. Table 1 lists the times required for maximum amount of bisisoimide group formation as well as the apparent isomerization rate constant (k_3). The k_3 varied from 0.76 min^{-1} in dry solvent to 9×10^{-4} min^{-1} in humidity-exposed solvent, representing acceleration of the reaction by a factor of over 800 in dry solvent.

The effect of temperature was studied with 0.5 wt % polyamic acid solution (1.5×10^{-2} M amic acid concentration) in dry solvent, where the concentrations of acetic anhydride and pyridine were 0.212 and 0.185 M, respectively. The kinetic parameters as well as the activation energies are summarized in Table 2. The activation energy for the conversion of bisisoimide group to bisimide group is 13.2 kcal/mol. The values for this polyamic acid are close to the values reported by Svirodor et al.[7]

When the concentration of polyamic acid decreased from 1.5×10^{-2} M (0.5 wt %) to 8×10^{-5} M, the time required for both stages of the reaction was reduced considerably as shown in Figure 4. While the maximum amount of bisisoimide group was about the same for all concentrations, lower polyamic acid concentration was

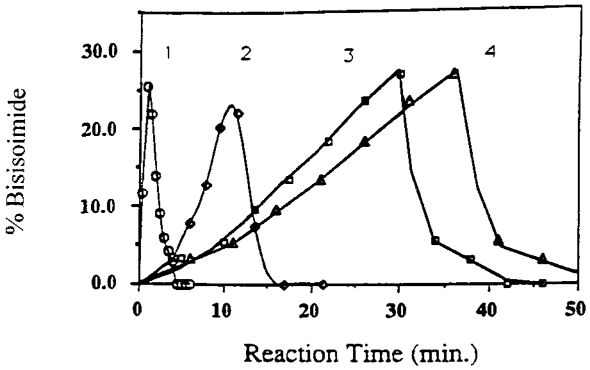

Figure 4. Effect of polyamic acid concentration as manifested in percentage bisisoimide group as a function of chemical imidization time, in dry NMP: (1) 0.0027 wt % (8.0 × 10^{-5}M); (2) 0.1 wt % (300 × 10^{-5}M); (3) 0.3 wt % (900 × 10^{-5}M); (4) 0.5 wt % (1500 × 10^{-5}M). The concentration in parentheses indicates amic acid unit concentration.

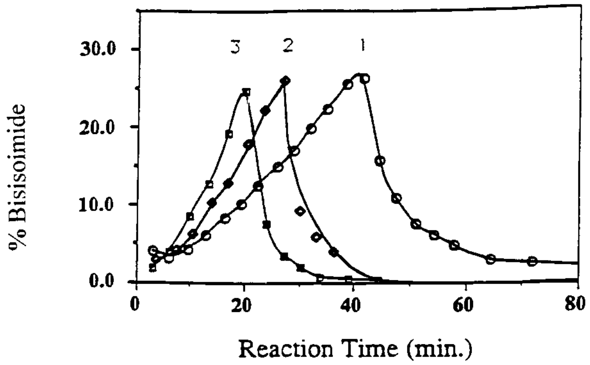

Figure 5. Effect of concentration of acetic anhydride concentration as manifested in percentage bisisoimide group as a function of chemical imidization time at 38 °C. Acetic anhydride concentration was (1) 0.212, (2) 0.318, and (3) 0.424 M, while pyridine concentration was 0.1855 M and polyamic acid concentration was 0.5 wt %, respectively.

found to accelerate the first stage of the reaction. The effect of polyamic acid concentration on the isomerization of bisisoimide group to bisimide group (k_3) is characterized by the less steep slopes after reaching maximum bisisomide group concentration in Figure 4, indicating reduced rates with increasing concentration. This trend is probably due to the reduced ionization of acetic acid, as more acetic acid is produced with increasing polyamic acid concentration.

2. Effect of Acetic Anhydride Concentration. Increasing acetic anhydride concentration was found to speed up the reaction at 38 °C in dry NMP, as shown in Figure 5. In this experiment, the ratio of acetic anhydride to amic acid ranged from 14.13 to 28.26, while the ratio of pyridine to amic acid was fixed at 12.37. The lowest ratio of acetic anhydride to pyridine was 4.0: 3.5, since it was reported to produce the optimum molecular weight by Vinogradova et al.[1] The concentration of the polyamic acid was 0.5 wt %.

It is noted in Figure 5 that doubling the anhydride concentration reduced the time required for maximum amount of isoimide by half, while the maximum amount did not change for all three concentrations of the acetic anhydride. As more acetic anhydride is used, the first three equilibrium reactions in Scheme 3 of the preceding paper[6] are shifted to the right, resulting in a high concentration of the mixed anhydride intermediate at the expense of amic acid. Reduced amic acid concentration makes the reaction faster as described in the preceding section, because of the reduced solution acidity which shifts the acid−base equilibrium reaction for the rate determining deprotonation step (reaction 4 in Scheme 3 of the preceding paper[6]) to the product side.

Scheme 2. Chemical Structure of the Acyl Ammonium Ion of 1,8-Diazobicycle[5.4.0]under-7-ene (DBU) Resonance Structure

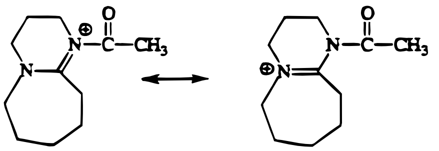

Table 3. Apparent Rate Constants and the Times to Reach the Maximum Concentration of Bisisoimide with Different Acetic Anhydride Concentrations on 0.5 wt % Polyamic Acid Reaction in Dry NMP at 38 °C[a]

acetic anhydride concentration (M)	time for max bisisoimide (min)	apparent rate constant k_3 (min^{-1})[b]
0.212	41	0.12
0.318	29	0.14
0.424	20	0.18

[a] Pyridine concentration = 0.185 M. [b] Definition of k_3 is shown in Scheme 1.

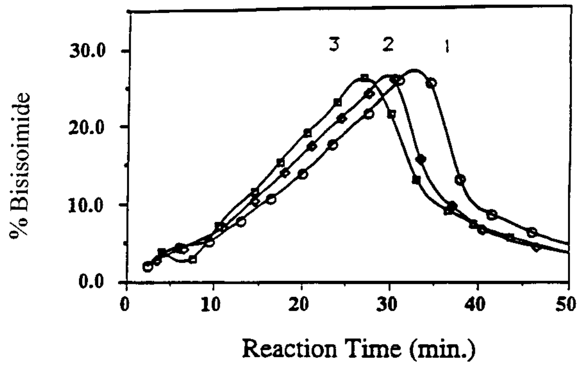

Figure 6. Effect of concentration of pyridine as manifested in percentage bisisoimide group during 0.5 wt % polyamic acid chemical imidizations in dry NMP.

Unlike the results of Vinogradova et al.,[1] GPC on reaction mixture showed little change in MW or MWD in this range of acetic anhydride. Table 3 lists the time required for maximum fraction of bisisomide group and the rate constant (k_3) for isomerization of isoimide group to imide group. With higher acetic anhydride concentration, k_3 also increases due to the equilibrium shifted to the right in the deprotonation step, resulting in higher concentration of the acetate ion. This ion is catalyzing the isomerization and, therefore, is responsible for faster rate.

3. Effect of Pyridine Concentration. Increasing pyridine concentration also has a similar effect as to increase acetic anhydride concentration as shown in Figure 6. Also, as was the case for acetic anhydride, isomide group concentration stayed the same in different pyridine concentration. Pyridine concentration was not doubled as was the case for the acetic anhydride, due to increasing UV absorption by pyridine.

The ratio of pyridine to amic acid was varied from 12.37 to 17.32, while the ratio of acetic anhydride to amic acid was fixed at 14.13. The polymer concentration was at 0.5 wt % and the reactions were at 38 °C in dry NMP. The reason for the pyridine concentration dependence is analogous to the case of acetic anhydride, as described in the preceding section. No significant

Table 4. Apparent Rate Constants and the Time To Reach the Maximum Concentration of Bisisoimide for Different Pyridine Concentrations on 0.5 wt % Polyamic Acid Reaction in Dry NMP at 38 °C[a]

pyridine concentration (M)	time for max bisisoimide (min)	apparent rate constant k_3 (min^{-1})[b]
0.185	34	0.079
0.222	30	0.076
0.259	27	0.11

[a] Acetic anhydride concentration = 0.212 M. [b] Definition of k_3 is shown in Scheme 1.

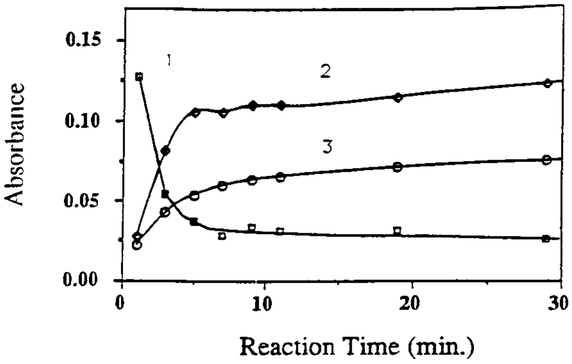

Figure 7. IR absorbance for (1) amic acid band at 1540 cm^{-1}, (2) imide band at 1364 cm^{-1}, and (3) isoimide band at 980 cm^{-1} as a function of chemical imidization time with polyamic acid film using 0.424 M acetic anhydride and 0.37 M pyridine in dry cyclohexane using FT-IR–ATR method.

change in MW or MWD as indicated by GPC was observed in this range of pyridine concentration. Table 4 lists the time required for maximum bisisomide group formation and the rate constant, k_3 for isomerization of isomide group to imide group, when the reaction was run with pyridine.

4. Chemical Imidization of Polyamic Acid Film by the FT-IR ATR Technique. The industrial procedure for the chemical imidization usually involves polyamic acid films. A previously reported study[8] on films required about 48 h between taking out the film from the imidizing mixture and the time its IR spectrum was determined. This long time was necessary to remove imidizing species from the film by diffusion in fresh solvent and subsequent solvent removal under reduced pressure at room temperature due to thermal instability of isoimide units. Such a handling could also introduce errors due to hydrolytic instability of isoimide moieties.

To eliminate the time delay and potential complications involved during handling of the film, we designed an in situ experiment based on the FT-IR attenuated total reflection (ATR) method. This technique allowed us to monitor reaction in real time by using a germanium ATR element on which polyamic acid film was cast. After removing most of the solvent by vacuum from the cast film, the imidizing mixture as described in the Experimental Section was injected on the other side of the film, in a liquid tight compartment as shown in Figure 1. The reaction was monitored by taking an IR–ATR spectra of the film as a function of time. Figure 7 shows the changes in the absorbance values corresponding to amic acid at 1540 cm^{-1} due to the amide II band,[8] imide at 1364 cm^{-1} due to the C–N stretching band,[8] and isoimide at 980 cm^{-1} due to the isoimide ring bending mode[8] as a function of the reaction time. This figure shows a simultaneous conversion of amic acid to both imide and isoimide, which occurs rather fast. The reaction reaches a plateau in about 30 min. The second stage of the reaction, isoimide group isomerization, was not monitored due to the longer reaction time, since the film was not prepared under dry conditions.

Table 5. Effect of Catalyst Structure and Base Strength on the Chemical Imidization of 0.5 wt % Polyamic Acid, in Dry NMP

catalyst	pK_a (H_2O 25 °C)[a]	time required for 95% conversion	$k_1 + k_2$ (min^{-1})
pyridine	5.23	100 min	0.074
triethylamine	10.72	250 min	0.018
methylpyrrolidine	10.46	<2 min	–
triethylenediamine	8.60	<2 min	–
N,*N*-(dimethyl)-aminopyridine	6.09	not determined	–
DBU	~13	no reaction	–
N-methylpyrrole	0	~ year	–

[a] Cited from ref 12b.

The results by this experiment offered supporting evidence for UV–visible deconvolution results and confirmed that cyclization of polyamic acid, by using acetic anhydride/pyridine mixture as a dehydrating mixture, leads to the simultaneous formation of both an imide group and an isoimide group.

5. Effect of Catalyst Structure and Base Strength. Pyridine was used in the preceding sections as the catalyst for chemical imidization. Since the effect of catalyst on the chemical imidization process was not extensively reported, we decided to investigate the effect of catalyst structure and base strength on the reaction. This study will also provide important insights on the underlying kinetics and mechanisms.

In this section, the effect of the tertiary amine catalyst structure and base strength on the chemical imidization of polyamic acid is investigated, using acetic anhydride as a dehydrating agent and dry NMP as a solvent. The concentrations of catalyst, acetic anhydride, and polyamic acid were 0.185 M, 0.212 M, and 0.5 wt % (1.5×10^{-2}M amic acid unit concentration), respectively. All reactions were run at 38 °C. Table 5 lists the types of the tertiary amine catalysts studied and their base strengths.

A. Triethylamine. Several differences are found when triethylamine is used instead of pyridine. First, the starting UV–visible spectrum of polyamic acid in the presence of triethylamine, before acetic anhydride is added, is red-shifted from 330 nm in comparison to 315 nm in pyridine, probably due to ionization of polyamic acid. UV–visible spectral deconvolution based on the spectra of polyamic acid and the sodium salt of bisamic acid revealed that the initial polyamic acid spectrum to be about 52% ionized. Second, no bisisoimide formation was observed during the chemical imidization reaction, as can be seen by the absence of UV–visible band around 380 nm for isoimide group. Third, UV–visible spectra for the reaction show conversion of the half-ionized polyamic acid to polyimide directly, as illustrated in Figure 8 for the composition. Fourth, the reaction does fit pseudo-first-order kinetics.

To compare the relative rates of imidization, Table 5 lists the time required for 95% conversion to polyimide. As can be seen in Table 5, the triethylamine-catalyzed reaction is slower than the pyridine-catalyzed reaction, even though the former is more basic than the latter. This result could be attributed to the difficulty to form the acylammonium ion intermediate due to the in-

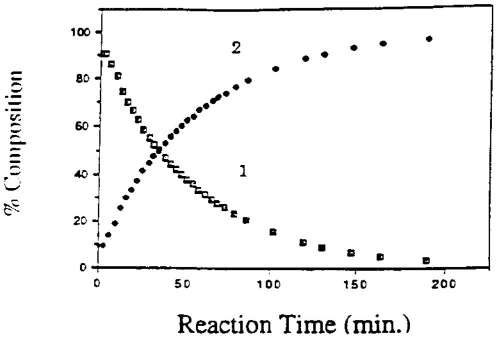

Figure 8. Composition profiles as a function of chemical imidization time for triethylamine catalyzed chemical imidization: (1) 50% ionized bisamic acid group; (2) bisimide group.

creased steric crowding generated by the three ethyl groups attached to the nitrogen atom. Similar steric hinderence was also reported in the case of benzoylammonium intermediate by Litvineko et al.[9] Smith studied triethylamine as a catalyst with fluorinated polyamic acid but did not provide a comparison to the case with pyridine.[10]

The reason that the bisisoimide was not formed, as reported also by others[11] can be explained in view of Scheme 3 in the preceding paper. When triethylamine is used as a catalyst, the acidity of the protonated triethylamine ($pk_\alpha = 9.25$) is less than that of polyamic acid ($pk_\alpha = 8.8$). Thus, the acidity of the reaction mixture is represented more by that of the protonated triethylammonium ion and therefore reduced in the case of pyridine, where polyamic acid acidity is the deciding factor. This means that the ionization of the acetic acid byproduct occurs more readily, effectively catalyzing the isomerization of isoimide group to imide group.

B. 1,8-Diazobicyclo[5.4.0]undec-7-ene (DBU). Although this base is one of the strongest organic bases known, it failed to catalyze the chemical imidization reaction, even after monitoring the reaction for about 2 weeks. UV−visible spectrum of the reaction mixture initially was that of partially ionized amic acid, which changed color to green after 3 h, followed by dark brown to black on the second day.

When this base reacts with acetic anhydride, the generated acylammonium ion, unlike other acylammonium ions, has a deactivated carbonyl group due to resonance stabilization of the positive charge next to the carbonyl, as can be seen in Scheme 2. This may explain the reason for this base's lack of a catalytic effect.

C. *N*-Methylpyrrole. This amine makes the reaction to be extremely slow. *N*-methylpyrrole is a very weak base due to the engagement of the lone electron pair on the nitrogen in resonance with the B double bonds, giving the five-membered ring the six electrons needed for aromatic resonance observed in pyrroles.[12a] Thus, the lone electron pair on the nitrogen is not available most of the time to contribute in chemical reactions, making pyrrols very weakly basic. ($pk_\alpha \approx 0$). Also it is very difficult to form the acylammonium ion needed for chemical imidization, leading to a very slow reaction.

D. *N*-methylpyrrolidine. This amine is less sterically hindered than triethylamine with a basicity similar to that of triethylamine. This base is much stronger than pyridine, leading to a very fast reaction. The spectra obtained after 2.5 min showed the reaction to be complete. When the reaction was monitored in situ in a 3.3 mm path length cuvette with half the normal concentration of polyamic acid (7.5×10^{-3} M), the absorption at 380 nm due to the bisisoimide group reached the maximum value at about 10 s, followed by isomerization to the bisimide group in less than 1 min.

With this base, less steric crowding allows the acylammonium ion to form much more easily, resulting in very fast formation of mixed anhydride, which is quickly converted to polyimide. This result is in constrast to the case with triethylamine, which has difficulty in forming the acylammonium ion due to the steric problem. The GPC result shows that this catalyst does not change the molecular weight or its distribution significantly.

E. Triethylenediamine. This amine is even less sterically hindered than *N*-methylpyrrolidine with a base strength stronger than pyridine but weaker than *N*-methylpyrrolidine. Reaction with this catalyst was also very fast and similar to results obtained with *N*-methylpyrrolidine. The reaction was complete in less than 1.5 min. In situ monitoring supported similarly fast formation of the bisisoimide group and its conversion to bisimide group as in *N*-methylpyrrolidine. Again, a similar GPC result was obtained as in the case of *N*-methylpyrrolidine.

Acknowledgment. We acknowledge the financial support of this work by the National Science Foundation (Grant DMR 8703908), the Army Research Office (Contract DAA L03-89-K-0081), the Office of Naval Research, and NASA (Grant NAG-1-931).

References and Notes

(1) (a) Vinogradova, S. V.; Vygodskii, Y. S.; Vorobev, V. D.; Churochkina, N. A.; Chudina, L. I., Spirina, T. N. Korshak, N. N. *Vysokomol. Soyed.* **1974**, *A16* (3), 506. (b) Sonnett, J. M.; Gannett, T. P. *Plast. Eng. (NY)* **1996**, *36*, 151.

(2) Koton, M. M.; Meleshko, T. K.; Kudryavtsev, V. V.; Nechayev, P. P.; Kamzolkina, T. V.; Bogorad, N. N. *Vysokomol. Soyed.* **1976**, *A18* (7), 1647.

(3) Kailani, M. H.; Sung, C. S. P.; Huang, S. J. *Macromolecules* **1992**, *25*, 3751.

(4) Kailani, M. H. Investigation of the Chemical Imidization Process for Polyimide. Ph.D. Dissertation, The University of Connecticut, 1993.

(5) Mirabella, F. M., Jr.; Harrick, N. J. *Internal Reflection Spectroscopy: Review and Supplement*; Harrick Scientific Corp.: Ossining, NY, 1985; Chapter 1 p 12.

(6) Kailani, M. H.; Sung, C. S. P. *Macromolecules* **1998**, *31*, 5771−5778.

(7) Sviridov, E. B.; Lamskaya, E. V.; Vasilenko, N. A.; Kotov, B. V. Doklady *Akad. Nauk USSR* **1988**, *300* (2), 404; *Chem. Abstr.* **1988**, *109*, 55407n.

(8) Koton, M. M.; Meleshko, T. K.; Kudryavtsev, V. V.; Nechayev, P. P.; Kamzolkina, T. V.; Bogorad, N. N. *Vysokomal. Soyed.* **1982**, *A24* (4), 715; *Chem. Abstr.* **1982**, *97*, 24311f.

(9) Litvineko, L. M.; Kirichenko, A. I. *Dokl. Akad. Nauk USSR*, **1967**, *176* (1), 97. *Chem. Abstr.* **1968**, *68*, 68325u.

(10) Smith, C. D. In *Proceedings of 4th European Technical Symposium on Polyimides and High Performance Polymers*; Abadie, M. T. M., Sillion, B., Eds.; University of Montpellier: Montpellier, France, 1996; 177.

(11) Angelo, R. J.; Golike, R. C.; Tatum, W. E.; Kreuz, J. A. *Proceedings of the Second International Conference of Polyimides*; Society of Plastics Engineers: Brookfield Center, CT, 1985; p 631.

(12) (a) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn and Bacon, Inc., Boston, MA, 1983; p 1270. *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A. Ed.; McGraw-Hill: New York, 1985; Tables 5−8, Section 5.

MA9800966