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Chemical Imidization Study by Spectroscopic Techniques. 1. Model Amic Acids

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ABSTRACT: UV−visible spectroscopy and H NMR spectroscopy were used to investigate the kinetics and the mechanisms of the chemical imidization for low molecular weight model monoamic acid and bisamic acid. Acetic anhydride and pyridine were used as the dehydrating mixture. The reaction was found to proceed by simultaneous formation of imide and isoimide through a mixed anhydride intermediate. The isomerization of isoimide to imide was found to take place only after the amic acid starting material has been completely consumed. The isomerization was very sensitive to the solvent's (NMP) exposure to humidity. In humidity-exposed NMP, the isomerization was very slow, while it occurred at a much faster rate in dry NMP. The main reason for the humidity effect on isomerization is due to the hydrogen bonding of the acetate ion (a final byproduct) by water, making the acetate ion a weak catalyst. A high concentration of the mixed anhydride was detected by H NMR during in-situ monitoring of reaction in 50/50 deuterated DMSO/deuterated toluene mixture. This result indicates that the rate-limiting step of the reaction to be the deprotonation of the mixed anhydride rather than the formation of the mixed anhydride. This result also provides the explanation for the kinetic deviation observed in the UV−visible experiment when a high concentration of amic acid was used as the starting material.

Introduction

Polyimides that are important high-performance polymers can be made by either thermal imidization or by chemical imidization, starting from poly(amic acids).[1] Thermal imidization has been extensively characterized for its kinetics and mechanisms.[2,3] In chemical imidization, cyclization is facilitated by using a dehydrating agent, such as aliphatic acid anhydride in combination with a base catalyst under mild conditions.

While chemical imidization has many advantages over thermal imidization, such as a faster conversion to polyimides, the maintenance of mechanical strength, and the shape integrity of the product, the reaction mechanisms are not clearly understood. There are conflicting reports as to how the reaction proceeds. Some suggested that the amic acid is first cyclized to isoimide, which isomerizes to the desired imide through consecutive reactions.[4] Others suggested that the reaction proceeds by the simultaneous formation of imide and isoimide and that the isoimide isomerizes to imide via a slow equilibrium reaction.[5] There is also another suggestion for the independent routes for the formation of both imide and isoimide.[6] These various reports are in part due to the difficulty in gathering fast kinetic information during chemical imidization. Furthermore, the experimental factors such as the type of solvent, temperature, the concentration of amic acid, and the composition of the imidizing mixture (dehydrating agent and catalyst) may be factors influencing the course of the reaction.

More recently, Smith et al. used fluorine-19 NMR to distinguish between different imidization products during chemical imidization in NMP and compared the effect of different base catalysts on the imidization process.[5b,c] However, fluorine-19 NMR technique applies only to fluorinated aromatic compounds.

To investigate the kinetics and the mechanisms of chemical imidization, UV−visible spectroscopy and NMR techniques have been applied in this study for the monoamic acid and bisamic acid. In the following paper, we will describe the chemical imidization of poly (amic acid) as a function of concentration, temperature, catalyst structure, and base strength. In our previous studies[3,7] to characterize various reactions involved during thermal and chemical imidization, several model compounds have been synthesized and characterized from 1,5-diaminonaphthalene (DAN) and phthalic anhydride. UV−visible and fluorescence spectral data were used to carefully investigate thermal imidization. In addition, some results of the chemical imidization of polyamic acid at one concentration using an acetic anhydride−pyridine mixture were reported.[7]

Experimental Section

Solvents and Reagents. The following materials were purchased from Aldrich with the specified purity: 1-methyl-2-pyrrolidinone (NMP, 99+% HPLC grade), trifluoroacetic anhydride (99+%), triethylamine (99+%), pyridine (99+%), and acetic anhydride (99+%). 1,5-Diaminonaphthalene (DAN, ≥98 to purity) was purchased from Fluka Chemical.

Purification and Special Handling. DAN from Fluka Chemical was recrystallized from acetone−petroleum ether, followed by sublimation. HPLC grade NMP from Aldrich was dried over 4D molecular sieves, vacuum distilled over P_2O_5, and stored under dry argon. To avoid moisture contamination during distillation of NMP, special care was taken as described in ref 8.

Synthesis of Model Compounds. Due to the limited solubility of the diamic acid compound in NMP, monofunctional amic acid, synthesized from DAN and phthalic anhydride, and the corresponding reaction products were synthesized and characterized, according to the general scheme, Scheme 1. They are given (from the top) in Scheme 1 as *N*-(1-naphthyl)phthalamic acid (**1**), its sodium salt (**2**), *N*-(1-naphthyl)phthalimide (**3**), *N*-(1-naphthyl)phthalisoimide (**4**),

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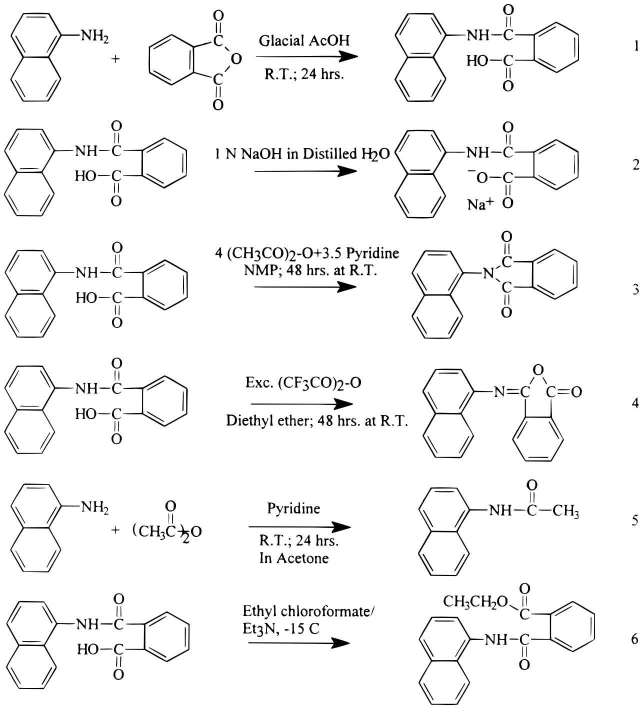
Scheme 1. Synthetic Reactions Used to Obtain Monofunctional Compounds



N-(1-naphthyl)acetamide (**5**) and the ethyl ester of *N*-(1-naphthyl)phthalamic acid (**6**).

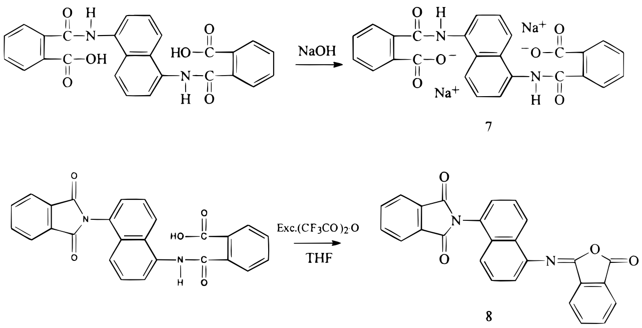
(1) *N*-(1-Naphthyl)phthalamic Acid. To a 1-naphthylamine (5.93 g) solution in 200 mL of glacial acetic acid was added 7.37 g of phthalic anhydride. After the reaction was stirred overnight, the precipitate was vacuum filtered and rinsed with glacial acetic acid until little color could be extracted. The precipitate was rinsed with 200 mL of distilled water before drying under vacuum at room temperature for 9 days. It was further purified by recrystallization from refluxing absolute ethanol, rinsed with petroleum ether, and vacuum-dried to yield fluffy needle-shaped white crystals. DSC shows a melting endotherm at 200 °C. This material was pure by H NMR and IR. The UV spectrum in distilled NMP shows an absorption peak at 296 nm with an extinction coefficient of 8860 L/(mol cm). No fluorescence was observed in NMP.

(2) Sodium Salt of *N*-(1-Naphthyl)phthalamic Acid. This was prepared by adding 1.156 g (3.94 mmol) of *N*-(1-naphthyl)phthalamic acid to 4 mL of distilled water, followed by 4 mL of 4 N sodium hydroxide (16 mmol solution). The sodium salt was precipitated by dropwise addition of the solution to 200 mL of acetone and was vacuum filtered and rinsed with two 100 mL batches of fresh acetone. The UV spectrum shows a red shift from 296 nm for the amic acid to 316 nm. No fluorescence was observed in NMP. The IR spectrum shows ionized amic acid bands, similar to those observed for the sodium salt of bisamic acid. The DSC thermogram is similar to that of the sodium salt of bisamic acid, and this compound does not show melting behavior, which is typical for ionic salts of alkali metals.[9]

(3) *N*-(1-Naphthyl)phthalimide. This was made by chemical imidization of *N*-(1-naphthyl)phthalamic acid. First 0.30 mL (3.65 mmol) of pyridine and 0.40 mL of acetic anhydride (4.18 mmol) were added to 0.152 g (0.522 mmol) of recrystallized *N*-(1-naphthyl)phthalamic acid, and reacted for 7 days at room temperature. The imide was precipitated in 200 mL of vigorously stirred distilled water, filtered, and vacuum-dried. H NMR, DSC, and FTIR show this material to be pure. The DSC thermogram shows a sharp melting endotherm at 180 °C. The UV spectrum has an absorption maximum at 281 nm with an extinction coefficient of 10400 L/(mol cm). No fluorescence was observed in NMP.

(4) *N*-(1-Naphthyl)phthalisoimide. To 0.168 g (0.58 mmol) of recrystallized *N*-(1-naphthyl)phthalamic acid were added 8 mL of anhydrous diethyl ether and 2.0 mL (14.2 mmol) of trifluoroacetic anhydride, and they were reacted for 48 h. The yellow precipitate was rinsed twice with 5 mL batches of petroleum ether and then dried under dry argon and under vacuum for 24 h. H NMR, FTIR, and DSC showed the product to be pure. The DSC thermogram shows a sharp melting endotherm at 131 °C. The UV spectrum in distilled NMP shows an absorption maximum at 367 nm with an extinction coefficient of 8390 L/(mol cm). No fluorescence was observed.

Scheme 2. Synthetic Reactions Used to Obtain New Difunctional Compounds



(5) *N*-(1-Naphthyl)acetamide. First, red impurities from 1-naphthylamine were removed by washing with acetone. The colorless crystalline 1-naphthylamine (0.15 g) in 5 mL of acetone was reacted by the addition of 0.5 mL of pyridine and 1.0 mL of acetic anhydride overnight. The excess solvent and reagents were removed under vacuum to give white needles. H NMR and DSC confirmed the purity. This amide shows a UV absorption peak at 297 nm and a weak fluorescence emission at 357 nm, with about 3% of the fluorescence intensity in comparison to 1-naphthylamine. A DSC thermogram shows a sharp melting endotherm at 158 °C.

(6) Ethyl Ester of *N*-(1-Naphthyl)phthalamic Acid. The procedure used for this compound was based on a method by Cotter et al.[10] but slightly modified. To 0.768 g of *N*-(1-naphthyl)phthalamic acid in 10 mL of chloroform was added 0.38 mL of triethylamine. After two drops of methanol were added and the reaction was cooled to −15 °C, 0.95 mL of ethyl chloroformate was added in small increments over a 30 min period. After overnight stirring and filtering to remove precipitate (presumably triethylammonium hydrochloride), the product was obtained by precipitating the filtrate in 40 mL of anhydrous diethyl ether. The H NMR spectrum confirmed the structure of this compound by the correct integration ratio between aromatic and ethyl aliphatic protons. An FT IR spectrum shows bands characteristic of ester and amide groups. A DSC thermogram shows a sharp melting peak at 132 °C. The UV spectrum shows an absorption maximum at 295 nm, which is similar to that of *N*-(1-naphthyl)phthalamic acid and *N*-(1-naphthyl)acetamide.

For bis-functional model compounds, most of their syntheses and characterization have already been published.[7] Two additional bis-functional model compounds such as imide-isoimide and the sodium salt of bisamic acid (**7**) and imide−isoimide **8** were synthesized as illustrated in Scheme 2.

(7) Sodium Salt of Bisamic Acid of 1,5-Naphthalene. A 1.156 g (3.94 mmol) sample of bisamic acid in 4 mL of distilled water was dissolved by adding 3.0 mL of 4 N NaOH (12 mmol). Dropwise addition of this solution to 250 mL of acetone resulted in a white precipitate which was vacuum filtered, washed with acetone, and vacuum-dried. The FT-IR spectrum supported the structure. The NMR spectrum could not be obtained due to insolubility. The UV spectrum shows a red shift from the bisamic acid parent compound to 341 nm. No fluorescence was observed. A DSC thermogram did not show melting, which is typical for the ionic salts of alkali metals.[9]

(8) 1-(Phthalimido)-5-(phthalisoimido)naphthalene. To a few milligrams of imide−amic acid compound[7] in a glass vial were added 5 mL of anhydrous diethyl ether and 0.5 mL of trifluoroacetic anhydride. After 3 days, the remaining volatile components were evaporated under a stream of dry nitrogen, and the resulting yellow product was dried under vacuum for 24 h. The UV−visible spectrum shows a long absorption typical of isoimides with a peak maximum at 365 nm.

Chemical Imidization Procedure. Two different experimental procedures were used; one (procedure A) with exceptional care given with regard to the reagent's exposure to humidity, the second (procedure B) with less precautionary measures. Exposure of the solvent used to humidity was found to have a significant influence on the course of the kinetic studies, as will be mentioned in later sections of this paper. The solvent (*N*-methyl-2-pyrrolidinone (NMP)) was always vacuum distilled over P_2O_5 in order to remove impurities in the commercial material which caused the absorption peak in the UV−vis spectrum of the bisamic acid model compound to be red shifted from 318 to 340 nm, if the impurities (most probably amine compounds) were not removed by vacuum distillation over P_2O_5. Since the stored distilled solvent was observed to have the tendency to develop this behavior over time (especially if stored over molecular sieves, which prevented us from doing so), we always checked the UV−vis spectrum of bisamic acid before using the distilled solvent in kinetic studies, as a precautionary measure.

Procedure A. The solvent used was vacuum distilled over P_2O_5 and was prevented from contact with atmospheric air/humidity sources using special conditions which included the following. (1) The internal surfaces of all glassware used to make the vacuum distillation apparatus (and subsequent storage of the distilled solvent in the receiving flask) were dried at 240 °C for at least 6 h, to get rid of absorbed water molecules on the internal surfaces of the glassware, and were prevented from direct contact with atmospheric air by connecting the distillation apparatus while hot, one piece at a time in such a manner that dry argon gas prevented atmospheric air from contacting the inner surfaces while they were cooling. The distillation setup was kept under a positive pressure of dry argon gas while it was loaded, and at the end of the distillation the vacuum was released with dry argon gas. The distilled solvent was stored in the receiving distillation flask under dry argon gas, and when used, the storage flask was kept under a steady stream of argon gas. This procedure was also applied to other reagents used (acetic anhydride, pyridine). Glasswares used, such as the reaction flask and glass pipets used to draw solvent to perform the kinetic studies, were also dried in an oven and stored in a desiccator filled with Drierite and filled with dry argon gas, until used. The argon gas used was dried by passing through a Drierite gas-drying unit ($2\,^{5}/_{8}$ in. o.d. × $11\,^{3}/_{8}$ in.) purchased from Fisher Scientific. Thus the sources of humidity contamination were carefully reduced.

Procedure B. The commercial solvent (HPLC grade) was vacuum distilled over P_2O_5 in clean glassware which had been dried in an oven and left to cool under the atmospheric conditions. After the vacuum distillation was complete, the vacuum in the distillation apparatus was released with atmospheric air passing through a Drierite trap. The distilled solvent was poured under atmospheric conditions into a brown glass bottle for storage. When the solvent was used for the kinetic studies and as a solvent for diluting the aliquots taken from the reaction mixture to monitor the reaction by UV−vis spectroscopy, no precautionary measures were taken to prevent the atmospheric air from entering the bottle. Thus the solvent was exposed to humidity.

As for chemical imidization procedures, different procedures were used for different concentrations. Dilute solutions were monitored directly by UV−visible spectroscopy of the reaction mixture in a cuvette with a 1.0 cm path length. For more concentrated solutions, aliquots were taken and diluted in solvent at regular time intervals. Most experiments were performed at 38 °C and in 0.212 M acetic anhydride and 0.185 M pyridine using NMP as a solvent. The details of the imidization procedure is described in the ref 8.

H NMR Spectroscopy. Since NMP has strong H NMR signals, experiments were performed either in 50/50 deuterated toluene/deuterated DMSO mixed solvent or in pure deuterated DMSO. DMSO was used as received. The reaction mixture was prepared by mixing 0.5 mL of the dehydrating mixture (composed of 0.424 M of acetic anhydride and 0.371 M of pyridine) and 0.5 mL of *N*-(1-naphthyl)phthalamic acid (0.06 M). After mixing, the NMR tube containing the mixed solution was quickly placed in the 270 MHz instrument. The concentration in the solution for acetic anhydride, pyridine and amic acid corresponds to 0.212, 0.185, and 0.030 M, respectively. Amide protons were quantified by weighing the peak areas.

Table 1. UV−Visible Absorption Maxima in NMP for Model Compounds

compound (no. in Scheme 1 or 2)	abs max (nm)
monoamic acid (**1**)	296
sodium salt of monoamic acid (**2**)	316
monoimide (**3**)	281
monoisoimide (**4**)	367
1-naphthylacetamide (**5**)	297
ethyl ester of monoamic acid (**6**)	295
disodium salt of diamic acid (**7**)	341
imide−isoimide (**8**)	295 and 361
1-naphthylamine	336

Table 2. Amide H NMR Chemical Shifts (in ppm) in Deuterated DMSO for Monofunctional Model Compounds

compound (no. in Scheme 1)	chemical shift (ppm)
monoamic acid (**1**)	10.39
sodium salt of monoamic acid (**2**)	7.75 and 7.98
1-naphthylacetamide (**5**)	9.93
ethyl ester of monoamic acid (**6**)	10.47

Table 1 summarizes the UV−visible absorption maximum of monofunctional and bisfunctional model compounds in NMP at room temperature. Table 2 summarizes the H NMR results for the amide proton chemical shifts for monofunctional model compounds in deuterated DMSO.

Results and Discussions

To understand chemical imidization mechanisms for polyamic acid, it is useful to start out with a low molecular weight amic acid. Even though bisamic acid and its intermediate species closely resemble the reaction species formed during chemical imidization of polyamic acid, the limited solubility of bisamic acid does not allow it to be studied in a concentration equivalent to even 1 wt % of polyamic acid solution. Therefore, monoamic acid and its derivations were synthesized and characterized as summarized in Tables 1 and 2 for UV−visible spectral maximum and proton NMR chemical shifts.

In the chemical imidization study reported in this paper, all of the reactions were carried out in NMP at 38 °C, with acetic anhydride and pyridine concentrations of 0.212 and 0.185 M, respectively, unless otherwise indicated.

1. Chemical Imidization of a Monoamic Acid, *N*-(1-Naphthyl)phthalamic Acid, by UV−Visible Spectroscopy. Reactions in dry NMP and NMP exposed to ambient air and thus humidity were found to be very different. Therefore, we will first describe reactions in the latter case.

(a) Reactions in NMP Exposed to Ambient Air.[11] The reaction was performed at two amic acid unit concentrations of 5.4×10^{-5} M and 3.0×10^{-2} M. The latter is equivalent to 1.0 wt % of polyamic acid in amic acid unit concentration. The UV−visible spectra during the reaction of 3.0×10^{-2} M solution of the monoamic acid show both an increase in absorption at 367 nm due to the formation of the isoimide and a simultaneous shift of the amic acid band from 296 to 281 nm due to the

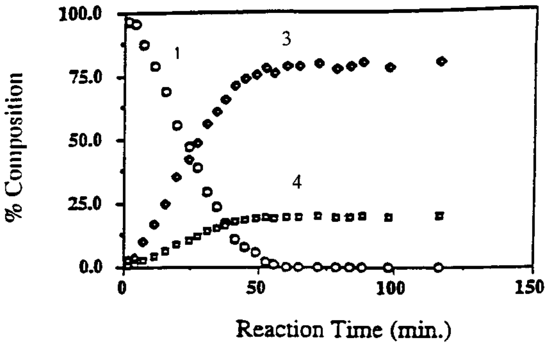


Figure 1. Composition profiles of amic acid (**1**), imide (**3**), and isoimide (**4**) as a function of chemical imidization time from the reaction of *N*-(1-naphthyl)phthalamic acid (3.0×10^{-2} M) at 38 °C in humidity-exposed NMP.

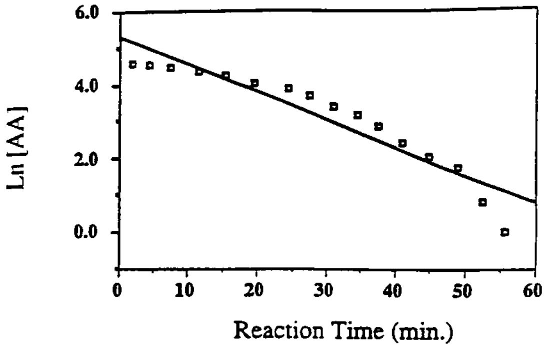


Figure 2. First-order kinetic plot for chemical imidization of 3.0×10^{-2} M *N*-(1-naphthyl)phthalamic acid at 38 °C in humidity-exposed NMP, showing deviation of amic acid composition from first-order kinetics.

formation of the imide. The deconvolution of the UV−visible spectra based on the spectra of the three model compounds of the monoamic acid (compound **1**), the isoimide (compound **4**), and the imide (compound **3**) provided the percent composition of each species as summarized in Figure 1.

Figure 1 shows the consumption of the monoamic acid with simultaneous increase in the imide and the isoimide. The ratio of the imide and the isomide was found to be 4:1 throughout the reaction, consistent with the mechanism of the simultaneous formation of imide and isomide. Since the composition did not change even after a few days of reaction, the reaction can be considered complete when the amic acid is consumed in about 75 min.

The consumption of the amic acid did not fit the pseudo-first-order kinetics which is expected from the large concentration ratio (>10) of acetic anhydride and pyridine to that of amic acid, as can be seen in Figure 2. This trend can be explained in view of the mixed anhydride (amide−anhydride) formed as an intermediate during the reaction (see reaction 3 in Scheme 3). Since the UV spectra for the amic acid is expected to be similar to that of the mixed anhydride, the amic acid composition obtained by UV spectral deconvolution will represent the sum of the actual amic acid and the mixed anhydride, thus being responsible for the deviation. Because the apparent rate constants for this reaction for 3.0×10^{-2} M concentration could not be obtained from Figure 2, the reaction time at which the maximum isoimide concentration is reached will be used as an indicator of the relative speed of the reaction as listed in Table 3.

Chemical imidization in lower concentration (5.4×10^{-5} M) of monoamic acid produced similar UV−visible spectral trends. Deconvolution of the UV−visible spectra based on the three species of the amic acid, the imide, and the isoimide gives a percent composition plot for the reaction, as shown in Figure 3. The results from this lower concentration turn out to follow the simultaneous parallel reaction as illustrated in Scheme 4 with k_1 and k_2 representing the apparent rate constant for the formation of imide and isoimide, respectively. The reason for this trend is explained in a later NMR section, following the discussions of the reaction mechanisms. For such parallel reactions, the following equations can be used:

$$[\text{amic acid}] = \mathrm{e}^{-(k_1+k_2)t}$$

$$[\text{isoimide}] = [k_2/(k_1 + k_2)]\mathrm{e}^{-(k_1+k_2)t}$$

$$[\text{imide}] = [k_1/(k_1 + k_2)]\mathrm{e}^{-(k_1+k_2)t}$$

Also, the ratio of the k_1/k_2 will be equal to the ratio of the concentration of imide/isomide. The consumption of monoamic acid in this lower concentration reaction was found to follow pseudo-first-order kinetics, as shown by the excellent fit of the plot of log [amic acid] vs reaction time. Its slope gives ($k_1 + k_2$). The rate constants k_1 and k_2 determined for a 5.4×10^{-5} M amic acid concentration are listed in Table 4 for the reaction at 38 °C as well as at 30 and 47 °C. The activation energy for the imide formation is 13.5 kcal/mol while 17.5 kcal/mol is found for isoimide formation. These values are comparable to those reported in the earlier literature.[5] In this low concentration, the conversion of isomide to imide in humidity-exposed NMP was not observed even in longer time scales.

(b) Reactions in Dry NMP. When care was taken to prevent ambient air from coming in contact with the solvent (NMP), the isomide absorption at 367 nm decreases due to isomerization to imide in the second stage of the reaction. In the first stage, the simultaneous formation of isoimide and imide in this concentration (1.5×10^{-2} M) was analgous to the preceding case of 3.0×10^{-2} M where NMP was exposed to ambient air. The deconvolution of the UV−visible spectra provides the percent composition as a function of reaction time as shown in Figure 4, which is consistent with the trends described from the spectra. The parallel reaction from the amic acid to isoimide and imide does not follow pseudo-first-order reaction kinetics, as in the humidity-exposed NMP case for a similar concentration. The time for the maximum isoimide formation is also used as an indicator of the relative speed of the reaction in this case, as listed in Table 3. Comparison of the time required for maximum isoimide formation in Table 3 indicates that the reaction in dry solvent is about twice as fast as the reaction in humidity-exposed solvent. The isomerization of isoimide to imide in dry solvent obeys first-order kinetics with the rate constant listed also in Table 3.

2. Chemical Imidization of Bisamic Acid in Humidity-Exposed NMP by UV−Visible Spectroscopy. Due to the limited solubility of this compound, only one concentration was studied. The UV−visible spectra during the reaction of 8.0×10^{-5} M diamic acid solution show both an increased absorption at 380 nm due to the formation of the bisisoimide and a simulta-

Scheme 3. Proposed Reaction Mechanism

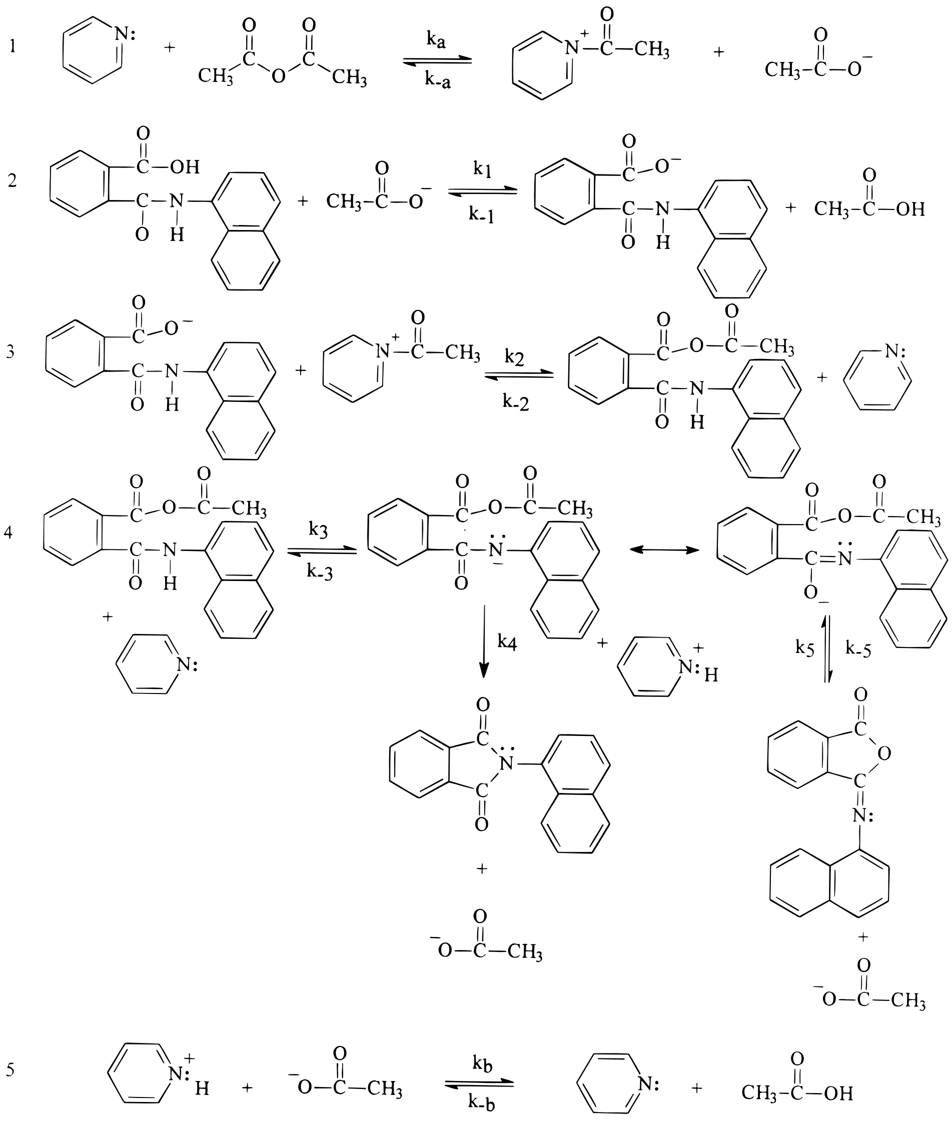


Table 3. Apparent Rate Constants[b] and the Times To Reach the Maximum Concentration of Isoimide, for Chemical Imidization of *N*-(1-Naphthyl)phthalamic Acid in Both Humidity-Exposed and Dry NMP[a]

amic acid concn ($\times 10^{-5}$ M)	time for max isoimide (min)	app rate constant $k_1 + k_2$ (min.$^{-1}$)	app rate constant k_3 (min.$^{-1}$)
	Air-Exposed Solvent		
5.4	≈75	6.02×10^{-2}	*c*
3000	≈75		*c*
	Dry Solvent		
1500	≈30		9.2×10^{-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] Definitions of k_1 and k_2 are shown in Scheme 4. k_3 is the rate constant for isomerization of isoimide to imide. [c] Isomerization too slow to be observed even after a few days.

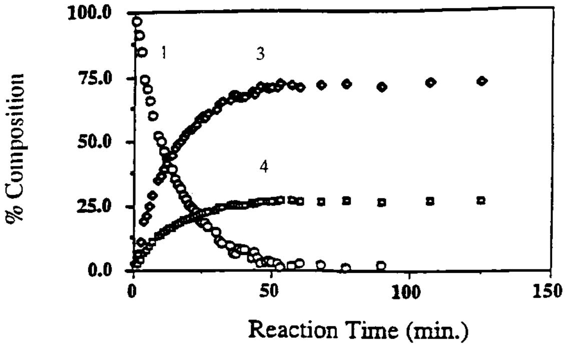


Figure 3. Composition profiles of amic acid (**1**), imide (**3**), and isoimide (**4**) as a function of chemical imidization time from the reaction of *N*-(1-naphthyl)phthalamic acid (5.4×10^{-5} M) at 38 °C in humidity-exposed NMP.

neous shift of the bisamic acid absorption band from 318 to 289 nm due to the formation of the bisimide. The deconvolution of the spectra using the spectra of the bisamic acid, the bisimide, and the bisisoimide provides a percentage composition plot as shown in Figure 5. This figure shows consumption of the bisamic acid with simultaneous increases in both bisimide and bisisoimide. The ratio of bisimide to bisisoimide was 3:1, which does not change during the reaction.

It was found that the results fit nicely with parallel pseudo first-order kinetics at this concentration, a trend similar to the monoamic acid reaction in a similar concentration. The rate constants, k_1 and k_2, are listed in Table 5 for 38 °C reaction, as well as at 30 and 47 °C reactions. Higher temperature resulted in both faster bisisoimide formation (k_2) and higher bisisoimide concentration at the end of the reaction. Isomerization of bisisoimide to bisimide was not observed within a few

Scheme 4. Simplified Mechanistic Scheme Describing the Chemical Imidization of *N*-(1-Naphthyl)phthalamic Acid at a Concentration of 5.4×10^{-5} M, Using Acetic Anhydride Pyridine Mixture in Humidity-Exposed NMP

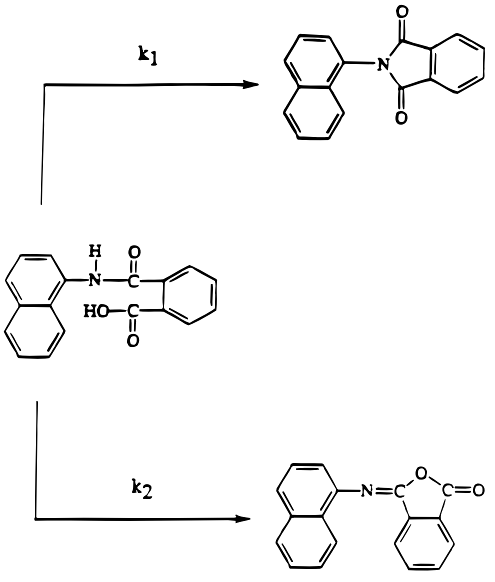


Table 4. Kinetic Parameters[b] for Chemical Imidization of *N*-(1-Naphthyl)phthalamic Acid (5.4×10^{-5} M) in Humidity-Exposed NMP[a]

temp (°C)	k_1 (min^{-1} × 10^2) for imide	k_2 (min^{-1} × 10^2) for isoimide	k_2/k_1
30	2.71	0.78	0.29
38	4.28	1.74	0.40
47	8.78	3.61	0.41
E_a (kcal/mol)	13.5	17.5	

[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] Definitions of k_1 and k_2 are shown in Scheme 4.

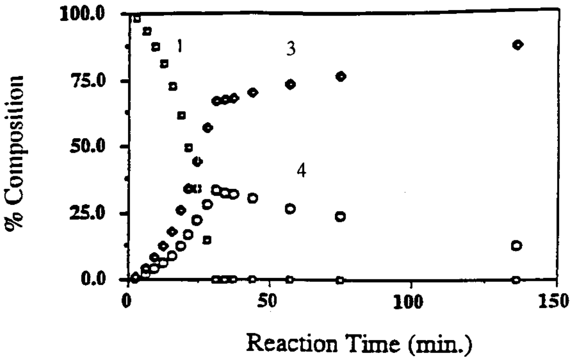


Figure 4. Composition profiles of amic acid (**1**), imide (**3**), and isoimide (**4**) as a function of chemical imidization time at 38 °C for the reaction of *N*-(1-naphthyl)phthalamic acid in dry NMP.

days of the reaction. The activation energy of 13.9 kcal/mol for bisimide formation and 15.7 kcal/mol for bisisoimide formation are similar to those observed for imide and isoimide formation starting from monoamic acid.

3. Proposed Reaction Mechanism. A detailed mechanistic scheme for acetic anhydride/pyridine induced chemical imidization is shown in Scheme 3, which is expanded from a mechanism proposed by Harris.[12] Reaction 1 in this scheme, the formation of acylpyridinium ion, was confirmed to be a very important step from a study of the effect of catalyst structure and base strength, as will be described in the following paper. As can be seen, this overall scheme, Scheme 3, contains several acid−base equilibria. The position of the various equilibria involved and hence the active species in the reaction can be estimated from the relative acidities of the individual species present in the solvent.

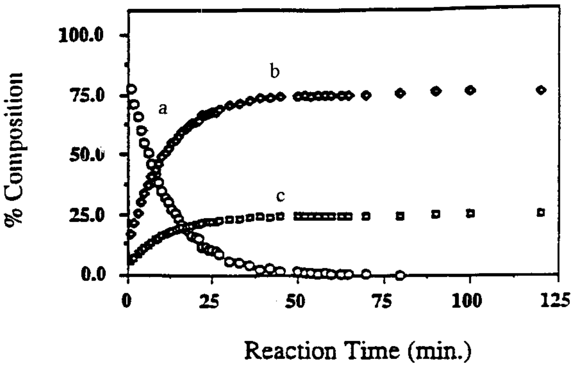


Figure 5. Composition profiles of bisamic acid (a), bisimide (b), and bisisoimide (c) as a function of chemical imidization time for the reaction of bisamic acid model compound at 38 °C in humidity-exposed NMP.

Table 5. Kinetic Parameters[b] for Chemical Imidization of Diamic Acid (8.0×10^{-5} M) in Humidity-Exposed NMP[a]

temp (°C)	k_1 (min^{-1} × 10^2) for imide	k_2 (min^{-1} × 10^2) for isoimide	k_2/k_1
30	3.64	1.06	0.29
38	6.19	2.03	0.33
47	12.2	4.19	0.34
E_a (kcal/mol)	13.9	15.7	

[a] Concentrations of acetic anhydride and pyridine for all reactions are 0.212 and 0.185 M, respectively. [b] Definitions of k_1 and k_2 are shown in Scheme 4.

Amic acid is a stronger acid (pk_a = 8.8 in DMF)[13] in comparison to the acetic acid (pk_a = 13.5 in DMF),[13] which is formed at the end (reaction 5) of Scheme 3. Therefore, the acidity of the reaction will be mostly determined by the concentration of the amic acid at the start of the reaction. In dipolar aprotic solvents such as NMP, acetic acid becomes a much weaker acid due to the poor solvation of the negative acetate ion which is normally solvated by H-bonding. Therefore, such an acid is normally present as undissociated in dry NMP. In humidity-exposed NMP, the acetate ion is H-bonded. Acylpyridinium ion formation is enhanced in the presence of high acid concentration, as supported by Fersht and Jencks.[14] Since amic acid is a much stronger acid than acetic acid, reaction 2 in Scheme 3 occurs where the acetate ion is protonated by amic acid. As a consequence, the reverse reaction 1 in Scheme 3 with k_{-a} is reduced. The presence of high concentration of acylpyridinium ion with the amic acid conjugate ion causes the reaction to generate the mixed anhydride in reaction 3 in Scheme 3. Reaction 3 in Scheme 3 is particularly favorable in the presence of higher amic acid concentration.

When the mixed anhydride is deprotonated in reaction 4 in Scheme 3, two different resonance structures are obtained for the resulting mixed anhydride anions, as can be seen in the right side of reaction 4 in Scheme 3. Intramolecular attack by the negatively charged nitrogen in the anion result in imide formation with the rate constant of k_4, while the attack by the oxygen

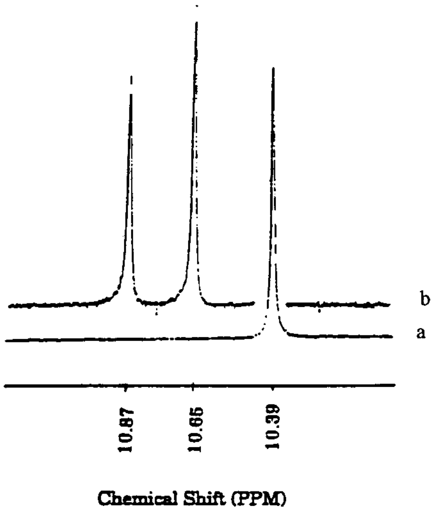


Figure 6. H-NMR spectra showing amide N−H peaks for (a) 3.0×10^{-2} M *N*-(1-naphthyl)phthalamic acid solution in deuterated DMSO and (b) the first spectrum of reaction mixture obtained after 7.5 min of chemical imidization at room temperature.

results in isoimide formation with the rate constants k_5 and k_{-5}. Since negatively charged nitrogen is a better nucleophile than negatively charged oxygen, imide formation is favored. This explained why the product ratio of imide/isoimide was found to be about 4/1 to 3/1. The acetate ion generated by the cyclization reactions in reaction 4 is quickly protonated when amic acid starting material is still present during the reaction, therefore preventing the reverse reaction from taking place. After amic acid has been consumed, acetate ion is generated from acetic acid ionization according to reaction 5 in Scheme 3. The imide group is chemically stable toward acetate ion attack. However, acetate ion is capable of attacking isoimide (reaction characterized by k_{-5} in reaction 4 in Scheme 3) at the carbonyl group to regenerate the mixed anhydride anion, which is cyclized to the more stable imide group. This occurs when the conditions for such attack are favorable such as when no amic acid starting material is present, or in dry solvent. In humidity-exposed NMP, the acetate ion may be stabilized by H-bonding by the water present, thus reducing its ability to attack the isoimide to be converted to imide. This may explain why the isomerization was observed as described in the previous section when discussing the reactions in dry NMP reaction.

It is not clear whether the rate determining step for chemical imidization is the formation of the mixed anhydride (reaction 3 in Scheme 3) or the deprotonation of the amide group in the mixed anhydride (reaction 4 in Scheme 3). To clarify this point, we carried out some H NMR experiments, which can follow the formation of the mixed anhydride, separately from the amic acid, since it was not possible to distinguish the mixed anhydride from the amic acid in UV spectra.

4. H NMR Studies for the Amic Acid Reaction. In-situ H NMR experiments were carried out to study the 3.0×10^{-2} M monoamic acid reaction. Figure 6 shows two amide bands at 10.65 and 10.87 ppm in spectrum b, which is obtained after 7.5 min at room temperature reaction in deuterated DMSO. Spectrum a in Figure 6 corresponds to that of the amic acid in deuterated DMSO before adding acetic anhydride and pyridine. The peak at 10.65 ppm was due to amic acid in the chemically imidizing environment, while the peak at 10.87 ppm was assigned to the mixed anhydride by Angelo et al.[6]

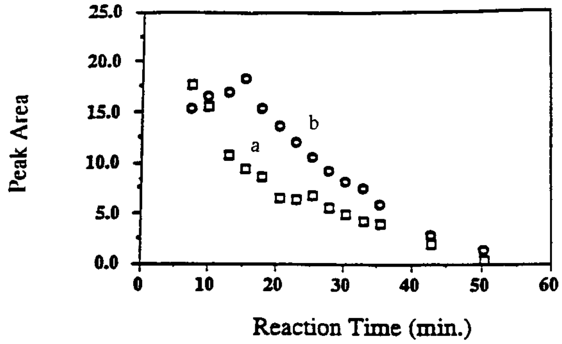


Figure 7. Peak areas during chemical imidization of 3.0×10^{-2} M *N*-(1-naphthyl)phthalamic acid in 50/50 deuterated DMSO/toluene mixture as a function of time at room temperature: (a) peak at 10.65 ppm; (b) peak at 10.87 ppm.

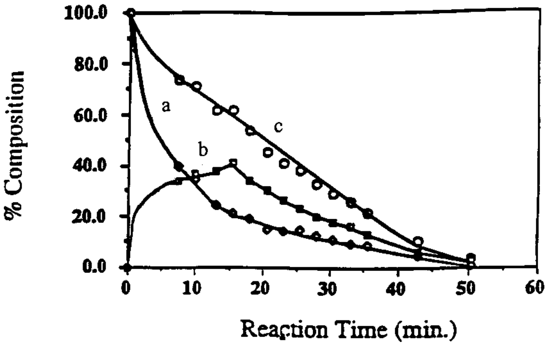


Figure 8. Composition profiles for (a) amic acid, (b) mixed anhydride, and (c) the sum of amic acid and anhydride during chemical imidization of 3.0×10^{-2} M *N*-(1-naphthyl)phthalamic acid in 50/50 deuterated DMSO/toluene at room temperature as a function of time.

These two peaks are found to change during the reaction, as illustrated in Figure 7, when the reaction was carried out in a 50/50 deuterated DMSO/toluene mixture. This mixture was chosen to approximate the polarity of NMP since DMSO is more polar than NMP. The chemical imidization behavior in this mixture was found to be similar by UV−visible spectroscopy in the composition profiles of intermediate products, such as isoimide as obtained in NMP.

When converted to the percentage composition based in Figure 7, we obtain the composition profiles by NMR such as Figure 8 where the amic acid (curve a), the mixed anhydride (curve b), and the sum of the amic acid and the mixed anhydride (curve c) are plotted as a function of reaction time. The mixed anhydride has a maximum concentration of 40% of the initial amic acid concentration. The build up of this high concentration of the mixed anhydride in 3.0×10^{-2} M solution indicates that its formation is not the rate limiting step in the reaction, suggesting that the deprotonation is likely to be the rate-limiting step.

The sum of the amic acid and the mixed anhydride concentration by NMR is found not to follow pseudo-first-order kinetics, as was the case for the amic acid in UV−visible results. On the other hand, the amic acid composition from NMR peak at 10.65 ppm is found to follow pseudo-first-order reaction kinetics. Therefore, the deviation observed in UV−visible experiments at high amic acid concentration is due to the high concentration of the mixed anhydride. At a low amic acid concentration of 5.4×10^{-5} M, the low acidity caused by the starting amic acid concentration was not enough to cause complicated kinetics, since the reactions were observed to follow pseudo-first-order kinetics.

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