Reactivity of Poly(amic acid) Isomers in Thermal Imidization

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ABSTRACT: The reactivity of isomers of poly(amic acid) prepared from 4,4'-oxydianiline and pyromellitic dianhydride in thermal imidization was investigated both in solution and in solid state at 130°C. FT-NMR was the main tool used to measure the mole fraction of various species formed in partial imidization, using diphenyl pyromellitimic acid as a model compound to verify its applicability. The results were modeled by kinetic equations. It showed that the terephthalamide isomer reacted 4.14 times faster than isophthalamide isomer when imidized in solution. On the other hand, the isophthalamide isomer reacted 3.25 times faster than the terephthalamide isomer when reacted in solid state.

KEY WORDS Poly(amic acid) / Imidization / Kinetics /

Aromatic polyimides have outstanding thermal, electrical and mechanical properties. They are an important class of high-performance polymers, applied extensively in insulation film for electrical equipment and electronic devices, such as flexible printed circuit board and multilevel metallization of LSIs.

Polyimides, in general, show a lack in thermoplasticity and solubility for processing. These materials are usually processed in the form of their precursors, the poly(amic acid)s, in solution, followed by thermal imidization. The reaction kinetics of imidization have been studied extensively.¹⁻¹⁷ Several ideas have been proposed to account for the apparent two-step cyclization, including a two-stage physico-chemical process⁸ in which both the molecular mobility of polymer matrix and the physical state of intrachain groups transformed into the imide rings play an important role, and the nonequivalent kinetic state of amic acid groups. However, it is yet to be possible to decide which, if any, of these ideas is

responsible for the kinetic behavior of imidization since the method used, mostly based on infrared spectroscopy, only provided overall imide ring concentration which cannot distinguish the different species from imidization. Recently, Pyun *et al.*¹⁰ used UV spectroscopy to distinguish the PAI and PII containing conjugated chromophores, and suggested a two-step kinetics to model the imidization reaction.

PAI

PII

In this paper, we used the high resolution FT-NMR spectrometer to characterize the isomeric structures and to investigate the

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reaction kinetics of thermal imidization of a polyamic acid prepared from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA).

EXPERIMENTAL

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), both supplied by TCI of Japan, were purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP) of Merck reagent grade was dried over P_2O_5 and distilled before use.

Poly(amic acid) (PAA) was prepared by dissolving ODA in NMP, followed by the

addition of an equivalent amount of PMDA, added in several portions. The reaction was carried out at room temperature for 4 h under nitrogen. The solid content of the solution was approximately 20%. The inherent viscosity of the prepared PAA was found to be 1.5 dl g^{-1} at a concentration of 0.5 g dl^{-1} in NMP.

A part of the above PAA solution was poured slowly into methanol with stirring. The precipitated PAA was filtered on a sintered glass, washed thoroughly with methanol, then dried under reduced pressure at ambient temperature.

Diphenyl pyromellitic acid (DPPA) was prepared from PMDA and an excess aniline

Figure 1. The NMR spectra of PMDA/ODA poly(amic acid): (a) before imidization; (b) partially imidized in NMP solution; (c) partially imidized in the solid state.

under the same conditions described above.

Partial imidization was proceeded by heating the PAA either in NMP solution or in the solid state at 130°C for a desired period. The specimens, precipitated in methanol in the case of PAA in NMP solution, were dissolved in DMSO-*d*₆ for nuclear magnetic resonance spectral analysis, recorded with a Bruker AM 400 spectrometer.

RESULTS AND DISCUSSION

Characterization of PAA Structure

The reaction of PMDA and ODA produced PAA with repeating units in two isomeric structures, *i.e.*, terephthalamide (**1a**) and isophthalamide (**1b**) shown below:

The amount of **1a** and **1b** in PAA can be analyzed by NMR spectroscopy,^{18,19} wherein H₁ of **1a** and H₂ of **1b** give singlet signals at 7.97 ppm and 8.30 ppm respectively (Figure 1a). From their signal intensities relative to the total intensities of the aromatic protons, it was found that the PAA prepared from PMDA and ODA in NMP solution consisted of repeating units 54% in **1a** structure and 46% in **1b**

Figure 2. The NMR spectra of diphenyl pyromellitic acid: (a) before imidization; (b) partially imidized in NMP solution-soluble fraction.

structure.

Partial Imidization of DPPA

Diphenyl pyromellitic acid was used as a model compound to test the applicability of NMR spectroscopy to the kinetic study on the

thermal imidization of PAAs. Figure 2 shows the NMR spectra of DPPA before (a) and after (b) partial imidization (130°C/20 min). The additional signals appeared in Figure 2b at 8.57 ppm and 8.68 ppm were attributed to H₇ and H₈ of **IIc** shown below:

The signal of H₉ was not observed in the spectrum since **IIc** was insoluble in the solvent used. This signal should be shifted further to the lower field since the imide ring has a stronger influence on the chemical shift of the nucleus protons on PMDA. The influence of the substituents on the chemical shift appeared to be in the following order:

[imides] > imide/carboxyl > imide/amide
> carboxyls > carboxyl/amide > amides

Table I gives the results of DPPA partially imidized in NMP solution at 130°C for 30 min.

The insoluble fraction amounted to 12.83% by weight, which was identified as **IIc** since its infrared spectrum was identical to that of fully imidized DPPA (350°C/2 h). The mole fractions of **IIa** and **IIb** were based on the reduced signal intensities of H₁ and H₂, both normalized for the insoluble fraction. **IIc** was either derived from the normalized signal intensities of H₇ and H₈, which gave a value of 0.198, or from the reduced signal intensity of the amide proton (NH) by the following relationship:

$$\text{IIc} = 2(\text{NH}-\text{H}_1-2\text{H}_2)/(\text{NH})_0 \quad (1)$$

Table I. Partial imidization of diphenyl pyromellitic acid in solution

	Before imidization	Imidized in NMP
(I) Precipitation II d (wt)/DPPA (wt)	0	12.83/100
(II) Soluble fraction signal intensity ^a		
NH	2.0 (NH) ₀	1.77
H ₁	1.0	0.71
H ₂	0.5	0.42
H ₇ + H ₈	0	0.46
Degree of imidization %		
Overall	0	23.97
II a	0	39.00
II b	0	27.84
Mole fraction		
II a	0.5	0.305
II b	0.5	0.361
II c ^b	0	0.198
II c ^c	0	0.189
II d ^d	0	0.141
II d ^e	0	0.145

^a Signal intensity was based on the total intensity of the aromatic protons as 12.

^b Based on the normalized signal intensity of H₇ and H₈.

^c Calculated from eq 1.

^d Based on the normalized weight of precipitation.

^e Calculated from eq 2.

which gave a value of 0.189. The mole fraction of **II**d was obtained from the insoluble fraction, which gave a value 0.141, against a value of 0.145 calculated by the following equation:

$$\text{II}d = 1 - (\text{II}a + \text{II}b + \text{II}c) \quad (2)$$

in which **II**c was calculated from eq 1. A good agreement of the results showed the applicability of NMR spectroscopy to the imidization reactions of PAAs derived from PMDA.

Partial Imidization of PAA

The poly(amic acid) prepared from PMDA and ODA was partially imidized either in NMP solution (20%) or in the solid state at a temperature of 130°C for a duration of

Table II. Relative reactivity of PAA isomers in partial imidization

	PAA (PMDA/ODA)	Imidized in NMP solution	Imidized in solid state
Signal intensity ^a			
NH	1.98	1.56	1.58
H ₁	1.08	0.61	0.91
H ₂	0.46	0.40	0.27
Degree of imidization			
Overall		21.2%	20.2%
I a		43.5%	15.7%
I b		13.0%	41.3%
Mole fraction			
I a	0.54	0.305	0.455
I b	0.46	0.400	0.270
I c	0	0.150	0.130
I d	0	0.145	0.145

^a Signal intensity was based on the total intensity of the aromatic protons as 10.

approximately 0.5 h. The results from NMR spectral analysis are given in Table II. The signal intensities were based on the total intensities of the 10 aromatic protons in each repeating unit. The overall degree of imidization was based on the reduction in signal intensity of the amide protons, and the degrees of imidization of **I**a and **I**b were based on the reduction in signal intensity of H₁ and H₂ as shown in Figures 1b and 1c. Since the signals of H₇, H₈, and H₉ were not well resolved in the spectrum, the mole fraction of **I**c was derived from eq 1, and that of **I**d from eq 2.

Unlike the results obtained from the model compound, where the two isomers, **II**a and **II**b, showed a slight difference in reactivity in partial imidization, a much greater difference in reactivity between the isomers was observed from the PAA. And their reactivities in solution were diagonally opposite to that in the solid state.

Partial imidization of the PAA was also carried out in *N,N*-dimethylacetamide (DMAc) solution. The result was comparable to that obtained in NMP solution. The amide solvents

form hydrogen bonds with the PAA. However, these hydrogen bonds are broken in the temperature range of 60–80°C.¹⁹ The nature of the solvent is not expected to play any important role in the imidization reactions. Therefore, the observed differences in reactivity between the isomers in solution and the isomers in the solid state must be resulted from their differences in chain conformation, although its exact mechanism is yet to be understood.

Kinetics of Imidization

Kinetic study on the imidization of PAA (PMDA/ODA), both in NMP solution and in the solid state, was carried out at 130°C for a duration of 1 h, sampled at intervals of every 6 min. The maximum degree of imidization was about 40%. Beyond that the samples became insoluble in DMSO. The data from NMR spectral analysis were treated as follows:

Case 1. Imidization was considered as first-order reactions. All the reactions were irreversible. The effect of end groups and side reactions were negligible. The reaction scheme is shown below:

Where **Ia**, **Ib**, **Ic**, and **Id** represent the mole fraction of each structural unit in the partially

imidized specimen. The above reaction scheme gave the following kinetic equations:

$$-d[\text{Ia}]/dt = 2k_1[\text{Ia}] \quad (3)$$

$$-d[\text{Ib}]/dt = 2k_2[\text{Ib}] \quad (4)$$

$$d[\text{Ic}]/dt = 2k_1[\text{Ia}] + 2k_2[\text{Ib}] - k_3[\text{Ic}] \quad (5)$$

where k_1 , k_2 , and k_3 are the rate constants. Integration of the above equations to give:

$$[\text{Ia}] = [\text{Ia}]_0 \times \text{Exp}(-2k_1t) \quad (6)$$

$$[\text{Ib}] = [\text{Ib}]_0 \times \text{Exp}(-2k_2t) \quad (7)$$

$$[\text{Ic}] = [\text{Ia}]/(k_{31}-1) + k_{21}C_1[\text{Ia}]^{k_{21}} / (k_{31}-k_{21}) + C_2[\text{Ia}]^{k_{31}} \quad (8)$$

where $[\text{Ia}]_0$ and $[\text{Ib}]_0$ are the initial mole fractions of **Ia** and **Ib**. C_1 and C_2 are constants, $k_{21} = k_2/k_1$, and $k_{31} = k_3/2k_1$.

The values of $[\text{Ia}]_0$, $[\text{Ib}]_0$, $[\text{Ia}]$, $[\text{Ib}]$, and $[\text{Ic}]$ were obtained from spectral analyses. Equations 6, 7, and 8 can be solved by the non-linear least square method with the 10 sets of experimental data. The results are given in Table III.

Case 2. Water formed from imidization reactions was retained in the system, which caused hydrolysis of the imides, *i.e.*, the reaction became reversible.

A similar treatment of the experimental data gave the results shown in Table IV. The rate constant of the reverse reactions was several orders lower than the corresponding rate constant of the forward reaction. In practice,

Table III. Rate constants for irreversible thermal imidization of PMDA/ODA

	Imidization in solution	Imidization in solid state
k_1 / min^{-1}	0.00939	0.00271
k_2 / min^{-1}	0.00227	0.00882
k_3 / min^{-1}	0.04042	0.04976
C_1	0.53405	3.40905
C_2	-1.9881	-88.51043
$t_{1/2}$, Ia	73.8 min	255.7 min
$t_{1/2}$, Ib	305.3 min	78.6 min

Table IV. Rate constants for reversible thermal imidization of PMDA/ODA

	Imidization in solution	Imidization in solid state
k_1 / min^{-1}	$9.81 \cdot 10^{-3}$	$2.65 \cdot 10^{-3}$
$k_{-1} / \text{min}^{-1} \text{ mol}^{-1}$	$2.35 \cdot 10^{-6}$	$4.73 \cdot 10^{-6}$
k_2 / min^{-1}	$2.51 \cdot 10^{-3}$	$8.76 \cdot 10^{-3}$
$k_{-2} / \text{min}^{-1} \text{ mol}^{-1}$	$2.61 \cdot 10^{-6}$	$8.25 \cdot 10^{-6}$
k_3 / min^{-1}	$4.21 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$
$k_3 / \text{min}^{-1} \text{ mol}^{-1}$	$5.65 \cdot 10^{-6}$	$1.02 \cdot 10^{-7}$

water formed from imidization would be evaporated, at least partly, at the experimental temperature. The mole fraction of the various species, calculated from the kinetic equations and indicated by the solid curves in Figure 4, showed greater variations from the experimental data as compared to those shown in Figure 3. Thus for all practical purpose, imidization of PAAs can be regarded as irreversible reactions.

The dotted lines in Figures 3 and 4 are calculated from the rate constants. They are not expected to have much significance since vitrification will take effect at higher degrees of imidization.

From the results given in Table III, k_1 had a value of 0.00939 min^{-1} which was 4.14 times that of k_2 , when imidization was carried out in NMP solution. On the other hand, k_2 had a value of 0.00882 min^{-1} which was 3.25 times that of k_1 , when imidization was carried out in the solid state. From the values of $t_{1/2}$ shown

Figure 3. Kinetics of irreversible thermal imidization of poly(amic acid).

Figure 4. Kinetics of reversible thermal imidization of poly(amic acid).

in Table III, the **Ib** isomer was rate-determining in the imidization of PAAs in solution. On the other hand, imidization of the **Ia** isomer became the bottle neck in the solid state. These results signified the importance of preventing rapid evaporation of solvent during the cure of cast films from PAA solution. Indeed, Ginsburg and Susko⁶ have reported that thick films cured faster because of solvent retention.

Attempt was also made to analyze the experimental data by second-order, self-catalyzed reactions. It was difficult to ascertain the concentration of the catalytic species, espe-

cially in the case of solid-state imidization, in which only catalytic species in the proximity of the reaction center would be effective. Although solutions can be found from any set of kinetic equations, we did not think that this laborious treatment will provide any real insight of the imidization reaction.

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