

Effects of Various Factors on the Formation of High Molecular Weight Polyamic Acid

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Synopsis

The reaction of pyromellitic dianhydride (PMDA) and aromatic diamine in an aprotic solvent such as dimethylacetamide (DMAc) gives a solution of poly(amic acid). The effects of certain variables on the polymerization and some additives on the stability and imidization of the poly(amic acid)s were studied. It was found that the addition of PMDA portionwise to the solution of diamine always keeps the excess diamine in solution and enables one to obtain the highest molecular weight of poly(amic acid). When the addition process was reversed, either by the change or dehydration of solvent, a high molecular weight was not attained. The inevitable water in the solvent or the reaction medium is the major factor, and the more the water content in the solvent or the reaction medium, the larger is the probability of destruction of PMDA during the reaction and hence low molecular weight is obtained. If very pure monomers were used in the polymerization, the 1:1 of molar ratio is the optimum value. Excess diamine or dianhydride results in the exchange reaction with poly(amic acid) and causes a rapid degradation of polymer chain. This exchange reaction was proved by NMR measurements. The presence of electrophilic agents or the nucleophilic agents containing active protons in the poly(amic acid) solution promotes the decomposition of polymer and causes the brittleness of polyimide film in the curing process. Using acetic anhydride (A) to convert the poly(amic acid) to polyimide, pyridine (P) can protect the polymer chain from the nucleophilic attack by the anhydride. The mixture with proper ratio of A/P (1/1–15/1) can be used as good dehydrating agents. Meanwhile, according to the results of experiments, we suggested the probable reaction mechanisms about how the water, amine, and anhydride destroy the polyamic acid chains.

INTRODUCTION

The preparation and properties of various polyimides have been described by several authors in the 1960s.^{1,2} The typical method is the two-stage polycondensation of a dianhydride with a diamine in an aprotic solvent, such as dimethylacetamide (DMAc). A soluble polyamic acid is obtained as polyimide prepolymer in the first stage; then cyclodehydration of this intermediate polymer, either by heat or chemical reagents, yields the insoluble polyimide.

Attainment of high molecular weight polyimide depends on the successful application of some controlling factors in the first stage of polycondensation. Sroog and his co-workers^{2,3} showed that molecular weight of poly(amic acid) depends on extremely pure monomers, rigorous exclusion of moisture, choice of solvent, and maintenance of reaction temperature. Besides, the order in the addition of the monomers is another important factor. It has been observed^{1,3,4} that the higher molecular weight polyamic acid was obtained when PMDA was added to the solution of the diamine than the

reverse addition. They assumed that in the latter case premature hydrolysis of PMDA may occur before aminolysis is initiated and that possible complex formation of PMDA and solvent reduces the PMDA reactivity.

The intrinsic viscosity and molecular weight reduce gradually when the poly(amic acid) solutions are aged, and the rate of decline is found to increase at higher temperatures, dilute polymer concentration, and in the presence of water or excess PMDA and DAPE.^{1,2} Frost and Kesse⁵ found that a rapid drop in viscosity is due to exchange reactions of amine or anhydride groups with the *o*-carboxamide linkage of poly(amic acid), but they didn't produce more direct evidence to account for this phenomenon.

In this study we will discuss in detail the effects of water on the achievement of high molecular weight poly(amic acid); the effects of various additives on the stability of poly(amic acid) and the curing of polyimide film will be studied also. Besides, according to the rapid decline of poly(amic acid) by the excess amine and anhydride and the measurements of NMR spectra, we prove that there is an exchange reaction between the amine or anhydride and poly(amic acid). In addition, we also propose a probable reaction mechanism.

EXPERIMENTAL

Reagents

Pyromellitic dianhydride (PMDA) (TCI-GR), 4,4'-diaminodiphenyl ether (DAPE) (TCI-GR) and 4,4'-diaminodiphenyl methane (DAPM) (TCI-GR) were used in the preparation of poly(amic acid), where PMDA was recrystallized by acetic anhydride before use and diamines were used without further purification. Dimethylacetamide (DMAc) and dimethylformamide (DMF), solvents used in the course of polymerization, were first dried by keeping over CaH_2 , P_2O_5 , or anhydrous MgSO_4 for several days and then distilled and stored over 4 Å molecular sieves.

Other laboratory grade reagents were used as additives: Among them were aniline, *p*-toluidine, *p*-phenetidine, phthalic anhydride (PA), maleic anhydride (MA), pyromellitic acid, benzoic acid, trichloroacetic acid, terephthalic acid, isophthalic acid, phenol, benzoyl chloride, bisphenol-A, 3,3',5,5'-tetrabromobisphenol-A, and pyridine.

Measurements

The viscosity of polyamic acid solution was determined at 30°C in DMAc by using a Ubbelohde suspended level viscometer. The water content of solvents was titrated by the Karl-Fischer reagent with a Karl-Fischer Titrator. NMR spectra were recorded on a JEOL-JNM-PMX 60 NMR Spectrometer instrument. The chemical shift (δ) is given in ppm with tetramethylsilane (TMS) as the internal standard.

Experimental Methods

Effect of Process of Addition of Monomers on Molecular Weight

(1) By using the general process of polymerization, first the diamine DAPE was dissolved into the DMAc, and then the equivalent amount of PMDA

was added to the solution within different times to obtain viscous solution of polyamic acid. The effect of the rate of PMDA's addition on the viscosity of polymer solution was observed.

(2) After dissolving DAPE into DMAc and then adding twice equivalent quantities of PMDA to the solution once at the same time, we made up the unbalanced quantity of DAPE either immediately or 10 min after the complete dissolution of PMDA to study the effects of the anhydride group standing in solution on the ultimate viscosity in terms of time length.

(3) Using the reverse process of (1), DAPE was added to the solution of PMDA to carry out the polymerization. The ultimate viscosity of the polymer solution was determined and compared with the results obtained from (1).

Effects of the Dehydration and Change of Solvent on the Molecular Weight of Poly(amic Acid) Formed

According to the methods described in literature,⁶ DMAc was dried by keeping over CaH_2 or P_2O_5 while DMF was dried by keeping over anhydrous MgSO_4 . Then the solvents were distilled, stored over 4 Å molecular sieves and titrated by Karl-Fischer Titrator to determine the water content in them. The reaction of PMDA and DAPE was carried out in the dried and undried DMAc by the general and reverse processes described in the previous subsection respectively to compare the differences of viscosity. Further, according to the processes described in Table IV, the copolymerization of PMDA with the mixture of DAPE/DAPM (1:1) proceeded in the dehydrated DMF to prepare the random and alternating copolymers and to compare the viscosities of their solutions.

Effect of Adventitious Water on the Formation of Poly(amic Acid)

Three portions of molar stoichiometric quantities of diamine DAPE (0.250 g) dissolved in DMAc (5mL); 1%, 2%, and 4% (vol %) of water was added to diamine solution, respectively. Then an equivalent amount of PMDA (0.272 g) was added to the above medium to carry out the reaction and to compare the ultimate viscosities of each polymer solution.

Effect of Reactant Ratio on Reaction of PMDA and DAPE

First 0.96 time of equivalent quantity of PMDA was added to the solution of DAPE in DMAc, and, after the ultimate viscosity of polymer solution had been determined, PMDA and DMAc were made up to keep the 10 wt % concentration of solution and change the PMDA/DAPE molar ratio into 0.98/1, 1.00/1, 1.01/1, 1.02/1, 1.04/1, 1.06/1, and 1.08/1 step by step. The ultimate viscosity of polymer solution at each stage was determined and the effect of monomers' ratio on reaction was studied.

Effects of Additives on Stability of Poly(amic Acid) Solution

A solution of 2.98 g DAPE in 60 mL DMAc was stirred rapidly while 3.25 g PMDA was added gradually. The mixture was stirred for 1 h to give a clear, viscous solution (with $\eta_{sp}/C = 2.82$ dL/g, $C = 0.5$ g/dL, 30°C in DMAc),

from which 5 mL aliquots were taken. Additions were made to these samples as listed in Table VII. These samples were aged at room temperature (25°C), with periodic viscosity measurements.

NMR Measurements to Observe the Exchange Reactions of Amine and Anhydride with Poly(amic Acid)

(1) **Exchange Reaction of Amine with Amic Acid.** Three equal portions (1.23 g of each) of phthalic anhydride (PA) reacted respectively with 0.78 g of aniline, 0.89 g of *p*-toluidine, and 1.44 g of *p*-phenetidine in DMAc (5 mL of each), to yield solutions of amic acid with $C = 30$ wt %, from which 0.6 mL sample of each solution was transferred to a NMR tube and their NMR spectra were recorded. Next we took four 0.6 mL aliquots of PA-aniline amic acid solution into 4 NMR tubes, respectively, and added equal and twice equivalent quantities of *p*-toluidine and equal and twice equivalent quantities of *p*-phenetidine to each tube to observe the changes of NMR spectra periodically and to compare the rate of exchange of amine with amic acid.

(2) **Exchange Reaction of Anhydride with Poly(amic Acid).** 0.5 g PMDA (2.29×10^{-3} mol) and 0.306 g DAPE (1.53×10^{-3} mol) were dissolved in 7.8 mL DMAc to produce a low molecular weight polyamic acid solution with concn = 10 wt %, from which 0.6 mL of poly(amic acid) was taken for NMR measurement. Five times equivalent quantities of maleic anhydride (0.1 g) was then added to the above-mentioned polyamic acid solution in the NMR tube, and the changes of NMR spectra were observed periodically.

Effects of Additives on the Polyimide-Curing Properties

(1) **Thermal Cyclodehydration.** Equimolar quantities of PMDA and DAPE were dissolved in DMAc to obtain a 5 wt % polyamic acid solution ($\eta_{sp}/C = 3.0$ dL/g, $C = 0.5$ g/dL, 30°C in DMAc), from which 5 mL aliquots were taken. Additions were made to these samples as listed in Table X. In the presence of various additives, these solutions were cast into polyamic acid films at 80°C and further converted to polyimides by heating to 250°C gradually. The effects of various additives on polyimide-curing properties were investigated.

(2) **Cyclodehydration by Chemical Reagents.** Equimolar quantity of PMDA was added to the solution of DAPM in DMAc to prepare a viscous polyamic acid solution, from which three 2 g aliquots were taken, and 0.5 mL each of acetic anhydride (A), pyridine (P), and the mixture of A/P = 2/1 (vol ratio) were mixed with these samples, respectively. The mixtures were spread on glass plates, forced dried at 80°C and then cured by heating to 250°C gradually, and kept at this temperature for 20 min to compare each polyimide-curing property.

In addition, PMDA-DAPM poly(amic acid) solution was spread on glass plate and dried at 80°C to give a polyamic acid film. These films were cured in the mixtures of A and P with different volume ratios. We then observed the changes of polyimide film property during the course of treatment.

RESULTS AND DISCUSSION

Effects of the Process of Monomers' Addition on the Molecular Weight of Poly(amic Acid)

In the preparation of polyamic acid from aromatic dianhydride and diamine, the order of addition of the monomers is an important requirement for successful polymerization.^{1,3,4} The general process is to add solid PMDA to the solution of diamine in an aprotic solvent such as DMAc to conduct a heterogeneous reaction. A viscous solution with high molecular weight can be obtained. If the order is reversed, i.e., the diamine is added slowly to a solution of PMDA, a high viscosity will not be obtained. The explanation for this fact is still confusing. In general, there are two interpretations: The one is that in the latter case premature hydrolysis of PMDA takes place,^{4,6} and the other is related to the reduction of PMDA reactivity by solvent-PMDA complex formation.^{1,3} This experiment made more detailed study on the effects of the process of addition. The results of viscosity measurements of poly(amic acid) prepared from various processes of addition are summarized in Table I. It is found that, first, in the reaction conducted by adding PMDA to the solution of DAPE in DMAc, the higher viscosity is obtained if PMDA is added at longer intervals, second, the longer the excess anhydride groups exist in the solution, the lower the viscosity of polymer is formed, and, third, by using the reversed process to add DAPE to the PMDA solution, we obtained polymer solution of the lowest viscosity.

The lower viscosity of polymer prepared from the procedures of d, e, and f in Table I may be owing to the fact that excess anhydride is easily destroyed by water in the reaction medium, so that the polycondensation cannot be carried out when the unbalanced DAPE is made up and hence a higher molecular weight is not obtained. In addition, the longer the anhydride groups exist in solution, the more seriously are they destroyed, and therefore the lower is the molecular weight. While the polymerization is conducted by general process (such as a, b, and c in Table I), the solvent DMAc, being sufficiently polar, thereby acts as Lewis base under anhydrous conditions, and increases the nucleophilicity of the dissolved aromatic diamine to attack the dianhydride carbonyl. As a result there is less chance of hydrolysis of anhydride group.⁷ Furthermore, from simple measurements of the rate at which heat is liberated during reactions, it is found that⁴ the reactivity ratio of diamine and water with PMDA in solution is approximately 5; i.e., with the diamine present in large excess, very little hydrolysis will occur. If PMDA is added in some portions to the DAPE solution, the chance of hydrolysis is still less, and hence a highly viscous polyamic acid solution can be obtained.

Effects of Dehydration and Change of Solvent on the Formation of Poly(amic Acid)

Solvents are dehydrated by CaH_2 , P_2O_5 , and anhydrous MgSO_4 , respectively, and the water contents of them are determined by Karl-Fischer Titrator. The results of water content measurements are listed in Table II. The reaction of PMDA and DAPE is carried out in the dehydrated and

TABLE I
Effect of the Process of Monomers' Addition on the Viscosity and Molecular Weight of Poly(amic Acid)

Sample	Process ^a	Viscosity ^b (dL/g)			$\bar{M}_w \times 10^{-4}$ ^c
		$\eta_{sp}/C, C = 0.5 \text{ g/dL}$	$[\eta]$	$[\eta]$	
a	DAPE/DMAc → PMDA was added at the same time	2.54	1.88	10.20	
b	2 DAPE/DMAc + 1 PMDA → 1 PMDA was added immediately after the previous solid has been dissolved	4.45	2.50	14.57	
c	DAPE/DMAc → PMDA was added portionwise within 30 min	5.14	2.71	16.11	
d	1 DAPE/DMAc + 2 PMDA → 1 DAPE was added immediately after the PMDA has been dissolved	1.35	0.89	4.01	
e	1 DAPE/DMAc + 2 PMDA → 1 DAPE was added 10 min after the PMDA has been dissolved	0.74	0.57	2.29	
f	PMDA/DMAc → DAPE was added after the complete dissolution of PMDA	0.64	0.51	1.99	

^a 0.239 g DAPE, 0.261 g PMDA, and 4.5 g DMAc were used in each process.

^b Viscosity was determined at 30°C in DMAc.

^c The Mark-Houwink equation for PMDA-DAPE poly(amic acid) is $[\eta] = 1.84 \times 10^{-4} \bar{M}_w^{0.8}$ (see Ref. 8).

TABLE II
 Water Contents of Solvents

Solvent	Water content (wt %)
Undried DMAc	0.127
DMAc, dried by CaH ₂	0.003 max
DMAc, dried by P ₂ O ₅	0.004 max
DMF, dried by anhydrous MgSO ₄	0.005 max

undehydrated DMAc by the general and reverse processes, respectively. The results of viscosity measurements of each polymer solution are summarized in Table III. It is found that the molecular weight of polyamic acid obtained in dehydrated DMAc is larger than that obtained in undehydrated DMAc, a result that indicates that the less the water in the reaction medium, the less the chance of hydrolysis of anhydride groups in the course of polymerization and hence a higher molecular weight polymer can be obtained. However, the reaction through the reverse addition, (b) in Table III, still cannot obtain a high molecular weight polymer.

PMDA reacted with the mixture of DAPE/DAPM (1:1) in the DMF which was dried with anhydrous MgSO₄, and the results of viscosity measurements of polymers obtained are shown in Table IV. The viscosity behavior is similar to that described in the previous subsection. If the anhydride groups exist in excess amount in either DMAc or DMF in the absence of amino group in solution, the chance of hydrolysis of anhydride groups is greatly raised, and thereby a high viscosity polymer solution is not obtained, even though the water content is very low.

The solvents are not easy to be dried completely. Besides, DMAc or DMF is apt to absorb moisture from the atmosphere. A little water may be liberated in the course of polymerization, for any amic acid may be converted to imide. As a result there is always some water inevitably present in the reaction medium. If excess anhydride groups are present in the solution, they will be destroyed by the water and become inactive; therefore, either by exchanging or by dehydrating the solvent, it is difficult to obtain high molecular weight of poly(amic acid) by using a reversed addition.

 TABLE III
 Effect of the Dehydration of Solvent on the Molecular Weight of Poly(amic Acid)

Process	DMAc	Viscosity (g/dL) ^a		$\bar{M}_w \times 10^{-4}$
		η_{sp}/C^b	$[\eta]$	
(a) DAPE/DMAc $\xrightarrow{\text{PMDA}}$	Undried	2.54	1.88	10.20
	Dried by CaH ₂	4.45	2.50	14.57
	Dried by P ₂ O ₅	3.04	2.27	12.91
(b) PMDA/DMAc $\xrightarrow{\text{DAPE}}$	Undried	0.64	0.51	1.99
	Dried by CaH ₂	1.60	1.09	5.16
	Dried by P ₂ O ₅	1.57	1.07	5.04

^a Viscosity was determined at 30°C in DMAc.

^b C = 0.5 g/dL.

TABLE IV
Comparison of the Viscosities of Random and Alternating Copolymers

Process ^a	Sequences of polymer chain	Viscosity ^b η_{sp}/C (dL/g)
DAPE/DMF + 2 PMDA $\xrightarrow{\text{DAPM}}$	Alternating	1.45
(DAPE+DAPM)/DMF $\xrightarrow{2 \text{ PMDA}}$	Random	4.46

^a DMF was dried by anhydrous MgSO_4 .

^b Viscosity was determined at 30°C in DMF, with concn = 0.5 g/dL.

Effects of Adventitious Water on the Formation of Poly(amic Acid)

Intentionally adding water in the reaction medium to study the effect of adventitious water on the formation of polymer, we find again that the presence of water has an important influence upon the molecular weight of polymer formed. The more the water is added into the DMAc solution of DAPE, the larger is the chance of hydrolysis of anhydride groups when PMDA is added; hence, the lower is the viscosity and molecular weight of poly(amic acid) obtained. The viscosity values of polymers prepared in different water content mediums are shown Table V.

Thus from the above results in this and the previous subsections, it is observed that the exclusion of moisture is very important factor in the acquisition of a high molecular weight poly(amic acid), and it also indicates that, in the investigation of the effect of the additions' order of monomers on the molecular weight of polymer, water indeed plays an important role and that the effect is to be attributed to the presence of water appears more apparently important than another presumed cause—the reduction of reactivity by the formation of PMDA–solvent complex.

Effect of Reactant Ratio on Reaction of PMDA and DAPE

In a previous paper⁵ Frost and Kesse utilized the mixture of PMDA/DAPM with different molar ratios to prepare the poly(amic acid) by adding all the PMDA to DAPM solution at the same time and found that when the PMDA/DAPM ratio was in the range of 1.02–1.03 the viscosity of poly(amic acid) obtained was the largest, and, as the ratio got smaller than 1.02 or larger than 1.03, the viscosity of polymer decreased greatly. The ratio given indicated that the purity of PMDA was a little inferior to that

TABLE V
Effect of Water Added to the Reaction Medium on the Viscosity of PMDA–DAPE Poly(amic Acid) Solutions

Amount of water added (vol %)	Viscosity of poly(amic acid) η_{sp}/C (dL/g), $C = 0.5$ g/dL
None	2.54
1	1.82
2	1.08
4	0.38

of DAPM. Thus the procedure used gave viscosity values that were dependent upon the reactant ratio, and, of course, this ratio was directly relative to the purity of monomers. In the present experiment, PMDA and DAPE with different ratios were used in the preparation of polyamic acid (Table VI). When the ratio of PMDA/DAPE was 0.98, the viscosity value reached to only $\eta_{sp}/C = 1.13$ dL/g ($C = 0.5$ g/dL, 30°C in DMAc). While the ratio was increased to 1.00 by adding complementary PMDA, the viscosity rose rapidly to $\eta_{sp}/C = 4.82$ dL/g, indicating that high molecular weight of poly(amic acid) had been formed. Hereafter, adding portionwise PMDA again, the viscosity of polymer never rose; on the contrary, it tended to fall rapidly, and it became brittle when polyimide film was cast by heating the solution to which the excess PMDA was added (with PMDA/DAPE = 1.08/1). The brittleness may be due to the fact that the excess PMDA accelerates the degradation of polymer, and this phenomenon will be studied in detail later.

From the results listed in Table VI, it is observed that when the ratio of PMDA/DAPE is 1/1, the resulting polymer possesses the largest viscosity value, thus indicating that the purity of PMDA treated by recrystallization is corresponding to that of DAPE. At the lower ratios (such as 0.96 and 0.98), a higher viscosity was not obtained and the product was presumably a polymer of low molecular weight, with terminal amine groups. Therefore, it is predictable that if the ratio of PMDA/DAPE is larger than 1 and if all PMDA is added to the DAPE solution at the same time, the polymer attained will possess a low molecular weight, with terminal anhydride or dicarboxylic acid groups.

Effects of Additives on the Stability of Poly(amic Acid)

When poly(amic acid) is stored in an aprotic solvent, the amide and carboxylic acid groups in the *o*-carboxamide linkage will attach each other and result in the intermediates 1 and 2 as shown in Scheme 1 (in the subsection Suggested Mechanism). These intermediates are easily attacked by electrophilic agents (such as anhydrides) or nucleophilic agents (such as water and amines), and hence the amic acid linkage is cleaved. In the aprotic solvent, the water is the most difficult to be prevented; hence, poly(amic acid) degrades gradually during its storage in solution. It is evident from the above observation in the previous subsection that the addition of excess

TABLE VI
Effect of Reactant Ratio on Viscosity of PMDA-DAPE Polymer Solutions at 25°C

Molar ratio, PMDA/DAPE	Viscosity, η_{sp}/C (dL/g), $C = 0.5$ g/dL
0.96/1	0.64
0.98/1	1.13
1.00/1	4.82
1.01/1	4.60
1.02/1	4.33
1.04/1	4.21
1.06/1	3.97
1.08/1	3.32

dianhydride tends to cause a rapid degradation of the polymer; thereby, further investigation was conducted by adding PMDA and various additives (Table VII) to the poly(amic acid) solutions in order to study their effects upon the stability of polymer. First PMDA, phthalic anhydride, maleic anhydride, and DAPE (b, c, d, and e in Table VII) was each added to the poly(amic acid)s which were prepared from PMDA and DAPE in DMAc; observing the decline of viscosity periodically, we found that these four additives all accelerate the rate of decay (Fig. 1). A reduction of intrinsic viscosity and molecular weight was noted by Bower and Frost¹ when polypyromellitic acid solutions were aged, and the rate of decline was found to increase at higher temperatures and in the presence of water or excess PMDA. Then, Frost and Kesse⁵ made further examinations and suggested that there was an exchange reaction between PMDA or DAPE and poly(amic acid), but they didn't propose any direct evidence for the exchange reaction. We will prove that the exchange reaction does take place by NMR measurements later on.

In the course of experiment it had been wrongly recognized that the excess anhydrides would be hydrolyzed to the corresponding acids in the solution and would accelerate the degradation of poly(amic acid). Hence, with the similarly structural acid compounds, such as isophthalic acid (f), benzoic acid (g), and pyromellitic acid (h), added to the poly(amic acid) solutions, the changes of viscosity were observed periodically; but it was found that their addition, actually, didn't accelerate the rate of decline. For easy distinction we summarize the results in another figure (Fig. 2).

The results of the effects of the other additives, such as phenol (i), trichloroacetic acid (j), and benzoic chloride (k), on the stability of poly(amic acid) are also listed in Figure 2. The strong bases (such as benzoyl chloride) and strong acids (such as trichloroacetic acid) may react with polymer chain and decompose it; therefore, both additions destabilize the polyamic acid. While, the addition of the weaker acid such as phenol, which behaved in the same way as weaker acids as reported above, didn't cause a rapid decline in viscosity.

TABLE VII
Additives for the Study on Their Effects on the Stability of Poly(amic Acid) Solutions

Sample	Material added (g)	Mol additive/unit mol polymer
a	None	None
b	DMAc, 0.89 + maleic anhydride, 0.03	0.25
c	DMAc, 0.89 + phthalic anhydride, 0.03	0.16
d	DMAc, 0.89 + PMDA, 0.03	0.11
e	DMAc, 0.86 + DAPE, 0.0275	0.11
f	DMAc, 0.79 + isophthalic acid, 0.019	0.09
g	DMAc, 0.89 + benzoic acid, 0.03	0.19
h	DMAc, 0.98 + pyromellitic acid 2H ₂ O, 0.04	0.11
i	DMAc, 0.73 + phenol, 0.012	0.10
j	DMAc, 0.78 + trichloroacetic acid, 0.018	0.08
k	DMAc, 0.74 + benzoyl chloride, 0.014	0.08

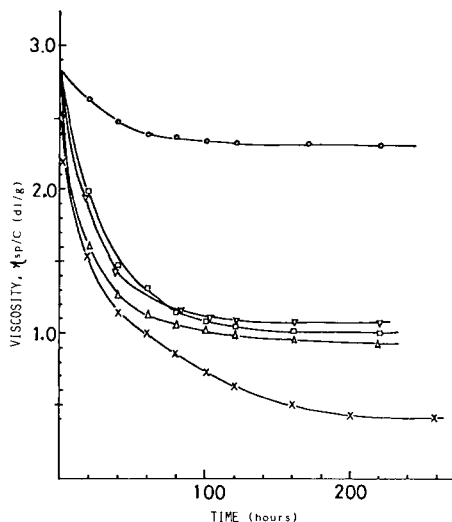


Fig. 1. Effect of additional anhydrides and diamine on stability of 10 wt % PMDA-DAPE poly(amic acid) in DMAc at 25°C: (○)(a) blank; (□)(b) MA; (▽)(c) PA; (△)(d) PMDA; and (X)(e) DAPE; viscosity was determined at 30°C in DMAc, $C = 0.5$ g/dL.

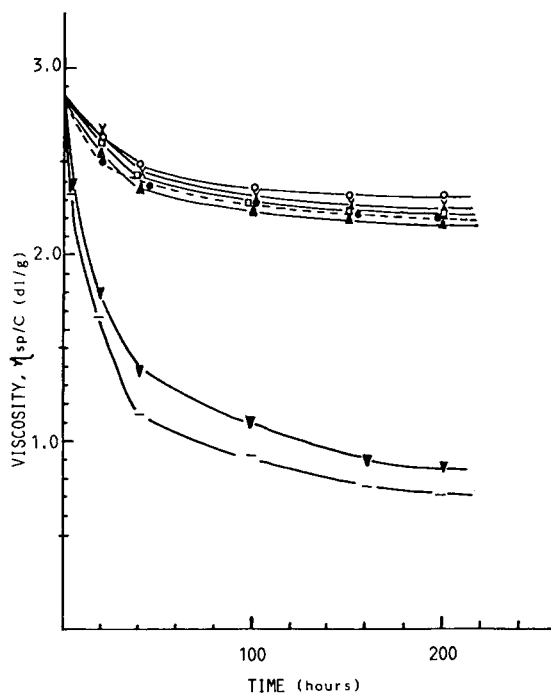


Fig. 2. Effect of additional acids and bases on the stability of poly(amic acid): (○)(a) blank; (X)(f) isophthalic acid; (□)(g) benzoic acid; (▲)(h) pyromellitic acid · 2H₂O; (●)(i) phenol; (▼)(j) trichloroacetic acid; and (—)(k) benzoyl chloride; viscosity was determined at 30°C in DMAc, with concn 0.5 g/dL.

NMR Measurements to Prove the Exchange Reactions of Amine and Anhydride with Poly(amic Acid)

Exchange Reaction of Amine with Amic Acid

Phthalic anhydride (PA) reacted with different amines to obtain the PA-amine amic acids which have different chemical shift of the protons on the amide linkage for the different functional groups bound to benzene ring of amines (Table VIII). For the inductive effect, the absorption peak of amide protons shifts to a higher magnetic field when R is an electron-donor group and to a lower magnetic field when R is an electron-withdrawing group.

Hence, when another amine is added into the solution of PA-amine amic acid and if the exchange reaction takes place, in view of the fact that the chemical shifts of various amide protons are different, the original single peak will transform to double peaks in the lower magnetic field (10–11 δ_{ppm}) of NMR spectra. Take the reaction of PA-aniline amic acid and *p*-toluidine, for example, when *p*-toluidine was added to the solution of PA-aniline amic acid, the absorption peak of carboxylic protons ($-\text{COOH}$), which was in the lower magnetic field originally, would shift to a higher magnetic field ($\delta_{7.3 \text{ ppm}}$) [Fig. 3(A)] due to the formation of amine salt ($-\text{NH}_3^{\oplus}\text{OOC}-$), and if twice the amount of *p*-toluidine was added, the absorption peak of amine salts would shift to a still higher magnetic field ($\delta_{6.2 \text{ ppm}}$) [Fig. 3(B)] In the other steady peaks, 10.30 ppm belongs to the resonance of amide protons and the complicated peaks in the range 6–8 ppm are related to the presence of aromatic protons of free amine and amic acid. Because the adventitious *p*-toluidine exchanged with PA-aniline amic acid to produce another PA-*p*-toluidine amic acid, the intensity of original 10.30 ppm peak decreased and another amide proton peak appeared at 10.20 ppm gradually (Figs. 3 and 4). Similarly, adding *p*-phenetidine into the PA-aniline amic acid would yield another amide protons peak at 10.13 ppm, too.

The exchange rate of amine and amic acid can be evaluated by the change of the absorption intensity of two kinds of amide protons. Because these two peaks are too close, and the integrator of the NMR instrument cannot distinguish clearly, the height of absorption peaks is used to evaluate the ratio of two amic acids present in the solution. The ratio value can be

TABLE VIII
Chemical Shift of Amide Protons of PA-Amine Amic Acid,

R	Chemical shift of $-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\text{N}}-$ (δ_{ppm})
- H	10.30
- CH_3	10.20
- OC_2H_5	10.13

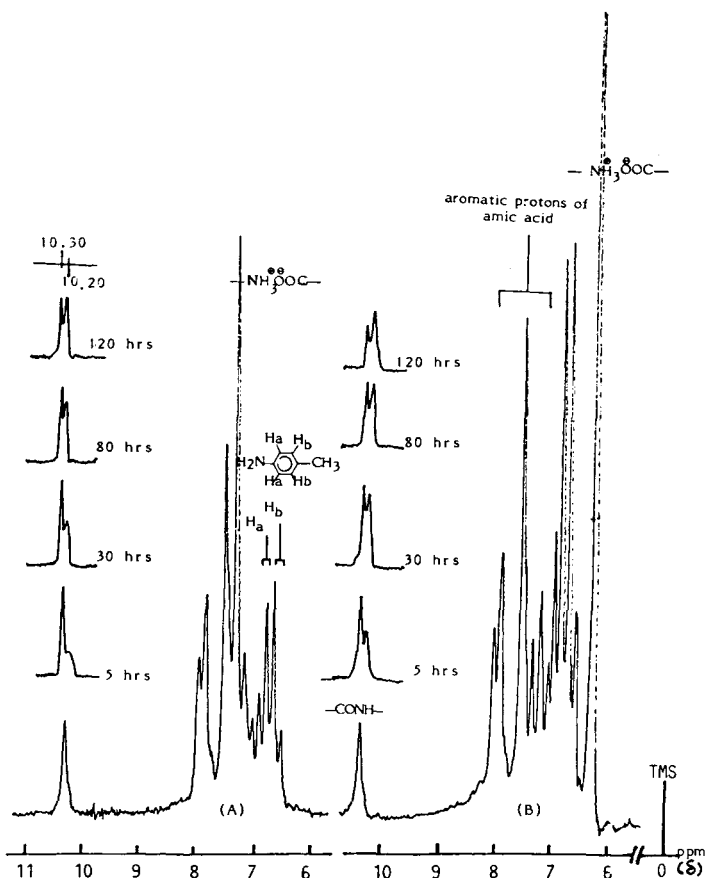


Fig. 3. $^1\text{H-NMR}$ spectra (60 MHz) of PA-aniline amic acid in DMAc after addition of *p*-toluidine [(A) 1 eq.; (B) 2 eq.] and changes of amide protons peaks.

transferred to the amount of amic acid exchanged by amine; Figure 5 shows the exchanged amounts of PA-aniline amic acid by different quantities of *p*-toluidine and *p*-phenetidine at various periods of time. The more the amine added, the faster is the exchange rate; but the ratio of two amic acids will reach an equilibrium value finally because the exchange reaction is reversible. The equilibrium value is related to the amount of amine added and the reactivity of amine. In the case of equimolar amine and amic acid, the equilibrium value is approximately as follows: $[\text{PA-aniline amic acid}]/[\text{PA-}p\text{-toluidine amic acid}] = 45/55$ and $[\text{PA-aniline amic acid}]/[\text{PA-}p\text{-phenetidine amic acid}] = 40/60$.

From the above model exchange reaction, it can be known that the exchange reaction of diamine and polyamic acid is feasible, and hence the excess DAPE will accelerate the degradation of polyamic acid.

Exchange Reaction of Anhydride with Poly(amic Acid)

When maleic anhydride was measured by NMR spectra in DMAc, the absorption peak at $\delta_{7.5 \text{ ppm}}$ could be detected, which is relative to the protons

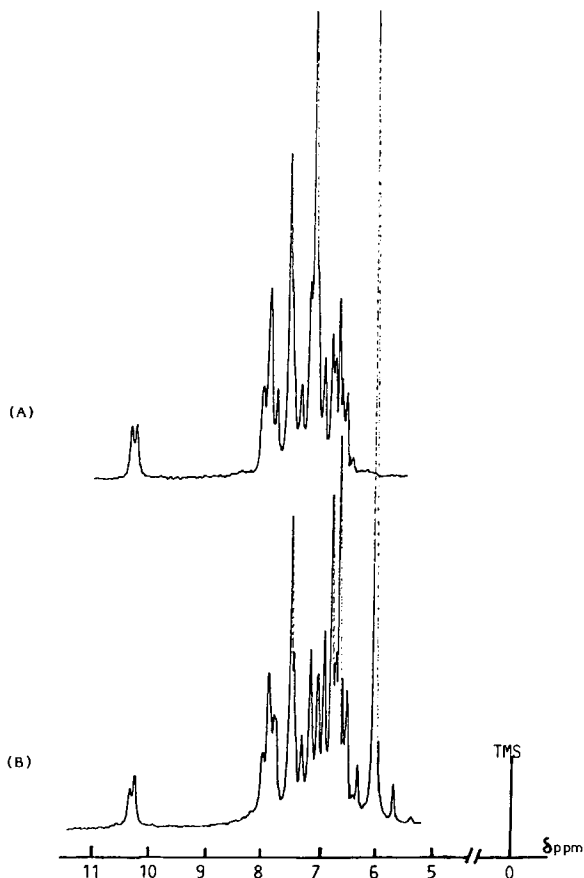


Fig. 4. $^1\text{H-NMR}$ spectra (60 MHz) of PA-aniline amic acid in DMAc at 120 h after addition of *p*-toluidine [(A) 1 eq.; (B) 2 eq.]; sweep width = 1200 cps.

bound to the C=C double bond, and if it reacted with water to the corresponding maleic acid, the chemical shift of protons bound to C=C double bond would shift to 6.3 ppm. And, when maleic anhydride reacted with aniline to corresponding maleamic acid, in its NMR spectra two AB doublets of the protons bound to C=C appeared at 6.8 and 6.44 ppm, respectively, as well as a singlet of amide protons appearing at 10.90 ppm.

Hereafter, the NMR spectra of polyamic acid solution, which is prepared from PMDA/DAPE with molar ratio $3/2$ was recorded. As shown in Figure 6, H_1 ($\delta_{7.76}$ ppm) and H_2 ($\delta_{7.93}$ ppm) are related to the aromatic protons of DAPE component in polymer chain. The signals of aromatic protons of PMDA component in polymer chain appear at three positions due to the symmetry of *o*-carboxamide linkage, H_3 ($\delta_{7.76}$) and H_6 ($\delta_{8.43}$) being peculiar to aromatic protons of *cis* form and H_4 ($\delta_{8.0}$) being peculiar to that of *trans* form. H_5 ($\delta_{8.24}$) belongs to the aromatic protons of terminal anhydride; H_7 ($\delta_{10.6}$) and H_8 ($\delta_{10.7}$) belong to the amide protons in the middle and terminal part of polymer chain, respectively; and the broad hump H_9 ($\delta_{13-13.8}$) has been interpreted by the presence of carboxylic groups ($-\text{COOH}$).

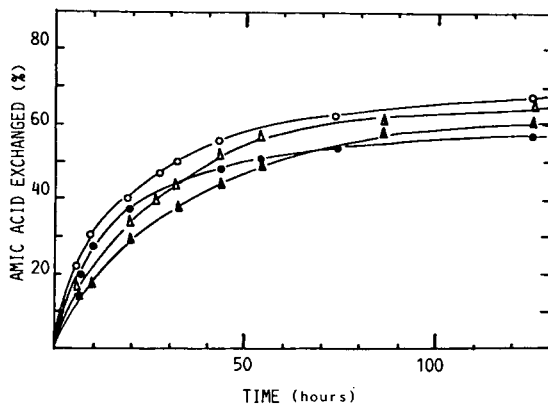


Fig. 5. Amount of PA-aniline amic acid exchanged by *p*-toluidine [(○) 2 eq.; (●) 1 eq.] and *p*-phenetidine [(△) 2 eq.; (▲) 1 eq.] vs. time.

When maleic anhydride was added to the poly(amic acid) solution, the strong resonance signal of protons bound to C=C would appear at $\delta_{7.5}$ ppm and the signal of —COOH would shift to lower magnetic field ($\delta_{13.9}$) under anhydrous condition; hereafter, maleic anhydride reacted with water in the solution or might take water from *o*-carboxamide linkage of amic acid. So, in addition to the signal at 7.5 ppm, there was another signal at 6.3 ppm which was related to the protons bound to C=C. This mixture was kept for 2 days, and it was found that the intensity of 7.5 ppm decreased and 6.3 ppm increased, while in the range of 6.3–7.0 ppm no characteristic absorption of maleamic acid protons was observed [Fig. 7(A)]. This indicates that the exchange amount of maleic anhydride with the *o*-carboxamide linkage is very small in a short time (e.g., several days), so the reaction can't be detected by NMR measurement. But, with this tube well-sealed and kept at room temperature for a longer period of time, the exchange reaction showed clearly on the NMR spectra. As shown in Fig. 7(B), after the mixture had been stored for 2 months the characteristic signals of protons bound to C=C of maleamic acid appeared at 6.45 and 6.60 ppm; meanwhile, because the original *o*-carboxamide linkages converted partly to imide groups and were exchanged partly to maleamic acid by maleic anhydride, the intensity of original absorption 10.60 ppm of amide protons decreased, and another signal of amide protons emerged at 10.97 ppm. Thus the NMR measurements enable us to prove that anhydride group has exchanged with poly(amic acid) and to further explain why the excess dianhydride has accelerated the degradation of poly(amic acid).

Now that we have proved the exchange reactions of amine and anhydride with poly(amic acid), let us recall that the excess PMDA and DAPE accelerate the decline of viscosity of polyamic acid. As shown in Figure 1 above, the excess diamine causes a faster degradation of polymer. In addition, the ultimate viscosity of polymer is lower than that of polymer solution with excess dianhydride. We may attribute this fact to the presence of water in the polymer solution. The water may come from the solvent; besides, some

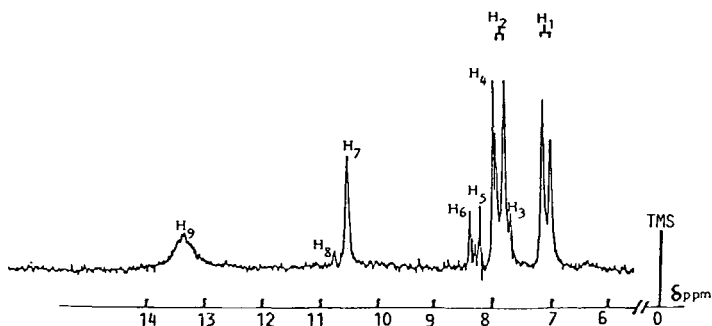
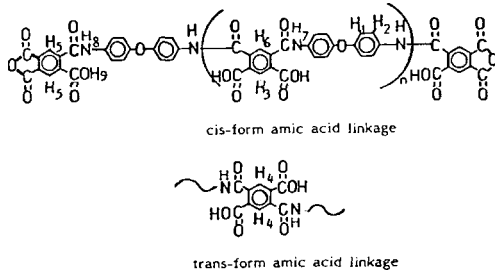
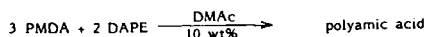


Fig. 6. $^1\text{H-NMR}$ spectrum (60 MHz) of 10 wt % PMDA-DAPE poly(amic acid) in DMAc (PMDA/DAPE = 3/2, molar ratio); sweep width = 1200 cps.

amic acid groups may convert to imides, releasing water in the course of polymerization or storage. Excess anhydride and anhydride terminated polymer are apparently destroyed or inactivated by water; therefore, although the excess PMDA causes a rapid degradation of poly(amic acid), the water slows the rate down. Furthermore, from the exchange reaction we may further investigate the effects produced by water in the course of polymerization. In case there is excess diamine in the poly(amic acid) solution, the polymer will be broken down into shorter chains as the degradation by exchange reaction proceeds. However, the amine-terminated polymer or oligomer remains active toward anhydride, and hence if the complementary dianhydride is added, the high molecular weight of polymer can still be obtained. On the contrary, if there is excess anhydride in the course of polymerization, as long as the solvent contains a little water or takes moisture from the atmosphere, excess anhydride or anhydride-terminated polymer will be destroyed or inactivated. Therefore, even though the unbalanced diamine is made up, the amic acid linkage still cannot be formed on the inactivated terminal. Thus high molecular weight of polyamic acid cannot be attained in this case, unless there are a complete dehydration of solvent, a rigorous exclusion of moisture from the environment, and a consistent maintenance of a low temperature to prevent amic acids from cyclodehydrating to imides.

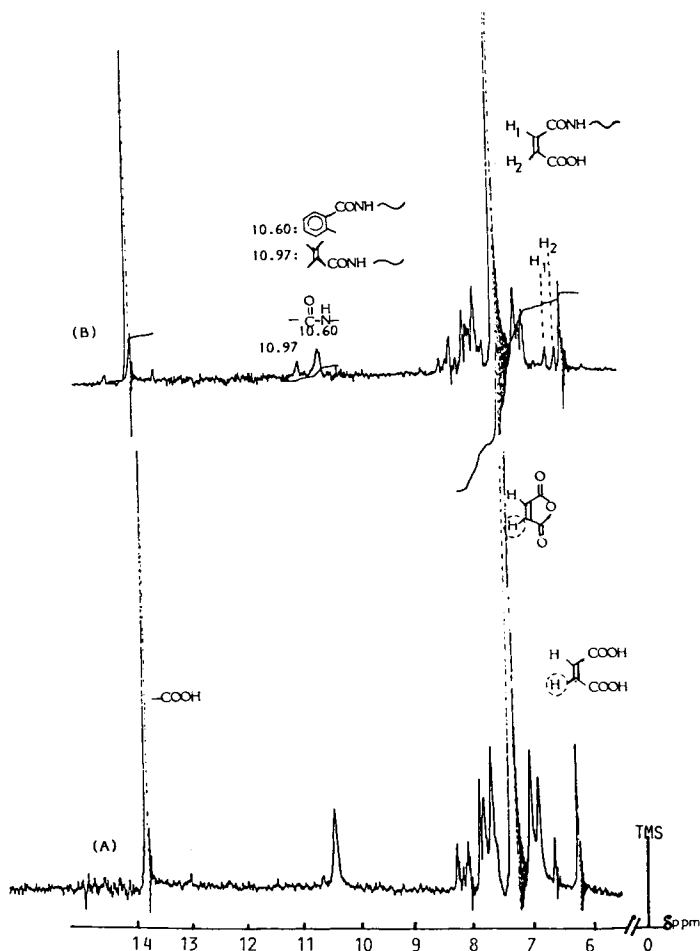


Fig. 7. $^1\text{H-NMR}$ spectra (60 MHz) of 10 wt % PMDA-DAPE polyamic acid in DMAc after addition of maleic anhydride [(A) 2 days later; (B) 2 months later], with sweep width = 1200 cps.

Effects of Additives on the Polyimide-Curing Properties

Thermal Cyclodehydration

As described earlier, when an excess amount of PMDA is added to PMDA-DAPE polyamic acid (with PMDA/DAPE = 1.08), the polymer solution will acquire a brittle film at the time of curing. Thus it becomes desirable to investigate the effects exerted by the equal or somewhat equivalent quantities of additives upon the curing of polyamic acid into polyimide, taking the added amount of PMDA as a reference. The results are shown in Table IX. The additions of additives such as 2, 3, 4, and 5 in Table IX, which could exchange with poly(amic acid) at room temperature, resulted in brittle films in the process of curing. It is presumed that a rapid exchange reaction of these additives and poly(amic acid) might take place at high temperature

TABLE IX
Effects of additives on the Film-Curing Properties of PMDA-DAPE Poly(amic Acids)

Sample	Additives	Amount	Mole additive/unit mole of polymer	Film property ^a	
				Poly(amic acid)	Polyimide
1	PMDA	0.005 g. (2.3×10^{-5} mol)	0.04	F	F
2	PMDA	0.010 g. (4.6×10^{-5} mol)	0.08	F	B
3	DAPE	0.009 g. (4.6×10^{-5} mol)	0.08	B	B
4	Phthalic anhydride	0.013 g. (9.2×10^{-5} mol)	0.16	B	B
5	Maleic anhydride	0.009 g. (9.2×10^{-5} mol)	0.16	B	B
6	Pyromellitic acid $2H_2O$	0.013 g. (4.6×10^{-5} mol)	0.08	F	B
7	Benzoic acid	0.03 g. (2.54×10^{-4} mol)	0.41	F	F
8	Terephthalic acid	0.04 g. (2.4×10^{-4} mol)	0.40	F	F
9	Bisphenol A	0.03 g. (1.31×10^{-4} mol)	0.22	F	F
10	3,3',5,5'-tetrabromobisphenol-A	0.03 g. (5.47×10^{-5} mol)	0.09	F	F

^a The film was judged to be flexible (F) if it could be creased without cracking; brittle (B) if it cracked on creasing.

to decompose polymer, making the films obtained brittle and deficient in mechanical strength. The additions of 3, 4, and 5 being especially deleterious, their additions resulted in brittle films of polyamic acid when cured at 80°C.

In the case of smaller added amount of PMDA and other additives such as 7, 8, 9, and 10 in Table IX, which didn't exchange with polyamic acid, these additives acted as fillers and didn't produce a very bad effect on film casting. While the addition of 6 also resulted in a brittle film, it is probable that pyromellitic acid carrying two crystallized water would raise the chance of hydrolysis of poly(amic acid) in the course of heating. It is also likely that pyromellitic acid might dehydrate to anhydride and exchange with uncyclized amic acids, thus degrading polyamic acid.

Treatment by Chemical Dehydrating Agents

From the literature⁹ anhydrides and tertiary amines can be used as dehydrating agents to cyclize amic acid. While the mixture of acetic anhydride and pyridine at 1:1 ratio was usually used in the cyclodehydration of poly(amic acid) to polyimide,^{4,5} no further explanation has been given for the ratio. In the present experiment mixtures of acetic anhydride (A) and pyridine (P) at different ratios were used as dehydrating agents to test the film properties of PMDA-DAPE polyamic acid on treatment.

After 0.5 mL acetic anhydride was added into 2 g of viscous poly(amic acid) solution and evenly mixed, the blend was spread on a glass plate and cured at 80°C. The edge of resulted film was found to be a little fragile. This film was rather brittle after further curing at a higher temperature. The process indicates that acetic anhydride, acting like PMDA and PA, exchanges with poly(amic acid) and decomposes it. While after pyridine was added to the same polymer solution and the films were cast by heating, both poly(amic acid) and polyimide films obtained were flexible. In the course of curing, pyridine volatilized as a solvent, didn't react with polymer and hence didn't affect the polyimide curing. If a proper amount of the mixture of A/P at 2/1 volume ratio was added to poly(amic acid) solution, polymer gelled at once and squeezed the solvent out. After the volatilization of the solvent by heating, a tough and hard polyimide bulk was obtained by further heating at 250°C. This indicates that, under the catalysis of pyridine, poly(amic acid) can be cyclodehydrated by acetic anhydride without any cleavage of polymer chain. This characteristic enables us to obtain polyimide with good strength. Since polyimide is insoluble in DMAc, a considerable amount of solvent was squeezed out at the same time when the gelation occurred.

Furthermore, the cured poly(amic acid) films were immersed in the solution of A/P at different ratios. The results of film curing and the phenomena observed during the process of curing are listed in Table X. The immersion of the poly(amic acid) film in pure acetic anhydride resulted in red and brittle pieces, while the heating of cyclodehydrated polyimide immersed in acetic anhydride didn't bring about any change. This indicates again that poly(amic acid) will react with acetic anhydride and decompose; however, it is very stable and doesn't react with acetic anhydride after it

TABLE X
Effect of Acetic Anhydride (A)/Pyridine (P) Ratio on the Imidization of PMDA-DAPM Poly(amic Acid) Films

Vol ratio A/P	Film property on Time after Addition into dehydrating agents at 25°C		Film property on 30 min after heating at 90°C
	10 min	1 h	
1/0	Exhibited some strength	Brittle	Red and brittle pieces
40/1	Turned to yellow	Yellow	Yellow, with poor strength
30/1	Opaque	Yellow	Yellow, with some strength
20/1	Transparent	Transparent	Turned partly to yellow, but with good strength
15/1			
10/1			
3/1	Transparent, with good strength		
2/1			
1/1			
1/2	Turned to yellow	Yellow	Yellow, with poor strength
1/3	Turned to yellow	Yellow	Yellow, with poor strength
0/1	Dissolved	—	—

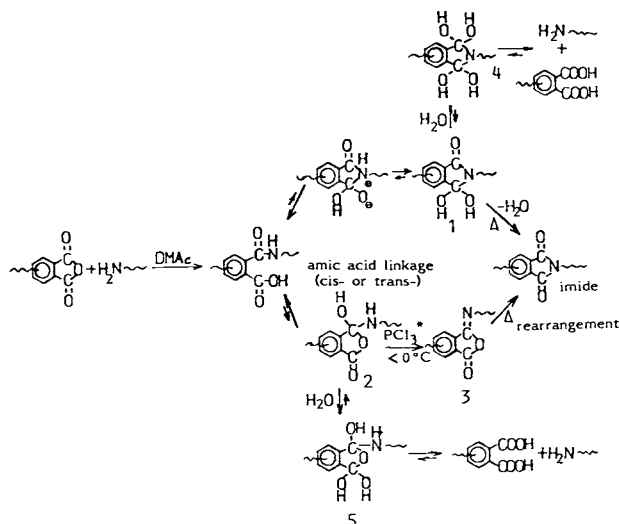
is cyclized to polyimide. Ten minutes after poly(amic acid) was immersed in pyridine, the film dissolved in it and ended up a clear solution. In case some drops of acetic anhydride were added into the solution, the yellow gel of polyimide was found to appear in it. In the mixture of A/P at a ratio of $1/2$ or $1/3$, the film, immersed for 30 min at room temperature, turned yellow but didn't fracture, and still possessed strength. On the other hand, while in the solution of A/P = 1/1, the film treated was clear and possessive of good strength. This fact may account for the ratio of 1:1 so commonly mentioned in the literature. Increase the proportion of acetic anhydride and we find that as long as small amounts of pyridine is present, the film won't become brittle during the curing. However, when pyridine is too small in amount, the film would be partially degraded by acetic anhydride, as seen from the change of color and the decay of strength.

Thus, if we want to convert polyamic acid to polyimide by acetic anhydride and pyridine, it is necessary to note the following three facts: (1) if the acetic anhydride is used singly without the protection of pyridine, the anhydride will react with polymer and cause the degradation of polymer; (2) when A/P is smaller than 1, the excess pyridine will cause a partial dissolution of polymer, thus ending up in a film yellow in color and weak in strength; and (3) in the mixture of A/P with ratios ranging in 1/1-15/1, the polyimide film obtained is clear, and possesses good strength; but when the ratio is above 15/1, the film becomes opaque and weak.

Suggested Mechanism

The polar solvent DMAc, acting as Lewis base under anhydrous conditions, increases the nucleophilicity of the dissolved aromatic diamine; therefore, the addition of PMDA to the solution of diamine will result in a rapid polymerization, and the monomers are largely converted to poly(amic acid) in a few minutes. Because the position of the dianhydride carbonyl attacked

by the amino group may be different, it may produce a *cis* or *trans* form of *o*-carboxyamide linkage in the polymer chain. The amide and carboxylic groups may react to each other and then result in the intermediates 1 and 2 as shown in Scheme 1, where the structure 1 is presumed to be an intermediate in the normal curing process and can be converted to polyimide by thermal cyclodehydration, and the intermediate 2 can be dehydrated to give intermediate iminolactone 3, which rearranges to imide on heating:



Scheme 1. Reactions of poly(amic acid) in polar solvent DMAc: (*) see Ref. 4.

Dine-Hart and Wright⁴ proposed that the amic acid first rearranged in an enol structure in DMF, and then it was dehydrated by PCI₃ at the temperature below 0°C to give an iminolactone such as the structure of 3 in Scheme 1. Kumar⁶ also mentioned this intermediate in his suggested mechanism for the imidization of polyamic acid. However, the isoimide structure¹⁰ was easily converted to *n*-imide by heat.

The reactions of two possible paths in the course of curing can also occur at the room temperature. Frost and Kesse⁵ found that about 20% imidization of 10% polyamic acid solution occurred in 4826 h of aging at 35°C. Therefore, when the polyamic acid solution is aged at room temperature, the intermediates 1 and 2 may be attacked by water which may come from the solvent or be released during the imidization of amic acid to give the intermediates 4 and 5 respectively, and then decompose to acid compound and amine. This is different from the presumption proposed by Frost and Kesse.⁵ They thought that the intermediate 2 might split out the amino group at a slow rate to give an anhydride before water attacked the anhydride group in competition with amine to hydrolyze the polyamic acid. However, the reaction rate of aminolysis in DMAc is 5 times that of hydrolysis, so that the probability of the polymer's hydrolysis in this way is very slim; therefore, it is presumed that poly(amic acid) is hydrolyzed through the intermediates 4 and 5 as mentioned above.

In the course of polymerization, if the amount of amine is excess, the product is presumably a polymer of low molecular weight with terminal

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