The Effects of Reaction Temperature and Hydrolysis on Polyamic Acids and Polyimides

E. L. JOHNSON, *The Bendix Corporation, Kansas City Division, Kansas City, Missouri 64141*

Synopsis

For some time, polyimides have enjoyed a significant degree of superiority over the other classes of thermo-oxidatively stable polymers. This superiority is, however, offset by the tremendous difficulty associated with the processing of polyimides. In an effort to understand these difficulties and their causes, several experiments were performed which reflect the roles that reaction temperature and hydrolysis (caused by the presence of water) play during amidization and imidization. Temperatures between 0° and 120°C were found to result in progressively lower-viscosity polyamic acids whose equivalent weights varied only slightly with increasing reaction temperatures. The presence of hydroxide ions from water were shown to cause degradation of the polymer, and the combination of temperatures above 120°C and hydroxide ions results in the rapid degradation of the polymer and lower molecular weight polyimides.

INTRODUCTION

Polyimides may be prepared by a number of reaction routes.[1–5] Among these are polyamide salts, trialklammonium salts, diesters of tetrabasic acids, and others.[6–9] This paper, however, deals with the preparation of polyimides (PI's) and polyamic acids (Paa's) by reacting diamines and tetrabasic acid dianhydrides together directly in solvents such as dimethylformamide (DMF) and dimethylacetamide (DMAc).

Polyimides have been in use for some time and have been found to exhibit several desirable properties. Among these properties are their tremendous electrical insulating capabilities and their unusually high thermo-oxidative stability. However, these exceptional properties are, in many cases, offset by the problems associated with processing. In almost all of these problems, the cause can be related to the water of condensation that is liberated during curing (imidization) and hydrolysis of the Paa which causes lower molecular weight polymers. This problem is usually approached from the standpoint of synchronizing the rates of volatile formation and water removal in an attempt to minimize the lowering of the molecular weight.

The major objective of this paper is to describe the chemical reactions involved in the preparation of PI's and Paa's and to relate the chemical mechanisms of amidication, imidization, and polymer hydrolysis (deg-

radation) with one another. It is hoped that by obtaining a better understanding of the chemistry involved in the preparation, application, curing, and degradation of PI's, those who are interested in the use of PI's will be able to combat the problems that are usually associated with the processing of polyimides.

EXPERIMENTAL

Materials

The materials used during this study were commercial materials of the highest available purity. The benzophenonetetracarboxylic acid dianhydride (BTDA) and the pyromellitic dianhydride (PMDA) were obtained from Gulf Chemical Company and Princeton Chemical Company, respectively. The diamines used were also obtained from various chemical companies as reagent-grade chemicals. These diamines are listed in Table I. The solvent used, dimethylacetamide (DMAc), was obtained

TABLE I
List of Abbreviations

Symbol	Name
PCH₂P	bis(4-aminophenyl)methane
POP	bis(4-aminophenyl) ether
p-øDA	p-phenylenediamine
BTDA	benzophenonetetracarboxylic acid dianhydride
PMDA	pyromellitic dianhydride
DMAc	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
Paa	polyamic acid

from Eastman Organic Chemical Company. Since all of these chemicals were obtained as reagent-grade chemicals they were used without further purification.

Equipment

All reactions were run in 1- to 4-liter reaction vessels or 250- to 500-ml round-bottom flasks equipped with an air motor-driven Teflon stirrer, a tachometer, a thermometer, and a dry nitrogen flush system (Fig. 1).

Viscosity measurements were made using a Brookfield viscometer (LVF) at the indicated temperature. Spindle No. 2 was used in all instances, and a speed of either 6, 12, 30, or 60 rpm was used.

Potentiometric titrations were carried out in the determination of equivalent weight values. A Beckmann Expandomatic pH Meter was used to carry out these operations.

Equivalent Weight Determinations

Polyamic acid equivalent weight values were obtained by dissolving 1.0-g samples of the resin in 50 ml of N,N-dimethylacetamide and adding 50.0 ml of 0.1N potassium hydroxide. This mixture was allowed to
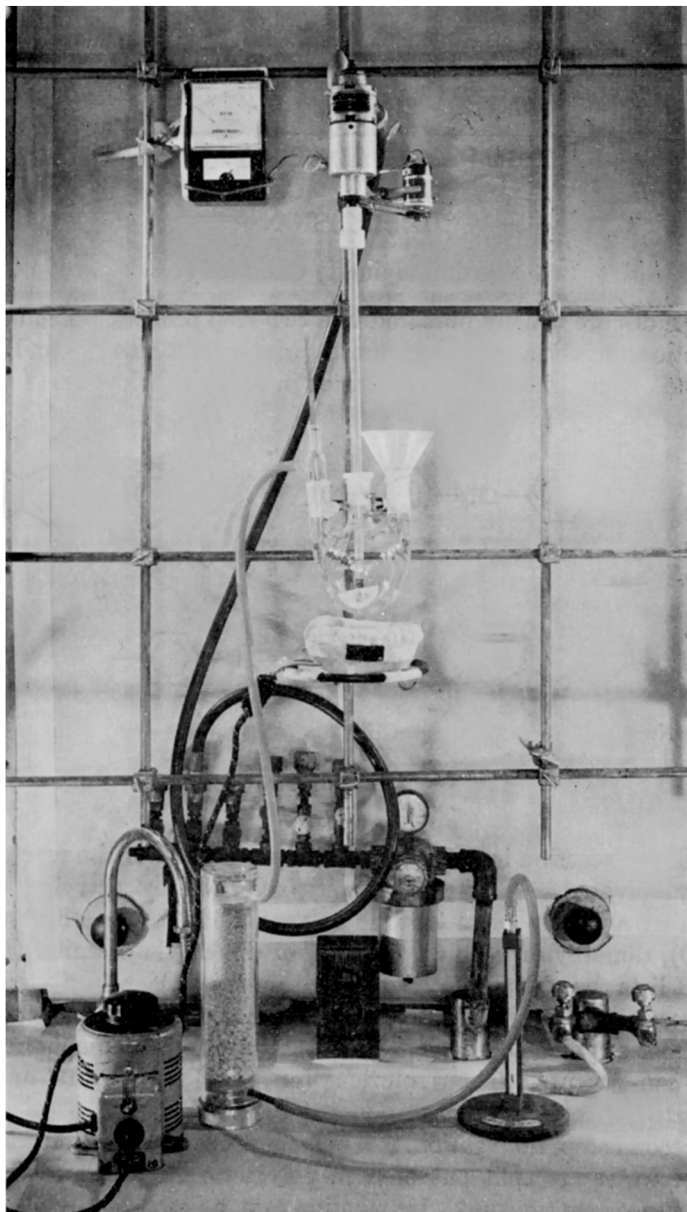

Fig. 1. Apparatus used to prepare polyamic acids.

stir for 3.0 min, and then the unreacted base was back-titrated with 0.1N hydrochloric acid. Sample calculations are shown below:

sample weight:	1.00 g
milliliters of KOH:	50.00
milliliters of HCl:	30.00
acid and base normality:	0.10

$$\text{equivalent weight} = \frac{\text{sample weight}}{(\text{ml of KOH} - \text{ml of HCl}) \cdot (\text{normality}) \cdot 10^{-3}}$$

$$= \frac{1.000 \text{ g}}{(50.0 \text{ ml} - 30.0 \text{ ml}) \cdot (0.10N) \cdot 10^{-3}} = 500 \text{ g/equivalent}$$

DISCUSSION

Basic Polyimide Chemistry

Polyimides are usually prepared in a two-step process. The first step, amidization, involves the reaction of a primary diamine (I) and a tetrabasic acid dianhydride (II) as illustrated in eq. (1):


(1)
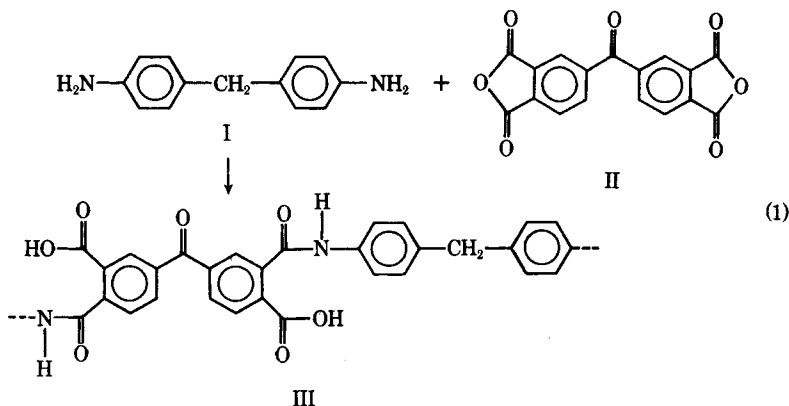
The addition reaction is spontaneous and exothermic if the reactants are properly solvated.[1,2,3] This is usually achieved by carrying out the reaction in a highly polar aprotic solvent such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or dimethylacetamide (DMAc). (Table I lists the abbreviations used in this report.)
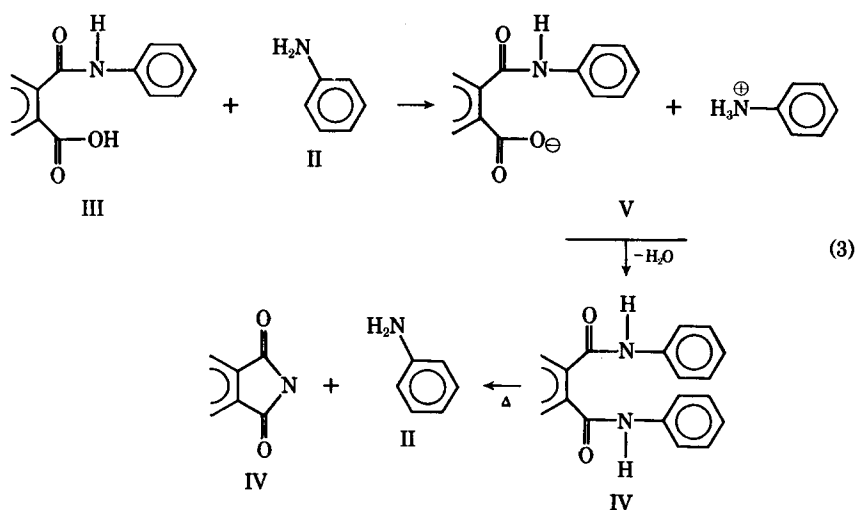
The resulting polyamic acids (III) vary in color from bright yellow to dark amber or green solutions, depending upon the chromophoric nature of their constituents. These solutions (or resins) may be cast or shaped, then heated to form their corresponding PI articles.

The second step, imidization, is a polycondensation reaction where two moles of water are split out of each polymeric unit. The imidization process is not spontaneous. Its reaction rate, as reported by others, was found to be proportional to the reaction temperature and has been found

to reach a maximum value between 120° and 140°C (278° and 280°F).[4] This direct intramolecular elimination of water is shown in eq. (2) and constitutes the main imidization (curing) process:
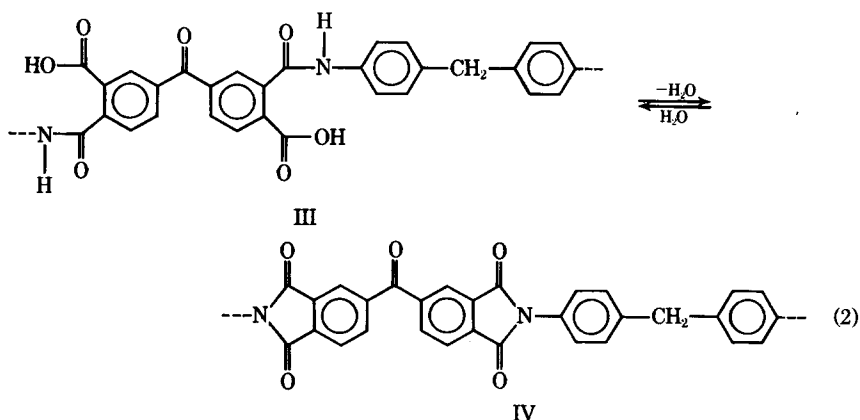
Hergenrother and co-workers[4] have shown that the ammonolysis of the anhydride to form Paa is a bimolecular reaction involving the nucleophilic attack of the amino group upon the anhydride. It was also reported that equilibrium is attained in Paa formation, eqs. (3) and (4), when 78 mole-% of the dianhydride had been added to 100 mole-% of the diamine. This conclusion was also based on infrared (IR) spectral analyses performed by Hergenrother. The remaining 22 mole-% of diamine reacts to form a nylon-like salt (V) through the available carboxylic acid groups (III). This was further substantiated by the observation of —NH_3^+ and/or —O^- absorption bands at 3.78 and 3.95 μ after the reaction mixture was allowed to stand for 10 min.

$$O + DMAc \xrightarrow{k_5} \quad O + H_2N \quad \longleftarrow \quad H_2N \quad + DMAc$$

II

$$\downarrow k_1$$

(4)

These salts, eq. (3), are believed to further react when heat is supplied to form the corresponding diamide (VI) and finally the corresponding imide (IV), with the elimination of free primary amine. The imidization process was found to be the source of our greatest difficulties.

The intramolecular elimination of water shown in eq. (2) represents the main imidization (curing) process. This constitutes a 5.2% weight loss. This is further complicated by the elimination of 2 moles of complexed DMAc per mer.[5] Thus, a total of 30.2% weight loss takes place, eq. (2), in a relatively short period. Polyimides are relatively nonporous materials, and this inherent characteristic minimizes the rate at which the volatiles of condensation may be evolved. Thus efforts to prepare thick polyimide films and moldings often result in parts filled with bubbles, voids, and/or cracks.

To abate these problems efforts were made to synchronize the rate of volatile removal with imidization. Cure cycles were developed for coatings, films, and adhesives which synchronized these processes and minimized bubbling as well as its associated problems. In casting films, aluminum foil can be placed over the films. As the DMAc is evolved, the atmosphere immediately above the film's surface becomes saturated with DMAc. This enhances the permeability of the films' surface, thus abating bubbling.

Imidization may be carried out by chemical as well as thermal means.[6] Polyamic acid films were prepared, then steeped in a mixture of acetic

anhydride, pyridine, and cyclohexane.[7] The acetic anhydride acted as a water scavenger by reacting with the eliminated water, eq. (2), from the imidization process. The removal of this water minimizes the hydrolytic degradation of the polymer which results in chain cleavage. The chemical removal of water, as opposed to driving it off by heating, appears to lower the activation energy of the imidization process. This allows imidization to take place at lower temperatures. This method was not pursued because the resulting films had to be dried at 300°C (670°F) to 320°C (683°F), as did those made by conventional methods.[1-5] Also the steeping process was inconvenient.

Various Heterogeneous Methods of Preparing Polyamic Acids

In an effort to evaluate various methods of preparing polyamic acids which might improve their processibility and to learn more about polyimides, the following polyamic acid synthesis methods were evaluated.[1,2] These methods involved the addition of one or both reactants to the reaction solvent as solids and are therefore called heterogeneous methods. The powdered diamine and/or the dianhydride are reacted stoichiometrically in the solvent, herein denoted A, B, and C, respectively. The three methods evaluated are shown below as 1, 2, and 3, where C (the solvent) is always in excess:

1. A + BC → ABC (A is added to a solution of B in C)
2. B + AC → ABC (B is added to a solution of A in C)
3. AB + C → ABC (A and B are first blended dry then slowly added to C)

In agreement with other works, method 3 was found to be more practical and to yield solutions of higher molecular weights, as indicated by viscosity measurements.[1] For these reasons, method 3 was used most extensively to prepare polyamic acids. Throughout these evaluations equipment similar to that shown in Figure 1 was used to prepare polyamic acids.[7-12]

Polyamic acid powders were prepared by precipitation from DMAc using a nonpolar solvent, such as benzene or diethyl ether, or by reacting the diamine and the dianhydride in anhydrous tetrahydrofuran (THF).[1] The THF precipitation method was found to be less time consuming and much more efficient for preparing unsolvated polyamic acids. In this method the diamine and the dianhydride were each suspended (or dissolved) in enough THF to yield 30% suspension (or solutions). These were then placed in separatory funnels and simultaneously added to enough THF with stirring to yield a 25% suspension of polyamic acid in THF. (Efforts were made to keep the molar rates of addition equal.) The resultant polyamic acid powder was a grey-green material which turned gray-tan after washing with ether and drying in a vacuum oven.

The fact that the polyamic acids are not complexed by the THF is evidenced by the observation that the polymer precipitates from THF

while it is soluble in DMAc.   These realities indicate that the solvent–solute interaction is greater in the DMAc/Paa than in the THF/Paa. The enormous interaction between the polymer and the DMAc is also evidenced by the tremendous distortions in the infrared and ultraviolet spectra of the solvated and unsolvated polymers and model compounds.[13]

This method of preparing uncomplexed (or solvent-free) Paa's was very interesting in that Paa's could be prepared that were not complexed with DMAc.   Also, as reported by others, the rate of amidization appeared to be a function of the rate of solution of the reactants.[1,3]

Effects of Reaction Temperature and Hydrolysis in Preparing Polyamic Acids and Polyimides

The effects of preparing polyamic acids at various temperatures were also evaluated.   Polyamic acids were prepared at various temperatures between 0° and 160°C.   Figure 2 shows a relatively steady decline in viscosity as the reaction temperature is raised and reflects the relationship between reaction temperature and viscosity.

Polymer propagation takes place as part of the amidization process. Figure 3 shows a plot of polyamic acid equivalent weight as a function of reaction temperature for POP/PMDA (system C) as an 8.81% solution. It should be noted that the equivalent weight changed very little until a reaction temperature of 120°C was used.   At this point, a sudden increase in equivalent weight was observed.   This indicates that as the reaction temperature is increased from 0° to about 110°C, the number of free carboxylic acid groups does not change significantly.   Beyond this point, the number of free acid groups decreases rapidly, denoting a drastic
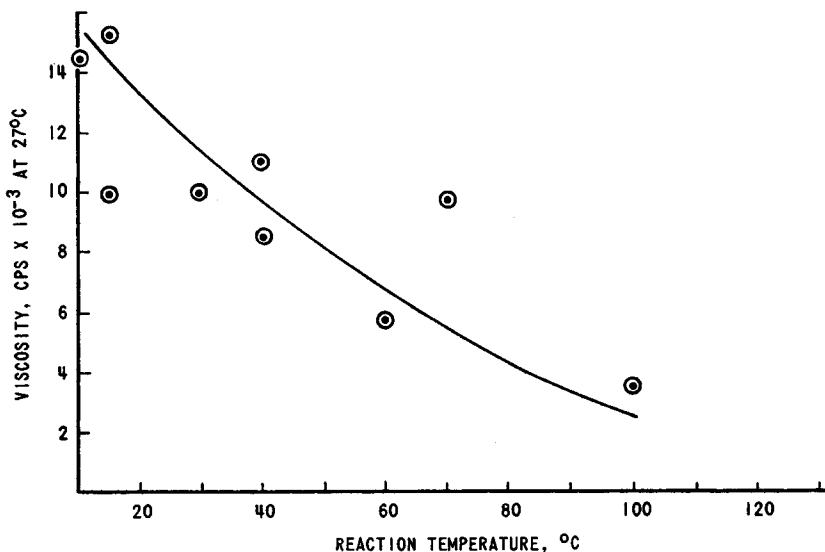

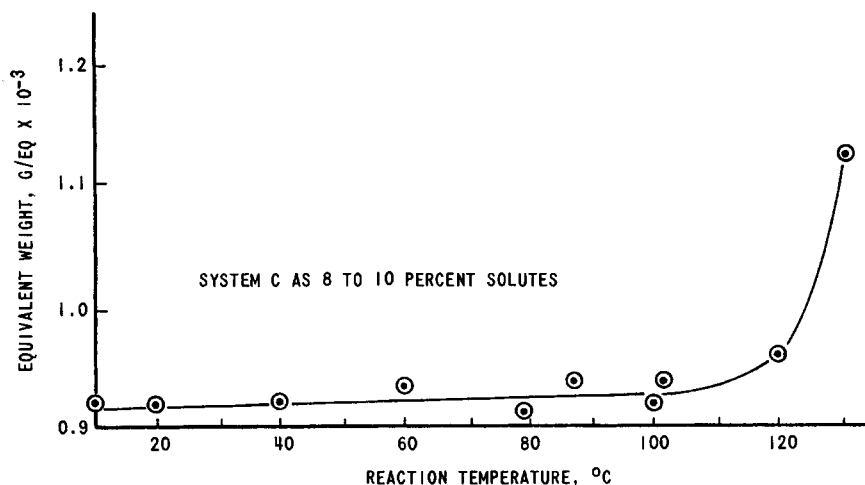Fig. 2. Polyamic acid viscosity as a function of reaction temperature.

Fig. 3. Typical plot of equivalent weight as a function of reaction temperature.
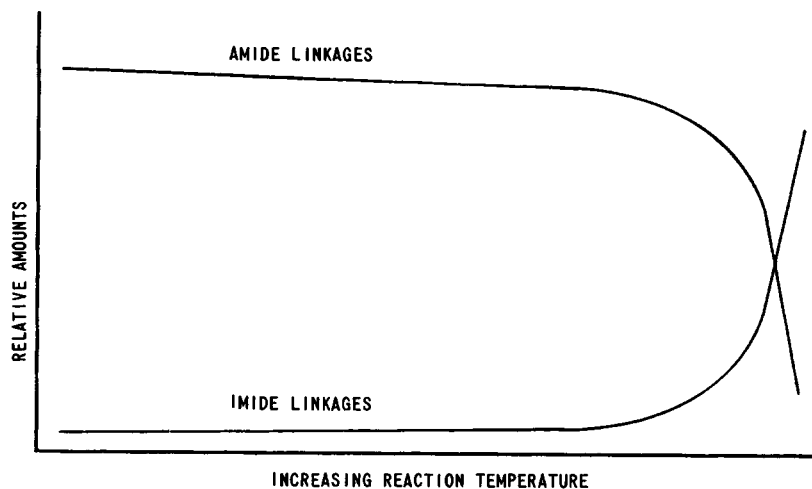

Fig. 4. Hypothetical plot of the rate of imidization and amidization as a function of time.

increase in the rate of imidization. The solutions prepared above 120°C contained a suspension of a tan powder which was identified as polyimide. Similar products have been obtained by others.[3] At temperatures below 120°C, imidization also takes place but at a much slower rate. This is indicated in Figure 3 where the equivalent weight remains relatively constant until a 120°C reaction temperature is reached. If imidization were taking place at a significant rate below 120°C, the equivalent weight would increase progressively with reaction temperature, since imidization consumes carboxylic acid groups. Also, since amidization of the solvated reactants is spontaneous, the relative number of amide linkages probably

remains constant, if side reactions do not interfer, until imidization begins to take place.   When the rate of imidization does become significant, the number of amide linkages begins to decrease.   Also, as the temperature is increased, the possibility of amide and imide hydrolysis increases. Amide hydrolysis results in chain cleavage and ultimately lower molecular weight polyimides.   Ignoring hydrolysis and the possibility of salt formation, the relative number of amide and imide linkages in a system was plotted hypothetically as a function of reaction temperature in Figure 4.

As expected, polyamic acids are soluble in bases and react with them to form their corresponding salts.   Thus, titration of polyamic acids with potassium hydroxide solutions is possible to determine the number of unreacted carboxyl groups in the polymer system.   This number per unit
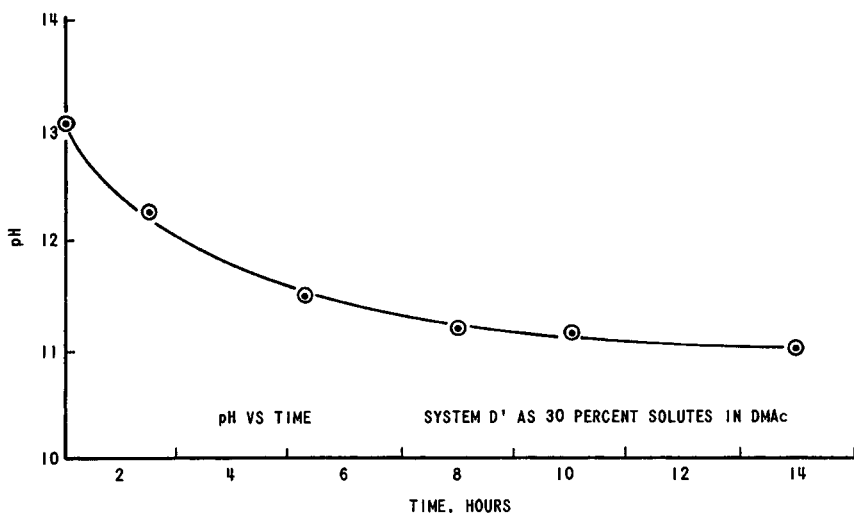

Fig. 5. Plot of pH vs. time for 1.0 g PCH₂P/BTDA dissolved in a mixture of 50 ml 0.1N KOH and 50 ml DMAc.

mass can be than used to determine the equivalent weight of the resin. The equivalent weight value, therefore, reflects just how far imidization has proceeded.

Titration is, however, complicated by the attack of the hydroxide ions of the KOH on the amide linkages of the polyamic acid as well as the DMAc to form benzophenonetetracarboxylic acid and acetic acid, respectively.   Thus, the equivalent weight values obtained in this direct manner were found to be time dependent and to vary with the length of time the polyamic acid was allowed to react with the KOH.   In Figure 5, this relationship is illustrated in a plot of pH as a function of time.   A steady decline in pH was noted over a 14-hr period when 1.0 g PCH₂P/BTDA (system D′) as a 30% solution in DMAc was dissolved in 50 ml 0.10N KOH and 50 ml DMAc.   This indicates that carboxylic acid groups are being generated as the solution is stirred, thus reacting with the KOH
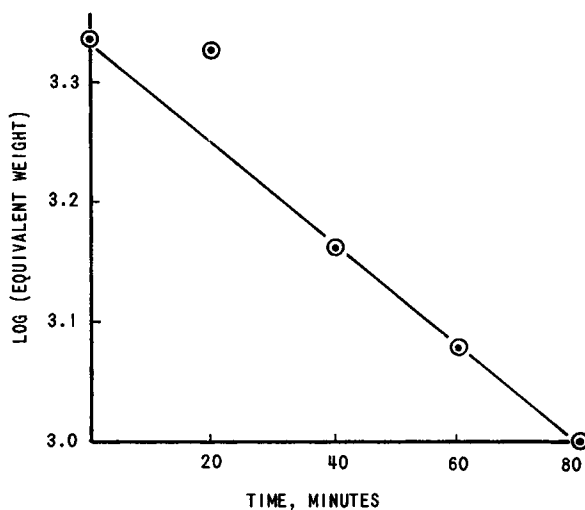
Fig. 6. Log equivalent weight of a typical polyamic acid plotted as a function of time.

to form the corresponding potassium salt and water and causing the observed decrease in pH.

In order to fully evaluate the time dependence of the equivalent weight (eq wt) determinations and the hydrolysis of Paa's and PI's, hydrolysis rate constants were determined by plotting log eq wt as a function of time as hydrolysis proceeded. Polyamic acid samples (5 g each) were dissolved in 1.00N KOH and back-titrated with 1.00N HCl, one sample was withdrawn and back-titrated every 20 min from 0 to 80 min. These results are summarized in Figure 6 and Table II. Figure 6 is a plot assuming first-order kinetics. The slope of this plot yields a first-order rate constant of 9.12×10^{-3} min^{-1}. Although these data suggests first-order kinetics, one should bear in mind that the hydroxide ions that attack the amide and imide linkages are in excess. For this reason, their relative amounts change very little. Thus, the hydrolysis reaction in this instance is pseudo-first order.

The value of 9.12×10^{-3} min^{-1} for the hydrolysis rate constant is significant in that it indicates that the hydrolysis reaction does proceed

TABLE II
Polyamic Acid Potassium Hydroxide Hydrolysis

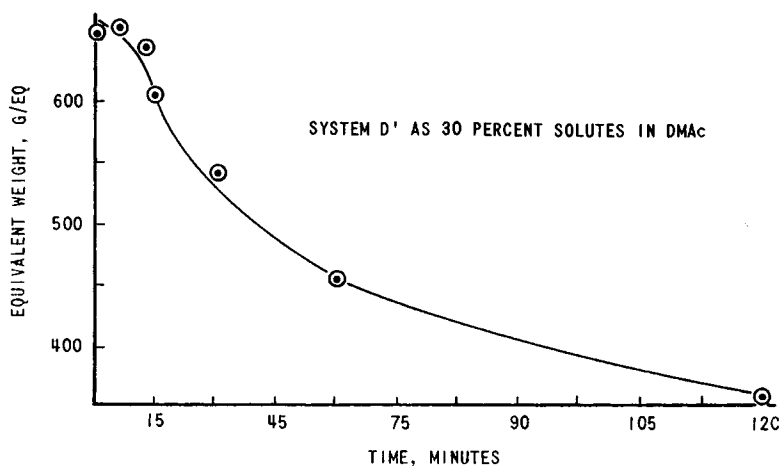| Time, min	HCl, meq	KOH, meq	Equivalent weight, g/eq	Log equivalent weight
0.0	7.61	2.39	2,090	3.32
20.0	7.30	2.70	1,852	3.27
40.0	6.50	3.50	1,428	3.15
60.0	5.85	4.15	1,205	3.08
80.0	4.90	5.10	980	2.99

Fig. 7. Equivalent weight values plotted as a function of reaction time.
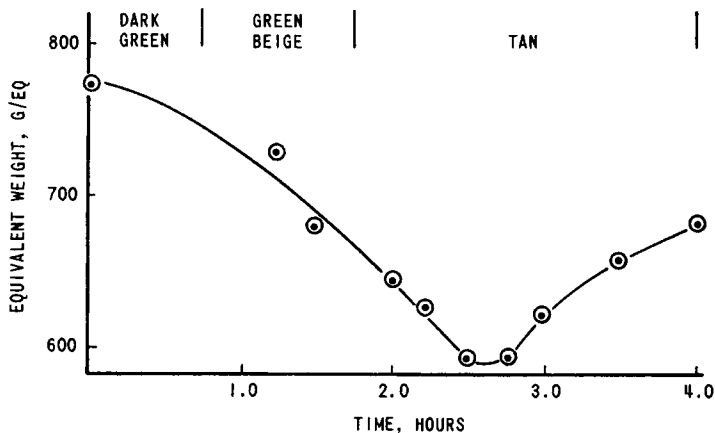
Fig. 8. Plot of equivalent weight vs. time: 8.81% solution of system C.

rapidly.   This was also suggested in Figure 5 where pH was plotted as
a function of time for a Paa dissolved in KOH.   The pH changed from
14.0 to 11.3 in a 14-hr period, indicating that hydrolysis was taking place
and generating new carboxylic acid groups.

Thus, the reaction temperature and the amount of water present are
very important in considering Paa molecular and equivalent weights.
Lower temperatures and anhydrous reactions are most favorable for ob-
taining high molecular weight Paa's and PI's.

Dissolving the polyamic acid in a known amount of 0.10N KOH and
back-titrating the unreacted KOH with 0.10N hydrochloric acid proved to
be the most efficient way of obtaining equivalent weight values.   Values
were obtained for various reaction time intervals, averaged, and plotted
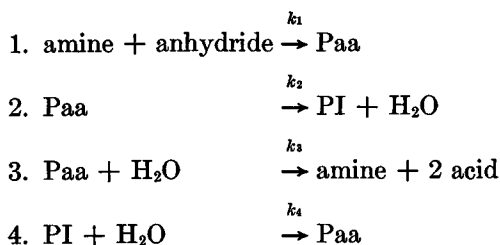as a function of reaction time in KOH and then extrapolated to zero time

to obtain the polyamic acid equivalent weight. Results for system D' as a 29 to 30% resin are shown in Figure 7.

Figure 8 is a plot of the equivalent weight of a Paa as a function of reflux time and temperature. These relationships were obtained by refluxing 500 ml of an 8.81% solution of p-ϕDA/PMDA (system E) and withdrawing 1.0-ml samples from the reflex vessel every 15 min during a 4-hr period. Equivalent weight determinations were made on each sample to ascertain the equivalent weight (the number of carboxylic acid groups per unit mass) of the refluxing solution. An initial decrease in equivalent weight was observed denoting an increased number of carboxylic acid groups, since equivalent weight equals the number of grams of material necessary to yield one equivalent of carboxylic acid groups and since equivalent weight is inversely proportional to the number of carboxylic acid groups per unit mass. After approximately 2.5 hr, a minimum value was obtained and the equivalent weight began to increase, denoting a decrease in the number of carboxylic acid groups per unit mass. This increase in equivalent weight continued at a steady rate to the end of the 4-hr period. During this period, the color of the refluxing solution changed from dark green to green-beige and finally to a tan flocculent precipitate, as indicated in Figure 8. These results are also summarized in Table III.

TABLE III
Effects of Refluxing 500 ml of an 8.81% Solution of System C (POP/PMDA)

Time, hr	Temp., °C	Carboxylic acid equivalent weight, g/eq	Color
	8	769.5	dark green
0.25	59		
0.50	115		
0.75	154		green-beige
1.00	161		
1.25	161	725.0	
1.50	160	675.0	
1.75	160	642.0	tan
2.00	160	640.0	
2.25	160	623.0	
2.50	160	589.0	
2.75	160	589.0	
3.00	160	619.0	
3.25	160	642.0	
3.50	160	655.0	
3.75	160		
4.00	160	676.0	

The following explanation of these events is offered. There are four basic reactions taking place: (1) amidization; (2) imidization; (3) Paa hydrolysis; and (4) PI hydrolysis:

1. amine + anhydride $\xrightarrow{k_1}$ Paa

2. Paa $\xrightarrow{k_2}$ PI + H$_2$O

3. Paa + H$_2$O $\xrightarrow{k_3}$ amine + 2 acid

4. PI + H$_2$O $\xrightarrow{k_4}$ Paa

The relationships of these reactions to one another are illustrated in eq. (4). (Since the solvent DMAc plays an active role in these reactions, many species are shown here in their solvated states.)

Two other important reactions also take place. These involve the solvation of the amine and anhydride by the DMAc and are prerequisite to all other reactions. Thus they play an intricate part in the four basic reactions as well as all other reactions and will be referred to here as reaction 6 and 5, respectively.
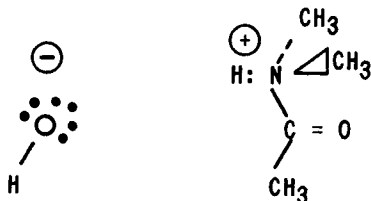
Fig. 9.

In eq. (4), the amine and anhydride spontaneously react to form the corresponding Paa *if they are properly solvated,* indicating that the rate of reaction for reaction 1 (r_1) is relatively large.[1,3] This also indicates that reactions 5 and 6 are prerequisite to all others. Basically, the Paa may participate in three possible reactions: reaction 3, which is the hydrolysis of the Paa; reaction 2, which eliminates water to form the corresponding imide; and reaction 7, which yields the Paa amine salt. Equilibrium is most likely established between these species, and their abundance is a function of the reaction conditions, which dictate the values of r_2, r_3, r_7, and r_7 of eq. (4).

The following assumptions are to be made: (1) $r_6 \geq r_5 > r_1$, r_2, $r_3 r_4$; (2) $r_2 \gg r_1 + r_3 + r_4$ if reaction temperature is above 120°C; (3) $r_1 \gg r_2 + r_3 + r_4$ if reaction temperature is below 120°C; (4) reactions 1, 3, and 4 generate carboxylic acid groups; (5) reaction 2 consumes carboxylic acid groups. Therefore, if during the heating period to 120°C reaction 3 proceeds at a rate greater than the rate of reaction 2, the observed increase in carboxylic acid groups is explained. At temperatures above 120°C, reaction 2 must proceed at a rate greater than reactions 1, 3, and 4 since the number of carboxylic acid groups present per unit mass is decreasing, as denoted by the increasing equivalent weight values.

As previously mentioned, the hydrolysis reaction is believed to result in the formation of amine salts as depicted in reactions 3 and 7 of eq. (4).[1] This hydrolytic degradation is enhanced because of the polar aprotic nature of the solvent (DMAc). The DMAc becomes strongly complexed with any hydrogen ions (H$^+$) in the system and this results in an increase in the strength of the hydroxide ions (OH$^-$) liberated during imidization in the formation of water. Thus, water as we know it, H$_2$O, is not actually formed, but exists as OH$^-$ and H$^+$ complex with DMAc as shown in Figure 9.

These amine salts when heated form their corresponding PI as illustrated in reactions 9 and 10 of eq. (4). The amine salts are greatly solvated by the DMAc and often cause decreases in solution viscosity since intermolecular secondary bonding forces are diminshed.[1,4,5]

As previously mentioned, the hydrolysis reaction is believed to result in the formation of amine salts as depicted in reactions 3 and 7 of eq. (4).[1] When heated, these amine salts form their corresponding PI as illustrated in reactions 9 and 10 of eq. (4). The hydrolytic degradation of the polymer is enhanced by the polar nature of the DMAc.

References

1. R. A. Dine-Hart, *The Preparation and Fabrication of Aromatic Polyimides,* AD-482530 DDC, Royal Aircraft Establishment, Oct. 1965.

2. J. K. Fincke, G. R. Wilson, R. E. DeBrunner, and R. F. Pietrzok, *Synthesis of New and Improved Thermally Stable Polyimide Laminating Reports and Adhesives,* AD 804 267 DDC, Monsanto Research Corporation, May 1966.

3. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Beer, W. M. Edwards, and K. L. Olivier, *J. Polym. Sci. A,* **3,** 1373 (1965).

4. P. M. Hergenrother, W. J. Wrasidlo, and H. H. Levine, *High Temperature Structural Adhesives,* DDC-AD 602 679, Narmco Research and Development, April 1964.

5. G. M. Bower and L. W. Frost, *J. Polym. Sci. A,* **1,** 3135 (1963).

6. W. M. Edwards and A. L. Endry (to E. I. du Pont) Brit. Pat. 903,271 (1962).

7. A. L. Endry (to E. I. du Pont) U. S. Pat. 3,179,630 (April 20, 1965).

8. A. L. Endry (to E. I. du Pont) U. S. Pat. 3,179,632 (April 20, 1965).

9. A. L. Endry (to E. I. du Pont) U. S. Pat. 3,242,136 (March 22, 1966).

10. R. J. Angelo (to E. I. du Pont) U. S. Pat. 3,282,897 (November 1, 1966).

11. W. M. Edwards and I. M. Maxwell (to E. I. du Pont) U. S. Pat. 2,880,230 (March 1, 1959).

12. G. G. Fritz (to E. I. du Pont) U. S. Pat. 3,376,260 (April 2, 1968).

13. E. W. Crandall and E. L. Johnson, Bendix Corporation, unpublished work.