JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 1039-1051 (1964)

Spontaneous Degradation of Aromatic Polypyromellitamic Acids*

L. W. FROST and I. KESSE, *Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*

Synopsis

The reaction of pyromellitic dianhydride with a solution of a primary diamine in a solvent such as dimethylacetamide gives a viscous solution of a polypyromellitamic acid of high molecular weight. The viscosity of the solution decreases greatly when it is aged at 35°C. Higher temperatures or the presence of water, excess amine or excess anhydride accelerate the rate of decline. A rapid early drop in viscosity has been found to be due primarily to hydrolysis by adventitious water and to exchange reactions of amine or anhydride groups with the *o*-carboxyamide linkage. Slow decline over a long period of time results from hydrolysis by water produced in the slow conversion of polypyromellitamic acid to polypyromellitimide. Degradation by hydrolysis also occurs when polyimide films are cast by heating the solution. The effect can be minimized by casting thin films, from which water can diffuse rapidly, or by using a chemical method, such as treatment with acetic anhydride and pyridine, to remove the water produced in imidization.

INTRODUCTION

The preparation and properties of aromatic polyimides have been described by several authors.[1-3] Typically, the preparation is performed in two steps. A dianhydride, such as pyromellitic dianhydride (PMDA), is first added to a solution of a primary diamine at a temperature below about 50°C. to give a solution of a poly(*o*-carboxyamide).[4] Dehydration of this intermediate polymer, either by heat or by chemical means, produces the insoluble polyimide.

It has been reported by Edwards and Endrey that highly purified reactants and anhydrous solvents are necessary for best results,[3,4] but no further explanation was given. A reduction of intrinsic viscosity and molecular weight was noted by Frost and Bower when polypyromellitamic 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.[1] The present paper extends these observations and proposes a mechanism for the degradation of polypyromellitamic acids in solution and during cure.

---

* Presented at the 144th American Chemical Society meeting, Los Angeles, April 1963.

RESULTS AND DISCUSSION

In a previous paper[1] Frost and Bower reported the viscosity changes which occurred when PMDA was added slowly to a solution of 4,4′-methylenedianiline (MDA). The procedure used gave viscosity values that were dependent upon both the reactant ratio and the time of aging of the solution. In order to separate these variables, a series of experiments have been made with the same reactants with dimethylacetamide (DMAC) as solvent, but with addition of the total amount of PMDA at once and

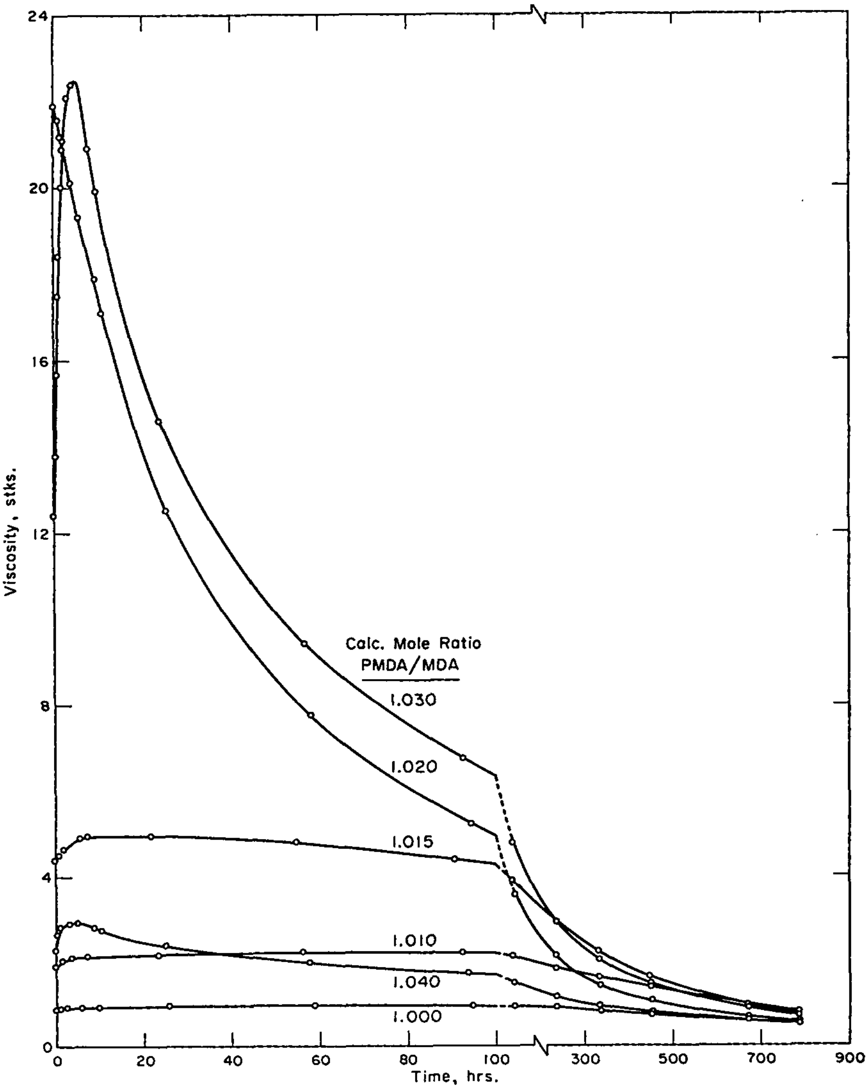


Fig. 1. Effect of reactant ratio on viscosity behavior of 12% MDA-PMDA in DMAC at 35°C.

TABLE I
Effect of Reactant Ratio on Viscosity of MDA–PMDA Polymer Solutions at 35°C.

Mole ratio, PMDA/MDA (calc.)	Maximum viscosity, stokes	Time to maximum, hr.	Viscosity at 2140 hr., stokes
1.000	0.946	60	0.227
1.010	2.195	58	0.369
1.015	4.95	12	0.372
1.020	>21.91	<0.3	0.357[a]
1.030	22.39	4.2	0.309
1.040	2.892	4.2	0.316

[a] Value at 1420 hr., when sample was lost. Viscosity was essentially constant after 1100 hr.

then following of the change in viscosity with time. Six different reactant ratios were used, and viscosities were observed for 2140 hr., with the results shown in Figure 1 and Table I. The graph was not continued beyond 800 hr. because the lines became too close to distinguish, but the final viscosities are given in Table I. The PMDA/MDA ratios given assume equal purity of the reactants and are believed to be about 1% high, so that the range actually covered includes ratios on both sides of the equivalence point. Each of the curves shows a maximum, suggesting that simul-

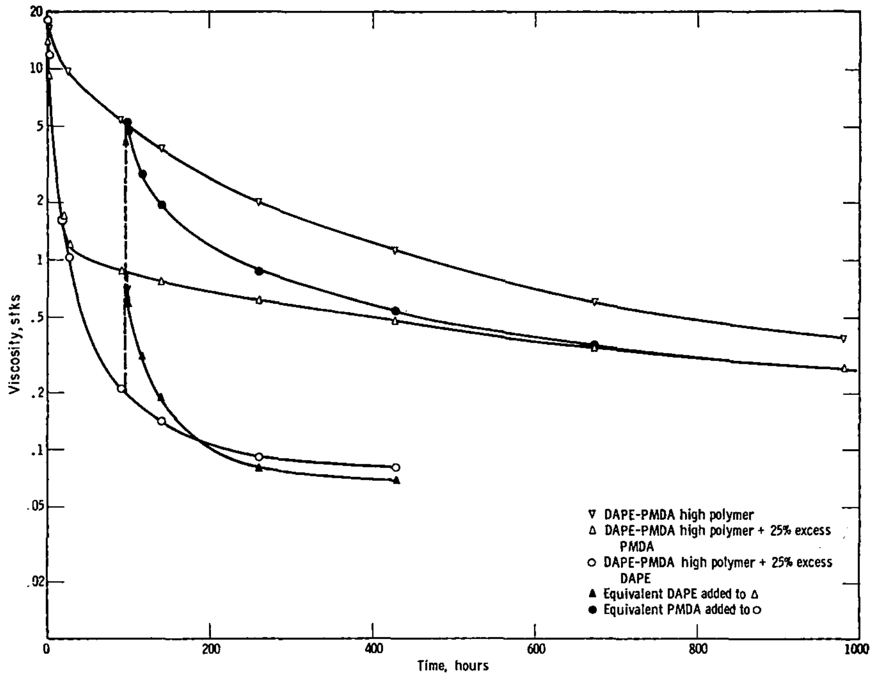


Fig. 2. Effect of additional DAPE and PMDA on 10% DAPE–PMDA in DMAC at 35°C.

taneous polymerization and degradation reactions were occurring. At the lower ratios a high viscosity was not attained and the product was presumably a polymer of low molecular weight, with terminal amine groups. The viscosity continued to increase for about 60 hr. at the lower ratios. This effect may simply indicate that the condensation reaction was continuing very slowly, or secondary effects such as solvation of the polymer may have contributed to the late viscosity rise. As the ratio was increased, the maximum viscosity was reached earlier and was much higher. Finally, when the ratio was increased to 1.04, the maximum viscosity decreased, indicating that a low polymer with anhydride endgroups was produced.

Earlier work[1] has shown that excess PMDA degrades the polymer in solution, and this effect undoubtedly contributed to the rapid decline of viscosity of a ratio of 1.04. A further examination of the effect of both anhydride and amine on viscosity was made, with the use of a 10% DMAC solution of a high polymer prepared from PMDA and 4,4'-diaminodiphenyl ether (DAPE). One portion of the solution was used as prepared. A second portion was mixed with a 25% excess of PMDA, and a third portion was mixed with a 25% excess of DAPE. The three solutions were aged simultaneously at 35°C., with periodic measurements of viscosity. The results are shown in Figure 2. Both DAPE and PMDA caused a very rapid decline in viscosity relative to the blank. However, the PMDA curve changes slope rather sharply at about 30 hr. and becomes roughly parallel to the blank curve, while the DAPE curve continues to drop steeply for a longer time and levels out more gradually. Readings beyond about 400 hr. could not be made on the solutions containing excess amine because of the formation of a black sludge. Two similar experiments were performed in which aniline and phthalic anhydride (0.5 mole/unit mole of polymer) were used as the additives. The curves obtained were essentially identical to that shown for added DAPE.

At the end of 97 hr. of aging, aliquots were taken from the solutions containing added PMDA and DAPE. To each was added an equivalent quantity of the complementary reagent, together with enough solvent to restore the original concentration. Viscosity measurements on these solutions are included in Figure 2. When PMDA was added to the solution containing excess DAPE the viscosity rose immediately to that of the blank and then declined normally. Addition of DAPE to the solution containing added PMDA, however, caused a very rapid drop to the equilibrium viscosity reached with excess DAPE.

It is evident from these observations that the addition of either amine or anhydride causes a rapid degradation of the polymer. This degradation presumably occurs through redistribution reactions, such as those shown in eqs. (4) and (5), which would be expected to lead finally to an equilibrium molecular weight and a stable viscosity. In all samples tested, however, the viscosity has continued to decline as long as observations were made (2140 hr.). Furthermore, excess anhydride is apparently destroyed or inactivated in about 30 hr. of aging, so that it neither attacks the polymer nor reacts with added amine. Excess diamine, however, remains active toward both anhydride and polymer, and apparently reaches equilibrium with the polymer in about 200 hr.

Hydrolysis has previously been implicated[1,3,4] as contributing to polymer degradation and is also a logical cause of anhydride destruction. Another relevant observation is that, in all of the aging experiments, the solutions slowly darkened, becoming essentially black after a few hundred hours. Since these solutions had been exposed to air repeatedly and since the darkening was most rapid when excess amine was present, it seemed probable that the coloration was due to oxidation of amine groups.

In order to observe viscosity behavior in the absence of hydrolyzing and oxidizing conditions, an experiment was conducted in a sealed, evacuated system, with the use of a 10% solution of DAPE–PMDA polymer in dried DMAC containing about 0.02% water (0.04 mole of water per unit mole of polymer). Figure 3 shows the viscosity changes occurring in this essentially anhydrous system at 35°C., compared with experiments in which the solvent was used as received (0.12% H_2O) and in which water was deliberately added (4.4% H_2O). The anhydrous system showed much less decline in viscosity than the others, and the solution remained pale yellow after 4750 hr. of aging. However, the viscosity did decrease from 12.30 to 0.932 stokes during this time, and was still declining when the viscometer was finally opened. PMDA was added in small increments to the aged solution, and the viscosity rose immediately, reaching a maximum value of 1.385 stokes with the addition of an amount equal to 2.5% of the PMDA originally used. The viscosity then declined rapidly with continued aging, as shown in Figure 3. It appears from these experiments that the viscosity decline is essentially equivalent to the removal of PMDA from the polymer to give amine-terminated fragments.

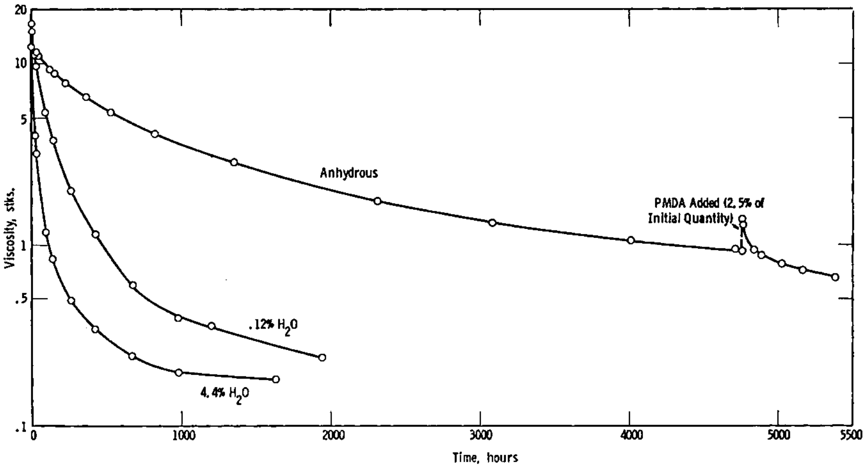


Fig. 3. Effect of water on viscosity of 10% DAPE–PMDA in DMAC at 35°C

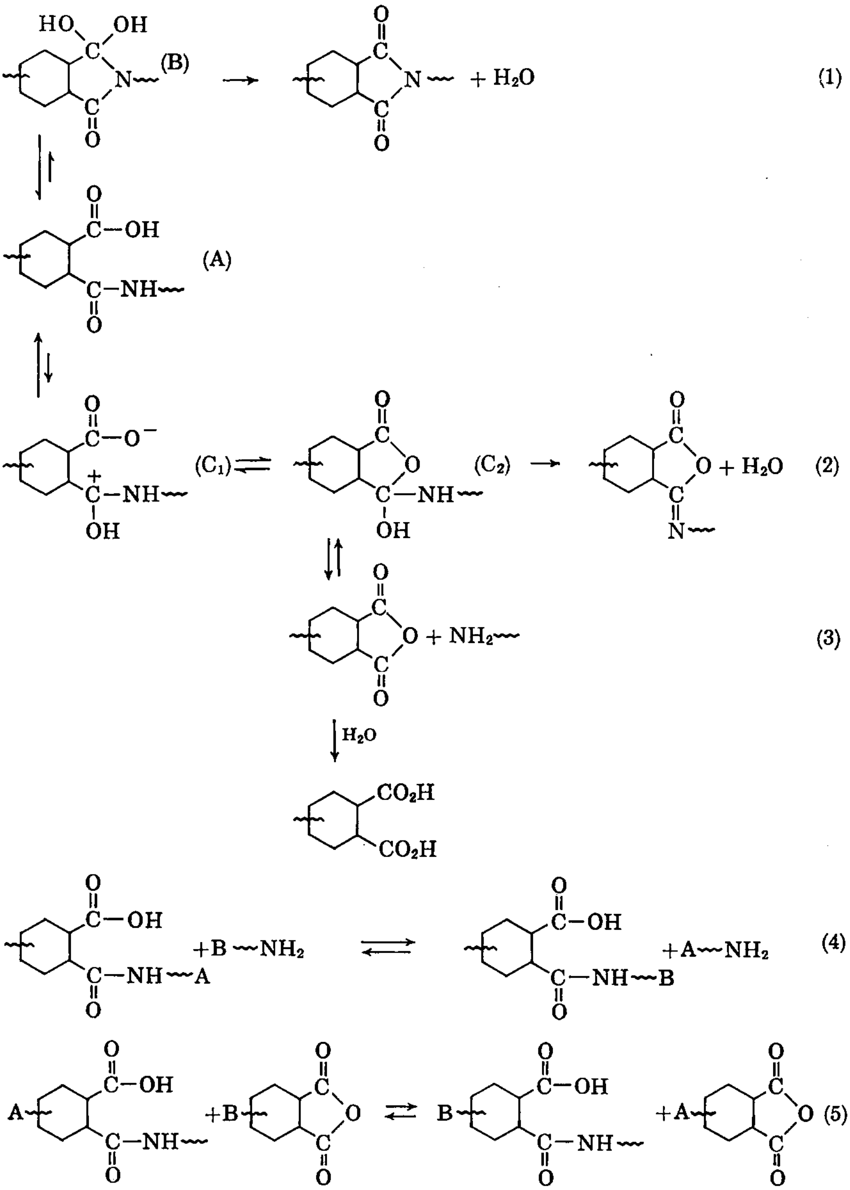
In previous work[1] the conversion of polypyromellitamic acid to polyimide in solution at 35°C. was too small to be detected in 55 hr. However, in the present case it was found that about 20% imidization had occurred in 4826 hr. of aging at 35°C. The analysis was performed by a comparison of the infrared spectra of a fresh sample of polymer, the aged sample, and the aged sample after heating to complete the imidization. The infrared spectra also gave qualitative indication of the presence of amine groups and of pairs of *o*-carboxyl groups (converted to anhydride upon heating) in the aged sample. The amount of water generated by the spontaneous imidization reaction in 4826 hr. was about 10 times the amount originally present as an impurity, and would have given a final water concentration of 0.19% if none were consumed.

The usual method of casting polyimide films is to heat a thin layer of a solution of amic acid polymer to accelerate the imidization reaction and to drive off solvent and water. When thick films are cast in this way, the resin becomes brittle and a yellow powder forms on the under side of the cast piece. A similar powder is obtained as a precipitate when the solution is heated in bulk.[1] It has been reported[3] that films can be cured at room temperature by treatment with a mixture of acetic anhydride and pyridine. We have found that when this method of cure was used in bulk, the cured polymer was obtained as a gel rather than as a powdery precipitate. A 10% solution of DAPE–PMDA polymer in DMAC was mixed with enough of a 1:1 mixture of pyridine and acetic anhydride to provide 4 moles of anhydride per unit mole of polymer. In less than 10 min., a soft gel had formed, which shrank and squeezed out part of the solvent over a period of several hours. The product was a firm, tough, dark red solid. The remaining solvent was removed by heating under vacuum to give a hard, black, solid resin.

CONCLUSIONS

A reaction scheme that is consistent with the observations presented is summarized in eqs. (1)–(5). The initial reaction between PMDA and a diamine is very rapid, and the reactants are largely converted to polypyromellitamic acid (A) in a few minutes. However, as the reaction approaches completion, the concentrations of amine and anhydride groups become very small, and the rate of reaction approaches zero. If nothing else were happening, the viscosity and molecular weight would slowly rise to a limiting value determined by the reactant ratio. However, as the rate of polymerization becomes very slow, reactions which were negligibly slow in the early stages become significant. Among these are the attack of both amine and anhydride groups upon the amic acid linkage [eqs. (4) and (5)]. Amine exchanges of this type have been reported by Spring and Woods,[5] Tingle and Rolker,[6] and Porai-Koshits,[7] and the present work shows a similar exchange with anhydrides.

As PMDA and a diamine react, the rate of condensation will be proportional to the product of amine and anhydride concentrations. If we assume that both amine and anhydride groups exchange with the polymer at the same rate (approximately true, according to Fig. 2), the rate of the degradation reaction will be proportional to the product of the concentration of amic acid links with the sum of the concentrations of amine and anhydride groups. The condensation rate, then, is large at the beginning and becomes very small as the reaction nears completion. The degradation rate begins at zero, rises to a maximum and then declines, although much



less rapidly than the condensation rate. The overall result is that the molecular weight of the polymer and the viscosity of the solution rapidly reach maximum values and then decline. The maximum is most sharply defined when the reactants are used in equivalent quantities, since an excess of either one prevents the attainment of a high viscosity. Because of the method of preparation, the early maximum from this mechanism is eliminated when excess amine is used. Since PMDA is added to a solution of the diamine, amine groups are always present in excess, and the molecular weight never exceeds the equilibrium value for the reactant ratio used. When excess PMDA is used, however, a finite time is required for it to dissolve and become complexed with the solvent, so that the polymer can build up to a fairly high molecular weight before the last of the PMDA becomes available. Thus, in Figure 1 the curve at a 1.04 ratio reaches an early maximum, while that at a ratio of 1.00 does not. If either amine or anhydride monomer is added to a high polymer solution, equilibration to low polymer occurs rapidly. If water is present, hydrolysis of the anhydride may stop its action before equilibrium is established.

Another set of reactions that contributes significantly to viscosity decline in the later stages of aging is summarized in eqs. (1)–(3). The structure B is presumed to be an intermediate in the normal curing reaction, shown in eq. (1). Although this reaction is slow at room temperature, it is essentially irreversible and becomes important as aging proceeds. A second largely irreversible reaction [eq. (2)] may occur to a small extent to give the isoimide.[8,9] The structure C_2 not only eliminates water to form the isoimide, but also [eq. (3)] splits out the amine group at a slow rate to give an anhydride. Early in the preparation, this reversal of the condensation reaction is negligible, but in the later stages the concentration of amine groups is so low that water begins to compete significantly for the anhydride so generated. If water is originally present in a considerable amount, degradation by this mechanism proceeds rapidly from the beginning, as shown in Figure 3. If the initial system is essentially anhydrous, however, the hydrolysis rate will be dependent upon the rate of generation of water by eqs. (1) and (2), and the degradation will be less rapid. The hydrolysis mechanism of eqs. (2) and (3) is essentially that proposed by Bender, Chow, and Chloupek for the hydrolysis of *o*-carboxybenzamide.[10]

As the degradation by hydrolysis proceeds, the polymer is broken down into shorter chains terminated by amine or carboxyl groups. Terminal amine groups are oxidized to colored products if air is present, and the solutions become very dark. The carboxyl groups produced by the degradation are unreactive at the aging temperature, but can be converted to anhydride by heating, and this reaction was observed by infrared spectroscopy. The viscosity of a solution of degraded polymer can be restored to some extent by reaction of the terminal amine groups with PMDA. However, only about 25% of the molecules would be expected to have amine groups at both ends and thus be convertible to high polymer. Therefore, the viscosity was only partially restored by PMDA addition to degraded polymer (Fig. 3), but a decrease due to equilibration with excess amine was fully restored with PMDA (Fig. 2).

When the resin is cured by heating, the reactions shown occur at an increased rate. Thin films can be cast successfully because the water produced diffuses away rapidly enough that little hydrolysis occurs. When a thick layer of solution is heated, however, extensive hydrolysis occurs before the water can escape, and the cured polymer is obtained as a powder of low molecular weight. Thick pieces can be cured without degradation by treatment with acetic anhydride, since no free water is produced in this method and hydrolysis does not occur.

EXPERIMENTAL

Materials

The source and grades of PMDA have been described.[1]

DAPE and MDA were obtained from Distillation Products Div., Eastman Kodak Co. DAPE was purified by vacuum distillation, followed by recrystallization from ethyl acetate to give white crystals, m.p. 190.5–191.5°C. MDA was purified by recrystallization from benzene, giving white crystals, m.p. 92–92.5°C.

DMAC was obtained from E. I. du Pont de Nemours & Co. The solvent as received contained about 0.05% water, but with normal handling, the water content reached 0.1–0.5% in use.

Effect of Reactant Ratio on Reaction of MDA and PMDA

Six simultaneous runs were made, in each of which a solution of 12.13 g. of MDA in 186.9 g. of DMAC was stirred at room temperature in a Waring Blendor while a weighed amount of pulverized PMDA was added quickly (Table II).

The mixtures were stirred for 1 min., giving clear yellow solutions. A sample of each was quickly transferred to a calibrated Ostwald viscometer which was immersed in a constant temperature bath at 35.0°C. Periodic viscosity measurements were made on the six solutions for 2140 hr., and the results are given in Table I and Figure 1. The viscometers were stoppered except during the measurements. The solutions became progressively darker with age and were very dark brown at the end of the experiment.

TABLE II

Mole ratio, PMDA/MDA	PMDA used, g.
1.000	13.36
1.010	13.49
1.015	13.56
1.020	13.63
1.030	13.76
1.040	13.89

Effect of Additives on Viscosity Decline of DAPE–PMDA Solutions

A solution of 20.00 g. of DAPE in 306.5 g. of DMAC (0.12% H_2O) was stirred rapidly while 22.00 g. of pulverized PMDA was added at once. The mixture was stirred for 3 min. to give a clear, viscous solution, from which 34.85 g. aliquots were taken. Additions were made to these samples as listed in Table III.

TABLE III

Sample	Material added, g.	Moles additive/unit mole of polymer
A	DMAC, 6.97	None
B	DMAC, 5.17 + H_2O, 1.80	10 (4.4% H_2O in solution)
C	DMAC, 6.47 + DAPE, 0.50	0.25
D	DMAC, 6.42 + PMDA, 0.55	0.25

A portion of each sample was transferred to a calibrated Ostwald viscometer immersed in a constant temperature bath at 35.0°C., and viscosities were determined periodically for about 1900 hr. The viscometers were stoppered except during measurements. In the case of sample C, a precipitate began to form in about 400 hr., and further readings could not be made. A similar effect limited the observation of sample B to 1600 hr.

The remaining portions of samples C and D were aged with the viscosity samples at 35.0°C. At the end of 97 hr. of aging a 10-g. portion of sample C (viscosity 0.20 stokes) was mixed with 0.13 g. of PMDA and 1.17 g. of DMAC to give a clear solution having a viscosity of 5.24 stokes. Part of this solution was transferred to a viscometer, and its viscosity at 35.0°C. was followed as a function of time. At the same time a 10-g. portion of sample D (viscosity 0.86 stokes) was mixed with 0.12 g. of DAPE and 1.08 g. of DMAC to give a solution with a viscosity of 0.64 stokes. This sample was also aged at 35.0°C., with periodic viscosity measurements, until the formation of a precipitate prevented further determinations after about 400 hr.

All of the samples, originally light yellow, became very dark brown on aging. Samples B, C, and the sample obtained by adding DAPE to D darkened most rapidly. The viscosity measurements are given in Figures 2 and 3.

TABLE IV

Aging time, hr.	Viscosity of solution A, stokes	Viscosity of solution B, stokes
0.62	8.69	9.31
6.85	3.19	3.52
22.92	0.88	0.91
47.6	0.37	0.37
119	0.14	0.15

A second batch of the DAPE–PMDA stock solution was prepared by the procedure described. A 69.7-g. aliquot was mixed with 13.3 g. of DMAC and 0.93 g. of aniline to give solution A. A second 69.7-g. aliquot was mixed with 12.7 g. of DMAC and 1.48 g. of phthalic anhydride to give solution B. The solutions were aged for 120 hr. at 35.0°C., and the viscosity measurements listed in Table IV were made.

Degradation of DAPE–PMDA Polymer in an Anhydrous Solution

A solution of 20.0 g. of DAPE in a mixture of 600 g. of DMAC and 200 g. of toluene was dehydrated by distilling it at reduced pressure until the residual solution weighed 372 g. The water content of a solution dehydrated in this way has been shown by infrared spectroscopy to be about 0.02%. A 9.5926-g. portion of the solution was transferred to a dried Zhukov viscometer, and 0.5902 g. of granular PMDA was added. This ratio of reactants had been previously determined to give a high viscosity. The viscometer was flushed twice with dry air, evacuated to 15 mm., and sealed. The solution was agitated until the PMDA had dissolved, and the viscometer was immersed in a constant temperature bath at 35.0°C. Viscosity measurements were made periodically for 4751 hr., during which time the viscosity dropped from 12.30 to 0.932 stokes. The viscometer was then opened and 0.010 g. of PMDA was added, whereupon the viscosity rose quickly to 1.343 stokes and then continued to rise more slowly, reaching 1.385 stokes in 137 min. An additional 0.005 g. of PMDA was added, and the viscosity began to drop, reaching 1.303 stokes after 307 min. from the time of the first addition. Further changes of viscosity with time are shown in Figure 3. The viscometer was sealed again after each PMDA addition.

A second sample of the dehydrated solution of DAPE, weighing 10.0870 g., was mixed with 0.6301 g. of PMDA, sealed in a second viscometer under anhydrous conditions, and aged at 35.0°C. with the first sample. At the end of 4826 hr., the sample was removed and analyzed by infrared spectroscopy. At the same time, a fresh sample of the same composition was prepared for comparison. It was found to contain no imide a few days after preparation.

Both aged samples remained clear and light yellow throughout the aging treatment.

The infrared analyses were performed with a Perkin-Elmer Model 221 infrared spectrophotometer with prism-grating interchange. The sample solutions were smeared on sodium chloride crystals as thin films, and the solvent was removed by vacuum treatment for 24 hr. at room temperature. After determination of the spectra of these samples, the same specimens were heated for 90 min. at 220°C. under vacuum. This treatment has been found to give complete conversion to the imide. The spectra were then determined again, and the ratios of the imide peak heights before and after imidization were measured to give the extent of imidization. Two imide absorption bands were found to be useful in this determination, one at 1775 cm.$^{-1}$ and the other at 720 cm.$^{-1}$. Both gave essentially the same results.

Additional qualitative information was obtained from the spectra of the samples that had been heated to 220°C. A small anhydride peak at 1860 cm.$^{-1}$ was observed for the aged sample, but not for the fresh one. The spectrum of the aged sample, when examined with a 10× expansion factor, showed a shoulder at about 3320 to 3410 cm.$^{-1}$ which was absent in the fresh sample. This absorption is believed to be due to amine N-H stretching.

Polyimide Cure with Acetic Anhydride and Pyridine

A solution of 100 g. of DAPE in 1881 g. of DMAC was stirred while 107 g. of PMDA was added. When solution was complete additional small increments of PMDA were added until a viscosity of 55.7 stokes at 25°C. was reached. A mixture of 204 g. of acetic anhydride and 204 g. of pyridine was added, and the solution was stirred for 5 min. and then divided equally between two 3-liter beakers. In another 3 min. it had set to a soft gel. After 3 hr. at room temperature the gel had become quite firm. Some shrinkage had occurred, giving two dark-colored cylinders, 12.5 cm. in diameter and 9 cm. high. A considerable amount of solvent had been squeezed out. The specimens were heated for 64 hr. at 50°C. under vacuum to give very firm and tough cylinders weighing 1585 g. (12% solids). Further heating under vacuum for 7 hr. at 100°C., 16 hr. at 120°C., and 47 hr. at 175°C. reduced the weight to 240 g. (79.5% solids). Finally the pieces were heated for 7 hr. at 300°C. in a forced draft oven, to give a product weighing 187 g. (1% loss of resin). The samples were hard, black, shrunken and slightly cracked.

References

1. Frost, L. W., and G. M. Bower, *J. Polymer Sci.*, **A1**, 3135 (1963).
2. Jones, J. I., F. W. Ochynski, and F. A. Rackley, *Chem. Ind. (London)*, **1962**, 1686.
3. Edwards, W. M., and A. L. Endrey, Brit. Pat. 903,271 (1962).
4. Edwards, W. M., Brit. Pat. 898,651 (1962).
5. Spring, F. S., and J. C. Woods, *J. Chem. Soc.*, **1945**, 625.
6. Tingle, J. B., and H. F. Rolker, *J. Am. Chem. Soc.*, **30**, 1882 (1908).
7. Porai-Koshits, B. A., *J. Gen. Chem. (USSR)*, **7**, 611 (1937) (from *Chem. Abst.* **31**, 5787^4 (1937)).
8. Sherrill, M. L., F. L. Schaeffer, and E. P. Shoyer, *J. Am. Chem. Soc.*, **50**, 474 (1928).
9. Cotter, R. J., C. K. Sauers, and J. M. Whelan, *J. Org. Chem.*, **26**, 10 (1961).
10. Bender, M. L., Y.-L. Chow, and F. J. Chloupek, *J. Am. Chem. Soc.*, **80**, 5380 (1958).

Résumé

La réaction du dianhydride pyromellitique avec une solution d'une diamine primaire dans un solvant tel que le diméthylacétamide donne une solution visqueuse d'un acide polypyromellitique de poids moléculaire élevé. La viscosité de la solution diminue fortement lorsqu'elle est vieillie à 35°C. Des températures élevées ou la présence d'eau, un excès d'amine ou un excès d'anhydride accélèrent la vitesse de diminution de viscosité. On a trouvé qu'une chute rapide de la viscosité est due principalement à une hydrolyse par de l'eau accidentelle et à des réactions d'échange des groupes amine ou anhydride avec le lien *o*-carboxyamide. Une diminution lente pendant une longue période de temps résulte de l'hydrolyse par l'eau produite lors de la lente conversion de l'acide polypyromellitamique en polypyromellitimide. Une dégradation par hydrolyse a lieu également lorsque les films de polyimide sont recuits en chauffant la solution. L'effet peut être minimisé en recuisant les films minces d'où l'eau peut diffuser rapidement ou bien en employant une méthode chimique, comme le traitement à l'anhydride acétique et à la pyridine pour enlever l'eau produite lors de l'imidization.

Zusammenfassung

Bei der Reaktion von Pyromellitsäure-dianhydrid mit der Lösung eines primären Diamins in einem Lösungsmittel wie Dimethylacetamid entsteht eine hochviskose Lösung einer "Polypyromellitamidsäure" von hohem Molekulargewicht. Alterung der Lösung bei 35°C führt zu einer starken Abnahme der Viskosität. Höhere Temperaturen oder die Anwesenheit von Wasser, überschüssigem Amin oder überschüssigem Anhydrid erhöhen die Geschwindigkeit der Abnahme. Ein früher, rascher Abfall der Viskosität geht in erster Linie auf Hydrolyse durch etwa vorhandenes Wasser und auf Austauschreaktionen des Amins oder der Anhydridgruppen mit der *o*-Carboxyamidbindung zurück. Die über längere Zeit him erfolgende langsame Abnahme wird durch die hydrolytische Wirkung des bei der langsamen Umwandlung von "Polypyromellitamidsäure" in Polypyromellitimid entstehenden Wassers verursacht. Auch beim Giessen von Polyimidfilmen unter Erhitzen der Lösung tritt hydrolytischer Abbau ein. Der Effekt lässt sich weitgehend einschränken, wenn man entwder dünne Filme giesst, aus denen das Wasser rasch herausdiffundieren kann, oder durc eine chemische Methode, wie etwa der Behandlung mit Acetanhydrid oder Pyridin, das bei der Imidbildung entstehende Wasser entfernt.

Received April 3, 1963