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THERMAL ANALYSIS OF A POLY(AMIC ACID)-POLYIMIDE SYSTEM*

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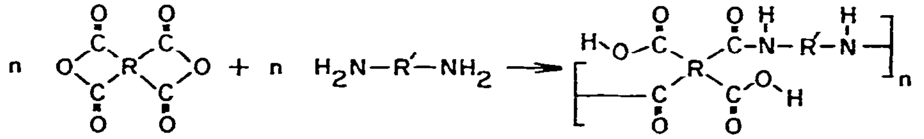
ABSTRACT

The thermal cyclization of a poly(amic acid) powder to polyimide and the thermal decomposition of the polyimide have been studied using thermal analysis. Activation energies for the thermal cyclization and decomposition are reported in both oxidative and non-oxidative atmospheres. Compositions of the pyrolysis residue consistent with previously postulated decomposition mechanisms are reported.

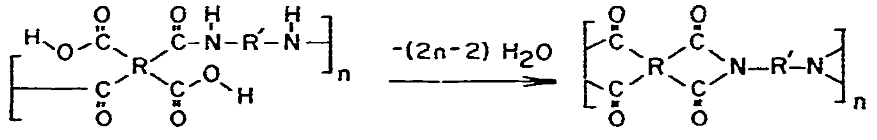
INTRODUCTION

Polyimides are a relatively new class of commercially available polymeric materials. The development of polyimides was prompted by the need for reliable thermally stable materials, consequently, the thermal behavior of polyimides has been studied by a number of investigators[1–12].

Polyimides are prepared by a two stage polycondensation reaction. In the first stage of the reaction, a dianhydride and diamine are reacted, usually in an aprotic dipolar solvent, as shown in Eqn. (1).


(1)

This soluble poly(amic acid) is processed to the desired form or shape needed in the final application and then converted to the nearly always infusible and insoluble polyimide by heat or chemical means as shown in Eqn. (2).


(2)

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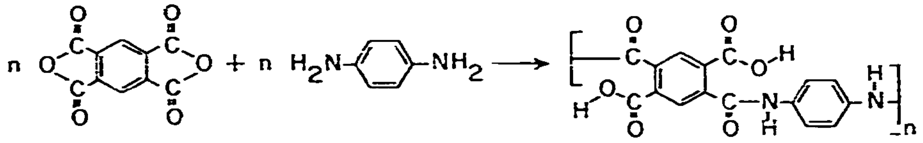
In Eqns. (1) and (2), R and R′ can be either aliphatic or aromatic groups, however, the most thermally stable polymers are based on aromatic dianhydrides and diamines.

The poly(amic acid) and polyimide used in this study were from 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride, PMDA) and 1,4-diaminobenzene (*p*-phenylenediamine, PPD). A detailed thermal analysis of this system has not yet appeared in the literature. This study reports an apparent activation energy and reaction order for the thermal cyclization of this poly(amic acid) to polyimide and activation energies for the decomposition of the polyimide in both oxidative and non-oxidative atmospheres. Compositions of the pyrolysis residue and probable structures for the residue are presented.

EXPERIMENTAL

Polymer preparation

Poly-(*p*-phenylene pyromellitamic acid)s used in this study were synthesized by a method similar to those reported in the literature[13–22]. Solid PMDA was added to a solution of PPD in *N*,*N*-dimethylformamide (DMF) as shown in Eqn. (3).



(3)

All syntheses were conducted at a concentration of 5% solids; reaction temperatures were varied from 5 to 50°C. After a 2-h reaction time, the poly(amic acid) solution was diluted by a 5:1 addition of 2-methoxyethanol (ethylene glycol monomethyl ether). The polymer was precipitated by dropwise addition of the polymer solution into benzene. The poly(amic acid) was recovered by filtration, washed with benzene, and frozen in liquid nitrogen. The polymers were placed on a freeze-drier for 72 h to remove as much solvent as possible. Poly-(*p*-phenylene pyromellitamic acid)s prepared by this method were very fine amorphous yellow powders. A detailed description of this synthesis procedure is available[23].

Characterization techniques

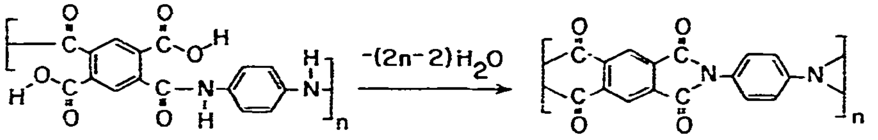
Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were obtained using a Mettler Thermoanalyzer. Analyses were made in 8-mm platinum crucibles on samples weighing approximately 40 mg. The heating rate was 4°C/min. Both flowing-air (5.7 liters/h) and flowing-argon (4.6 liters/h) atmospheres were used. Aluminium oxide (Al_2O_3) was used as the reference material for DTA measurements.

IR spectra were obtained using a Beckman IR-12 Infrared Spectrophotometer. Spectra were obtained by preparing KBr pellets of the polymers. Sample concentration was approximately 0.7 weight per cent; path length of the pellets was about 0.5 mm.

Scanning electron microscopy (SEM) of the poly(amic acid) powders was performed using a JEOLCO JSM-2 Scanning Electron Microscope. Samples were adhered to copper sample mounts with a conductive silver paste. Since the polymers were non-conductors, a thin gold film was vapor deposited onto the surface.

DISCUSSION AND RESULTS

Solvents for poly(amic acid)s must be capable of very strong polymer–solvent interactions. Consequently, when poly(amic acid)s are precipitated, solvent molecules remain bound to the polymer molecules[17–19,22–25]. Solid poly-(*p*-phenylene pyromellitamic acid)s subjected to thermal analysis had DMF molecules associated along the polymer molecule, the association presumably due to hydrogen bonding between the carbonyl oxygen of the DMF and the hydrogen of the carboxyl groups in the polymer[24,26]. Since the dissociation energy of the hydrogen bonds between the DMF and the polymer is lower than the dissociation energy of the covalent bonds in the polymer backbone, heating the polymer should free it of associated solvent before polymer degradation occurs. Heating the poly-(*p*-phenylene pyromellitamic acid) should also convert the polymer to poly-(*p*-phenylene pyromellitimide) as shown in Eqn. (4) prior to the occurrence of polymer degradation.



(4)

Therefore, the TG curve obtained on heating the polymer shows weight losses due to dissociated DMF molecules and water eliminated in polyimide formation, followed by weight loss due to polymer degradation.

Thermal analysis in air

A typical TG curve for poly-(*p*-phenylene pyromellitamic acid)–poly-(*p*-phenylene pyromellitimide) is shown in Fig. 1. The TG curve can be divided into four essentially linear regions. These regions are numbered I–IV in Fig. 1.

Weight loss regions I and II could be due either to associated solvent (DMF) being released as hydrogen bonds are dissociated, or to the escape of water formed during the conversion of poly(amic acid) to polyimide. A series of experiments were designed using TG and IR to determine the mechanism causing the weight loss in regions I and II. Individual samples were heated to 50, 75, 100, 125, 150, 175, and 200 °C and maintained at their respective temperatures until they reached constant weight. IR spectra were then obtained on the polymer remaining after the heating procedure. Fig. 2 shows the portion of the IR spectrum from 2500 cm^{-1} to 3400 cm^{-1} for poly(amic acid) samples heated at 100, 125, 150, and 175 °C. The peak at 2920–2930 cm^{-1} can be assigned to aliphatic C–H stretch which is attributed to the asso-

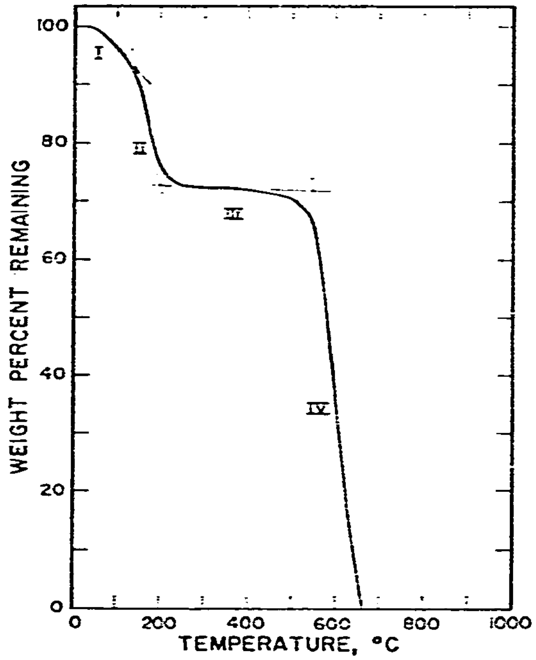


Fig. 1. Thermogravimetry of poly-(*p*-phenylene pyromellitamic acid)-poly-(*p*-phenylene pyromellitimide) in air.

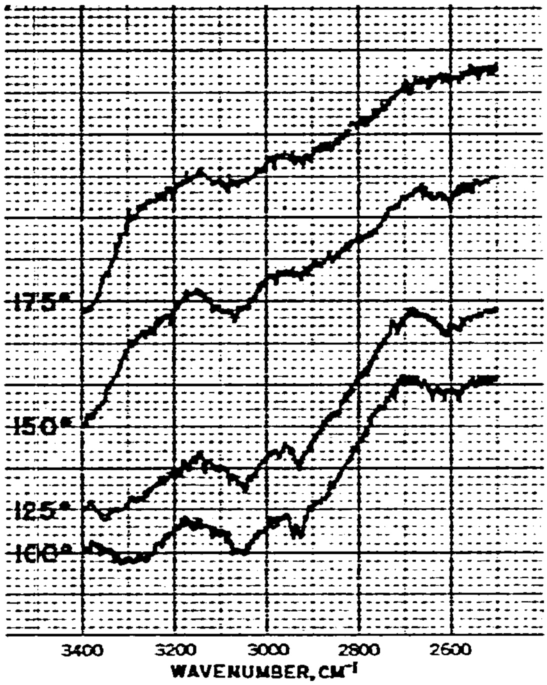
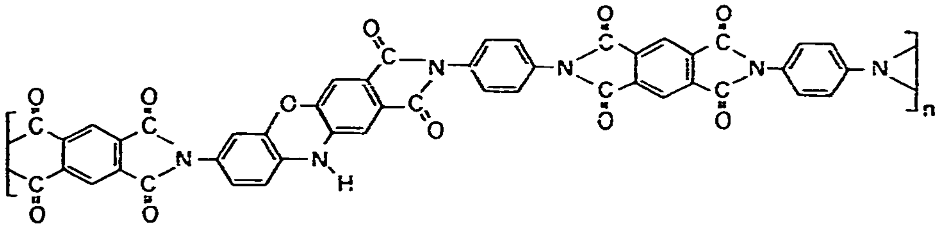


Fig. 2. Changes in the IR spectrum of poly-(*p*-phenylene pyromellitamic acid) during cyclization, 2500–3400 cm^{-1}.

ciated DMF. Examination of Fig. 2 shows the disappearance of this peak between 125 and 150°C indicating that much of the associated DMF has escaped. Fig. 3 shows the portions of the IR spectra from 700–750 cm^{-1} and 1600–1850 cm^{-1} for poly(amic acid) samples heated at 75, 100, 125, 175, and 200°C. Conversion of poly(amic acid) to polyimide can be followed by the disappearance of the amide peak at 1660 cm^{-1} and appearance of imide peaks at 725 and 1779 cm^{-1}. Examination of Fig. 3 shows that cyclization (ring closure) begins near 100°C and continues up to 200°C. Appreciable cyclization occurs from 175–200°C. These infrared studies indicate that region I in the TG curve, shown in Fig. 1, is predominately due to the escape of DMF which was associated with the polymer. Region II is predominantly due to the escape of water eliminated during the conversion of poly(amic acid) to polyimide. Extrapolation of the linear weight loss portions of the TG curve results in the intersection of region I and region II at about 135±5°C.

Region III shows only a small weight loss and represents the region in which the polyimide is thermally stable. All possible cyclization and solvent removal have occurred prior to this region but oxidative decomposition has not yet begun. The slight weight loss ($<3\%$) in the linear portion of region III could be due, in part, to removal of the last amounts of water and solvent or decomposition of low molecular weight polymer. As shown in Fig. 1, region III extends from about 210±10 to 545±20°C.

The polymer undergoes total decomposition in region IV. Rapid decomposition begins at about 545±20°C and continues until the polymer is totally decomposed at 670±15°C. An elemental microanalysis of the partially pyrolyzed residue remaining after heating to 600°C was obtained. Approximately 50% of the polyimide (material present at 350°C) remains at 600°C in air. The composition of the residue is: C, 66.19%; H, 1.62%; N, 11.62%, and O, 20.57%; (by difference)* and can be represented by the empirical formula $(C_{13.3}H_{3.9}N_2O_3)_x$. The theoretical composition for the polyimide $(C_{16}H_6N_2O_4)_x$ is C, 66.21%; H, 2.08%; N, 9.65%; and O, 22.05%. The microanalysis shows that the composition of the residue has not changed a great deal upon heating, even though about half of the polyimide present at 350°C has decomposed. Much of the polymer must still have its original composition. A possible structure for several repeat units of the polymer, which is consistent with the decomposition mechanism proposed by Bruck[4], and the composition of the residue after pyrolysis in argon (to be discussed in the next section) is:



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*Elemental microanalysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

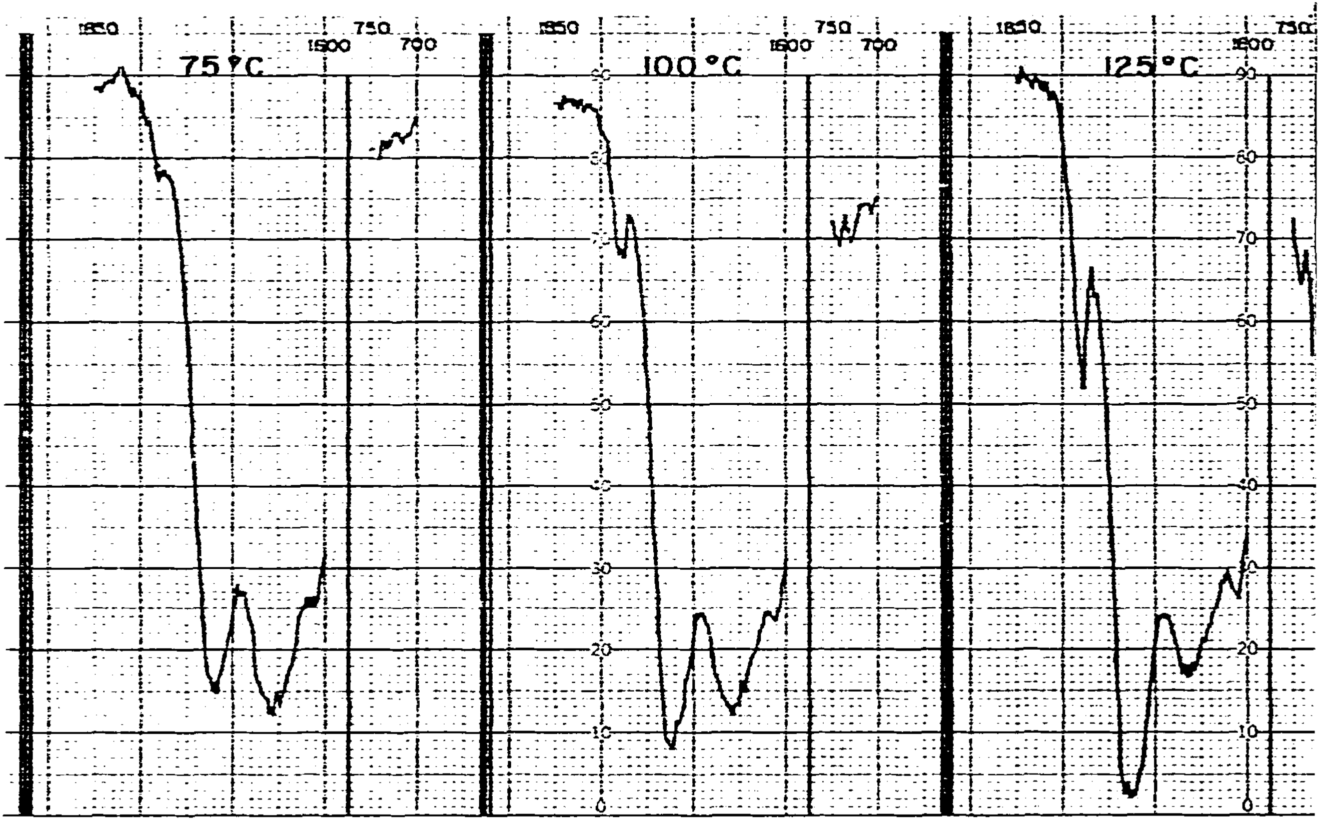


Fig. 3. Changes in the IR spectrum of poly-(p-phenylene pyromellitamic acid) during cyclization, 700–750 cm^{-1} and 1600–1850 cm^{-1} at five different temperatures.

The composition of this structure approaches the composition of the residue. The high oxygen content of the residue indicates that chain scission with release of CO or CO_2 is probably not the principal mode of decomposition. A unit-by-unit destruction of the polymer molecules proposed by Scala and Hickam[7] and supported by Shulman and Tusing[9] provides a decomposition mechanism which allows the polymer chains to remain intact. The unit-by-unit mechanism involves a chain depolymerization (unzippering) with oxidation of the fragments.

Weight loss data were obtained from the TG curves as functions of both time and temperature in the cyclization and decomposition regions. Data from the initial portion of a weight loss region [shape of the derivative thermogravimetric (DTG) curve is negative] were used in a kinetic analysis. The data were found to obey Arrhenius-type kinetics. A typical Arrhenius plot for the cyclization and decomposition reactions is shown in Fig. 4.

The apparent activation energy for decomposition of poly-(p-phenylene pyromellitimide) over the temperature range 475–585 °C is 41.9 kcal/mole (standard deviation

Fig. 3. See opposite for caption.

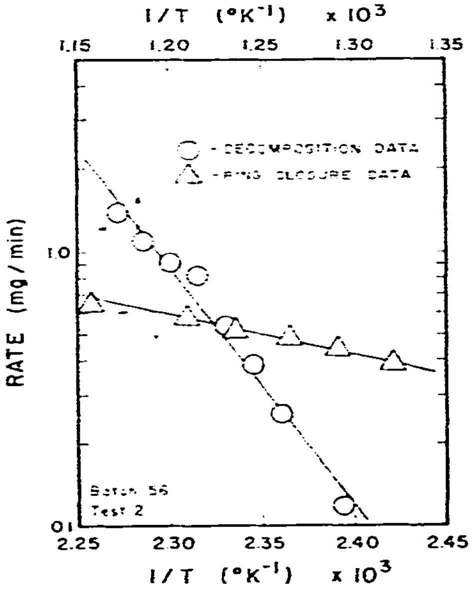


Fig. 4. Arrhenius-type plots for poly(amic acid) cyclization (ring closure) and polyimide decomposition.

= 3.6 kcal/mole for 5 samples). Activation energies for the decomposition in air of duPont's H-film (from PMDA and 4,4′-diaminodiphenyl ether) have been published. Bruck[1-3] has reported activation energies of 31 and 33 kcal/mole, and Heacock and Berr[5] have reported a value of 39.9 kcal/mole for the decomposition.

The apparent activation energy for the cyclization reaction of poly-(*p*-phenylene

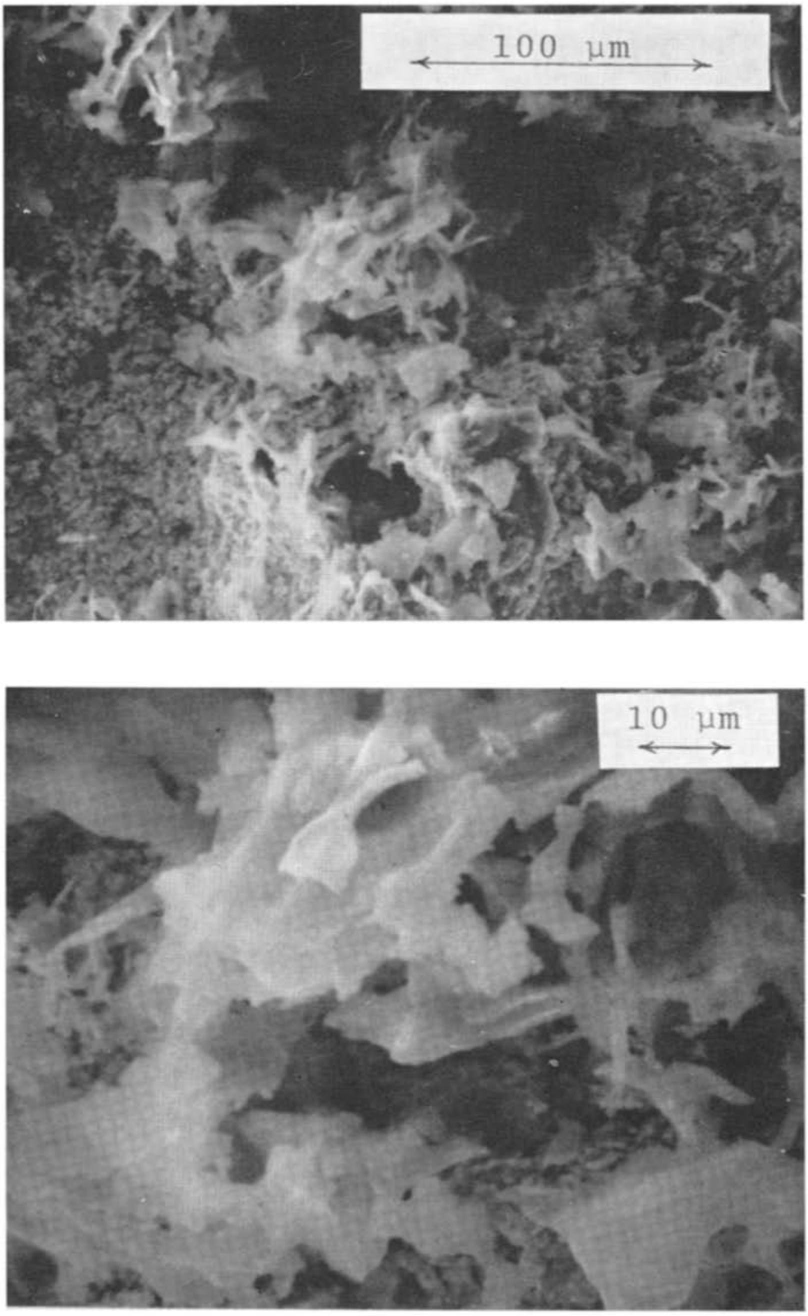


Fig. 5. SEM micrographs of poly-(*p*-phenylene pyromellitamic acid).

pyromellitamic acid) over the temperature range 130–175°C is 7.1 kcal/mole (standard deviation = 0.7 kcal/mole for 5 samples). Although this value is well within the range of values of activation energies for gases diffusing through polymers[27], diffusion control is believed to be unimportant. The average value of 7.1 kcal/mole was obtained on analyses of polymers passing a 100-mesh screen (149-micron opening). An average apparent activation energy of 6.9 kcal/mole (standard deviation = 1 kcal/mole for 4 samples) was obtained upon analyses of polymers passing a 325-mesh screen (44-micron opening). The activation energies are not statistically different. Scanning electron microscopy of the poly(amic acid) (Fig. 5), shows that the polymer particles are thin platelets with an estimated thickness of 0.1–0.2 μm and planar dimensions of 3–4 × 1–2 μm. SEM also revealed that the particles exist as loosely bound agglomerates and that the products passing the 100- and 325-mesh screens differed only by the sizes of the agglomerates. The loosely bound agglomerates and thin particles would be less likely to result in a diffusion controlled process than thicker particles. Kinetic data for the thermal cyclization of this poly(amic acid) have not appeared in the literature; however, data have been published for the poly(amic acid) from PMDA and 4,4′-diaminodiphenyl ether. Kruez *et al.*[24] studied cyclization of poly(amic acid) films and reported a two step cyclization, a slow step below 150°C with an activation energy of 23 ± 7 kcal/mole followed by a rapid step with an activation energy of 26 ± 3 kcal/mole. Laius *et al.*[28] reported activation energies of 23–30 kcal/mole, the activation energy increasing as the cyclization reaction progressed. Kolesnikov[29] reported an activation energy of 24.0 kcal/mole for the cyclization reaction.

Some of the kinetic data were treated by the method proposed by Friedman[30] in order to estimate an apparent kinetic order for the cyclization reaction. Friedman's method yielded small positive values (<0.08) or negative values for the reaction order indicating that the cyclization reaction obeys zero order kinetics over the 130–175°C temperature range subjected to kinetic analysis. If the cyclization reaction obeys zero order kinetics, the rate of decrease in weight of the polymer with respect to time would be represented by $-\mathrm{d}m/\mathrm{d}\theta = k$, where k is a rate constant. Since the reaction apparently follows Arrhenius-type kinetics, the effect of temperature on the rate constant is represented by the Arrhenius equation $k = A\mathrm{e}^{(-E_a/RT)}$. The two equations may be combined to yield Eqn. (5)

$$-\mathrm{d}m/\mathrm{d}\theta = A\,\mathrm{e}^{(-E_a/RT)} \tag{5}$$

which is the non-isothermal rate equation for a zero order reaction. For the 7.1 kcal/mole activation energy found in this study, Eqn. (5) predicts that the rate of weight loss during the thermal cyclization of the poly(amic acid) should be essentially constant from 130°C to 200°C, varying less than 0.2%. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are reproduced in Fig. 6. Examination of Fig. 6 shows that the TG curve is linear and the DTG curve is constant from approximately 155–185°C. These TG results are consistent with zero order kinetic behavior. Deviation from zero order kinetics is observed below 150–155°C and above 185–190°C. Departure from zero order kinetic behavior below 155°C could be due to the presence of

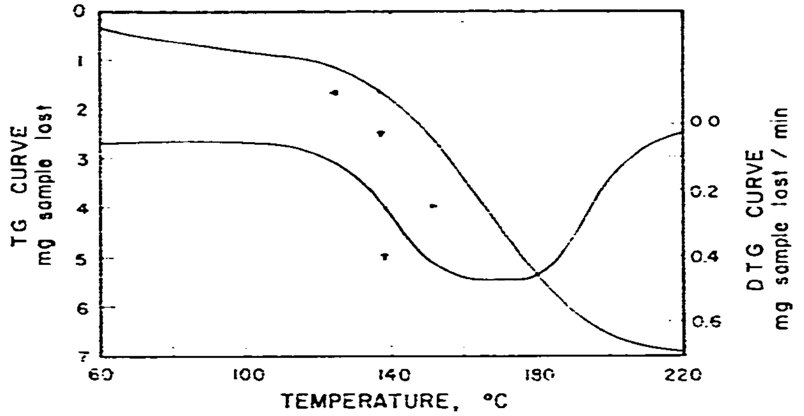


Fig. 6. Thermogravimetry and derivative thermogravimetry for poly(amic acid) cyclization.

residual solvent. If DMF remains hydrogen bonded to some of the carboxyl groups of the poly(amic acid), the cyclization of these groups to imide linkages may follow somewhat different kinetic behavior to that which would result if the associated solvent were not present. The departure from zero order kinetics above 185°C could result from the decreased chain mobility, which would result as poly(amic acid) was converted to polyimide. Localized stiffness in the polymer chains could retard proper orientation of the amide and carboxylic acid groups for cyclization. Zero order kinetics also indicates that the observed behavior in the cyclization step is not diffusion controlled. If the process were diffusion controlled, the rate of weight loss would be proportional to the concentration of the diffusing species and would not display apparent zero order kinetic behavior. Studies of the reaction order for cyclization of other poly(amic acid)–polyimide systems reported in the literature have been contradictory. IR studies of the thermal cyclization of the poly(amic acid) from PMDA and *m*-phenylenediamine in dilute solution yielded a reported[31] order of 1.10. Kruez *et al.*[24] studied thermal cyclization of the poly(amic acid) from PMDA and 4,4'-diaminodiphenyl ether by IR. Their data did not allow an unequivocal determination of the reaction order; however, first order behavior was assumed on the basis of studies with model compounds. They point out, however, that kinetic similarities between poly(amic acid) and model compound cyclizations are limited. Laius *et al.*[28], in IR studies of the PMDA–4,4-diaminodiphenyl ether system, reported a reaction order changing from 2.2 to 3.2 between 160°C and 250°C.

The DTA curves for polymers heated in air were all very similar. A broad endotherm exists between 100±20 and 200±20 °C with its peak near 170±10°C. This endotherm may be part of a broader endotherm which begins below 50°C. If this broader endotherm exists, there is a second, less-intense peak at 70±10°C. A definite statement as to the existence of this second peak can not be made. This possible broad endotherm begins immediately after the start of the analysis. Consequently, an initial baseline for the DTA curve can not be obtained after analysis is begun. Definite determination of the DTA baseline is also complicated since there is probably a difference in heat capacities of the poly(amic acid) and polyimide which would cause a change in the DTA baseline during the broad endotherm. The DTA curve does show that the net process of imide ring formation, dissociation of hydrogen bonds between the solvent and polymer, and escape of solvent and water is endothermic. A broad, intense exotherm occurs from the onset of rapid oxidative decomposition of the polyimide near 475°C until decomposition is complete. The peak of this exotherm is at 580 ± 10°C.

Thermal behavior in argon

A typical TG curve for thermal analysis of the poly(amic acid) is shown in Fig. 7. The sample was heated to 900°C and maintained at 900°C for 100 min. The TG curve in argon can also be divided into four distinct regions.

Region I of Fig. 7 corresponds to region I and II of Fig. 1. In this region, the hydrogen bonds associating DMF along the polymer chain are dissociated and the cyclization reaction occurs. Region I extends to approximately 215 ± 10°C, nearly the same temperature marking the end of solvent removal and cyclization in air.

Region II of Fig. 7 corresponds to region III of Fig. 1 representing the temperatures at which the polyimide is thermally stable. This region extends to about 600 ± 25°C, about 50°C higher than the temperature for an oxidative atmosphere.

In region III the polyimide undergoes rapid degradation. The rapid degradation occurs between 600 ± 25°C and 650 ± 25°C.

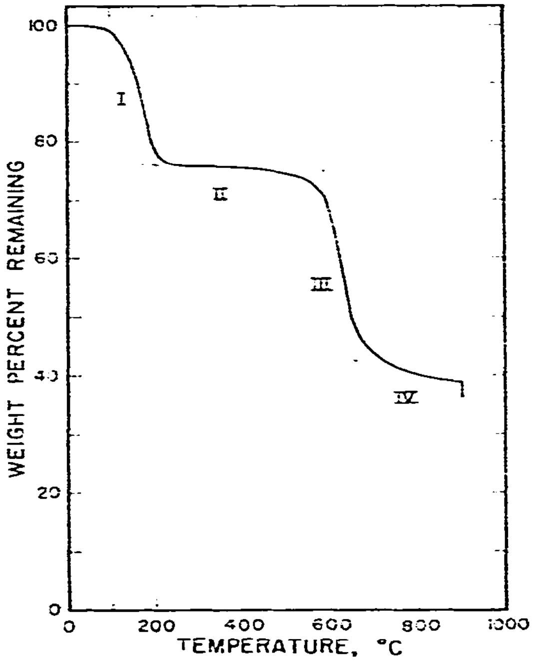
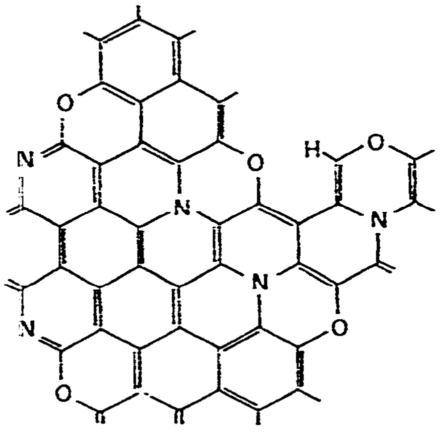


Fig. 7. Thermogravimetry of poly-(*p*-phenylene pyromellitamic acid)-poly-(*p*-phenylene pyromellitimide) in argon.

Above 700 °C in region IV, the pyrolyzed residue resulting from the polymer exists. Approximately 48–50% of the material present at 350 °C remains after heating the polyimide to 900 °C and maintaining the 900 °C temperature for a minimum of 60 min. An elemental microanalysis of the pyrolysis residue was obtained and shows the residue composition to be: C, 84.48%; H, 0.10%; N, 6.39%; O, 9.03%; (by difference)*. An empirical formula for the residue is $(C_{70.9}HN_{4.6}O_{5.7})_x$. The only possible structure for such a carbonized residue would be the fused aromatic structure proposed by Bruck[4].



The weight loss data obtained from the TG curves were subjected to the same type of kinetic treatment used in analysis of samples heated in air. The data obeyed Arrhenius-type kinetics with Arrhenius plots similar to those for heating in air shown in Fig. 4.

The apparent activation energy for decomposition of poly-(*p*-phenylene pyromellitimide) in argon over the temperature range 540–630 °C is 53.9 kcal/mole (standard deviation = 5.0 kcal/mole for 4 samples). Activation energies for the non-oxidative degradation of H-film have been reported by Bruck to be 73–74 kcal/mole for degradation in vacuum[1–3]. Heacock and Berr[5] found activation energies of 54.0 kcal/mole in helium.

The apparent activation energy for the cyclization reaction in argon of poly-(*p*-phenylene pyromellitamic acid) is 6.3 kcal/mole over the temperature range 130–175 °C (standard deviation = 1.3 kcal/mole for 4 samples). This value is not statistically different than the value for cyclization in air. The weight loss data in argon appear to follow zero-order kinetics. The similar results obtained in argon and air suggest that the cyclization reaction is independent of the atmosphere.

The DTA curves for polymers heated in argon and air are identical up to 350 °C, showing a broad endotherm. Above 350 °C, the DTA curve in argon shows a very broad but weak exotherm from about 500 to 650 °C, the same temperature range over which the rapid degradation of polyimide occurs.

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*Elemental microanalysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

CONCLUSION

The thermal cyclization of poly-(*p*-phenylene pyromellitamic acid) powders follows zero order kinetic behavior and has an apparent activation energy of approximately 6–7 kcal/mole. The apparent activation energies for decomposition of poly-(*p*-phenylene pyromellitimide) are approximately 42 kcal/mole in air and 54 kcal/mole in argon. Composition of the pyrolysis residue indicates a unit-by-unit oxidative degradation. The residue resulting after pyrolysis in argon appears to be primarily an aromatic carbon matrix.

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