Kinetics of Imidization of Poly (Amic Acid) in Miscible and Immiscible Polymer Blends

S. M. MAKHIJA, E. M. PEARCE, and T. K. KWEI

Departments of Chemistry and of Chemical Engineering, and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201

SYNOPSIS

Blends of commercial poly (amic acid), LARC-PAA polymer were prepared with thermoplastic polyimide P84. The blends were shown to be miscible over a certain composition range. Chemical imidization of LARC-PAA in the blends leads to phase separation. Thermal imidization of LARC PAA in the blends was carried out in the solid state. Miscible compositions of the blend remained miscible after imidization and showed a single glass transition for each blend. Immiscible compositions after imidization remained immiscible and showed two glass transition temperatures in the DSC scans. The kinetics of thermal imidization of PAA to polyimide (PI) in the solid state were studied using FTIR. In the immiscible blend the kinetics remained unaffected while in the miscible state the rate of imidization became faster than that of the pure PAA.

INTRODUCTION

Polymer blends are physical mixtures of polymers. The morphology and properties of polymer blends are controlled by the miscibility and phase behavior of the mixture. The two topics have evolved into a major area for polymer research in the last two decades. In recent years, polymer blends have been used successfully in an increasing number of applications due to their cost effectiveness and the relative ease with which new material systems meeting new applications can be tailor-made.[1,2]

Although a large number of polymer blends have been successfully commercialized, there are few examples for high temperature polymer systems so far. Among the high temperature polymers studied, a subclass containing various thermally stable heterocyclic units in the backbones and no pendant oxidizable groups has commanded a great deal of attention. The presence of aromatics or heterocyclic units leads to restricted rotation around skeleton bonds and gives high T_g. Polyimides are examples of such polymers.[3-9] Considering these rigid structures one would expect that certain polyimides may

not mix, or mix only with difficulty with other polymers. However in the last few years it has been found that several polyimides form miscible blends with polybenzimidazoles,[10] poly (aryl ether ketone),[11] polysulfones,[12] and polyethersulfones.[13] Many polyimides have limited solubilities or decompose during melting. However, the precursor of polyimides (PI) *viz.* poly (amic acid) (PAA) are usually soluble in many common solvents. Therefore mixing PAA with another polymer and then imidizing the PAA to PI in the blend can be a viable route to obtain PI blends. During imidization the PAA is undergoing a chemical change, and this change in chemical structure is expected to change the miscibility behavior of the polymer blend. Nevertheless, the situation is simpler than that encountered in the epoxy resin-polyethersulfone system.[14] Polyethersulfones formed miscible blends with the epoxy resins before crosslinking but phase separation took place during the cure. During the cure of epoxy resin there is a change in the chemical structure as well as a change in the molecular weight of the polymer, and both factors affect miscibility. In the PAA case there is no change in the molecular weight of the polymer. The only factor which contributes to the change in miscibility behavior is the change in the chemical structure. A more complicated case is where both components

are undergoing chemical change. For example, in a mixture of two poly (amic acids), Feger[15] studied the curing of binary mixtures of PAAs and showed that the mixture underwent exchange reactions in solution and in solid state. After curing, poly (amic acid) mixtures produced either polyimide blends, polyimide block copolymers/blends, or polyimide copolymer. Similar conclusions were reached by Jou and Huang.[16] In our PAA/PI blends, however, the cyclization reaction of PAA is not expected to have any effect on the already formed PI.

LARC-TPI/P84 SYSTEM

LARC-TPI (*Langley Research Center Thermoplastic Polyimide*) is a thermoplastic. It is based on benzophenonetetracarboxylic acid dianhydride reacted with 3,3'-diaminobenzophenone as shown in Figure 1. LARC-TPI is made by Mitusui Toatsu Co., Japan, and Rogers Corporation, Connecticut, USA. It has a glass transition temperature of about 260°C and shows a crystalline melting peak at about 313°C. It is available both in the poly (amic acid) form and in the fully imidized form. In the poly (amic acid) form it is soluble in NMP, DMAc, and other solvents. In the fully imidized form it can be dissolved

P84 (Lenzing, Tg = 315 °C)
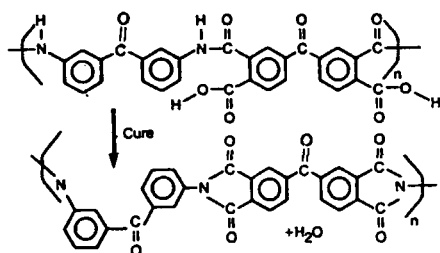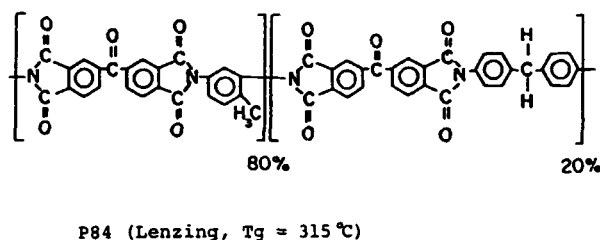
Figure 1   LARC-PAA (Before Curing) and LARC-PI (After Curing). Chemically cured LARC-PI is semicrystalline with T_m = 313°C.

in NMP only under high pressure and high temperatures (200–230°C).

P84 (Lenzing Corp., Austria) is an amorphous thermoplastic based on benzophenonetetracarboxylic acid and two types of diisocyanates (Fig. 1). It is soluble in aprotic polar solvents such as NMP, DMAc, DMF at room temperature. It has a glass transition temperature of about 313°C.

A BRIEF REVIEW OF IR STUDIES OF KINETICS OF IMIDIZATION

The most widely used technique to study the kinetics of cyclization of poly (amic acids) (PAA) is infrared spectroscopy.[17-21] Typically, polyimides show four characteristic imide bands at 1800 cm^{-1}, 1720 cm^{-1}, 1370 cm^{-1}, and 721 cm^{-1}. The bands at 1800 cm^{-1} and 1720 cm^{-1} are assigned to symmetric imide carbonyl stretching. The band at about 1370 cm^{-1} results from imide carbon-nitrogen stretching and the band near 721 cm^{-1} from the bending of the imide ring. Recently Pryde[22] has shown that bands near 1800 cm^{-1} and 721 cm^{-1} are affected by the presence of anhydride which is formed when PAA is heated. This interference can result in significant errors in determining the degree of cure. The carbonyl bands at 1800 cm^{-1} and 1720 cm^{-1} cannot be used for quantitative studies, since they deviate from the Beer-Lambert Law, as a result of hydrogen bonding.[23] According to Pryde,[22] the best band to follow the kinetics of imidization of PAA is the one at 1370 cm^{-1} which does not appear to suffer direct interference from any other peak. Furthermore, the absorbance in the 1370 cm^{-1} region shows little effect from anisotropy as the reaction proceeds. Accordingly, the 1370 cm^{-1} was used in this study to monitor the kinetics of imidization. For quantitative IR studies, a reference band is used whose absorbance only depends upon the thickness of the sample. In polyimides both the 1500 cm^{-1} and 995 cm^{-1} bands can be used as references. In the present study the band at 995 cm^{-1} was used as the reference band.

EXPERIMENTAL

Miscibility Studies

LARC in the poly (amic acid) form was diluted with 1-methyl pyrrolidinone (NMP) solvent. This was then precipitated by pouring slowly into water. After filtration the powder was dried under high vacuum at about 70°C overnight. The dried powder was re-

dissolved in NMP solvent. LARC-TPI was dissolved in NMP in a high pressure reactor at 250°C and 80 psi. P84 was dissolved in NMP at room temperature. For DSC studies blend films were prepared by casting from 4% to 8% solutions of the respective polymer mixture on a glass plate. The solvent was removed by drying under vacuum at 90°C overnight. These blend films were then imidized according to a thermal cycle as shown in Figure 2.

The chemical imidization was carried out by preparing a 10% solution of PAA and its blends in NMP solvent.[24] An equal volume of pyridine was added and the mixture was stirred for one hour. A volume of acetic anhydride equal to that of pyridine was added and stirring continued for another hour. The contents of the reaction vessel was poured into a volume of distilled water about four times that of the reaction mixture. After precipitation occurred the solid blend was collected by filtration. The material was then dried and differential scanning calorimetry (DSC) experiments were conducted.

Isothermal Kinetics Study

It is well known that if the water formed during the imidization reaction is not removed rapidly from the reaction zone, it may cause hydrolytic cleavage of the macromolecules and a decrease in the molecular weight of the polymer. The imidization of poly (amic acids) therefore was carried out in thin films of less than 30 μm for FTIR studies. These films were cast from 4% solution directly on KBr windows. In order for the samples to have the same thermal history prior to measurements, all the films were cast at 85°C for 15 min in a vacuum oven. Further solvent

removal and conversion to polyimide was followed by using a Digilab Fourier Transform Infrared spectrophotometer (FTS60) system using 64 scans. A high temperature high pressure FTIR cell from AABSPEC, (New York) was used with a transmission probe. The heater was placed inside the probe and connected to a temperature controller. The temperature of the sample can be monitored by using a thermocouple inserted from the top inlet of the cell, and controlled to within ±1°C. Imidization was carried out under a stream of nitrogen gas, so that water formed during the reaction could be removed easily. The temperature of the sample was quickly raised to the desired value and spectra were recorded at different times to monitor the reaction isothermally.

RESULTS AND DISCUSSIONS

Miscibility Data

The LARC-TPI purchased from Rogers displayed a melting endotherm at 315°C. After cooling, a second scan showed a glass transition at 257°C and no melting peak at 315°C. This is attributed to the residual crystallinity in the LARC introduced by the chemical imidization.[25] This crystallinity is destroyed if LARC heated above the melting point or dissolved in the solvent. Our chemically imidized LARC-PAA showed a crystalline peak at 302°C (Fig. 5). The position of this peak depends upon the way the chemical imidization is carried out. The LARC-PAA chemically imidized in presence of P84 in the ratio of LARC/P84 80/20 and 50/50 also showed
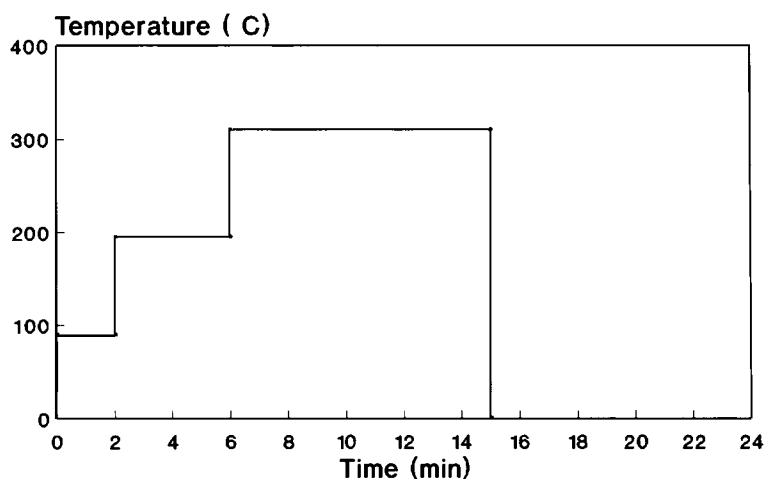

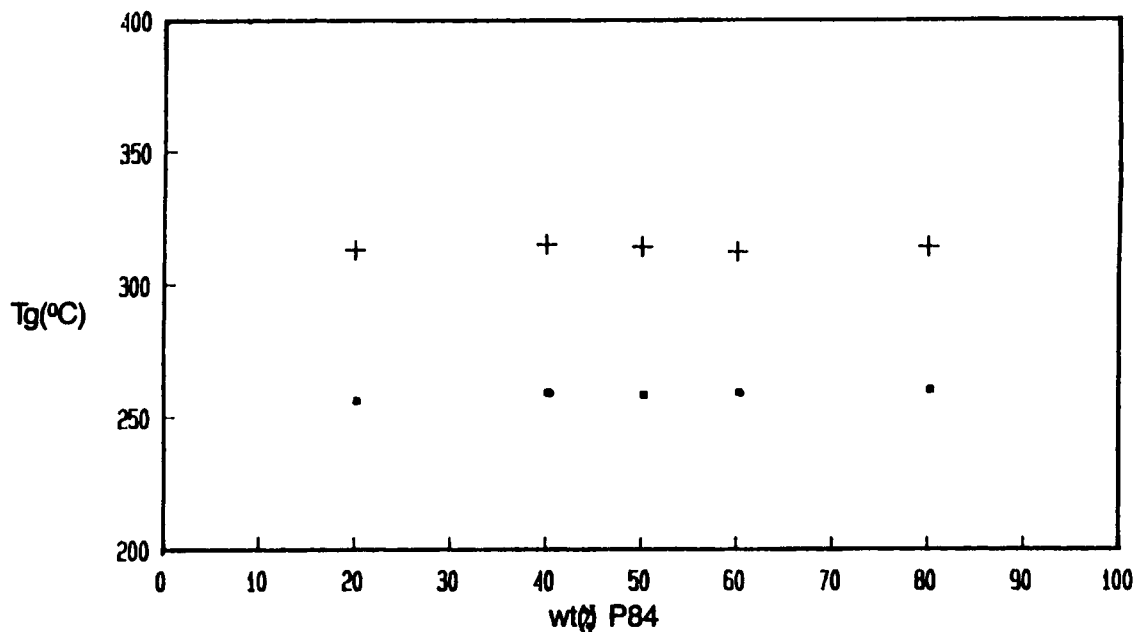**Figure 2** Thermal cycle used for cyclization of PAA and its blends.

Figure 3 T_g vs. composition of LARC-TPI/P84 blends.

crystalline peaks at the same temperature. During the second run, two glass transitions, one corresponding to LARC-TPI and the other corresponding to P84, were noted as shown in Figure 3. From Figure 3 we conclude that chemically imidized blends of LARC/P84 were phase separated. Blend films of the two polyimides (LARC-TPI/P84) were heterogeneous when seen under an optical microscope. These blends showed two glass transitions in DSC experiments, one corresponding to that of LARC-TPI around 257°C and the other at 313°C corresponding to that of P84 as shown in Figure 4.
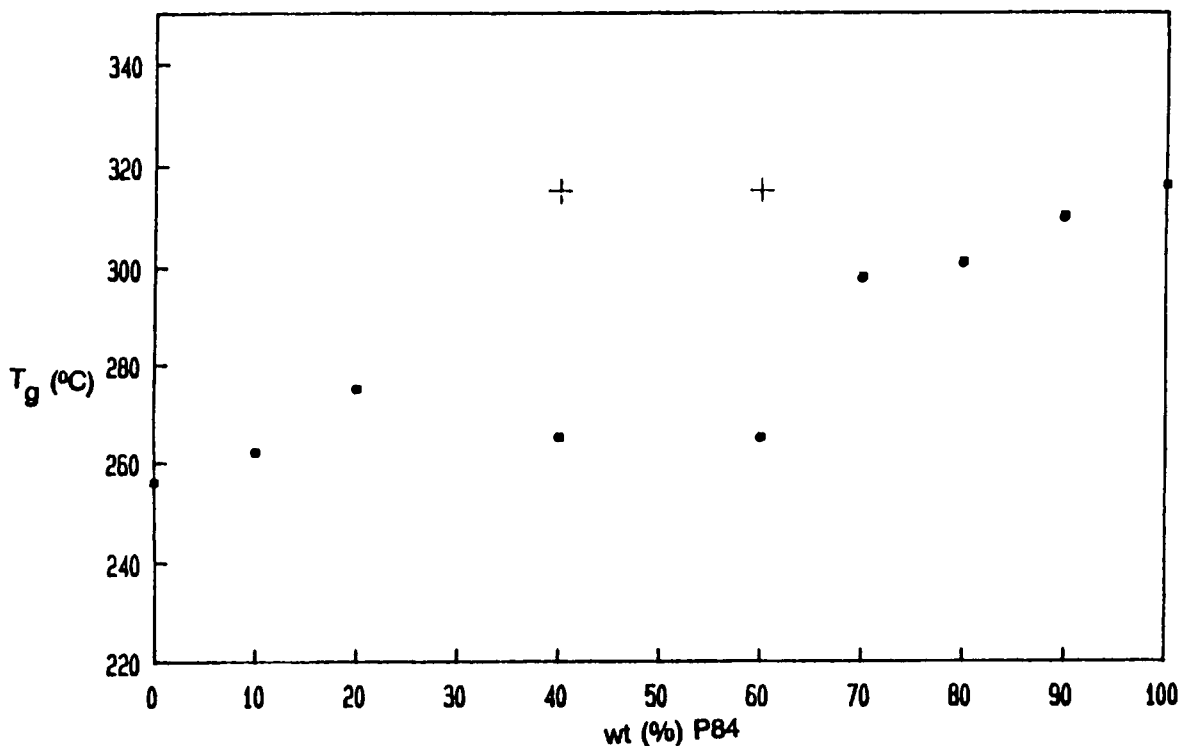

Figure 4 Glass transition temperature vs. composition of thermally imidized D100/P84 blends.

Films of PAA/P84 (poly amic acid form of LARC-TPI/P84) were examined by optical microscope using cross polars. Clear and transparent films were obtained when the PAA content was either above 70% by weight or below 40%. Films having PAA compositions between 40% and 70% were opaque and showed distinct phases. All the blends, homogeneous or heterogeneous, were then subjected to thermal imidization. Thermal imidization of the films was carried out in the DSC cell using a thermal cycle shown in Figure 2. After imidization the blends were cooled and were scanned again to determine T_g. Again, blends having composition between 40/60 and 70/30 showed two glass transitions temperatures corresponding to those of pure LARC and pure P84. Blend compositions below 40% PAA or above 30% P84 showed a single glass transition for each composition. The glass transition temperatures are shown in Figure 5 as a function of composition.

In this figure it can be seen that the initially miscible PAA/P84 blends remained miscible after imidization. Since LARC-TPI was immiscible with P84 at all compositions, one would expect that as PAA in the blends of PAA/P84 imidized to PI, the blend

would become heterogeneous. However our DSC data did not show this. Possibly, the relatively rigid polyimide chains may not have enough mobility in the solid state to undergo phase separation under the conditions of our experiment. Therefore kinetic factors are believed to contribute to the apparent miscibility. However, a complicating factor in determining the miscibility of a cast film is the "solvent effect" and a detailed study is needed to understand the phase separation.

Kinetics Study

Thermal imidization was followed by the change in intensity of 1370 cm^{-1} band in the infrared. Figure 6 shows the FTIR spectra of the pure LARC at 200°C at different times during the course of imidization. The area under the 1370 cm^{-1} peak was seen to increase with time. The conversion (α) is calculated from eq. (1).

$$\alpha = \frac{(A_{1365}/A_{995})_t}{(A_{1365}/A_{995})_{t=\infty}} \tag{1}$$

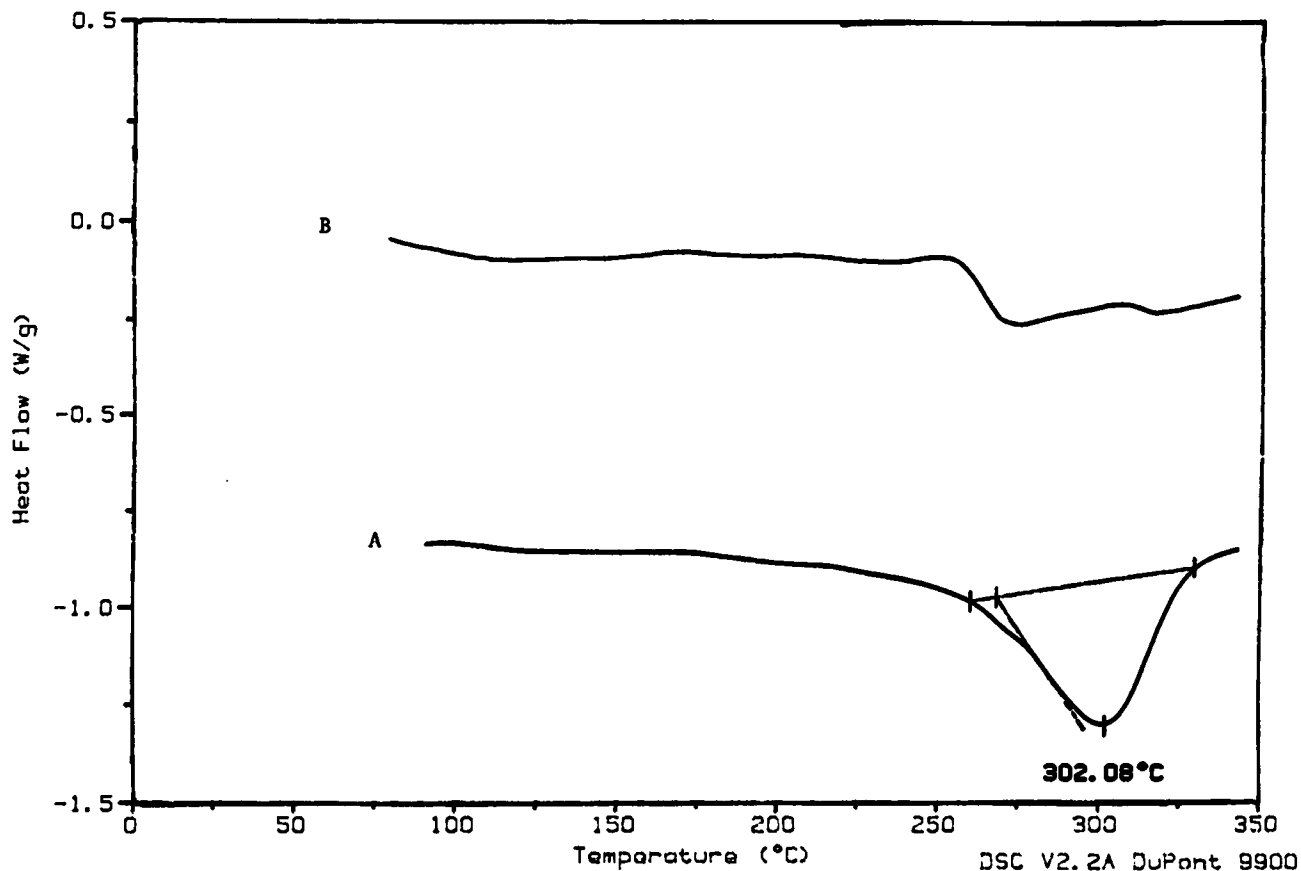where $(A_{1365}/A_{995})_t$ represents the ratio of area under

Figure 5 Chemically imidized LARC-PAA. (A) First run (B) Second run.

the peak at 1365 cm^{-1} to that of 995^{-1} at time t. This ratio after complete imidization is designated as $t = \infty$ (the highest value in the series of experiments). Before the imidization reaction is started there was no or very little polyimide formed (2–4%). The above equation is based upon the Beer-Lambert Law, $A = a \cdot b \cdot c$ where A is the absorbance of a particular peak, a is the absorbtivity of that peak, b is the path length, and c is the concentration of that peak. Absorbance can be used for quantitative calculations when the peaks are well separated and symmetrical. Under these conditions the area under the peak is proportional to the height of that peak, that is, to the absorbance. However, in the present study it was found that during the later stages the relationship between area and absorbance was not linear as shown in Figure 7. Therefore areas were used for all calculations instead of normally used absorbance.

In carrying out the same calculation in the blend, we need to take into account the presence of P84 which absorbed in the same region. The conversion (α) was calculated by a simple modification of eq. (1).

$$\alpha = \frac{(A_{1365}/A_{995})_t - (A_{1365}/A_{995})_{t=0}}{(A_{1365}/A_{995})_{t=\infty} - (A_{1365}/A_{995})_{t=0}} \quad (2)$$

where $(A_{1365}/A_{995})_{t=0}$ is the contribution due to P84 present in the blend. Implicit in the above equation is the assumption that both components follow the Beer-Lambert law individually and in the blend and that the temperature dependence of the absorbtivity is the same for 1370 cm^{-1} and 995 cm^{-1} peaks.

Figures 8 and 9 show the spectra of a miscible blend of 80/20 PAA/P84 and an immiscible blend of 50/50 of PAA/P84 at 200°C at different times during cyclization.

The position of the relevant peaks remain the same throughout the reaction. Quantitative calculations of the conversion from these spectra are plotted in Figure 10. From this figure it can be seen that the rates of cyclization of PAA in the immiscible blend are very similar to that of the pure LARC. On the other hand, the maximum conversions obtained, as well as the rates (slope of the curve) of cyclization in the miscible blends are higher than the values for the pure LARC or for the 50/50 immiscible blend. Similar results were obtained at higher tempera-
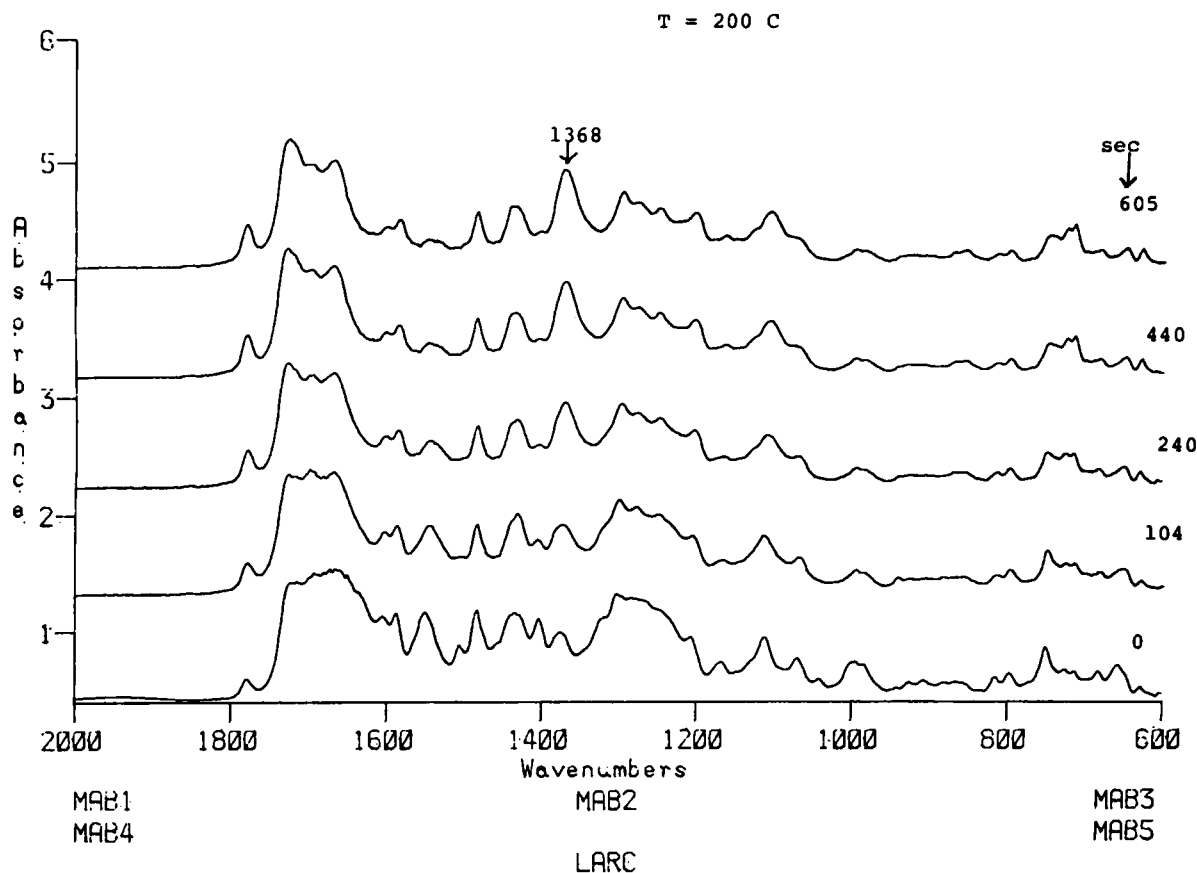

Figure 6 FTIR spectra of PAA during cyclization at 200°C at various times.
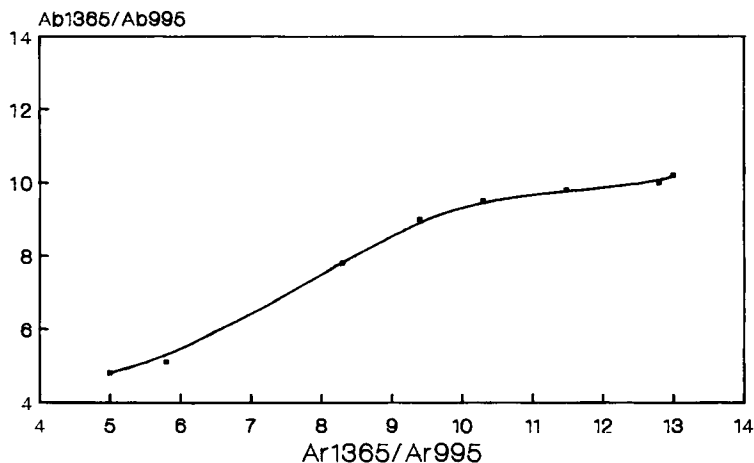
Blend of PAA/P84, 50/50 at 200 °C

Figure 7   Blend of PAA/P84, 50/50 at 200°C.

tures. The maximum conversion obtained at different temperatures are plotted in Figure 11. From Figures 10 and 11 we can make the following observations.

1. The rate of imidization in the immiscible blend was very similar to that in the pure

LARC. This is easy to understand because in the immiscible blend LARC behaves as if the other component is not present.

2. Higher levels of conversion were obtained in the miscible blend with a higher rate of imidization. Although the reasons for the acceleration of the imidization rate are not well
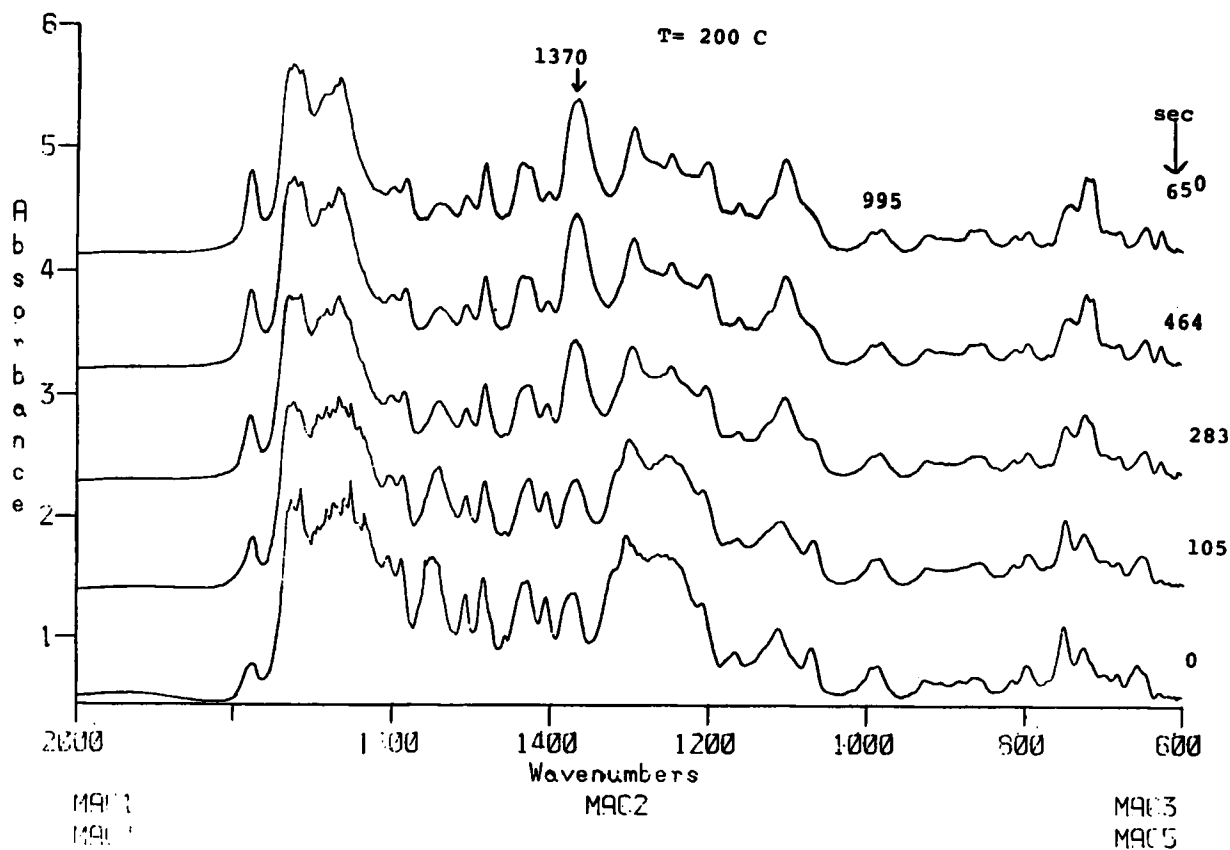

Figure 8   FTIR spectra of LARC/P84 (80/20) blend at 200°C at various times.
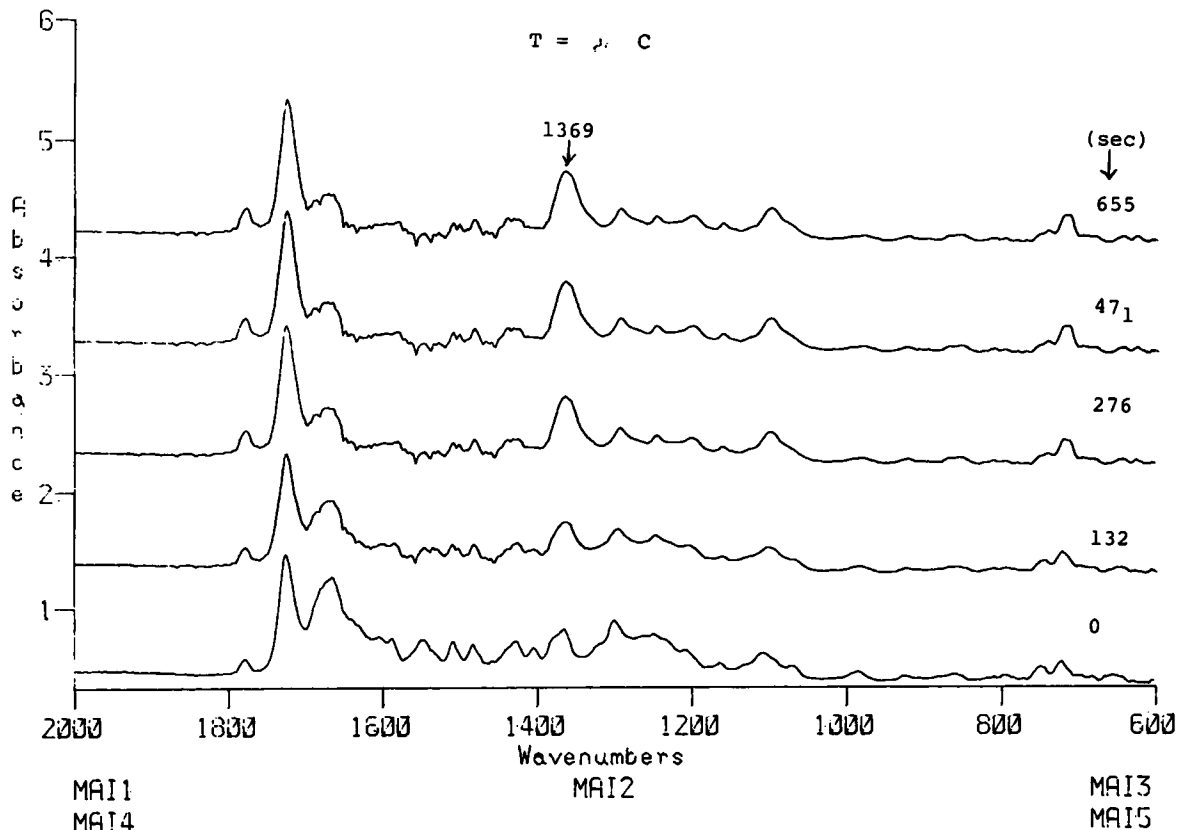
Figure 9 50/50 LARC/P84 blend.

understood, we hypothesize that the presence of another component in the immediate vicinity of LARC PAA may influence the conformations of the amide or the carbonyl group so that cyclization becomes more favorable.

CONCLUSIONS

The polyimide P84 is shown to be miscible with LARC poly (amic acid) over certain composition ranges. The miscibility of the blend is retained after
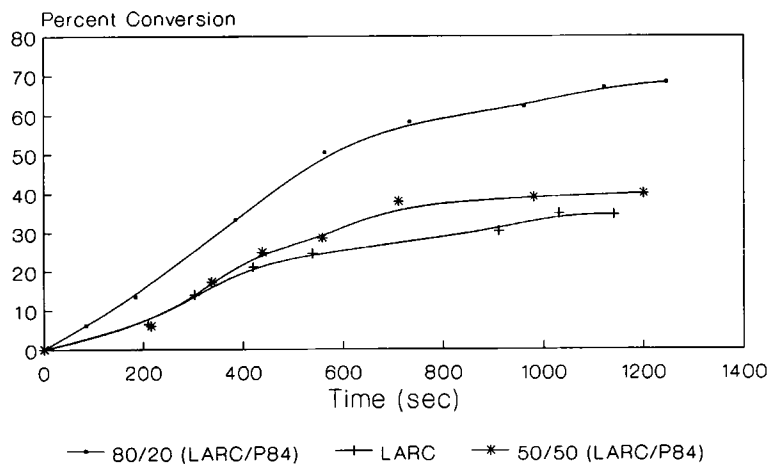

Figure 10 Kinetics of imidization of LARC and its blends at T = 150°C.
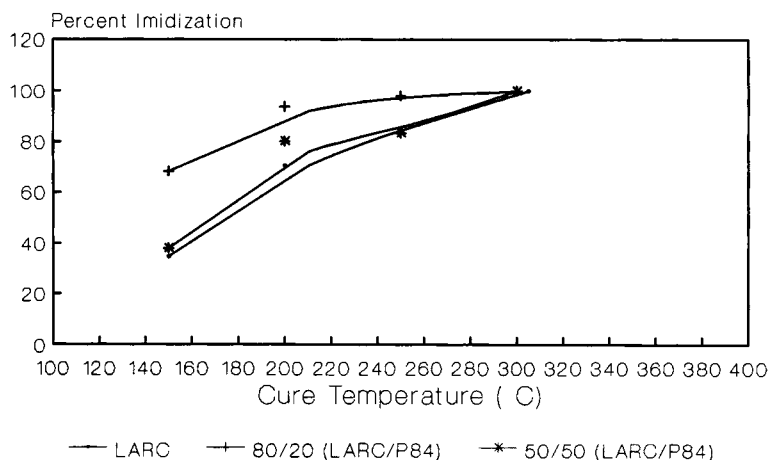
Figure 11 Degree of imidization as a function of cure temperature.

thermal imidization. Chemical imidization of the blend leads to phase separation. The kinetics of thermal imidization was studied using FTIR. The kinetics are unaffected in the immiscible blend. In the miscible blend the rate of imidization becomes faster and the final maximum conversion higher. The reasons for this are not well understood.

REFERENCES

1. D. R. Paul, and S. Newman, Eds., *Polymer Blends,* Academic Press, New York, 1978.
2. K. Solc, Ed., *Polymer Compatibility and Incompatibility: Principles and Practices,* Published for MMI Press by Harwood Academic Publisher, 1982.
3. P. M. Hergenrother, N. T. Wakelyn, and S. J. Havens, *J. Polym. Sci., Polym. Chem., A.,* **25,** 1093 (1987).
4. P. Hergenrother and S. J. Havens, *Sci. Adv. Matl. Proc. Engr. Series,* **33,** 451 (1988).
5. P. E. Cassidy, *Thermally Stable Polymers,* Marcel Dekker, New York, 1980.
6. J. P. Critchley, G. J. Knight, and W. W. Wright, *Heat Resistant Polymers,* Plenum, New York, 1983.
7. P. M. Hergenrother, "Heat Resistant Polymers," in *Encyc. Polym. Sci. Eng.,* H. Mark, Ed., 2nd Ed., Vol. 7, John Wiley and Sons, New York, 1987, p. 639.
8. P. M. Hergenrother and S. J. Havens, in *Polyimides, Synthesis, Characterization and Applications,* K. Mittal, Ed., Plenum, New York, 1984, p. 453.
9. P. M. Hergenrother, "Polyquinooxalines," in *Encycl. Polym. Sci. Eng.* 2nd Ed., Vol. 13, John Wiley and Sons, New York, 1988, p. 55.

10. P. Musto, F. E. Karasz, and W. J. MacKnight, *Polymer,* **30,** 1012 (1989).
11. J. McGrath, *Symposium on Recent Advances in Polyimides and Other High Performance Polymers,* Division of Polymer Chemistry, ACS, San Diego, January 1990.
12. W. J. MacKnight and F. E. Karasz, AIChE, San Francisco, Nov. 1989.
13. S. Makhija, Unpublished research, Polytechnic University, Brooklyn, New York (1991).
14. K. Yamanaka and T. Inoue, *Polymer,* **30,** 662 (1989).
15. C. Feger, *Symposium on Recent Advances in Polyimides and Other High Performance Polymers,* Division of Polymer Chemistry, ACS, San Diego, January 1990.
16. J. H. Jou and P. T. Huang, *Polym. J.,* **10,** 909 (1990).
17. P. D. Frayer, in *Polyimides, Synthesis, Characterization and Applications,* K. Mittal, Ed., Plenum, New York, 1984, p. 273.
18. P. R. Young, *SAMPE Prepr.,* **30,** 889, (1985).
19. M. Navarre, in *Polyimides: Synthesis and Characterization,* K. Mittal, Ed., Plenum, New York, 1984, p. 259.
20. R. Ginsberg and J. R. Susko, in *Polyimides: Synthesis and Characterization,* K. Mittal Ed., Plenum, New York, 1984, p. 237.
21. S. Numata, K. Fujisaki, and N. Kinjo, in *Polyimides: Synthesis and Characterization,* K. Mittal, Ed., Plenum, New York, 1984, p. 273.
22. C. A. Pryde, *J. Polym. Sci.: Part A,* **27,** 711 (1989).
23. J. A. Kreuz, A. L. Endrey, F. P. Gay, and C. E. Sroog, *J. Polym. Sci., Part A-1,* **4,** 2607 (1966).
24. T. H. Hou, J. M. Bai, and T. L. St. Clair, in *Polyimides: Materials, Chemistry and Characterization,* C. Feger, M. M. Khojasteh and J. E. McGrath, Eds., Elsevier, Amsterdam, 1989, p. 169.
25. J. Wang, A. T. DiBenedetto, J. F. Johnson, S. J. Huang, and J. L. Cercena, *Polymer,* **30,** 718 (1989).