

Effect of Cure Conditions on Probimide 32 Polyamide–Imide

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ABSTRACT: We report on a curing study of Probimide 32, a preimidized polyamide–imide. The polymer was in a solution of *N*-methyl pyrrolidone (NMP) and xylene and was spun cast or doctor-bladed to form films for study. The films were cured by drying under a variety of conditions to effect solvent removal. We characterized the effects of cure by thermogravimetric analysis, dynamic mechanical analysis, Fourier transform infrared spectroscopy, and differential scanning calorimetry. Index of refraction was measured by waveguide prism coupling. Although the polymer did not require postprocessing thermal closure of its imide group, the physiochemical makeup of the system, and consequently, the properties of the Probimide 32 films, were highly dependent upon the curing temperature and environment. The properties/thermal stability improved as residual solvent was driven from the films. In the films hard baked at 300°C, the extent of thermally induced crosslinking was substantially greater in air-cured films than in nitrogen-cured films. The crosslinking markedly affected the properties and relaxation behavior of the material. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1113–1126, 1997

INTRODUCTION

Polyimides are important members of the class of high temperature heterocyclic polymer materials.^{1–3} They are well known for their outstanding thermal stability, mechanical and electrical properties, and chemical resistance. Polyimides are used in electronic, display, and aerospace applications.

Polyamide–imides⁴ are related polymers whose repeat units contain an imide ring linkage and an amide linkage. Polyamide–imides are less expensive than polyimides, readily processed from solutions, and still have outstanding properties. There is expanding interest in polyamide–imides as engineering plastics⁴ as materials for molecular composites,^{5,6} and as liquid crystal display (LCD) alignment films.⁷

Polyimides generally require high temperature treatments that are necessary for ring closure of the polyamic acid precursor and for the removal of high boiling point solvents. Studies have shown^{8–16} that the chemical and physical properties of polyamic acid precursor systems change substantially as they are cured, primarily because of the chemical conversion from polyamic acid to polyimide. Unlike most polyimides, polyamide–imides are available in solutions of their fully converted (i.e., fully imidized) form. The fully imidized polyamide–imides systems do not require postprocessing heat treatment to effect closure of the imide ring.

It is important that the outstanding features, as well as the limitations, of polyamide–imides be well understood. It is furthermore crucial to understand these materials from a processing–structure–properties perspective. Because reducing the cure temperature of polyimides may reduce processing cost and time as well as allowing

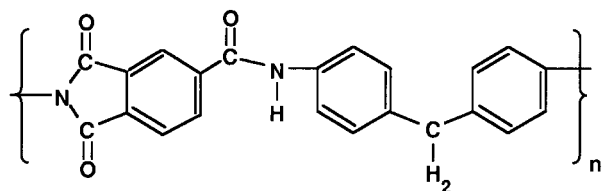
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their compatibility with inexpensive low temperature materials, it is interesting to learn how these systems respond to differing thermal treatments. Thus, this work explored the effects of cure temperature and environment on the properties and structure of a preimidized polyamide-imide system. Our goal was to learn how the preconverted polymer changes physically and chemically during its cure treatment. We report here the processing-structure-property relationships in Probimide 32 polyamide-imide as part of an ongoing evaluation of the material for liquid crystal alignment applications.

EXPERIMENTAL

We studied the material Probimide 32, a fully imidized polyamide-imide resin produced by OCG Microelectronic Materials, Inc. The polymer was provided in an *N*-methyl pyrrolidone (NMP)/xylene solution with 21% solids content by weight. The material has the following chemical repeat unit:



To form bulk films, the Probimide 32 solution was dropped onto a glass plate and wiped with a 1-mm gap doctor blade. The wet films were dried to a tack free condition under a dry air current at room temperature overnight. The films were then progressively cured at 100°C for 6 h, 200°C for 3 h, and 300°C for 3 h. Thermal cures of 100 and 200°C were performed in air with the polymer on glass, while the 300°C cures (which we will call hard cures) were performed on free-standing film in either air or nitrogen environments. Film thicknesses were on the order of 100 μm . All films were amorphous, because the samples exhibited no Bragg scattering peaks when examined by wide angle X-ray scattering.

Thin films were formed by spin casting the Probimide 32 solution on glass or KBr at 4000 rpm for 30 s. The samples were immediately soft baked at 100°C for 15 min in air. The samples appeared to be dry after soft curing. The samples then progressively underwent 1-h cures at 200 and

300°C. The 200°C cures were performed in air, while the 300°C cures were performed either in air or in nitrogen.

A Seiko TG/DTA320 was used for thermogravimetric analysis (TGA) of the bulk films. Samples were scanned from room temperature to 575°C at 10°C/min in flowing air (300 mL/min).

Dynamic mechanical analysis (DMA) was performed in tension mode on the bulk films using a Seiko DMS200. Samples were scanned under nitrogen at 2°C/min from room temperature to above glass transition temperature, T_g , at which breakage occurred. Frequencies of 1, 2, 5, 10, and 20 Hz were used.

The index of refraction at $\lambda = 632.8$ nm was measured using a Metricon PC-2000 prism coupler. Refractive index was measured by determination of the critical angle. Both in-plane n_{TE} and out of plane n_{TM} indices were measured. Average refractive index n_{avg} was calculated as the average of the indices along three orthogonal axes as shown in eq. (1):

$$n_{\text{avg}} = (1/3)(2n_{\text{TE}} + n_{\text{TM}}) \quad (1)$$

Refractive index measurements were taken for the free-standing films and the thin films spin coated on glass slides.

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 510P. FTIR spectra were taken for the Probimide 32 thin films spin coated on KBr.

Differential scanning calorimetry (DSC) measurements were made for bulk films using a Perkin-Elmer DSC-7 calibrated to zinc and indium standards. The scan rate was 20°C/min.

RESULTS AND DISCUSSION

Coloration and Brittleness

The changes in coloration and brittleness in Probimide 32 thick films that occurred with subsequent cures are summarized in Table I. The films were considered brittle if they were easily broken upon flexing. Probimide 32 became progressively darker as it was cured to higher temperatures, and it was darkest when cured at 300°C in air. The polymer was brittle after it was cured at only 100°C. However, the brittleness receded when cured to 200°C. The film then became brittle if cured at 300°C in air, but it did not become brittle

Table I Color and Brittleness in Films Cured at Progressively Higher Temperatures

Temp. (°C)	Environment	Color	Brittleness
100	Air	Yellow	Very brittle
200	Air	Brown	Flexible
300	Air	Dark, reddish brown	Brittle
300	N ₂	Brown	Flexible

if cured at 300°C in nitrogen. The brittleness and dark coloration of the air cured, hard baked film suggests that abundant chemical crosslinks had formed.

TGA

Thermogravimetric spectra of Probimide 32 bulk films charted the removal of solvent and water from the films, and also indicated decomposition of the polymer. Our primary goal was to observe solvent content as a function of cure conditions. We demonstrate here how the solvent was progressively removed from the bulk polymer films as they were cured at 100, 200, and 300°C.

Polyimide Solvents

Polyimide solvents typically have very high boiling points: NMP boils at 202°C and xylene boils at 138–144°C. However, while solvents unbound to polymer typically evaporate at temperatures below their boiling points, solvents bound to polymer may require higher temperatures in order to vaporize. In the 10°C/min thermogravimetric scan of the NMP (Fisher Scientific) in Figure 1, all solvent has evaporated by about 190°C.

Probimide 32

In Figure 2(a–d) thermogravimetric and derivative scans of Probimide 32 treated at room temperature, 100, 200, and 300°C, respectively, are compared. The scans depict the water loss at 80°C, loss of residual solvent at about 200°C, and the decomposition of the polymer above 350°C. The films lost about 3% of their initial weight below 150°C due to the removal of water. All samples treated at or below 200°C had a large loss in weight in the 150–350°C region due to vaporization of residual solvent. For the derivative curves, the higher the cure temperature, the higher the

temperature at which the maximum rate of weight loss of the solvent occurred. While the rate of weight loss was maximal at around 200°C in the room temperature cured sample, the rate of weight loss was maximal at almost 300°C in the 200°C cured sample. The peak height decreased as the cure temperature increased. In the 150–350°C region, the room temperature cured sample [Fig. 2(a)] had the largest weight loss, the 100°C cured sample less [Fig. 2(b)], and the 200°C cured sample even less [Fig. 2(c)]. Thus, each cure at a progressively higher temperature removed more solvent from the film. There was apparently no residual solvent remaining in the 300°C cured film [Fig. 2(d)]. The weight loss curves showed a plateau until the temperature exceeded 400°C, at which point film degradation began.

This study demonstrates that there is a distribution of solvent removal temperatures ranging from below 150 to above 350°C. Solvent molecules that are removed at or below the boiling point of the solvent represent loosely bound species that readily vaporize, while molecules that are removed at temperatures far above the boiling point represent species that are physically bound to the polymer. Thus, as the material is cured, low boiling species are removed and the distribution of removal temperatures of residual solvent species is pushed to higher temperatures.

Cure time also affects the residual solvent in the polymer film. Figure 3 depicts thermogravimetric scans of Probimide 32 treated for 1, 6, and 24 h at 100°C. As cure time increased, the amount of residual solvent decreased. There was also a small shift in the distribution of solvent removal

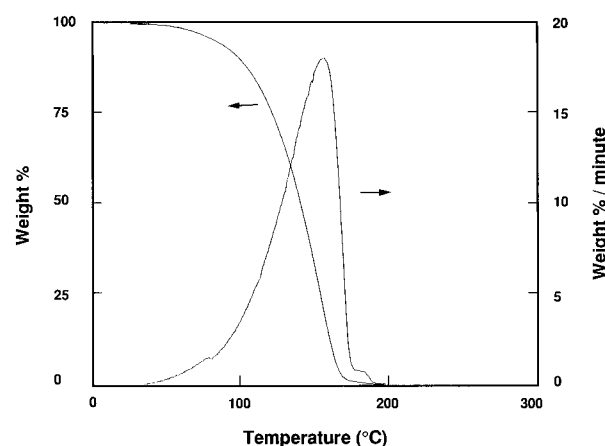


Figure 1 Weight loss and derivative of weight loss vs. temperature for *N*-methyl pyrrolidone (NMP).

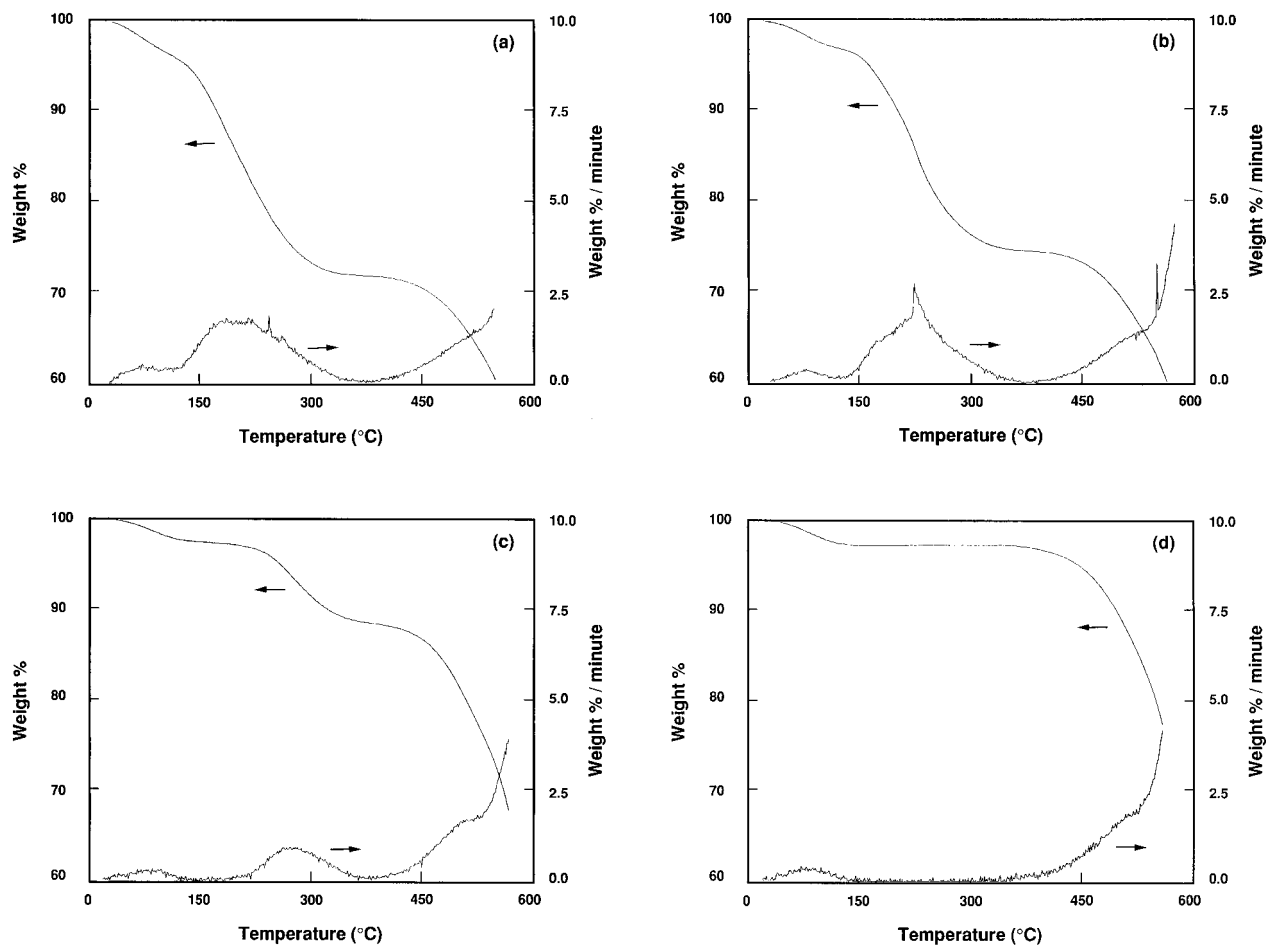


Figure 2 Weight loss and derivative of weight loss vs. temperature for Probimide 32 thick films: (a) dried under an air current at room temperature, (b) then baked 6 h at 100°C, (c) then 3 h at 200°C, (d) then 3 h at 300°C.

temperatures between 1 and 6 h and a larger shift after 24 h of cure.

As Figures 2 and 3 show, at around 450°C decomposition of the polymer begins, as indicated by a large loss in weight. If we arbitrarily define the decomposition temperature as the temperature above 350°C at which the time derivative of weight loss equals 3%/min (scanning at 10°C/min), the decomposition temperature of Probimide 32 was about 550°C in flowing air. The manufacturer reports a decomposition temperature of 494°C.¹⁷

DMA

The dynamic mechanical relaxation of Probimide 32 films provides a wealth of property and structure information. The DMA data for our films demonstrated how the glassy regions, the relaxation regions, and the rubbery regions of the DMA

scans were affected during the cure and how they were dependent upon the cure environment. The changing dynamic mechanical spectra can be attributed to changing solvent content and changing degrees of crosslinking.

The DMA spectra for Probimide 32 are shown in Figure 4(a–d) for samples cured at 100, 200, and 300°C in air, and 300°C in nitrogen, respectively. Young's modulus E' and loss factor $\tan \delta$ are shown as functions of temperature. For brevity, only measurements at 1 Hz are shown.

The glassy Young's modulus at 25°C was affected by the cure conditions of the polymer film. The glassy modulus of film treated at 100 and 200°C [Fig. 4(a,b)] was 1.9–2.0 GPa. The glassy modulus of Probimide 32 film treated at 300°C in nitrogen [Fig. 4(d)] was somewhat higher, 2.7 GPa, which agrees with reported values of the modulus.¹⁷ It appears that residual solvent in the

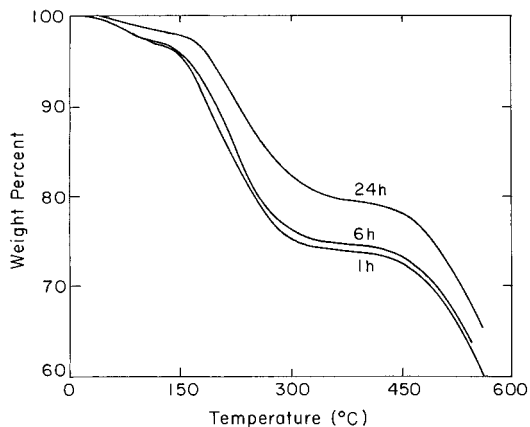


Figure 3 Weight loss and derivative of weight loss vs. temperature for Probimide 32 thick films baked at 100°C for 1, 6, and 24 h.

films cured at 100 and 200°C plasticized the films, lowering the glassy modulus. The measured glassy modulus of film treated at 300°C in air [Fig. 4(c)] was fairly low, 1.3 GPa. This was either because of oxidative damage inflicted upon the polymer during the cure, or because of an inability to make an accurate measurement due to the brittleness of the film.

In Figure 4(a,b) Young's modulus for samples cured at 100 and 200°C drops by about 2 orders of magnitude as a result of polymer relaxation. In the $\tan \delta$ curves, two relaxations are seen in these samples. The first relaxation in each scan occurred at about the curing temperature, while the second relaxation occurred just below 300°C. The material was highly plasticized by the residual solvent, giving the material a low softening tem-

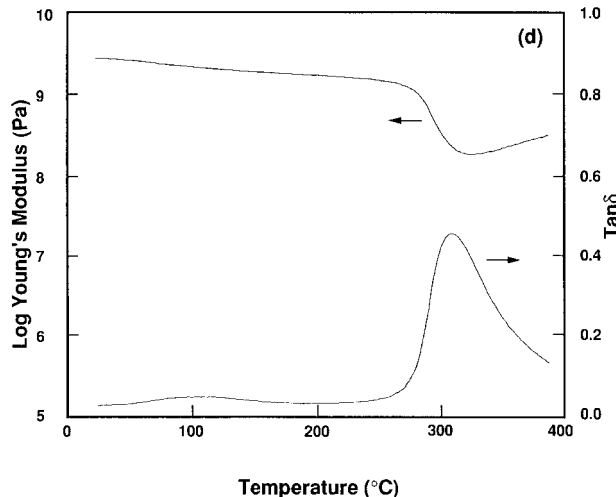
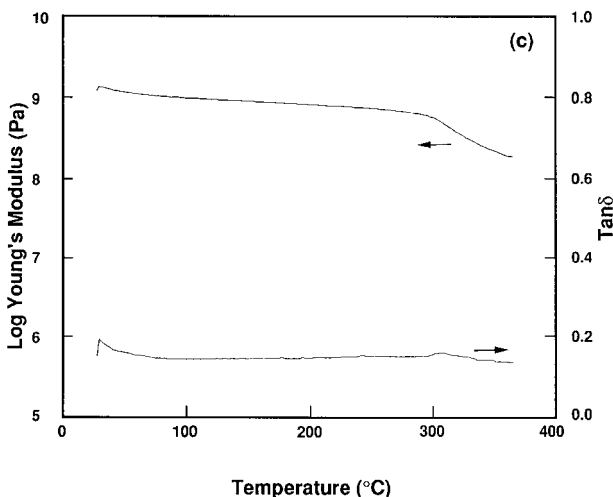
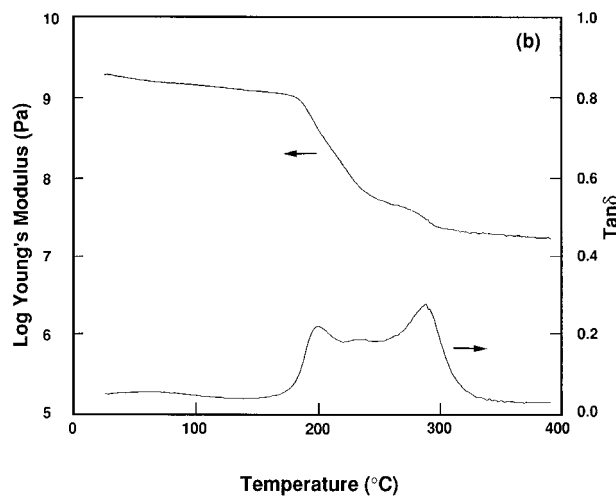
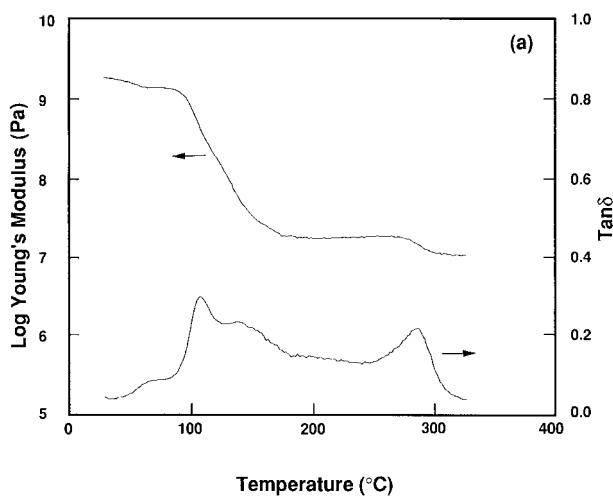


Figure 4 Young's modulus and dissipation factor, $\tan \delta$, for Probimide 32 thick films: (a) cured 6 h at 100°C, (b) then 3 h at 200°C, then 3 h at 300°C in either (c) air or (d) nitrogen.

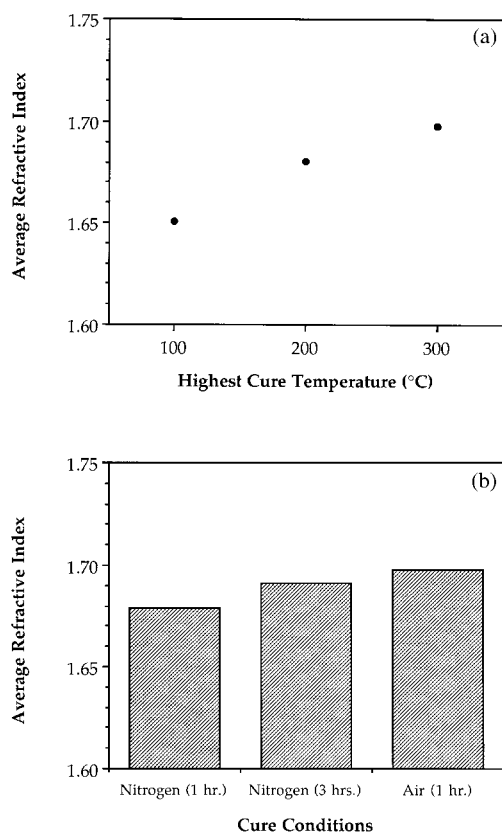


Figure 5 (a) Indices of refraction of spin coated Probimide 32 films vs. highest cure temperature in air. Cure cycle was 15 min at 100°C, 1 h at 200°C, 1 h at 300°C. (b) Refractive indices for different cure conditions at 300°C.

perature. Once the solvent was driven out, the material again relaxed at the glass transition temperature of the unplasticized polymer.

In Figure 4(c,d) the samples treated at

300°C, in air or in nitrogen, have only a single relaxation. The glass transition relaxation was centered above 300°C in the air-treated sample. The $\tan \delta$ peak was shallow, suggesting the sample was highly crosslinked by the 300°C cure in air. The sample treated under nitrogen at 300°C, on the other hand, had a well-defined glass transition relaxation at 300°C. Thus, it was apparent that the degree of crosslinking in Probimide 32 was substantially greater when hard cured in air than when hard cured under flowing nitrogen.

The rubbery modulus region was also very different in the Probimide 32 films. The films cured at 100 and 200°C had extremely low rubbery moduli, the 200°C cured film having a slightly greater rubbery modulus than the 100°C treated film. In the 300°C nitrogen-treated material, the rubbery Young's modulus reached a minimum value of 0.16 GPa shortly after relaxation. This rubbery modulus was about 10 times greater than that observed in the 100 and 200°C treated films. Apparently, the 300°C cure in nitrogen not only increased the glass transition temperature but also provided reinforcement to the rubbery state, probably as a result of backbone crosslinks that formed during the hard cure. The rubbery modulus of the film cured at 300°C in nitrogen slowly increased with temperature because the high temperatures induce more nonoxidative crosslinks in the polymer. In the film cured at 300°C in air, no rubbery region was clearly observed because the gel network had already formed before the polymer relaxed. Instead, the modulus slowly declined and did not appear to flatten entirely before the sample broke.

Table II IR Absorption Regions of NMP and Xylene

Compound	Peak Location or Approx. Region (cm ⁻¹)	Tentative Assignment	Peak Strength
NMP	2800–3000	$\nu(\text{C—H})$	S
	1680	$\nu(\text{C=O})$	S
	1380–1500	$\delta(\text{C—H}), \delta(\text{N—CH}_3)$	S
	1300	$\nu(\text{C—N})$	S
	1110	$\nu(\text{C—N})$	M
	980	$\beta(\text{ring})$	M
Xylene	2900–3100	$\nu(\text{C—H})$	S
	1380–1650	$\nu(\text{C=C})$	S
	1000–1050	Aryl $\delta(\text{C—H})$	M
	790, 760, 740, 690	δ ring substitution bands	S

S, strong; M, medium.

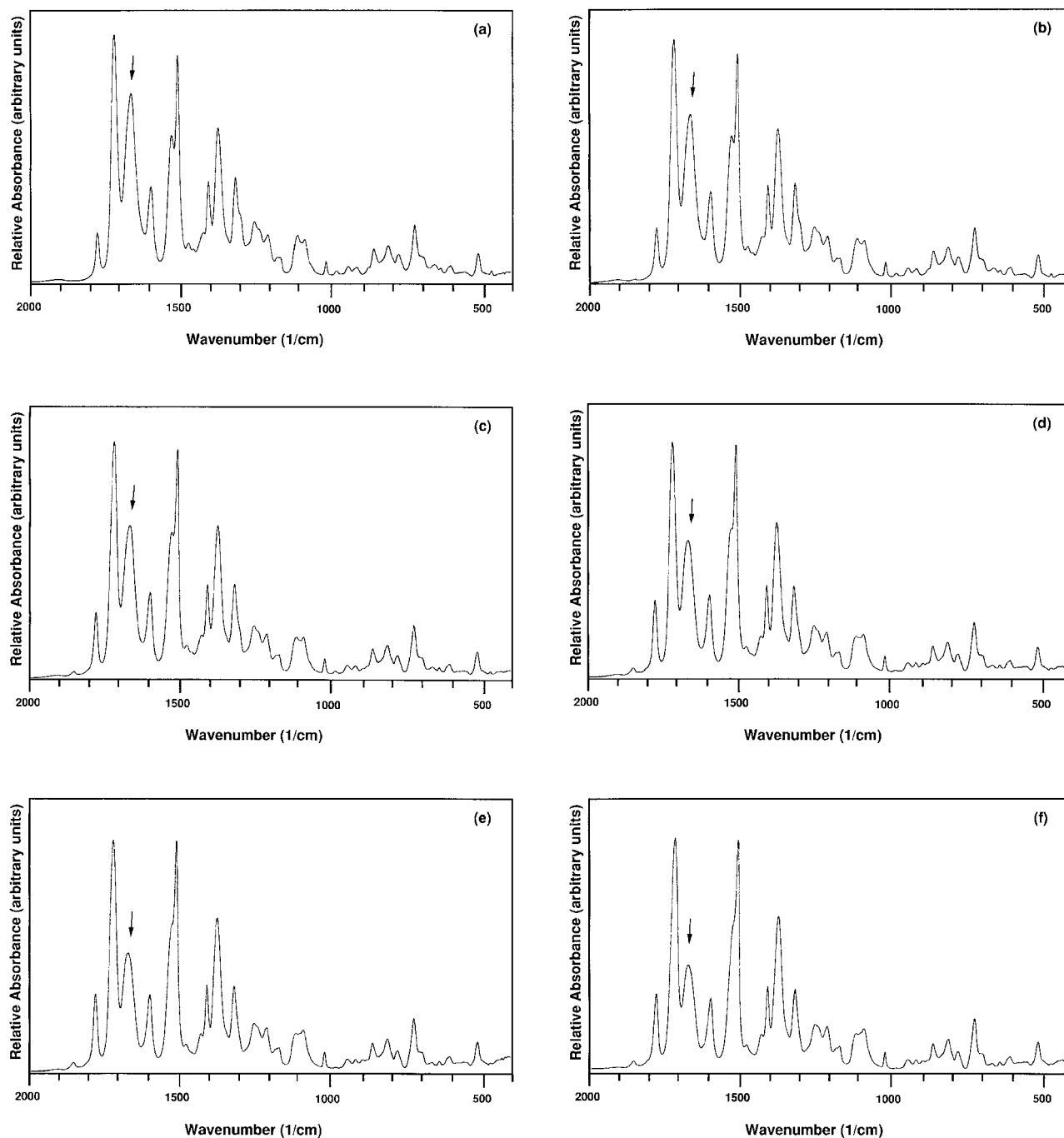


Figure 6 Relative absorbance vs. wave number for spin coated Probimide 32 films: (a) baked 10 min at 100°C, (b) then 10 min at 120°C, (c) then 10 min at 140°C, (d) then 10 min at 160°C, (e) then 10 min at 180°C, (f) then 10 min at 200°C.

In a polyimide that is not preconverted, the modulus and glass transition temperature increase as the polymer is cured. This is not surprising, because the conversion of polyamic acid to polyimide increases the stiffness of the chemical backbone. This study shows, however, that even

in a fully converted system, residual solvent can also have a marked effect on the mechanical properties of the material. The study also demonstrates that the extent of interchain covalent bonding strongly impacts the mechanical behavior of the polyamide-imide.

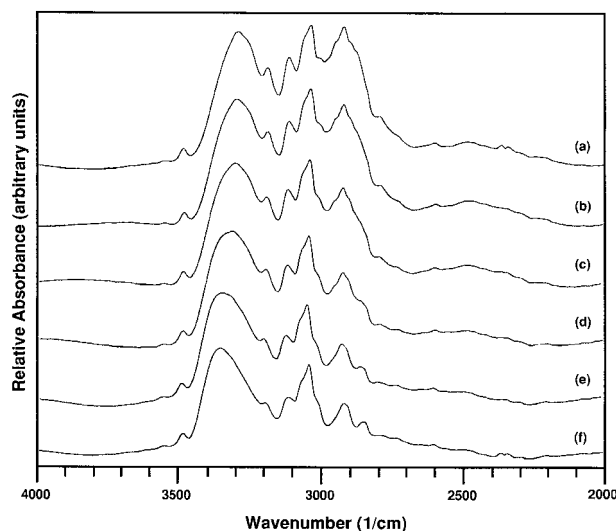


Figure 7 Relative absorbance vs. wave number for spin coated Probimide 32 films: (a) baked 10 min at 100°C, (b) then 10 min at 120°C, (c) then 10 min at 140°C, (d) then 10 min at 160°C, (e) then 10 min at 180°C, (f) then 10 min at 200°C.

Index of Refraction

The optical properties of Probimide 32 are also cure dependent. They change with cure temperature and cure environment. The indices of refraction of thin films of Probimide 32 spin coated on glass are presented in Figure 5(a,b). The average indices of refraction of the bulk films were identical to those of the thin films.

Average indices of refraction of spin coated films are plotted against the highest cure temperature in air in Figure 5(a). There was a general increase in refractive index with increasing cure temperature. These changes coincided with the observed changes in coloration described in Table I. The increase in index is associated with increased density and/or electronic polarizability due to a combination of several factors: loss of solvent, crosslinking, and increased interchain interaction.

Average indices of films cured at 300°C are shown in Figure 5(b) as a function of 300°C cure conditions. The hard baked films under nitrogen had slightly lower average refractive indices than those treated in air. This suggested that the crosslinking reaction at 300°C was faster in air than in nitrogen.

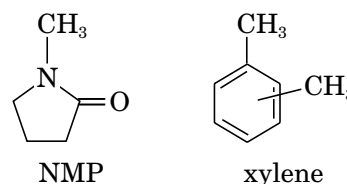
FTIR Spectroscopy

FTIR spectroscopy is a powerful method of examining the progress of a polyimide cure. This is

especially true in polyamic acid precursor materials, which undergo significant changes in their IR spectra as they are converted to polyimides. Our fully preconverted polyamide-imide, on the other hand, gave us an interesting opportunity to observe the effects of solvent removal and oxidative crosslinking in the absence of the amic acid to imide conversion. We demonstrate here how the FTIR spectrum of Probimide 32 evolved during curing. The study below suggests a technique for monitoring the cure in fully converted polyimide and related systems.

Solvent Spectra

NMP and xylene were the two solvents used in the Probimide 32 system. Their chemical structures are shown below.



FTIR spectra of these compounds can be found in most IR spectra atlases.¹⁸ The main IR absorption regions and our peak assignments are shown in Table II.

The three chemicals in the Probimide 32 system, the polyamide-imide polymer, NMP, and xylene, have a number of chemical units in common. For example, the polyamide-imide and NMP contain an amide unit, the polymer a secondary amide, and the NMP a tertiary amide. The carbonyl bond of the amide group in both molecules contributes an extremely strong IR absorption band at about 1680 cm^{-1} . Also, the xylene and the polyamide-imide contain aromatic bonds that have a number of IR absorption bands, which are listed in Table II. One key spectral peak, due to carbon-carbon skeletal stretching of the aromatic ring, appeared at around 1500 cm^{-1} . There can be multiple bands in this region at slightly different absorption frequencies, depending upon the ring substituents. In addition, all three substances have carbon-hydrogen bonds. These bonds typically have broad absorption in the locality of 3000 cm^{-1} .

Probimide 32 Spectra

FTIR spectroscopy of spin coated thin films of Probimide 32 on KBr, shown in Figures 6–9, revealed two processes that take place in the system upon

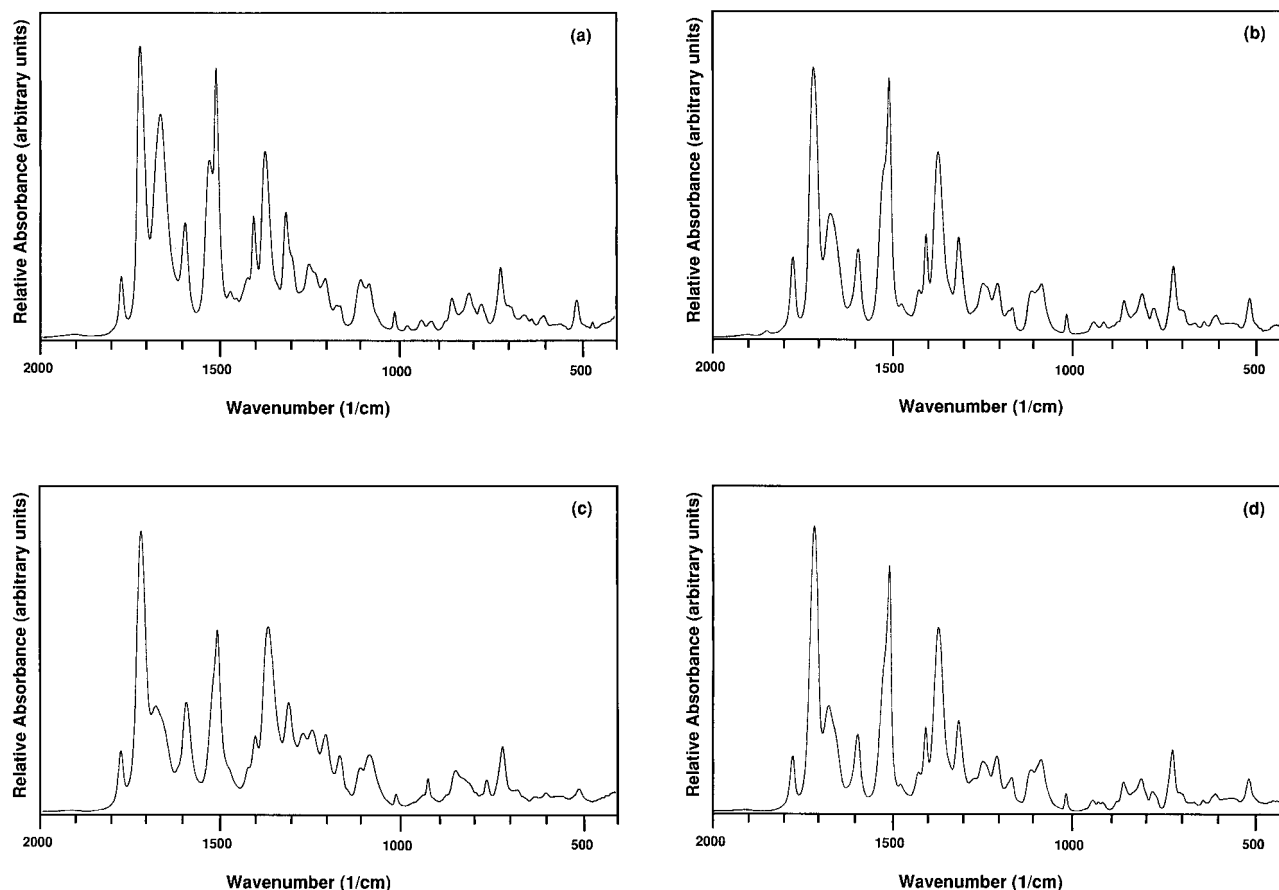


Figure 8 Relative absorbance vs. wave number for spin coated Probimide 32 films: (a) baked 15 min at 100°C, (b) then 1 h at 200°C, then 1 h at 300°C in either (c) air or (d) nitrogen.

curing. The first process is the systematic removal of solvent. The second is crosslinking and degradation at 300°C in air. Assignments of the main absorbance bands in the polyamide-imide polymer are shown in Table III.

The presence and removal of residual solvent was apparent in the “finger print” region of the FTIR scans. Figure 6(a–f) shows the 400–2000 cm^{-1} region of Probimide 32 samples treated for 10 min at 20°C intervals between 100 and 200°C. As the sample was cured from 100 to 200°C [Fig. 6(a–f)], a number of peaks declined or disappeared. These changes were consistent with removal of solvent. The most important peak was associated with the amide carbonyl bond, which was present in the polyamide-imide and the NMP solvent and strongly absorbed at about 1680 cm^{-1} . This strong absorption peak gradually declined (Fig. 6) as NMP was removed from the polymer by treating it to progressively higher temperatures.

Observation of the strong reflection at 1510 cm^{-1} due to aromatic skeletal stretching also proved to be quite interesting. As the polymer was treated to higher temperatures, an overlapping side peak systematically receded. The best explanation for this occurrence is that NMP or xylene, either of which could contribute to this side peak, was systematically removed. When the solvent was eliminated, a shoulder to the peak at 1510 cm^{-1} remained, reflecting the fact that there are two differing aromatic substitution environments in the polyamide-imide.

As the polymer was cured, we also observed the gradual disappearance of a shoulder peak near 1300 cm^{-1} , the decline of a peak at around 1110 cm^{-1} , and the disappearance of a small peak at about 980 cm^{-1} . All three of these changes were consistent with the gradual removal of NMP from the system.

We also saw an increase in the band at 1770

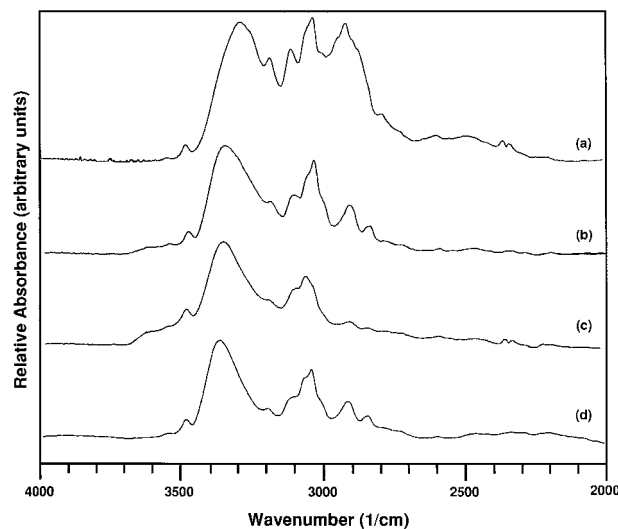


Figure 9 Relative absorbance vs. wave number for spin coated Probimide 32 films: (a) baked 15 min at 100°C, (b) then 1 h at 200°C, then 1 h at 300°C in either (c) air or (d) nitrogen.

cm^{-1} associated with in-phase stretching of the imide ring carbonyl. However, there did not seem to be an obvious explanation for this.

The 2000–4000 cm^{-1} region is shown in Figure 7. Two marked changes were observed. First, there was decline in absorption in a broad range around 3000 cm^{-1} . This indicated a decrease in hydrocarbon bonds, thus being consistent with the removal of solvent. Second, there was a gradual shifting of the N—H amide peak from about 3300 to almost 3400 cm^{-1} . It is typical for the location of this band in amide compounds to exist

at a lower wave number in the solid state than in the solution state as a result of increased hydrogen bonding.¹⁹ However, a shift to a higher wave number as the solvent was removed suggested that the polymer formed stronger hydrogen bonds with the NMP than it did with itself.

In Figure 8(a–d) 400–2000 cm^{-1} FTIR scan regions of Probimide 32 treated at 100, 200, and 300°C in air, and 300°C in nitrogen, respectively, are shown. The effects of solvent removal described above were clearly seen in these scans as the films were treated above 100°C. Also, we noted that the peak at 1770 cm^{-1} , corresponding to in-phase stretching of the imide carbonyl, increased as the polymer was heated from 100 to 200°C, but returned to its original height after treating at 300°C in either air or nitrogen. Again, there did not seem to be an obvious explanation for this.

The 2000–4000 cm^{-1} region is shown in Figure 9. Reduced absorption near 3000 cm^{-1} , as well as shifting of the amide peak from 3300 to 3400 cm^{-1} , both a result of solvent removal, were again apparent as the material was treated above the soft bake temperature.

Previously, we showed that a 300°C treatment in air initiated substantial chain crosslinking, while the same thermal treatment in nitrogen did not. There were noticeable differences in the FTIR spectra of Probimide 32 films treated at 300°C in air [Figs. 8(c), 9(c)] and at 300°C in nitrogen [Figs. 8(d), 9(d)]. These changes suggested possible mechanisms for the oxidative crosslinking reaction. The most apparent difference was a reduction in the air-treated sample in C=C phenyl

Table III Partial List of IR Absorbance Bands in Probimide 32 Polyamide-Imide

Peak Location or Approx. Region (cm^{-1})	Tentative Assignment	Peak Strength
3100–3400 (broad)	$\nu(\text{N—H})$	W
3000–3100 (broad)	$\nu(\text{C—H})$	W
1770	$\nu(\text{C=O})$ (imide)	M
1720	$\nu(\text{C=O})$ (imide)	S
1680	$\nu(\text{C=O})$ (amide)	S–M
1600	$\nu(\text{C=C})$ (phenyl)	M
1510	$\nu(\text{C=C})$ (phenyl)	S
1410	$\nu(\text{C=C})$ (phenyl)	M
1380	$\nu(\text{N—C})$ (imide)	S
1320	$\nu(\text{N—C})$ (amide)	M
720	δ phenyl substitution	M

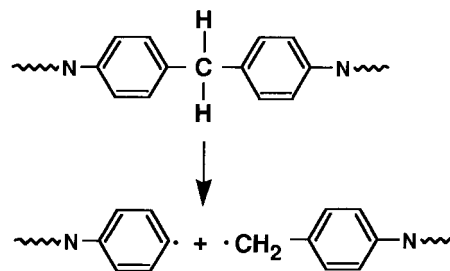
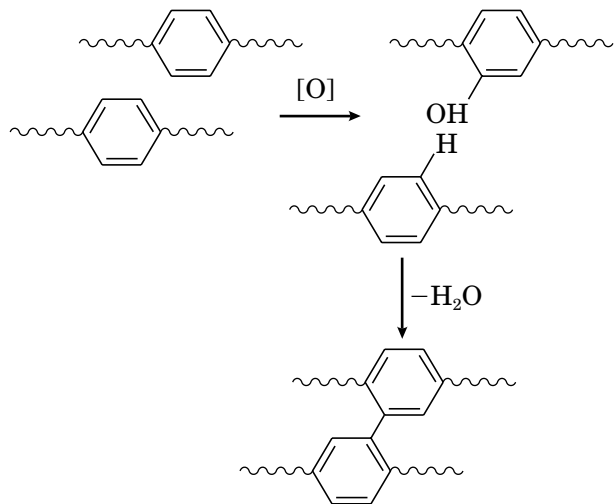
S, strong; M, medium; W, weak.

stretching near 1510 cm^{-1} . This was accompanied by a drop in C—H stretching near 3000 cm^{-1} . In fact, two distinct hydrocarbon peaks near 2900 cm^{-1} were nearly eliminated. The amide C=O peak at 1680 cm^{-1} appeared to become nearly a shoulder of the imide C=O peak at 1720 cm^{-1} . Also, there was an increase in the C=C phenyl vibration at 1600 cm^{-1} .

Kuroda and Mita²⁰ also observed a large drop in the 1510 cm^{-1} phenyl vibration, accompanied by an increase in the 1600 cm^{-1} phenyl vibration, in their studies of thermooxidative degradation of a polyimide. They interpreted the decline in the 1510 cm^{-1} peak as the cleavage of $\phi\text{—CH}_2$ bonds. Kuroda and Mita²⁰ suggest a complex series of crosslinking reactions which also involve alkyl C—H breakage and peroxide formation. The authors speculated that the increase in the vibration at 1600 cm^{-1} might be associated with the formation of diphenyl crosslinks.

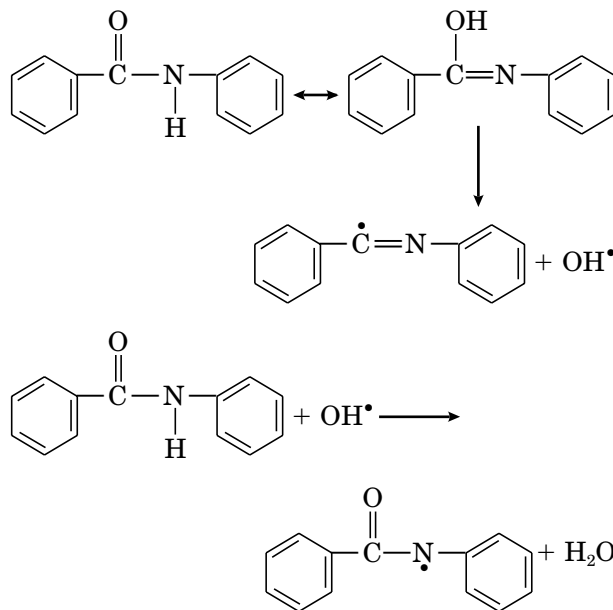
Dine-Hart et al.,^{21,22} in their investigations of the oxidative curing of PMDA-ODA polyimide, concluded that the main crosslinking reaction appeared to be the intermolecular coupling of phenyl rings in the diamine segments of the main chains. This occurred by the formation of phenolic groups that subsequently react. The phenolic bonds were formed either by direct dehydrogenation of the phenyl rings, as shown in Scheme 1, or by scissioning of aryl-ether bonds.

The reduction in the 1510 cm^{-1} phenyl vibration, increase in the 1600 cm^{-1} phenyl vibration, and reduction in C—H stretching near 3000 cm^{-1} in the Probimide 32 polyamide-imide might be associated with the formation of the crosslinks



shown in Scheme 1. The diphenyl crosslinks must occur in the diamine portion of the polyamide-imide repeat unit, because the 1510 cm^{-1} vibration is associated with 1,4- C_6H_4 groups,²³ while the 1600 cm^{-1} band can be attributed to more highly substituted phenyl groups.²³ The interchain crosslinks in Scheme 1 might occur in conjunction with the intrachain breakage of 1,4-phenyl-alkyl bonds in the diamine, as shown in Scheme 2. The radicals in Scheme 2 may subsequently undergo oxygen-facilitated crosslinking reactions.

Broadbelt et al.²⁴ reviewed the various reactions that may occur on the amide linkage of an aromatic amide model compound as the substance undergoes elevated temperature treatments. A reaction mechanism that would be consistent with an increase in molecular weight would be a [1, 3] sigmatropic shift (see Scheme 3) followed by



random radical recombination reactions. It is also likely that many of the other reactions could simultaneously take place, including various bond homolyses of the amide bond followed by random radical recombinations that do not result in a net increase in molecular weight.

If the sigmatropic shift and random crosslinking at the amide bond were to occur in the polyamide-imide during its 300°C treatment in air, we would expect to see decreases in amide C=O stretching at 1680 cm^{-1} and in N—H stretching in the 3100–3400 cm^{-1} region. These changes appear to have occurred in the FTIR spectra for the 300°C air treatment in Figures 8(c) and 9(c).

The above data suggest that cure can be monitored in the polyamide-imide system by FTIR. This could be an especially valuable tool if, for example, a new processing scheme and cure cycle were to be tested for solvent removal effectiveness. The most apparent change in the FTIR spectrum as solvent is eliminated is the decline of the amide carbonyl peak at 1680 cm^{-1} . In Figure 10, the peak height at 1680 cm^{-1} relative to that at 1370 cm^{-1} is plotted against the highest cure temperature for FTIR data shown in Figures 6 and 8. The ratio declined steadily with increasing cure temperature. Because the spin coated films were thin, we expected the films to be nearly free of solvent after the 1 h cure at 200°C. The drop in peak height after the 300°C cure could be due to either further removal of high boiling point solvent species or to nonoxidative crosslinking at the amide carbonyl. The films appeared to be solvent free when the relative absorbance ratio was about 0.6–0.7.

DSC

The calorimetric relaxation response of Probimide 32 was studied as a function of cure temperature and environment in order to gain further insight into the processes that take place during curing. DSC scans of Probimide 32 bulk films treated at 100, 200, and 300°C (air and N_2) are shown in Figure 11(a–d). Several physical phenomena can be observed in these scans: the vaporization of water, the vaporization of solvent, and transition from the glassy to the rubbery state.

Vaporization of water contained by the polymer, also observed in the TGA scans in Figures 2 and 3, is seen in all DSC scans in Figure 11. It appears as a broad endothermic response near 100°C.

Vaporization of residual solvent was observed

in the 100°C treated sample, [Fig. 10(a)] as indicated by the large endothermic response seen in the scan between 150 and 300°C. It is possible that the spikes observed were a consequence of instrument noise caused by the violent vaporization occurring in the encapsulated sample. Any glass transitions that might have occurred in the 100°C treated sample were hidden by the strong vaporization response. Solvent vaporization was not clearly indicated in any other sample.

In the 200°C treated sample [Fig. 11(b)] a glass transition was seen at about 200°C, as indicated by the step increase in heat capacity. A weak response at about 300°C was also seen. These data are in good agreement with the DMA results shown in Figure 4(b).

In the 300°C air-cured and nitrogen-cured samples, glass transitions were seen at 300°C. The transition in the air-treated sample [Fig. 11(c)] was broader and slightly shifted to a higher temperature, as compared to the transition in the nitrogen-treated film [Fig. 11(d)]. This is consistent with the DMA scans shown in Figure 4(c,d). However, in the DSC scans, a weak step in the heat capacity was seen at about 330°C, where no comparable change in mechanical modulus was observed in the DMA data.

CONCLUSIONS

Although the polyamide-imide Probimide 32 undergoes no thermal imidization reaction during curing, the structure and properties of the polymer system are dependent upon its curing conditions. The effects of progressive cure conditions

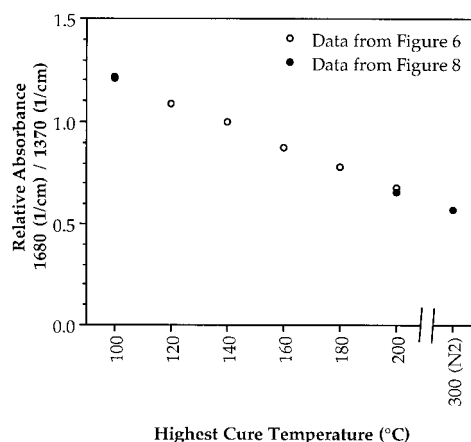


Figure 10 Relative absorbance of peak at 1680 cm^{-1} vs. peak at 1370 cm^{-1} vs. highest cure temperature.

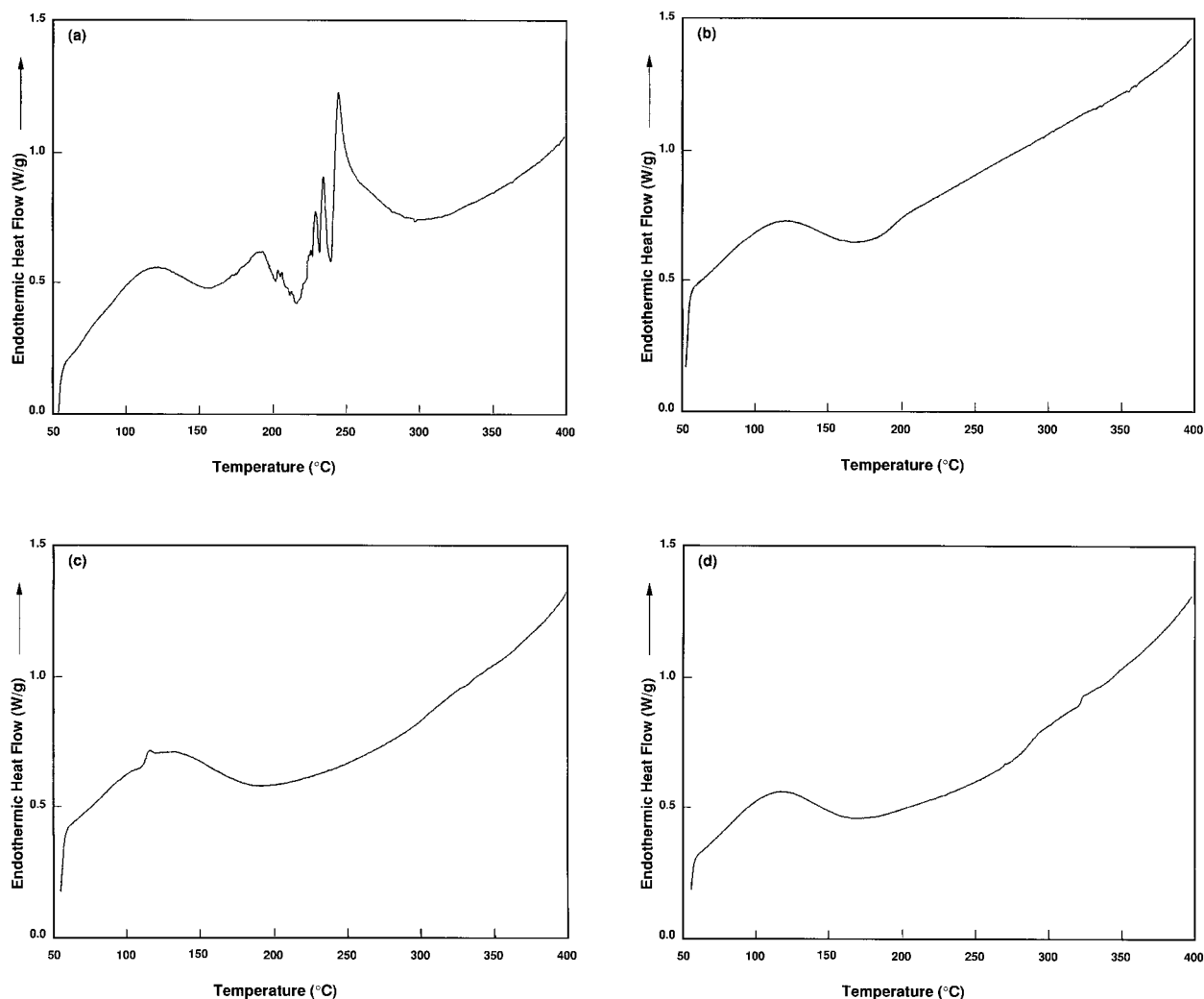


Figure 11 Endothermic heat flow vs. temperature for Probimide 32 thick films: (a) baked 6 h at 100°C, (b) then 3 h at 200°C, then 3 h at 300°C in either (c) air or (d) nitrogen.

on the properties and physiochemistry of the polymer were studied by several characterization methods. When bulk films of Probimide 32 were treated at only 100°C, a great deal of solvent remained. The residual solvent affected the properties and deteriorated the thermal stability of the material. The volume of residual solvent was reduced and the properties and thermal stability improved when the polymer was cured to 200°C. Samples treated at 300°C were solvent free and highly thermally stable. However, substantial oxidative crosslinking occurred if the polymer was cured at 300°C in air rather than in an inert environment such as nitrogen.

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