Investigation of the Crosslinking Efficiency of Some Additional Curing Polyimides

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Synopsis

The thermal properties of a PMR (polymerization of monomer reactants) polyimide resin chain terminated with various reactive monomers has been studied. Vinyl groups appear as efficient as ethynyl in providing crosslinks that are more thermally stable than those resulting from nadic ester endcapping. Terminal nitrile groups were found to be unreactive. Evidence for the curing mechanism of these resins is presented from infrared, thermogravimetric, and liquid chromatographic analyses.

INTRODUCTION

In high-performance structural composites, matrix resins that possess the desired thermomechanical properties are required. However, utility of some polymers, such as the polyimides, for these applications is seriously compromised by poor handling and processing characteristics. A solution for polyimides are PMR (polymerization by monomeric reactants) resins such as PMR-15 and LARC 160.[1,2] In this approach, chemical precursors for the polyimide such as diamines and the half-ester of dianhydrides are used in conjunction with a chain terminator (endcapper). The latter is nonfunctional in regard to amine or anhydride structure but possesses another functional species that can be used to crosslink the polymer after imide formation occurs. In the PMR system, the endcapper has a very important role in that the quantity employed determines the oligimer chain length and the reactivity of the other functional group as a crosslink establishes the ultimate thermomechanical properties of the cured system.

Typical structures for endcappers would be amines or anhydrides containing reactive unsaturated species. The half-ester of nadic anhydride is a common endcapper and is used in both PMR-15 and LARC-160. It is thought to form crosslinks via a ring-opening mechanism. Of the other type of chain terminators, those containing ethynyl groups[3,4] or nitriles[5] are particularly attractive candidates in that they offer a potential crosslink which might occur by the formation of bridging aromatic structures such as benzene or triazine. The formation of this type of structure should enhance thermostability of the cured composite.

This paper describes an investigation of various compounds that might be considered candidate endcappers for a high-temperature structural PMR polyimide resin. Endcappers studied include *p*-aminobenzonitrile (ABN), *p*-aminostyrene (AS), *m*-aminophenylacetylene (APA), and nadic ester (NE). The effectiveness of these endcappers was studied in the du Pont NR-150 polyimide precursor system composed of the diethyl ester of 4,4'-(hexafluoroisopropylidene)bis(phthalic acid) (HFDE) and *p*-phenylenediamine (PPDA).

The thermal properties of this resin with nadic encapping have been reported.[6]

EXPERIMENTAL

Materials

The basic polyimide resin used was du Pont NR-057, a 60% solids ethanol solution of HFDE/PPDA in a 5/4 molar ratio. Commercially available p-aminostyrene, m-aminophenylacetylene, or p-aminobenzonitrile was added to the NR-057 solution to give a molar stoichiometry of 5/4/2 of HFDE/PPDA/endcapper for the formulated resins. The properties of these materials were compared to the nadic ester-encapped system, du Pont PMR-15-II, supplied by U.S. Polymeric, Santa Ana, California, with a stoichiometric composition of 4/5/2 of HFDE/PPDA/NE.

Characterization

Neat resin softening temperatures were measured by the probe penetration technique using the Perkin–Elmer TMS thermomechanical analyzer. Specimens approximately 0.1 mm thick were heated at 20°C/min with a probe pressure of 7 kg/cm² under flowing helium. The point of maximum change of slope of the displacement-versus-temperature curve was taken as the softening point.

Thermogravimetric analysis of curing and decomposition was performed using the du Pont 951 TGA. Weight change of specimens 10–12 mg was recorded at 5°C/min under nitrogen atmosphere.

Infrared spectra were recorded from 4000 to 200 cm⁻¹ on a Beckman 4250 dual beam spectrophotometer. Resin films cast on KBr discs were placed in a linear temperature programmed oven set at 1.5°C/min. At intervals of 25°C, the KBr disc was removed from the oven, the oven set to hold, and a spectra of the film taken. This procedure was carried out from room temperature to 400°C.

Chromatographic separation of the PMR ingredients was made with a Spectra Physics 3500B liquid chromatograph system. Water–methanol solvent gradients containing Waters Associates PIC-A ion pair reagent were used with a Whatman Partisil 10, ODS-2 column.

RESULTS AND DISCUSSION

Thermomechanical Data

The relative crosslinking efficiency of the various PMR chain terminators was determined by studying the effect of cure schedule on neat resin softening temperature. Before curing, the resin mixtures were vacuum dried at 60°C for 24 hr to remove the ethyl alcohol solvent. Polymerization was then carried out as a function of cumulative cure time at three successive temperature levels of 121°C (250°F), 205°C (400°F), and 330°C (626°F). Specimens were withdrawn at various times during the three cure stages and the softening temperature was measured. Data for the softening behavior of the four resins are presented in Figure 1.
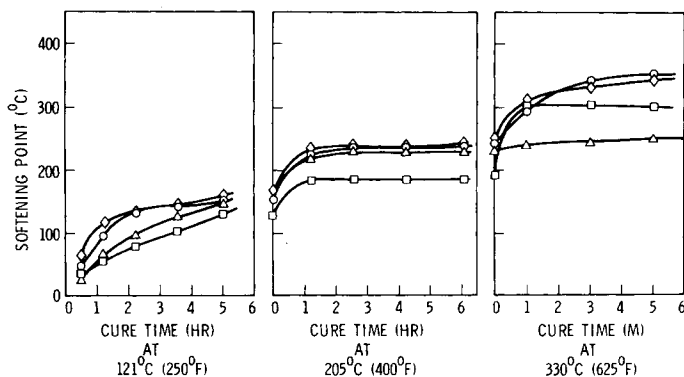
Fig. 1. Softening behavior of PMR polyimide resins: (□) PMR-15-II; (◊) NR-057/AS; (O) NR-057/APA; (△) NR-057/ABN.

The three aromatic amine-endcapped resins show a similar increase in softening temperature during cure at 121 and 205°C. The PMR-15-II resin, however, shows a somewhat lower softening point under these conditions. Assuming that no crosslinking takes place at 205°C, the lower softening points of this system may be caused by its lower formulated molecular weight resulting from ester-versus-amine endcapping. On the other hand, if complete crosslinking is achieved in the 330°C curing step this lower formulated molecular weight should produce a tighter network with a higher distortion temperature. The lower softening temperature of the PMR -15-II system subsequent to the 330°C curing step may indicate a lack of reactivity of the ester endcap or an inherently greater flexibility for this type of crosslink.

Two other important results from thermomechanical analysis were obtained during the 330°C cure stage where crosslinking would be expected to occur. First, the APA and AS show almost identical thermomechanical behavior. Recent studies[4] postulate that the cure reaction of ethynyl-terminated polymers is quite complex and that simple trimerization into an aromatic crosslink does not play an important role. The comparable crosslinking behavior observed here for vinyl and ethynyl groups might be an indication that double bonds are as effective as triple bonds in the reaction pathways proposed as alternates to aromatic formation. Substitution of vinyl for ethynyl termination could then offer a simpler and less expensive means for chain extension and crosslinking of high-temperature polymers in general.

Another significant result of the thermomechanical analysis is the apparent lack of any effective crosslinking reaction in the ABN-terminated resin. As shown in Figure 1, the softening temperature of this resin never rose much above the value it attained at the 205°C dwell, where no crosslinking was anticipated. In the ideal reaction sequence for PMR polymerization shown in Figure 2, the ABN should react first to endcap the polyamide acid oligomers. Imide structures form in the next step, followed at higher temperature by crosslinking through the chain-terminating groups.

The lack of nitrile crosslinking in the present system is apparently caused by the inability of ABN to terminate the polyamide acid oligomers. This conclusion is supported by liquid chromatographic analysis. Figure 3 shows two chromatograms of the same material, one taken before heating and one taken after
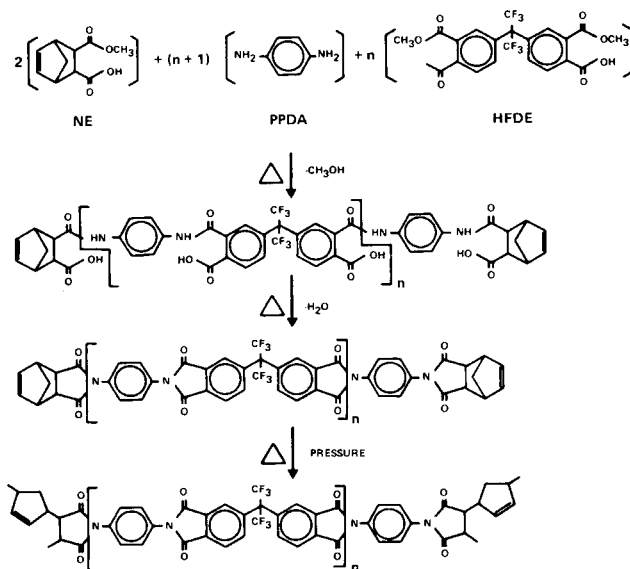
Fig. 2. Idealized reaction sequence for PMR polyimide polymerization.

5 hr of heating at 121°C. As can be seen, after heating the PPDA and HFDE reacted to form a new group of peaks identified as polyamide acid; the ABN, however, was still present as a monomer. Similar studies of the other resins showed no unreacted APA or AS monomer present after 5 hr of cure at 121°C. Even after the 330°C curing step, the ABN-terminated resin remained soluble and free endcapper was detected by liquid chromatographic analysis. Additional studies of the curing behavior of du Pont NR-057 resin without a chain terminator showed it to have a higher softening temperature than the ABN-endcapped system after 330°C cure. This suggests that the ABN is unreacted and acting as a plasticizer rather than a crosslinking agent for the resin. A possible explanation for the low reactivity of ABN might be the markedly reduced basicity of its amine group as a result of the electron-withdrawing character of the nitrile group in the para position. (An interesting experiment for future consideration would be to compare the p-ABN results with a resin formula which employed m-ABN. The effect of meta-substituted nitrile should be quite different from that of para substituted nitrile.)

In the event ABN were able to endcap the polyamide acid oligomers, the addition reactions of nitrile groups are not favored thermodynamically and generally require an initiator or catalyst to occur.[7] Crosslinking of nitrile groups has been reported to occur by thermal[5] and electroinitiated[8] mechanisms.

Infrared Spectra

Further characterization of the mechanism of PMR polymerization was made by infrared analysis. Figure 4 shows two typical PMR-15-II IR spectra, (a) taken approximately at the beginning of the temperature cure cycle at 100°C and (b) toward the middle of the cycle at 225°C. Several obvious differences between these two spectra can be seen, as indicated by the arrows in Figures 4(a) and 4(b).
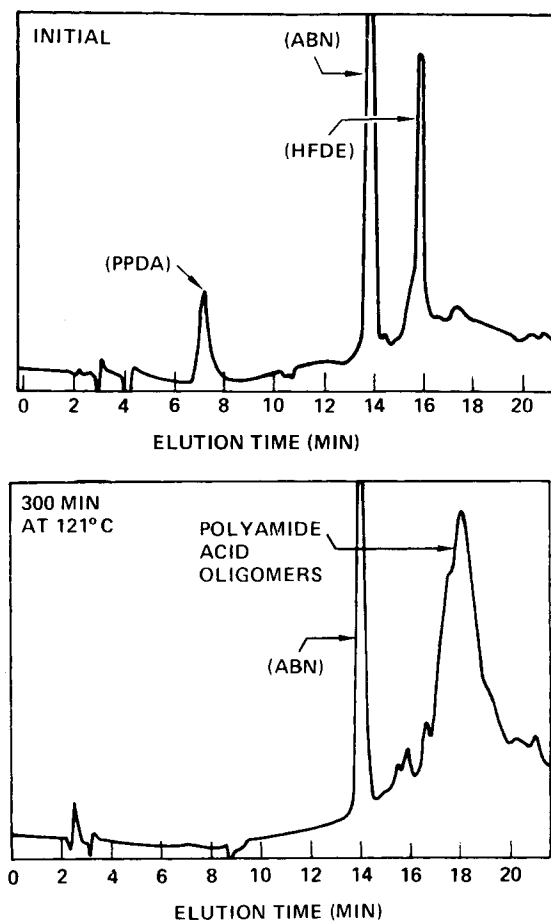
Fig. 3. Liquid chromatographic separation of NR-057/ABN polyimide resin.

Several sets of absorption bands were monitored. Between 2500 and 4000 cm^{-1}, three very broad absorptions result from CH, NH, and OH stretches, inhomogeneously broadened by hydrogen bonding interactions. These absorptions are characteristic of the monomeric species and of the amide–acid oligomer. The polyimide oligomer should not absorb in these regions. Figure 5 shows the hydrogen stretches of PMR-15-II and NR-057/AS resin as a function of temperature. (In Figs. 5, 6, and 7 the absorption intensity of a given absorption band at any temperature is normalized to its greatest intensity.) It should be noted that the major features of the two sets of curves are quite similar. The stretching absorptions are essentially absent at just beyond 200°C, with the maximum rate of change occurring at about 150–200°C.

A second set of two absorption peaks indicates the appearance of imide structure in the resin. These occur at ~720–730 cm^{-1}, and ~1360–1370 cm^{-1}, shifting slightly as the curing process progresses. The 1360–1370 cm^{-1} peak is probably an aromatic ring-nitrogen stretching vibration, while the 720–730 cm^{-1} peak might be associated with an out-of-plane motion of the imide nitrogen. These data are shown in Figure 6 for PMR-15-II and NR-057/AS. The imide
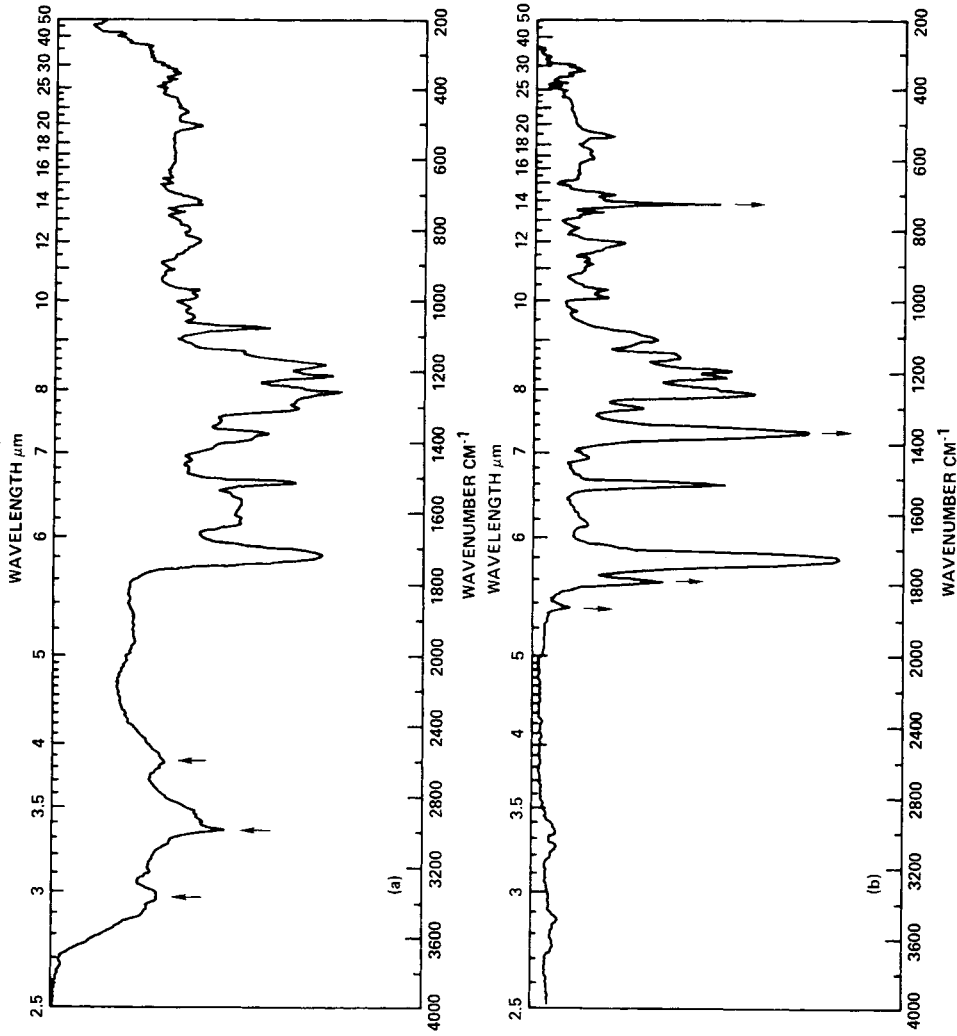
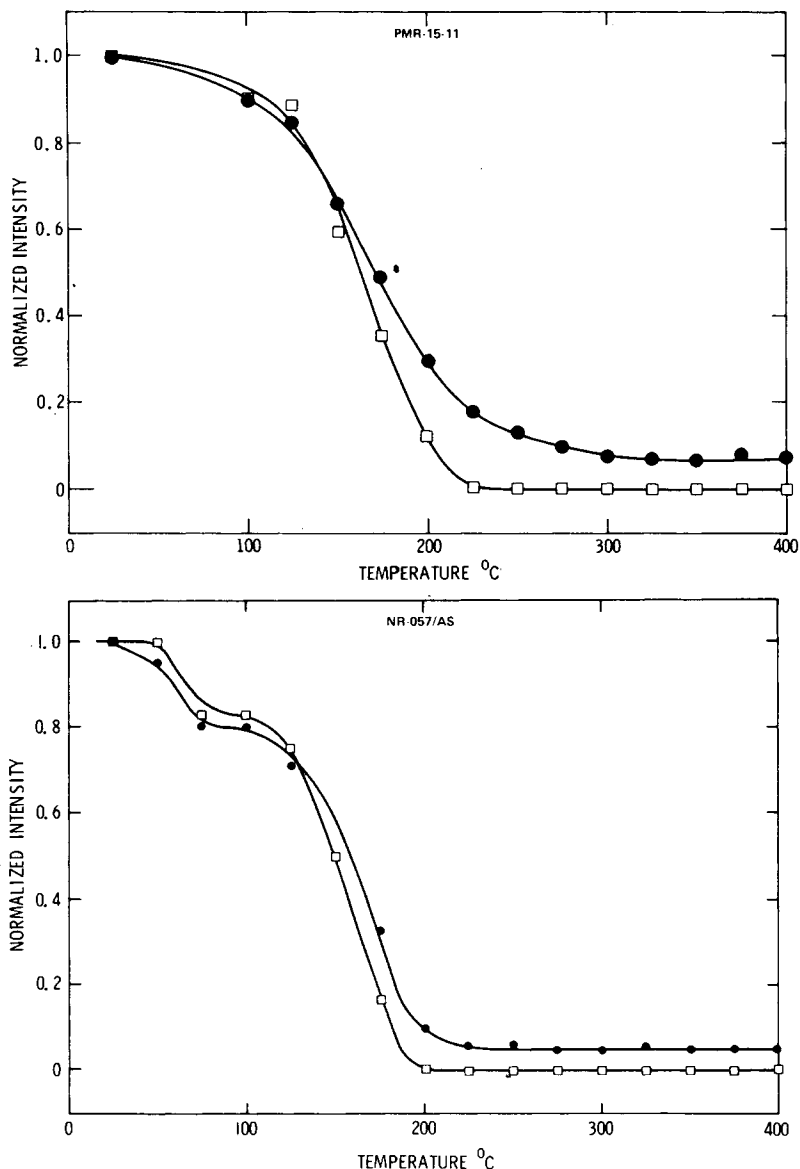Fig. 4. Infrared spectrum of PMR-15-II: (a) at 100°C; (b) at 225°C.

Fig. 5. Effect of cure temperature on hydrogen stretching absorption bands for PMR polyimides: (□) 2600 cm^{-1}; (●) 3000 cm^{-1}

absorptions reach a maximum intensity at just beyond 200°C and have a maximum rate of change at about 175–200°C.

A third set of absorptions (Fig. 7) indicate the development of other than the ideal PMR reaction sequence. The region between ~1900 and ~1700 cm^{-1}, contains absorptions readily recognized as C=O stretching vibrations. A characteristic of cyclic structures that contain two C=O groups is two split C=O stretching vibrations, those corresponding to symmetric and antisymmetric
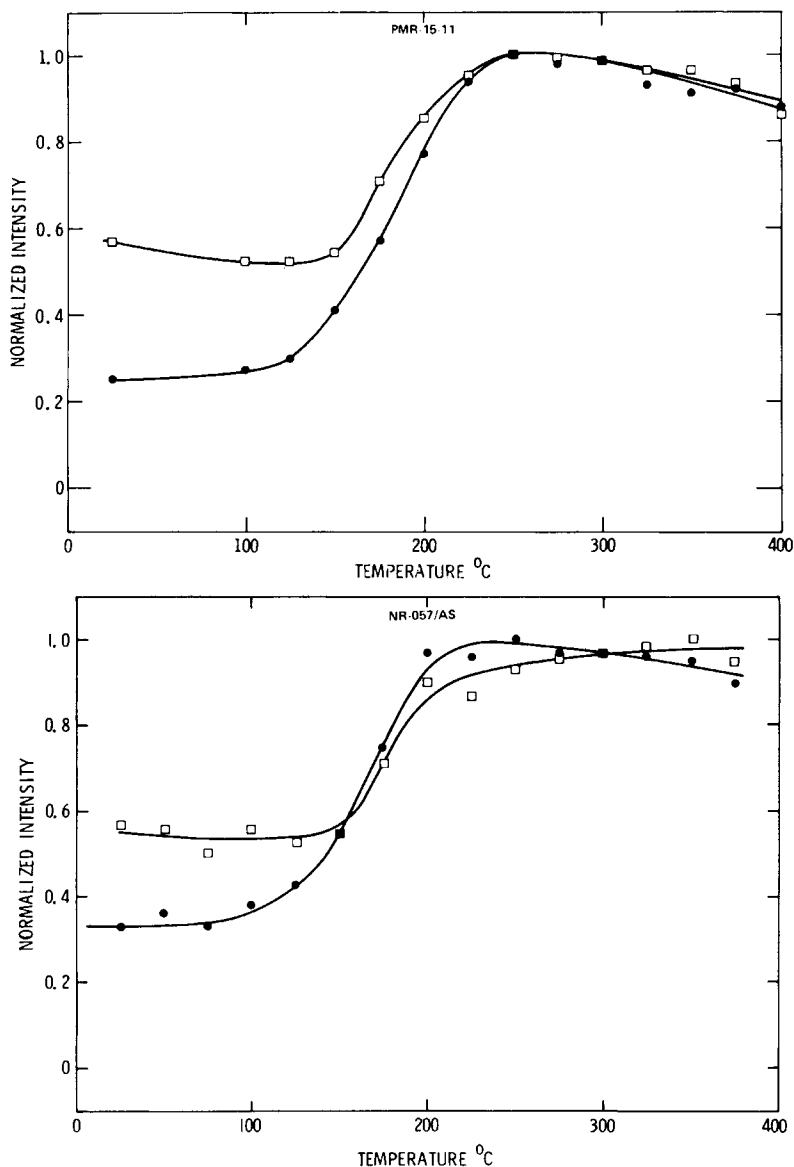
Fig. 6. Appearance of imide absorption bands with cure temperature for PMR polyimides: (●) ~730 cm^{-1}; (□) ~1380 cm^{-1}.

combinations of the two local C=O stretching modes. Five-member cyclic anhydrides have a distinctive pair of such C=O absorptions at about 1850 and 1790 cm^{-1}. A five-member cyclic imide, on the other hand, has characteristic C=O absorptions about 1790 and 1695 cm^{-1}. The IR spectra shown in Figure 4(b) show two absorptions, at about 1790 and 1860 cm^{-1}, which first appeared at about 125 and 175°C, respectively. Figures 7(a) and 7(b) show the behavior of these absorption bands in the PMR-15-II and NR-057/AS resin systems, respectively. Both these absorptions reach a maximum intensity at about 200 and 225°C and
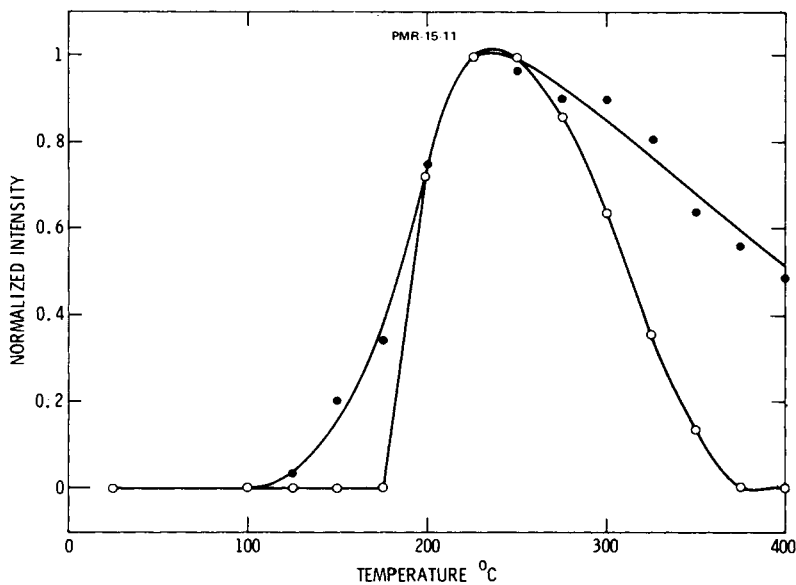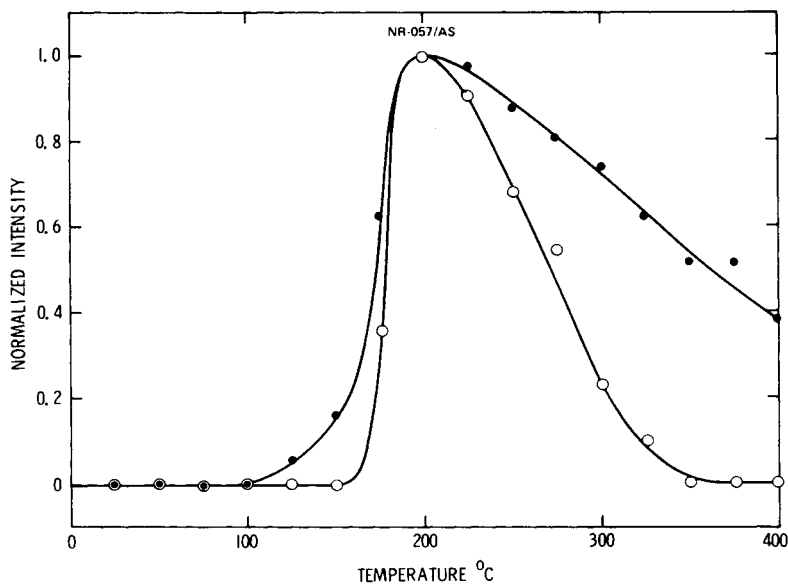
Fig. 7. Effect of cure temperature on behavior of anhydride absorption bands for PMR polyimides: (●) ~1790 cm^{-1}; (○) ~1860 cm^{-1}.

decline as the temperature rises. While the 1790 cm^{-1} band is probably due to absorption by both imide and anhydride five-member ring structures, the ~1860 cm^{-1} absorption is undoubtedly an anhydride absorption. The presence of anhydrides in the curing specimen would indicate that the desired endcapping process is not occurring ideally. The infrared spectra of these two resins, as well as the other two endcapped material, are very similar. Unfortunately, the

spectral properties of the endcap compound could not be detected clearly enough to follow its behavior separately during cure.

Thermogravimetric Data

Thermogravimetric analysis revealed another interesting feature of the curing behavior of these resins. Two regions of rapid weight loss occurred similarly for all systems. The rate of weight loss as a function of temperature is given in Figure 8 for the four PMR resin systems. Between 150–250°C, amide-acid oligomer formation accompanied by imidization resulted in the evolution of condensation by-products (H_2O and C_2H_5OH). At temperatures greater than about 500°C, pyrolysis that produced a very high rate of weight loss in all the resins occurred. A smaller but significant weight loss was evident in the PMR-15-II resin at intermediate temperatures between 250 and 400°C. This behavior was not found in the other PMR resins and might be associated with the nadic endcapper. Dissociation of the nadic endcap by a reverse Diels–Alder reaction has been discussed by others.[9,10] Unless sufficient pressure is maintained during processing to suppress this reaction, the evolution of volatile by-products by resins using the nadic endcapper can produce voids or defects in the cured laminate.

Polymerization Mechanism

Based on information derived from the preceding experiments, some conclusions can be drawn concerning the mechanism of PMR polymerization. Infrared analysis of hydrogen stretching bands (Fig. 5) indicates that the first step
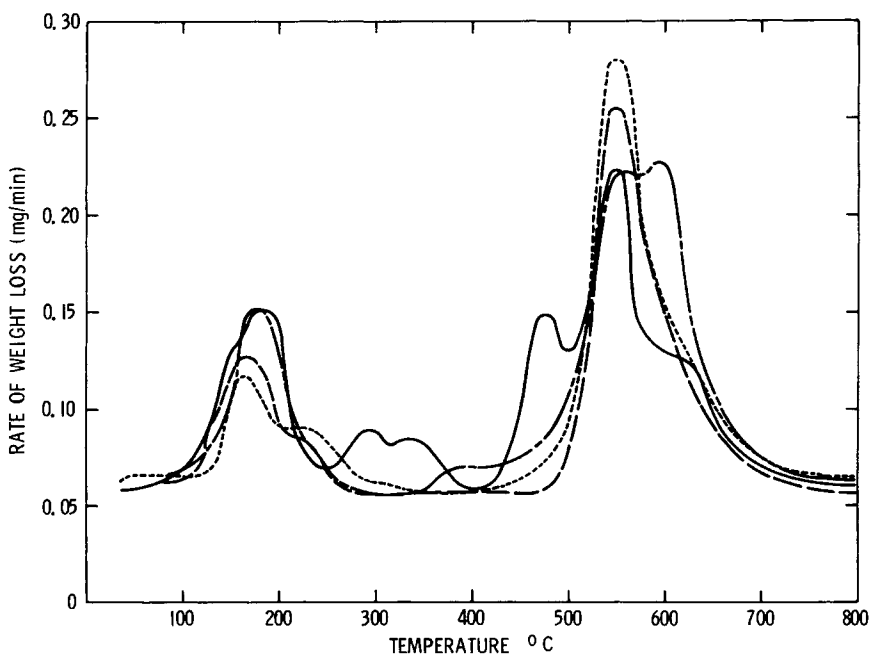

Fig. 8. Thermogravimetric analysis of PMR polyimide curing: (——) PMR-15-II; (·····) NR-057/AS; (-··-) NR-057/ABN; (- - -) NR-057/APA.

in PMR polymerization, polyamide acid formation, is completed by 200°C. Collaborative evidence was obtained by liquid chromatographic determination of unreacted monomer concentration as a function of cure temperature in the NR-057/APA system. It was found that HFDE, PPDA, and APA were completely incorporated as polyamide acid oligomer by 200°C.

Infrared (Fig. 6) and thermogravimetric data (Fig. 8) show that imidization and polyamide acid formation occur concurrently. Imidization begins near 150°C, while chain extension of polyamide acid is still occurring, and continues to about 250°C.

The generation of anhydride structures during reaction at 200–225°C appears to result from the reversal of the reaction by which the amic acid was produced. It is probably influenced by the presence of free amine, which is capable of salt formation with the acid. Subsequent attack of the carboxylate amine on the amide attached to the adjacent carbon will then result in anhydride formation. As the cure reaction proceeds to higher temperature, less and less amine is available, so that salt formation occurs much less frequently and and anticipated reaction (cyclization to form the imide) is favored.

CONCLUSIONS

This investigation has examined the curing behavior and crosslink efficiency of some PMR polyimide resins containing various endcapper or chain terminator compounds. Several significant conclusions can be drawn from the results obtained.

The crosslinking effectiveness of vinyl endgroups is comparable to that of ethynyl endgroups in these resins. Evidently crosslinking by the formation of aromatic ring structures is not an important crosslink route for the ethynyl group. This conclusion demonstrates the suitability of the generally less expensive vinyl compounds as effective endcappers and crosslinking agents.

A competitive pathway to imide formation was revealed by the presence of cyclic anhydride structures at intermediate temperatures (~200°C) in the curing resin. The formation of such structures might be aided by the acid amino salts which undoubtedly form early in the cure.

The p-aminobenzonitrile compound proved to be quite unreactive and therefore unsuitable as an endcapper. Its inactivity is probably due to the electron-withdrawing character of the nitrile group.

Finally, more evidence was found that suggests that the nadic acid ester might decompose near the temperature at which crosslinking occurs. An unusually high rate of weight loss was observed at the crosslinking temperature, which suggests some volatile evolution.

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