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KINETICS OF IMIDIZATION AND CROSSLINKING IN PMR-POLYIMIDE RESIN

by Richard W. Lauver
Lewis Research Center
Cleveland, Ohio 44135

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by Richard W. Lauver

Lewis Research Center
Cleveland, Ohio 44135

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by Richard W. Lauver

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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SYNOPSIS

Infrared spectroscopy and differential scanning calorimetry were employed to study the imidization and crosslinking kinetics of norbornenyl-capped, addition-type polyimide resins (designated PMR for polymerization of monomer reactants). The spectral and thermal analyses were performed on resin specimens which had been isothermally aged at temperatures appropriate for imidization (120° to 204° C) and crosslinking (275° to 325° C). Imidization occurs rapidly ($\sim 10^{-2}$ min^{-1}) at short times, while at times longer than ~0.5 hr, the rate decreases significantly ($\sim 10^{-4}$ min^{-1}). The crosslinking reaction exhibits first order kinetics during the initial portion of the reaction and its rate appears to be limited by the reversion of the norbornenyl Diels-Alder adduct. Both the first order dependence and the activation energy (~44 kcal) are consistent with this interpretation. The total heat evolved per mole of endcap during crosslinking shows an inverse dependence on the molecular weight of the imide prepolymers. This reflects the effect of endcap dilution and decreased mobility of the larger oligomers.

STAR Category 23

INTRODUCTION

The purpose of this investigation was to investigate the reaction kinetics of thermally induced imidization and crosslinking in PMR-polyimide resin. These are the most critical reactions in the application of this resin because they directly affect processing parameters (such as flow and gellation) and ultimate resin properties (such as strength and thermal stability). The polymer employed in this study was the high temperature resistant, addition-type, polyimide resin system (designated PMR for polymerization of monomer reactants) developed at Lewis Research Center (Ref. 1). The resin uses three monomer reactants (Fig. 1): monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and dimethylester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE). In practice, an alcohol solution of the monomers is used to impregnate reinforcing fibers; most of the solvent is driven off, but it is assumed that no chemical reaction occurs at this stage. In the next stage of the process, the impregnated material is heated to initiate the condensation reactions which give the amide and the imide prepolymers (Fig. 1). In the idealized sequence, these condensation reactions would be complete prior to the thermal crosslinking step; however, in many processing situations, the imidization may not be advanced to completion so that other processing characteristics such as resin flow can be maintained. During the final stage of the process, the material is heated under pressure to a temperature adequate to initiate the addition crosslink reaction of the norbornenyl endcaps. The reaction sequence of

PMR-polyimide resin has been discussed previously (Refs. 2 to 5); however, the pertinent reaction rates have not been reported. Rate data have been reviewed for thermally induced imidization in several linear, aromatic polyimide resins (Refs. 6 and 7). The kinetics of crosslinking in maleic capped polyimides has been studied (Ref. 8), however, no direct analog was found in the literature for thermally induced reaction of the norbornenyl endcaps.

EXPERIMENTAL

Reagents

The monomethylester of 5-norbornene-2, 3-dicarboxylic acid (NE), the 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA), the 4, 4'-methylenedianiline (MDA), and the 4, 4'-oxydianiline (ODA) were commercially available materials used without further purification. Anhydrous, electronic grade methanol was employed. Monomer solutions of dimethylester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (BTDE) were prepared by refluxing BTDA in methanol for approximately two hours. The solutions were formulated to give 50 weight percent BTDE at the end of the reaction.

Resin solutions were prepared by adding NE, MDA, and methanol to give nominal 50 weight percent solutions with monomers in the ratio 2(NE):(n+1)(MDA):n(BTDE). The number of moles, n, was chosen to give the desired formulated molecular weight. Dried resin samples were isolated at ambient conditions by drying resin solution on heat cleaned glass cloth. Two doubly-capped model compounds (2NE:1MDA; 2NE:1ODA) were isolated by heating the solution to 204° C to remove solvent and form the respective imide.

Instrumental Measurements

Infrared spectral measurements were made on a commercial, double-beam spectrometer. PMR resin was cast as a thin film on NaCl salt plates for spectral monitoring. The salt plates were heated in forced air ovens at appropriate temperatures (±5° C) and removed intermittently for spectral measurements. Changes in transmittance (peak minimum to adjusted baseline) were recorded at 1840, 1780, and 1370 cm^{-1} and converted to absorbance. Data for each sample were normalized to a standard state (assumed complete imidization) associated with 15 minute exposure at 316° C).

Differential scanning calorimetry (DSC) was performed on a commercial thermal analysis unit employing a high pressure DSC attachment. Pressures in excess of 6.9×10^5 N m^2 (100 psi) are required for reproducible observation of PMR-polyimide cure. The large amounts of methanol and water evolved during imidization cause excessive thermal noise due to bubbling or "cavitation" at lower pressures; and, similarly, undesirable volatilization of short chain imides and reaction intermediates can cause erratic endotherms in the crosslink region at lower pressures. Sample size ranged from approximately 5 to 10 mg. Aluminum sample pans were employed; the pans were covered, but not crimped closed. A static pressure of approximately 2.1×10^6 N m^2 (300 psi) of dry nitrogen was maintained over the sample. A heating rate of 10° C per minute was used for all thermal scans. For isothermal exposures the samples were pressurized, heated to the designated isothermal temperature at 50° C per minute, held for designated times, quenched by removing heat and pressure (nominally 5 minutes for cooling to 200° C), and then scanned at 10° C per minute from 200° to 450° C. The exotherm centered near 340° C was integrated with a planimeter. Baseline curvature was chosen to approximate a scan of a completely cured sample. Data for each isothermal temperature were normalized to (1) sample mass and (2) total peak area for a sample cured in a 10° C per minute scan.

Calculations

The quantification of the data in this study was based on two assumptions: (1) that the concentration of imide groups formed is directly proportional to the absorbance, I, observed at 1370 cm^{-1} (the linearity of this relationship has been discussed in Ref. 6); (2) that the concentration of reacted endcaps is directly proportional to the heat, ΔH, evolved. The linearity of this relationship may be questioned for the latter stages of reaction because reactivity is expected to change with the extent of the polymerization. In the imidization experiments, I_{iso} was observed and plotted as Fraction Imidized = I_{iso} I_{total}; where I_{total} = total absorbance at 1370 cm^{-1}, or imide concentration, of a completely imidized prepolymer, and I_{iso} = the imide concentration of a prepolymer imidized at a chosen isothermal condition. In the crosslinking experiment, ΔH_r was observed and plotted as Fraction of Heat Evolved = ΔH_{iso} ΔH_{total} = $(\Delta H_{total} - \Delta H_r)$ ΔH_{total}; where ΔH_{total} = total heat evolved during complete crosslinking of all endcaps and ΔH_r = heat evolved during completion of crosslinking for a sample which had previously been subjected to isothermal crosslinking. The rate constants were determined from plots of ln (I_r/I_{total}) vs. time where $I_r = I_{total} - I_{iso}$, and ln $(\Delta H_r/\Delta H_{total})$ vs. time, respectively, to test the first order dependence of the data. The first order rate constants were then plotted as a reciprocal function of absolute temperature and fitted with the simplest Arrhenius form of the rate constant:

$$k = A \exp(-E_a/RT)$$

where

k	rate constant (min^{-1} or sec^{-1})
A	pre-exponential factor (same units as k)
E_a	activation energy (cal)
R	gas constant (1.987 cal/K° mole)
T	temperature (K°)

RESULTS AND DISCUSSION

Thermochemistry of PMR-Polyimide

A differential calorimeter scan of the overall cure of PMR-polyimide (Fig. 2) shows four thermal transitions which occur during the process. This scan serves to identify the temperature ranges of interest in this study. The initial endotherm (below 100° C) results from the melt of the monomers and loss of residual solvent. It has been shown (Refs. 4 and 5) that chemical reaction leading to chain extension do not occur below 100° C, however it appears that the monomers do associate in the melt, possibly forming a salt. The second endotherm (centered near 140° C) results from loss of methanol and water as the condensation reactions occur to form imide prepolymers. The assignment of this thermal transition to imidization is verified by the appearance of imide bands in the infrared spectrum of the material after exposure at temperatures near 140° C. It should be noted that sequential amide and imide formation is not resolved. The kinetics of imidization will be considered in more detail below. The third endotherm appears to be related to the melt and flow of the prepolymers. This thermal transition has not been examined in detail, but does correspond to a region in which flow is observed in large scale processing (Ref. 9) The exotherm centered near 340° C is due to the addition crosslink reaction of the norbornenyl endcaps. The assignment of this exotherm can be more explicitly ascertained by comparing the DSC scans of two simple, doubly capped imides shown in Figure 3. These compounds show only two major transitions below 400° C: (1) characteristic melt endotherms and (2) crosslink exotherm. The exotherms occur in the same temperature range as the imide prepolymer. This crosslink reaction will also be examined in more detail.

Imidization Kinetics

The rate of formation of imide was monitored using infrared spectroscopy The 1370 cm^{-1} imide ring absorption was employed to quantify the rates discussed below because (as discussed in Ref. 6) the imide carbonyl band at 1780 cm^{-1} does not follow Beer's Law. Neither the precision of the intensity data nor the control of temperature in the laboratory ovens used were adequate for a detailed kinetic analysis; however, the results are consistent with published data as discussed below. The curves of Figure 4 are isotherms for the extent of imidization with time for PMR-polyimide (1500 formulated molecular weight). Figure 5 shows first order rate plots of the quantity I_r/I_{total} for these isotherms.

These data exhibit two distinct stages of the imidization reaction. Initially, the reaction rate is rapid; however, the rate decreases dramatically as the reaction proceeds. Rate constants for the initial reaction were not determined in this study but appear to be approximately 10^{-2} min^{-1} or one to three orders of magnitude larger than the rate constants of the slower reaction discussed below. The slower reaction rate was of principal interest in this study because the time scale of resin processing is relatively slow (times of several minutes or even a few hours may be involved).

Rate constants for the slower kinetic region are given in Table 1. These constants were determined from the slopes of the simple, first order plots of Figure 5. An Arrhenius plot of these data is given in Figure 6. The activation energy determined from the slope of this curve is, $E_a = 24 \pm 6$ kcal/mole, and the intercept gives $A \approx 1.4 \times 10^7$ sec^{-1} for the Arrhenius pre-exponential factor. In the classical sense, this small A value (compared to a theoretical value of $\sim 10^{13}$ sec^{-1}) implies a large negative entropy of activation for the reaction.

Similar two-stage imidization has been described by Kreuz, et al. (Ref. 10) for a linear, aromatic polyimide system. The first order rate constants reported by Kreuz are comparable to those discussed above. A similar activation energy ($E_a \approx 25$ kcal/mole) was found by Kreuz for both fast and slow reaction stages and it was suggested that the principal difference in the rate expressions describing the two stages is a large, negative entropy factor for the slower reaction.

The cause of the observed two-stage imidization kinetics can only be speculated. Such physical phenomena as strong association (hydrogen bonding or salt formation) could facilitate more rapid initial reaction. Also, initial melt and flow followed by gellation or crystallization could contribute to the difference in rates. Stiffening of oligomer chains as imidization progresses could also contribute to the observed decrease in entropy.

The two-stage behavior of this reaction offers a significant advantage for PMR-polyimide resin processing. It allows stepwise staging or partial imidization to be obtained by choice of temperature rather than careful control of exposure times. The extent of imide formation after one hour is plotted as a function of temperature in Figure 7. A near linear relationship exists in the temperature range 100° to 200° C because of the slow rate of the second stage of imidization. This relationship does not vary significantly for imidization times in the range of thirty minutes to several hours. The only obvious complication is that long time exposure at temperatures near 200° C can also cause appreciable reaction of the norbornenyl endcaps in PMR-polyimide (Ref. 5). Employing changes in both refractive index and density, Adrova, et al. (Ref. 6, pp. 148-149) have followed the extent of imidization in some linear, aromatic polyamide acids. These investigators observed an analagous change in the extent of reaction in the identical temperature range.

The achievement of complete imidization is often a point of concern [illegible] linear, aromatic polyimides (Refs. 7 and 11). In general, complete reaction may be inhibited by various factors such as competing reactions, interacting solvents, poor mobility of reactants, and hydrolysis of products. It appears that imidization of the PMR-polyimide resin is not seriously plagued by these problems; however, in the initial stages of reaction (particularly at higher temperatures), a peak due to acid anhydride is observed near 1840 cm^{-1} in the vibrational spectrum. This peak is diminished with time and it appears that the imidization of the PMR-polyimide oligomers goes to completion (within the sensitivity of conventional spectroscopy)

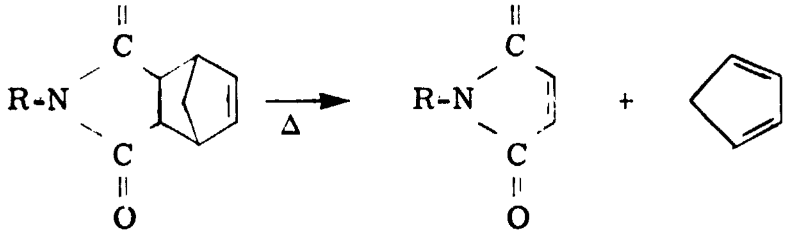
These data show that the temperature range, kinetics, and energetics of imidization for PMR-polyimide and most linear, aromatic polyamide acids are analagous. Hence the rate of imide formation in PMR-polyimide resin is not hindered by the reaction to form amide and this suggests that the rate controlling step in the imidization reaction is the final ring closure.

Kinetics of Crosslink Reaction

Thermally induced crosslinking of the norbornenyl capped PMR-polyimide resins exhibits a characteristic exotherm as shown in Figures 2 and 3 This thermal transition was used to monitor the extent of reaction as a function of temperature. Figure 8 shows a set of normalized isotherms for the bis-nadimide of MDA. The high purity, the moderate melting temperature, and the high concentration of endcaps make this an ideal model compound for analyzing the crosslink reaction. The data were fit with a simple first order kinetic model. Plots of ln (ΔH_r, ΔH_{total}) as a function of time (Fig. 9) are linear for a significant portion of each isotherm. Isothermal rate constants determined from these data are listed in Table 2. Analagous data are given in Figure 10 and Table 3 for PMR-polyimide resins having formulated molecular weights of 1000 and 1500. These data show the same trend as those for the model compound, but the logarithmic plots (not shown) do deviate from first order at smaller extents of reaction. This deviation might be expected with the decreasing mobility of the larger oligomers. Within the precision of these data, however, the data for both 1000 and 1500 formulated molecular weight materials coincide.

An Arrhenius plot of these rate constants is shown in Figure 11. The plot includes data for all three materials discussed above. The linearity of the plot is reasonable considering the overlapping data. The slope of the curve defines an activition energy, E_a=44±2 kcal/mole, and the intercept gives a pre-exponential term, $A \approx 4.24\times10^{13}$ sec^{-1}.

While the detailed nature of the thermally induced crosslink reaction has not been defined, these kinetic and energetic observations do provide insight into the rate controlling step of the reaction. It is generally presumed that thermally induced reactions of the norbornenyl moiety are initiated by the reverse Diels-Alder reaction:



If one assumes the reverse Diels-Alder reaction to be the rate limiting reaction (precedents for this assumption are given in Ref. 12), first order kinetics must be observed. The observed classical vibrational value of the pre-exponential factor ($A \approx 10^{13}$ sec^{-1}) is also expected for a simple, first order thermal fission reaction such as the reverse Diels-Alder reaction. The values for the pre-exponential factor and the observed activation energy ($E_a \approx 44$ kcal/mole) are in agreement with data tabulated by Benson (Ref. 13) for unimolecular thermal fission reactions of molecules to stable products. Diels-Alder adducts are a typical species in this classification. Wasserman (Ref. 14) discusses the reversion of several Diels-Alder adducts which have activation energies in the range 26-57 kcal/mole and pre-exponential factors in the range 10^{11} -10^{14} sec^{-1}. Thus, it appears that the rate controlling step in the overall crosslink reaction is the Diels-Alder reversion of the norbornenyl endcaps. Subsequent crosslinking most likely proceeds by a free radical mechanism, however, these rate data do not address the questions of initiation or propagation of the radical reaction directly.

It should be noted that, while the data in Figure 10 show that different formulations of PMR-polyimide react to the same relative extent as a function of time and temperature, the total heat evolved (per norbornenyl endcap) is not the same. Figure 12 shows the variation of total heat of crosslinking (per mole of endcap) as a function of formulated molecular weight. The linear decrease in total heat evolution with increasing molecular weight can be explained by the effective dilution of endcaps in the larger oligomers and the decrease in mobility of the longer chains.

SUMMARY OF RESULTS AND CONCLUSIONS

The kinetics and energetics for imidization and crosslinking of PMR-polyimide resin were determined. From these results it is concluded that:

1. Imidization of PMR-polyimide occurs in the temperature range of 100° to 200° C and exhibits two kinetic regions (initial rate nominally 10^{-2} min^{-1} and final rate nominally 10^{-4} min^{-1}). Both regions exhibit first order kinetics with an activation energy of ~25 kcal/mole.

2. The rate of imidization in PMR-polyimide resin is analagous to the rates observed for linear polyamide acids. Hence, it appears that the rate is limited by imide ring closure.

3. For times longer than ~0.5 hour, the extent of imidization is effectively a linear function of temperature. Only small changes in extent of imidization occur at longer times.

4. The rate of crosslinking in PMR-polyimide is nominally 3×10^{-2} min^{-1} at 300° C and exhibits overall first order kinetics over more than half the reaction.

5. The activation energy (~44 kcal/mole), the pre-exponential factor ($\sim 10^{13}$ sec^{-1}) and the first order rate dependence are consistent with a reaction model in which the reverse Diels-Alder reaction of the norbornenyl endcaps is the rate limiting step in the crosslink reaction.

6. The total heat evolved during crosslinking reflects the effect of endcap dilution in PMR-polyimide resins having higher formulated molecular weights.

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TABLE 1. - FIRST ORDER RATE CONSTANTS FOR IMIDIZATION OF PMR-POLYIMIDE (SLOW REACTION)

Temperature, °C	k, min^{-1}
121	8.0×10^{-5}
149	5.0×10^{-4}
163	8.0×10^{-4}
190	8.5×10^{-3}

TABLE 2. - FIRST ORDER RATE CONSTANTS FOR CROSSLINKING OF BIS-NADIMIDE MODEL COMPOUND

Temperature, °C	k, min^{-1}
275	5.50×10^{-3}
288	1.37×10^{-2}
300	3.85×10^{-2}
313	8.33×10^{-2}
325	1.67×10^{-1}

TABLE 3. - FIRST ORDER RATE CONSTANTS FOR CROSSLINKING OF PMR-POLYIMIDE RESINS

Temperature, °C	k, min^{-1}
288	1.11×10^{-2}
300	2.38×10^{-2}
313	5.88×10^{-2}

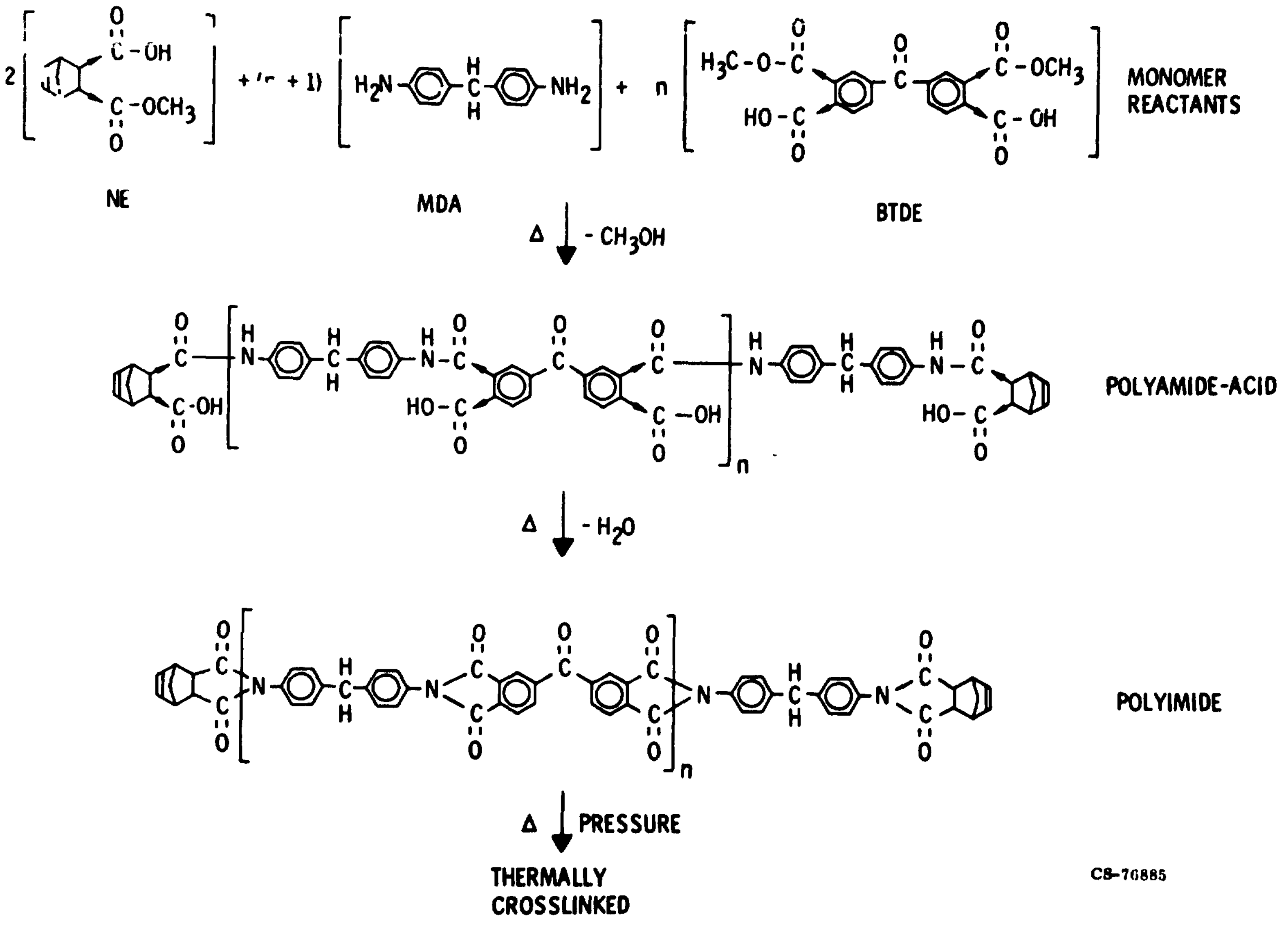

Figure 1. - Reaction sequence for PMR-polyimide resin.

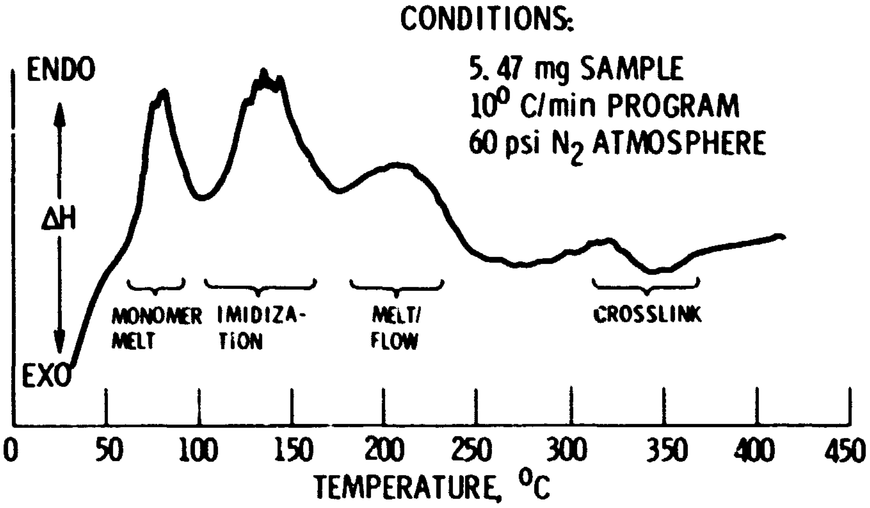

Figure 2. - Differential calorimeter scan of PMR-polyimide cure.

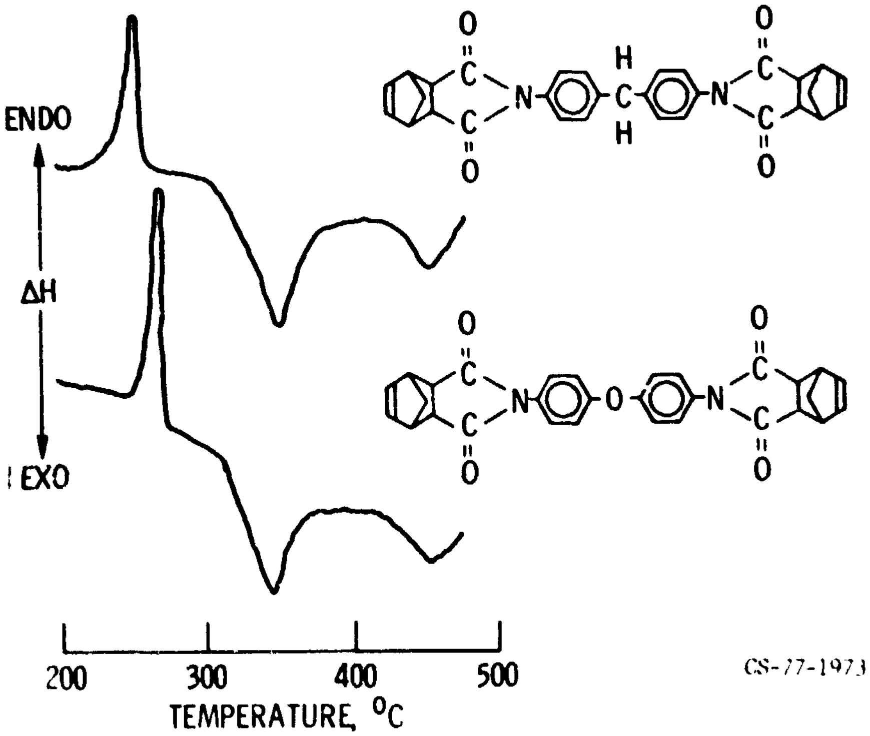

Figure 3. - Differential calorimeter scans of imide model compounds.

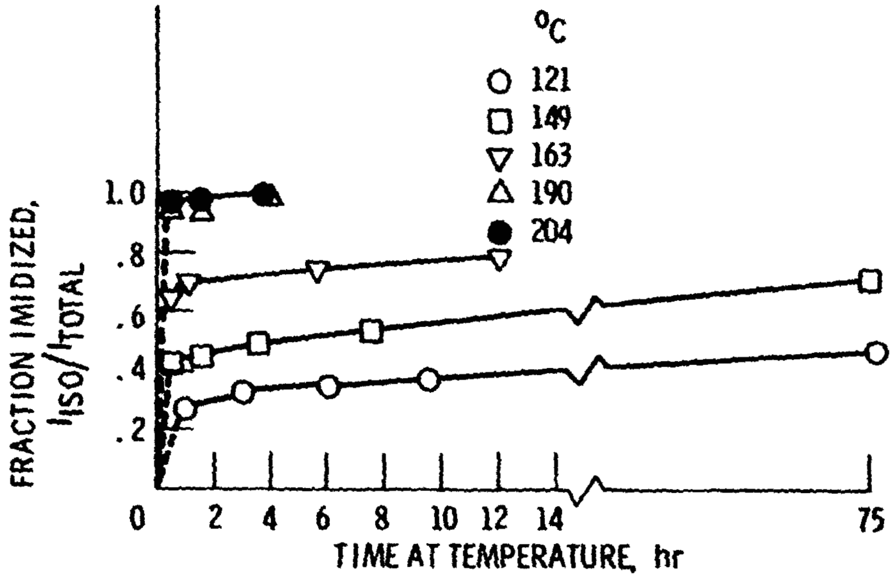

Figure 4. - Extent of imidization after isothermal cure of PMR-polyimide resin.

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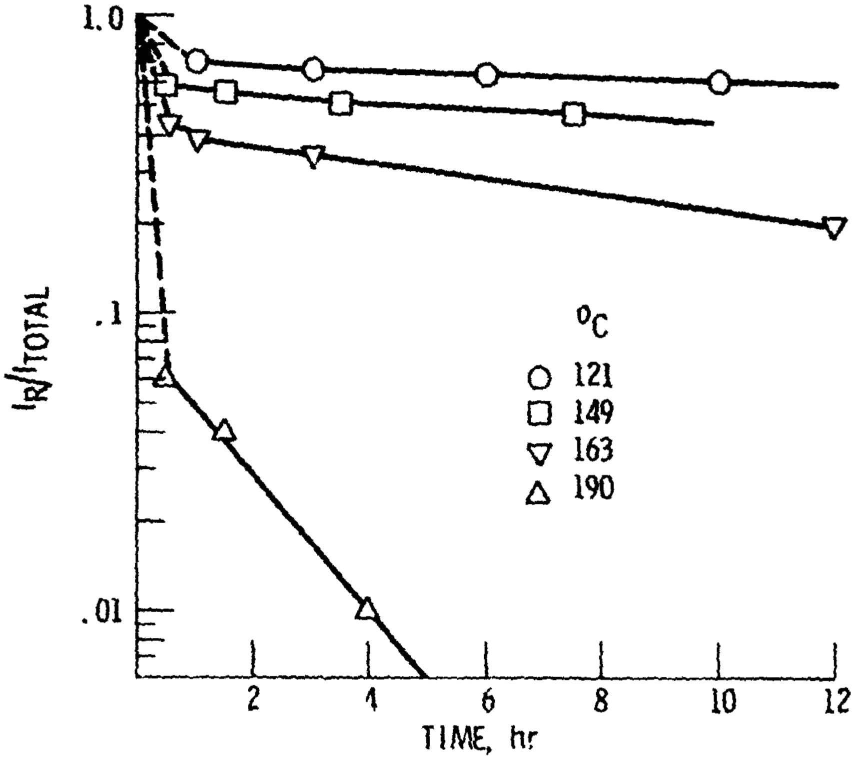

Figure 5. - First order rate plots for imidization of PMR-polyimide at selected temperatures.

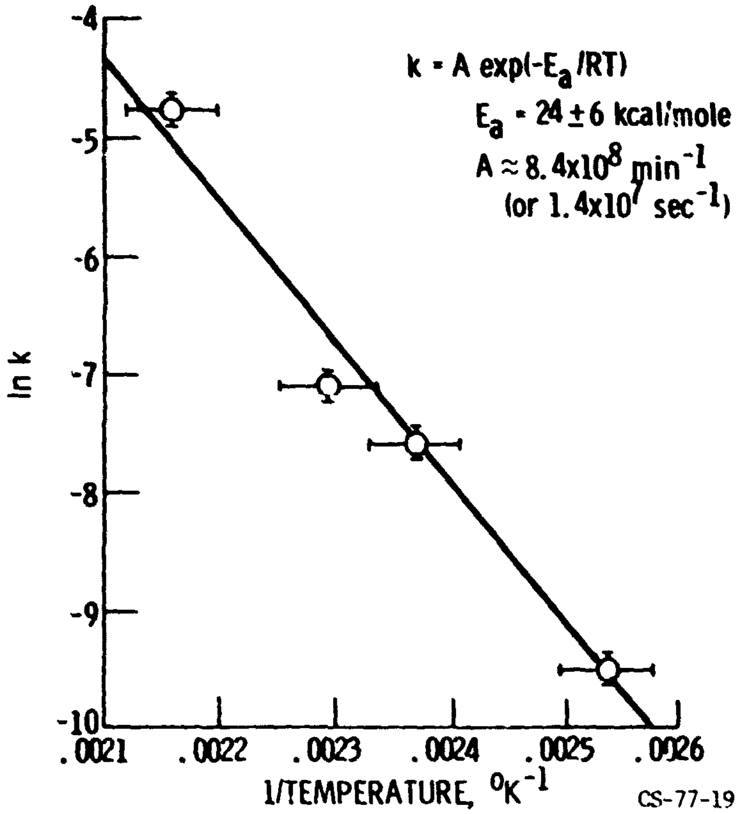

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Figure 6. - Arrhenius plot of first order rate constants for imidization of PMR-polyimide.

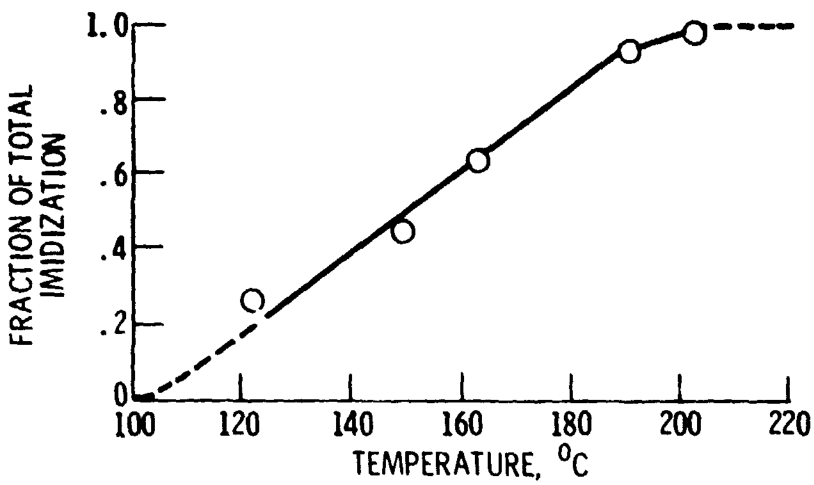

Figure 7. - Fraction of total imidization of PMR-polyimide after one hour at selected temperatures.

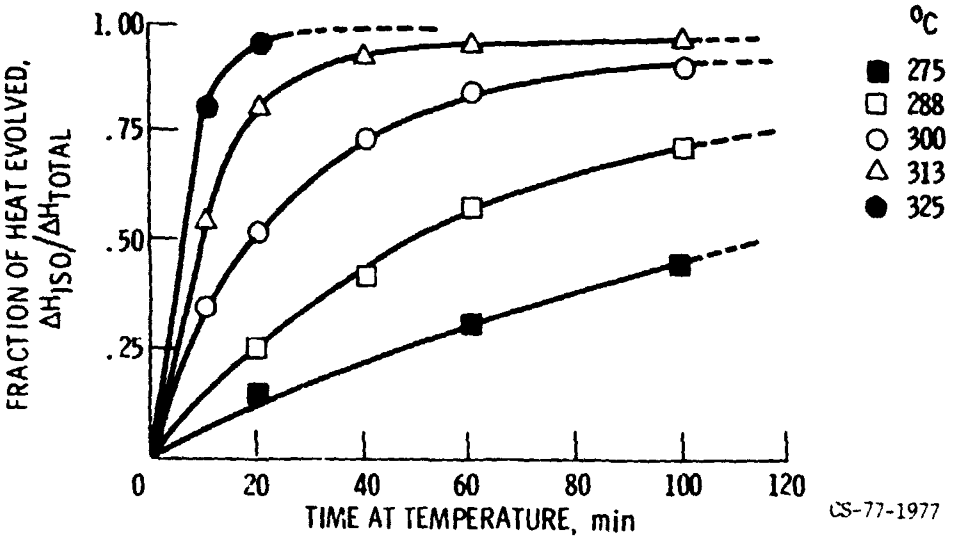

Figure 8. - Extent of crosslinking in bis-nadimide of MDA at selected temperatures.

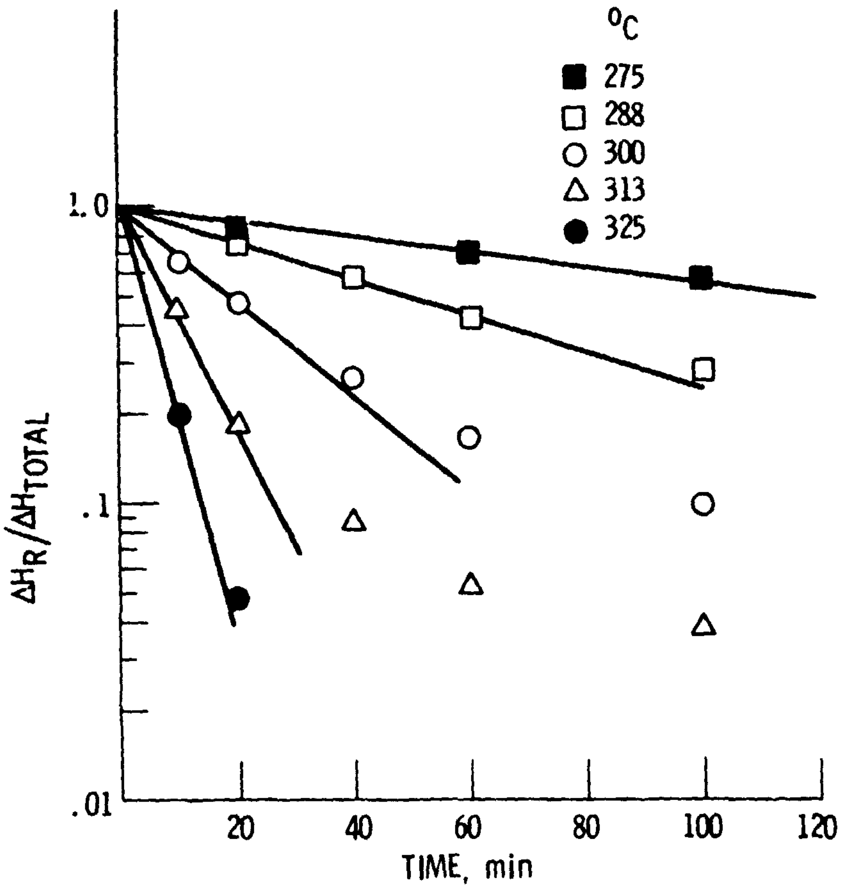

Figure 9. - First order rate plots for bis-nadimide of MDA at selected temperatures.

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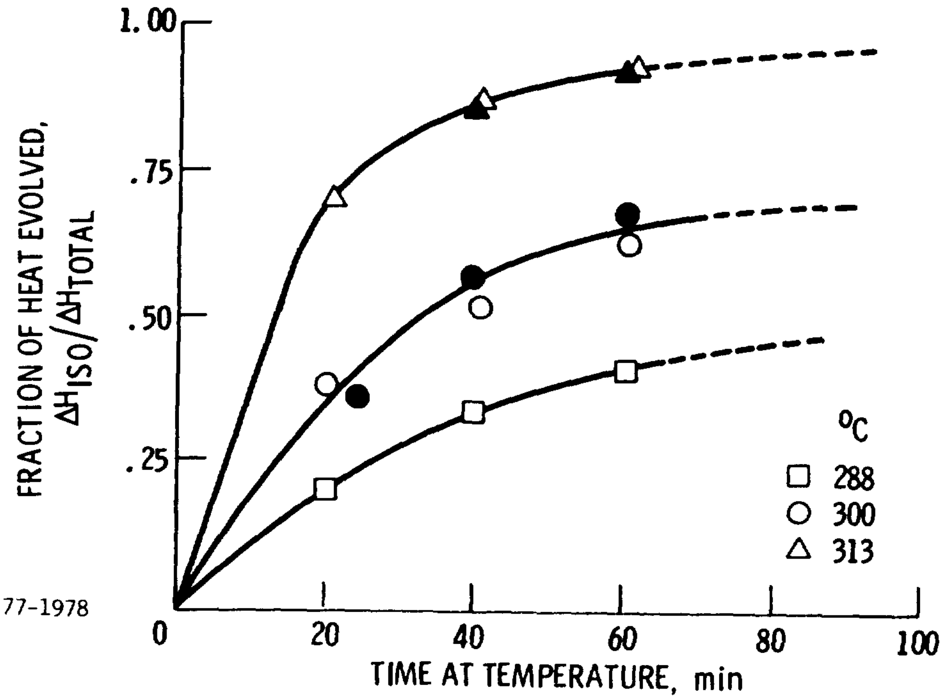

Figure 10. - Extent of crosslinking in PMR-polyimide resins at selected temperatures (solid symbols - 1000 FMW; open symbols - 1500 FMW).

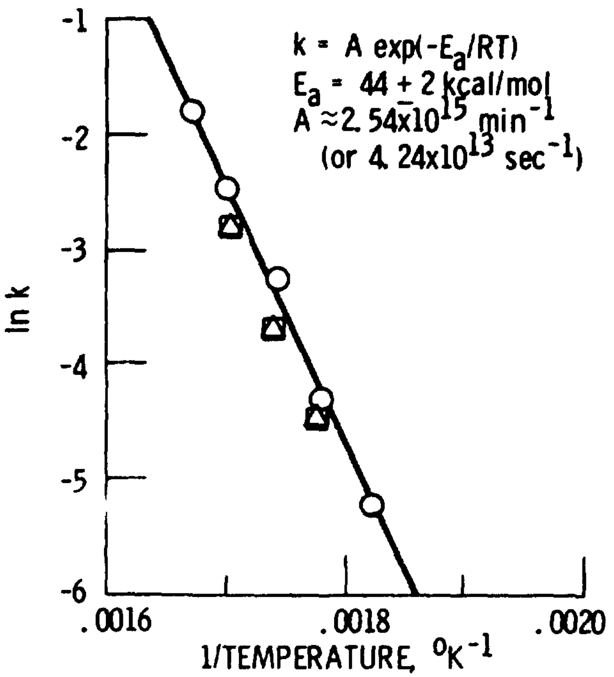

Figure 11. - Arrhenius plot of first order rate constants for PMR-polyimide resins. (○ - model imide compound (2NE + MDA); □ - PMR-polyimide, 1500 FMW; △ - PMR-polyimide, 1000 FMW).

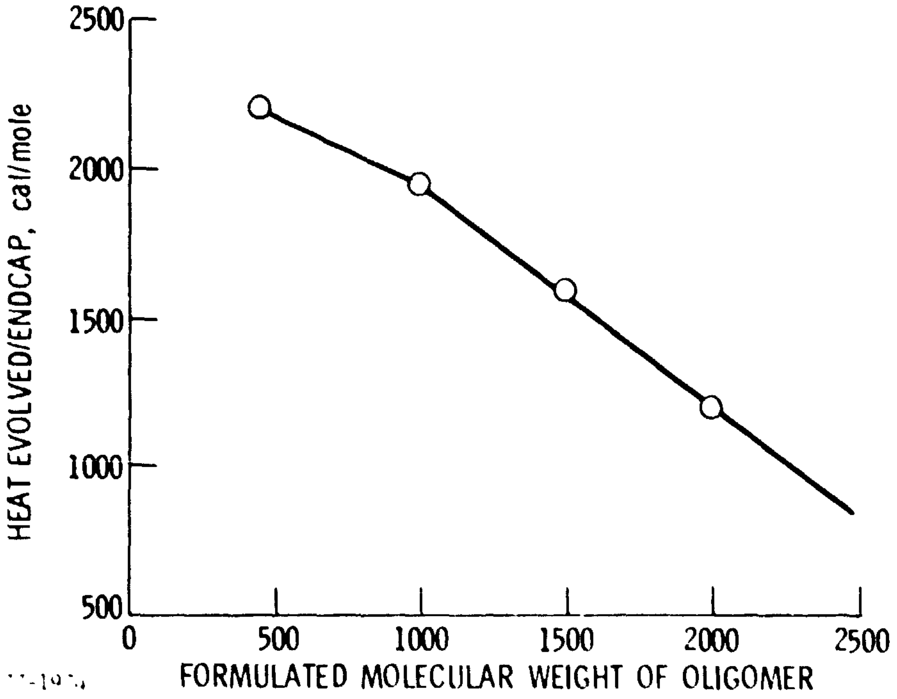

Figure 12. - Effect of formulated molecular weight on heat evolution during crosslinking of PMR-polyimide resins.