

Cure kinetics of a multisubstituted acetylenic monomer

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A polyfunctional arylacetylenic monomer, 1,2,4-tris(phenylethynyl)benzene, thermally polymerizes by a free-radical mechanism to a highly crosslinked structure of interest as a precursor matrix for carbon/carbon composites. The polymerization reaction was characterized by Fourier transform infra-red spectroscopy and differential scanning calorimetry (d.s.c.). The disappearance of the acetylenic stretching band at 2212 cm^{-1} was used successfully to monitor the cure reaction. The cure reaction follows first-order kinetics with an overall activation energy of 135 kJ mol^{-1} . Dynamic d.s.c. analysis carried out to estimate the activation energy of the cure reaction yields a value of 137 kJ mol^{-1} .

(Keywords: acetylene-terminated resin; char yield; cyclotrimerization)

INTRODUCTION

Acetylene-terminated resins undergo thermal polymerization to yield a highly crosslinked structure¹. Interest in these resins stems from the fact that they can be processed into void-free components and the cured resins possess excellent thermal stability as well as good mechanical properties. These properties render acetylenic resins useful as matrices for high temperature composite applications² and also as precursors for carbon matrices in carbon/carbon (C/C) composites.

We have synthesized several new acetylenic resins with the primary goal of developing carbon-based materials that can afford high char yield^{3–6}. As a resin matrix for C/C composites, these resins have low melt viscosity which enables easy impregnation of carbon fibres. In addition, the high char yield is particularly desirable from the processing viewpoint as it can reduce the number of densification cycles needed in C/C composite processing. The cure chemistry of some of these resins has been addressed earlier from a molecular structure and cure activation energy standpoint⁷. The aim of this work is to address the kinetics of the acetylenic cure reaction. In general, the dielectric and mechanical properties of thermoset matrices are dependent on the degree of cure. Because the degree of cure is defined by the reaction kinetics, understanding the cure kinetics of these matrices becomes essential for defining final properties, process development and quality control. In this paper, we present the results of cure studies of a polyfunctional arylacetylenic resin, 1,2,4-tris(phenylethynyl)benzene, the structure of which is shown in *Figure 1*. This compound will be referred to hereafter as 124, based on its substitution pattern on the benzene ring. Its detailed synthesis and thermal characterization results have been reported⁶. Isothermal Fourier transform infra-red (FTi.r.) spectroscopy and differential scanning calorimetry (d.s.c.)

techniques have been employed to monitor the cure reaction and obtain the various kinetic parameters.

THEORY

Cure kinetics of many thermosetting systems have been elucidated by d.s.c. using isothermal and dynamic scanning methods⁸ and by FTi.r. spectroscopy⁹. In this work, kinetic analysis is performed using a generic n th order reaction model. The general rate equation may be written as:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

where α is the fractional conversion (degree of cure), t is the reaction time and n is the order of the reaction. k is the rate constant defined by the Arrhenius relationship:

$$k = A\theta^{-E/RT} \quad (2)$$

where A is the frequency factor, E is the activation energy, R is the universal gas constant and T is the temperature. Combining the above equations and taking the natural logarithm yields:

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + n \ln(1 - \alpha) \quad (3)$$

Thus, from a plot of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$, k can be estimated from the intercept. Also, with the knowledge of k at different temperatures, the activation energy of the cure reaction can be estimated using equation (2).

The non-isothermal d.s.c. analysis for estimation of the activation energy E capitalizes on the variation in peak exotherm temperature (T_p) with the heating rate (ϕ). A simple relationship between activation energy, heating rate and peak exotherm temperature, based on the work

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of Ozawa^{10,11} and Doyle^{12,13} is presented as:

$$E = \frac{-R \Delta \log \phi}{0.4567 \Delta(1/T_p)} \quad (4)$$

From peak exotherm temperatures as a function of heating rate, the activation energy can be calculated⁸ with a precision of 2–3%.

EXPERIMENTAL

1,2,4-Tris(phenylethynyl)benzene was synthesized in our laboratory from the corresponding tribromobenzene in the presence of activated Pd catalyst⁶. FTi.r. studies were conducted with a Perkin–Elmer model 1800 spectrophotometer using a thin film of the monomer on a KBr plate. The film was deposited by placing a drop of the sample solution in methylene chloride on a salt plate, evaporating the solvent gently under a stream of argon gas and momentarily placing it in an oven maintained at 240°C to melt the sample. The scan obtained with this sample is used as the initial $t=0$ spectrum. Spectra were collected in a quantitative mode using 4 cm⁻¹ resolution and 16 scans. Isothermal cure was carried out for various times in an air-circulating oven at 240, 260, 280 and 300°C. Differential scanning calorimetric experiments were carried out in a Perkin–Elmer 7500 calorimeter under a nitrogen atmosphere. Isothermal scans employed a heating rate of 10°C min⁻¹ and 5–7 mg of the sample. Dynamic d.s.c. runs were obtained at heating rates of 5, 10, 20 and 30°C min⁻¹. Viscosity measurements were carried out on a Bohlin rheometer using a modified 40 mm parallel-plate geometry. Approximately 1 g of the monomer was melted, a gap of 0.4 mm was maintained and data were collected at a frequency of 1 Hz in a dynamic oscillatory mode.

RESULTS AND DISCUSSION

The thermal polymerization of acetylenic resins is believed to proceed via a radical polymerization reaction to yield a polyene network structure¹⁴. The initiating radicals may be derived from thermal homolysis of

impurities including peroxides or hydroperoxides formed due to the presence of oxygen¹⁵. The monomer used in this study was rigorously purified by flash chromatography followed by recrystallization⁶, therefore peroxides and hydroperoxides formed are the likely initiators for this high temperature cure reaction. Cyclotrimerization to form trisubstituted benzene has been proposed for chain growth in polysulfones that contain 1,3-enyne linkages in the backbone¹⁶, acetylene-terminated arylsulfone¹⁷ and (3-phenoxyphenyl)acetylene¹⁴. Cyclization has also been proposed as the mechanism for the thermal¹⁸ and photochemical¹⁹ polymerization of acetylenes. Sefcik *et al.*²⁰ investigated the mechanism of polymerization of an acetylene-terminated polyimide by magic-angle ¹³C n.m.r. They concluded that even after prolonged post-cure only 30% of the acetylenic end-groups undergo cyclotrimerization in the crosslinking process. However, the exact cure mechanism is still obscure because of the numerous ways in which polymerization can proceed, combined with the fact that few characterization techniques are available to study these complex thermoset structures. In the present study, FTi.r. and d.s.c. studies have been conducted to monitor the cure reaction and derive insight into the cure kinetics.

An absorbance FTi.r. spectrum of the 124 compound is shown in Figure 1. Spectra of the 124 acetylenic monomer subjected to isothermal polymerization at 280°C for various times are shown in Figure 2. Since all the possible reaction routes involve the consumption of acetylenic groups, vibrational modes which are associated with the C≡C bond can be used to monitor the degree of cure. The isolated band at 2212 cm⁻¹, associated with the C≡C triple bond stretching mode, was chosen for our quantitative study. The aromatic =C–H stretching at 3058 cm⁻¹ was used as an internal standard band. The polymerization reaction was monitored over a temperature range of 240–300°C. Figure 3 shows the intensity of the 2212 cm⁻¹ band scaled to the intensity of the internal standard and normalized with respect to the initial intensity, as a function of reaction time for the isothermal cure at 240°C. Figure 4 is a plot of the extent of the conversion as a function of time for reaction temperatures of 240, 260, 280 and 300°C. This plot reveals

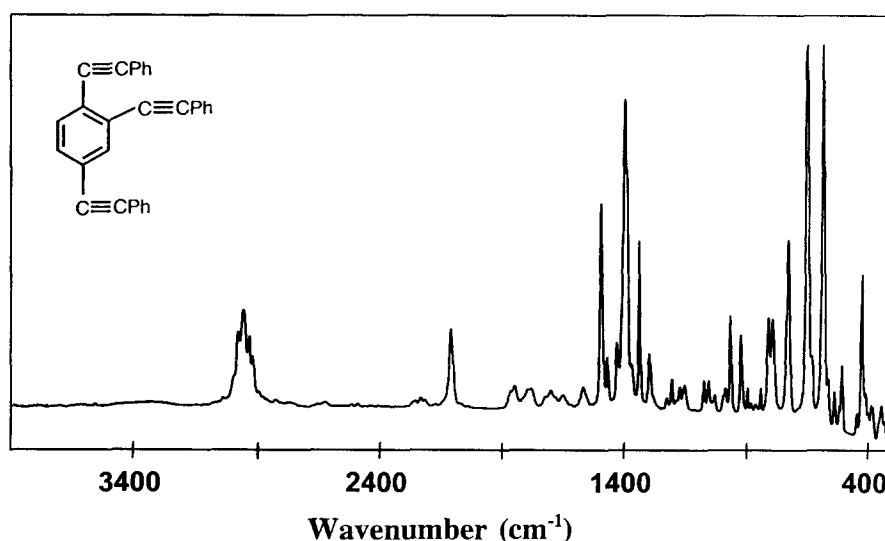


Figure 1 FTi.r. spectrum of the acetylenic resin 124

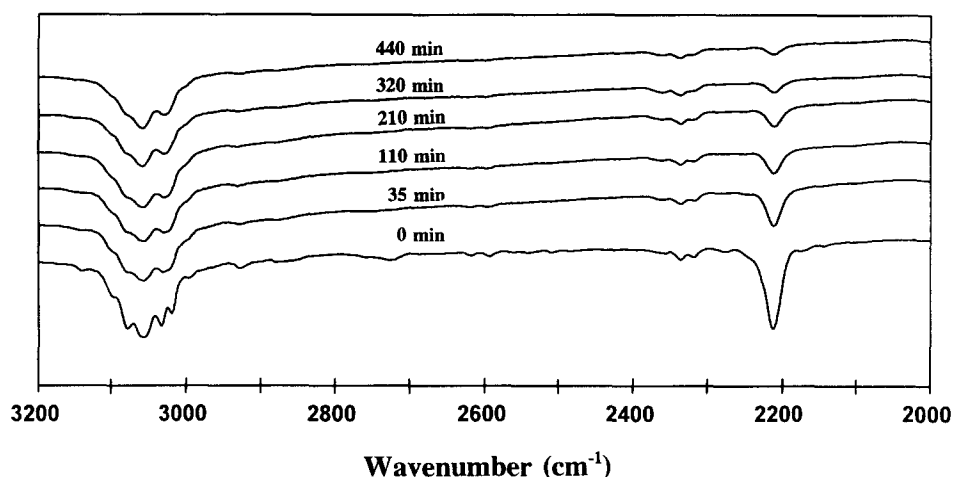


Figure 2 FTIR spectra showing the gradual disappearance of the acetylenic peak with time at 280°C

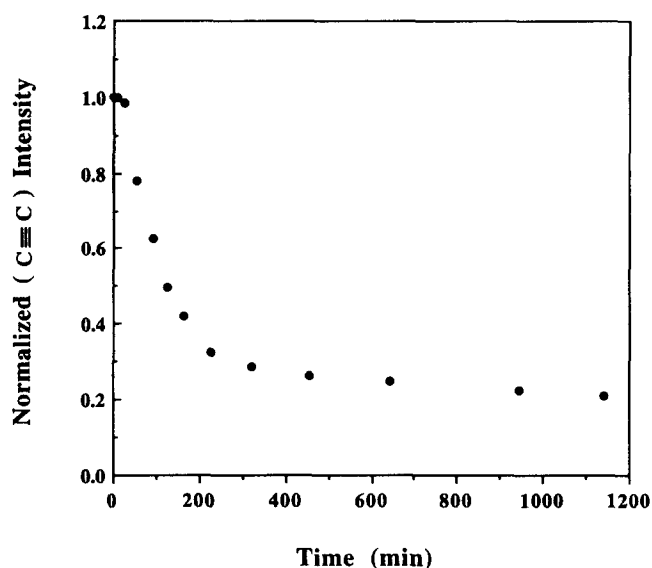


Figure 3 Typical plot of normalized acetylenic intensity 2212 cm^{-1} absorbance band as a function of time for the isothermal reaction temperature of 240°C

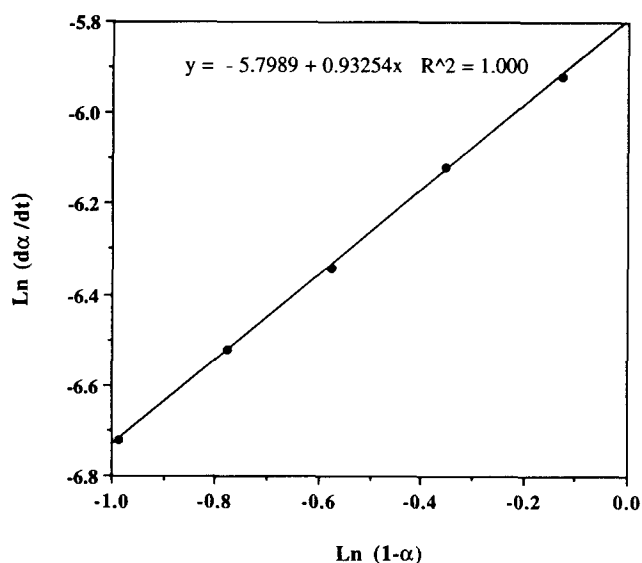


Figure 5 Acetylenic conversion data for 240°C plotted in the form of equation (3). Linear regression analysis to determine the values $\ln(k) = -5.8$ and $n = 0.93$

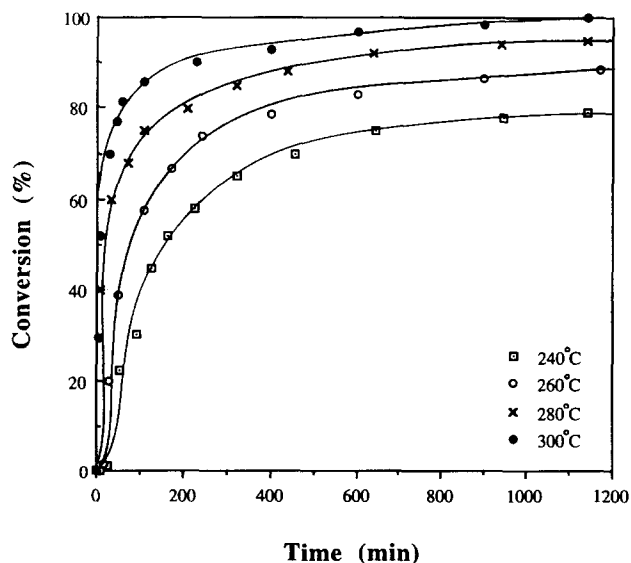


Figure 4 Conversion versus time plots for the isothermal reaction temperatures 240, 260, 280 and 300°C

that the rate of cure reaction increases with increased reaction temperature. Within the experimental time-scale of 20 h, a 100% conversion is observed only when the reaction temperature is 300°C. Lower temperatures clearly necessitate very long reaction times to drive the reaction to completion. The initial steep rise in the conversion *versus* time plot, followed by a very gradual increase, is suggestive of the kinetic behaviour of a diffusion-limited system. The viscosity of the medium increases dramatically with the initial reaction of three reactive acetylenic groups present on the monomer. Combining the effects of the decrease in both the concentration of reactive ends in the medium and the ability for diffusive movement of these ends, the rate of the reaction should begin to diminish once these effects become substantially inhibiting. The effect of the viscosity increase can be minimized and higher degree of conversion achieved as the cure temperature is raised.

Figure 5 shows a representative plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ for the reaction at 240°C, the intercept of which gives the order of the cure reaction. The average

order of the reaction obtained from these studies is approximately one. Similar studies have been conducted on 3-phenoxyphenylacetylene¹⁴ and diethynyldiphenylmethane⁹ and both are reported to show a first-order cure reaction. The fact that the mono-, di- and triacetylenic resins all show first-order kinetics suggests that the order n may not be a function of the number of acetylenic groups on the resin. However, at this stage, the exact cure mechanism to account for the observed value of $n=1$ in these thermal polymerizations is unclear. Finally, a plot of the rate constants determined for the reaction at different temperatures with linear regression to a straight-line fit is shown in Figure 6. From this analysis, the reaction has a calculated overall activation energy of 135 kJ mol^{-1} and a frequency factor of $3 \times 10^9 \text{ s}^{-1}$.

Isothermal d.s.c. studies were carried out with the aim of corroborating the FTi.r. studies. A d.s.c. scan of 124 obtained at a heating rate of $10^\circ\text{C min}^{-1}$ is shown in Figure 7. The compound melts at around 110°C into a

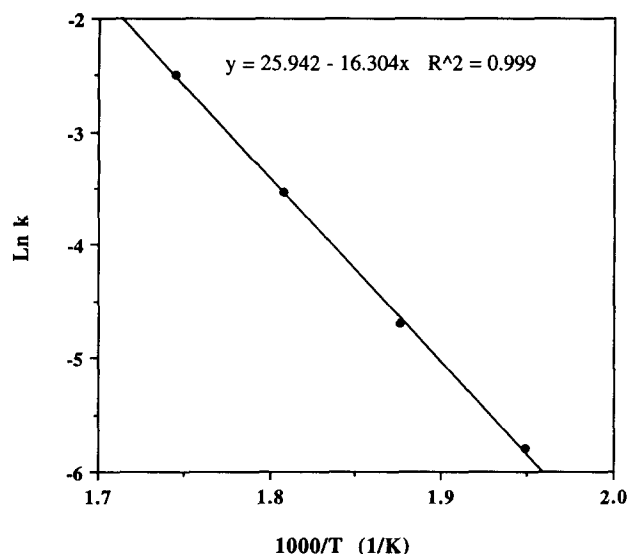


Figure 6 Arrhenius plot for the acetylenic cure reaction. Plot in the form of equation (2) yields $E = 135 \text{ kJ mol}^{-1}$

low viscosity fluid, has a processing window over a 110°C range and shows a broad cure exotherm between 240 and 350°C . Based on the area under the exotherm, the heat of polymerization is 298 kJ mol^{-1} . Two isomeric disubstituted acetylenic compounds, 1,2-bis(phenylethynyl)benzene and 1,4-bis(phenylethynyl)benzene, were synthesized to serve as model compounds using the methodology reported in the literature²¹. The heat of polymerization for these diacetylenic compounds is about 230 kJ mol^{-1} , i.e. 115 kJ mol^{-1} of acetylenic groups. In reference to cyclotrimerization of acetylenic groups as a possible pathway of polymerization in these resins, the theoretically predicted ΔH_p value based on bond energy calculations²², for the cyclization of three acetylenic groups is $189 \pm 10 \text{ kJ}$. The fact that the experimentally determined heats of polymerization for the di- and triacetylenic resins involved in this study are less than the predicted enthalpy of cyclotrimerization, suggests that trimerization of the acetylenic groups may not be the preferred reaction pathway, at least during the initial stages of polymerization. Furthermore, trimerization of these secondary acetylenic groups to form hexasubstituted benzene rings appears to be a sterically unfavourable process. The bulky phenyl moieties linked to the acetylenic groups would probably preclude achievement of the necessary orientation for the trimerization reaction. The likely product formed in the initial state of polymerization is a branched polyene, which could subsequently undergo a variety of addition reactions to yield a crosslinked polymer²⁰.

D.s.c. scans after isothermal dwells at 240°C are shown in Figure 8. The area under the exotherm progressively diminishes with time, suggestive of the increasing extent of cure reaction. However, the extent of cure could not be assessed accurately from the area under the curve. For instance, even though the d.s.c. trace showed no significant area under the cure exotherm after annealing for 3 h at 240°C , the FTi.r. scan does show the presence of an acetylenic peak at 2212 cm^{-1} . The area under the exotherm and the intensity of the acetylenic peak, both of which depend on the extent of cure, could not be easily correlated. The limiting factor for the d.s.c. technique is probably the diffusion-controlled nature of the advanced

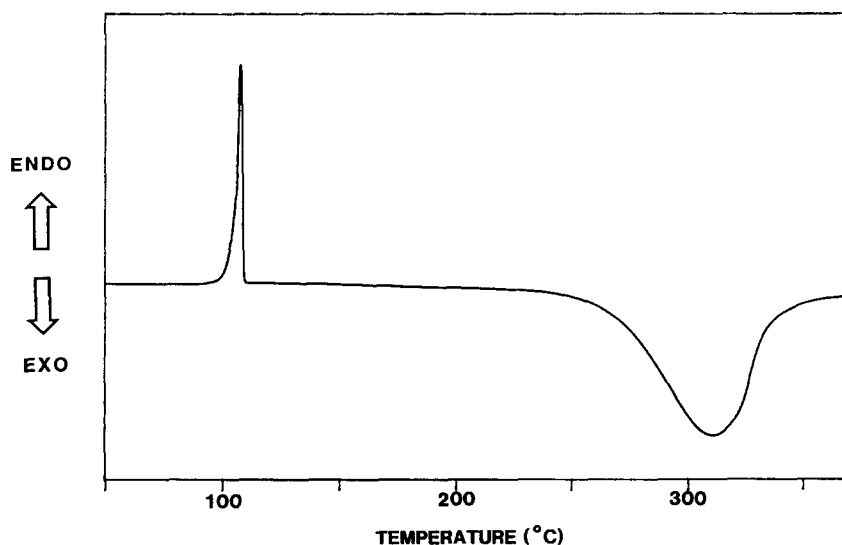


Figure 7 D.s.c. scan of the acetylenic monomer at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere

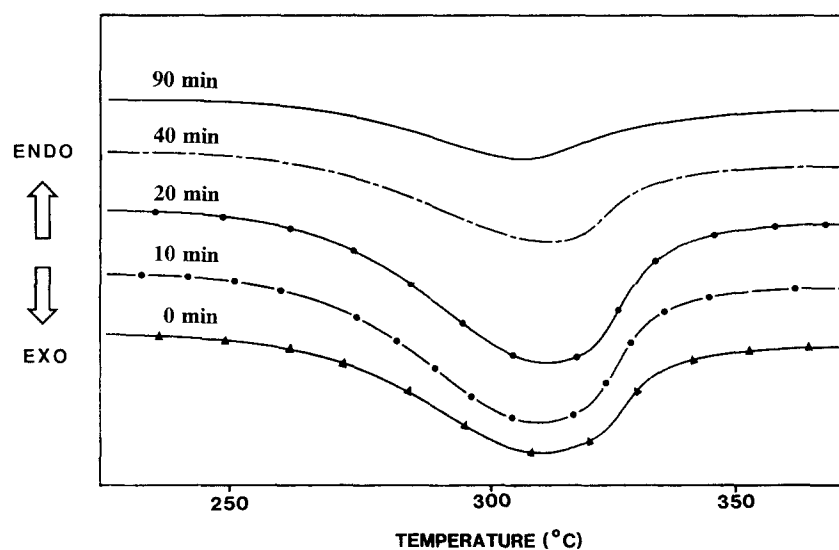


Figure 8 Isothermal d.s.c. scans at 240°C as a function of time

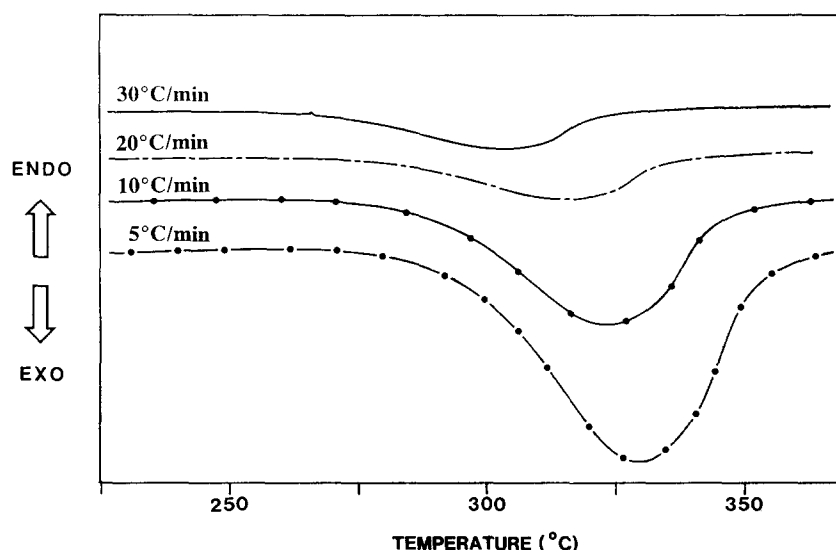


Figure 9 Dynamic d.s.c. scans showing a shift in peak position as a function of heating rate of 5, 10, 20 and 30°C min⁻¹

cure reaction which leads to very low reaction rates at higher conversions. Furthermore, based on the estimated ΔH value of 115 kJ mol⁻¹ of the acetylenic group for compounds 12 and 14, the total ΔH_p for the trifunctional 124 monomer would be three times this value, i.e. 345 kJ mol⁻¹, whereas the actual measured ΔH_p from the d.s.c. scan is only 298 kJ mol⁻¹. This discrepancy supports the fact that the measured enthalpy value of 124 from d.s.c. studies is that of an incomplete cure reaction.

Dynamic d.s.c. experiments were conducted on 124 resin to obtain the activation energy of the cure reaction. The d.s.c. scans revealing the shift in peak position as a function of heating rate are shown in Figure 9. A plot of log(heating rate) versus inverse of peak temperature ($1/T_p$) is shown in Figure 10. The activation energy calculated from the slope of this plot using equation (4) is 137 kJ mol⁻¹. This value of the activation energy is in close agreement with that obtained from isothermal FTi.r. study. Thus, FTi.r. studies lend indirect support to the accuracy of dynamic d.s.c. analysis for estimation

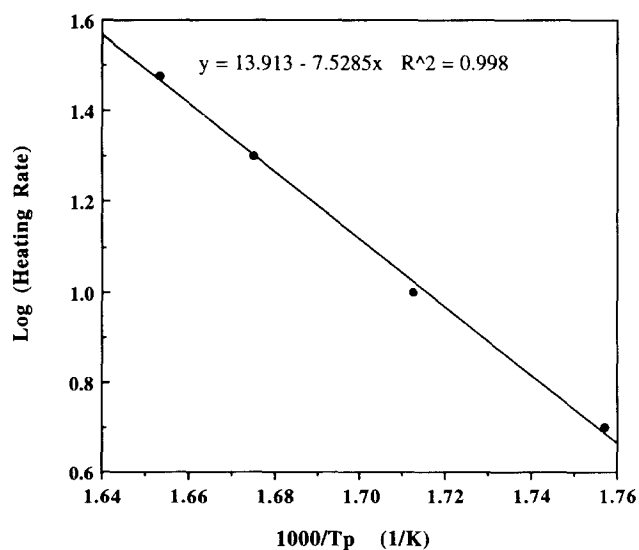


Figure 10 Plot of log(heating rate) versus $1/T_p$ for 124 resin

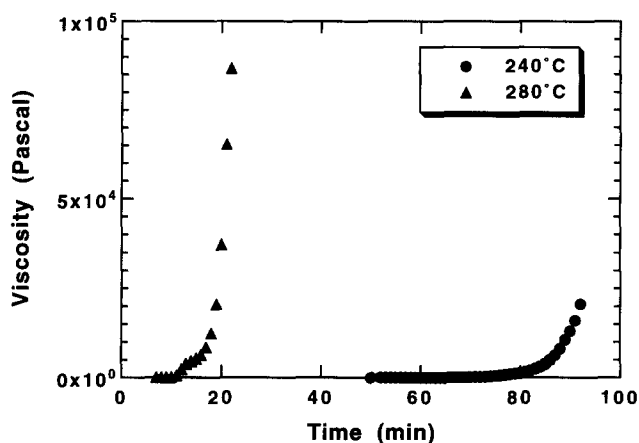


Figure 11 Plot of viscosity versus time for 124 cure reaction

of the activation energy, as well as to our n th order cure reaction model.

Finally, the viscosity of the acetylenic cure reaction as a function of time is shown in Figure 11. The rise in viscosity of the melt is dependent largely on the temperature of cure. A greater degree of mobility at higher temperatures presumably enables a proportionately greater number of acetylenic sites to react. The steep rise in viscosity after 20 min at 280°C is in tune with the sharp increase in the extent of conversion seen in Figure 4.

CONCLUSIONS

A kinetic characterization using FTi.r. and d.s.c. techniques was performed on 1,2,4-tris(phenylethynyl)benzene. The disappearance of the acetylenic peak at 2212 cm^{-1} was used successfully to monitor the cure reaction. The extent of cure is dependent on the reaction temperature. Lower temperatures need very long reaction times to drive the reaction to completion. The long times involved for full conversion even at higher temperatures (280 and 300°C) are probably because of the vitrification of the resin and thus the decreased diffusion rates of the reactants. A frequency factor of $3 \times 10^9\text{ s}^{-1}$, an order of one and an activation energy of 135 kJ mol^{-1} are observed for the cure reaction. The activation energy derived from dynamic d.s.c. analysis is in excellent agreement with that

obtained by conventional isothermal analysis. D.s.c. studies using the residual heat of reaction to follow the extent of cure were not in agreement with FTi.r. studies because of the extremely low reaction rates at high conversions.

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