Copolymerization of di- and trifunctional arylacetylenes

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The copolymerization of a difunctional arylacetylene, 4,4′-diethynyldiphenylmethane (DEDPM), with trifunctional arylacetylene monomers is characterized by differential scanning calorimetry, Fourier transform infra-red spectroscopy and microdielectrometry, and compared with the homopolymerization of DEDPM. The addition of trifunctional monomer is found to increase the rate of reaction during the early stages of polymerization. However, as the extent of crosslinking increases, the increased viscosity attributable to formation of highly branched polymer results in a slower overall reaction rate relative to the difunctional monomer. Incorporation of trifunctional groups was found to be helpful in controlling the melt rheology during the early stages of polymerization.

(Keywords: arylacetylenes; 4,4′-diethynyldiphenylmethane; differential scanning calorimetry; Fourier transform infra-red spectroscopy; microdielectrometry; cure; reaction kinetics)

INTRODUCTION

Polyfunctional arylacetylenes polymerize thermally to form rigid, highly crosslinked resins which are stable to >400°C in an oxidizing environment. As such, these monomers are of interest as high-temperature composite matrix resins[1]. The difunctional monomer, 4,4′-diethynyldiphenylmethane (DEDPM), melts at 60°C to a low-viscosity liquid, and polymerizes above 120°C by a free-radical mechanism. The reaction kinetics and mechanism of DEDPM polymerization are described in detail elsewhere[2].

It is expected that DEDPM also would copolymerize with other arylacetylene monomers, and that the incorporation of trifunctional monomer units might influence the crosslink density, and hence the physical and mechanical properties of the resulting matrix resin.

The present study investigates the copolymerization of DEDPM with two trifunctional acetylene monomers, 1,3,5-triethynyltriphenylbenzene (TETPB) and 4,4′,4″-triethynyltriphenylmethane (TETPM). Both are solids at room temperature, and melt at 74–84°C and 39–44°C respectively. Monomer structures are shown in *Figure 1*. The TETPB molecule is bulkier than TETPM, and hence would be expected to diffuse more slowly; however, its acetylene groups are farther apart, and therefore TETPB is not as subject to steric hindrance by the growing polymer to the reaction of the second and third functional groups. The central phenyl of TETPB offers a more highly conjugated structure for stabilization of a free radical than does the architecture of TETPM. Hence, both reaction kinetics and final network structure might be influenced by the choice of trifunctional monomer.

Polymerization reactions were characterized by differential scanning calorimetry (d.s.c.) using a combined isothermal and scanning technique, Fourier transform infra-red (*FT*i.r.) spectroscopy and microdielectrometry. Homopolymerization of monomer was studied, as were copolymer blends of DEDPM with either of the trifunctional monomers.

As in the case of the homopolymerization of DEDPM, the terminal acetylenic groups of TETPB and TETPM can be expected to polymerize thermally via a number of possible routes[3–16]. Cyclotrimerization to form trisubstituted benzenes has been deduced to be a minor component formed at low extent of polymerization. Glaser coupling, where $-C\equiv C-C\equiv C-$bonds are formed, is not found on polymerization of DEDPM, based on disappearance of the 2104 cm^{-1} band in the infra-red, assigned to the $C\equiv C$ bond. Linear or branched polymerization to form conjugated linkages is probably the major product[2].

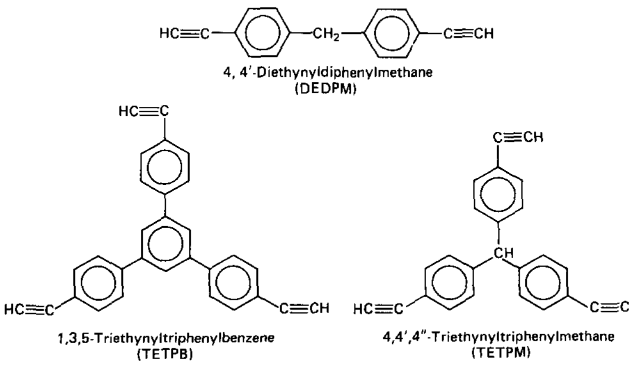

Figure 1 Arylacetylene monomers

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EXPERIMENTAL

4,4'-Diethynyldiphenylmethane (DEDPM), 1,3,5-triethynyltriphenylbenzene (TETPB) and 4,4',4''-triethynyltriphenylmethane (TETPM) were purchased from Chem Biochem Research Inc., Salt Lake City, Utah. All were >92% pure, as determined by reverse phase chromatography, and were used without further purification.

Homopolymerization of each of the monomers was characterized. Copolymers of DEDPM with 10 and 20wt% additions of either of the trifunctional monomers were studied. These monomer blends would correspond to 5.9 and 12.3 mol% TETPB and 7.2 and 14.8 mol% TETPM if the constituents were 100% pure. The compositions of the blends can also be represented as 8.6 and 17.4 mol% ethynyl groups contributed by trifunctional monomer for TETPB addition, and 10.4 and 20.7 mol% ethynyl groups from trifunctional monomer when TETPM is used. Throughout the remainder of the paper, per cent composition refers to weight per cent for simplicity.

Differential scanning calorimetry experiments were carried out using a DuPont 1090 calorimeter. Samples of nominally 2.5 mg were sealed in Teflon-coated aluminium pans that had first been annealed at 350°C. Scanning experiments were conducted at a heating rate of 10°C min^{-1} to determine the total enthalpy of reaction (ΔH_t). Samples also were scanned isothermally at 120 and 180°C for varying times and the reaction quenched using liquid nitrogen. Residual heats of reaction (ΔH_r) were found by scanning the quenched samples at a heating rate of 10°C min^{-1}. The heat evolved during the isothermal portion of the curve (ΔH_p) was determined by the difference:

$$\Delta H_p = \Delta H_t - \Delta H_r \qquad (1)$$

A horizontal baseline was then constructed so that the area under the isothermal dH/dt vs. time curve was equal to ΔH_p. The extent of reaction, α, as a function of time was found by partial area integration of the isothermal curves, using the relationship:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_t}\frac{dH}{dt} \qquad (2)$$

where α ranges from 0 to 1. Integrating,

$$\alpha = \frac{1}{\Delta H_t}\int_0^t \frac{dH}{dt}\,dt \qquad (3)$$

For *FT*i.r. studies, a thin film of monomer or blend was melted between two potassium bromide (KBr) salt plates. The monomer-coated KBr plates were fitted in a specially designed heating cell. The temperature of the sample was monitored by two chromel/alumel thermocouples cemented into grooves on the inner surface (in contact with the monomer film) of one of the KBr plates, and controlled to ±1°C. The cell was mounted in a Digilab FTS-20E Fourier transform infra-red spectrometer using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectrometer was constantly purged with dry nitrogen gas to reduce atmospheric moisture.

In an isothermal experiment, the sample was rapidly heated to 173°C and then held at that temperature for 190 min. Scanning was started immediately at the time at which the isothermal temperaure was reached, designated time $t = 0$. The sample was scanned every 5 min during the first hour, and every 20 min thereafter. These spectra were obtained at 4 cm^{-1} resolution and 40 scans, using double-precision software.

In other experiments, samples of monomer blend sandwiched between two KBr plates were placed in glass vials and heated in an oven at 120°C. After desired periods of time, the vials were taken out of the oven and immediately quenched in ice–water. Spectra of these samples were obtained at room temperature with 2 cm^{-1} resolution and 200 scans, using double-precision software.

Dielectric monitoring was accomplished using a Micromet Eumetric System II microdielectrometer. The monomer or blend was placed on the 2 × 3 mm sensor surface as a powder. A d.s.c. cell was used to control temperature. Measurements were made at 1, 10, 100, 1000 and 10 000 Hz. A complete set of data were recorded every 90 s.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Heat evolution as a function of temperature for samples of DEDPM, TETPB and TETPM scanned at a heating rate of 10°C min^{-1} are shown in *Figure 2*. The activation energy for DEDPM, as determined previously[2] from

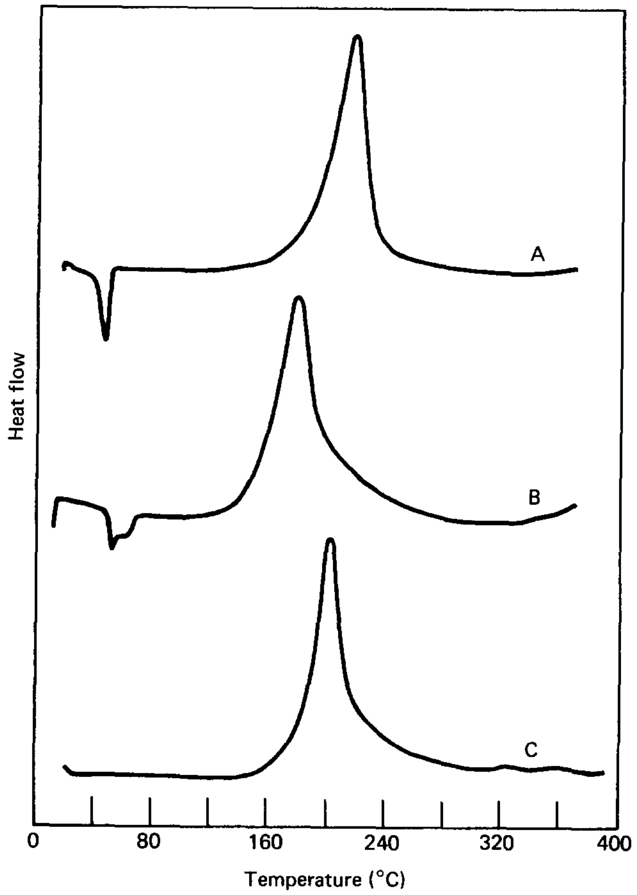

Figure 2 Heat evolution as a function of temperature for (A) DEDPM, (B) TETPB and (C) TETPM scanned at a heating rate of 10°C min^{-1}

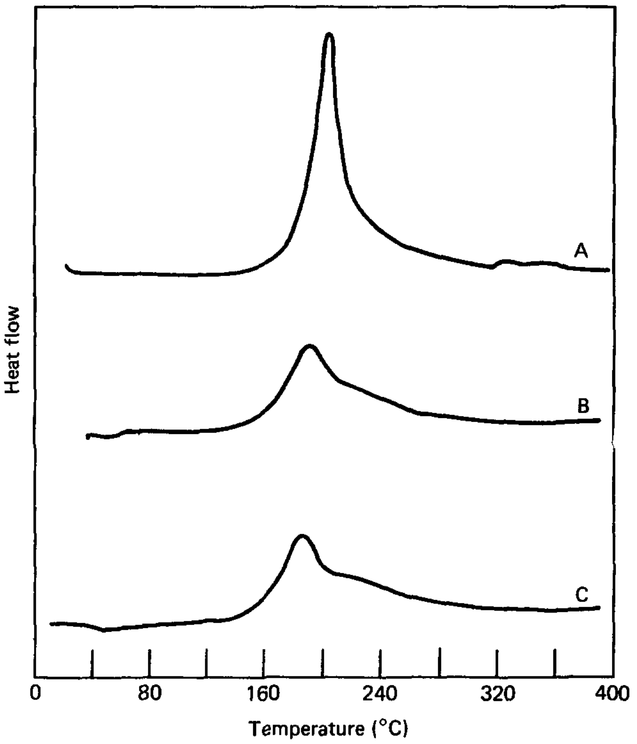

Figure 3 D.s.c. scane of TETPM obtained at 10°C min^{-1} showing decreasing peak area with ageing time of (A) as received, (B) 20 months and (C) 30 months

isothermal d.s.c. data obtained at 170, 180, 190 and 200°C, is 126 kJ mol^{-1}. The maxima of the exotherms for the TETPB and TETPM homopolymerizations are shifted to lower temperature relative to DEDPM, indicative of lower activation energies for the trifunctional monomers.

The heat of reaction of DEDPM, ΔH_t, as determined from the area under the exotherm, is 254 kJ mol^{-1} of DEDPM, or 127 kJ mol^{-1} of acetylene. On the basis of the number of moles of acetylenic groups present, an expected heat of reaction for TETPB and TETPM can be calculated. Comparison of the measured and calculated heats of reaction shows that only 59% of the ethynyl groups react on homopolymerization of TETPB and 81% in the case of TETPM, most probably as a result of vitrification, with the smaller TETPM molecule allowing a greater extent of reaction before onset of vitrification.

It was noted that the heat of reaction for the homopolymerization of TETPM decreases on ageing. D.s.c. scans of TETPM obtained over a period of 30 months showed a decrease in ΔH_t from an initial value of 958 J g^{-1} to 724 J g^{-1} after 20 months and 655 J g^{-1} after 30 months (*Figure 3*). This decrease in area is most likely attributable to polymerization at room temperature, possibly initiated by u.v. radiation from laboratory lighting, and would correspond to an average rate of reaction of 1% of the ethynyl groups per month. As the major exothermic peak decreases in area, a second, higher-temperature peak becomes more pronounced, and might correspond to further reaction of already polymerized material. Sublimation of TETPM at room temperature also was noted; ground material would reform into large chunks.

Expected heats of reaction if all ethynyl groups were to react were calculated for each of the blends based on the number of ethynyl groups present. With the addition of 10 or 20% of either trifunctional monomer to DEDPM, the measured heat of reaction equalled the expected value.

Heat evolution as a function of time for copolymerization at 180°C is shown in *Figure 4*. All four monomer compositions show an initial rapid reaction during the first 5 min, followed by a region of more slowly decreasing reaction rate. Between 40 and 60 min the rate of reaction slows somewhat more rapidly, and then levels off. This sharper decrease is more pronounced with 20% addition of trifunctional monomer than it is at the 10% level. This 'step' change in the rate of heat evolution is not observed in the homopolymerization of DEDPM, and might arise from rapid viscosity changes with corresponding decreases in diffusion rate. Alternatively, trifunctional monomer might react preferentially and the change in rate could correspond to the point at which all trifunctional monomer has been consumed. If this is the case, the resulting matrix inhomogeneity might explain the poorer composite mechanical properties observed for the DEDPM/TETPM copolymer matrix as compared with DEDPM alone or the DEDPM/TETPB blend[1]. Grinding together of DEDPM and TETPM monomer powders proved difficult, and this also might contribute to this inhomogeneity.

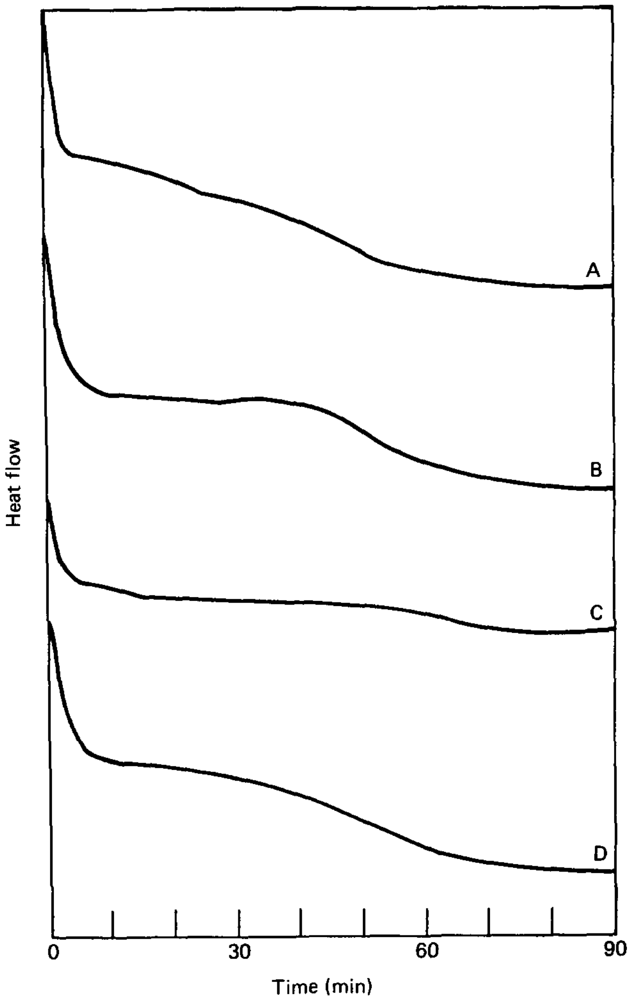

Figure 4 Heat evolution with time at 180°C for (A) 0.1 TETPB/0.9 DEDPM, (B) 0.2 TETPB/0.8 DEDPM, (C) 0.1 TETPM/0.9 DEDPM and (D) 0.2 TETPM/0.8 DEDPM blends

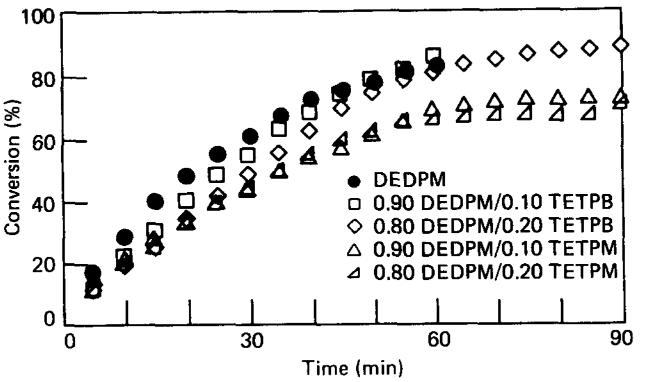

Figure 5 Extent of reaction as a function of time at 180°C for DEDPM and copolymers, as determined by d.s.c.

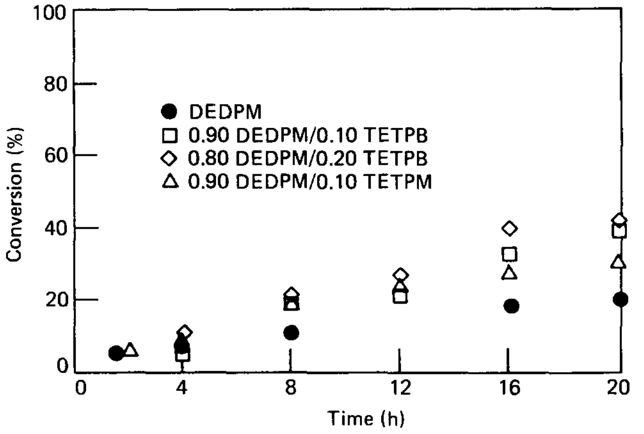

Figure 6 Extent of reaction as a function of time at 120°C for DEDPM and copolymers, as determined by d.s.c.

The extent of reaction, α, was obtained by isothermal d.s.c. measurement of the rate of heat evolution with time at 120 and 180°C, as indicated in equations (1)–(3). Per cent conversion with time for the copolymers is compared with that for the homopolymerization of DEDPM in *Figures* 5 and 6.

At 180°C (*Figure* 5), addition of trifunctional monomer slows the rate of reaction relative to DEDPM. This is probably the result of increased viscosity on the addition of trifunctional reactants, with a corresponding decrease in diffusion rate, as well as steric hindrance arising from the introduction of growing branched polymer at trifunctional sites. The TETPB copolymers attain the same extent of reaction observed for the DEDPM homopolymer. In contrast, conversion curves for the TETPM copolymers level off at slightly more than 60% conversion. This difference might be explained by increased steric hindrance to reaction of the third ethynyl group on the TETPM molecule as a result of its small size relative to TETPB. The rate of reaction is higher with TETPB addition than with TETPM at both concentrations; this also might be the result of more extensive electron delocalization in the TETPB radical, which could enhance its stability and thus its tendency to form polymer.

At 120°C (*Figure* 6) addition of trifunctional monomers increases the rate of reaction relative to DEDPM. Reaction is again more rapid with TETPB than TETPM. This again might arise from the greater stability of the TETPB radical, or may result from some homopolymerization of TETPM. (The 120°C data were obtained ~6 months after the 180°C d.s.c. data.) At low extent of reaction, as characterized by the 120°C data, viscosity would be expected to be fairly low; therefore diffusion rate should not be as strong an influence as at higher extents of reaction, as seen in the 180°C data.

It is noted that DEDPM heated for 16 h at 120°C is still fluid, whereas with 10% addition of either TETPB or TETPM the copolymer has gelled. The gel point is estimated to occur between 25 and 30% conversion (*Figure 6*).

Fourier transform infra-red spectroscopy

Representative spectra of TETPB during an isothermal polymerization reaction at 173°C are shown in *Figure* 7. Vibrational modes that are associated with the C=C bond are used to monitor the degree of cure. The band at 3295 cm^{-1}, due to the C–H stretching mode of the acetylenic end groups, and the one at 2104 cm^{-1}, attributed to the C≡C stretching mode, were chosen for our study. The band at about 940 cm^{-1}, which is characteristic of a C–H stretching mode of a terminal acetylenic group, was not used because of the severe overlapping of the bands in this vicinity and the broadening of the bands due to the elevated temperature of the experiment.

The integrated intensities of the two bands, 3295 cm^{-1} and 2104 cm^{-1}, were obtained. The degree of isothermal conversion at a time t can be calculated based on each band by

$$R_t\,(\%) = [(I_0 - I_t)/I_0] \times 100$$

where R_t is the conversion at time t, I_0 is the integrated intensity of the band at time $t=0$ (before reaction started), and I_t is the integrated intensity of the band at time t. The degrees of isothermal conversion calculated from each band are plotted as functions of time in *Figure 8*. Within experimental error, data from the two bands coincide. As in the case of the difunctional DEDPM, the parallel continuous decrease in the areas of

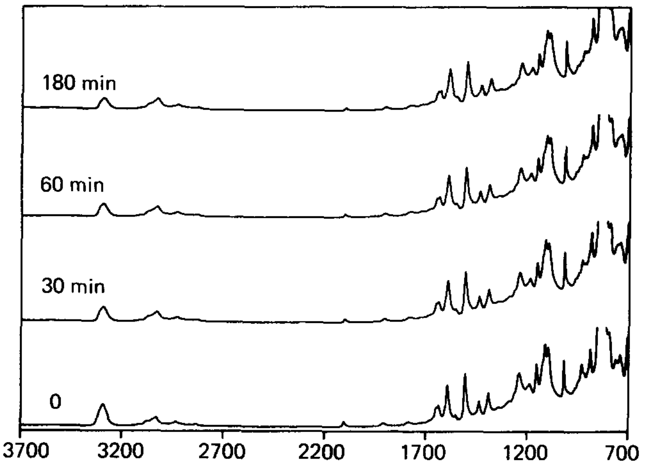

Figure 7 *FT*i.r. spectra for isothermal reaction of TETPB heated at 173°C for different times (indicated on spectra)

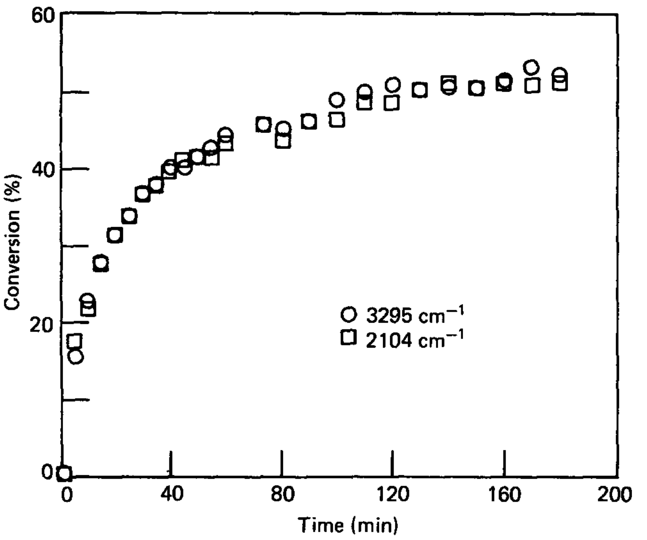

Figure 8 Extent of reaction as function of time for the homopolymerization of TETPB as determined by *FT*i.r.

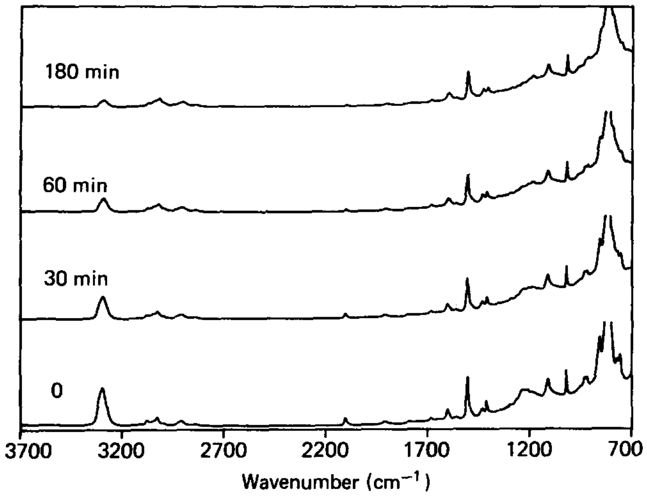

Figure 9 *FT*i.r. spectra for isothermal reaction of 0.1 TETPB/0.9 DEDPM mixture polymerized at 173°C for different times (indicated on spectra)

both bands rules out the formation of $-C{\equiv}C-C{\equiv}C-$ due to Glaser coupling.

Figure 8 shows that, at 173°C, only about 50 % of the total terminal acetylenic groups have reacted after 3 h. Compared to the reaction of DEDPM at the same temperature, the 'equilibrium' conversion of TETPB is much lower (50 % *versus* 85 % of the ethynyl groups have reacted). Hedberg *et al.*[17] have indicated that the curing reaction of terminal acetylene groups may be diffusion-controlled. In that case, the size of the TETPB molecules is large enough that at 50 % conversion the system is already vitrified to the point that the molecules cannot diffuse to the active sites to continue the reaction. D.s.c. data (see above) would indicate that only ~60 % of the TETPB ethynyl groups react on scanning to 400°C.

The spectra of the 10 % TETPB blend, which were taken at 173°C as the reaction proceeded, are shown in *Figure 9*. The degree of conversion, calculated from decrease in area of the 3295 and 2104 cm^{-1} peaks, is shown as a function of time in *Figure 10*. Calculations based on the two bands agree very well. The equilibrium degree of conversion is approximately 80 %, which is near that of pure DEDPM. This reflects the fact that 90 % of the monomer mixture is DEDPM. It also corroborates the observation that the curing reaction is diffusion-controlled.

Another sample was cured isothermally at 120°C and the reaction was stopped at 2, 4 and 8 h so spectra could be obtained at room temperature. The spectra are shown in *Figure 11*. The data from this set of experiments show that the integrated intensities of the 3295 and 2104 cm^{-1} bands increase after 2 h of curing. The increase in intensities is found to be about 30 %. Intermolecular conjugation between the terminal acetylenic moieties, which would occur on cyclotrimerization, as postulated in the homopolymerization of DEDPM[2], would explain the increase in intensities in the early stage of curing at 120°C.

The presence of the vibrational modes due to the formation of 1,3,5-trisubstituted aromatic rings may be masked by those characteristic of the benzene rings of TETPB, if their intensities are weak. Hence it has to be

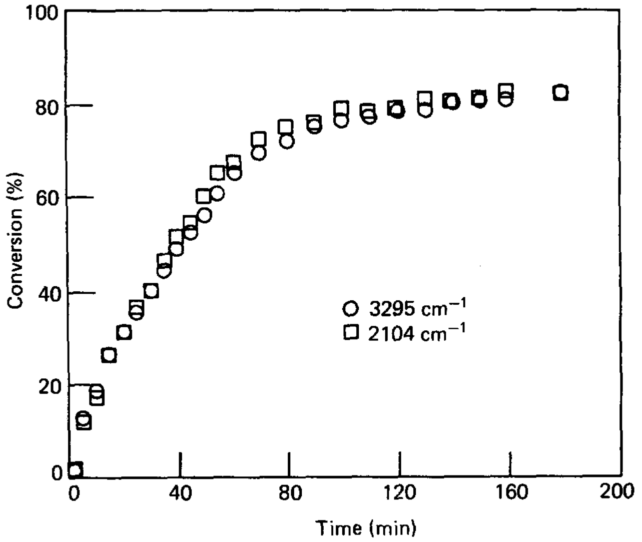

Figure 10 Extent of reaction time at 173°C for 0.1 TETPB/0.9 DEDPM copolymer as determined by *FT*i.r.

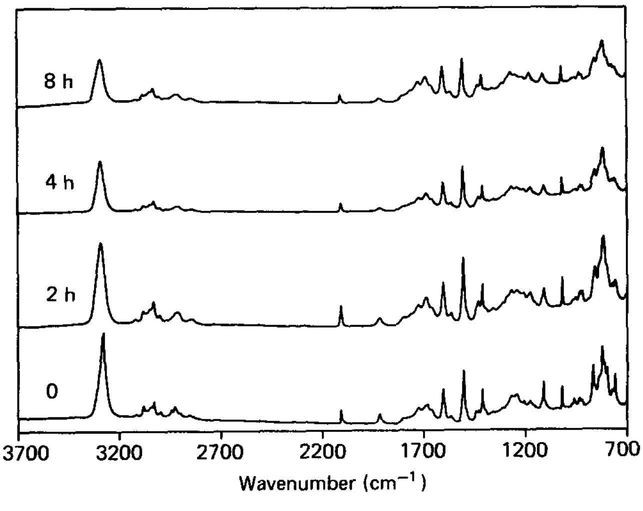

Figure 11 *FT*i.r. spectra for isothermal reaction of 0.1 TETPB/0.9 DEDPM blend at 120°C for different times (indicated on spectra)

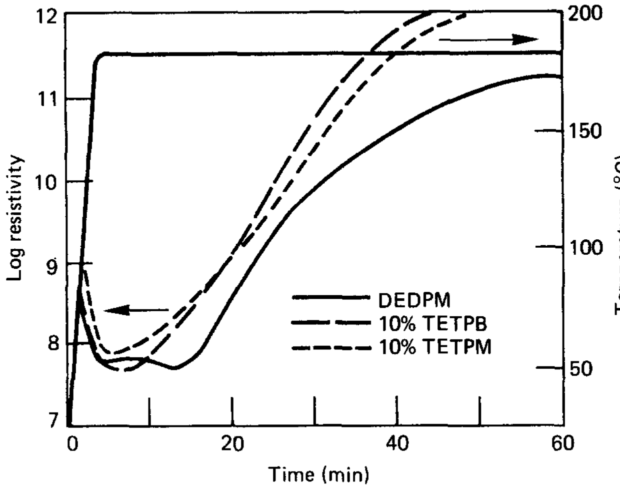

Figure 12 Changes in resistivity with curing time at 180°C for DEDPM alone and with 10% trifunctional monomers

concluded that the degree of cyclotrimerization is also low for the trifunctional TETPB. The major reaction product is again a linear conjugated structure.

Microdielectrometry

Measurement of the dielectric loss at several frequencies enables separation of the ionic conductivity from dipole contributions using the relationship[18]:

$$\varepsilon''\varepsilon_0\omega = \sigma + (\text{dipole term}) \times \varepsilon_0\omega \qquad (4)$$

where ε'' = loss factor, ε_0 = permittivity of free space ($8.85 \times 10^{-14}\,\mathrm{F\,cm^{-1}}$), σ = conductivity = (resistivity)$^{-1}$ and $\omega = 2\pi f$, where f is the frequency of measurement.

Resistivity is plotted as a function of time for both the homopolymerization of DEDPM and the copolymerization of DEDPM with 10% TETPB or TETPM polymerized isothermally at 180°C and 120°C (*Figures 12* and *13*). At 180°C (*Figure 12*), addition of trifunctional reactant produces an almost immediate increase in viscosity once the isothermal temperature is reached. After slightly more than 30 min reaction time this viscosity difference is almost an order of magnitude. Comparison of dielectric (*Figure 12*) and d.s.c. data (*Figure 4*) reveals that fewer ethynyl groups have reacted in the higher-viscosity copolymer system than for the DEDPM homopolymerization, supporting our earlier conclusion of a decrease in diffusion rate with incorporation of trifunctional reactants.

At 120°C (*Figure 13*), the DEDPM homopolymerization shows a decrease in viscosity (increase in ionic conductivity) during the first 2 h of reaction, which has previously been attributed to the formation of a cyclic trimer intermediate[2]. This increase in conductivity is not seen on addition of trifunctional monomer. Comparison with d.s.c. data at 120°C (*Figure 6*) shows that in this case the viscosity increase for the copolymers coincides with a more rapid incorporation of ethynyl groups into the growing polymer chain.

CONCLUSIONS

Addition of small quantities of trifunctional arylacetylene monomers to DEDPM can be used to control the rheology of the polymerization reaction through the influence of branching on polymer viscosity. Incorporation of trifunctional monomers also influences the rate of reaction. At low extent of conversion (<20%), based on the 120°C data, the reaction is more rapid on trifunctional addition. At higher extents of conversion, as seen at 180°C, viscosity increases rapidly and the reaction becomes diffusion-controlled; chain growth is slowed by the incorporation of trifunctional groups that give rise to more bulky branched polymers.

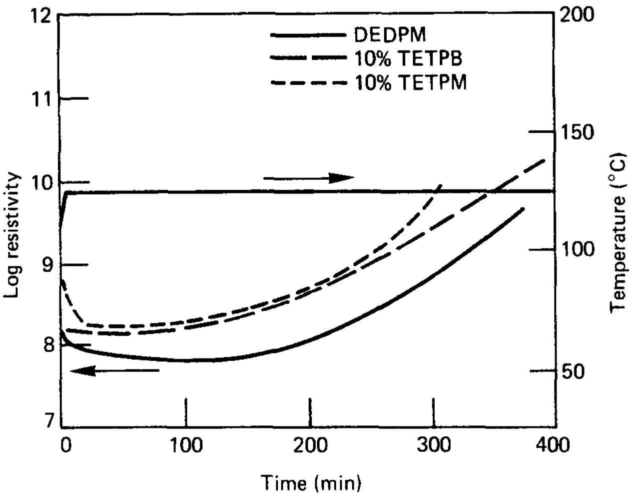

Figure 13 Changes in resistivity with curing time at 120°C for DEDPM alone and with 10% trifunctional monomers

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