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POLYMERISATION OF DIETHYLENE GLYCOL BIS-ALLYL CARBONATE UP TO HIGH DEGREES OF CONVERSION

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Abstract—The polymerisation of diethylene glycolbis-allyl carbonate to high conversion was investigated by ESR, FTIR and DMA techniques. The ESR spectrum was simulated using a two line, a three line and a broad line spectral component. These spectral components were assigned to the propagating radical, a mobile allyl radical and a less mobile allyl radical formed on a crosslink. The change in the resonance frequency of the ESR cavity during polymerisation was demonstrated to be sensitive to gel formation. ESR and FTIR data show that the restriction in the mobility of the system occurred well after gel formation making this system different from the vinyl systems. The ESR and FTIR data were used to calculate the rate constants for propagation, termination, transfer and reinitiation at high conversion. The chain transfer constant was not found to change with conversion. The DMA data shows that the extent of cyclisation during the polymerisation is about 20–25%. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The advantages of diethylene glycol bis-allyl carbonate commonly known as CR39, for optical purposes have been known for a long time. Various authors [1–3] have investigated the polymerisation of CR39 initiated by peroxydicarbonate or peroxide. In these studies it was shown that a high conversion of double bonds could be obtained in CR39 polymerisation. Schnarr and Russell [4] investigated the polymerisation of CR39 at low conversion by measuring the molecular weights and polymer structure by NMR. They observed little cyclisation, and found a degree of polymerisation of seventy and they measured the value of the chain transfer constant to be 0.014 at 50°C. O'Donnell and Sullivan [5] used laser Raman spectroscopy to study CR39 polymerisation up to high conversion. The rate of consumption of double bonds was found to be approximated by first order kinetics up to 80% conversion.

Portwood and Stejney [6], using FTIR to follow the conversion, found that in CR39 at low initiator concentrations and low conversion the reaction followed the reaction rate law found for vinyl polymerisation, but at high conversion and high initiator concentration there appeared to be evidence of allylic abstraction and chain transfer. They also found that increasing the polymerisation temperature decreases the extent of chain transfer. Photo-polymerisation of CR39 was also reported [7] and $k_p/(k_t)^{\frac{1}{2}}$ values of $1.5 \pm 0.05\ \mathrm{L}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{s}^{-1/2}$ were obtained when the system was treated as a normal vinyl polymerisation.

Chain transfer to monomer [8], anomalous head-to-head (HH) addition [9] and cyclisation [10] are some of the additional reactions which need to be considered in free radical polymerisation of allylic monomers as compared to vinyl monomers. As a result, the kinetic analysis is more complicated. The nature of the radicals and the variation in the radical concentration with polymerisation time in bulk polymerisation for CR39 was investigated by Hill *et al.* [11] using ESR. An eight line spectrum was observed in the initial stages of polymerisation, which was assigned to the allyl radical. This confirmed the presence of chain transfer in the polymerisation of CR39 and thus the need to consider these reactions in any kinetic analysis of polymerisation of this monomer. A study of the radicals present beyond the gel point in some other multi allyl monomers was also reported [12]. A radical trapping technique used to study [13] the reaction of *t*-butyl radicals with CR39 indicated extensive hydrogen abstraction from ethylene groups of the glycol moiety instead of from the allylic carbon atom.

A recent publication [14] from this group presented the kinetics of polymerisation of several mono and diallyl monomers to low conversion. A six line propagating radical and an eight line allyl radical were observed in the ESR spectra. The percentage of cyclisation in some diallyl monomers was calculated, and in CR39 cyclisation was found to be 25% during the initial stages of polymerisation. Monomers with longer alkyl side chains were found to undergo more reinitiation by the chain transfer radical. Rate constants for propagation, termination and transfer were estimated in the study.

In the present study ESR, FTNIR and DMA data were used to analyse the polymerisation behaviour and calculate rate parameters for CR39 polymerisation at high conversion.

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EXPERIMENTAL

Materials

The monomer, CR39, was provided by SOLA International Holdings, Adelaide, Australia. It was used as supplied. The initiator benzoyl peroxide (BPO) was purified by recrystallising twice from methanol and the isopropyl peroxydicarbanate (IPP) and dicumyl peroxide (DICUP) were used as obtained. Samples were prepared in 5 mm glass tubes (for FTIR) or in 3 mm quartz tubes (for ESR), which were degassed through at least three freeze–thaw cycles, after which they were sealed under vacuum.

Electron spin resonance spectroscopy (ESR)

ESR spectra were obtained on a Bruker ER-200 ESR spectrometer, operating in the X-band frequency range, at a modulation frequency of 100 kHz, in the TE-101 mode. A sweep width of 20 mT was scanned over 200 s, 1024 data points were acquired, at a modulation amplitude of 0.2 mT. The microwave power used was typically 2 mW. A correction was applied for changes in the cavity sensitivity during the polymerisation, which results from the change in the dielectric constant of the system during polymerisation. A more thorough description of this procedure has been previously published [15]. The cavity temperature was controlled by a Bruker VT-100 temperature controller/power supply, which was calibrated by insertion of a digital thermocouple in an ESR tube filled with silicon oil directly into the ESR sample cavity. A strong pitch secondary calibration standard was used for the determination of the radical concentrations.

Radical measurements were made *in situ*. This method of polymerisation describes the procedure in which the sample tube was inserted into the preheated ESR cavity at the desired polymerisation temperature. Spectral acquisitions were carried out at prescribed time intervals. At the higher conversions which are of interest to this paper, a single scan was sufficient to obtain a spectrum with good *S*/*N*.

Infrared spectroscopy

Conversion data were obtained using a Perkin-Elmer 1600 spectrometer operating in the NIR region and fitted with an external bench MCT detector. The intensity of the band at 6150 cm^{-1} was used to monitor the double bond concentration. A sample in a 5 mm o.d. tube was placed in a custom built, thermostatted aluminium heater block, with an entry and exit port designed to cater for the infrared beam. Accumulation of 32 scans at a resolution of 8 cm^{-1} was repeated every 5 min to give a single data point in the conversion profile.

Dynamic mechanical analysis

Samples were prepared in sealed 5 mm o.d. glass tubes and polymerised in the block heater in the FTIR spectrometer to the required conversion. Samples were then quenched in liquid nitrogen to stop the reaction and left in liquid nitrogen until required for measurements. Samples were taken out of liquid nitrogen just before measurements were made using a Perkin-Elmer DMA 7 instrument. Measurements were carried out in the parallel plate mode on a cylindrical sample of 1.5 mm height. Samples cured to 25% conversion in the FTIR spectrometer were used in isothermal DMA scans at the polymerisation temperature. For the isothermal scans, the sample cavity was heated to the required temperature, the sample was introduced as quickly as possible and the cavity was closed immediately, a few minutes were allowed for the temperature to stabilise and the analysis was started. The chamber usually reached thermal stability within 2 min.

RESULTS AND DISCUSSION

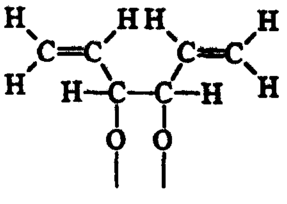
Radical spectra

The ESR spectra of the radicals formed at low conversion in the polymerisation of allyl monomer were discussed in a previous paper [14]. At low conversions, the allyl radical and the propagating radical are formed in the reaction mixture. As the polymerisation proceeds, the spectral shape changes [11]. First a combination of a broad spectrum and a sharp allylic radical spectrum was observed. The spectrum then changes at higher conversion into a broad three line spectrum, and then at very long reaction times, the fine structure of the spectrum is lost and a broad single line spectrum was observed.

The ESR spectra of CR39 at 80% conversion polymerised at 70 and 90°C using BPO and at 130C° using DICUP are shown in Fig. 1. The figure indicates the loss of the fine structure in the spectrum as the temperature of the polymerisation is increased. This indicates that the ESR spectra at this stage of polymerisation consist of at least two types of radicals; one a more mobile radical, which gives rise to the fine structure, and the other, a more restricted radical, which gives rise to a broad spectrum. The spectrum obtained at 90°C could be simulated considering three radicals as shown in Fig. 2. The three radicals used in this simulation are: a three line spectrum (20%, $a_{H\alpha} = 1.1$ mT, $\Delta H = 0.9$ mT), a two line spectrum (10%, $a_{H\alpha} = 2.3$ mT, $\Delta H = 1.2$ mT) and a broad line (70%, $\Delta H = 3.4$ mT). The increased reactivity of the radicals responsible for the two and the three line spectra, result in the low concentrations of these radicals present at the higher polymerisation temperatures.

At any temperature the percentage of the broad line radical was found to be much higher than that of the two mobile radicals. These two mobile radicals may be due to the head and tail addition radicals of the CR39 molecule. The tail addition radical has one α proton and the head addition radical has two α protons, thus the two-line and three-line ESR spectra could be assigned to these tail and head addition radicals, respectively. However, considering the splitting constant of 1.1 mT, it is unlikely that the three line spectrum is due to an alkyl radical, for which splitting constants of 2.0 mT or above usually are found [16]. The three line spectrum is therefore more likely to be due to an allyl radical, where splitting constants in this range have been reported [17].

The sharp eight line spectrum of an allyl radical may be expected to reduce to a four line spectrum of splitting of 1.4 mT in a glassy environment [18]. However, the introduction of even 5% of a four line spectrum distorted the simulated spectrum from that of the observed spectrum. The distance D (Fig. 3a) is reduced with this modification to the radical distribution. As reported earlier [14], the proportion of allyl radicals to propagating radicals at low conversion was about 5%. Thus the contribution of the allyl radicals giving rise to the four lines in the spectra at high conversion should be less than 5%. Since we have observed allyl radical recombination to occur in the early stages of the reaction, there should be a significant concentration of A–A structures (I) in the system at conversions above 60%. The allyl radicals formed in the A–A structures have only two α protons and, therefore, should be characterised by a spectrum of three lines with splitting constant of around 1.1 mT. Thus, these radicals are the most likely source of the three line spectrum.



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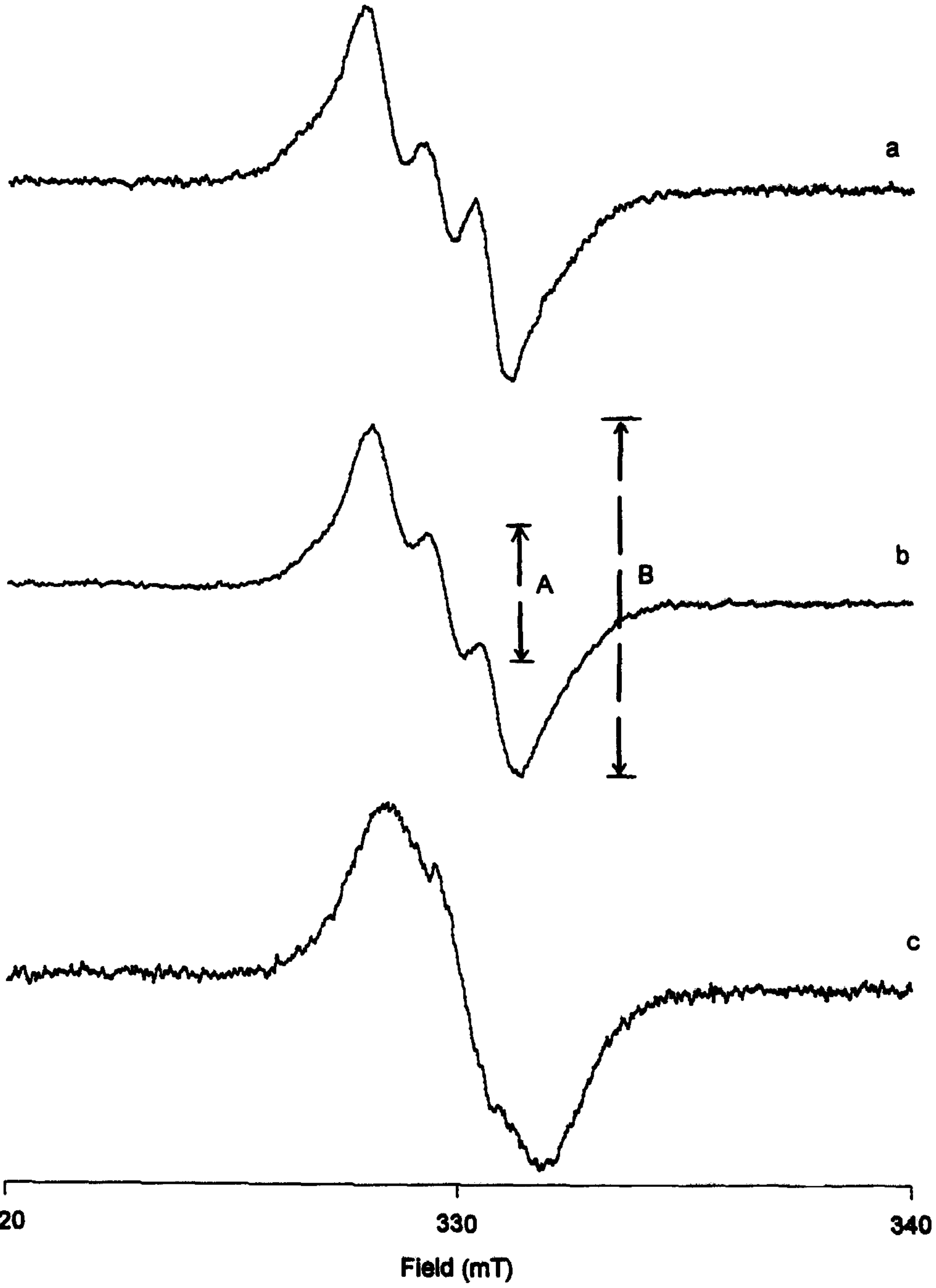


Fig. 1. ESR spectra during polymerisation at (a) 70, (b) 90 and (c) 130°C at 80% conversion.

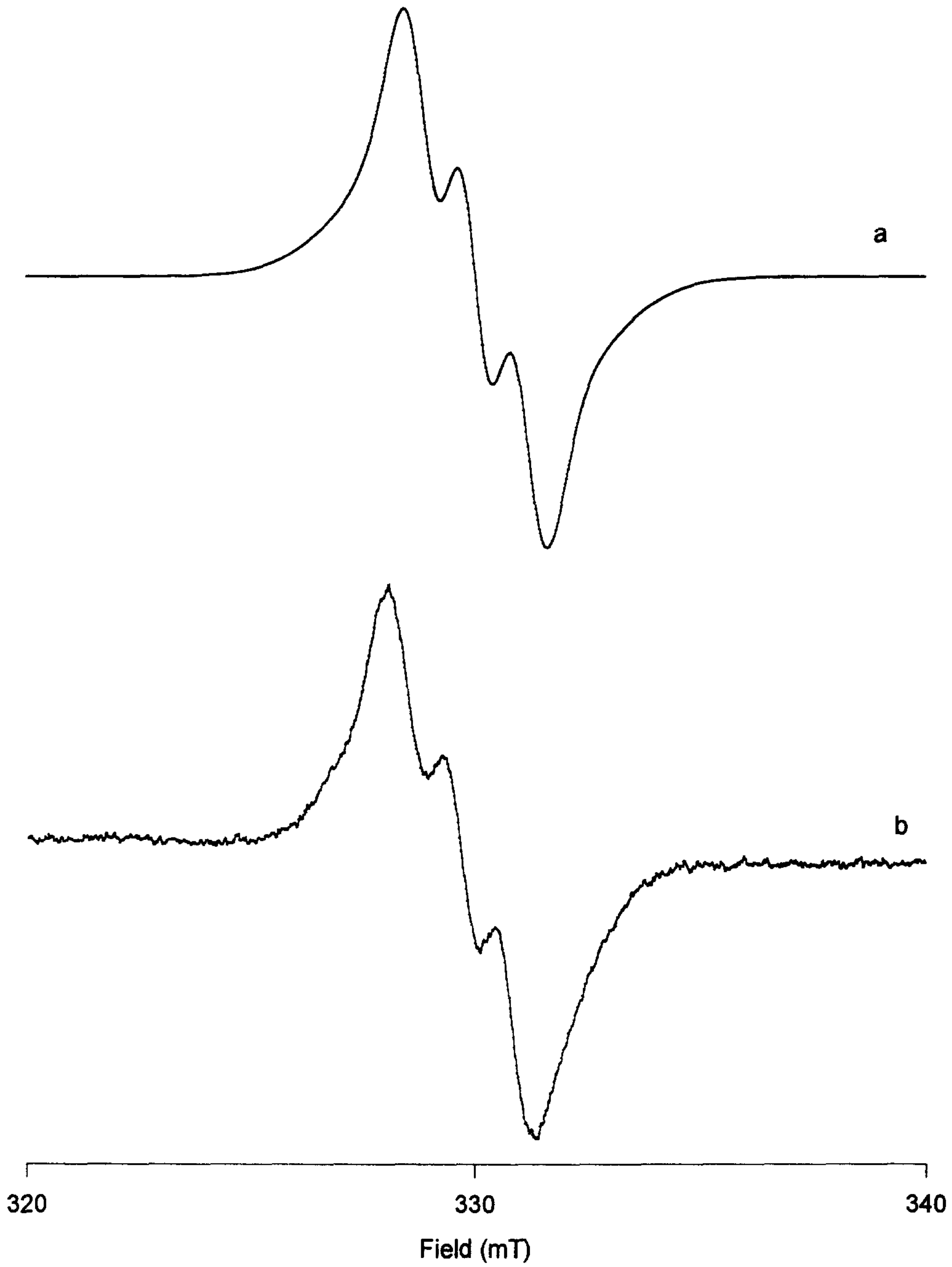
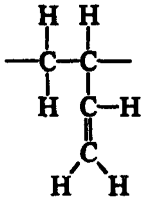


Fig. 2. ESR spectra (a) simulated (b) experimental at 90°C.

ESR spectra simulated using the above mentioned splitting parameters and different radical percentages are shown in Fig. 3. Increasing the contribution of the two line component by 5% and reducing that of the three line component by a corresponding amount, has the effect of reducing the height of the central line (A/B in Fig. 3) as observed clearly in Fig. 3(b and c). While the spectrum in Fig. 3(b) matches the spectrum observed when the polymerisation temperature is 70°C (Fig. 2a), the spectrum in Fig. 3(c) matches the spectrum obtained when the polymerisation temperature is 90°C (Fig. 2b). This indicates that the increase in the polymerisation temperature from 70 to 90°C causes a reduction in the contribution of the mobile propagating radical and an increase in the contribution of the allyl radical. This may be expected, since an increase in the polymerisation temperature generates more radicals initially, first the propagating radical then the allyl radical, thus more recombination with the formation of A–A structures will occur during the initial stages. Therefore, when the polymerisation reaches high conversion, a polymerisation carried out at a higher temperature will contain more A–A structures, which in turn would give rise to more three-line radicals. Alternatively, the increase in the contribution in the allyl radical may be due to increased chain transfer and/or reduced allyl radical termination at the higher polymerisation temperatures. Reduced allyl radical termination at higher initial polymerisation rates is later discussed in more detail.

The proportion of A/B was found to increase as the extent of polymerisation increases as shown in Fig. 4 for polymerisations at 70 and 90°C. This corresponds to an increase in the propagating radical concentration as the polymerisation proceeds. This is not surprising since, as the reaction proceeds, depletion in the concentration of the allylic hydrogen occurs in the system.



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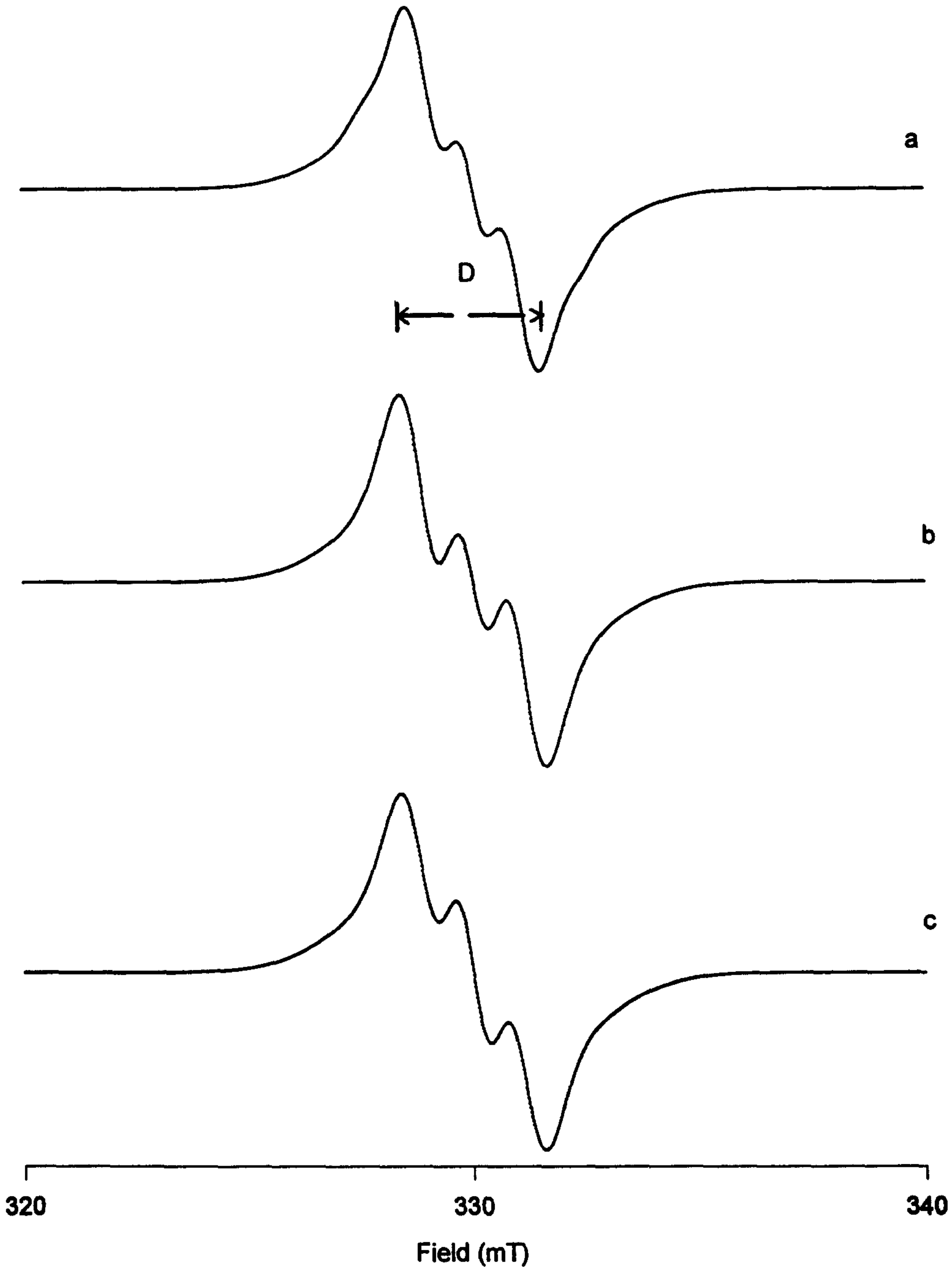


Fig. 3. Simulated ESR spectra using (a) 20, 10, 65, 5, (b) 15, 15, 70, 0 (c) 20, 10, 70, 0 percentages of three line, two line, broad singlet and four line spectra, respectively.

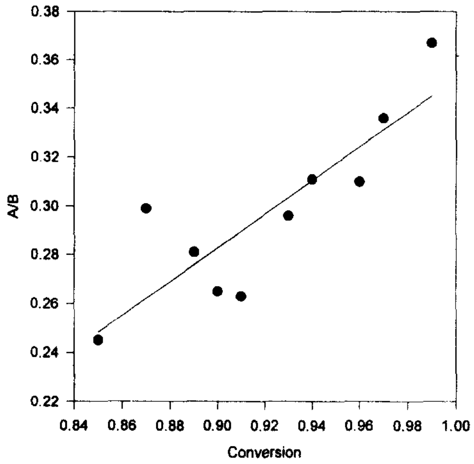


Fig. 4. Relationship of A/B (refer to Fig. 1) and conversion at 5% BPO for polymerisation at 90°C.

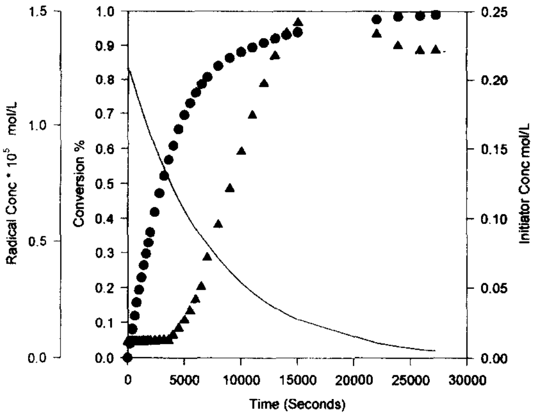
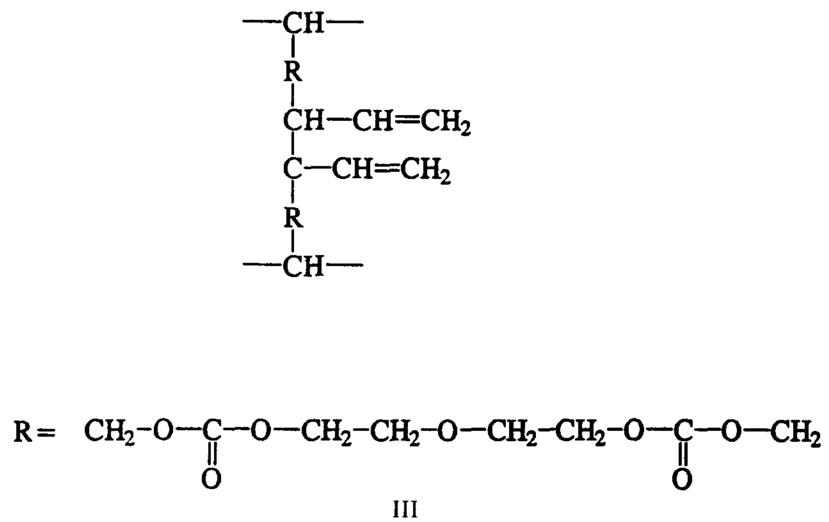


Fig. 5. (●) Conversion, (▲) radical concentration, (–) initiator concentration for polymerisation at 5% BPO and 90°C.

The third spectral species that was used to simulate the experimental spectrum is the broad line singlet with a 3.4 mT peak width. In diacrylates and dimethacrylates such a broad line is not observed at any conversion. The peaks in spectra of these systems always showed hyperfine splitting. However, it is known [19] that the allylic radical of butadiene in the glassy state has a broadened spectrum. In this case the spectra correspond to the allylic radicals formed in both of the 1,4- and 1,2-butadiene structures. The allylic structure of 1,2-butadiene (**II**), is similar to the structures observed in CR39 when the allyl unit is bound to the network through an allylic radical recombination to give a crosslink in the network. This arises as discussed in our previous paper [14], by first radical transfer to a pendent double bond to form an allylic radical, followed by recombination of two of these allylic radicals to give a inter or intra molecular crosslink. For explanation purposes we refer this process as forming structure **III** (this allylic radical is different to the species giving rise to the three line spectrum, where the unbound A–A structures are considered). The maximum concentration of the radicals formed in this way ($\approx 10^{-5}$ mol L^{-1}) is only a very small fraction (1.9×10^{-4}%) of the initial double bond concentration, hence the presence of allylic type radicals at the final stages of reaction is not impossible. This was also confirmed by gamma-irradiating a fully polymerised poly-CR39 sample which gives rise to a multi-line ESR spectrum.



$$R = CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2$$

III

Monomer conversion

Monomer conversion, initiator concentration and radical concentration vs time plots are given in Fig. 5 for the polymerisation of CR39 with 5% BPO at 90°C. The consumption of BPO was calculated according to the first order decomposition [20] with $k_d = 1.36 \times 10^{-4}\,s^{-1}$. The polymerisation of CR39 can be divided into several regions; first a pre-gel

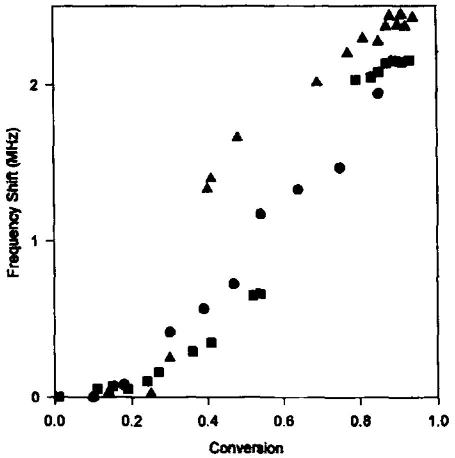


Fig. 6. Relationship between frequency shift and conversion during the polymerisation at (●) 70, (■) 80 and (▲) 90°C and 5% BPO.

period (0–20% conversion) not observed in the plots shown in Fig. 5, a gel to vitrification region (20–60% conversion), a glassy region (60–98% conversion) and a post cure region.

There is a change in the resonance frequency of the microwave cavity in the ESR during the polymerisation of CR39 due to the change in the real part of the dielectric constant [21]. A similar change has been used to monitor the conversion during the polymerisation of methyl methacrylate [15]. During the polymerisation, the Q factor of the resonance cavity also changes as the monomer is consumed. Due to the dependence of the Q factor on the dielectric constant, the sensitivity of the instrument increases during the conversion of the monomer. These two changes (resonance frequency and sensitivity) were measured [15] during the polymerisation of CR39 using manganese(II). The typical relationship between the peak area of Mn(II) and the resonance frequency of the cavity vs conversion during CR39 polymerisation is shown in Fig. 6. The sensitivity of the cavity increases two-fold between 25 and 100% conversion. In the case of methyl methacrylate this increase was about three-fold [15].

In the calculation of radical concentration given in Fig. 5, this correction for instrument sensitivity was applied. The sensitivity and the resonance frequency of the cavity started to increase at about 25% conversion. This change corresponds to a decrease in the absorption of microwaves, which accompanies the polymerisation. The change is due to the decrease in the real part of the dielectric constant of the polymerising mixture as the more mobile polar monomer is converted to gel and eventually to a glassy polymer, in which the mobility of the polar bonds, including the double bonds, are greatly reduced. In the case of CR39 the gel point occurs at about 23% conversion, and corresponds to the formation of the network [22]. It is clear from the above experiment that the ESR cavity sensitivity commences to change only after the formation of the gel.

Unlike methacrylates, the onset of gel formation was not evident in either the conversion or radical concentration curves obtained by FTIR and ESR (see Fig. 5). This is due to the low limiting degree of polymerisation obtained in the allylic systems. Even after the three-dimensional network is formed, the change in the mobility of the system is not sufficient to result in a significant change in the polymerisation rate. Vitrification occurs at about 60% conversion for CR39. Here the mobility of the system starts to affect the reaction rate and the radical concentration starts to increase. In the glassy region, above 60% conversion, the radical concentration steadily increases. Finally, in the post cure period, the radical concentration starts to drop, even at a polymerisation temperature as low as 70°C. This observation again differs from that for the methacrylates, where the radicals were found to be more stable at such temperatures [23]. In Fig. 5 it can be observed that the radical concentration remains very low up to the end of stage 2. In this region a quasi-steady-state-hypothesis (QSSH) may be expected to be valid, and the polymerisation rate can be described by chemically controlled reactions. Therefore, diffusion controlled termination becomes effective only well after gel formation, unlike the behaviour in methacrylates.

In the initial period of stage three of the polymerisation of CR39, a broad line starts to appear in the ESR spectrum and the radical concentration starts to increase. This transition in the ESR spectra suggests that the reaction system is approaching a glassy state. In the glassy state the reaction mass is heterogeneous. Therefore, at least two populations of radicals exist as we mentioned before. One population is resident in a tightly crosslinked network and the other in a loose network or soluble region. Free monomer translational diffusion and bound monomer segmental diffusion is reduced in the regions where the network is tightly crosslinked. It is generally considered that in allylic monomer polymerisation reactions, the termination of the propagating radicals occurs by chain transfer to an allylic group of a monomer unit. The allylic radicals then can reinitiate polymerisation or terminate by recombination. The rate constant for reinitiation was shown to be very low compared to that for recombination [14]. The development of the radical concentration, particularly the broad line component due to the allylic radical, indicates that the termination by radical recombination is blocked or reduced in this region of the polymerisation. This is because most of the remaining monomer (double bond) is bound to the network at these conversions.

In crosslinking systems, the polymer produced at low conversion is soluble, because the polymer chains are either linear or only slightly branched. When the conversion reaches a certain point, the first insoluble polymer is formed. Once a gel molecule is nucleated, it grows rapidly following four reactions: (a) propagation of a gel radical with monomer, (b) reaction of a gel radical with a pendent double bond of a soluble chain component, (c) reaction of a gel radical with

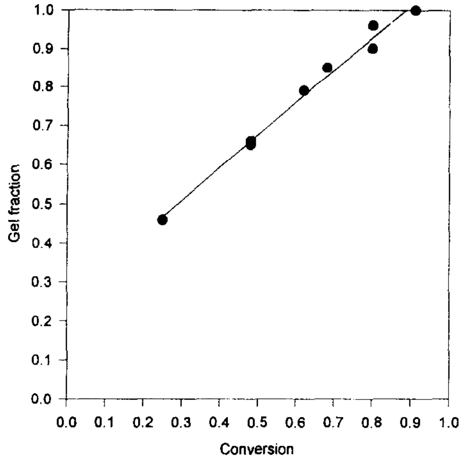


Fig. 7. Relationship between gel fraction and conversion at 5% BPO and 90°C.

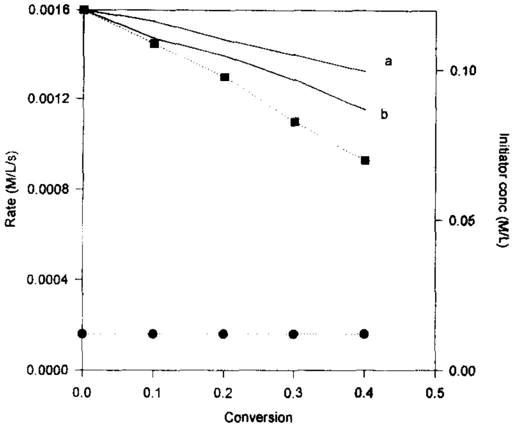


Fig. 8. Relationship between conversion and the rate of polymerisation at (●) 70, (■) 90°C with 3% BPO and the initiator concentration at (a) 70, (b) 90°C.

a pendent double bond of a soluble chain component, (d) sol–gel radical recombination to form an insoluble network. In the sol phase (e) sol radicals can react with monomer or a pendent double bond on a chain in the sol, and in (f) sol radicals recombine. In the case of allylic monomers, chain transfer is an additional reaction which can take place in either the sol or gel phases. Up to very high conversion, the allylic radical that is formed by chain transfer will remain either in the sol or on the pendent end of a monomer unit, thus the mobility is enhanced. The plot of gel fraction vs conversion shown in the Fig. 7 indicates that most of the monomer has entered the network at about 85% conversion. At 50–60% conversion, when the radical concentrations commence to increase, the gel fraction is about 70–80%.

The conversions at which stage 2 changes to stage 3 during CR39 polymerisation for different initiation rates are given in Table 1. These values were calculated by extrapolating the radical concentration/time curve in stage 3 to zero radical concentration. The higher the initiation rate, the lower is the conversion at which stage 3 begins. We have demonstrated [14] that the higher the reaction rate, the lower is the gel fraction at a particular conversion and the higher is the crosslink density. This is similar to micro gelation. Therefore, the termination of the allylic radicals which are formed from structures of type I, which will be bound to the network, is reduced since allylic radicals in two micro gel particles have to participate in the termination reaction. As a result, the intensity of the broad line of width 3.4 mT, which is due to allylic radical on structure **III**, starts to increase in the ESR spectrum. This effect is also observed in the rate vs conversion curves in Fig. 8, where the drop in the rate is steeper when the initial rate is higher. In fact, what is observed [11] in the early period of stage three is the development of the broad line of width 3.4 mT.

Kinetic analysis

Important steps in the polymerisation of allyl monomers have been identified [8] as:

Initiation:			I	$\rightarrow$	$2I^{\cdot}$			k_d
	$I^{\cdot}$	$+$	M	$\rightarrow$	$M^{\cdot}$			
Propagation	$M^{\cdot}$	$+$	M	$\rightarrow$	$P^{\cdot}$			k_p
Chain transfer	$P^{\cdot}$	$+$	M	$\rightarrow$	P	$+$	$A^{\cdot}$	k_{tr}
Reinitiation	$A^{\cdot}$	$+$	M	$\rightarrow$	$M^{\cdot}$			k_{ri}
Termination	$A^{\cdot}$	$+$	$A^{\cdot}$	$\rightarrow$	$A—A$			k_{ta}

In any crosslinking system, since the radicals are in different network environments, they will have different reactivities. It is assumed here that all the radicals have equal reactivity. Thus this assumption means that only an apparent rate constant can be calculated.

Table 1. Conversion at which radical concentration commences to increase for polymerisation of CR39

Temperature (°)	Initial rate (mol L^{-1} s^{-1})	Conversion (%)
70	0.0002	80–84
80	0.0008	76–79
90	0.0014	78–81
90	0.002	69–74
100	0.005	62–74
70	0.01	58–65

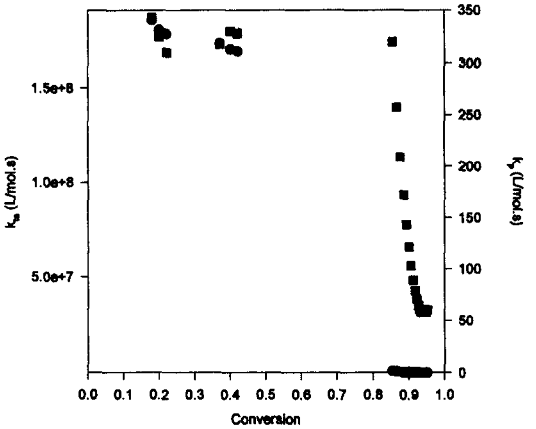


Fig. 9. Variation of k_{ta} and k_p with conversion at 90°C.

The value of k_{ta} can be calculated [14] from the equation $k_{ta} = (2fkd[I] - dR^{\cdot}/dt)/[A^{\cdot}]^2$, and the values for 5% BPO polymerisation reaction at 90°C are given in Fig. 9. The results indicate that the apparent value of k_{ta} drops during the whole range of conversion. The values of the termination rate constant for CR39 at low conversion are much higher than those for other vinyl monomers, such as MMA [24]. The higher values were explained as being due to the more mobile nature of the short chain terminating allyl radicals in CR39, compared to the large molecular weight propagating radicals in MMA. Thus, the attachment of an allyl radical onto the network after gel formation in CR39 would lead to reduction in the termination rate. The only way an allyl radical formed on the structure III could terminate is either by the movement of the radical site by hydrogen hopping or by the diffusion of a mobile short chain allylic radical to the site of the network allyl radical.

The rate equation for the loss of double bonds [14] can be rearranged as;

$$Rp/([A^{\cdot}][M]) = k_p([M^{\cdot}]/[A^{\cdot}]) + k_{ri}$$

Thus, by plotting $Rp/([A^{\cdot}][M]$ vs $[M^{\cdot}]/[A^{\cdot}]$, as given in Fig. 10 for very high conversion (95%), k_p and k_{ri} can be derived. These calculations give a value of about 150 for k_p and a value of zero for k_{ri} for 5% BPO at 90°C. Assuming that k_{ri} remains very low during the whole range of polymerisation (the k_{ri} value calculated [14] at low conversion is 22), the values of k_p could be calculated from the simplified equation, $k_p = Rp/([M^{\cdot}]M])$. The values of k_p so obtained are given in Fig. 9. The results indicate that the k_p values remain unchanged up to about 80% conversion, then they start to drop.

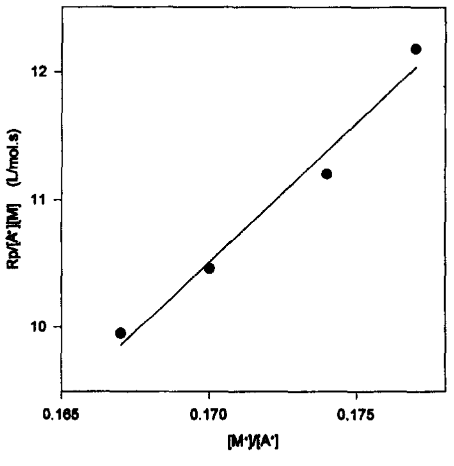


Fig. 10. Relationship between $Rp/[A^{\cdot}][M]$ and $[M^{\cdot}]/[A^{\cdot}]$ for polymerisation at 5% BPO and 90°C.

Since k_{ri} is zero at 95% conversion, k_{tr} could be evaluated from the equation, $k_{tr} = (d[A^{\cdot}]/dt + k_{ta}[A^{\cdot}]^2)/[M^{\cdot}][M]$. A value of 5 was obtained for k_{tr}, which is similar to the value at low conversion [14]. This confirms that the allyl radical build up is not due to an increase in the rate of chain transfer, but is due to a reduced rate of termination. This contradicts a previous observation [6] that there is more chain transfer at high conversion and at higher initiator concentrations. An increase in the chain transfer at high conversion may be expected because of the greater availability of methylene hydrogens in the glycol moiety. Therefore, when the propagation is reduced due to diffusion restrictions, the propagating radical may abstract a methylene hydrogen, thus increasing the rate of chain transfer. However, this was not found to be the case.

Another interesting observation was the effect of a plasticiser on the polymerisation of CR39. When a solvent was added, CR39 did not go to 100% conversion under conditions of 5% BPO at 90°C. Instead the polymerisation stopped at about 80% conversion, and no build up of the radicals was observed in the ESR experiment. This may be due to the reduction of the T_g by the plasticiser. However, a build up of radicals was observed at temperatures above T_g (130°C) without plasticiser. This indicates that termination during the CR39 polymerisation involves species which are not bound to the network. Without the plasticiser present these species find it difficult to diffuse to the network bound allyl radical. In the presence of the plasticiser, the network is swollen, thus allowing the terminating mobile species to migrate in the network. The lack of a build up in the radical concentration in CR39 is similar to that observed in the polymerisation of monoallyl monomers, where at low final conversions there is no build up of radicals [14].

Network formation

From elementary rubber elasticity theory,

$$G = (dRT)/M_c,$$

where G is the measured dynamic storage modulus obtained from the DMA analysis, d is the sample density, R is the gas constant, T is the absolute temperature and M_c is the average weight between crosslinks. While this expression is based on a very simple model of rubber elasticity that neglects, for example, entanglement effects, it has been shown to be an adequate first approximation in many other cases [25]. Since the molecular weight of the chains in poly(CR39) has been shown to be very low, the effects of entanglement should be negligible, and thus this model should suit the CR39 system better than other vinyl systems. It should also be pointed out that the

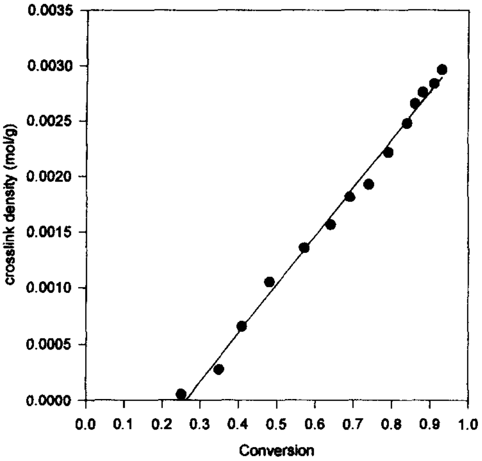


Fig. 11. Relationship between crosslink density and conversion at 5% BPO at 90°C.

relationship would only true for the "rubbery" plateau above the T_g. Since the experiment was conducted at 90°C, it is reasonable to assume that the sample was always above T_g, as reaction would cease when the T_g of the mixture reached the experimental polymerisation temperature. The crosslink density calculated from the DMA, storage modulus data are plotted against the extent of reaction in Fig. 11. The density values at different conversion [3] were used in the calculations. The figure indicates that the crosslink density is a linear function of the extent of conversion throughout the whole range.

The total concentration of the double bonds at the commencement of the reaction was 0.00742 mol g^{-1}. This corresponds to 0.00371 mol g^{-1} of monomer units. Thus if it is assumed that the crosslinks are formed only through the reaction of double bonds, the maximum crosslink density achievable is 0.00371 mol g^{-1}. At 90% conversion, the experimentally determined value was 0.0034 mol g^{-1}. Therefore, the experimental value is about 82% of the maximum value. When the crosslinks formed through allyl radical recombination are taken into account, the results indicate that there is about 20–25% cyclisation during the polymerisation, which agrees with the cyclisation value calculated at low conversion [14].

CONCLUSIONS

The ESR spectrum observed at high conversion of ethylene glycol bis-allyl carbonate could be deconvoluted in to three components. They are the propagating radical, a mobile allyl radical and a restricted allyl radical. Only restricted allyl radicals were observed at high temperatures. The proportion of propagating radicals to mobile allyl radicals changed with experimental conditions and conversion.

The resonance frequency of the ESR cavity was found to be sensitive to gel formation during polymerisation of CR39 gel formation. The rate of the frequency change was higher after the gel point. Unlike the observations for vinyl monomers, gel formation was not obvious in the radical concentration and monomer conversion vs time curves.

Chain transfer was found to be independent of conversion, but at very high conversions the reinitiation rate constant was found to be zero. The rate constant for termination decreased with conversion whereas for propagation the rate constant remained constant until 80% conversion. Addition of a solvent was found to reduce the final conversion. The extent of cyclisation was estimated to be 20–25% throughout the reaction.

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