ELSEVIER

S0032-3861(96)00560-5

Polymer Vol. 38 No. 3, pp. 695–702, 1997

0032-3861/97/$17.00+0.00

Copolymerization of methyl methacrylate and diethylene glycol bis(allyl carbonate)

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(Received 6 March 1996; revised 8 May 1996)

The free radical copolymerization of MMA and CR39 was investigated using Fourier transform infra-red spectroscopy, electron spin resonance (e.s.r.), nuclear magnetic resonance and gel permeation chromatography. The data obtained from these techniques were used to evaluate the rate constants, the reactivity ratios and chain transfer to the CR39 allyl groups. The copolymerization reaction proceeds in two major steps or regions, first the predominant polymerization of MMA with only a few CR39 units entering the polymer molecules. This is followed by predominate CR39 polymerization and crosslinking, with the remaining few MMA molecules entering the polymer molecule. In the first region, the propagation rate constant of MMA was found to be unaffected by the presence of CR39, while the termination rate constant decreased with increasing CR39 content. Very little chain transfer from the propagating MMA radical to the CR39 molecule was found during this stage. The presence of CR39 also results in the propagating MMA radical being found to be predominantly in the 13-line e.s.r. confirmation up to a much higher conversion that in the case of homopolymerization of MMA. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: methyl methacrylate; radical polymerization; copolymerization)

INTRODUCTION

Copolymerization of methyl methacrylate (MMA) and diethylene glycol bis(allyl carbonate) (CR39) has been reported in many optical applications. One such application is in plastic fibres[1], where a monofunctional methacrylate, acrylate or other vinyl monomer may be copolymerized with CR39 or another diallyl monomer, dimethacrylate or diacrylate polyfunctional monomer. Another application[2–4] is in optical cable or light conduit, where a methacrylate is usually polymerized with a polyfunctional monomer such as CR39. In all these cases the polyfunctional reactant is used to obtain the required crosslinking to improve the thermal properties of the resultant product and in some cases the flexibility.

Copolymerization of acrylate, methacrylate and other vinyl monomers, with dimethacrylate, diacrylates and other vinyl monomers has been extensively studied[5–11]. For example, copolymers of MMA with divinyl monomers, such as ethylene glycol dimethacrylate (EGDMA), are crosslinked to an extent which depends on the properties of the divinyl monomer, with consequent changes in properties. Any divinyl monomer decreases the gel time of MMA polymerization and increases the initial rate of polymerization.

There is a vast difference in the homopolymerization of MMA and CR39. Homopolymerization of MMA to high conversion in bulk can be divided into three stages. In the first region, the pre-gel region (0–30% conversion at 60°C), k_p and k_t are independent of the extent of conversion. In the second region, above the gel point (30–80% conversion at 60°C), the polymer chains become entangled, so increasing the viscosity and reducing the termination rate constant. This increases the radical concentration, thus increasing the polymerization rate. In the third region (above 85% conversion at 60°C), the polymer becomes a glass and the T_g of the mixture reaches the polymerization temperature. Both k_p and k_t decrease through this region.

By contrast, in the polymerization of allylic monomers, including CR39, chain transfer to the monomer occurs[12], considerably limiting the kinetic chain length of polymerization (to less than 30). The reaction rates for the allylic monomers are much smaller than for MMA, and the double bond conversion–time plots do not show[13,14] any clearly different regions during polymerization. However, in diallyl monomers the shape of the electron spin resonance (e.s.r.) spectra change at about 60% conversion as the radical concentration starts to rise. The gel point of CR39 is about 23% conversion. Further, reactivity ratios for MMA (M_1) and allyl acetate (M_2) copolymerization have been evaluated[15] to be $r_1 = 41$ and $r_2 = 0.024$, so $r_1 r_2 \approx 1$ which requires that the incorporation of the two monomers in the polymer is close to random.

In view of these differences in the behaviour of the vinyl and allyl monomers, and the industrial interest in the final product, a study was undertaken to obtain more information on the copolymerization of MMA and CR39. The aim of the study was to investigate whether a 'true copolymer' is formed, and, if it is, to determine the reactivity ratios and to calculate the individual kinetic rate parameters.

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EXPERIMENTAL

Materials and sample preparations

BASF grade MMA and AKZO Neuset 200 grade CR39 were used in the study. MMA was vacuum distilled to remove the inhibitor and CR39 was used as received. Benzoyl peroxide, BPO, obtained from Aldrich Chemicals Co., was purified by recrystallization from a chloroform–methanol mixture.

The required quantities of distilled MMA, CR39 and BPO were accurately weighed into a flask in the dark and mixed thoroughly. Samples of this solution were then added to glass tubes and vacuum thaw degassed four times and the tubes were then sealed under vacuum. 5 mm o.d. pyrex tubes were used for *in situ* Fourier transform infra-red spectroscopy (*FT*i.r.), 3 mm o.d. quartz tubes were used for e.s.r. (*in situ* and quenched), and large glass ampoules were used to prepare low conversion samples for gel permeation chromatography (g.p.c.) and nuclear magnetic resonance (n.m.r.) analysis. After polymerization to 10% conversion, the samples for g.p.c. and n.m.r. analysis were added to methanol to stop the reaction. The precipitated polymer was dissolved in acetone and reprecipitated twice.

Electron spin resonance spectroscopy

E.s.r. 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 TE-101 mode. A spectral width of 20 mT was swept over 200 s, acquiring 1024 data points, at a modulation amplitude of 2 or 10 dB. The microwave power used was typically 2 mW. A correction for changes in cavity sensitivity during the polymerization, as a result of changes in the dielectric constant of the system, was applied. A more thorough description of this procedure has been previously published[16]. The sample temperature was controlled by a Bruker VT-100 temperature controller/power supply, which was calibrated by insertion of a digital thermocouple directly into the sample cavity in an e.s.r. tube with silicon oil as conductant. A strong pitch secondary calibration standard, previously calibrated against a DPPH primary standard, was used in determination of the radical concentration.

Two methods of obtaining e.s.r. spectra were used. *In situ* polymerization describes the method whereby the sample tube was inserted into the preheated e.s.r. cavity at the desired polymerization temperature and multiple scan acquisitions were carried out until a signal to noise ratio adequate for reliable quantitative estimation of the radical concentration was obtained. The second method is referred to as the quenching method. In this instance, a sample was polymerized outside the e.s.r. cavity at the desired temperature for a prescribed period of time, after which the sample was quickly quenched in liquid nitrogen, so stopping the polymerization. Acquisitions of the e.s.r. spectra were subsequently carried out in the frozen glassy state at 143 K.

Nuclear magnetic resonance spectroscopy

N.m.r. spectra were obtained using a JEOL GX400 NMR spectrometer, operating at 100 MHz for carbon detection and 400 MHz for proton detection. Proton spectra were obtained by accumulating 8 K data points over a spectral width of 4400 Hz, using a 7.0 μs, 90° pulse with a recycle delay of 4 s between acquisitions. ^{13}C n.m.r. spectra were obtained with accumulation of 32 K data points covering a spectral width of 22 000 Hz, and a 9.1 μs, 90° pulse. Samples were prepared in $CDCl_3$ at a concentration of 10% (w/v), using TMS as an internal reference which was defined as 0 ppm for both carbon and proton chemical shifts.

Infra-red spectroscopy

Conversion data were obtained using a Perkin-Elmer 1600 spectrometer operating in the near infra-red (n.i.r.) region fitted with an external bench MCT detector. The intensity of the band at around 6150 cm^{-1} was used, arising from the reacting double bond. The sample in a 5 mm o.d. tube was placed in a custom built, thermostated aluminium heater block, with an entry and exit port for the infra-red beam, and polymerized at the desired temperature. Accumulation of 32 scans at a resolution of 2 cm^{-1} was repeated to give a single data point every 2 min in the conversion profile.

Gel permeation chromatography

G.p.c. studies were made with a Waters Chromatograph with microstyragel columns (10^2–10^6 Å) and a refractive index detector. The elution solvent was tetrahydrofuran at a temperature at 21°C. The columns were calibrated with polystyrene standards.

RESULTS AND DISCUSSION

Measurement of conversion

A typical *FT*n.i.r. spectrum of the mixture of MMA/CR39 is shown in *Figure 1*. The absorption peak is broad which indicates the presence of two overlapping peaks which can be deconvoluted as shown in the figure. By collecting the spectra of pure MMA and CR39 monomers, the peak at 6165 cm^{-1} was assigned to the overtone band of the double bond of MMA and the peak at 6130 cm^{-1} to the CR39 double bond overtone. By peak fitting using a software program called GRAMS, it is possible to follow the reaction of the individual monomers. A typical conversion plot obtained from the data is shown in *Figure 2*.

Figure 2 shows the individual MMA and CR39 conversion curves for the 50/50 MMA/CR39 sample at 60°C with 1% BPO as the initiator. Very little polymerization of CR39 is indicated until MMA reaches about 50% conversion. Significant polymerization of CR39 then commences, but it is still at a much lower rate than that of MMA, until MMA reaches about 90% conversion. The reaction rates of MMA and CR39 were then similar. The homopolymerization of MMA and CR39 under similar conditions are shown in *Figure 3*. Comparing the two figures indicates that the gel effect commences about 50% conversion in the copolymerization, compared to about 30% conversion in the homopolymerization of MMA. However, the conversion reaction in the pre-gel period was faster in the presence of CR39. This is due to the increase in viscosity of the mixture in the presence of CR39. The values are given in *Table 1*.

The difference between these observations and the homopolymerization of CR39, as indicated by *Figures 2* and *3*, is also interesting. The reaction rate for the homopolymerization of CR39 is very low and remains low, even after 11 000 s (3 h). To obtain reasonable polymerization rates for CR39, normally BPO concentrations of

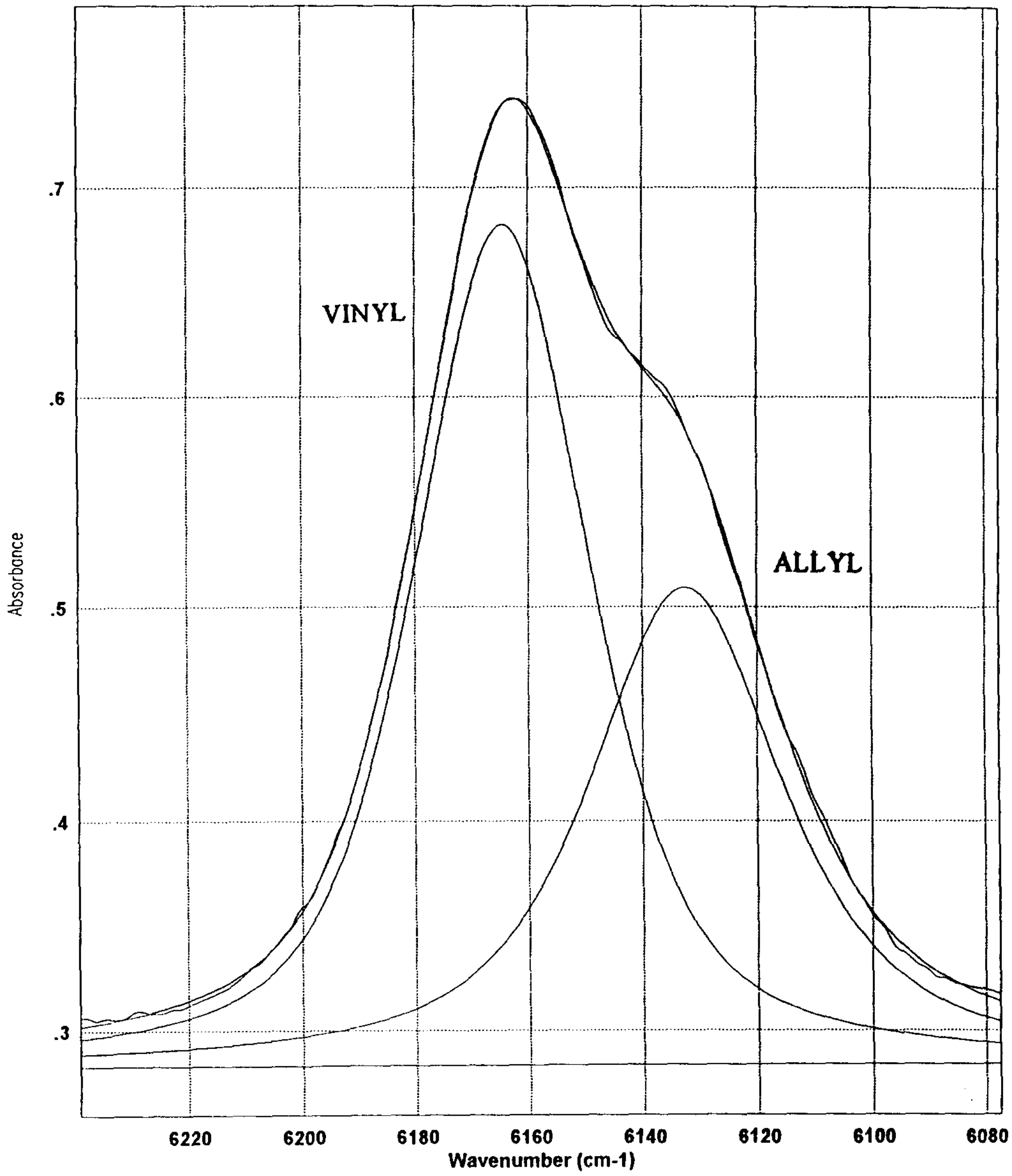

Figure 1 N.i.r. spectrum of 50/50 mixture of MMA and CR39 showing the MMA and CR39 double bond overtone peaks

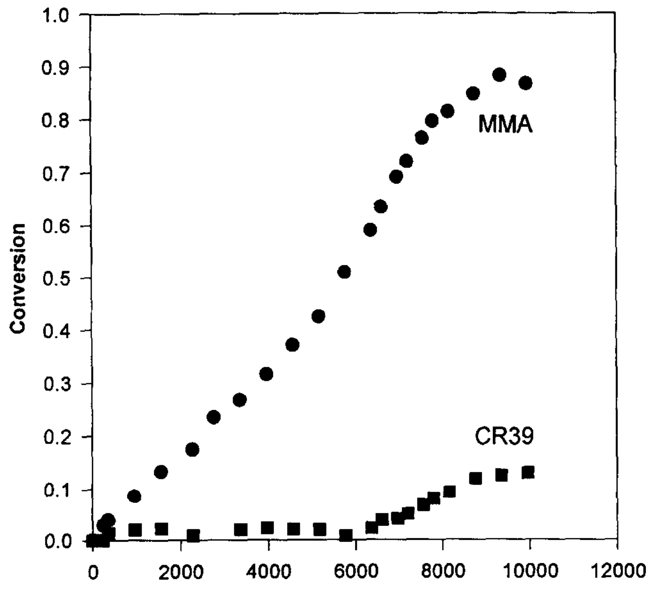

Figure 2 Conversion of MMA and CR39 double bonds in a 50/50 mixture at 60°C with 1% BPO

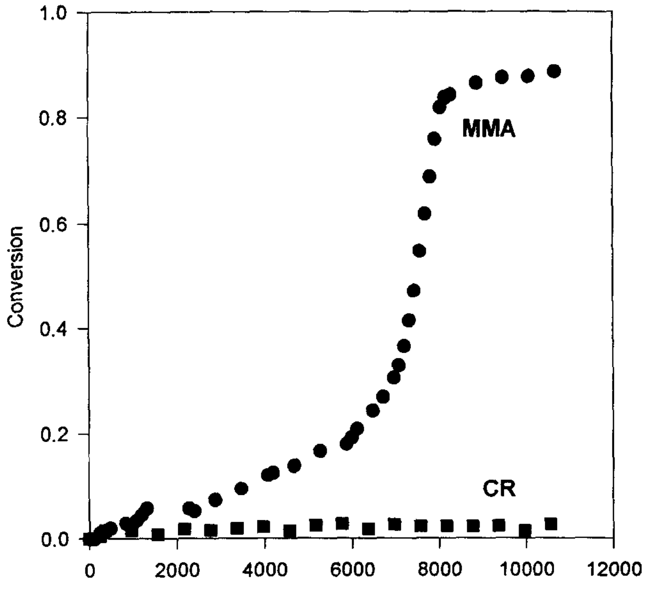

Figure 3 Conversion of MMA and CR39 double bonds in a homopolymerization at 60°C with 1% BPO

Table 1 Viscosity and initial polymerization rates of mixtures of MMA and CR39

MMA (%)	Initial $R_p \times 10^{-4}$ (mol l^{-1} s^{-1})	Initial viscosity (mPa s)
100	2.72	0.6
90		2.29
75	3.0	4.83
50	4.1	8.55
25	2.4	13.28

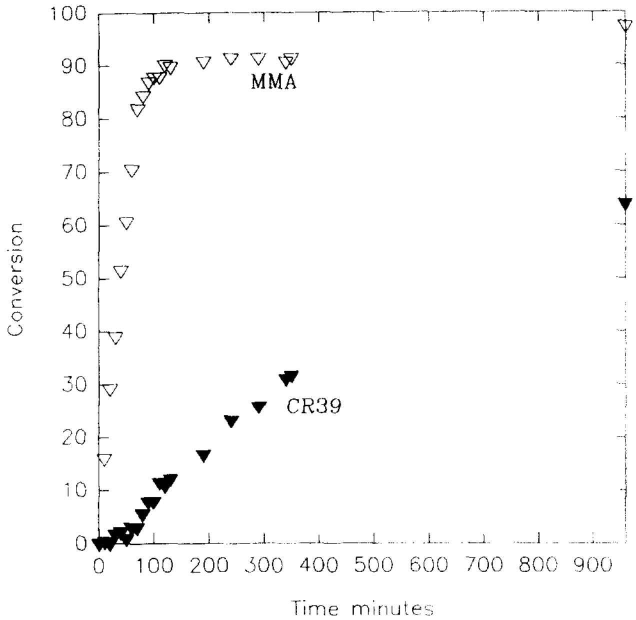

Figure 4 Conversion of MMA and CR39 double bonds in a 50/50 mixture at 75°C with 1% BPO

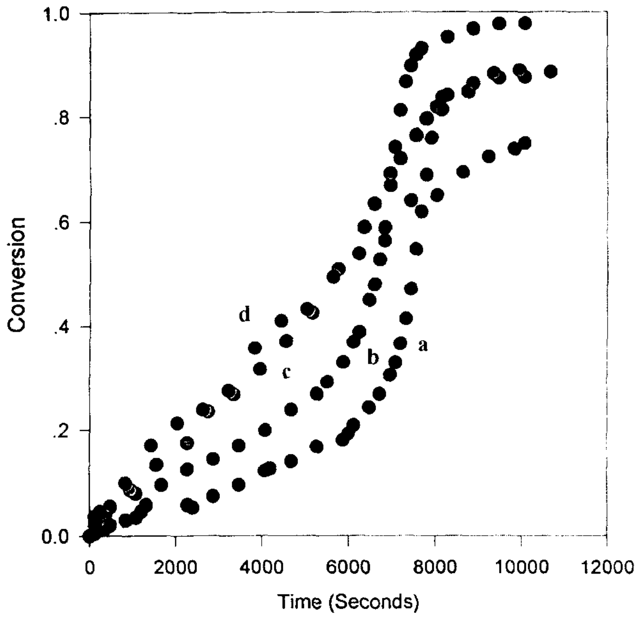

Figure 5 Conversion of MMA double bonds (a) 1/0, (b) 3/1, (c) 1/1 and (d) 1/3 MMA/CR39 proportions at 60°C with 1% BPO

about 3% and a temperature of 75°C was used. Under the conditions in *Figure 2* in the presence of MMA, the rate of polymerization of CR39 increases at about 6000 s (less than 2 h). This is as a result of the increase in the viscosity of the system with the formation of the poly(MMA), thus reducing radical termination and chain transfer.

An increase in the reaction temperature from 60 to 75°C, makes only a small change to the reaction features (*Figure 4*), other than an increase in rate. However under these conditions, CR39 seems to undergo reaction at low MMA conversion; the reaction rate of CR39 starts to increase at about 60% MMA conversion. In both cases, when MMA reaches 90% conversion, CR39 has reacted only to about 15% conversion. The reaction of CR39 then continues at a higher rate, while the rate of reaction of MMA begins to slow.

Conversion of MMA in the presence of different proportions of CR39 is shown in *Figure 5*. The known sigmoidal shape for MMA polymerization is observed in the composition range 0% to 25% CR39. That is, there is a gel effect in the presence of 25% CR39. However, by contrast, at 25% CR39, the MMA reached 100% conversion, but for homopolymerization of MMA only 90% conversion was reached under similar conditions. At 50% and 75% CR39 contents no gel effect was observed, but the reaction rates at high conversion become smaller and the polymerization takes much longer to reach full conversion of MMA. For similar polymerization time intervals, 90% conversion was reached for 50% CR39 composition, while less than 80% conversion was observed for 75% CR39. CR39 undergoes crosslinking during polymerization and it forms a network (gel) at about 23% conversion. The drop in the limiting conversion is due to increased crosslinking at the higher CR39 contents. On the other hand, the presence of a similar mole fraction of divinyl monomer, such as EGDMA, increases the initial rate of polymerization and decreases the time to the onset of the gel acceleration in the rate. Further, the monomer conversion at which auto-acceleration starts, decreases with increasing divinyl monomer content. The limiting conversion, increases with the amount of divinyl monomer to a maximum of 98% at 1% EGDMA, and then it decreases with a further increase in the divinyl monomer content. In the case of CR39, the final conversion reaches a maximum (98%) at much higher CR39 contents (25%).

Rates of MMA consumption during the initial period were calculated and are given in *Table 1*. There is an increase in the rate to a maximum with increasing CR39 content, and then it reduces. All of these above observations can be understood by considering the well known free radical polymerization steps; initiation, propagation, termination and chain transfer. The polymer radicals grow rapidly by propagating and then, when one radical centre meets another, they can terminate. At low conversion the bimolecular termination process has been postulated to consist of three steps: translational diffusion, segmental diffusion and chemical reaction. Free radicals are highly reactive species, therefore the magnitude of the rate constant for termination depends on the first two steps. At low conversion, it is controlled by segmental diffusion, but after sufficient polymerization occurs, the polymer molecules become entangled and or chemically crosslinked, and then the termination reaction becomes translational diffusion controlled. This diffusion control of the termination reaction gives rise to the auto-acceleration effect when the termination rate decreases,

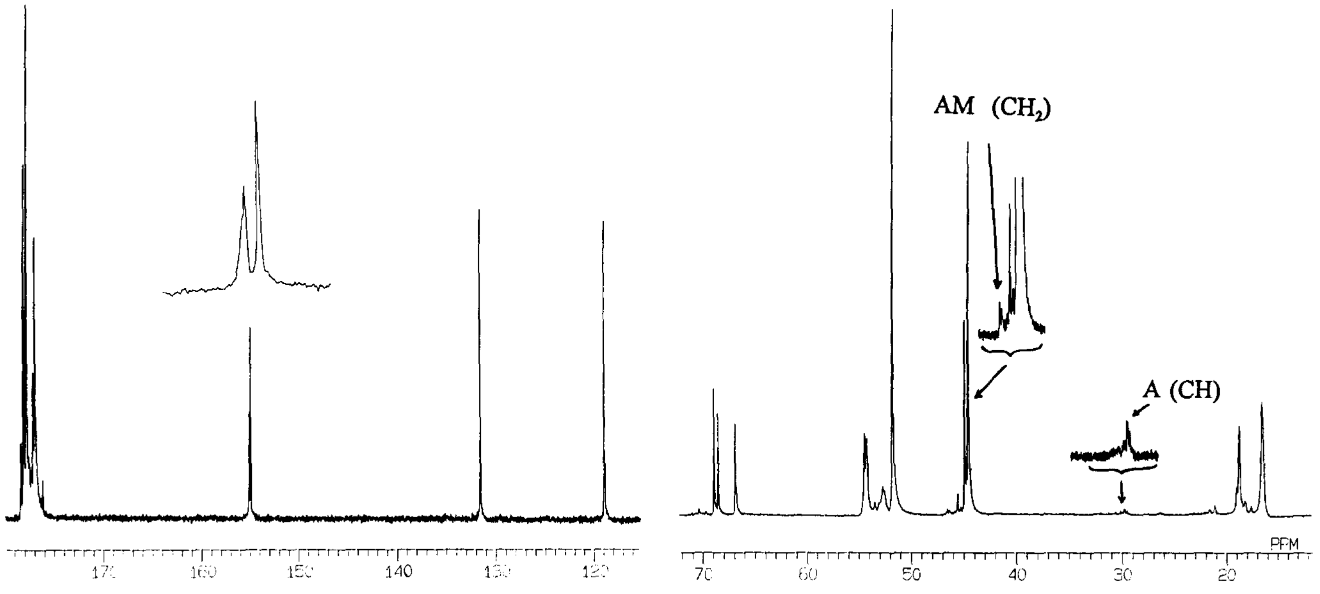

Figure 6 ^{13}C n.m.r. spectrum of MMA/CR39 1/3 mixture cured for 10% conversion

which leads to a rapid increase in the radical concentration. The increase in the radical concentration produces an increase in the propagation rate.

Addition of CR39 to MMA increases the viscosity of the system as shown in *Table 1*. The increase in the viscosity lowers the termination rate constant, which in turn increases the radical concentration, as will be discussed later, and so increases the rate of polymerization. However, at a content of 75% CR39 the amount of MMA in the feed is such that the polymerization rate is lower than that for pure MMA. Since during the initial stages of polymerization, MMA polymerizes predominantly, the concentration of PMMA in the system at a particular time is smaller for increasing CR39 contents. Furthermore, unreacted CR39 plasticizes the system, so that for the polymerization of 50/50 and 25/75 MMA/CR39 mixtures, the viscosity is not lowered during the polymerization to the point where k_t decreases sufficiently so as to increase the radical concentration rapidly and induce an auto-acceleration. At very high conversions, in samples containing CR39, the system is sufficiently mobile for the MMA molecules to diffuse readily and polymerize to complete conversion of this monomer. However, since CR39 undergoes crosslinking, with increasing CR39 content, the density of crosslinking increases at any given double bond conversion. The crosslinking would reduce the reaction rate, hence the polymerization rates are lower at high conversion in 50% and 75% CR39 samples. Further, as we discussed in the introduction, allylic monomers undergo chain transfer to the monomer during polymerization, and addition of a chain transfer agent to the MMA/EGDMA system is known[9] to reduce the final double bond conversion.

Structure of the product

The ^{13}C n.m.r. spectrum of the 10% conversion product of the 25/75, MMA/CR39 sample is given in *Figure 6*. In spite of the high concentration of CR39 in the feed, the spectrum resembles that of PMMA except for the peaks at 66–70 ppm, 119, 132 ppm and 156 ppm, which are due to CR39, and two very small peaks at 30 ppm and 46.5 ppm. The peak at 46.5 ppm is due to the CH_2 of the backbone in a CM dyad and the peak at 30 ppm is due to the backbone CH of the CR39 group[15]. In the CC dyad, the backbone CH_2 should appear at 35–39 ppm[17]. Since this peak is not observed, it is apparent that the CR39 units are isolated in the polymer. However, the presence of the CM dyad resonance confirms the formation of a copolymer.

Once the formation of a copolymer was confirmed, the data from *FT*i.r. experiments were used to determine the copolymer composition at each feed composition. These values were then used to calculate the terminal model reactivity ratios, which were $r_C = 0.032$ and $r_M = 32.0$. The product $r_C r_M = 1.01$ indicates that the copolymer is statistical and the copolymerization conforms to Bernoullian statistics, whereby the probability of adding a particular monomer is independent of the unit at the chain end.

Therefore during the copolymerization of MMA and CR39, initially the MMA reacts predominantly, with few CR39 units becoming incorporated in the polymer chains. However once the MMA conversion reaches 90%, the polymerization of the CR39 commences. In these late stages of polymerization, the polymer chains are predominantly of CR39 with few MMA units in the chains. Thus the end product contains predominantly two components; namely poly(MMA) chains with few randomly located CR39 units, and poly(CR39) chains with few MMA units randomly located in the chains. The copolymer chains may be held together by crosslinks that are formed through the CR39 molecules in both chain types.

Molecular weight changes

The molecular weights of the polymers at 10% total conversion with different proportions of MMA and CR39 are given in *Table 2*. At 10% total conversion all of these samples are in the pre-gel period, hence the values could be compared. As observed in the n.m.r. at this stage of polymerization the polymers are predominantly PMMA with very few CR39 molecules in the structure. Thus the contribution of CR39 to determining the molecular weights of polymers containing only a small amount of CR39 may be considered to be negligible.

The role of the CR39 in the feed in determining the

Table 2 Molecular weights of polymer formed at 10% conversion

MMA (%)	$M_n 10^5$ (g mol^{-1})	M_w/M_n
100	1.1	1.78
90	2.7	1.52
75	3.1	1.5
50	2.4	1.7
25	2.1	1.8

polymer molecular weight can be attributed to two factors. First the increase in the viscosity reduces[18,19] the termination rate, thus increasing the molecular weight. The change in viscosity and initial rates of reactions are given in *Table 1*. The termination rate constant k_t for MMA polymerization at 30°C is known[19] to change from 6.3×10^4 to $1.9 \times 10^4\,\mathrm{l\,mol^{-1}\,s^{-1}}$. Second, the possibility of chain transfer to a CR39 molecule will reduce the polymer molecular weight. Due to the difficulty in identifying the individual contributions of termination and chain transfer, it was not possible to estimate the chain transfer rate constant from the molecular weight data. However, since the molecular weights are of the order of 10^5 compared to 10^2 for homopolymerization of CR39, it is reasonable to assume that the rate of chain transfer from the MMA propagating radical to the allyl monomer is small compared to that for propagation.

Radical measurements

Information regarding the nature and the concentration of radicals formed during free radical polymerization is required for estimation of the kinetic rate parameters. The e.s.r. spectrum obtained during the polymerization of a 50/50 mixture of MMA and CR39 is shown in *Figure 7*. In the polymerization of MMA, in the pre-gel region, where the viscosity of the polymerizing mixture is low, a 13 line spectrum is observed, but near the gel-point (25% conversion), where the viscosity is much higher, this 13 line spectrum changes to a nine line spectrum[20]. In the polymerization of a MMA/CR39 mixture of composition 3/1, the nine line spectrum is not observed up to a conversion of approximately 75%. At this conversion, almost all of the MMA monomer has reacted. For a MMA/CR39 mixture of composition 1/1, the nine line spectrum cannot be observed through the whole conversion range. Even when an auto-acceleration is observed in the polymerization of a MMA/CR39 mixture of 3/1, the radicals with 13 line conformation were observed.

At 60% total conversion, the eight line spectrum of the allylic radical[13,14] was observed, followed at further conversion by the broad three line spectrum which has been assigned[21] to a mixture of allyl and propagating radicals of CR39. At very high conversion the broad

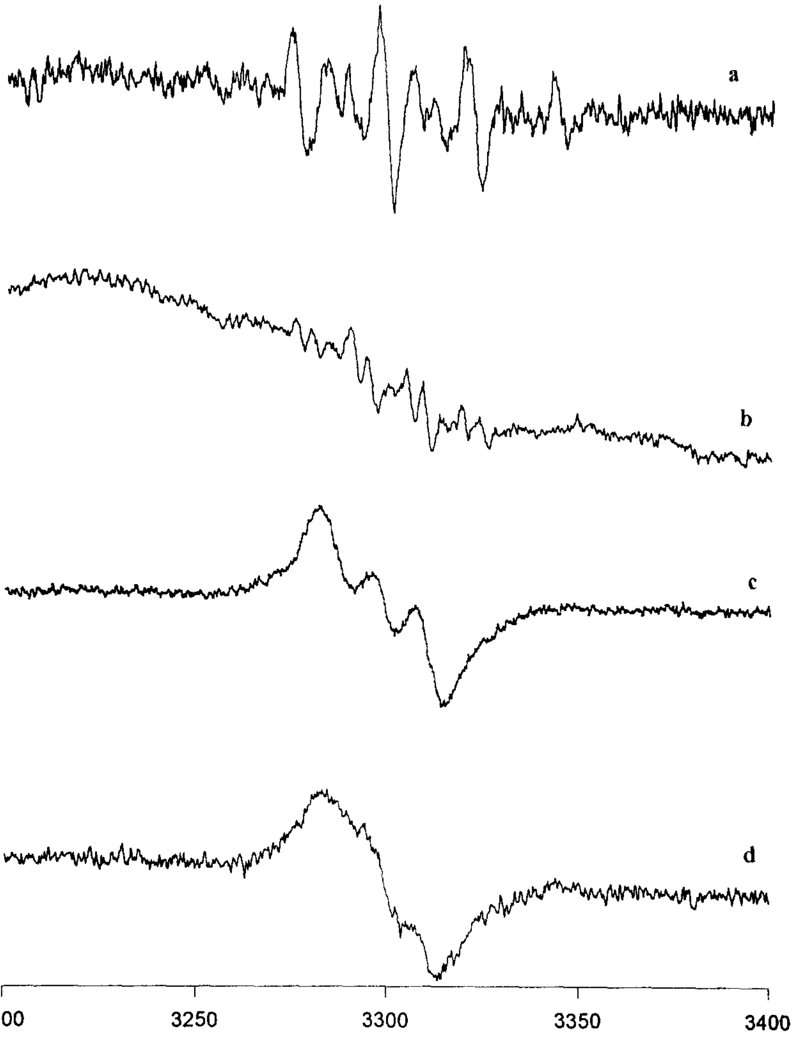

Figure 7 E.s.r. spectra of a MMA/CR39 1/1 mixture at 60°C with 1% BPO at (a) 30, (b) 60, (c) 67 and (d) 98% total conversions

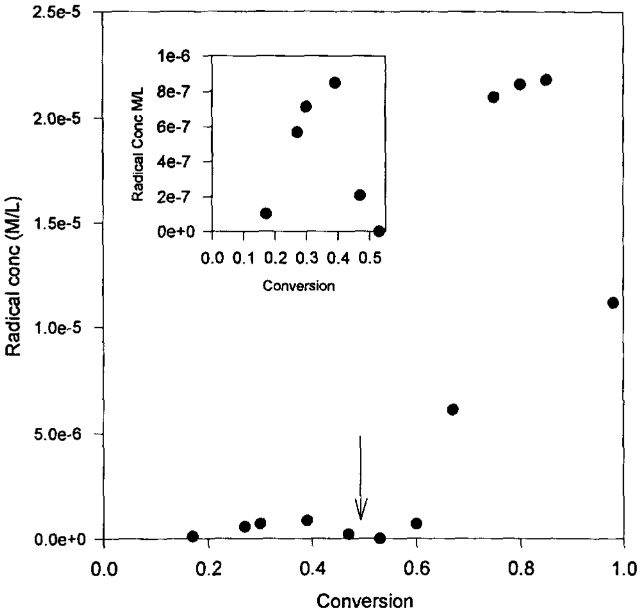

Figure 8 Radical concentration vs conversion of a MMA/CR39 1/1 mixture at 60°C with 1% BPO

spectrum of the trapped CR39 allyl radicals[21] are observed.

The radical concentration measured by integrating the e.s.r. peaks are given in *Figure 8* for the MMA/CR39 mixture of composition 1/1. An initial increase in the radical concentration at conversions where only the MMA propagating radical is observed, is followed by a drop to zero at 50% total conversion. From the conversion data described above, most of the MMA has reacted at this total conversion. The polymerization of CR39 then commences with the observation of the typical allylic radical spectrum. When the spectrum becomes broader, the radical concentration starts to increase. Finally, at about 90% total conversion, the radical concentration starts to drop once again. The increase and then the decrease in the radical concentration between 0–50% total conversion is indicative of the mobile nature of the system even at high MMA conversions. This is due to the plasticizing effect of the CR39 in the system. The maximum MMA propagating radical concentration is observed at 40% total conversion, which corresponds to about 90% reaction of the MMA in the system. Similarly in the 3/1 and 1/3 MMA/CR39 systems, the maximum for the MMA propagating radical concentration was observed at about 90% MMA conversion.

This pattern in the variation of the radical concentration with conversion is completely different from that which was observed[8] in the polymerization of MMA, with or without added dimethacrylate or diacrylate crosslinkers. In these systems a rapid increase in the radical concentration was observed at about 30% conversion, due to the onset of the well documented auto-acceleration. However, no similar increases in radical concentrations were observed at these conversions for the MMA/CR39 copolymerizations. Thus a reduction in the termination rate due to the presence of physical entanglements or crosslinking is not observed here. As for the homopolymerization of CR39, the increase in the radical concentration commences after about 60% total conversion. Further, by contrast with the MMA/EGDMA system in the MMA/CR39 polymerization, the radical concentration starts to drop at high conversion.

Kinetic analysis

The kinetic equations for copolymerization can be represented by the following scheme, where M_1 is MMA and M_2 is CR39.

$$\text{Initiation } I \rightarrow 2R^{\cdot}\ k_d \tag{1}$$

$$R + M_1 \rightarrow M_1^{\cdot} \tag{2}$$

$$\text{Propagation } M_1^{\cdot} + M_1 \rightarrow M_1^{\cdot}\ k_{p11} \tag{3}$$

$$M_1^{\cdot} + M_2 \rightarrow M_2^{\cdot}\ k_{p12} \tag{4}$$

$$M_2^{\cdot} + M_1 \rightarrow M_1^{\cdot}\ k_{p21} \tag{5}$$

$$M_2^{\cdot} + M_2 \rightarrow M_2^{\cdot}\ k_{p22} \tag{6}$$

$$\text{Chain transfer } M_1^{\cdot} + M_2 \rightarrow P + A^{\cdot}\ k_{tr} \tag{7}$$

$$\text{Termination } M_1^{\cdot} + M_1^{\cdot} \rightarrow P\ k_n \tag{8}$$

$$A^{\cdot} + A^{\cdot} \rightarrow A\text{–}A\ k_{ta} \tag{9}$$

$$M_1^{\cdot} + A^{\cdot} \rightarrow P\ k_{tb} \tag{10}$$

$$M_2^{\cdot} + M_2^{\cdot} \rightarrow P\ k_{t2} \tag{11}$$

As shown by the n.m.r. data, the copolymer produced in the initial stages is composed mostly of the MMA. Equations (4), (6) and (11) can therefore be ignored in these early stages of polymerization. This yields $r_M = k_{p11}/k_{p12} = 32$. Even though $r_C = k_{p22}/k_{p21} = 0.032$ indicates a high k_{p21} value, because there is no evidence for significant concentrations of CR39 propagation radicals, equations (5) and (11) also may be ignored. The very low polymerization rate of CR39 compared to MMA in the initial stages of polymerization, supports the assumption that the initiator fragments are transferred to MMA propagating radicals as shown in equation (2). Thus the corresponding equation for CR39 can be ignored. The g.p.c. results indicate that chain transfer from the MMA propagating radical to a CR39 molecule is also negligible. Therefore to a first approximation, equation (7) may also be ignored. This also eliminates equations (9) and (10). Therefore, the initial period of the polymerization, to a first approximation, can be treated as being similar to the normal homopolymerization kinetics of MMA, including only equations (1), (2), (3) and (8). Thus,

$$k_p = k_{p11} = R_p/([M][M^{\cdot}]) \tag{12}$$

$$k_t = k_{t1} = 2fk_d[I]/[M^{\cdot}]^2 \tag{13}$$

The values of k_p and k_t for the pre-gel period calculated using equations (12) and (13) are given in *Table 3*. In these calculations it was assumed that the initiator efficiency, $f = 0.85$ and initiator decomposition rate constant, $k_d = 2.44 \times 10^{-6}\,s^{-1}$. The calculated values indicate that there is no change in k_p for MMA polymerization in the presence of CR39. However, as expected, the k_t drops with increasing CR39 content because of the increase in the viscosity of the comonomer mixture.

CONCLUSIONS

The presence of CR39 eliminates the gel effect in the polymerization of MMA/CR39 mixtures. However the presence of the comonomer was found to increase the

Table 3 Radical concentrations and rate constants at low conversion

MMA (%)	$[M_1] \times 10^{-7}$ (mol l^{-1})	k_p (l mol^{-1} s^{-1})	$k_t \times 10^{-7}$ (l mol^{-1} s^{-1})
100	9.3	323	1.8
75	4.0	300	0.5
50	1.0	340	0.08
25	3.6	335	0.13

polymerization rate of each monomer at different stages of polymerization.

The n.m.r. studies indicate the partial incorporation of CR39 units to the polymer during the early stages of the copolymerization. The reactivity ratios for the free radical copolymerization of MMA and CR39 were evaluated using n.i.r. data. They confirm the low tendency towards copolymerization of the allylic double bond.

The g.p.c. data indicate very little chain transfer takes place from the MMA propagating radical to the CR39 monomer.

The e.s.r. spectra show that the presence of CR39 in the mixture ensures that the 13 line confirmation of the MMA propagating radical is present to much higher conversions than is the case for homopolymerization of MMA.

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