Conformation, environment and reactivity of radicals in copolymerization of methyl methacrylate/ethylene glycol dimethacrylate

Y. Tian, S. Zhu and A. E. Hamielec*
Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

D. B. Fulton and D. R. Eaton
Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4L7

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The electron spin resonance (e.s.r.) spectra of radicals observed during the copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) consist of 13 lines in the initial liquid phase, but change to 9 lines as the copolymerization proceeds. The experimental spectra have been simulated by use of a model based upon a Gaussian distribution of dihedral angles about a most stable conformation. The simulations suggest that the e.s.r. spectra are superpositions of spectra arising from three types of radicals: a liquid-phase radical giving rise to a 13-line spectrum and two solid-phase radicals giving rise to two slightly different 9-line spectra. The two types of 9-line spectra correspond to terminal radicals on EGDMA and MMA residues. The ratio of the two types of solid-phase radicals is correlated with the degree of disorder of the reacting system, which accounts for the observed dependence of both initiator efficiency and final radical concentration upon the weight fraction of EGDMA. When copolymerization proceeded to medium conversion, ultra-violet irradiation of the samples reinitiated the reaction and caused a temporary reappearance of the 13-line spectrum, indicating that some propagating radicals are trapped in the polymer matrix.

(**Keywords: conformation; radical; copolymerization; electron spin resonance; modelling; methyl methacrylate; ethylene glycol dimethacrylate**)

INTRODUCTION

It has long been recognized that physical factors such as diffusion, heterogeneity and solvation play an important role in determining the reaction kinetics of polymerizing systems. In a free-radical polymerization, the autoacceleration effect, the glass transition effect and the trapping effect are typical examples of the complexities encountered. E.s.r. has a special advantage in the study of these effects because it can be used to investigate directly both radical concentrations and environments. However, there exist two difficulties in its application. First, the e.s.r. instrument must be sufficiently sensitive to measure the low radical concentrations (about 10^{-7} mol l^{-1}) that commonly occur in low-conversion free-radical polymerizations. This problem, to some extent, has been solved by the use of special e.s.r. cavities[1–3]. Secondly, the e.s.r. spectra must be correctly interpreted. Methods for simulating e.s.r. spectra have advanced significantly since the 1950s, but their application to polymerization systems has lagged.

This work is part of a continuing study of the mechanism and kinetics of the copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA)[4–8]. The present objective is to clarify the relationship between the e.s.r. spectra and the radical conformations, environments and reactivities.

EXPERIMENTAL RESULTS

For convenience, we introduce terminology to describe the e.s.r. spectra of MMA/EGDMA radicals. Two kinds of e.s.r. spectra were observed, shown in *Figures 1a* and *1b*: a '13-line' spectrum, arising from radicals in the initial liquid material, and a '9-line' spectrum, arising from radicals in the polymerized glassy material. The 13 lines of the first type of spectrum can be divided into two groups: an inner eight lines (relative intensities 1, 1, 3, 3, 3, 3, 1, 1) and an outer five lines (1, 4, 6, 4, 1). The 9-line spectrum can also be divided into two groups of lines: an inner four lines (1, 3, 3, 1) and an outer five lines (1, 4, 6, 4, 1). The intensity ratio of the inner and outer lines is given by Y/X, defined in *Figures 1c* and *1d* for both types of spectrum.

On-line e.s.r. spectra were recorded during copolymerization of reaction systems containing various concentrations of MMA and EGDMA (0, 1, 3, 5, 10, 15, 25, 50 and 100 wt% EGDMA), and 0.3 wt% azobisisobutyronitrile (the decomposition rate constant at 70°C is 3.12×10^{-5} s^{-1} (ref. 9), i.e. the half-life is

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* To whom correspondence should be addressed

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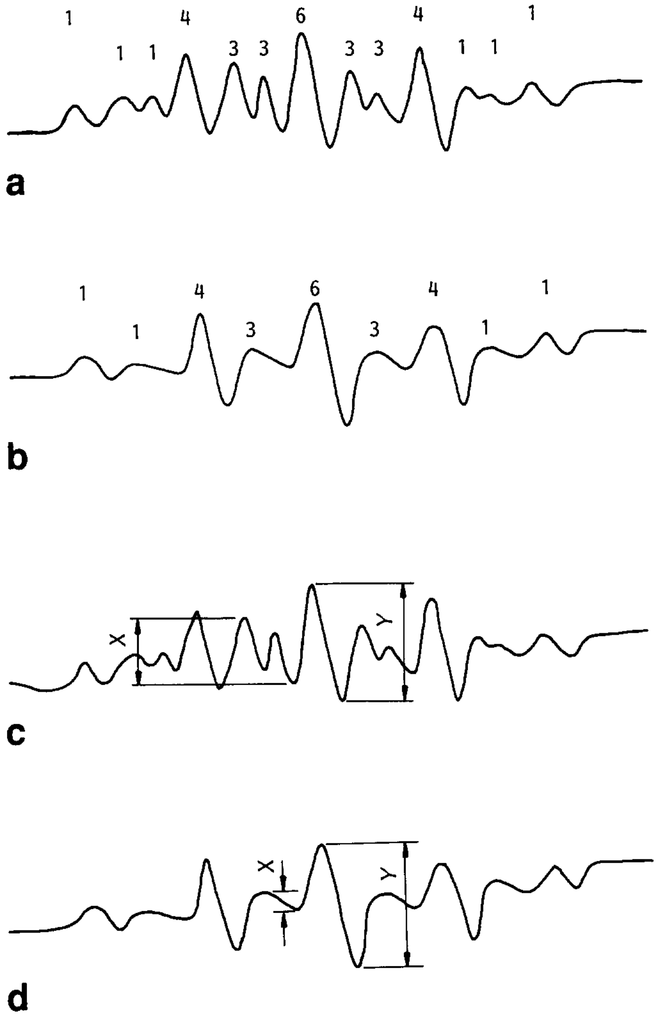

Figure 1 Typical e.s.r. spectra of radicals during MMA/EGDMA copolymerization: (a) typical '13-line' spectrum; (b) typical 'nine-line' spectrum; (c) definition of X and Y for 13-line spectra; (d) definition of X and Y for nine-line spectra. All spectra herein were recorded at X-band (microwave frequency, 9.45 GHz) using a TE102 cavity

about 6 h) as initiator. The reactants were purified, degassed and sealed in Pyrex ampoules as is described in ref. 4. The reaction mixtures were kept in a liquid-nitrogen bath until copolymerization was initiated in the e.s.r. cavity by raising the sample temperature to 70 ± 0.5°C. In each case, in addition to a general increase in signal intensity due to the growing radical concentration, the spectral lineshapes changed during the course of the reaction. The spectra for 15 wt% EGDMA, shown in *Figure 2a*, are typical. Initially the 13-line spectrum was observed. The inner eight lines broadened and finally coalesced to produce the nine-line spectrum. It is evident from *Figure 2a* that appreciable change in lineshape occurred during the sweep-time (about half a minute) required to record each spectrum. Therefore partial spectra, requiring a shorter sweep-time (about 10 s), were also recorded (*Figure 3a*). These spectra display the region of interest, i.e. one of the coalescence regions, and are subject to less distortion from polymerization during the sweep-time. Computer simulations of the experimental spectra were generated (*Figures 2b* and *3b*), based on a model described in detail in the next section.

The intensity ratio of inner and outer lines, Y/X, was measured as a function of time for each reaction system (*Figure 4a*). The value of Y/X levelled off during the final stage of copolymerization, as each system approached its glassy state. When the monomer weight fraction of EGDMA was increased, the following trends were observed in the 9-line spectra measured during the final stage of copolymerization: (1) the limiting Y/X value increased (*Figure 4b*) and (2) the widths of the inner four lines decreased (*Figure 5*).

The polymerized samples were kept at room temperature for two months and the residual radical concentrations of each were then measured (*Table 1*) by integrating their e.s.r. spectra. In pure poly(MMA) about 80% of the radicals disappeared, whereas in pure poly(EGDMA) the radical concentration was unchanged.

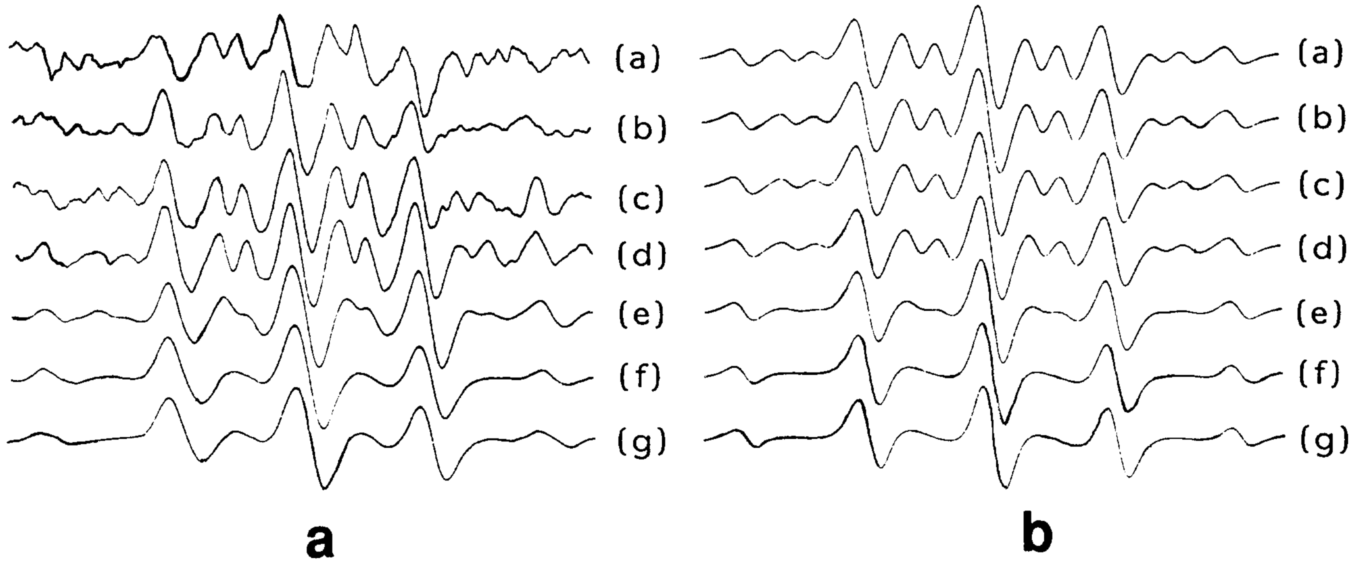

Figure 2 (a) Experimental e.s.r. spectra of radicals in the copolymerization of MMA/EGDMA with weight fraction 85/15. Experimental parameters: microwave frequency, 9.45 GHz; modulation frequency, 100 kHz; modulation amplitude, 3.2 Gpp; sweep-time, 30 s; scan range, 3310 to 3439 G; polymerization time (min), (a) 12, (b) 13, (c) 13.33, (d) 13.66; (e) 14, (f) 14.33; (g) 15; $T = 70°C$; AIBN, 0.3 wt%. (b) Simulated e.s.r. spectra of MMA/EGDMA radicals, consisting of superpositions of a 13-line spectrum (liquid 65/55 conformation) and a nine-line spectrum (65/55 plus 60/60 conformations with a Gaussian distribution). Simulation parameters: linewidth, 4 G; halfwidth of Gaussian distribution of solid radical, 10.5°; ratio of 60/60 to 65/55 conformation of solid radical, 85:15; ratio of liquid radical to solid radical, (a) 1:10, (b) 1:5, (c) 3:10, (d) 2:5, (e) 85:100, (f) 98:100, (g) 0:100

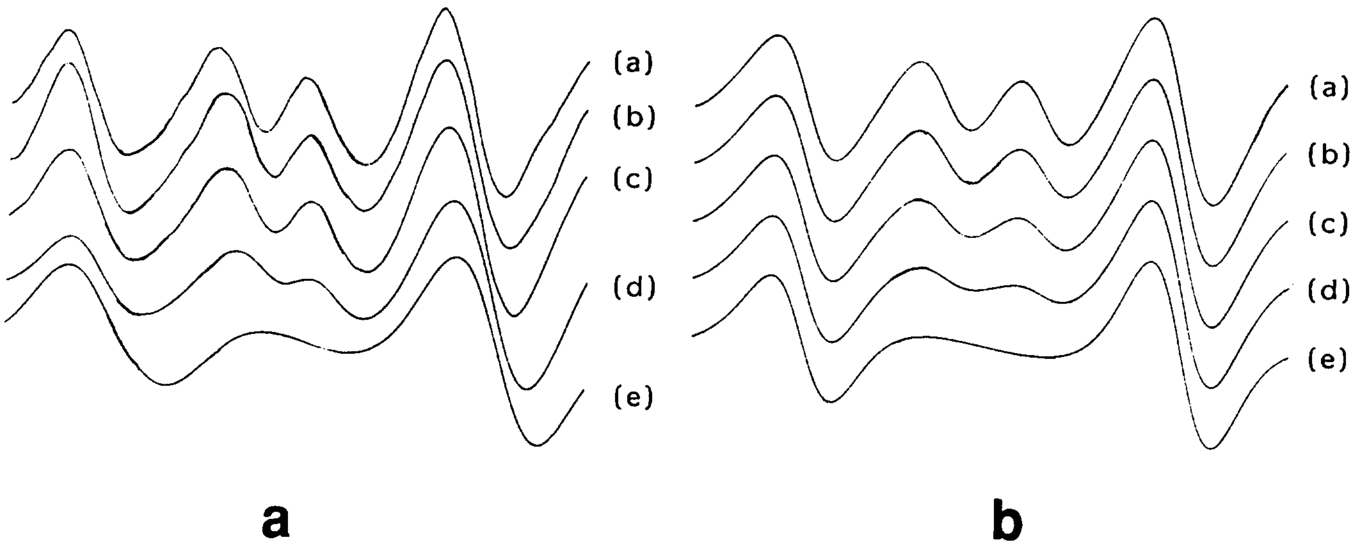

Figure 3 (a) Experimental e.s.r. spectra of radicals in the copolymerization of MMA/EGDMA with weight fraction 85/15. Experimental parameters as for *Figure 2a* except: sweep-time, 10 s; scan range, 3352 to 3392 G; reaction time (min), (a) 13.5, (b) 13.67, (c) 13.83, (d) 14, (e) 14.33. (b) Simulated e.s.r. spectra of MMA/EGDMA radicals. Simulation parameters as for *Figure 2b* except: ratio of liquid radical to solid radical, (a) 100:0, (b) 3:1, (c) 1:1, (d) 1:3, (e) 0:100

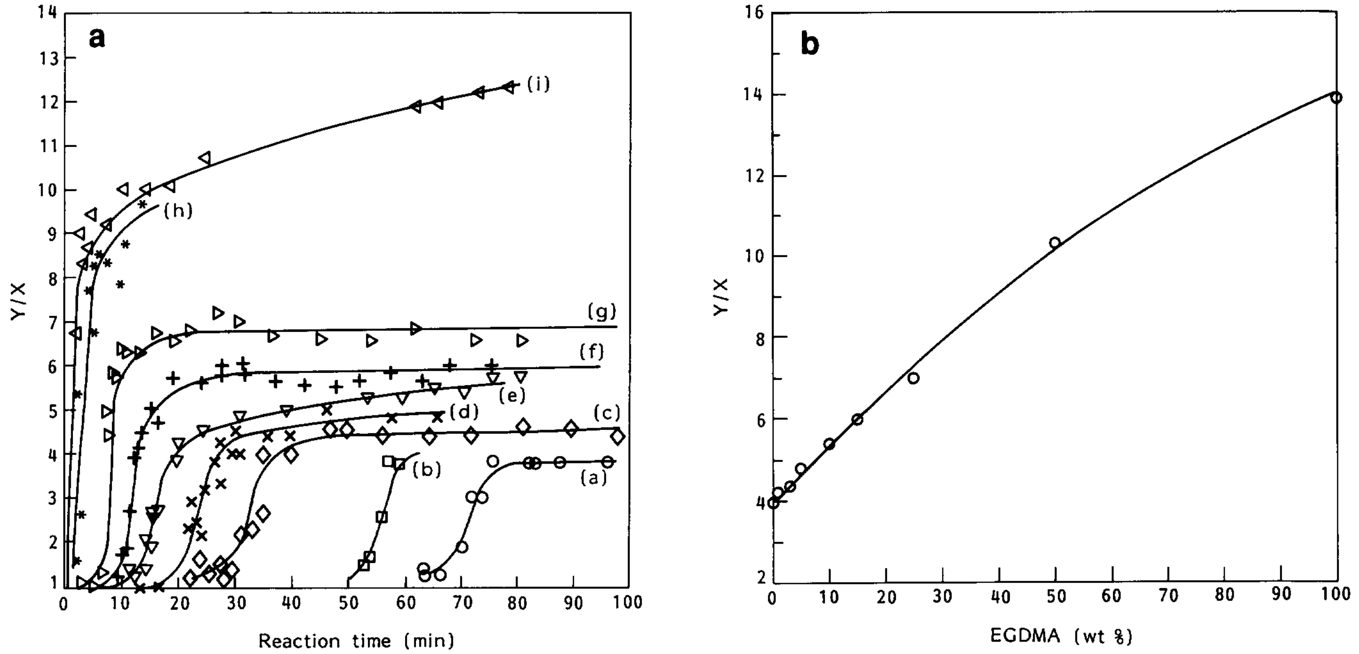

Figure 4 (a) The ratio of the intensity of inner four lines and outer five lines (Y/X) *versus* polymerization time for various EGDMA levels. Temperature, 70°C; AIBN, 0.3 wt%; EGDMA (wt%), (a) 0.0, (b) 1.0, (c) 3.0, (d) 5.0, (e) 10.0, (f) 15.0, (g) 25.0, (h) 50.0, (i) 100.0. (b) Limiting Y/X as a function of EGDMA level; data are from *Figure 4a*

DISCUSSION

Interpretation of the e.s.r. spectra

The e.s.r. spectra of poly(MMA) radicals have been interpreted in terms of a model, depicted in *Figure 6a*. The unpaired electron density ($S = 1/2$) is assumed to be localized in a p-orbital on the α-carbon, and there is a hyperfine coupling with α-protons on the adjacent methyl group and β-protons on the adjacent methylene group. The α-protons are assumed to be magnetically equivalent owing to free rotation of the methyl group, whereas rotation of the methylene group is assumed to be hindered, so that the β-protons are inequivalent and have hyperfine coupling constants[10] given by:

$$A_q = B\cos^2(\Theta_q)$$

where $q = 1$, 2 and dihedral angles Θ_1, Θ_2 are defined in *Figure 6b*.

The radical sites on crosslinked EGDMA residues are thought to have a structure similar to that shown in *Figure 6a* for MMA radicals, but with a different ester group. We therefore assume that the e.s.r. spectra of EGDMA radicals can also be described by the above model, with slight alterations to the model parameters.

Three elaborations of the above model have been proposed to account for the observed transition from

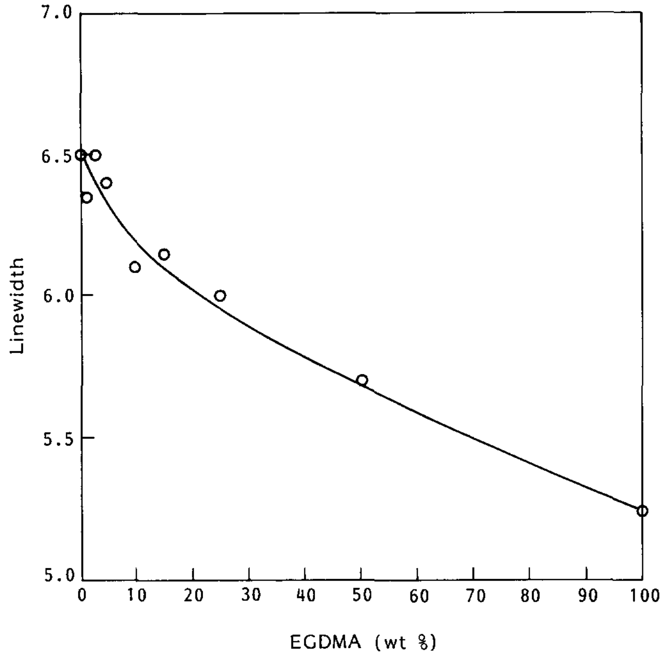

Figure 5 Linewidth of inner four lines of the e.s.r. spectra of MMA/EGDMA radicals observed at high conversion *versus* EGDMA level

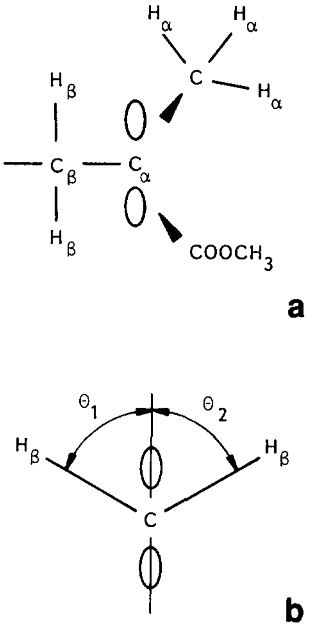

Figure 6 (a) Structure of MMA radical showing the α- and β-protons. (b) Projection of MMA radical structure along the α-carbon–β-carbon axis showing dihedral angles Θ_1 and Θ_2

13-line to 9-line spectra: (1) exchange broadening of two stable conformations[11]; (2) the superposition of spectra due to two or more stable conformations[12,13]; and (3) a Gaussian distribution of the dihedral angles about a most stable conformation[14,15]. In this paper, they are referred to as models 1, 2 and 3, respectively. Simulated spectra based on each of these models were generated and compared with the experimental spectra of the copolymer systems.

Calculations by Kamachi *et al.*[12] indicate that MMA radicals exist in three stable conformations with $\Theta_1 = 60$, 65, 75° ($\Theta_2 = 120° - \Theta_1$), i.e. 60/60, 65/55 and 75/45 conformations, using the notation Θ_1/Θ_2. Exchange between conformations may conceivably occur via bond rotation (model 1). Spectra, broadened by exchange processes among the above conformations, were simulated using calculations based upon a modified form of the Bloch equations[15]. The calculations show that the 65/55 conformation exchanging with the 55/65 conformation gives a spectrum in good agreement with the experimental 13-line spectrum, in the slow exchange limit. As the exchange rate increases, there is a transition to a 9-line spectrum (*Figure 7*). However, simulations based on model 1 predict that the inner four lines of a 9-line spectrum narrow as the exchange rate is increased, which was not experimentally observed. Furthermore, it seems unlikely that the conformational exchange rate, which involves bond rotation, would increase during the transition from liquid to solid. Model 1 has therefore been rejected.

Spectra based on model 2 with various ratios of the 60/60, 65/55 and 75/45 conformations have also been calculated. For some ratios, the calculated spectra consisted of 9 lines, but it was not possible to calculate a spectrum in which both the widths and the intensity distribution of the inner four lines agreed with the experimental spectra. In addition, this model does not account for the change of the spectra from 13 to 9 lines. Model 2 was therefore also ruled out.

Iwasaki *et al.*[11] have reported that simulated spectra based on a Gaussian distribution of dihedral angles about the 65/55 conformation (model 3) show a transition from 13 to 9 lines as the halfwidth of the distribution is increased. The series of spectra shown in *Figure 8* were calculated using this model. The inner eight lines broaden uniformly as the distribution halfwidth increases. The experimental spectra (*Figure 2a*) display somewhat different behaviour: one of each pair of the inner lines (those with relative intensity 3) broadens more rapidly than the other. Also, the simulation based on the 65/55 conformation gives a nine-line spectrum in which the width of the inner four lines is 5 G, whereas in the experimental nine-line spectrum this linewidth varied

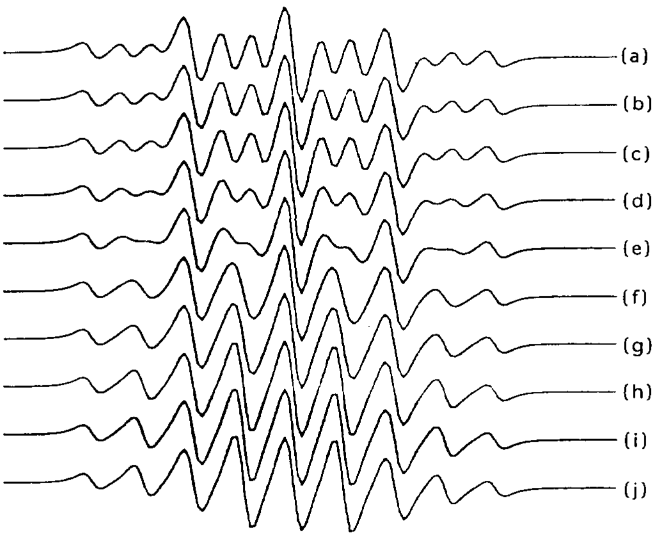

Figure 7 Simulated spectra of MMA radicals with exchange between 65/55 and 55/65 conformations. Relaxation time (s): (a) 1.0×10^{-10}, (b) 5.0×10^{-10}, (c) 1.0×10^{-9}, (d) 5.0×10^{-9}, (e) 1.0×10^{-8} (f) 5.0×10^{-8}, (g) 1.0×10^{-7}, (h) 5.0×10^{-7}, (i) 1.0×10^{-6}, (j) 5.0×10^{-6}

from 7 G for pure MMA polymer to 5.3 G for pure EGDMA polymer. However, simulations based on a distribution about the 60/60 conformation give 9-line spectra in which the width of the inner four lines is 7 G. Clearly, model 3 is also not satisfactory.

We propose that the experimental spectra can be described by a model that is a composite of models 2 and 3, i.e. superpositions of three different Gaussian distributions. The initially observed 13-line spectrum can be simulated by a narrow distribution about the 65/55 conformation. The 9-line spectrum observed at the completion of copolymerization is a superposition of spectra due to (wider) distributions about the 65/55 and 60/60 conformations, corresponding to radicals on EGDMA and MMA residues, respectively. The ratio of the two conformations is proportional to the weight per cent of EGDMA (see *Figures 9a* and *9b*). The half-width of the dihedral angle distribution is also taken to be a function of the weight per cent of EGDMA (*Figure 10*). We found that it was necessary to vary both of these parameters to reproduce the trends of *Figures 4b* and *5* in the simulated 9-line spectra. Finally, the intermediate spectra observed during copolymerization are superpositions of the 13-line and nine-line spectra described above (see *Figures 2a*, *2b*, *3a* and *3b*).

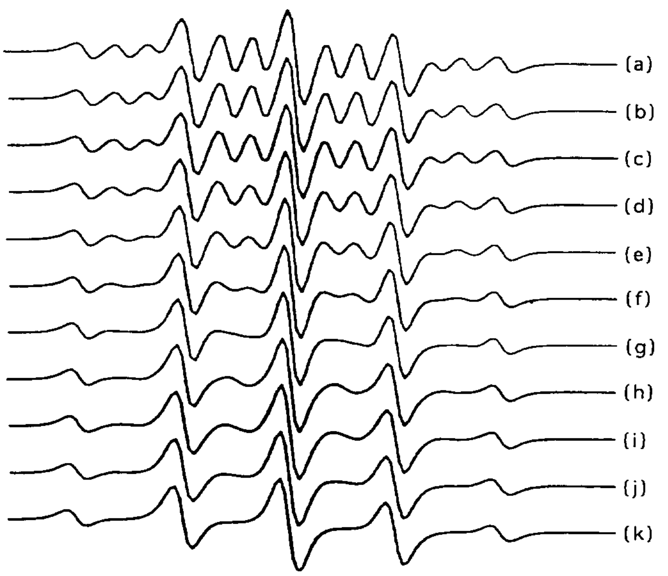

Figure 8 Simulated spectra of MMA/EGDMA radicals with a Gaussian distribution of dihedral angles about the 65/55 conformation. Halfwidth of Gaussian distribution (deg): (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5, (g) 6, (h) 8, (i) 10, (j) 12, (k) 14

This model accounts for the 9- to 13-line transition, the linewidth variation during copolymerization and the different final linewidths observed in the 9-line spectra. The implication of this model is that 13-line and 9-line spectra correspond to two distinct populations of radicals (see below).

Effect of polymer structure on reactivity

The effects observed during the MMA/EGDMA copolymerizations as the level of EGDMA was increased can be interpreted in terms of the influence of EGDMA on the structure of the copolymer. The polymer matrix of EGDMA is less ordered than the linear polymer of pure MMA. The proposed model for interpreting the e.s.r. spectra suggests that, in copolymers, EGDMA radicals exist in conformations close to the 'liquid' 65/55 conformation, and MMA radicals exist in conformations close to the 'vitreous' 60/60 conformation. As is shown in *Figure 10*, the width of the Gaussian distributions about these conformations increases with EGDMA level, indicating a higher degree of disorder in the EGDMA-rich copolymer matrix.

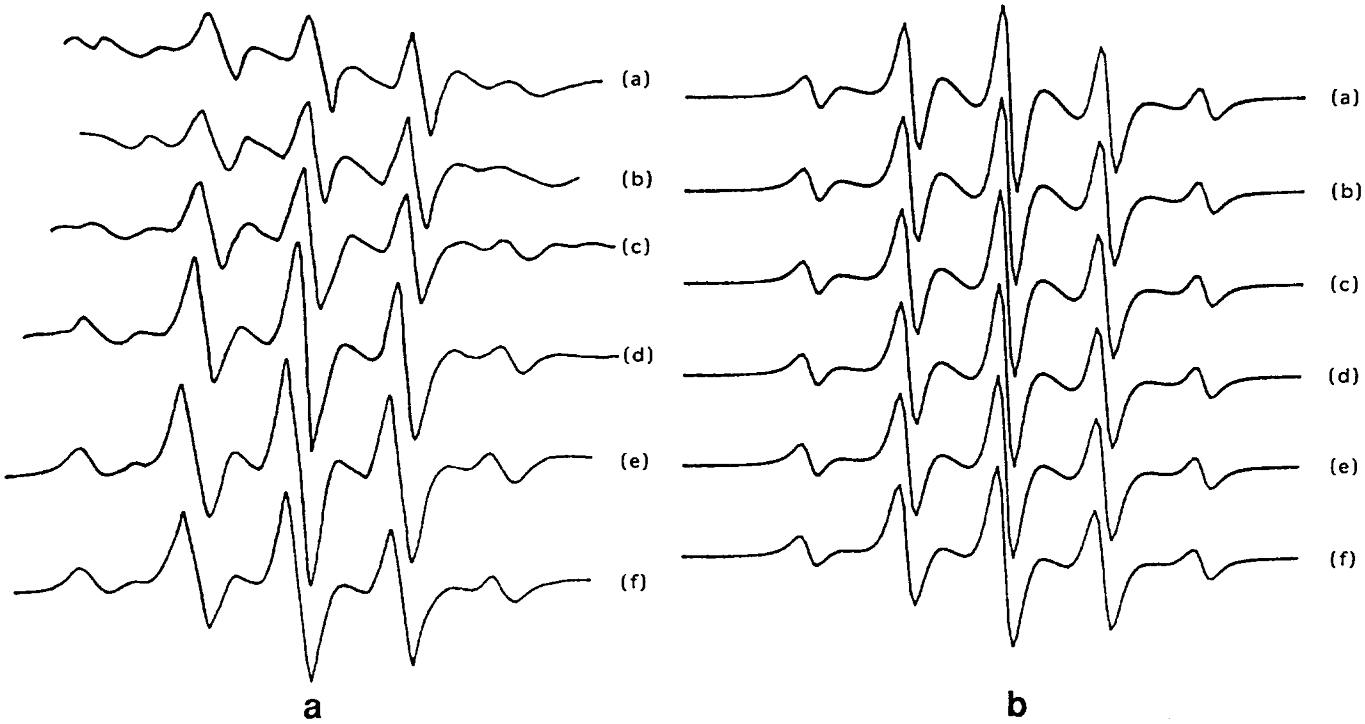

Figure 9 (a) The nine-line spectra observed at different EGDMA levels. EGDMA (wt%) and polymerization time (min): (a) 0.0, 85.0; (b) 5.0, 30.0; (c) 15.0, 95.5; (d) 25.0, 126.0; (e) 50.0, 15.2; (f) 100.0, 80.0. (b) Simulated e.s.r. spectra for different EGDMA levels. Linewidth 4 G. Halfwidth of Gaussian distribution and ratio of 60/60 to 65/55 conformation: (a) 10.0, 100:0; (b) 10.3, 95:5; (c) 10.54, 85:15; (d) 10.75, 75:25; (e) 11.0, 50:50; (f) 11.2, 0:100

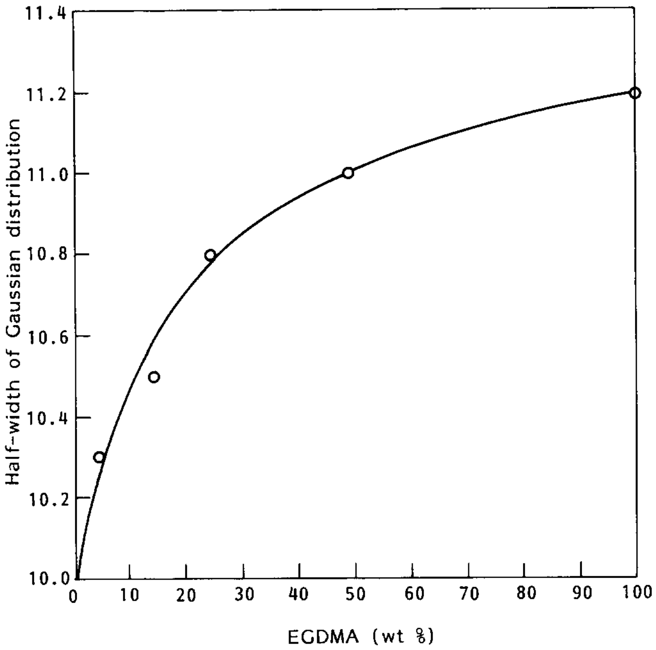

Figure 10 Halfwidth of dihedral angle distribution giving best fit *versus* EGDMA level

Table 1 The variation of the MMA/EGDMA radical concentration (mol l^{-1}) in polymer matrix for two months. AIBN 0.3 wt%; reaction temperature 70°C

EGDMA (wt%)	[R]	$[R]_{2 \text{ months later}}$
0.0	2.76×10^{-6}	5.26×10^{-7}
5.0	6.87×10^{-6}	6.02×10^{-7}
15	1.79×10^{-5}	1.34×10^{-5}
25	5.93×10^{-5}	1.11×10^{-5}
50	4.83×10^{-4}	3.94×10^{-4}
100	1.06×10^{-3}	1.06×10^{-3}

The structural influence of EGDMA can explain the trends observed as EGDMA levels were increased: higher limiting radical concentrations (*Figure 4b*) and lower termination rate (*Table 1*). The higher crosslink density and increased structural disorder in the EGDMA-rich copolymers hinders macroradical diffusion, but may permit free diffusion of small molecules such as primary radicals and monomer. Thus initiator efficiency in high-EGDMA copolymers may be high, but the termination rate in the later stages of copolymerization is low.

Termination rates may also be influenced by EGDMA level through the effect of pendant double bonds. During copolymerization of EGDMA, many double bonds remain unreacted because they are pendant to macromolecular chains and cannot diffuse as easily as, for example, a MMA monomer. When a primary radical is produced in EGDMA copolymerization, it can encounter a pendant double bond and become a macroradical. Because such macroradicals are unlikely to terminate, the radical concentration will increase until the supply of pendant double bonds is exhausted.

Heterogeneity of reaction system

The model used to interpret these experimental results suggests that the copolymerization process is heterogeneous, involving two distinct populations of radicals (those associated with the 13- and 9-line spectra, respectively), which differ markedly in stability and reactivity.

The 13-line spectrum, observed in the early stages of copolymerization, is apparently due to very reactive radicals in a 'liquid' environment, i.e. radicals in a monomer-rich environment.

The appearance of the 9-line spectrum is coincident with local reductions in the rates of monomer conversion and radical concentration[4]. The 9-line spectrum apparently arises from radicals trapped in a solid environment. The reactivity of these radicals is lower than that of radicals in the liquid phase, since their e.s.r. signal persists long after completion of polymerization.

The proposed model suggests that there are two types of trapped radicals in MMA/EGDMA copolymers. Those arising from MMA monomers exist in the 60/60 conformation with a Gaussian distribution, while those arising from EGDMA monomers exist in a 65/55 conformation also with a Gaussian distribution. The changes in the e.s.r. spectra over the course of the reaction could best be simulated by varying the ratio of 13-line and 9-line spectra (rather than by varying the distribution width). This suggests that disappearance of 'liquid' radicals and the appearance of trapped radicals are discrete rather than continuous processes. That is, as the viscosity of the polymerization system increases, there is not a smooth variation of radical conformation from a distribution about a 65/55 conformation to one based on a 64/56, to 63/57, and finally to a 60/60 conformation. The trapped radical fraction during any point of copolymerization may be estimated from the ratio of 65/55 to 60/60 used in the simulation of the corresponding e.s.r. spectrum (*Figure 11*).

The physical interpretation of the proposed model is that polymeric radicals become entangled by other macromolecules and can no longer diffuse freely in the polymer matrix, resulting in greatly reduced bimolecular termination rates and a dramatic increase in polymer

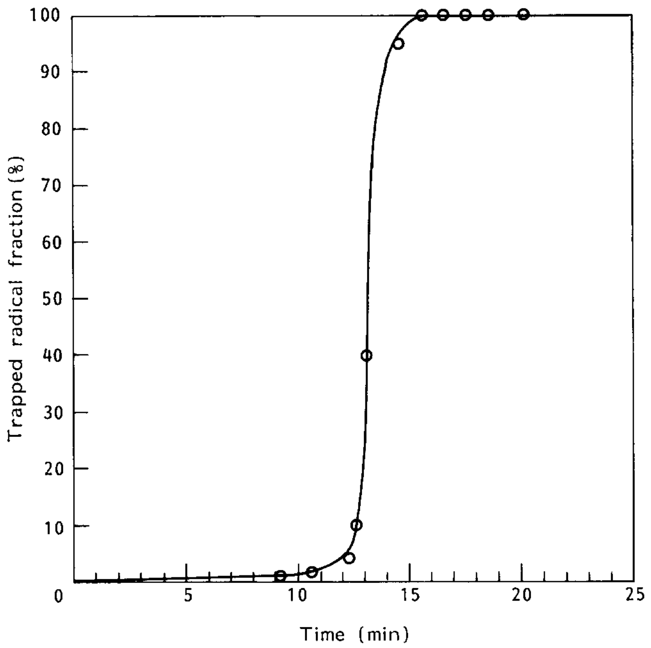

Figure 11 Trapped fraction of propagating radicals in the MMA/EGDMA matrix *versus* polymerization time for copolymerization of 15 wt% EGDMA and 85 wt% MMA, at $T = 70$°C

radical concentration. Some polymer radicals become starved of monomer and the environment around the radical centre becomes glassy. This affects the vibrations of neighbouring atoms and causes the e.s.r. signal to change from 13 to nine lines. From then on the polymerization becomes heterogeneous as more and more radicals experience the same fate.

The use of a better solvent may reduce this trapping effect by allowing radicals to diffuse more rapidly from the solid into solution. A reduced autoacceleration effect would be expected in such systems.

Related experiments are consistent with the heterogeneous nature of the polymerization process[6,16]. The polymerization of MMA was carried out in the e.s.r. cavity using u.v. initiation. During irradiation, the autoacceleration effect appeared and the e.s.r. spectra still showed 13 lines. The u.v. lamp was then turned off to stop initiation and the e.s.r. spectrum monitored. The e.s.r. spectrum of the residual radicals changed to the 9-line pattern. When initiation was resumed by turning on the u.v. lamp, a 13-line spectrum again appeared. This demonstrates that, even after the appearance of the 9-line spectrum, there still exists solution phase in the polymerization system.

CONCLUSIONS

The high radical concentrations in EGDMA/MMA copolymers result from crosslinking. The reaction system is heterogeneous, consisting of two populations of radicals: reactive (13-line) radicals in a liquid (monomer-rich) environment, and unreactive (9-line) radicals trapped in the copolymer matrix at high conversion. When the reaction proceeds from low to high conversion the e.s.r. spectrum changes from a 13-line to a 9-line pattern. The intermediate spectra are due to the coexistence of radicals in monomer-rich and glassy environments.

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