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Application of ESR spectroscopy to the kinetics of free radical polymerization of methyl methacrylate in bulk to high conversion

R. Wayne Garrett, David J.T. Hill, James H. O'Donnell*, Peter J. Pomery, and Catherine L. Winzor

Polymer and Radiation Group, Department of Chemistry, University of Queensland,
Brisbane 4067, Australia

SUMMARY

The concentration of propagating radicals during the free radical polymerization of methyl methacrylate in bulk to high conversion at 60°C was determined - (1) by "in situ" measurements in the spectrometer, and (2) using a cryogenic quenching procedure. The radical concentration showed a sigmoidal relationship with polymerization time, and the conformation of the radical was different below and above the gel point of *ca.* 30 % conversion. A value of $k_t = 2.5\ (\pm 0.3) \times 10^7$ l mol^{-1} s^{-1} was obtained below the gel point. The variation in k_t, without allowance for a decreasing efficiency factor (f), was determined over the entire conversion range.

INTRODUCTION

Most fundamental studies of the kinetics of free radical polymerizations have been limited to low conversion, but recently there has been increasing interest in polymerizations to high conversion. Several theories have been proposed to explain the features of high conversion polymerizations, most notable among them being those of Dionisio and O'Driscoll (1), Marten and Hamielec (2), Soh and Sundberg (3), Tulig and Tirrell (4), Soong *et al* (5) and Gilbert *et al* (6). However, to date these theories have not been adequately tested. We have previously reported a kinetic study of the emulsion polymerization of methyl methacrylate (7,8) which we now extend to the bulk polymerization of the same monomer to high conversion.

Free radical polymerizations to high conversion in bulk can be divided into three stages: (i) a low conversion region in which the steady state radical concentration is very low (10^{-7} - 10^{-8} M) and k_p and k_t are independent of conversion to a first approximation; (ii) a region above the gel point where the polymer chains become entangled and where the increased viscosity of the polymerization mixture results in a marked change in the diffusion characteristics of the growing polymer radicals - these two effects cause a rapid decrease in the magnitude of k_t and an increase in the radical concentration, consequently the polymerization rate begins to rise rapidly - the Trommsdorf effect; (iii) a region at high conversion where the polymerizing mixture becomes a glass and diffusion of monomer becomes restricted, thus resulting in a marked decrease in the polymerization rate.

In this paper we demonstrate, for the first time, how ESR spectroscopy can be utilized to measure the concentration of the propagating radicals throughout the course of the bulk polymerization of methyl methacrylate and thus, in conjunction with conversion measurements, yield directly values of the kinetic parameters.

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*To whom correspondence should be addressed

EXPERIMENTAL

Methyl methacrylate was distilled under 24 kPa of nitrogen at 60°C and the appropriate amount of freshly recrystallized azobisisobutyronitrile (AIBN) was added to give a concentration of 0.1 mol AIBN / l monomer. The mixture was freeze-thaw degassed several times and the samples were transferred under vacuum into 4 mm diam., high-purity quartz (Spectrasil) ESR tubes, sealed and stored under liquid nitrogen. All sample preparations were carried out in the absence of light.

A Bruker ER200D ESR spectrometer interfaced to an IBM PC/XT compatible microcomputer was used to obtain spectra of the methyl methacrylate propagating radicals. Two methods were used to obtain ESR spectra during polymerization. (1) The sealed, evacuated tube containing methyl methacrylate and initiator was polymerized "*in situ*" in the spectrometer at 60°C and spectra of the propagating radical recorded at different times during the polymerization. (2) Multiple samples were polymerized in a thermostatt at 60°C and individual samples were removed at various times; the polymerization was rapidly quenched by freezing to -196°C in liquid N_2. The ESR spectra of these quenched samples were subsequently obtained in the solid state at -133°C, where the Boltzmann distribution is more favourable than at 60°C and where spectral accumulation can be used to improve the signal to noise ratio.

Conversion of monomer to polymer was measured by ^1H NMR. Monomer/initiator samples were polymerized in a thermostatt at 60°C, and quenched in liquid N_2 as described above. The samples were crushed while still frozen, then dissolved in $CDCl_3$. ^1H NMR spectra were obtained on a JEOL GX400 spectrometer at 400 MHz using a recycle time of 20 s. Conversion was followed by the loss of vinyl ($=CH_2$) protons.

RESULTS AND DISCUSSION

ESR "*In Situ*" Measurements

The steady-state radical concentration in the early stage of the polymerization was too low to allow spectra to be obtained from single scans. Only after the radical concentration had begun to rise, and the conversion had reached approximately 30 % , could spectra be obtained in the liquid phase. A typical spectrum obtained at conversions of about 30 % is shown in Figure 1a. It is characterized by thirteen lines and is similar to that reported by Kamachi *et al* (9) in solution, and may be attributed to the presence of two conformations of the methyl methacrylate propagating radicals.

When the conversion exceeded 30 % the spectrum was transformed to the well-known nine-line spectrum of the methacrylate propagating radical (Figure 1b), indicating that, as the molecular mobility decreases even further, the radical adopts one preferred conformation. This conformation is that in which the methyl groups on the ultimate and penultimate units are in a trans orientation.

In order to obtain radical concentrations from these first differential spectra, each spectrum was doubly integrated and the area under the absorption peak compared with that of a suitable reference standard (strong pitch calibrated against diphenylpicryl hydrazyl/benzene). Allowance must be made for the changing sensitivity of the ESR cavity as the polymerization mixture changes from a liquid to a gel and then to a

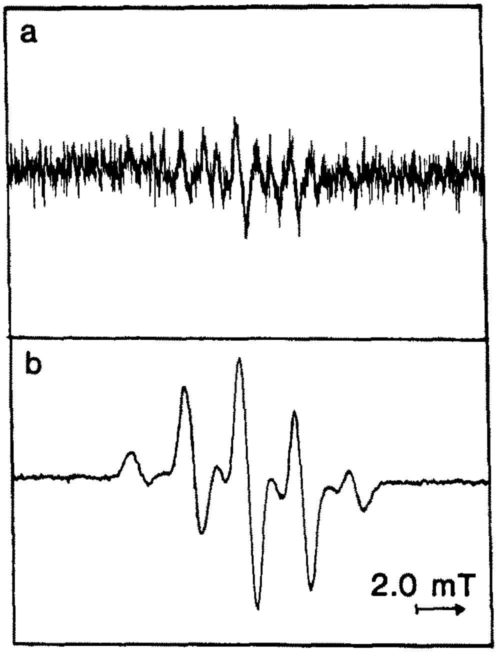

Figure 1 ESR spectra recorded for methyl methacrylate polymerized *in situ* at 60°C; (a) 30 % conversion; (b) 90 % conversion.

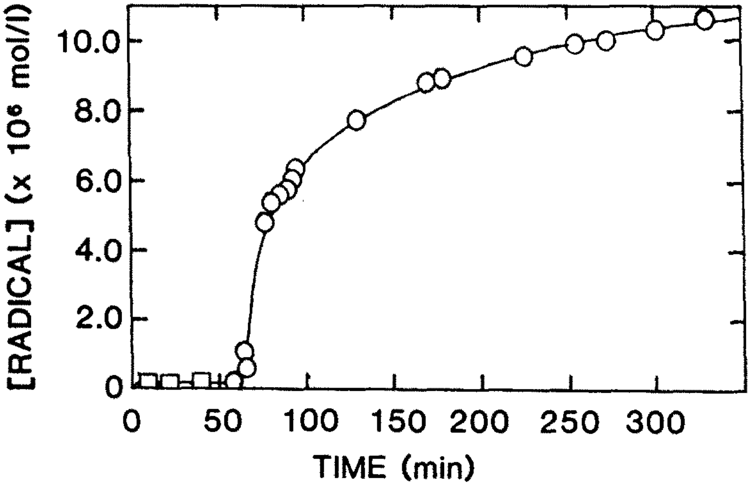

Figure 2 Variation of radical concentration with time for methyl methacrylate polymerized at 60°C. (○) *in situ* measurements, (□) polymerization quenched cryoscopically.

glass. This was done by using a reference of manganese oxide, which was coated on the outside of the ESR tube. Care was also taken to avoid saturation of the radical signals by operating the spectrometer at a suitably low microwave power level. The absolute variation in radical concentration with polymerization time obtained by *in situ* measurements is shown in Figure 2.

ESR Cryoscopic Measurements

ESR spectra with improved signal to noise ratio compared to single scans from "*in situ*" measurements could be obtained at 140 K. Spectra were obtained before the Trommsdorf region after accumulation at 140 K. These spectra comprised nine lines, indicating the presence of only one stable radical conformation at this temperature. Because all the samples at 140 K were in the solid state, the dielectric was constant and therefore independent of the extent of conversion of monomer to polymer. However, low microwave power must be used to avoid saturation. The spectra were integrated and compared with a pitch standard to determine radical concentrations. The spectra obtained from samples polymerized to conversions lower than the gel point were of low intensity making integration difficult, and the radical concentrations in these samples were determined in many cases from the peak to peak height of the central line in the spectrum, using an appropriate calibration curve between peak height and spectrum area.

The relationship between radical concentration obtained cryoscopically and polymerization time agreed well with the "*in situ*" measurements.

Radical Concentrations

In the initial stage of the polymerization the radical concentration remained approximately constant at 1.5×10^{-7} M until the conversion increased to about 30 %. Beyond this conversion, the radical concentration increased rapidly, as also did the conversion. These rapid increases have been attributed to decreasing k_t resulting from the onset of chain entanglement and decreasing molecular mobility due to the increasing viscosity.

When the conversion reached about 80 %, the rate of increase in the radical concentration declined markedly and the polymerization rate decreased to near zero above the glass transition. These changes have been attributed to the onset of diffusion control of the propagation reactions, because of reduced diffusion of monomer and to a decrease in the initiation efficiency of the initiator due to the enhanced cage recombination of initiator radicals. The variation in the rate of formation of propagating radicals with conversion has a maximum at approximately 50 % conversion. Figures 2 shows that the rate of formation of radicals is approximately zero in the initial stage of the polymerization when the reaction mixture is a liquid. For this stage we can write equations of the form:

$$\frac{d[R\cdot]}{dt} = 2k_d.f.[I] - 2k_t[R\cdot]^2 = 0 \qquad [1]$$

Therefore:

$$[R\cdot]^2 = f\,\frac{k_d[I]}{k_t} \qquad [2]$$

Using this relationship yields a value for f/k_t of 2.4×10^{-8} mol l^{-1} assuming a value for k_d of 9.9×10^{6} s^{-1} for AIBN at 60°C (1) in the early stage of the polymerization . If a value for "f" of 0.6 is assumed at low conversion, then a value for k_t of $(2.5 \pm 0.3) \times 10^{7}$ l mol^{-1} s^{-1} is obtained. This can be compared with a literature value of 2.6×10^{7} l mol^{-1} s^{-1} calculated from data given by O'Driscoll (1).

From measurement of radical concentrations and conversion of monomer to polymer, it is possible to calculate k_t across the entire conversion range, if the variation of the efficiency factor (f) with conversion is known. However, the dependence of f on conversion has not been reported, so only an apparent k_t for a constant f can be obtained. The variation of k_t with conversion is shown in Figure 3. Above the gel point (approximately 25 % conversion) k_t decreases rapidly until the conversion reaches approximately 80 %. Above this point, when the monomer/polymer is a glass, k_t decreases rapidly to near zero.

A comprehensive treatment of the relationship between radical concentration and polymerization rate, and a comparison of our experimental results with predictions based on different theories of polymerization will be presented in a subsequent paper.

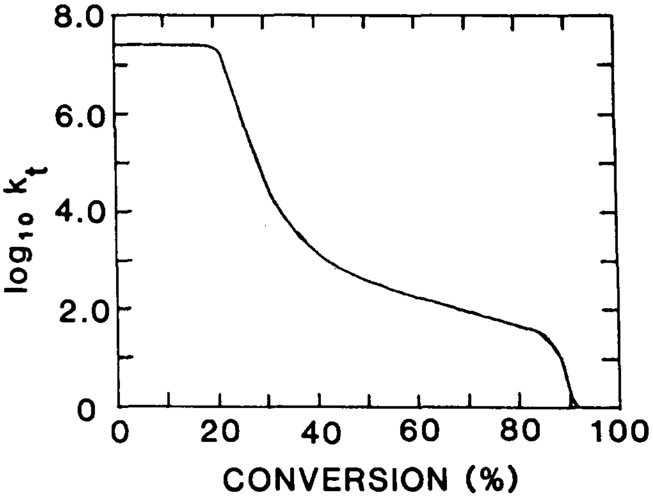

Figure 3 Variation of the apparent value of k_t with conversion for methyl methacrylate polymerized at 60°C

Acknowledgements

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