Kinetic parameters for polymerization of methyl methacrylate at 60°C

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Fourier transform infrared spectroscopy (*FT*i.r.) and electron spin resonance spectroscopy (e.s.r.) have been used to follow the kinetics of the polymerization of methyl methacrylate to high conversion at 60°C. The *FT*i.r. absorbance at 6152 cm^{-1} was used to monitor the time dependence of the concentration of double bonds, and the concentration of the polymer-chain propagation radicals was monitored using the e.s.r. absorption spectrum. These data were analysed to obtain instantaneous estimates of the kinetic rate parameters for propagation and termination across the range of conversion, and of the initiator efficiency at high conversion. The kinetic parameters were found to be consistent with values obtained by other methods and with the predictions of recent theories.

(Keywords: kinetic parameters; polymerization; methyl methacrylate)

INTRODUCTION

Several models have been proposed to describe the polymerization of vinyl monomers, such as methyl methacrylate, to high conversion[1–14], but these require accurate measurements of the variation in the double bond and radical concentrations with polymerization time to provide an adequate test of the description of the system. While there have been numerous studies reporting the variation in the double bond concentration, there have been relatively few studies of the corresponding variation in the radical concentration.

Here we report a study of the polymerization of methyl methacrylate to high conversion at 60°C using 2,2′-azoisobutyronitrile (AIBN) as initiator, in which we have monitored the double bond concentration by near i.r. spectroscopy, and the radical concentration by electron spin resonance (e.s.r.) spectroscopy. These data have been used to obtain instantaneous values for the propagation and termination rate constants, k_p and k_t respectively, and for the initiator efficiency factor, f, at high conversion.

EXPERIMENTAL

Methyl methacrylate monomer was distilled under an atmosphere of nitrogen and AIBN was recrystallized from methanol immediately before use. Oxygen was removed by bubbling the solutions with high purity nitrogen gas and then sealing. All preparation steps were carried out under minimal light conditions to avoid photoinitiation. Polymerizations were carried out in 3 mm i.d. pyrex or quartz tubes at 60°C using an initiator concentration of 0.1 mol dm^{-3}.

Double bond concentrations were obtained, as described elsewhere[15], by monitoring the first overtone band of the C=CH vibration at 6152 cm^{-1}, using a Mattson Sirius 100 *FT*i.r. spectrometer. The spectra were obtained at a resolution of 4 cm^{-1} with a signal to noise ratio of 300, by averaging 32 interferograms in 10 s. The double bond concentration was calculated from the absorbance of the peak by application of the Beer–Lambert law.

Radical concentrations were obtained on a Bruker ER200D spectrometer using techniques described previously[16]. In the pregel region, polymerizations were quenched rapidly to 77 K and e.s.r. spectra were acquired subsequently at 140 K by accumulating multiple scans to enhance the signal to noise. Beyond the gel region, satisfactory spectra could be obtained from single scans when the polymerization was conducted in the cavity of the spectrometer. In the post-gel region the results obtained from single scans in the cavity and those obtained by the quenching technique were in excellent agreement.

RESULTS AND DISCUSSION

The important kinetic steps in the bulk polymerization of vinyl monomers such as methyl methacrylate are:

Initiation

$$I \xrightarrow{k_d} 2I\cdot \qquad (1)$$

Propagation

$$P_{\dot{n}} + M \xrightarrow{k_p} P_{\dot{n}+1} \qquad (2)$$

Termination

$$P_{\dot{n}} + P_{\dot{m}} \xrightarrow{k_t} P_{n+m} \quad \text{or} \quad P_n + P_m \qquad (3)$$

It follows from these chemical equations that the instantaneous rate of polymerization and the net rate of formation of radicals are given by equations (4) and (5) respectively, where f is the initiator efficiency factor, and $[P\cdot]$ and $[M]$ are the concentrations of polymer radicals

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and monomer respectively.

$$-\frac{d[M]}{dt} = k_p[P\cdot][M] \qquad (4)$$

$$\frac{d[P\cdot]}{dt} = 2k_d f[I] - 2k_t[P\cdot]^2 \qquad (5)$$

Thus the time dependence of the polymer radical and monomer concentrations can yield values of k_p and k_t, provided the values of k_d and f are known. The value of k_d, the rate constant for decomposition of the initiator, remains constant during polymerization, but the value of the initiator efficiency factor will begin to decrease beyond the gel point, because the probability for cage recombination of initiating radicals increases as the system changes from a liquid to a glass.

Monomer concentration

Fourier transform near i.r. spectroscopy offers several advantages over mid-range i.r. spectroscopy for determination of double bond concentration in vinyl polymerizations. For example, Pyrex glass cells can be used because Pyrex does not absorb in the near i.r. region of the spectrum, and path lengths of several millimetres can be employed to improve sensitivity. Scattered light effects are negligible in this region, and the accumulation function available on modern *FT*i.r. spectrometers provides spectra with high signal to noise ratio. A typical spectrum of methyl methacrylate is shown in *Figure 1*, with the C=CH band at 6152 cm^{-1}. The double bond concentration can be determined from the absorbance of this peak.

Results obtained by the *FT*i.r. technique have been shown to agree closely with those determined by other methods[17]. The variation in the double bond conversion with polymerization time is shown in *Figure 2*. The curve shows that the rate of polymerization remains approximately constant up to a conversion of about 25% (the gel point) where the polymerizing mixture becomes very viscous. Beyond the gel point the polymerization rate increases rapidly and passes through a maximum at approximately 65% conversion. The rate of polymerization decreases rapidly beyond the glass point (approximately 80% conversion) to a small and almost constant value of approximately 10^{-5} mol dm^{-3} s^{-1}.

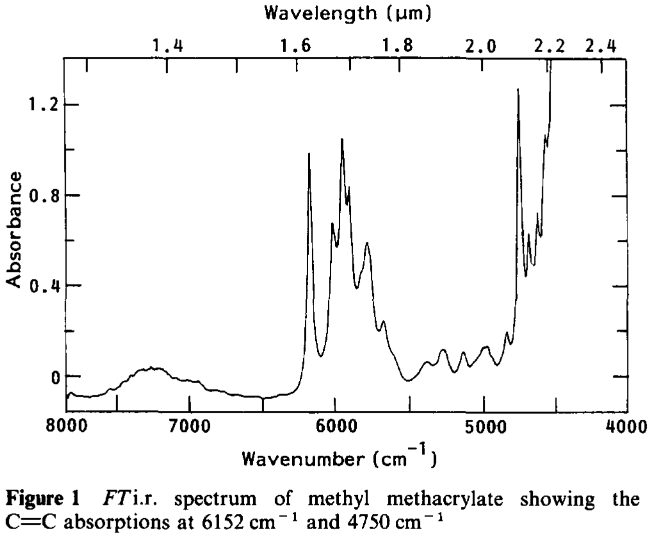

Figure 1 *FT*i.r. spectrum of methyl methacrylate showing the C=C absorptions at 6152 cm^{-1} and 4750 cm^{-1}

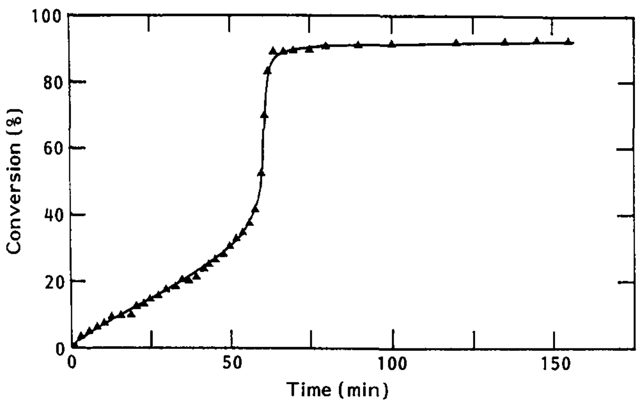

Figure 2 Plot of conversion *versus* time for polymerization of methyl methacrylate at 60°C using an AIBN concentration of 0.1 molar

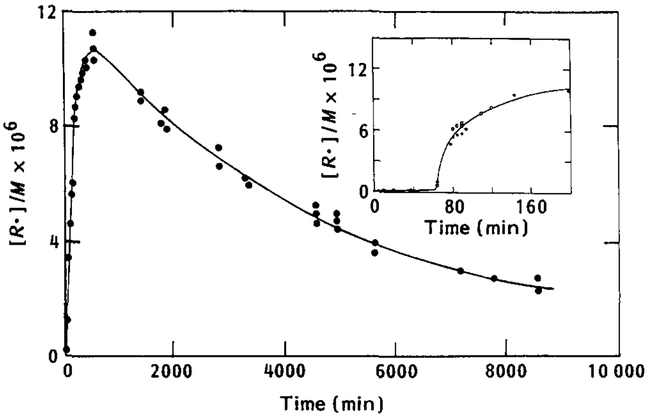

Figure 3 Plot of the radical concentration *versus* time for polymerization of methyl methacrylate at 60°C using an AIBN concentration of 0.1 molar

Radical concentration

The radical concentration can be determined using the e.s.r. techniques described previously[16]. At conversions below 25% the steady state radical concentration was too low to be obtained from a single scan, so the polymerization was rapidly quenched and the e.s.r. spectrum acquired at 140 K using accumulation of repeated scans to improve signal to noise. We have previously shown[16] that rapid quenching prevents any significant loss of radicals by termination during cooling. Beyond the gel point, relatively noise-free e.s.r. spectra could be obtained from single scans of a polymerizing mixture held at constant temperature in the variable temperature cavity of the e.s.r. spectrometer.

Figure 3 shows the variation in the radical concentration with time. At conversions below 25% the radical concentration remains approximately constant, with a value of 1.5×10^{-7} mol dm^{-3}. Beyond the gel point the radical concentration increases rapidly until the glass point is reached, where the rate of increase in the radical concentration begins to slow. Eventually the radical concentration reached a maximum value. This occurs when the rate of initiation is equal to the rate of termination. At longer polymerization times, the radical concentration steadily falls as shown in *Figure 3*.

Kinetic parameters

Instantaneous values of the apparent rate constants k_p and k_t can be calculated from equations (4) and (5) using the experimental information displayed in *Figures 2* and *3*. In the pregel region the values of k_p and k_t were found to remain approximately constant at 510 ± 100 $dm^3\,mol^{-1}\,s^{-1}$ and $(2.1 \pm 0.2) \times 10^7\,dm^3\,mol^{-1}\,s^{-1}$ respectively. These values agree with those reported in the literature[18] for polymerizations to very low conversion and obtained by rotating sector methods at this temperature: $k_p = 686\,dm^3\,mol^{-1}\,s^{-1}$ and $k_t = 3.4 \times 10^7\,mol\,dm^{-3}\,s^{-1}$.

Beyond the glass point the calculated value of k_p begins to decrease as shown in *Figure 4*. The values of $\ln(k_p/k_{p_0})$ agree closely with those predicted by Ballard *et al.*[19] on the basis of the theoretical model proposed by Soh and Sundberg[9–12], using the assumption that the diffusion coefficient for the monomer is $10^{-6}\,cm^2\,s^{-1}$.

The value of k_t begins to fall rapidly when the gel point is reached because the viscosity of the polymerizing mixture increases. The value of f would also decrease because the probability for recombination of the initiating radicals within the cage provided by the viscous matrix will also increase. However, once the glass point is reached, the nature of the matrix does not change very rapidly with polymerization time, because the rate of polymerization in this region is small. Thus, both f and k_t will be slowly changing functions of time in this region, and hence can be considered to be constant over short time intervals.

If equation (5) is rearranged as in equation (6) below, it follows that a plot of the left-hand side of the equation *versus* $[P\cdot]^2/[I]$ should be linear over short time intervals. This relationship is demonstrated in *Figure 5* for the range of polymerization times between 80 min (the glass point) and 8000 min. The instantaneous initiator concentration $[I]$ can be calculated[20] at each polymerization time from the concentration of the initiator originally and the known rate constant, k_d.

$$\frac{d[P\cdot]}{dt}\bigg/[I] = 2k_d f - 2k_t[P\cdot]^2/[I] \qquad (6)$$

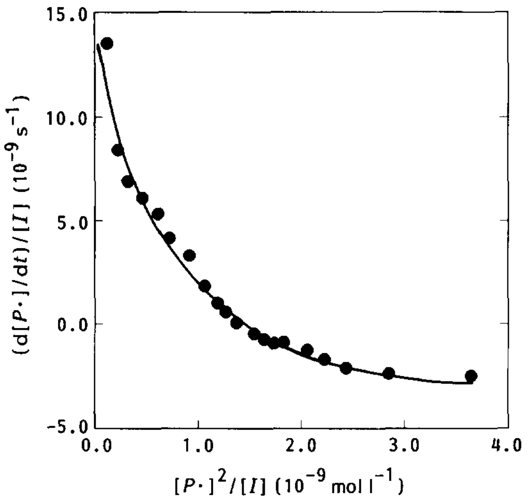

Figure 5 Analysis of experimental data using equation (6)

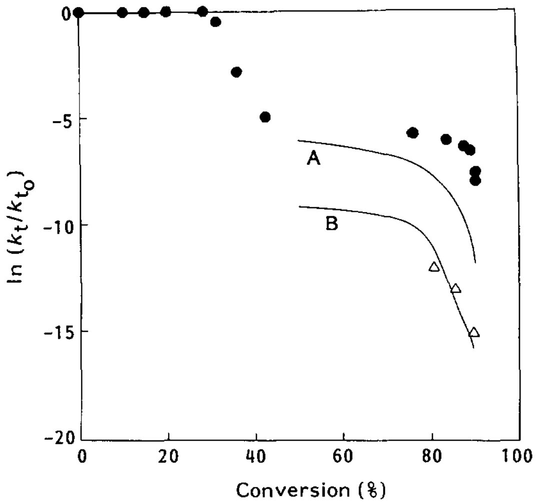

Figure 6 Plot of k_t/k_{t_0} *versus* conversion for polymerization of methyl methacrylate at 60°C using an AIBN concentration of 0.1 molar: theoretical models from Russell *et al.*[21] for A, flexible chains and B, rigid chains. Experimental values calculated for $f = 0.6$ (●) and $f = 10^{-3}$ (△)

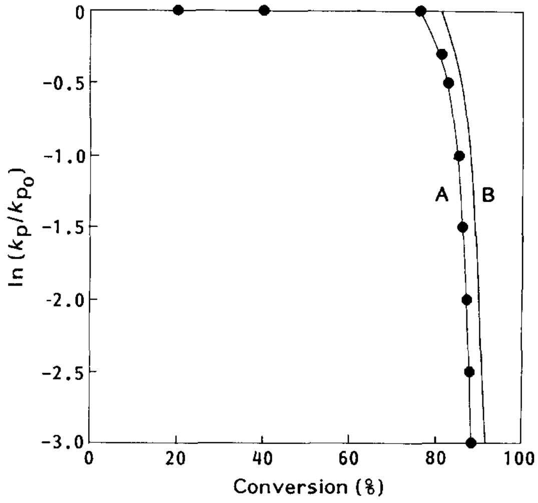

Figure 4 Plot of $\ln(k_p/k_{p_0})$ *versus* conversion for polymerization of methyl methacrylate at 60°C using an AIBN concentration of 0.1 molar: theoretical models from Ballard *et al.*[19] for monomer diffusion coefficients of A, $10^{-5}\,cm^2\,s^{-1}$ and B, $10^{-6}\,cm^2\,s^{-1}$. ●, Experimental values

The plot in *Figure 5* is distinctly curved, indicating that either or both f and k_t vary significantly with time in this region. However, over small time intervals, it is possible to obtain estimates of the values of both f and k_t from the slope and intercept of linear sections of this plot. For example, in the region just beyond the glass point (corresponding to polymerization times between 100 and 3000 min) the values calculated for f and k_t are 10^{-3} and $3.5\,dm^3\,mol^{-1}\,s^{-1}$, respectively. The monomer conversion over this range of polymerization times (between 100 and 1000 min) is 90–95%.

This value of k_t is approximately seven orders of magnitude smaller than that found in the pregel region, $2.1 \times 10^7\,dm^3\,mol^{-1}\,s^{-1}$. The large decrease in k_t beyond the gel point is consistent with the behaviour predicted by recent theoretical models, see *Figure 6*. The value obtained for f in the region beyond the glass point is also much less than that for the pregel region. This observation is also consistent with the predictions based upon theoretical models, although the value calculated here is somewhat larger than that predicted by Russell *et al.*[21] for polymerizations of methyl methacrylate at 50°C.

Buback[14] has recently reported a modification of the theory of Russell *et al.*[21] in which he expresses the residual termination rate constant, k_{tRD}, (which is equivalent to k_t in the glassy region) in terms of the propagation rate constant, k_p, and the fraction of double bonds remaining $(1 - U)$:

$$k_{tRD} = C_{RD}k_p(1 - U) \qquad (7)$$

The proportionality constant C_{RD} was calculated by Buback to be approximately 187 at 60% conversion for polymerizations of methyl methacrylate, and fairly independent of temperature. Calculation of C_{RD} using the data reported herein at 60% conversion yields a value of 276. This value is of similar magnitude to that reported by Buback, which was based on data for emulsion polymerizations at 50°C and bulk polymerizations at 0°C. Considering the likely errors in the experimental data, the two estimates of C_{RD} can be considered to be in reasonable agreement.

SUMMARY

The kinetic parameters for the polymerization of methyl methacrylate have been determined at 60°C using *FT* i.r. spectroscopy to measure the conversion and e.s.r. spectroscopy to measure the propagating radical concentration over the range from zero to approximately 95% conversion. The initiator efficiency has been shown to be much smaller in the post-glass region than it is in the pregel region of the polymerization.

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