Aspects of high-conversion free-radically initiated polymerizations: 1. Initiator efficiency in the homopolymerization of acrylonitrile and methyl acrylate in dimethylsulfoxide with azobisisobutyronitrile as initiator*

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The kinetic mechanism of the free-radically initiated homopolymerization of acrylonitrile and methyl acrylate in dimethylsulfoxide solution has been examined. All reactions have been taken to high conversions of monomer. It has been found that the initiator efficiency is unity before the β scission of primary radicals occurs and is dependent on monomer concentration after that reaction. A kinetic mechanism that explains the changes in the initiator efficiency with conversion has been proposed, which makes use of the cage-effect concept. The proposed mechanism has made it possible to explain quantitatively the experimentally observed variation in monomer concentration with time, which has not been possible previously. It has also been found that the termination step is not significantly diffusion-controlled in the homopolymerizations.

(Keywords: high-conversion polymerization; kinetic mechanism; initiator efficiency)

INTRODUCTION

There have been numerous kinetic studies of free-radically initiated polymerizations in solution where the reactions have been taken to relatively low conversions, either because of the difficulties of obtaining good experimental data at high conversions, or because it has not been deemed necessary to take reactions to high conversion in order to arrive at a mechanism appropriate for situations where side reactions or deviations from ideal physical conditions are not complicating factors. Obviously, high-conversion studies are more appropriate, indeed essential, for a quantitative understanding of technically important polymerizations. Furthermore, much interesting new information can be obtained about polymerization mechanisms by exploring the deviations that occur at higher conversions.

It is known that the initiator efficiency in free-radically initiated polymerizations carried out in solution can be dependent on the concentration of monomer when reactions are taken to high conversion of monomer. Moad *et al.*[1] suggested that, in the case of the polymerization of styrene, the initiator efficiency of azobisisobutyronitrile (AIBN) decreases with increasing conversion because of recombination between primary radicals. Fink[2] proved that recombination of primary radicals takes place within a solvent cage in the presence of styrene. Russell *et al.*[3] reported that the initiator efficiency of AIBN changes drastically at high conversions in bulk polymerization of methyl methacrylate. Attempts have been made to express the variation in initiator efficiency in terms of rigorous mathematical kinetic models. Ito[4] outlined a kinetic model that explained the changes in initiator efficiency in terms of the diffusion control of primary-radical reactions. Munzer[5] used an approach in which the kinetic steady-state assumption for radical concentrations is used in order to derive expressions that allow the calculation of the initiator efficiency with conversion.

The work reported here also makes use of the steady-state assumption. The kinetic mechanism of high-conversion homopolymerization of acrylonitrile and methyl acrylate has been examined with dimethylsulfoxide (DMSO) as solvent. Experimental reaction rates have been obtained by ^{13}C nuclear magnetic resonance (n.m.r.) measurements. A computer algorithm has been constructed, which makes possible the prediction of the changes in monomer concentration in reactions taken to high conversion where the initiator efficiency varies with conversion. Comparisons have been made between the

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theoretical predictions and experimental observations using a common modelling approach for the two monomers that have been examined.

EXPERIMENTAL

Materials

Acrylonitrile (AN) and methyl acrylate (MA) (BDH Chemicals Ltd) were refluxed with calcium hydride for 7 h, and distilled twice at atmospheric pressure. 2,2'-Azobisisobutyronitrile (AIBN) (BDH Chemicals Ltd) was dissolved in methanol at 35°C and recrystallized at low temperature (2°C). Deuterated dimethylsulfoxide (d_6-DMSO) (Goss Scientific Instruments Ltd) was refluxed over a molecular sieve (3 Å) (BDH Chemicals Ltd), and distilled twice under reduced pressure.

Real-time ^{13}C n.m.r. measurement

Polymerizations of AN and MA were carried out in the n.m.r. instrument at 60°C over a period of 14 h. Known quantities of monomer (AN or MA), AIBN, d_6-DMSO and hexamethylenedisiloxane (HMDS) as standard were dissolved in d_6-HMSO (2.5 ml) at the concentration specified in the captions to the figures where the results are reported. Each solution was introduced into an n.m.r. tube (10 mm diameter), which was sealed and set in the probe of an n.m.r. instrument (JEOL GX270) in the usual way. Spectra were automatically accumulated with time. The distortionless enhancement by polarization transfer (d.e.p.t.) technique was employed to estimate monomer loss. The pulse delay time was 3.0 s, the sampling time 0.9 s and the irradiation time 12.0 μs. At least 300 spectra were accumulated, each represented by 33 000 data points.

A typical ^{13}C n.m.r. spectrum taken during the homopolymerization of AN is shown in *Figure 1*. The

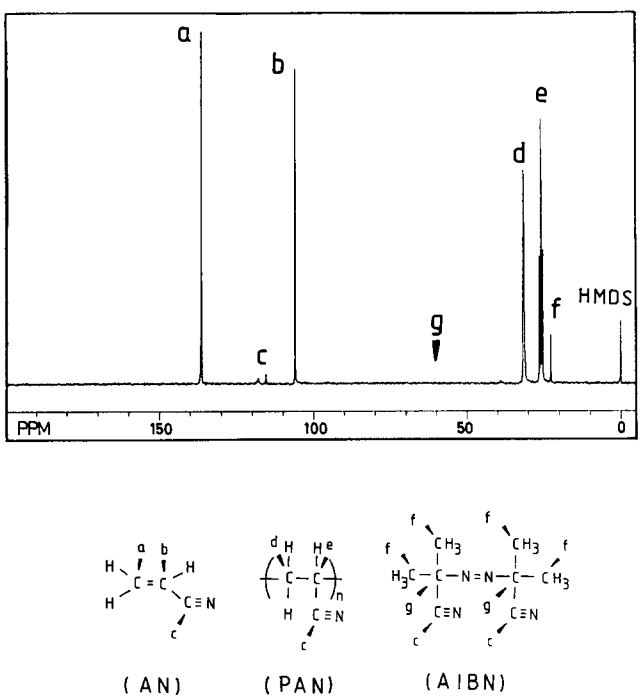

Figure 1 A typical real-time ^{13}C n.m.r. spectrum acquired during the homopolymerization of AN in d_6-DMSO at 60°C (polymerization time, 2220 s; initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2})

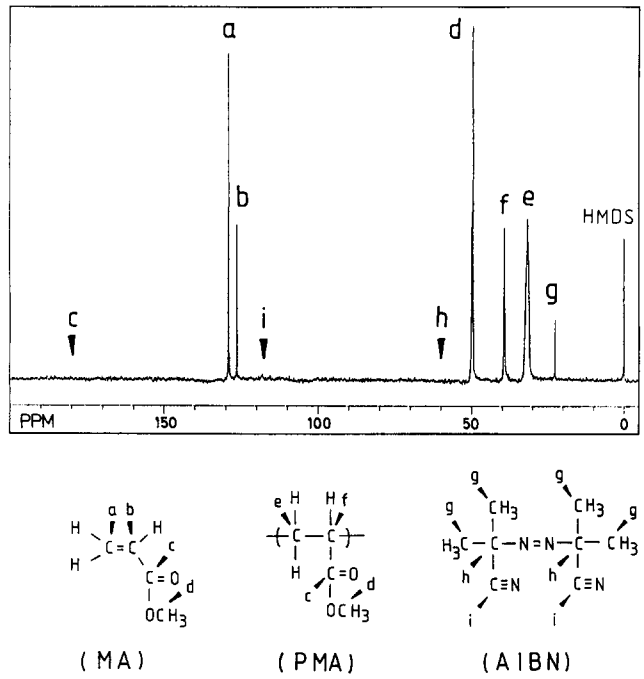

Figure 2 A typical real-time ^{13}C n.m.r. spectrum acquired during the homopolymerization of MA in d_6-DMSO at 60°C (polymerization time, 1860 s; initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2})

peak in the vicinity of 27 ppm (e) has been assigned to a CH carbon in the polymer, and the peak around 33 ppm (d) to a CH_2 carbon in the polymer. The peaks at 136 ppm (a) and at 106 ppm (b) are attributable to the carbon–carbon double bond in the AN. The concentrations of AN at selected time intervals have been determined by taking the ratio of the area of peak a to that of the HMDS peak. The peak at 22.5 ppm (f) has been assigned to the CH_3 carbon in the AIBN. This peak can be clearly distinguished from that at 20.2 ppm, which arises from by-products of the decomposition of AIBN. Although the impurity peak, which is attributed to the CH_3 carbon in tetramethylsuccinodinitrile, was clearly seen when initiator decomposition was followed in the absence of monomer, it was not the case during the polymerization studies except at very high conversion of monomers, and then only in trace quantities. The concentrations of AIBN at selected time intervals have been determined by taking the ratio of the intensity of peak f to that of the HMDS peak. A typical ^{13}C n.m.r. spectrum obtained during the homopolymerization of MA is shown in *Figure 2*. The peak at 40 ppm (f) has been assigned to a CH carbon in the polymer, and that at 33 ppm (e) to a CH_2 carbon in the polymer. The peaks at 129 ppm (a) and at 126 ppm (b) have been attributed to the carbon–carbon double bond in the MA. The concentrations of MA at selected time intervals have been determined by taking the ratio of the area of peak a to that of the HMDS peak. It was checked, by weighing, that there was no loss of reactants from the n.m.r. tube during the experiment. Although it was not possible to measure the temperature in the n.m.r. tube during polymerization, it is believed that good isothermal conditions were maintained during polymerization as the surface area of the n.m.r. tube is large in relation to the volume of reagents used and the overall reaction time was generally over 5 h or more. A critical account of the

n.m.r. method used for following homopolymerizations, copolymerizations and multicomponent polymerizations will be presented elsewhere[6].

RESULTS AND DISCUSSION

Rate of initiation

The rate of loss of initiator at 60°C in the presence of AN in d_6-DMSO is shown in *Figure 3*. The best exponential fit for ^{13}C n.m.r. experimental data gave a rate constant for decomposition (k_d) of AIBN of $2.0 \times 10^{-5}\ s^{-1}$. The fact that k_d is constant over the entire range of reaction supports the view that isothermal conditions have been maintained in the case of the homopolymerization of AN. Bamford *et al.*[7] have reported the value of $2fk_d$ for AIBN in dimethylformamide (DMF) at 60°C to be $1.54 \times 10^{-5}\ s^{-1}$. The value for $2fk_d$ in DMSO is larger than that in DMF, assuming that f is unity in DMSO. It has been reported that $f = 1.0$ in the case of AN polymerization in ethanol[8]. In the work reported below, it was found necessary to assume that $f = 1.0$ up to a certain monomer conversion in order to achieve agreement between the experimental kinetic data and the simulated data from the model that has been proposed for the polymerization reactions. There is no obvious justification that can be given for assuming that the values in DMSO and ethanol are the same other than this, although it should be possible to determine initiator efficiency in DMSO using a radioactively labelled initiator. The difference between the reported values of $2fk_d$ in different solvents may actually be the result of a genuine solvent effect on k_d and/or f. This will be discussed in greater detail elsewhere[9].

Kinetics of homopolymerization

The rate of homopolymerization can be expressed as follows[10]:

$$-d[M]/dt = k_p[M](2fk_d[I]/k_t)^{0.5} \quad (1)$$

Here, [M] and [I] are the concentrations of monomer and initiator, respectively, and k_p and k_t are the rate constants for propagation and termination, respectively.

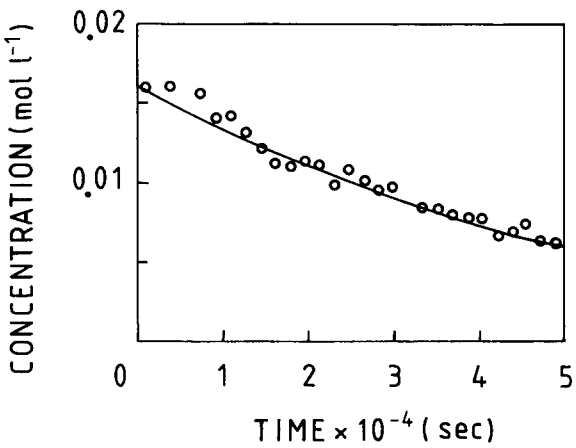

Figure 3 The time dependence of AIBN concentration in the homopolymerization of AN in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}): (○) ^{13}C n.m.r. experimental data; (——) the best exponential fit for the experimental data ($k_d = 2.0 \times 10^{-5}$)

Table 1 Rate constants for transfer reactions of homopolymerization

	AN	MA
Monomer	2.6×10^{-5} [a]	3.6×10^{-6} [b]
Solvent	1.1×10^{-5} [c]	No data
Initiator	0[a]	No data
Polymer	3.5×10^{-4} [d]	5.0×10^{-5} [e]

[a] Bulk polymerization at 60°C, ref. 11
[b] Bulk polymerization at 60°C, ref. 12
[c] Solution polymerization in DMSO at 50°C, ref. 13
[d] Bulk polymerization at 60°C, ref. 14
[e] Bulk polymerization at 60°C, ref. 15

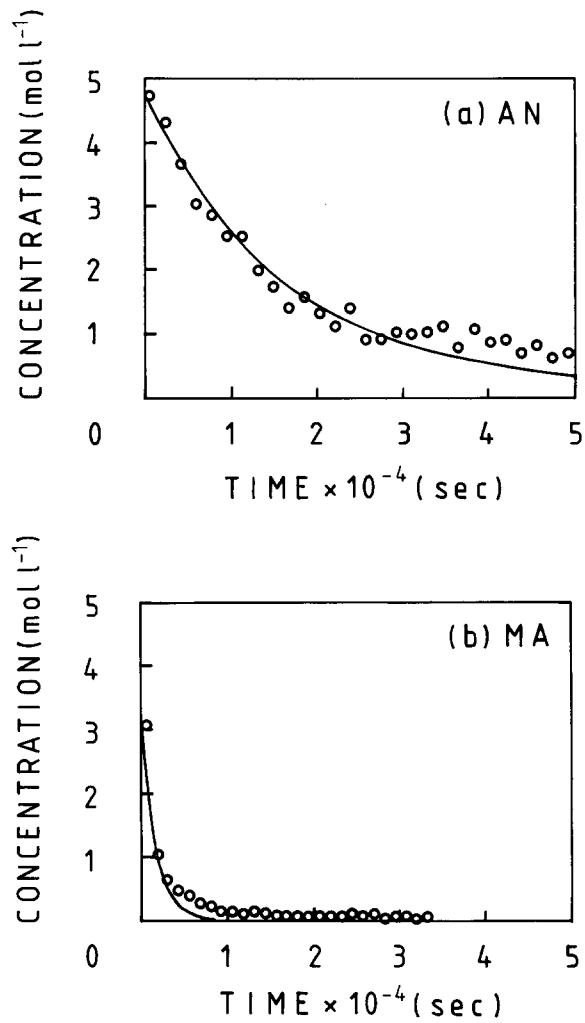

Figure 4 A plot of monomer concentration against time in the high-conversion homopolymerization in d_6-DMSO at 60°C: (a) AN (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}); (b) MA (initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2}); (○) ^{13}C n.m.r. experimental data; (——) computer simulation data with $f = 1$

Transfer reactions to monomer, initiator, polymer and solvent have been ignored, since the rate constants for the transfer reactions are small, as is shown in *Table 1*. High-conversion homopolymerization of AN and MA has been carried out to examine the kinetic mechanism throughout the reaction. *Figures 4a* and *4b* show the ^{13}C n.m.r. experimental data and simulation data for monomer concentration change with time in the homopolymerization of AN and MA, respectively. The simulation data were obtained using a computer program

based on the following equation:

$$[M]_i = [M]_{i-1} \exp\{-k_p(2fk_d[I]/k_t)^{0.5}\} \quad (1 \leqslant i \leqslant 1000) \tag{2}$$

where $[M]_i$ is the concentration of monomer at a given instant in time i and $[M]_{i-1}$ is the concentration at the previous time $i-1$, the time interval being dt. The initiator efficiency has been assumed to be unity over the whole range of conversion. The values of $k_p/k_t^{0.5}$ for AN and MA have been determined using experimental data at relatively low conversion, assuming that the initiator efficiency is unity. Despite the fact that the experiments have not been carried out under absolutely identical conditions, e.g. the same concentration of solvent or precisely the same molecular weight of the polymer and other possible factors of this sort, which might influence the termination step of the reaction, the values are in good agreement with published data, as can be seen in *Table 2*. It should be noted that there is an internal inconsistency in the paper by White and Zissell[13] in which they report the polymerization of AN in DMSO, i.e. the values of k_p and k_t reported are not consistent with the $k_p/k_t^{0.5}$ quoted in the same paper. In the computer simulations described below, the values of $k_p/k_t^{0.5}$ for AN and MA that have been used are those determined in this work. The total conversion time was divided into 1000 equal time intervals (dt) and the values of [M] and [I] were calculated for each time interval. The total volume of all reagents (V_i) has been determined at each time interval i by using the equation:

$$V_i = V_0 + V_{i-1}([M]_{i-1} - [M]_i)M_w(\rho_p^{-1} - \rho_m^{-1}) \tag{3}$$

in which V_0 is the initial total volume of all reagents, and ρ_m and ρ_p are the densities of the monomar (AN, 0.80 g ml^{-1}; MA, 0.95 g ml^{-1}) and the polymer (1.10 g ml^{-1}), respectively. V_{i-1} is the total volume of all reagents at previous time $i-1$, the time interval being dt, and M_w is the molecular weight of monomers (AN, 53; MA, 86). Simulations were carried out by using an Olivetti personal computer (model M380). The program was written in Quick Basic. The simulation and ^{13}C n.m.r. experimental results diverge as the conversion increases, as can be seen from the fact that the two plots in *Figures 4a* and *4b* do not coincide at higher conversions. Because the polymerization of MA is relatively fast compared with the speed of data capture in the n.m.r. experiment, it is not possible to treat those data with the same degree of confidence as for the case of AN.

Initiator efficiency

Initiator concentration can be expressed with time as follows:

$$[I] = [I]_0 \exp(-k_d t) \tag{4}$$

Table 2 Values of $k_p/k_t^{0.5}$ for homopolymerization of AN and MA at 60°C

	AN	MA
This work	0.0836	0.745
Literature	0.0842[a]	0.678[b]

[a] Solution polymerization in DMSO, ref. 13 (k_p, 11 600 l mol^{-1} s^{-1}; k_t, 1.9×10^{10} l mol^{-1} s^{-1})
[b] Solution polymerization, ref. 16 (k_p, 2090 l mol^{-1} s^{-1}; k_t, 9.5×10^6 l mol^{-1} s^{-1})

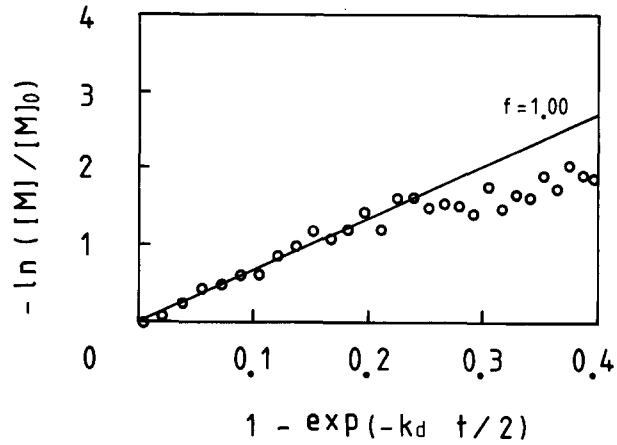

Figure 5 A plot of $-\ln([M]/[M]_0)$ against $\{1-\exp(-k_d t/2)\}$ in high-conversion homopolymerization of AN in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}): (○) ^{13}C n.m.r. experimental data; (——) the value of 1.0 as the initiator efficiency

Here, $[I]_0$ is the initial concentration of iniator. From equations (1) and (4), it follows that:

$$-\ln([M]/[M]_0) = 2k_p(2f[I]_0k_d/k_t)^{0.5}\{1-\exp(-k_d t/2)\} \tag{5}$$

where $[M]_0$ is the initial concentration of monomer. The initiator efficiency can be obtained from a plot of $-\ln([M]/[M_0]$ against $\{1-\exp(-k_d t/2)\}$. *Figure 5* shows this plot for the high-conversion polymerization of AN together with a calculated line for behaviour when the initiator efficiency is 1.0. There is no *a priori* reason why this plot should be linear over the complete range of monomer conversion range. However, it is apparent that a plot for the situation where $f=1.0$ does fit the curve up to a certain conversion, beyond which agreement rapidly becomes very poor. It is possible to fit further tangents to the curve at higher conversions with values of f less than unity. All previous theories concerning initiator efficiency have suggested that there is some decrease in f with increasing conversion. However, it is not possible to explain the new experimental observations of a very rapid reduction in the value of f at approximately 75% conversion of monomer seen in this work. This phenomenon can be explained quantitatively if the mechanism of initiation reaction involving AIBN is considered in more detail. The decomposition of AIBN can be described as a two-step reaction, as shown in *Figure 6*. A cyanopropyl radical and a diazenyl radical are produced from an AIBN molecule in the first step. Then, a cyanopropyl radical and a nitrogen are produced from a diazenyl radical in the second step (β scission)[17]. The kinetic scheme for this reaction can be expressed as follows:

$$-d[I]/dt = k_{d1}[I] - k_{d1}^{-1}[\text{cage-A}] \tag{6}$$

$$-d[\text{cage-A}]/dt = k_{d2}[\text{cage-A}] + k_{d1}^{-1}[\text{cage-A}] - k_{d1}[I] \tag{7}$$

$$d[\text{cage-B}]/dt = k_{d2}[\text{cage-A}] \tag{8}$$

in equations (6)–(8), [cage-A] represents the concentration in the solvent cage[18] that includes a cyanopropyl radical and a diazenyl radical, and [cage-B] the concentration in the solvent cage that includes two

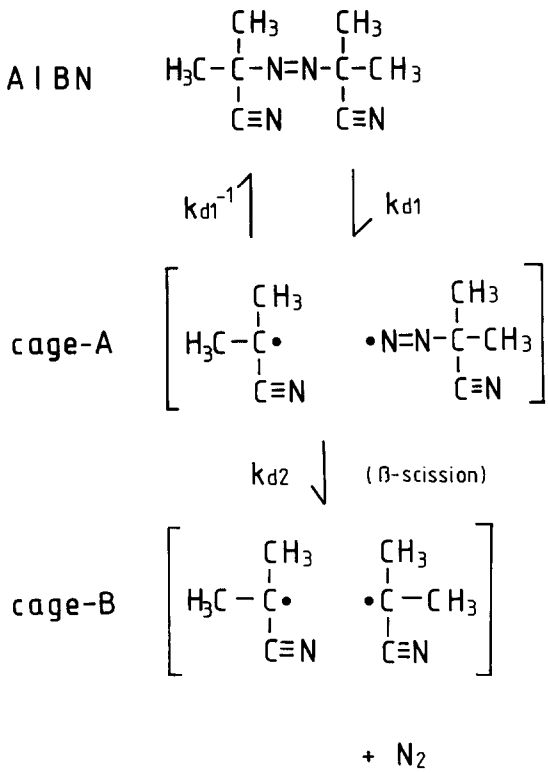

Figure 6 The kinetic scheme for decomposition of AIBN

cyanopropyl radicals. Individual rate constants have been defined as shown in *Figure 6*. The rate of decomposition of AIBN can be described by a first-order equation to a very good approximation since the rate constant of decomposition of AIBN is almost constant during the homopolymerization of AN, as shown in *Figure 3*. It is therefore possible to conclude that the value of k_{d2} must be much greater than that of k_{d1} and k_{d1}^{-1}. When $k_{d2} \gg k_{d1}^{-1}$, equations (6)–(8) can be simplified as follows:

$$-d[I]/dt = k_{d1}[I] \quad (9)$$

$$-d[\text{cage-A}]/dt = k_{d2}[\text{cage-A}] - k_{d1}[I] \quad (10)$$

$$d[\text{cage-B}]/dt = k_{d2}[\text{cage-A}] \quad (11)$$

If initiation of polymerization takes place before the cage-B situation is produced, initiator efficiency must be unity because recombination between cyanopropyl radicals and diazenyl radicals does not give any by-products, as only AIBN molecules are regenerated. However, if initiation occurs after the establishment of the cage-B situation, by-products will be produced alongside initiation, causing a decrease in initiator efficiency. At the point in the monomer conversion where the value of the initiator efficiency changes rapidly from 1.0 to a much lower value, the following equation is applicable:

$$k_i[M]_c[\text{cage-A}] = k_{d2}[\text{cage-A}] \quad (12)$$

In equation (12), k_i is the rate constant for initiation, and $[M]_c$ is the concentration of monomer at the critical point. When $k_i[M] > k_{d2}$, initiator efficiency is always unity. When $k_i[M] \leqslant k_{d2}$, initiator efficiency is not unity, and recombination of cyanopropyl radicals takes place alongside the initiation reaction. Two cyanopropyl radicals produced from an AIBN molecule are likely to recombine inside the 'cage' rather than outside[1,2], since the likelihood of one primary radical meeting another in the presence of monomer is very low, given that the radical concentration is approximately 10^{-9} mol l^{-1} and monomer concentration is in the range from 10^{-2} to 1 mol l^{-1}. Even when the monomer concentration is low at high conversion, the primary radical will be substantially outnumbered by monomer molecules. Reactions within the solvent cage can be expressed as follows:

$$I \xrightarrow{k_d} (2R^*)$$

$$(2R^*) + M \xrightarrow{k_i} R\text{–}M^* + R^*$$

$$(2R^*) \xrightarrow{k_z} R\text{–}R$$

$$(2R^*) \xrightarrow{k_{dif}} 2R^*$$

where the parentheses indicate species within the solvent cage, and k_z and k_{dif} are the rate constants for recombination and for diffusion from solvent cage, respectively. The decomposition of initiator is defined as a one-step reaction here. This must be a good approximation since the rate of decomposition of AIBN can be described as a simple first-order reaction, as shown in *Figure 3*. In the case where AIBN is the initiator, recombination can occur in two ways, namely, to yield tetramethylsuccinodinitrile or dimethyl-*N*-(2-cyano-2-isopropyl) ketenimine[1]. Disproportionation, which gives rise to methacrylonitrile and isobutyronitrile, is a minor reaction of the primary radicals from AIBN[19]. However, since ketenimine will give rise to new propagating radicals[1] and the disproportionation reaction amounts only to approximately 10% of all cage reactions that lead to by-products[19], the value of k_z mainly accounts for the rate constant of the production of tetramethylsuccinodinitrile. As initiator concentration is always low (0.016 mol l^{-1}), methacrylonitrile produced from AIBN would not affect the polymerization kinetics. Given these assumptions, the concentration of primary radicals at steady state within the solvent cage can be arrived at as follows:

$$d[(2R^*)]/dt = k_d[I] - R_i - R_z - R_{dif} = 0 \quad (13)$$

where the rates of initiation (R_i), recombination (R_z) and diffusion (R_{dif}) are given by:

$$R_i = k_i[(2R^*)][M] \quad (14)$$

$$R_z = k_z[(2R^*)] \quad (15)$$

$$R_{dif} = k_{dif}[(2R^*)] \quad (16)$$

Hence, the concentration of primary radicals within the solvent cage is given by:

$$[(2R^*)] = \frac{k_d[I]}{k_i[M] + k_z + k_{dif}} \quad (17)$$

If the reaction of primary radicals outside the solvent cage is given by the expression:

$$R^* + M \xrightarrow{k_i} R\text{–}M^*$$

then the concentration of primary radicals outside the solvent cage can be given by:

$$d[R^*]/dt = R_{dif} + R_i - R_i' = 0 \quad (18)$$

and the rate of the initiation reaction outside the solvent

cage (R_i') by:

$$R_i' = k_i[R^*][M] \tag{19}$$

It follows that the concentration of primary radicals outside the solvent cage can be expressed as:

$$[R^*] = \frac{k_i[M] + k_{dif}}{k_i[M]}[(2R^*)] \tag{20}$$

and the ratio of initiation reaction (f) to recombination reaction ($1-f$) by:

$$\frac{f}{1-f} = \frac{R_i + R_i'}{R_z} \tag{21}$$

When equations (14), (15), (17), (19) and (20) are combined, it can be shown that:

$$f = \frac{2k_i[M] + k_{dif}}{2k_i[M] + k_z + k_{dif}} \tag{22}$$

Where the value of k_{dif} has been assumed to be much smaller than the value of $2k_i[M]$, then equation (22) can be rewritten as:

$$f = \frac{2k_i[M]}{k_z + 2k_i[M]} \tag{23}$$

Initiator efficiency can be expressed over the whole range of monomer conversion by:

$$\begin{aligned} f &= 1 && \text{when } [M] > k_{d2}/k_i \\ f &= 2k_i[M]/(k_z + 2k_i[M]) && \text{when } [M] \leqslant k_{d2}/k_i \end{aligned} \tag{24}$$

It is noteworthy that Scott and Senogles[20] reported that the bulk polymerization kinetics of alkyl acrylates are characterized by monomer orders of 1.5 or greater. This can be clearly explained in terms of the magnitude of the initator efficiency. For example, by substituting equation (24) into equation (1), the following equation is obtained:

$$\begin{aligned} -d[M]/dt &= k_p[M](k_d[I]/k_t)^{0.5} && (\text{when } f = 1) \\ -d[M]/dt &= k_p[M]\{4k_i[M]/(k_z + 2k_i[M]) \times (k_d[I]/k_t)\}^{0.5} && (\text{when } f \neq 1) \end{aligned} \tag{25}$$

When the initiator efficiency is equal to 1.0, the rate of polymerization is characterized by a monomer order of 1.0, as can be seen from the above equation. When the initiator efficiency is not equal to 1.0, it is dependent on monomer concentration. From equation (25) in the case of $f \neq 1$, assuming that $k_z \gg 2k_i[M]$, then:

$$\begin{aligned} -d[M]/dt &= k_p(k_d[I]/k_t)^{0.5} \times (4k_i[M]/k_z)^{0.5}[M] \\ &= k_p(k_d[I]/k_t)^{0.5} \times (4k_i/k_z)^{0.5}[M]^{1.5} \end{aligned} \tag{26}$$

Therefore, when the value of k_z is much greater than that of $2k_i[M]$, the rate of polymerization is proportional to $[M]^{1.5}$. The monomer order is dependent on the difference in values between k_z and $2k_i[M]$. This is a new way of explaining the observations reported by Scott and Senogles[20]. In the work reported here, when initiator efficiency changes with monomer conversion, the order of reaction with respect to monomer must also change automatically in agreement with the experimental observation of Scott and Senogles. This fact lends further support to the proposals that are made here.

Termination reaction in high-conversion homopolymerization

It has been recognized by some workers that the termination step in free-radically initiated polymerization can be diffusion-controlled. Benson and North[21] first reported in 1959 that k_t is inversely proportional to the viscosity of the medium over a wide range in homopolymerization of methyl methacrylate (MMA) at 40°C, although k_p is independent of viscosity. They also claimed that k_t was independent of viscosity at low viscosity, and became more dependent on viscosity at increasing conversions in the homopolymerization of butyl acrylate at 30°C. This behaviour has been interpreted in terms of a model involving competitition between translational diffusion and chemical reaction. North and Reed[22] confirmed the inverse dependence of k_t in the homopolymerization of MMA on the viscosity of the medium at 30°C, using various esters as solvents. Subsequently, they proposed a mathematical expression for k_t, which made use of a diffusion-controlled model[23]. Burnett and colleagues[24] also observed that k_t is proportional to the inverse of the viscosity of the medium in homopolymerization of styrene in various solvents at 25°C. Bamford and Brumby[25] reported similar findings for the homopolymerization of MMA at 25°C in various aromatic solvents, although they suggest that this is not the general rule because of the narrow range of viscosity and the magnitude of errors in k_t.

When termination is a diffusion-controlled reaction, then k_t decreases with increasing conversion of monomer as the viscosity of the medium increases. However, it can be seen from *Figure 5* that the slope of the plot of $\{1-\exp(-k_d t/2)\}$ *versus* $-\ln([M]/[M]_0)$ remains constant up to very high conversion (75%) in the case of the homopolymerization of AN in DMSO at 60°C. The slope in this figure is given by $2k_p(2f[I]_0 k_d/k_t)^{0.5}$ as can be seen from equation (5). One might think that the value of $k_t^{0.5}$ is counterbalanced with the value of fk_p; then initiator efficiency is not equal to 1.0 with $fk_p/k_t^{0.5}$ constant up to very high conversion in the homopolymerization. This argument has no substance, however, since the value of $fk_p/k_t^{0.5}$ should deviate from a constant value gradually if it is to deviate at all. The experimental evidence is that the value of $fk_p/k_t^{0.5}$ changes quite sharply at very high conversion as is shown in *Figure 5*. Hence, it is reasonable to assume that k_p, k_t and f are constant with conversion when the initiator efficiency of AIBN is equal to 1.0. A recent electron spin resonance (e.s.r.) study shows that k_p is constant over the whole range of conversion and k_t starts to decrease at approximately 40% conversion of monomer in bulk polymerization of styrene at 70°C[26]. In the case of bulk polymerization of MMA at 70°C, k_p is constant up to approximately 70% conversion, beyond which the value decreases with conversion, and k_t does not change significantly up to approximately 35% conversion, at which autoacceleration starts[27]. These two results show that k_p and k_t do not change significantly with increasing conversion of monomer when the viscosity of the medium is not too high. Since the homopolymerizations have been carried out in solution with initial monomer concentrations of less than 5 mol l^{-1}, it is not thought that the viscosity of the medium is sufficient to cause autoacceleration even at 100% conversion of monomer.

Surprisingly, the termination reaction in the homopolymerization of AN in DMSO at 60°C is apparently

not diffusion-controlled to any significant extent, at least under the experimental conditions that have been used. When the temperature of the reaction medium is decreased, or the viscosity of the medium is substantially increased, such as in bulk polymerization of MMA, the diffusion reaction becomes significant. It is also possible that changes in the molecular weight of the polymer that might occur owing to different reaction conditions or reagent concentrations might play a role in the diffusion control processes. This aspect of the problem has not been explored.

Computer simulation for high-conversion homopolymerization

Figure 7a shows a plot of $-\ln([M]/[M]_0)$ against $\{1-\exp(-k_d t/2)\}$ for the homopolymerization of AN, and *Figure 7b* shows that for the homopolymerization of MA. The full lines are the plots obtained when the value of the initiator efficiency is taken as 1.0, and the broken lines show the best fits to the experimental data that are shown by the filled circles. The experimental data shown by the open circles can be best described by a value of 1.0 for the initiator efficiency. Initiator efficiencies for the experimental data shown by the filled circles can be estimated from the slopes in *Figures 7a* and *7b*, and these are 0.18 and 0.10 for AN and MA, respectively. Further tangents could be obtained at other conversions, but discussion will be limited to those illustrated. The values of k_{d2}/k_i for both homopolymerizations can be estimated from the intersection point of the two lines in *Figures 7a* and *7b*. The values of k_z/k_i can be estimated from equation (24). The values of k_{d2}/k_i and k_z/k_i are shown in *Table 3*.

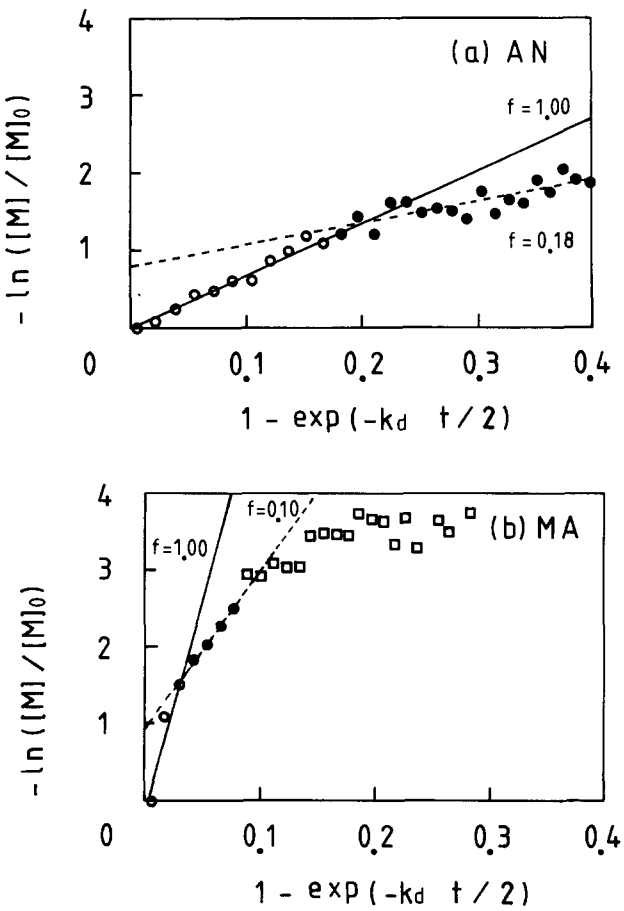

Figure 7 A plot of $-\ln([M]/[M]_0)$ against $\{1-\exp(-k_d t/2)\}$ in high-conversion homopolymerization in d_6-DMSO at 60°C: (a) AN (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}); (b) MA (initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2}); (○) ^{13}C n.m.r. experimental data that agree with computer simulation data in *Figure 4*; (●) ^{13}C n.m.r. experimental data that do not agree with computer simulation data in *Figure 4* and used for the estimation of the initiator efficiency; (□) ^{13}C n.m.r. experimental data that do not agree with computer simulation data in *Figure 4* and not used for the estimation of the initiator efficiency; (——) the value of 1.0 as the initiator efficiency; (– – –) the best fit for the ^{13}C n.m.r. experimental data that are indicated by a filled circle (●)

Table 3 Values of k_{d2}/k_i and k_z/k_i for homopolymerization of AN and MA

	AN	MA
k_{d2}/k_i	1.18	0.61
k_z/k_i	8.56	7.74

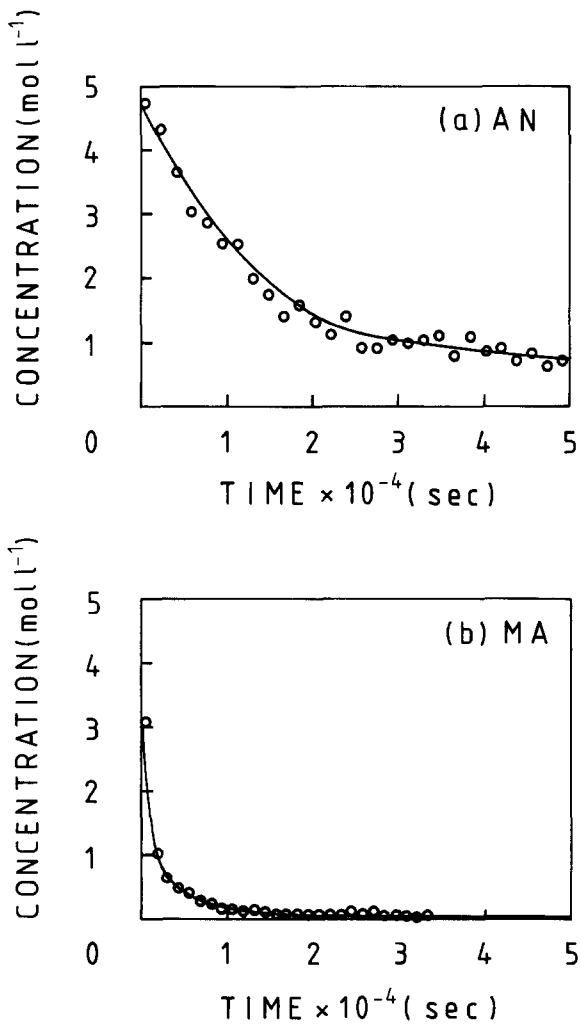

Figure 8 A plot of monomer concentration against time in high-conversion homopolymerization in d_6-DMSO at 60°C: (a) AN (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}); (b) MA (initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2}); (○) ^{13}C n.m.r. experimental data; (——) computer simulation data

Computer simulations for homopolymerizations of AN and MA have been carried out by using the values of k_d, $k_p/k_t^{0.5}$ and initiator efficiency determined as described above (see equation (24)). *Figure 8a* shows the simulation data together with the ^{13}C n.m.r. experimental data for

the homopolymerization of AN. *Figure 8b* shows the corresponding information for the homopolymerization of MA. The simulation data and experimental data agree more closely than was the case prior to the initiator efficiency being taken into account. *Figures 9a* and *9b* are the profiles of initiator efficiency with time. There appears to be a step change in efficiency. This stems from the fact that only two tangents were taken to the plot shown in *Figures 7a* and *7b*. If a series of tangents had been taken to the curve, then the change in initiator efficiency would have been somewhat more gradual, as illustrated by the broken curve. *Figures 10a* and *10b* are the profiles of initiator efficiency with conversion in homopolymerization of AN and MA, respectively. The comments concerning the number of tangents used apply to this figure also.

In order to confirm that initial monomer concentration does not affect the validity of the kinetic theory described above, the homopolymerization of AN was repeated with different initial monomer concentrations, i.e. 4 and 3 mol l^{-1}. Computer simulations have been carried out using k_d and $k_p/k_t^{0.5}$ determined in this work and the values of k_z/k_i and k_{d2}/k_i shown in *Table 3*. *Figures 11* and *12* show ^{13}C n.m.r. experimental data together with the simulated data for the homopolymerization with the initial monomer concentrations of 4 and 3 mol l^{-1}, respectively. It can be seen from these results that the proposed theory for initiator efficiency variation is applicable at least in the monomer concentration range from 3.00 to 4.74 mol l^{-1}. The fact that the initiator efficiency is independent of the initial monomer concentration also indicates that initiator efficiency of AIBN is not significantly diffusion-controlled in the

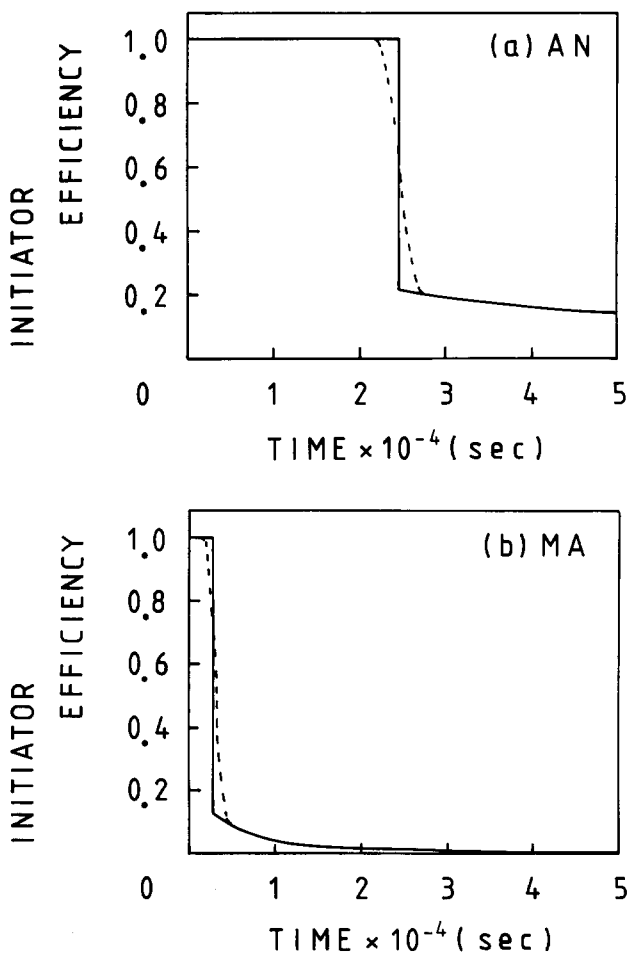

Figure 9 A plot of initiator efficiency of AIBN against time in homopolymerization in d_6-DMSO at 60°C: (a) AN (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}); (b) MA (initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2})

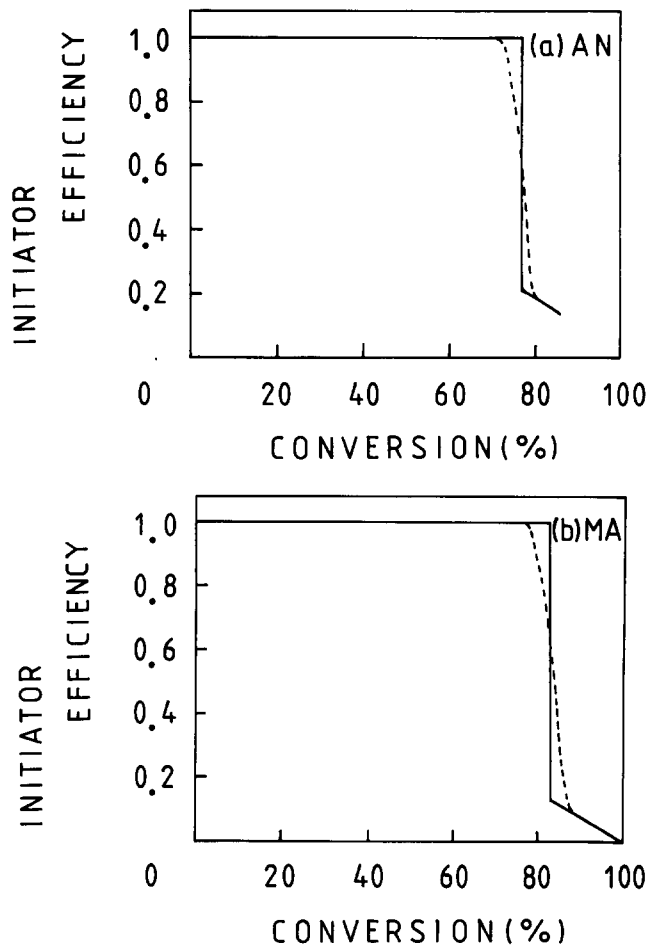

Figure 10 A plot of initiator efficiency of AIBN against conversion in homopolymerization in d_6-DMSO at 60°C: (a) AN (initial concentration of reagents (mol l^{-1}), AN 4.74, AIBN 1.6×10^{-2}); (b) MA (initial concentration of reagents (mol l^{-1}), MA 3.08, AIBN 1.6×10^{-2})

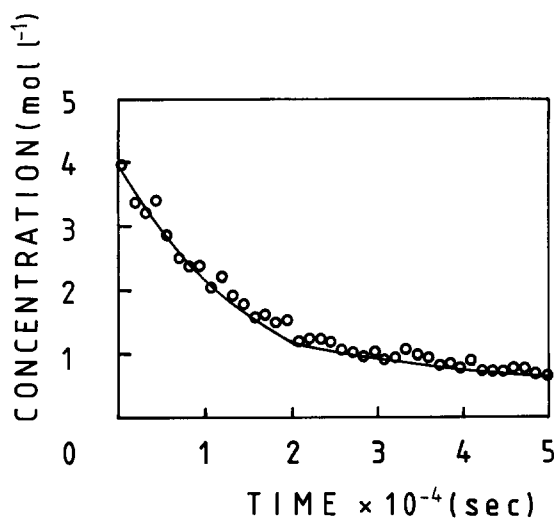

Figure 11 A plot of monomer concentration against time in high-conversion homopolymerization of AN in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 4.00, AIBN 1.6×10^{-2}): (○) ^{13}C n.m.r. experimental data; (——) computer simulation data

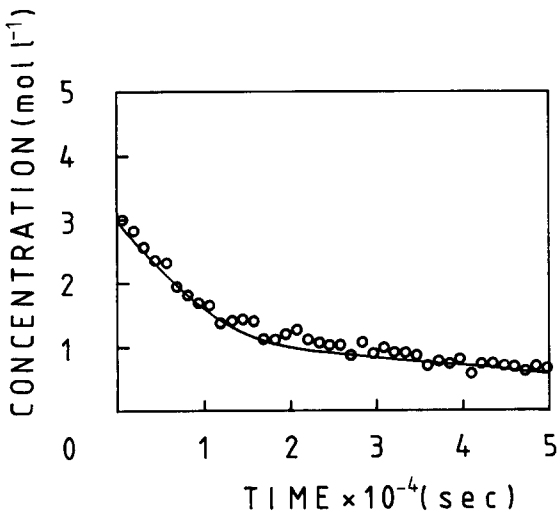

Figure 12 A plot of monomer concentration against time in high-conversion homopolymerization of AN in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 3.00, AIBN 1.6×10^{-2}): (○) ^{13}C n.m.r. experimental data; (——) computer simulation data

homopolymerization in this monomer concentration range, because the point of onset of the relatively sharp change of initiator efficiency must be dependent on initial monomer concentration when it is dependent on the medium viscosity.

The good agreement that has been achieved between the theory and experimental data means that it is not necessary to invoke diffusion-controlled reaction rates as a result of an increase in viscosity of the polymerization medium during reaction, at least under the conditions that have been used.

The experimental and theoretical approach described here have been found to be applicable to the copolymerization of AN with MA, and this work will be described in part 2 of this series[28].

CONCLUSION

New experimental evidence has been found for deviations from the classical free-radical polymerization reaction mechanism associated with the AIBN-initiated polymerization of AN and MA in DMSO when reactions are taken to high conversions, i.e. a significant reduction in the reaction rate occurs late in the isothermal polymerization process. On the basis of the novel suggestion for a solution polymerization process that the initiator efficiency can change sharply at relatively high monomer conversions, it has been possible to achieve good agreement between a kinetic mechanism that makes use of the steady-state assumption for primary radicals in a solvent 'cage' and experimental kinetic data obtained by real-time monitoring of polymerization by ^{13}C n.m.r. The initiator efficiency is only unity for both monomers when initiation takes place before β scission occurs. For both monomers, the initiator efficiency is very dependent on the concentration of monomer under all conditions other than the above. It has not been necessary to invoke the concept of diffusion-controlled reaction rates despite the fact that reactions were carried out with relatively high initial monomer concentrations in the batch reactor (3.0–5.0 mol l^{-1}) and that reactions were taken to conversions that were always greater than 85%. It is likely that this situation would not pertain at a lower polymerization temperature or a higher initial monomer concentration in the reaction mixture. The rate constant for the decomposition of AIBN in DMSO at 60°C has been found to be 2.0×10^{-5} s^{-1}.

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