Aspects of high-conversion free-radically initiated polymerizations: 2. Copolymerization of acrylonitrile with methyl acrylate in dimethylsulfoxide using azobisisobutyronitrile as initiator*

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The kinetic mechanism of the high-conversion free-radically initiated copolymerization of acrylonitrile with methyl acrylate in dimethylsulfoxide has been examined by using real-time ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy to monitor individual monomer conversions. Computer simulation techniques have been used to generate model predictions for comparison with experimental data. It has been found that the kinetic behaviour of the copolymerization can be explained by using Walling's kinetic model with $\phi = 1$ over the complete range of conversion without the necessity to invoke the concept of the penultimate-unit effect. However, it has been found that the initiator efficiency decreases very significantly around 80% conversion, and this has a considerable impact on the experimentally observed reaction rates over the last 20% conversion of monomers. The mathematical equations used to describe the influence of the initiator efficiency on the copolymerization reaction are an extension of those which successfully described the kinetic behaviour of the monomers in high-conversion homopolymerization reactions.

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

INTRODUCTION

There have been numerous studies of free-radically initiated copolymerization reactions. Walling[1] proposed the copolymerization kinetic model with a single adjustable parameter, the cross-termination factor ϕ; and the value of ϕ has been reported for some comonomer systems subsequently. Atherton and North[2] have suggested that Walling's kinetic model is not appropriate for some copolymerizations, and they proposed an alternative diffusion-controlled termination model in which termination reactions are not a function of the chemical properties of polymer radical and monomer. In addition to those models, Fukuda, Ma and Inagaki[3,4] have suggested that the influence of the penultimate units in the growing copolymer chains does have to be taken into account in order to explain the kinetic behaviour of some copolymerizations, and the available literature data for copolymerization rates were reinterpreted on the basis of the penultimate-unit effect model[5]. It was found that the smaller the value of the product r_1r_2, the more significant was the penultimate-unit effect, r_1 and r_2 being the monomer reactivity ratios. Kuchanov[6] and Fukuda[7] have recently provided excellent overviews of the theories of radically initiated copolymerization reactions.

In this work, the kinetic mechanism of the azobisisobutyronitrile-initiated copolymerization of acrylonitrile (AN) with methyl acrylate (MA) in dimethylsulfoxide solution has been explored in a batch reactor, paying particular attention to the kinetic characterization of the reaction when taken to high monomer conversions. It has recently been demonstrated in our laboratories that the initiator efficiency decreases rapidly and significantly at high conversions in homopolymerizations of both acrylonitrile and methyl acrylate[8]. It is shown that a similar variation in the initiator efficiency has to be invoked in order to explain the copolymerization kinetics. Computer simulation methods have been used to generate conversion and other information for the theoretical model that has been explored. Experimental kinetic data were generated by following the reactions in real-time ^{13}C n.m.r. spectroscopy. As this method of measurement makes it possible to assess 'instantaneous' monomer concentration, it is considered to be more accurate than relying on off-line measurements on either residual monomers or copolymer composition. A critical evaluation of the n.m.r. technique for monitoring

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polymerization reactions will be presented elsewhere[9]. Transfer reactions to monomer, polymer, initiator and solvent have all been considered to be negligible in this work, as the relevant rate constants are small[10–14].

THEORY

Walling's kinetic model

The overall rate of a copolymerization reaction can be described by using Walling's kinetic model as follows[1]:

$$-\frac{\mathrm{d}([\mathrm{M}_1]+[\mathrm{M}_2])}{\mathrm{d}t}=\frac{R_i^{0.5}(r_1[\mathrm{M}_1]^2+2[\mathrm{M}_1][\mathrm{M}_2]+r_2[\mathrm{M}_2]^2)}{(r_1^2\delta_1^2[\mathrm{M}_1]^2+2\phi r_1r_2\delta_1\delta_2[\mathrm{M}_1][\mathrm{M}_2]+r_2^2\delta_2^2[\mathrm{M}_2]^2)^{0.5}} \quad (1)$$

with

$$\delta_1=k_{\mathrm{t}1}^{0.5}/k_{11}$$
$$\delta_2=k_{\mathrm{t}2}^{0.5}/k_{22}$$
$$\phi=k_{\mathrm{t}12}/(k_{\mathrm{t}11}k_{\mathrm{t}22})^{0.5}$$

Subscripts 1 and 2 indicate monomer units 1 and 2, respectively, $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$ are the monomer concentrations, R_i is the initiation rate at time instant i and k_{pq} is the propagation rate constant with p and q representing the terminal and monomer units, respectively ($p, q=1$ or 2). The termination rate constants for homopolymerizations are given by $k_{\mathrm{t}1}$ and $k_{\mathrm{t}2}$ and the cross-termination rate constant is expressed as $k_{\mathrm{t}12}$. For a short time interval $(t_{i-1}-t_i)$, the overall monomer concentration can be expressed with time as:

$$[\mathrm{M}]_i=[\mathrm{M}]_{i-1}\exp\left(-R_{i-1}^{0.5}\frac{r_1f_1^2+2f_1f_2+r_2f_2^2}{(r_1^2\delta_1^2f_1^2+2\phi r_1r_2\delta_1\delta_2f_1f_2+r_2^2\delta_2^2f_2^2)^{0.5}}(t_{i-1}-t_i)\right) \quad (2)$$

with

$$f_1=\frac{[M_1]_{i-1}}{[\mathrm{M}_1]_{i-1}+[\mathrm{M}_2]_{i-1}}$$
$$f_2=\frac{[M_2]_{i-1}}{[\mathrm{M}_1]_{i-1}+[\mathrm{M}_2]_{i-1}}$$

where $[\mathrm{M}]_i$ is the overall concentration of monomer at a given instant in time i and $[\mathrm{M}]_{i-1}$ is the concentration at a previous time $i-1$, the time interval being $(t_{i-1}-t_i)$, $[\mathrm{M}_1]_i$ and $[\mathrm{M}_2]_i$ are concentrations of individual monomers at a given instant in time, and $[\mathrm{M}_1]_{i-1}$ and $[\mathrm{M}_2]_{i-1}$ are the concentrations at a previous time, the time interval being $(t_{i-1}-t_i)$. The concentration of individual monomers in the copolymerization can be obtained from equation (2) as follows:

$$[\mathrm{M}_1]_i=[\mathrm{M}_1]_{i-1}\exp\left(-R_{i-1}^{0.5}\frac{r_1f_1+f_2}{(r_1^2\delta_1^2f_1^2+2\phi r_1r_2\delta_1\delta_2f_1f_2+r_2^2\delta_2^2f_2^2)^{0.5}}(t_{i-1}-t_i)\right) \quad (3)$$

$$[M_2]_i=[\mathrm{M}_2]_{i-1}\exp\left(-R_{i-1}^{0.5}\frac{r_2f_2+f_1}{(r_1^2\delta_1^2f_1^2+2\phi r_1r_2\delta_1\delta_2f_1f_2+r_2^2\delta_2^2f_2^2)^{0.5}}(t_{i-1}-t_i)\right) \quad (4)$$

Simulation program

A computer simulation program based on the above model has been constructed. The total conversion time was divided into 1000 equal time intervals (dt) and the values of monomer and initiator concentrations were calculated for each time interval. The total volume of all reagents (V_i) has been determined at each time interval i by using:

$$V_i=V_0+V_{i-1}\{(\rho_\mathrm{p}^{-1}-\rho_1^{-1})([\mathrm{M}_1]_{i-1}-[\mathrm{M}_1]_i)\mathrm{M}_{\mathrm{w}1}+(\rho_\mathrm{p}^{-1}-\rho_2^{-1})([\mathrm{M}_2]_{i-1}-[\mathrm{M}_2]_i)M_{\mathrm{w}2}\} \quad (5)$$

in which V_0 is the initial volume of all reagents, and ρ_1, ρ_2 and ρ_p are densities of AN (0.80 g ml^{-1}), MA (0.95 g ml^{-1}) and the copolymer (1.10 g ml^{-1}), respectively. V_{i-1} is the total volume of all reagents at previous time $i-1$, time difference being dt. The terms $M_{\mathrm{w}1}$ and $M_{\mathrm{w}2}$ are molecular weights of AN (53) and MA (86), respectively. Simulations were carried out by using an Olivetti personal computer (model M380). The programs were written in Quick Basic.

EXPERIMENTAL

Materials

Acrylonitrile (AN) and methyl acrylate (MA) (BDH Chemicals Ltd) were each 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 molecular sieves (3 Å) (BDH Chemicals Ltd), and distilled twice under reduced pressure.

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

The real-time n.m.r. method that has been used to follow high-conversion polymerization processes has been outlined in part 1 of this series[8]. A more detailed description of n.m.r. for evaluating the kinetics of polymerization processes will be described elsewhere[9]. A typical ^{13}C n.m.r. spectrum taken during the copolymerization of AN with MA in DMSO is shown in *Figure 1*.

RESULTS AND DISCUSSION

Monomer reactivity ratios

The kinetic scheme for propagation steps of copolymerization of the terminal model can be expressed as follows[15]:

$$\mathrm{M}_1^*+\mathrm{M}_1\xrightarrow{k_{11}}M_1M_1^*$$
$$\mathrm{M}_1^*+\mathrm{M}_2\xrightarrow{k_{12}}M_1M_2^*$$
$$\mathrm{M}_2^*+\mathrm{M}_1\xrightarrow{k_{21}}M_2M_1^*$$
$$\mathrm{M}_2^*+\mathrm{M}_2\xrightarrow{k_{22}}M_2M_2^*$$

where M_1 and M_2 are the respective monomers, the asterisk (*) represents active centres and k_{pq} is the rate constant for the terminal sequence with p and q representing terminal and monomer unit, respectively.

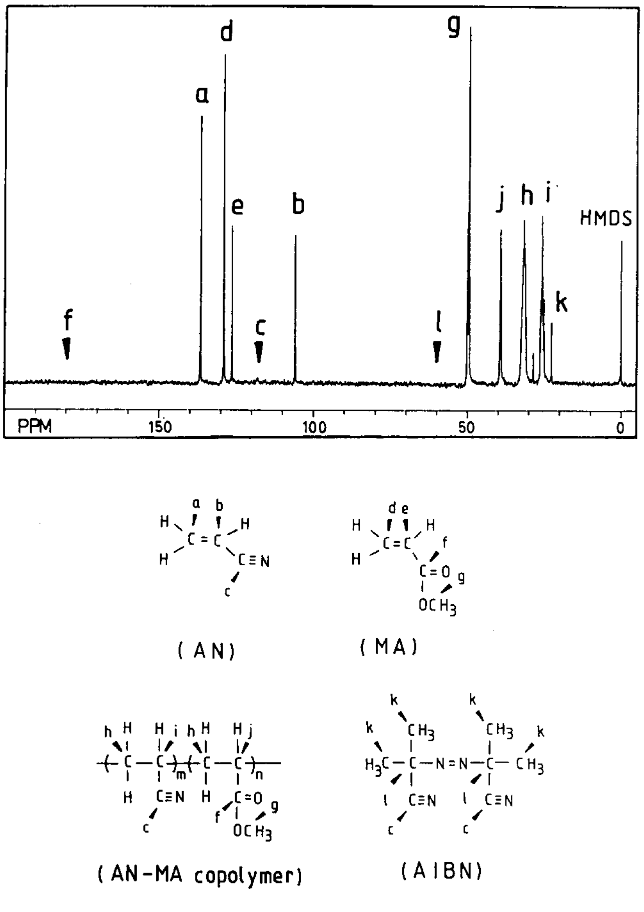

Figure 1 A typical real-time ^{13}C n.m.r. spectrum acquired during copolymerization of AN with MA in d$_6$-DMSO at 60°C (polymerization time, 6900 s; initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016)

The individual polymerization rate of monomers can be determined as follows:

$$-\mathrm{d}[\mathrm{M}_1]/\mathrm{d}t = k_{11}[\mathrm{M}_1^\bullet][\mathrm{M}_1] + k_{21}[\mathrm{M}_2^\bullet][\mathrm{M}_1] \tag{6}$$

$$-\mathrm{d}[\mathrm{M}_2]/\mathrm{d}t = k_{12}[\mathrm{M}_1^\bullet][\mathrm{M}_2] + k_{22}[\mathrm{M}_2^\bullet][\mathrm{M}_2] \tag{7}$$

Here, square brackets mean concentration of each species. For those situations where the monomer feed composition does not change significantly during copolymerization, i.e. when the changes in concentration of both monomers are small in comparison with the absolute concentrations of both monomers, the ratio of $[\mathrm{M}_1]$ to $[\mathrm{M}_2]$ can be assumed to be constant. When the rate of initiation does not change significantly during copolymerization, the total concentration of radicals ($[\mathrm{M}_1^\bullet] + [\mathrm{M}_2^\bullet]$) can be assumed to be essentially constant. When these conditions are applicable, the change in the concentrations of the individual monomers in copolymerizations can be described by an exponential curve as follows:

$$[\mathrm{M}_1] = [\mathrm{M}_1]_0 \exp(-\alpha t) \tag{8}$$

$$[\mathrm{M}_2] = [\mathrm{M}_2]_0 \exp(-\beta t) \tag{9}$$

with

$$\alpha = k_{11}[\mathrm{M}_1^\bullet] + k_{21}[\mathrm{M}_2^\bullet]$$

$$\beta = k_{22}[\mathrm{M}_2^\bullet] + k_{12}[\mathrm{M}_1^\bullet]$$

Here, $[\mathrm{M}_1]_0$ and $[\mathrm{M}_2]_0$ are initial concentrations of monomers. From equations (8) and (9), the individual rates of copolymerizations can be expressed as:

$$-\mathrm{d}[\mathrm{M}_1]/\mathrm{d}t = -\alpha[\mathrm{M}_1]_0 \exp(-\alpha t) \tag{10}$$

$$-\mathrm{d}[\mathrm{M}_2]/\mathrm{d}t = -\beta[\mathrm{M}_2]_0 \exp(-\beta t) \tag{11}$$

From equations (10) and (11):

$$\frac{\mathrm{d}[\mathrm{M}_1]}{\mathrm{d}[\mathrm{M}_2]} = \frac{\alpha[\mathrm{M}_1]_0 \exp(-\alpha t)}{\beta[\mathrm{M}_2]_0 \exp(-\beta t)} = \frac{\alpha[\mathrm{M}_1]}{\beta[\mathrm{M}_2]} \tag{12}$$

Copolymer composition can be described by using r_1 and r_2 as follows:

$$\frac{\mathrm{d}[\mathrm{M}_1]}{\mathrm{d}[\mathrm{M}_2]} = \frac{r_1[\mathrm{M}_1] + [\mathrm{M}_2]}{[\mathrm{M}_1] + r_2[\mathrm{M}_2]}\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} \tag{13}$$

By determining the values of α and β in the system where $[\mathrm{M}_1]/[\mathrm{M}_2]$ is maintained constant, it is possible to calculate monomer reactivity ratios r_1 and r_2 using equations (8)–(13).

Figure 2 shows the change in monomer feed composition with time during copolymerization of AN with MA in DMSO at 60°C. It can be seen that monomer feed composition remains almost constant during the period studied: $[\mathrm{AN}]/([\mathrm{AN}]+[\mathrm{MA}]) = 0.59 \pm 0.01$, $[\mathrm{MA}]/([\mathrm{AN}]+[\mathrm{MA}]) = 0.41 \pm 0.01$. Therefore equations (8)–(13) are applicable to this copolymerization. *Figure 3* shows experimental data for concentrations of AN and MA with time during the copolymerization, together with the best first-order exponential curves. The values of α and β for AN and MA in equations (8) and (9) are 8.533×10^{-5} and 6.410×10^{-5}, respectively. Then, when these values are used in equations (8)–(13), r_1 and r_2 are 1.33 and 0.76, respectively. The results are shown in *Table 1* together with the relevant literature values obtained from copolymer composition analysis[16]. The method described above should be more reliable than copolymer composition analysis. It is easier to measure instantaneous monomer concentration than to draw conclusions from accumulated information of copolymer composition at a given time.

Initiator efficiency

It has been suggested[8] that the reactions of primary radicals should be considered with some care in

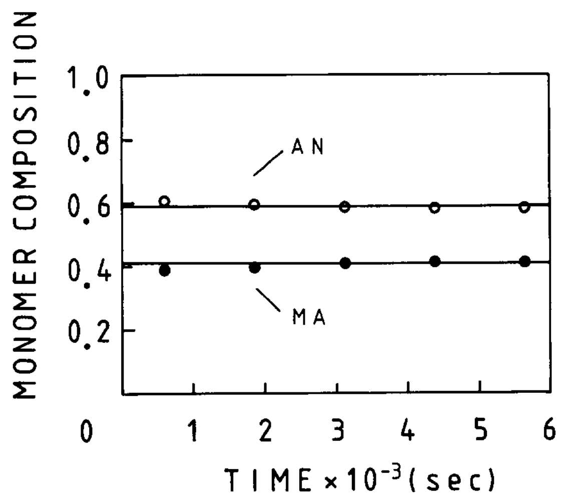

Figure 2 Plots of monomer feed compositions against time in copolymerization of AN with MA in d$_6$-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 2.39, MA 1.54, AIBN 0.016): (○) ^{13}C n.m.r. experimental data for AN; (●) ^{13}C n.m.r. experimental data for MA; (——) average values (0.59 for AN, 0.41 for MA)

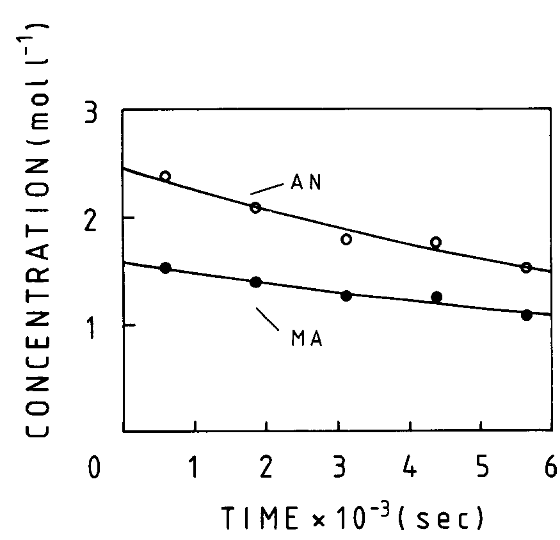

Figure 3 Plots of monomer concentrations against time in copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 2.39, MA 1.54, AIBN 0.016): (○) ^{13}C n.m.r. experimental data for AN; (●) ^{13}C n.m.r. experimental data for MA; (——) the best exponential curves

Table 1 Monomer reactivity ratios for copolymerization of AN with MA in DMSO

	r_{AN}	r_{MA}	$r_{AN}r_{MA}$
This research (60°C)	1.33	0.76	1.01
Literature^a (50°C)	1.02±0.02	0.70±0.02	0.71±0.04

^{a}Ref. 16

order that the kinetics of the high-conversion AIBN-initiated homopolymerizations of AN and MA might be adequately explained, i.e. the nature of the addition to monomer (initiation), and primary radical recombination reactions inside the solvent cage. An expression describing the initiator efficiency in copolymerization reactions can be derived using the same general logic as that which has been described for homopolymerization reactions[8]. The kinetic scheme for reactions involving primary radicals in copolymerization can be expressed as follows:

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

$$(2\mathrm{R}^*)+\mathrm{M}_1 \xrightarrow{k_{i1}} \mathrm{R{-}M}_1^* + \mathrm{R}^*$$

$$(2\mathrm{R}^*)+\mathrm{M}_2 \xrightarrow{k_{i2}} \mathrm{R{-}M}_2^* + \mathrm{R}^*$$

$$(2\mathrm{R}^*) \xrightarrow{k_z} \mathrm{R{-}R}$$

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

Here, the parentheses are used to indicate that the species are within a solvent cage, and the subscripts 1 and 2 represent monomers 1 and 2, respectively. The rate constants for the initiation reactions are given by k_{i1} and k_{i2}, a single constant for all recombination steps is given by k_z, and the rate constant for diffusion from the solvent cage is given by k_{dif}. The decomposition of AIBN is regarded as a two-step reaction that includes β scission. However, this reaction may be reasonably approximated as a one-step reaction, as the rate of β scission is much faster than that of the first scission in the steady state[8]. The concentration of primary radicals within the solvent cage can be expressed as:

$$d[(2R^*)]/dt = 2k_d[I] - R_i - R_z - R_{dif} = 0 \qquad (14)$$

The rates of initiation (R_i), of recombination (R_z) and of diffusion from the solvent cage (R_{dif}) can be expressed as:

$$R_i = k_{i1}[(2R^*)][M_1] + k_{i2}[(2R^*)][M_2] \qquad (15)$$

$$R_z = k_z[(2R^*)] \qquad (16)$$

$$R_{dif} = k_{dif}[(2R^*)] \qquad (17)$$

It follows that the concentration of primary radicals within the solvent cage is given by:

$$[(2R^*)] = \frac{k_d[I]}{k_{i1}[M_1] + k_{i2}[M_2] + k_z + k_{dif}} \qquad (18)$$

The kinetic expressions for the reaction of primary radicals outside the solvent cage can also be described:

$$\mathrm{R}^* + \mathrm{M}_1 \xrightarrow{k_{i1}} \mathrm{R{-}M}_1^*$$

$$\mathrm{R}^* + \mathrm{M}_2 \xrightarrow{k_{i2}} \mathrm{R{-}M}_2^*$$

In the steady state it follows that:

$$d[R^*]/dt = R_{dif} + R_i - R_i' = 0 \qquad (19)$$

where the rate of initiation reaction outside the solvent cage (R_i') is given by:

$$R_i' = k_{i1}[R^*][M_1] + k_{i2}[R^*][M_2] \qquad (20)$$

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

$$[R^*] = \frac{k_{i1}[M_1] + k_{i2}[M_2] + k_{dif}}{k_{i1}[M_1] + k_{i2}(M_2]}[(2R^*)] \qquad (21)$$

Then the ratio of initiation to recombination, $f/(1-f)$, can be derived as follows, where f is initiator efficiency:

$$\frac{f}{1-f} = \frac{R_i + R_i'}{R_z} \qquad (22)$$

When the expression for f is combined with equations (15), (16), (18), (20) and (21), one obtains:

$$f = \frac{2k_{i1}[M_1] + 2k_{i2}[M_2] + k_{dif}}{2k_{i1}[M_1] + 2k_{i2}[M_2] + k_z + k_{dif}} \qquad (23)$$

The magnitude of k_{dif} can be much smaller than that of ($2k_{i1}[M_1] + 2k_{i2}[M_2]$), and was found to be negligible in the case of the homopolymerization of AN and MA[8]. If it is assumed that the same situation pertains in the copolymerization of these monomers, then equation (23) can be reduced to:

$$f = \frac{2k_{i1}[M_1] + 2k_{i2}[M_2]}{2k_{i1}[M_1] + 2k_{i2}[M_2] + k_z} \qquad (24)$$

The values of k_z/k_{i1} and k_z/k_{i2} have been determined previously[8], and are given in *Table 2*. When initiation takes place before β scission occurs, the initiator efficiency is always unity[8]. At the point where the initiator efficiency rapidly starts to deviate from unity, the following equation applies:

$$k_{i1}[M_1][\text{cage-A}] + k_{i2}[M_2][\text{cage-A}] = k_{d2}[\text{cage-A}] \qquad (25)$$

Table 2 Values of k_z/k_i and k_{d2}/k_i for homopolymerizations of AN and MA[a]

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

[a] Ref. 8

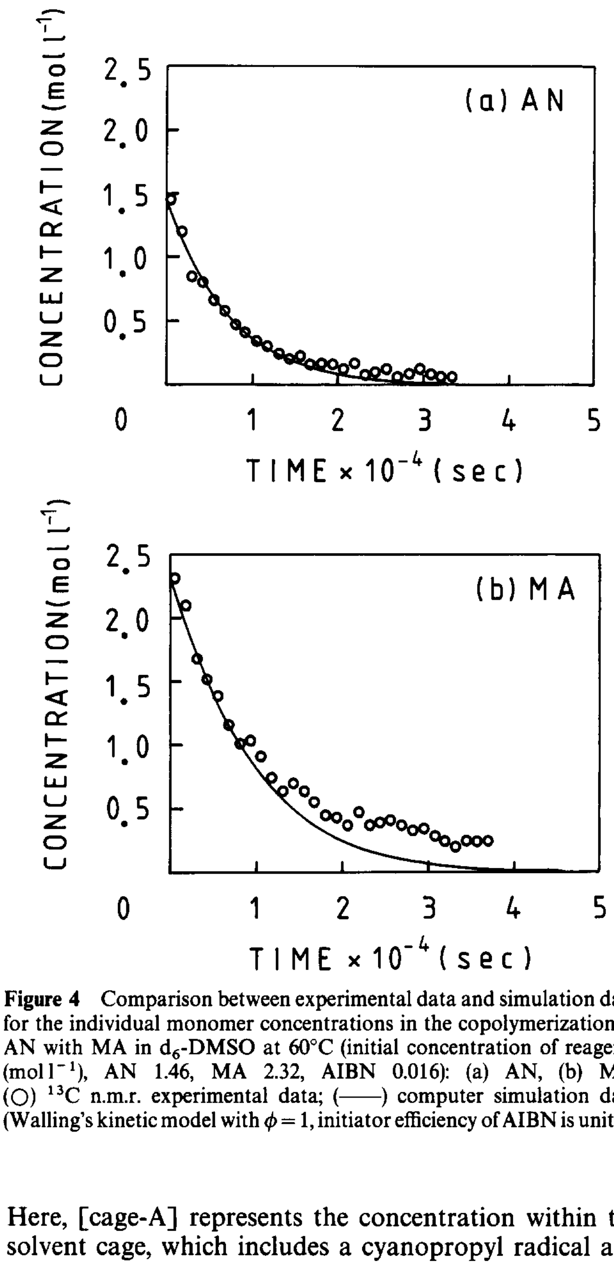

Figure 4 Comparison between experimental data and simulation data for the individual monomer concentrations in the copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016): (a) AN, (b) MA; (○) ^{13}C n.m.r. experimental data; (——) computer simulation data (Walling's kinetic model with $\phi = 1$, initiator efficiency of AIBN is unity)

Here, [cage-A] represents the concentration within the solvent cage, which includes a cyanopropyl radical and a diazenyl radical, and k_{d2} is the rate constant for β scission described in *Figure 3*. From equations (24) and (25) it is possible to arrive at the equations:

$$f = 1 \quad \text{when } (k_{d2}/k_{i1})^{-1}[M_1] + (k_{d2}/k_{i2})^{-1}[M_2] > 1$$

$$f = \{1 + (2[M_1](k_z/k_{i1})^{-1} + 2[M_2](k_z/k_{i2})^{-1})^{-1}\}^{-1} \quad \text{when } (k_{d2}/k_{i1})^{-1}[M_1] + (k_{d2}/k_{i2})^{-1}[M_2] \leqslant 1 \qquad (26)$$

Computer simulation for high-conversion copolymerization

A computer simulation of the rate of the copolymerization has been carried out usig Walling's kinetic model, equations (3) and (4). In the simulation model the value of ϕ was assumed to be unity, i.e. there is no preference for cross-termination or termination by like radicals. This assumption was made, not for any specific mechanistic reason, but simply as a starting point for the simulation. The value of other parameters used in the simulation are summarized in *Table 3. Figures 4a* and *4b* show the concentrations of AN and MA in the copolymerization, which have been determined by ^{13}C n.m.r., together with computer simulation data, which have been obtained by using a constant value for the initiator efficiency of unity. Experimental data coincide with simulation data at relatively low monomer conversion. However, it is apparent that experimental data and simulation data diverge at relatively high conversion. This deviation has been attributed to a decrease in initiator efficiency with conversion of monomers[8]. *Figure 5* shows a plot of the initiator efficiency with time for the copolymerization, calculated using equation (26). *Figure 6* shows a plot of the initiator efficiency with total monomer conversion. It can be seen that the initiator efficiency decreases significantly around 80% conversion of both monomers. As described in part 1[8], in reality the change in initiator efficiency would be somewhat more gradual, as illustrated by the broken curve. The conversion at which the change in initiator efficiency occurs depends on the instantaneous composition of monomers. In *Figures 7a* and *7b*, experimental data for the concentrations of AN and MA in the copolymerization are plotted against time, together with computer simulation data in which the change in initiator efficiency has been taken into account. In *Figure 8* are given the corresponding time–conversion plots. It can be seen that the kinetic behaviour of AIBN-initiated copolymerization of AN with MA can be described in terms of Walling's classical kinetic model

Table 3 Parameters that have been used in computer simulations

Parameter	Value	Ref.
k_d	2.0×10^{-5} s^{-1}	8
$k_p/k_t^{0.5}$(AN)	0.0836 $l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	8
$k_p/k_t^{0.5}$(MA)	0.745 $l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	8
r_{AN}	1.33	This work
r_{MA}	0.76	This work

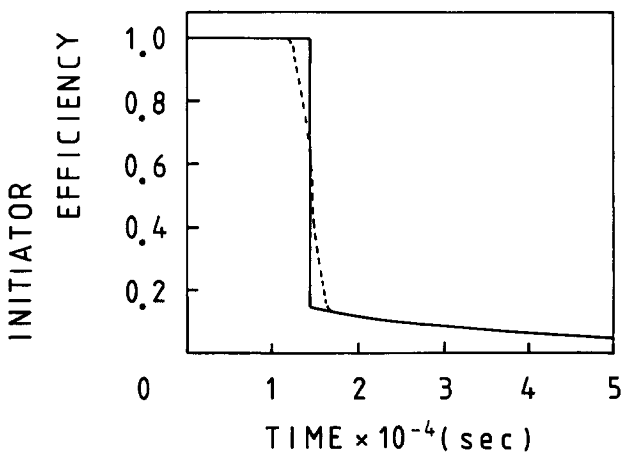

Figure 5 A plot of initiator efficiency of AIBN against time in the copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016)

with $\phi = 1$ over the whole range of total monomer conversion provided the changes in initiator efficiency with conversion are taken into account. There is no penultimate-unit effect in the copolymerization of AN with MA in DMSO. Since $r_1 r_2 = 1.0$ (see *Table 1*), the copolymerization can be described as an 'ideal copolymerization'.

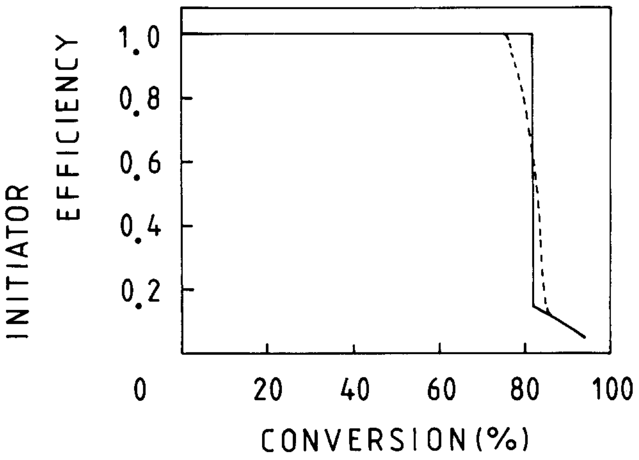

Figure 6 A plot of initiator efficiency of AIBN against conversion in the copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016)

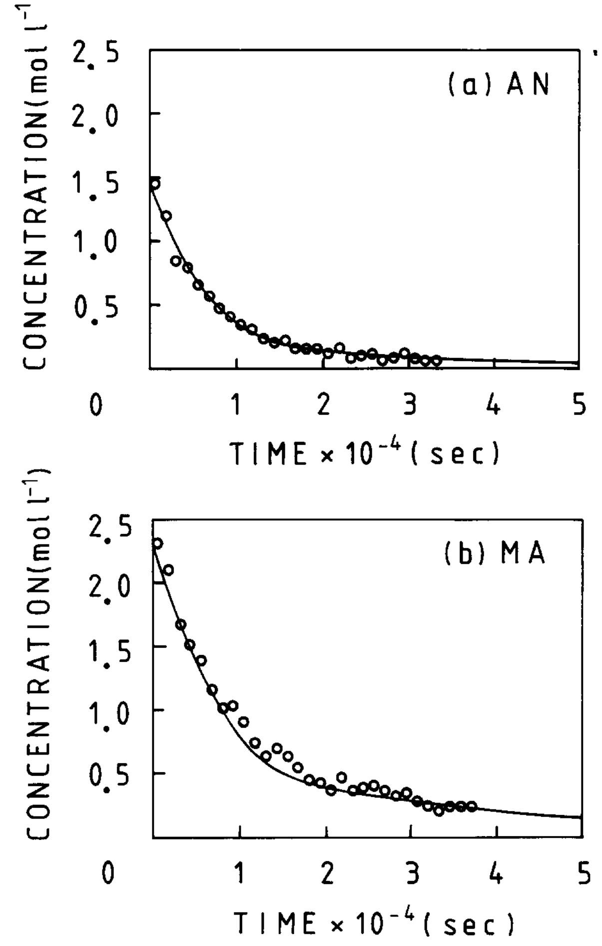

Figure 7 Comparison between experimental data and simulation data for the individual monomer concentrations in the copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016): (a) AN, (b) MA; (○) ^{13}C n.m.r. experimental data; (——) computer simulation data (Walling's kinetic model with $\phi = 1$)

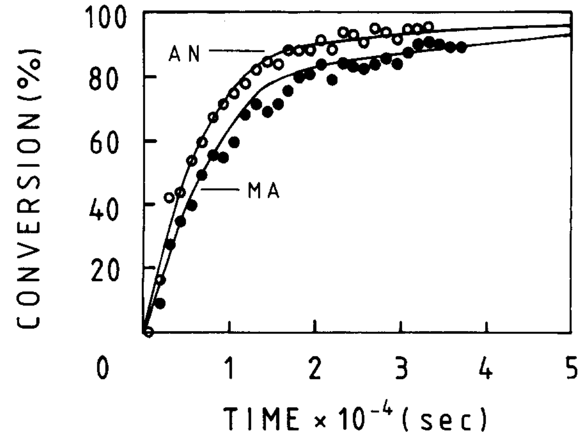

Figure 8 Comparison between experimental data and simulation data for the individual monomer conversions in the copolymerization of AN with MA in d_6-DMSO at 60°C (initial concentration of reagents (mol l^{-1}), AN 1.46, MA 2.32, AIBN 0.016): (○) ^{13}C n.m.r. experimental data; (——) computer simulation data (Walling's kinetic model with $\phi = 1$)

The diffusion-controlled model has been tested, but with little success. This work will be reported elsewhere[17] when considering the impact of monomer composition on the observed kinetic behaviour for the AN+MA system.

CONCLUSION

It is uncommon to find experimental data for the kinetic behaviour of individual monomers in a copolymerization reaction. It has been shown that it is possible to use these data in order to arrive at a more detailed understanding of high-conversion processes. The mechanism of the free-radically initiated copolymerization of AN with MA in DMSO solution can be explained by using Walling's kinetic model with $\phi = 1$ over the whole range of conversion provided the change in the initiator efficiency, which occurs at approximately 80% conversion, is taken into account. The penultimate-unit effect is not significant in the AN+MA system and there is no preference for cross-termination or for termination by like radicals. It has been found that computer simulations are helpful in analysing copolymerization kinetic behaviour. The monomer reactivity ratios for AN (monomer 1) and MA (monomer 2) in copolymerization in DMSO initiated by AIBN at 60°C, determined by following the kinetics of copolymerization, are $r_1 = 1.33$ and $r_2 = 0.76$, respectively.

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