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Instantaneous Copolymer Composition in High Conversion Copolymerization of Acrylonitrile and Methyl Acrylate Assessed by in Situ ^{13}C NMR Measurements of Individual Monomer Reaction Rates

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ABSTRACT: The copolymerization of acrylonitrile with methyl acrylate initiated by azobis(isobutyronitrile) in dimethyl sulfoxide at 60 °C has been investigated to high conversion using in situ ^{13}C NMR spectroscopy. The focus has been on the relative rates of individual monomer consumption as a function of time up to as high a conversion as experimentally feasible. It has been found that the relative rates of monomer consumption, i.e., the instantaneous copolymer composition, cannot be described by the low conversion values of the monomer reactivity ratios r_1 and r_2. These findings are discussed within the framework of possible effects of monomer diffusion rates and explicit penultimate unit effects in connection with monomer composition drift.

Introduction

High conversion free radical copolymerizations of many different monomer combinations are of great commercial importance, but despite this fact, the kinetics of many processes at high conversions still remain relatively poorly understood. Electron spin resonance spectroscopy (ESR)[1] and pulsed-laser polymerization combined with size-exclusion chromatography for the analysis of the molecular weight distribution (PLP−SEC)[2] has allowed the determination of propagation (k_p) and termination rate coefficients (k_t) as functions of conversion for many radically initiated homopolymerizations, and there is an increasing body of data available for the conversion dependences of k_p and k_t.[2−13] The kinetics of copolymerization systems are thus far considerably less well-understood, especially at high conversion of monomers.[14−20]

An interesting aspect of high conversion free radical copolymerization is the extent to which the copolymer composition can be predicted as a function of conversion using the terminal model monomer reactivity ratios (r_1 and r_2) as estimated at low conversion. Good agreement has been reported for several copolymerization systems over various conversion ranges based on the cumulative copolymer composition (e.g., by use of the integrated copolymerization equation[21]).[14,22−28] Without disputing these important findings, this type of analysis should not be treated as a strict test of the validity of the low conversion terminal model at high conversion with regards to copolymer composition due to the relative insensitivity of the cumulative copolymer composition to possible changes in the instantaneous copolymer composition over a relatively narrow high conversion range. It is therefore instructive to examine the instantaneous copolymer composition in reactions taken to high conversion even though this quantity can be difficult to access directly by any experimental method. However, it is possible to monitor the individual rates of monomer consumption up to high conversion much more readily. Several models of high conversion bulk free radical copolymerization of various degrees of complexity have been reported where comparisons between computed and experimental copolymer compositions have been made, but none of these have focused on instantaneous copolymer compositions at high conversion.[29−35]

In this paper, an in situ ^{13}C NMR investigation of the high conversion copolymerization of acrylonitrile and methyl acrylate in dimethyl sulfoxide is reported. This monomer pair is interesting because methyl acrylate (and possibly also acrylonitrile, although accurate k_p data are not available) is a monomer with a high k_p, and thus diffusion-controlled propagation would be expected to commence at a lower conversion than for a monomer with a lower k_p, e.g., styrene. When the propagation step (one or more of the four separate propagation steps using the terminal model as basis) becomes diffusion-controlled, the low conversion reactivity ratios will no longer be meaningful, and the monomer "reactivities" will instead be governed by the monomer diffusion coefficients.[15] As far as we are aware, this prediction has to date not been substantiated experimentally. Moreover, in view of the fact that an explicit PUE has been detected in the copolymerization of styrene and acrylonitrile,[36] one might anticipate that an explicit PUE is operative also in the acrylonitrile/methyl acrylate system. In order for constant values of r_1 and r_2 to be consistent with the instantaneous copolymer composition as a function of conversion, it is a requirement that any penultimate unit effects (PUE) are implicit in nature if the monomer feed composition

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Table 1. Copolymerizations of Acrylonitrile/Methyl Acrylate in d_6-DMSO Initiated by 0.016 M AIBN at 60 °C

experiment	$[AN]_0$ (M)	$[MA]_0$ (M)	$[M]_{tot,0}$ (M)	$f_{AN,0}$
A	3.06	0.81	3.87	0.79
B	2.39	1.54	3.93	0.61
C	1.46	2.32	3.78	0.39
D	0.72	3.05	3.77	0.19

changes with conversion (as it normally does). In the case of an explicit PUE, r_1 and r_2 will depend on conversion if the monomer feed composition changes with conversion. In addition to analyzing the instantaneous copolymer composition as a function of conversion, the lumped parameter $k_p(f/k_t)^{0.5}$ has been evaluated as a function of conversion and monomer feed composition.

Experimental Section

Materials. Commercial acrylonitrile (AN) and methyl acrylate (MA) (BDH Chemicals Ltd.) were refluxed with calcium hydride for 7 h and distilled twice at atmospheric pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN; BDH Chemicals Ltd.) was recrystallized in methanol. d_6-Dimethyl sulfoxide (d_6-DMSO; Goss Scientific Instruments Ltd.) was refluxed over molecular sieves (BDH Chemicals Ltd.) and distilled twice under reduced pressure.

Real-Time ^{13}C NMR. Copolymerizations were carried out at different initial monomer feeds initiated by 0.016 M AIBN in d_6-DMSO at 60 °C (Table 1). Monomer concentrations as functions of time were obtained by real-time in situ ^{13}C NMR measurements. Polymerizations were carried out in the NMR cavity (JEOL GX270) in sealed NMR tubes (10 mm diameter) at 60 °C. Hexamethylenedisiloxane (HMDS) was used as an internal standard. Spectra were automatically accumulated with time. Distortionless enhancement by polarization transfer (DEPT) was employed to measure the monomer concentration. The pulse delay time was 3.0 s, the sampling time 0.9 s, and the irradiation time 12.0 μs. In one polymerization run, at least 300 spectra were accumulated, each consisting of 33 000 data points. Baseline correction and smoothing (19 point moving average) were applied to each spectrum. The accumulation time for one spectrum was 21 min, and the resulting data point was assigned the time corresponding to the arithmetic average of the time passed from the beginning of the polymerization between the start and the end of the sampling time. A typical spectrum has been has been given in a previous report of related work.[16] The AN concentration was computed from the ratio of the area of one (136 ppm) of the two peaks (136 and 106 ppm) corresponding to the carbon−carbon double bond to that of the HDMS peak. The MA concentration was computed from the ratio of the area of one (129 ppm) of the two peaks (129 and 126 ppm) corresponding to the carbon−carbon double bond to that of the HDMS peak. After each polymerization run, it was confirmed by weighing that no loss of material had occurred.

Conversion by Gravimetry. To verify the NMR data, overall conversion−time data were obtained by gravimetry for a selected copolymerization of 2.39 M AN and 1.54 M MA initiated by 0.016 M AIBN in d_6-DMSO at 60 °C in a water bath taken to close to 80% conversion (over 300 min reaction time). The polymer obtained was precipitated in a 10-fold excess of methanol and purified by reprecipitation twice using a DMSO/methanol mixture and subsequently dried over P_2O_5. The results revealed near perfect agreement between the two methods throughout the entire conversion range investigated (Figure 1).

Results and Discussion

Relative Rates of Individual Monomer Conversion. The individual conversions of AN and MA in the copolymerizations of Table 1 as obtained by real-time in situ ^{13}C NMR measurements are displayed in Figures 2−5.

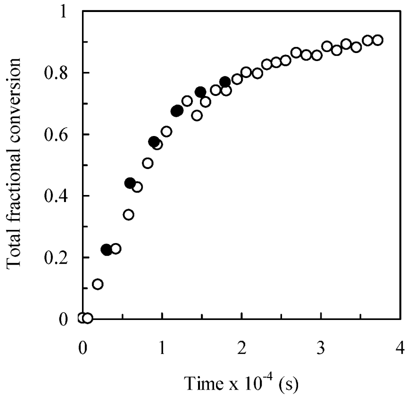

Figure 1. Comparison of total fractional conversion obtained by gravimetry (●) and ^{13}C NMR (○) for the copolymerization of AN and MA ($f_{AN,0}$ = 0.61) in dimethyl sulfoxide initiated by 0.016 M AIBN at 60 °C. The ^{13}C NMR conversions in this figure refer to the weight of polymer formed as a fraction of the weight of polymer at complete conversion of both monomers (differences in molar mass of monomers considered).

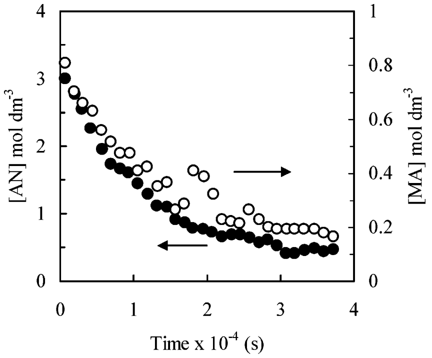

Figure 2. Monomer concentrations vs time for the copolymerization of AN (●) and MA (○) with $f_{AN,0}$ = 0.79 in dimethyl sulfoxide initiated by 0.016 M AIBN at 60 °C.

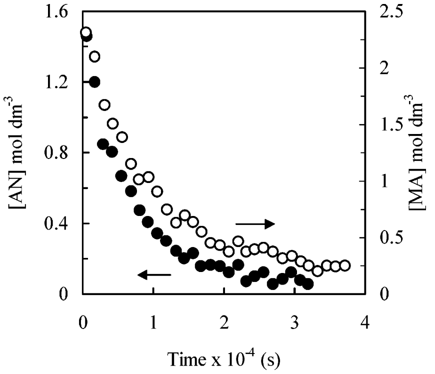

Figure 3. Monomer concentrations vs time for the copolymerization of AN (●) and MA (○) with $f_{AN,0}$ = 0.39 in dimethyl sulfoxide initiated by 0.016 M AIBN at 60 °C.

The experimental instantaneous copolymer composition, $F_{1,\mathrm{inst(exp)}}$, can be obtained as a function of conversion from the individual monomer consumption rates using eq 1:

$$F_{1,\mathrm{inst(exp)}} = \left(\frac{d[M_1]}{dt}\right) \Big/ \left(\frac{d[M_1]}{dt} + \frac{d[M_2]}{dt}\right) \qquad (1)$$

According to the terminal model, the instantaneous copolymer composition as a function of the instanta-

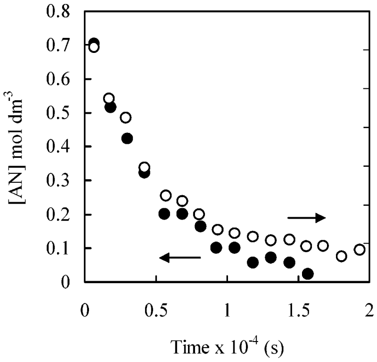

Figure 4. Monomer concentrations vs time for the copolymerization of AN (●) and MA (○) with $f_{\text{AN},0} = 0.19$ in dimethyl sulfoxide initiated by 0.016 M AIBN at 60 °C.

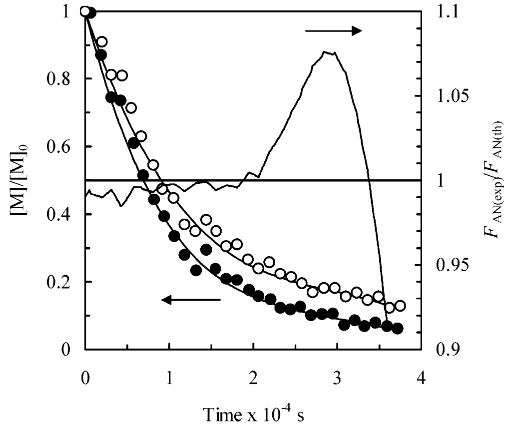

Figure 5. Monomer concentrations vs time (expressed as [M]/[M]$_0$, where [M] is the instantaneous and [M]$_0$ the initial monomer concentration) for the experiment with $f_{\text{AN},0} = 0.61$ (MA (○); AN (●)). The lines through the data points are the polynomials fits, based on which the relative consumption rates were obtained. The quantity $F_{\text{AN(exp)}}/F_{\text{AN(th)}}$ (eqs 1 and 2) is based on the terminal model with $r_{\text{AN}} = 1.33$ and $r_{\text{MA}} = 0.76$.

neous monomer feed composition can be expressed in terms of r_1 and r_2 according to eq 2:

$$F_{1,\text{inst(model)}} = \frac{f_1(r_1 f_1 + f_2)}{r_1 f_1^{\,2} + r_2 f_2^{\,2} + 2 f_1 f_2} \qquad (2)$$

where f_1 and f_2 denote the molar fractions of monomers 1 and 2 in the feed. Thus, $F_{1,\text{inst(model)}}$ is calculated from the low conversion values of r_1 and r_2 and f_1 and f_2 as obtained from the experimental data of individual monomer concentration vs time. If the terminal model and the input values of r_1 and r_2 provide a correct description of the copolymerization, the quantity $F_{1,\text{inst(exp)}}/F_{1,\text{inst(model)}}$ should have a value of unity throughout the copolymerization. The monomer reactivity ratios as defined by the terminal model were evaluated from the low conversion portion of the monomer concentration vs time data to give $r_{\text{AN}} = 1.33$ and $r_{\text{MA}} = 0.76$ as reported previously.[16] These values are close to recently reported values of $r_{\text{AN}} = 1.29 \pm 0.2$ and $r_{\text{MA}} = 0.96 \pm 0.2$ in dimethylformamide at 62 °C.[37] The values of $F_{1,\text{inst(exp)}}/F_{1,\text{inst(model)}}$ vs conversion for the copolymerizations summarized in Table 1 are displayed in Figure 6. There appears to be reasonable agreement with the terminal model predictions in all experiments at low and intermediate conversions, but deviations occur at conversions higher than 70−80%. The normalized monomer concentrations ([M]/[M]$_0$) for the experiment with $f_{\text{AN},0} = 0.61$ are plotted vs time together with $F_{1,\text{inst(exp)}}/F_{1,\text{inst(model)}}$ in Figure 5 to more clearly illustrate at what point in the copolymerization process the deviations occur.

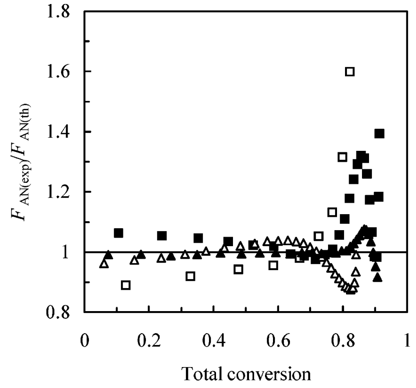

Figure 6. The quantity $F_{\text{AN(exp)}}/F_{\text{AN(th)}}$ vs total monomer conversion, where $F_{\text{AN(th)}}$ is based on the terminal model with $r_{\text{AN}} = 1.33$ and $r_{\text{MA}} = 0.76$. $f_{\text{AN},0} = 0.79$ (△); $f_{\text{AN},0} = 0.61$ (▲); $f_{\text{AN},0} = 0.39$ (■); $f_{\text{AN},0} = 0.19$ (□).

The question undoubtedly arises whether these deviations are real or merely stem from experimental error. The level of scatter in the monomer concentration vs time data is acceptable even at high conversion (Figures 2−5), although systematic error cannot be excluded. The lack of a common pattern in the deviations at high conversion may suggest experimental error rather than a mechanistic cause. However, considering also the good agreement between the NMR and gravimetric data up to close to 80% conversion, it is considered likely that the deviations are real. An alternative way to present these results is to plot $F_{1,\text{inst(exp)}}$ against f_1 (where f_1 is based on experimental data) separately for all copolymerizations and make comparisons with the theoretical copolymer composition plot of F_1 vs f_1 according to the terminal model (eq 2). The results are most easily interpreted in experiments B and C which cover the widest instantaneous monomer feed compositions, where it can be clearly seen how the experimental and theoretical lines are close to being superimposable up to conversions of 70−80% after which deviations occur (Figure 7).

Two possible origins of these deviations will now be discussed: (i) an explicit penultimate unit effect (PUE) and (ii) diffusion-controlled propagation.

Penultimate Unit Effect. The significance of PUEs[38,39] within the context of the present work is that if an explicit PUE[40,41] is operative, the reactivity ratios will be functions of the monomer feed composition (f_1) according to eq 3:

$$\bar{r}_i = \frac{r_{ji}(f_i r_{ii} + f_j)}{(f_i r_{ji} + f_j)} \qquad i, j = 1,2\ (i \neq j) \qquad (3)$$

An implicit PUE affects the rate of polymerization but not the relative rates of consumption of the two monomers. There are, to the best of our knowledge, no data available for PUEs in the copolymerization of AN with MA. However, the copolymerization of AN with both St[36,42] and methyl methacrylate[42] (MMA) do exhibit PUEs. In the case of the copolymerization of AN with St, it is an explicit PUE. (This may well be the case also for AN/MMA, although thus far only an implicit effect has been reported.) It thus appears very likely that the there is a PUE operating for the AN + MA system, and

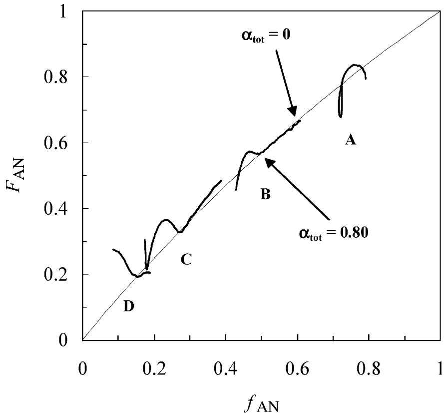

Figure 7. Experimental instantaneous copolymer composition estimated from the instantaneous individual rates of monomer consumption vs instantaneous monomer feed composition (thick lines) compared with the copolymer composition curve according to the terminal model with $r_{AN} = 1.33$ and $r_{MA} = 0.76$ (thin line). The value of f_{AN} decreases as with increasing total conversion (α_{tot}) as indicated with arrows for experiment B. A: $f_{AN,0} = 0.79$; B: $f_{AN,0} = 0.61$; C: $f_{AN,0} = 0.39$; D: $f_{AN,0} = 0.19$.

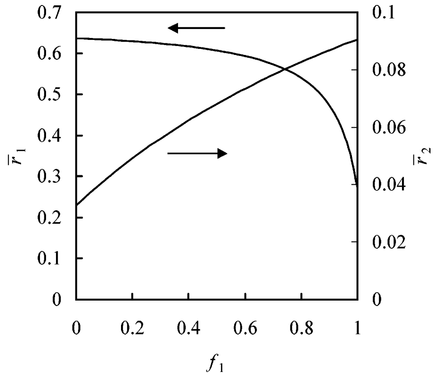

Figure 8. Dependence of r_1 and r_2 on f_1 according to eq 3 based on the explicit penultimate unit effect model monomer reactivity ratios reported by Hill et al.[36] for AN(1)/styrene(2) ($r_{11} = 0.039$, $r_{21} = 0.091$, $r_{22} = 0.229$, $r_{12} = 0.634$).

furthermore, it could possibly be explicit in nature. Consequently, the quantity $F_{1,\mathrm{inst(exp)}}/F_{1,\mathrm{inst(model)}}$ may deviate from unity as a result of the monomer feed composition changing with conversion. As a rough guide with regards to what magnitude of deviation might be expected in the event of an explicit PUE, the system AN(1) + styrene(2) was examined by simulations using the explicit PUE model monomer reactivity ratios reported by Hill et al.:[36] $r_{11} = 0.039$, $r_{21} = 0.091$, $r_{22} = 0.229$, $r_{12} = 0.634$. As can be seen in Figure 8, $\bar{r}_i$ depends strongly on f_i. However, in the system of monomers of interest in this work, there is no major change in f_1 over the course of the polymerizations (Figure 7). In polymerization C, f_1 decreases from 0.39 to 0.17 over the conversion range studied. In the case of the work reported by Hill (Figure 8), this would correspond to an increase in r_1 from 0.088 to 0.090 (a 2.3% increase) and a decrease in r_2 from 0.43 to 0.33 (a 23% decrease). This would translate to a much smaller deviation in F_1 compared with the terminal prediction with constant r_1 and r_2 with conversion than observed experimentally in this work. The system AN + MA may of course exhibit a different explicit PUE (if any at all) to that for AN + St; nonetheless, in view of the above reasoning, it does seem unlikely that an explicit PUE is the sole cause of the conversion dependence of the quantity $F_{\mathrm{AN(exp)}}/F_{\mathrm{AN(th)}}$, although some minor influence cannot be totally excluded.

Diffusion-Controlled Propagation. In the case of the bulk homopolymerization of St and MMA, a dramatic decrease in the experimentally observed k_p is observed at approximately 70−80% conversion.[5−10,12] The value of k_p is often expressed as a function of the chemically controlled (k_{p0}) and the diffusion-controlled propagation rate coefficient ($k_{p,\mathrm{diff}}$) according to eq 4:[43,44]

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \frac{1}{k_{p,\mathrm{diff}}} \tag{4}$$

The conversion level at which the rate of monomer diffusion begins to influence the overall propagation rate is affected by the magnitude of the chemically controlled propagation step, and direct comparison with the St and MMA bulk systems is not possible; the higher k_{p0}, the earlier is the onset of diffusion-controlled propagation. Extrapolation using the Arrhenius parameters of k_{p0} for the homopolymerization of MA from pulsed-laser polymerization (PLP) data yields $k_{p0} = 2.78 \times 10^4$ M^{-1} s^{-1} at 60 °C,[45] i.e., almost 2 orders of magnitude greater than for St.[46] Acrylate polymerization is complex as it proceeds in the presence of the "normal" propagating species as well as midchain radicals resulting from inter- and/or intramolecular hydrogen abstraction.[47] These midchain radicals exhibit significantly lower reactivity than the normal propagating radicals, and thus the "true" k_{p0} (i.e., excluding any effects of midchain radicals) may well be even higher than reported. The data available for the k_{p0} for AN homopolymerization are less reliable; values of the order 10^3 M^{-1} s^{-1} at 25−50 °C in DMSO have been reported.[48] The cross-propagation rate coefficients would be of similar magnitude as the homopropagation rate coefficients based on $r_{AN} = 1.33$ and $r_{MA} = 0.76$.[16] PUEs (radical reactivity ratios s_1 and s_2 not reported for the AN/MA system) may result in lowering of the homopropagation rate coefficients with a different monomer unit in the penultimate position (i.e., s_1, $s_2 < 1$). The value of k_p as a function of conversion in the current study was estimated from eqs 4−6 following the approach of Buback:[44]

$$k_{p,\mathrm{diff}} = k^0_{p,\mathrm{diff}}/\mu_r \tag{5}$$

$$\ln \mu_r = C_\mu \alpha \tag{6}$$

where μ_r is the reduced viscosity, $k^0_{p,\mathrm{diff}}$ is a second-order rate coefficient for a transport or orientational process at zero conversion, α is the fractional monomer conversion, and C_μ is a constant. To correct for the fact that the current study was carried out in solution and not in bulk, the monomer conversion in eq 6 was multiplied by the factor 0.3 (because 100% conversion at the current conditions corresponds to approximately 30% conversion in bulk in terms of polymer content). The calculated k_p vs conversion is plotted in Figure 9 using $k_{p0} = 2.78 \times 10^4$ M^{-1} s^{-1}, $k^0_{p,\mathrm{diff}} = 5 \times 10^9$ M^{-1} s^{-1},[49] and $C_\mu = 27$.[44] It thus appears possible that monomer diffusion rates may begin to exert a small influence on k_p at high conversion under the current conditions, although it must be emphasized that this is merely an approximate treatment.

The experimental value for the product $k_{p\phi_i}$ (where ϕ_i is the primary quantum yield) obtained from SP−PLP

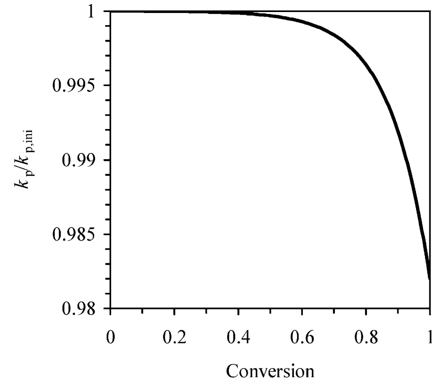

Figure 9. Calculated values of $k_p/k_{p,ini}$ (where $k_{p,ini}$ is k_p at zero conversion) according to eq 4 for $k_{p0} = 2.78 \times 10^4$ M^{-1} s^{-1} and $k^0_{p,diff} = 5 \times 10^9$ M^{-1} s^{-1} (see text for further details).

for butyl acrylate at 50 °C indicate that k_p (assuming ϕ_i is independent of conversion) remains approximately constant up to conversions as high as 80%.[50] This k_p will, however, be an apparent value for the reasons outlined above; i.e., it is a function of the midchain radical content which has been shown to vary with conversion.[47]

Recent data on the initiator efficiency (*f*) for *tert*-butyl peroxide in the bulk polymerization of St at 120 °C[7] have indicated that a drastic fall occurs at approximately 80% conversion, despite this initiator being considerably less susceptible to side reactions that result in lower *f* values than azoinitiators.[43] In the same study, it was observed that k_p also falls dramatically at approximately 80% conversion, i.e., at conversion levels similar to those at lower temperatures,[6,8−10,12] despite the fact that the temperature of reaction is above the glass transition temperature (T_g). This suggests it may not be possible to predict the conversion dependence of k_p from the rate of monomer diffusion alone by comparing the experimentally obtained value of k_p and monomer diffusion data[51] as previously suggested by Faldi et al. for the bulk polymerization of MMA at temperatures below T_g. The rate of monomer diffusion was found to be much too high for diffusion-controlled propagation to be the main reason for the dramatic fall in k_p at high conversion. The findings of Faldi et al. suggest that a new explanation for the observations is required, and this would be relevant in relation to the results reported in this study. One obvious implication is that, even in the absence of diffusion-controlled propagation, a dramatic fall in k_p may occur, a suggestion supported by the fact that k_p falls dramatically in the case of the bulk polymerization St at approximately 80% conversion at 70 °C and also at 120 °C.[7,8]

Another factor that may have been at least partly responsible for the effects observed in Figure 6 (although considered less likely than an explicit PUE and diffusion-controlled propagation) is chain-length-dependent composition. It has recently become known that k_{p0} decreases with propagating radical chain length up to some critical chain length.[52−54] If the chain length of the propagating radicals change with conversion, and if each monomer exhibits a different k_{p0} chain length dependence (not known), the copolymer composition would be affected. Moreover, if the chains formed at high conversion are very short, then the relative rate of addition of the cyanoisopropyl radicals generated by AIBN decomposition may also have an effect on the copolymer composition.

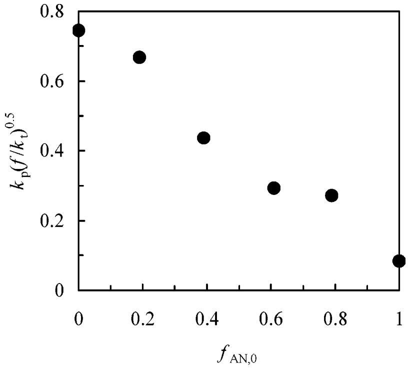

Figure 10. Initial (low conversion) values of $k_p(f/k_t)^{0.5}$ vs monomer feed composition estimated from eq 7. The data points at $f_{AN,0} = 0$ and 1 are from ref 57.

Solvent effects on the propagation step in free radical polymerization are generally relatively small.[55] It is however conceivable that the results observed in this paper (in particular Figure 6) may be somewhat different in bulk or other solvents, considering that a significant solvent effect of DMSO on the propagation step in MMA homopolymerization has been detected.[56]

In concluding this section, it remains difficult to make any definitive statement with regards to the possible influence of monomer diffusion rates on the propagation rates reported here. The very high values of the chemically controlled k_p in methyl acrylate polymerization together with the assessment of diffusion-controlled propagation using eq 4 indicate that it is possible for monomer diffusion rates to affect the experimentally observed propagation rates. On the other hand, the k_p vs conversion data for butyl acrylate in bulk, as well as the work by Faldi et al.,[51] suggest that this should not be the case.

Evaluation of $k_p(f/k_t)^{0.5}$. On the basis of classical kinetics and the steady-state assumption with regards to the propagating radical concentration, the overall rate of polymerization can be expressed according to eq 7, where [M] and [P•] denote the total monomer and propagating radical

$$-\frac{d[M]}{dt} = k_p[P^\bullet][M] = k_p[M]\left(\frac{f k_d[I]_0 \exp(-k_d t)}{k_t}\right)^{0.5} \quad (7)$$

concentrations, respectively, k_p and k_t are the overall propagation and termination rate coefficients, respectively, f is the initiator efficiency, and k_d is the rate constant for thermal initiator decomposition. The steady-state treatment to high conversion has been confirmed to be valid using electron spin resonance (EPR) data for bulk polymerization of St at 70 and 120 °C despite significant variations of [P•] with conversion because $d[St^\bullet]/dt \ll 2f k_d[I]_0 \exp(-k_d t)$.[3,7] Thus, the lumped parameter $k_p(f/k_t)^{0.5}$ can be estimated as a function of conversion using a value of k_d determined by ^{13}C NMR measurements of [AIBN] as a function of time in the homopolymerization of AN in DMSO at 60 °C ($k_d = 2.0 \times 10^{-5}$ s^{-1}).[57] The initial (low conversion) values of $k_p(f/k_t)^{0.5}$ decrease in an essentially linear manner with increasing $f_{AN,0}$ over almost 1 order of magnitude (Figure 10). This correlates fairly well with k_p for the respective homopolymerizations (MA: $k_p \approx 2.78 \times 10^4$ M^{-1} s^{-1}; AN: $k_p \approx 10^3$ M^{-1} s^{-1}—see above) and suggests that the variation in the overall k_p may be the main

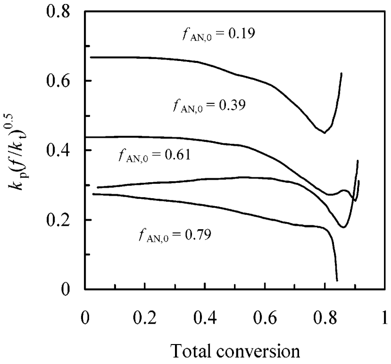

Figure 11. Conversion dependence of $k_p(f/k_t)^{0.5}$ estimated from eq 7 for different initial monomer feed compositions for the copolymerization of AN and MA in DMSO initiated by 0.016 M AIBN at 60 °C.

factor in governing the monomer feed dependence of $k_p(f/k_t)^{0.5}$. The full dependence is, however, also a complex function of penultimate unit effects (s_1 and s_2) as well as the monomer feed composition dependence of the overall k_t. The variation in f is believed to be of less importance in this context.

The conversion dependences of $k_p(f/k_t)^{0.5}$ are influenced by not only the expected decrease in k_t and f with conversion but also the monomer composition drift that occurs during polymerization (Figure 11). The value of k_t in bulk homopolymerization of MA at 40 °C and 1000 bar remains almost constant up to 20% conversion,[20] whereas no data are available for the conversion dependence of k_t during AN homopolymerization. The values of $k_p(f/k_t)^{0.5}$ remain relatively constant up to approximately 70% conversion, whereas significant conversion dependence is seen for all samples in the highest conversion regime despite the relatively low weight fraction of polymer compared to a bulk system. This is the same conversion range where $F_{AN(exp)}/F_{AN(th)}$ deviated from unity (Figure 6) and might thus suggest that variations in k_p may not be negligible with regards to the conversion dependence of $k_p(f/k_t)^{0.5}$ in this particular case.

Conclusions

In situ ^{13}C NMR spectroscopy has been employed to carefully monitor the individual monomer concentrations as functions of time to high conversion in the copolymerization of acrylonitrile with methyl acrylate initiated by azobis(isobutyronitrile) in dimethyl sulfoxide at 60 °C. Comparison of total conversions with time from ^{13}C NMR and gravimetry revealed that the ^{13}C NMR technique yields reliable data to high conversion and is a much more convenient technique if somewhat demanding of instrument time. To investigate whether the low conversion terminal model monomer reactivity ratios r_1 and r_2 are applicable also at very high conversion with regards to copolymer composition, the instantaneous copolymer compositions have been examined via the relative rates of individual monomer consumption. This approach is significantly more sensitive to any deviations in the apparent r_1 and r_2 values than the commonly used approach of examining the cumulative copolymer compositions to high conversion. It has been found that significant deviations from terminal model kinetics are present at conversion levels beyond 70% conversion despite this corresponding to a weight fraction of polymer of only approximately 20%. These findings have subsequently been examined in terms of possible influences of explicit penultimate unit effects and the rates of monomer diffusion affecting the propagation rates. It has been shown that due to the high propagation rate coefficient for the chemical reaction step of methyl acrylate (and possibly also acrylonitrile), it is possible that the rate of monomer diffusion may affect the relative monomer consumption rates, although no definitive statement can be made. Explicit penultimate unit effects may also contribute, although these effects are likely to be very small in this particular case. Inevitably, further work is required in order to fully reveal the underlying mechanisms responsible for the reported experimental findings.

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