Kinetic Analysis of the ^{60}Co γ Ray-Initiated Inverse Emulsion Polymerization of Sodium Acrylate Solutions

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ABSTRACT: The kinetics of the ^{60}Co γ ray-initiated inverse emulsion polymerization of aqueous sodium acrylate solutions in kerosene with Span 80 as the emulsifier was investigated. The conversion−time curves were analyzed using the equation $[\epsilon x/(1 - \epsilon) - \ln(1 - x)] = B$ (constant) $+ [\bar{n}k_p/(V_{p\infty}N_A)]t$, derived on the basis of a monomer droplet nucleation mechanism. The following expressions were obtained for $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ under the experimental conditions investigated: $K \propto$ [dose rate]$^{0.9}$[sodium acrylate]$^{0.5}$ [Span 80]$^{0.4}$, which was simplified to $\bar{n} \propto$ [dose rate]$^{0.9}$, $\bar{n}k_p \propto$ [sodium acrylate]$^{0.5}$, and $\bar{n}/V_{p\infty} \propto$ [Span 80]$^{0.4}$. The polymerization rate during the steady state (approximate conversion range 20−80%) could be expressed by $R_p = KxC_0 \propto$ [dose rate]$^{0.9}$[sodium acrylate]$^{1.5}$[Span 80]$^{0.4}$. The kinetic analysis suggests a dose rate independent polymerization process for the system studied such that, at any time, there was only one active passage of radiation through a droplet, viz., all polymer radicals resulting from a radiation passage were terminated before another passage.

Introduction

In contrast to detailed studies on conventional oil-in-water emulsion polymerization,[1−3] inverse water-in-oil emulsion polymerization has been less thoroughly investigated, partially because only a few water-soluble monomers can be polymerized by inverse emulsion polymerization. After the pioneering work of Vanderhoff et al.,[4] inverse emulsion polymerization has attracted considerable attention more recently, with the increasing application of synthetic water-soluble polymers such as polyacrylamide, polyacrylate salt, and their copolymers, because of its main advantages: (1) high molecular weight polymers are readily prepared with high polymerization rate, and (2) the obtained polymers are easily dissolved in water by phase inversion of the polymer latex. Despite numerous studies on the polymerization mechanisms and kinetics of inverse emulsion polymerization,[4−26] detailed analysis of the polymerization kinetics has been sparse. We have studied the kinetics of the inverse emulsion polymerization of sodium acrylate solutions in kerosene containing Span 80 as the emulsifier with ^{60}Co γ ray[20,21,25] and potassium persulfate initiation[26] and proposed a kinetic model to analyze the conversion−time curves.[25] In this report, we present a more detailed analysis of the kinetics of the ^{60}Co γ ray-initiated inverse emulsion polymerization of sodium acrylate solutions.

Experimental Section

Acrylic acid was distilled under reduced pressure just before use. Kerosene and Span 80 (sorbitan monooleate, reagent grade) and other chemicals (analytical grade) were used as supplied. Sodium acrylate solutions were prepared by neutralizing acrylic acid with sodium hydroxide (the pH was adjusted to 7.0 ± 0.1) and were emulsified in kerosene containing Span 80 by stirring under nitrogen purging. The monomer emulsions were then vacuum-degassed. Polymerization was carried out at controlled temperatures with a 6 kCi ^{60}Co γ source, which provided dose rates in the range of 0.08−0.3 Gy s^{-1}, as determined by the standard Fricke dosimeter with a radiation chemical yield of G[Fe(III)] = 1.62 μmol J^{-1},[27] and was continuously followed with an automatic dilatometer remotely as described elsewhere.[20,23] The obtained polymer latexes were diluted with petroleum ether (bp 30−60 °C), and the polymers were precipitated and washed three times with methanol and then vacuum-dried below 80 °C. The molecular weights of the polymers were determined by measuring the intrinsic viscosity with a capillary viscometer in 1.25 mol dm^{-3} NaSCN aqueous solutions at 30 °C, with $[\eta] = 0.121\bar{M}_v^{0.50}$ dm^{-3} kg^{-1}.[28] The particle sizes of the monomer emulsions and the polymer latexes were observed with an Olympus BX-2 optical microscope.

Results and Discussion

Conversion−Time Curves and Particle Sizes of Monomer Emulsions and Polymer Latexes. The volume contraction constant upon polymerization for sodium acrylate has been estimated as $(1.59 \pm 0.01) \times 10^{-2}$ dm^3 mol^{-1} sodium acrylate at 30 °C, and the temperature dependence of the volume contraction constant was estimated as -4.4×10^{-5} dm^3 mol^{-1} K^{-1} in the temperature range of 19−30 °C.[26] Thus, the volume contraction constant, δ (dm^3 mol^{-1}), at a given temperature θ (°C) was obtained as $\delta = [(1.59 - 4.4) \times 10^{-3}(\theta - 30)] \times 10^{-2}$ dm^3 mol^{-1} for all temperatures studied in the present study by assuming the same temperature dependence. Polymerization was followed continuously with a dilatometer, and the percentage conversion of monomer was calculated by assuming that the volume contraction constant did not change with the emulsion ingredients under our experimental conditions. The conversion−time curves were generally S-shaped. Induction times were normally observed, typically 3−30 min, depending mainly on the dose rate, presumably owing to the existence of oxygen in the monomer emulsions. The shape of the conversion−time curves was apparently not affected by the induction period above about 5% monomer conversion, though it was obviously affected below about 5% conversion. Preliminary study shows that the monomer emulsions and polymer latexes were quite stable, probably due to relatively high water/oil phase ratios and relatively low monomer and/or polymer contents in the aqueous phase. And the polymer latexes (up to weeks or even months) were much more stable than the monomer emulsions (up to days or even weeks). But no detailed study on

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the stability of the monomer emulsions or polymer latexes was attempted, because the present system was quite stable during polymerization. The monomer emulsions and the polymer latexes were diluted with kerosene containing Span 80 and observed by optical microscope. No apparent change in particle size was observed after polymerization. The particle diameters of the monomer emulsions and the polymer latexes were estimated as around 1 μm, without significant change with the emulsion ingredient and the polymerization condition, as observed by optical microscope. The distribution was rather narrow, though no quantitative estimation was made. Unfortunately, more precise information on particle size was not obtainable because of experimental limitations.

Kinetic Model. In our previous studies, a monomer droplet nucleation mechanism has been proposed for the present system,[20,21,25] viz., the polymerization locus is the pre-existing droplets. The polymerization is expected to be initiated in the monomer droplets since the radiolysis of water in the monomer droplets generates e_{aq}^-, $^\bullet$OH, and $^\bullet$H, with a radiation chemical yield of $G(e_{aq}^- + {}^\bullet OH + {}^\bullet H) = 0.6$ μmol J^{-1} in pure water[29] (estimated as 1.0 μmol J^{-1} for the present system because of the scavenging effect of sodium acrylate, see below), which react very rapidly with sodium acrylate, and the radiolysis of the continuous oil phase (kerosene, mixed alkanes) generates alkyl radicals with $G \approx 0.5$ μmol J^{-1}, typical for pure alkanes,[30] which are water insoluble and thus of marginal importance in initiating polymerization because the monomer sodium acrylate is insoluble in the oil phase. The polymerization proceeds in the compartmentalized monomer droplets independently (by hypothesis), which is supported by the results that the particle sizes are almost unchanged after polymerization. The present inverse emulsion polymerization process resembles a suspension or microsuspension polymerization process, except for the smaller sizes of the monomer and polymer droplets for the present system. Similar systems of acrylamide solutions have been classified as inverse microsuspension polymerization.[31] Efforts have been made to provide criteria for the categorization of inverse emulsion and microsuspension polymerizations,[32] but a clear-cut categorization is still difficult. Since the monomer emulsions and the polymer latexes are very much similar to those of the conventional oil-in-water emulsion polymerization, and the upper limit of the particle size of about 1 μm is well in the particle size range conventionally considered for emulsion polymerization,[3] the present system is preferably considered as an inverse emulsion polymerization process rather than a suspension or microsuspension polymerization process.

On the basis of the above description, it is further assumed that (1) the droplets neither coalesce nor split during polymerization, (2) the droplets are of the same size, (3) the monomer conversion is the same in all droplets, and (4) the average number of polymerizing radicals in a droplet reaches a steady-state value after the conversion reaches a certain value. Thus, the polymerization rate is expressed by eq 1,[25] by analogy

$$-\mathrm{d}(CV_p)/\mathrm{d}t = (\bar{n}/N_A)k_pC \qquad (1)$$

with seeded conventional emulsion polymerization,[33] where C is the monomer concentration (mol dm^{-3}) in the droplets at time t, V_p is the volume of a droplet (dm^3) at time t, t is the polymerization time (s), $\bar{n}$ is the average number of polymerizing radicals in a droplet, N_A is the Avogadro number, and k_p is the propagation rate constant (dm^3 mol^{-1} s^{-1}). Equation 1 is also obtainable by analogy with Smith−Ewart case III kinetics for conventional emulsion polymerization.[3]

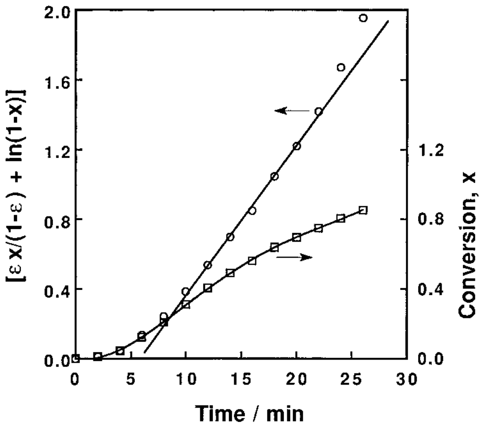

Figure 1. Conversion of sodium acrylate (x) and [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] as a function of time. Ingredients: aqueous phase (70.0 wt %), 2.78 mol dm^{-3} sodium acrylate, pH = 7.04; oil phase (30.0 wt %), 6.03 wt % Span 80 in oil phase (Span 80 + kerosene); polymerization temperature, $\theta = 23$ °C; dose rate, 0.188 Gy s^{-1}.

Assuming that $\bar{n}$ and k_p are constant in the steady state, eq 2 is obtained by integrating eq 1, where V_{p0}

$$\epsilon x/(1-\epsilon) - \ln(1-x) = B + [\bar{n}k_p/(V_{p\infty}N_A)]t \qquad (t \geq t_b) \quad (2)$$

$$B = \epsilon x_b/(1-\epsilon) - \ln(1-x_b) - [\bar{n}k_p/(V_{p\infty}N_A)]t_b \quad (3)$$

and $V_{p\infty}$ are the respective volumes (dm^3) of a droplet at zero and 100% conversion, ϵ is the volume contraction coefficient, which equals $(V_{p0} - V_{p\infty})/V_{p0} = \delta C_0$, with C_0 being the monomer concentration in the droplets before polymerization and δ the volume contraction constant of sodium acrylate (dm^3 mol^{-1}), and x and x_b are the conversions of monomer at t and t_b, respectively, with t_b being the beginning time of the steady state.

Thus, a plot of [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] against t should be linear, with a slope of $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ (s^{-1}). An example is shown in Figure 1. In a wide range of conversion, $x = 0.2-0.8$ (corresponds to [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] values of about 0.2−1.6), [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] is linear in t. The slopes of $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ thus obtained are used below to characterize the polymerization kinetics. Although it is assumed that $\bar{n}$ and k_p are constant in the steady state in deriving eq 2, this equation is still valid if only the product $\bar{n}k_p$ is constant in the steady state. No direct experimental evidence is available to prove that both $\bar{n}$ and k_p are constant in the range of $x = 0.2-0.8$, where [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] is linear in t. Since the monomer concentrations in the droplets are relatively low (1.8−2.8 mol dm^{-3}) in the present study, presumably k_p does not change significantly with monomer concentration and conversion for the present system. Principally, the number of polymerizing radicals per droplet, $\bar{n}$, that characterizes the polymerization process can be estimated from the slope K, provided that k_p and $V_{p\infty}$ are known.

Effect of Dose Rate and Monomer and Emulsifier Concentrations on *K*. The conversion−time curves at various dose rates are shown in Figure 2. These curves were analyzed according to eq 2 as shown in Figure 3. The change of $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of dose rate is shown in Figure 4, which yields

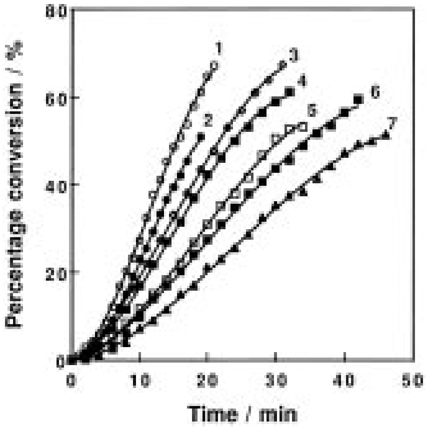

Figure 2. Percentage conversion of sodium acrylate as a function of time at different dose rates. Ingredients: aqueous phase (75.0 wt %), 2.93 mol dm^{-3} sodium acrylate, pH = 6.94; oil phase, 1.7 wt % Span 80 and 23.3 wt % kerosene; polymerization temperature, θ = 23 °C; dose rate, (1) 0.295, (2) 0.235, (3) 0.188, (4) 0.132, (5) 0.115, (6) 0.0996, and (7) 0.0834 Gy s^{-1}. Induction times are not shown.

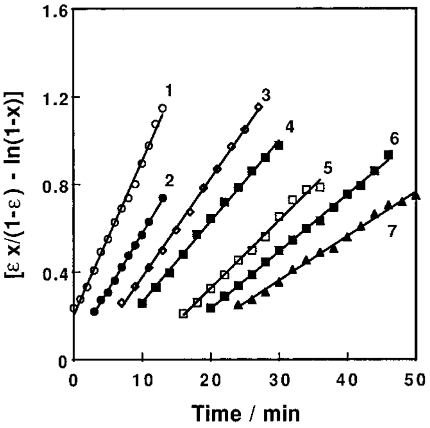

Figure 3. [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] as a function of time. See Figure 2 for ingredients and polymerization conditions. Curves are shown only for the linear part with conversion above about 20% and shifted arbitrarily in time for clarity.

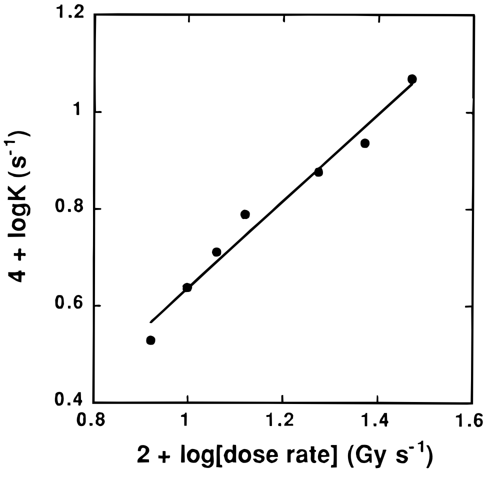

Figure 4. $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of dose rate. See Figure 2 for ingredients and polymerization conditions.

$K \propto$ [dose rate]$^{(0.90\pm0.06)}$. The dose rates used in the calculation of this expression are the dose rates in the dosimeter solutions. Since k_p and $V_{p\infty}$ are not expected to change with dose rate, $\bar{n} \propto$ [dose rate]$^{0.9}$. Under the same conditions, $\bar{M}_v \propto$ [dose rate]$^{-0.1}$.[20]

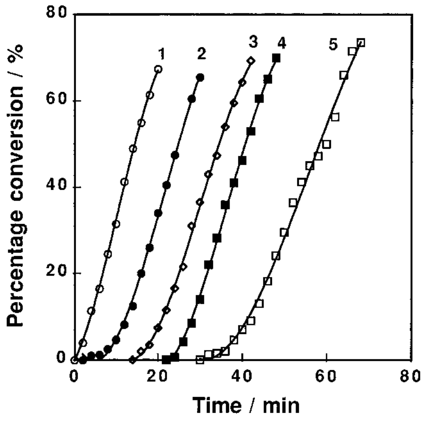

Figure 5. Percentage conversion of sodium acrylate as a function of time at different monomer concentrations. Ingredients: aqueous phase (69.45 wt %), 1.78–2.78 mol dm^{-3} sodium acrylate, pH = 7.0 ± 0.1; oil phase, 1.85 wt % Span 80 and 28.70 wt % kerosene; polymerization temperature, θ = 23 °C; dose rate, 0.188 Gy s^{-1}. Sodium acrylate concentrations: (1) 1.78, (2) 2.00, (3) 2.22, (4) 2.50, and (5) 2.78 mol dm^{-3}. Induction times are not shown. Curves are shifted arbitrarily in time for clarity.

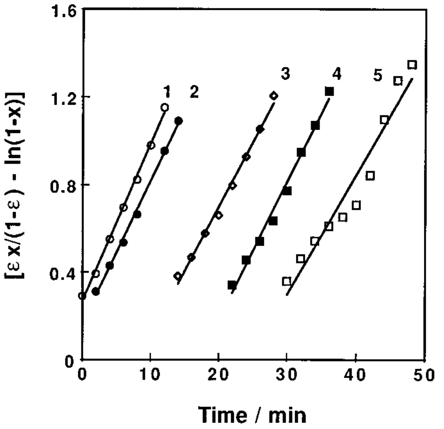

Figure 6. [$\epsilon x/(1 - \epsilon) - \ln(1 - x)$] as a function of monomer concentration. See Figure 5 for ingredients and polymerization conditions. Curves are shown only for the linear part with conversion above about 30% and shifted arbitrarily in time for clarity.

The conversion–time curves at various monomer concentrations are shown in Figure 5. These curves were analyzed according to eq 2 as shown in Figure 6. The change of $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of monomer concentration is shown in Figure 7, which yields $K \propto$ [sodium acrylate]$^{(0.51\pm0.16)}$. The monomer concentrations used in the calculation of this expression are the monomer concentrations in the aqueous phase before polymerization. Since $V_{p\infty}$ is not expected to change significantly with monomer concentration, $\bar{n}k_p \propto$ [sodium acrylate]$^{0.5}$. Under the same conditions, $\bar{M}_v \propto$ [sodium acrylate]$^{2.9}$.[20,21]

The conversion–time curves at various emulsifier concentrations are shown in Figure 8. These curves were analyzed according to eq 2 as shown in Figure 9. The change of $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of emulsifier concentration is shown in Figure 10, which yields $K \propto$ [Span 80]$^{(0.38\pm0.13)}$. The Span 80 concentrations used in the calculation of this expression are the weight percentages of Span 80 in the oil phase (Span 80 + kerosene). Since k_p is not expected to change significantly with emulsifier concentration, $\bar{n}/V_{p\infty} \propto$ [Span 80]$^{0.38}$. Under the same conditions, $\bar{M}_v \propto$ [Span 80]$^{-0.1}$.[20]

Average Number of Polymerizing Radicals per Droplet, $\bar{n}$. Before discussing the influence of dose

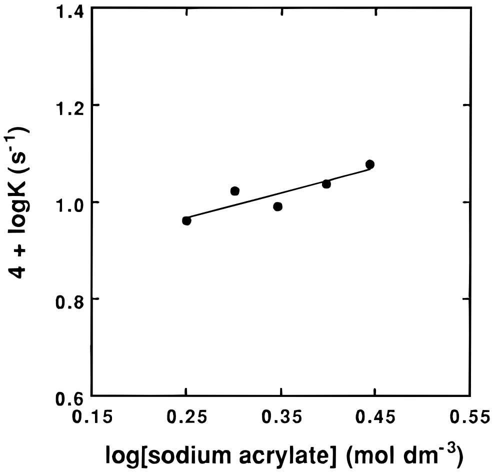

Figure 7. $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of monomer concentration. See Figure 5 for ingredients and polymerization conditions.

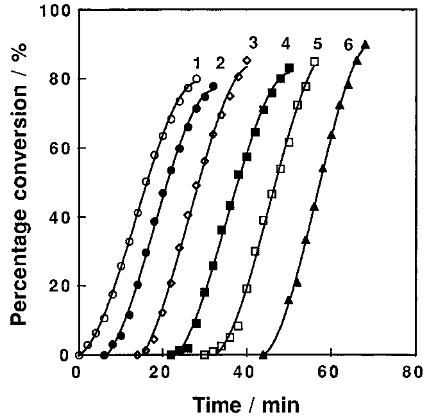

Figure 8. Percentage conversion of sodium acrylate as a function of time at different emulsifier concentrations. Ingredients: aqueous phase (68.0–71.0 wt %), 2.778 mol dm^{-3} sodium acrylate, pH = 7.04; oil phase, 3.5–9.3 wt % Span 80 in oil phase (Span 80 + kerosene); polymerization temperature, θ = 23 °C; Span 80 concentrations: (1) 3.54, (2) 4.82, (3) 6.03, (4) 7.07, (5) 8.25, and (6) 9.28 wt % in oil phase. Induction times are not shown. Curves are shifted arbitrarily in time for clarity.

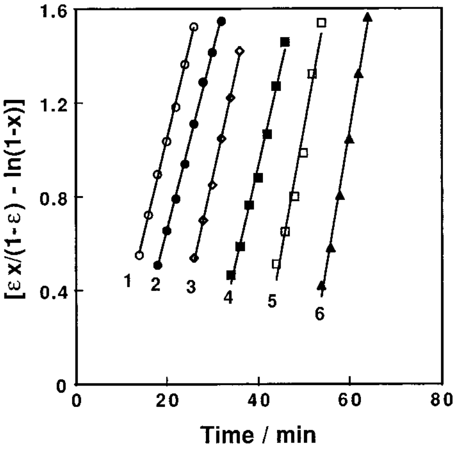

Figure 9. $[\epsilon x/(1-\epsilon) - \ln(1-x)]$ as a function of time. See Figure 8 for ingredients and polymerization conditions. Curves are shown only for the linear part with conversion between about 30 and 80% and shifted arbitrarily in time for clarity.

rate and monomer and emulsifier concentrations on K (and thus on $\bar{n}$, k_p, and $V_{p\infty}$), it is of considerable interest to estimate the value of $\bar{n}$, the average number of polymerizing radicals per droplet. Let us consider a typical system in Figure 2 [designated hereafter as system I (curve 3); ingredients: aqueous phase (75.0 wt %), 2.93 mol dm^{-3} sodium acrylate, pH = 6.94; oil phase, 1.7 wt % Span 80 and 23.3 wt % kerosene; polymerization temperature, θ = 23 °C; dose rate, 0.188 Gy s^{-1}] with a droplet average diameter of d = 1 μm. The radiolysis of water generates e_{aq}^-, $^{\bullet}$H, and $^{\bullet}$OH radicals in the droplets by reactions 4 and 5, with reaction 4 being the predominant process and any processes other than reactions 4 and 5 negligible.[34]

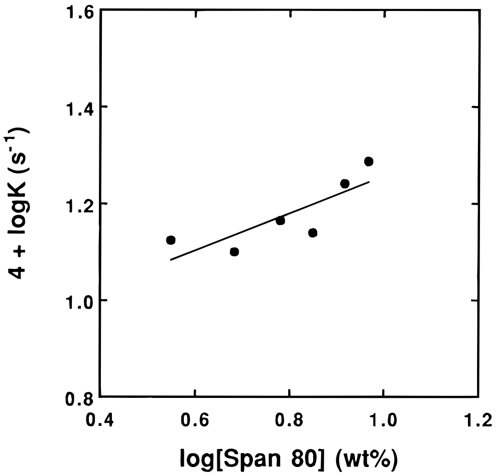

Figure 10. $K = [\bar{n}k_p/(V_{p\infty}N_A)]$ as a function of emulsifier concentration. See Figure 8 for ingredients and polymerization conditions.

$$H_2O \xrightarrow{\text{radiolysis}} H_2O^+ + e^- \rightarrow {}^{\bullet}OH + e_{aq}^- + H^+ \quad (4)$$

$$H_2O \xrightarrow{\text{radiolysis}} H_2O^* \rightarrow {}^{\bullet}OH + {}^{\bullet}H \quad (5)$$

The production rate of water radiolysis radicals in a droplet, N_R (radicals s^{-1}), is given by eq 6, where G is

$$N_R = 10^{-6} G D V_p \rho N_A \quad (6)$$

the radiation chemical yield (μmol J^{-1}), D is the dose rate (Gy s^{-1}), V_p is the volume of the droplet (dm^3), ρ is the density of the droplet (kg dm^{-3}, $\rho \approx 1$), and N_A is the Avogadro number.

The radicals from water radiolysis react with sodium acrylate to yield the α-carbon radicals (α-R$^{\bullet}$) by reactions 7–9, with $k_7 = 5.3 \times 10^9$ dm^3 mol^{-1} s^{-1},[35,36] $k_9 = 5.7 \times 10^9$ dm^3 mol^{-1} s^{-1},[36,37] and k_8 similar to k($^{\bullet}$H + CH$_2$=CHCOOH) = 3.3×10^9 dm^3 mol^{-1} s^{-1}.[36,38] Radical **I** has a pK_a of 4.9, compared to pK_a = 4.88 for CH$_3$CH$_2$-COOH.[39] Radical **II** is expected to have a similar pK_a value for the carboxylic acid group.

$$e_{aq}^- + CH_2{=}CHCOO^- \rightarrow [CH_2{=}CHCOO^-]^{\bullet -} \xrightarrow{H_2O} \underset{\textbf{(I)}}{CH_3C^{\bullet}HCOO^-} + OH^- \quad (7)$$

$$^{\bullet}H + CH_2{=}CHCOO^- \rightarrow \underset{\textbf{(I)}}{CH_3C^{\bullet}HCOO^-} \quad (8)$$

$$^{\bullet}OH + CH_2{=}CHCOO^- \rightarrow \underset{\textbf{(II)}}{HOCH_2C^{\bullet}HCOO^-} \quad (9)$$

The radiation chemical yields (G) of e_{aq}^-, $^{\bullet}$OH, and $^{\bullet}$H for system I are higher than those for pure water because of the scavenging effect of sodium acrylate, and they presumably change with conversion since the polymer only competes for $^{\bullet}OH$ radicals. The rate constant for $^{\bullet}OH$ radical reaction with a monomeric unit $[-CH_2CH(COO^-)-]$ in polyacrylate salt has been reported as 2.2×10^8 dm^3 mol^{-1} s^{-1} for the dissociated form and as 9.0×10^7 dm^3 mol^{-1} s^{-1} for the undissociated form[40] to yield α- and β-carbon polymer radicals.[41] The rate constants are significantly lower than the estimate of 1.13×10^9 dm^3 mol^{-1} s^{-1}, obtained by summarizing the reactivity of $^{\bullet}OH$ toward $^{\bullet}H$ atoms at α and β positions as evaluated from aliphatic carboxylate.[42] Approximately, $G(e_{aq}^- + {}^{\bullet}OH + {}^{\bullet}H) = 1.0$ μmol J^{-1} was estimated for system I at 50% conversion by using the yield–scavenging effect curves of water radiolysis.[34] The volume of the droplet $V_p = (4/3)\pi(d/2)^3 = 5.24 \times 10^{-16}$ dm^3. Thus, $N_R \approx 60$ radical s^{-1} for $D = 0.188$ Gy s^{-1}.

The formation rate of polymer chains, N_P (polymers s^{-1}), in a droplet is estimated by eq 10, where V_p is the

$$N_P \approx V_p C_0 (x_2 - x_1) N_A M_w / [\bar{M}_n (t_2 - t_1)] \qquad (10)$$

volume of the droplet (dm^3), C_0 is the initial monomer concentration (mol dm^{-3}) in the aqueous phase, x_2 and x_1 are the conversions at polymerization time t_1 (s) and t_2 (s), respectively, N_A is the Avogadro number, M_w is the molecular weight of monomer, and $\bar{M}_n$ is the number-average molecular weight of polymers produced between t_1 and t_2, which is approximated by $\bar{M}_v/2$. For system I, $x_1 = 0.274$ at $t_1 = 780$ s, and $x_2 = 0.674$ at $t_2 = 1860$ s, with $\bar{M}_v = 6 \times 10^6$ g mol^{-1}. Thus, $N_P \approx 10$ polymers s^{-1}. The disappearance rate of polymer radicals, N_{PR} (polymer-radicals s^{-1}), will be twice as large, $N_{PR} \approx 20$ polymer-radicals s^{-1}, assuming combination for chain termination, which suggests that only one-third of the primary water radiolysis radicals became polymer radicals of average molecular weight 3×10^6 g mol^{-1}. Because of the uncertainty in relating $\bar{M}_n$ to $\bar{M}_v$, direct comparison of radical production rate, N_R, and polymer radical termination rate, N_{PR}, is of no significant meaning. Information on molecular weight distribution at different conversions is desirable.

The average lifetime of a polymer radical at time t, τ (s), can be estimated by eq 11 by assuming a combination termination, where $\bar{M}_n'$ is the number-average

$$\tau \approx \bar{M}_n'/(2CM_w k_p) \approx \bar{M}_v/(4CM_w k_p) \qquad (11)$$

molecular weight of polymers produced at time t, approximated by $\bar{M}_v/2$, and all other parameters have their above-defined meanings. The k_p value for sodium acrylate depends on the pH and electrolyte concentration of the solution. It has been reported that $k_p = 6.5 \times 10^2$ dm^3 mol^{-1} s^{-1} at pH = 7.9, with [sodium acrylate] = 1.2 mol dm^{-3}, and $k_t = 2.6 \times 10^6$ dm^3 mol^{-1} s^{-1} for sodium acrylate in aqueous solutions.[43,44] The value of k_p increased to 3.15×10^3 dm^3 mol^{-1} s^{-1} with addition of 1.5 mol dm^{-3} NaCl, while k_t was unchanged.[44] The k_p value for the present system was presumably higher than the latter k_p value of 3.15×10^3 dm^3 mol^{-1} s^{-1} since the monomer (an electrolyte) concentration was higher. In the aqueous solution copolymerization of acrylamide (AM) and sodium acrylate (A) in an inverse microemulsion system, where there is no complication of monomer distribution, $r(\mathrm{AM}) = 0.92$ and $r(\mathrm{A}) = 0.89$ independent of conversion,[45] which suggests that k_p should be similar for sodium acrylate and acrylamide. Thus, $k_p \approx 10^4$ dm^3 mol^{-1} s^{-1} is suggested for sodium acrylate in the present system, considering the k_p values (6.0×10^3 dm^3 mol^{-1} s^{-1} at pH 5.5,[43,46,47] and 7.9×10^4 dm^3 mol^{-1} s^{-1} [43,48]) for acrylamide in aqueous solutions. Because of the large uncertainties in the measurement of k_p values, citation of a single k_p value is discouraged.[43b] For system I, the polymer radical lifetime was estimated as $\tau \approx 1.2$ s with $k_p \approx 10^4$ dm^3 mol^{-1} s^{-1}, with $\tau \approx 0.15$ s with $k_p = 7.9 \times 10^4$ dm^3 mol^{-1} s^{-1} as a low limit and $\tau \approx 19$ s with $k_p = 650$ dm^3 mol^{-1} s^{-1} as a high limit at 50% conversion. Thus, for system I, the number of radicals in a droplet is estimated by τN_{PR} or τN_R to be $\bar{n} \approx 24-70$, with $\bar{n} \approx 3-9$ as a low limit range and $\bar{n} \approx (0.38-1.1) \times 10^3$ as a high limit range.

Similar estimation of $\bar{n}$ can be obtained from K values. For system I, $K = 7.5 \times 10^{-4}$ s^{-1}. Thus, $\bar{n}$ is estimated by $\bar{n} = KV_{p\infty}N_A/k_p$ to be $\bar{n} \approx 24$ with $k_p \approx 10^4$ dm^3 mol^{-1} s^{-1}, with $\bar{n} = 3$ with $k_p = 7.9 \times 10^4$ dm^3 mol^{-1} s^{-1} as a low limit and as $\bar{n} = 3.6 \times 10^2$ with $k_p = 650$ dm^3 mol^{-1} s^{-1} as a high limit for a droplet diameter of $d = 1$ μm. Mainly because of the uncertainty in k_p, the estimation of $\bar{n}$ gives only a rough range, which is too large to be of any quantitative meaning, but of considerable importance in the discussion of the polymerization kinetics.

Dose Rate Dependence of $\bar{n}$. The dose rate dependence of $\bar{n} \propto [\text{dose rate}]^{0.9}$ and $\bar{M}_v \propto [\text{dose rate}]^{-0.1}$ suggests a dose rate independent polymerizing radical termination process or a dose rate independent polymerization process. A dose rate independent termination process should be first-order in polymer radical. Two cases can be considered:

(1) Chain Transfer. Chain transfer from the polymerizing radical to monomer and/or emulsifier seems unlikely, since $\bar{M}_v$ increases greatly with monomer concentration and does not change appreciably with emulsifier concentration. The radiolysis of water also produces H_2O_2 with a radiation chemical yield of $G(H_2O_2) = 0.06$ μmol J^{-1} in pure water [29] (estimated as 0.016 μmol J^{-1} for the present system because of the scavenging effect of sodium acrylate[34]). The polymerization was terminated in 20–40 min, and the accumulated H_2O_2 would be less than 2 μmol dm^{-3}. The rate constant of chain transfer to H_2O_2 for the polymerization of acrylamide in aqueous solution has been estimated as 9.1 dm^3 mol^{-1} s^{-1}.[49] The reactivities of H_2O_2 toward poly(sodium acrylate) radical and polyacrylamide radical are expected to be similar in aqueous solutions. Presumably, chain transfer to H_2O_2 was of little importance in the present study. Chain transfer to polymer (intra- or interpolymer) and other chain transfer reactions, if present, do not lead to first-order disappearing kinetics for polymerizing radicals in the whole system, though they do lead to first-order termination kinetics for individual radicals.

(2) Polymer Radical Trapping. The polymerizing radical may be trapped without being terminated by meeting a radical partner and thus lose its activity in carrying out polymerization. From the authors' unpublished results on aqueous solution polymerization of sodium acrylate, the polymer presumably precipitates after a certain conversion (the solution became turbid) and redissolved at higher conversions (the solution became transparent), depending on the initial monomer concentration. It is probable that the polymerizing radical was trapped by polymer precipitation. However, this mechanism cannot explain the increase in molecular weight of polymers with monomer concentration since polymerizing radical trapping is expected to be more effective with increasing monomer concentration and thus to stop chain propagation more effectively. The precipitation phenomenon was system specific and was not studied in more detail. Further discussion is too speculative. In the potassium persulfate-initiated aqueous solution polymerization of sodium acrylate, the polymerization rate is one-half order with respect to initiator concentration.[48] Although this reaction order has been obtained at lower monomer concentration and lower conversion than the present system, this result suggests that first-order termination or deactivation of polymerizing radicals might not be true.

A dose rate independent polymerization process can be understood as follows. The ^{60}Co γ rays make tracks when they pass through the solutions. Suppose that at any time there is, at most, only one active passage of radiation (including the incident γ rays, and all subsequent γ rays and electrons produced) through a droplet, viz., all polymer radicals from a radiation passage are terminated before another passage. Thus, an increase in dose rate only increases the number of active droplets that have polymerizing radicals. As a result, $\bar{n}$ changes linearly with dose rate, and $\bar{M}_v$ is independent of dose rate. The radiation chemical consequences of energy loss are arbitrarily classified into three categories: spurs (<100 eV), blobs (100−500 eV), and short tracks (500−5000 eV).[51,52] The fraction of energy loss in spurs, blobs, and short tracks depends on the medium and the type and energy of radiation. For 1 MeV electrons in liquid water, 52% of the energy loss is in spurs, 19% in blobs, and 29% in short tracks.[53] The energies of ^{60}Co γ rays are 1.17 and 1.33 MeV. The energy loss processes are similar for fast electrons and ^{60}Co γ rays of similar energies because of their similar LETs (linear energy transfers). The efficiencies in initiating polymerization are expected to be very low for short tracks, low for blobs, and high for spurs, which suggests that spurs are of primary importance for the present system. This largely explains why only one-third of the water radiolysis radicals become polymer radicals of high molecular weights. The LET of average Compton electrons from ^{60}Co γ rays for liquid water is 0.026 eV Å^{-1}.[54] The mean energy loss for 1 MeV incident electrons in liquid water has been estimated as $E_s = 56.8$ eV, which is roughly considered as the absorbed energy in a spur.[53] Thus, the interspur distance for ^{60}Co γ rays is about $d_s = 0.46\ \mu$m. For a sphere of 1 μm diameter, the number of spurs produced is approximated by $n_s = [(4/3)\pi(d/2)^3]/[\pi(d/2)^2 d_s] = (2/3)d/d_s = 1.45$. Thus, on average, about 8 radicals are produced in a droplet by a passage of radiation if all the energy absorbed leads to the formation of radicals. The polymerization process induced by one passage of radiation in a droplet is not affected by dose rate. This requires a low $\bar{n}$ value of less than about 8, corresponding to $k_p \geq 3 \times 10^4$ dm^3 mol^{-1} s^{-1}, as estimated for system I from the K value, which is not unreasonable. If this is the case, the present system is an interesting example in which reaction volume size has a significant effect on reaction kinetics. An alternative explanation is that there might be more than one active spur, blob, or short track in a droplet at any time, but no spur, blob, or short track overlapping occurs during polymerization. Since the lifetime of a polymer radical is as long as seconds, the distribution of polymerizing radicals in a droplet is preferably considered as homogeneous. Thus, this explanation is not preferred.

Monomer Concentration Dependence of $\bar{n}k_p$. The monomer concentration dependence $\bar{n}k_p \propto$ [sodium acrylate]$^{0.5}$ and $\bar{M}_v \propto$ [sodium acrylate]$^{2.9}$ is more appropriately explained by a dose rate independent polymerization mechanism. The effect of monomer concentration on k_p is unknown. Increase in k_p with addition of molar amount of salt has been reported for sodium acrylate at pH 7.9.[43,44] The dissociation constant for poly(acrylic acid) has been reported as $K_d \approx C_m\alpha^2 = 1.7 \times 10^{-6}$ mol dm^{-3} at 25 °C in very diluted solutions (polymer molecular weight $= 2 \times 10^6$ g mol^{-1}), where C_m (mol dm^{-3}) is the equivalent concentration of monomer units, and α is the fraction of dissociated charges of poly(acrylic acid).[55] The pK_a value of poly(acrylic acid) has been reported as 6.4, and the presence of monomer increases the pK_a by about 2 units.[56] Thus, the polymer is expected to be only slightly dissociated under our conditions of pH 7. The end carboxyl group of the polymer radical presumably has the same pK_a value as other carboxyl groups in the polymer chain, since α-carbon radicals of aliphatic carboxylic acid have almost the same pK_a values as the parent molecules.[39] The effect of monomer on the pK_a value of the end radical moiety is unknown. Presumably, the radical end carboxyl group was dissociated to a larger extent. Thus, ionic strength is expected to have a significant influence on the propagation reaction. However, under our conditions with 1.8−2.8 mol dm^{-3} sodium acrylate, the ionic strength effect is expected not to change significantly, since there is a relatively high concentration of sodium acrylate even at relatively high conversions. Thus, k_p is expected to increase only slightly with monomer concentration and approximately $\bar{n} \propto$ [sodium acrylate]$^{0.5}$. This increase of $\bar{n}$ and $\bar{M}_v$ with monomer concentration is probably due to the polymer concentration increase with monomer concentration, which increased the viscosity of the droplets and thus decreased the polymer radical termination rate.

Effect of Emulsifier Concentration. The emulsifier concentration probably affects the droplet sizes. Since a change in droplet size should not affect k_p significantly, we can approximate $\bar{n}/V_{p\infty} \propto$ [Span 80]$^{0.4}$. If the droplet size did not change with emulsifier concentration or had no effect on polymerization, then $\bar{n}N_d$ should depend only on dose rate and should not change with emulsifier concentration, where N_d is the number of droplets for a unit volume V_a (1 dm^3) of aqueous phase and $N_d = V_a/V_{p\infty}$. Thus, $\bar{n}/V_{p\infty}$ should not change with emulsifier concentration, which is inconsistent with the experimental results, suggesting that the droplet size changed with emulsifier concentration. The longer the lifetime of the polymer radical, the higher the $\bar{n}$ value and the molecular weights of the polymers, suggesting that $\bar{n}$ and $\bar{M}_v$ should change in the same direction, which is in disagreement with the experiment results. There is no clear explanation for this discrepancy. The results may suggest the existence of polymer radical chain transfer to emulsifier that might have resulted in a molecular weight decrease with emulsifier concentration. Span 80 has been found to increase the molecular weight of polymer in the aqueous solution polymerization of acrylamide.[31] It has been suggested that a polymer radical can abstract a hydrogen atom from the hydrophilic portion of the emulsifier to form a dead polymer chain and an emulsifier radical. When the emulsifier radical polymerizes, it would produce a polymer chain with a terminal double bond, which could later react to form a branched polymer and thus increase the molecular weight of the polymer.[31] However, in the present system, the possibility of further reaction of the terminal double bond (if present) in the hydrophobic portion of the emulsifier is presumably much lower than that in aqueous solution polymerization, since the hydrophobic portion is oriented in the oil phase in which the monomer is insoluble, which may result in a decrease in molecular weight of the polymer.

Rate of Polymerization. The polymerization rate, R_p (mol dm^{-3} s^{-1}), at a given conversion x during the steady state can be given by eq 12, where all parameter have their above-defined meanings. Thus, $R_p \propto$ [dose

$$R_p = \bar{n}N_d k_p x C_0/N_A = \bar{n}k_p x C_0/(V_{p\infty}N_A) = KxC_0 \quad (12)$$

rate]$^{0.9}$[sodium acrylate]$^{1.5}$[Span 80]$^{0.4}$. In our previous studies, the maximum rate of polymerization, R_{pmax} (mol dm^{-3} s^{-1}), at about 20−30% conversion, which corresponds to the beginning of the steady state, has been used to characterize the polymerization kinetics. The following expression has been obtained, $R_{pmax} \propto$ [dose rate]$^{0.78}$[sodium acrylate]$^{1.6}$[Span 80]$^{0.2}$,[20,21] which is very similar to the equation obtained from the present treatment. However, the present treatment describes the polymerization in a wide range of conversion from 20 to 80%, while the previous treatment described only that at a certain conversion.

Principally, the present treatment provides a feasible way to estimate $\bar{n}$ that characterizes the polymerization if k_p and $V_{p\infty}$ are known. Unfortunately, this was unsuccessful because of the large uncertainties in k_p and $V_{p\infty}$. More precise measurement of k_p and particle sizes are desirable in order to take advantage of the present treatment. Nevertheless, a better presentation of the experimental data has been achieved by the present treatment, and more specific and insightful information is believed to have been obtained.

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