On Loci of Acrylonitrile Polymerization with Bisulfite-Persulfate Initiators under the Conditions of Low Water/Monomer Ratio

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Synopsis

In the preparation of acrylonitrile–vinylacetate copolymer (93:7 in weight) by continuous polymerization in aqueous medium using the complete mixing type reactor, the author and co-workers studied the effects of the water/monomer ratio on polymer properties and polymerization. They reported that the structure of a polymer particle becomes more compact with decreasing water/monomer ratio. This was noted in studying the physical properties of the polymer and the formation of polymer particles in this system.[1,2] Here the author has performed kinetic studies based on the results of polymerization to determine the loci of the polymerization in the range of water/monomer ratio roughly from 1.75 to 4.0. Most of the primary radicals from the initiators attack the monomers in the aqueous phase to form monomer radicals attached to initiator fragments, and most of the monomer radicals grow to form polymer radicals until termination occurs in the aqueous phase. Hence, the loci of polymerization in this system are not the surfaces and inner parts of the polymer particles, the diameters of which are roughly from 20 to 60 μm observed by a microscope, but the aqueous phase excluding these particles.

INTRODUCTION

The continuous polymerization in aqueous medium using the persulfate–bisulfite redox system has been important in production of acrylonitrile (AN) polymers. Studies[3-6] on low water/monomer ratio in this polymerization system have been previously reported, but studies on effects of water/monomer ratio on the polymer properties and polymerization seemed insufficient. The author and co-workers performed some studies[1] on properties of the polymer and the polymerization in the range of water/monomer ratio 1.5–4.0 in the preparation of acrylonitrile (AN)–vinylacetate (VAc) copolymer (93:7 in weight). The author further studied the above polymerization including the loci of polymerization and the kinetics thereof. In this paper the loci of the polymerization in the range of water/monomer ratio 1.5–4.0 is dealt with.

EXPERIMENTAL

Procedures

The reactor and the procedure were the same as those previously described.[1,7,17] A reactor having a capacity of 83 L of complete mixing type was used for polymerization. Monomer blend, potassium persulfate (KPS),

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sulfur dioxide (SO_2), sodium bicarbonate ($NaHCO_3$), and ferrous sulfate ($FeSO_4$) in aqueous solutions were fed to the reactor at a rate to maintain the given polymerization condition including water/monomer, KPS/monomer, SO_2/monomer, SO_2/KPS, SO_2/$NaHCO_3$, Fe/monomer, and dwell time. The slurries from the reactor were taken for evaluation in 6–8 h after the start of polymerization. The weight average diameters of polymer particles were measured by microscopic observations of short stopped slurries from the reactor. Osmotic measurement for $\overline{Mn}$ and end-group analysis were performed by procedures previously described.[7,17]

RESULTS AND DISCUSSION

The observation of the short stopped slurry by a microscope immediately after sampling the overflowed slurry from the reactor into a beaker of dilute stopper solution showed polymer to disperse in a round discrete particle the diameter of which is roughly from 20 to 60 μm, (Fig. 1). The short stopped overflowed slurry from the reactor under the polymerization condition (Table I) can be easily filtered by filter cloth such as nylon cloth and the filtrate is transparent. Hence, most of the polymer in the reactor slurry is not dispersed in emulsion, but in suspension of discrete particles, diameters of which are from 20 to 60 μm. This particle is packed with secondary particles, diameters of which are roughly from 0.5 to 2 μm observed by scanning electron micrographs.[1] These secondary particles are composed of primary particles, diameters of which are roughly from 0.1 to 0.2 μm observed by transmitting electron micrographs.[1]

These primary particles correspond to the particle prepared under the conditions of high water/monomer ratio described in the proceeding papers.[8-10] These primary particles are formed in the aqueous phase of the polymerizing system. The process of the formation of polymer particles in the polymerizing system was studied by simulation in the recent paper.[2] From the observation and studies above it was considered that the aqueous phase plays an important role in polymerization and formation of primary particles.

Initiation of Monomer

In this polymerization system, primary radicals from the initiators form in aqueous phase, since the initiators are water-soluble. Primary radicals follow three courses: addition to monomers to initiate polymerization; recombination with each other; capture of polymer particles. The scheme of the production of primary radicals can be shown from the previous study[11-14]:

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^- + Fe^{3+} + SO_4^{2-} \tag{1}$$

$$HSO_3^- + Fe^{3+} \longrightarrow HSO_3 + FE^{2+} \tag{2}$$
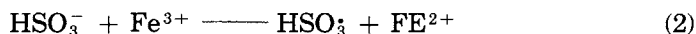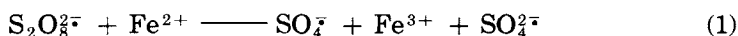
Consequently, the following expression is obtained:

$$S_2O_8^{2-} + HSO_3^- \longrightarrow SO_4^- + SO_4^{2-} + HSO_3 \tag{3}$$
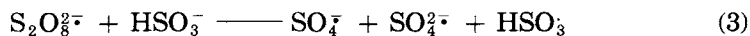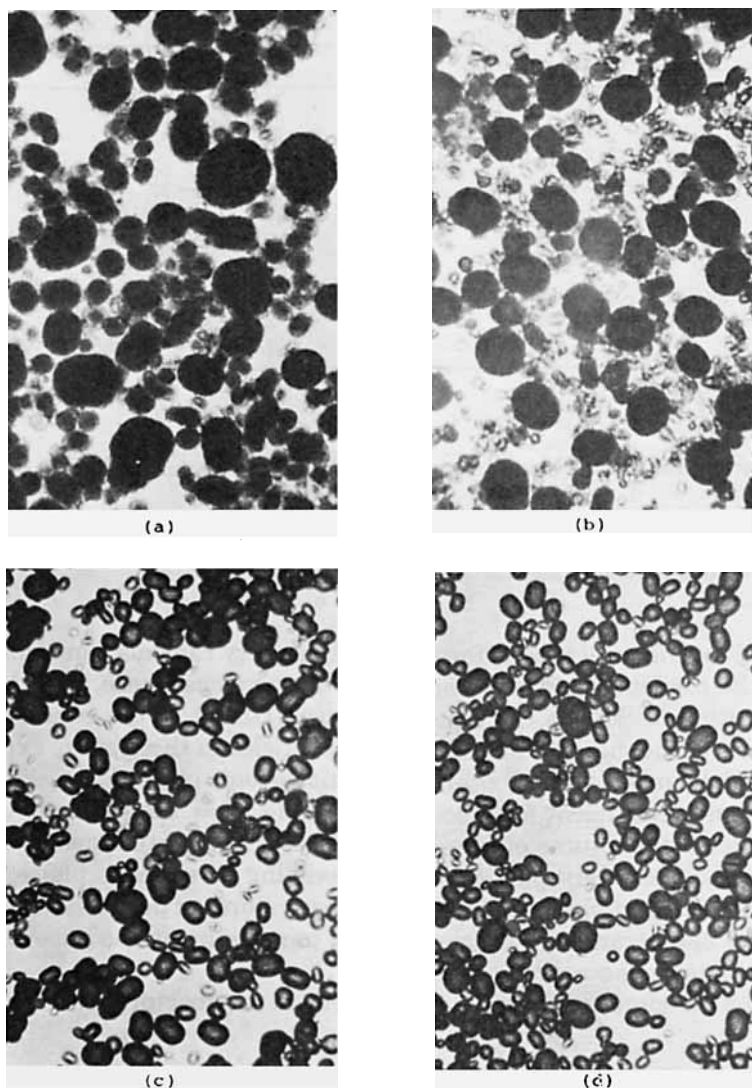
Fig. 1. Micrographs of polymer particles in slurry prepared under various water-to-mono-mer ratios. Polymerization conditions of a, b, c, d, correspond to expt. no. 5, 3, 2, 1, respectively.

Primary radical concentration in aqueous phase can be estimated from the following equation, since mutual reactions of primary radicals seem negligible from the previous studies[7]:

$$\frac{1}{2}\rho = k_{pi}[M]_l(SO_4^{\overline{\cdot}})_l + 4\pi r^2 \cdot k_L(SO_4^{\overline{\cdot}})N + 4\pi r_x^2 \cdot k_{Lx}(SO_4^{\overline{\cdot}})_l N_x + \frac{SO_4^{\overline{\cdot}}}{\theta} \quad (4)$$

$$\frac{1}{2}\rho = k_{pi}[M]_l(HSO_3)_l + 4\pi r^2 \cdot k_L(HSO_3)_l N$$

$$+ 4r_x^2 k_{Lx}(HSO_3)_l N_x + \frac{(HSO_3)_l}{\theta} \quad (5)$$

TABLE I

Expt. no.	1	2	3	4	5
Water/monomer[a]	1.75	2.0	2.5	3.0	4.0
Dwell time	89	82	70	60	60
KPS/monomer (%)[b]	0.44	0.49	0.50	0.50	0.525
SO_2/KPS[c]	10	10	10	10	10
Nsp[d]	0.201	0.186	0.202	0.213	0.196
Conversion (%)	90.1	82.6	80.0	81.5	71.3
SAG $\times 10^5$ (eq/g)[e]	3.82	3.97	3.73	3.88	4.10
$M_n \times 10^{-4}$ [f]	2.59	2.60	2.05	2.11	2.09
VAc (%)[g]	7.17	7.06	7.02	7.60	6.77

[a] Weight ratio.
[b] Wt %.
[c] Molar ratio.
[d] Nsp denotes the reduced viscosity multiplied by 0.1 of 0.5% solution of polymer in DMF at 25°C.
[e] SAG denotes the strong acid groups content in polymer.
[f] Number average molecular weight.
[g] Vinyl acetate content in polymer expressed as wt %.

where k_{pi} = the total rate of formation of primary radicals from initiators, [M] = the concentration of monomer in the aqueous phase, $[SO_4^-]$ = the concentration of SO_4^- in the aqueous phase, $[HSO_3^-]$ = the concentration of HSO_3^-, r = the mean radius of polymer particles in the system, expressed as the weight mean radius obtained by microscopic observation, k_L = the mass transfer coefficient for a polymer particle, N = the numbers of polymer particles per volume of liquid in the system, r_x = the mean radius of primary and secondary particles freely existing in aqueous phase, N_x = the numbers of particles mentioned above per volume of liquid in the system, k_{Lx} = the mass transfer coefficient of the particle mentioned above, and θ = dwell time in the reactor.

Average monomer concentration of slurry in the reactor [M] is expressed by

$$[M] = (1 - V_p)[M]_l + V_p \cdot m \quad (6)$$

where V_p is the volume fraction of polymer in the slurry and m is average monomer concentration absorbed onto polymer phase.

In this polymerization system, $V_p \cdot m/[M]$ is estimated roughly 0.05–0.15 by experimental data. Hence eq. (7) is obtained as an approximation:

$$[M] \approx (1 - V_p)[M]_l \quad (7)$$

Hence, the value of $[M]_l$ is calculated from

$$[M]_l = [min](1 - z)\varphi \cdot f_{rv} \quad (8)$$

where [min] is the monomer concentration in the feed, z is the conversion

rate,

$$f_{rv} = \frac{R + 1.25}{R + 1} \tag{9}$$

f_{rv} is the correction factor by change of the volume from the feed to the overflow, R is the water/monomer ratio,

$$\varphi = 1/(1 - V_p) \tag{10}$$

V_p is the volume fraction of polymer in the polymerization system,

$$V_p \approx 0.053[\text{min}] \cdot Z \tag{11}$$

The values of N and N_x are calculated from eqs. (12) and (14):

$$N = \frac{W_p}{\frac{4}{3} \pi r^3 \rho_p} \tag{12}$$

where W_p is the weight of polymer per unit volume in the system and ρ_p is the density of a polymer particle.

$$X_w \approx 0.053[\text{min}] Z \cdot f_{rv} \varphi \tag{13}$$

where [min] is the monomer concentration in the feed and Z is the conversion rate.

$$N_x = \frac{W_{px}}{\frac{4}{3} \pi r x^3 \rho_p} \tag{14}$$

where W_{px} is the weight of particles mentioned above. ρ_p is the density thereof. ρ is estimated from eq. (15) based on the literature[14]:

$$\rho = 2k_1[\text{Fe}^{2+}]_l[\text{C}]_l \tag{15}$$

$$[\text{C}] = \frac{[\text{C}_{in}] \cdot \varphi \cdot f_{rv}}{(1 + k_1[\text{Fe}^{2+}]_l \theta)} \tag{16}$$

$$[\text{Fe}^{2+}]_l \approx [\text{Fe}_{in}] \varphi \cdot f_{rv} \tag{17}$$

where k_1 is the rate constant of eq. (1), $[\text{Fe}^{2+}]_l$ is the concentration of Fe^{2+} in aqueous phase, [C] is the concentration of $S_2O_8^{2-}$ in aqueous phase, $[\text{C}_{in}]_l$ is the concentration of $S_2O_8^{2-}$ in the feed, and $[\text{Fe}_{in}]_l$ is the concentration of iron in the feed. Hence,

$$\rho = \frac{2k_1[\text{Fe}_{in}][\text{C}_{in}][\varphi \cdot f_{rv}]^2}{1 + k_1[\text{Fe}_{in}] \cdot \theta[\varphi \cdot f_{rv}]} \tag{18}$$

ρ is the compared with $(R_i)_l$ obtained as follows: In this system the chain transfer of polymer radical to bisulfite ion is well known in the literature.[14] Hence,

$$\frac{R_i}{R_p} + \frac{R_{tr}}{R_p} = \frac{1}{\overline{DP}} \tag{19}$$

Then

$$R_i = \frac{R_p}{\overline{DP}}\left(\frac{1}{1+k}\right) \tag{20}$$

$$k = \frac{R_{tr}}{R_i} \tag{21}$$

where R_p is the rate of propagation, R_{tr} is the rate of chain transfer to HSO_3^-, R_i is the rate of formation of primary radicals from initiators, and, $\overline{DP}$ is the average degree of polymerization of polymer obtained. Then the rate of initiation in aqueous phase $(R_i)_l$ is calculated by

$$(R_i)_l = R_i \cdot \varphi \tag{22}$$

Here the aqueous phase is defined as the liquid phase excluded by polymer solid phase. In eq. (20), r_p and k are calculated as follows:

$$R_p = \frac{[M_{in}]Z}{\theta} \cdot f_{rv} \tag{23}$$

k is obtained from the following:

$$\frac{f_{tr} \cdot R_{tr} + R_i/2}{f_{tr} \cdot R_{tr} + R_i} = \frac{SAG_1}{SAG_1 + SAG_2} = f_a \tag{24}$$

where f_{tr} is the efficiency of initiation by bisulfite ion chain-transferred, SAG_1 = the sulfonate end groups in polymer (eq/g), SAG_2 = the sulfate end groups in polymer (eq/g), and f_a is estimated by end group analysis. Therefore,

$$k = \frac{(R_{tr})_l}{(R_i)_l} = \left(\frac{f_a - 0.5}{1 - f_a}\right) \cdot \frac{1}{f_{tr}} \tag{25}$$

The measured values of f_a were roughly 0.7 when SO_2/KPS ratio is 10. The value of f_{tr} is assumed as 0.65 from eq. (25) and experimental results. Then $k \approx 1$. k_L is obtained by[15]

$$k_L = 0.13(\gamma P_M)^{0.25} Sc^{-2/3} \tag{26}$$

where γ is kinematic viscosity; P_M, energy dissipation; Sc, Schmidt Number, γ/D; D, molecular diffusion coefficient of primary radicals.

In the case of this system

$$P_M \simeq 4.30 \times 10^4 \ (\text{cm}^2 \ \text{s}^{-3})$$

$$\gamma \simeq 0.01 \ (\text{cm}^2 \ \text{s}^{-1})$$

D is roughly the order of 10^{-5} $(\text{cm}^2 \ \text{s}^{-1})$. Therefore,

$$k_L \simeq 6 \times 10^{-3} \ (\text{cm} \ \text{s}^{-1})$$

k_{pi} is assumed to be roughly equal to the propagation rate constant (k_p) of AN in water at 50°C:

$$k_p = 5 \times 10^4 \ (\text{mol}/l \ \text{s})^{16}$$

$$= 8.3 \times 10^{-17} \ (1/\text{cm}^3 \ \text{s})$$

From eqs. (4) and (5), eq. (27) is obtained.

$$[\text{SO}_4^-]_l = [\text{HSO}_3^-]_l = \frac{0.5\rho}{k_{pi}[M]_l + 4\pi r^2 k_L \cdot N + 4\pi r^2 x k_{Lx} N_x} \tag{27}$$

where

$$\frac{4\pi r_x^2 N_x}{4\pi r^2 N} = \frac{W_{px}}{W_p} \cdot \frac{r}{r_x} \tag{28}$$

From experimental observations of the reactor slurry mentioned above,

$$\frac{W_{px}}{W_p} \leq 0.01\text{--}0.001 \tag{29}$$

$$\frac{r}{r_x} \leq 300 \tag{30}$$

Hence,

$$\frac{4\pi r_x^2 N_x}{4\pi r^2 N} \leq 10^2\text{--}10^3 \tag{31}$$

$$k_L \geq k_{Lx} \tag{32}$$

Hence in eq. (27), if

$$k_{pi}[M]_l >> 4\pi r^2 k_L N + 4\pi r_x^2 k_{Lx} N_x \tag{33}$$

Then,

$$[\text{SO}_4^-]_l = [\text{HSO}_3^-]_l = \frac{0.5\rho}{k_{pi}[M]_l} \tag{34}$$

Values of $[SO_4^-]_l$ and $[HSO_3^-]_l$ can be calculated as shown in Table II by introducing data in Table I into eq. (27).

From the calculated values in Table II

$$k_{pi}[M]_l > > 4\pi r^2 k_L \cdot N + 4\pi r_x^2 k_{Lx} N_x \tag{35}$$

Equation (35) will hold, even if $[M]_l$ decreases due to the absorption of monomer onto polymer particles and $4\pi r^2 k_{Lx} N_x$ increases within the range of variations in the number of primary and secondary particles freely dispersed in the system. Hence, it is apparent that initiation of monomer occurs mainly in the aqueous phase in this system.

Behavior of Polymer Radicals

From the above-described consideration, the monomer initiated by primary radicals grows as a polymer radical. The polymer radicals follow mainly two courses: termination either by mutual reaction or by chain transfer to HSO_3^- in aqueous phase; absorption onto polymer particles. Polymer radical concentration in the aqueous phase can be estimated from following:

$$\rho = k_t[P\cdot]_l^2 + 4\pi r^2 k_L[P\cdot]_l \cdot N + 4\pi r_x^2 k_{Lx}[P\cdot]_l \cdot N_x \tag{36}$$

TABLE II[a]

Expt. no.	1	3	5
Water/monomer (R)	1.75	2.5	4.0
[min] (mol/L)	6.22	4.98	3.55
Z	0.90	0.80	0.71
ϕ^b	1.426	1.266	1.149
$f_{rv}{}^c$	1.09	1.07	1.05
θ (s)	5340	4200	3600
$\rho \times 10^{-15\,d}$ (cm^{-3} s^{-1})	0.940	0.697	0.354
$(R_i)_l \times 10^{-15\,e}$ (cm^{-3} s^{-1})	1.04	1.04	0.668
$[M]_l \times 10^{-20\,f}$ (cm^{-3})	5.86	8.18	7.53
$r^{\,g}$ (μm)	14	26	31
$N \times 10^{-6\,h}$ (cm^{-3})	54.5	6.42	2.55
$k_{pi}[M]_l \times 10^{-4\,i}$ (s^{-1})	4.86	6.79	6.25
$4\pi r^2 k_L N^{\,j}$ (s^{-1})	7.98	3.27	1.85
$[SO_4{}^+]_l \times 10^{-10\,k}$ (cm^{-3})	1.93	0.51	0.28

[a] All values obtained as moles are expressed as numbers obtained by multiplying moles by Avogadro number.

[b] Calculated from eq. (10).

[c] Calculated from eq. (9).

[d] Calculated from eq. (18).

[e] Calculated from eq. (22), putting $k \approx 1$ and using values of $\overline{DP}$ listed in Table I.

[f] Calculated from eq. (8).

[g] Weight mean radius of polymer particles.

[h] Calculated from eq. (12).

[i] The value of k_p was used as that of k_{pi}.

[j] k_L was calculated from eq. (26).

[k] Calculated from eq. (27).

where $[\text{P·}]_l$ = the polymer radical concentration in aqueous phase, k_t = the rate constant of termination of radicals, and ρ_1, r_1, N, r_x, and N_x are the same symbols as in eq. (4). k_L and k_{Lx} are the mass transfer coefficient respectively for a polymer particle and a primary or secondary particle existing freely in aqueous phase. In eq. (36)

$$\frac{4\pi r_x^2 N_x}{4\pi r^2 N} = \frac{W_{px}}{W_p} \cdot \frac{r}{r_x} \tag{37}$$

From experimental observations mentioned above and some study on the formation of polymer particles,[2]

$$\frac{W_{px}}{W_p} \leq 0.01\text{–}0.001 \tag{38}$$

$$\frac{r}{r_x} \leq 300 \tag{39}$$

can be assumed. Hence,

$$\frac{4r_x^2 N_x}{4r^2 N} \leq 0.3\text{–}3 \tag{40}$$

On the other hand,

$$k_L \geq k_{Lx} \tag{41}$$

Then

$$\frac{4r_x^2 k_{Lx} N_x}{4r^2 k_L N} \leq 3 \tag{42}$$

From eq. (36)

$$[\text{P·}]_l = \frac{-(2\pi r^2 k_L N + 2r_x^2 k_{Lx} N_x) + \{(2\pi r^2 k_L N + 2\pi r_x^2 k_{Lx} N_x)^2 + k_t \cdot \rho\}^{1/2}}{k_t} \tag{43}$$

where $k_t = 2 \times 10^9$ (Lmol^{-1} s^{-1})[16], or $k_t = 3.33 \times 10^{-12}$ (cm^2 s^{-1}) and $k_L = 6 \times 10^{-3}$ (cm s^{-1}). $2r^2 k_L N$, k_{pt}, and $[\text{P·}]_l$ are calculated in Table III.

$$k_t \rho >> (2\pi r^2 k_L N + 2\pi r_x^2 k_{Lx} N_x)^2 \tag{44}$$

$$\therefore \ [\text{P·}]_l \approx (\rho/k_t)^{1/2} \tag{45}$$

Therefore, most polymer radicals will terminate in the aqueous phase before they reach surfaces of not only polymer particles, the diameters of which are roughly from 10 to 70 µm, but also before they reach primary and

secondary particles existing freely in aqueous phase, the concentration of which is estimated roughly below 0.01–0.001 based on total polymer weight. From calculated $[P \cdot]_l$, the rate of polymerization in aqueous phase $\{(R_p)_{l2}\}$ is calculated from

$$(R_p)_{l2} = k_p[P \cdot]_l \cdot [M]_l \qquad (46)$$

The overall rate of polymerization is calculated from eq. (47) which is equal to eq. (23):

$$(R_p)_{0v} = \frac{[min]}{\theta} f_{rv} \qquad (47)$$

As shown in Table III, the value of $(R_p)_{0v}$ is comparable to $(R_p)_l \ (1 - V_p)$. Hence $[P \cdot]_l$ calculated is reasonable and polymer radicals can propagate in aqueous phase before they will be caught by polymer particles. The rate of monomer diffusion to growing radicals (I_m) is calculated from

$$I_m = 4\pi r_R D_m[M] \qquad (48)$$

where, r_R = the radius of a maximum sphere that can envelope a growing radical in aqueous phase and D_m = the molecular diffusion coefficient of monomer. If r_R is roughly 2×10^{-3} μm and D_m is roughly

$$2 \times 10^{-5} \ (\text{cm}^2 \ \text{s}^-)$$

then

$$I_m \approx 3 \times 10^{10} \ (\text{s}^{-1})$$

TABLE III

Expt. no.	1	3	5
Water/monomer	1.75	2.5	4.0
$\rho \times 10^{-15\,a}$ (cm^{-3} s^{-1})	0.940	0.697	0.354
$2\pi r^2 k_L N^b$ (s^{-1})	3.99	1.64	0.93
$k_t \rho \times 10^{-3\,c}$ (cm^{-1} s^{-2})	3.13	2.32	1.18
$[P \cdot]_l \times 10^{-13\,d}$ (cm^{-3})	1.68	1.45	1.03
$(R_p)_{l1} \times 10^{-17\,e}$ (cm^{-3} s^{-1})	9.88	7.79	5.12
$(R_p)_{l2} \times 10^{-17\,f}$(cm^{-3} s^{-1})	8.17	9.84	6.44
●$(R_p)_{l2}/\Phi\} \times 10^{-17}$ (cm^{-3} s^{-1})	5.73	7.77	5.60
$(R_p)_{0v}^{\ g}$ (cm^{-3} s^{-1})	6.93	6.16	4.46

[a] Same as those values listed in Table 1.
[b] Calculated in the same manner as those in Table 1.
[c] $k_t = 3.33 \times 10^{-12}$.
[d] Calculated from eq. (45).
[e] Calculated from the equation $(R_p)_{l1} = ([min]Z/\theta) f r v \cdot \Phi$.
[f] Calculated from eq. (46). where $k_p = 8.3 \times 10^{-17}$ (cm^{-3} s^{-1}), values of $[P \cdot]_l$ and $[M]_l$ were used those in Tables III and II, respectively.
[g] Overall rate of propagation calculated from eq. (47).

On the other hand, the rate of monomer addition to a growing radical v_{kp} is calculated from

$$v_{kp} = k_p[M]_l \tag{49}$$

where $k_p = 8.33 \times 10^{-17}$ and $v_{kp} \approx 5.7 \times 10^4$ (s^{-1}). Hence

$$I_m >> v_{kp} \tag{50}$$

Therefore, monomer diffusion control might never occur in the aqueous phase.

Based on the above-described results and considerations, the main process of polymerization considered is as follows: Primary radicals produced from bisulfite and persulfate ion initiation system add to monomer to form monomer radicals, which grow to polymer radicals in aqueous phases. Most growing radicals terminate in aqueous phase not only before they reach surfaces of polymer particles, the diameters of which are roughly from 20 to 60 μm, but also before they reach the primary and secondary particles freely existing in the aqueous phase. Hence, the loci of polymerization in this system is mainly the aqueous phase excluding both polymer particles mentioned above and secondary and primary particles freely existing in the aqueous phase. In the aqueous phase, particles smaller than primary particles possibly exist in emulsion, though the concentration thereof is low. It cannot be denied that they give a loci of polymerization in this system as emulsion particles.

References

1. S. Ito and K. Yoshida, *Kobunshi Ronbunshu*, **40**, 307 (1983).
2. S. Ito, *Kobunshi Ronbunshu*, to appear.
3. W. M. Thomas and W. C. Mallison, *Petroleum Refiner*, **40**(5), 211 (1961).
4. W. C. Mallison, U.S. Pat. 2,777,832 (1957); U.S. Pat. 2,847,405 (1958).
5. C. C. Ketter, U.S. Pat. 2,974,123 (1961).
6. M. Q. Webb and Williamson, U.S. Pat. 2,992,209 (1961).
7. *J. of Appl. Polym. Sci.*, in press.
8. W. M. Thomas, *Fortschr. Hochpolym.-Forsch.*, **2**, 401 (1961).
9. S. Yugushi and M. Watanabe, *Chem. High Polym.*, **17**, 108 (1960).
10. S. Yamasaki, M. Fukuda and M. Hamashima, *Chem. High Polym.*, **27**, 459 (1970).
11. J. Ulbricht and P. Fritzsche, *Faserforsch. Textiltechn.*, **14**, 320 (1963).
12. P. Fritzsche and J. Ulbricht, *Faserforsch. Textiltechn.*, **14**, 517 (1963).
13. P. Fritzsche and J. Ulbricht, *Faserforsch. Textiltechn.*, **15**, 93 (1964).
14. L. H. Peebles, Jr., *J. Appl. Polym. Sci.*, **17**, 113 (1973).
15. J. T. Davies, *Turbulence Phenomena*, Academic, New York and London, 1972, pp. 148, 368.
16. F. S. Dainton and R. S. Eaton, *J. Polym. Sci.*, **39**, 313 (1959).
17. *J. Appl. Polym. Sci.*, in press.