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Kinetics and Mechanisms of O/W Microemulsion Polymerization of Styrene

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Summary: To clarify the kinetics and mechanisms of o/w microemulsion polymerization, the o/w microemulsion polymerizations of styrene were carried out with different kinds and types of initiators and surfactants. The number of polymer particles and the molecular weight of polymer formed were not affected by the kinds and types of initiators and surfactants. The rate of polymerization with different kinds of azo-type oil-soluble initiators with widely different water-solubility was almost the same, but was much lower than that with KPS. A kinetic model proposed by us could mostly explain the kinetic behavior except for the difference in the polymerization rate with KPS and that with oil-soluble initiators.

Introduction

Polymerization in microemulsion (microemulsion polymerization) is a relatively new, but an attractive field, because it can produces nano-scale polymer particles with extraordinary high molecular weight polymer. Many papers have been published to date on the o/w microemulsion polymerization of styrene (St), and some models for kinetics and mechanisms of the o/w microemulsion polymerization have been proposed. However, a consistent kinetic picture of this polymerization system is still missing. In order to clarify the kinetic picture of the o/w microemulsion polymerization of St in more detail, the o/w microemulsion polymerizations of St were conducted by changing the type of initiators (water-soluble and oil-soluble initiators) and also by changing the type of emulsifiers (anionic and cationic).

Experimental Part

Materials

Anionic and cationic emulsifiers used were sodium lauryl sulfate (NaLS, Nacalai) and dodecyl trimethyl ammonium bromide (DTAB, Tokyo Kasei), respectively. 1-Pentanol (Wako) was used as cosurfactant in the case where NaLS was used as surfactant. Water-soluble initiator used was potassium persulfate (KPS, Wako). Oil-soluble initiators with widely different water-solubility used were 2,2'-Azobis(2-methyl-butyronitrile) (V-59),

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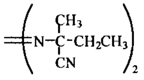
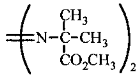
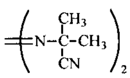
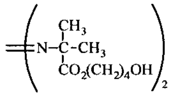
2,2'-Azobis (methyl 2-methylpropionate) (V-601), 2,2'-Azobis(2-methyl-propionitrile) (V-60=AIBN), 2,2'-Azobis(4-hydroxybutyl 2-methylpropionate) (HB-AIBE), respectively. They are all obtained from Wako Pure Chemical Industries Ltd. Their water-solubilities and partition coefficients between the monomer (St) and water phases, λ were measured at 25°C by the same method as described in the previous paper[1], and are listed in Table 1.

Table 1. Properties of oil-soluble initiators used.

Name	Structural formula	$\lambda^{a)}$ at 25°C	$k_d f$ [10^{-7} s^{-1}]	% in water phase $^{b)}$
V-59	 $\left(=N-C(CH_3)(CN)-CH_2CH_3\right)_2$	2560	8.4	0.6 %
V-601	 $\left(=N-C(CH_3)(CO_2CH_3)-CH_3\right)_2$	595	13	2.4 %
AIBN	 $\left(=N-C(CH_3)(CN)-CH_3\right)_2$	120	8.4	11.1 %
HB-AIBE	 $\left(=N-C(CH_3)(CO_2(CH_2)_4OH)-CH_3\right)_2$	2.8	29	84.2 %

a) Partition coefficient between St and water phases ($\lambda=[I]_{oil}/[I]_{water}$).
b) % of initiator dissolved in the water phase.

The values of thermal decomposition rate constant times the initiator efficiency, $k_d f$ at 50°C for V-59, V-601 and HB-AIBE, relative to that for AIBN were determined by comparing the rate of bulk polymerization of St initiated by each initiator at 50°C with that initiated at 50°C by AIBN, the $k_d f$ value of which is already known,[1] and are listed in Table 1.

Procedure of Polymerization and Characterization

All polymerizations were carried out at 50°C under a high purity nitrogen atmosphere (purity>>99.995%). The recipe for the polymerization used in this study is shown in Table 2.

Table 2. Recipe of the O/W microemulsion polymerization of St employed.

Styrene 20.65 g ;		Water 350g ;		Initiator variable ;	
(1) Surfactant	NaLS	38.5g ;	Cosurfactant	1-pentanol	16.36g ;
(2) Surfactant	DTAB	54.9g ;	Cosurfactant	none	

The monomer conversion was determined gravimetrically with methanol as precipitant for polystyrene (PSt). The molecular weight of PSt produced was measured by gel-permeation chromatography. The volume average diameter of polymer particles produced was determined by transmission electron microscopy.

Results and Discussion

Polymerization with anionic emulsifier (NaLS) and water-soluble initiator (KPS)[2,3]

In our microemulsion polymerization systems, the amounts of monomer and emulsifier initially charged are usually comparable. Therefore, the number of micelles left in the system at any stage of the reaction is regarded to be far greater during the whole course of the polymerization than the total number of polymer particles so far produced (N_T). Full and Puig et al.[4] have directly demonstrated from SANS spectra of polymerized St microemulsions that only less than 1% of the monomer-swollen micelles present in the parent St microemulsion forms polymer particles, the rest coexisting with polymer particles as empty micelles. So, we proposed a simple mathematical kinetic model based on the following kinetic picture [2,3]: (A) Almost all the radicals in the water phase diffuse into monomer-swollen micelles, at least in the beginning of the reaction, to transform them into polymer particles containing a growing radical (active polymer particles), (B) with negligible radical termination in the water phase and (C) with negligible radical entry into the preformed polymer particles. Considering the kinetic picture given by (C), we can deduce that (D) all chain-stopping events in the active polymer particles are the chain transfer to monomer or some chain transfer agent, and (E) growth of the polymer particles is stopped only when the low-molecular weight radical generated by the chain transfer reaction desorbs out from the particles.

According to the kinetic picture presented above, the monomer conversion, X_m can be derived in the following way. Since loss of radicals via bimolecular termination is negligible and almost all the radicals in the water phase participate in forming new polymer particles, the number of the active polymer particles N^* is roughly equal to the total number of radicals generated so far from the beginning of the polymerization and can be expressed as:

$$N^* = r_i\, t \qquad (1)$$

where r_i is the generation rate of radicals effective for nucleating new polymer particles and t is the reaction time. In the case where water soluble initiator like KPS is used, effective radical generation rate can be expressed as:

$$r_i = 2\, k_d f\, I_0\, N_A / M_I \qquad (2)$$

where I_0 is the amount of initiator charged initially in unit of g/cc-water, N_A is the Avogadro's number, M_I is the initiator molecular weight, and k_d is the thermal decomposition rate constant for initiator, and f is the initiator efficiency.

It is assumed that monomer is consumed dominantly by the propagation reaction in the active polymer particles. Thus the rate of polymerization, R_p can be expressed as:

$$R_p = \left(\frac{M_0 N_A}{M_g}\right)\frac{dX_m}{dt} = k_p[M]_p N^* \tag{3}$$

where M_0 is the amount of monomer charged initially in unit of g/cc-water, M_g is molecular weight of monomer, X_m is monomer fractional conversion, k_P is the propagation rate constant, $[M]_P$ is the monomer concentration in the polymer particles. According to Guo et al.[5], the monomer concentration in the polymer particles can be approximated as:

$$[M]_p=[M_0]_p\,(1-X_m) \tag{4}$$

where $[M_0]_p$ is the monomer concentration in the polymer particles in the beginning of the polymerization. Substituting Eqs. (1), (2) and (4) into Eq.(3) and integrating the resultant equation gives the following expression for the monomer conversion X_m.

$$X_m = 1 - exp\left(-\frac{k_p[M_0]_p M_g r_i}{2M_0 N_A} t^2\right) \tag{5}$$

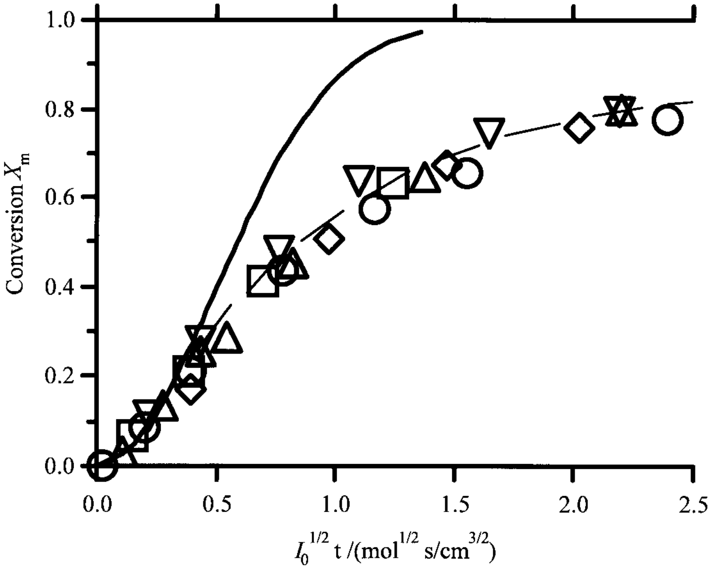


Figure 1. Plot of X_m versus $I_0^{1/2}$ t observed in the O/W microemulsion polymerization of St with SDS/1-pentanol at different initial KPS concentrations, I_0 (x10^{-7}mol/cm^3-water): 4.18(○), 8.37(△), 16.7(□), 33.4 (▽), 91.9 (◇); Solid line: predicted by Eq.(5).

Eq.(5) expects that a plot of experimental X_m versus a new parameter, ($I_o^{1/2} \cdot t$) falls on the same line, irrespective of the initial initiator concentration. The validity for this is demonstrated by the experimental results shown in Fig.1. However, the values predicted by Eq.(5), which is shown by the solid line in Fig. 1, only explains X_m in the range less than *ca.* 30%. The reason for this is not yet explained quantitatively.

According to our kinetic picture proposed previously, dominant chain stopping event is chain transfer to monomer or to chain transfer agent (CTA). In this polymerization system, there are no special CTAs and hence, the chain transfer reaction occurs mainly to monomer. Therefore, the number and weight average molecular weight of polymer formed is predicted as:

$$\overline{M}_n = M_g / C_M , \quad \overline{M}_w / \overline{M}_n = 2 \qquad (6)$$

where C_M is the chain transfer constant to monomer, $\overline{M}_n$ and $\overline{M}_w$ are the number and weight average molecular weight, respectively. Eq.(6) indicates that $\overline{M}_n$ and $\overline{M}_w$ are independent of both the initial initiator concentration and the monomer conversion.

Fig. 2 shows the experimental results for $\overline{M}_w$ observed at different initiator concentration. $\overline{M}_w$ is almost independent of the monomer conversion and the initial initiator concentration, which agrees with the prediction of the kinetic picture proposed by us. The solid line in Fig.2 is the value calculated by Eq.(6), assuming C_M= 3x10^{-5} although the literature value of C_M scatters in the range from 1x10^{-5} to 5x10^{-5}. A fairly good agreement between the predicted and experimental values indicates the validity of our kinetic picture (D).

Based on the proposed kinetic picture (E), the average size of the polymer particles containing no radical (dead polymer particles) produced in this microemulsion polymerization can be

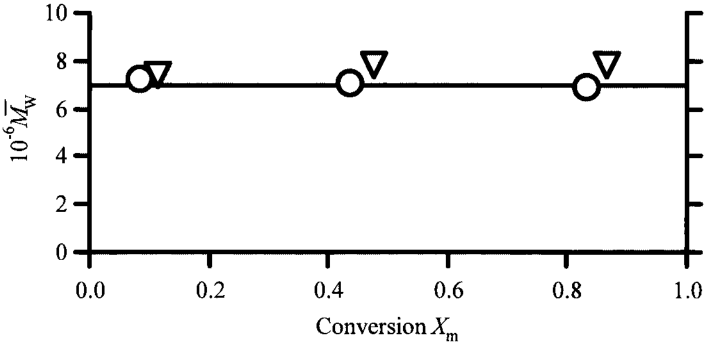


Figure 2. Weight average molecular weight of polymer $\overline{M}_w$ versus X_m obtained with SDS and KPS; Symbols are the same as in Fig. 1.

estimated as follows: The average lifetime of an active polymer particle, starting by entry of a radical into a micelle followed by initiation and ending by desorption of a monomer radical produced by the chain transfer reaction to monomer, is given by the reciprocal of the desorption rate coefficient, k_f. Therefore, the average number of monomer units incorporated into a polymer chain during the average lifetime, n_p is expressed by the rate of propagation per radical times the average lifetime of the active particle, as shown by

$$n_p = \frac{k_p[M]_p}{k_f} \tag{7}$$

Thus, the volume average diameter of the dead polymer particles, d_v is given by

$$d_v = \left(\frac{6M_g}{\pi\rho_p N_A}\right)^{1/3} n_p^{\ 1/3} \tag{8}$$

where ρ_p is the density of the polymer. In the case where re-entry of desorbed radicals into polymer particles can be neglected, k_f is known to be expressed as[6]

$$k_f = K_o\left(\frac{k_{mf}[M]_p}{K_o + k_p[M]_p}\right) \tag{9}$$

where k_{mf} is the rate constant for chain transfer reaction to monomer, and K_0 is the diffusion rate coefficient for monomer radicals out of polymer particles given by

$$K_o = \left(\frac{12D_w\delta}{m_d d_p^{\ 2}}\right), \quad \delta = \left(1 + \frac{D_w}{m_d D_p}\right)^{-1} \tag{10}$$

where D_w and D_p are the diffusion coefficients of monomer radicals in the water phase and in the active polymer particles, respectively, m_d the partition coefficient for monomer radicals between the water and active polymer particle phases, δ the ratio of the water side to the overall resistances for monomer radicals to diffuse out of the polymer particles into the water phase, and d_p the average diameter of polymer particle from which the radical desorbs.

By solving Eqs.(7) to (10), we can predict the volume-average diameter of the dead polymer particles so far generated. To make the treatment simpler, we use the volume average diameter, d_v in place of d_p in Eq.(10). Furthermore, $[M]_p$ changes in accordance with Eq.(4). Therefore, the average particles diameter will also change with the monomer conversion. By using the values listed in Table 3 and Eq.(4), the average particle diameter can be predicted to be 46 nm at X_m=0 and 31 nm at X_m=0.5. Thus, we can regard that particles with average diameter of about 40 nm are produced in this system at least in the range of monomer conversion less than 50%. As seen in Fig. 3, the volume average diameter of polymer particles observed is almost constant around 40nm, independently of both the initial initiator concentration and the monomer conversion, and also is in good agreement with the predicted value shown by the solid line (40 nm). This fairly good agreement indicates the validity of our kinetic picture proposed for the o/w microemulsion polymerization of St.

Considering that the probability of radical desorption is higher in a smaller polymer particle than in a larger one, the average particle size of the dead polymer particles would be somewhat smaller than that of the active polymer particles.

Table 3. The values of numerical constants at 50°C used.

Constants	Value	Unit	Source
k_p	236	$dm^3\ mol^{-1}s^{-1}$	Gilbert et al.[7]
$k_d f$	$6.7x10^{-7}$	s^{-1}	Nomura et al.[8]
$[M_0]_p$	7.0	$mol\ dm^{-3}$	Guo et al.[5]
C_M	$3\ x10^{-5}$	-	Nomura et al.[2]
D_W	$1.2\ x10^{-5}$	$cm^2\ s^{-1}$	Nomura et al.[8]
m_d	1300	-	Nomura et al.[8]
δ	0.04 a)	-	Penboss et al.[9]
ρ_p	1.05	$g\ cm^{-3}$	Polymer Handbook[10]

a) estimated by Eqs.(9) and (10) using the literature data[9] that k_f=$5.5x10^{-4}$ s^{-1} at 50°C for latex with d_p=154 nm and the constants listed in this table.

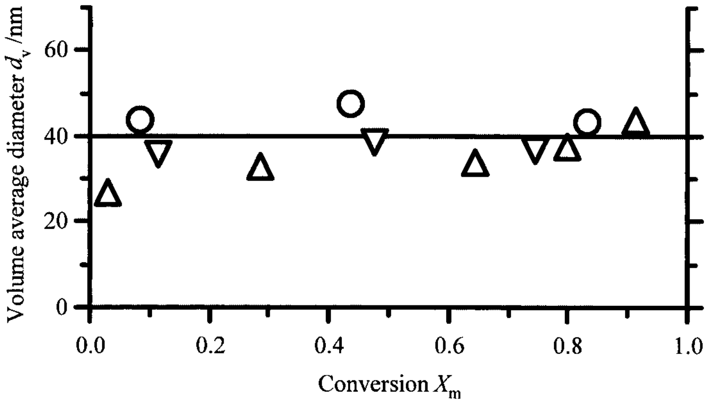


Figure 3. Volume average diameter of polymer particles versus monomer conversion obtained with SDS and KPS; Solid line is model prediction; Symbols are the same as those in Fig.1.

Polymerization with anionic emulsifier (NaLS) and oil-soluble initiators[11]

Oil-soluble initiators partition in the monomer-swollen micelle, polymer particles and water phases, respectively. Hence, oil-soluble initiators generate radicals in these three phases. A pair of radicals generated in such a small space as a polymer particle and a micelle may terminate very rapidly with each other or with a propagating radical, so that the number of radicals effective for the polymerization may depends on the water-solubility of the oil-soluble initiator. These factors would affect the rate of polymerization, the molecular weight of polymer produced and the particle size. To clarify the effects of these factors on the kinetics of o/w microemulsion polymerization, we carried out the o/w microemulsion polymerization of St initiated by the oil-soluble initiators listed in Table 1 with NaLS and 1-pentanol as surfactant and cosurfactant, respectively. All the monomer conversion data obtained with these oil soluble initiators gathered around the same line regardless of the water-solubility of the oil-soluble initiators, when they were plotted against the value of $r_i^{1/2} \cdot t$ with the value of r_i changing very widely. A representative result obtained with V-59 is shown in Fig.4. This agrees well with the prediction by Eq.(5).

Nomura et al. reported that in the emulsion polymerization of St initiated by an oil-soluble initiator, AIBN, the rate of polymerization and the number of the polymer particles generated could be explained quantitatively by the amount of initiator dissolved in the water phase.[12]

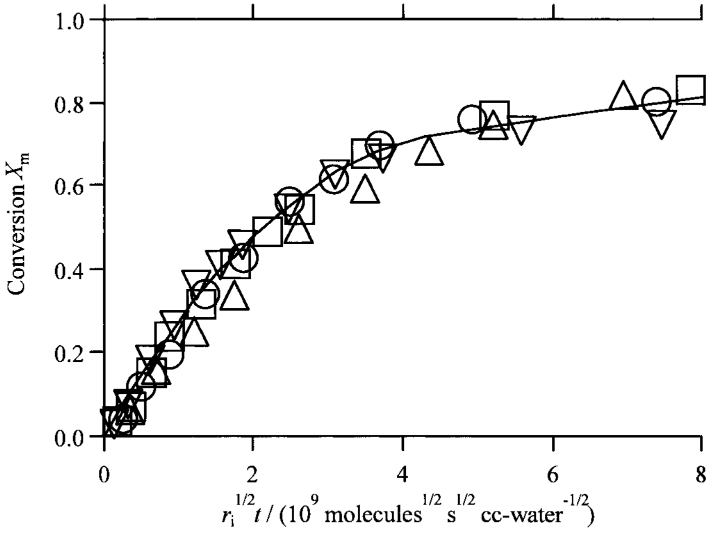


Figure 4. Plot of X_m versus $r_i^{1/2}t$ for the O/W microemulsion polymerization of St initiated by V-59 with NaLS; r_i = 1.07(▽), 2.1(□), 4.2(○), 8.4(△) x 10^{12} molecules/cc-water.s.

They pointed out that the reason for this may be due mainly to that a pair of radicals generated in a small locus like a polymer particle and a micelle mostly terminates bimolecularly as soon as they have appeared. They also show that the number of particles generated is determined almost only by the amount of initiator dissolved in the water phase[13]

Contrary to the emulsion polymerization of St, the water-solubility of oil-soluble initiators did not affect the rate of polymerization, the number of polymer particles produced and the molecular weight of polymer produced in the o/w microemulsion polymerization of St, as shown in Figs.5, 6 and 7, respectively. This suggests that the radicals formed both in the organic phase like micelles and polymer particles and in the water phase are equally effective for the polymerization. However, the rate of polymerization with the oil-soluble initiators is only *ca.* 1/3 of that with KPS, even if the value of r_i is kept the same in every system. Considering that the rate of polymerization is proportional to the square root of the rate of radical generation, the efficiency of the radicals produced from these oil-soluble initiators is about 1/9 of that of the radicals produced from KPS. The reason for this is not clarified yet.

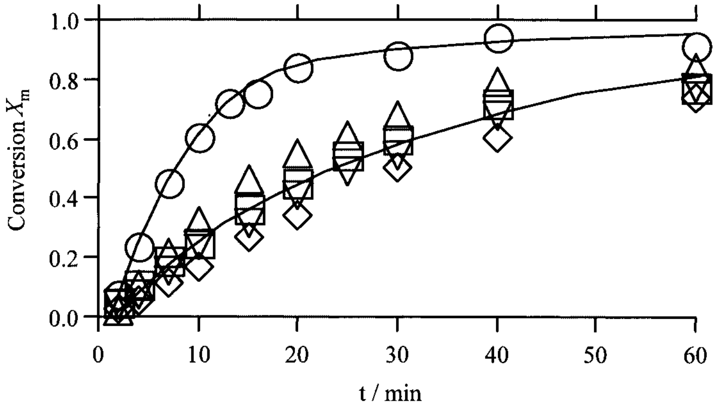


Figure 5. Time-conversion curves obtained in the O/W microemulsion polymerization of St at r_i=2.1x10^{12} molecules/cc-water.s; Initiators: V-59(▽), V-601(△), AIBN(□), HB-AIBE(◇), KPS(○), with NaLS as surfactant and 1-pentanol as cosurfactant, respectively.

On the other hand, the weight average molecular weight of polymer produced, $\overline{M}_w$ and the volume average diameter, d_v observed in the microemulsion polymerization of St initiated by all the initiators used are plotted against the value of r_i in Fig.6 and Fig.7, respectively. The average values of $\overline{M}_w$ and d_v observed are almost independent not only of the monomer conversion, but also of r_i and the type and kind of initiators. That the molecular weight of polymer produced is not affected by the value of r_i demonstrates that bimolecular termination in the polymer particles is negligible, which was presumed in our kinetic picture, (C) and (E).

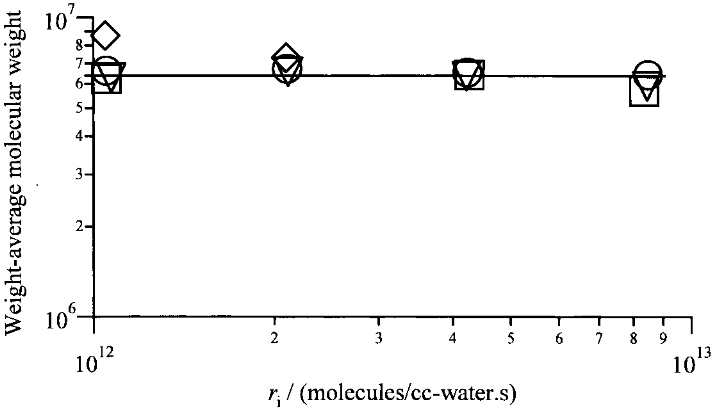


Figure 6. Effect of r_i and the kind of initiators on weight average molecular weight of polymer obtained with SDS; Symbols are the same as those in Fig. 5.

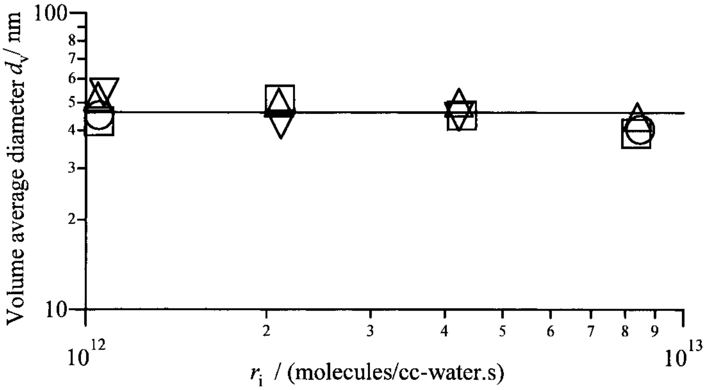


Figure 7. Effect of r_i and the kind of initiators on volume average diameter of polymer particles obtained with SDS; Symbols are the same as those in Fig. 5.

Polymerization with cationic emulsifier (DTAB) and water-soluble initiator (KPS)[14]

Our kinetic aspect to o/w microemulsion polymerization is that as far as the number of micelles present is far larger than the number of polymer particles produced throughout the polymerization, the kinetic behavior would be the same as that pictured by Eqs.(1) to (10), even though the kind and type of surfactant used is different. To see whether this presumption is correct or not, we carried out the o/w microemulsion polymerization of St initiated by KPS with DTAB as surfactant and with the polymerization recipe shown in Table 2.

Fig. 8 shows a plot of the monomer conversion versus $I_0^{1/2}t$, which shows that all the monomer conversion data fall on a line regardless of the initial initiator concentration. The solid line is the same one obtained in Fig.1 for the o/w microemulsion polymerization of St with NaLS as surfactant. This result demonstrates that the polymerization in this system also proceeds according to Eq.(5). One can regard, therefore, that the kinetics of the o/w microemulsion polymerization of St with DTAB as surfactant is almost the same as that with NaLS as surfactant and 1-pentanol as cosurfactant, respectively.[2] Furthermore, we found that the molecular weight of polymer and the average diameter of polymer particles observed with DTAB were, although not shown here, also equal to those obtained with NaLS and 1-pentanol.[14] We can conclude, therefore, that the kind of emulsifier does not affect the kinetic behavior of the o/w microemulsion polymerization of St. This supports the validity of our kinetic picture proposed in the previous section.

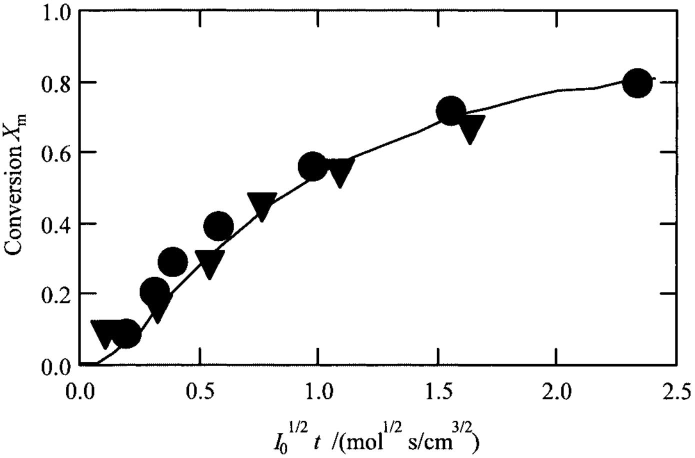


Figure 8. Plot of X_m versus $I_0^{1/2}t$ at different initial KPS concentration with DTAB, I_0 (mol/cc-water): I_0=4.18x10^{-7}(●), 3.34x10^{-6}(▼); Solid line is the broken line in Fig.1.

Conclusion

We proposed a kinetic picture for the o/w microemulsion polymerization with the assumptions that: (A) almost all the radicals in the water phase enter monomer-swollen micelles to transform them into polymer particles, (B) with negligible radical termination in the water phase and (C) with negligible radical entry into the preformed polymer particles, and hence, (D) chain-stopping events in the polymer particles are only the chain transfer to monomer. Thus, (E) the growth of a polymer particle is stopped only by desorption of a monomer radical generated by chain transfer to monomer into the water phase.

Based on this kinetic picture, a quantitative kinetic model was proposed. We demonstrated the validity of the model by showing that the model quantitatively explains the kinetic behavior of the o/w microemulsion polymerization of St initiated by KPS and with NaLS as surfactant and 1-pentanol as cosurfactant at least in the early stage of the polymerization. Furthermore, the validity of the model was tested by changing the kinds and types of emulsifiers and initiators employed. As the model predicts, particle diameter and the molecular weight of polymer formed were independent of the initial emulsifier, initiator and monomer concentrations regardless of the kinds and types of emulsifiers and initiators employed. However, the rate of polymerization with azo-type oil-soluble initiators was much lower than that predicted by the model, and also was much lower than that with KPS, even if the polymerization was carried out with the same value of r_i. These experimental results could not be explained by the proposed kinetic model. Moreover, the model could not explain properly the fact that the rate of polymerization with azo-type oil-soluble initiators with widely different water-solubility did not change with their water-solubility. This may suggest that a pair of radicals generated in such a small space like a micelle and a polymer particle can survive mutual termination by desorbing out of them. Thus, it is still a important problem to clarify the role of the water and organic phases in radical generation for oil-soluble initiators.

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