An Experimental Study on the Kinetics and Mechanisms of Styrene Polymerization in Oil-in-Water Microemulsion Initiated by Oil-Soluble Initiators

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SUMMARY: In order to clarify the kinetic role of oil-soluble initiators in microemulsion polymerization, the oil-in-water (O/W) microemulsion polymerizations of styrene are carried out using four kinds of azo-type oil-soluble initiators with widely different water-solubility. The results are compared with those observed when a water-soluble initiator, potassium persulfate (KPS) is used. For all the oil-soluble initiators used, the molecular weight of polymers and the average size of polymer particles do not change with the monomer conversion and the initial initiator concentration. The monomer conversion is expressed as a function of $r_i^{0.5}t$, where r_i is the rate of radical generation in the whole reaction system and t is the reaction time. These characteristics are quite the same as those observed when KPS is used as an initiator. When the polymerizations are carried out with the rate of radical generation in the whole reaction system fixed at the same value, the rates of polymerization are almost the same for all the oil-soluble initiators employed, irrespective of their water-solubility, but are significantly lower (*ca.* 1/3) than that with KPS. Then, the following conclusions are given: (1) The radicals generated not only in the aqueous phase, but also in the micelle and polymer particle phase are almost equally effective for the polymerization. However, (2) only a small portion (*ca.* 1/9) of the radicals generated in both phases participate in the polymerization. (3) Bimolecular termination of a growing radical in the polymer particle with an entering radical and with a pair of radicals generated in the polymer particles is negligible, and hence, the molecular weight of polymers is determined only by chain transfer to monomer.

Introduction

We carried out the polymerization of styrene initiated by a water-soluble initiator, KPS in the O/W microemulsion composed of sodium dodecylsulfate (SDS) as surfactant and 1-pentanol as cosurfactant[1] and reported that; (a) The rate of polymerization at any

given conversion is proportional to the 0.5 power of the rate of radical generation. (b) The weight-average molecular weight of polymers obtained is almost constant at *ca.* 6×10^6 independently of the initial initiator concentration and the monomer conversion. (c) The average particle size is almost constant around 40 nm independently of the initial initiator concentration and the monomer conversion. Based on these experimental findings, we proposed a kinetic model for the O/W microemulsion polymerization of styrene initiated by KPS [1,2], where we assumed that (1) all the radicals generated in the aqueous phase enter the monomer-swollen micelles with negligible termination in the aqueous phase to form new polymer particles, and (2) with negligible radical entry into the preformed polymer particles. The model is developed by assuming also that (3) a dominant chain-stopping event of growing polymer in the polymer particle is the chain transfer reaction to monomer and (4) the growth of polymer particle is stopped only by desorption of monomeric radicals generated by chain transfer to monomer from the polymer particles. The model can predict fairly well the conversion versus time history, the molecular weight and the particle size. Thus, we have succeeded in clarifying the kinetic role of KPS in the O/W microemulsion polymerization of styrene.

Instead of water-soluble initiators, oil-soluble initiators are also often used in microemulsion polymerization. Oil-soluble initiators, unlike water-soluble initiators, dissolve mainly in micelles and polymer particles and generate a pair of radicals inside them, although a small portion of the oil-soluble initiator dissolves also in the aqueous phase and generate radicals there. When a pair radical is generated in such small spaces as a micelle or a polymer particle, they may quickly terminate bimolecularly with each other and hence, they may not contribute to the polymerization. On the contrary, if these pair radicals can desorb out of the micelles and the polymer particles very rapidly before terminating bimolecularly with each other, they may all be effective for the polymerization. Thus, in order to understand the kinetics and mechanisms of microemulsion polymerization initiated by oil-soluble initiators, we have to clarify especially the kinetic role of the radicals generated in the organic phase such as micelles and polymer particles. At the present stage, however, it is not clear yet how the radicals generated in the micelles and the polymer particles are effective for the polymerization. With an aim of clarifying the kinetic role of oil-soluble initiators in microemulsion polymerization, we conducted the O/W microemulsion polymerization of styrene initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN) [3,4]. We observed the same

characteristics as those found in the KPS system, except that the rate of polymerization with AIBN is only *ca.* 1/3 of that with KPS even though the total rate of radical generation in the whole reaction system is fixed at the same value in both systems. Considering that the rate of polymerization is proportional to the 0.5 power of the total rate of radical generation, the percentage of radicals which effectively contribute to the polymerization is *ca.* $(1/3)^{1/0.5} = 1/9$. The percentage of AIBN dissolved in the aqueous phase is around 10 %, which is very close to 1/9.   From these experimental results, we pointed out the possibility that only the radicals stemming from the portion of the initiator dissolved in the aqueous phase are effective for the O/W microemulsion polymerization of styrene in the case where AIBN is used as an oil-soluble initiator.

In this paper, we aim to clarify the kinetic role of the oil-soluble initiator distributed in the organic phase such as micelles and polymer particles in more detail. For this purpose, we carried out the O/W microemulsion polymerization of styrene initiated with oil-soluble initiators with varying the percentage of the initiator distributed in the organic phase by adopting several kind of oil-soluble initiators with widely different water-solubility.

Experimental

Oil-Soluble Initiators Used

The oil-soluble initiators used are: (1) 2,2'-Azobis(2-methyl-butyronitrile) (V-59), (2) 2,2'-Azobis (methyl 2-methylpropionate) (V-601), (3) 2,2'-Azobis(2-methyl-propionitrile) (AIBN=V-60), and (4) 2,2'-Azobis(4-hydroxybutyl 2-methylpropionate) (HB-AIBE). These initiators were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan. The water-solubility and the partition coefficient between the monomer (styrene) and the water phases, λ, were measured at 25°C by the same method as described in the previous paper[5] and are listed in Table 1. The value of partition coefficient, λ', between the polymer particle and the water phases is considered to be approximately equal to the value of λ.

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 styrene initiated by each initiator at 50°C

Table 1. Properties of oil-soluble initiators used.

Name	Structural formula	$\lambda^{a)}$ at 25°C	k_df / 10^{-7} s^{-1}	% in the aqueous phase
V-59	$\left(N-\underset{\underset{CN}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_2CH_3\right)_2$	2560	8.4	0.6 %
V-601	$\left(N-\underset{\underset{CO_2CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3\right)_2$	595	13	2.4 %
AIBN	$\left(N-\underset{\underset{CN}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3\right)_2$	120	0.84	11.1 %
HB-AIBE	$\left(N-\underset{\underset{CO_2(CH_2)_4OH}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3\right)_2$	2.8	29	84.2 %

a) Partition coefficient between styrene and water phases ($\lambda=[I]_{oil}/[I]_{water}$)

with that initiated at 50°C by AIBN, the k_df value of which is already known[5].
This is based on the fact that the rate of the bulk polymerization of styrene can be expressed by

$$r_p = k_p[M]\left(\frac{2k_df}{k_t}\right)^{1/2}[I_0]^{1/2} \tag{1}$$

where k_p is the propagation rate constant, $[M]$ the monomer concentration, k_t the termination rate constant, $[I_0]$ the initial initiator concentration. The values of the rate constants except for k_df are regarded to be the same independently of the kind of initiators. The values of k_df thus determined are listed in Table 1. The water soluble initiator, KPS, was also used for the polymerization for comparison.

Polymerization Procedure

Polymerizations were conducted with the same reactor and procedure as those described in the previous paper[1] except that the initiator was charged in the form of monomer solution or microemulsion into the reactor. Impeller speed was 400 rpm unless otherwise stated. All the polymerization experiments were carried out at 50°C under a

high purity nitrogen atmosphere. The recipe employed in this study was: Water=350g, styrene=20.65g, SDS=38.5g, 1-pentanol=16.36g and initiator=variable. The monomer conversion was determined gravimetrically with methanol as precipitant for polystyrene. The molecular weight of polymers produced was measured by gel-permeation chromatography (GPC). The diameter of polymer particle was measured by a transmission electron microscope. The volume-average diameter of polymer particles was calculated using the following equation.

$$\overline{d_v} = \left(\frac{\sum n_i d_{pi}^3}{\sum n_i} \right)^{1/3}$$ (2)

where n_i is the number of the particles whose diameter is d_{pi}.

Experimental Results and Discussion

Rate of Polymerization

Figure 1 shows an example of the monomer conversion versus time histories observed when V-59 is used with varying the total rate of radical generation, r_i widely.
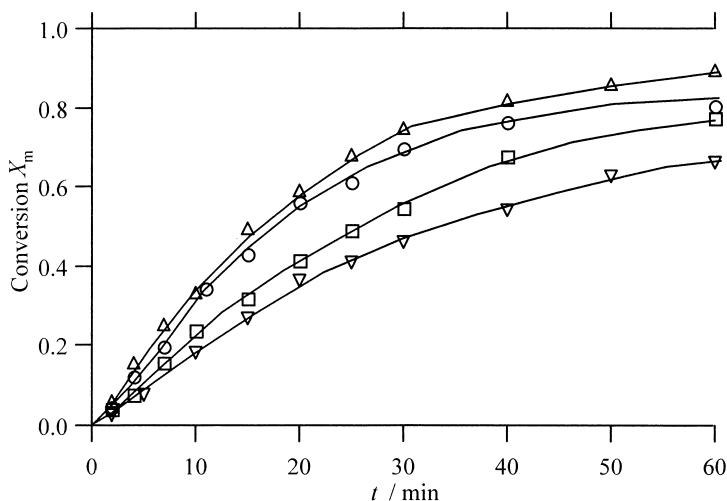

Fig. 1: Conversion versus time histories for the O/W microemulsion polymerization of styrene initiated by V-59; The total rate of radical generation, r_i=1.07 ($\triangledown$), 2.1 ($\square$), 4.2 ($\bigcirc$), 8.4 ($\triangle$) x10^{12} molecules/cc-water.s

The rate of polymerization is seen to increase with the total rate of radical generation. The total rate of radical generation, r_i, was calculated using the following defining expression.

$$r_i = 2k_d f I_o \tag{3}$$

where I_o is the amount of initiator initially charged per unit volume of water.

According to the kinetic model proposed previously by us for the O/W microemulsion polymerization of styrene initiated by KPS[1], the monomer conversion X_m is given by

$$X_m = 1 - \exp\left(-\frac{k_p[M]_{po} r_i}{2M_0} t^2\right) \tag{4}$$

where $[M]_{po}$ is the initial monomer concentration in the polymer particles expressed in moles of monomer, M_0 the amount of monomer initially charged per unit volume of water, and t the reaction time. Eq.(4) indicates that the monomer conversions observed at different total rate of radical generation fall on the same line when they are plotted against $r_i^{1/2}t$. The validity of this expression was experimentally demonstrated in the O/W microemulsion polymerization of styrene initiated by KPS[1] and also by AIBN[4].

The monomer conversions in Fig.1 are replotted against $r_i^{1/2}t$ in Fig.2.   The solid line is the correlation result obtained for the AIBN system with the same plot. It is seen that all the monomer conversions obtained with V-59 at different r_i also gather approximately around the solid line. On the other hand, the dotted line shows the correlation result obtained for the KPS system. The monomer conversions observed with HB-AIBE and V-601 also gathered around the solid line with the same plot, although not shown here. These results directly show that the rate of polymerization is approximately proportional to the 0.5 power of the total rate of radical generation for all the oil-soluble initiators, similar to the case where KPS is used as an initiator. It is clear from Fig. 2 that the rate of polymerization with V-59 is almost the same as that with AIBN as long as the total rate of radical generation is the same, even though V-59 and AIBN have about 20 times difference in the water-solubility. Moreover, it should be pointed out that the rates of polymerization obtained with V-59 and AIBN are far lower than that obtained with KPS, although the total rate of radical generation is kept at the same value among these three systems.
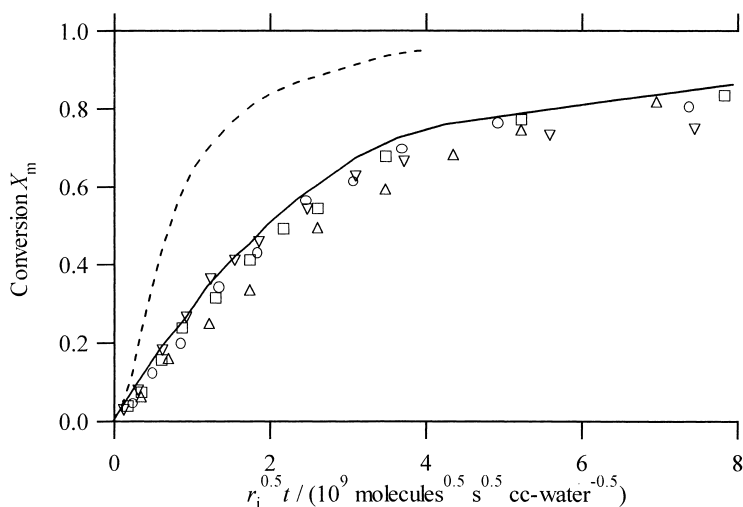
Fig. 2: Plot of monomer conversion X_m against $r_i^{0.5}t$ for the O/W microemulsion polymerization of styrene initiated by V-59; r_i=1.07 ($\triangledown$), 2.1 ($\square$), 4.2 ($\bigcirc$), 8.4 ($\triangle$) x10^{12} molecules/cc-water.s; Solid line=Correlation result for AIBN system[4]; Dotted line=Correlation result for KPS system[1]

Figure 3 shows the monomer conversion versus time histories observed with the total rate of radical generation fixed at 2.1x10^{12} molecules/cc-water.s for all the initiators.
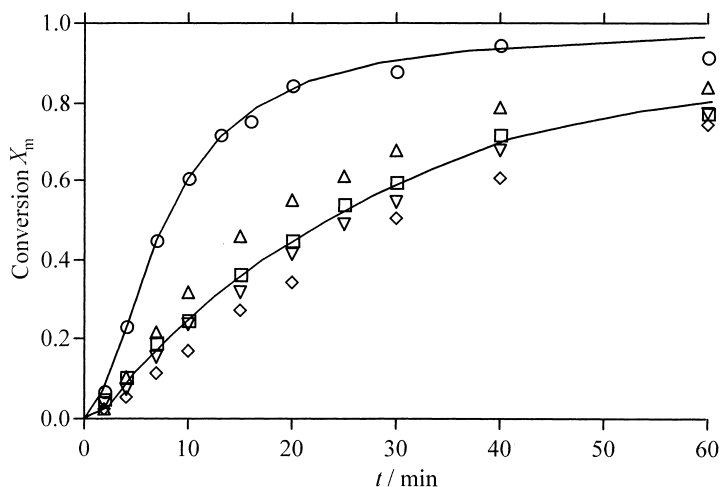

Fig. 3: Conversion versus time histories observed in the O/W microemulsion polymerization of styrene carried out with the total rate of radical generation fixed at r_i = 2.1x10^{12} molecules/cc-water.s. Initiators=V-59($\triangledown$), V-601 ($\triangle$), AIBN ($\square$), HB-AIBE ($\diamondsuit$), KPS ($\bigcirc$)

The rates of polymerization observed with the oil-soluble initiators, V-59, V-601, AIBN and HB-AIBE are roughly equal to each other irrespective of their water-solubility. The percentage of radicals generated in the aqueous phase can be calculated by using the partition coefficient listed in Table 1 and the recipe, and they are listed in Table 1. In the case of HB-AIBE, about 84% radicals are generated in the aqueous phase, while in the case of V-59, 99.4% radicals are generated in the micelle and polymer particle phase. Nevertheless, no appreciable difference is observed between the rate of polymerization with HB-AIBE and that with V-59. This suggests that the difference in the locus of radical generation does not affect the rate of polymerization in this polymerization system when the oil-soluble initiator is used, and that the radicals generated in both the micelle and particle phase and the aqueous phase are equally effective for the polymerization.

These experimental results contradict our expectation that only the radicals generated from the portion of initiators dissolved in the aqueous phase would be effective for the polymerization because we expected that a pair of radicals generated in such a small space as a micelle and a polymer may terminate with each other rapidly before desorbing out of them.

However, the rates of polymerization observed with these oil-soluble azo-type initiators are significantly lower than that obtained with a water-soluble initiator, KPS, even at the same total rate of radical generation. The initial rates of polymerization observed with these oil-soluble initiators at r_i=2.1x10^{12} molecules/cc-water.s are all roughly 1/3 of that observed with KPS at the same rate of radical generation. Considering that the initial rate of polymerization is proportional to the 0.5 power of the initial initiator concentration, only *ca*. 1/9 of the radicals generated from the oil-soluble initiators participates in the polymerization. This means that the apparent initiator efficiency of these oil-soluble initiators is roughly 1/9 of that of KPS.

From these experimental results, we can conclude that; (1) The radicals generated not only in the aqueous phase, but also in the micelle and polymer particle phase are almost equally effective for the polymerization, because the water-solubility does not affect the rate of polymerization, However, (2) they are less effective than KPS radicals. (3) Considerable portion of pair radicals generated in such small spaces as micelles and polymer particles can survive bimolecular-termination through radical desorption from

the micelles and the polymer particles. However, (4) only a small portion (*ca.* 1/9) of the radicals generated in both phases can participate in the polymerization.

Molecular Weight of Polymers

The molecular weight of polymer produced in this polymerization system does not change with the monomer conversion at least in the range higher than around 40% for all the initiators used. Therefore, the weight-average molecular weight of polymers obtained at the monomer conversion around 50% using V-59, AIBN, HB-AIBE, and KPS is plotted against the total rate of radical generation in Fig.4. It is interesting to point out that the weight-average molecular weight of polymers observed in this polymerization system is almost independent of the total rate of radical generation and the water-solubility of the initiators used, and is quite the same as that observed in the KPS system. This implies that the O/W microemulsion polymerization of styrene initiated by these oil-soluble initiators proceeds according to a scheme very similar to that initiated by KPS.

Moreover, the weight-average molecular weight observed in this polymerization system agrees well with the value predicted by the following expression[1].

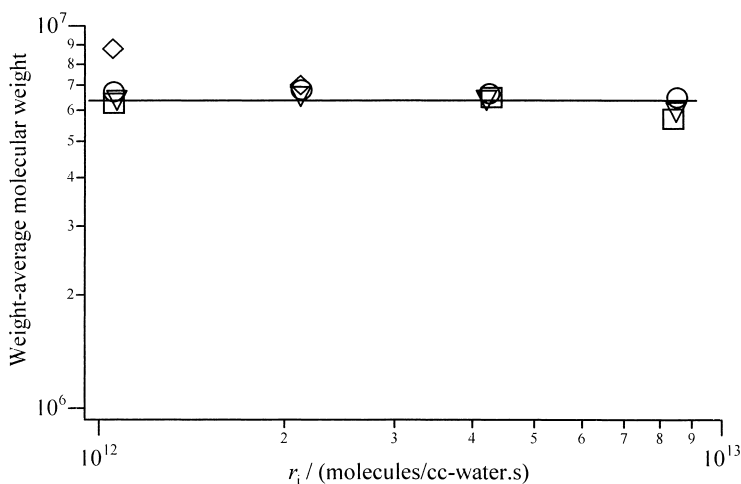$$\overline{M}_w = 2\, M_g\, /\, C_M \tag{5}$$

Fig. 4: The weight-average molecular weight of polymers obtained at the monomer conversion around 50% in the O/W microemulsion polymerization of styrene initiated at 50°C with V-59($\bigtriangledown$), AIBN ($\square$), HB-AIBE ($\diamondsuit$), KPS ($\bigcirc$).

which is obtained by assuming that the sole chain stopping event in the polymer particles is the chain transfer to monomer and the chain transfer constant to monomer, C_M, is 3.0×10^{-5}. Here, M_g is the molecular weight of monomer. This suggests that the probability of bimolecular termination of a growing radical with an entering radical or with a pair of radicals generated in the polymer particles can be neglected compared to the probability for a growing radical to chain transfer to monomer. Thus, we can say that the chain-stopping event in the polymer particles is only the chain-transfer to monomer, just like in the KPS system[1].

Average Particle Size

The volume-average diameter of polymer particles measured by TEM was almost constant throughout the polymerization, irrespective of the kind and the initial concentration of the oil-soluble initiators used. Therefore, the volume-average particle diameters obtained at the monomer conversion around 50% using V-59, V-601, AIBN and KPS are plotted against the total rate of radical generation in Fig. 5. The volume-average particle diameter obtained with V-59, V-601, and AIBN are quite the same independently of the total rate of radical generation and the kind of initiators, i.e. the water-solubility of the initiators.

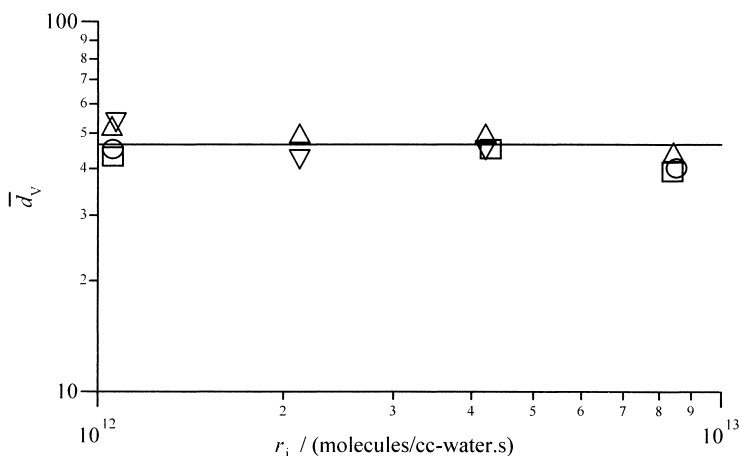Furthermore, they are the same as those obtained with a water-soluble initiator, KPS and

Fig. 5: The volume-average diameter of polymer particles, $\overline{d}_v$ versus the total rate of radical generation, r_i observed at the monomer conversion around 50%. Initiators: V-59($\triangledown$), V-601 ($\triangle$), AIBN ($\square$), KPS ($\bigcirc$)

are close to a constant value of *ca.* 40 nm predicted by our kinetic model proposed for the KPS system. This also suggests that the O/W microemulsion polymerization of styrene initiated by these oil-soluble initiators proceeds according to a scheme very similar to that initiated by KPS[1], that is, that the second radical entry into the preformed polymer particles is negligible and only the desorption of oligomeric radical generated by chain transfer to monomer in a polymer particle stops the growth of the polymer particle.

Discussion

In the O/W microemulsion polymerization of styrene carried out with the total rate of radical generation fixed at the same value, the rates of polymerization are almost the same for all the oil-soluble initiators employed, independently of the water-solubility of the initiators. Moreover, the rates of polymerization are proportional to the 0.5 power of the total rate of radical generation. One possible polymerization mechanism that may explain these experimental results is that radical entry into and desorption from the micelles and the polymer particles are so rapid that the polymerization proceeds according to the pseudo-homogeneous polymerization mechanism similar to the mechanism of suspension polymerization. It is clear that the pseudo-homogeneous mechanism with rapid radical entry into and desorption from the micelles and the polymer particles cannot explain the experimental results on the average molecular weight. In order to clarify the difference between the suspension and microemulsion polymerizations, however, we carried out the suspension polymerization of styrene with the same recipe as that of the microemulsion polymerization except that no surfactant (SDS) is added. The monomer conversion versus time histories for the suspension polymerization of styrene initiated with V-59, AIBN, and HB-AIBE are shown in Fig.6 along with those for the microemulsion polymerization of styrene. It is clear from Fig. 6 that the rates of the microemulsion polymerizations with the oil-soluble initiators are much faster than those of the suspension polymerizations even at the same radical generation rate.

Since the weight-average molecular weight of polymers produced in suspension polymerization decreases with the monomer conversion, the values of the weight-
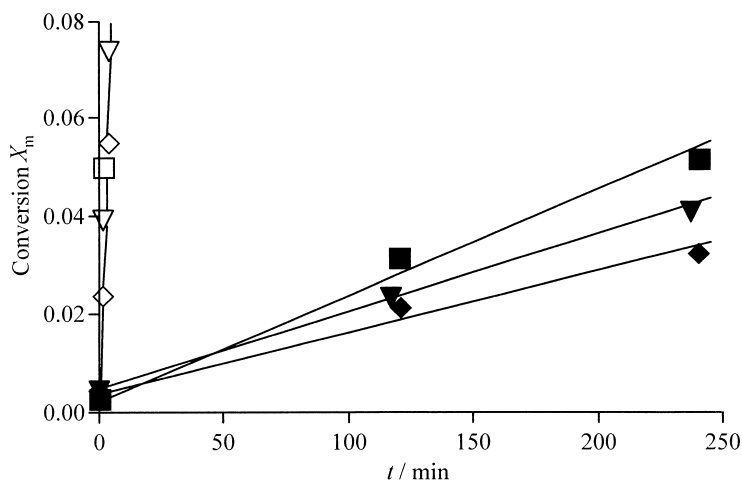
Fig. 6: Comparison of the monomer conversion versus time histories for the suspension and microemulsion polymerizations of styrene at the total rate of radical generation, r_i= 2.1×10^{12} molecules/cc-water.s. Initiators=V-59(▼ ▽), AIBN (■ □), HB-AIBE (◆ ◇); Open keys = Microemulsion polymerization, Closed keys = Suspension Polymerization.

Table 2. The weight-average molecular weight of polymers obtained with suspension and microemulsion polymerizations at $r_i = 2.1 \times 10^{12}$ molecules/cc-water.s

Polymerization	Initiator	X_m	$\overline{M}_w$
Suspension	V-59	0.090	· 8.0×10^4
Suspension	HB-AIBE	0.059	8.4×10^4
Microemulsion	V-59	0.49	6.6×10^6
Microemulsion	HB-AIBE	0.51	7.3×10^6

average molecular weight of polymers obtained below 10% conversion are listed in Table 2 along with those observed around 50% conversion in the microemulsion polymerization.The molecular weight of polymers produced in microemulsion polymerization is about two orders of magnitude higher than those produced in suspension polymerization. These results directly deny the explanation that the O/W microemulsion polymerization proceeds according to the pseudo-homogeneous polymerization mechanism similar to suspension polymerization. The main difference between microemulsion and suspension polymerizations is in the size of polymerization site. In microemulsion polymerization, polymerization starts in the monomer-swollen

micelles (microemulsion droplets) the diameter of which is in the order of 10 nm, while in suspension polymerization, polymerization takes place in the monomer droplets whose diameter would be larger than 10,000 nm. It is interesting to note that the difference in the size of polymerization site causes such significant differences in the rate of polymerization and the molecular weight of polymer produced.

From the experimental results and the discussion so far presented, we can conclude that the O/W microemulsion polymerization initiated by the oil-soluble initiators employed in this work proceeds according to the heterogeneous polymerization mechanism very similarly to that initiated with KPS. The molecular weight of polymers and particle size can be explained by the mechanism on which our kinetic model is based. However, our model, which could mostly explain the kinetic behaviors of the O/W microemulsion polymerization of styrene initiated by KPS, cannot explain the reason why the rate of polymerization initiated by the oil-soluble initiators is much lower than that initiated by KPS, even with keeping the total rates of radical generation in both systems fixed at the same value. The key point to understand the kinetics and mechanisms of the O/W microemulsion polymerization of styrene initiated by the oil-soluble initiators employed in this study will be to clarify the quantitative role of the radicals generated in both the micelle and polymer particle phase and the aqueous phase. At the present stage, however, our experimental results so far obtained are not enough to explain the kinetic role of the radicals generated in each phase. Thus, further quantitative study is expected to establish the kinetics and mechanisms of the O/W microemulsion polymerization of styrene initiated with oil-soluble initiators.

Conclusion

In order to clarify the kinetic role of oil-soluble initiators in microemulsion polymerization, the O/W microemulsion polymerization of styrene was carried out using four kinds of azo-type oil-soluble initiators with widely different water-solubility. The monomer conversion versus time histories, the weight-average molecular weight of polymers and the average diameter of polymer particles were measured and compared with those observed when a water-soluble initiator, KPS is used. It was found that the weight-average molecular weight of polymers and the average diameter of polymer particles are almost constant independently of the monomer conversion and the water-solubility and the total rate of radical generation of the oil-soluble initiators used. The

monomer conversion is expressed as a function of the product of square root of the total rate of radical generation and the reaction time for all the oil-soluble initiators used. These characteristics are quite the same as those observed when a water-soluble initiator, KPS is used. It was also found that when the total rate of radical generation is kept at the same value, the rates of polymerization observed are almost the same for all the oil-soluble initiators used, but are only 1/3 of that for KPS. From the experimental results, we can obtain the following conclusions: (1) The radicals generated in the micelle and polymer particle phase and those generated in the aqueous phase are almost equally effective for the polymerization. (2) Only a small portion (*ca.* 1/9) of the radicals generated in both phases can participate in the polymerization. (3) Bimolecular termination of a growing radical with an entering radical or with a pair of radicals generated in the polymer particles can be neglected compared to chain transfer of a growing radical to monomer.

At the present stage, however, we cannot propose any definite polymerization scheme that can explain the reason why the rate of polymerization initiated by the oil-soluble initiators is much lower than that initiated by KPS, even though the total rate of radical generation in both systems is kept at the same value. In order to clarify the kinetic role of oil-soluble initiators in microemulsion polymerization, we still need further quantitative kinetic study.

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