The Polymerization of Vinyl Monomers in the Presence of Surface Active Agents. III. The Rate of the Polymerization of Styrene

Teruzo Asahara, Manabu Senō, Shinsaku Shiraishi, and Yoshikazu Arita
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo

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Styrene polymerized in the presence of sodium tetrapropylenebenzenesulfonate in an aqueous system without any ordinary initiators. The rate of the polymerization was dependent on the concentration of the surfactant and on the initial monomer concentration. The apparent activation energy of the polymerization was about 13.9 kcal/mol. The polymerization was inhibited by adding hydroquinone to the reaction system.

Imoto and Takemoto[1] have reported the homo- and graft polymerization of methyl methacrylate (MMA) onto fibers with hydroxylic pendant groups, especially onto cellulose. In their paper, they have also described that styrene (St) polymerized only with difficulty under the same reaction conditions. We ourselves have previously reported that the polymerization of MMA in the presence of anionic surface active agents, such as sodium tetrapropylenebenzenesulfonate and 2-dodecylbenzenesulfonate, in an aqueous system without any ordinary initiators gave a stable emulsion of poly(methyl methacrylate) (PMMA) with an unusually high molecular weight, and that the resultant polymer was recovered in a good yield.[2,3] During the course of the investigation, we found that styrene also polymerized in the presence of sodium tetrapropylenebenzenesulfonate about three times or more as much as in the case of MMA in an aqueous medium.

In this paper, we will describe the kinetic study of the polymerization of styrene; we will also consider the reaction in some detail.

Experimental

Materials. Styrene and acrylonitrile (AN) were purified by usual methods. Sodium tetrapropylenebenzenesulfonate (ABS) was purified according to the procedure described in our previous paper.[2]

Polymerization. In a four-necked, 100 ml, flat-bottomed flask equipped with a condenser, a dropping funnel, a nitrogen inlet tube, and a rubber stopper, given amounts of deionized water and ABS were placed; the mixture was then preheated to the reaction temperature (80°C except otherwise stated) for 40 min, during which period a slow stream of nitrogen was introduced into the mixture. A definite amount of a monomer was then added to the mixture through the dropping funnel and allowed to polymerize. For a kinetic experiment, 2 g portions of the reaction mixture were withdrawn by means of a syringe at definite time intervals, weighed accurately, and poured into 10 ml of methanol in order to precipitate the polymer formed. The polymer was collected by filtration, thoroughly washed with methanol, dried at 60°C under a vacuum, and weighed. The rate of polymerization was determined from the time-conversion curves. The molecular weight, $\overline{M}$, of the polystyrene thus obtained was determined from the intrinsic viscosity, $[\eta]$, by using this equation:[4]

$$[\eta] = 1.2\times 10^{-5}\,\overline{M}^{0.71}.$$

The viscosity of the polymer solutions in toluene was measured according to an ordinary method at 30°C.

Determination of Number of Particles. For particle-size determination, a sample of about 1 g was taken from the reaction mixture and diluted 10 times by water containing 0.01% of hydroquinone to minimize any further change. It was deposited onto a collodion substrate in minute droplets approximately 2 microns in radius. The specimen was directly photographed by using a JEM-5Y electron microscope of 9800 magnification at 80 kV. A photograph was enlarged in length as much as 2 times. The diameter of the particles was measured by a Scale Lupe of 5 magnification on 50 to 100 particles on the enlarged photograph, and the average diameter was calculated. The number of particles in the reaction mixture was calculated from the average diameter and the density of the particles, which was approximated as 1.0.

Results and Discussion

As has been reported previously,[2] we have found that MMA polymerized in the presence of ABS in an aqueous system without any ordinary initiators. The initiation mechanism, however, has not yet been elucidated. Knowledge of whether or not this polymerization technique is applicable to other monomers may throw some light on the problem; thus, we attempted the polymerization of St in a manner similar to that used for MMA. It was found that St polymerized in an aqueous system in the presence of ABS as much three times or more as in the case of MMA. The polymerization reaction of St was inhibited by adding hydroquinone. This result shows that the polymerization reaction of St proceeds *via* a free radical mechanism.

The relationship between the rate of polymerization of St and the concentration of ABS was investigated. As is shown in Fig. 1, an approximately linear relation was found between the rate of polymerization, R_p, and the ABS concentration, [ABS], in the range studied.

$$R_p \propto [\mathrm{ABS}] \qquad (1)$$

Equation (1) did not agree with either the equation of the polymerization of MMA or that of the Smith-Ewart theory, but it was consistent with the equation

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[1] M. Imoto and K. Takemoto, *Kogyo Kagaku Zasshi*, **70**, 1851 (1967).

[2] T. Asahara, M. Senō, S. Shiraishi, and Y. Arita, This Bulletin, **43**, 3895 (1970).

[3] T. Asahara, M. Senō, S. Shiraishi, and Y. Arita, *ibid.*, **45**, 2862 (1972).

[4] T. Oyama, K. Kawahara, and M. Ueda, *Nippon Kagaku Zasshi*, **79**, 727 (1958).

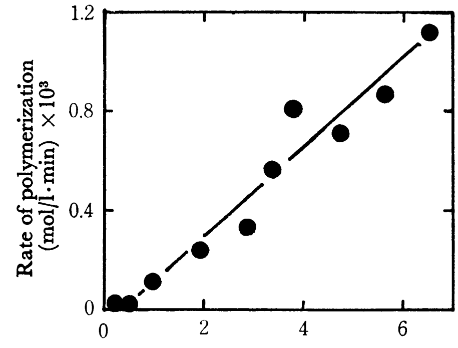

Fig. 1. Dependence of polymerization rate (mol/l·min) on ABS concentration (wt%).

of Medvedev,[5] as will be shown below.

Medvedev argued that the surface area was the most important parameter of the emulsion polymerization and developed a kinetic expression; in which R_P was proportional to the emulsifier concentration when primary radicals were formed in adsorbed emulsifier layers.

Therefore, the surface area may in a sense be one of the important parameters of the present polymerization system. Furthermore, the number of micelles may be considered to be another important parameter,because the number of micelles increases with an increase in the ABS concentration. Supposing that the radicals are generated only on the surface of the micelle, the number of radicals may increase with an increase in the number of micelles in our system.

In the case of AN, the polymerization did not occur even at higher concentration of ABS as is shown in Table 1. The solubility of AN in water, higher than that of St, is responsible for this behavior. This result, together with the fact reported before[2] that the polymerization of MMA did not occur in the medium of organic solvents, suggests that the formation of micelles may be essential for the polymerization in the present system.

TABLE 1. POLYMERIZATION OF ACRYLONITRILE

ABS (g)	AN (g)	Temp. (°C)	Time (hr)	Yield (%)
1.0	10.0	80	2	0
1.0	10.0	70	2	0
1.0	20.0	70	3	trace
2.0	10.0	75	3	trace[a]
3.0	10.0	75	2	0

water 100 g; under nitrogen atmosphere.

a) water 90 g and benzen 10 g under nitrogen atmosphere

The number of polymer molecues was calculated from the yields and the molecular weights of the polymers. The effects of the concentrations of ABS and St and of the reaction temperature on the number of polymer molecules are shown in Figs. 2 and 3 and in Table 2. It was noticeable that the number of polymer molecules increased with an increase in the concentration of ABS and a rise in the reaction temperature, but were nearly independent of the concentration of the monomer in the range above 1.5 mol%. This result suggests that the number of initiation species increased with an increase in the concentration of ABS and the reaction temperature.

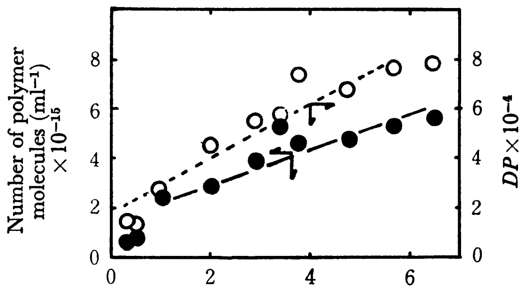

Fig. 2. Dependence of number of polymer molecules (ml⁻¹) and *DP* on ABS concentration (wt%).

St 10 g/aqueous phase 100 g, 2 hr, 80°C under nitrogen atmosphere.

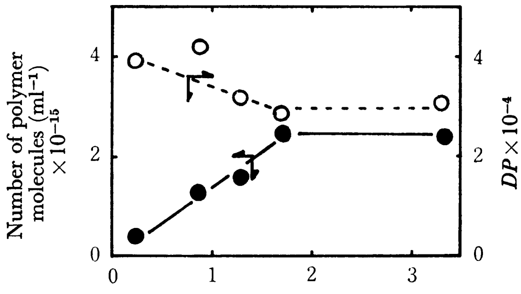

Fig. 3. Dependence of number of polymer molecules (ml⁻¹) and *DP* on initial monomer concentration (mol%). ABS 1 wt%, 80°C, 2 hr, under nitrogen atmosphere.

TABLE 2. EFFECT OF REACTION TEMPERATURE ON POLYMERIZATION RATE, *DP* AND NUMBER OF POLYMER MOLECULES

Reaction temperature (°C)	Polymerization rate (mol/l·min) × 10³	*DP* × 10⁻⁴	Number of polymer molecules (ml⁻¹) × 10⁻¹⁵
70	0.74	4.22	1.04
80	1.14	2.82	2.43
85	1.14	2.44	2.76
90	2.30	2.61	5.16
100	3.50	2.20	11.3

St 10g/100g aqueous phase, ABS 1wt% under nitrogen atmosphere.

The reaction mixture was observed by means of an electron microscope, and the particle sizes were determined at reaction times of 30, 60, and 120 min at ABS concentrations of 1 and 3 wt%. The results are shown in Table 3. The particle sizes were nearly constant, most of them lying in the range from 300 to 400 Å, independent of the concentration of ABS and the reaction time. The maximum particles were from 1000 to 1200 Å in size, and new particles with smaller radii appeared at each reaction time, as is shown in Fig. 4. The number of polymer particles per unit of volume was about 1×10^{15}, which is of the same order as the number of polymer molecues esti-

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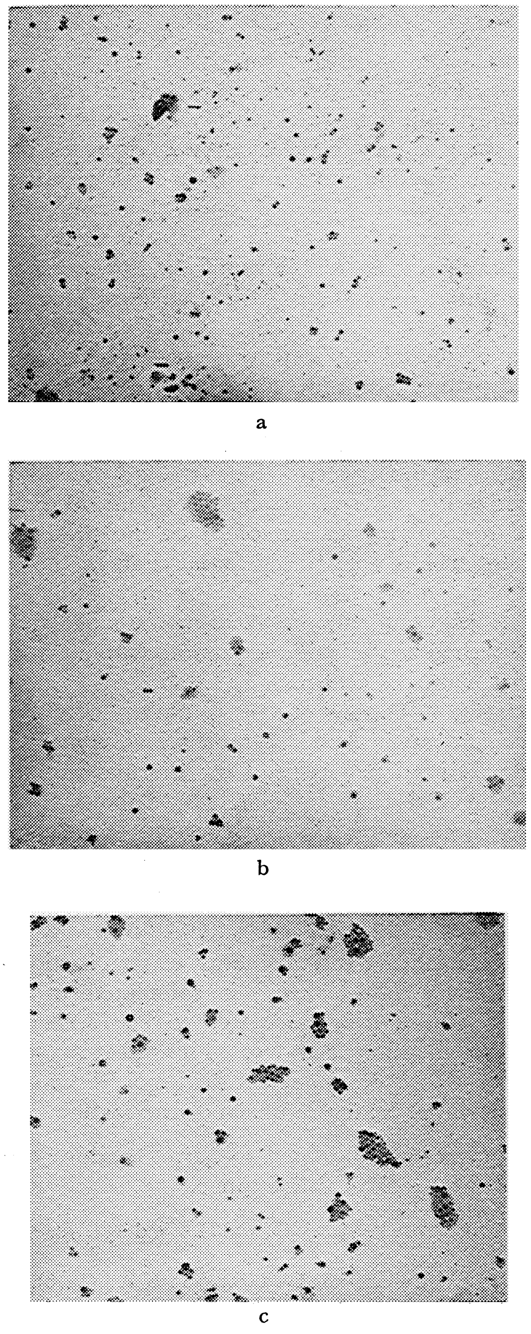
[5] G. E. Ham, "Vinyl Polymerization, Part II," Marcel Dekker, New York (1969), p. 19.

TABLE 3.

ABS (wt%)	Reaction time (min)	Average diameter (Å)	Number of polymer particles (ml^{-1})	Number of polymer molecules (ml^{-1})
1	30	345		
	60	407		
	120	384	0.52×10^{15}	3.3×10^{15}
3	30	427		
	60	410		
	120	414	0.94×10^{15}	3.8×10^{15}

St 10g/100g aqueous phase at 80°C under nitrogen atmosphere.


a

b

c

Fig. 4a, b, c. Electron micrographs of polystyrene latices. The samples are at reaction time; 30 min(a), 60 min(b), and 120 min(c).
ABS 3 wt%, St 10 g/aqueous phase 100 g (19600×).

mated previously. These results can be explained from the following considerations. The loci of the polymerization reaction are the interfaces between the micelles and the continuous medium; the radicals generated at the interface enter into the micelle, and hence the polymerization occurs.

By assuming that one polymer is formed in one micelle, the number of micelles can be calculated by:

$$N = (W/\bar{M}) \times 6 \times 10^{23},$$

where W is the yield of the polymer in grams and where $\bar{M}$ is the average molecular weight of the polymer.

The number of particles was about (0.7 to 4.0)$\times 10^{15}$ ml^{-1} of the solution; this value was of the same order as in the general emulsion polymerization.[6]

From the above discussion, it can be concluded that the formation of micelles is an important factor in the generation of radicals and that the radicals do not enter into the particle from the water phase, but are generated only in the micelle. The ABS concentration was thought to be a factor in the production of radicals, and it was quantitatively understood that the relationship between the ABS concentration and the number of polymer particles was linear.

The rate of emulsion polymerization was usually independent of the initial monomer concentration and proportional to the monomer concentration in the polymer particles or micelles, but in our system the relationship between the rate of polymerization and the initial monomer concentration, $[M]_0$, defined in mol% calculated from the composition in the initial reaction mixture, was as is shown in Fig. 5. The dependence of R_p on $[M]_0$ was more remarkable than in the case of MMA. The apparent relationship can be written by:

$$R_p \propto [St]_0^{0.64}.$$

However, the dependence of R_p on the initial monomer concentration was small compared with that on the ABS concentration, as R_p may be considered to be almost independent of the initial monomer concentration in the range above 0.85 mol%, as is shown in Fig. 5.

These results may be well understood by suposing the following relation:

$$R_p \propto [M]_0[ABS]/([M]_0 + [ABS]).$$

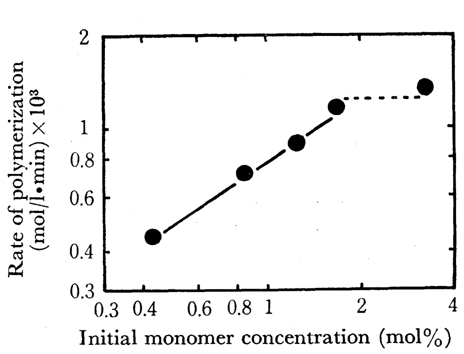


Fig. 5. Dependence of polymerization rate (mol/l•min) on initial monomer concentration (mol%).
ABS 1 wt%, 80°C under nitrogen atmosphere.

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[6] P. J. Flory, "Principles of Polymer Chemistry" Princeton Univ. Press (1953), p. 215.

When the experiment is conducted under the condition of $[M]_0 \gg [ABS]$, R_p is apparently expressed by $R_p \propto [ABS]$. On the other hand, when [ABS] is constant, R_p is almost constant in the range of $[M]_0 \gg [ABS]$, but R_p is slightly dependent on $[M]_0$ in the range where $[M]_0$ is not sufficiently larger than [ABS]. This explains the apparent relationship of $R_p \propto [St]_0^{0.64}$. The plot of R_p *vs.* $[ABS]/([M]_0+[ABS])$ also gave a straight line (Fig. 7); this shows a better linearity than the plot of R_p *vs.* [ABS].

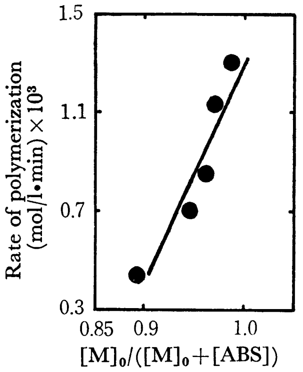

Fig. 6. Dependence of polymerization rate (mol/l•min) on $[M]_0/([M]_0+[ABS])$
ABS 1 wt%, 80°C under nitrogen atmosphere.

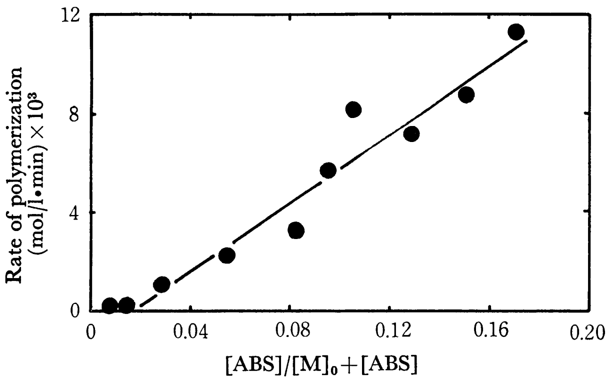

Fig. 7. Dependence of polymerization rate (mol/l•min) on $[ABS]/([M]_0+[ABS])$
St 10 g/aqueous phase 100 g, 80°C under nitrogen atmosphere.

From the relation between the polymerization rate and the reaction temperature shown in Table 2, the activation energy was calculated to be about 13.9 kcal/mol. This value is somewhat smaller than that of ordinary radical polymerization.

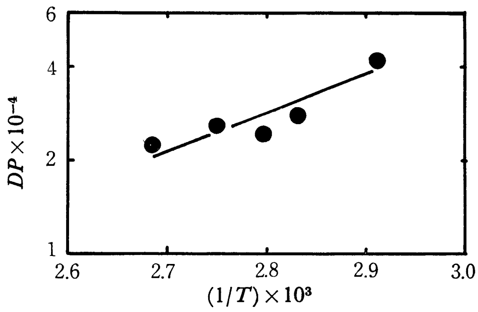

Fig. 8. Dependence of *DP* on $1/T$.
St 10 g/aqueous phase 100 g, ABS 1 wt%, 2 hr, under nitrogen atmosphere.

The average degree of polymerization, *DP*, calculated from the intrinsic viscosity was plotted against the ABS concentration, the initial monomer concentration, and the reaction temperature. As is shown in Figs. 2, 3, and 8, *DP* increases with an increase in the ABS concentration, and it is nearly independent of the concentration of the monomer, but decreases with the rise of the reaction temperature. *DP* is expressed by:

$$DP = R_p/(R_t+R_{tr}) = R_p/R_i$$

where R_p, R_t, R_{tr}, and R_i are the rates of the propagation reaction, the termination reaction, chain transfer to the monomer, and the initiation reaction respectively. Therefore, the activation energy derived from the temperature dependence of the *DP*, E_{DP}, is expressed as follows:

$$E_{DP} = E_p - E_i,$$

where E_p and E_i are the activation energies of propagation and initiation respectively. In general, E_i is larger than E_p, and therefore *DP* decreases with a rise in the reaction temperature, as is shown in Fig. 8. As is shown in Fig. 8, the activation energy of *DP* was calculated to be about −5.2 kcal/mol. On the other hand, the E_p of the emulsion polymerization of St was found by Morton[7] to be 7.4 kcal/mol. Using the values of E_{DP} and E_p mentioned above, E_i was calculated to be 12.6 kcal/mol, which is considerably smaller than those values found for the thermal polymerization or polymerization by radical initiators. The reason for the difference is not clear, but it may be attributed to the effect of the surfactant added to the polymerization system. Hohenstein and Mark investigated the polymerization of St in the presence and in the absence of soap; they found that, in the case of emulsion polymerization by potassium persulfate, E_i is about 17 kcal/mol, about 8 kcal/mol smaller than the value in the case of polymerization without soap.[8]

If this value, 8 kcal/mol, is applied to our system, the activation energy of the initiation of St in the absence of soap is 20.6 kcal/mol, which almost agrees with the activation energy of the thermal initiation of the St polymerization calculated by Tobolsky.[9]

It has been shown that, in the case of thermal and radical polymerization, the overall activation energy, E, can be calculated by the following equation:[10]

$$E = (1/2)E_i + [E_p-(1/2)E_t],$$

where E_t is the activation energy of termination. By this equation, $[E_p-(1/2)E_t]$ is calculated to be 7.6 kcal/mol because E is calculated to be 13.9 kcal/mol, as has been mentioned above. This value agrees with Tobolsky's value of about 6.3 kcal/mol,[11] which was found for the ordinary radical polymerization of St.

The authors are indebted to Mr. Toshihiro Shibata for his helpful technical assistance.

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7) M. Morton, P. P. Salatiello, and H. Landfield, *J. Polym. Sci.*, **8**, 279 (1952).

8) W. P. Hohenstein and H. Mark, *ibid.*, **1**, 549 (1946).

9) K. E. Russel and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **75**, 5052 (1953).

10) T. Otsu and K. Takemoto, "Experiments of Vinyl Polymerization," Kyoritsu Schuppan, Tokyo (1964), p. 256.

11) A. V. Tobolsky and B. Baysal, *J. Polym. Sci.*, **11**, 471 (1953).

56