BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2862—2866 (1972)

Polymerization of Vinyl Monomers in the Presence of Surface Active Agents. II. The Rate of Polymerization of Methyl Methacrylate

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(Received January 22, 1972)

The polymerization of methyl methacrylate in the presence of sodium tetrapropylenebenzenesulfonate(ABS) in an aqueous system without any ordinary initiators was examined kinetically. The rate of polymerization of methyl methacrylate is dependent on the initial concentrations of methyl methacrylate and ABS, and expressed by the equation:

$$R_p \propto [\mathrm{ABS}]^{0.37}[\mathrm{MMA}]^{0.32}$$

The apparent activation energy of the polymerization is about 3 kcal/mol. It was confirmed by electron microscopic observation that the number of polymer molecules is in the same order as that of the micelle particles in the polymerization system.

We reported previously on the polymerization of methyl methacrylate (MMA) in the presence of anionic surface active agents such as alkylbenzenesulfonate (ABS) in an aqueous system without any ordinary initiators. This system gave a stable emulsion of poly(MMA) with an unusually high molecular weight in a good yield.[1)]

In this paper, the results of a kinetic study of the polymerization of MMA in the presence of ABS in an aqueous system will be described.

Experimental

Materials. Methyl methacrylate and sodium tetrapropylenebenzenesulfonate (ABS) were purified according to the method described previously.[1)] Diphenylpicrylhydrazyl (DPPH) of G.R. grade was used without further purification.

Determination of the Rate of Polymerization. 100 g of deionized water and a desired amount of ABS were placed in a four-necked, flat bottomed 100 m*l* flask equipped with a condenser, a dropping funnel, a nitrogen inlet tube and a rubber stopper. The mixture was then preheated at a prescribed reaction temperature for 40 min, a slow stream of nitrogen being introduced into the mixture. MMA was then added through the dropping funnel and allowed to polymerize. About 2 g of the reaction mixture was withdrawn by a syringe and accurately weighed at regular time intervals. The weighed sample was poured into 10 m*l* of methanol in order to precipitate the polymer formed, which was collected by filtration, washed with methanol, dried at 60°C under a vacuum and weighed. The rate of polymerization was determined from the weight of the precipitate.

Determination of Number of Particles. Particle size determination was carried out on a sample of about 1 g which was withdrawn from the reaction mixture and diluted with 10 times as much water containing 0.01% of hydroquinone which was used to minimize further change. The diluted sample was deposited onto the collodion substrates in the form of minute droplets of approximately 2 micron in radius. The specimen was shadow-cast with carbon, and the electron micrographs were taken with a JEM-5Y electron microscope of magnification 9800 at 80 kV. The surface average dia-

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

meters of particles were obtained on 50—100 particles in an enlarged (×2) photograph using a Scale Lupe of magnification 5. The number of particles was calculated from the volume average diameter and the density of particles which was approximated to be 1.0.

Measurement of the Generated Radicals. 50 m*l* of water or an organic solvent (THF or ethyl acetate), 0.3 g of ABS, and 1 m*l* of MMA or ethyl acetate, each containing 5.0 mg of DPPH, were placed in an apparatus as shown in Fig. 1. If the mixture was not a clear solution, a few drops of octaoxyethylene nonylphenyl ether were added as a solubilizer. The mixture was shaken well and subsequently frozen in a liquid nitrogen bath. It was then brought to a vacuum below 10^{-3} Torr in order to degas, and then allowed to melt. This freeze-thaw procedure was repeated three times to attain complete degassing. The degassed mixture was then heated in an oil bath at 80±0.2°C and the absorption of each sample at 530 mμ was measured at regular time intervals.

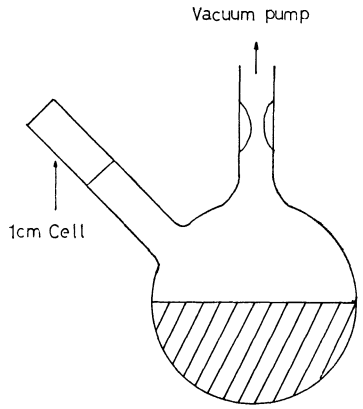


Fig. 1. Apparatus for measurement of generated radicals.

Results and Discussion

We found[1] that MMA polymerized readily in the presence of an anionic surface active agent in water without any ordinary initiators. The mechanism of the polymerization, however, has not been clarified yet. A kinetic approach to the polymerization was attempted and the relationship between the rate of polymerization and the initial monomer concentration or the ABS concentration was investigated. The quantity of the free radicals generated in the reaction system was also measured spectrometrically by using DPPH in order to obtain information on the initiation mechanism of the polymerization.

For a case of usual emulsion polymerization, Smith and Ewart presented the following equation for the rate of polymerization:[2]

$$R_p = k_p[\mathrm{M}]/N/2, \quad (1)$$

where k_p is the rate constant of the propagation reaction, [M] is the monomer concentration in the particles which is supposed to remain constant until the excess monomer droplets disappear in the system, and N is the number of particles. Thus R_p is dependent only on N. Smith and Ewart also pointed out that the relationship between N and the concentration of emulsifier was as follows:

$$N = k(\mathrm{CsAs})^{3/5}(\rho/\mu)^{2/5} \quad (2)$$

where As is the surface area of a particle, Cs is the concentration of the emulsifier present, ρ is the rate of generation of radicals, μ is the rate of volume increase of the particles and k is a constant with value 0.37—0.57.

Their theory, however, cannot be applied to our reaction system, in which R_p depends on the initial monomer concentration $[\mathrm{M}]_0$, which is defined as an apparent molarity calculated from the composition in the initial reaction mixture. A plot of log R_p against log $[\mathrm{M}]_0$ is found to be linear as shown in Fig. 2. The relationship can be expressed by the equation:

$$R_p \propto [\mathrm{M}]_0^{0.32}$$

The result may imply that the monomer concentration in the particles does not remain constant in the present reaction system.

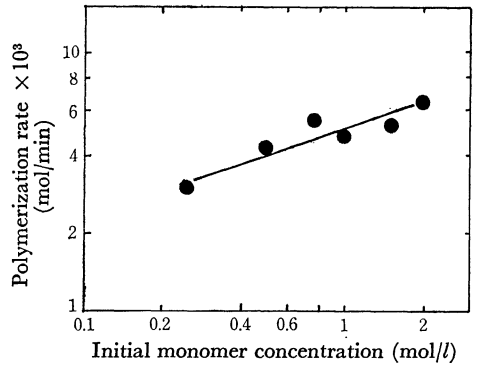


Fig. 2. Dependence of polymerization rate (mol/min) on initial monomer concentration (mol/*l*).
ABS 0.3 g/100 g of water, 80°C, under nitrogen atmosphere. Slope of line 0.32.

While Smith and Ewart also showed that the value of R_p was proportional to 0.6th power of the concentration of the emulsifier, Lee and Longbottom[3] have proposed the following equation:

$$R_p \propto [\mathrm{Cs}]^{0.18-0.55}$$

The rate of polymerization of our system depends on the concentration of ABS. As seen from Fig. 3, the relation between R_p and [Cs] is given by

$$R_p \propto [\mathrm{Cs}]^{0.37}$$

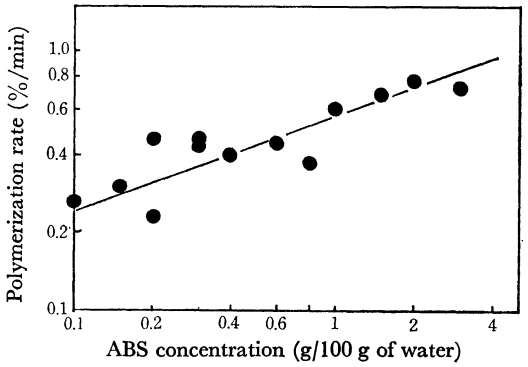


Fig. 3. Dependence of polymerization rate (%/min) on ABS concentration.
MMA 10 g, 80°C, under nitrogen atmosphere. Slope of line 0.37.

2) W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

3) P. I. Lee and H. M. Longbottom, *J. Appl. Polym. Sci.*, **14**, 1377 (1970).

The rate of polymerization was measured at temperatures 70—100°C and the results are shown in Table 1. The activation energy of the overall polymerization reaction is about 3 kcal/mol. This value is very small compared to the values reported hitherto for the radical polymerization of MMA. The polymerization rate decreased at 100°C. This might be due to the increase of the rate of termination reaction or the reduced stability of particles caused by boiling of the reaction mixture. The induction period decreased with an increase of reaction temperature, but an estimation of the activation energy of the initiation reaction from the period was not successful.

The average degree of polymerization of the poly(MMA), DP, was obtained from the intrinsic viscosity measurement[1] and the result is plotted against the initial monomer concentration and the ABS concentration (Figs. 4 and 5). The DP is almost independent of both ABS and $[M]_0$. It tends to increase slightly with a rise in reaction temperature, presumably because the rate constant of the propagation increases with an increasing temperature (Table 1). In every case, DP is very high as we have emphasized.[1] It might be explained as follows: The number of generated radicals is very small, radicals rarely exist simultaneously in the same particle and the termination by radical coupling hardly takes place.

This is rationalised by a comparison of the number of polymer molecules formed with that of the polymer particles. The number of polymer molecules was calculated from polymer yields and molecular weight.

Table 1. Effect of reaction temperature on polymerization rate and DP

Reaction temperature (°C)	Polymerization rate (mol/min)	DP
70	4.42×10^{-3}	5.48×10^{-4}
80	4.59	5.90
85	4.39	5.50
90	6.05	6.80
100	5.38	6.31

MMA 10 g; water 100 g; ABS 0.3 g under nitrogen atmosphere.

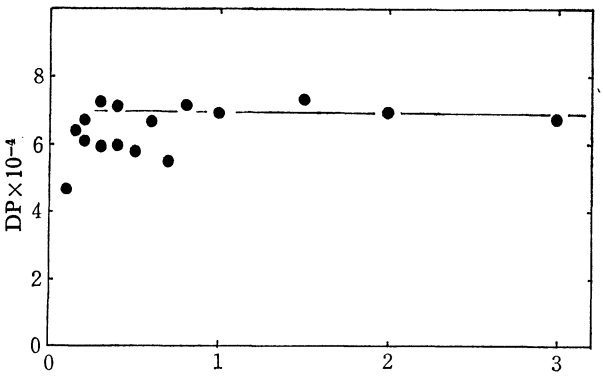


Fig. 4. Dependence of DP on ABS concentration.
MMA 10 g, 80°C, 2 hr, under nitrogen atmosphere.

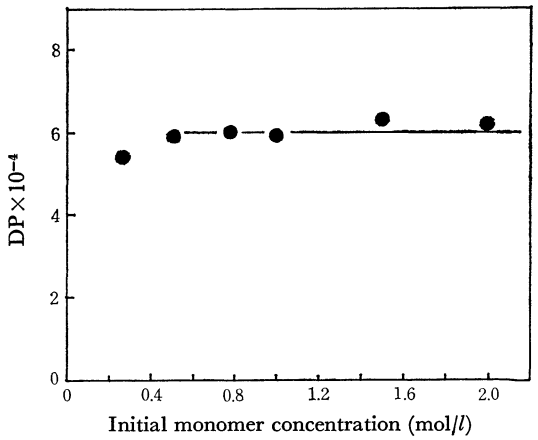


Fig. 5. Dependence of DP on initial monomer concentration.
ABS 0.3 g, water 100 g, 80°C, 2 hr, under nitrogen atmosphere.

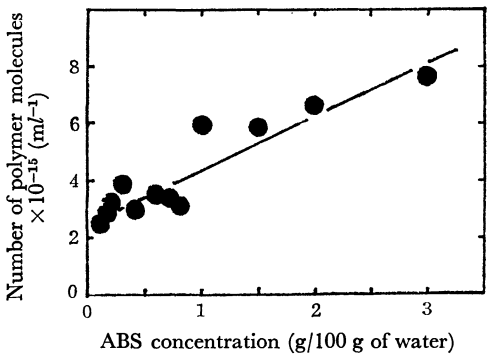


Fig. 6a. Dependence of number of polymer molecules on ABS concentration.
MMA 10 g, water 100 g, 80°C, 2 hr, under nitrogen atmosphere.

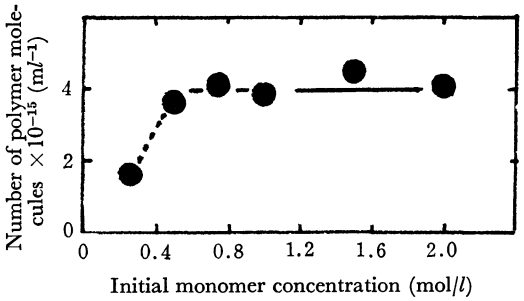
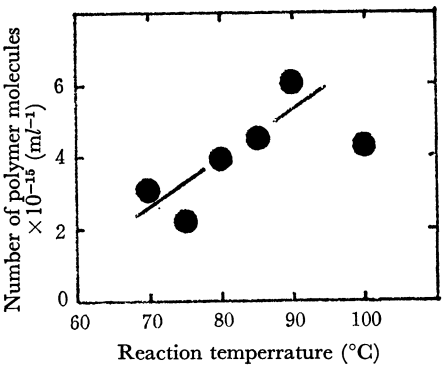


Fig. 6b. Dependence of number of polymer molecules on initial monomer concentration.
ABS 0.3 g, water 100 g, 80°C, 2 hr, under nitrogen atmosphere.



Fgi. 6c. Dependence of number of polymer molecules on reaction temperature.
ABS 0.3 g, MMA 10 g, water 100 g, 2 hr, under nitrogen atmosphere.

The effects of the concentrations of ABS and monomer and of the reaction temperature on the number of polymer molecules are shown in Figs. 6a, b, and c. The number of polymer molecules increased with the increasing concentration of ABS and increasing reaction temperature, but was not affected by the concentration of monomer in the concentration range above 0.5 mol/*l*. We see from the results that the generated radicals increased with the increasing concentration of ABS and temperature.

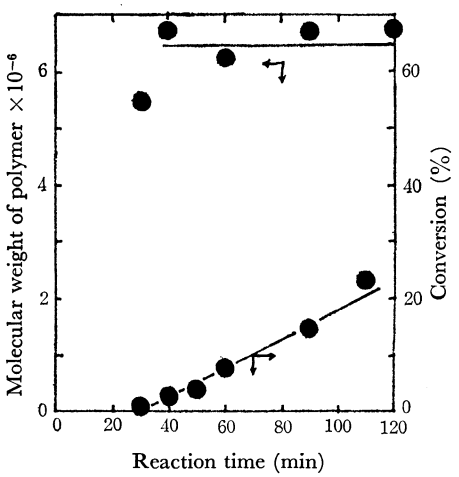


Fig. 7. Dependence of molecular weight of polymer on reaction time.
MMA 50 g, ABS 2.5 g, water 500 g, 80°C, under nitrogen atmosphere.

When a steady state was reached (Fig. 7), direct determination of particle size was attempted with an electron microscope. The samples were prepared under the conditions; reaction time 30, 60, and 120 min, the ABS concentration 1 g and 3 g per 100 g of water.

The results are shown in Fig. 8 and Table 2. The result in Table 2 shows that the particle size is in the relatively narrow range 300—400 Å independent of the concentration of ABS and the reaction time. The maximum particle size is 1000—1200 Å and the particles which are supposed to be generated newly were observed at every reaction time. The number of polymer particles per unit volume is about 1×10^{15}, which is in the same order as the number of polymer molecules calculated above. Since poly(MMA) scatter electrons poorly and give electron micrographs of a low contrast, we used the shadow-casting with carbon.

Table 2. Particle size of MMA latices

ABS (g)	Reaction time (min)	Average diameter (Å)	Number of polymer particles (ml^{-1})	Number of polymer molecules[a] (ml^{-1})
1	30	414		
1	60	462		
1	120	472	0.95×10^{15}	4.5×10^{15}
3	30	363		
3	60	411		
3	120	438	1.40×10^{15}	5.5×10^{15}

MMA 10 g; water 100 g; at 80°C under nitrogen atmosphere.
a) Calculated from molecular weight and yield of polymers.

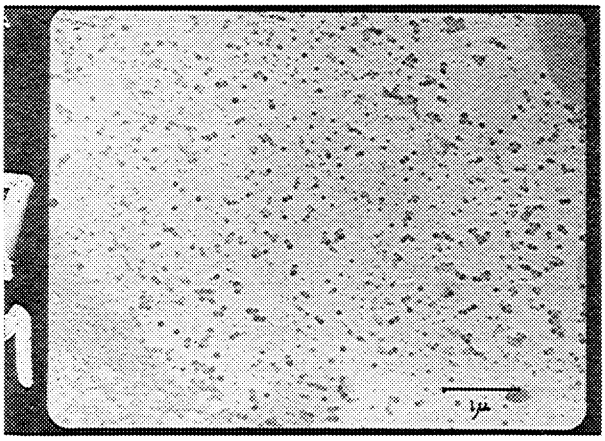


Fig. 8a

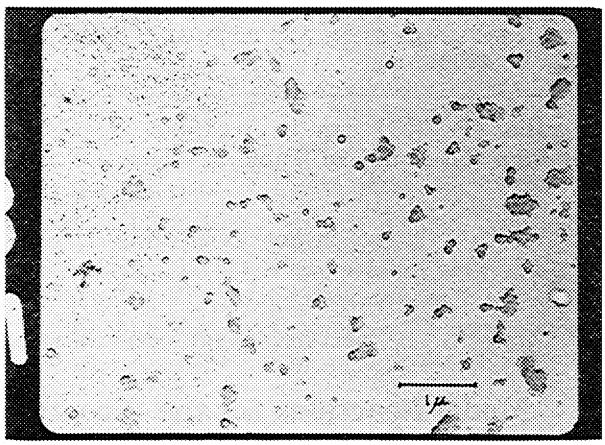


Fig. 8b

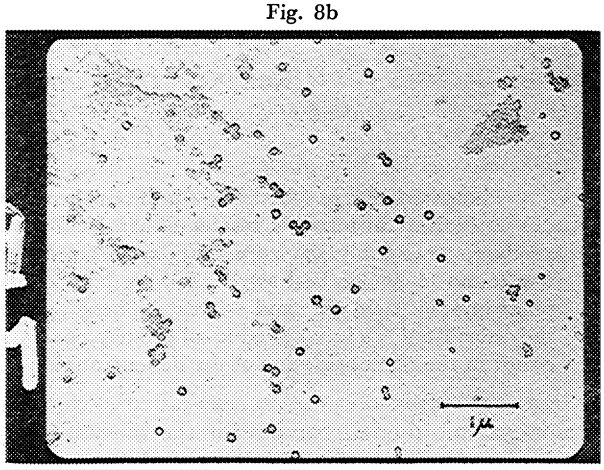


Fig. 8c

Fig. 8. Electron micrographs of MMA latices. The samples are at reaction time; 30 min (a), 60 min (b), 120 min (c). ABS 1 g/100 g water. (×19600).

It may be presumed that the polymerization in particles proceeds in a similar way to that in bulk polymerization. Thus the relation between the degree of polymerization and the initial monomer concentration can be represented by the equation:

$$DP = k_p/\{k_t[P\cdot]/[M]+k_{tr}\}$$

where k_p, k_t, and k_{tr} are rate constants of propagation, termination and chain transfer to monomer, respectively, and [P·] and [M] are concentration of growing radical and monomer in the particle, respectively.

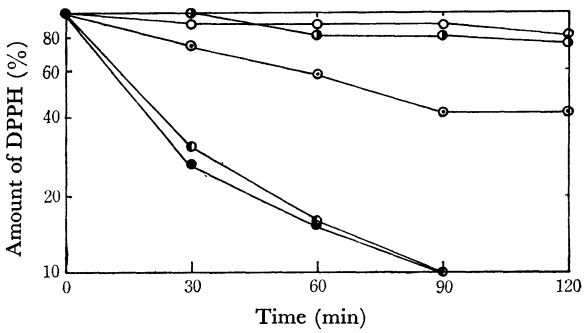


Fig. 9. Time changes of disappearance of DPPH in various system.
◐ H_2O 50 m*l*; ABS 0.3 g; MMA 1 m*l*; DPPH 5 mg
⊙ THF 50 m*l*; ABS 0.3 g; MMA 1 m*l*; DPPH 5 mg
◑ THF 50 m*l*; ABS none; MMA 1 m*l*; DPPH 5 mg
● H_2O 50 m*l*; ABS 0.3 g; ethyl acetate 1 m*l*; DPPH 5 mg
○ ethyl acetate 50 m*l*; ABS 0.3 g; ethyl acetate 1 m*l*; DPPH 5 mg

The ratio [P·]/[M] can be regarded as negligibly small from the results in Table 2. Thus $DP \simeq k_p/k_{tr}$ which is constant. In fact, DP is independent of monomer concentration as shown in Fig. 5, which gives $k_p/k_{tr}=6\times10^4$.

Measurement of the generated radicals was carried out by using DPPH as a radical scavenger in MMA or ethyl acetate. The absorption of DPPH in the presence of water or organic solvents was measured at 530 mμ with a spectrophotometer. As shown in Fig. 9, when an organic solvent such as THF or ethyl acetate was used instead of water, the amount of DPPH remained almost constant. In an aqueous system, in spite of the presence of MMA, the absorption of DPPH decreases markedly in intensity in the presence of ABS. These results are seen to reflect a specific role of the interface, and are consistent with the fact that a surfactant shows the surface activity only in an aqueous medium.

Thus, it is plausible that the polymerization is initiated at the surface of the micelle particles.

The authors are indebted to Mr. Shigeki Shiozawa for his technical assistance.