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

Teruzo Asahara, Manabu Senō, Shinsaku Shiraishi and Yoshikazu Arita

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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Methyl methacrylate polymerized in the presence of a surface active agent in an aqueous system without any ordinary initiators. Anionic surface active agents, such as sodium tetrapropylenebenzenesulfonate and sodium 2-dodecylbenzenesulfonate, markedly effected the polymerization of methyl methacrylate in the presence of water. The polymerization was inhibited by adding hydroquinone to the reaction system and was also affected adversely by oxygen. Water as a reaction medium was found to be indispensable. The polymerization in organic solvents afforded hardly any polymeric products.

The polymerization of methyl methacrylate (MMA) has been extensively investigated by many workers. Imoto and Takemoto[1] have reported the homo and graft polymerization of MMA onto fibers with hydroxylic pendant groups, especially onto cellulose. They proposed that the initiation step of the polymerization is mainly connected with the formation of a ternary complex of the hydroxyl group, water, and MMA, and also reported that the use of a surface active agent in the polymerization had a slight effect on the reaction. Matsumoto *et al.*[2] reported the polymerization of MMA in an aqueous medium in the presence of poly(methacrylic acid) and proposed that initiation is due to the peroxide of the MMA monomer.

We ourselves have previously reported the polymerization of MMA in the presence of an inorganic substance with a hydroxylic surface, such as clay or silica.[3] During the investigation, we have found that MMA polymerizes readily in the presence of an anionic surface active agent in water, without either hydroxylic surfaces or any ordinary radical initiators, to give poly(methyl methacrylate) with an unusually high molecular weight in a good yield. In this paper, the polymerization of MMA with various surface active substances will be described, and some consideration will be given to the reaction mechanism.

Experimental

Materials. *Monomer.* Methyl methacrylate was purified by the usual method and was stored in a refrigerator until use.

Anionic Surfactants. Sodium tetrapropylenebenzenesulfonate (ABS) was purified by the recrystallization of the methanol-soluble part of a commercial substance (from Lion Fat & Oil Co.) from ether. Sodium 2-dodecylbenzenesulfonate (LAS) was recrystallized from 2-propanol. Sodium lauryl sulfate (SLS) was purified by the procedure used for ABS. Sodium oleate (SO) was recrystallized from ethanol. These purified surfactants were all dried under a vacuum.

Nonionic Surfactants. Octaoxyethylene nonylphenyl ether and polyoxyethylene dodecyl ether were supplied by Kao Soap and Chem. Co. and were used without further purification.

Cationic Surfactant. Cetylpyridinium chloride (CPC) was purified by recrystallization from benzene.

Polymerization. *Method 1.* Into a four-necked, 100-m*l*, round-bottomed flask equipped with a condenser, a dropping funnel, a nitrogen inlet tube, and a thermometer, 0.15 g of a surfactant and 60 m*l* of deionized water were placed; the mixture was then preheated at the desired reaction temperature for 40 min, during which period a slow stream of nitrogen was introduced into the mixture. MMA was then added through the dropping funnel, after which the mixture was heated and stirred continuously under a nitrogen atmosphere for the desired reaction period. At the end of the period, the resultant mixture was poured into 300 m*l* of methanol in order to precipitate the polymer formed, which was filtered, washed with methanol, and dried at 60°C under a vacuum.

Method 2. In a 100-m*l*, round-bottomed flask were placed MMA, a surfactant, and water. The mixture was shaken well and subsequently frozen in an acetone-dry ice bath. It was then subjected to a vacuum below 10^{-3} mmHg in order to degas it, and then allowed to melt. The procedure described above was repeated three times to get a complete degassing. The degassed mixture was then heated at the desired reaction temperature in order to carry out the polymerization reaction. The subsequent procedure to polymerization was the same as that described above.

Determination of Molecular Weight. The molecular weight, $\overline{M}$, of the polymer thus obtained was

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

[2] T. Matsumoto, I. So and A. Izutsu, *Kobunshi Kagaku*, **26**, 234 (1969).

[3] M. Seno and T. Asahara, Proceedings of the Vth International Congress on Surface Active Substances, p. 983 (1969).

determined from the intrinsic viscosity, $[\eta]$, by using this equation:

$$[\eta]=5.2\times10^{-5}\,\overline{M}^{0.76}.$$ 4)

The viscosity of the polymer was measured in benzene at 30°C.

Analysis of Peroxide. The amount of peroxide in the materials used was determined by Wagner's method.5)

Results and Discussion

The polymerization of MMA in the presence of various types of surfactants in an aqueous system was investigated. Among the surfactants used, all the anionic surfactants except sodium oleate were markedly effective in the polymerization, as is shown in Fig. 1. When either ABS or SLS was used, the polymer yield had a tendency to increase with the reaction time over a period of 6 hours. Sodium oleate, polyoxyethylene nonylphenyl ether, and cetylpyridinium chloride had little effect on the polymerization of MMA compared with the case in which no surfactant was used (Table 1).

The effects of the polymerization temperature and also of the reaction atmosphere were investigated. In the reaction temperature range from 60 to 100°C, a maximum in the polymer yield was observed at 80°C in every case, as may be seen in Fig. 2. The figure also shows that LAS had a higher efficiency in polymer yield throughout the reaction temperature range investigated than did the other surfactants.

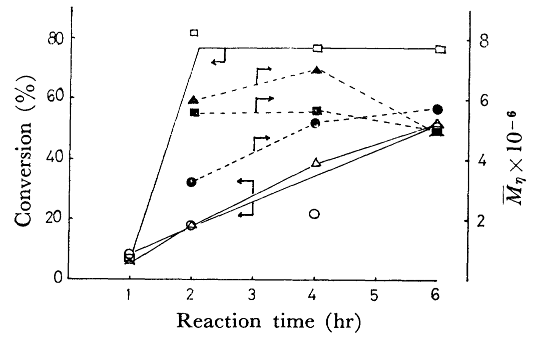

Fig. 1. Effect of Surfactants on polymer yield and molecular weight of Poly(methyl methacrylate) formed.
MMA, 5 g; surfactant, 0.15 g; water 60 m*l*; at 80°C under N_2.

	Conv.	$\overline{M}_\eta$
ABS	—△—	···▲···
SLS	—○—	···●···
LAS	—□—	···■···

Table 1. Effect of surfactants on polymer yield

Surfactant used	Reaction time (hr) 2	6
Octaoxyethylene nonylphenyl ether	1.6	0.2
SO	0.2	0.2
CPC	0.0	0.0
None (control)	0.0	0.2

MMA, 5g; surfactant, 0.15 g; water, 60 m*l*; at 80°C; under N_2.

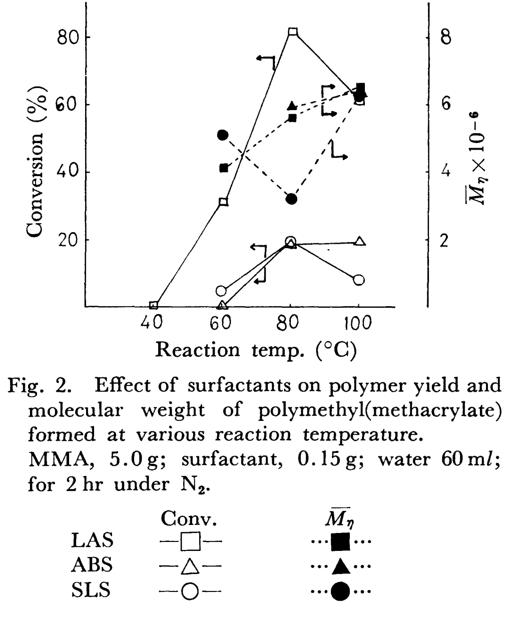

Fig. 2. Effect of surfactants on polymer yield and molecular weight of polymethyl(methacrylate) formed at various reaction temperature.
MMA, 5.0 g; surfactant, 0.15 g; water 60 m*l*; for 2 hr under N_2.

	Conv.	$\overline{M}_\eta$
LAS	—□—	···■···
ABS	—△—	···▲···
SLS	—○—	···●···

The polymerization was conducted under different reaction atmospheres; the results are summarized in Table 2. The polymerization *in vacuo* gave the highest yield and the highest molecular weight polymer. Under nitrogen or carbon dioxide, a high molecular weight polymer was obtained, but in a smaller yield. When air was passed through into the reaction mixture, however, no polymerization was observed. The addition

Table 2. Effect of reaction atmosphere on the polymerization of MMA

Reaction atmosphere	Polymer yield (%)	Molecular weight $\overline{M}$
N_2	18.4	5.94×10^6
CO_2	22.0	6.03×10^6
Air	0	—
in vacuo (1× 10^{-3} mmHg)	24.0	7.24×10^6

MMA, 5.0 g; ABS, 0.15g ; water, 60 m*l* ; at 80°C for 2 hr.

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4) "Analytical Chemistry of Polymers", Interscience Publishers, New York (1962), Part II, p. 17.

5) C. D. Wagner and R. H. Smith, *Ind. Eng. Chem. Anal. Ed.*, **19**, 976 (1947).

TABLE 3. POLYMERIZATION IN VARIOUS ORGANIC MEDIUMS

Solvent	Reaction temp. (°C)	Polymer yield (%)	Molecular weight $\overline{M}$
Water	80	18.4	5.94×10^6
Methanol	65 (reflux)	—*	—
Ethanol	78 (reflux)	—	—
THF	65 (reflux)	—	—
Benzene	80	—	—

MMA, 5.0 g; ABS, 0.15 g; solvent, 60 m*l*; for 2 hr.
* No detectable solid product was obtained.

of hydroquinone or diphenylpicrylhydrazyl to the reaction mixture also inhibited the polymerization. In each polymerization under a vacuum or a nitrogen or carbon dioxide atmosphere, the polymer formed was recovered as a fine powder by pouring the resultant mixture, which was a rather stable emulsion, into methanol.

The polymerization was also carried out in a non-aqueous medium, such as methanol, ethanol, tetrahydrofuran or benzene, but no polymerization was observed (Table 3). From these results, it is conceivable that water is inevitable for the polymerization under the present conditions, and also that the formation of a micelle may be an essential part of the polymerization reaction. The polymerization undoubtedly proceeds *via* a radical mechanism, in view of the experimental facts presented above.

In order to clarify the initiation step of the polymerization, the peroxide values of the surfactants used and of MMA were determined by Wagner's method. The results are summarized in Table 4. LAS, which afforded the highest efficiency in the polymerization, had the highest peroxide value. The approximate total amount of free radicals appearing in the reaction system is 10^{-6}—10^{-7} mol, as calculated from the molecular weight and the yield of the polymer formed, presuming only a radical coupling for the termination reaction of the polymerization. This value is roughly consistent with the peroxide value of the surfactant. It has not been, however, clear that the peroxides of the surfactants used participate in the initiation step, because no polymerization occurred in organic reaction media. At any rate, the presence of a charged interface in the reaction system may be very important for the propagation and/or initiation step. The most likely effect of anionic surfactants was also observed in the emulsion polymerization of MMA, with di-*t*-butyl peroxide used as a radical initiator, as may be seen in Fig. 3. However, the sulfonate anion itself is not very effective in the polymerization, judging from the results of the polymerization, of MMA with sodium *p*-toluenesulfonate and a nonionic surfactant, shown in Fig. 4.

TABLE 4. ANALYSIS OF PEROXIDE IN THE SURFACTANTS USED AND IN MMA

Material	Peroxide (mol/100 g)
LAS	2.7×10^{-3}
ABS	3.9×10^{-4}
SLS	3.6×10^{-5}
MMA	1.7×10^{-5}

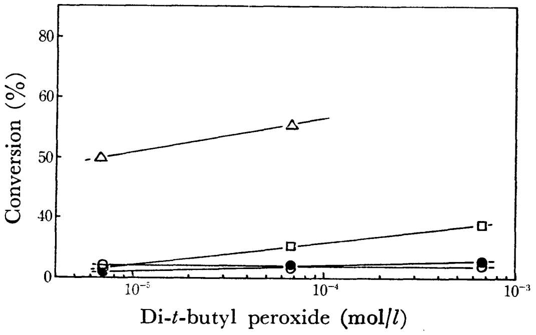

Fig. 3. Effect of surfactants on the polymerization of MMA with di-*t*-butyl peroxide in aqueous system.
MMA, 5.0 g; surfactant, 0.15 g; water, 60 m*l*; at 80°C for 2 hr under nitrogen atmosphere.
△ ABS, □ CPC, ○ octaoxyethylene nonylphenyl ether, ● none.

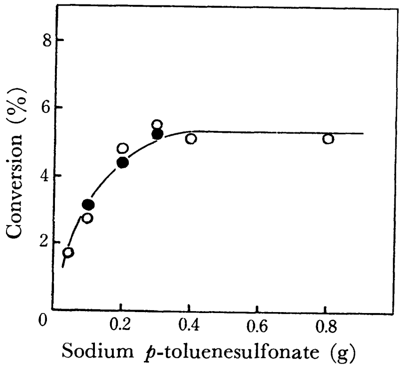

Fig. 4. Effect of sodium *p*-toluenesulfonate on the polymerization of MMA without any ordinary initiators.
MMA, 5.0 g; water, 60 m*l*; at 80°C for 2 hr under nitrogen atmosphere.
○ Sodium *p*-toluenesulfonate only.
● With 3 g of polyoxyethylene dodecyl ether.

The effort to detect free radicals in the reaction system by the ESR technique has not been successful. This might be because of the concentration of radicals was too low for them to be detected in such an aqueous emulsion system. The poly(methyl methacrylate) obtained had the same structure as that obtained by a conventional free radical polymerization, judging from the results of the IR and NMR measurements.

A further mechanistic study of the polymerization and also of the variation of monomers is now in progress and its results will be presented in the near future.

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