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The Polymerization of Vinyl Monomers in the Presence of Surface-active Agents. V. The Copolymerization of Methyl Methacrylate with Styrene

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In the previous papers of this series, we have reported the polymerization of methyl methacrylate (MMA)[1,2] and styrene (St)[3] in the presence of a surface-active agent in an aqueous medium without any ordinary initiators. The polymerization reactions were considered to proceed via a radical mechanism, because the polymerizations were inhibited by the addition of hydroquinone or diphenylpicrylhydrazyl and also by passing air continuously into the reaction system during the reaction period. In this paper we will present the results of the copolymerization of MMA with St; we attempted this in order to confirm that the present reaction proceeds *via* a radical mechanism and also to ascertain some particular aspects of this reaction system if possible.

Experimental

Materials. MMA and St were purified by ordinary procedures and were stored in a refrigerator until use. The sodium tetrapropylenebenzenesulfonate(ABS from the Lion Fat & Oil Co.) was purified by recrystallization from aqueous acetone.

Copolymerization. The copolymerization of MMA with St was carried out in a manner similar to that described in a previous paper.[2]

Characterization of the Copolymers. The composition of the copolymers was determined by the IR technique. The calibration curve for the quantitative analysis was prepared by measuring the intensity of the C=O absorption at 1725 cm^{-1} of 1% chloroform solutions of mixtures of poly(MMA) and poly(St) in various ratios by using a cell 0.268 mm thick. The curve was expressed by this equation:

$$\log (I_0/I) = 0.61[C]$$

where I_0 is the percentage transmission of the solvent only, where I is that of the solution, and where [C] is the concentration of the MMA component in copolymers (g/100 ml of a chloroform solution).

The composition of the copolymers was also determined by elementary analyses, which gave the same results as obtained by the IR techniques afore-mentioned.

The NMR spectra were measured at 34 °C with 3% solutions in carbon tetrachloride using a Hitachi-Perkin Elmer R-20A Spectrometer working at 60 MHz, with tetramethylsilane as the internal standard.

Results and Discussion

The copolymerization of St(M_1) with MMA(M_2) has been widely investigated, and the monomer reactivity ratios have been reported to be $r_1=0.52$ and $r_2=0.46$ for a bulk polymerization at 60 °C,[4] $r_1=0.54$ and $r_2=0.42$ for a solution polymerization in benzene at 60 °C,[5] and $r_1=0.56$ and $r_2=0.50$ for an emulsion polymerization at 35 °C.[6] In the present report, the copolymerization of St with MMA in the presence of ABS without any ordinary initiators will be examined. The results are summarized in Table 1. As is shown in Table 1, the rate of the copolymerization of St with MMA is much smaller than that of the polymerization of MMA. This phenomenon has also been observed in the usual radical copolymerization of St with MMA. Therefore, the propagation reaction may proceed in the same way as the usual radical copolymerization, though the initiation reaction may be different from usual in the point of the necessity for the micelles to be formed in our present polymerization system.

TABLE 1. COPOLYMERIZATION OF MMA WITH St

MMA/St[a]	Conversion (%)	$[\eta]$[b]
∞	52.3	8.20
4.00	19.9	5.09
2.33	16.3	3.70
1.50	16.4	3.87
1.00	14.4	3.87
0.67	11.1	3.87
0.43	22.5	4.20
0.25	13.9	3.85
0	15.3	4.85

a) Reactant mole ratio. b) In benzene solution at 30°C. Water 100 g, ABS 1 g, comonomer 0.1 mol, at 80°C, 2 hr, under nitrogen atmosphere.

The polymers obtained were fractionated by precipitation from a 2% benzene solution by ethanol; all of the polymers in the solution precipitated out in the precipitation range (volume ratio of the precipitant to the polymer solution) of 0.9 to 1.2, which indicated that the polymer was exclusively the copolymer of the two monomer components.[7] The dependence of the composition of the copolymers on initial ratio of monomers was examined. The composition of the resulting copolymers was determined by the IR technique using the calibration equation described above. The copolymer composition curve

1) T. Asahara, M. Senō, S. Shiraishi, and Y. Arita, This Bulletin, **43**, 3895 (1970).
2) T. Asahara, M. Senō, S. Shiraishi, and Y. Arita, *ibid.*, **45**, 2862 (1972).
3) T. Asahara, M. Senō, S. Shiraishi, and Y. Arita, *ibid.*, **46**, 249 (1973).
4) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1519 (1948).
5) C. C. Price and J. G. Walsh, *J. Polym. Sci.*, **6**, 239 (1951).
6) F. T. Wall, T. E. Florin, and C. J. Delbeq, *J. Amer. Chem. Soc.*, **72**, 4769 (1950).
7) K. Tomioka and Y. Shinohara, *Kobunshi Kagaku*, **21**, 83 (1964).

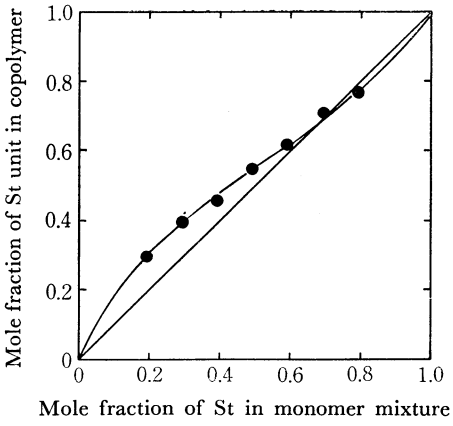

Fig. 1. Copolymerization of MMA with St, Copolymer composition curve.
Water 100 g, ABS 1 g, comonomer 0.1 mol, 80 °C, 2 hr, under nitrogen atmosphere.

thus obtained is shown in Fig. 1.

The apparent monomer reactivity ratios (mrr) were calculated to be $r_1=0.71\pm0.03$ and $r_2=0.40\pm0.03$ by Mayo and Lewis' intersection method. These values were very different from Mayo's data.

According to Wall's investigation into the solubility of St and MMA in water,[6] we calculated the monomer ratios in the oil phase in the present system and corrected the copolymer composition curve and reactivity ratio. The corrected values were $r_1=0.61\pm0.03$ and $r_2=0.48\pm0.03$, which apparently approached Mayo's data. The values were still slightly different from the usual mrr, but it is considered that these values show that the copolymerization proceeds *via* a radical mechanism.

8) K. Ito and Y. Yamashita, *J. Polym. Sci., Part B*, **3**, 625 (1965).

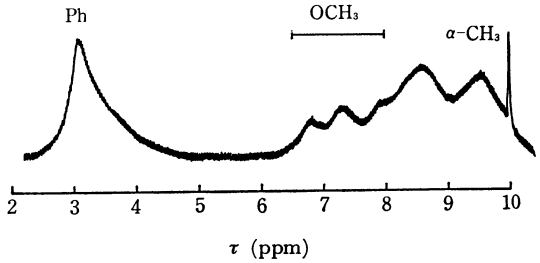

Fig. 2. NMR spectrum of MMA-St cooplymer of reactant mole ratio 1.0 at 60 MHz, at 34 °C in CCl_4 solution.

The NMR spectrum of the copolymer gave results similar to those of Yamashita's investigation.[8] As is shown in Fig. 2, the α-methyl proton resonance of the MMA unit appears at 9.2—9.1 ppm and the methoxy proton resonance is resolved into three peaks, which is a characteristic feature of the copolymers of St and MMA formed through a radical mechanism.

The results presented above and those of the previous reports[1,2,3] definitely confirmed that the polymerization of our reaction system proceeds *via* a radical mechanism. It was also clarified that, in the emulsion copolymerization, the mrr of each monomer component obtained by the usual copolymerization technique must be modified by considering their solubility parameters, especially the distribution coefficient.