

Studies on Suspension and Emulsion. XLVI. Emulsifier-Free Emulsion Polymerization of Styrene in Acetone–Water

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Synopsis

Emulsifier-free emulsion polymerization of styrene in acetone–water medium was carried out using potassium persulfate as initiator. Below acetone content of 40 vol %, stable emulsion was prepared and polymerizations were remarkably fast compared with those in pure water. The particle size decreased from 0.5 to 0.17 μm with an increase in acetone content in the range 0–40 vol %, and the distributions were very sharp. The optimum polymerization for the preparation of the stable emulsion was: styrene, 20 vol %; acetone/water, 40/60 (v/v); KPS, 3.4×10^{-3} mole/l; temp., 90°C.

INTRODUCTION

Emulsifiers in emulsion polymerization are mainly sites for the locus of polymerization and the stabilization emulsion particles. The preparation of the stable emulsifier-free emulsion for hydrophobic monomer (styrene¹) and hydrophilic monomer (ethyl acrylate^{2,3}) was investigated. In the latter case, the stable emulsion was prepared at high polymer content in a short time optimum polymerization conditions. In the former case, however, the stable emulsion was prepared only at low polymer content; and therefore, polymerization required a longer period of time. In order to increase the rate of polymerization for styrene, a small amount of emulsifier-free poly(ethyl acrylate) particles² was utilized as the locus of polymerization. The stable emulsion was obtained in short time at high polymer content.⁴ This improved method, however, cannot be applied when pure polystyrene emulsion is required.

In this article the emulsifier-free emulsion polymerization for styrene was used in the acetone–water system in which the monomer solubility increases. Acetone is infinitely miscible with water and with styrene monomer and is a nonsolvent for polystyrene. The results are compared with those Homola et al.⁵ in which methanol has been used for the same purpose.

EXPERIMENTAL

Materials

Styrene purified by distillation under reduced pressure in nitrogen was stored in a refrigerator. The deionized water and acetone were also distilled. Potassium persulfate (KPS) was analytical grade.

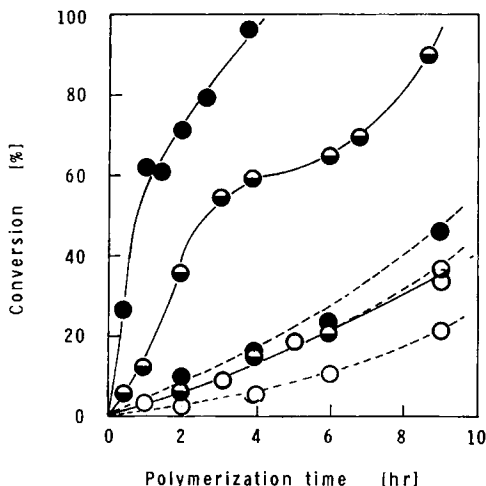


Fig. 1. Effect of polymerization temperature on the polymerization rate of styrene in water and acetone-water system: Styrene, 20 vol %, KPS, 1.8×10^{-2} mole/l; (O) 70°C; (◐) 80°C; (●) 90°C; (---) in water; (—) in acetone-water system (40/60, v/v).

Polymerization was conducted in a sealed test tube (diameter: 16 mm, empty volume: 40%). Ingredients were weighed into the test tube at room temperature to give a total reaction volume of 15 ml. The mixture, which was purged with nitrogen and sealed off, was maintained at the appropriate temperature with shaking at ~ 180 cycles/min. Conversion was determined by solid content. Particle size was determined by electron microscopy. The particle diameters from 100 to 150 particles were measured in each sample.

Solubility of styrene monomer in acetone-water medium under the same conditions for polymerization was determined. Styrene was added to different mixtures of acetone and water by use of a micro syringe. The mixture was sealed and placed at 70°C. After 1 hr it was observed whether or not a styrene monomer phase existed. This procedure was repeated changing the amount of styrene monomer added.

RESULTS AND DISCUSSION

Figure 1 shows the time-conversion curves of emulsifier-free emulsion polymerization of styrene in water and acetone-water at 70, 80, and 90°C. The rates of polymerization in the acetone-water system were greater than those in water and increased with temperature. The rate of polymerization in acetone-water at 90°C was comparable to that of the usual emulsion polymerization with emulsifier. The solubility of styrene in acetone-water is shown in Table I. It increased with increase in acetone content and an elevation in temperature. For example, the degree of solubility of styrene monomer was greater by a factor of about 15 than that in pure water at 90°C. Its value was nearly equal to that of ethyl acrylate in pure water, from which emulsifier-free emulsion polymerization can be smoothly carried out in a short time.² The rate of decomposition of KPS in 40 vol % acetone was greater by a factor of about 3.5 than that of KPS in pure water (Table II).

The formation of particles utilized as the locus of polymerization proceeds

TABLE I
 Solubility of Styrene in Acetone-Water Systems^a

Acetone content, vol %	Temperature, °C			
	20	70	80	90
0	0.027	0.04	0.07	0.10
10	0.10	0.11	0.13	0.15
20	0.16	0.20	0.23	0.25
30	0.26	0.58	0.72	0.96
40	0.57	1.25	1.30	1.54
50	1.31	2.10	2.80	3.40

^a In g/100 ml.

smoothly in the acetone-water system owing to the increase of monomer solubility and the rate of decomposition of the initiator.

Figure 2 shows the effect of acetone content on the conversion achieved after 9 hr at different temperatures. The conversion increased with increase in acetone content until about 40 vol % of the emulsions were stable. Acetone content giving a maximum conversion was getting smaller with polymerization temperature. Above 50 vol %, the polymerization did not proceed in the emulsion state and its rate was very slow. This phenomenon is based on the fact that polymer particles nucleated at the beginning of polymerization easily aggregate with each other in high acetone content above 50 vol %.

 TABLE II
 Increase of Decomposition Rate of KPS with Acetone Content in Acetone-Water System^a

Acetone content, vol %	Temperature, °C		
	60	70	80
0	1	1	1
30	1.6	3.2	2.7
40	2.1	3.4	3.51
50	4.0	4.0	4.2

^a The value is shown as the ratio of initial decomposition rate with that in pure water. All experiments were conducted in 1.1×10^{-3} mole/l. KPS.

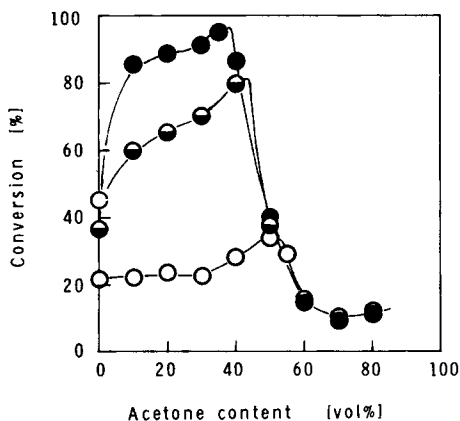


Fig. 2. Effect of acetone content in acetone-water system on the conversion achieved after 9 hr: styrene, 20 vol %; KPS, 1.8×10^{-2} mole/l; (○) 70°C; (◐) 80°C; (●) 90°C.

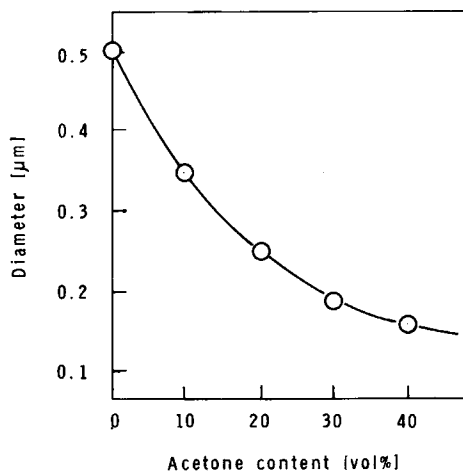


Fig. 3. Effect of acetone content in acetone-water system on size of particles obtained below 40 vol % acetone content at 80°C in Fig. 2.

Figure 3 shows the relationship between acetone content and particle size formed below 40 vol % acetone content. Particle size decreased with an increase in acetone content. The same tendency was observed in emulsifier-free emulsion polymerization of styrene in methanol-water by Homola et al.⁵ In their results, particle size decreased only from 0.6 to 0.5 μm in methanol content of 0–100 vol %. On the other hand, in our experiment, it changed more widely (from 0.5 to 0.17 μm) in an acetone content of 0–40 vol %. This difference occurs since the ability of acetone to increase the solubility of styrene monomer is greater than that of methanol.

Figure 4 shows the effect of the initiator concentration on the rate of polymerization and particle size. As the initiator concentration increased, the polymerization rate increased and particle size decreased to 0.2 μm . The rate of polymer particle nucleation increases with an increase of initiator concentration.

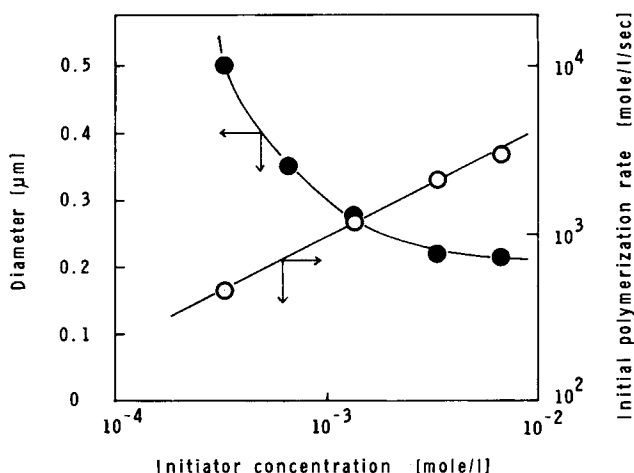


Fig. 4. Effect of initiator concentration on particle size and initial polymerization rate: styrene, 20 vol %; acetone/water, 40/60 (v/v); polymerization temperature, 80°C.

The optimum polymerization conditions for stable emulsion were as follows: styrene monomer, 20 vol %; acetone/water, 40/60 (v/v); KPS, 3.4×10^{-3} mole/l.; temp., 90°C. The number-average diameter of emulsion particles prepared under these conditions was 0.16 μm , and its distribution was very sharp. There was no precipitation in the ultracentrifuge at 27,000 g. The emulsion stability did not change after six months and after the evaporation of acetone from this system. The stability is derived from sulfate initiator endgroups at the surface of the particles.

References

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