Particle Size Control in Suspension Copolymerization of Styrene, Chloromethylstyrene, and Divinylbenzene

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Synopsis

The particle size distribution of suspension copolymers of styrene, chloromethylstyrene, and divinylbenzene prepared with gelatin and poly(diallyldimethylammonium chloride) as suspension stabilizers can be varied widely by variation of the relative amounts of monomer and aqueous phases, the stirring speed, and the amount of added anionic surfactant sodium dodecylbenzenesulfonate.

INTRODUCTION

The suspension method is used widely in polymerization of styrene, vinyl chloride, vinyl acetate, acrylate, and methacrylate monomers. Suspension polymerization has been reviewed by Munzer, Trommsdorf, and Schildknecht.[1,2] The major factors controlling particle size are surface tension, densities of aqueous and monomer phases, viscosities of aqueous and monomer phases, diameters of stirrer and kettle, and stirring speed. Generally, the intensity of mixing determines droplet size when the dispersion is first prepared, before polymerization begins, and polymerization only increases the densities of the droplets as they are transformed to solid beads. In the most extensive investigation reported on the parameters controlling bead size, Hopff and co-workers[3,4] found that the relative volumes of the aqueous and monomer phases affected bead size when small amounts of the protective colloid, poly(vinyl alcohol), were used for polymerization of methyl methacrylate. Bead size was not affected when large amounts of poly(vinyl alcohol) were used. In our experiments with styrene copolymers and a mixture of a cationic polyelectrolyte and gelatin as dispersants, the relative amounts of the two phases and the presence of an anionic surfactant are the critical variables affecting particle size. Anionic surfactants have been used before to reduce particle sizes of styrene–divinylbenzene suspension copolymers.[5,6]

Our research on particle size effects in polymer-supported organic synthesis and polymer-supported phase transfer catalysis[7,8] requires crosslinked polystyrenes of a wide range of sizes with chloromethyl groups that can be converted easily to polymer-bound esters and thiolesters and to quaternary ammonium and phosphonium ions. Instead of the usual method of chloromethylation of crosslinked polystyrene, we copolymerize styrene, chloromethylstyrene, and divinylbenzene to avoid use of the cancer suspect agent chloromethyl methyl ether. Crosslinked chloromethyl polystyrenes are generally useful for ion ex-

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change resins,[9,10] supported catalysts, solid-phase peptide synthesis, and poly-mer-supported organic synthesis. Suspension polymerization is the conventional method of preparation. Polymerizations in bulk and in solution produce ma-terials of irregular shape that are not as useful as spherical beads in ion exchange columns. The recently reported precipitation polymerization method for crosslinked polymers offers promise as an alternative to suspension polymer-ization, but it has been carried out only on a very small scale.[11]

EXPERIMENTAL

Materials

Styrene (Aldrich), vinylbenzyl chloride (Dow, 60/40 m/p), and 55% active divinylbenzene (Polysciences) were used as received without removal of inhib-itors. They did not contain any material that precipitated on addition to methanol. Azobisisobutyronitrile (AIBN, Aldrich), gelatin (Knox Gelatin Co., pharmaceutical grade, lime hydrolyzed), poly(diallyldimethylammonium chloride) (Calgon Corp., Catfloc T), Triton X-100 (Rohm and Haas), and sodium dodecylbenzenesulfonate (Polysciences) were used without purification.

Polymerization

This is a typical procedure for a 2% divinylbenzene, 25% vinylbenzyl chloride, and styrene copolymer using 165 g monomers and 450 g water. In 60 ml deion-ized water, 2.70 g gelatin is dissolved at 50–60°C with magnetic stirring. In the remaining water, 0.0816 g sodium dodecylbenzenesulfonate, 24.6 g Catfloc T, and 5.1 g boric acid are dissolved (in that order) at room temperature. The pH of the latter solution is adjusted to 10.0 with 25% aqueous sodium hydroxide, and 0.10 g sodium nitrite is added. Only after the pH adjustment does the aqueous mixture become clear. The hot gelatin solution is mixed into the rest of the aqueous phase, and the entire mixture is added carefully (to prevent foaming) to a 1000-ml three-neck round-bottom flask fitted with reflux condenser, me-chanical stirrer, and thermocouple connected to a proportional temperature controller (Love Controls Corp., model 49). A solution of 117.75 g styrene, 41.25 g vinylbenzyl chloride, 6.10 g divinylbenzene, and 0.825 g AIBN is added slowly to the flask. Both the aqueous phase and the monomer phase must be used right away; they cannot be stored. Nitrogen is swept through the flask for 30 min, and a slight positive pressure of nitrogen is maintained throughout the poly-merization. The stirrer has a curved stainless steel blade with a tip-to-tip dis-tance of 80 mm. The blade is positioned with its top at the aqueous/organic interface of the quiet mixture. The stirrer is driven by a Con-torque stirring motor (Eberbach Corp., model 7225) with a clutch capable of maintaining speed at ±5 rpm in the range 0–400 rpm. Stirring speed is measured with a tachometer. Stirring is started at room temperature. Stirring may be stopped to sample the mixture and examine droplet sizes under a microscope. Average droplet size may be decreased by increasing the stirring speed. The mixture is stirred at least 10 min at room temperature before heating to 70°C over a period of 40–60 min. Temperature is maintained with a heating mantle on an air-driven hydraulic jack (I²R Corp., Jack-O-Matic) connected to the temperature controller. Al-

ternating heat (with the mantle adjusted to provide only a small excess of heat) and cool air maintain the temperature at 70 ± 0.5°C. The polymer passes through a gel point usually after about 60 min at 70°C. After 36 h, the mixture is cooled and filtered through a fine-porosity Corning glass frit (4–5.5 μm) under vacuum. The filtration takes many hours.

The filtered polymer is washed with water, methanol, acetone, and methanol until the wash solution does not turn cloudy upon addition to water. The washed polymer is dried at 60°C in a shallow pan and separated into fractions with 40, 60, 100, 200, 325, and 400 mesh U.S. standard sieves using a sieve shaker (Fritsch Analysette type 13501). With 8-in.-diameter sieves, only about 20 g dry polymer can be separated at one time without clogging one of the sieves. Often repetition is necessary to complete the separation. If the polymer exhibits electrostatic cling, the static charge can be neutralized with a trace of magnesium silicate powder.

Basically the same procedure was used for all of the experiments in Tables I and II, which are representative but are only a small fraction of the suspension polymerizations carried out in our laboratory. When no surfactant is used, the polymer is filtered and washed directly on a 400-mesh sieve, avoiding the slow filtration step used to collect 5–37 μm particles. Low yields reported in Tables I and II are due primarily to sieving losses and with added SDBS, to production of sizable amounts of particles <5 μm in diameter which are not isolated by filtration through a fine glass frit.

RESULTS AND DISCUSSION

The most important experimental parameters we have used to regulate particle size are relative amounts of monomer and aqueous phases, stirring speed, and presence or absence of anionic surfactant. Table I shows the effects of surfactants. The nonionic Triton X-100 has no major effect, but the anionic sodium dodecylbenzenesulfonate (SDBS) at or below its critical micelle concentration in water (1.10 × 10^{-3} M)[10] causes formation of a large fraction of particles smaller than 74 μm (200 mesh) and prevents formation of particles larger than 250 μm (60 mesh). The exact amount of SDBS does not appear to be critical. Variations in particle size distributions between the SDBS runs are probably random, due primarily to lack of thoroughness of the sieving procedure.

Table II shows the effects of relative amounts of aqueous and organic phases and the stirring speed on particle size distribution. With a monomer charge of 300 g per 450 g water and no surfactant, one can obtain only traces of particles smaller than 46 μm (325 mesh). With a smaller monomer charge, of 165 g, there is a shift to many more 75–150 (200 mesh) and 37–75 μm (400 mesh) particles. With still smaller monomer charges, it should be possible to produce even smaller particles at the expense of efficiency of reactor use. There is a general trend toward smaller particles as stirring speed increases, but the changes are not large over the range of speeds investigated. The effect of stirring speed on particle size in polymerization mixtures containing surfactant was not studied because of difficulty with foaming at >300 rpm.

In the course of these preparations, a number of the other experimental parameters were explored, and none of them had any marked effect on particle size distribution. Divinylbenzene content was varied from 0.5 to 10 wt %, and vin-

TABLE I
Effect of Surfactants on Particle Size Distribution[a]

Run	Surfactant concn, M	Reaction time, h	Wt of product, g	\% polymer on mesh sieve size					
				60	100	200	325	400	-400
MT-102B[b]	none	17.5	139	29	60	11	0	0	0
TB-10A	Triton X-100, 1.2×10^{-4}	18	c	10	60	25	—5—		0
TB-10B	SDBS, 1.10×10^{-3} [d]	18	90	0	17	44	17	11	11
TB-14A	SDBS, 5.5×10^{-4}	36	111	0	28	36	13	5	18
TB-14B	SDBS, 2.75×10^{-4}	36	107	0	12	56	17	6	9

[a] All polymers contained 2% DVB and 25% VBC by weight using 165 g monomer charge and 0.5 wt % AIBN at a stirring speed of 300 rpm, unless otherwise noted.
[b] Contained 150 g monomers and 10% divinylbenzene.
[c] Not determined.
[d] Critical micelle concentration = 1.10×10^{-3} M. See Ref. 12.

TABLE II
Effect of Stirring Speed and Monomer Charge on Particle Size Distribution[a]

Run	Stirring speed, rpm	% DVB	% AIBN	Wt of monomers, g	Wt of product, g	Reaction time, h	% polymer on mesh sieve size				
							60	100	200	325	400
WF-124A[b]	269	0.5	1.0	300	215	18	64	33	2	0	0
WF-124B[b]	271	1.0	1.0	300	209	18	87	12	1	0	0
WF-115B	304	6.0	0.5	300	c	21	45	43	11	1	c
WF-115A	322	4.0	0.5	300	c	21	31	51	16	2	c
WF-107A	366	2.0	0.5	300	c	17	31	49	18	2	c
TB-89	340	10.0	0.5	165	146	36	—58—		32	7	3
TB-90	400	10.0	0.6	165	147	36	—58—		32	7	4
TB-91	440	6.0	0.5	165	139	36	—32—		60	5	3

[a] All runs contained no surfactant and 25 wt % VBC.
[b] Contained 50% as much gelatin and Catfloc as other runs.
[c] Not determined.

ylbenzyl chloride content was varied from 25 to 75%. Such monomer variations could in principle have altered the surface tension of the organic droplets. Reduction by 50% of the amounts of gelatin and poly(diallyldimethylammonium chloride) had little effect.

Several changes in experimental parameters led to some clustered particles instead of entirely to the desired spherical beads: increase in AIBN to 1.0 wt %, increase in temperature to 80°C, and reduction in stirring speed after the droplet size was set but before heating. These variables were not explored further. When polymerizations were stopped after 17–21 h, the products still had a styrene odor. No odor was noticed after a reaction time of 36–40 h. Yields of recovered polymer were somewhat lower with the shorter reaction times, but the major variations in yields are due to losses during sieving and production in the presence of surfactant of particles smaller than 5 μm, too small to be isolated by our filtration method.

References

1. M. Munger and E. Trommsdorff, in *Polymerization Processes*, C. E. Schildknecht and I. Skeist, Eds., Wiley-Interscience, New York, 1977, pp. 106–142.

2. E. Trommsdorff and C. E. Schildknecht, in *Polymer Processes*, C. E. Schildknecht, Ed., Interscience, New York, 1956, pp. 69–109.

3. H. Hopff, H. Lussi, and P. Gerspacher, *Makromol. Chem.*, **78**, 24, 37 (1964).

4. H. Hopff, H. Lussi, and E. Hammer, *Makromol. Chem.*, **82**, 175, 184 (1965).

5. R. H. Wiley, K. S. Kim, and S. P. Rao, *J. Polym. Sci. Part A-1*, **9**, 805 (1971).

6. F. Wolf and H.-J. Mallon, *Z. Chem.* (Leipzig), **11**, 388 (1971).

7. M. Tomoi and W. T. Ford, *J. Am. Chem. Soc.*, **102**, 7140 (1980); *ibid.*, **103**, 3721, 3728 (1981).

8. T. Balakrishnan and W. T. Ford, *Tetrahedron Lett.*, **22**, 4377 (1981).

9. H. C. Hamman and D. H. Clemens, U.S. Pat. 3,728,318 (1973).

10. R. L. Albright, U.S. Pat. 4,185,077 (1980).

11. C. H. Bamford, A. Ledwith, and P. K. Sen Gupta, *J. Appl. Polym. Sci.*, **25**, 2559 (1980).

12. K. Shinoda, in *Colloidal Surfactants*, K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, Eds., Academic, New York, 1963, p. 50.