

### Particle Size Control in Dispersion Polymerization

For certain end use applications it is desirable to produce particles with dimensions in the 1-10 micron range. The classical particle-producing polymerization methods normally yield particle sizes much below these limits (emulsion polymerization) or significantly above (suspension polymerization). To achieve this range, the method considered in this study is a modified suspension polymerization technique which Schildknecht<sup>1</sup> defines as dispersion polymerization. This technique entails the use of relatively high concentrations of dispersant and high stirring speeds.

The formation of a particulate polymer system with a predetermined particle size is complicated because of the large number of variables which necessarily accompany a nonhomogeneous system. In this respect the findings of Hopff, Lussi, and Hammer<sup>2</sup> are encouraging, but the range of particle sizes reported is in excess of the above goal. These authors have demonstrated the possibility of approaching the range in question by the use of increasing concentrations of poly(vinyl alcohol) and higher stirring speeds. Winslow and Matreyek<sup>3</sup> reported the production of an average spheroid diameter of 5 microns using a homogenizing mixer. This was the lower limit of their investigations.

The following tabulated results (Tables I, II, and III) were obtained from a series of polymerizations carried out in standard 2-liter round-bottom flasks equipped with paddle stirrer, argon purge, and sampling tubes. The aqueous phase was premixed and stirred at high speed as the monomer was introduced. After dispersion, the stirring speed was generally reduced to 300 rpm. Periodic samples were taken to determine conversion, and stirring was continued during the cooling phase to prevent agglomeration due to settling out of the particles. Polymer particles were recovered by repeated washings with water to remove the poly(vinyl alcohol) followed by freeze drying.

TABLE I  
Dispersion Polymerization of Polystyrene. Effect of Stirring Speed on Particle Size

Initial stirring speed, rpm	Organic phase ratio	Poly(vinyl alcohol) concn., %	Average particle size, $\mu$
700	0.1	2.0	1.5
500	0.1	1.0	2.0
300	0.2	3.0	2.0
200	0.1	1.0	2.5*

\* Agglomeration took place; only separate particles measured.

TABLE II  
Dispersion Polymerization of Poly(vinyl Acetate).  
Effect of Stirring Speed on Particle Size

Initial stirring speed, rpm	Organic phase ratio	Poly(vinyl alcohol) concn., %	Range of particle diameters, $\mu$
1000	0.22	3.0	5-25
1000	0.11	3.0	1-10
800	0.11	3.0	5-20
800	0.13	3.0	1-25
300	0.10	2.5	30-120
300	0.10	2.0	10-130

TABLE III  
Effect of Poly(vinyl Alcohol) Concentration on Poly(vinyl Acetate) Particle Size

PVA1c concn., %	Range of diameters, $\mu$
2.0	3-30
3.0	5-45
3.0	10-80
3.0	5-30
4.0	2-18
4.0	5-30
5.0	5-60

The following observations were made. In a well-stabilized system, the final particle size was determined by the initial dispersion conditions. Maintaining high dispersion speeds throughout the polymerization did not further reduce particle size. Therefore, it is possible to size the particles at the beginning of the polymerization and subsequently reduce the stirring speed to a level sufficient to keep the polymer particles from settling. The stability of the dispersion significantly decreased with increasing phase ratio and lower poly(vinyl alcohol) concentrations. Higher catalyst concentration and polymerization temperature reduce the tendency to agglomerate by shortening the time the particles are in a partly polymerized state.

The results lead to the conclusion that the particle size obtained is very dependent on the monomer used. Stirring speed has a significant effect on particle sizes in the 100-micron and above range, but becomes proportionately less effective in the 10-micron range, possibly reaching a limiting size. Although Hopff et al.<sup>2</sup> found a significant decrease in particle size with an increase in poly(vinyl alcohol) concentration in the 0.5% to 2.0% range, increasing the concentration from 2.0% to 5.0% (Table III) did not produce any significant change in the case of poly(vinyl acetate).

These conclusions generally confirm the results of previous studies and, in addition, introduce the concept of a limiting particle size. The final particle size obtained is determined to a large extent by the interaction of the dispersed phase with the dispersant and by the amount of shear it is possible to exert upon the monomer droplets. It is fortunate that the shear effect is proportional to particle size, as this will lead to a narrowing of the particle distribution. Once a particular set of conditions is determined, the production of the predictable, relatively narrow-distribution particle size should be possible. The significant difference between monomers is probably due to their individual ability to interact with the dispersing agent. The difference in the surface tensions of the monomers used above are significant, but the results are contrary to what one would expect simply from the consideration of surface tension.

#### References

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2. H. Hopff, H. Lussi, and E. Hammer, *Makromolek. Chem.*, **82**, 175, 184 (1965).
3. F. H. Winslow and W. Matreyek, *Ind. Eng. Chem.*, **43**, 1108 (1951).

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