
ON PARTICLE SIZE DISTRIBUTION IN SUSPENSION POLYMERIZATION OF STYRENE

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Experiments were conducted on some of factors affecting the polymerized particle size distribution in suspension polymerization of styrene. Polymerization experiments with styrene at 80°C showed that the final polystyrene product size distribution is strongly affected by the stabilizer concentration, the type and the speed of impeller, and the hold-up fraction.

One of the most important unit process in polymer industry is the suspension polymerization. During this, monomers are dispersed by agitation into water containing a suspending or stabilizing agent. The major advantages of suspension polymerization lie in the relatively high heat transfer out of the reacting monomer droplets and the ability to control the size of produced polymer beads.

There are many factors affecting the particle size distribution in suspension polymerization, i.e. the concentration of stabilizer, the geometry and the speed of impeller, the hold-up fraction etc. In the past, it was assumed that the particle sizes are determined at the beginning of the experiment, before a noticeable conversion can take place¹. On the contrary, Langner et al.² showed that the resulting particle sizes are not irreversibly determined at the beginning but are changing during the whole polymerization process. The particle size attained in an agitated dispersion is analogous to the drop size distribution of liquid dispersions in agitated vessels. The latter is a dynamic process where there is continuously droplet coalescing and breaking taking place. A review of this area is given by Tavlarides and Stamatoudis³.

One of the factors that affect the particle size distribution produced by suspension polymerizations is the stabilizer concentration. Suspension polymerization experiments conducted by methyl methacrylate⁴⁻⁶, vinyl acetate⁷, and styrene⁷⁻⁹ monomers show that increasing the concentration of stabilizer results in a decrease of particle sizes.

Other important factors affecting the produced particle sizes are the impeller geometry and the impeller speed. Work done^{4,5,7,10-14} shows that different particle size distributions are obtained by different impeller geometry^{12,13} and impeller size^{4,5,7,10,11,14}. In particular, increasing the impeller size results in the production

of smaller particles. The effect of impeller speed on the particle size distribution in dispersion polymerization has been given a lot of attention^{2,4-7,10-13}. Experiments of dispersion polymerization in agitated vessels of methyl methacrylate^{4-6,10,11}, vinyl acetate^{2,7}, styrene^{2,7,12}, and styrene/divinylbenzene¹³ show that the particle sizes decrease with the increase of impeller speed. A different picture is given by Lewis and Johnson¹⁵, who found that particle sizes produced in the dispersion polymerization of vinyl chloride initially decrease with impeller speed reaching a minimum and start increasing again. Similarly, Tanaka and O'shima⁹ conducting suspension polymerization of styrene in a loop reactor found an increase of particle sizes with the increase of impeller speed.

The effect of hold-up fraction on particle size distribution produced by suspensions polymerization of methyl methacrylate⁵, styrene⁸, and styrene/divinylbenzene¹³ has also been studied. It was observed that the increase of hold-up fraction results in the production of greater particle sizes. Almost all previous work done on particle size distribution produced by suspension polymerization was focused at the relatively high hold-up fractions ($\Phi > 0.1$) and high concentrations of stabilizer. It is of great interest to investigate the size distribution at lower hold-up fraction and low stabilizer concentration and this is the goal of the present work.

EXPERIMENTAL

The apparatus consisted of a reactor, an agitator and a temperature controller. The covered two-liter glass reactor (made by Normschliff Geratebau, West Germany) was rounded bottom and had a 15 cm inner diameter. It was provided with a jacket, inside which water of controlled temperature was circulated to keep the reactor temperature constant. The temperature of the circulating water was controlled by a Julabo PC circular. Four vertical stainless steel baffles of 1.5 cm were used to hinder vortex forming and consequently air entrainment into the agitated fluid. Three stainless steel impellers were used, (i) a vertical six-blade disk style impeller (impeller diameter, D , 7 cm, blade width, W , 1.4 cm, blade length, l , 2.8 cm, disk diameter 4.8 cm); (ii) a vertical six-blade open style impeller ($D = 7$ cm, $W = 1.4$ cm) and (iii) a 45° pitched six-blade open style impeller ($D = 7$ cm and $W = 1.4$ cm). The impellers were fixed on a vertical shaft and they were located in the center of the agitated dispersion. It was driven by a variable speed drive (Normschliff Geratebau, West Germany). At the shaft speeds used in this work there was no air entrainment into the agitated dispersion. The impeller speed was measured by a 725 DIGI-BETA stroboscope (made by Mayer and Wonisch, West Germany).

The dispersion volume in all experiments was kept at 2 l (giving a filling height about 11 cm). Distilled water was used as the continuous phase and styrene as the dispersed one. The styrene and the rest of chemicals were manufactured by Merck. Experiments were conducted for hold-up fraction, Φ , 0.01, 0.05 and 0.1 and for shaft speeds equal to 150, 200 and 250 r.p.m. A water soluble stabilizer, poly(vinyl alcohol), was applied at mass concentrations, c , 0, 0.15, 0.3, and 0.6 g l⁻¹ (related to the volumes of distilled water) to prevent particle (drop) coalescence. The reactor temperature was kept at 80°C. The polymerization reaction was initiated by adding 0.13 mol α, α' -azobis(isobutyronitrile) per liter of styrene and the reaction was terminated after 6 h when the polymer consisted of solid beads. At the end, the dispersion was cooled, filtered and dried.

The final particle size distribution was measured by photographing a sample of 100–300 of final particles through a Sz-Tr Olympus Zoom Stereo Microscope. The slides were projected on a screen and the particles measured by a ruler. The results were analyzed by a computer. The Sauter mean diameter, a_{32} , was calculated by

$$a_{32} = \frac{\sum n_i a_i^3}{\sum n_i a_i^2},$$

where n_i is the number of drops of diameter a_i in the sample. Attempts to photograph the drops in situ (during the reaction) after the first hour were unsuccessful due to the difficulty in distinguishing the drops inside the polymerizing dispersion.

RESULTS AND DISCUSSION

Some of the experimental results showing the effect of stabilizer concentration on the particle size distribution are given in Figs 1*a, b*. It is seen that increasing this concentration results in a decrease of particle sizes regardless of impeller type, impeller speed and hold-up fraction. One reason is the resulted increase of the hindering of the droplet coalescence at higher stabilizer concentration at the early stages of polymerization. The other reason is the decrease of interfacial tension with the increase of stabilizer concentration resulting in less stable droplets again at the early stages of reaction. This observation agrees with the results of other work in the literature^{4–9}.

Figs 2*a, b* show the effect of impeller type (geometry) on the particle size distribution. There is a significant effect of the type of impeller regardless of its speed, stabilizer concentration and hold-up fraction. The pitched open style impeller has the largest droplets due to the lowest shear rates present with those impellers. Even though other investigators^{12,13} have found a noticed difference between size distributions produced by different types of impellers, no one in the past has compared the effect of presently used three types of impellers.

It is observed that the particle sizes increase with impeller speed regardless of impeller, stabilizer concentration and hold-up fraction (Figs 3*a, b*). These observations are contrary to the observations for agitated non-polymerizing two-liquid phase systems where an increase of impeller speed results in a decrease of droplet sizes. The difference probably lies in the greater difficulty in breaking polymerizing particles than liquid droplets. It must be remembered that the drop (particle) size distribution is the dynamic result of the two competing processes, the breakages and the coalescences. Thus, while in the non-polymerizing agitated systems an increase of impeller speed will result in an increase of drop coalescence rate tending to increase the drop sizes, the increase of breakage rate (due to higher shear rates) will outweigh the previous effect of coalescence resulting in a net production of smaller drops. In the case of polymerization taking place while again the increase of impeller speed will increase

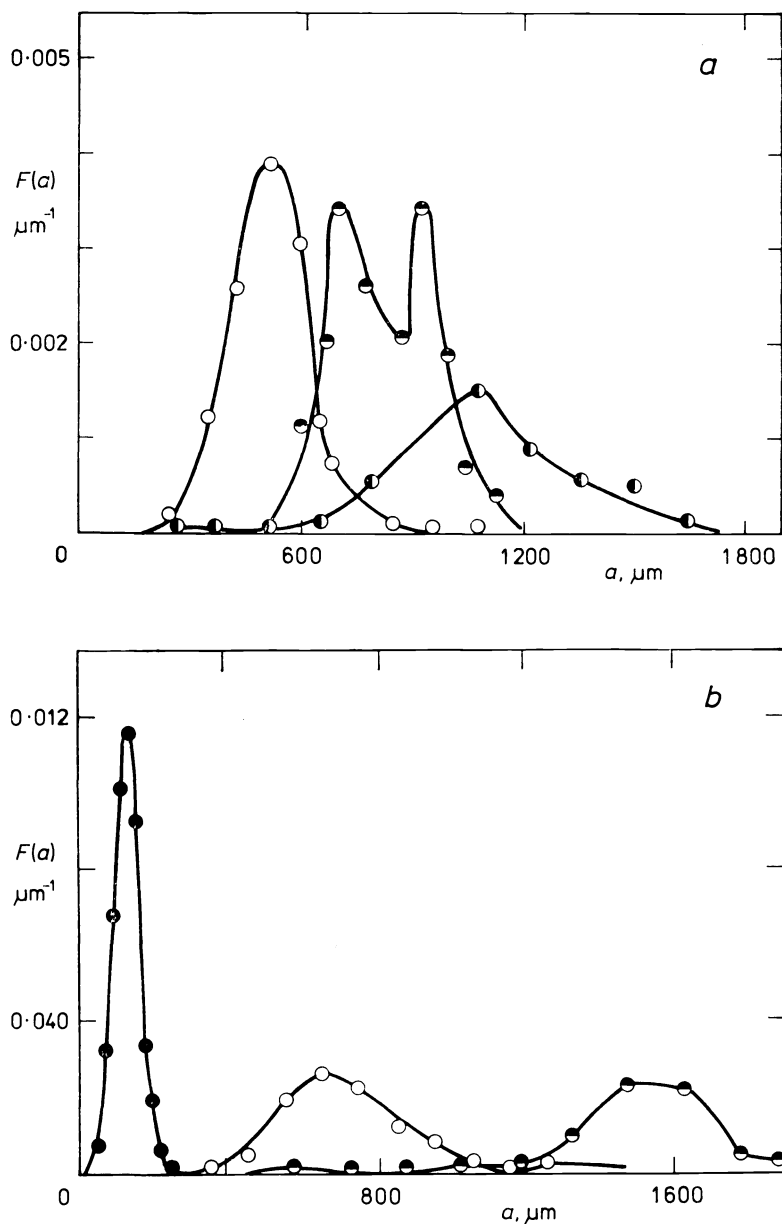


FIG. 1

Polystyrene particle size distribution ($F(a) da$ is the fraction of drops of diameter between a and $a + da$) for different mass concentrations (c) of the stabilizer (PVA). *a* Hold-up fraction, $\Phi = 0.01$, disk type impeller, 250 r.p.m., c , g l^{-1} (a_{32} , μm): 0, 1 151 (\bullet); 0.15, 875 (\ominus); 0.3, 566 (\circ). *b* $\Phi = 0.05$, pitched open type impeller, 250 r.p.m., c , g l^{-1} (a_{32} , μm): 0.15, 1 574 (\ominus); 0.3, 801 (\circ); 0.6, 148 (\bullet)

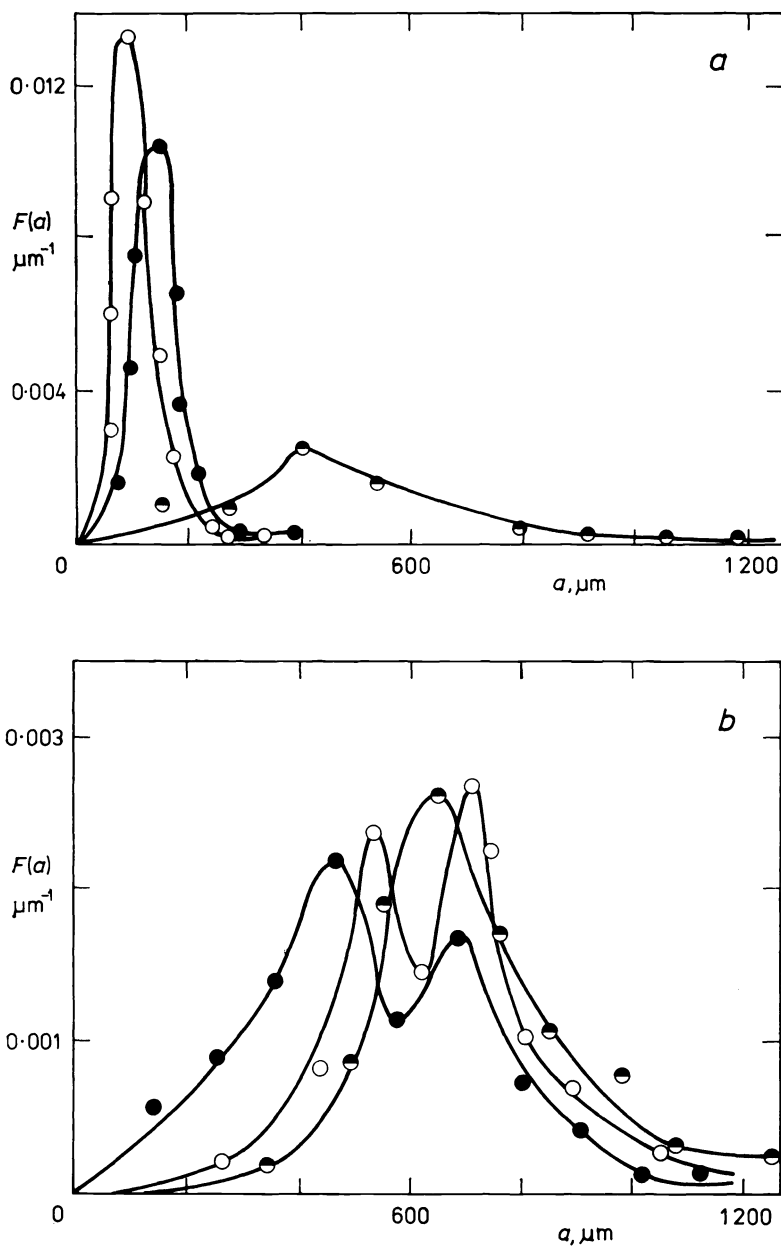


FIG. 2

Polystyrene particle size distribution for various type of impellers (● disk, ◐ pitched open, ○ vertical open) at $\Phi = 0.05$ and $c = 0.3 \text{ g l}^{-1}$. Impeller speeds: a 150 r.p.m., a_{32} , μm : 148 (○), 201 (●), 741 (◐); b 250 r.p.m., a_{32} , μm : 704 (●), 765 (○), 801 (◐)

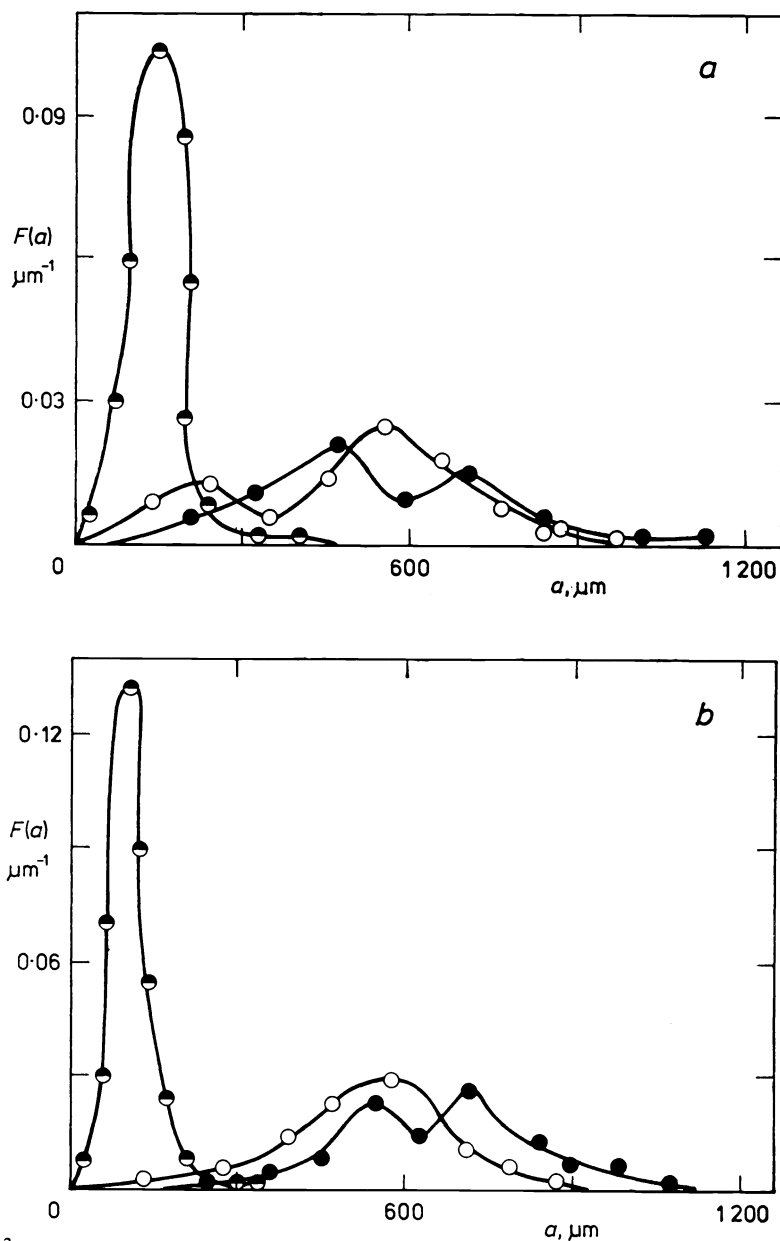


FIG. 3

Polystyrene particle size distribution for different impeller speeds ($\phi = 0.05$, $c = 0.3 \text{ g l}^{-1}$),
 a Disk type impeller, impeller speed, r.p.m. (a_{32} , μm): 150, 201 (●); 200, 631 (○); 250, 704 (●).
 b Vertical open type impeller, impeller speed, r.p.m. (a_{32} , μm): 150, 148 (●); 200, 610 (○); 250, 765 (●)

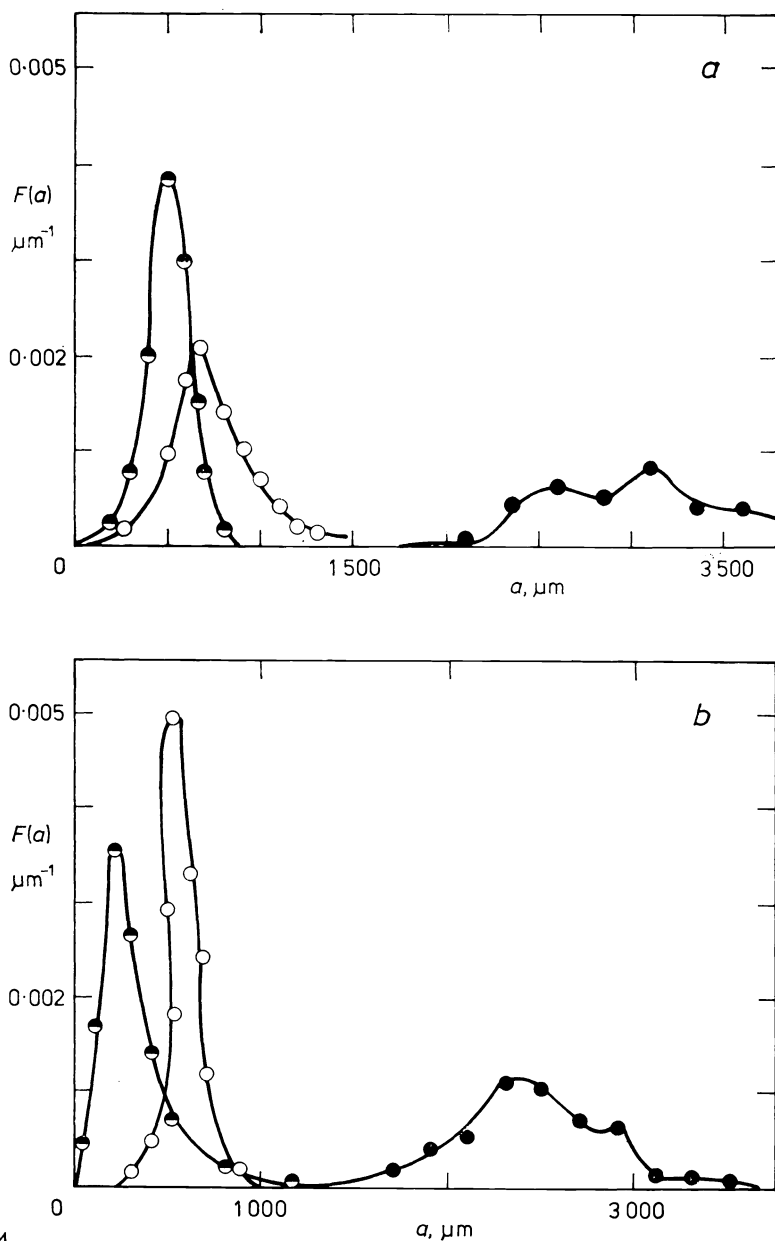


FIG. 4

Polystyrene particle size distribution for different hold-up fraction of styrene at impeller speed 250 r.p.m., *a* Disk type impeller, $c = 0.3 \text{ g l}^{-1}$, $\Phi (a_{32}, \mu\text{m})$: 0.01, 566 (●); 0.05, 704 (○); 0.10, 3 241 (●). *b* Vertical open type impeller, $c = 0.6 \text{ g l}^{-1}$, $\Phi (a_{32}, \mu\text{m})$: 0.01, 532 (●); 0.05, 574 (○); 0.10, 2 590 (●)

the coalescence rate tending to increase the particle size, the breakage rate (of polymerizing "drops") will not increase substantially to overcome the increase of coalescence rate and thus having as result the dynamic equilibrium to reach at larger particle sizes. Even though the observation of the present work that the particle sizes increase with the impeller speed is in agreement with some^{9,15} of the literature work, it disagrees with the rest of them^{2,4-7,10-13}. The disagreement can not be explained fully because the other literature works were done at much higher hold-up fraction, higher stabilizer concentration and different impeller geometry, and different monomers.

The particle size increases with the increase of hold-up fraction regardless of impeller type and of stabilizer concentration (Figs 4a, b). This is expected due to the greater number of droplets at higher Φ which result in greater coalescence rates and greater sizes. These observations are in agreement with the other literature work^{5,8,13}.

The experimental results in this work show that the produced polystyrene particle size by suspension polymerizations

- a) is decreasing with the increase of stabilizer concentration,
- b) is affected by the type of impeller used (the pitched open type impeller is the least effective thus giving the largest particles),
- c) is affected by the speed of impeller giving larger sizes at higher speeds,
- d) is affected by the hold-up fraction giving larger sizes at higher hold-up fractions.

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