

Monodisperse Poly(butadiene/styrene) Particles by Dispersion Polymerization

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SYNOPSIS

Experimental conditions for preparing monodisperse, micron-size poly(butadiene/styrene) particles by dispersion polymerization were investigated. After some initial recipe development, the following variables were fixed: butadiene/styrene weight ratio (90/10), dispersion medium (ethanol), polymeric stabilizer [poly(vinyl pyrrolidone), K-30], costabilizer (sodium dioctyl sulfosuccinate), initiator (2,2'-azobisisobutyronitrile), and polymerization temperature (70°C). The primary process variables investigated were the monomer/ethanol ratio (M/S), the rpm of the bottle polymerizer, and the amount of free space (FS) in the polymerization bottles. The particle size varied from 0.77 to 1.8 μm and was found to increase with increasing M/S and rpm, and decreasing FS. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The ability to prepare monodisperse micron-size polymer particles has become of great commercial interest for applications in polymer modification, coatings, inks, dry toners, biomedical treatment, chromatography, and microelectronics. Presently, micron-size particles are usually prepared by one of the following three methods: suspension polymerization,¹ dispersion polymerization,²⁻⁵ and seeded emulsion polymerization.^{6,7} Suspension polymerization is usually used for the production of spherical particles having diameters between 20 and 1000 μm . The particle-size distributions are typically broad because of the broad droplet-size distributions produced by mechanical homogenization and the coalescence of the droplets/particles during polymerization. Seeded emulsion polymerization, with or without a swelling promoter, has proven to be a successful technique for producing monodisperse micron-size particles. This procedure, however, is tedious and often difficult to carry out. Dispersion polymerization is a simple and efficient one-step method for the preparation of monodisperse latex

particles in the 1–15 μm size range.^{2-5,8-12} The distinct features of dispersion polymerization include that (1) the monomer is soluble in the nonaqueous reaction medium while the polymer is insoluble; (2) the initiator is soluble in the medium; and (3) an uncharged steric stabilizer is used. Sometimes, a costabilizer is also added to improve the monodispersity. From the previous work on dispersion polymerization,¹³ the dispersion medium can be polar, such as alcohols, or nonpolar, such as hydrocarbons. The stabilizer must be selected based on its suitability for the solvent system used as the dispersion medium. Usually poly(isobutylene-*co*-isoprene), poly(lauryl methacrylate), and polystyrene-*block*-poly(hydrogenated butadiene) are used in hydrocarbon media and poly(vinyl pyrrolidone) (PVP), hydroxypropyl cellulose (HPC), and poly(acrylic acid) are used in polar media. Sometimes, a costabilizer such as sodium dioctyl sulfosuccinate (Aerosol OT) is also added when using a polar medium.

To date, most of the studies have focused on the dispersion polymerization of styrene and methyl methacrylate. No work has been published on the preparation of micron-size polybutadiene particles by dispersion polymerization. The objective of this work was to investigate the feasibility of preparing uniform micron-size polybutadiene-based particles

by dispersion polymerization. Such particles are required for conducting systematic studies of the role of rubber particle size on the toughening properties and mechanisms in modified thermoplastics such as polystyrene.

EXPERIMENTAL

Materials

Butadiene (Matheson Gas Products, Inc.) and styrene (Aldrich) were purified by passing them through Ascarite II (Thomas Scientific) and aluminum oxide (Aldrich) columns, respectively. The remaining materials were used without further purification. The initiator was 2,2'-azobisisobutyronitrile (AIBN, Kodak). The stabilizer was poly(vinyl pyrrolidone) with a molecular weight of 40,000: PVP K-30 (GAF Chemicals Corp.). Aerosol OT (sodium dioctyl sulfosuccinate, American Cyanamid Co.) was used as a costabilizer. The dispersion medium was ethanol (200 proof, Midwest Grain Products Co.).

Dispersion Polymerizations

The dispersion polymerizations were carried out in 250 mL pressure bottles by a batch process. PVP and Aerosol OT solutions in ethanol were prepared first and added to the bottles. Then, a fresh solution of AIBN in ethanol was charged into the bottles. The total volume of the reaction mixture was adjusted by the addition of ethanol. After adding the styrene monomer, the bottles were purged with N₂ and then placed in a -10°C freezer for about 30 min. Finally, the condensed butadiene was charged into the bottles. The bottles were capped with a crown cap and rubber gasket and placed in a bottle polymerizer maintained at 70°C for 24 h. After screening some parameters such as stabilizer type and concentration, monomer concentration, and initiator concentration, two recipes (I and II) having different monomer/solvent ratios were developed to obtain particles with narrow particle-size distributions, as shown in Table I.

Particle-size Measurements

The average particle size and particle-size distribution of the poly(butadiene/styrene) (PBS) particles were determined using images recorded from an Etec Autoscan scanning electron microscope (SEM). Each latex sample was centrifuged to remove most of the PVP stabilizer. The particles were then

Table I Recipes for the Dispersion Polymerization of 90/10 Butadiene/Styrene

Component	Recipe I (g)	Recipe II (g)
Ethanol	80	75
Bd/St(90/10)	20	25
AIBN ^a	0.1	0.19
PVP K-30 ^b	8	14
Aerosol OT ^c	0.5	0.63

^a AIBN: 2,2'-azobisisobutyronitrile.

^b PVP K-30: poly(vinyl pyrrolidone), $M_w = 40,000$ g/mol.

^c Aerosol OT: sodium dioctyl sulfosuccinate.

redispersed in distilled-deionized water and stained with osmium tetroxide (OsO₄). One drop of the treated latex was spread onto a metal stub and the water was evaporated at room temperature. The dried particles were coated with a thin layer of Au—Pt using a Polaron E5100 sputter coater in an argon atmosphere. Three different micrographs were taken for each latex sample at 2000× magnification. The particle sizes and particle-size distributions were determined by measuring the diameters of at least 300 particles for each sample from the micrographs using a Zeiss MOP-3 analyzer.

RESULTS AND DISCUSSION

The resulting particle sizes and particle-size distributions and polydispersity indexes ($PDI = D_w/D_n$) are reported in Table II. It can be seen that micron-size PBS particles with narrow particle-size distributions were obtained. A combination of factors such as monomer/solvent ratio (M/S), rotation speed of the bottle polymerizer (rpm), and the free space (FS) in the bottle were found to influence the final particle size. Figure 1 shows SEM micrographs of these samples.

It can be seen from Table II and Figure 1 that the particle sizes were larger for the higher ratio of monomer to solvent. This finding has been documented previously for polystyrene¹⁴ and poly(methyl methacrylate).¹⁵ However, the magnitude differs for each of these polymer systems. Since the mechanism of particle formation in dispersion polymerization is a complex function of the polymerization system and conditions, different monomer systems are expected to behave differently in terms of particle formation. Generally, the final particle size and particle-size distribution are determined by the specific features of particle nucleation. For dispersion po-

Table II Particle Size Results Obtained for PBS Particles Prepared Under Varying Conditions

Sample	M/S	rpm	FS ^a (%)	D_n (μm)	PDI
A	20/80	16	55	0.77	1.02
B	20/80	32	55	0.93	1.02
C	20/80	32	44	1.2	1.01
D	25/75	16	53	1.8	1.01
E	25/75	32	53	2.2	1.03

^a FS: free space, defined as the initial volume of the polymerization bottle that is not occupied by the liquid and is given as a percentage of the total volume of that bottle.

lymerization, four possible nucleation mechanisms have been proposed¹⁶: (a) micellar, (b) self-nucleation or homogeneous nucleation, (c) aggregative nucleation, and (d) coagulative nucleation. The micellar entry approach assumes that nucleation takes place by entry of a free radical formed by decomposition of the initiator into monomer-rich micelles comprising the polymeric stabilizer. Since in dispersion polymerization the monomer and stabilizer and/or costabilizer are all soluble in the dispersion medium and the system is clear and homogeneous before polymerization, it is not likely that nucleation occurs by this approach. In the self-nucleation process, the free radical undergoes propagation in the continuous phase. These oligomeric radicals are initially soluble in the dispersion medium until a critical chain length is reached by which they precipitate to form particle nuclei. These are stabilized by adsorption or grafting of the stabilizer. In this process, each oligomer formed will create a new particle and higher initiator concentrations should result in smaller particle sizes. Aggregative nucleation is a variation of the self-nucleation model, where the oligomers associate with each other, undergoing aggregation to form the particle nuclei. At the same time, the stabilizer adsorbs onto the aggregates to form stable particle nuclei of a certain size. In the coagulative nucleation mechanism, it is postulated that the oligomer chains are formed first and grow to the point where they reach their solubility limit, collapse, and form unstable precursor particles. After the formation of the precursors, there are several ways to form stable nuclei,¹⁷ such as (1) the collision with another precursor resulting in homocoagulation; (2) collision with a stabilizer followed by the propagative growth of the polymer chain; and (3) growth of the size of the precursor by polymerization takes place within the preformed unstable precursor particle due to monomer absorption. The nucleation

process is terminated when oligomers, precursors, or nuclei formed in solution are captured before they can become stable, mature polymer particles. From the available experimental data,⁴⁻¹⁵ as the initiator concentration is increased, the final particle size increases, which implies that particle formation in dispersion polymerization takes place by the aggregative or coagulative nucleation mechanism. Each nucleation mechanism can result in a different particle size and distribution. After the nucleation step, the particles can also grow by several means: monomer polymerization within the monomer-swollen particles, oligomer capture, and heterocoagulation.¹⁶ Variations in the monomer concentration can have a major effect on the nucleation process. Increasing the monomer concentration increases the solvency of the dispersion medium for the polymer with the consequence that the oligomers grow to a longer chain length before precipitation or adsorption. In addition, the propagation rate of the oligomeric chains is faster at higher monomer concentrations. Therefore, the size of the particle nuclei increases and the final particle size is larger. For recipe II, the initiator concentration was also increased along with the monomer concentration. Increasing the initiator concentration increases the number of free radicals formed, which, in turn, increases the number of oligomeric radicals available for aggregation into larger particle nuclei, and as a result, larger final particles are formed.

It has also been noted that the polymerizations carried out in the bottle polymerizer operated at different rotation speeds, 16 and 32 rpm, resulted in different particle sizes. The higher the rotation speed, the larger the resulting particle size. This effect was more pronounced for the higher monomer/ethanol ratio (i.e., compare the particle size of sample E with sample B). In addition, the amount of free space in the bottle has an effect on the resulting particle size and distribution, as well. The free space (FS) is defined as the initial volume of the polymerization bottle not occupied by the liquid at room temperature and is given as a percentage of the total volume of the bottle. When the free space was 55%, the resulting particle size was smaller and the particle-size distribution was narrower than those produced with a free space of 44%. Both the rpm and the FS affect the nucleation since each of these help determine the local shear rate in the system. A higher rotation speed leads to higher shear rates, which, in turn, may cause an increase in the rate of aggregation of the nuclei and, therefore, larger size particles will be formed. However, the effect of the FS is not fully understood at the present time, al-

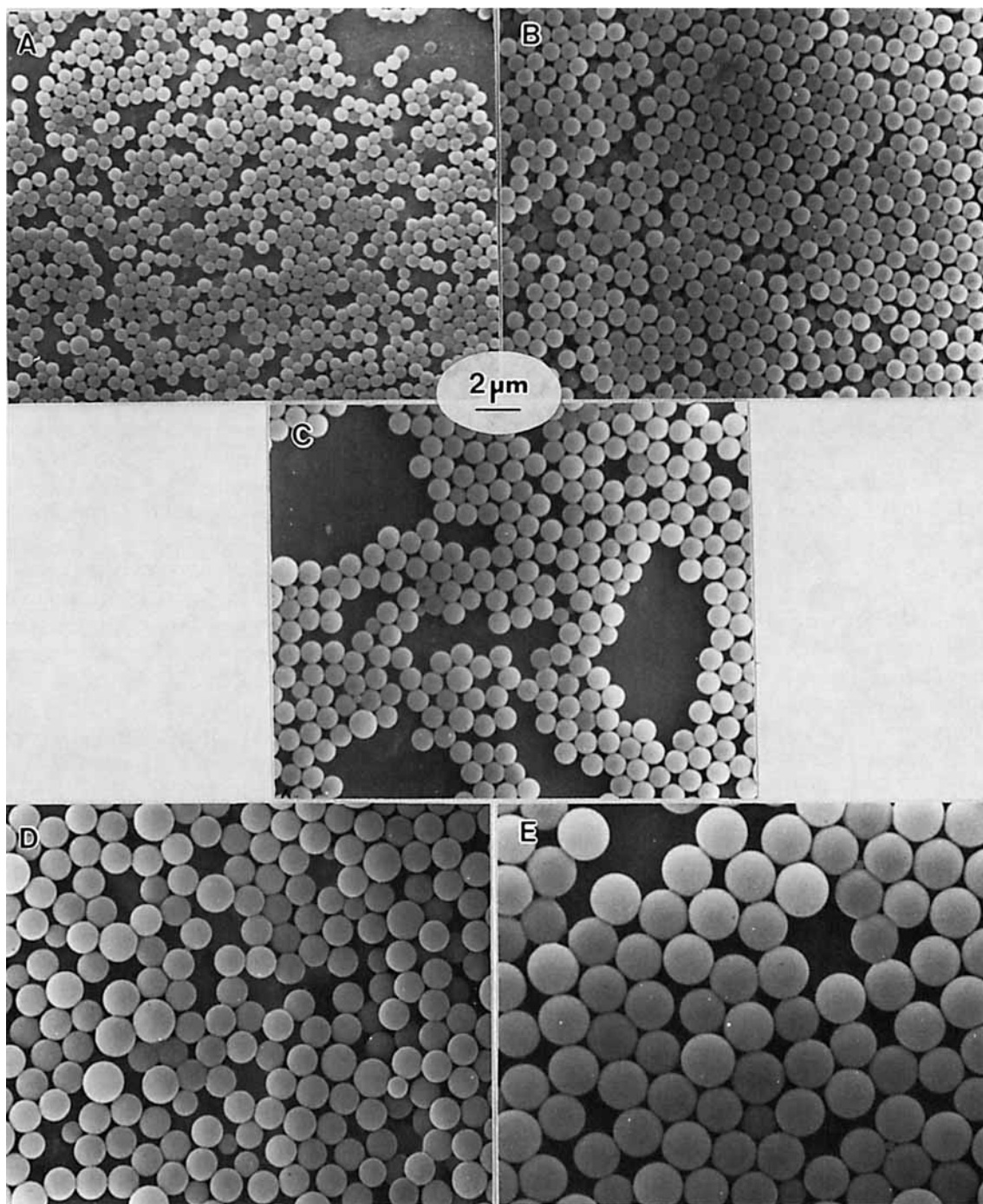


Figure 1 SEM micrographs of PBS (90/10) particles: (A) M/S = 20/80, rpm = 16, FS = 55%; (B) M/S = 20/80, rpm = 32, FS = 55%; (C) M/S = 20/80, rpm = 32, FS = 44%; (D) M/S = 25/75, rpm = 16, FS = 53%; (E) M/S = 25/75, rpm = 32, FS = 53%.

though it should also be related to the rheological behavior of the system and the local shear rate in the bottles brought about by the end-over-end rotation and their influence on the aggregation rate of the nuclei. Since the mechanism of particle nucleation in dispersion polymerization is still not fully

understood, it is difficult at this point to fully explain the results that we obtained for the butadiene/styrene monomer system.

The objective of this note was to define the operating parameters for the preparation of uniform micron-size rubber particles. Future work must be

done to examine the role of shear rate on particle nucleation in dispersion polymerization.

CONCLUSIONS

This study defined conditions under which micron-size polybutadiene-based particles (Bd/St = 90/10) with narrow particle-size distributions could be prepared by dispersion polymerization using ethanol as the solvent and PVP as the stabilizer. The particle size was affected by the rotation speed of the bottle polymerizer and the free space in the bottle. The shear rate in the system was considered to play a dominant role in the determination of the resulting particle size and particle-size distribution.

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