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Morphological Investigations of Polymer Microspheres Prepared by Dispersion Copolymerization

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SUMMARY: In the dispersion copolymerization system of styrene and glycidyl methacrylate, the procedures for preparing the microspheres influence the particle size and size distribution. Increasing the stabilizer concentration and the fraction of styrene in the monomer feed causes some decrease in the particle size. In addition, Styrene/Acrylamide and Styrene/N-vinyl carbazole dispersion copolymerization systems were investigated preliminarilly.

Introduction

Monodisperse polymer microspheres have found lots of applications in such fields as standard calibration, biomedical and clinical examinations, HPLC fillers, catalyst carriers, coating and ink additives, information storage materials, and so on [1,2]. Several techniques for preparation of monodisperse micron-size beads have been developed.

Dispersion polymerization is a very attractive method to prepare micron-size monodisperse polymer particles due to the inherent simplicity of its single-step process. It is most suitable for preparation of beads in the diameter range of 1-15μm [3,4]. Recently, much attention has been directed towards the formation of dispersion polymer particles containing functional monomer or comonomer, such as formylstyrene, styrene sulfonylchloride, chloromethylstyrene, 2-hydroxyethylmethacrylate (HEMA), and acrylic acid, etc [5].

In this paper, the morphology of micron-size copolymer microspheres consisting of styrene and glycidyl methacrylate prepared by dispersion copolymerization is studied in detail. Besides, Styrene/Acrylamide and Styrene/N-vinyl carbazole dispersion copolymerization systems are investigated prelimінerilly.

Experimental

Materials

Styrene (St) and glycidyl methacrylate(GMA) were purified by distillation under reduced pressure before polymerization. Acrylamide(Am) was purified by recrystallization in chloroform. N-vinyl carbazole (NVC), supplied from Merck corporation. 2,2-

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Azobisisobutyronitrile (AIBN), was purified by recrystallization in ethanol. Polyvinylpyrolidone (PVP, Mw = 360,000) was supplied from BASF corporation. Deionized water was used throughout this work. Ethanol (EtOH) was used as received.

Preparation of copolymer microspheres by dispersion copolymerization

Two different procedures of polymerization were studied in this work, described as follows:

Procedure 1 (P1) The stabilizer, PVP was dissolved in a mixture of ethanol and deionized water in a 250mL four-necked round-bottom flask equipped with a mechanical stirrer, thermometer, a reflux condenser, and a nitrogen gas inlet and outlet. Then a solution of AIBN in a mixture of monomers was added under stirring. Under nitrogen atmosphere, the mixture was stirred for 30 min. Then the flask was placed in an oil bath at 70 °C, and the polymerization was carried out for 24hr at 70 °C.

Procedure 2 (P2) PVP was dissolved in a mixture of ethanol and deionized water, then the mixture of monomers was added. Under nitrogen atmosphere, the mixture was stirred for 30 min, then the flask was placed in an oil bath at 70 °C. When the system was heated to 70 ℃, a solution of AIBN in ethanol was added under stirring. Polymerization was carried out for 24hr, and the reaction temperature was maintained at 70 °C.

After centrifugal purification the microspheres were redispersed into ethanol/water (v/v=1:1) for use.

Characterization of the particles

Morphology analysis was carried out on a Hitachi S-520 Scanning Electron Microscopic (SEM). The particle size and size distribution were measured on a Coulter LS230.

Results and discussion

Effect of the Procedures for Preparing the microspheres

In table 1 are shown the results obtained by using the two procedures to prepare the copolymer microspheres. It is found that the particles obtained by P1 were smaller and with a narrower size distribution than that by P2, such as G1 and G4 (Figure 1). This is due to the fact that the reaction temperature (nucleation temperature) influences the particle size and size distribution. The system temperature in P1 went up from room temperature to 70℃. But the system temperature in P2, because the solution of AIBN was added into the mixture system at 70℃, first went down from 70℃ to about 65℃, and then went up to 70℃. Thus, P1 only went through a temperature rise process, and the P2 went through a temperature fall and then rise process. The initial nucleation temperature was about 65 °C (translucent) in P1, lower than 70℃. In P2, the initial nucleation was instantaneous at 70 °C with the addition of AIBN solution, then the system temperature went down to about 65 °C, and some particles also formed during the temperature decreasing. With increasing temperature the particle size increases and size distribution broadens [4, 6], so the particles prepared by P2 were bigger and in broader distribution than that by P1. Saenz [7] found that if the temperature is increased only after the beginning of the nucleation, the new nucleation can be avoided. Therefore, in the following experiments, P1 was chosen as the experiment process.

Table 1 Effect of the procedures on particle size and size distribution a)

Sample	Procedure	EtOH/H_2O (g/g)	$\bar{D}_v$(μm) b)	CV(%) c)	Init δ d) $(cal/cm^3)^{1/2}$
G1	P1	80/5	2.4	17	12.9
G2`	P1	77.5/7.5	1.6	15	13.2
G3	P1	75/10	1.5	15	13.5
G4	P2	80/5	2.8	27	12.9
G5	P2	77.5/7.5	2.8	54	13.2
G6	P2	75/10	1.8	16	13.5

a: 15%(w/w) monomer relative to total mixture, St/GMA(w/w) =12/3; 1% (w/w) AIBN relative to monomers; 4.5% (w/w) PVP relative to monomers.

b: Diameter is measured by Coulter LS230; $\bar{D}_v$ is volume-average diameter .

c: CV: the coefficient of variation of volume-average diameter.

d: Init δ: initial solubility parameter.

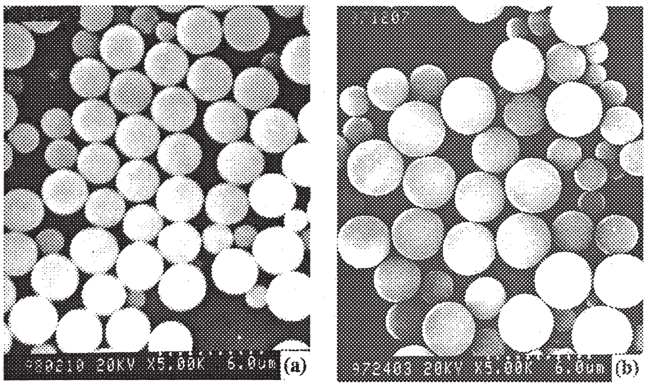

Figure 1. SEM photographs: (a)G1 by Procedure 1; (b)G4 by Procedure 2.

Effect of Stabilizer concentration

The stabilizer plays an important role in the preparation of monosized particles by dispersion polymerization [3, 6, 8]. From table 2 and Figure 2, one sees that the particle size decreases slowly with increasing concentration of the PVP stabilizer. An increase in the concentration of PVP increases the viscosity of the medium and the rate of physical adsorption of PVP, as well as the rate of adsorping of the grafted stabilizer since the amount of grafted stabilizer increases too. All these would reduce the extent of aggregation of the nuclei and reduce the particle size. When the PVP concentration was 2.5%, some irregular particles such as doublets, triplets had been obtained (Figure 2.a). This might be due to the fact that less PVP could not provide enough stabilization for particle growing. But for very high PVP concentrations, after the stage of nucleation, there was still a significant amount of PVP in the continuous phase, then the polymer formed in the continuous phase would easily adsorb the stabilizer, leading to new stable and smaller particles (Figure 2.d).

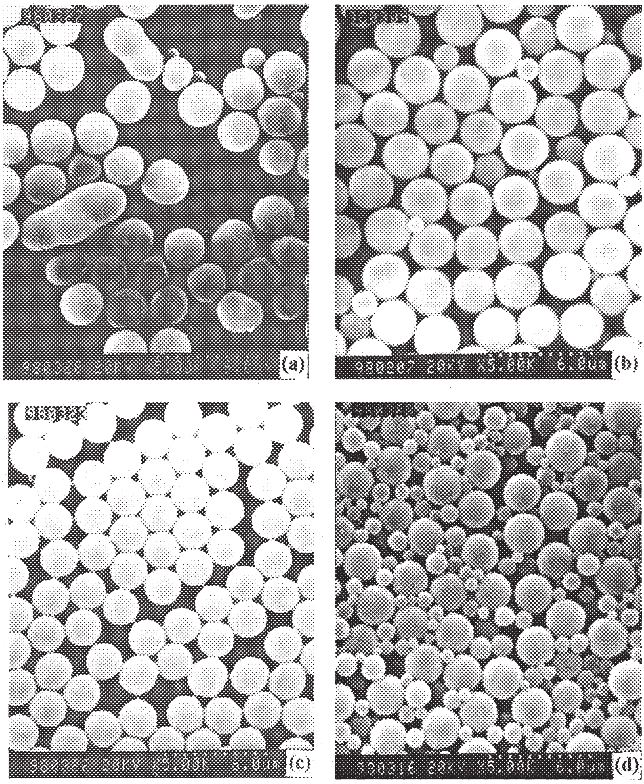

Figure 2. Effect of stabilizer concentration on particle morphology: (a)G7; (b)G8; (c)G9; and (d)G10.

Table 2 Effect of stabilizer concentration on particle size and size distribution a)

Sample	PVP concentration b) (%)	$\bar{D}_v$(μm)	CV(%)
G7	2.5	2.6	23
G8	4.5	2.4	17
G9	6.5	2.2	12
G10	8.5	2.1	52

a: EtOH/H_2O(w/w)= 80/5, 15%(w/w) monomer relative to total mixture, St/GMA(w/w)=12/3; 1% (w/w) AIBN relative to monomers.

b: PVP concentration relative to monomers (w/w).

Effect of Comonomers

Table 3 Effect of comonomers on particle size and size distribution

Sample	Comonomer	St/ Comonomer (g/g)	$\bar{D}_v$ (μm)	CV(%)
G11	GMA a)	15/0	1.4	14
G12		14/1	2.0	16
G13		13/2	2.3	29
G14		12/3	2.4	17
G15		10/5	3.6	35
A1	Am b)	15/0	1.4	17
A2		14.5/0.5	1.1	24
A3		14/1	1.3	23
A4		13/2	1.6	35
A5		11/4	- d)	-
A6		9/6	- e)	-
N1	NVC c)	20/0	1.1	23
N2		19/1	1.2	18
N3		17/3	1.0	30
N4		15/5	1.2	18

a: 15%(w/w) monomer relative to total mixture; EtOH/H_2O(w/w)= 80/5; 1% (w/w) AIBN relative to monomers; 4.5% (w/w) PVP relative to monomers.

b: 15%(w/w) monomer relative to total mixture; EtOH/H_2O(w/w)= 80/5; 2% (w/w) AIBN relative to monomers; 4% (w/w) PVP relative to monomers.

c: 20%(w/w) monomer relative to total mixture; EtOH/H_2O(w/w)= 78/2; 2% (w/w) AIBN relative to monomers; 5% (w/w) PVP relative to monomers.

d: The polymerization system was translucent and a lot of particles were obtained when the temperature went down from 70 °C to room temperature.

e: The polymerization system was solution polymerization.

GMA, Am and NVC were incorporated in the dispersion polymerization as a comonomer in three series, and the results are shown in Table 3. With increasing the amount of GMA in the monomer mixture, the particle size increases. Especially, when the fraction of GMA in the monomers was 0.33, some slightly dented particles were obtained. The reason for this is still not clear (Figure 3.a). The difference in particle size might result from the polarity of the copolymer P(St-GMA). The polarity of the resultant copolymer rich in PGMA is higher than that rich in PS. The copolymer richer in PGMA is more soluble in ethanol-water, thus the critical chain length would become longer with increasing the amount of GMA, and the particle size would increase. A similar result was obtained by Frechet et al. in the system of St/BMA [6].

As shown in Table 3, when Am is incorporated in the polymerization system, the particle size first decreases, then increases with increasing the fraction of Am. The size distribution widens with increasing the fraction of Am (Figure 3.b). Because polyacrylamide acts as co-stabilizer, it may result in decrease of particle size. For example, in the emulsifier-free emulsion polymerization system of St/Am, an increase of Am fraction in monomer caused some decrease in the particle size [9]. Moreover, PAm could dissolve in ethanol-water at the reaction temperature, and the copolymer richer in PAm is more soluble, thus leading to larger particles. When the fraction of Am is 4/15 (A5), the polymerization system was half-muddy and a lot of particles were obtained when the temperature went down from 70 ℃ to room temperature. Especially, when the fraction of Am is 0.4 (A6), the polymerization system was transparent and acted as solution polymerization at 70℃. In A6, when the system temperature went down from 70℃ to room temperature after the polymerization, no particles but gel-like polymers were obtained at room temperature.

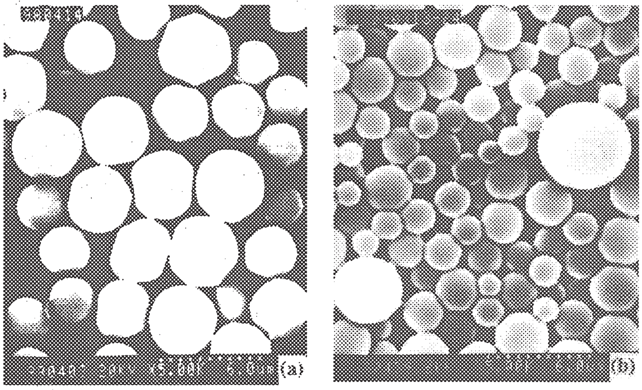

Figure 3. SEM photographs: (a)G15; (b)A4.

In St/NVC copolymerization, the particle size had been little affected with increasing the fraction of NVC (see Table 3). Because the polarity and hydrophilicity of Poly(N- vinyl carbazole) (PVK) are all near to those of PS, the critical chain length of the copolymer richer in PVK may be close to that rich in PS, thus the particle size wouldn't change when changing the ratio of St/NVC.

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