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ORIGINAL CONTRIBUTION

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Dispersion copolymerization of styrene and glycidyl methacrylate in polar solvents

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Abstract Monodispersed copolymer microspheres consisting of styrene and glycidyl methacrylate have been prepared by dispersion polymerization. The effects of various polymerization parameters on the particle size and size distribution were systematically investigated. The initial solubility parameter of the system had a significant effect on the final particle size and size distribution. With decreasing initial solubility parameter, the particle size increased and the size distribution broadened. The particle size decreased with increasing stabilizer concentration, the amount of styrene in the monomer mixture, and decreasing initiator concentration.

Key words Dispersion copolymerization – Micron-sized monodispersed polymer particles – Styrene – Glycidyl methacrylate

Introduction

Micron-sized monodispersed polymer microspheres are used in a wide variety of fields such as standard calibration, biomedical and clinical examinations, HPLC fillers, catalyst carriers, coating and ink additives, information storage materials, and so on [1–3]. Several techniques for the preparation of monodispersed micron-sized beads have been developed. Vanderhoff et al. [4] used a successive seeding method to obtain micron-sized monodispersed polymer particles. Similar sized particles were also prepared by Ugelstad et al. [5] by a two-step swelling method. However, both approaches were tedious and typically required several reaction steps.

Dispersion polymerization is a very attractive method to prepare micron-sized monodispersed polymer particles due to the inherent simplicity of the single-step process. It is most suitable for the preparation of beads in the diameter range 1–15 μm [6–10]. The preparation of micron-sized monodispersed homopolymer particles has been extensively studied, especially the polystyrene (PS) system and the poly(methyl methacrylate) system; however, very few studies on unseeded batch dispersion copolymerization have been reported [11–14]. One reason is that dispersion polymerization is highly sensitive to small changes in the numerous reaction parameters involved in the process. The behavior of the polymerization may change when another monomer is present in the reaction medium; even the different comonomer ratio should be treated as a new polymerization system. In 1987, Ober and Lok [12] prepared large monodispersed copolymer particles of styrene (St) and *n*-butyl methacrylate (BMA) by unseeded batch dispersion copolymerization in ethanol/water. Further study on this system was carried out by Horak et al. [13]. Recently, dispersion copolymerization of St and butyl acrylate in polar solvents was also reported [14].

The unseeded batch dispersion copolymerization of St and glycidyl methacrylate (GMA) in ethanol/water medium was employed to prepare functionalized micron-sized monodispersed polymer microspheres, and the influences of various polymerization parameters such as the initial solubility parameter, stabilizer concentration, initiator concentration, and the composition of the monomer mixture on the particle size and size distribution were investigated.

Experimental

Materials

St and GMA were purified by distillation under reduced pressure before polymerization. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization in ethanol. Polyvinylpyrolidone (PVP, $M_w = 360\,000$) was supplied by BASF. Deionized water was used throughout this work. Ethanol was used as received.

Preparation of copolymer microspheres by dispersion copolymerization

In a typical example, 0.675 g PVP was dissolved in a mixture of 80 g ethanol and 5 g deionized water in a 250 mL four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet and outlet. Then a solution of 0.15 g AIBN in a mixture of 12 g St and 3 g GMA was added under stirring. Under a nitrogen atmosphere, polymerization was carried out at 70 °C for 24 h. After centrifugal purification the microspheres were dispersed 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. The particle size and size distribution were measured on a Coulter LS230.

Results and discussion

Effect of initial medium polarity

The reaction medium of dispersion polymerization should be able to dissolve the steric stabilizer but not to dissolve the resultant polymer. In dispersion polymerization, medium polarity plays a crucial role and influences the particle size and size distribution because it controls the critical molecular weight above which the polymer will precipitate. One method of estimating the polarity of a mixture of miscible liquids involves averaging the solubility parameter of the components [15]. The solubility parameter, δ, is an empirical quantity that permits the calculation of a value representing the polarity of a solvent medium. The calculation of δ for a solvent mixture is done by taking the average based on the volume fraction of solvent in the mixture [16]. The average used in the calculations is given by

$$\delta = \left(\Sigma\Phi_i\delta_i^2\right)^{1/2},$$

where Φ_i is the volume fraction of component i. Neither the polymeric stabilizer nor the initiator is used in the estimation since they are present in small quantities. The polymer produced from the monomers is not included in the calculation since it locates in another separated phase. The solubility parameters of the individual components used in this study are summarized in Table 1 [17].

The effect of the water content in the solvent mixture on the solubility parameter of the system is shown in Table 2. The solubility parameter increased with increasing water content [12]. As seen in Table 2 and Fig. 1, when the solubility parameter increased the particle size decreased and size distribution narrowed. Because the polarity of the copolymer P(St-GMA) is low, the critical molecular weight of the copolymer decreases with increasing polarity of the system. Thus, with increasing δ, the critical chain length decreases and the rate of adsorption of the stabilizer-grafted copolymer onto the nuclei increases, resulting in smaller particles. Meanwhile, the precipitation rate of the polymer chain increases, and the particle formation stage becomes shorter, resulting in a narrow distribution. The mechanism for the formation of nonspherical particles is still not clear (e.g. Fig. 1b).

With increasing monomer concentration, the initial solubility parameter decreased, and larger particles were obtained at higher monomer concentrations (Table 3): similar results have also been reported in the literature [7, 12, 13]. As the solubility parameter of both monomers is much lower than that of ethanol or water, a higher proportion of monomers will result in lower

Table 1 Solubility parameter of individual components

Component	Solubility parameter δ_i (cal/cm^3)$^{1/2}$
Styrene	9.3
Glycidyl methacrylate	8.9[a]
Ethanol	12.7
Water	23.4

[a] Calculated using the formula ($\rho\Sigma G/M$), where G is the molar attraction constant, ΣG is the sum for all the atoms and groupings in the molecules, ρ is the density and M is the molecular weight [17]

Table 2 Effect of dispersion medium on particle size and size distribution[a]

Sample	EtOH/H$_2$O (g/g)	$\bar{D}_v$ (μm)[b]	CV (%)[c]	Init δ[d] (cal/cm^3)$^{1/2}$
R1	85/0	3.3	49	12.3
R2	82.5/2.5	2.9	68	12.6
R3	80/5	2.4	17	12.9
R4	75/10	1.6	15	13.5

[a] 15% (w/w) monomer relative to total mixture, Styrene (St)/glycidyl methacrylate (GMA) (w/w) = 12/3; 1% (w/w) 2,2-azobisisobutyronitrile (*AIBN*) relative to monomers; 4.5% (w/w) polyvinylpyrolidone (PVP) relative to monomers

[b] Diameter measured by a Coulter LS230; $\bar{D}_v$ is the volume-averaged diameter

[c] The coefficient of variation of the volume-averaged diameter, $\bar{D} = \frac{\sum_{i=n}^{n} D_i}{n}$; standard deviation $= \sqrt{\frac{\sum_{i=1}^{n}(D_i - \bar{D})^2}{n-1}}$; CV(%) = (standard deviation)/$\bar{D}$

[d] Initial solubility parameter

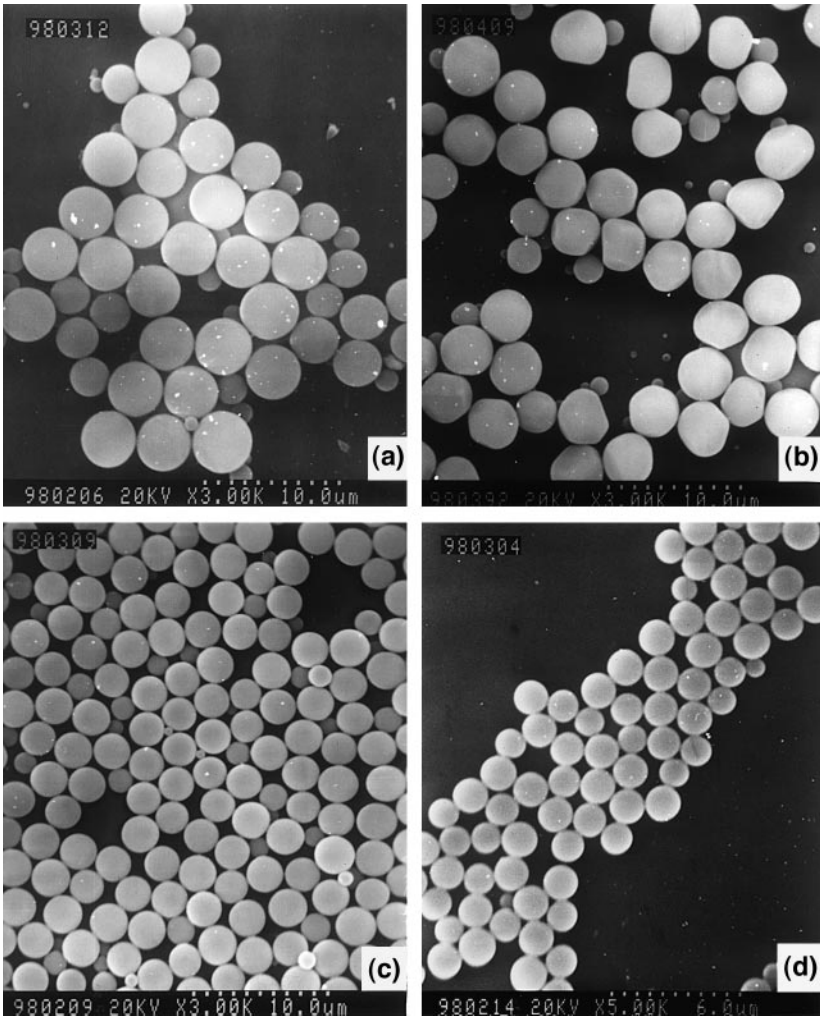

Fig. 1a–d Effect of dispersion medium on particle size and size distribution. **a** R1, **b** R2, **c** R3, **d** R4

Table 3 Effect of monomer concentration on particle size and size distribution[a]

Sample	Monomer concentration[b] (%)	$\bar{D}_v$ (μm)	CV (%)	Init δ^c $(\mathrm{cal/cm^3})^{1/2}$	$\delta_{\mathrm{final}} - \delta_{\mathrm{init}}{}^d$ $(\mathrm{cal/cm^3})^{1/2}$
R5	5	0.9	23	13.2	0.2
R6	10	2.0	13	13.1	0.3
R7	15	2.4	17	12.9	0.5
R8	20	2.9	68	12.8	0.6
R9	25	5.4	52	12.6	0.8

[a] St/GMA (w/w) = 4/1; EtOH/H_2O (w/w) = 80/5; 1% (w/w) AIBN relative to monomers; 4.5% (w/w) PVP relative to monomers

[b] Monomer concentration relative to total mixture (w/w)

[c] Initial solubility parameter

[d] The difference between the final solubility parameter and the initial solubility parameter

average solubility parameters, and decreasing solubility parameters will increase the critical chain length. Thus larger beads were obtained at higher monomer concentrations.

The polarity of the system increased during polymerization due to the consumption of monomers. For example, the initial solubility parameter of the system containing 25 wt% monomers was 12.6 $(\mathrm{cal/cm^3})^{1/2}$, and it was 13.4 $(\mathrm{cal/cm^3})^{1/2}$ after the monomers had been consumed. The difference between the initial solubility parameter and the final solubility parameter is shown in Table 3. At higher concentrations of monomer, the drift in δ is much greater with the changing of conversion ratio. With the increase in polarity of the medium, the species that do not nucleate early in the reaction system might do so now, thus some small particles would form, resulting in a broadening of the particle-size distribution (Fig. 2d, e) [13].

From Tables 2 and 3, we can find that when the initial solubility parameter $\delta \geq 12.9$ $(\mathrm{cal/cm^3})^{1/2}$, narrow distribution polymer microspheres would be obtained, and when the initial solubility parameter $\delta < 12.9$ $(\mathrm{cal/cm^3})^{1/2}$, only broad distribution polymer particles would occur. So, the initial solubility parameter is the key element that influences the particle size and size distribution.

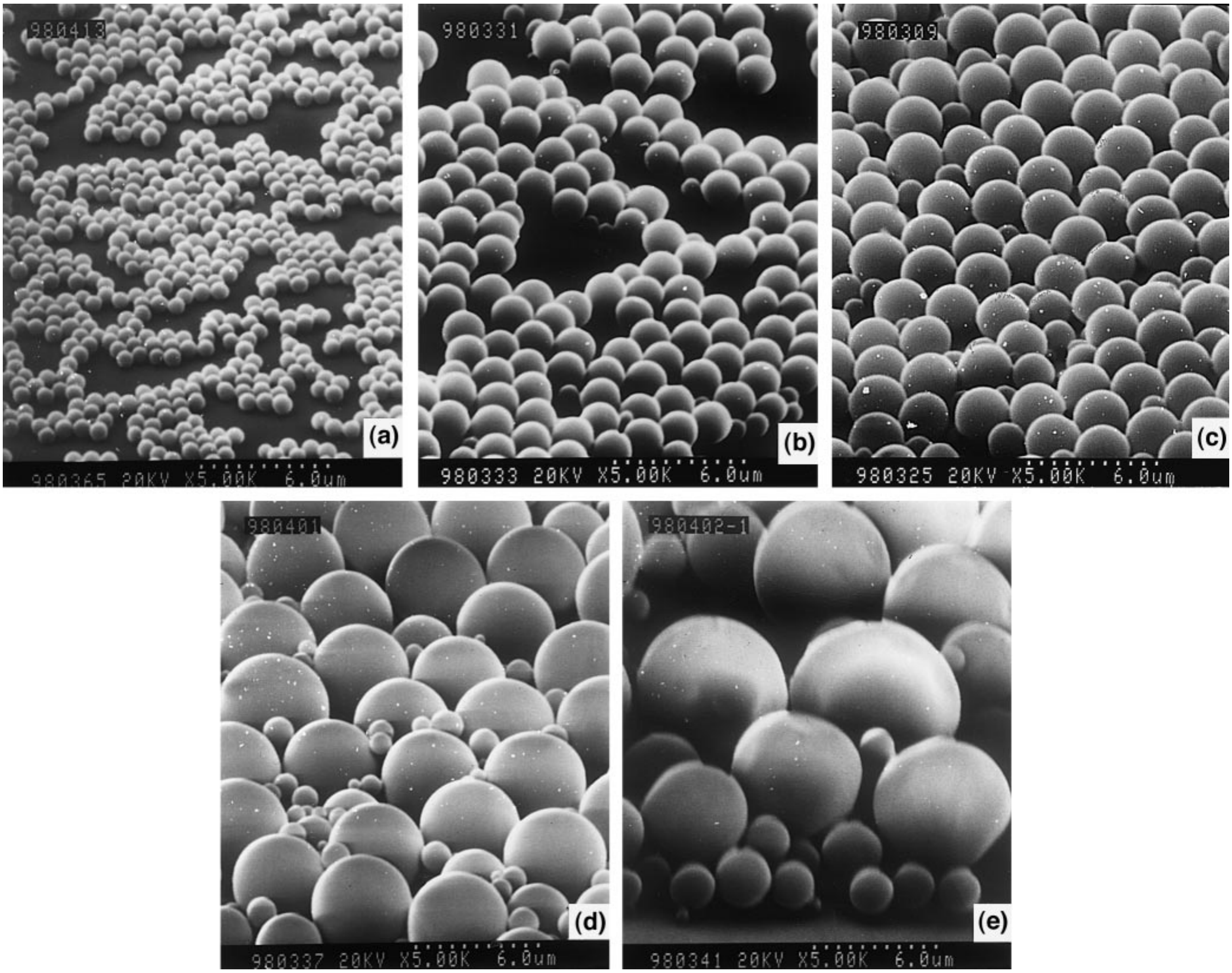

Fig. 2a–e Effect of monomer concentration on particle size and size distribution. **a** R5, **b** R6, **c** R7, **d** R8, **e** R9

Table 4 Effect of stabilizer concentration on particle size and size distribution[a]

Sample	PVP concentration[b] (%)	$\bar{D}$ (μm)	CV (%)
R10	2.5	2.6	23
R11	4.5	2.4	17
R12	6.5	2.2	12
R13	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] Relative to monomers (w/w)

Stabilizer concentration

The stabilizer plays an important role in the preparation of monosized particles by dispersion polymerization [7, 8, 11, 13]. From Table 4 it can be found that the particle size decreased slowly with increasing concentration of 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 anchoring adsorption of the grafted stabilizer, since the amount of grafted stabilizer increases. 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 and triplets were obtained (Fig. 3a). This may due to the fact that less PVP could not provide enough stabilization for particle growth. The particle-size distribution of R12 containing 6.5% PVP was narrower than that of R11 containing 4.5% PVP. In the higher PVP concentration system, the stage of the formation of stable particles became shorter, thus reducing the nucleation time, resulting in narrow size distribution samples (R11 and R12). When the concentration of PVP was 8.5%, a lot of small particles were produced (Fig. 3d). For the too high

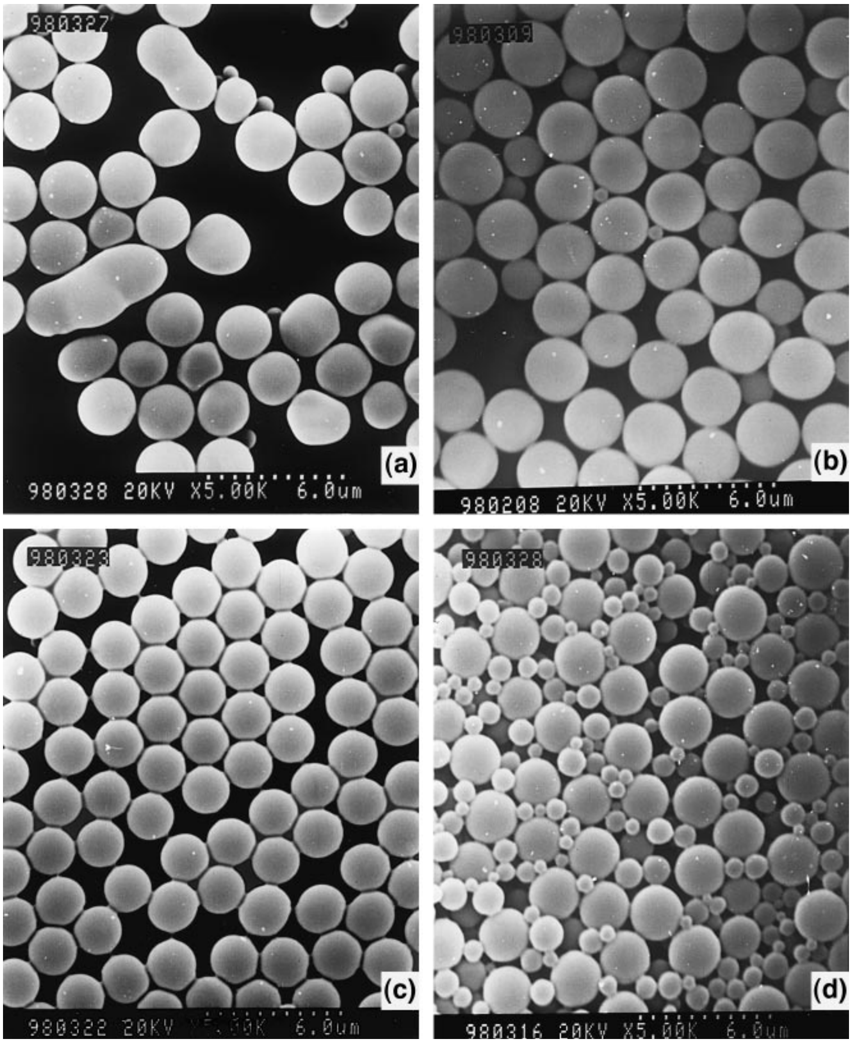

Fig. 3a–d Effect of stabilizer concentration on particle size and size distribution. **a** R10, **b** R11, **c** R12, **d** R13

PVP concentration, after the stage of nucleation there was still more PVP in the continuous phase, so the polymer formed in the continuous phase would easily adsorb the stabilizer and form new stable particles. This might lead to more small particles.

Initiator concentration

As seen in Table 5, it can be found that the particle size increased with increasing AIBN concentration. This may due to the fact that radical concentration increases with increasing initiator concentration; thus at the early stage of polymerization more polymer and nuclei would form. With increasing nuclei concentration, aggregation of the nuclei was stronger and larger stable particles were obtained. Meanwhile, at higher initiator concentration, lower molecular weight P(St-GMA) would be formed, and that makes the grafted stabilizer more soluble and less effective as a stabilizer [7, 8]. All these lead to larger particles at higher AIBN concentrations.

Table 5 Effect of initiator concentration on particle size and size distribution[a]

Sample	Initiator concentration[b] (%)	$\bar{D}_v$ (μm)	CV (%)
R14	0.5	1.7	20
R15	1.0	2.0	13
R16	1.75	2.4	11
R17	2.0	2.7	20
R18	3.0	3.1	21

[a] (EtOH + H_2O) is 90 g, EtOH/H_2O (w/w) = 80/5; 10% (w/w) monomer relative to total mixture, St/GMA = 4/1; 4.5% (w/w) PVP relative to monomers

[b] Initiator concentration relative to monomers (w/w)

Effect of the St/GMA ratio

The effect of the St/GMA ratio on the particle size is shown in Table 6. With increasing amount of GMA in the monomer mixture, the particle size increased. These results could not be explained by the initial solubility

Table 6 Effect of monomar component on particle size and size distribution[a]

Sample	St/GMA (g/g)	$\bar{D}_v$ (μm)	CV (%)
R19	15/0	1.4	14
R20	14/1	2.0	16
R21	13/2	2.3	29
R22	12/3	2.4	17
R23	10/5	3.6	35

[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

parameters because they are all about 12.9 (cal/cm^3)$^{1/2}$. 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 amount of GMA, and the particle size would increase. A similar result was obtained by Horak et al. [13] for the St/BMA system.

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