Effect of GMA on Monodisperse Epoxy-Functionalized Polymer Microsphere Particles by Dispersion Copolymerization of Styrene with Glycidyl Methacrylate

SUNG-SOO LEE,[1] KANG-YEOL PARK,[1] JU-YOUNG KIM,[2] KYUNG-DO SUH[1]

[1] Division of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

[2] Department of Material Engineering, Samchok National University, Kangwon 245-711, Korea

ABSTRACT: Monodisperse poly[styrene-*co*-glycidyl methacrylate (GMA)] microparticles were synthesized by dispersion copolymerization in a water–ethanol medium. The effects of various polymerization parameters on the particle size and size distribution of the dispersion copolymerization were investigated. The dispersion of polymer particles decreased when the GMA was added if the polystyrene homopolymer particles were polydispersed. The GMA acted as a comonomer as well as a costabilizer in the dispersion copolymerization of styrene with GMA. The solvency of the monomer increased with the concentration of GMA in the polymerization medium because GMA has a greater hydrophilicity than styrene, resulting in a large particle size and a slow polymerization rate. From an HCl–dioxane analysis of the poly(styrene-*co*-GMA) microparticles, great amounts of epoxy groups were detected after the completion of dispersion copolymerization. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1206–1212, 2001

Key words: dispersion copolymerization; monodisperse; GMA, styrene; comonomer; costabilizer

INTRODUCTION

There has been great interest in monodisperse polymer particles in the micron range, which have been found to have a wide variety of applications in coatings, inks, and dry toners and in instrument calibration, chromatography, biomedical treatment, and microelectronics.[1–7] Conventionally, monodisperse polymer microspheres have been prepared using the seeding polymerization, polymerization in the state of activated swelling, and dispersion polymerization methods.[8–10] Except for dispersion polymerization, these methods require a multistep polymerization process.

For the preparation of monodisperse homopolymer microspheres, dispersion polymerization in polar media is often used because of the simplicity of the process. Ober et al.,[11] Tseng et al.,[10] Okubo et al.,[12] and Paine et al.,[13] among others, have studied this method in order to control particle size and achieve a narrow particle-size distribution. The technological applications of monodisperse microsphere particles have been greatly increased by the use of copolymers. Typical combinations of monomers used to obtain these particles are styrene–butyl methacrylate,[14] styrene–divinylbenzene,[15] styrene–urethane acrylate,[16] styrene–methyl methacrylate,[17] and styrene–glycidyl methacrylate (GMA).[18] However,

very few reports in the literature deal with particles prepared by dispersion copolymerization. This is probably because of the complex nature of comonomer mixtures, in which each new comonomer ratio must be treated as a new polymerization system.[19] These comonomer systems are even more complicated if the comonomers polymerize at different rates or if they partition differently in the system once nucleation has taken place.

Until quite recently styrene with GMA has been copolymerized through emulsion polymerization in an aqueous medium. Various of its parameters have been studied, including the reactivity ratios for styrene and GMA copolymerization,[20] the main factors affecting size and morphology of the resulting copolymer particle,[21] and the effects of reaction conditions on surfactant-free emulsion polymerization.[22] Yang et al.[18] first reported forming epoxy-functionalized polymer particles of styrene with GMA by dispersion copolymerization in a water–ethanol medium using a stirring system. In their work, reaction conditions of dispersion copolymerization were observed when the polystyrene homopolymer particles were monodispersed.

This article reports on a study of dispersion copolymerization of styrene with GMA in a water–ethanol medium using a rotation system in order to evaluate GMA as a comonomer as well as a costabilizer when polystyrene homopolymer particles have been polydispersed. The effects of the comonomer ratio on the particle size, size distribution, morphology, and polymerization rate were investigated. The conventional HCl–dioxane method was used to determine the concentration of the remaining epoxy groups after the polymerization procedure.

EXPERIMENTAL

Materials

Inhibitor in styrene (Junsei Chemical Co., Japan) and GMA (Junsei Chemical Co.) was removed through a removing column (Aldrich Chemical Co., USA). 2,2- Azobisisobutyronitrile (AIBN; Junsei Chemical Co.) was recrystallized from methanol before use. Distilled deionized (DDI) water was used in all experiments. All other materials were used without further purification: ethanol (reagent grade, Junsei Chemical Co.), Poly(vinylpyrrolidone) (PVP K-30, M_w = 4.0 $\times 10^4$ g·mol^{-}1, Aldrich Chemical Co.), 1,4-dioxane

Table I   Standard Recipe for Dispersion Copolymerization[a]

Ingredient	Weight (g)
Styrene[b]	0.714
GMA[b]	0.286
PVP K-30[c]	0.070
AIBN[d]	0.010
Ethanol[e]	8.028
Water[e]	0.892

[a] 70°C; 24 h; 10 wt % of monomer concentration based on total weight.
[b] Weight ratio of GMA : styrene (2 : 5).
[c] 0.7 wt % of PVP K-30 (M_w = 4.0 $\times 10^4$ g mol^{-1}) based on total weight.
[d] 1 wt % of 2,2'-azobisisobutyronitrile (AIBN) based on monomer weight.
[e] Water–ethanol medium (water : ethanol = 10 : 90 wt %).

(Junsei Chemical Co.), potassium hydroxide (KOH; Junsei Chemical Co.), hydrochloric acid (HCl; Junsei Chemical Co.), and phenolphthalein (Shinyo Chemical Co., Japan).

Polymerization Procedure

AIBN, PVP, styrene, GMA, ethanol, and water were weighed into 20-mL glass vials. After being sealed in a nitrogen atmosphere, the vials were submerged in a thermostated water bath and slowly tumbled around its stem axis at a rotation speed of 40 rpm. The polymerization was carried out for 24 h at 70°C. The obtained microparticles were centrifuged for 10 min at 6000 rpm; then the supernatant was decanted, and the remaining precipitate was repeatedly washed by five redispersions/centrifugations. The microparticles were then dried under vacuum at ambient temperature. The recipe for the dispersion copolymerization of styrene with GMA in a water–ethanol medium is listed in Table I.

Characterization

Particle size was measured with a field-emission scanning electron microscope (FE-SEM, JSM-6340F, JEOL). An average was taken of the more than 200 individual particle diameters measured from the SEM photographs. A polydispersity index (PDI) was obtained as follows[23]:

$$D_n = \frac{\sum\limits_{i=1}^{n} d_i}{N} \qquad (1)$$

$$D_w = \frac{\sum\limits_{i=1}^{n} d_i^4}{\sum\limits_{i=1}^{n} d_i^3} \qquad (2)$$
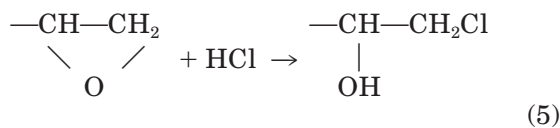
$$\text{PDI} = \frac{D_w}{D_n} \qquad (3)$$

where, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number counted, and d_i is the diameter of particle i.

Conversion-time curves for this set of polymerizations were calculated as[24]

$$\text{Conversion (\%)} = \frac{M_2 - M_1 \times (w_2 + w_3)}{M_1 \times w_1} \times 100 \qquad (4)$$

where M_1 is the weight of the sample before drying, M_2 is the weight of the sample after drying, w_1 is the weight percent of the styrene and GMA in the reactor, w_2 is the weight percent of the PVP in the reactor, and w_3 is the weight percent of the AIBN in the reactor.

The HCl-dioxane method[25,26] was used to determine the remaining concentration of epoxy groups after the completion of the polymerization procedure. This method utilizes the reaction of HCl with epoxy groups. The reaction produced a chlorohydrin while consuming the acid.

$$\begin{matrix} \text{—CH—CH}_2 & & \text{—CH—CH}_2\text{Cl} \\ \diagdown\ \diagup & + \text{ HCl} \rightarrow & | \\ \text{O} & & \text{OH} \end{matrix} \qquad (5)$$

With our method, excess 0.1M HCl was added to a known mass of particles that dissolved in 1,4-dioxane and allowed reacting for 3 h with stirring at 30°C. The concentration of unreacted HCl was then determined by titration with 0.1M KOH using phenolphthalein as the indicator. The reaction of HCl with the epoxy rings, followed by titration of the residual HCl with the KOH, was used as a method of measuring the remaining epoxy content of the particle. The difference between the number of moles of HCl initially added and the number of moles determined by titration corresponds to the number of moles of HCl that reacted with the epoxy groups. A minimum of five

Table II   Effect of GMA on Poly(styrene-*co*-GMA) Average Particle Sizes and Size Distribution with Concentration of Great Amount of PVP and Low Amount of PVP[a]

| Sample[b] | Particle Size (μm) | | PDI (D_w/D_n) | Remarks |
	D_n	D_w		
G/S1-0/5	1.571	1.573	1.001	Monodisperse
G/S1-1/5	1.791	1.793	1.001	Monodisperse
G/S1-2/5	1.931	1.935	1.002	Monodisperse
G/S1-3/5	2.455	2.459	1.002	Monodisperse
G/S2-0/5	1.983	2.453	1.237	Doublet
G/S2-1/5	3.041	3.047	1.002	Monodisperse
G/S2-2/5	3.714	3.721	1.002	Monodisperse
G/S2-3/5	4.149	4.788	1.154	Polydisperse

[a] 70°C; 24 h; water–ethanol medium (water : ethanol = 10 : 90 wt %); 10 wt % of monomer concentration based on total weight; 1 wt % of AIBN, based on monomer weight.
[b] G : Sα–β : γ; α-PVP concentration (1–4 wt %, 2–0.7 wt %) based on total weight; β : γ weight ratio of GMA : styrene.

duplicate analyses were performed for each sample.

RESULTS AND DISCUSSION

EFFECT OF GMA

Poly(styrene-*co*-GMA) (PSG) particles were synthesized at the different weight ratios of styrene: GMA in a water–ethanol medium (water:ethanol = 10:90 wt %) at 70°C for 24 h, where the concentration of PVP as a stabilizer was 0.7 and 4 wt %. Table II has the detailed recipe for the dispersion copolymerization. Figures 1 and 2 show the morphology of PSG particles prepared with different amounts of PVP in the preparation of copolymer particles. The PSG particles prepared with greater amounts of PVP show stable dispersion with a narrow particle-size distribution, in the range of 1.5–2.5 μm [Fig. 1(a–d)]. Some irregular polystyrene homopolymer particles such as doublets were obtained [Fig. 2(a)] when the preparation of PSG particles had a lesser amount of PVP (0.7 wt %), indicating that this weight percent is too small to exert a stabilizing effect on particle growth. On the other hand, as the weight ratio of GMA:styrene increased, the average diameter increased from less than 2 μm to abut 4 μm, with the particle-size distribution changing from poly-
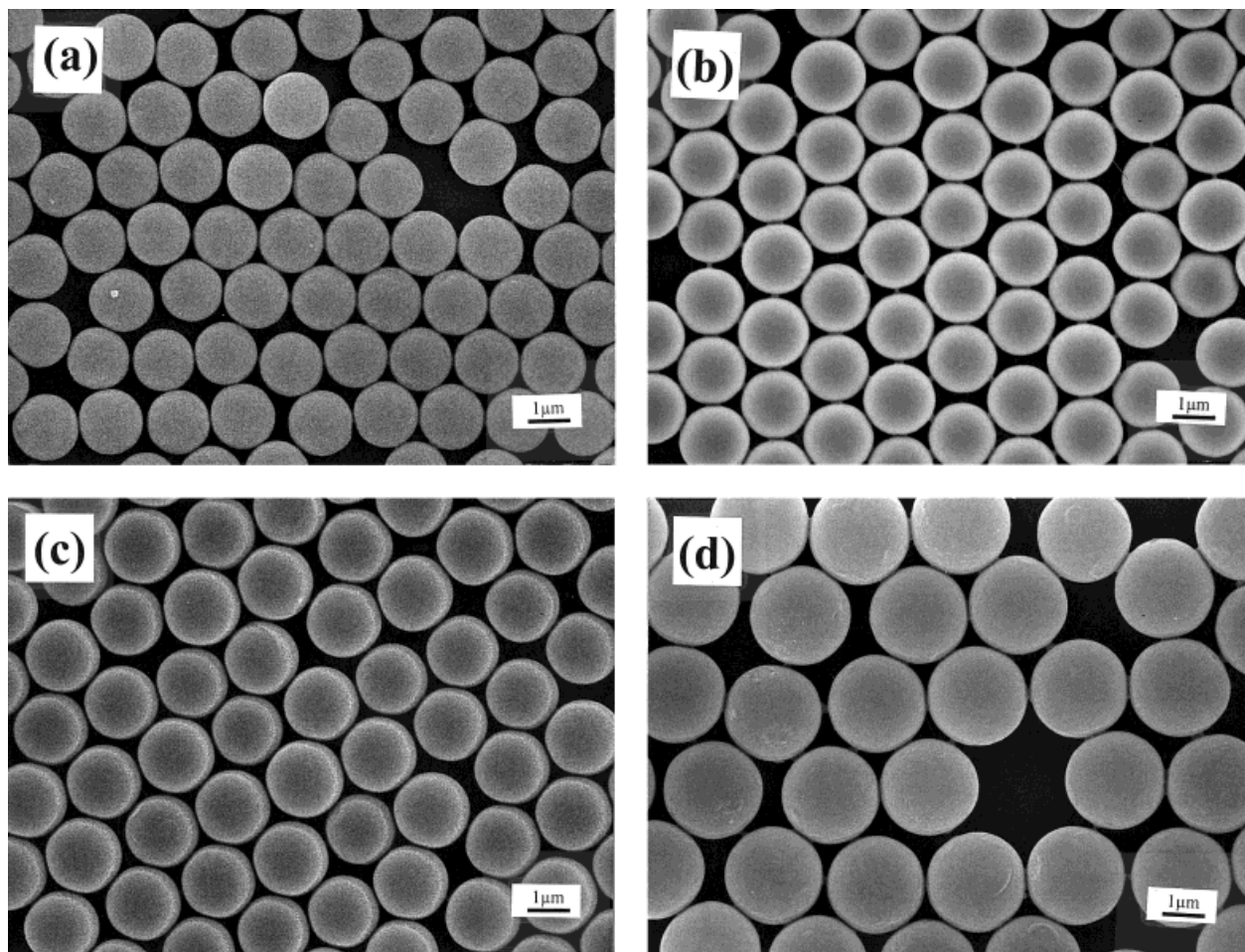
Figure 1 SEM photographs of poly(styrene-*co*-GMA) microparticles produced by dispersion copolymerization with a weight ratio of GMA:styrene in a large amount of PVP-dissolved water–ethanol medium as follows: (a) G:S1—0:5, (b) G:S1—1:5, (c) G:S1—2:5, (d) G:S1–3:5.

disperse to monodisperse. The PSG particles were spherical and monodisperse at this micron range [Fig. 2(b,c)], and their surface was smooth [Fig. 2(d)]. However, the particle size was polydispersed again and massive coagulation occurred when the weight ratio of GMA:styrene was greater than 3:5.

It is well known that in dispersion copolymerization, monodisperse poly(styrene-*co*-comonomer) microparticles have been obtained with the addition of more than 1 wt % comonomer for the styrene given the condition that the polystyrene homopolymer particles have been polydispersed.[10] These results are due to the stability improvement of the primary particle during dispersion copolymerization stemming from the costabilizing effect of the comonomer. In our experiments PSG particles were also more monodisperse and larger than the polystyrene ho-

mopolymer particles [Fig. 2 (a)]. This may indicate that the GMA used as a comonomer exerts a costabilizing effect on the primary particle at an optimum concentration, leading to a monodisperse morphology of the PSG particles.

The average size and distribution of PSG particles prepared with the greater concentration (Fig. 1) and the lower concentration (Fig. 2) of PVP are summarized in Table II. Because GMA has a greater hydrophilicity than styrene,[27] the monomer solvency in the medium increased with an increase in the concentration of GMA in the polymerization formulation, which caused an increase in the PSG particle size. Despite the increase in stability of the PSG particles from adding GMA, PSG particle size distribution broadened [Fig. 2(e)] when the GMA was used at more than optimum concentration. This polydispersed
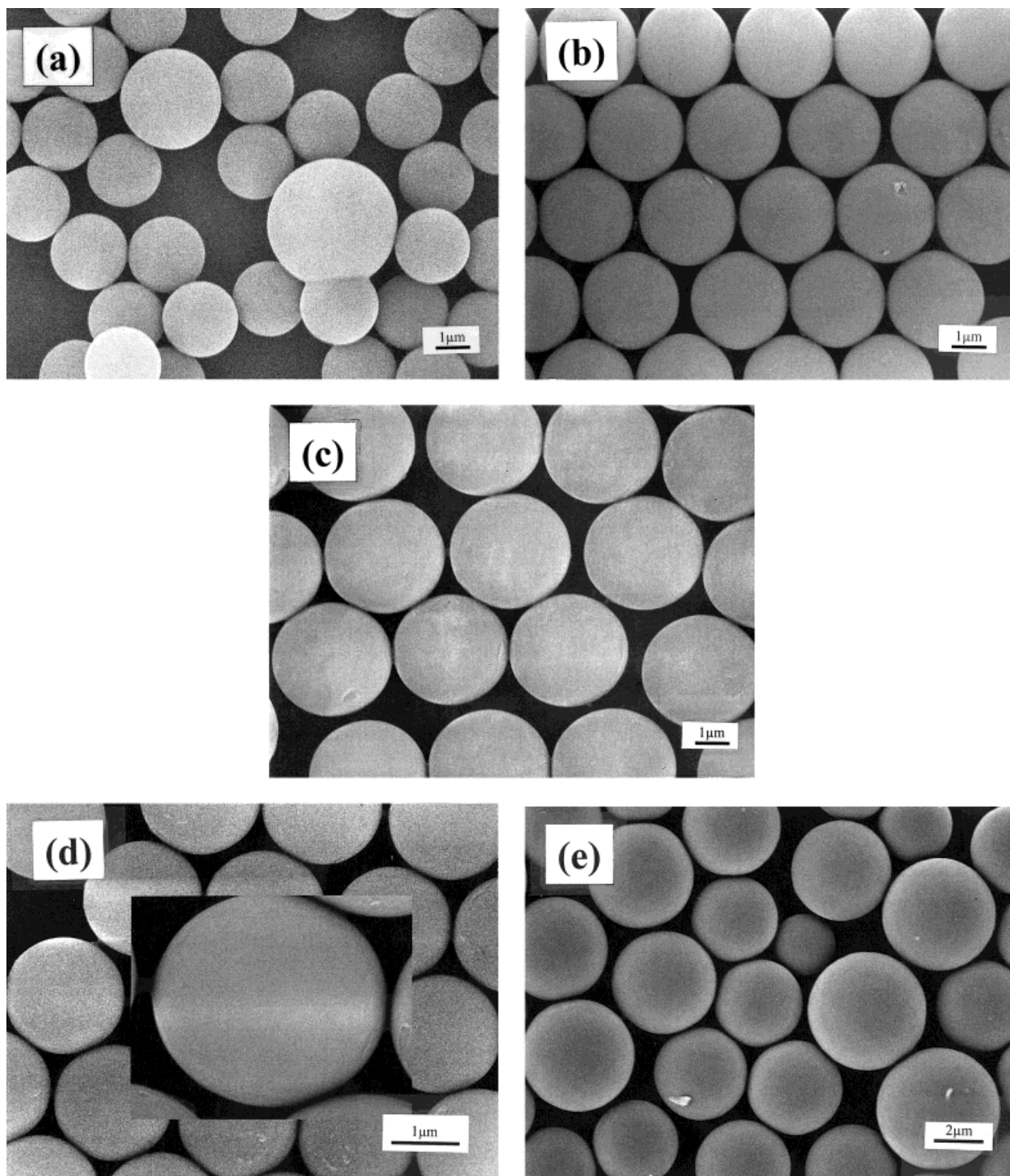
Figure 2   SEM photographs of poly(styrene-*co*-GMA) microparticles produced by dispersion copolymerization with a weight ratio of GMA:styrene in a small amount of PVP-dissolved water–ethanol medium as follows: (a) G:S2–0:5, (b) G:S2–1:5, (c) G:S2–2:5, (d) G:S2–2/5, (e) G:S2–3/5.

size distribution arose from an extended formation stage of new primary particles. These results clearly show that a balance between stability of the primary particle and the period of stable primary particle formation is important in preparing monodisperse particles.

Rate of Polymerization

Figure 3 shows a plot of conversion versus time for dispersion copolymerization in water-ethanol medium at different weight ratio of GMA/styrene (1/5, 2/5, and 3/5), compared with styrene dispersion polymerization (0/5) in water-ethanol medium. As the concentration of the GMA increases, the polymerization rate decreases. Because hydrophilicity of GMA is greater than that of styrene, the solvency of dispersion copolymerization of styrene with GMA in a water–ethanol medium increases with an increase in GMA concentration in the polymerization formulation. This increased solvency causes a decrease in the number of primary particles, indicating a decrease in the total surface area of particles. Therefore, the equilibrium distribution of monomer toward the particle phase was less favorable, which eventually results in a slow polymerization rate.

Determination of Epoxy Content

Table III represents the measured epoxy contents of PSG particles produced by dispersion polymerization according to the recipe in Table II. Th epoxy content data, reported as a percentage of the initial moles of epoxy in the recipe, indicate
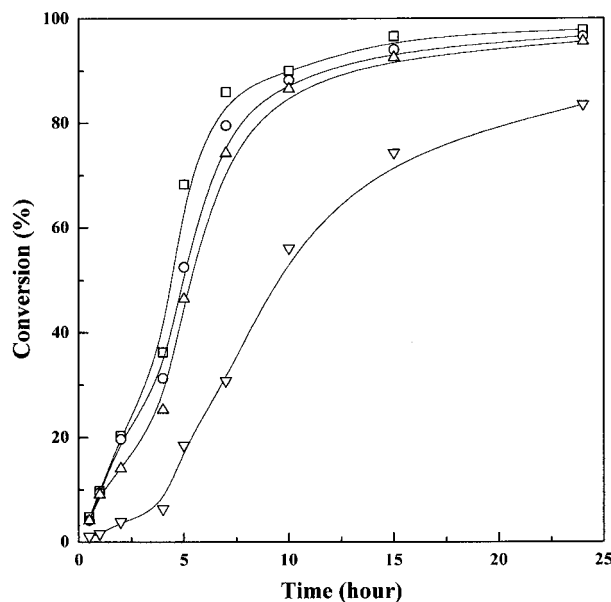

Figure 3 Polymerization rate for poly(styrene-*co*-GMA) microparticles with a weight ratio of GMA:styrene as follows: □ G:S2–0:5, ○ G:S2–1:5, △ G:S2–2:5, ▽ G:S2–3:5.

Table III   Remains of Epoxy Content of Poly(styrene-*co*-GMA) Particles[a]

Sample[b]	Remains of Epoxy Content (%)[c]
G/S2-0/5	—
G/S2-1/5	84.1 ± 5.1
G/S2-2/5	79.5 ± 3.1
G/S2-3/5	77.5 ± 4.7
G/S2-4/5	78.1 ± 2.5

[a] 70°C; 24 h; water–ethanol medium (water : ethanol = 10 : 90 wt %); 10 wt % of monomer concentration based on total weight; 1 wt % AIBN, based on monomer weight.
[b] G : Sα–β : γ; α-0.7 wt % PVP concentration based on total weight; β : γ weight ratio of GMA : styrene.
[c] Percentage based on initial charge of GMA, measured using the HCl–dioxane method.

that most epoxy groups remained after completion of dispersion copolymerization.

CONCLUSION

Micron-size polymer particles with a narrow size distribution were prepared by dispersion copolymerization of styrene with GMA. The size distribution of the copolymer particle was enhanced when GMA was added in a polymerization medium in which polystyrene homopolymer particles had a polydispersed morphology. The GMA played an important role as a costabilizer as well as a comonomer in the styrene with GMA dispersion copolymerization. The ability of GMA to be a costabilizer depends on the weight ratio of GMA to styrene. Because GMA has a greater hydrophilicity than styrene, the solvency of the monomer in the medium increased with an increase in GMA concentration, leading to a larger copolymer particle size and a slower polymerization rate as compared with those for the polymerization of homopolystyrene. In our copolymerization system it is likely the stable primary particles were formed because of the costabilizing effect of GMA during dispersion copolymerization. These stable primary particles grow without formation of new primary particles, resulting in the production of monodisperse polymer particles. After the dispersion copolymerization of styrene with GMA, large amounts of unreacted epoxy groups remained in the PSG particles, which will make these particles useful in many applications.

REFERENCES

1. Robin, J. L.; Hill, G. A.; Carle, B. N.; Carlquist, J. H.; Marcus, S. Proc Soc Exp Bio Med 1962, 109, 321

2. Margel, S.; Offarim, M. Anal Biochem 1982, 128, 342.

3. Grag, G. R. Anal Chem 1980, 52, 9R.

4. Van Den Hul, H. J.; Vanderhoff, J. W. J Coll Int Sci 1968, 28, 336.

5. Tokes, A. Z.; Rogers, K. E.; Rembaum, A. Proc Nut Acad Sci USA 1982, 79, 2026.

6. Ober, C. K.; Lok, K. P. U.S. Pat. 4,617,249 (1986).

7. Ugelstad, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T. N.; MØrk, P. C; Stenstad, P.; Hornes, E.; Olsvik, Ø. Prog Polym Sci 1992, 17, 87.

8. Sudol, E. D.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci 1986, 24, 3499.

9. Ugelstad, J.; MØrk, P. C.; Kaggerud, K. H.; Ellington, T.: Berge, A. Adv Coll Interf Sci 1980, 13, 101.

10. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci, Part A: Polym Chem 1986, 24, 2995.

11. Ober, C. K.; Lok, K. P. Can J Chem 1985, 63, 209.

12. Okubo, M.; Ikegami, K.; Yamamoto, Y. Colloid Polym Sci 1989, 267, 193.

13. Paine, A. J.; Luymens, W.; McNulty, J. Macromolecules 1990, 23, 3104.

14. Winnik, F. M.; Ober, C. K. Eur Polym J 1987, 23, 617.

15. Hattori, M.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 1993, 50, 2027.

16. Kim, J. W.; Suh, K. D. Colloid Polym Sci, 1988, 276, 870.

17. Shen, S.; El-Aasser, M. S.; Dimonie, V. L.; Vanderhoff, J. W.; Sudol, E. D. J Polym Sci, Part A: Polym Chem 1991, 29, 857.

18. Yang, W.; Hu, J.; Tao, Z.; Li, L.; Wang, C.; Fu, S. Colloid Polym Sci 1999, 277, 446.

19. Ober, C. K.; Lok, K. P. Macromolecules 1987, 20, 268.

20. Simms, J. A. J Appl Polym Sci 1991, 5, 58.

21. Zurkova, E.; Bouchal, K. ; Zdenkova, D.; Pelzbauer, Z.; Svec, F.; Kalal, J. J Polym Sci, Part A: Polym Chem 1983, 21, 2949.

22. Smigol, V.; Svec, F.; Kosoya, K.; Wang, Q.; Frechet, J. M. J. Angew Makromol Chem 1992, 195, 152.

23. Saenz, J. M.; Asua, J. M. J Polym Sci, Part A: Polym Chem 1996, 34, 1977.

24. Ho, C. H.; Chen, S. A.; Amiridis, M. D.; Van, Z. J. W. J Polym Sci, Part A: Polym Chem 1997, 35, 2907

25. Kline, G. M. Analytical Chemistry of Polymers; Interscience: New York, 1959; p 123.

26. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York 1982; p 42.

27. Kling, J. A.; Ploehn, H. J. J Polym Sci, Part A: Polym Chem 1995, 33, 1107.