

Effect of Polyurethane-Based Macromonomers in the Dispersion Polymerization of Styrene

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Received 7 October 2005; accepted 16 December 2005

DOI 10.1002/app.24713

Published online 12 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two different polyurethane-based macromonomers, a polyurethane macromonomer with methacrylamide (PUM-M) and a polyurethane macromonomer with acrylamide (PUM-A), were synthesized from poly(ethylene glycol)s (PEGs) of various molecular weights and two different amides, methacrylamide and acrylamide, and they were used for the dispersion polymerization of styrene. The structures of the macromonomers and polystyrene (PS) particles were verified with ^{13}C -NMR and Fourier transform infrared. The weight-average molecular weights of the PS particles increased with the macromonomer concentration but decreased with the PEG molecular weight. The average diameter of the PS particles increased with

the PEG molecular weights but decreased with the macromonomer concentration. The thermal stability of PUM-A-PS was enhanced, and its grafting ratio with 30 wt % PUM-A was much higher than that of PUM-M-PS. Thus, this study suggested that the polyurethane-based macromonomers act not only as reactive stabilizers but also as grafting agents in the dispersion polymerization. In addition, the acrylamide end group provided better thermal stability than methacrylamide. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2656–2664, 2008

Key words: dispersions; macromonomers; polystyrene; polyurethanes

INTRODUCTION

The use of macromonomers as reactive stabilizers¹ provides a facile route to control the molecular structures of polymers, including various types of crosslinked and branched copolymers.^{2–5} Macromonomers are a relatively new category of functionalized polymer materials having one or more reactive end groups.

Crosslinkable macromonomers composed of ethylene-butylene aliphatic hydrophobic chains and bifunctional terminal acrylic acid moieties have been synthesized^{6,7} and used as both costabilizers and crosslinking agents in the miniemulsion polymerization of *n*-butyl methacrylate. The most recent examples are methacryloxypropyl-terminal⁸ and vinyl-terminal polysiloxanes⁹ used in the dispersion polymerization of methyl methacrylate in nonpolar media. However, the development of bifunctional macromonomers based on ethylene oxide (PEO) or poly(ethylene glycol) (PEG) blocks is still unexploited.

In a previous study, novel bifunctional macromonomers consisting of PEO and urethane groups in the main chain and vinyl-terminal groups^{10,11} were

synthesized and applied to the dispersion polymerization of styrene. Polystyrene (PS) microspheres, having exceptionally high molecular weights, were prepared because of the possibility of crosslinking or grafting of the macromonomers.¹² In addition, various macromonomers consisting of PEGs with different number-average molecular weights and several terminal groups were synthesized, and the effects of the macromonomers on the synthesized PS prepared by dispersion polymerization were thoroughly investigated.¹³

In this study, vinyl-terminated polyurethane macromonomers with methacrylamide and acrylamide were synthesized and applied to the dispersion polymerization of styrene with various concentrations (5–30 wt %) of macromonomers. Then, the PEG number-average molecular weights and macromonomer-concentration-dependent characteristics of the PS particles, such as the conversion, weight-average molecular weight, weight-average diameter, uniformity, glass-transition temperature, thermal stability, and grafting ratio, were thoroughly investigated.

EXPERIMENTAL

Materials

PEGs with number-average molecular weights of 1000, 2000, 4000, and 8000 g/mol (PEG1000, PEG2000, PEG4000, and PEG8000, respectively) and

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Contract grant sponsor: Inha University (2005).

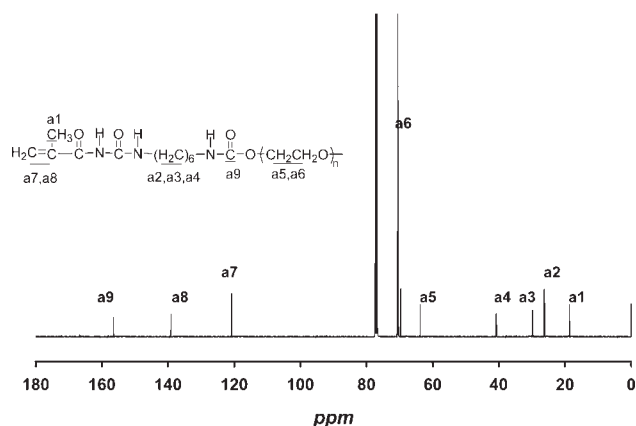


Figure 1 Representative ^{13}C -NMR spectrum of PUM(4000)-M.

bon ($\text{C}=\text{O}$) of the urethane group can be observed at 156.6 ppm (a9). The important characteristic signals of the vinyl carbon in the macromonomer can be detected between 120 and 140 ppm. The signals at 120.9 and 139.3 ppm (a7 and a8) can be attributed to methyl carbons ($\text{CH}_2=\text{CH}-$) of the terminal vinyl groups of the macromonomer. Therefore, Figure 1 clearly confirms the existence of the terminal vinyl groups in the synthesized macromonomer.

The calculated and experimental molecular weights of two macromonomers, PUM-M and PUM-A, as a function of the macromonomer concentration and the PEG molecular weights, and experimentally obtained polydispersity indices (PDIs) are listed in Table I. The experimental values are slightly higher than the calculated ones, and the PDIs become narrower with the PEG molecular weight.

PS prepared with the macromonomers

Figure 2(A–C) presents the FTIR spectra of the PUM(4000)-M macromonomer, PS synthesized with polyvinyl pyrrolidone (PVP, $M_w = 40$ K) and PS synthesized with the macromonomer, respectively. In Figure 2(A), the broad peaks at 3460–3400 and

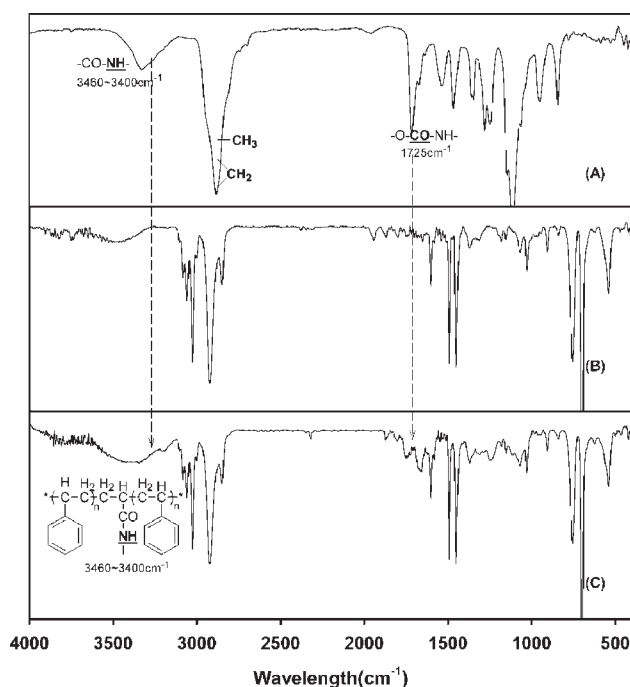


Figure 2 Representative FTIR spectra of (A) the PUM(4000)-M macromonomer, (B) PS synthesized with the commercial stabilizer PVP, and (C) PS synthesized with the macromonomer.

1725 cm^{-1} represent the characteristic peak of amine in the urea group ($-\text{NH}-\text{CO}-\text{NH}-$) and the carbonyl stretching peak of the urethane group ($-\text{NH}-\text{CO}-\text{O}-$), respectively. Figure 2(B) depicts the FTIR spectrum of PS synthesized with PVP; the small, broad peak of the urea group at 3460 cm^{-1} and the carbonyl stretching of the urethane group at 1725 cm^{-1} can be observed. In Figure 2(C), the PS particles prepared by the macromonomer show the typical functional group at $3460\text{--}3400\text{ cm}^{-1}$ and the carbonyl stretching peak at 1725 cm^{-1} of the urethane group. This is evidence that PVP and the macromonomer are incorporated into the PS particles.

Figure 3 depicts the conversion of the polymerization of PUM-M-PS and PUM-A-PS with the macromonomer concentration as a function of the

TABLE I
Comparison of the Calculated and Experimental Molecular Weights of Two Different Macromonomers

	Macromonomer							
	PUM-M				PUM-A			
M_n (g/mol) ^a	1000	2000	4000	8000	1000	2000	4000	8000
M_w ^b	1506	2506	4506	8506	1482	2482	4482	8482
M_w ^c	1806	2678	4895	9062	1625	1980	4850	8984
PDI	2.793	2.378	1.042	1.262	1.689	1.029	1.072	1.214

^a Number-average molecular weight of PEG.

^b Calculated weight-average molecular weight.

^c Weight-average molecular weight experimentally obtained with gel permeation chromatography.

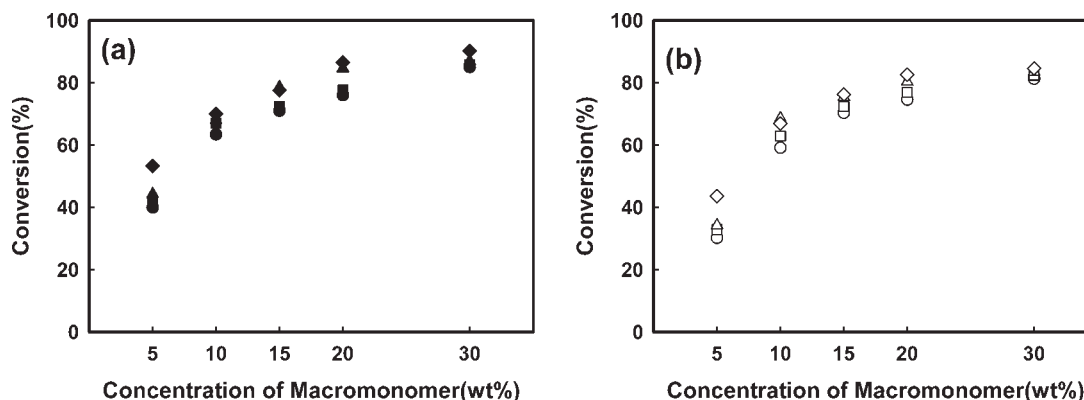


Figure 3 Conversion of PS prepared with various concentrations of (a) PUM-M and (b) PUM-A: (●) PUM(1000)-M-PS, (■) PUM(2000)-M-PS, (▲) PUM(4000)-M-PS, (◆) PUM(8000)-M-PS, (○) PUM(1000)-A-PS, (□) PUM(2000)-A-PS, (△) PUM(4000)-A-PS, and (◇) PUM(8000)-A-PS.

PEG molecular weight. In both systems, the higher the macromonomer concentration, the higher the conversion obtained, whereas no significant effect of the PEG molecular weight on the conversion was obtained. In addition, the conversion increased with the macromonomer concentration, and as a result, the maximum conversion was 82–90% with a 30 wt % concentration of the macromonomer in both systems.

Figure 4 depicts a representative ^{13}C -NMR spectrum of PS [for a specimen of PUM(4000)-M-PS] synthesized by a reaction of PEG4000, HDI, methacrylamide, and SM in dispersion polymerization at 70°C for 24 h. In Figure 4, the signal at 40.4 ppm (a'1) is attributed to methyl carbons ($-\text{CH}_2\text{CH}-$) of PS, and three peaks at 125.6, 127.9, and 145.1 ppm (a'3, a'4, and a'5, respectively) are the phenyl groups of PS stabilized by PUM(4000)-M. The repeating EO unit ($-\text{CH}_2\text{CH}_2\text{O}-$) results in 70.5 ppm (a'2). The carbons in the vinyl-functional group ($\text{C}=\text{C}$) at 121.0 and 139.3 ppm (a7 and a8) in Figure 1 are clearly absent in Figure 4. The disappearance of the vinyl groups in the macromonomer after polymerization is indicative of the reaction capability with SM.

Figure 5 shows the weight-average molecular weights of the synthesized polymers, PUM-M-PS and PUM-A-PS, as a function of the macromonomer concentration and the PEG molecular weight. In both systems, the molecular weight of PS increased with the macromonomer concentration, but inverse behavior was observed with the PEG molecular weight. However, for the PUM(8000)-M system, no particular effect of the macromonomer concentration on the PS molecular weight was observed. In addition, the molecular weights of PUM-M-PS were higher than those of PUM-A-PS.

Figure 6 depicts the representative SEM photographs of the synthesized PS (PUM-M-PS) prepared by the reaction of the macromonomer, PEGs of various number-average molecular weights (from 1000

to 8000), methacrylamide, and SM at 70°C for 24 h in 15 wt % ethanol. As expected, spherical particles were obtained, and this implied that the macromonomer acted as a reactive stabilizer in the dispersion polymerization. In addition, the average particle size increased with the increased molecular weight of the macromonomer. This indicated that the smaller the PEG molecular weight, the higher the stability observed; this means that a smaller particle size was obtained. This is typical behavior of ordinary stabilizers.

The average particle sizes of the representative PUM(4000)-M-PS and PUM(4000)-A-PS synthesized with various concentrations of the macromonomers are compared in Figure 7. The weight-average diameter of PUM(4000)-M-PS decreased from 2.85 to 2.4 μm with the macromonomer concentration increasing from 10 to 30 wt %, whereas that of PUM(4000)-A-PS decreased from 3.2 to 2.2 μm with the same range of macromonomer concentrations.

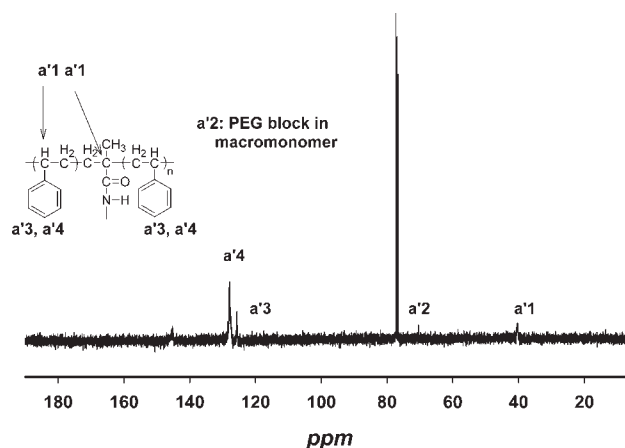


Figure 4 ^{13}C -NMR spectrum of PUM(4000)-M-PS.

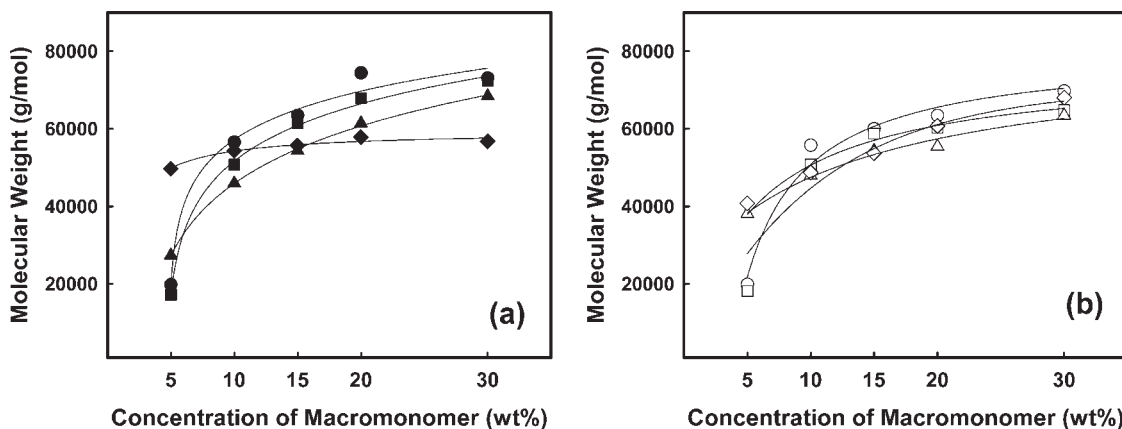


Figure 5 Weight-average molecular weights of PS prepared with various concentrations of (a) PUM-M and (b) PUM-A: (●) PUM(1000)-M-PS, (■) PUM(2000)-M-PS, (▲) PUM(4000)-M-PS, (◆) PUM(8000)-M-PS, (○) PUM(1000)-A-PS, (□) PUM(2000)-A-PS, (△) PUM(4000)-A-PS, and (◇) PUM(8000)-A-PS.

The overall variance of the weight-average diameter of the synthesized PS is quantitatively analyzed and plotted in Figure 8. The common feature is that the weight-average diameter decreases with the macromonomer concentration but increases with the PEG molecular weight. The weight-average diameter of PUM-A-PS is larger than that of PUM-M-PS, and this implies that acrylamide is better for making sta-

ble particles (small particles) than methacrylamide. This behavior is the inverse of the behavior of the molecular weight of the particles, as shown in Figure 5, but it is a consistent result typically obtainable in dispersion polymerization. This phenomenon indicates that the decrease in the particle size with the PEG molecular weight is pronounced because the macromonomer effectively stabilizes a greater sur-

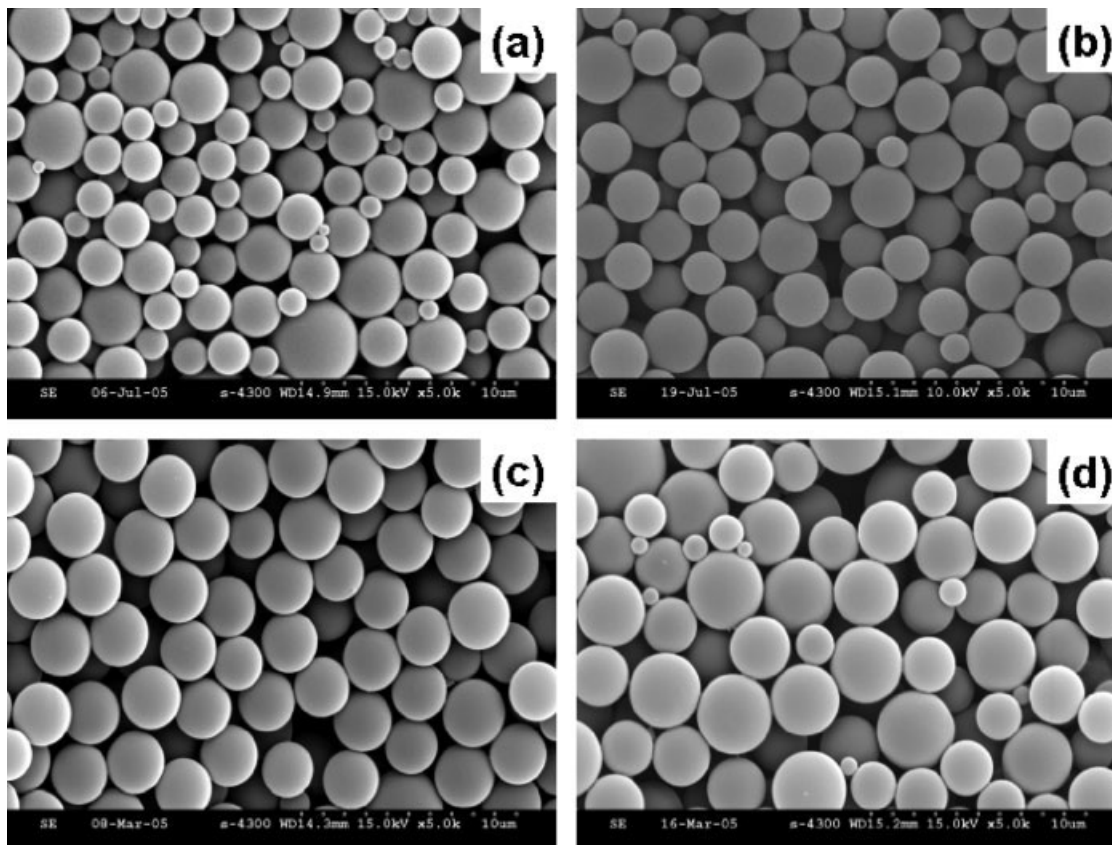


Figure 6 SEM photographs of synthesized PS microspheres prepared with various PUM-M macromonomers (15 wt %): (a) PUM(1000)-M, (b) PUM(2000)-M, (c) PUM(4000)-M, and (d) PUM(8000)-M.

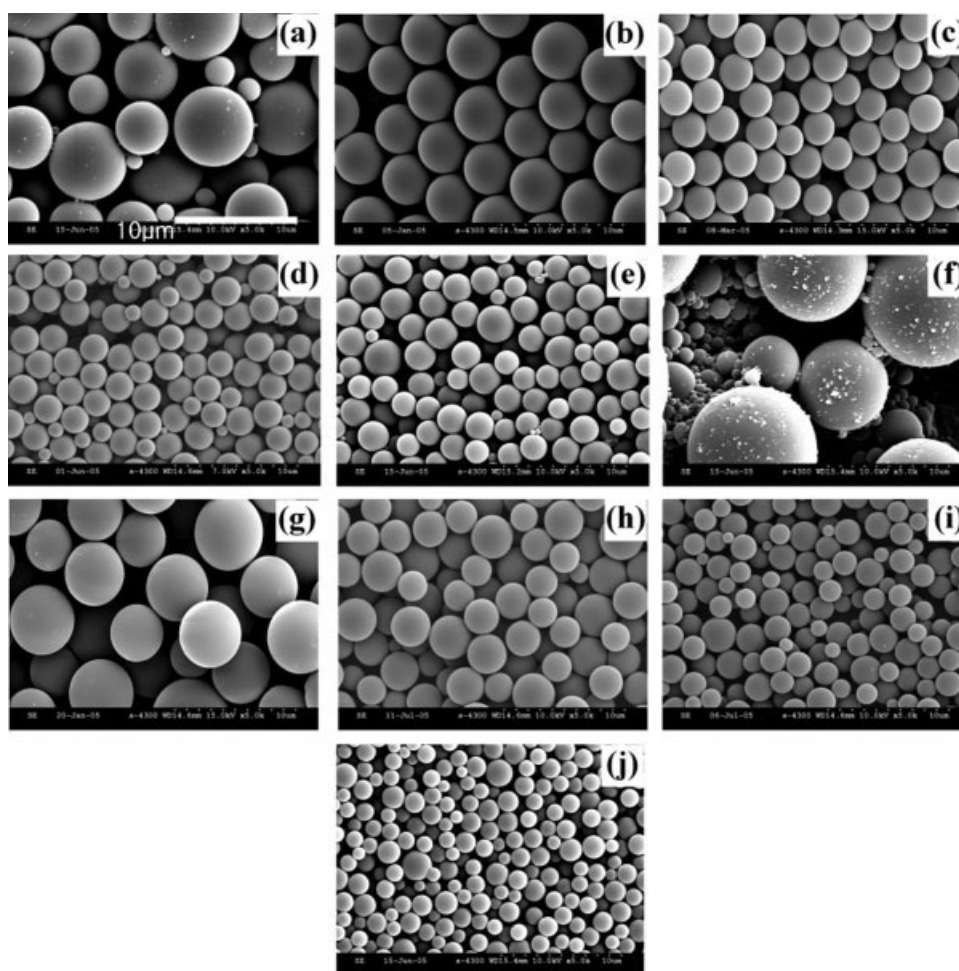


Figure 7 SEM photographs of synthesized PS microspheres prepared with PUM(4000)-M and PUM(4000)-A at various concentrations: (a) 5, (b) 10, (c) 15, (d) 20, and (e) 30 wt % PUM(4000)-M and (f) 5, (g) 10, (h) 15, (i) 20, and (j) 30 wt % PUM(4000)-A.

face area of the PS particles. In addition, when a relatively low concentration of the macromonomers (10 or 15 wt %) was used, the largest diameter of PUM-

M-PS and PUM-A-PS was obtained with PEG 4000, whereas when a relatively large amount of the reactive stabilizers (20 or 30 wt %) was used, the largest

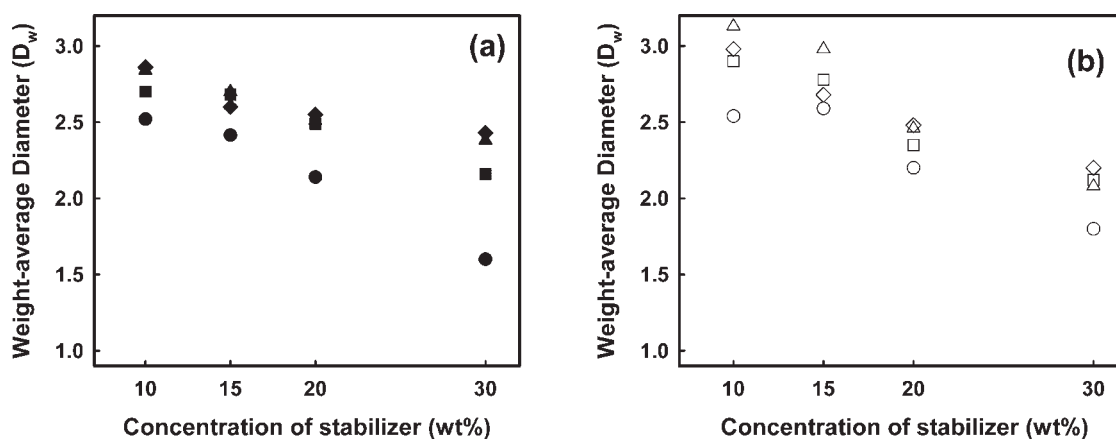


Figure 8 Weight-average diameters of PS prepared with various concentrations of (a) PUM-M and (b) PUM-A: (●) PUM(1000)-M-PS, (■) PUM(2000)-M-PS, (▲) PUM(4000)-M-PS, (◆) PUM(8000)-M-PS, (○) PUM(1000)-A-PS, (□) PUM(2000)-A-PS, (△) PUM(4000)-A-PS, and (◇) PUM(8000)-A-PS.

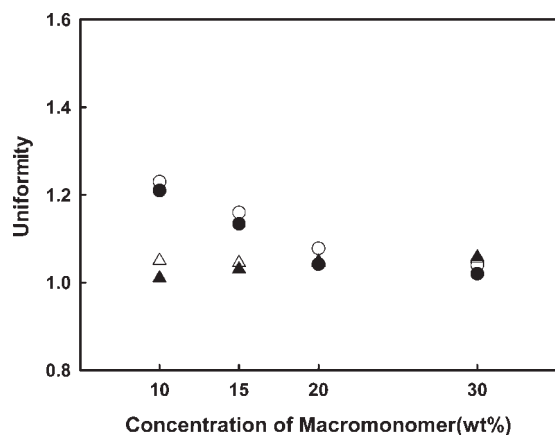


Figure 9 Uniformity of synthesized PS prepared with various concentrations of PUM-M (solid symbols) and PUM-A (open symbols): (●) PUM(1000)-M, (▲) PUM(4000)-M, (○) PUM(1000)-A, and (△) PUM(4000)-A.

diameter of both polymers was obtained with PEG8000.

Figure 9 depicts the representative uniformity (weight-average diameter/number-average diameter) (D_w/D_n) of the PS particles versus the macromonomer concentration between PEG1000 and PEG4000. The uniformity of the PS particles prepared with PEG1000 slightly decreased from 1.28 to 1.02 with the macromonomer concentration, but that of the PS particles prepared with PEG4000 slightly increased from 1.01 to 1.06 with the macromonomer concentration from 10 to 30 wt %. This implies that the uniformity increases with the PEG molecular weight and the macromonomer concentration.

Figure 10 shows the glass-transition temperatures of the synthesized PUM-M-PS and PUM-A-PS versus the macromonomer concentration and PEG molecular weight. The glass-transition temperature varied from 96 to 103°C for PUM-M-PS and from 97

to 103°C for PUM-A-PS; thus, no significant difference in the glass-transition temperature of the PS particles upon variations in the PEG molecular weight and macromonomer concentration was observed. Thus, the macromonomer was working not only as a reactive stabilizer but also as an agent enhancing the thermal properties of the polymers. This observation follows the theoretical background.

Grafting of the macromonomers with PS

The data were obtained by the calculation of the grafting ratio with the equation proposed by Shay et al.¹⁴ and with the ¹H-NMR spectra of the synthesized PS. Two broad peaks ranging from 6 to 7.2 ppm are mainly attributed to the aromatic protons of PS. The small, narrow peak at 3.7 ppm evidently originated from the methyl protons of the PEO block in the polyurethane macromonomer.¹⁵ Figure 11(a,b) depicts the calculated grafting ratio as a function of the macromonomer concentration and PEG molecular weight. No particular difference in the grafting ratio between PUM-M-PS and PUM-A-PS up to a 20 wt % concentration of the macromonomer with the PEG molecular weight was observed. However, the grafting ratios of the two polymers, PUM-M-PS and PUM-A-PS, with a 30 wt % concentration of the macromonomer were markedly different; the grafting ratio of the former PS varied from 0.05 to 0.16 with the PEG molecular weight changing from 8000 to 1000. Whereas that of PUM-A-PS varied from 0.03 to 0.27 for the same molecular weight range of PEG. The high grafting ratio of PUM(1000)-A-PS resulted in the low molecular weight of PS, as shown in Figure 5. Because the grafting ratio is calculated as the ratio of the reacted PEO to PS, the higher grafting ratio means that the amount of PEO

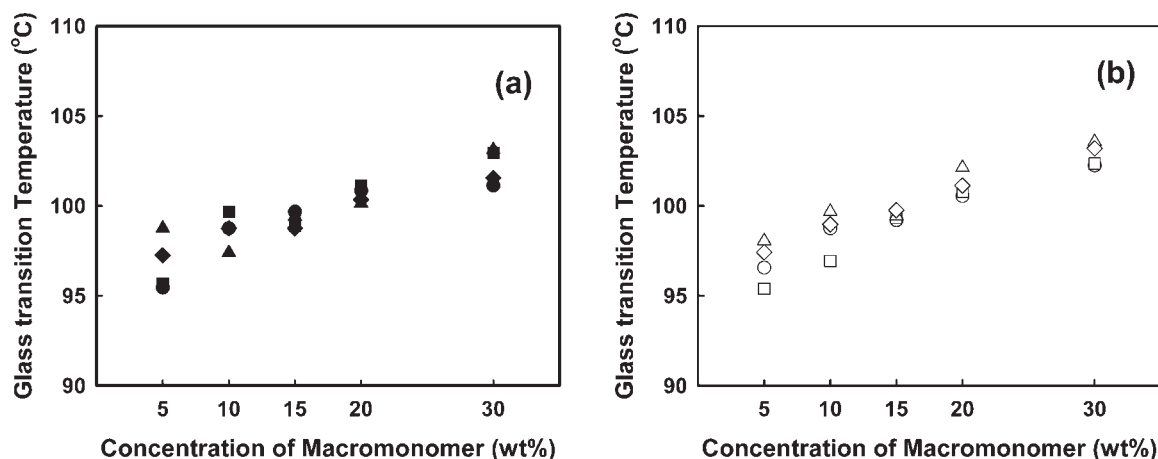


Figure 10 Glass-transition temperatures of PS prepared with various concentrations of (a) PUM-M and (b) PUM-A: (●) PUM(1000)-M-PS, (■) PUM(2000)-M-PS, (▲) PUM(4000)-M-PS, (◆) PUM(8000)-M-PS, (○) PUM(1000)-A-PS, (□) PUM(2000)-A-PS, (△) PUM(4000)-A-PS, and (◇) PUM(8000)-A-PS.

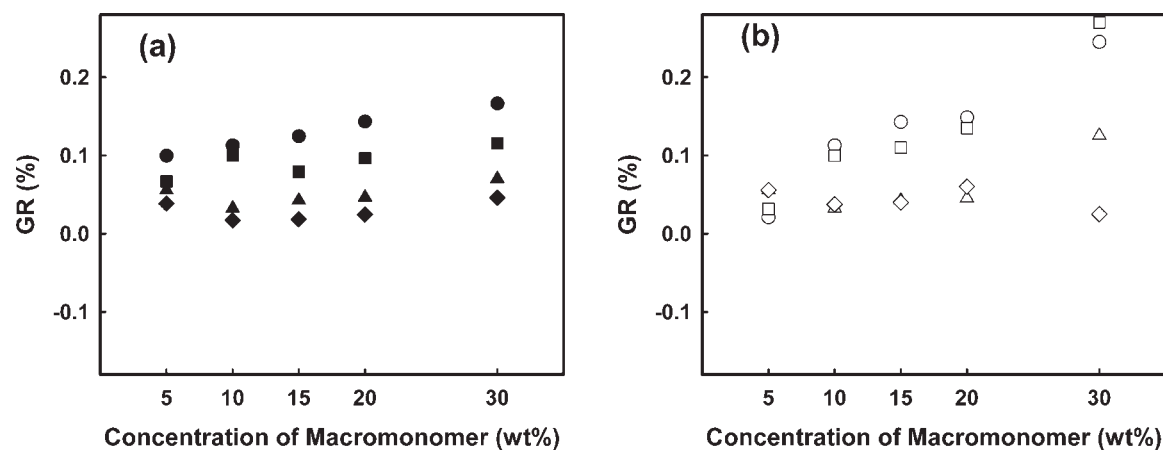


Figure 11 Grafting ratio (GR) of synthesized PS prepared with various concentrations of (a) PUM-M and (b) PUM-A: (●) PUM(1000)-M-PS, (■) PUM(2000)-M-PS, (▲) PUM(4000)-M-PS, (◆) PUM(8000)-M-PS, (○) PUM(1000)-A-PS, (□) PUM(2000)-A-PS, (△) PUM(4000)-A-PS, and (◇) PUM(8000)-A-PS.

is relatively large in comparison with styrene repeating units in PUM-A-PS versus PUM-M-PS. This phenomenon is rationalized by the fact that PUM-M consists of a methyl group, which is relatively bulky for reacting with SM; therefore, less grafting takes place, and this results in most polymerization occurring between SMs. In addition, it is thought that the reacted macromonomer molecules exist on the surface of the PS particles because the hydrophilic PEO blocks will prefer to migrate to the alcoholic (ethanol) medium.¹⁶ The small grafting ratio is ascribed to the high molecular weight of the macromonomer working as a grafting agent.

CONCLUSIONS

Vinyl-terminated polyurethane-based macromonomers were synthesized from PEGs of various molecular weights, HDI, and two different monomers, methacrylamide and acrylamide. The various concentrations of the macromonomers (PUM-M and PUM-A) from PEG1000, PEG2000, PEG4000, and PEG8000 were applied to synthesize the stable PS particles. The structural verification of the macromonomers and PS was confirmed with ¹³C-NMR and FTIR. The maximum conversion varied between 82 and 90% with 30 wt % concentrations of the macromonomer in both systems. The weight-average molecular weights of the PS particles increased with the macromonomer concentration but decreased with the PEG molecular weight. However, the weight-average molecular weight of PUM-M-PS was larger than that of PUM-A-PS. The average diameter of the PS particles increased with the PEG molecular weights but decreased with the macromonomer concentration. In addition, the average particle size of PS decreased with the macromonomer concentration

but increased with the PEG molecular weight. In particular, the particle size based on the monomers derived from methacrylamide was larger than that of the acrylamide derivative monomer. The inverse behavior between the molecular weight and the particle size is a typical characteristic of dispersion polymerization. The thermal degradation temperature of PUM-A-PS was higher than that of PUM-M-PS, and this indicated that acrylamide was favorable for higher thermal stability of the PS particles. The grafting ratio of PS calculated from ¹H-NMR spectra increased with the macromonomer concentration but decreased with the PEG molecular weight. In particular, the grafting ratio of PUM-A-PS with 30 wt % macromonomer dramatically increased from 0.03 to 0.27 with the PEG molecular weight. The thermal stability of PUM-A-PS was enhanced, and its grafting ratio with 30 wt % PUM-A was much higher than that of PUM-M-PS. Thus, our results suggest that the bifunctional macromonomers act not only as reactive stabilizers but also as grafting agents, enhancing the thermal properties. In addition, acrylamide end groups provide improved thermal stability in comparison with methacrylamide.

S. Choe thanks Inha University for the financial support.

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