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Macromonomers having different molecular weights of polyethylene glycol and end group functionalities in dispersion polymerization of styrene

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Abstract

Bifunctional polyurethane-based macromonomers (BPUM) were synthesized from various molecular weights of polyethylene glycol (PEG) and hexamethylene diisocyanate (HDI) with different end group functionalities. The synthesized BPUMs were applied to the dispersion polymerization of styrene in ethanol. Structures of various macromonomers and PS particles were investigated using ^{1}H NMR. Molecular weights of PEG 1000, 2000, 4000, and 8000 were able to provide stable particles of polystyrene (PS), whereas PEG 400 was not big enough to form stable particles. Although the final conversion was almost constant, average size of the PS microspheres increased with PEG molecular weights. The inverse relationship between the size of particles and molecular weight of PS was observed. In particular, the particle size based on the monomers derived with acrylamide was larger than acrylate derivative monomers. As the molecular weight of PEG increased, the thermal stability was enhanced and leveled off. The grafting ratio of the PS calculated from ^{1}H NMR spectra exponentially decreased from 1.05 to 0.18 mol% with the increased molecular weight of PEG. Thus, present study suggests that the bifunctional macromonomers act not only as reactive stabilizers, but also as grafting agents in dispersion polymerization.
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1. Introduction

The preparation of macromolecules with pre-defined structures of block, graft, and star copolymers has received an extensive attention due to their unique chemical and physical properties [1–4]. In the synthesis of such polymers, several polymerization techniques have been used including living ionic polymerizations [5] and controlled/living radical polymerization [6]. However, these methods require relatively stringent conditions during the polymerization.

Macromolecular monomers, so called macromonomers, have been introduced in the mid 1970s [7] as reactive stabilizers. The use of macromonomers provides a facile route to control the molecular structure of polymers including cross-linked and branched copolymers such as comb, star, brush, and graft types [8–11]. In addition, the macromonomers can be used in the preparation of polymer colloids instead of surfactants or steric stabilizers in heterogeneous polymerizations [12]. Compared to the conventional surfactants or stabilizers, the utilization of macromonomers is advantageous, since desorption and migration of the macromonomers from the latex is minimized due to their chemical binding with matrices. Therefore, the macromonomer could be employed when prolonged stabilization or preservation of the latex is needed [13].

Macromonomers are relatively new category of functionalized polymer materials having one or more reactive polymerizable end groups. The most intensively studied macromonomers consist of poly(ethylene oxide) (PEO) block functionalized with styryl, methacryloyl, thiol, maleate, vinyl, p-vinylphenylalkyl reactive end groups [14–17]. The

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advantage of PEO-derived macromonomers is a good solubility in water as well as various alcohols. It is worthy to note that these macromonomers are monofunctional. However, studies on the synthesis and utilization of bifunctional macromonomers, and their polymerization characteristics are still limited to date [18]. The most recent examples are methacryloxypropyl- [19] and vinyl-terminal [20] polysiloxanes used in the dispersion polymerization of methyl methacrylate (MMA) in non-polar media.

Lightly cross-linked polymer microspheres have been produced using bifunctional urethane acrylate as a cross-linking agent in the presence of conventional stabilizer in dispersion polymerization [21,22]. The bifunctional macromonomers consisting of ethylene–butylene aliphatic hydrophobic chain and bifunctional terminal acrylic groups have been used as a both co-stabilizer and cross-linker in the miniemulsion polymerization of *n*-butyl methacrylate [18].

Very recently, our group has synthesized novel bifunctional macromonomers consisting of PEO and urethane groups in the main chain and vinyl-terminal groups [23,24]. These macromonomers were applied to dispersion polymerization of styrene and the PS microspheres having exceptionally high molecular weights were prepared due to a possibility of cross-linking or grafting of the macromonomer [25].

In this article, we synthesized various macromonomers consisting of PEG with different molecular weights and several terminal groups using methacrylamide, hydroxyl ethymethacrylate, hydroxyl ethylacrylate, and acrylamide. Furthermore, the effects of molecular weights and terminal groups of the macromonomers on the dispersion polymerization of styrene were thoroughly investigated in terms of the conversion, molecular weights, size variation of the PS microspheres, thermal properties, and grafting ratio.

2. Experimental section

2.1. Materials

Poly(ethylene glycol) (PEG) having number-average molecular weights 400, 1000, 2000, 4000, and 8000 g/mol (each of them is called PEG400, PEG1000, PEG2000, PEG4000, and PEG8000, respectively) and hexamethylenediisocyanate (HDI) were supplied by Aldrich Co. (USA) and used as received. Methacrylamide (MAAM, Aldrich), hydroxyl ethylmethacrylate (HEMA), hydroxyl ethylacrylate (HEA), and acrylamide (AAM) were purified by recrystallization in methanol twice prior to use. The chemical structures of these chemicals are listed in Table 1. Highly pure acetone (Samchun Co., Korea) as the reaction medium for the synthesis of polyurethane and double-distilled deionized water (DDI) were used. Methyl ethyl ketone (MEK, Samchun) was used as received. As an initiator, analytical grade of 2,2-azobisisobutyronitrile (AIBN, Junsei, Japan) was used without further purification.

Styrene (SM, Junsei) and ethanol (99%; Samchun) were used as the monomer and medium for the dispersion polymerization, respectively.

2.2. Synthesis

The isocyanate-terminated polyurethane pre-polymer is synthesized by the reaction of 1:2 molar ratio of PEG with various molecular weights (for example for PEG400, 0.05 mol, 100 g) and HDI (0.1 mol, 4.21 g) in MEK at 80 °C. The macromonomers having different molecular weights were synthesized by the reaction of 1:2 molar ratio of isocyanate-terminated pre-polymer (0.025 mol, 104.21 g) and MAAM (0.05 mol, 2.13 g) in acetone medium. The details of the synthetic procedure and the confirmation of chemical structure of the macromonomer are described in our previous publication [23]. Scheme 1 illustrates a representative synthetic route of an isocyanate-terminated pre-polymer and resultant bifunctional vinyl-terminated polyurethane macromonomer of PUM–MAAM. The other macromonomers such as PUM–AAM, PUM–HEMA, and PUM–HEA (see Table 1 for the abbreviation) were synthesized in the same way.

Dispersion polymerization was carried out in a 50 mL capped scintillation vial with magnetic stirring under nitrogen atmosphere. Twenty-five grams of ethanol was first poured in the vial, 10 wt% SM (2.5 g) relative to the ethanol was charged. The concentration of macromonomers was fixed at 10 wt% to SM throughout the dispersion polymerization. The initiator, 0.1 wt% of AIBN (0.025 g) relative to SM, was used and the polymerization was carried out at 70 °C under nitrogen atmosphere for 24 h. During the polymerization, aliquots of sample were periodically taken from the reaction vessel for characterization. After completion of the polymerization, the resultant material was rinsed off with DDI water and methanol, then centrifuged repeatedly in order to remove the non-reacted residual macromonomer or monomer.

2.3. Characterization

In order to confirm the structure of the macromonomers and PS synthesized with the macromonomers, Varian 400 MHz ^{1}H NMR using CDCl$_3$ was used. The molecular weights of the PS microspheres were measured using Waters GPC (gel permeation chromatography) equipped with 510 differential refractometer and Viscotek T50 differential viscometer. 500, 10^2, and 10^3 Å μ-styragel packed high resolution-columns were employed. Before the measurement of the synthesized materials, the calibration was carried out using 10 polystyrene standard samples (Polymer Laboratories, UK) with molecular weight ranging 580–7,500,000 g/mol. The PS dissolved in THF were injected at a flow rate of 1.0 ml/min. Hitachi S-4300 of SEM (scanning electron microscopy) was used to investigate the morphology and size of the PS particles. The

Table 1
Chemical structure of acrylate and amide derivatives and their abbreviations used in this study

Isocyanate-terminated polyurethane pre-polymer (PUM)		Bifunctional polyurethane macromonomer (BPUM)		Polymer	
(PEG)	HDI	Monomer	Macromonomer	Monomer (styrene)	Polymer
M_n: 400, 1000, 2000, 4000, 8000	HDI	MAAM	PUM–MAAM	SM	PUM–MAAM–PS[a]
	HDI	AAM	PUM–AAM	SM	PUM–AAM–PS
	HDI	HEMA	PUM–HEMA	SM	PUM–HEMA–PS
	HDI	HEA	PUM–HEA	SM	PUM–HEA–PS
Chemical name (abbreviation)	Hexamethylene diisocyanate (HDI)	Methacrylamide (MAAM)	Acrylamide (AAM)	Hydroxyl ethylmethacrylate (HEMA)	Hydroxyl ethylacrylate (HEA)
Chemical structure	O=C=N(CH₂)₆– N=C=O	H₂C=C–C–NH₂ (CH₃)	H₂C=C–C–NH₂ (H)	H₂C=C–C–OCH₂CH₂OH (CH₃)	H₂C=C–C–OCH₂CH₂OH (H)
Molecular weight (g/mol)	168	85	73	130	116

[a] PUM (2000)–MAAM–PS means that the PS is prepared using PEG 2000, HDI, MAAM, and SM.

weight-average (D_w), number-average (D_n) diameter, and the uniformity (D_w/D_n) were obtained by counting 100 particles in SEM photographs using Scion Image Analyzer®. The monomer conversion to polymer was determined by ^{1}H NMR.

The thermal degradation temperature of the prepared PS microspheres was measured by means of Perkin–Elmer TGA-7 (thermal gravimetric analysis) at a heating rate of 20 °C/min from 0 to 800 °C under nitrogen environment. The onset of degradation temperature was determined at the point with a maximum derivative.

The grafting ratio (GR) was calculated from the ^{1}H NMR spectra of PS using the following equation [26]:
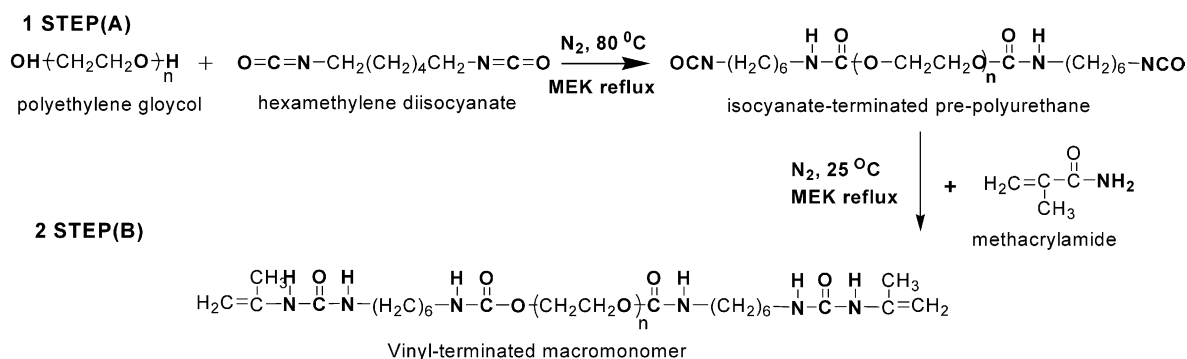
$$GR = \frac{5 \text{ protons per SM unit}}{\text{area under SM protons peaks}}$$

$$\times \frac{\text{area under EO proton peak}}{4 \text{ protons per EO unit}} \times \frac{1}{n_{EO}} \quad (1)$$

where n_{EO} denotes the number of ethylene oxide (EO) units in the macromonomer.

3. Results and discussion

3.1. Characterization of macromonomer

The structural verification is carried out using ^{1}H NMR. The representative confirmation of PUM(4000)-MAAM is shown in Fig. 1. The peak assignment is shown on the spectrum, in particular, the strong signal at 3.6 ppm (a) characterizes EO unit (–CH_2CH_2O–) of PEG, whereas the methylene protons (–CH_2–) of HDI are observed at 1.3, 1.5, and 3.2 ppm (e). The methylene protons (=CH_2) of vinyl group in PBUM are detected at 5.4 and 5.7 ppm (b) and (c) and the signal at 1.9 ppm (d) is a characteristic peak of the methyl protons (–CH_3) in PBTM. Although the protons of the urethane group (–NHCOO–) of BPUM are expected to appear at 8.07 ppm in this spectrum, they are not observed, since the number of urethane groups in a relatively gigantic BPUM molecule is quite small. However, we were able to detect those protons in the polyurethane macromonomers having a similar structure in our previous study [23]. Since the macromonomers are prepared by reacting polyol and isocynate, it is thought that urethane groups are inevitably

1 STEP(A)

OH(CH₂CH₂O)ₙH + O=C=N–CH₂(CH₂)₄CH₂–N=C=O →(N₂, 80 °C, MEK reflux)→ OCN–(H₂C)₆–N–C(O–CH₂CH₂O)ₙ–C–N–(CH₂)₆–NCO

polyethylene gloycol   hexamethylene diisocyanate   isocyanate-terminated pre-polyurethane

N₂, 25 °C
MEK reflux   +   H₂C=C–C–NH₂ (CH₃)

methacrylamide

2 STEP(B)

H₂C=C–N–C–N–(H₂C)₆–N–C–O(CH₂CH₂O)ₙC–N–(CH₂)₆–N–C–N–C=CH₂

Vinyl-terminated macromonomer

Scheme 1. A representative synthetic route for making vinyl-terminated macromonomer for PUM–MAAM.
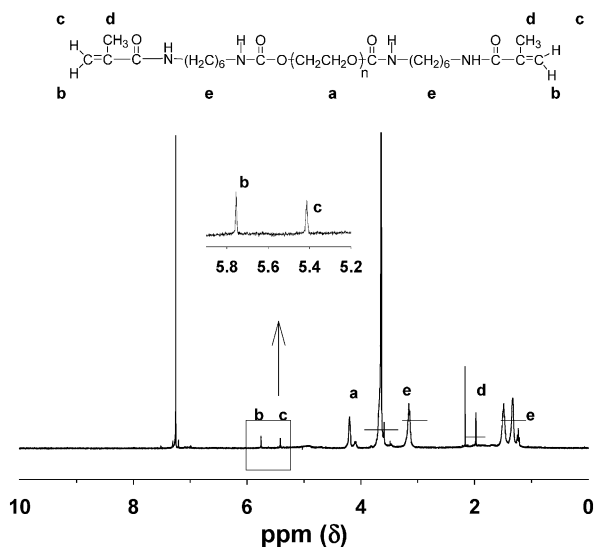
Fig. 1. Representative ^{1}H NMR spectrum for PUM(4000)–MAAM macromonomer.

Fig. 2. ^{1}H NMR spectrum for the confirmation of PUM (2000)–MAAM–PS.

developed. Throughout the investigation using ^{1}H NMR spectrum of each macromonomer, the structures of sixteen macromonomers are verified. The synthesized four BPUMs are abbreviated as PUM–MAAM, PUM–AAM, PUM–HEMA, and PUM–HEA and the specific molecular weight of PEG is presented as a number next to PUM. For example, if PEG 2000 is used for preparation of BPUM using MAAM, the abbreviation of the final product is PUM(2000)–MAAM.

Fig. 2 represents the ^{1}H NMR spectra of PS (for a representative specimen for PUM(4000)–MAAM–PS) synthesized by a reaction of PEG4000, HDI, MAAM, and styrene monomer (SM) in the dispersion polymerization at 70 °C for 24 h. The peak assignment is carried out, where only two-peak groups are interested in calculation of grafting ratio using the above Eq. (1). EO unit ($-CH_2CH_2O-$) of PEG is characterized in 3.65 ppm (a) and the two broad peaks located between 6 and 7.5 ppm primarily represent the aromatic protons of PS. Furthermore, it is clearly seen that the vinyl protons in BPUM at 5.4 and 5.7 ppm shown in Fig. 1 disappeared after polymerization, which means that the BPUM participates in the reaction with styrene during the polymerization. The terminal vinyl groups in BPUM are depleted after polymerization, since the vinyl protons are not detected from the ^{1}H NMR spectrum of PS in Fig. 2. Furthermore, the ^{1}H NMR spectrum reveals that BPUM molecules are grafted with PS chains to form the structure also shown in Fig. 2. Therefore, one can conclude that BPUM can serve both as a reactive stabilizer and a grafting agent. Although a cross-linking reaction is expected to occur due to the a symmetric vinyl groups in BPUM, we use the term of 'grafting' since the molecular weights of PS and formation of covalent bonds between BPUM and PS investigated in terms of grafting ratio are not significantly increased, which
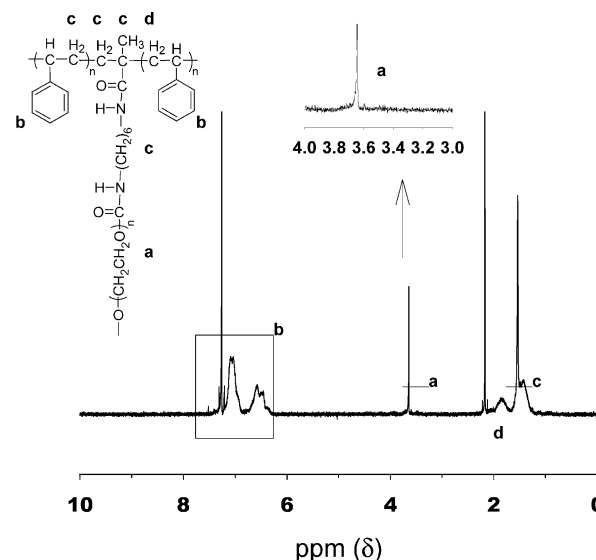
will be discussed in a following section. In fact, the choice of terminology between the cross-linking and grafting is still debatable in these systems. These may be the fact that relatively low concentrations of the macromonomers compared to that of monomer are used in our system. It is thought that the macromonomers possess reactive vinyl terminal group, the reaction between the macromonomers and growing PS molecules would be facilitated. Truly, when a significantly high concentration of a similar bifunctional macromonomer, which is 100 wt% of the macromonomer relative to styrene monomer, is reacted, the stable PS microspheres insoluble in THF have been prepared by a cross-linking reaction in dispersion polymerization [23].

Fig. 3 shows the representative SEM photographs of the synthesized PS (PUM–MAAM–PS) prepared by the reaction of BPUM with various molecular weights of PEG and methacrylamide with SM at 70 °C for 24 h in 10 wt% acetone. As usual, spherical particles are obtained, implying that BPUM acts as a reactive stabilizer in the dispersion polymerization except for PEG400. In addition, the average particle size increases with PEG molecular weight. In particular, for PS particles prepared with PEG4000 and PEG8000, the particle sizes are fairly monodisperse. For the polymers prepared with PEG400, however, the major part is formed in resin type by coagulation, implying the BPUM consisting of PEG400 is not sufficiently large enough for working as a steric stabilizer.

In Fig. 4, the SEM photographs of the synthesized PS (PUM–HEMA–PS) prepared by the reaction of various molecular weights of PEG with HDI and hydroxyl ethylmethactylate (HEMA). The trend in PUM–HEMA–PS system is almost the same as the PUM–MAAM–PS one; the formation of spherical particles depends on the PEG molecular weight and particle sizes increase with it, but no particles are formed with PEG 400 resulting resin type
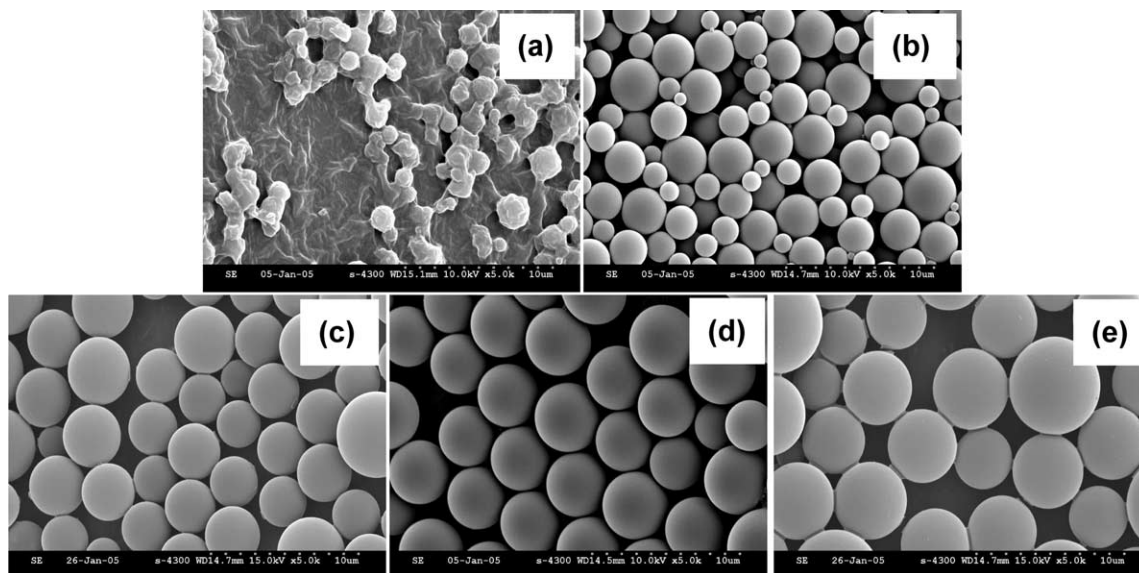
Fig. 3. SEM photographs of PUM–MAAM–PS with (a) PEG 400, (b) PEG 1000, (c) PEG 2000, (d) PEG 4000, and (e) PEG 8000.

polymer. The only difference between PUM–MAAM–PS and PUM–HEMA–PS systems is the molecular weight of the monomer between MAAM and HEMA, the functional group between amide and acylate, and the average particle sizes. Although we have not shown all the particles synthesized through this investigation, the average particle sizes prepared by MAAM and AAM are relatively larger than those by HEMA and HEA. Thus, amide group seems to favor making larger particles than acrylate group.

Fig. 5 shows the thermal degradation stability of a representative PUM–MAAM–PS system as a function of the molecular weight of PEG. The thermal degradation temperature of the polymer with PEG400 is observed at 325 °C, but the it is rapidly enhanced to 375 °C for PEG1000, then leveled at 380 °C for PEG2000, 4000, and 8000. This result indicates that once the particle is formed, no particular effect of the molecular weight of PEG exists and that BPUM is working not only as a particle stabilizer, but also as an agent enhancing thermal property of the polymers.

Fig. 6 represents the conversion and weight-average molecular weights of four different PS, PUM–MAAM–PS, PUM–AAM–PS, PUM–HEMA–PS, and PUM–HEA–PS, depending on the molecular weight of PEG. As seen in Fig. 6(a), the conversion is almost similar about 94–97% for all molecular weights of PEG and no end group functionality dependence between acrylamide and acrylate is observed. In addition, the weight-average molecular weights of synthesized four PS with different end group structures of BPUM are plotted in Fig. 6(b). The molecular
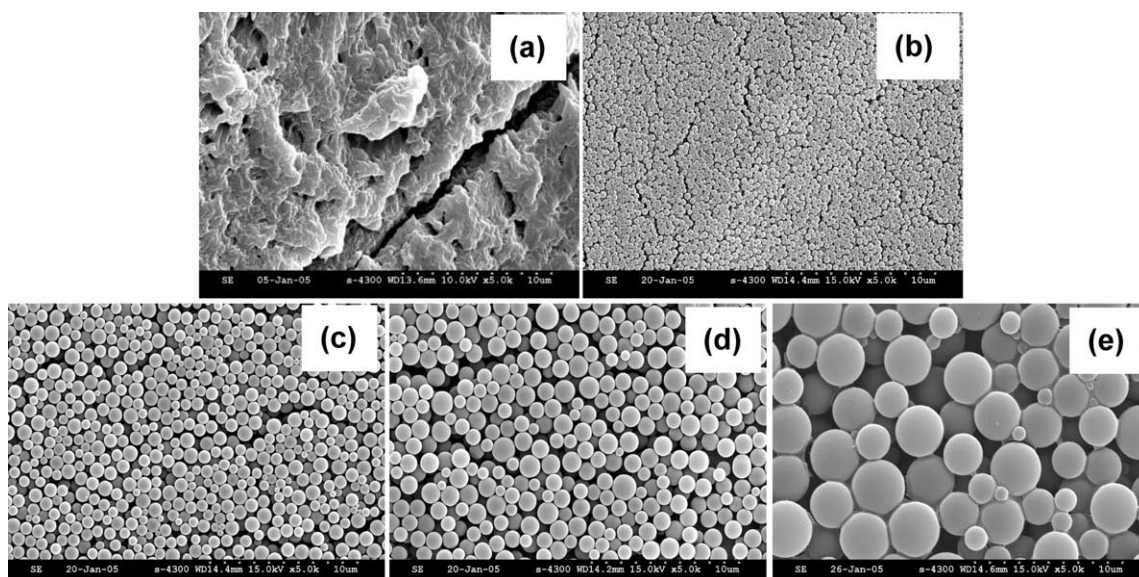

Fig. 4. SEM photographs of PUM–HEMA–PS with (a) PEG400, (b) PEG1000, (c) PEG2000, (d) PEG4000, (e) PEG8000.
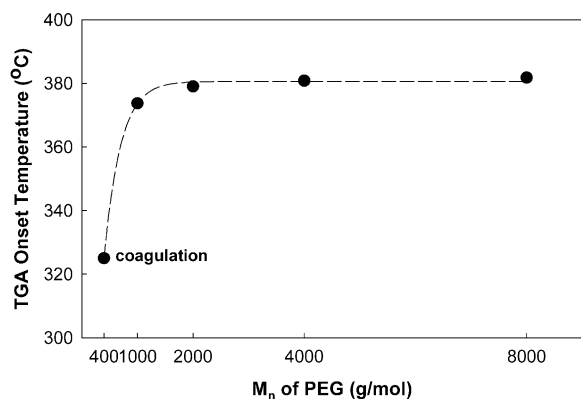
Fig. 5. The effect of the molecular weight of PEG on thermal degradation of PUM–MAAM–PS.

weight of the PS particles decreases with the PEG molecular weight. The molecular weights of acrylate-derived PS particles are higher than those of acrylamide-derived PS. Thus, the end group functionality and higher molecular weight of HEMA (130 g/mol) and HEA (116) than that of MAAM (85) and AAM (73) may be the factors giving high molecular weight of PS particles.

In Fig. 7(a), the weigh-average diameter (D_w) of the PS microspheres increases with the molecular weight of PEG. In addition, D_w of acrylamide-derived PS is higher at least 2.5 folds than that of acrylate-derived polymer. The inverse behavior is observed from the molecular weight of the PS and this is a characteristic in dispersion polymerization.

The uniformity (D_w/D_n) of the PS microspheres upon the molecular weight of PEG drawn in Fig. 7(b) decreases up to PEG4000, then increases at PEG8000. This implies that optimum molecular weight of macromonomer, which is PEG4000 in this study, is necessary to give narrow distribution of PS particles. This phenomenon indicates that the decrease in particle size with the molecular weight of PEG is pronounced, since BPUM effectively stabilizes a greater surface area of the PS particles.

3.2. Grafting of macromonomer with polystyrene

^{1}H NMR technique has been used in order to verify the PEO macromonomers grafted with polymer latex particles [16,27]. The data is obtained by calculating the grafting ratio using the Eq. (1) proposed by Shay et al. [26] from the ^{1}H NMR spectra of PS reacted with BPUM and SM. 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 is evidently originated from the methylene protons of PEO block in the polyurethane macromonomer [28].

Fig. 8 depicts the calculated grafting ratio as a function of PEG molecular weight, where a representative case of PUM–MAAM is investigated. Considering a greater reactivity of acrylate than that of amide group, higher grafting ratio is expected for acrylate. The grafting ratio is exponentially decreased from 1.05 to 0.18 with the
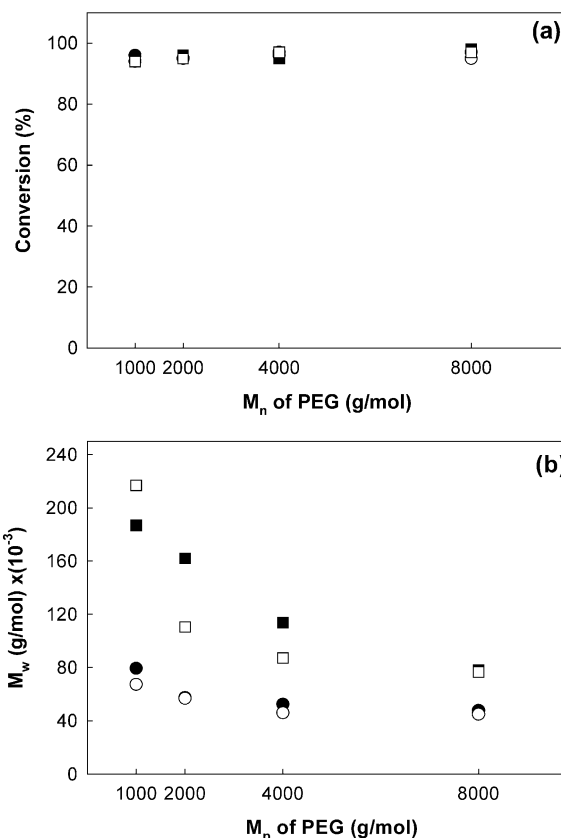

Fig. 6. Conversion (a) and weight-average molecular weigh (b) of synthesized PS with various PEG.s. (●) PUM–MAAM–PS, (○) PUM–AAM–PS, (■) PUM–HEMA–PS, (□) PUM–HEA–PS.

molecular weight of PEG, i.e. molecular weight of macromonomer. It is noted that the high grafting ratio of PS with PEG400 is caused by the low molecular weight of PS resin in Fig. 3(a). Since the grafting ratio is calculated by the ratio of the reacted PEO to PS, the amount of PEO is relatively large compared to polystyrene due to small molecular weight of PS. Additionally, it is thought that the reacted macromonomer molecules exist on the surface of the PS particles since the hydrophilic PEO blocks will prefer to migrate to the alcoholic medium [29]. The small grafting ratio is ascribed to the high molecular weight of the macromonomer working as a grafting agent, considering the molecular size of a typical grafting agent such as divinylbenzene.

4. Conclusion

Bifunctional polyurethane-based macromonomers (BPUM) are synthesized from various molecular weights of PEG. Various BPUMs from different molecular weights of PEG and PS prepared with the BPUMs are conformed using ^{1}H NMR. The macromonomers from PEG1000, 2000, 4000 and 8000 and styrene monomer are used to synthesize the stable PS particles, but PEG400 is not working to
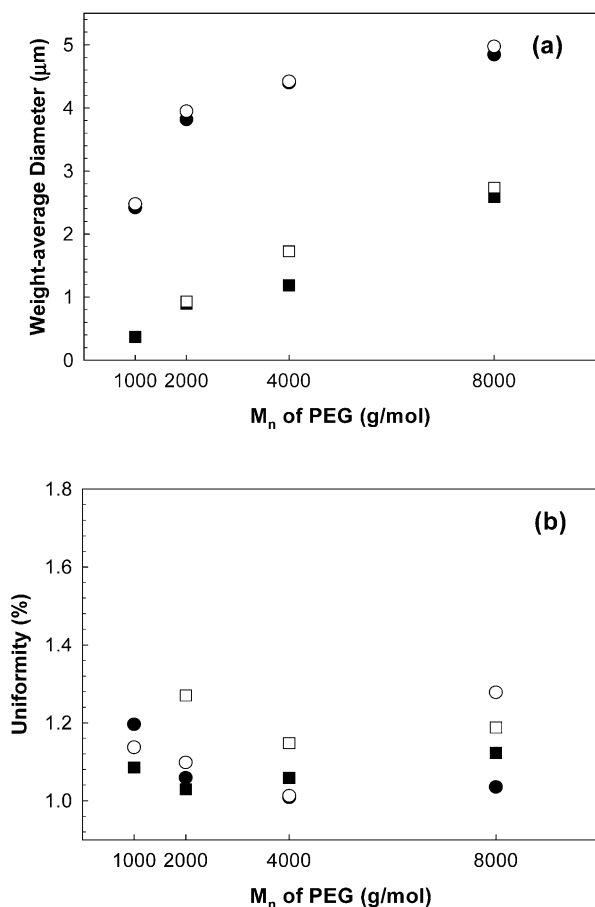
Fig. 7. Weight-average diameter (a) and uniformity (b) of synthesized PS upon PEG molecular weight. (●) PUM–MAAM–PS, (○) PUM–AAM–PS, (■) PUM–HEMA–PS, (□) PUM–HEA–PS.

form stable particles in dispersion polymerization. The conversion in the polymerization of styrene using BPUMs having different molecular weights is similarly ranging in 94–97%. Average particle size of the PS particles increases with PEG molecular weight, but the molecular weight of the PS particles decreases. In particular, the particle size based on the monomers derived with acrylamide is larger than
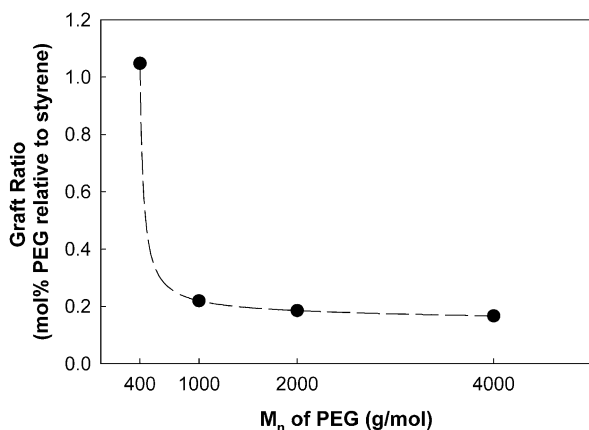

Fig. 8. Grafting ratio of PUM–MAAM–PS upon PEG molecular weight.

acrylate derivative monomer, but the inverse behavior is observed in the molecular weight. Thus, the higher molecular weights of HEMA and HEA than MAAM and AAM give higher molecular weight of PS, but smaller particle size. In addition, the thermal degradation temperature of the polymer with PEG 400 is observed at 325 °C, but it rapidly increases to 375 °C for PEG1000, then levels off at 380 °C for PEG2000, 4000, and 8000. The grafting ratio of the polystyrene calculated from ^{1}H NMR spectra exponentially decreases from 1.05 to 0.18 mol% with the different molecular weights of PEG, i.e. molecular weight of macromonomer. This may be a consequence of grafting behavior of macromonomer. Thus, our result suggests that the bifunctional macromonomers act not only as reactive stabilizers, but also as grafting agents.

Acknowledgements

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