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Crosslinkable functional moiety for the formation of highly crosslinked stable microspheres in the precipitation polymerization

Minhye Ha, Kangseok Lee, Soonja Choe*

Department of Chemical Engineering, Inha University, Yonghyundong 253, Namgu, Incheon 402-751, Republic of Korea

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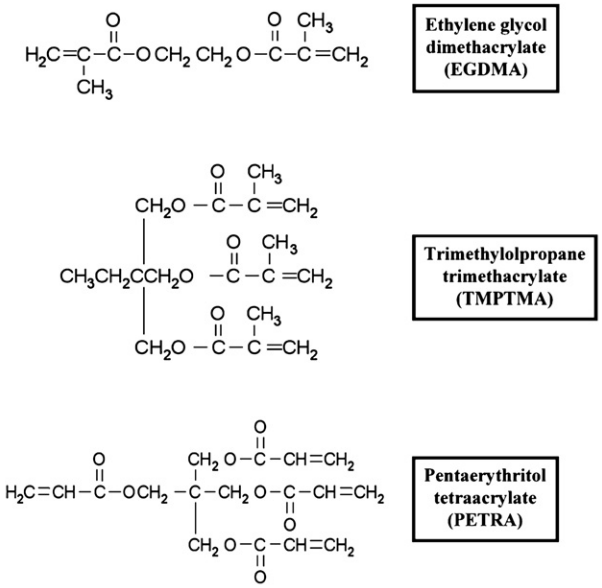
ABSTRACT

The highly crosslinked stable spherical microspheres were successfully synthesized using styrene and three crosslinking agents having different number of crosslinkable functional moiety in comonomer using the precipitation polymerization. The crosslinking agents are ethylene glycol dimethacrylate (EGDMA), trimethylolpropane trimethacrylate (TMPTMA) and pentaerythritol tetraacrylate (PETRA). The maximum and minimum concentrations for forming the stable spherical particles were ranging at 20–90 mol% for EGDMA, 15–80 mol% for TMPTMA, and 5–40 mol% for PETRA, respectively. The number-average diameter of stable poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA), and poly(S-*co*-PETRA) particles varied 4.1–3.06, 3.94–3.03 and 2.77–1.66 μm, respectively. Since the prepared microspheres are highly crosslinked, no glass transition temperature was observed. The TGA onset point of the thermal degradation temperature increased with the concentration of crosslinking agent and the number of crosslinkable functional moiety, which is EGDMA < TMPTMA < PETRA. As a result, the minimum and maximum concentrations for the formation of stable spherical particles of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA), and poly(S-*co*-PETRA), the particle size and its distribution, CV, yield and the TGA onset point are significantly affected by the number of the crosslinkable functional moiety. Thus, the number of the crosslinkable functional moiety and the different reactivity as well as the different copolymerization parameters of styrene with (meth)acrylates would influence the composition as well as the rate of formation of stable microspheres.

1. Introduction

Polymer colloids have been used in vast areas such as various coatings, adhesives, inks, leather finishings, constructions and so forth [1]. Nowadays, the applications of such polymer particles were broadened to more advanced fields such as information technology, electric and electronic science, and biotechnology including biochemicals and biomedicals [2–4]. In accord with the expansion of their applications, the precise control of properties of the polymer colloids has become more important. Their size, uniformity of size, functionality of the base polymer, morphology of the polymer beads, and the degree of crosslinking, etc. are the main concerns in controlling properties.

Highly crosslinked micron-sized spherical polymer particles have been received much attention since they possess unique applications due to their superior strength, thermal and solvent resistance, and anti-slip properties [5]. In addition, uniformly sized and highly crosslinked polymeric microspheres in micron size are considered as specialty materials such as packing materials in



Scheme 1. The chemical structures of the three crosslinking agents used.

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* Corresponding author.
E-mail address: sjchoe@inha.ac.kr (S. Choe).

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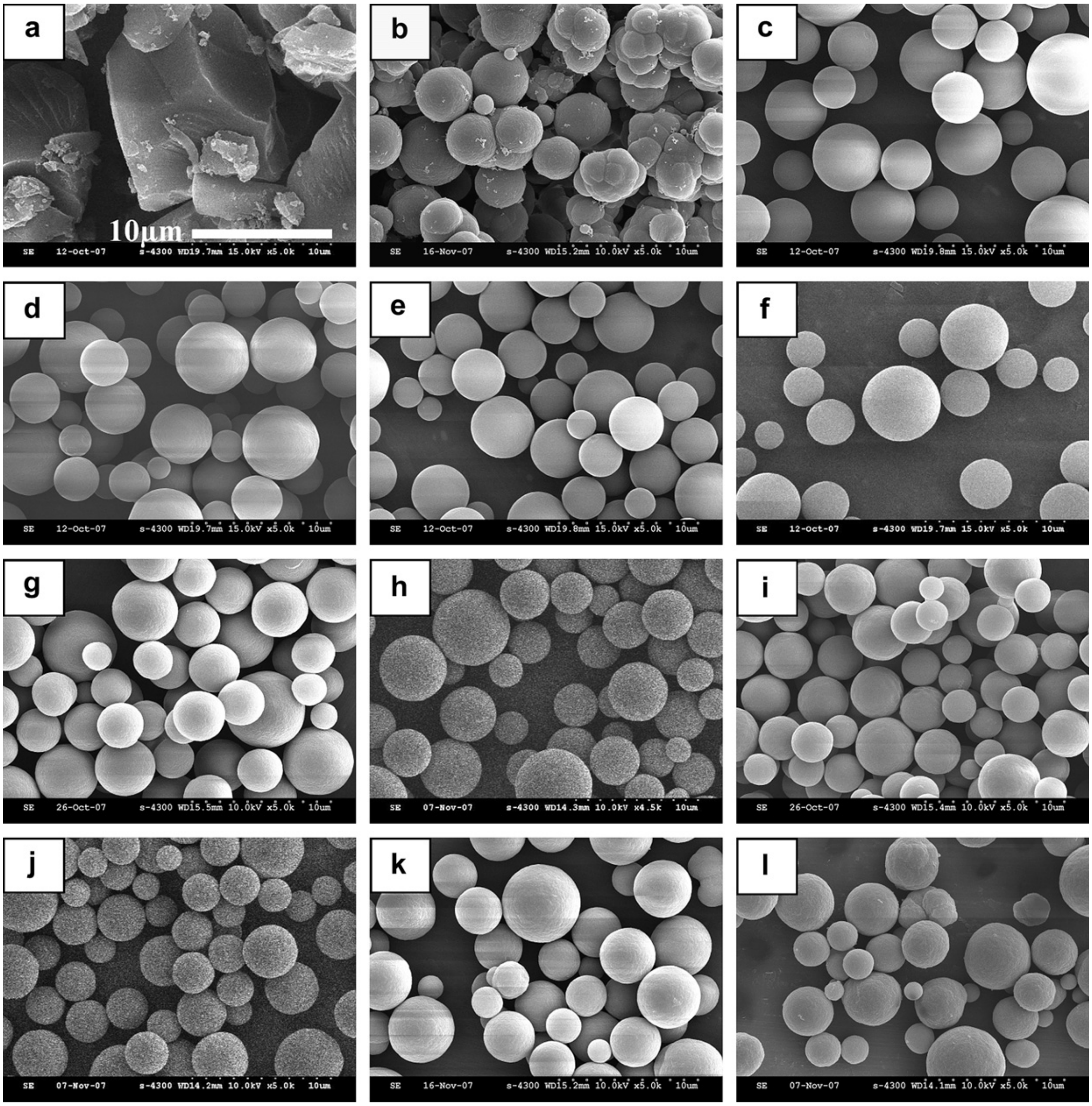
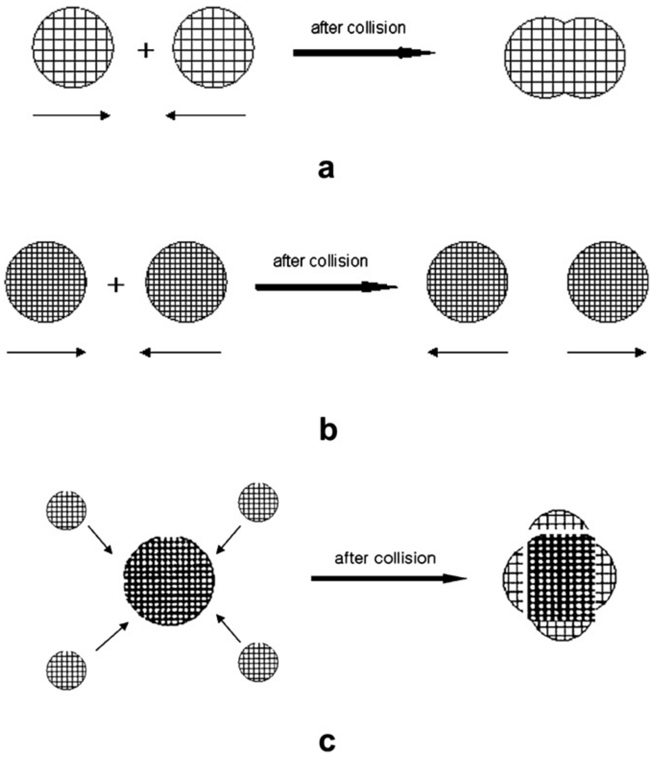


Fig. 1. SEM photographs of poly(S-*co*-EGDMA) particles composed of various concentrations of EGDMA with 2 wt% AIBN in acetonitrile at 70 °C in the precipitation polymerization. EGDMA concentrations: (a) 10, (b) 15, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70, (i) 80, (j) 90, (k) 95, (l) 100 mol%.

column chromatography [6] and spacers in liquid crystal display [7,8]. Therefore, the development of simple technique to synthesize micron-sized highly crosslinked polymer particles has been a subject of intensive research in polymer colloid fields. Recently, Winnik and Song [9] studied the effect of crosslinking agents on the size and size distribution of polystyrene particles prepared by dispersion polymerization and prepared monodisperse polystyrene particles containing 1 wt% ethylene glycol dimethacrylate (EGDMA).

Stöver's group [10–12] has introduced a method to synthesize the fully crosslinked polymer beads in micrometer scale by the precipitation polymerization of single crosslinkable monomer such as divinylbenzene and multiple monomers with crosslinkable monomer in the absence of stabilizer in organic medium. Several monomers including methacrylate and maleic anhydride have been copolymerized with divinylbenzene by the precipitation polymerization, resulting in microspheres. The morphology of the polymer is governed by the aggregation mechanisms, mostly depending on the parameters which may affect the stability of colloidal particles formed upon precipitation of the polymers. In addition, both precipitation and dispersion polymerizations start with a homogeneous system, in which the initiator (radical generator) is soluble. More recently, Héroguez et al. [13] studied the precipitation polymerization of divinylbenzene monodisperse crosslinked particles functionalized with vinylbenzylchloride. They reported that highly crosslinked functional polymer particles with narrow size distribution have been produced by precipitation copolymerization of divinylbenzene, ethylene glycol dimethacrylate and vinylbenzylchloride using a simple reflux protocol and investigated the influences of particles size, specific surface area and packing conditions on the separation behavior.

Choe's group [14–16] has widely investigated a method to synthesize the highly crosslinked poly(styrene-*co*-divinylbenzene), poly(methyl methacrylate-*co*-divinylbenzene) and poly(glycidyl methacylate-*co*-divinylbenzene) particles. The polymerization yield is relatively low about 50 mol% and at least 20 mol% of



Scheme 2. Schematic illustration of the formation of polymer particles with different levels of crosslinking after collision in the precipitation polymerization. (a) Aggregated unstable particles with low level of crosslinking agent, (b) stable spherical particles with high level of crosslinking agent, (c) unstable spherical particles with too high level of crosslinking agent having bulky side group.

divinylbenzene is needed for stable spherical crosslinking particles. Recently, we reported the role of the acetone/methanol and acetonitrile/2-methoxyethanol media for the formation of the stable P(S-*co*-DVB) spheres in the absence of acetonitrile. This behavior is explained in terms of the three parameters such as the solubility parameter, polarity, and viscosity of the polymer and solvents [17].

In this study, the preparation of highly crosslinked polymeric spheres in the precipitation polymerization is continued using styrene monomer and various chemical structures of crosslinking agents as a comonomer. The highly crosslinked stable poly[styrene-*co*-ethylene glycol dimethacrylate (EGDMA)], poly[styrene-*co*-trimethylolpropane trimethacrylate (TMPTMA)] and poly[styrene-*co*-pentaerythritol tetraacrylate (PETRA)] microspheres were successfully synthesized in the precipitation polymerization in the presence of acetonitrile. Then, the polymerization parameters affecting the particle characteristics such as the concentration window of crosslinking agents (EGDMA, TMPTMA, PETRA) for the formation of stable spherical particles, yield, particle size and the distribution, thermal properties of the particles in terms of the number of functional moiety, which is acrylate, are investigated.

2. Experimental

2.1. Materials

Styrene (Junsei Chemicals, Tokyo, Japan) was purified using an inhibitor removal column (Aldrich Chemical Co., WI, USA) and stored at −5 °C prior to use. Ethylene glycol dimethacrylate (EGDMA; Aldrich Chemical Co., WI, USA), trimethylolpropane trimethacrylate (TMPTMA; Aldrich Chemical Co., WI, USA) and pentaerythritol tetraacrylate (PETRA; Aldrich Chemical Co., WI, USA) were stored at −5 °C prior to use. As an initiator, analytical grade of 2,2-azobisisobutyronitrile (AIBN; Junsei, Tokyo, Japan) was used without further purification. As the polymerization media, analytical grade acetonitrile (Aldrich Chemical Co., WI, USA), methanol (Samchun, Seoul, Korea), ethanol (Samchun, Seoul, Korea), acetone (Samchun, Seoul, Korea) were used. The chemical structures of the used three crosslinking agents are drawn in Scheme 1.

2.2. Polymerizations

The polymerization ingredients simply consist of medium, various compositions of styrene and EGDMA, TMPTMA, PETRA, and AIBN. The total amount of monomers was 4 wt% of the medium. The concentration of AIBN was 2 wt% with respect to the total amount of the monomers. After charging 30 mL of polymerizing mixture in glass vial, nitrogen was purged for 15 min and sealed. Polymerization was carried out in a shaking water bath with an agitation speed at 30 rpm and 70 °C for 12 h. After completion of the polymerization, the resultant particles were obtained by centrifugation and washed with methanol repeatedly and dried in vacuum at 70 °C.

2.3. Characterization

The yield of the polymerization was determined gravimetrically. Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to characterize the morphology of the particles. SEM images were obtained on samples coated with a thin layer of gold, to a depth of approximately 20 nm, under vacuum. The number-average diameter (D_n) and size distribution of the spherical particles were measured by means of laser diffraction (LS230, Beckman Coulter, CA, USA). The solution samples were put in Coulter Counter entrance up to 40% value and measured D_n, D_w (weight-average diameter), uniformity. Differential scanning calorimetry (DSC; Perkin–Elmer DSC-7, UK) was used to measure the glass transition temperature (T_g) of the particles. The samples were heated at a heating rate of 20 °C/min under a nitrogen atmosphere and quench cooled at a maximum cooling rate, and then reheated for the second time. Thermal degradation of the crosslinked microspheres was studied using a thermogravimetric analyzer (TGA; TA Instrument Q50) under the high purity nitrogen gas atmosphere. The TGA onset temperature of the degradation temperature was determined at the transition point as the curve passes the maximum negative slope.

3. Result and discussion

Fig. 1(a)–(l) shows the SEM microphotographs of poly(styrene-*co*-EGDMA) spheres prepared by the precipitation polymerization with 2 wt% AIBN at 70 °C for 12 h in the presence of acetonitrile. When up to 15 mol% EGDMA was used, unstable particles with doublet or triplet shape were observed due to the lack of stability upon low concentration of crosslinking agent, EGDMA, as seen in Fig. 1(a) and (b). Whereas when 20–90 mol% EGDMA was used, very clear and smooth surface of spherical particles was obtained. However, when 95 and 100 mol% of EGDMA were added, slightly coagulated and less stable particles were observed. This is surprising because the higher the concentration of crosslinking agent, the higher the stable spherical particles were expected. The coagulation with 95 and 100 mol% of EGDMA would be related with the bulky side group in EGDMA. This will be explained in detail in the later section.

Some of the characteristics of the precipitation polymerization are similar to those of the dispersion polymerization in which all polymerization ingredients are soluble in medium, but the resulting polymers are not soluble in the medium. However, unlike the

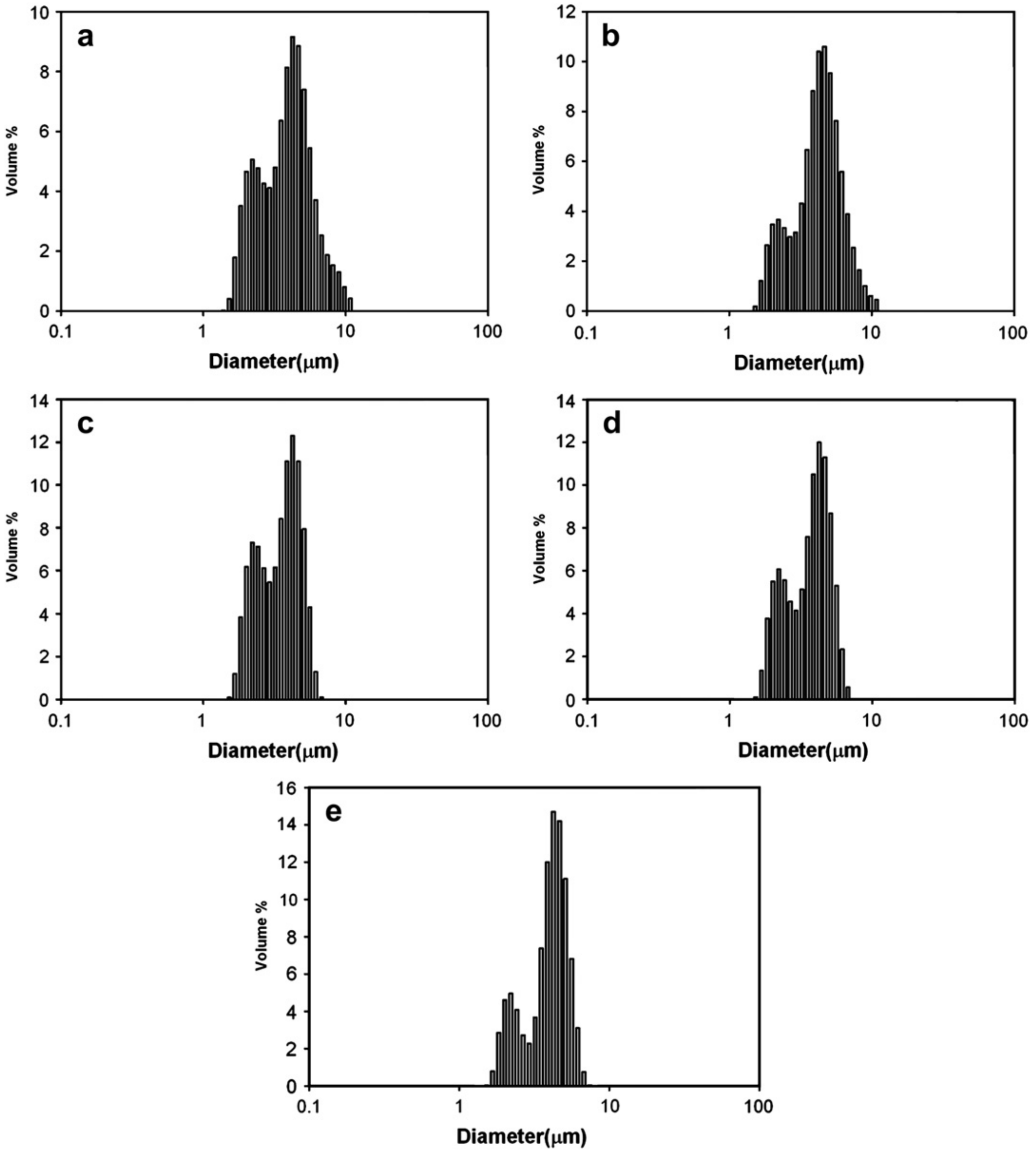


Fig. 2. EGDMA content dependent particle size distribution of poly(styrene-*co*-ethylene glycol dimethacrylate (EGDMA)) spheres prepared by the precipitation polymerization with 2 wt% AIBN in acetonitrile at 70 °C. EGDMA concentration: (a) 20, (b) 30, (c) 50, (d) 70, and (e) 90 mol%.

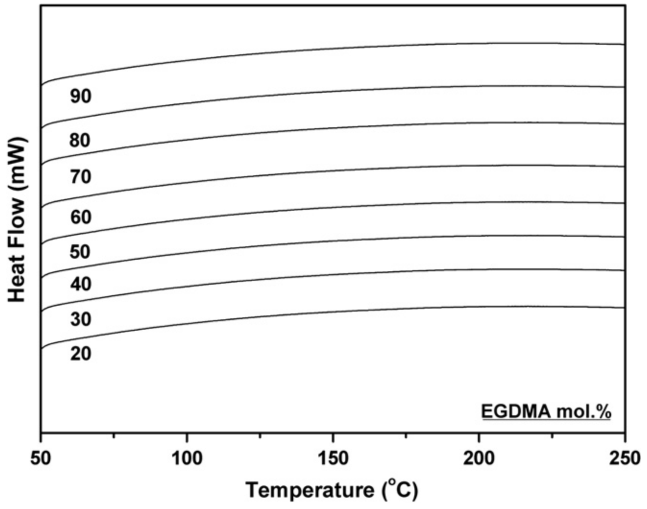


Fig. 3. DSC thermograms of poly(S-*co*-EGDMA) prepared with various concentrations of EGDMA in acetonitrile at 70 °C.

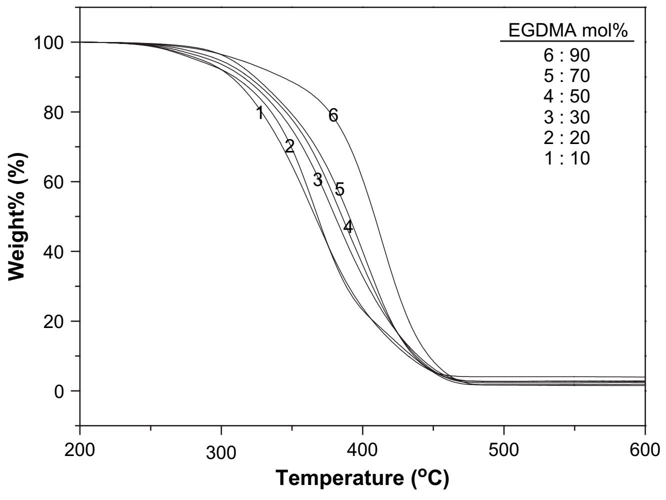


Fig. 4. TGA thermograms of poly(S-*co*-EGDMA) prepared with various concentrations of EGDMA with 2 wt% AIBN in acetonitrile at 70 °C for 12 h.

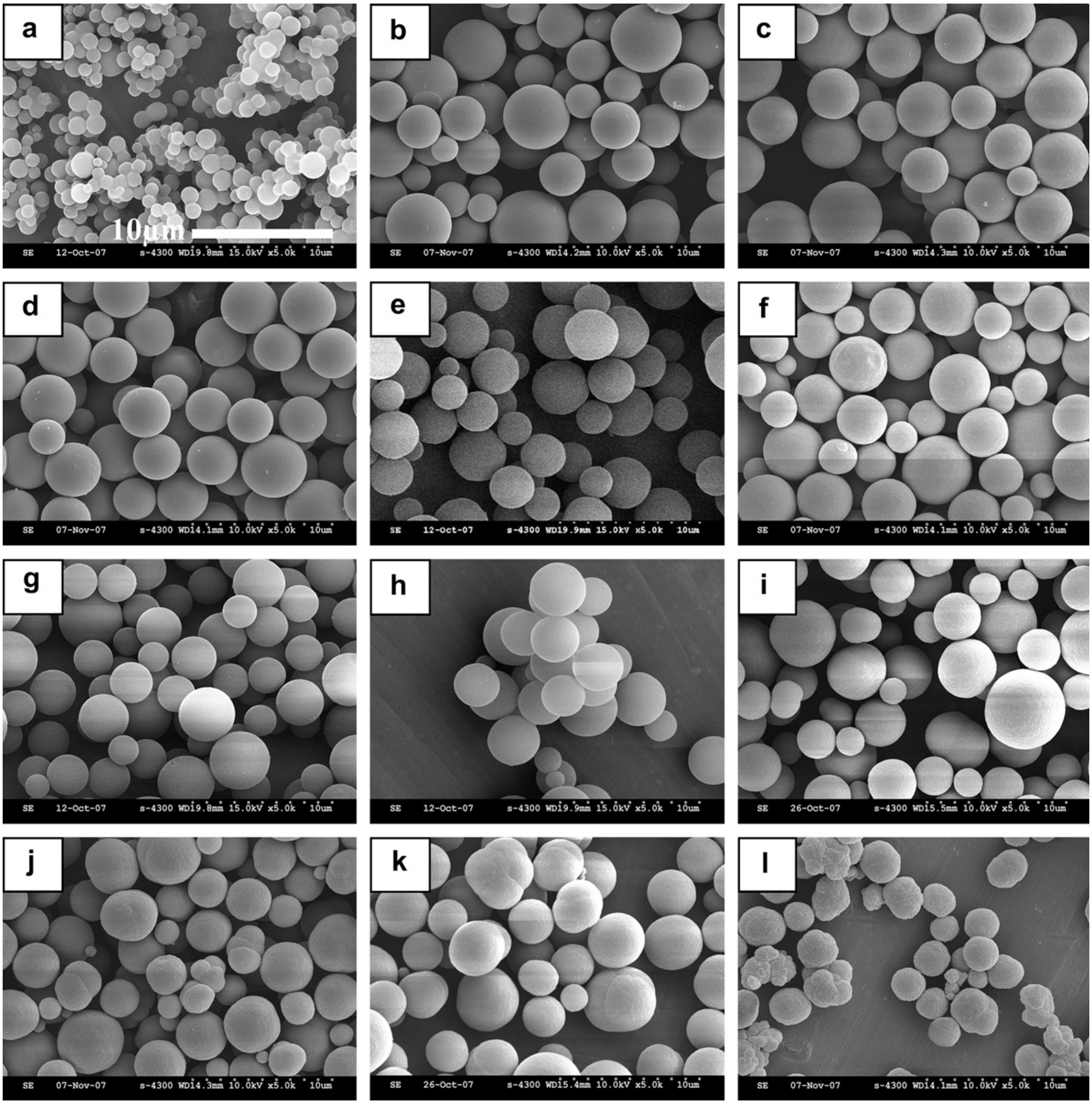


Fig. 5. SEM photographs of poly(styrene-*co*-TMPTMA) particles composed of various concentrations of TMPTMA with 2 wt% AIBN in acetonitrile at 70 °C prepared by precipitation polymerization. TMPTMA concentrations: (a) 10, (b) 15, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70, (i) 80, (j) 85, (k) 90, (l) 100 mol%.

dispersion polymerization, the precipitation polymerization provides stable spherical particles without an aid of surface stabilizing agent such as steric stabilizers, polyvinylpyrrolidone (PVP) or polyvinylalcohol (PVA). The use of crosslinkable monomers such as divinylbenzene (DVB), EGDMA, TMPTMA, and PETRA is an essential feature in the precipitation polymerization in acetonitrile medium. The formation of stable spherical particles in the precipitation polymerization is strongly dependent on the degree of crosslinking of the particles. The high degree of crosslinking within the polymer particles prepared in the course of the precipitation polymerization prevents from fusion (i.e. coagulation) between the particles due to the improved hardness and resilience of individual particles as represented in Scheme 2. The highly crosslinked stable poly (styrene-*co*-divinylbenzene) microspheres were prepared in the precipitation polymerization and the novel mechanism was proposed by Choe's group [18]. It was found that particle size grew continuously without an abrupt change, implying that the aggregation or coagulation was not taking place and that the particles formed in the early stage of the polymerization kept growing to the final stage.

The particle size distribution of poly(S-*co*-EGDMA) prepared at 70 °C for 12 h was analyzed as a function of the EGDMA content between 20 and 90 mol% and plotted in Fig. 2. When 20–30 mol% EGDMA is incorporated as seen in Fig. 2(a) and (b), the slightly broad distribution of the particle size is observed. On the other hand, as the concentration of EGDMA further increased between 50 and 90 mol% in Fig. 2(c)–(e), the size distribution improved with narrow distribution and the average particle size also decreased. In overall, the particle size shows bimodal distribution between 3.5 and 6.6 μm. This may arise from the different crosslinking densities upon different contents of EGDMA, of which the reaction mechanism in the precipitation polymerization was proposed in this laboratory [18]. At the initial stage of precipitation polymerization, the primary stable particles are generated by the aggregation of the primary nucleus particle, and then grow in size by absorbing oligomeric species.

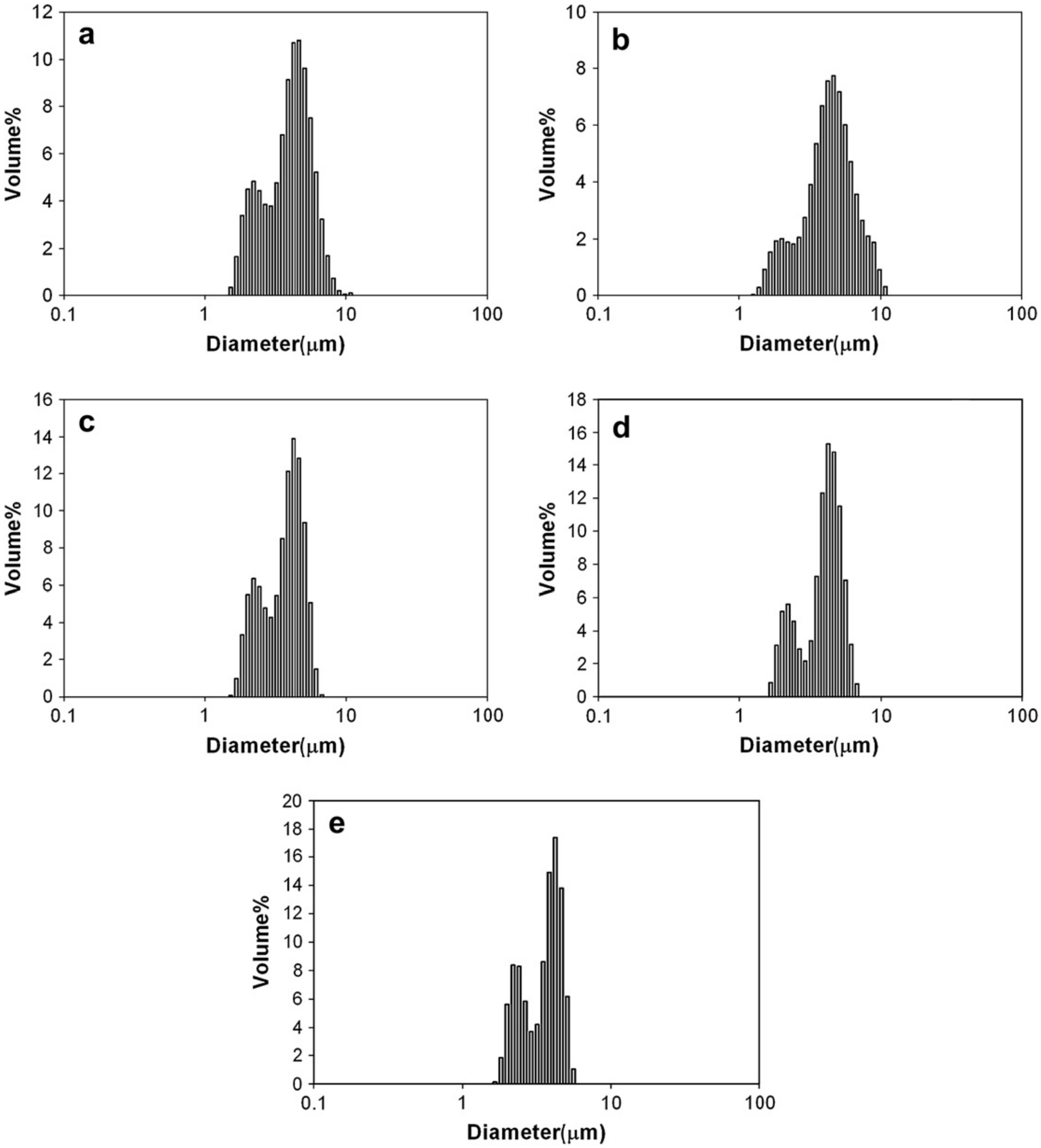


Fig. 6. The TMPTMA content dependent particle size distribution of the poly(S-*co*-TMPTMA) spheres prepared by the precipitation polymerization with 2 wt% AIBN in acetonitrile at 70 °C. TMPTMA concentrations: (a) 15, (b) 30, (c) 50, (d) 70, and (e) 80 mol%.

The thermal properties of the poly(S-*co*-EGDMA) spheres obtained from the precipitation polymerization were characterized using DSC. The DSC thermograms of the spherical particles containing various concentrations of EGDMA are demonstrated in Fig. 3. A broadening and an increase in the endothermic transition and followed by the disappearance of the glass transition temperature with increasing concentration of EGDMA were initially expected. However, no existence of the endothermic transition representing the glass transition temperature was observed for all examined samples as seen in this figure. This may indicate that the whole compositions of poly(S-*co*-EGDMA) would be highly crosslinked in the molecular level. In our previous study, the glass transition temperatures of the poly(S-*co*-DVB) particles prepared by emulsion polymerization were well observed for the divinylbenzene contents between 2 and 10 mol% [19]. Thus, poly(S-*co*-EGDMA) seems to be higher degree of crosslinking than poly(S-*co*-DVB).

Fig. 4 depicts the TGA thermograms of the poly(S-*co*-EGDMA) particles prepared with various concentrations of EGDMA from 10 to 90 mol% in acetonitrile at 70 °C. The numbers from 1 to 6 represent the various concentration of EGDMA from 10 to 90 mol%, respectively. For the whole samples of poly(S-*co*-EGDMA) with 10–90 mol% EGDMA, the weight loss of the samples between 250 and 460 °C is dramatically improved, but no enhancement less than 250 and higher than 460 °C were observed. This indicates that the higher content of EGDMA improves the thermal stability of poly(S-*co*-EGDMA) particles due to increased level of crosslinking between styrene and EGDMA.

Fig. 5(a)–(i) represents the SEM photographs of poly(styrene-*co*-TMPTMA) particles. When TMPTMA was used up to 10 mol%, aggregated particles were obtained due to the lack of the crosslinking agent. However, when between 15 and 80 mol% of TMPTMA was added, stable spherical particles with smooth surface were obtained because of high crosslinking density. The only difference between poly(S-*co*-EGDMA) and poly(S-*co*-TMPTMA) is the degree of crosslinkable functionality moiety between EGDMA and TMPTMA, respectively. From this difference, poly(S-*co*-EGDMA) system induces the stable spherical particles with EGDMA between

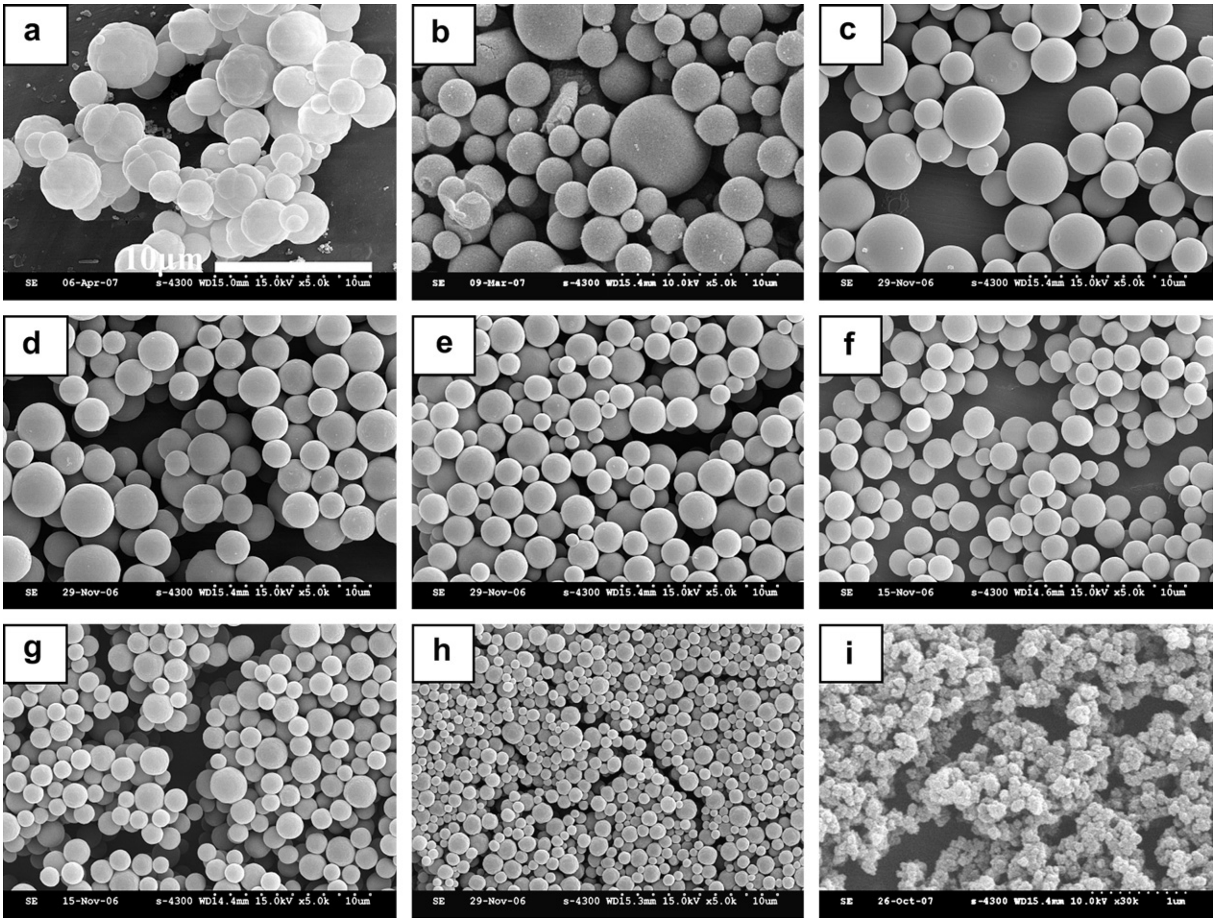


Fig. 7. SEM photographs of poly(styrene-*co*-PETRA) particles composed of various concentrations of PETRA with 2 wt% AIBN in acetonitrile at 70 °C prepared by precipitation polymerization. PETRA concentrations: (a) 3, (b) 4, (c) 5, (d) 10, (e) 20, (f) 30, (g) 40, (h) 45, (i) 100 mol%.

20 and 90 mol%, whereas poly(S-*co*-TMPTMA) system induces the stable spherical particles with TMPTMA between 15 and 80 mol%. Thus, it would be interpreted as the following: the higher the degree of crosslinkable functionality moiety, the lower the moiety concentration would form stable spherical particles, whereas the higher the moiety concentration would induce unstable aggregated particles. This is obviously evidenced when TMPTMA, which has trimethacrylate, is used.

Fig. 6 shows the representative particle size distribution of the poly(S-*co*-TMPTMA) particles containing 15, 30, 50, 70 and 80 mol% TMPTMA, respectively. As mentioned above, the size uniformity is enhanced as the concentration of TMPTMA increases. In particular, when 50, 70 and 80 mol% TMPTMAs were used, bimodal shape of distribution was observed.

Fig. 7 shows the SEM photographs of the poly(styrene-*co*-PETRA) particles prepared by the precipitation polymerization in acetonitrile with 2 wt% AIBN at 70 °C. Fig. 7(a) and (b) representing the PETRA concentrations of 3 and 4 mol% and (h) and (i) representing the PETRA concentration of 45 and 100 mol%, respectively, show unstable aggregated particles. On the other hand, stable spherical particles were obtainable between 5 and 40 mol% of PETRA. This is comparable with EGDMA and TMPTMA systems, of which stable spherical particles were obtainable with 20–90 and 15–80 mol% of EGDMA and TMPTMA, respectively. Since PETRA contains four crosslinking functional moieties, tetraacrylate, it has an advantage of forming stable spherical particles with low concentration of PETRA, but has a disadvantage of it with high concentration of PETRA due to bulkiness of the crosslinking moiety. In overall, the following discussions are suggested in the precipitation polymerization between polystyrene and multifunctional crosslinkable moieties, as the number of the crosslinkable functional moieties increases, the formation of stale spherical particles is possible with lower concentration of the crosslinkable functional moieties. On the other hand, the higher concentration of the crosslinkable (meth)acrylates induces unstable spherical particles. In addition, the different reactivity between styrene and (meth)acrylates as well as the different copolymerization parameters of styrene with (meth)acrylates comonomers can also influence the composition as well as the rate of formation of stable microspheres.

Fig. 8 shows the particle size distribution of the stable spherical poly(S-*co*-PETRA) particles upon PETRA concentrations. As the PETRA concentration increases, the particle size distribution becomes narrow, in particular at 30 and 40 mol% PETRA, the size distribution is relatively narrow following the single Gaussian distribution with the coefficient of variation (CV) less than 15. This kind of behavior may come from the high degree of crosslinking with tetraacrylate moiety.

Fig. 9 represents the number-average particle size of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) spheres with increasing concentrations of the crosslinking agent in the precipitation polymerization at 70 °C in acetonitrile. The number-average particle diameter of poly(S-*co*-EGDMA) slightly decreased from 4.01 to 3.06 μm for between 20 and 90 mol% of EGDMA, respectively. In addition, the number-average particle diameters of poly(S-*co*-TMPTMA) decreased from 3.93 to 3.03 μm with increasing concentrations of TMPTMA between 15 and 80 mol%, respectively. Whereas, for poly(S-*co*-PETRA), it decreased from 2.77

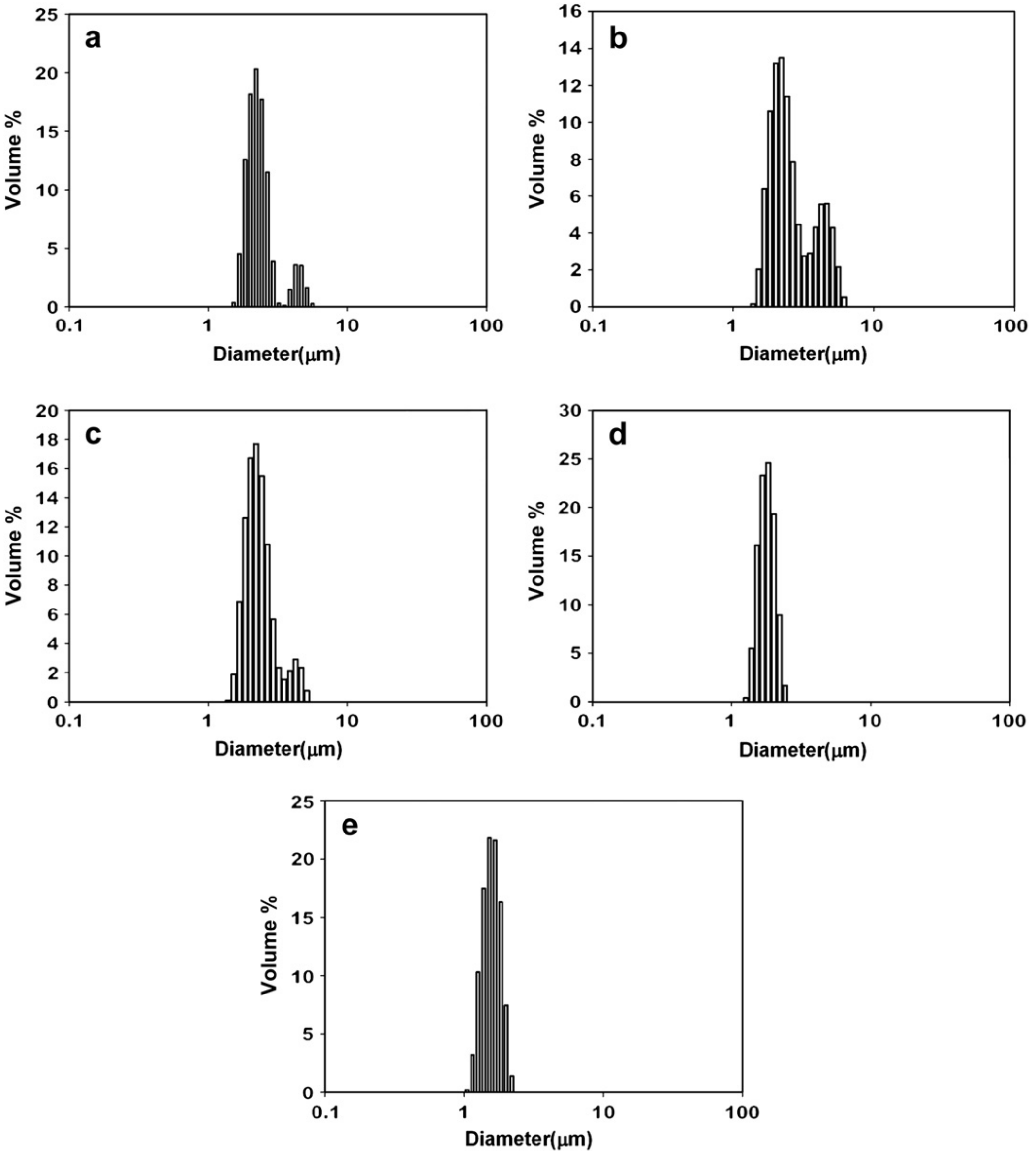


Fig. 8. PETRA content dependent particle size distribution of poly(S-*co*- PETRA) spheres in the precipitation polymerization with 2 wt% AIBN in acetonitrile at 70 °C. PETRA concentrations: (a) 5, (b) 10, (c) 20, (d) 30, (e) 40 mol%.

to 1.66 μm for between 5 and 40 mol% PETRA, respectively. This implies that the particle size decreases due to increased degree of crosslinking. This behavior is similar to that of poly(S-*co*-DVB) [14].

The interesting feature is the concentration window for the formation of stable spherical particles. It is between 20 and 90 mol% for EGDMA, between 15 and 80 mol% for TMPTMA, and between 5 and 40 mol% for PETRA. Thus, the lower and upper limits simultaneously decreased from 20 to 5 mol% and from 90 to 40 mol% of the crosslinking agent, respectively. This is interpreted as the following: as the number of the functional moiety, which is bulky acrylate group, increased from 2 to 4, the minimum concentration of it decreased from 20 to 5 mol% and the maximum concentration of it also decreased from 90 to 40 mol%. This means that the number of the crosslinkable functional moieties strongly influences the formation of stable spherical particles. That is, the smaller the number of the crosslinkable functional moieties in the crosslinking agent, the higher the concentration of crosslinking agent was needed for the formation of stable spherical particles. On the other hand, the larger the number of the crosslinkable functional moieties, the lower the concentration of it was needed. In

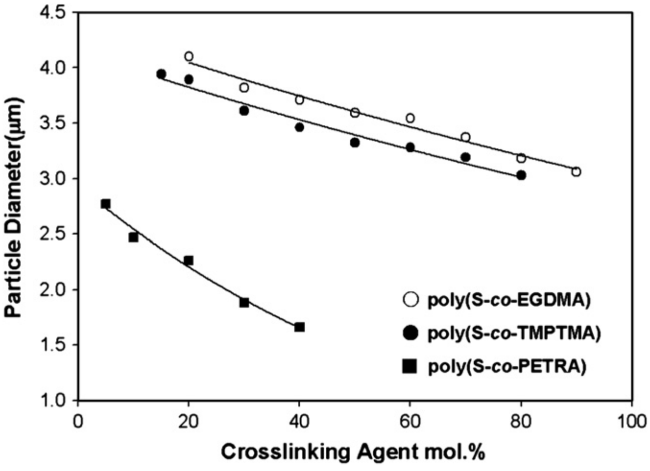


Fig. 9. The number-average particle size of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) spheres with increasing concentrations of crosslinking agents (EGDMA, TMPTMA, PETRA) in the precipitation polymerization. The symbols are the experimental results and the solid lines are the extrapolated ones.

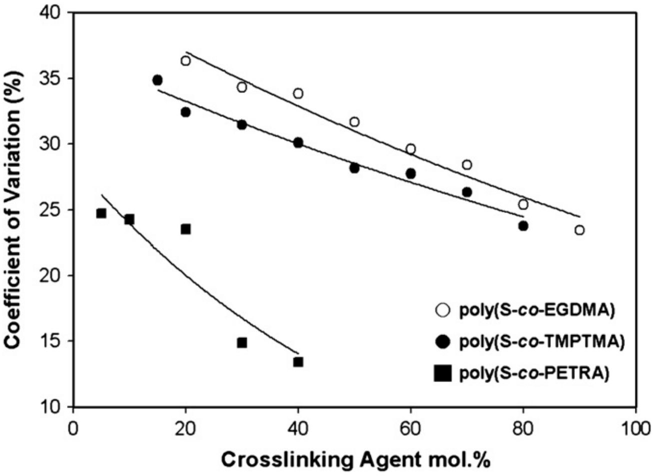


Fig. 10. The coefficient of variation of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA), and poly(S-*co*-PETRA) spheres with increasing concentrations of crosslinking agents (EGDMA, TMPTMA, PETRA) in the precipitation polymerization. The symbols are the experimental results and the solid lines are the extrapolated ones.

addition, according to the "Like dissolves like" principle, the solubility of the crosslinking agent will be dependent on the bulkiness of the molecules, resulting in less solubility in the system with PETRA than EGDMA, as an example.

Fig. 10 shows the coefficient of variation (CV) of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) prepared at 70 °C as a function of each crosslinking agent. The CV of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) varied from 36.3 to 23.4, from 34.9 to 23.7 and from 24.7 to 13.4, respectively, implies that the particle uniformity improved with the increasing concentration of each crosslinking agent.

Fig. 11 depicts the yield of the polymerization of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA). In these three cases, the yield was 91.5% for 90 mol% EGDMA, 92.7% for 80 mol% TMPTMA, and 91.3% for 40 mol% PETRA, respectively. Thus, the maximum yield was almost same although the upper limit of the concentration of each crosslinking agent is different. In our previous study on poly(S-*co*-DVB) system, the yield was obtained 63.5% for 75 mol% DVB [14]. The only difference between the former and present studies is the comonomers having different functional moieties. In present study, two, three and four crosslinkable functional moieties in EGDMA, TMPTMA and PETRA, respectively, are connected with flexible aliphatic unit. Whereas, the two-vinyl group in DVB is connected with rigid phenyl group in our previous study. Thus, the residual vinyl group on the gel and out-layer of the poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) was more favorable and easier to react with the monomer and oligomer to result in the growth of the polymer particles and lead to higher yield with EGDMA, TMPTMA and PETRA than with DVB [20].

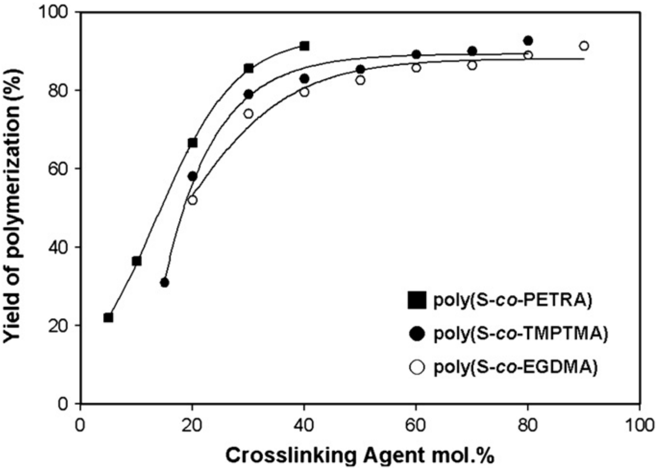


Fig. 11. The comparison of the yield of the polymerization of styrene with three different crosslinking agents: poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA). The symbols are the experimental results and the solid lines are the extrapolated ones.

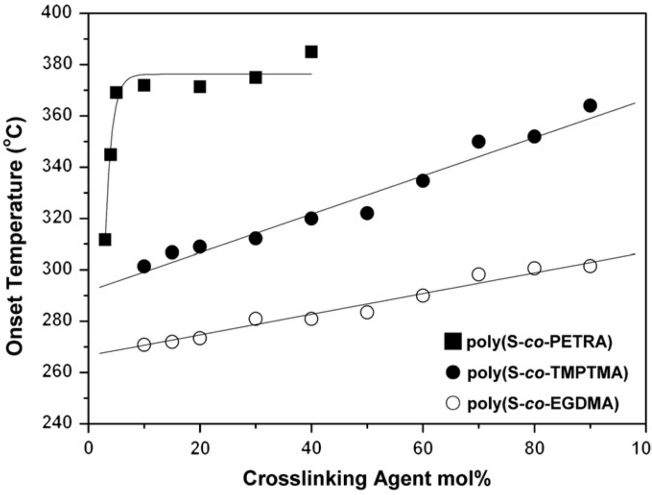


Fig. 12. Comparison of the TGA onset temperature of poly(S-*co*-crosslinking agents) spheres with EGDMA, TMPTMA, and PETRA in the precipitation polymerization in acetonitrile at 70 °C for 12 h. The symbols are the experimental results and the solid lines are the extrapolated ones.

Fig. 12 represents the TGA onset temperature of the thermal degradation of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) spheres with increasing concentrations of crosslinking agent. The degradation temperature, which is determined at the transition point as the curve passes the maximum negative slope, varied from 351.2 to 394.6 °C for 20 and 90 mol% EGDMA. In addition, for the poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) spheres, the TGA onset point was observed between 359.5 and 415.1 °C for between 15 and 80 mol% TMPTMA, and between 420.9 and 438.5 °C for between 5 and 40 mol% PETRA, respectively. As seen in this figure, as the number of the crosslinkable functional moieties increased, the thermal stability enhanced, indicating that the effect of the number of the crosslinkable functional moieties is the same as discussed in the previous section.

Fig. 13 shows the concentration window giving the stable spherical particles of poly(S-*co*-crosslinking agent) prepared with

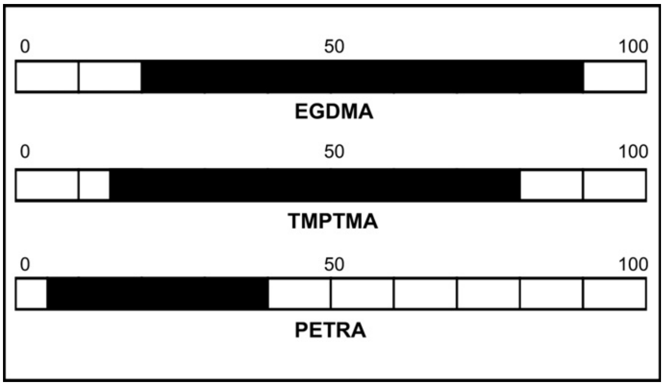


Fig. 13. Concentration window for the formation of stable spherical poly(S-*co*-crosslinking agents) particles with various crosslinking agents (EGDMA, TMPTMA, PETRA).

2 wt% AIBN in acetonitrile at 70 °C in the precipitation polymerization. The minimum and maximum concentrations for the formation of the stable spherical particles are 20 and 90 mol% for EGDMA, 15 and 80 mol% for TMPTMA, and 5 and 40 mol% for PETRA, respectively. Since each of EGDMA, TMPTMA, and PETRA has two, three, and four crosslinkable functional (meth)acrylates, respectively, the minimum and maximum concentrations of each crosslinkable comonomer are lowered with increased number of the functional moiety resulting in high degree of crosslinking. Thus, the higher the crosslinkable functional moiety, the lower the concentration of the crosslinkable monomer is required and the higher the thermal stability was observed. In our previous study with poly(S-*co*-DVB) system, the minimum concentration for forming stable spherical particles is 40 mol% DVB [14]. As discussed above, this observation would be from the difference in the crosslinkable functional moiety and different reactivity of the (meth)-acrylates as well as the different copolymerization parameters of styrene with (meth)acrylates. These three parameters can influence the composition as well as the rate of formation of stable microspheres.

4. Conclusions

The highly crosslinked stable poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA) and poly(S-*co*-PETRA) microspheres composed of various concentrations of crosslinking agents based on styrene were prepared in the precipitation polymerization in neat acetonitrile. Doublet or triplet particles after inter-collision were frequently observed at low concentrations of crosslinking agents since particles are soft enough during a growing stage in polymerization. On the other hand, unstable aggregated particles were also obtained with extremely high concentrations of crosslinking monomers. The stable spherical particles were obtained at 20–90 mol% for EGDMA, 15–80 mol% for TMPTMA, and 5–40 mol% for PETRA. The number-average particle diameters are in the range of 4.01–3.06 μm for poly(S-*co*-EGDMA), 3.94–3.03 μm for poly(S-*co*-TMPTMA), and 2.77–1.66 μm for poly(S-*co*-PETRA). The average particle sizes decrease with the concentration of the crosslinking agents and the number of the crosslinkable functional moiety. In addition, the yield of the polymerization was 91.4% for 90 mol% EGDMA, 92.7% for 80 mol% TMPTMA, and 91.3% for 40 mol% PETRA. Furthermore, the yield increased with the number of the crosslinkable functional moiety at a constant concentration of the crosslinking agent. In the measurements of the endothermic transition using DSC, no glass transition temperature was observed for the whole samples synthesized in this study, implying that all polymer spheres are highly crosslinked. The TGA onset point of the thermal degradation temperature increased with the concentration of crosslinking agent and the number of crosslinking functional moiety, which is EGDMA < TMPTMA < PETRA. From the above result, it is obvious that the minimum and maximum concentrations for the formation of stable spherical particles of poly(S-*co*-EGDMA), poly(S-*co*-TMPTMA), and poly(S-*co*-PETRA), particle size and its distribution, CV, yield and the TGA onset point are significantly affected by the number of the crosslinkable functional moiety, which is the number of the (meth)acrylates in each crosslinking agent. In overall, the difference in the crosslinkable functional moiety and the different reactivity as well as the different copolymerization parameters between styrene and (meth)acrylates would influence the differences in the composition as well as the rate of formation of stable microspheres.

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