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Soap-free emulsion polymerization of styrene using poly(methacrylic acid) macro-RAFT agent

Yeonhwa Wi, Kangseok Lee, Byung Hyung Lee, Soonja Choe*

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

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ABSTRACT

A well-defined poly(methacrylic acid) (PMAA) macro-RAFT agent has been synthesized by the bulk polymerization using 4-toluic acid dithiobenzoate as a RAFT agent and successfully employed as a reactive emulsifier in the soap-free emulsion polymerization of styrene, leading to a formation of stable latex. The amphiphilic block copolymer, prepared from the in situ micelle formation, contains a hydrophilic PMAA block and a hydrophobic PS block, via styrene monomer transfer reaction to the dithioester function in PMAA macro-RAFT agent during the nucleation step. The chemical structure of the synthesized PS with the PMAA macro-RAFT agent was confirmed using FTIR and NMR. In addition, it was confirmed that the macro-RAFT agent is present on the particle surface via the ESCA measurement. The reaction mechanism was proposed that the stable spherical particles enlarged by the aggregation of small particles, which were also produced by the chemical or physical bonding between the tiny small particles. The results indicate that the PMAA macro-RAFT agent is used as emulsifier for the formation of PS particles and block copolymer [P(S-*b*-MAA)] in situ.

1. Introduction

Nano-sized polymeric particles with monodisperse size distribution have been utilized in various applications such as ion adsorbents [1], fillers in polymers, pigments, instrument calibration standards [2], diagnostics and drug carriers [3], reaction catalysis [4], environmental protection [5], etc. Water-borne polymerizations such as emulsion and suspension polymerizations are of great importance in industrial application as they provide environmental friendly processes, remove the reaction heat easily during polymerization, and assure the feasible handling of the final product having a low viscosity [6–8].

Research in controlled/living free-radical polymerization (LFRP) has been increased significantly during the past two decades. Based on the radical capping mechanism and agents, controlled/living radical polymerizations are generally classified as the nitroxide-mediated polymerization (NMP) [9,10], metal catalyzed atom transfer radical polymerization (ATRP) [11,12], and the reversible addition–fragmentation chain transfer (RAFT) [13,14] methods. Among the LFRPs, the RAFT polymerization allows the controlled polymerization of a wide variety of monomers at convenient temperatures. In the previous studies, we have reported the LFRP techniques using NMP [15,16] and RAFT [17–22] emulsion/dispersion polymerization to synthesize polymers with well-defined end groups and narrow molecular weight distributions. All these methods rely on a reversible activation–deactivation of the growing polymer chains. Although LFRP in bulk or solution polymerization was well studied previously, the implementation of LFRP in the dispersed aqueous media and especially in the emulsion polymerization has reported one or more of the following problems; poor colloidal stability, high polydispersity, poor molecular weight control. The first attempts to conduct LFRP in aqueous dispersions logically used emulsion polymerization. However these attempts generally failed, leading to the use of miniemulsions, which have proven to be quite robust for all forms of LFRP. In recent years, there have been several exciting and innovative developments in LFRP aqueous dispersions. Understanding of the interaction of the LFRP chemistry within a colloidally dispersed environment has progressed to the stage where processes are approaching commercial viability [13,23–25].

With the advance of LFRP methods, a variety of amphiphilic block copolymers have been studied as potential stabilizers in the emulsion polymerization. Common surfactants such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide possess critical micelle concentrations (CMCs) on the order of 10^{-3}–1 mol L^{-1} [26]. In the heterogeneous polymerization, lower concentration of amphiphilic block copolymers can be used than that of the conventional surfactants or stabilizers [27]. Amphiphilic block copolymers having both hydrophobic and hydrophilic blocks can form a micellar structure. For the efficient anchoring in amphiphilic

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* Corresponding author. Tel.: +82 32 860 7467; fax: +82 32 876 7467.
E-mail address: schoe@inha.ac.kr (S. Choe).

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block copolymer, the hydrophobic block has to be long enough, however, this might lead to a difficulty in solubilizing the block copolymer in water solution prior to polymerization. An alternative route is then to employ a reactive hydrophilic polymer capable to react during the polymerization course, hence affording an in situ amphiphilic block copolymer stabilizer.

Charleux et al. [28,29] reported a new approach to carry out miniemulsion polymerization. The amphiphilic diblock copolymer is used to emulsify the monomer phase in water, stabilize the particles, and initiate the polymerization of a third monomer for the preparation of ABC triblock copolymers using AGET (activator generated by electron transfer) ATRP. In addition, the RAFT-mediated non-aqueous dispersion polymerization of methyl acrylate in isododecane, which is a nonsolvent for poly(methyl acrylate), was carried out by using soluble poly(2-ethylhexyl acrylate) macromolecular RAFT agents, containing either a dithiobenzoate reactive function or a trithiocarbonate one. The soap-free emulsion polymerization of styrene was acted in the presence of comonomer (sodium acrylate) and RAFT agent (dibenzyltrithiocarbonate). The new process based on a spontaneous phase inversion mechanism overcomes the slow diffusion of the RAFT agent [30]. The water-soluble polymers carrying a thio end group such as poly(dimethylaminoethyl methacrylate), poly(ethylene oxide), and poly(ethylene oxide)-*b*-poly(dimethylaminoethyl methacrylate) have been estimated as precursors of stabilizers in soap-free emulsion polymerization of styrene under acidic conditions to form ionically stabilized polystyrene latex particles [31,32].

In our previous study, the crosslinked poly(divinylbenzene) [PDVB] particles were synthesized in the presence of poly(styrene-*block*-4-vinylpyridine) copolymer in aqueous media. The block copolymer consisting of the RAFT agent is used as an emulsifier and reactive stabilizer as well, but the process is carried out using two-step polymerizations [33].

In this study, we were able to obtain submicron-sized monodisperse spherical particles using a small amount of block copolymer of the poly(methacrylic acid) (PMAA) macro-RAFT agent as a precursor of emulsifier in the in situ one-step polymerization. The mechanism is proposed on the basis of the formation of particle, particle size, and the content of oxygen on the particle surface and follows the previously proposed micelle formation in our previous study [31]. This work does not only intend to apply the controlled free-radical polymerization in an aqueous dispersed system but also takes advantage of the RAFT technique to create a well-defined emulsifier with a high chain-end reactivity. Such reactive hydrophilic polymers can be considered as a new class of macromolecular emulsifier, which will be able to afford new developments in soap-free emulsion polymerization.

2. Experimetal

2.1. Materials

Styrene (Junsei Chemicals, Tokyo, Japan) and methacrylic acid (99% purity, Aldrich Chemical Co., WI, USA) were purified using an inhibitor removal column (Aldrich Chemical Co., WI, USA) and stored at −5 °C prior to use. 2,2-Azobis(isobutyronitrile) (AIBN, Junsei Chemicals, Tokyo, Japan) was used without further purification. Double-distilled deionized (DDI) water was used as the polymerization medium. Tetrahydrofuran (THF, Acros, Gheel, Belgium) employed in the synthesis of a RAFT agent was freshly distilled using sodium and benzophenone. Phenylmagnesium bromide (3.0 M in diethyl ether, Aldrich Chemical Co., WI, USA), carbondisulfide (99.9% purity, Aldrich Chemical Co., WI, USA), and α-bromo-*p*-toluic acid (97% purity, Aldrich Chemical Co., WI, USA) were purchased from Aldrich Co. Silica used in column chromatography was kieselgel-60 (Merck, Germany).

2.2. Synthesis of the RAFT agent

A RAFT agent, 4-toluic acid dithiobenzoate, was synthesized in the laboratory according to the previous work [34].

2.3. Synthesis of the poly(methacrylic acid) (PMAA) macro-RAFT agent

The 4-toluic acid dithiobenzoate is used as the chain transfer agent (CTA). A solution containing methacrylic acid (36 mL, density; 1.015), AIBN (0.014 g), and 4-toluic acid dithiobenzoate (0.12 g) was prepared under an anhydrous condition. The solution was degassed using nitrogen for 30 min. Then, a vial was sealed and completely submerged in an oil bath at 60 °C for 12 h. After the polymerization, the reaction product was dissolved in DDI water, and the polymer was precipitated in acetone/diethyl ether and purified by repeated precipitation and washing process. The product was dried in a vacuum oven at 70 °C. In order to verify the difference between the block copolymer of P(S-*b*-MAA) and the mixture of homopolymers of PS and PMAA, the bulk polymerizations of styrene and methacrylic acid were carried out in a 20 mL capped scintillation vial with styrene (10 g), methacrylic acid (0.36 g) and AIBN (0.1 g) under a nitrogen atmosphere, respectively.

2.4. Soap-free emulsion polymerization of styrene using the PMAA macro-RAFT agent

Soap-free polymerization of styrene was carried out in a 50 mL capped scintillation vial with magnetic stirring under a nitrogen atmosphere. DDI water (30 g) was first added in the scintillation vial and 10 wt% of styrene (3 g) relative to the medium was charged. The amount of AIBN (0.03 g) was fixed at 1 wt% relative to the monomer. The concentration of the PMAA macro-RAFT agent was varied from 0.2 to 10 wt% (0.3 g) relative to styrene. The polymerization temperature was set at 70 °C in an oil bath and the vial was stirred with a magnetic stirrer. During the polymerization, aliquots of the product were periodically taken from the reaction vessel for the characterization. After completion of the polymerization, the resultant material was rinsed off with water and ethanol, and then centrifuged repeatedly to remove the residual PS and PMAA macro-RAFT agent.

2.5. Characterizations

The molecular weight and polydispersity index (PDI) were characterized using a GPC (gel permeation chromatography, Waters viscotex, USA) equipped with a 510 differential refractometer and Viscotek T50 differential viscometer, using THF or water as running solvents, separately. The GPC using THF as the solvent is for polystyrene. A universal calibration curve (RI detector) was obtained using 10 polystyrene standard samples (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g/mol. In order to prepare the GPC sample, an aliquot of the sample taken from the reaction vessel was washed with excess water and centrifuged at 9000 rpm, repeatedly. Then, they were dissolved in THF, and the solution was passed through a 0.45 μm filter and then injected into the GPC column at a flow rate of 1.0 mL/min. For water based GPC, the samples were dissolved in water, the solution was passed through a 0.45 μm filter and then injected into the GPC column at a flow rate of 1.0 mL/min. A universal calibration curve was obtained using 10 polyethylene glycol (PEG) standard samples (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g/mol. The chemical structure of the synthesized polymer was verified by a Varian 400 MHz ^{1}H NMR (Unity INOVA400, Palo Alto, USA) using $CDCl_3$ as a solvent and an FTIR spectrum obtained using a Bruker series FTIR spectroscopy (Vertex

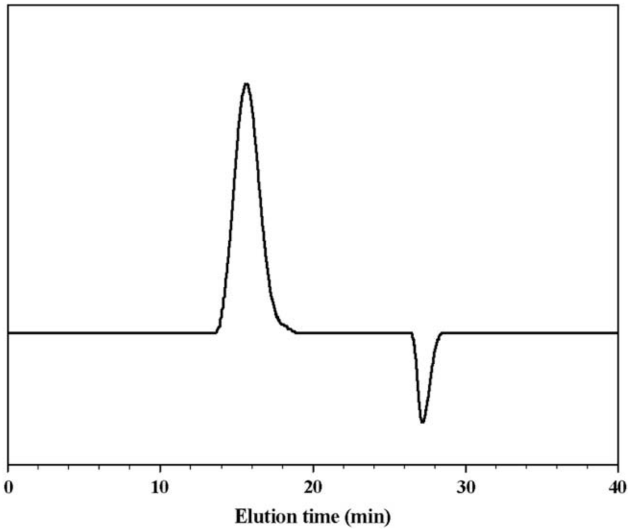


Fig. 1. GPC traces for poly(methacrylic acid) macro-RAFT agent prepared by bulk polymerization using water as a solvent at 60 °C.

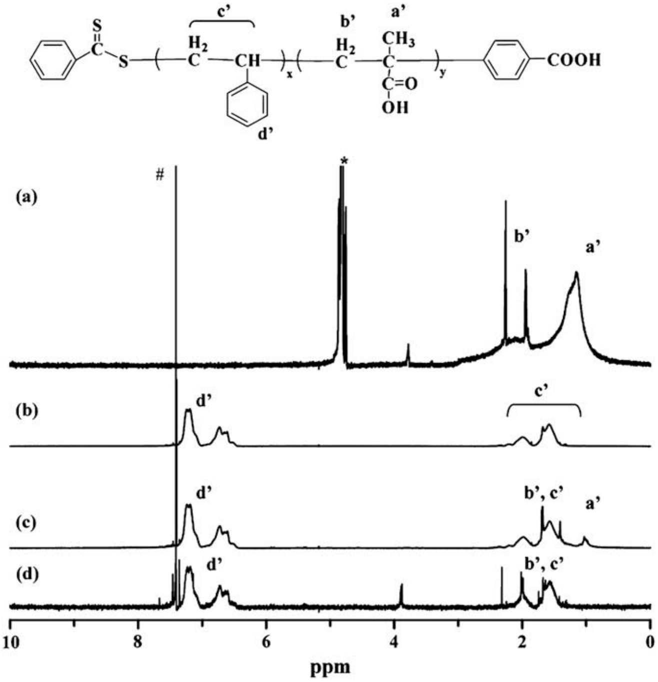


Fig. 2. ^{1}H NMR spectra of (a) pure PMAA (b) pure PS (c) Poly(S-*b*-MAA) (5 wt% PMMA relative to monomer) copolymers (d) mixed homopolymers (pure PS:pure PMMA = 95:5) [solvent peaks: *(D$_2$O), $^\#$(CDCl$_3$)].

80 V, Bruker Optics, Germany). All infrared spectra were recorded for 20 s for each specimen. SEM (scanning electron microscopy, S-4300, Hitachi, UK) was used to observe the morphology of the PS particles. The samples were prepared with a drop of diluted suspension on an aluminum tape. Then each sample was sputter-coated with platinum. The particle size and its distribution were measured using a particle size analyzer (Mastersizer 2000, Marvern, UK). The fractional conversion was calculated gravimetrically. The number-average diameter (D_n), and the coefficient of variation (Cv) were obtained using Scion Image Analyzer (SIA) software (Scion Corporation, Frederick, Maryland, USA) by counting 200 individual particles from the SEM photographs using the formula as described previously [35]. The compounds on the surface of the PS particles were analyzed using an ESCA (Electron Spectroscopy for Chemical Analyzer, VG Multilab 2000, Thermo electron corporation, UK). It utilized X-rays (source; Mg Kα) with low energy (anode voltage 14.9 keV) to knock off photoelectrons from atoms of the sample through the photoelectric effect. The energy content of these ejected electrons was then analyzed by a spectrometer to identify the elements where they came from.

3. Result and discussion

3.1. *Effect of the presence of PMAA macro-RAFT agent on the emulsion polymerization*

The weight-average molecular weight (M_w) and polydispersity index (PDI) of PMAA macro-RAFT agent were measured using GPC; the M_w of the macro-RAFT agent is 316,160 g/mol and the PDI is 1.21 (Fig. 1). The conversion was 38% in 12 h. The low molecular weight distribution of PMAA confirms that the RAFT method successfully worked for the preparation of macro-RAFT agent.

^{1}H NMR spectroscopy is used to verify the chemical structure of the synthesized PMAA macro-RAFT agent, polystyrene (PS), and PS synthesized using the PMAA macro-RAFT agent [P(S-*b*-MAA)]. Fig. 2(a) and (b) shows the spectrum of PMAA and PS prepared by the bulk polymerization, respectively. Fig. 2(c) is a spectrum of P(S-*b*-PMAA) prepared by the RAFT method. In the characteristic peaks of PMAA in Fig. 2(a), the resonance of the methyl protons (a′) shows a multiplet around 0.8–1.7 ppm and the H–C sp^3 signal expansion in the interval of 0–4 ppm. It is due to H–C sp^3 signal repetition in the homopolymeric chain [36]. For PS in Fig. 2(b), two multiplets were observed at 6.2–7.2 ppm for five protons of the phenyl ring (d′) and methane and methylene of the PS were observed at 1–2 ppm [37]. Fig. 2(c) shows the same characteristic peaks of PS and PMAA as observed in (a) and (b), respectively. Based on the ^{1}H NMR spectra, it was confirmed that P(S-*b*-MAA) was successfully synthesized implying that the block copolymer contains styrene and PMAA block. In addition, Fig. 2(d) shows the spectrum of the mixed homopolymers (pure PS:pure PMMA = 95:5 wt%). This spectrum shows some similarities to Fig. 2(c), but doesn't show a peak (a′) from (c).

Fig. 3 compares the FTIR spectra of PMAA prepared by the bulk polymerization and the PS particles with different concentrations of the PMAA macro-RAFT agent in the emulsion polymerization in water at 70 °C. In Fig. 3(a) showing the FTIR spectra of pure PMAA, the absorption peak of extension vibration of C═O at 1708 cm^{-1} is

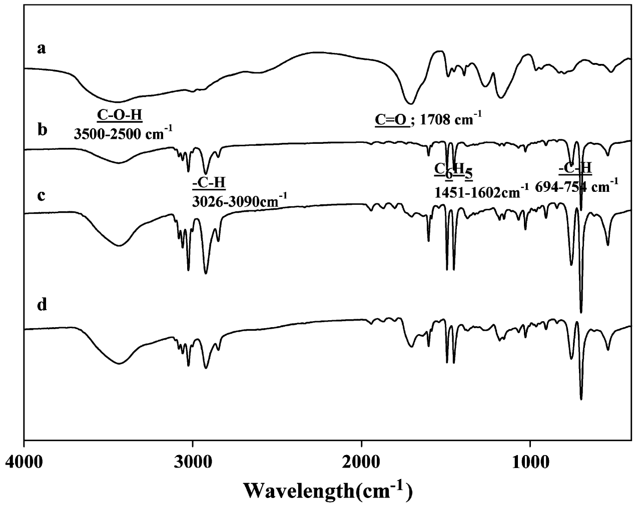


Fig. 3. FTIR spectra of the PMAA macro-RAFT agent prepared by the bulk polymerization (a), neat PS prepared by the bulk polymerization (b), P(S-*b*-MAA) (2 wt% relative to monomer) (c), and P(S-*b*-MAA) (5 wt% relative to monomer) prepared by the emulsifier-emulsion polymerization in water (d).

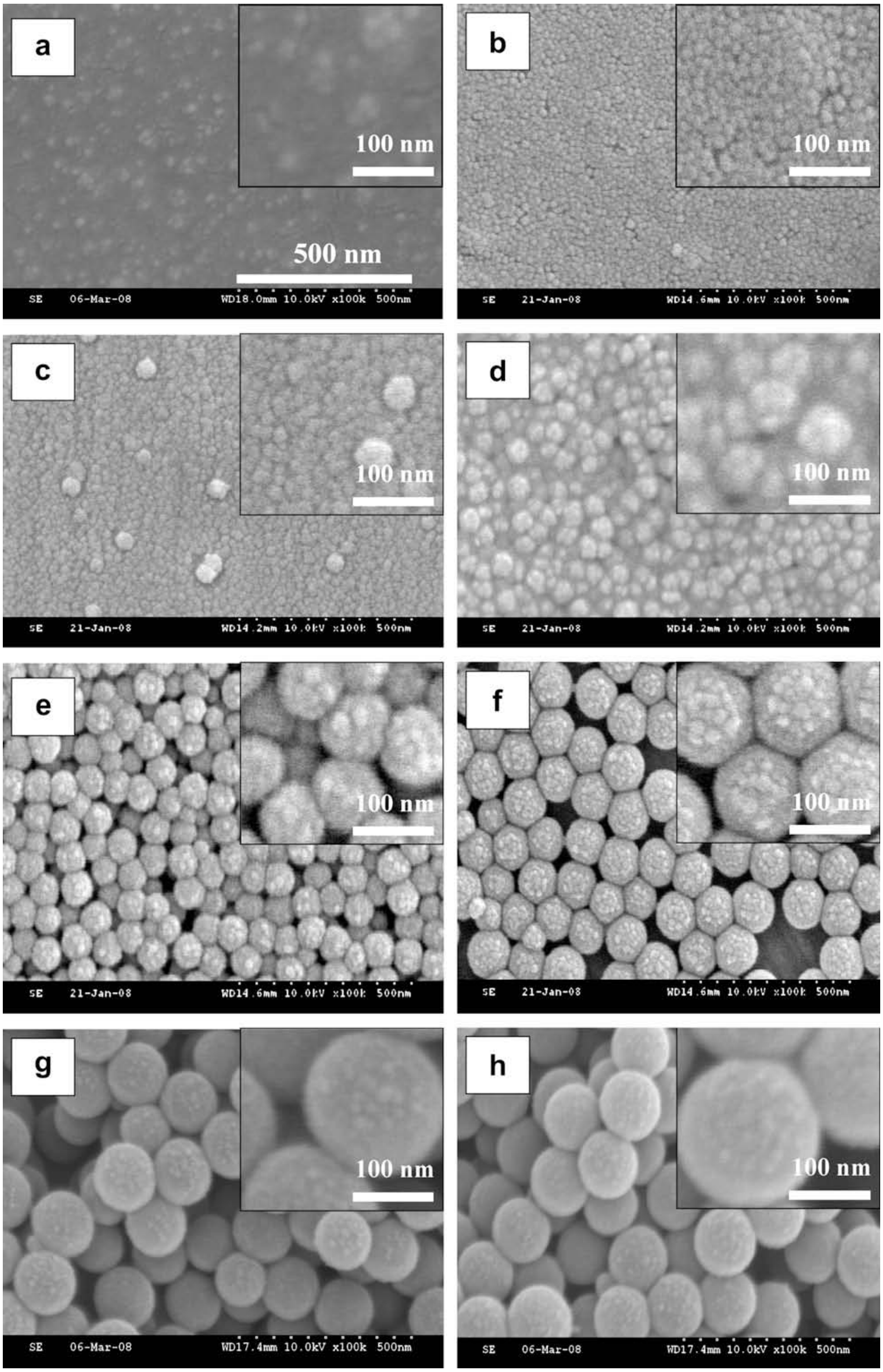


Fig. 4. SEM photographs of particle diameter formed with 1 wt% AIBN and 2 wt% PMAA macro-RAFT agent at 70 °C for 24 h at different polymerization times: (a) 10 min (b) 30 min (c) 1 h (d) 2 h (e) 4 h (f) 8 h (g) 12 h (h) 24 h.

strengthened. At 3500–2500 cm^{-1}, a very broad peak is observed, which is caused by the C–O–H extension vibration of hydroxyl group. In Fig. 3(b) representing the pure PS prepared by the bulk polymerization, the absorption peaks of extension vibration of –C–H on the benzene ring at 3026–3090 cm^{-1}, framework of benzene ring at 1451–1602 cm^{-1}, and the absorption peaks of bending vibration of –C–H on the benzene ring at 694–754 cm^{-1} were observed. In addition, the characteristic peaks of PS with 2 and 5 wt% of PMAA macro-RAFT agent are compared in Fig. 3(c) and (d), respectively. Since the composition of the macro-RAFT agent in PS particles is different between 2 and 5 wt%, the peak intensity of the extension vibration of C=O at 1708 cm^{-1} and C–O–H at 3500–2500 cm^{-1} is slightly increased. From the above observation, one can suggest the existence of the PMAA macro-RAFT agent on the PS particles. Therefore, the PMAA macro-RAFT agent is working as a precursor of emulsifier in this study.

For the supplementary validation of the proposed mechanism of the formation and growth of the particles in the medium using

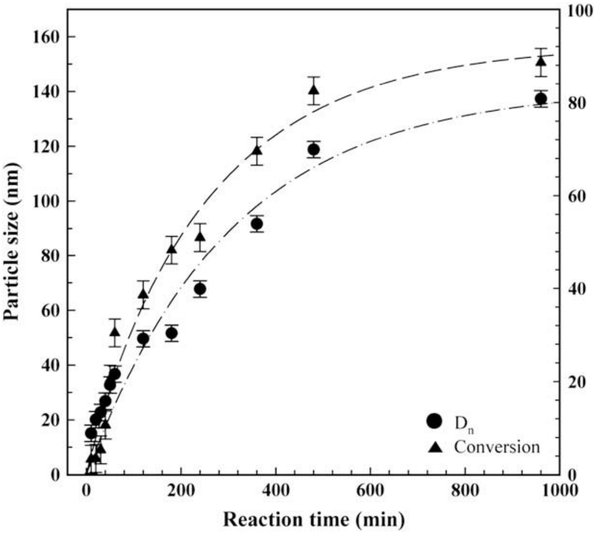


Fig. 5. Particle size and conversion of the PS spheres in the presence of 2 wt% PMAA macro-RAFT agent at 70 °C at different reaction times (10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 2 h, 4 h, 6 h, 8 h, 12 h, 24 h).

PMAA macro-RAFT agent, several experiments are carried out based on the formation of micelles, particle size and conversion at various reaction times (10 min–24 h). In these experiments, monomer (styrene) contents are 10 wt% relative to the medium (water), initiator (AIBN) contents are 1 wt% relative to the monomer (styrene) and the PMAA macro-RAFT agent contents are 2 wt% relative to the monomer. The particle shape and size are characterized, and the results are shown in Figs. 4 and 5.

Fig. 4 shows the SEM photographs of the PS spherical particles prepared with 1.0 wt% AIBN and 2.0 wt% PMAA macro-RAFT agent as a function of the reaction time for 24 h. When the ingredients including the PMAA macro-RAFT agent and styrene are reacted for 10 min in water medium, the P(S-*b*-MAA) copolymer containing styrene leads the formation of micelles of the average size of 15 nm consisting of the hydrophobic PS block inside and the hydrophilic PMAA block toward outside [Fig. 4(a)]. After this stage, the micelle size increases to 20 nm in 30 min [Fig. 4(b)]. When the polymerization of styrene is taking place at 70 °C, a propagating radical undergoes chain transfer with a sulfur atom on dormant species of the PMAA macro-RAFT agent, which subsequently reacts with styrene in the continuous phase. As a result, the P(S-*b*-MAA) copolymer is formed. After this point, the sulfur atom and the carboxylic acid group which is located in the side chain of the P(S-*b*-MAA) block copolymer react with unreacted styrene monomer, oligomer, or

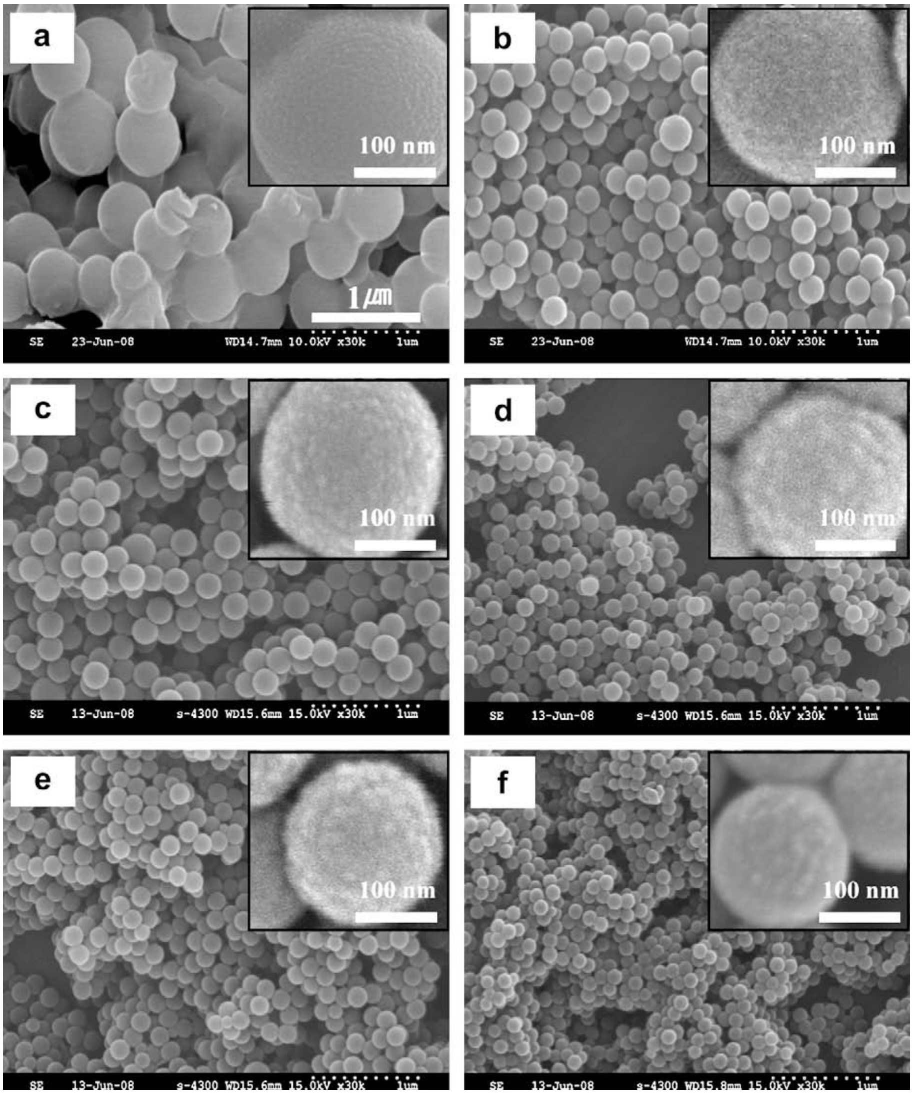


Fig. 6. SEM photographs of PS microspheres prepared with (a) 0.1 (b) 0.2 (c) 0.3 and (d) 0.6 (e) 1 (e) 2 wt% PMAA macro-RAFT agent for 24 h.

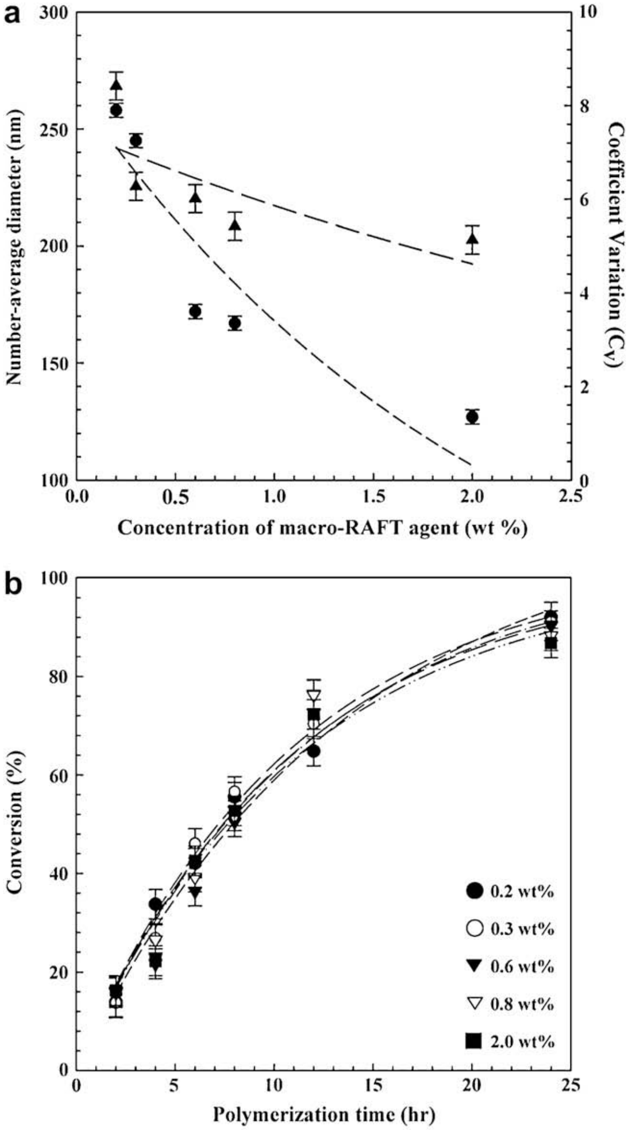


Fig. 7. (a) Number-average diameter (D_n; ●), coefficient variation (C_v; ▲)and (b) conversion of PS microspheres prepared by emulsifier-free emulsion polymerization with varying concentrations of 0.2–2 wt% PMAA macro-RAFT agent in water at 70 °C.

growing block copolymer in another particle. The tiny small particles with living character in the presence of the PMAA macro-RAFT agent and block copolymer are physically and chemically bonded after 1 h [Fig. 4(c)]. Since the block copolymer, in particular the reactive PMAA block, exists on the surface of the particles, the growing particles can be chemically bonded by the propagation of styrene monomer. Although the termination reaction is negligible in the RAFT polymerization, it is limited to the polymerization of mono-functional monomers. This would lead to the coagulation of particles. At last, the particles are formed by the aggregation and chemical or physical bonding, which is obviously seen in Fig. 4(d). Furthermore, the particles enlarged by the aggregation of the small particles. Because of the existence of the additional reactive site, the polymerization of styrene can take place to form oligomers, resulting in the filling of the uneven particle surface [33].

In Fig. 5, the particle size and conversion were plotted as a function of the reaction time. As the reaction time increased from 0 to 24 h, the particle diameter increased from 15.1 to 137.3 nm, respectively, and the conversion went up from 5.32 (10 min) to 88.58% (24 h), respectively.

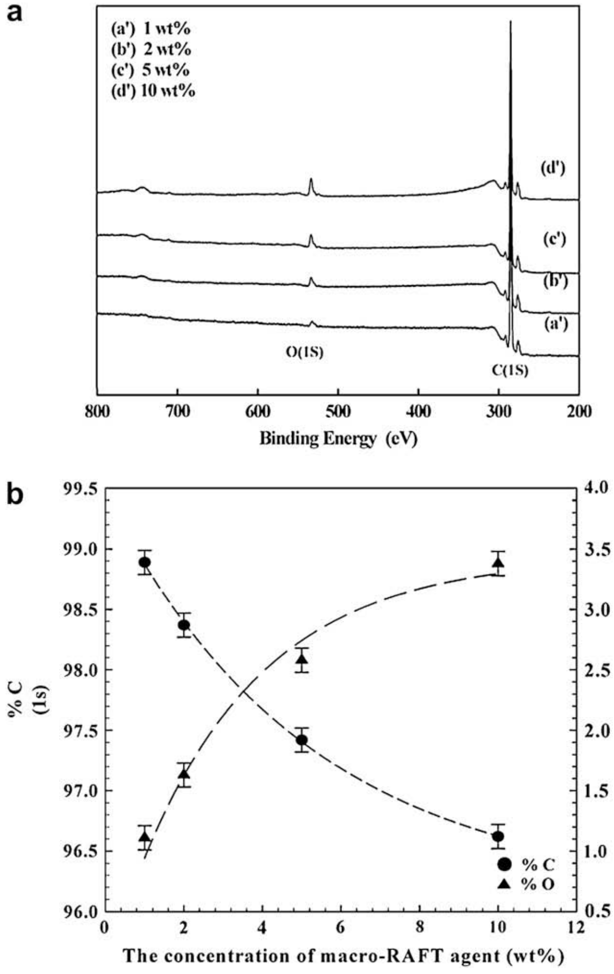


Fig. 8. (a) ESCA spectrum of PS spheres with 1–10 wt% PMAA macro-RAFT relative to monomer agent in water at 70 °C for 24 h. (b) The plots of 1S oxygen and 1S carbon as a function of the PMAA macro-RAFT agent.

3.2. Effect of the concentration of the PMAA macro-RAFT agent on the polymerization

Fig. 6 represents the SEM photographs of the PS spherical particles prepared with 0.1–2.0 wt% PMAA macro-RAFT agent referring to monomer in water at 24 h. The coagulation was observed with 0.1 wt% macro-RAFT agent, possibly due to the low concentration of the PMAA macro-RAFT on the formation of stable spherical particles, in Fig. 6(a). On the other hand, the spherical particles of P(S-*b*-MAA) were observed with 0.2–2.0 wt% PMAA macro-RAFT agent as seen in Fig. 6(b)–(f), respectively. In addition, the particle size decreased with increasing concentration of the macro-RAFT agent. This indicates that the PMAA macro-RAFT agent is working as a precursor of emulsifier inducing stable spherical particles. The resulting number-average diameter and the coefficient of variation (C_v) from Fig. 6 are plotted in Fig. 7. In Fig. 7(a), the particle diameter decreased from 258 to 127 nm and the C_v also decreased from 8.4 to 5.2 as the concentration of the macro-RAFT agent increased from 0.2 to 2.0 wt%, respectively. This tells that the macro-RAFT agent is working well as a precursor of emulsifier in this emulsion polymerization. In Fig. 7(b), the conversion increased with the polymerization time, however, no particular concentration dependency of the macro-RAFT agent on the conversion was observed.

Fig. 8 compares the XPS spectrum using the ESCA for the PS particles prepared with 1, 2, 5, 10 wt% PMAA macro-RAFT agent in the emulsion polymerization in water at 70 °C. In Fig. 8(a), there are two peaks of 1S oxygen and 1S carbon at 280 and 520 eV,

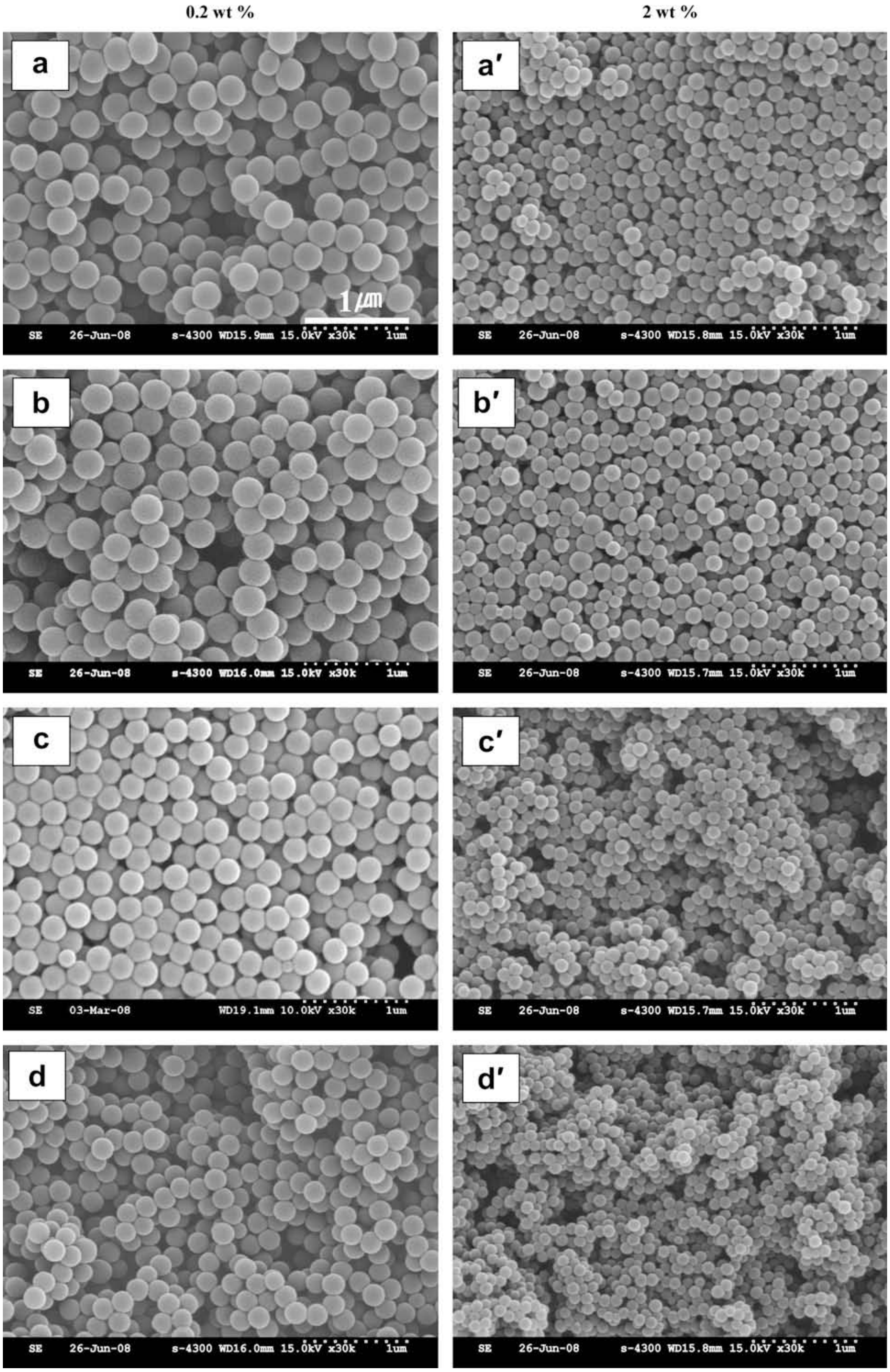


Fig. 9. The representative SEM photographs of PS microspheres at different AIBN concentrations in the presence of 0.2 (left) and 2 wt% (right) of PMAA macro-RAFT agent relative to monomer at 70 °C for 24 h in water medium. (a), (a′) 0.5; (b), (b′) 1.0; (c), (c′) 2.0; (d), (d′) 3.0 wt% AIBN relative to the monomer.

respectively. From these curves, the contents of 1S oxygen and 1S carbon are plotted in terms of the concentration of the macro-RAFT agent in (b). In this figure, as the contents of the macro-RAFT agent increase, the content of 1S carbon decreases from 98.89 to 96.62%, but the content of 1S oxygen increases from 1.11 to 3.38%. This suggests that the PMAA macro-RAFT agent exists on the surface of PS particles since the oxygen atom only exists in PMAA. Thus, the larger the content of the macro-RAFT agent, the higher the macro-RAFT agent exists on the particle surface inducing the formation of small particles due to the increased stability of the micellar structure of the agent.

3.3. The effect of the initiator concentration on the polymerization

Since the RAFT agent acts as a chain transfer agent (CTA), the effect of the concentration of AIBN and macro-RAFT agent on the polymerization characteristics was studied. The representative SEM photographs of PS spherical particles at various concentrations of AIBN between 0.5 and 3.0 wt% at 0.2 and 2.0 wt% PMAA macro-RAFT agent are shown in Fig. 9 (left) and (right), respectively. The common feature is that the particle sizes decrease with the increased concentration of AIBN and PMAA macro-RAFT agent, simultaneously.

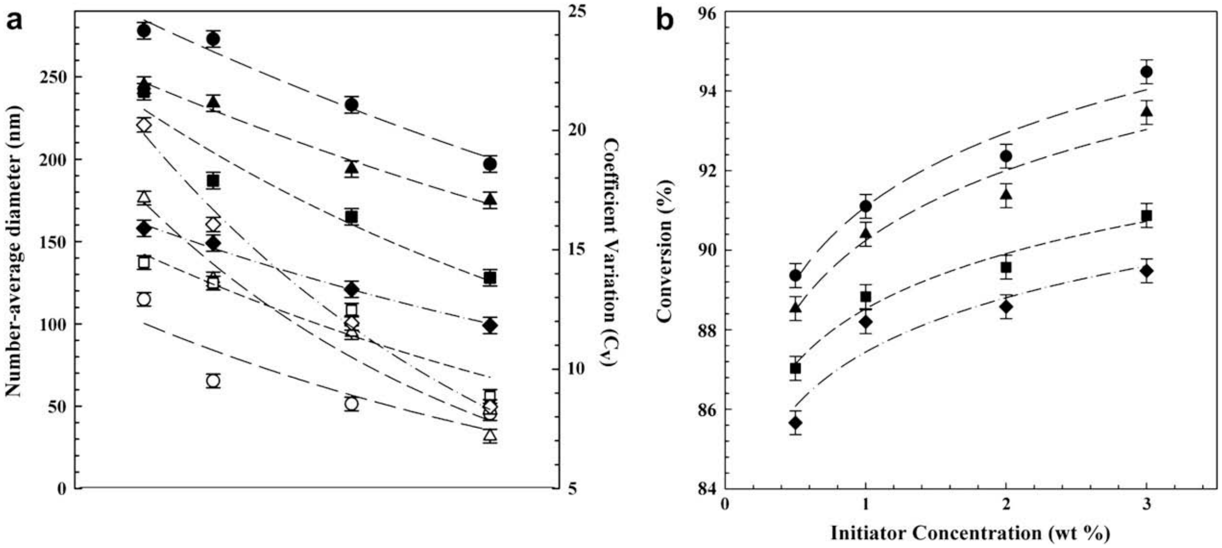


Fig. 10. (a) Number-average diameter (D_n: solid symbol), coefficient variation (C_v: open symbol) and (b) Conversion of PS microspheres prepared by emulsifier-free emulsion polymerization with various concentrations of initiator (0.5–3 wt%) and PMAA macro-RAFT agent in water at 70 °C. (concentrations of PMAA macro-RAFT agent: ● ○, 0.2 wt%; ▲ △ 0.3 wt%; ■ □, 1.0 wt%; ◆ ◇, 2.0 wt% relative to monomer).

In Fig. 10, the particle size, C_v and the conversion were plotted as a function of the concentration of initiator between 0.5 and 3.0 wt% and the RAFT agent between 0.2 and 2.0 wt%. The number-average diameter (D_n) of PS at different concentrations of AIBN and PMAA macro-RAFT agent decreases from 278 to 197 for 0.2 wt% RAFT agent, from 245 to 175 for 0.3 wt% agent, from 241 to 128 nm for 1.0 wt% RAFT agent, and from 158 to 99 nm for 2.0 wt% RAFT agent. The increased amount of initiator induces a large number of

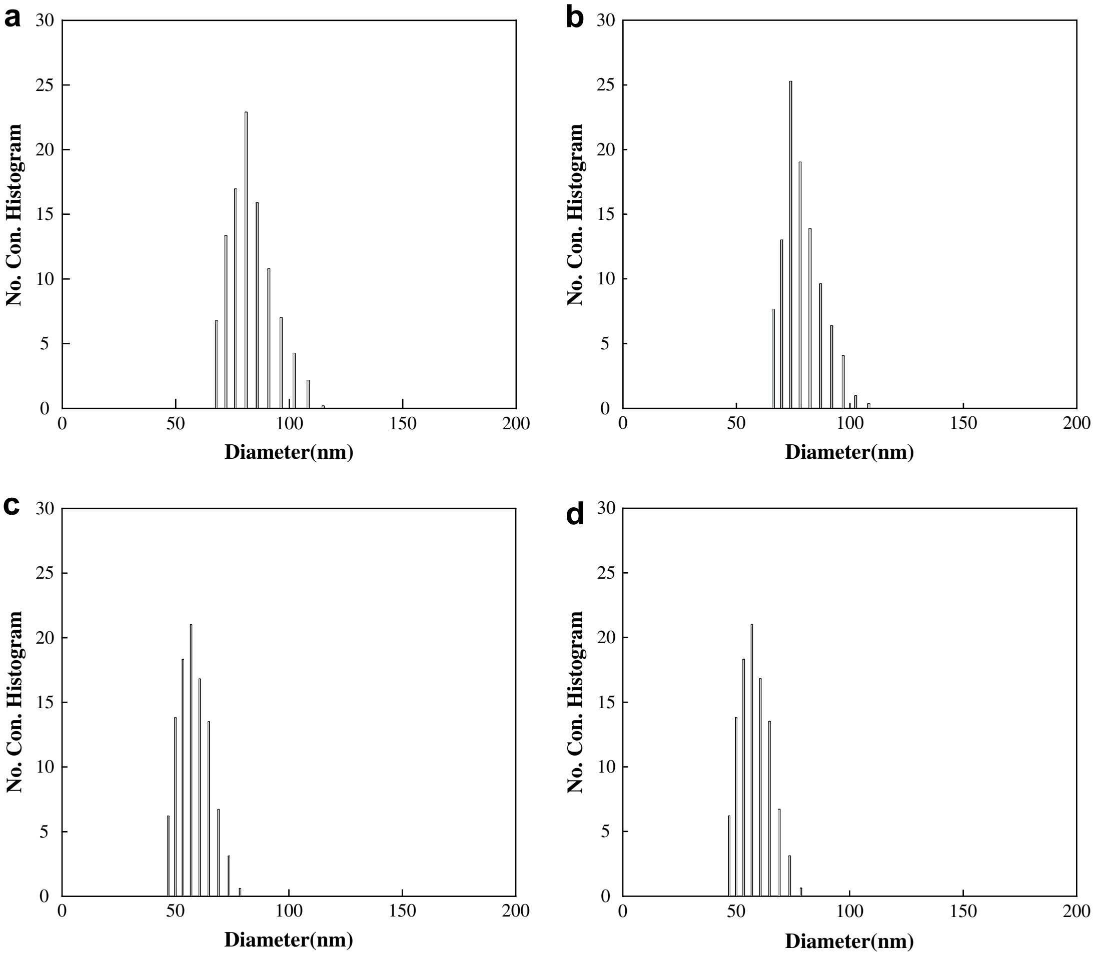
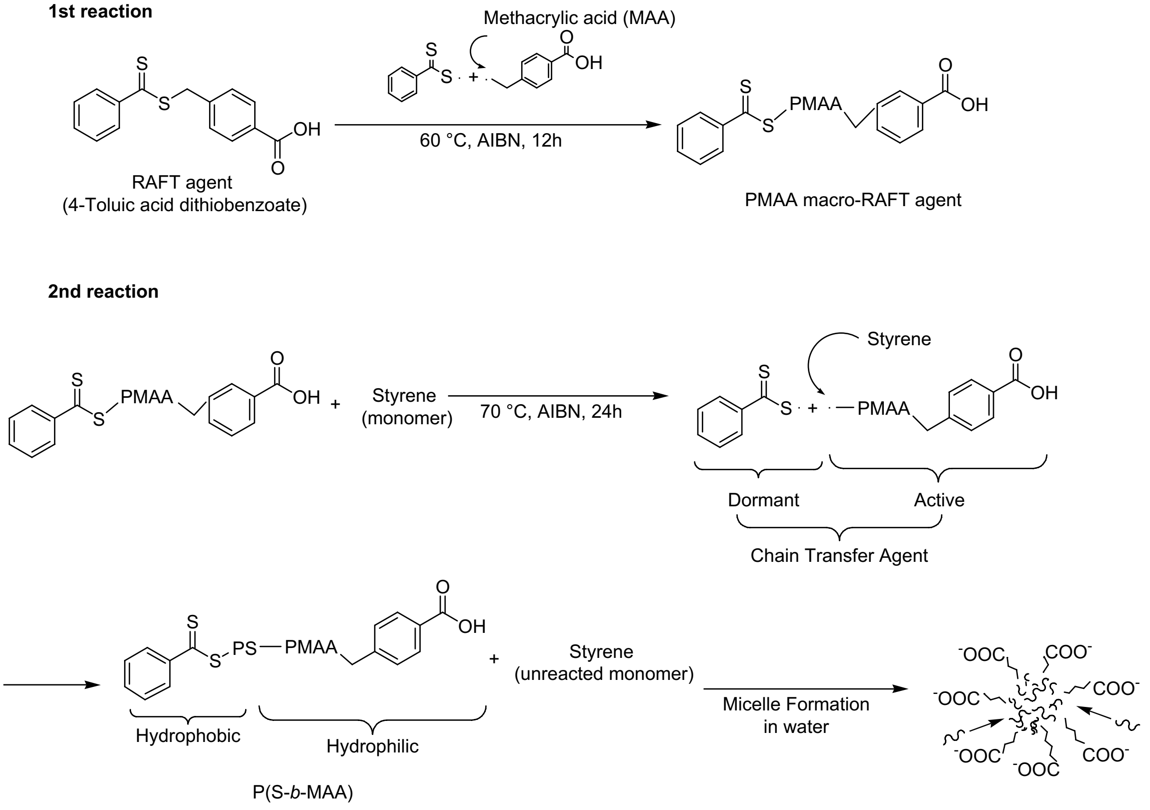


Fig. 11. The representative particle size distribution of the P(S-*b*-MAA) copolymer obtained from 2 wt% RAFT agent and different concentrations of initiator: (a) 0.5 wt% (b) 1 wt% (c) 2 wt% (d) 3 wt% relative to monomer.



Scheme 1. The mechanism of the formation of micelle in situ polymerization using a PMAA macro-RAFT agent.

polymeric particles, which leads to smaller individual particle sizes. On the other hand, the conversion increases with increasing initiator concentration, respectively. Thus, it is confirmed that the size of PS spherical particles reduced with the increased content of the macro-RAFT agent and initiator because the amount of the formed nuclei increased.

Fig. 11 is the representative particle size distribution data of the P(S-*b*-MMA) copolymer obtained from 2 wt% RAFT agent and different concentrations of initiator: (a) 0.5 wt% (b) 1 wt% (c) 2 wt% (d) 3 wt% relative to monomer. In this figure, the distribution becomes narrower when the content of the initiator increases. Thus, 2 wt% of AIBN would be proper to synthesize the submicron-sized P(S-*b*-MAA) particles.

*3.4. The proposed mechanism of the formation of poly(S-*b*-MAA) using the PMAA macro-RAFT agent*

From the above observation, the mechanism of the formation of the stable PS spherical particles was proposed as seen in Scheme 1. As seen in Scheme 1, the PMAA macro-RAFT agent is decomposed in water and severed into a dormant and active species through a homolytic cleavage of the carbon–sulfur bond. The active species carrying carboxyl group undergoes further propagation. As the hydrophobic monomer reacts with the active species, the length of a hydrophobic aliphatic backbone of oligomer becomes longer, making the intermediate surface-active because it contains both hydrophilic and hydrophobic moieties. Therefore, the intermediate could form micelles which serve as a locus of polymerization for the emulsion polymerization. The hydrophilic moiety is aligned outwards and the hydrophobic oligomeric chains are placed inside of the micelles. In addition, the growth of particles occurs by monomer transportation from monomer droplet to the micelles or monomer-swollen particles. This mechanism is quite similar to the emulsifier-free emulsion polymerization where initiators such as water-soluble initiators (i.e. KPS, APS) generate a surface-active oligomeric intermediate [38]. At this point, the sulfur atom and the vinyl group which is located in the side chain of the block copolymer react with partially unreacted styrene monomer or polymer. This reaction induces the chemical or physical bonding resulting in between the tiny small particles. Finally, stable spherical polymer particles can be produced by the aggregation of small particles. This phenomenon may follow the previously proposed mechanism of the micelle formation [33].

4. Conclusions

In this study, poly(methacrylic acid) (PMAA) macro-RAFT agent has been synthesized by the bulk polymerization using 4-toluic acid dithiobenzoate as a RAFT agent and used in the soap-free emulsion polymerization of styrene. In order to prevent this phenomenon that water-soluble initiator such as potassium persulfate (KPS) forms oligomeric radical and reacts with hydrophobic monomer as an emulsifier in emulsion polymerization, water-insoluble initiator, AIBN, is used for the polymerization. The chemical structure of the synthesized PS with the PMAA macro-RAFT agent was confirmed using FTIR and NMR. The polymerization in aqueous media with water-insoluble monomer and initiator is a typical suspension polymerization, providing the monodisperse submicron-sized spherical particles. It was confirmed that the macro-RAFT agent is present on the particle surface via the ESCA measurement. The size of PS spheres reduced as the amount of the macro-RAFT agent and the concentration of initiator increased because the amount of nuclei formation increased. The reaction leads to stable latex, as a result of the in situ micelle formation of an amphiphilic block copolymer stabilizer containing a hydrophilic PMAA block and a hydrophobic PS block, via styrene monomer transfer reaction to the dithioester functions in PMAA macro-RAFT agent during the nucleation step. It was confirmed that the macro-RAFT agent is present on the particle surface via the ESCA measurement. The reaction mechanism is proposed that the stable spherical particles enlarged by the aggregation of small particles, which were also produced by the chemical or physical bonding between the tiny small particles. The results indicate that the PMAA macro-RAFT agent could be a precursor of an effective emulsifier for the formation of submicron-sized polystyrene particles.

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