

Ab Initio Dispersion Polymerization of Styrene in the Presence of the Poly(methacrylic acid) Macro-RAFT Agent

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Abstract: Stable, spherical, polystyrene particles were synthesized in ab initio dispersion polymerization by using the poly(methacrylic acid)[PMAA] macro-RAFT agent. The presence of the PMAA macro-RAFT agent on the polystyrene (PS) particles was confirmed by NMR and FTIR spectroscopy. The PS particle size was influenced by the concentration of the RAFT agent and monomer due to the initial nucleation. When the concentration of the PMAA macro-RAFT agent was increased from 2 to 10 wt% relative to the monomer, the average particle size decreased from 2.31 to 1.36 μm , the conversion decreased from 93.3 to 88.9%, the weight-average molecular weight increased from 46,300 to 150,200 g mol^{-1} and the PDI decreased from 2.79 to 1.94, respectively. In particular, the incorporation of 10 wt% of PMAA macro-RAFT agent produced monodisperse PS spheres of 1.36 μm with a coefficient of variation (CV) of 6.44%. Thus, the PMAA macro-RAFT agent worked as a reactive steric stabilizer providing monodisperse, micron-sized, PS particles.

Keywords: dispersion polymerization, poly(methacrylic acid) macro-RAFT agent.

Introduction

Micron-sized monodisperse polymeric spheres are used for various applications such as toners, standard samples for instrument calibration, column packing materials in chromatography, microelectronic materials, and biomedical analysis.¹⁻⁵ Dispersion polymerization in a single step is one of the methods used for the preparation of micron-sized monodisperse polymer particles for the last two decades.^{6,7}

In the synthesis of polymer colloids, various stabilizing agents are essentially used such as surfactants in emulsion, dispersants in suspension, and steric stabilizers in dispersion polymerization. The polymerization mechanisms are different in each case. In emulsion polymerization, the surfactants provide not only a colloidal stability but also a polymerization locus in aqueous media. In suspension polymerization, protective stabilizers, also called dispersants, are used to endow colloidal stability of the monomer droplets by physical adsorption in aqueous media. Steric stabilizers in dispersion polymerization serve as precursors in particle nucleation and give stability to the formed particles in organic media.

Steric stabilizers frequently used in dispersion polymerization can be classified into three different types; homopolymers,^{8,9} macromonomers,¹⁰ and block¹¹ or graft copolymers. The most effective steric stabilizers are based on the graft or

block copolymers those incorporate a segment soluble to the dispersing solvent, or those adsorbed or anchored on to the dispersed phase. Among them, amphiphilic block copolymers with low critical micelle concentrations (CMC) and diffusion coefficients are strongly fixed on the colloidal particles. The structure of amphiphilic block copolymer consists of two parts; one segment is an anchor to the surface of polymer particles while the other hydrophobic segment is extended into the continuous phase. It can be inferred that the amphiphilic block copolymers provide steric barrier that prevents the coagulation of the polymer particles. The early studies of block copolymers as stabilizers in the dispersion polymerization were carried out by many researchers.^{6,12,13} In most cases, relatively high concentrations (from 10 to 30 wt% in weight to monomer) of stabilizers (homopolymers or macromonomers) were used.¹⁴ However, the use of a small fraction of stabilizers is important in the industrial point of view in order to minimize possible side reactions. Wang *et al.* studied that only 6% of the introduced PVP ($M_w=3,600,000 \text{ g mol}^{-1}$) is grafted on the surface of the final poly(*n*-butyl acrylate) latex particles. This low grafting yield essentially results from a low transfer constant to the polymer (from 10^{-4} to 10^{-3}).¹⁵ As the grafting reactions occur along the precursor chains of the stabilizer, the stabilizers grow to become grafted copolymers.¹⁶ Furthermore, a number of monomers are used in the synthesis of block copolymers using controlled/living free radical polymerization (LFRP) under less rigorous experimental conditions than in the

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ionic polymerization. LFRP has been known to be a useful technique for preparing well-defined polymer structure. The three main techniques that induce living behaviors are nitroxide mediated polymerization (NMP),^{17,18} atom transfer radical polymerization (ATRP),^{19,20} and reversible addition-fragmentation chain transfer (RAFT) polymerization.^{21,22} Among these, the RAFT method provides with wide range of choices among variety of monomers along with high tolerance to the functional groups, which make the RAFT method suitable for synthesizing well-defined polymeric architectures. According to the mechanism proposed by Rizzardo *et al.*, the polymers obtained by the RAFT method contain a reactive terminal group which can be used further as polymerizable macroinitiator.²³

In our previous study, poly(styrene-*block*-4-vinylpyridine) [P(S-*b*-4VP)] was used as an effective steric stabilizer in providing the monodisperse polymer particles in the two-step dispersion polymerization of methyl methacrylate.²⁴ Poly(methyl methacrylate) (PMMA) particles having number-average diameter (D_n) of 4.3 μm and the coefficient of variation (C_v) of 2.14% were obtained in the presence of 2 wt% of P(S-*b*-4VP). In addition, the crosslinked poly(divinylbenzene) (PDVB) particles were synthesized in the presence of P(S-*b*-4VP) copolymer in aqueous media. The block copolymer consisting of RAFT agent was used as both an emulsifier and a reactive stabilizer, but the process was carried out using two-step polymerizations.²⁵

Recently, Bathfield *et al.*²⁶ carried out the first experiments under the dispersion polymerization conditions using macro-RAFT agents as only precursors of stabilizers. Their ultimate goal was to prepare functional latex particles that show bio-related surface groups, rather than to control the polymerization inside the particles. The proposed method was applied to the synthesis of hairy latex particles that incorporate a carbohydrate derivative. In addition, a well-defined poly(methacrylic acid) (PMAA) macro-RAFT agent was synthesized by the bulk polymerization using 4-toulic acid dithiobenzoate as a RAFT agent and was successfully employed as a reactive emulsifier in the soap-free emulsion polymerization of styrene, leading to the formation of stable latex.²⁷ The macro-RAFT agent was confirmed to be present on the particle surface and the proposed reaction mechanism suggested that the stable spherical particles be enlarged by the aggregation of small particles.

In this study, the small amount of PMAA macro-RAFT agent was applied to the dispersion polymerization of styrene. Until now, there is no particular report on the use of macro-RAFT agent in the dispersion polymerization. The characteristics of the resulting polystyrene (PS) particles were investigated in terms of the concentrations of the monomer, initiator and of PMAA macro-RAFT agent, and various solvents. Then, the role of the PMAA macro-RAFT agent as an effective steric stabilizer was verified.

Experimental

Materials. Styrene (Junsei Chemicals, Tokyo, Japan) and methacrylic acid (Aldrich Chemical Co., WI, USA) were purified using an inhibitor removal column (Aldrich Chemical Co., WI, USA) and stored at $-5\text{ }^\circ\text{C}$ prior to use. 2,2-azobis(isobutyronitrile) (AIBN, Junsei Chemicals, Tokyo, Japan) was used without further purification. Ethanol (Samchun Chemical, Korea) was used as the polymerization medium. Methanol, propanol, butanol, pentanol, and heptanol (all from Samchun Chemical, Korea) were also used for the polymerization media, too. Tetrahydrofuran (THF, Acros, Gheel, Belgium) employed during the synthesis of a RAFT agent was freshly distilled using sodium and benzophenone. Phenylmagnesium bromide, carbondisulfide, and α -bromo-*p*-toluic acid were purchased from Aldrich Chemical Co., WI, USA and used for synthesis of the RAFT agent. Silica used in column chromatography was Kieselgel-60 (Merck, Germany).

Synthesis of the RAFT Agent and the Poly(methacrylic acid) (PMAA) Macro-RAFT Agent. The RAFT agent, 4-toulic acid dithiobenzoate (TADB), and the PMAA macro-RAFT agent were synthesized in this laboratory according to the previous publications,^{27,28} respectively. The weight-average molecular weight (M_w), PDI and the conversion of the PMAA macro-RAFT agent was 316,200 g mol^{-1} , 1.21 and 38 % for 12 h, respectively.²⁷

Dispersion Polymerization of Styrene Using the PMAA Macro-RAFT Agent. Dispersion polymerization was carried out in a 50 mL capped scintillation vial with magnetic stirring under a nitrogen atmosphere at $70\text{ }^\circ\text{C}$ for 24 h. Ethanol (25 g) was first added in the scintillation vial and 10 wt% of styrene (2.5 g) relative to the medium was charged. The amount of AIBN (0.025 g) was fixed at 1 wt% relative to the monomer. The concentration of the PMAA macro-RAFT agent was varied from 0.5 to 10 wt% relative to styrene. The polymerization temperature was fixed at $70\text{ }^\circ\text{C}$ in an oil bath and a magnetic stirrer was used for stirring. During the polymerization, aliquots of the sample were periodically taken from the reaction vessel for the characterization. After the polymerization was completed, the resultant was rinsed off with ethanol and then centrifuged repeatedly to remove the residual PS and PMAA macro-RAFT agent.

Characterizations. The molecular weights and polydispersity index (PDI) of the PS were measured using a Waters GPC (gel permeation chromatography) equipped with a 510 differential refractometer and a Viscotek T50 differential viscometer by flowing PS-dissolved THF at a flow rate of 1.0 mL/min. A universal calibration curve (RI detector) was obtained using 10 PS standard samples (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g mol^{-1} . The chemical structure of the synthesized polymer was verified by a Varian 400 MHz ^1H NMR (Unity INOVA400, Palo Alto, USA) using CDCl_3 as a solvent

and a FTIR spectrum was obtained using a Bruker series FTIR spectroscopy (Vertex 80V, Bruker Optics, Germany). SEM (scanning electron microscopy, S-4300, Hitachi, UK) was used to observe the morphology of the PS particles. The particle size and its distribution were measured using a particle size analyzer (Mastersizer 2000, Marvern, UK), while the fractional conversion was calculated gravimetrically. The number average diameter (D_n) and the coefficient of variation (C_V) 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 described previously. The surface of the PS particles was analyzed using an ESCA (Electron Spectroscopy for Chemical Analyzer, VG Multilab 2000, Thermo electron corporation, UK). It utilized X-Rays (source; Mg K α) 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 where those elements came from.

Results and Discussion

The chemical structures of the synthesized materials, PMAA macro-RAFT agent and PS particles, were confirmed from the ^1H NMR spectrum, where the characteristic peaks were assigned. It is noted that the hydrogen atom in carboxyl group that was expected to observe above 10 ppm was not discernable due to the weak signal intensity. The ^1H NMR spectra of the copolymers consisting of 95–90 wt% styrene and 5–10 wt% PMAA macro-RAFT agent, respectively, were studied. However, no difference between the previous study in the emulsion polymerization²⁷ and the present system in the dispersion polymerization was observed, because the constituents were exactly same with different roles of the RAFT agent.

Figure 1 shows the FTIR spectra of the neat PS and PMAA macro-RAFT agent prepared by the bulk polymerization, and the PS particles prepared using different concentrations (1–10 wt%) of the PMAA macro-RAFT agent with 1 wt% AIBN relative to the monomer in ethanol at 70 °C for 24 h in the dispersion polymerization. The characteristic peaks of PS with 1.5, 2, 5 and 10 wt% PMAA macro-RAFT agent were compared in Figures 1(c), 1(d), 1(e) and 1(f), respectively. Since the content of the macro RAFT agent increased from 1 to 10 wt%, the peak intensities of the extension vibration of C=O at 1708 cm^{-1} and that of C-O-H at 3500–2500 cm^{-1} relatively increased. This verifies that the PMAA macro-RAFT agent exists on the PS particles. Therefore, the PMAA macro-RAFT agent works as a stabilizer not only physically adsorbed on the surface of particles but also chemically bound by forming a covalent bond with polymer molecules. The existence of the stabilizer molecule on the resulting polymer particles was verified and reported that 1.1 wt% of total added stabi-

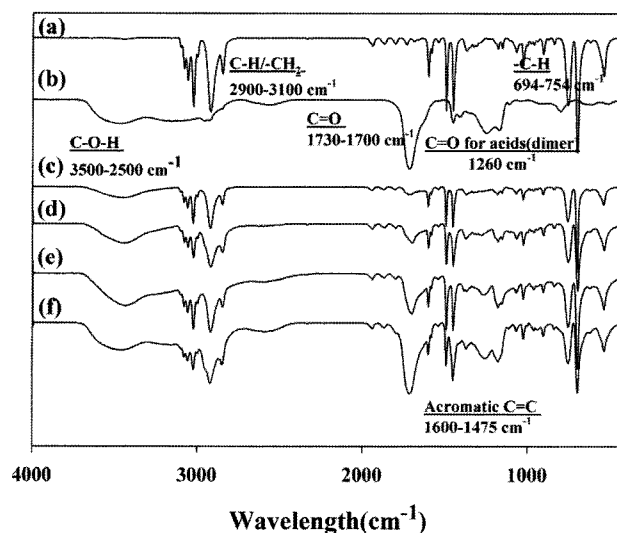


Figure 1. (a) FTIR spectra of neat PS prepared by the bulk polymerization, (b) PMAA macro-RAFT agent prepared by the bulk polymerization, (c) PS particles prepared with the PMAA macro-RAFT agent at 1.5, (d) 2, (e) 5, and (f) 10 wt% relative to the monomer in ethanol at 70 °C for 24 h.

lizer was adsorbed on PS particles prepared by the dispersion polymerization.^{3,9}

Figure 2 represents the SEM photographs of the PS spherical particles prepared with 1.5–10 wt% PMAA macro-RAFT agent and 1.0 wt% AIBN referring to the monomer in ethanol at 70 °C for 24 h. Partial coagulum was obtained with 1.5 wt% of the RAFT agent. The spherical particles were obtained from 2.0 wt% of the RAFT agent and the particle size decreased as the concentration of the macro-RAFT agent increased from 2.0 to 10.0 wt%. This indicates that the PMAA macro-RAFT agent is working as a stabilizer by inducing large particle surface with stability.

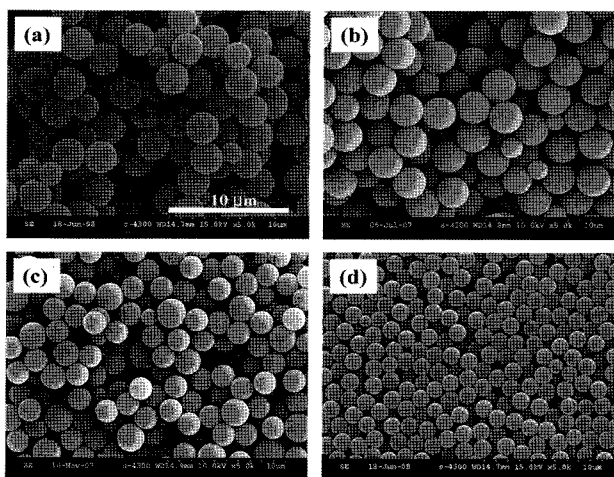


Figure 2. SEM photographs of PS microspheres prepared with (a) 1.5, (b) 2, (c) 5, and (d) 10 wt% PMAA macro-RAFT agent in ethanol at 70 °C for 24 h.

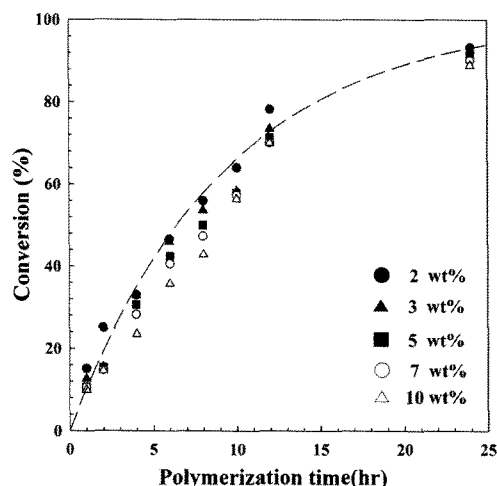


Figure 3. Conversion of PS microspheres prepared by the dispersion polymerization with varying concentrations of 1.5~10 wt% PMAA macro-RAFT agent in ethanol at 70 °C.

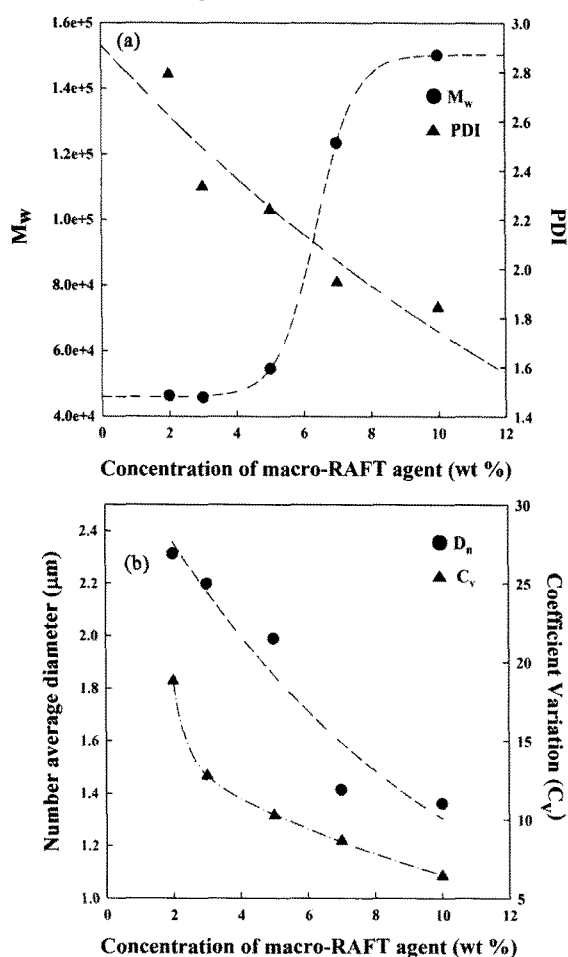


Figure 4. (a) Weight-average molecular weight (M_w , ●) and polydispersity index (PDI, ▲), and (b) number-average diameter (D_n , ●) and coefficient of variation (C_v , ▲) of PS microspheres prepared by the dispersion polymerization of styrene (10 wt%) and AIBN (1.0 wt%) with various concentrations of 2~10 wt% PMAA macro-RAFT agent in ethanol at 70 °C.

In Figure 3, the final conversion obtained for 24 h decreased from 93.3 to 88.9% as the concentration of the macro-RAFT agent increased from 2.0 to 10 wt%, respectively. However, no correlation between the concentration of the macro-RAFT agent and the conversion was observed. Figure 4(a) shows the effect of the macro-RAFT agent concentration on the weight-average molecular weight (M_w) and PDI at 70 °C for 24 h. The M_w increased from 46,300 to 150,200 g mol⁻¹ and the PDI decreased from 2.79 to 1.94 as the concentration of the macro-RAFT agent varied from 2.0 to 10 wt%, respectively. The resulting number-average diameter (D_n) and the coefficient of variation (C_v) were plotted in Figure 4(b). The particle diameter decreased from 2.31 to 1.36 μm and the C_v decreased from 18.80 to 6.44% with the increased macro-RAFT agent from 2.0 to 10 wt%, respectively. This indicated that the macro-RAFT agent was working well as a steric stabilizer in the dispersion polymerization.

Figure 5 shows the representative particle size distribution of the PS particles obtained from 2.0 to 10 wt% of the macro-RAFT agent and the same recipe described in the experimental section. The distribution became narrower as the concentration of the PMAA macro-RAFT agent increased, implying that the macro-RAFT agent was appropriate for

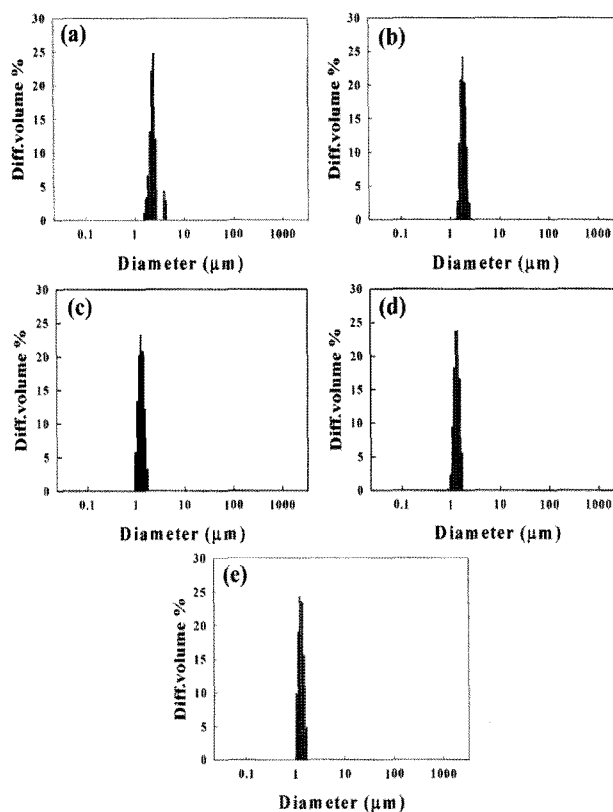


Figure 5. The representative particle size distribution of the PS particle with different concentrations of the PMAA macro-RAFT agent: (a) 2, (b) 3, (c) 5, (d) 7, and (e) 10 wt% relative to the monomer in ethanol at 70 °C.

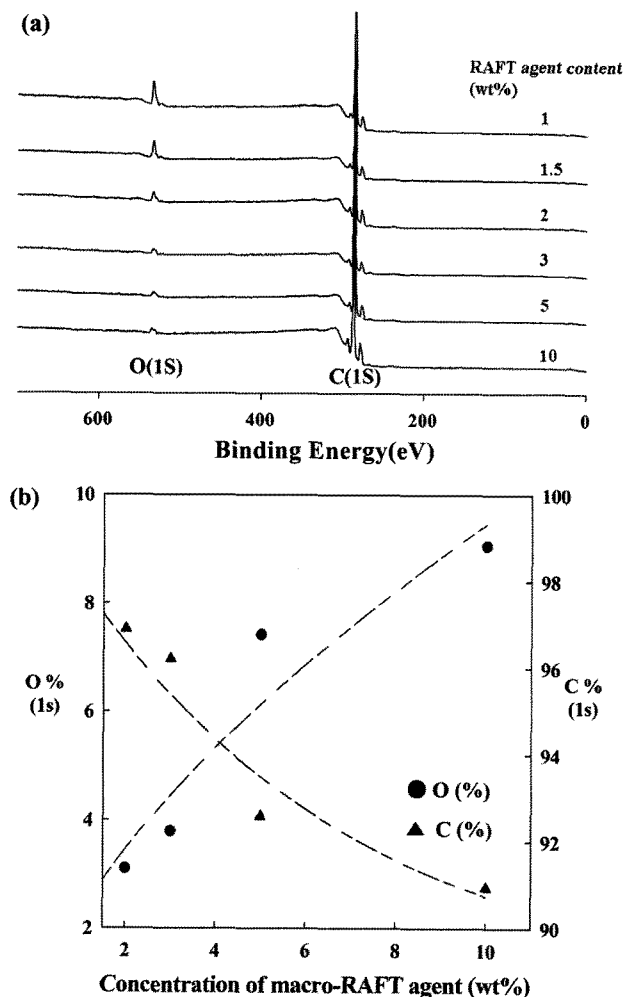


Figure 6. (a) XPS spectrum of PS spheres with 1.0–10.0 wt% PMAA macro-RAFT agent relative to the monomer in ethanol at 70 °C for 24 h, and (b) the plots of 1S oxygen (●) and 1S carbon (▲) as a function of the PMAA macro-RAFT agent.

the preparation of micron-sized PS particles.

Figure 6 exhibits the XPS spectrum of the PS particles prepared with 2.0–10 wt% of the macro-RAFT agent and 1.0 wt% AIBN referring to the monomer. The 1S oxygen and 1S carbon at 280 and 520 eV were observed, respectively, in Figure 6(a) and the contents of them were plotted as the function of the macro-RAFT agent in Figure 6(b). The content of 1S carbon decreased from 98.3 to 90.9%, while the content of 1S oxygen increased from 1.7 to 9.1% with the increasing contents of the macro-RAFT agent from 2 to 10 wt%, respectively. This suggests that the PMAA macro-RAFT agent exist on the surface of PS particles since the oxygen atom exists only in the PMAA macro-RAFT agent. Thus, the larger the content of the macro-RAFT agent, the more the macro-RAFT agent exists on the particle surface. This may imply that smaller particles were formed due to the increased macro-RAFT agent (as a stabilizer) and that the

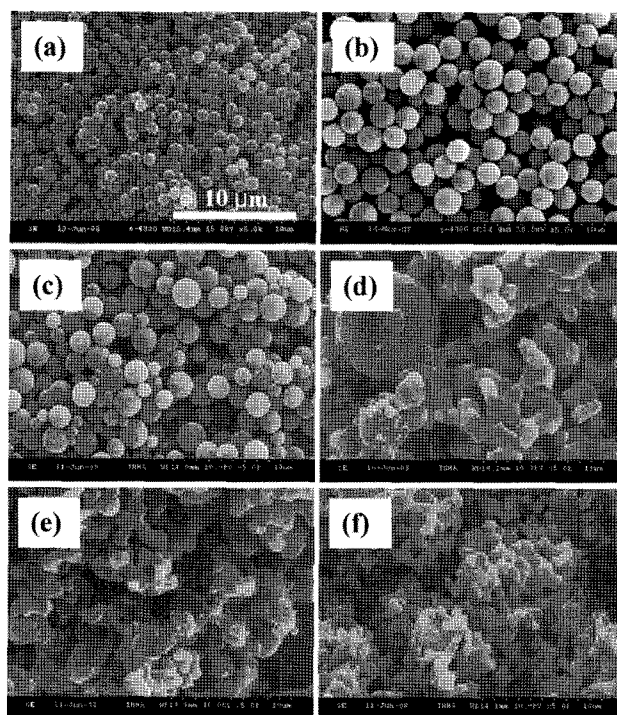


Figure 7. SEM photographs of PS microspheres prepared by the dispersion polymerization with 5 wt% macro-RAFT agent in various media at 70 °C for 24 h. (a) methanol, (b) ethanol, (c) propanol, (d) butanol, (e) pentanol, and (f) heptanol.

PS particles grafted with the PMAA macro-RAFT agent.

The dispersion polymerization was carried out using various alcoholic media including methanol, propanol, butanol, pentanol and heptanol using 5 wt% macro-RAFT agent at 70 °C for 24 h. Figure 7 represents the SEM photographs of the PS particles, prepared in the presence of 5 wt% PMAA macro-RAFT agent and 1.0 wt% AIBN referring to the monomer in various alcoholic media. The particle size increased from 0.86 (Figure 7(a)) to 4.15 μm (Figure 7(b)) with narrow size distribution. However, the solubility was lowered as the number of carbon in alcoholic medium increased (over 4). As a result, no spherical particles were observed with butanol, pentanol and heptanol since PMAA macro-RAFT agent was not soluble in the above three alcohols. In dispersion polymerization, the solvents that show better monomer solubility tend to yield larger particles since less number of nuclei is produced. The size of the PS particles remained uniform as the solubility parameter increased.

Figure 8 shows the SEM photographs of the PS spherical particles prepared with 5 wt% PMAA macro-RAFT agent referring to monomer along with various initiator concentrations from 0.5 to 3 wt% at 70 °C for 24 h. The particle size increased from 1.78 to 2.09 μm with the increased initiator concentrations from 0.5 to 2.0 wt%, respectively. However, unstable and coagulated PS particles were obtained with 3.0 wt% of AIBN. Overall, higher initiator concentra-

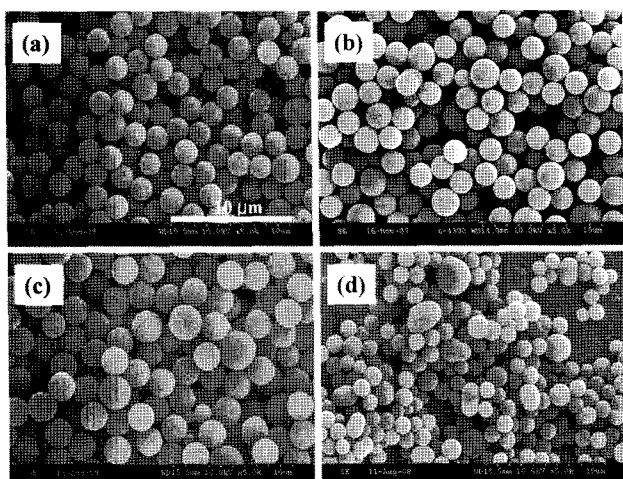


Figure 8. SEM photographs of PS microspheres prepared with 5 wt% poly(methacrylic acid) macro-RAFT agent referring to the monomer in various initiator concentrations (a) 0.5, (b) 1, (c) 2, and (d) 3 wt% in ethanol at 70 °C for 24 h.

tion induced grafting the shorter chain length, which showed greater solubility in the reaction medium. The delayed adsorption of the grafted stabilizer on the particle surface led to larger particle size.

The dispersion polymerization of styrene in ethanol using 5.0 wt% RAFT agent and 1.0 wt% AIBN referring to monomer was carried out with various concentrations of monomer at 70 °C for 24 h. As the monomer concentration increased from 10 to 100 wt%, the average particle sizes increased from 1.41 to 5.75 μm and the C_V varied from 8.66 to 52.07%, respectively, implying that the particle size distribution broadened. In addition, deformed spherical particles were observed due to the lack of the stabilizer, which is 5 wt% PMAA macro-RAFT agent.

Conclusions

The stable spherical polystyrene particles were synthesized in ab initio dispersion polymerization by using the poly(methacrylic acid) [PMAA] macro-RAFT agent without using any particular stabilizer. The presence of the PMAA macro-RAFT agent on the PS particles was confirmed by the NMR and FTIR spectroscopy. In addition, it was confirmed the presence of IS oxygen atom on the PS particle surface via the ESCA and verified the role of the PMAA macro-RAFT agent as a reactive stabilizer in this system. As the PMAA macro-RAFT agent content increased from 2 to 10 wt% referring to the monomer, the weight-average molecular weight increased from 46,300 to 150,200 g mol^{-1} . In addition, the PDI decreased from 2.79 to 1.94, the particle diameter decreased from 2.31 to 1.36 μm , and the C_V decreased from 18.80 to 6.44 %, respectively. In particular, when 10 wt% of the PMAA macro-RAFT agent was used

relative to the monomer, the very narrow distribution of particle sizes was obtained. In addition, the particle size was influenced by both the concentration of the RAFT agent and the monomer due to initial nucleation. Thus, the PMAA macro-RAFT agent was working as an effective steric stabilizer providing the monodisperse distribution of the particle size. This is comparable to the previous report that was used as an emulsifier in the soap-free emulsion polymerization.

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