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The effect of polystyrene-*block*-poly(4-vinylpyridine) prepared by a RAFT method in the dispersion polymerization of MMA

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Abstract

The dispersion polymerization of methyl methacrylate (MMA) has been carried out using polystyrene-*block*-poly(4-vinylpyridine) copolymer [P(S-*b*-4VP)], which was prepared by a reversible addition–fragmentation chain transfer (RAFT) method, as a steric stabilizer in an alcohol media. The stable polymer particles were obtained when the block copolymer concentrations increased from 1 to 10 wt% relative to the monomer and the average particle sizes decreased from 5.3 to 3.4 μm with the increasing concentration of the block copolymer. In particular, the incorporation of 2 wt% polystyrene-*block*-poly(4-vinylpyridine) produced 4.3 μm of monodisperse PMMA particles with 2.14% of C_v. Thus, the P(S-*b*-4VP) block copolymer prepared by the RAFT method is working not only as a steric stabilizer, but also in providing monodisperse micron-sized PMMA particles.

Keywords: RAFT; Polystyrene-*block*-poly(4-vinylpyridine); Dispersion polymerization

1. Introduction

The production of micron-size monodisperse microspheres has received much industrial and synthetic attention due to a wide variety of applications such as toners, instrument calibration standards, column packing materials for chromatography, microelectronic materials, and support materials for biomedical and biochemical analysis [1–5]. For most of these applications, size control and narrow size distribution are of key importance. Manufacture of micron-sized monodisperse microspheres is tough by conventional emulsion and/or suspension polymerization because these methods are unable to control the particle size and uniformity simultaneously. Therefore, numerous variations have been studied for the preparation of monodisperse micron sized particles. Vanderhoff et al. [6] and Ugelstad et al. [7] produced particles using emulsion polymerization using seeding or two-stage swelling method. Omi et al. [8] and Kamiyama [9] studied modified suspension polymerizations, while Okubo et al. [10] developed the dynamic monomer swelling method. However, most of these processes for making polymer particles have their own limitations. They are usually complicated and also difficult to implement on a large scale. On the other hand, dispersion polymerization has been used to prepare micrometer-scale monodisperse polymer particles in a single and easy process for the past three decades [11–13].

In dispersion polymerization, all reaction materials are dissolved in the reaction medium at the beginning stage of the reaction, then insoluble spherical polymer particles stabilized by steric stabilizer molecules are formed and dispersed in the reaction medium. Therefore, stabilizer, monomer, solvent, initiator, and temperature are important factors influencing the particle size, molecular weight of polymer particles, and kinetics of the polymerization process. Among the many factors, choosing a suitable stabilizer and reaction medium are very important for a satisfactory polymerization. In addition, large amounts of stabilizer affect the property and production cost of the resultant materials. In dispersion polymerization, frequently used steric stabilizers are homopolymers [14–18], macromonomers [19], and block [20] or graft polymers. Among them, amphiphilic block copolymers with low critical micelle concentrations (CMC) and diffusion coefficients are strongly fixed on the colloidal particles. Since, the structure of amphiphilic block copolymer constitutes of two parts, one segment is an anchor to the surface of polymer particles and the other lipophilic segment extends into the continuous phase. It can be inferred that the amphiphilic block copolymers provide a steric barrier to prevent the coagulation of the polymer

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particles. The early studies of block copolymers as a stabilizer in dispersion polymerization have been carried out by Barrett [11], Winnik et al. [21] and Piirma [22]. After them, many researchers studied with various block copolymers under different reaction conditions [20,23]. Thus, the controlled molecular weight and molecular weight distribution of block copolymers are important factors for carrying out successful dispersion polymerization. To date, block copolymers have been usually synthesized through ionic living polymerization. However, ionic living polymerizations require stringent conditions and are limited to a relatively small number of monomers. In order to overcome these disadvantages, attempts have been recently made to synthesize block copolymers employing simple and easy techniques.

Controlled/‘living’ radical polymerization has been known as useful technique for the preparation of a well-defined polymer structure by controlling molecular weight, molecular weight distribution, and tailored architecture. Based on the radical capping mechanism and agents, controlled/living radical polymerizations are generally classified as nitroxide-mediated polymerization (NMP) [24,25], metal catalyzed atom transfer radical polymerization (ATRP) [26,27], and the reversible addition-fragmentation chain transfer (RAFT) method [28,29]. Because the RAFT method has been discovered more recently, it has several advantages over NMP or ATRP. One of the advantages of the RAFT polymerization over other competing controlled/living radical systems is a tolerance of a very wide range of functionality in monomer and solvent.

Pyridine-containing polymers have attracted interests in recent years because they can be used in various applications such as water-soluble polymers and coordination reagents for transition metals. Recently, a controlled/living radical polymerization for the 4-vinylpyridine homopolymer [30] and block copolymer [31] has been reported using various methods. Although the synthesis of a 4-vinylpyridine-contained block copolymer was reported, the study of using polystyrene-*block*-poly(4-vinylpyridine) as stabilizers in dispersion polymerization has not been reported yet.

In this study, P(S-*b*-4VP) was successfully synthesized by the RAFT method and used in the dispersion polymerization of MMA in an alcoholic media as a steric stabilizer. Then the characteristics of the resultant PMMA particles were investigated in terms of the concentration of the monomer and P(S-*b*-4VP).

2. Experimental section

2.1. Materials

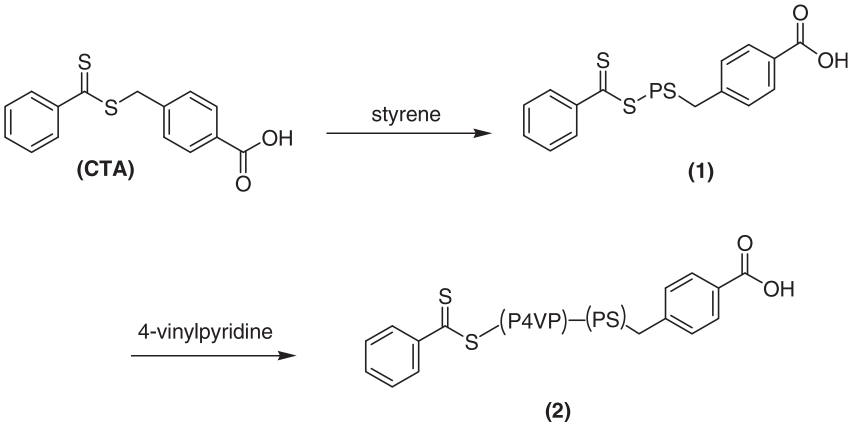
Methyl metacrylate, styrene (Junsei Chemicals, Japan) and 4-vinylpyridine (Aldrich, USA) were purified using an inhibitor removal column (Aldrich, USA) and stored at −5 °C prior to use. 2,2-Azobis(isobutyronitrile) (AIBN, Junsei) was used without further purification. Methanol (Samchun Chemical, Korea) was used as the polymerization media. Tetrahydrofurane (THF) employed in 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 Co. silica used in column chromatography was Kieselgel-60 (Merck, Germany).

2.2. Synthesis of the RAFT agent

4-Toluic acid dithiobenzoate (CTA3) was prepared by a modification of procedures described elsewhere [32].

2.3. Polymerization of P(S-b-4VP)

Scheme 1 shows the synthetic procedure of the block copolymer in detail. The PS was prepared in a controlled manner using a reversible addition–fragmentation chain transfer (RAFT) method and 4-toluic acid dithiobenzoate is used as the chain transfer agent (CTA). A solution containing styrene (40 ml), AIBN (0.0112 g), and 4-toluic acid dithiobenzoate (0.39 g) was prepared under an anhydrous condition. The solution was degassed using nitrogen for 15 min. Aliquots (5 ml) of the mixture were transferred to scintillation vials. Then, the vials were sealed and completely submerged in an oil bath at 70 °C. After the polymerization, the reaction mixture was dissolved in THF and the polymer was precipitated in



Scheme 1. Synthesis of polystyrene-*block*-poly(4-vinylpyridine).

methanol and purified by repeated precipitations. The product was dried in a vacuum oven. Then a stock solution of PS (1 g), AIBN (0.02 g), 4-vinylpyridine (7 ml), and DMF (10 ml) was prepared under an anhydrous condition. The solution was degassed by nitrogen for 15 min. Aliquots (5 ml) of the mixture were transferred to scintillation vials. Then, the vials were sealed and completely submerged in an oil bath at 70 °C. After the polymerization, the reaction mixture was precipitated and purified by repeated precipitations. Then the polymer dried in a vacuum oven. The final product was obtained in a pink powder form.

2.4. Dispersion polymerization of MMA using P(S-b-4VP)

Dispersion polymerization was carried out in a 50 ml capped scintillation vial with magnetic stirring under a nitrogen atmosphere. Twenty-five grams of methanol was first poured in the scintillation vial and 10 wt% of methyl metacrylate (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 block copolymer was varied from 1 to 10 wt% (0.25 g) relative to methyl metacrylate and the polymerization temperature was fixed at 60 °C in an oil bath.

The P(S-*b*-4-VP), monomer, initiator, and alcohol were all added into a capped scintillation vial. Once the solution became homogeneous, it was degassed by bubbling nitrogen gas at room temperature for 15 min. Then the vial was placed in a 60 °C oil bath and stirred with a magnetic stirrer. During the polymerization, aliquots of the sample were periodically taken from the reaction vessel for characterization. After completion of the polymerization, the resultant material was rinsed off with methanol, then centrifuged repeatedly to remove the residual MMA and block copolymer.

2.5. Characterizations

The fractional conversion was calculated gravimetrically. The chemical structure of the synthesized block copolymer was confirmed by a Varian 400-MHz ^{1}H NMR using $CDCl_3$ as the solvent. The molecular weight and polydispersity index (PDI) were characterized using a Waters GPC (gel permeation chromatography) equipped with a 510 differential refractometer and Viscotek T50 differential viscometer. 10^5, 10^3, and 10^2 Å μ-styragel packed high-resolution columns were employed. A universal calibration curve was obtained using 10 polystyrene standard samples (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7,500,000 g/mol. A FTIR spectrum was obtained using a Bruker 48 series FTIR spectroscopy. All infrared spectra were recorded for 20 s for each specimen. A Hitachi SEM (scaning electron microscopy) S-4300 was used to observe the morphology of the PMMA particles. The samples were prepared with a drop of diluted suspension on an aluminum tape. Then each sample was sputter-coated with platinum. The weight-average diameter (D_w) and coefficient of variation (C_v) were obtained using a Scion Image Analyzer Software by counting 100 individual particles from the SEM microphotographs. The surfaces of the PMMA particles were analyzed using a XPS (X-ray photoelectron spectrometer), model ESCALAB 220i-XL, and the atomic concentrations were calculated based on the program (spectral data processor v 4.1).

3. Results and discussion

3.1. Characterization of the block copolymer

^{1}H NMR spectroscopy is used to confirm the chemical structure of the synthesized P(S-*b*-4VP). Fig. 1 shows the ^{1}H NMR spectra of the PS, P4VP and P(S-*b*-4VP), respectively. Fig. 1(A) and (B) showed the spectrum of polystyrene and P4VP prepared by the solution polymerization. The characteristic peaks of PS were observed at 6.1–7.1 ppm for five protons of the phenyl ring. For P4VP, two multiplets at 6.1–6.8 ppm and 8.2–8.5 ppm for four protons of pyridine ring were observed. In addition, Fig. 1(C) is a spectrum of P(S-*b*-4VP) prepared by the RAFT method. This figure showed the same characteristic peaks of PS and P4VP simultaneously as observed in Fig. 1(A) and (B). Based on the ^{1}H NMR spectra, it was confirmed that P(S-*b*-4VP) was successfully synthesized.

The molecular weights and polydispersity of PS and P(S-*b*-4VP) were measured using GPC; the number-average molecular weight of the PS homopolymer is about 11,000 g/mol and the molecular weight distribution is 1.12, while those of the block copolymer are about 98,000 g/mol and 1.28, respectively. This implies that the block copolymer contains a long poly(4-vinylpyridine) block and a short polystyrene block. The GPC curves of the prepared block copolymer showed a single peak without other peaks, which

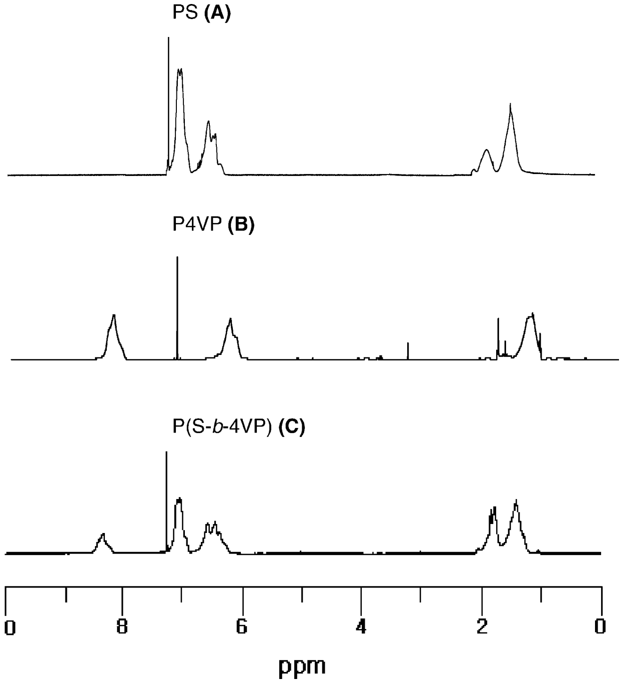


Fig. 1. ^{1}H NMR spectra of PS, P4VP and P(S-*b*-4VP) polymers.

means that there is no significant homopolymer or other impurities in the block copolymer. The low molecular weight distribution of the block copolymer confirms that the RAFT method successfully worked for the preparation of the block copolymer. The successful preparation by the RAFT method and various confirmations of the structure from ^{1}H NMR and GPC indicated that the polymerization was followed by the controlled/living radical mechanism.

3.2. Effects of the block copolymer concentration

Fig. 2(A)–(C) shows the FTIR spectra of PMMA prepared by the bulk polymerization without using any solvent or stabilizer, the block copolymer of P(S-*b*-4VP), and PMMA microspheres with the 10 wt% block copolymer prepared by the dispersion polymerization in methanol at 60 °C, respectively. Fig. 2(A) shows the representative characteristic peaks of PMMA; carbonyl stretching at 1725 cm^{-1} and aliphatic CH and CH_2 stretching at 2900–3100 cm^{-1}. The aromatic CH at 3063 cm^{-1} and aliphatic CH and CH_2 stretching at 2900–3100 cm^{-1} of styrene repeating unit and a strong absorption peak at 3500 cm^{-1}, representing a characteristic peak of C–N stretching of 4-vinylpyridine are observed in Fig. 2(B). In addition, the characteristic peaks of styrene with 4-vinylpyridine and PMMA are combined in Fig. 2(C); since PMMA particles are synthesized using 10 wt% block copolymer, the composition of styrene unit in PMMA particles is too small, thus the peak intensity of C–N peak of P(S-*b*-4VP) and carbonyl stretching is relatively large.

Fig. 3 shows the effect of the block copolymer concentration on the conversion of MMA monomer to PMMA microspheres by the dispersion polymerization in methanol at 60 °C using various concentrations of P(S-*b*-4VP) for 24 h. The conversion increases with the increasing concentration of the block copolymer since less termination occurred in the high stabilizer-containing system. The conversion to PMMA is strongly dependent on the concentration of the block copolymer. In the case of 10 wt% of P(S-*b*-4VP), the final conversion reached 98% for 24 h.

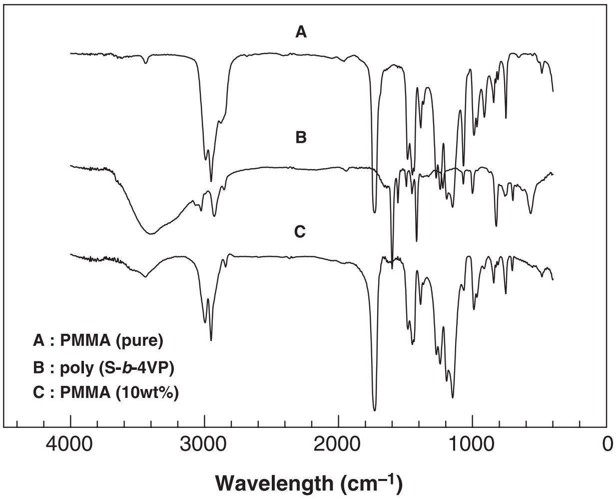


Fig. 2. FTIR spectra of the PMMA prepared by the bulk polymerization (A), block copolymer P(S-*b*-4VP) (B) by solution polymerization, and PMMA microspheres (C) with the 10 wt% block copolymer prepared by the dispersion polymerization in methanol at 60 °C for 24 h.

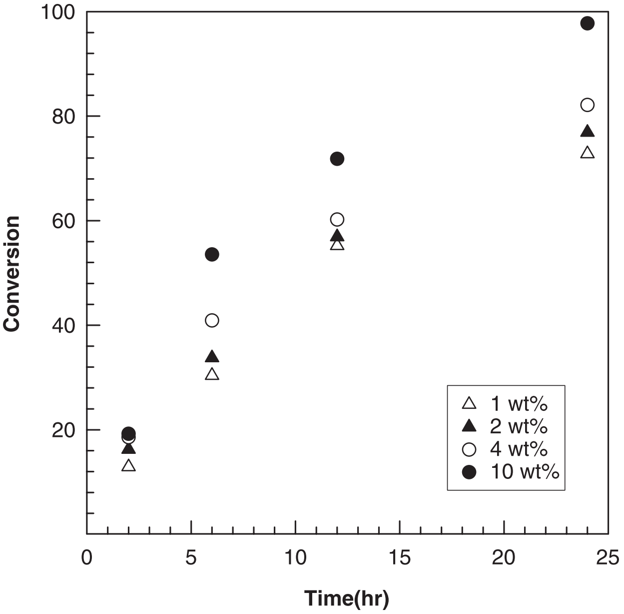


Fig. 3. Conversion of PMMA microspheres prepared by dispersion polymerization with varying concentrations of 1, 2, 4, and 10 wt% P(S-*b*-4VP) block copolymer in methanol at 60 °C.

Fig. 4 represents the scanning electron microscopy (SEM) photographs of the PMMA microspheres prepared with 1–10 wt% block copolymer referring to monomer at 24 h. By observing the spherical particles, the use of P(S-*b*-4VP) is proven to be working as a stabilizer.

The characteristics of Fig. 4 are analyzed and plotted in Fig. 5, which shows the relationship between the weight-average diameter (D_w) and coefficient of variation (C_v) along the P(S-*b*-4VP) concentration. As the block copolymer concentration increased, the size of PMMA microspheres decreased due to the favorable formation of more primary nuclei in the early stages of polymerization at higher concentrations of the stabilizer. This kind of behavior was also observed in previous works [33–35]. In addition, C_v dramatically decreased from 7.82 to 2.14% for 1–2 wt% P(S-*b*-4VP), then slightly increased to 4% for 4 and 10 wt% P(S-*b*-4VP). In the dispersion polymerization using conventional stabilizers such as poly-(*N*-vinylpyrrolidone) (PVP) or hydroxylpropyl cellulose (HPC), the monodisperse micron-sized microspheres were obtained with a large amount of stabilizer. Typically, the window is 10–15 wt% of stabilizer for styrene and around 30 wt% for MMA based on the amount of the monomer [36–38]. However, very promising results were obtained in our study: highly monodisperse PMMA micrispheres having 4.3 μm of weight-average diameter and 2.14% of C_v were obtained at 2 wt% of block copolymer. In addition, 2–10 wt% of P(S-*b*-4VP) copolymer was sufficient to produce monodisperse PMMA microspheres without a formation of

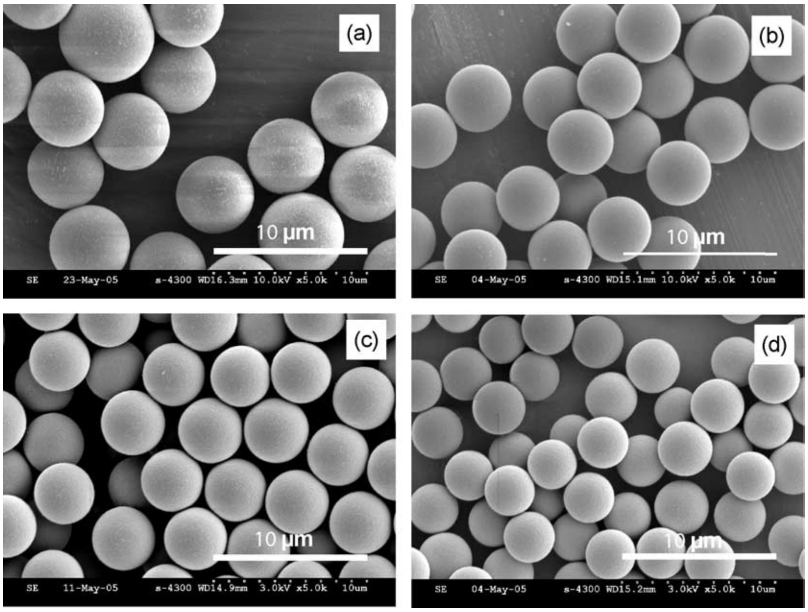


Fig. 4. SEM photographs of PMMA microspheres prepared with (a) 1 (b) 2, (c) 4 and (d) 10 wt% P(S-*b*-4VP) for 24 h.

coagulation or secondary particles. This result implies that the use of P(S-*b*-4VP) is more efficient than the conventional stabilizer for providing not only PMMA microspheres with a low content of stabilizer but also very narrow particle size distributions. Since, P(S-*b*-4VP) contains hydrophobic PS and hydrophilic P4VP units, it is thought that the block copolymer molecules are preferentially located on the surface of the microspheres by physical absorption; the PS block is inside of the PMMA particles and the P4VP block is outside of the particles as a tail.

Fig. 6 compares the X-ray photoelectron spectroscopy (XPS) spectrum of the PMMA particles prepared with 2 and 10 wt% P(S-*b*-4VP) by the dispersion polymerization in methanol at 60 °C. In Fig. 6(A) showing PMMA prepared with 2 wt% of P(S-*b*-4VP), there are two strong peaks of 1S oxygen and 1S carbon at 280 and 520 eV, and a very small peak of 1S nitrogen at 400 eV, respectively. In Fig. 6(B) for

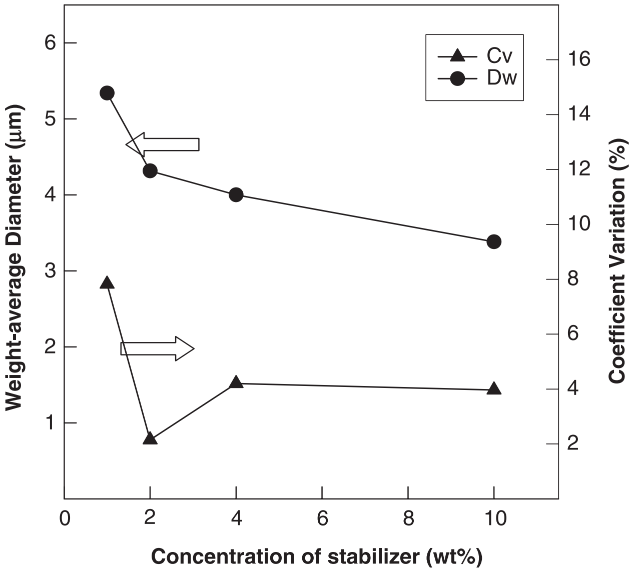


Fig. 5. Effect of the concentration of the stabilizer, P(S-*b*-4VP), on the weight-average diameter and coefficient of variation of PMMA microspheres in dispersion polymerization in methanol at 60 °C for 24 h.

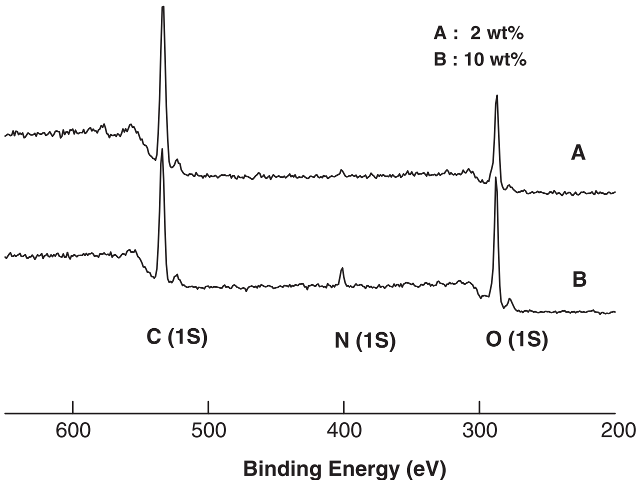


Fig. 6. XPS spectrum of PMMA microspheres prepared with 2 and 10 wt% block copolymer by dispersion polymerization in methanol at 60 °C 24 h.

Table 1
Contents of carbon, nitrogen and oxygen in PMMA microspheres using various concentrations of block copolymer

ESCA results			
Block copolymer concentration (wt%)[a]	% C	% N	% O
1	51.9 (55.21)	1.1 (1.17)	47.0 (50)
2	46.6 (45.60)	2.2 (2.15)	51.1 (50)
4	39.7 (34.52)	2.8 (2.43)	57.5 (50)
10	58.1 (78.94)	5.1 (6.93)	36.8 (50)

[a] Numbers in parenthesis indicate the normalized quantity of the component relative to oxygen.

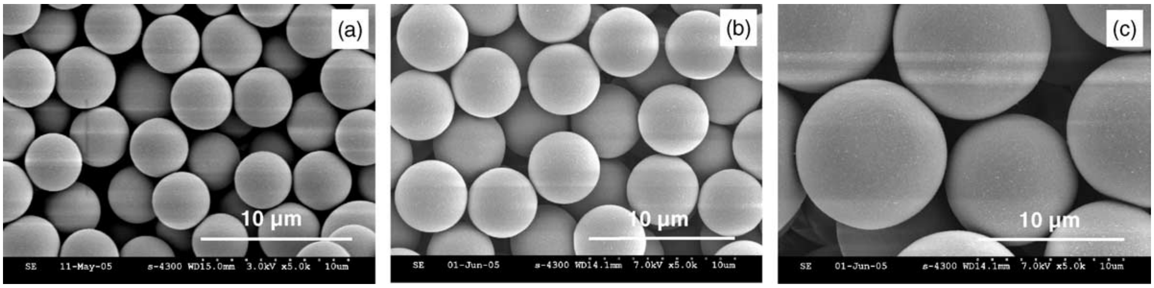


Fig. 7. SEM photographs of PMMA microspheres prepared with (a) 10, (b) 20, and (c) 30 wt% of monomer refer to solvent.

PMMA with 10 wt% of P(S-*b*-4VP), two strong peaks of 1S oxygen and 1S carbon at 280 and 520 eV, and a relatively enlarged 1S nitrogen peak at 400 eV were observed, respectively. From these two figures, the following can be suggested; the P(S-*b*-4VP) block copolymer exists on the surface of PMMA particles since the nitrogen atom only exists in 4-vinylpyridine and the larger the P(S-*b*-4VP) concentration, the higher the peak intensity was observed. Table 1 list that the calculated atomic concentrations based on the program (spectral data processor v 4.1) and the nitrogen content on the PMMA microsphere surface increases from 1.17, 2.15, 2.43 and 6.93 for the addition of 1, 2, 4, and 10 wt% P(S-*b*-4VP), respectively. This result confirms that the use of higher concentrations of the block copolymer results in the higher concentration of poly (4-vinylpyridine) units on the surface of the PMMA particles.

Fig. 7 represents the scanning electron microscopy (SEM) photographs of the PMMA microspheres prepared with various concentrations of monomer referring to solvent for 24 h at 60 °C. As the monomer concentration increased from 10, 20 to 30 wt%, the size of the PMMA particle increased from 4.3, 4.97 to 10.22 μm, and the C_v varied from 2.14, 4.24 to 7.34%, respectively. It is surprising that up to 20 wt% of monomer concentration produces fairly monodisperse PMMA particles and this may be the effect of the P(S-*b*-4VP) prepared by the RAFT technique.

4. Conclusions

In this study, we have demonstrated that polystyrene-*block*-poly(4-vinylpyridine) copolymers are effective steric stabilizers in the dispersion polymerization of MMA. The block copolymers were synthesized by the RAFT method using the bulk and solution polymerization. The chemical structure of the synthesized block copolymer was confirmed using ^{1}H NMR and FTIR, of which the block copolymer contains a long poly(4-vinylpyridine) block and a short polystyrene block. In this block copolymer, the polystyrene segment functions as an anchor to the surface of polymer particles and the poly(4-vinylpyridine) segment extends into the continuous phases, providing a steric barrier to prevent the coagulation of the polymer particles. We confirmed that the block copolymers are present on the particle surface via the XPS result. The increasing peak intensity of nitrogen was observed with the increasing concentration of the block copolymer. As the block copolymer content increased from 1 to 10 wt% referring to monomer, the conversion of PMMA particle reached up to 98% for 24 h of reaction in the dispersion polymerization. As a result, polymerization of MMA in the presence of 1–10 wt% of P(S-*b*-4VP) in methanol produced fairly monodisperse particles ranging 5.3–3.4 μm. Stable and spherical particles are obtained without coagulum or secondary particles in the all systems. In particular, highly monodisperse microspheres having 4.3 μm of the weight-average diameter with 2.14% of C_v were obtained with a small amount of stabilizer, 2 wt% of P(S-*b*-4VP). Monomer concentration dependent particle size increased from 4.3 to 4.97 μm for 10–20 wt% monomer with the remaining the C_v between 2.14 and 4.25, respectively. Our results indicate that P(S-*b*-4VP) can be effective steric stabilizer and the particle size is influenced by stabilizer and monomer concentration due to initially nucleation of particle is very important factor in polymer process.

Acknowledgements

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