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Mechanism of the Formation and Growth of the Cross-Linked Poly(divinylbenzene) Spheres Using Poly(styrene-*block*-4-vinylpyridine)

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ABSTRACT: The cross-linked poly(divinylbenzene) [PDVB] particles were synthesized in the presence of poly(styrene-*block*-4-vinylpyridine) [P(S-*b*-4VP)] copolymer in aqueous media at 70 °C. The block copolymer consisting of the RAFT agent is used as an emulsifier and reactive stabilizer as well. The mechanism of the formation and growth of the cross-linked PDVB microspheres using the block copolymer was proposed on the basis of the evidence shown by the formation of micelles, morphology and internal structure of the particles, particle size and distribution, and the content of nitrogen on the particle surface. The block copolymer formed micelles with DVB in ethanol and water due to the amphiphilic character. When the polymerization is taking place inside the micelles and at the living site of the block copolymer, the growing poly(4-vinylpyridine) [P4VP] block propagates by the addition of DVB, and the chemical bonding of DVB occurs in the P(S-*b*-4VP) block copolymer. As a result, the P(S-*b*-4VP-*b*-DVB) triblock copolymer is formed, inducing tiny small particles. The tiny small particles having the living character due to the diblock and triblock copolymers are enlarged by chemical bonding and coagulation showing the coretex-like macropores of the particle surface and become smoother upon filling with the DVB oligomers.

Introduction

Cross-linked micron-sized spherical particles are being used in various applications, such as medical applications, polymer-supported reagents, electronic materials, and packing chromatographic instruments.[1,2] These microspheres have been synthesized by various methods, such as suspension, dispersion, precipitation, and two-stage seeded polymerization.[3−6] The suspension polymerization technique is useful for the preparation of cross-linked particles in the range 20−2000 μm in size. In suspension polymerization, medium-insoluble monomers are suspended in medium. The monomer droplets are generated by a strong mechanical shear force, i.e., agitation, and stabilized by means of a protective colloid such as poly(vinyl alcohol). The polymerization takes place in the confined monomer droplets, and the mechanism is similar to that of bulk polymerization. Although the synthesis of highly cross-linked polymer microspheres is possible using suspension polymerization, it is quite difficult to make narrow size distribution. Dispersion polymerization is other way to prepare stable microspheres with low degree of cross-linking, but particles with high degree of cross-linking lead to a rough surface or even popcorn shape.[7] Cross-linked stable microspheres are obtainable within a limited solvent and monomer content in the precipitation polymerization.[8] Seeded polymerization is one of the methods used to prepare cross-linked microspheres. The seed particles prepared by either an emulsion or dispersion polymerizations are used in the subsequent monomer-swollen process.[9] In spite of many efforts, each of the processes used for making cross-linked microspheres has its own limitation.

Amphiphilic block copolymers composed of both hydrophobic and hydrophilic block can form a micellar structure. 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}.[10] Whereas, in the heterogeneous polymerization, lower concentration of amphiphilic block copolymers can be used than that of the conventional surfactants or stabilizers.[11,12] Charleux et al. used the diblock, triblock, and star block copolymers of polystyrene (PS) and poly(acrylate salt) as emulsifiers in the emulsion polymerization.[13] The study of stable PS/poly(acrylic acid) micelle consisting of cross-linked poly(acrylic acid-*co*-ethylene glycol diacrylate) core and PS shell via the RAFT copolymerization was reported.[14]

The block copolymer, polystyrene-*block*-poly(4-vinylpyridine) [P(S-*b*-4VP)], has attracted increasing attention in recent years since polymers containing pyridine can be used in various applications such as water-soluble polymers or coordination reagents for transition metals. Moreover, because of the solubility difference between PS and P4VP, P(S-*b*-4VP) has an ability to form micelles in a wide range of organic solvents. In our previous study, the P(S-*b*-4VP) block copolymer used as an effective steric stabilizer in providing monodisperse PMMA particles in the dispersion polymerization,[15] resulting in the number-average diameter (D_n) of 4.3 μm and coefficient of variation (C_v) of 2.14% in the presence of 2 wt % P(S-*b*-4VP).

Recently, 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 ionic polymerization. The LFRP techniques such as nitroxide-mediated polymerization (NMP),[16] atom transfer radical polymerization (ATRP),[17] and reversible addition−fragmentation chain-transfer (RAFT)[18] polymerization are widely used to synthesize complex macromolecular architectures with well-defined end groups and narrow molecular weight distributions. Among these, the RAFT method allows us to choose varieties of monomers with a high tolerance to the functional groups that make them suitable for synthesizing well-defined polymeric architectures. According to the mechanism proposed

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Table 1. Standard Recipe Used in Polymerization at 70 °C for 2 h

ingredient	amount (g)	remark
P(S-*b*-4VP)	0.1	5 wt % relative to monomer
DVB	2	10 wt % relative to medium
AIBN	0.02	1 wt % relative to monomer
water	10	50 wt % relative to total medium
ethanol	10	50 wt % relative to total medium

by Rizzardo et al., the polymers obtained by the RAFT method contain a reactive terminal group which can be further used as a polymerizable macroinitiator.[18]

In this study, highly cross-linked [PDVB] particles were prepared in the presence of P(S-*b*-4VP) copolymer in the aqueous phase with ethanol, and the mechanism of the formation and growth of the cross-linked PDVB particles using the block copolymer was proposed on the basis of the formation of micelles, morphology and internal structure of the particles, particle size and distribution, and the content of nitrogen on the particle surface.

Experimental Section

Materials. Divinylbenzene (55% mixture of isomers, Aldrich Chemical Co.), styrene (Junsei Chemicals, Japan), and 4-vinylpyridine (Aldrich Chemical Co.) were purified using an inhibitor removal column (Aldrich Chemical Co.) and stored at −5 °C prior to use. 2,2-Azobis(isobutyronitrile) (AIBN; Junsei Chemicals, Japan) was used without further purification. Ethanol (Samchun Chemical Co., Korea) and double distilled deionized (DDI) water having a pH of 6.75 were used as the polymerization medium.

Synthesis of the RAFT Agent. A RAFT agent, 4-thiobenzoylsulfanylmethylbenozic acid, was synthesized in this laboratory according to the previous publication.[19]

Polymerization of P(S-*b*-4VP). The polystyrene-*block*-poly(4-vinylpyridine) [P(S-*b*-4VP)] copolymer was synthesized by the reversible addition−fragmentation chain transfer (RAFT) polymerization of styrene and 4-vinylpyridine. The detailed process and characterization were mentioned in our previous publication.[15]

Preparation of Poly(divinylbenzene) [PDVB] Micropheres Using P(S-*b*-4VP). The polymerization recipe used in this study is given in Table 1. All polymerizations were carried out in a 50 mL capped scintillation vial with magnetic stirrer under a nitrogen atmosphere. This polymerization was made two steps: First, the P(S-*b*-4VP), monomer, initiator, and ethanol were simultaneously added into a vial. Then the water was added to the mixture. The stirred solution was degassed by bubbling nitrogen gas at room temperature for 15 min. The sealed vial was immersed in an oil bath at stirring speed of 200 rpm at 70 °C for 2 h. The polymerizing aliquots of the samples (0.8 mL) were periodically taken from the reaction vessel for characterization. After completion of the polymerization, the polymerization was stopped by soaking the vial in ice water bath. To remove the small-sized particles (100∼300 nm), the latex sample was centrifuged at 8000 rpm for 1 min. Approximately 3−5 wt % of the fraction of supernatant including small-sized particle was eliminated upon centrifugation of three times. The elimination of small-sized particles was confirmed using scanning electron microscopy (SEM) and a particle size analyzer, LS230. The precipitated fraction was redispersed in an excess amount of ethanol. The remnants of the samples were dried in a vacuum oven.

Characterization. SEM (S-4300, Hitachi) was used to observe the surface morphology of the synthesized PDVB microspheres. The samples were prepared with a drop of diluted suspension on an aluminum tape and sputter-coated with platinum. Transmission electron microscopy (TEM; JEM 2100F, Philips) was used to observe the internal structure of PDVB. For analysis, the dried samples were fixed in epoxy resin, and the thin section was cut serially (50 nm) by an ultramicrotome (MTX, RMC) and mounted on 100 mesh grids. Micelle diameters were measured using a laser light particle sizer (LLS, sys 700, Malvern Instrument). The ultrasonic homogenizer (UW 2200, BANDELIN) was used to study the structural stability of the synthesized spherical particles. The washed sample was redispersed in tetrahydrofuran (THF), and then ultrasonic homogenization was applied for 15 min. To verify the formation of cross-linked stable spherical particles, all the particles were immersed in various solvents such as THF, toluene, ethanol, and dimethylformamide (DMF) for 24 h and measured the particle size and distribution using a particle size analyzer, LS230. The glass transition temperature of the sample was measured using the differential scanning calorimeter (DSC; DSC-7, Perkin-Elmer). The samples were heated at a heating rate of 20 °C/min under a nitrogen atmosphere, quench cooled at a maximum cooling rate, and then reheated in the second time. The glass transition temperature (T_g) was collected at the midpoint of the transition region in the second scan. The size distribution was measured using a particle size analyzer (LS230, Beckman Coulter). The surface of the particles was analyzed using an XPS (X-ray photoelectron spectrometer) in a VG MultiLab2000 MK spectrometer with a Mg Kα X-ray source (1253.6 eV) with an energy analyzer set at a constant retardation ratio of 20. The specific surface area of the particles was measured using an ASAP 2O2O (Micrometrics Instrument Co.) using nitrogen as the absorption gas which has been degassed at 100 °C for 6 h prior to the measurement and calculated on the basis of the BET equation.

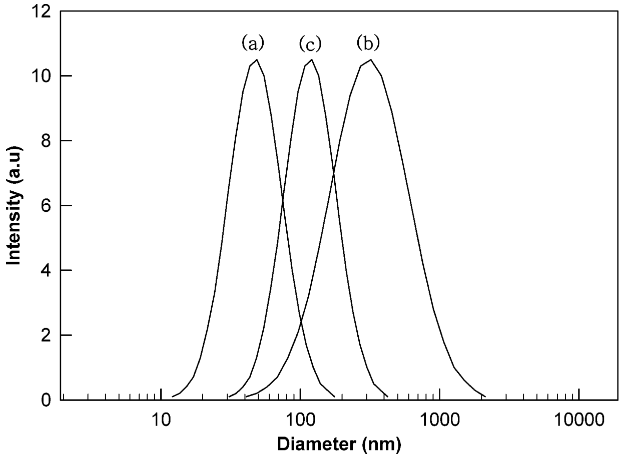


Figure 1. Micellar diameter formed with the (a) block copolymer and DVB in ethanol, (b) block copolymer and DVB in ethanol and water, and (c) block copolymer in ethanol and water. Diameters of P(S-*b*-4VP) micelles were prepared from standard recipe without AIBN and determined using a laser light particle sizer.

Results and Discussion

Proposed Mechanism for the Formation of Cross-Linked Microspheres. For the validation of the proposed mechanism of the formation and growth of the cross-linked PDVB particles in the mixtures of ethanol and water using P(S-*b*-4VP) block copolymer, further experiments are carried out based on the formation of micelles, specific surface area of the PDVB spheres, particle size and distribution, and the content of nitrogen and carbon on the particle surface at various reaction times. The number-average molecular weight and polydispersity index (PDI) of P(S-*b*-4VP) were 98,176 g/mol and 1.28, respectively, and those of the PS block in the block copolymer were 11,388 g/mol and 1.11, respectively.[15] This implies that the block copolymer contains a long hydrophilic poly(4-vinylpyridine) block and a short hydrophobic polystyrene block. The block copolymer is expected to form micelles with DVB in aqueous media due to the amphiphilic character.

In order to measure the micelle diameter upon ingredients, the samples (a), (b), and (c) were prepared with selected materials using the standard recipe. The size of micelles is characterized, and the results are shown in Figures 1a−c. The sample (a) represents the micelles with the P(S-*b*-4VP) block copolymer and DVB in ethanol, the sample (b) is the micelles consisting of the block copolymer and DVB in the mixtures of ethanol and water, and the sample (c) is the micelles of the block copolymer in ethanol and water mixture. The micellar diameter of the samples (a), (b), and (c) is 52.7, 407.2, and 117.0 nm, respectively. Figure 1a stems from a general character of amphiphilic block copolymers capable of the formation of nanometer- or micrometer-sized micelles in selective solvents.[14] On the other hand, when water is involved in the mixtures of sample (a), the diameter of the micelles abruptly increased to 407.2 nm, as seen in Figure 1b. This phenomenon resembles the well-known “like dissolves like” principle. The difference in the solubility parameters between DVB and the media becomes large upon the addition of water. The solubility parameters (δ) of DVB, ethanol, water, and polystyrene are 8.5, 12.7, 23.4, and 9.5 (cal/cm^3)$^{1/2}$, respectively.[20] It is noted that the solubility parameter of DVB was calculated from the Hansen group contribution method.[21] The solubility parameter of the mixtures containing DVB, ethanol, and water was calculated using the following equation:[22]

$$\delta_{\text{mixture}} = \sum \delta_i v_i \tag{1}$$

where δ_i and v_i denote the solubility parameter and volume fraction of the *i*th component, respectively.

When 10 g of water is added to the mixtures of DVB (2 g) and ethanol (10 g), the solubility parameter of the mixture increases from 12.1 to 16.6 (cal/cm^3)$^{1/2}$. Consequently, the solubility parameter of the reaction medium is far distinct from that of DVB. The addition of water brings the instability of micelles due to the change in the solubility parameter of the system, and the related result will be shown later in Figure 7e. Thus, a greater number of block copolymers are needed to maintain the stable micelle, and subsequently the average diameter of the micelle increased by the aggregation between the block copolymers and existing micelles. On the other hand, the micelle diameter of the sample (c) in the absence of DVB decreased to 117 nm in Figure 1c. As a consequence, the micelle diameter of the P(S-*b*-4VP) block copolymer is rather influenced by the incorporation of water than by that of DVB, and this is due to the difference in the solubility parameter.

Figures 2a−d show the typical surface morphology of the PDVB cross-linked particles obtained at various reaction times. At 30 min as seen in Figure 2a, the particle surface shows a corrugated macroporous structure resembling the cortex-like human brain. At 60 min in Figure 2b, the particle surface is still rough, but it looks smoother than in Figure 2a. When the polymerization is further proceed at 90 min and completed at 120 min as seen in parts c and d of Figure 2, respectively, the improved surface smoothness is obtained. The final form at 180 min as seen in Figure 2e is as well. The change in the degree of roughness can be confirmed from the measurement of the specific surface area of the particles. The calculated BET surface area is 79.2, 56.2, 45.6, and 41.2 m^2/g for 60, 90, 120, and 180 min, respectively. This implies that the surface area decreased with the polymerization time. The smooth surface obtained at 120 and 180 min still possesses a substantial surface area, indicating the presence of well-developed nanopores on the surface. We propose two distinct procedures for forming spherical particles having smooth surface; the first step is the particle enlargement by mainly chemical bonding of tiny small particles having the living character of P(S-*b*-4VP) block copolymer between parts a and b of Figure 2. The second step is the surface smoothness upon filling the pores with DVB oligomers. This will be verified using the particle distribution curve in Figure 3. Figure 3 shows the particle growth and size distribution of PDVB upon reaction times. When the reaction is taking place for 30 min, the majority of the particles are in the range of 0.1−1.0 μm, as seen in Figure 3a. However, when the polymerization proceeds for 60 min, the particle size grows 10 times larger in the average of 1−10 μm, and the distribution of the particle size seems unsymmetrial doublet type in Figure 3b. This suggests that the large particles are formed upon chemical bonding and simultaneous aggregation of tiny small particles. When the reaction further proceeds for 90 min in Figure 3c, no distinct particle growth is occurring for the larger particles (the latter peak in doublets) around 5−10 μm, but the peak intensity of the smaller particles (the former peak in doublets) around 1−5 μm becomes strong and the size distribution becomes narrow with time. For further reaction for 120 min in Figure 3d, no variance is observed except for a slightly narrow size distribution. Thus, the polymerization is expected to complete at 120 min. On the other hand, when the polymerization takes plase for 180 min, the small particles having the number-average diameter of 150 nm were observed as seen in Figure 3e. This is believed to arise from the exhaustion of the block copolymers so that they are not able to provide the living character for inducing large particles any longer. The distribution data in Figure 3 agree well with the surface morphology shown in Figure 2.

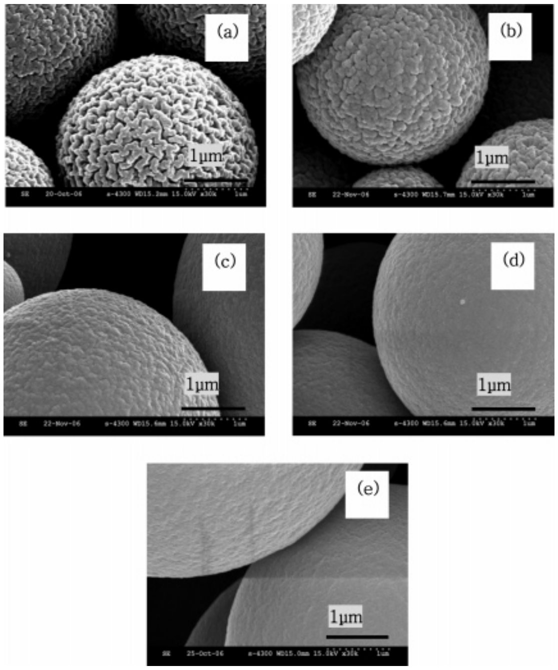


Figure 2. SEM photographs of cross-linked PDVB spheres with AIBN at 70 °C for 2 h at different polymerization times: (a) 30, (b) 60, (c) 90, (d) 120, and (e) 180 min.

In order to further support the mechanism for the formation and growth of the particles, the XPS measurement was analyzed as seen in Figure 4. The 1s carbon and 1s nitrogen are obtained at 285 and 400 eV, respectively, upon the polymerization time for 30, 60, 90, and 120 min. The calculated carbon contents are 95.80, 96.87, 97.61, and 97.65%, and the nitrogen contents are 4.23, 3.13, 2.39, and 2.35%, respectively. This indicates the following two points: The existence of nitrogen atom implies that the particle surface contains P(S-*b*-4VP) and the 4-vinylpyridine block. In addition, the decrease in nitrogen content with the polymerization time is an indication of the particle surface filled with DVB oligomers. These results agree well with the

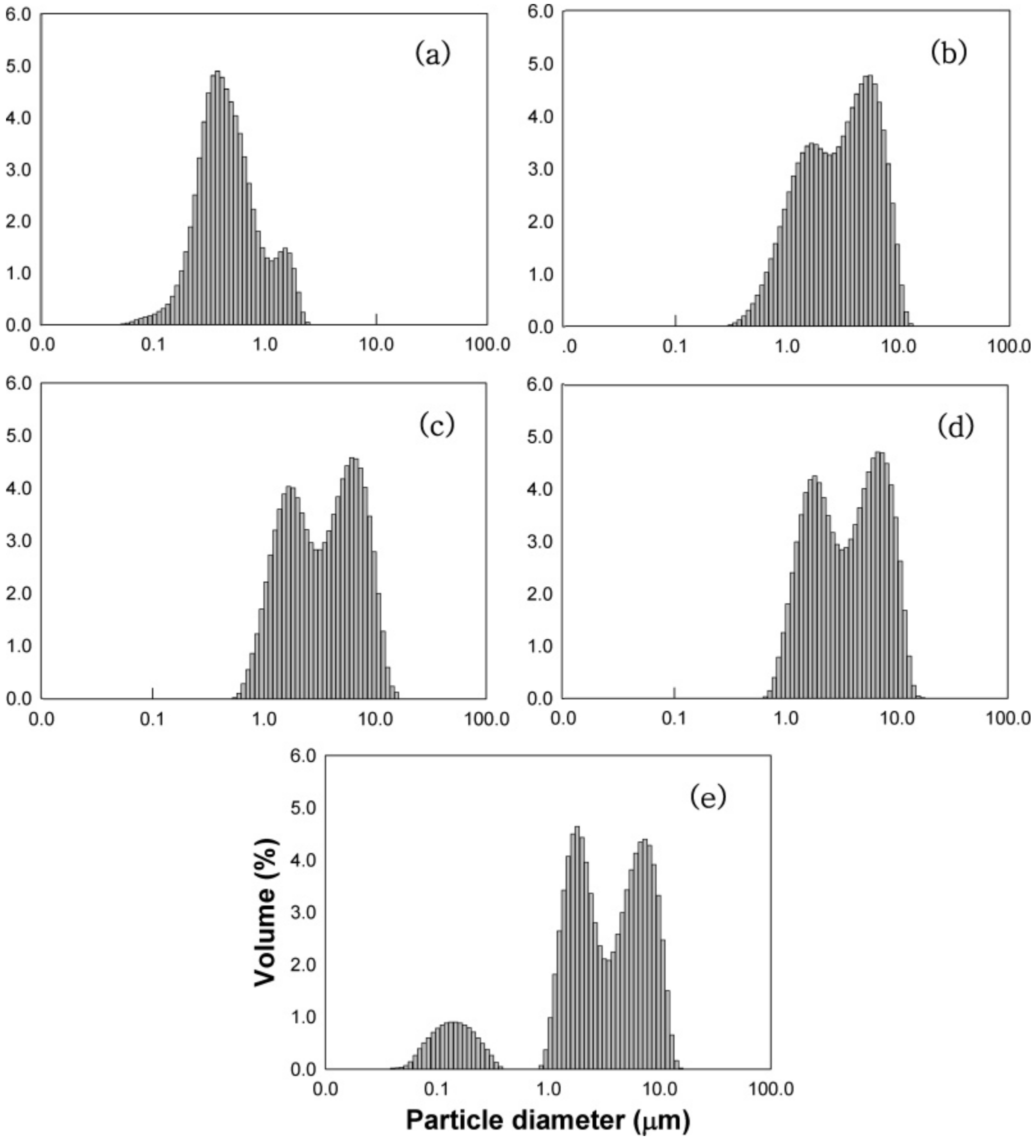


Figure 3. Particle size distribution of the cross-linked PDVB spheres in the presence of 5 wt % block copolymer at 70 °C at different reaction times: (a) 30 (b) 60, (c) 90, (d) 120, and (e) 180 min.

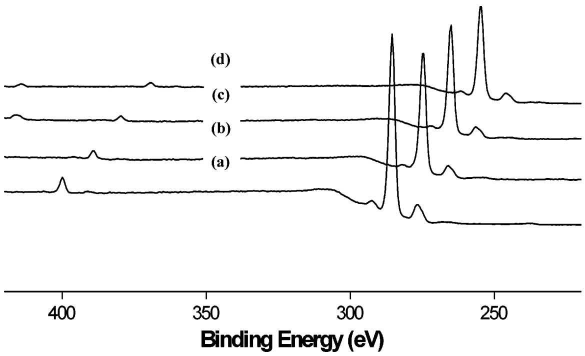
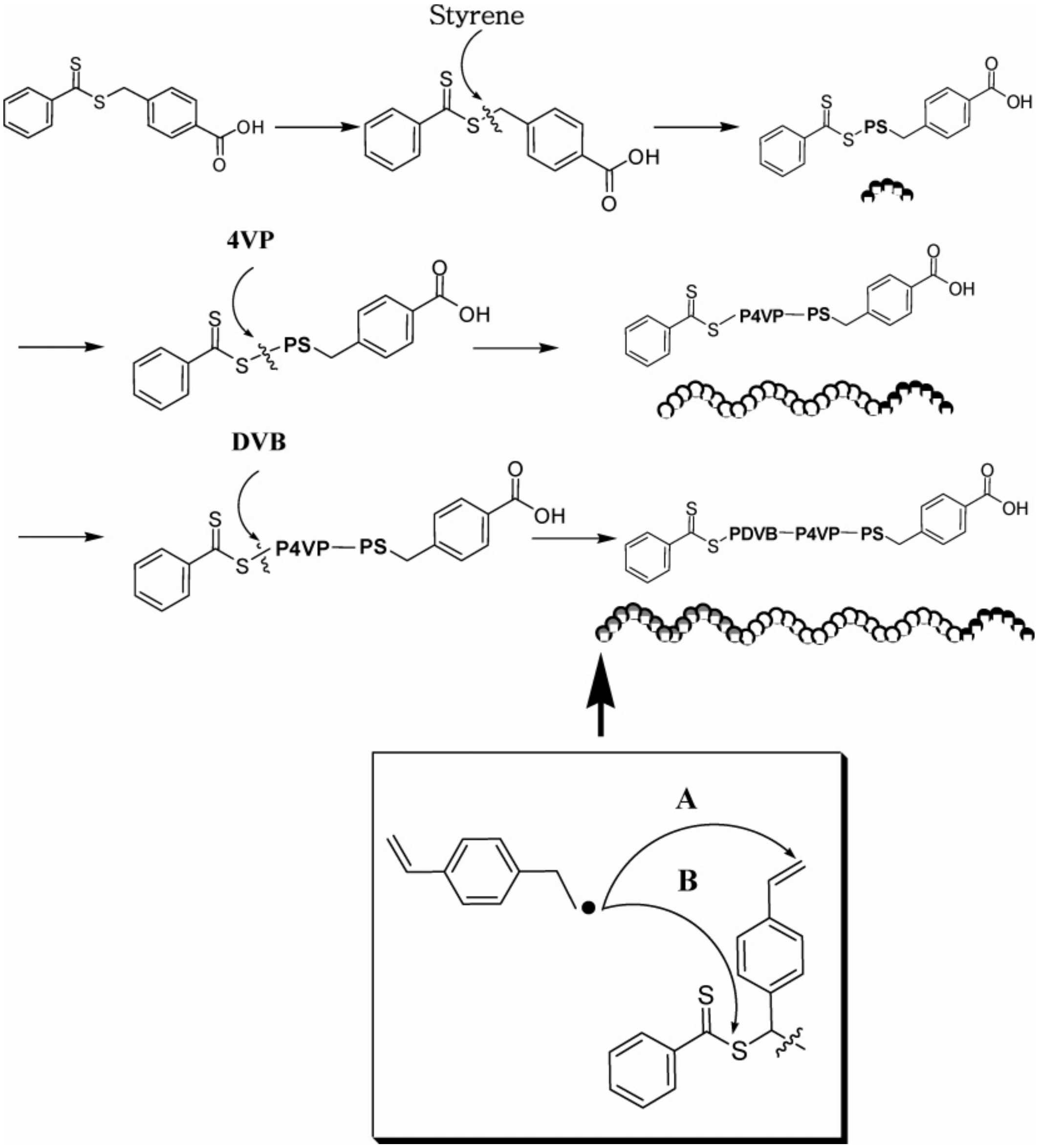


Figure 4. XPS spectrum of cross-linked PDVB spheres in presence of 5 wt % of block copolymer at 70 °C at different reaction times: (a) 30 (b) 60, (c) 90, and (d) 120 min.

SEM photographs explained in Figures 2a−d and the particle distribution shown in Figures 3a−e.

From the supplementary evidence between Figure 1 and Figure 4, Scheme 2 depicts the proposed mechanism for the formation and growth of the cross-linked PDVB particles in the mixtures of ethanol and water with AIBN using P(S-*b*-4VP) copolymer. When the ingredients including the block copolymer and DVB are mixed in ethanol medium, the P(S-*b*-4VP) copolymer containing DVB leads the formation of micelles of ∼53 nm consisting of the hydrophobic PS block inside and the hydrophilic P4VP block toward outside (Scheme 2a). When water is added into the mixtures of DVB, ethanol, and the block copolymers, the micelle size increases to 407.2 nm (Scheme 2b). At this stage, the DVB-swollen micelles are stabilized by a long P4VP fragment in an aqueous ethanol media. When the polymerization of DVB is taking place at 70 °C, a propagating radical undergoes chain transfer with a surfur atom on dormant species of RAFT agent, which subsequently reacts with DVB in the continuous phase. As a result, the P(S-*b*-4VP-*b*-DVB) triblock copolymer is formed, and this is drawn in Scheme 1. At this point, the surfur atom and the vinyl group which is located in the side chain (moiety of DVB) of the triblock copolymer react with initiated bifunctional DVB monomer, polymer, or growing triblock copolymer in another particle. This reaction induces the chemical bonding resulting in cross-linking between the tiny small particles (Scheme 2c). The tiny small particles having the living character in the presence of the diblock and triblock copolymer is chemically bonded. Since the triblock copolymer, in particular the reactive P4VP block, exists on the surface of the particles, the forming particles can be chemically bonded by propagation of bifunctional DVB.

Scheme 1. Proposed Formation of Triblock Copolymer



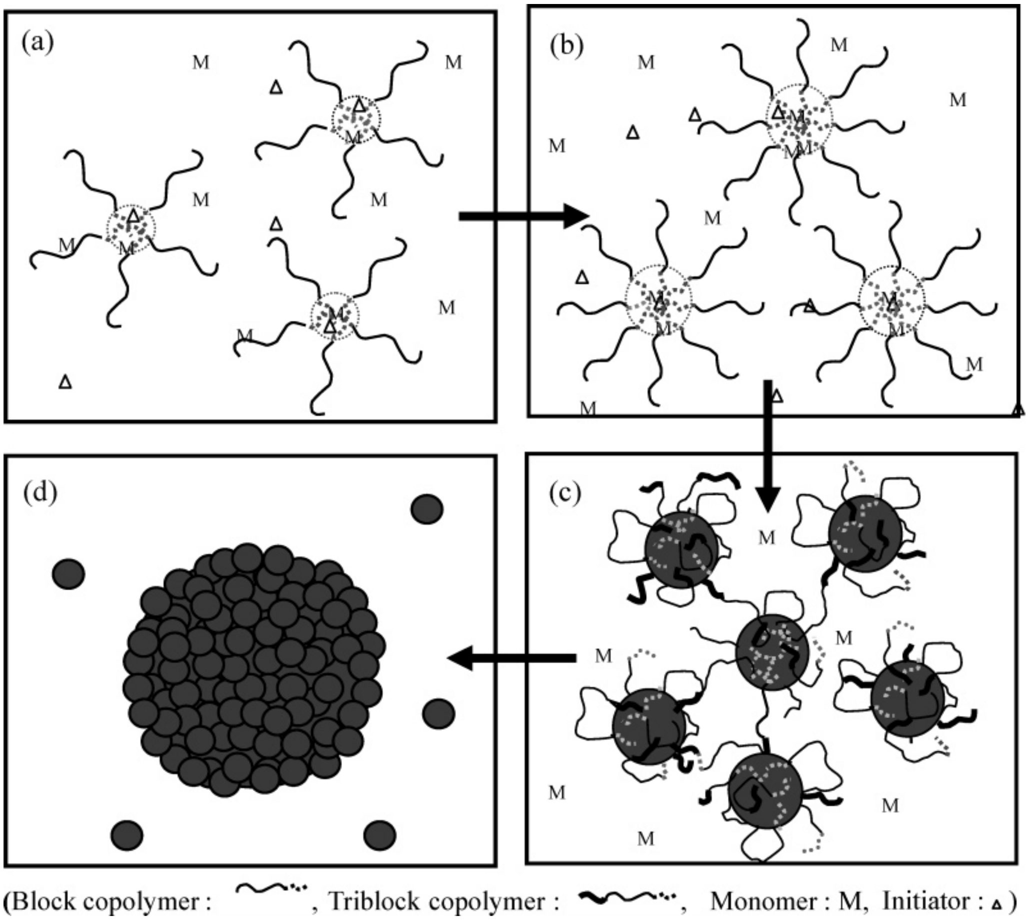
Although termination reaction is negligible in the RAFT polymerization, it is limited to the polymerization of monofunctional monomers. This would lead to the coagulation of particles as depicted in Scheme 2d. Finally, coagulation and chemical bonding will be formed between the particles. Because of the existence of the additional reactive site, the polymerization of DVB can take place to form oligomers, resulting in the filling the pores

Morphology and Stability of Microspheres. Parts a and b of Figure 5 show the scanning electron microscopy (SEM) of PDVB prepared by the standard recipe given in Table 1 and that of the broken particle under compression in a hot press without heating, respectively. Figure 5c is the transmission electron microscopy (TEM) photograph of the cross-sectional view of the internal structure of PDVB. At this point, a spherical small particle located inside of the broken particle in Figure 5b is not the core, but it is a small particle inserted upon breakage coincidently. For the detailed analysis of the internal structure, the particles were molded in an epoxy resin and microtomed to produce a 50 nm thick section for TEM analysis. According to the SEM and TEM photographs, the particles were composed of numerous tiny small particles.

In order to verify the structural stability of the synthesized particles, the particles were redispersed in tetrahydrofuran (THF) for 24 h and dried. Figure 5d shows no difference in the particle size, shape, and particle surface before and after solvent treatment. Moreover, the stability of the particles was examined by redispersing in THF and applying powerful ultrasonification (600 W, 20 kHz) for 15 min. The morphology of the particles after sonofication showed exactly the same particles as the original spherical shape (Figure 5e). In addition, no glass transition temperature of the samples was observed, indicating that PDVB spheres are highly cross-linked. Overall, this is the evidence that the PDVB microspheres are chemically bonded with small tiny particles.

The Role of P(S-*b*-4VP) Copolymer. In general, individually stable spherical particles are obtainable by the electrostatic stabilization in emulsion polymerization,[23] steric stabilization in suspension,[24] dispersion and seeded polymerization,[6,25] and self-stabilization by cross-linking in precipitation polymerization.[26] The role of the emulsifier or stabilizer has been important in the synthesis of spherical particles, except for the precipitation polymerization. To compare the ability of P(S-*b*-4VP) as a stabilizer, polymerization of divinylbenzene was carried out

Scheme 2. Proposed Mechanism of the Formation of Stable Cross-Linked Particles: (a) Mixtures of the Diblock Copolymer, Initiator, and DVB in Ethanol, (b) Mixtures of (a) with Water, (c) Formation of the Triblock Copolymer of P(S-*b*-4VP-*b*-DVB) in Aqueous Media with Ethanol, and (d) Formation of Large and Small Particles



using various stabilizers including poly(vinyl alcohol) (PVA), poly(*N*-vinylpyrrolidone) (PVP), sodium dodecyl sulfate (SDS), and P(S-*b*-4VP). As seen in Figure 6a, when no stabilizer was used, a resin type of PDVB was obtained due to the absence of the stabilizing moiety. Moreover, when PVP and PVA, the conventional stabilizers in dispersion and suspension polymerization, respectively, were used, the coagulated particulate resin was obtained due to the poor colloidal stability in Figure 6, b and c, respectively. Furthermore, the severely agglomerated resin was obtained with SDS in Figure 6d due to the lack of colloidal stability. On the contrary, the stable spherical particles were formed with P(S-*b*-4VP) as seen in Figure 6e. This result suggests that the role of P(S-*b*-4VP) be different from that of the other stabilizers, where the physical adsorption and chemical bonding of P(S-*b*-4VP) onto the PDVB surface are the main factors for the colloidal stability.

In addition, when the polymerization of DVB is taking place using AIBN in the presence of P(S-*b*-4VP) block copolymer at 70 °C, the growing P4VP block propagates by the addition of DVB units. Thus, the chemical bonding of DVB occurs between sulfur and 4-vinylpyridine segment in the block copolymer, resulting in the formation of the P(S-*b*-4VP-*b*-DVB) triblock copolymer as seen in Scheme 1 by the RAFT method.[27] Thus, P(S-*b*-4VP) is working not only as the steric stabilizer by physical adsorption but also as the reactive stabilizer by forming P(S-*b*-4VP-*b*-DVB) triblock copolymer.

Effects of the Water Content in the Medium Mixtures. One of the important factors affecting the formation of spherical particles is the characteristics of the solvent used in the polymerization. In particular, the formation of micelles originated from the P(S-*b*-4VP) block copolymer is affected by the selective solvents where the micelles further serve as the

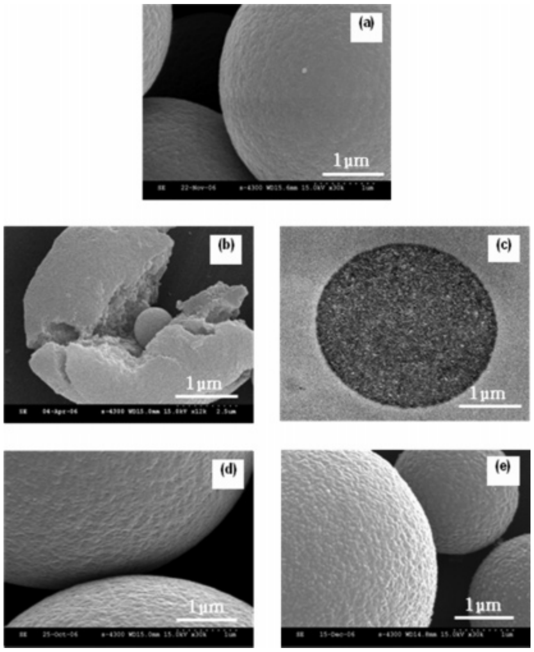


Figure 5. (a) SEM photograph showing the surface of the cross-linked PDVB microspheres. (b) SEM photograph of the internal structure of the PDVB upon broken by hot press. (c) TEM photograph of the internal structure of PDVB upon microtoming of (a). (d) SEM photograph of dispersed (a) in THF for 24 h. (e) SEM photograph of treated (a) with ultrasound in THF for 15 min.

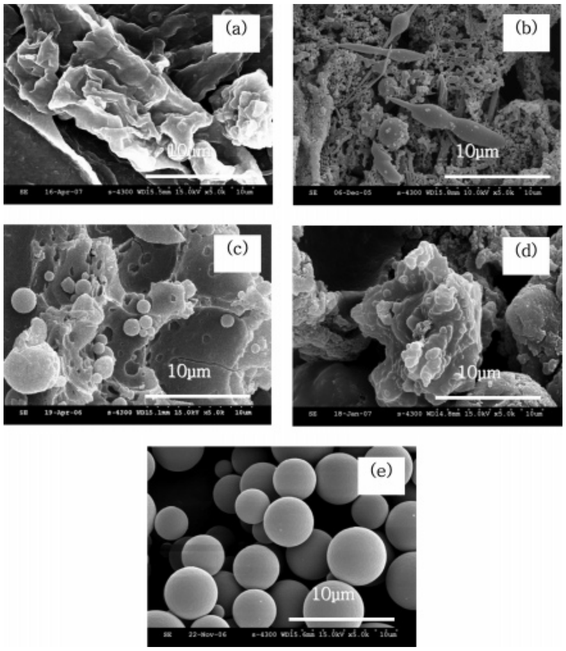


Figure 6. SEM photographs of synthesized PDVB using various stabilizers. The concentration of stabilizers was 5 wt % relative to monomer in mixtures of ethanol (10 g) and water (10 g) at 70 °C for 2 h: (a) no stabilizer, (b) PVP, (c) PVA, (d) SDS, and (e) P(S-*b*-4VP).

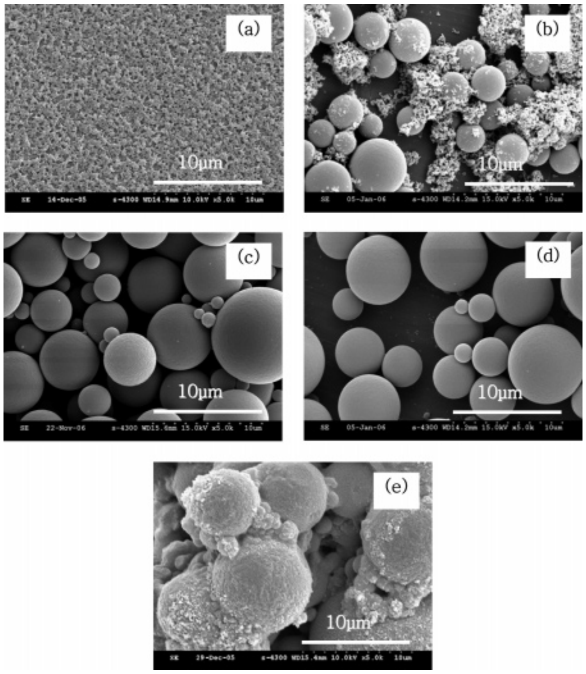


Figure 7. SEM photographs of the cross-linked PDVB spheres prepared with the water concentrations of (a) 30, (b) 40, (c) 50, (d) 60, and (e) 70 wt % relative to total media.

polymerization loci. Figure 7 shows the effect of the water contents in the medium mixtures on the formation of spherical particles using the standard recipe listed in Table 1. The water content varied from 30 to 70 wt % relative to the total media. When water content was 30 wt %, only tiny small particles are obtained as shown in Figure 7a. When the water content increased from 40 to 70 wt %, two different behaviors are observed: the stable spheres were obtained with 50 and 60 wt % of water in Figures 7c,d. On the other hand, the formation of small particles and aggregation of unstable particles were obtained with 40 and 70 wt % water as shown in parts b and e of Figure 7, respectively. These results indicate that the water content affects the surface energy and thereby micelle diameter of the block copolymer. The higher the water content in the medium mixtures, the higher the P(S-*b*-4VP) block copolymer content is needed to stabilize the micelles. As the water content increased, the number of P(S-*b*-4VP) molecules increased in each micelle. If a small number of the P(S-*b*-4VP) copolymer exists per micelle, the number of reactive living site decreases, and the coagulations of tiny primary particles by chemical bonding are suppressed significantly. Under such conditions, noncoagulated tiny particles exist as an independent entity as seen in Figure 7a. When an excess amount of water is present in the medium as seen in Figure 7e, the chemical affinity between the medium and the block copolymer/monomer becomes far distinct, giving severely agglomerated particles. Therefore, the optimum water content lies in the range 50−60 wt % with respect to the total media.

Conclusions

The polymerization method for the synthesis of highly cross-linked polymer microspheres with narrow size distribution in a single stage is limited. The most recent approach is to use precipitation polymerization without using stabilizer in organic media. However, precipitation polymerization has many demerits such as low final conversion (30−50%) and low monomer content (2−5%). On the other hand, our novel process is successful for preparing highly cross-linked microspheres with various advantages of short reaction time, high yield (65%), and controlled surface area using inexpensive and enviromental media. The stable cross-linked PDVB microspheres were prepared in the presence of the P(S-*b*-4VP) block copolymer, and the mechanism of the formation and growth of the PDVB particles was proposed. The significance of the polymerization is the use of the P(S-*b*-4VP) copolymer prepared by the RAFT method in the mixtures of ethanol and water. The formation of cross-linked PDVB particles strongly depends on the water content and the presence of the block copolymer. The morphology and internal structure of the particles are confirmed by SEM and TEM photographs. Before the initial stage, the P(S-*b*-4VP) copolymer was found to form micelles containing DVB in ethanol at room temperature. When the polymerization is taking place inside of the micelles and at the living site of the block copolymer at 70 °C, the growing P4VP block propagates by the addition of DVB and the chemical bonding of DVB occurs in the P(S-*b*-4VP) copolymer. As a result, the P(S-*b*-4VP-*b*-DVB) triblock copolymer is formed, inducing nanoparticles. The tiny small particles having the living character due to the diblock and triblock copolymer are enlarged, showing the cortex-like macropores by chemical bonding. As the reaction proceeds, the surface morphology of the particles becomes smoother since the surface pores are filled with the DVB oligomers.

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References and Notes

(1) Li, W.-H.; Hamielec, A. E.; Stöver, H. D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2029.
(2) Cheng, C. M.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 245.
(3) Yang, S.; Shim, S. E.; Choe, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1309.
(4) Mohanty, P. S.; Kesavamoorthy, R.; Matsumoto, K.; Matsuoka, H.; Venkatesan, K. A. *Langmuir* **2006**, *22*, 4552.

(5) Downey, J. S.; Frank, R. S.; Li, W. H.; Stöver, H. D. H. *Macromolecules* **1999**, *32*, 2838.
(6) Song, J. S.; Winnik, M. A. *Macromolecules* **2005**, *38*, 8300.
(7) Choi, J.; Kwak, S.-Y.; Kang, S.; Lee, S. S.; Park, M.; Lim, S.; Kim, J.; Choe, C. R.; Hong, S. I. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4368.
(8) Yang, S.; Shim, S. E.; Lee, H.; Kim, G. P.; Choe, S. *Macromol. Res.* **2004**, *12*, 519.
(9) Tillier, D. L.; Meuldijk, J.; Magusin, P. C. M. M.; Van Herk, A. M.; Koning, C. E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3600.
(10) Riess, G.; Labbe, C. *Macromol. Rapid Commun.* **2004**, *25*, 401.
(11) Gaillard, N.; Guyot, A.; Claverie, J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 684.
(12) Ma, Y.; Yang, W. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *42*, 2678.
(13) Burguière, C.; Pascual, S.; Bui, C.; Vairon, J.-P.; Charleux, B.; Davis, K. A.; Matyaszewski, K.; Bétremieux, I. *Macromolecules* **2001**, *34*, 4439.
(14) Zheng, G.; Zheng, Q.; Pan, C. *Macromol. Chem. Phys.* **2006**, *207*, 216.
(15) Lee, J. M.; Lee, B. H.; Choe, S. *Polymer* **2006**, *47*, 3838.
(16) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.
(17) Mühlebach, A.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1996**, *31*, 6046.
(18) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A. *Macromolecules* **2003**, *36*, 2273.
(19) Shim, S. E.; Shin, Y.; Jun, J. W.; Lee, K.; Jung, H.; Choe, S. *Macromolecules* **2003**, *36*, 7994.
(20) Barton, A. F. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1985; pp 94−109.
(21) Shim, S. E.; Yang, S.; Choi, H. C.; Choe, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 835.
(22) Barton, A. F. M. *Pure. Appl. Chem.* **1985**, *57*, 905.
(23) Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*; Wiley-Interscience: New York, 1999.
(24) Svec, F.; Fréchet, J. M. J. *Macromolecules* **1995**, *28*, 7580.
(25) Tuncel, A.; Tuncel, M.; Salih, B. *J. Appl. Polym. Sci.* **1999**, *71*, 2271.
(26) Jin, J. M.; Lee, J. M.; Ha, M. H.; Lee, K.; Choe, S. *Polymer* **2007**, *48*, 3107.
(27) Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 5457.

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