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Living radical dispersion photopolymerization of styrene by a reversible addition–fragmentation chain transfer (RAFT) agent

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Abstract

In this study, an addition–fragmentation chain transfer agent bearing dithioester group is synthesized and applied to conventional dispersion photopolymerization of styrene in ethanol medium in the presence of poly(*N*-vinylpyrrolidone) stabilizer with varying amounts of the RAFT agent and optionally with conventional initiator, azobisisobutyronitril (AIBN) at various temperatures. Monomer conversion, molecular weight evolution, polydispersity index (PDI), and final particle sizes are measured. The PDI of the formed polymer is between 1.5 and 2.5 in the presence of RAFT agent. Higher concentration of RAFT agent or elevated temperature leads to the acceleration of the polymerization rate resulting in fast conversion, and reducing molecular weight and PDI. Stable polystyrene beads above 1 μm in diameter are successfully prepared by means of RAFT method applied in dispersion polymerization. The weight average particle sizes are between 1.08 and 2.04 μm, and the uniformity (D_w/D_n) is ranged from 1.26 to 2.51.

Keywords: Living radical polymerization; Dispersion polymerization; RAFT

1. Introduction

Controlled/'living' radical polymerization has been known to be a useful technique for a preparation of well-defined polymer structure by controlling molecular weight, molecular weight distribution and tailored architecture. The revolutionized polymers prepared through the living radical polymerization possess vast applications for new or advanced materials including surfactants, coatings, adhesives, biomaterials, medical materials and microelectronics.

Several controlled/living radical polymerization methods have been developed: the representative methods are, in general, nitroxide-mediated polymerization (NMP) [1,2], metal catalyzed atom transfer radical polymerization (ATRP) [3,4], and reversible addition–fragmentation chain transfer (RAFT) method [5,6].

Although RAFT has been discovered more recently, it endows several advantages over NMP or ATRP. RAFT, in principle, has similar polymerization methods and reaction rates to conventional emulsion polymerization, since the number of free propagating radicals remains theoretically unaffected. In addition, compared to the limits of usable monomers in NMP or ATRP, RAFT method can be easily adopted to a wide range of monomers which can be polymerized by free radical methods [7]. For example, methacrylate monomers cannot be applied to NMP and vinyl acetate cannot be utilized in ATRP. As a consequence, intensive studies have been carried out for various monomers using RAFT technique [8–13].

Polymer particles above micron size have a wide range of applications including standard samples for instrument calibration, column packing materials in chromatography, support materials for biochemicals, and microelectronic materials [14–18]. Dispersion polymerization has been carried out in order to synthesize such micron sized monodisperse polymeric beads for the past three decades [19–21].

In a dispersion polymerization, all reaction ingredients are dissolved in the reaction medium at the beginning stage of reaction, then insoluble spherical polymer particles stabilized by steric stabilizer are formed and dispersed in the reaction medium. However, only a few studies have been reported on the living radical dispersion polymerization technique [22,23], where NMP method was used in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy

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(TEMPO). Since little has been known in the field of dispersion polymerization using RAFT method to date, conducting living radical polymerization via dispersion polymerization technique has remained as a challengeable area.

In our previous study on the living radical emulsion polymerization of methyl methacrylate using water-soluble 4-thiobenzoyl sulfanylmethyl benzoate carrying $-COO^{-}Na^{+}$ as a RAFT agent, uniform PMMA beads in a size range of 50–400 nm were prepared at a temperature range of 60–90 °C without any additional conventional initiator and optionally in the presence of sodium dodecyl sulfate (SDS) surfactant [24]. The number average molecular weight and polydispersity index (PDI) were 2.5×10^5–5.7×10^5 g/mol, and 1.2–1.7, respectively.

In the current study, the end group of 4-thiobenzoyl sulfanylmethyl benzoate was replaced by benzoic acid (i.e. $-COO^{-}Na^{+}$ was replaced by –COOH), which can be dissolved in alcohol. Dispersion polymerization of styrene was successfully carried out in ethanol medium with poly(*N*-vinylpyrrolidone) (PVP) stabilizer without or optionally with additional conventional initiator, AIBN, in order to produce micron sized polystyrene (PS) beads by living radical polymerization using a RAFT agent. The dependence of the RAFT agent concentration on the conversion, the molecular weight and its distribution, and the particle size at 70 °C, the influence of the added AIBN on the polymerization products, and the temperature dependent polymerization using the RAFT agent were investigated.

2. Experimental section

2.1. Materials

Reagent grade phenylmagnesium bromide, α-bromo-ρ-toluic acid, and carbon disulfide used in preparation of a RAFT agent were purchased from Aldrich Co. (USA). Anhydrous diethyl ether and methanol were purchased from J. T. Baker Co. (USA). Carbon disulfide and diethyl ether were distilled in order to remove existing impurities and water. Styrene (Junsei Chemicals, Japan) was distilled under reduced pressure and stored in a refrigerator prior to use. Poly(*N*-vinylpyrrolidone) (PVP; weight-average molecular weight = 40,000; Sigma Chemical Co.) was used. Ethanol (Samchun Chemical Co., Korea) was used as a reaction medium.

2.2. Synthesis of RAFT agent

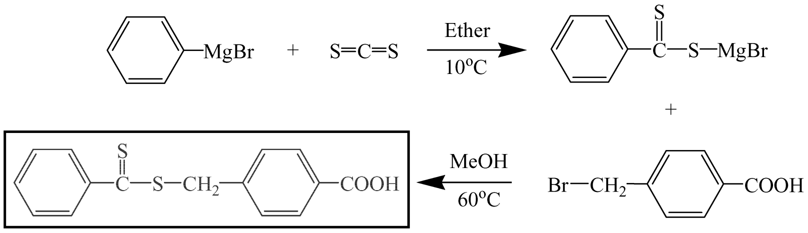
4-Thiobenzoyl sulfanylmethyl-benzoic acid RAFT agent was synthesized through two steps of reaction. First, 0.03 mol phenylmagnesium bromide and 0.045 mol carbon disulfide were reacted in dry diethyl ether at 10 °C for 6 h. After removing unreacted reagents by distillation, 1.7:1 molar ratio of (thiobenzoyl)sulfanyl magnesium bromide and α-bromo-ρ-toluic acid were added in methanol. The second step reaction was carried out at 60 °C for 24 h. Again, unreacted reagent and methanol were removed by distillation. Details of the procedure for the synthesis of the RAFT agent is described in Scheme 1.

2.3. Polymerization

A mechanical stirrer under nitrogen atmosphere carried out polymerization in a 500 ml of three-neck reaction vessel at a constant agitation speed of 150 rpm. The polymerization temperature was 50, 60, and 70 °C and the temperature was controlled using water bath circulator. 1 kW UV lamp having 365 nm wavelength was employed to initiate the polymerization. Styrene concentration was 10 wt% based on the reaction medium and the RAFT agent concentration was varied from 0.5 to 2.0 wt% based on styrene. In some cases, 1 and 2 wt% of AIBN based on styrene were added. The amount of PVP was fixed at 10 wt% throughout all experiments. The general procedure was as follows: ethanol and styrene were charged to the reaction vessel and nitrogen was purged for 30 min. When the temperature in the reaction vessel was reached to a desired level, the RAFT agent dissolved in the rest 10 ml of ethanol was added to the reactor, then the reaction was initiated by turning on the UV lamp. Polymerization was carried out for up to 16 h. During the polymerization, 4 ml of the sample was periodically taken from the reaction vessel to characterize the polymerization including conversion, molecular weight and PDI. After completion of the polymerization, the resultant was rinsed with methanol and final fine powder of white PS was obtained by filtration process.

2.4. Characterizations

The chemical structure of the synthesized RAFT agent was confirmed by Varian 400-MHz ^{1}H-NMR using $CDCl_3$ as the solvent. Molecular weight and PDI were characterized using Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotex T50 differential viscometer. 10^5, 10^3, and 10^2 Å μ-styragel packed high resolution-columns were employed. In order to avoid misleading results arisen from PVP, the solution sample withdrawn from the reaction vessel was rinsed with methanol and centrifuged repeatedly, then the PS powder was dried in vacuum oven for 24 h. PS dissolved in THF was injected at a flow rate of 1.0 ml/min. Calibration was based on ten polystyrene standard samples (Polymer Laboratories, UK) with molecular weight ranging 7,500,000–580 g/mol. Measurement of the FTIR spectra was performed using a Bruker 48 series FTIR spectroscopy. All infrared spectra recorded at 4 cm^{-1} 21 resolution and 16 scans were accumulated in 20 s for each specimen. Philips SEM (Scanning Electron Microscopy) 515 was used to investigate the morphology of PS particles. The monomer conversion to polymer was determined gravimetrically



Scheme 1. Synthesis of 4-thiobenzoyl sulfanylmethyl-benzoic acid RAFT agent.

appeared elsewhere [25]. Number and weight average diameter, D_n and D_w, and the uniformity were obtained using Scion Image® Analyzer Software by counting individual 100 particles from SEM microphotographs.

3. Results and discussion

3.1. Synthesis of a RAFT agent

Scheme 1 shows the procedure for the synthesis of 4-thiobenzoyl sulfanylmethyl-benzoic acid for the RAFT agent. The colour of the reaction solution turned into orange after the completion of the first step of the reaction and finally pink-colour powder was obtained after purification by distillation. The chemical structure of the successfully synthesized 4-thiobenzoyl sulfanylmethyl benzoic acid was confirmed from the proton NMR spectrum as shown in Fig. 1, where characteristic peaks were assigned. It is noted that hydrogen atom at the end carboxyl group expected to be observed above 10 ppm was not discernable due to a quite weak signal intensity.

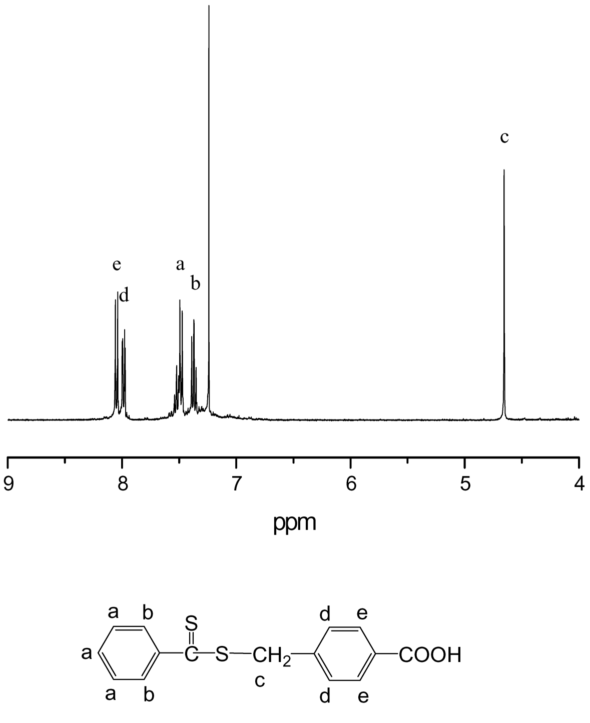


Fig. 1. ^1H NMR spectrum of the synthesized RAFT agent in $CDCl_3$.

3.2. RAFT agent concentration on the polymerization at 70 °C

Fig. 2 shows the effect of the RAFT agent concentration on the fractional conversion of styrene monomer as a function of reaction time with 12 wt% PVP at 70 °C. It is seen that the conversion of all the experimental sets exhibits a linear increase in fractional conversion with time. The linearity implies that the concentration of growing radicals is constant during polymerization. As expected, the conversion increases with increasing amounts of the RAFT agent since the RAFT agent behaves as a polymerization initiator upon the hemolytic cleavage of sulfur-carbon bond by UV radiation. However, it is observed that the extrapolated initial intercepts at zero polymerization time do not pass through the origin as seen in Fig. 2. It is known that polymeric stabilizer used in dispersion polymerization is not only physically adsorbed but also chemically bound by forming a covalent bond with monomer which cannot be removed from the polymer particles since nucleation starts on PVP molecules by abstraction of labile hydrogen [16]. El-Aasser et al. [26] reported that 1.1 wt% of total added PVP was physically adsorbed on poly(methyl methacrylate) particles prepared by dispersion polymerization.

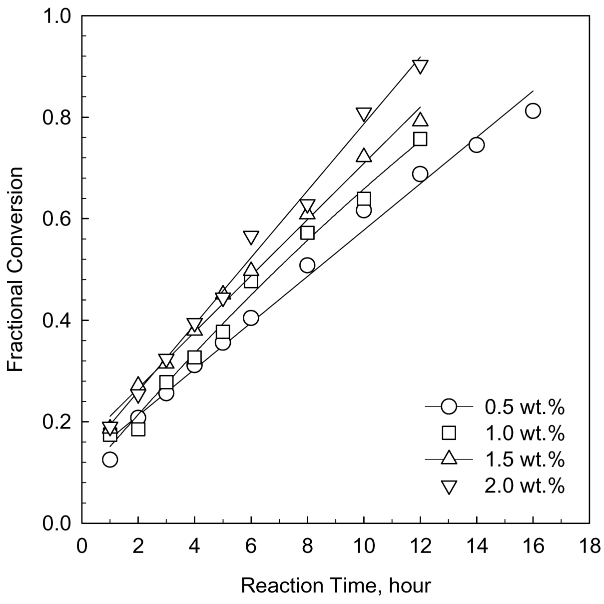


Fig. 2. Conversion of living radical dispersion photopolymerization of PS with 12 wt% PVP stabilizer with varying concentration of the RAFT agent at 70 °C.

In addition, they observed that the C=O peak at 1670 nm^{-1} in IR spectra of PVP still exists after washing off the PVP adsorbed on the prepared PS particles, which indicates that the PVP is grafted to the PS molecules. Thus, it is worthy mentioning that the behavior observed in the extrapolated initial intercepts maybe due to the formation of in situ grafted PVP–PS copolymer upon initiation process during nucleation stage.

Fig. 3(a)–(c) shows the FTIR spectra of the prepared PS by living radical dispersion photopolymerization in the presence and absence of PVP, and the pure PVP, respectively. In characterizing PVP molecules by means of FTIR method, the characteristic absorption band of PVP at 1660–1680 cm^{-1} is attributed to the combination of >C=O and C–N stretching [27] as seen in Fig. 3(c). Owing to this combination mode, this band occurred broadly at a lower wavenumber than the pure carbonyl band expected at 1750–1700 cm^{-1}. In the case of pure PS in Fig. 3(b), a characteristic C=C absorption band of benzene ring on PS weakly occurs at 1689 cm^{-1}. Whereas a stronger absorption peak at 1689 cm^{-1} for the prepared PS in the presence of PVP is observed in Fig. 3(a), implying the existence of PVP molecules on PS particles.

In Fig. 4(a), the evolution of number average molecular weight (M_n) linearly increases with fractional conversion throughout the polymerization, which is a key characteristic of living radical polymerization. It is well known that number average molecular weight is inversely proportional to the concentration of RAFT agent [28].

Although there exists a lack of publications regarding living radical dispersion polymerization, in the case of heterogeneous polymerizations including emulsion and miniemulsion polymerization using various RAFT agents, the same trend was found by several researchers [29–31]. As seen in Fig. 4(a), M_n decreases with an increase of RAFT agent concentration from 0.5 to 2.0 wt%. Again, extrapolated intercepts of the lines are not extended to the origin due to the in situ grafting of PVP on PS at initial polymerization stage as mentioned earlier (Table 1).

Fig. 4(b) represents the effect of concentration of RAFT agent on the molecular weight distribution of PS. As the polymerization proceeds, PDI tends to slightly increase for all RAFT agent concentrations. Additionally, a higher RAFT agent concentration yields a lower polydispersity. The PDI values lie higher than normally obtained ones in various homogeneous living radical polymerizations such as bulk and solution polymerization. The reason for this observation is investigated in the following experiments. Kanagasabapathy et al. [32] studied the RAFT polymerization of poly(4-acetoxystyrene) and poly(4-acetoxystyrene)-block-polystyrene by bulk, solution, and emulsion polymerization methods using various dithioester RAFT agents in conjunction with a conventional initiator. They found that the same RAFT agent used in this study yields 1.18 of PDI in bulk polymerization of poly(4-acetoxystyrene). The number average molecular weight and the conversion were 4501 g/mol and 29.7%, respectively, at 90 °C for 8 h. The molecular weight dependence of the RAFT agent concentration using the experimental data shown in Fig. 4(a) is recalculated at 80% conversion and plotted in Fig. 5. The PDI increases with the fractional conversion. In addition, it is found that the number average molecular weight is proportional to the RAFT agent molar concentration to the power of −0.602 (i.e. $M_n \alpha$ [RAFT agent]$^{-0.602}$).

Fig. 6 displays the SEM microphotographs of the PS beads prepared in ethanol medium at 70 °C upon various RAFT agent concentrations initiated by UV radiation. It is

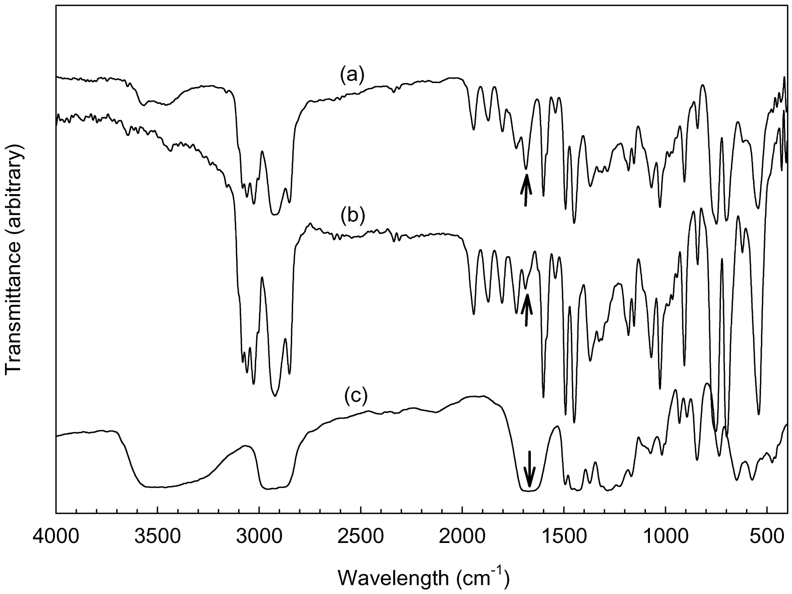


Fig. 3. FTIR spectra of pure PVP and PS prepared by living radical dispersion photopolymerization with 2 wt% of RAFT agent in ethanol at 70 °C. (a) PS prepared in the presence of PVP, (b) PS prepared in the absence of PVP, (c) pure PVP ($M_w = 40,000$ g/mol).

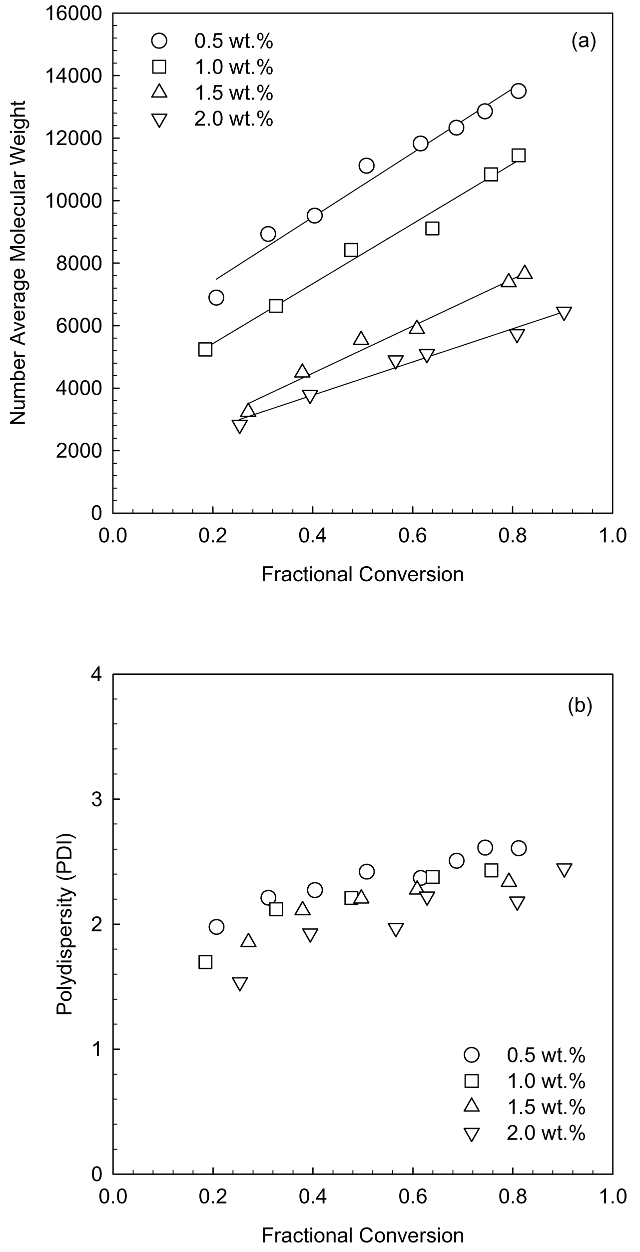


Fig. 4. (a) Number average molecular weight and (b) PDI of PS prepared by living radical dispersion photopolymerization with 12 wt% PVP stabilizer with varying concentration of RAFT agent at 70 °C.

Table 1
Polymerization conditions for living radical dispersion photopolymerization of styrene in ethanol

Run	RAFT agent[a] (wt%)	AIBN (wt%)	PVP[b] (wt%)	Temperature (°C)	Initiation
1	0.5	0	12	70	photo
2	1.0	0	12	70	photo
3	1.5	0	12	70	photo
4	2	0	12	70	photo
5	2.0	0	12	50	photo
6	2.0	0	12	60	photo
7	2.0	0	0	70	photo
8	1	1	12	70	photo
9	0	2	12	70	photo

Styrene concentration is 10 wt% based on ethanol.

[a] The amount of RAFT agent is based on styrene monomer.

[b] The amount of PVP is based on styrene monomer.

seen that stable PS beads are successfully prepared by this technique. The results of the number and weight average diameter, the uniformity, and the coefficient of variation (CV) of the beads are summarized in Table 2. The weight average particle sizes are between 1.08 and 2.04 μm, and the uniformity (D_w/D_n) is ranged from 1.26 to 2.51. In addition, as the RAFT agent concentration increases, the size of the beads tends to increase and the uniformity or CV values become greater, which is a common observation in dispersion polymerization using oil-soluble initiators such as AIBN or BPO. In a conventional dispersion polymerization, the increase in particle size and the broadening in particle size uniformity with initiator concentration have been often observed [33,34]. These phenomena have been explained by the fact that increased amount of initiator produces higher concentration of precipitated oligomer chains due to increased number of radicals, resulting in accelerating aggregation of nuclei and followed by a formation of larger particles. Since larger particles are lack of stabilizer or oligomer adsorbing capability due to lowered surface area, nucleation (i.e. formation of small particles) facilitated, therefore the particle size distribution becomes broader. In the case of TEMPO-mediated living radical dispersion polymerization of PS, the average particle sizes were reported in the range of 0.5–3.64 μm with the D_w/D_n ranging from 1.3 to 2.5 [22].

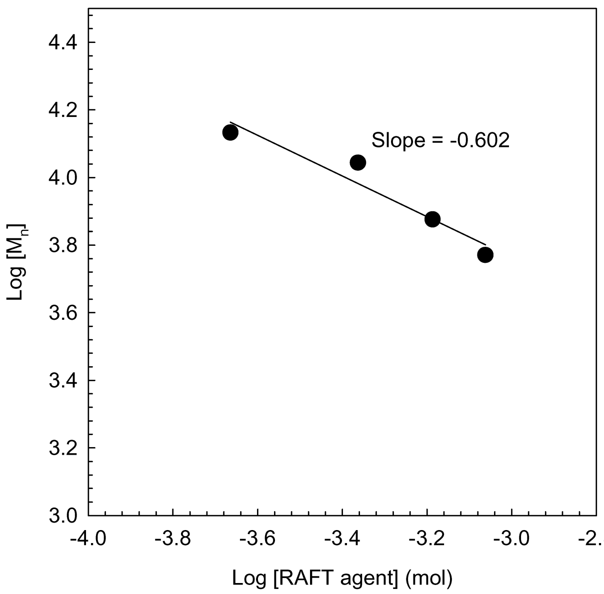
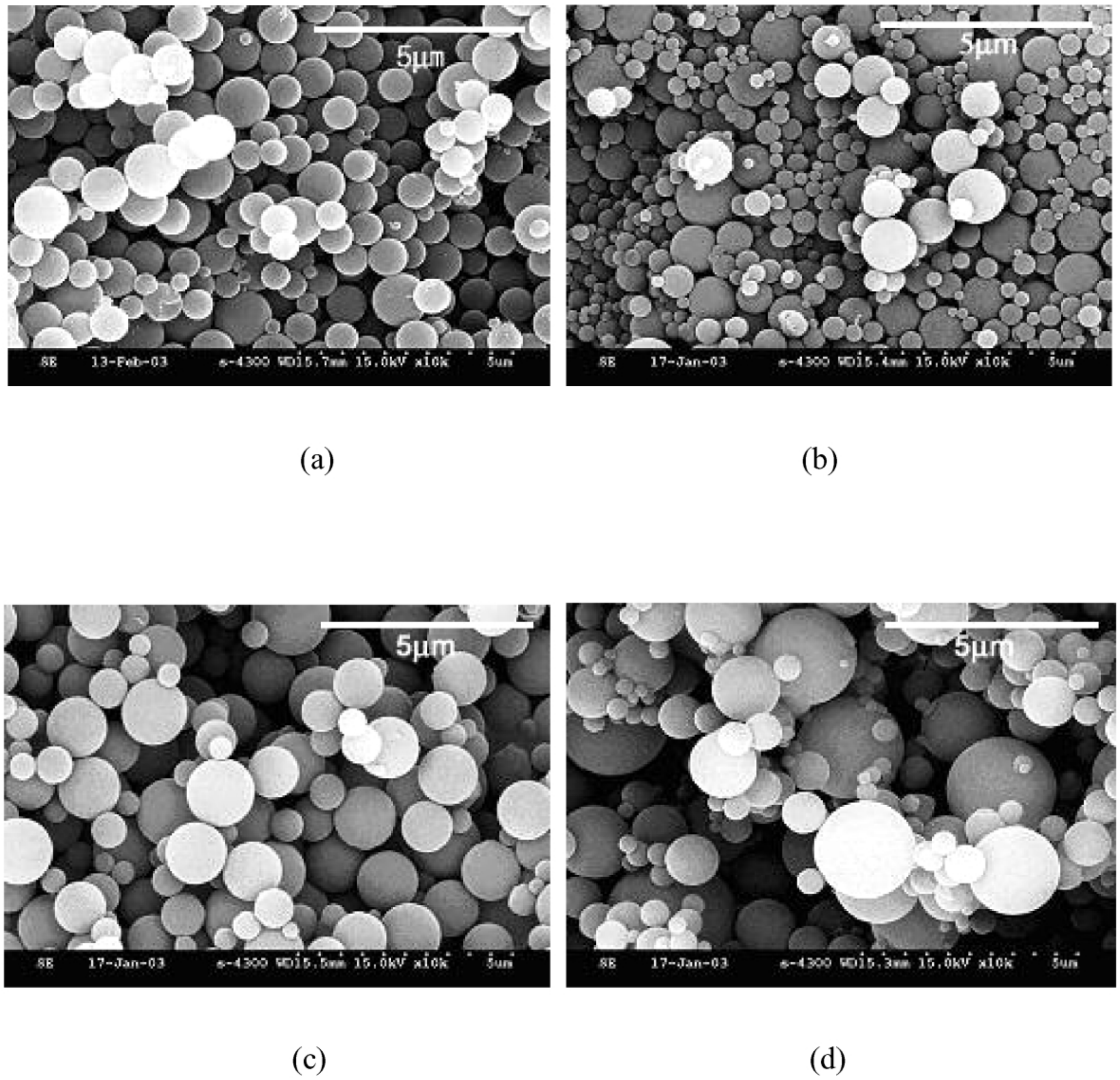


Fig. 5. Dependence of number average molecular weight, M_n, on RAFT agent concentration in the styrene dispersion living radical photopolymerization based on 80% conversion at 70 °C.



(a) (b)

(c) (d)

Fig. 6. SEM micro-photographs of PS beads prepared by living radical dispersion photopolymerization in ethanol medium at 70 °C with various amounts of RAFT agent (10 wt% styrene to ethanol, 12 wt% PVP to styrene). (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt%, and (d) 2.0 wt%.

Table 2
Size of PS beads prepared by living radical dispersion photopolymerization with 12 wt% of PVP stabilizer in ethanol at 70 °C

RAFT concentration (wt%)	D_n (μm)[a]	D_w (μm)[a]	Uniformity[b]	CV (%)[c]
0.5	0.86	1.08	1.26	34.1
1.0	0.68	1.13	1.66	52.3
1.5	0.99	1.36	1.37	40.5
2.0	0.81	2.04	2.51	71.8

Maximum bead size observed in SEM microphotograph.

[a] The number average diameter, $D_n = (\sum_{i=1}^{n} n_i D_i / n$; the weight average diameter, $D_w = [\sum_{i=1}^{n} (n_i D_i)^4] / \sum_{i=1}^{n} (n_i D_i)^3]$.

[b] Uniformity $= D_w / D_n$.

[c] The coefficient of the variation (CV) of the number average diameter = (standard deviation)/D_n, where standard deviation $= [\sum_{i=1}^{n} (D_i - D_n)^2 / (n-1)]^{\frac{1}{2}}$.

3.3. Added AIBN and the polymerization

In order to study the effects of AIBN along with the RAFT agent, small amounts of AIBN were introduced to the polymerization medium with 12 wt% of PVP at 70 °C. Fig. 7 shows the fractional conversion vs. reaction time with the RAFT agent:AIBN wt% ratios of 2:0, 1:1, and 0:2. It is noted that initiation was induced by UV radiation. When 2 wt% of AIBN is solely used, polymerization rate is the highest and the conversion reaches to 0.955 at 10 h and 0.983 at 14 h. Again, when 2 wt% of the RAFT agent is sorely used, the conversion of 0.903 is obtained at 12 h. In the case of 1:1 ratio of RAFT agent to AIBN, the polymerization rate is the lowest. It is believed that the initiation is primarily achieved by AIBN and the RAFT agent acts as a chain transfer agent.

Comparison of the molecular weight evolution and the polydispersity in the AIBN-added systems is shown in

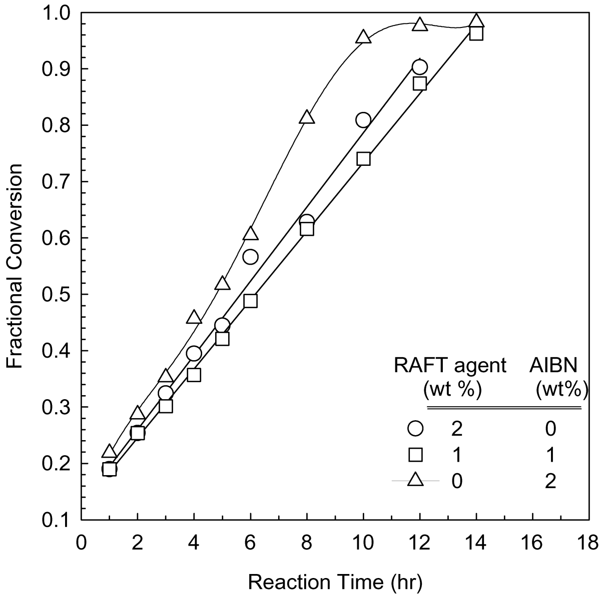
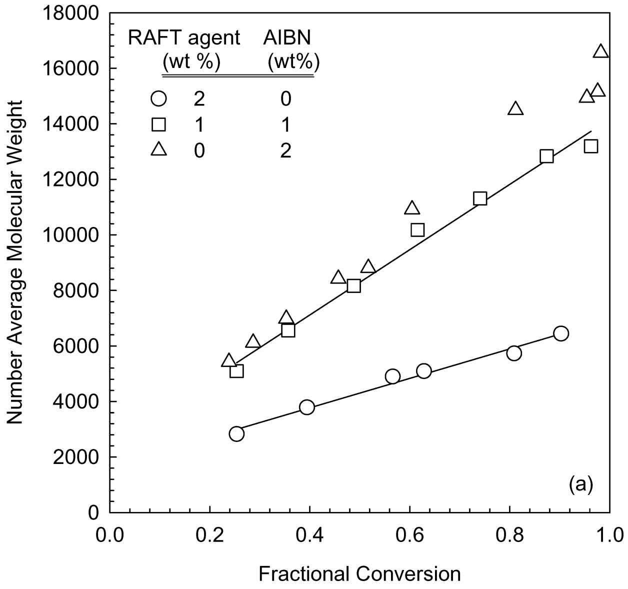


Fig. 7. Conversion of living radical dispersion photopolymerization of styrene with 12 wt% PVP stabilizer with varying concentration of RAFT agent and AIBN at 70 °C.

Fig. 8(a) and (b). When the RAFT agent is solely used, the number average molecular weight is quite low, whereas when AIBN is used in conjunction with the RAFT agent, the molecular weight significantly increases, which is similar to the case, where only AIBN is used. The molecular weight with the 1:1 ratio of RAFT agent to AIBN reaches to 11,312 g/mol at 10 h (conversion of 0.741) and 13,198 g/mol at 14 h (conversion of 0.963). In all cases, molecular weights of PS prepared in this study are similar to those achieved from living free radical miniemulsion polymerization [28], but lower than the usually obtained values using living free radical emulsion polymerization [35] since monomer transportation to the growing particles is suppressed by viscous reaction medium. Typical emulsion polymerization produces the weight average molecular weight in the range of 10^5-10^6 g/mol, whereas low molecular weight is obtained in dispersion polymerization due to this reason. In addition, termination of growing radicals could be readily achieved in dispersion polymerization compared to emulsion polymerization, where growing particles contain the average number of radicals of 0.5 in particle growing stage (i.e. Interval II).

The PDI of the polymerization initiated using various RAFT agent: AIBN ratios are depicted in Fig. 8(b). When the RAFT agent still exists in the polymerization system, the PDI sparingly increases with the conversion. But AIBN is sorely used, the PDI abruptly increases with increasing conversion, yielding high value up to 13.6 from 1.5. Rabek et al. reported photo-induced oxidative degradation of PVP [36]. Upon 4 h of UV irradiation in water solution, PVP itself degrades and PDI increases from 3.44 to 5.30. When radical generating species such as hydrogen peroxide is present, the PDI rises to 7.71 for 4 h. The significant increase in PDI in 0:2 ratio of the RAFT agent to AIBN system may be arisen from the photo-degradation of PVP. Furthermore, relatively high PDI values throughout the experiments might be caused from the degradation of PVP.



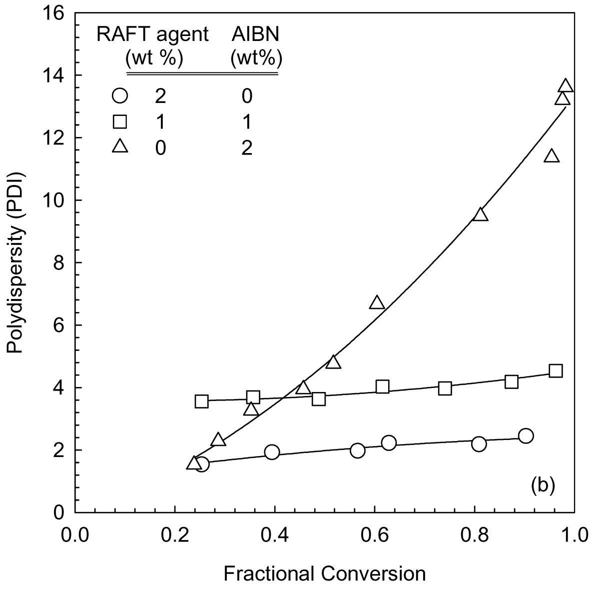
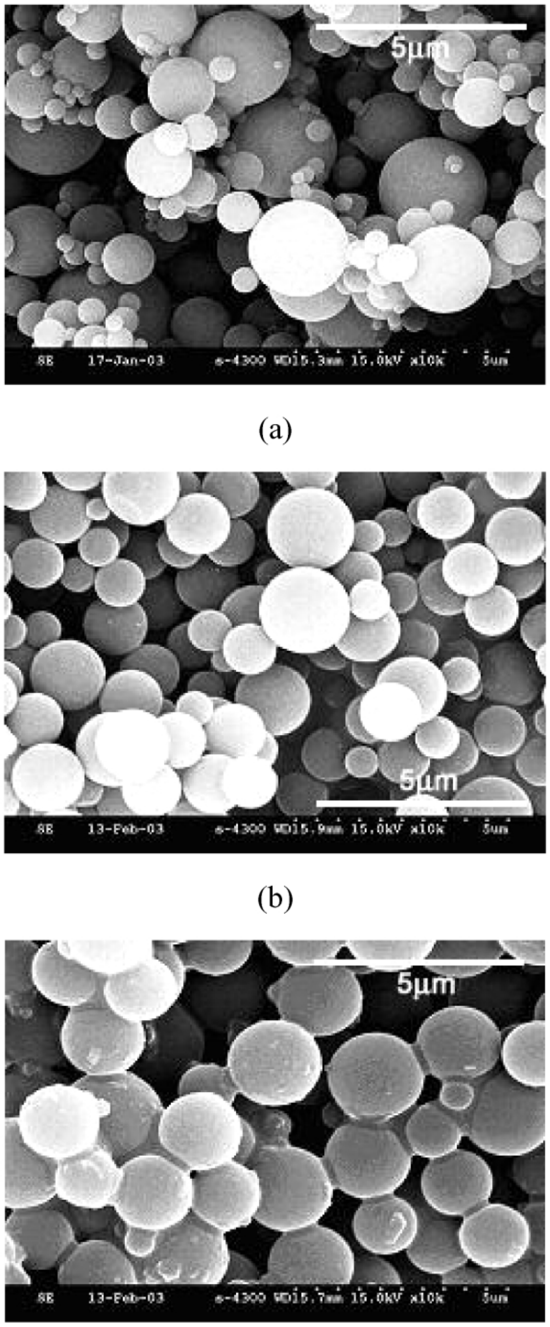


Fig. 8. (a) Number average molecular weight and (b) PDI vs. conversion of PS prepared by living radical dispersion photopolymerization with 12 wt% PVP stabilizer with varying concentration of RAFT agent and AIBN at 70 °C.

In Fig. 9, SEM images of the PS beads prepared by living radical dispersion photopolymerization in ethanol with various concentrations of RAFT agent and AIBN are exhibited. The number average particle diameters are 0.81, 1.22, and 1.67 μm for the 2:0, 1:1, and 0:2 ratios of RAFT agent to AIBN, respectively. As seen in Fig. 9, the particle size for the 0:2 ratio of RAFT agent to AIBN at 70 °C was 1.67 μm, whereas that of the 2:0 ratio of RAFT



(a)

(b)

(c)

Fig. 9. SEM microphotographs of PS beads prepared by living radical dispersion photopolymerization in ethanol medium at 70 °C with 12 wt% PVP stabilizer with with varying concentration of RAFT agent and AIBN at 70 °C (10 wt% styrene to ethanol, 12 wt% PVP to styrene). RAFT agent (wt%):AIBN (wt%) = (a) 2:0 (b) 1:1, and (c) 0:2.

agent to AIBN is reduced to 0.81 µm. In addition, particle coagulation on the surface of PS beads is observed in the case, where AIBN is solely used. The coagulation is thought to arise from the instability of the PS particles due to the significant degradation of PVP molecules during the UV radiation as seen in Fig. 8(b).

3.4. Temperature dependent polymerization

Fig. 10(a) and (b) demonstrate the effects of polymerization temperature on the fractional conversion and the number average molecular weights of PS prepared with 12 wt% PVP and 2 wt% RAFT agent, respectively. Elevated temperature leads to the acceleration of polymerization resulting in fast conversion and reduced molecular weight, while maintaining the linearity in conversion vs. reaction time and molecular weight vs. reaction time intact. In addition, increasing polymerization temperature induces the reduction of PDI as seen in Fig. 11.

In Fig. 12, SEM images of the PS beads prepared at various

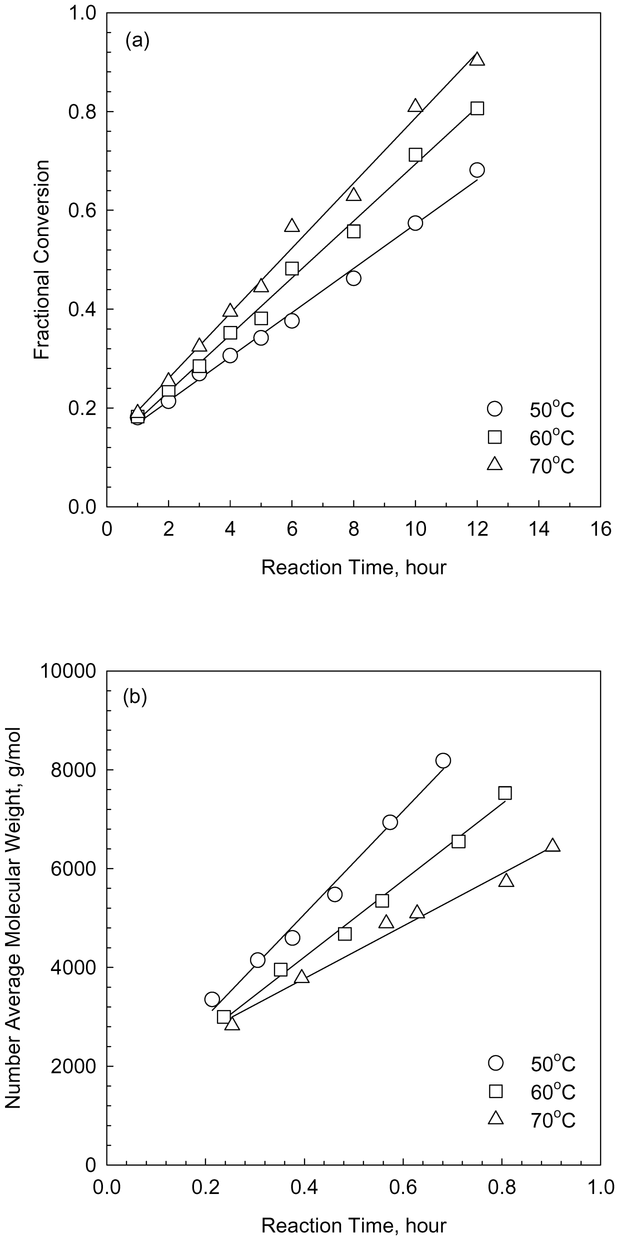


Fig. 10. (a) Fractional conversion, and (b) Number average molecular weight as a function of reaction time with 12 wt% PVP stabilizer and 2 wt% RAFT agent in ethanol medium at various temperatures.

temperatures are shown and the results are summarized in Fig. 13. As the polymerization temperature increases, weight average particle diameter increases, while the number average particle diameter increases at 50 and 60 °C, but decreases at 70 °C since the population of small particles, i.e. secondary particles, increases at 70 °C. The uniformity value abruptly increases at 70 °C due to these small particles. The secondary particles are produced in the case, where a nucleation period in the polymerization is long. Therefore, in dispersion polymerization, a short nucleation period is essential to obtain uniformly sized beads and the sizes are quite sensitive to the formulation of added ingredients [34,37].

In this study, micron sized stable PS beads are prepared by a living radical dispersion polymerization utilizing RAFT agent. However, the PDI is higher than those generally obtained by homogeneous living radical polymerization due to the photo-degradation of PVP during polymerization. In our laboratory, work is in progress to obtain micron sized monodisperse particles having low PDI values by thermal initiation.

4. Conclusions

In this study, an addition–fragmentation chain transfer agent bearing dithioester group is synthesized and applied to conventional dispersion photopolymerization of styrene with PVP stabilizer, varying amounts of the RAFT agent, and optionally with a conventional initiator, AIBN in ethanol medium at several temperatures. As the RAFT agent concentration increases, higher conversion, low molecular weight, and PDI are obtained. A linear increase in number average molecular weight with respect to the polymerization duration is observed, explicating the nature of living radical polymerization is also valid for dispersion polymerization using RAFT method. The number average molecular weight is inversely proportional to the RAFT agent molar concentration and the weight average particle sizes are between 1.08 and 2.04 μm, and the uniformity (D_w/D_n) is ranged from 1.26 to 2.51. In addition, it is found that the added RAFT agent significantly lowers the molecular weight distribution from 13.6 to ca 1.5–2.5. As the RAFT agent concentration

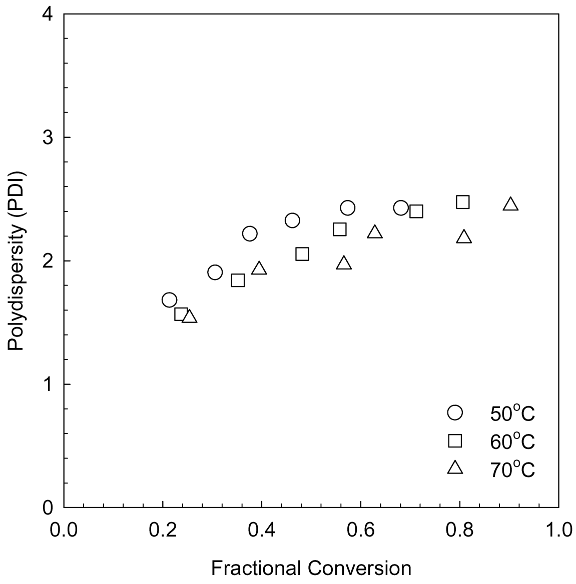
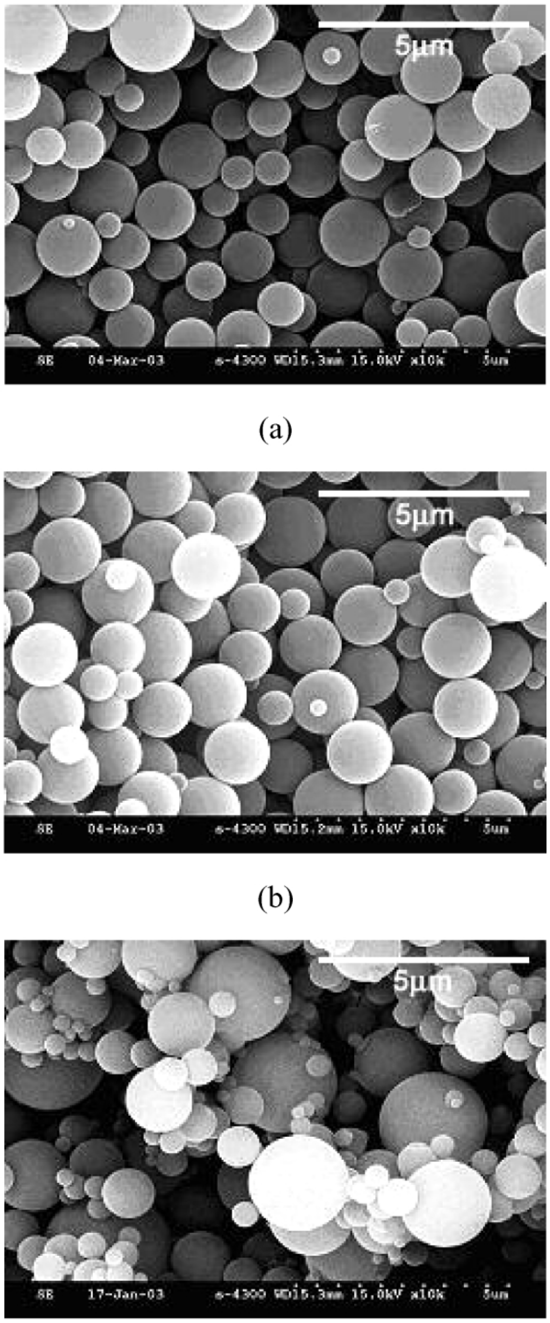


Fig. 11. PDI of polystyrene prepared by living radical dispersion photopolymerization vs. fractional conversion with 12 wt% PVP stabilizer and 2 wt% RAFT agent in ethanol medium at various temperatures.



(a)

(b)

(c)

Fig. 12. SEM microphotographs of PS beads prepared by living radical dispersion photopolymerization with 12 wt% PVP stabilizer and 2 wt% RAFT agent in ethanol medium at various temperatures. (a) 50 °C, (b) 60 °C, and (c) 70 °C.

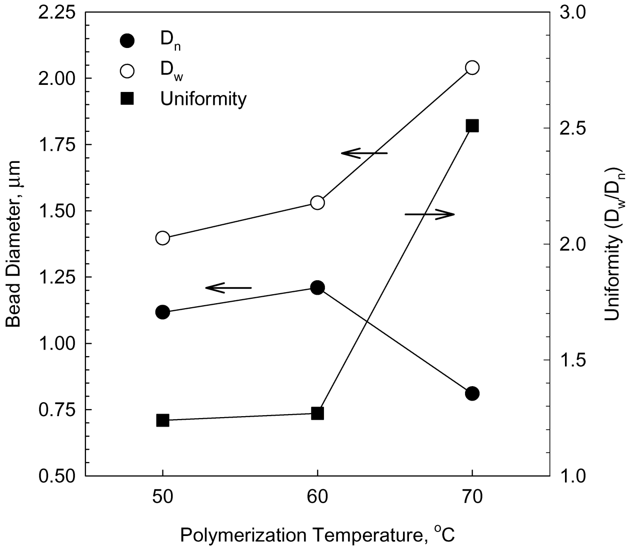


Fig. 13. Number (D_n) and weight (D_w) average particle diameter and uniformity (D_w/D_n) of PS beads prepared by living radical dispersion photopolymerization with 12 wt% PVP stabilizer and 2 wt% RAFT agent in ethanol medium at various temperatures.

increases, the bead sizes tend to increase and the uniformity or CV values become greater. The use of RAFT agent significantly suppresses the increase of PDI value caused by the photo-degradation of PVP. Addition of AIBN induces fast reaction rate and augments molecular weight without altering the average particle sizes. Elevated temperature leads to the acceleration of polymerization resulting in fast conversion, and reducing molecular weigh and PDI. In addition, as the polymerization temperature increases, weight average particle diameter increases, while the number average particle diameter increases at 50 and 60 at 70 °C, but decreases at 70 °C since the population of small particles, i.e. secondary particles, increases with temperature. Finally, stable PS beads above 1 μm in diameter are successfully prepared by a living radical dispersion polymerization utilizing RAFT agent initiated by UV radiation.

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