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Reversible Addition Fragmentation Chain Transfer Mediated Dispersion Polymerization of Styrene

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Summary: Polystyrene microspheres have been synthesized by the reversible addition-fragmentation chain transfer (RAFT) mediated dispersion polymerization in an alcoholic media in the presence of poly(*N*-vinylpyrrolidone) as stabilizer and 2,2′-azobisisobutyronitrile as a conventional radical initiator. In order to obtain monodisperse polystyrene particles with controlled architecture, the post–addition of RAFT agent was employed to replace the weak point from the pre-addition of RAFT. The feature of preaddition and postaddition of RAFT agent was studied on the polymerization kinetics, particle size and its distribution and on the particle stability. The living polymerization behavior as well as the particle stability was observed only in the postaddition of RAFT. The effects of different concentration on the postaddition of RAFT agent were investigated in terms of molecular weight, molecular weight distribution, particle size and its distribution. The final polydispersity index (PDI) value, particle size and the stability of the dispersion system were found to be greatly influenced by the RAFT agent. This result showed that the postaddition of RAFT agent in the dispersion polymerization not only controls the molecular weight and PDI but also produces stable monodisperse polymer particles.

Keywords: living radical dispersion polymerization; nucleation; particle size distribution; RAFT; stability

Introduction

Reversible addition-fragmentation chain transfer (RAFT)[1,2] polymerization has been one of the most promising recent advances in the controlled free radical polymerization (CRP) technique for both the homogeneous and heterogeneous system.[3,4] The mechanism of the RAFT has been established by a dynamic equilibrium between the active and the dormant species.[1,2] Although RAFT polymerizations were well developed in the heterogeneous media via emulsion,[2,5,6] miniemulsion[2,7,8] and *ab initio* emulsion[9] polymerization, RAFT emulsion polymerization was unsuccessful due to the slow polymerization rate, poor molecular weight control and high levels of coagulum and formation of thick red layers.[9,10] However, good control and colloidal stability were achieved only under limited conditions or by using different polymerization techniques.[5,8,11] In the *ab initio* RAFT emulsion polymerization, Gilbert et al.[12,13] reported the living character of polymers with controlled molecular weights and polydispersities without the loss of colloidal stability.

Living radical dispersion polymerization techniques have been explored to provide polymer dispersions with controlled morphology in contrary to the traditional free radical dispersion polymerization. Although living radical dispersion polymerization gives both the controlled molar mass and particle morphology, only a few studies have been reported with broad

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particle size distributions.[14–16] Mülhaupt et al.[14] carried out the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated dispersion polymerization of styrene in *n*-decane at 135 °C in presence of polystyrene-*block*-poly(ethene-*alt*-propene) ''Kraton'' block copolymers as a steric stabilizer, where a very broad particle size distribution ranging from 50 nm ~ 10 μm was reported. The synthesis of polystyrene (PS) latex via living free-radical dispersion polymerization with TEMPO in both the alcoholic and aqueous alcoholic media using poly(*N*-vinylpyrrolidone) (PVP) at 112–130 °C was reported.[15] In a recent study, Winnik et al.[17] reported living/controlled radical dispersion polymerization of styrene in the presence of perfluorohexyl iodide as a degenerative chain transfer (DCT) agent and 1-cyano-1-methylpropyl dithiobenzoate as a RAFT agent in ethanol and in ethanol-water mixtures. They obtained the characteristics of a living/controlled radical polymerization on the delayed addition of the chain transfer agents (DCT or RAFT) i.e. until the completion of the nucleation stage which they named as two-stage living radical dispersion polymerization.[17] In this methodology, they were able to obtain monodisperse micron-sized PS particles consisting of chain extendible low molar mass polymer. So, with the advantages of CRP techniques, the preparation of polymer particles in the dispersion polymerization has an important goal as monodisperse polymer particles have many important applications.[18] Here, we report the effect of RAFT agent on the dispersion polymerization of styrene to control not only the molecular weight and molecular weight distribution but also the uniformity of the PS particles. In the dispersion polymerization of styrene in an ethanol medium, the *tert*-butyl dithiobenzoate (*t*-BDB) was used as a chain transfer agent (CTA) and 2, 2′-azobisisobutyronitrile (AIBN) as a radical initiator in the presence of a steric stabilizer PVP. The CTA, *t*-BDB contains a better leaving group that resulted the faster fragmentation of the corresponding intermediate radical due to a better *tert*-butyl radical stability and to steric factors.[2,7,19] Initially, in the presence of a RAFT agent, the experimental condition was optimized for the formation of polymer particles and then the effect of concentration of the RAFT agent on molecular weight, particle size and their distributions were studied in the dispersion polymerization.

Experimental Part

Materials

S-(Thiobenzoyl) thioglycolic acid (Aldrich, 99% purity) and 2-methyl-2-propanethiol (Aldrich, 99%) were used as received for the preparation of the RAFT agent. Anhydrous diethyl ether and HPLC grade tetrahydrofuran (THF) were purchased from J. T. Baker Co. (USA) and distilled. Styrene (Junsei Chemicals, Japan) was purified using an inhibitor removal column and stored at −5 °C prior to use. AIBN (Junsei Chemicals, Japan) was purified by recrystallization in ethanol and dried *in vacuo*. PVP (weight-average molecular weight = 40,000; Sigma Chemical Co.) was used as a stabilizer. Ethanol (Samchun Chemical Co., Korea) was used as a reaction medium.

Synthesis of RAFT Agent

t-BDB was synthesized as reported earlier.[7]

Dispersion Polymerization

The dispersion polymerization was carried out in a capped 50-mL scintillation vial with magnetic stirring under nitrogen atmosphere. Ethanol was first poured into the vial, and 0.69 mol L^{-1} of styrene was charged. The amount of AIBN was fixed at 0.002 mol L^{-1} and the concentration of the RAFT agent was varied from 0.0017 to 0.0068 mol L^{-1}. The polymerization temperature in the oil bath was fixed at 70 °C. The amount of PVP concentration was fixed at 0.0002 mol L^{-1} throughout the experiments. The general procedure was as follows: Ethanol, AIBN and styrene were charged into the vial and degassed with bubbling nitrogen gas at room temperature for 30 min. Then, the RAFT agent dissolved in ethanol was introduced into the vial which was then placed in an oil bath at the desired temperature for a given time. During the polymerization, aliquots of the sample were periodically withdrawn through a degassed syringe for further characterization of the polymerization progress. After the completion of the polymerization, the resulting latex particles were centrifuged and redispersed in methanol. These centrifugation and redispersion cleanup cycles were repeated many times to ensure the removal of any excess stabilizer and unreacted styrene monomer.

Characterization

The chemical structure of the synthesized RAFT agent was confirmed with a Varian 400-Mhz ^{1}H NMR and ^{13}C NMR with $CDCl_3$ as the solvent. The monomer conversion to polymer was determined gravimetrically. The molecular weights and the polydispersity index (PDI) were measured using a Waters GPC (gel permeation chromatography) equipped with a 510 differential refractometer and Viscotek T50 differential viscometer. High resolution of 10^5-, 10^3-, and 10^2-Å μ-Styragel packed columns were employed. A universal calibration curve was obtained with 10 polystyrene (PS) standard samples (Polymer Laboratories, UK) with molecular weights ranging from 7,500,000 to 580 g/mol. The flow rate of the PS solution dissolved in THF was 1.0 mL/min. Scanning electron microscopy (SEM; S-4300, Hitachi) was used to study the morphology of the synthesized PS particles. The number- and weight-average diameters (D_n and D_w, respectively), uniformity (D_w/D_n) and the coefficient of variation (CV) were obtained using Scion Image Analyzer software (Scion Corp., Frederick, MD) by the counting 100 individuals particles from the SEM photographs.[16] The CV is calculated from the following equation:

$$CV = \frac{\left(\sum\left(d_i - \left(\sum n_i d_i / \sum n_i\right)\right)^2 / \sum n_i\right)^{1/2}}{\left(\sum n_i d_i / \sum n_i\right)} \times 100$$

where n_i is the number of particles with a diameter of d_i.

Results and Discussion

RAFT Behavior in the Dispersion Polymerization

Figure 1(a) and 1(b) show the SEM photographs of the PS particles prepared for 24 h in the presence of pre-addition and postaddition of 0.0034 mol L^{-1} of the RAFT agent. In general, in the dispersion polymerization, all reaction ingredients are dissolved in the medium, in which particles are generated from the oligomeric species and microspheres subsequently grown by the adsorption of oligomers and monomers

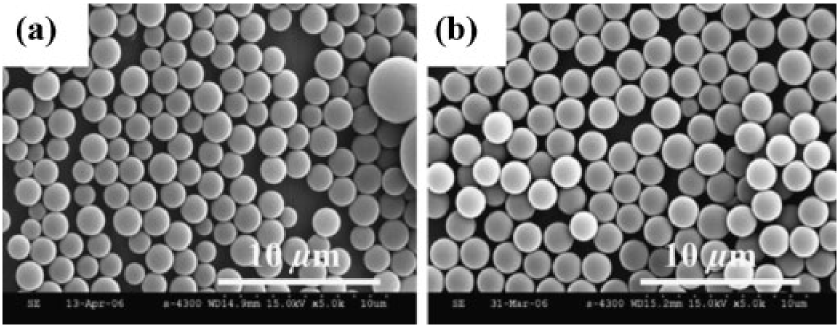

Figure 1.
PS microspheres prepared in the presence of 0.0034 mol L^{-1} of RAFT agent in the dispersion polymerization of styrene at 70 °C in an ethanol medium for 24 h; (a) pre-addition of RAFT (b) post-addition of RAFT.

from the medium. The process of dispersion polymerization is separated into two stages, nucleation and particle growing stage where the former is short, but complex and sensitive, whereas the latter is relatively long, simple and robust.[18] Herein, the pre-addition of RAFT is defined as the addition of RAFT agent at the beginning of the dispersion polymerization along with all the other ingredients whereas postaddition refers to the addition of RAFT agent after the completion of the sensitive nucleation stage. For the PS particle prepared in the pre-addition of RAFT at 24 h, as seen in the Figure 1(a), the final D_w, D_w/D_n and CV are 1.97 μm, 1.31 and 23.12% respectively. In this case, the nucleation period was much longer than to the nucleation period of normal dispersion polymerization and a pink coagulant at the bottom of the reactor was observed until the end of the reaction. This indicated no completion of the polymerization due to the phase separation and this could be one of the reasons for observing polydisperse PS particles at the end of the polymerization reaction in the preaddition of RAFT. In the seeded emulsion polymerization of styrene, the formation of the red layer was reported to be observed in the presence of a RAFT agent and explained it as due to the slow transportation of the RAFT agent into the particles.[10] However, in the postaddition of RAFT, monodisperse PS particles were obtained from the very beginning of the polymerization without any pink layer of precipitation. The particle instability in the early stage of the polymerization with preaddition of RAFT would be overcome with the postaddition of RAFT. The final D_w, D_w/D_n and CV of PS particle obtained in the postaddition of RAFT were 1.75 μm, 1.01 and 5.76% respectively. Thus, the postaddition of the RAFT agent controls the particle size and its distribution without changing the particle morphology. It is obvious that the particle numbers and its distribution are determined by the nucleation stage if no secondary particles or coagulum are formed during the particle growth.[18]

Figure 2 shows the kinetics of the dispersion polymerization for both the preaddition and postaddition of RAFT in an ethanol medium at 70 °C. The linear correlations between $\ln([M]_o/[M])$ and the polymerization time indicate that the polymerization is a first order reaction with respect to the monomer and that the number of radicals remains constant throughout the dispersion polymerization. It implies that the chain transfer agent influences the kinetics of the dispersion polymerization i.e. on the propagating species concentration. The rate of polymerization for the pre-addition and

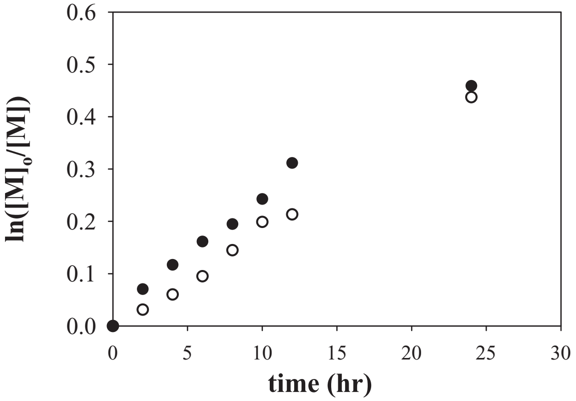

Figure 2.
Polymerization kinetics for the dispersion polymerization of styrene in the (○) preaddition and (●) postaddition addition of 0.0034 mol L^{-1} of RAFT at 70 °C in an ethanol medium.

postaddition of RAFT are similar to each other, though the polymerization in the postaddition of RAFT is slightly faster than that of preaddition of RAFT. More detailed kinetic data are needed to determine whether there is any significant effect of the RAFT concentration on the dispersion polymerization rate. The evolution of the number-average molecular weight (M_n) and PDI with the monomer conversion in the preaddition and postaddition of RAFT agent has been depicted in Figure 3(a) and 3(b), respectively.

The theoretical M_n was calculated with the following equation

$$M_{n(theo)} = ([\mathrm{Sty}]_o/[\mathrm{CTA}]_o)X_m M_m + M_{CTA}$$

where X_m is the fractional conversion, M_m is the molecular weight of the monomer and M_{CTA} is the molecular weight of the chain transfer agent.

An important aspect of living polymerization is the linear increase in the molecular weight with conversion. As seen in Figure 3(a), the M_n increased linearly with increased conversion and theoretical M_n values were in good agreement with the experimental one, indicating the "living" polymerization nature for both the preaddition and postaddition of RAFT. In the postaddition of RAFT, it was observed that the initial experimental M_n values were slightly higher than those of the theoretical M_n. This was due to the chemical

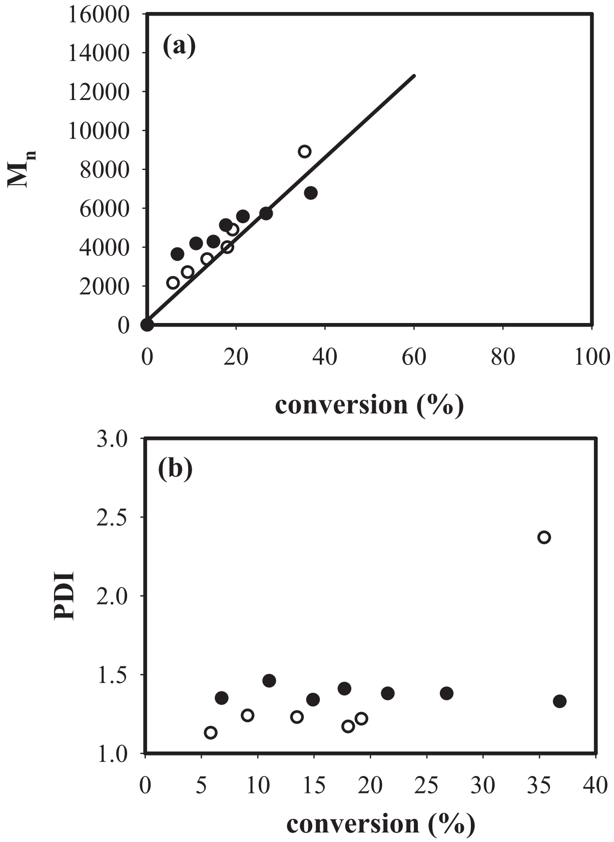

Figure 3.

(a) M_n and (b) *PDI* as functions of the conversion of PS microspheres prepared by living radical dispersion polymerization in the (○) preaddition and (●) postaddition of 0.0034 mol L^{-1} of RAFT in an ethanol medium at 70 °C. Solid line represents the theoretical M_n.

attachment of PVP on the polymer molecules, which significantly increased the molecular weight of PS, causing the deviation from the origin.[16] In the TEMPO-mediated dispersion polymerization of styrene, it also reported that the stabilizer, PVP, was not located exclusively on the outside of the PS latex particles, a significant proportion of the PVP was also located inside of the latex.[15] This might also be due to the non-controlled character of the polymer chains formed initially in the absence of chain transfer agent. However, in the preaddition of RAFT, as we see, the experimental M_n values have a good correlation to the theoretical one. In this case, turbidity was not observed for 4 h of reaction and no stable PS particles were obtained until the 8 h of polymerization. So, we assumed that initially at least, only solution polymerization occurred.[15] Although the stability improved with the preaddition of RAFT for 24 h, but broad particle size distribution was observed (Figure 1(b)). As soon as the stabilized PS particles were obtained for the pre-addition of RAFT, the final M_n value dramatically increased and deviated from the theoretical M_n value. It might be due to the chemical attachment of PVP to the PS particles, as unstable particles observed at the beginning of the reaction, with the results that the initial PVP-PS graft could be a poor stabilizer. A short nucleation period and an uniform growth of the primary particles are necessary for monodisperse polymer particles.[20] Thus, the broadening of the particle size distribution could be due to the prolonged nucleation time in the pre-addition of RAFT.[15]

The PDI of the PS microspheres prepared in the RAFT mediated dispersion polymerization in ethanol is shown in Figure 3(b). Fairly narrow PDI values are observed in the postaddition of RAFT which decreases to 1.33 with the final conversion. The sudden increased of PDI value to 2.37 with the higher conversion observed in the pre-addition of RAFT which might be due to the longer nucleation period. In fact, the initial low PDI values for the preaddition of RAFT reflects that the solution polymerization took place at the early stage while the dispersion polymerization occurred in the later stage.[15] Figure 4 shows the GPC traces of the final PS latex in the dispersion polymerization of styrene in preaddition and postaddition of RAFT. In the preaddition of RAFT, a bimodal distribution curve was observed

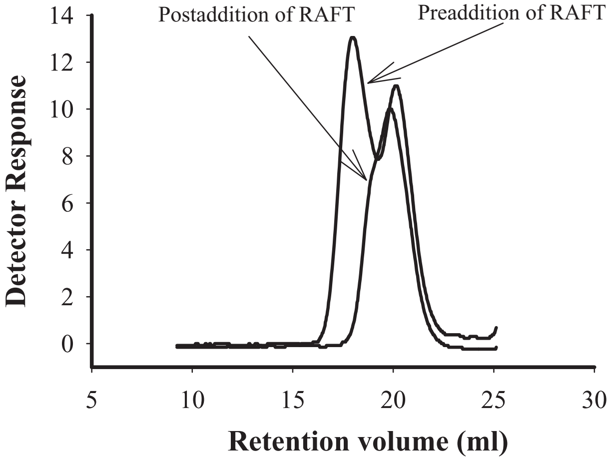

Figure 4.
GPC chromatograms of PS microspheres prepared by living radical dispersion polymerization of styrene in presence of preaddition and postaddition of 0.0034 mol L^{-1} of RAFT at 70 °C in an ethanol medium for 24 h.

which could be due to the nonhomogeneous distribution of the active species among the particles. It might also be due to the delayed nucleation that results in the broad distribution of particle size (Figure 1(a)). However, a narrow molecular weight distribution curve is observed with the postaddition of RAFT (Figure 4). In the RAFT miniemulsion polymerization of styrene, Luo et al.[21] also obtained a bimodal distribution for the final PS latex. They reported the formation of two kinds of particles in the polymer chains i.e. polymer particles and oligomer particles. Oligomer particles were larger in size and lower in molecular weight, leading to a bimodal distribution of both particle size and molecular weight. However, they reported to obtain narrow particle size and molecular weight distributions in the postaddition of surfactant in RAFT miniemulsion polymerization. So, the living behavior with controlled molecular weight, particle size and its distribution can only be obtained in the postaddition of RAFT agent in the dispersion polymerization.

Effect of the Post Addition of RAFT in the Dispersion Polymerization

To study the effect of the postaddition of RAFT in the dispersion polymerization, three experimental runs were designed for the synthesized of PS particles. Figure 5 shows the SEM photographs of PS microspheres prepared at three different concentrations of postaddition of RAFT with 0.0002 mol L^{-1} of PVP stabilizer. Table 1 summarized the results obtained with the postaddition of RAFT on conversion, M_n, M_w/M_n, D_w and CV. It is observed that PS particle are in spherical morphology with a good monodispersity (Figure 5).

The final D_w and D_w/D_n of the PS with respect to the RAFT concentrations are plotted in Figure 6. The particle size decreases with the increased concentration of the RAFT agent and good particle size uniformity was obtained in the presence of

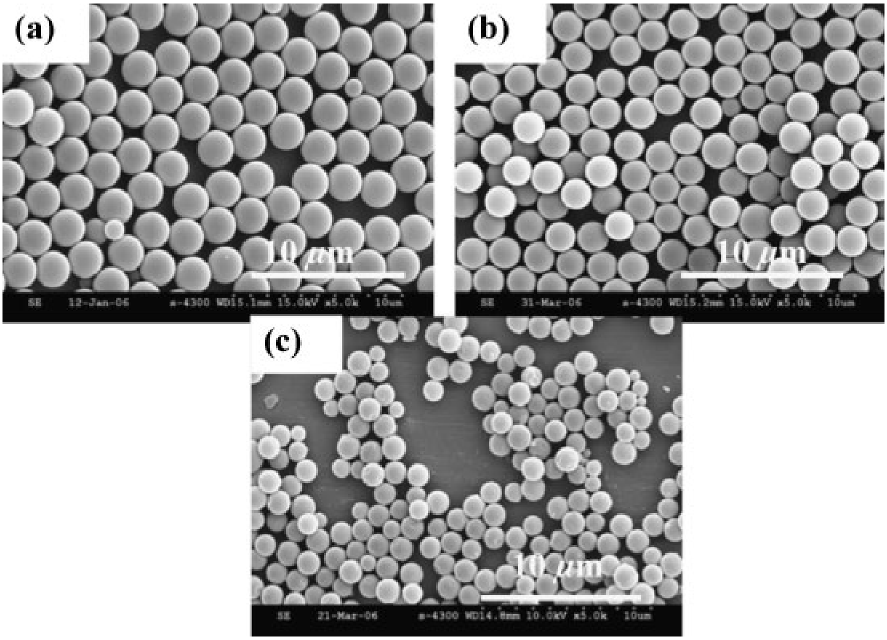

Figure 5.
SEM images of the PS microspheres prepared by living radical dispersion polymerization in an ethanol medium at 70 °C for 24 h in the presence of different concentrations of postaddition of RAFT: (a) 0.0017; (b) 0.0034; and (c) 0.0068 mol L^{-1}.

Table 1.
Properties of the PS microspheres prepared in the dispersion polymerization of styrene with various concentration of postaddition of RAFT.

RAFT (mol L^{-1})	Time (h)	M_n (theo) (g/mol)	M_n (GPC) (g/mol)	M_w/M_n (GPC)	Conversion (%)	D_w (μm)	CV (%)
0	24		27800	3.47	71.13	2.22	30.17
0.0017	4	6752	7600	1.44	15.06	1.48	3.82
	6	9355	7900	1.43	21.65		
	10	14171	8600	1.68	33.05		
	12	16186	14100	2.21	37.82	1.77	5.64
	24	23722	15600	3.34	55.6	2.04	8.43
0.0034	4	2522	4100	1.46	11.01	0.46	4.22
	6	3339	4300	1.34	14.90		
	10	4733	5500	1.38	21.54		
	12	5829	5700	1.37	26.76	1.32	4.61
	24	7937	6800	1.33	36.79	1.75	5.76
0.0068	12	1452	3600	1.35	11.83		
	24	2563	4200	1.28	22.40	1.24	4.79

RAFT agent. The growing radicals produced from the fragmentation of the RAFT agent exit the particles and reenter into the continuous phase to form new particles before the precipitation of the existing particles, thus increased the exit rate coefficient with RAFT concentration.[5] This induces the retardation of the polymerization due to the transfer of the RAFT agent to the particles and so the particle size decreases with the RAFT concentration. In the emulsion polymerization of styrene, the particle diameter decreased and the size distribution became narrower with the RAFT concentration.[9] However, a partial destabilization of the final latexes has been observed at 0.0068 mol L^{-1} concentration of RAFT (Figure 5(c)).

The molecular weight of the resulting polymer increased with the conversion but decreased with the increasing RAFT concentration (Table 1). At low concentration of RAFT (0.0017 mol L^{-1}), there was a marked deviation between the experimental and theoretical M_n. This could be due to the formation of dead polymeric materials via conventional termination that usually observed at lower concentrations of the RAFT.[22] With the increased RAFT concentration, M_n values were fairly close to

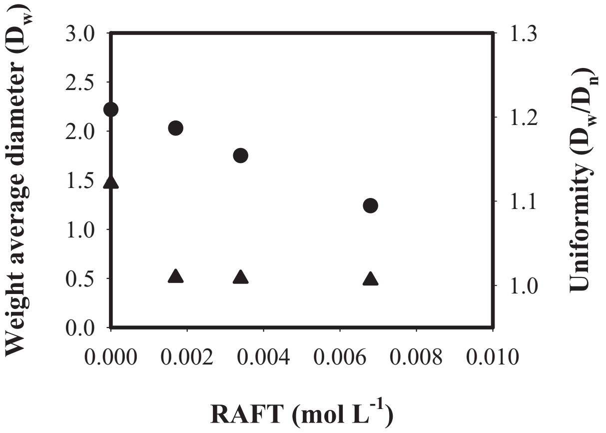

Figure 6.
Effect of postaddition of RAFT concentration on the weightaverage diameter (D_w; ●) and uniformity (D_w/D_n; ▲) of PS microspheres prepared in the dispersion polymerization of styrene in an ethanol medium at 70 °C for 24 h.

the theoretical ones. A deviation from the theoretical M_n was due to the polymeric stabilizer, which is not only physically adsorbed but also chemically bonded with the monomer. Stabilizer is not easily removal from the polymer particles since the nucleation starts on PVP molecules by abstraction of labile hydrogen.[15,16,23]

Regarding on the PDI, the initial value of PDI decreased to 1.43, and again increased to 3.34 with the conversion at 0.0017mol L^{-1} concentration of RAFT. This implies that the less amount of RAFT is insufficient to control the PDI in the dispersion polymerization of styrene. With the increased concentration of the RAFT, the PDI value decreased to 1.28, which is fairly narrow PDI value in the dispersion polymerization as compared to the homogeneous living radical polymerization in solution or bulk in presence of RAFT.[2,14]

Due to the presence of stabilizer PVP, slightly broad PDI values were obtained as narrow PDI value was obtained in the TEMPO-mediated dispersion polymerization of styrene without the use of PVP stabilizer.[15] From the obtained results it can be concluded that the addition of the RAFT agent in the dispersion polymerization not only controls the molecular weight and PDI but also produces stable polymer particles.

Conclusion

Living free radical dispersion polymerization has been successfully carried out using the RAFT agent *tert*-butyl dithiobenzoate. The strategy of preaddition and postaddition of RAFT agent in the dispersion polymerization was carried out and established that the postaddition of RAFT showed living polymerization behavior along with controlled particle size and its distribution. The concentration of the RAFT agent proved to be an important variable to control the molecular weight, particle size and distribution as well as its stability in the dispersion polymerization. Polymerization occurred in an uncontrolled manner in the presence of less amount of RAFT while particle destabilization observed with more amount of RAFT concentration. The effect of the RAFT agent on the particle size is currently poorly understood and needs further investigation. Finally, it can be concluded that the right tuning between the nucleation rate and concentration of the RAFT agent is essential to obtain the stable monodisperse polymer particles with controlled architecture in the living radical dispersion polymerization.

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