Particle Growth Behavior of Poly(methyl methacrylate) Nanoparticles Synthesized by the Reversible Addition Fragmentation Transfer Living Radical Polymerization Reaction

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ABSTRACT: PMMA nanoparticles with highly mono-dispersed size distribution were prepared using the RAFT living radical emulsion polymerization technique. A novel sur-iniferter for the RAFT reaction, DTBA, was synthesized and its chemical structure was identified using several spectroscopic techniques. The relationship between the particle size and the molecular weight of the polymer was investigated measuring the rate of growth of each during formation of particles, and was well explained by the simple random flight molecular conformation model. The particle size increased up to a certain value with decreasing sur-iniferter concentration and then leveled off, because the surface charge density of the growing particles was not high enough to stabilize the particles in aqueous medium above that value. The core-shell type di-block copolymer nanoparticles were also successfully prepared via RAFT reaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3816–3822, 2007

Key words: living radical polymerization; emulsion polymerization; particle size distribution; growth

INTRODUCTION

The living radical polymerization is known to be an effective method of controlling the molecular weight, molecular weight distribution, and end group structures of the resulting polymers. The nitroxide mediated polymerization (NMP) method was proposed by Solomon and Rizzardo et al., and was performed by means of 4-oxy TEMPO radicals. It has the drawback of leading to a low yield in the polymerization of acryl or methacrylate monomer systems, because the reaction temperature has to exceed 120°C for the initiation of the initiator.[1–6] The atom transfer radical polymerization (ATRP) was suggested by Matyjaszewsk and coworkers.[7–10] It works quite well for all monomer systems except vinyl acetate. It can be applied to bulk, emulsion, suspension and even solution polymerizations at reaction temperatures ranging from −20 to 150°C. The two main limitations of this method are in the difficult recycling or removal of metal catalyst from the polymer products and the hard application to vinyl acetate monomer systems. The reversible addition-fragmentation chain transfer (RAFT) reaction was proposed by Solomon and Rizzardo et al. The most important and effective reagents for RAFT polymerization are thiocarbonylthio type compounds. A group of them, benzyl N,N-diethyldithiocarbamate (BDC) can be used as a photo-initiator. This method can be applied to almost all monomer systems adapted to free radical polymerization.[11–21] For example, methacrylate monomers cannot be applied to NMP and vinyl acetate cannot be utilized in ATRP. The main advantage of this method is the possibility of possessing end groups at which a variety of functionalities can be attached.

Polymeric particles are usually prepared in heterogeneous phases such as emulsion, dispersion, or suspension.[22–30] A surfactant or dispersing stabilizer is usually used to provide interfacial stability between the monomer and dispersing medium phases for free radical polymerization systems. When a surfactant is used, the particle formation reaction starts simultaneously from not only inside but also outside micelles—the dispersing solvent, initial monomer droplets, etc, according to its concentration. Under those complex particle growing circumstances, particles with a mono-dispersed size distribution cannot be readily achieved just by controlling the molecular weight of the polymer product, even in the case of

traditional living radical polymerization. To control the particle size by adjusting the molecular weight, the formation of radicals should occur only inside the micelles.

In this contribution, the RAFT living radical reaction mechanism was applied to the formation of PMMA particles in the emulsion state using a sur-iniferter, wherein the function of surfactant was added to the conventional functions of an iniferter. The polymeric particles that were produced were expected to be highly monodisperse, since the initiation, chain transfer reaction, termination and emulsification are simultaneously brought about by the same reagent, confining the formation of the radicals to the interior of the micelles.

EXPERIMENTAL

Materials

The monomer, methyl methacrylate, was purchased from Aldrich Chemical Company (Milwaukee WI), and was purified before use by a butyl carbitol inhibitor—removing column. The water as a dispersing medium was purified at least twice before use by means of a water ultra-purification system (Aquamax, Younglin, Korea). 4-Bromomethyl benzoic acid (Tokyo Chemical, Tokyo, Japan) and sodium diethydithiocarbamate trihydrate (Aldrich) were used without further treatment for the synthesis of the sur-iniferter. Methanol (Daejung, Korea) was used as a solvent, and was purified before use by vacuum distillation.

Synthesis of sur–iniferter (DTBA)

A total of 0.1 mol of 4-bromomethyl benzoic acid and 0.1 mol of sodium diethydithiocarbamate trihydrate were dissolved in 250 mL of methanol, and the mixture was reacted at 70°C for 24 h. The product, 4-diethythiocarbonylsulfanylmethyl—benzoic acid (DTBA), was cooled to 4°C, and then the residual solvent (methanol) was removed using a rotary evaporator at room temperature. The un-reacted monomer and other impurities were completely eliminated by washing the product in distilled water. The product was then dissolved in NaOH solution, and re-crystallized in HCl solution. This purification process was conducted at least three times. The reaction scheme for the synthesis of DTBA is illustrated in Figure 1.

Preparation of PMMA nanoparticles

PMMA particles were prepared in the emulsion state using the synthesized DTBA sur-iniferter. Methyl methacrylate monomer in the concentration ranging from 10 to 15 wt % was dispersed in 150 mL water. The reactants were vigorously stirred at 700 rpm for
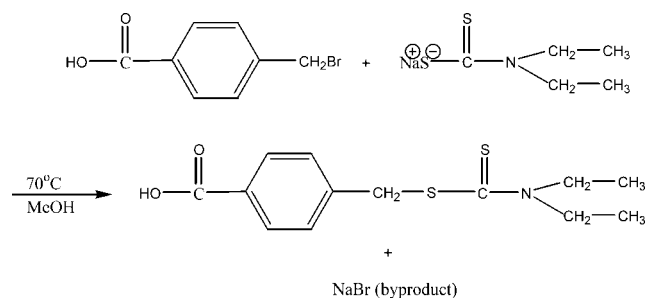

Figure 1 Synthetic route to the formation of 4-diethyl thiocarbonyl sulfanylmethyl-benzoic acid (DTBA).

18 h at room temperature under the radiation from a UV light source situated at a distance of 15 cm from the reactor. The concentration of the sur-iniferter was varied in order to control the molecular weight of the polymer products. The core-shell type di-block copolymer nanoparticles were prepared by adding 5 g of styrene monomer to the PMMA nanoparticles in water. The copolymerization reaction was performed for 12 h.

Characterization

[1]H-fourier transform nuclear magnetic resonance spectroscopy (^{1}H-FTNMR, Varian, Unit Inova 500, USA), Fourier transform infrared spectroscopy (FTIR, Magne, IR-560, Nicolet, USA), and UV spectroscopy (Hitachi, U-3210, Japan) were used to identify the chemical structure of the synthesized sur-iniferter. $DMSO_4$-d_6 was used to dissolve the samples used for NMR analysis. Scanning electron microscopy (SEM, Hitachi, S-2400, Japan) was used to observe the shape of the prepared PMMA particles after coating them with platinum. Dynamic light scattering (DLS, Brookhaven, BI-200SM, USA) was used to analyze the size distribution of the PMMA particles. Gel permeation chromatography (GPC, Waters 515, USA) was used to measure the molecular weights of the PMMA products. Tetrahydrofuran was used as a solvent and an injection flow rate was 1 mL/min. The monomer conversion rate during the polymerization reaction was determined from the gravitational measurements using eq. (1).

$$\text{Conversion } (\%) = \frac{W_p}{W_m/[(W_w + W_m)] \times W_s} \times 100 \quad (1)$$

Here, W_p, W_m, W_w, and W_s are the weights of the dried polymer, fresh monomer, water, and sample, respectively.

RESULTS AND DISCUSSION

Identification of sur-iniferter

Figure 2(a–c), show the structural identification results for the synthesized DTBA obtained using
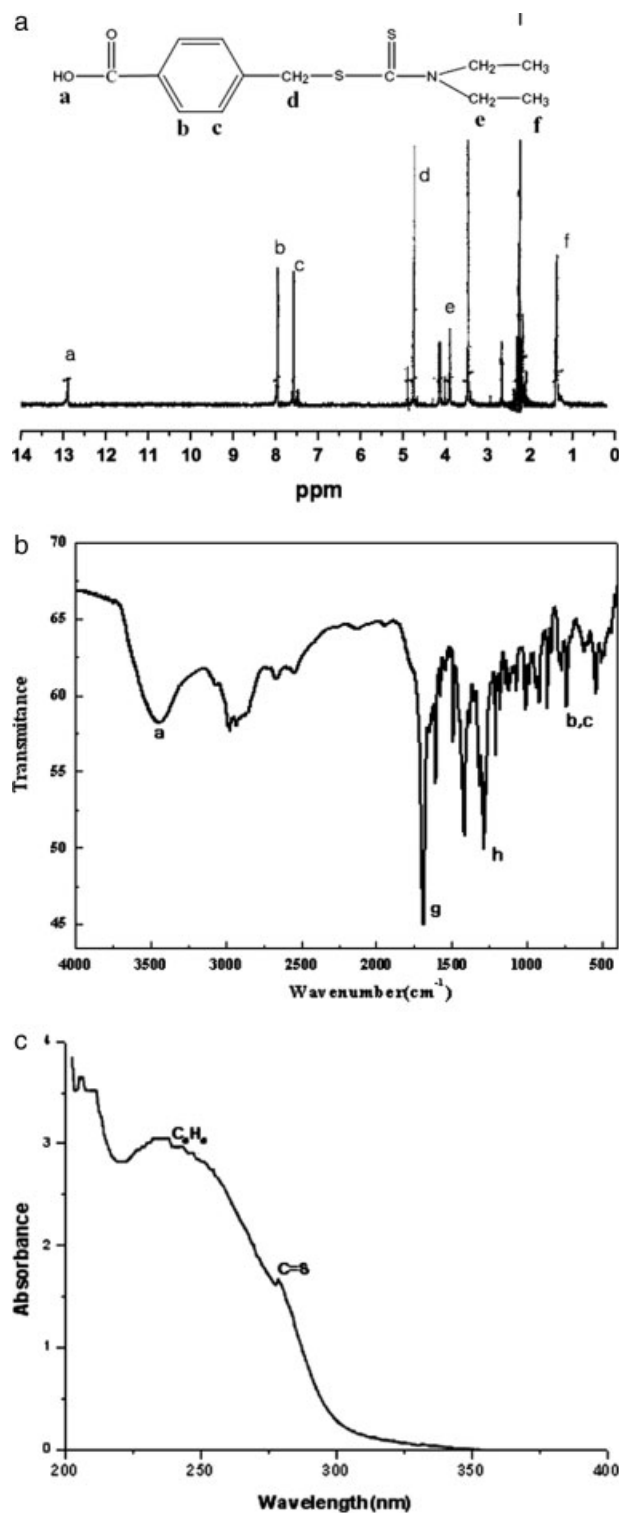
Figure 2 Structure of DTBA identified by (a) FTNMR, (b) FTIR, and (c) UV spectroscopy, respectively.

FTNMR, FTIR, and UV spectroscopy, respectively. DTBA has living radical functionality because of its reversibly reactive characteristics associated with the weak interaction between the dithio- and benzyl ether groups. NaBr was released during its produc-

tion. All of the protons in the DTBA were identified by analyzing the peak positions and the integration areas of the ^{1}H-NMR spectra shown in Figure 2(a). As shown in the FTIR spectra in Figure 2(b), the —COOH group, which plays an important role as an anionic surfactant, is observed at 3400 cm^{-1}. The UV spectra in Figure 2(c) also show a CS$_2$ absorption peak at a wavelength of 270 nm and a benzene absorption peak at 240 nm.
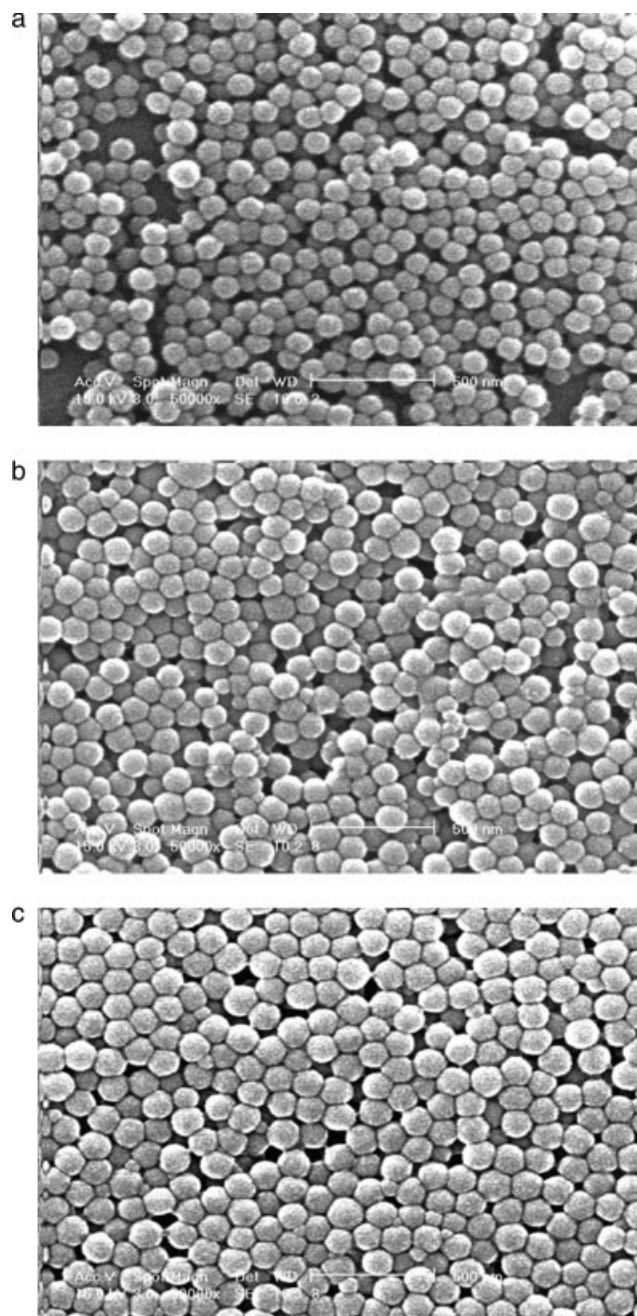

Figure 3 Microphotographs of PMMA particles prepared using different concentrations of DTBA; (a) 0.90, (b) 0.45, and (c) 0.40 wt %.
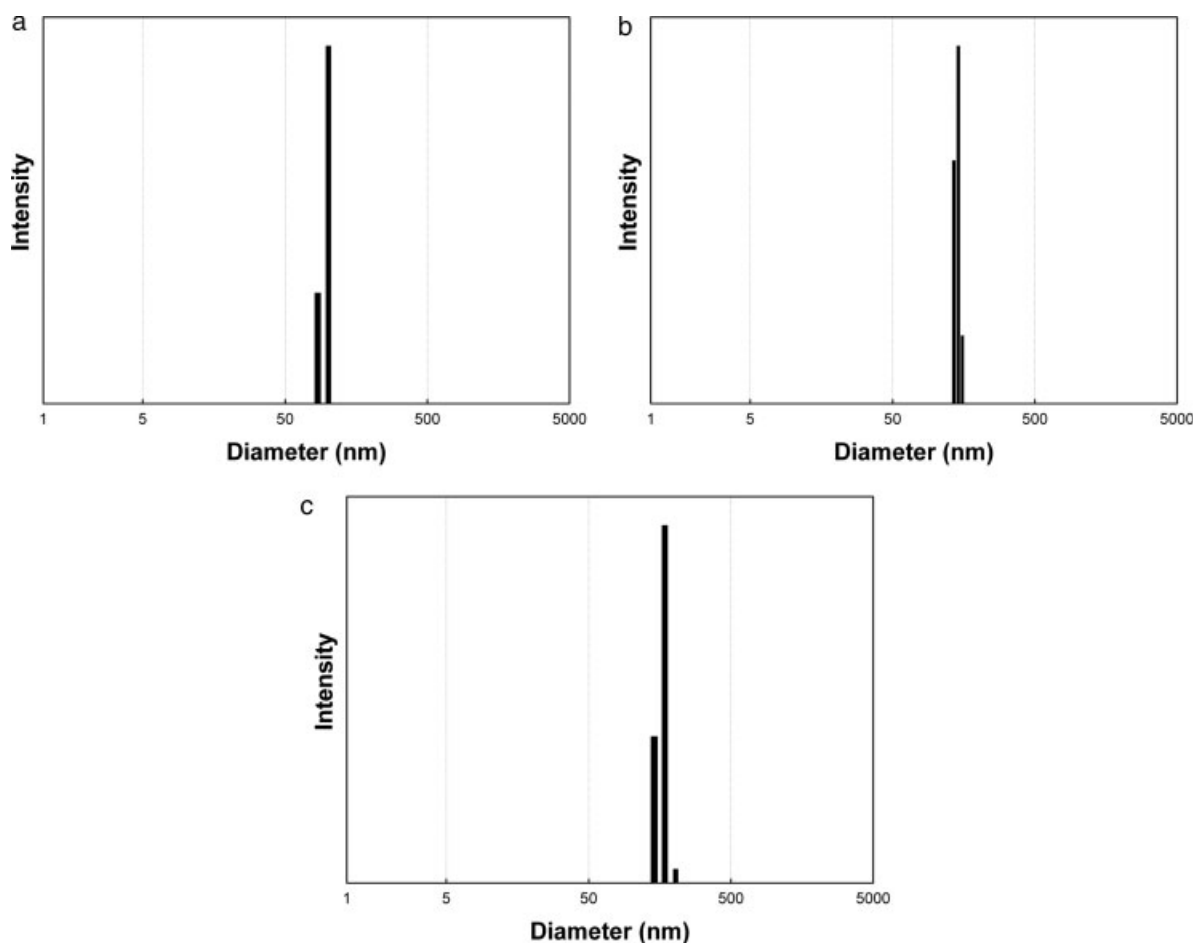
Figure 4 Size distribution of PMMA particles prepared using different concentrations of DTBA; (a) 0.90, (b) 0.45, and (c) 0.40 wt %.

Effect of the sur-iniferter concentration on the PMMA nanoparticle sizes

The SEM microphotographs of the prepared PMMA nanoparticles are shown in Figure 3. A comparison of Figure 3(a–c) shows that the particle shapes are well defined and that their sizes increased with decreasing sur-iniferter concentration. Figure 4 shows the particle size distribution of the synthesized PMMA nanoparticles measured using DLS. The particle sizes were quite monodispersed and the average particle diameters increased from 110 to 130 nm as the DTBA concentration decreased from 0.90 to 0.35 wt %, as observed in the SEM analysis.

As the radiation energy required for the generation of the radicals eventually induced the growth of the particles with the ions present at their surface, much more stable and monodispersed particles were obtained through the prevention of the coagulation of the particles due to the ionic repulsion forces associated with the surface charges.

Figure 5(a,b) show the SEM microphotographs obtained when the monomer contents were increased to 15%, while Figure 6(a,b) show the corre-sponding DLS results. When the monomer content was too high (when the sur-iniferter concentration was too low), in this case 10%, the growing particles coagulated or flocculated, because their surface charge density was not high enough to stabilize them in an aqueous medium. This was why no particles larger than 500 nm in diameter were able to be obtained in this experiment.

Polymer molecular weight and particle size

In general, the parameters that affect the particle size and molecular weight in radical emulsion or suspension polymerization are different: the former are mostly affected by the surfactant concentration and the latter by the initiator concentration. In this living radical polymerization method, however, the simultaneous reactions of initiation and termination take place continuously and proceed reversibly until all of the monomer is consumed.[31] If the concentration of living radicals and the polymerization activity are invariant regardless of the monomer concentration, the linier increase in the chain growth would be
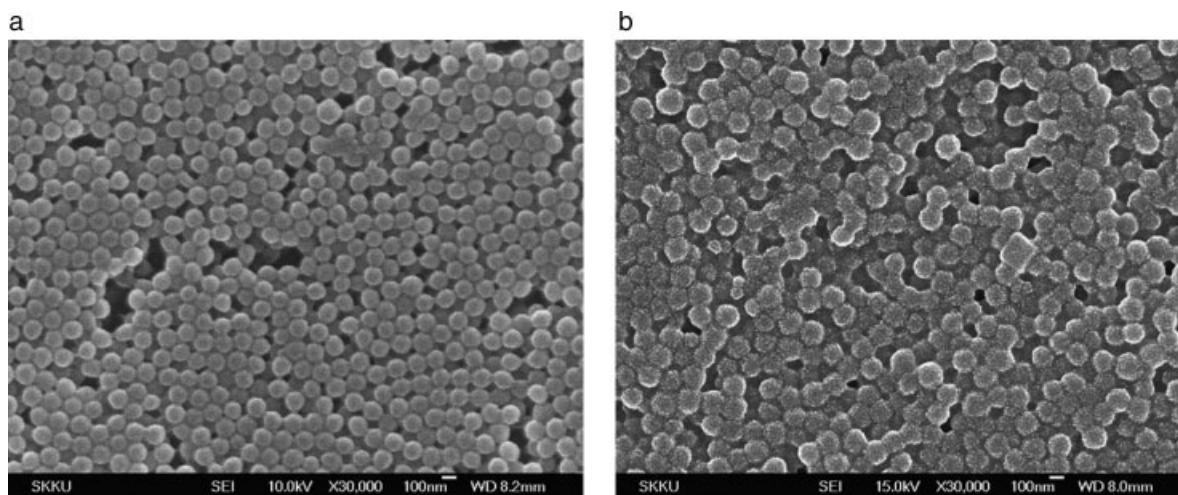
Figure 5 Microphotographs of PMMA particles prepared using different concentrations of DTBA; (a) 0.30 and (b) 0.45 wt % when the monomer contents were increased to 15%.

expected to result in a narrow molecular weight distribution. In view of the nature of the particle growth, the chain growing sites in this living radical system are confined to the interior of the micelles, because the initiator itself has surfactant functionality afforded by the hydrophilic group situated at the end of the molecule. Thus, the rate of growth of the particle size is highly correlated with the rate of increase in the molecular weight.

Figure 7 shows the relationship between the molecular weight of the polymer and the monomer conversion. The unique characteristic of the living radical polymerization is that the molecular weight increased linearly with the monomer conversion rate, as shown in Figure 7. It also decreased with increasing DTBA concentration. The molecular weight was difficult to measure after 60% conversion of the monomer, as the sample was not easily dis-

solved in THF due to the salt form of the hydrophilic end groups.

Figure 8 shows the growth rate of particle size during the polymerization of MMA. In Figure 8(a), the particle size increased but not in a linear manner. The growth rate of particle size (increase in diameter) decreased with the progress of the reaction, while the molecular weigh increased almost linearly as shown in Figure 8(b). The simplest model relating the radius gyration of the polymeric particles with the molecular weight in theta solvent is the random flight model, as shown in eqs. (2)–(4). The experimental result was in good accordance with the theoretical relationship, given that the particle diameter increased with the square root of the molecular weight of the polymer chains.[32]

$$R_g^2 = r^2/6 \text{ (for the random coil model)} \quad (2)$$
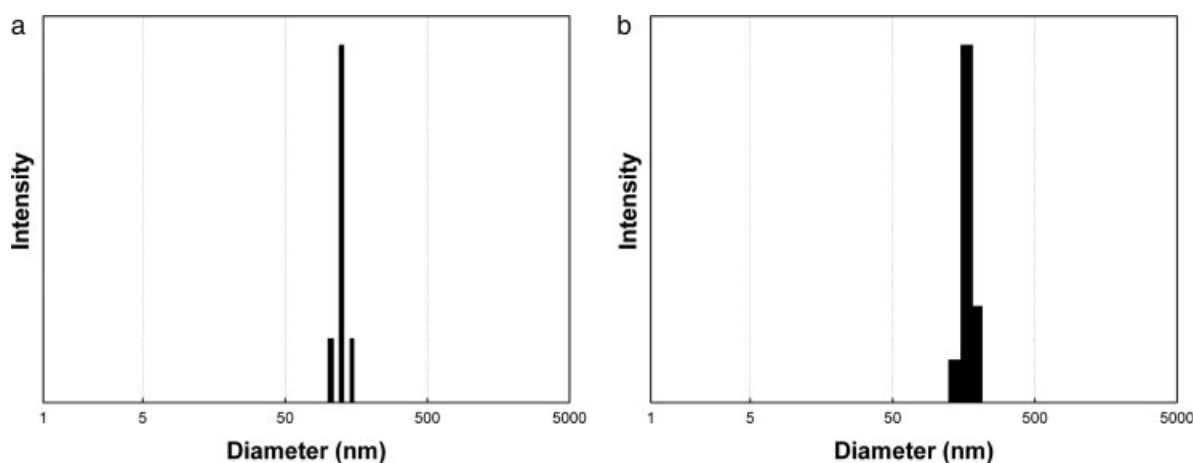

Figure 6 Size distribution of PMMA particles prepared using different concentrations of DTBA; (a) 0.30 and (b) 0.45 wt % when the monomer contents were increased to 15%.
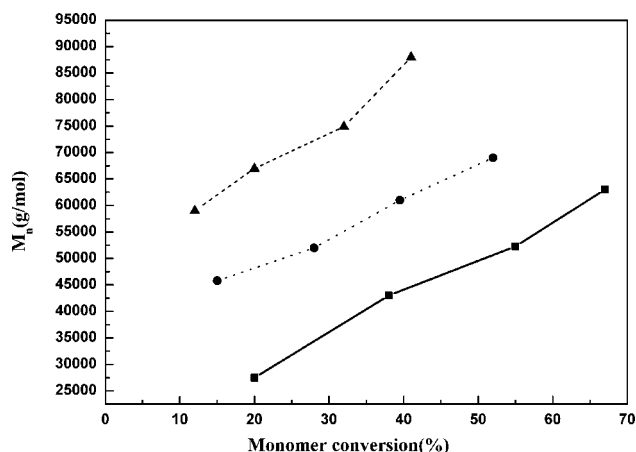
Figure 7 Molecular weight as a function of the conversion of MMA.

$$r^2 = CM \text{ (for a random coil obeying}$$
$$\text{Gaussian statistics)} \quad (3)$$
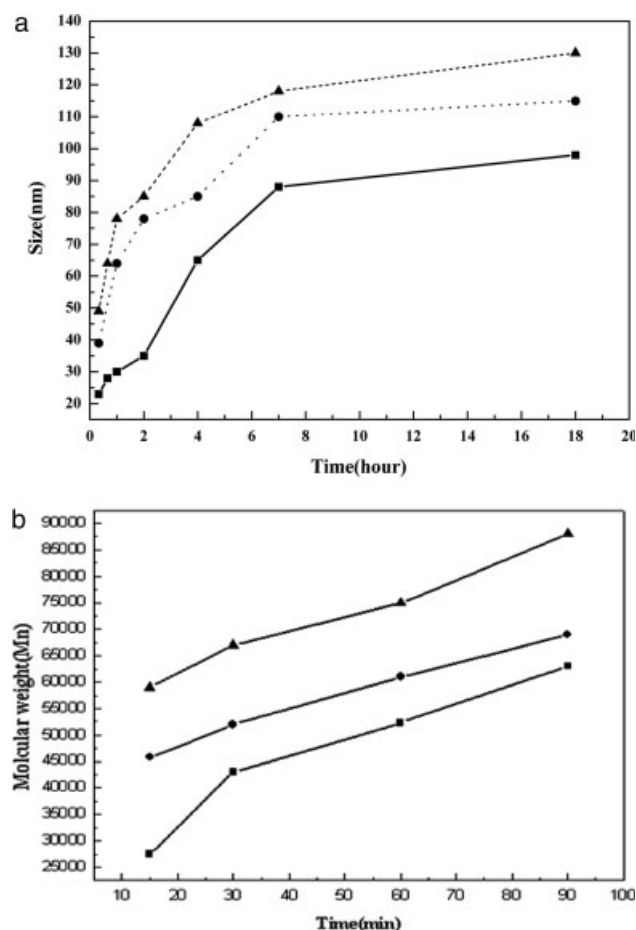$$R_g^2 \propto M \quad (4)$$

Figure 8 (a) Particle size and (b) molecular weight growth during the polymerization of MMA.

Here, C is a proportional constant depending on the chain molecular structure, R_g radius of gyration, and M molecular weight, respectively.

Core-shell type nanoparticles synthesized by di-block copolymerization

The main characteristic of living polymerization, namely living radical regeneration reactivity, was applied to synthesize core-shell type copolymer particles. Since polymers comprising particles possess living radicals, the second monomer can be reacted to produce di-block type copolymer particles. The second component of a block copolymer may form the shell layer of particles. Figure 9 shows the SEM microphotographs of the PMMA particles before and after the co-polymerization reaction of the second monomer, styrene. As shown in Figure 9, the particle size increased with the simple addition of the styrene monomers without any initiator. The size distribution of the particles produced in this way was still highly mono-dispersed. Figure 10 shows the ^{1}H-FTNMR spectrum of the PMMA-*b*-PS di-block type copolymer particles. As shown in Figure 10, all of the protons in the PMMA-*b*-PS di-block copolymer particles were identified by analyzing the peak posi-
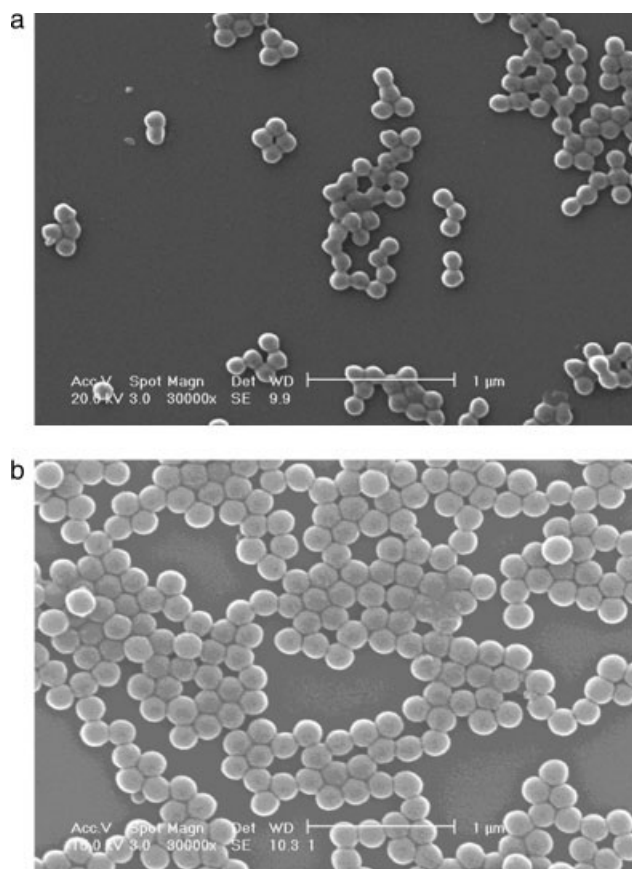

Figure 9 Microphotographs of PMMA particles (a) before and (b) after the addition of the styrene monomer.
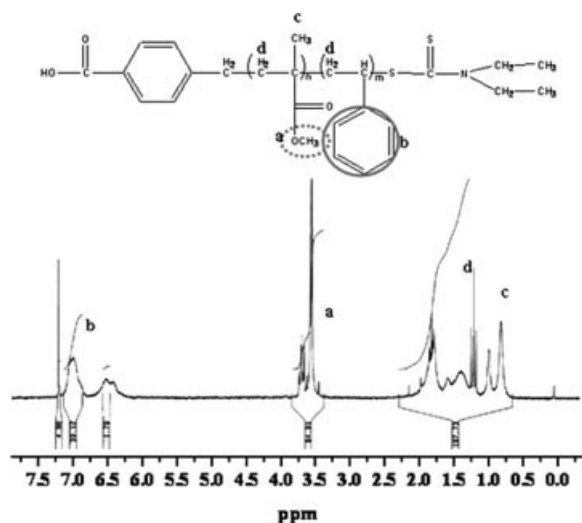
Figure 10 ^{1}H-FTNMR spectrum of the PMMA-*b*-PS copolymer particles.

tion and integration area of the ^{1}H NMR spectra. As the ^{1}H NMR spectra show that the mole ratio of PMMA to PS of the PMMA-*b*-PS block copolymer is 3, it can be inferred that nearly all amount of the styrene added, 5 g, was reacted.

CONCLUSION

Highly monodispersed PMMA nanoparticles were prepared by the RAFT emulsion polymerization method. DTBA was synthesized and used as a suriniferter by adding surfactant functionality to the iniferter for the RAFT emulsion system. The particle size increased with deceasing DTBA concentration. The relationship between the particle size and the molecular weight was analyzed by measuring the rates of growth of those during the formation of the particles, and was well explained by the simple random flight molecular conformation model. The main characteristic of living polymerization, namely the regenerative reactivity, was applied to synthesize core-shell type copolymer particles.

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