Macromolecules **2004,** *37,* 5565−5571

Synthesis of Functionalized Monodisperse Poly(methyl methacrylate) Nanoparticles by a RAFT Agent Carrying Carboxyl End Group

Sang Eun Shim, Huije Lee, and Soonja Choe*

Department of Chemical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon, Republic of Korea 402-751

Received January 9, 2004; Revised Manuscript Received May 19, 2004

ABSTRACT: A RAFT agent bearing a carboxylic acid group is applied to the miniemulsion polymerization of methyl methacrylate (MMA) in order to prepare the stability-enhanced functionalized latex. At the polymerization temperatures of 60, 70, and 80 °C, the polymerization kinetics, evaluation of the molecular weight, and PDI are found to be strongly dependent on the temperature. The higher the temperature, the faster the polymerization rate, the lower the molecular weight, and the lower the PDI are obtained. The PMMA nanoparticles prepared by the miniemulsion polymerization using this RAFT agent show some interesting characteristics. As the amounts of the RAFT agent increase, the magnitude of the zeta potential and the conductivity correspondingly increase and the size of the PMMA nanoparticle decreases from 118.8 to 49.5 nm. These results imply that the carboxyl group (or partially in anionic form) is present on the surface of the polymer particles, and therefore, the stability of the system is enhanced. Furthermore, no noticeable sign of creaming or destabilization of the PMMA nanoparticles was observed for at least several months by remaining as a homogeneous latex.

Introduction

Polymer colloids have been used in vast areas such as various coatings, adhesives, inks, leather finishing, construction, and so forth.[1] Nowadays, such polymer particles have broadened their applications to more advanced fields such as information technology, electric and electronic fields, and biotechnology including biochemicals and biomedicals.[2−4] In accord with the expansion of their applications, the precise control of the properties of the polymer colloids has become more important.

Charge-controlled colloids are being considered as important functionalized materials. To prepare such functional particles, several methods are utilized such as the (1) copolymerization with ionic monomers/comonomers,[5−7] (2) polymerization with charge endowing surfactants or initiators,[8−10] and (3) multistep process in which functional groups are incorporated into the polymer particles.[11,12] Such polymer particles are produced by the introduction of highly polar or ionic functional groups including aldehyde,[13,14] carboxylate,[15,16] chloromethyl,[17,18] amino,[19,20] and vinyl moiety.[21]

The living free radical polymerization (LFRP), triggered by a pioneering study of Otsu,[22] is quite efficient in preparing controlled molecular architectures in various polymers. With the advent of several revolutionizing LFRPs such as the nitroxide-mediated polymerization (NMP),[23,24] atom transfer radical polymerization (ATRP),[25,26] and reversible addition−fragmentation chain transfer polymerization (RAFT),[27,28] the synthesis of well-defined polymers/copolymers having desired structures has become realized in a convenient way. Therefore, the subject of molecular design of polymers by means of LFRPs has been a rapidly growing research area. Current research trends in LFRP are moving toward the synthesis of rather complex macromolecules and applying it to several heterogeneous polymerizations.

Contrary to the ATRP method, RAFT technique utilizes a chain transfer agent (CTA) in order to control the molecular evolution. The most frequently used CTAs are dithioester derivatives, S═C(Z)−SR. This type of CTA reacts with either the primary radical produced by an initiator or a propagating polymer species. In this process, controlled polymerization is achieved by the alternation of the activation and deactivation of the CTA between dormant and active moieties. The end group of the synthesized macromolecule depends on the functionality of the CTA in Z and R groups. To endow the versatility of the CTA and functionality of the synthesized macromolecules, a few CTAs bearing terminal carboxyl acid in the R group have been utilized.[29−31] Since the carboxyl acid group in R can be readily substituted by carboxylic anion which is soluble in water, water-soluble polymers have been successfully synthesized by the RAFT method.[31,32]

Miniemulsion polymerization is the most frequently used in association with the RAFT technique[33−37] among the several heterogeneous polymerizations since the miniemulsion polymerization is taking place inside the monomer swollen micelles, which is in the homogeneous phase. However, in these studies, the CTAs without end group functionality in R group have been used since their interests have been focused on the success of the process. In this article, we synthesized a CTA bearing carboxyl acid in the R group and used in miniemulsion polymerization of methyl methacrylate. It was found that the carboxyl group in CTA was located at the interface between the particle and water medium, and the colloidal stability was enhanced by the formation of carboxylic anions.

Experimental Section

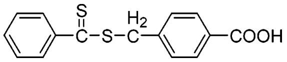
Materials. Reagent grade phenylmagnesium bromide, α-bromo-*ρ*-toluic acid, and carbon disulfide, used in the preparation of a RAFT agent, were purchased from Aldrich Co.. Anhydrous

---

* Corresponding author: e-mail sjchoe@inha.ac.kr; Tel +82-32-860-7467; Fax +82-32-876-7467.

10.1021/ma049930j CCC: $27.50

Scheme 1. Carboxylic Acid End-Functionalized RAFT Agent, 4-Thiobenzoyl Sulfanylmethylbenzoic Acid, Used in This Study



diethyl ether and methanol were purchased from J.T. Baker Co.. Carbon disulfide and diethyl ether were distilled in order to remove the existing impurities and water. MMA and styrene (Samchun Chemical Co., Korea) were purified using an inhibitor removal column (Aldrich) and stored at −5 °C prior to use. An initiator, analytical grade of 2,2-azobis(isobutyronitrile) (AIBN; Junsei Chemicals, Japan), was used without further purification. An anionic surfactant, sodium dodecyl sulfate (SDS), was purchased from Junsei Chemicals, and hexadecane (Aldrich), as a hydrophobe, was used as received. Double distilled deionized (DDI) water having the pH of 6.75 was used as a reaction medium.

Polymerization. A RAFT agent, 4-thiobenzoyl sulfanylmethylbenozic acid (99% purity) (Scheme 1), was synthesized in our laboratory according to the previous publication.[38] MMA concentration was 10 wt % (10 g) based on the reaction medium (DDI water, 100 g), and the concentration of the SDS was fixed at 10 mM. 2 wt % hexadecane (0.2 g) based on MMA was used. The amounts of SDS and hexadecane were chosen according to a typical recipe in miniemulsion polymerization.[39] 0.05 wt % AIBN (0.05 g) relative to MMA was used, and the molar ratio of [RAFT agent]/[AIBN] was varied from 0 to 5. Polymerization ingredients were charged to the reactor. Preemulsification was carried out as the following two steps: first, the polymerization reactor containing the right recipe was mechanically stirred at 1000 rpm, and then the ultrasonic homogenization was performed for 3 min. Upon the completion of the preemulsification, water-insoluble pink color RAFT agent was not observed as a precipitate since all the RAFT agent molecules were absorbed into micelles containing the monomer, initiator, and RAFT agent. Polymerization was carried out in a 500 mL three-necked reaction vessel with a mechanical stirrer at 60, 70, and 80 °C under a nitrogen atmosphere. A mild agitation of 220 rpm was applied throughout the polymerization. During the polymerization for 3 h, an aliquot of the sample was periodically taken from the reactor for further characterizations. In the beginning of the polymerization, the entire polymerization medium appeared pink color due to the RAFT agent; however, that color disappeared as the polymerization proceeded, followed by the formation of a milky latex upon the completion of the polymerization.

Characterization. The molecular weight and PDI were measured using a Waters GPC (gel permeation chromatograph) 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. The calibration was carried out using 10 polystyrene standard samples (Polymer Laboratories, UK) with molecular weight ranging from 580 to 7 500 000 g/mol. The latex solution sample withdrawn from the reaction vessel was rinsed with DDI water and centrifuged repeatedly, and then the PMMA powder was dried in a vacuum oven for 24 h. The PMMA was then dissolved in THF and injected at a flow rate of 1.0 mL/min. The monomer conversion to polymer was determined gravimetrically, and the average value of five measurements was used. The particle size and zeta potential of the polymer particles were monitored with a Malvern Zetasizer 4 (UK) at an angle of 90° at room temperature. The latex sample was diluted to 10 000 times with DDI water prior to the measurement. The average of five measurements was adopted for analyzing data. A Philips SEM (scanning electron microscope) 515 was used to investigate the morphology and size of the PMMA particles. Conductivity and pH of the continuous phase were immediately measured by sampling the latex from the reactor using a conductivity meter (GM-115, KEM Co., Japan) and a pH meter (TI 9000, Trans Instruments, Singapore), respectively, as described elsewhere.[40]

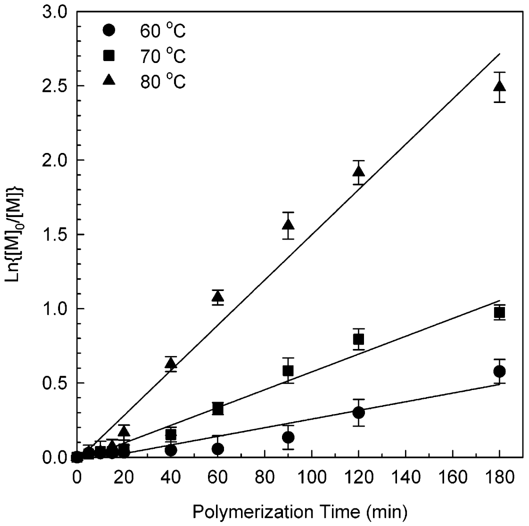


Figure 1. Polymerization kinetics of miniemulsion polymerization of MMA using a carboxylic acid end-functionalized RAFT agent at several temperatures. [RAFT]/[AIBN] = 1.0.

Results and Discussion

RAFT Miniemulsion Polymerization at Different Temperatures. Figure 1 represents the polymerization kinetics of the miniemulsion polymerization of MMA at 60, 70, and 80 °C. In all cases, pseudo-first-order kinetics are clearly observed, which indicates these polymerization systems obey the living radical polymerization. The linearity between the $\ln\{[M]_0/[M]\}$ vs polymerization time is an indicative, explaining that the concentration of the growing radicals is constant during the polymerization. It is also seen that the linearity is exhibited from the early stage of the polymerization at all temperatures. In the case where the polymerization temperature is not adequate, i.e., low, for a desired RAFT polymerization, a significant retardation has been reported.[41] Therefore, the chosen temperatures of 60, 70, and 80 °C seem to be appropriate to conduct the miniemulsion polymerization of MMA using this type of RAFT agent. Furthermore, the polymerization kinetics is strongly dependent on the temperature during the living free radical polymerization, as shown in Figure 1. The higher the temperature, the faster the polymerization rate is obtained. To date, a few studies on the temperature-dependent RAFT polymerization were conducted. For example, in the calculation of the theoretical molecular weight in RAFT system, the temperature term is excluded since the concentrations of the initiator, monomer, and chain transfer agent are considered to control the polymerization. Although Gaynor et al.[42] reported that the temperature is not a major factor influencing the living free radical polymerization of styrene and acrylate by means of an iodine degenerative method, other researchers have found that the living radical polymerization is dependent on the temperature.[43−45] Bai et al.[43] have reported that the conversion and molecular weight increased with increasing temperature but that the narrowest molecular weight distribution was achieved in the intermediate polymerization temperature in the bulk polymerization of methacrylate in the presence of dithiobenzoic acid as the chain transfer agent. According to Kanagasabapthy's result,[44] the plot of the conversion vs time indicated that the higher polymerization rate was observed at higher temperature by maintaining the living characteristics using a 4-acetoxystyrene in the

Table 1. Comparison of Molecular Weight Evolution in the Miniemulsion Polymerization[a] of MMA and Styrene with 1.0 Ratio of [RAFT Agent]/[AIBN] at 80 °C.

monomer	time (h)	conv (%)	$M_{n,theory}$[b] (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
MMA	2	85.3	28 000	48 100	1.62
styrene	8	52.0	17 100	18 800	1.24

[a] The same recipe was used: 100 g of DDI water, 10 g of monomer (MMA or styrene), 10 mM SDS, 0.05 g of AIBN, and 0.2 g of hexadecane. [b] $M_{n,theory} = M_{monomer} \times$ fractional conversion $\times$ $[monomer]_0 \times [RAFT]_0$.

presence of carboxylmethyl dithiobenzoate from 60 to 90 °C. Stenzel-Rosenbaum et al. reported that the increase of the polymerization temperature led to the higher conversion and reaction rate but reduced the molecular weight and PDI in the synthesis of star polymer using a RAFT technique.[45] In our previous study on the living free radical emulsion polymerization of MMA[38,46] and dispersion polymerization of MMA,[47] both in the presence of 4-thiobenzoyl sulfanylmethylbenzoic acid derivatives as a RAFT agent, the conversion, polymerization kinetics, molecular weight, and PDI were sensitively affected by the polymerization temperature. On the basis of these works, one can conclude that the polymerization temperature is one of the important parameters in living free radical polymerization. This temperature-dependent polymerization rate in the living free radical polymerization is also ascribed to the fast propagation of the free radicals, fast decomposition of the initiator, and better efficiency of a chain transfer agent at elevated temperature. In conventional radical polymerization, it is known that the activation energy in radical propagation is appreciably higher than that in termination process at higher temperature.[48] Thus, the increase in k_p/k_t (k_p and k_t represent the rate constants at propagation and termination, respectively) with temperature increase results in fast polymerization rate.

In Table 1, the polymerization characteristics in the miniemulsion polymerization of MMA and styrene under the identical polymerization procedure and recipe are compared. In the case of styrene system, the experimentally obtained ($M_{n,GPC}$) and theoretically calculated ($M_{n,theory}$) show a good agreement, and the PDI was 1.24. However, in the MMA system, the experimental molecular weight is much higher than the calculated one, and the PDI was 1.62. The relatively poor control in MMA system is ascribed to the different water solubility of monomer. In the most RAFT miniemulsion polymerizations, styrene is preferentially chosen as a model monomer due to its strong hydrophobic nature. In reality, MMA has approximately 12-fold greater water solubility than styrene ($C_{w,MMA}^{sat} = 6.1 \times 10^{-1}$ mol/dm^{-3} and $C_{w,styrene}^{sat} = 4.3 \times 10^{-3}$ mol/dm^{-3} at 50 °C).[49] de Brouwer et al.[28] have found the large deviation of experimentally obtained and theoretically calculated molecular weights of PMMA in the RAFT miniemulsion polymerization since uncontrolled homogeneous nucleation more likely occurs in a relatively hydrophilic MMA system. This explanation seems true since a significant discrepancy between the molecular weights in the MMA system was obtained as shown in Table 1.

Figure 2a,b depicts the effects of the polymerization temperature on the evolution of molecular weight and the corresponding molecular weight distribution during the RAFT miniemulsion process. The linear increase in the molecular weight with respect to the conversion also implies that this reaction is well controlled by the RAFT agent. The low molecular weight is obtained at high temperature, which is a common phenomenon in radical polymerization. The PDI of the synthesized polymer decreases with the temperature. Besides the increase in k_p/k_t with increasing temperature, the polymerization temperature plays an important role in the decomposition of initiator and the rate of chain transfer reaction. At high temperature, the concentration of the primary radicals generated by the initiator would significantly increase in the beginning of the reaction, which causes a termination reaction induced by the excess of radicals. Then the polymerization could undergo in a controlled manner by the RAFT agent. In addition, the efficiency of the reversible chain transfer by the RAFT agent may increase with the temperature, which ensures the uniform growth of the polymer chains and finally reduces the PDI. Since the conversion occurs fast and the PDI is intact with the living nature at 80 °C, this temperature was chosen for the subsequent experiments.

Effect of the RAFT Agent on the Polymerization. In the previous section, it was found that the polymerization kinetics, the molecular weight evolution, and the PDI were sensitively affected by the polymerization temperature. Here, we studied the effects of the concentration of the RAFT agent in the miniemulsion polymerization. The polymerization was conducted at 80 °C to achieve a fast conversion and a low PDI. The molar ratio of [RAFT]/[AIBN] was varied in the range of 0, 1.0, 2.0, and 5.0.

Figure 3 shows the polymerization kinetics with respect to the concentration of the RAFT agent. In the absence of the RAFT agent, the typical characteristics in radical polymerization are observed, and the conversion levels off in ca. 40 min. On the other hand, the polymerization is well controlled in a pseudo-first-order in the presence of the RAFT agent. Furthermore, the rate of the polymerization becomes slow with increasing RAFT agent since more chain transfer reaction occurs via the reversible addition and fragmentation mechanism at high concentration of the RAFT agent.

The evolution of molecular weight during the polymerization is depicted in Figure 4. The number-average molecular weight increases in a linear fashion with respect to the conversion in the presence of the RAFT agent, while a typical growth of the molecular weight is observed in the absence of the RAFT agent. As expected, the number-average molecular weight decreases with the concentration of the RAFT agent. The PDI of the PMMA prepared with various concentrations of the RAFT agent shows distinctive difference between the presence and absence of the RAFT agent. In the presence of the RAFT agent, the PDI is controlled throughout the polymerization, and the final PDI varies from 1.6 to 1.2 with the increasing molar ratio of [RAFT]/[AIBN]. Figure 5 represents the GPC traces of the PMMA obtained at the end of the polymerization using a various concentrations of the RAFT agent at 80 °C. The shift of each curve toward low molecular weight region is clearly seen as the amount of the RAFT agent increases. The final number-average molecular weight (g/mol)/PDI were 82100/3.4, 48100/1.6, 33300/1.4, and 21800/1.3 for 0, 1.0, 2.0, and 5.0 ratios of [RAFT]/[AIBN], respectively.

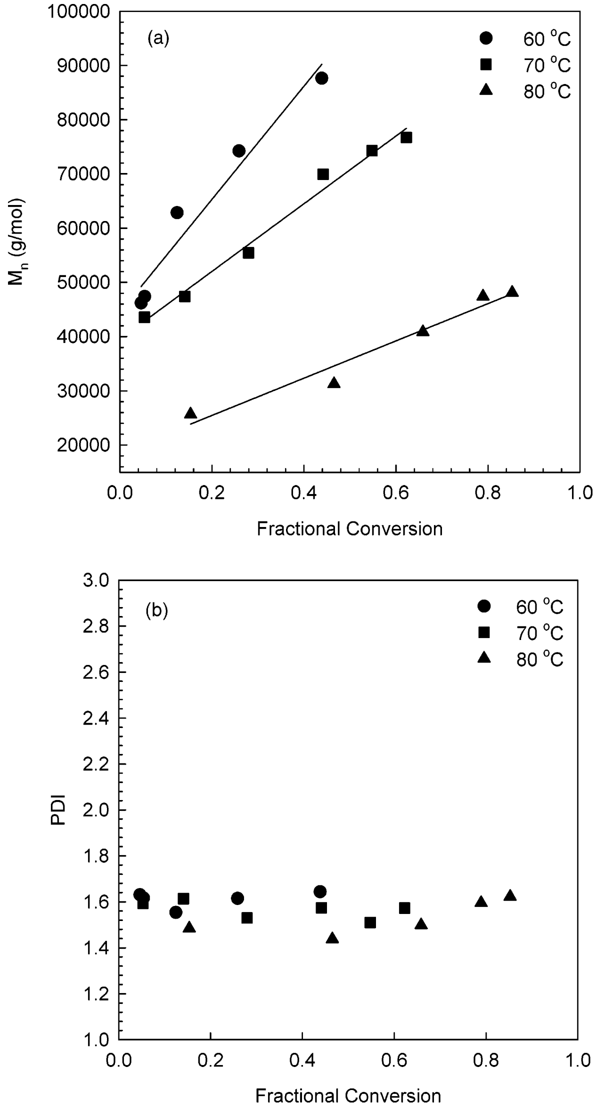


Figure 2. (a) Number-average molecular weight and (b) polydispersity index of PMMA prepared by RAFT miniemulsion polymerization at several temperatures. [RAFT]/[AIBN] = 1.0.

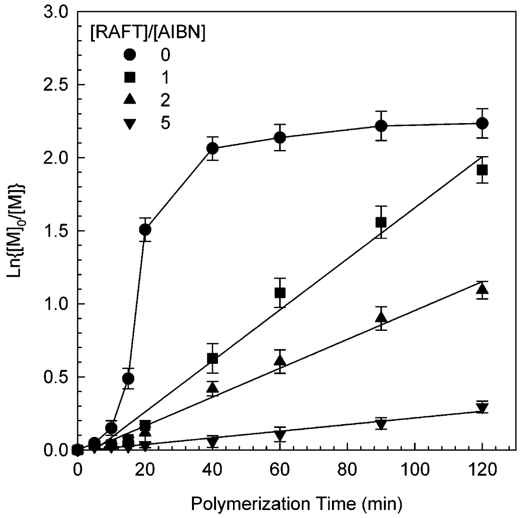


Figure 3. Effect of the concentration of the RAFT agent on the polymerization kinetics of miniemulsion polymerization of MMA at 80 °C, where [RAFT]/[AIBN] = variable.

Synthesis of Functionalized PMMA Nanoparticles. Scheme 2 illustrates a route to synthesize the functionalized PMMA latex via the miniemulsion polymerization using a RAFT agent carrying a carboxyl

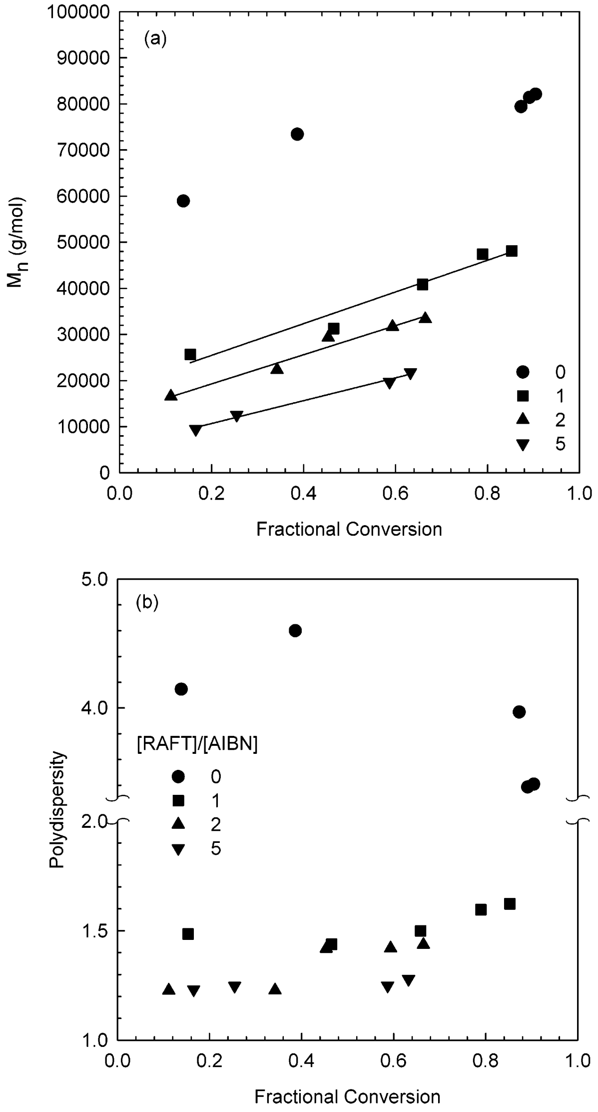


Figure 4. (a) Number-average molecular weight and (b) polydispersity index of PMMA prepared by RAFT miniemulsion polymerization at 80 °C, where [RAFT]/[AIBN] = variable.

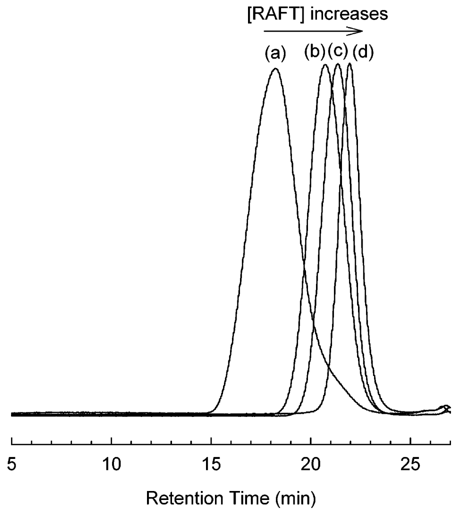


Figure 5. GPC traces of PMMA prepared by RAFT miniemulsion polymerization at 80 °C, where [RAFT]/[AIBN] = (a) 0, (b) 1.0, (c) 2.0, and (d) 5.0.

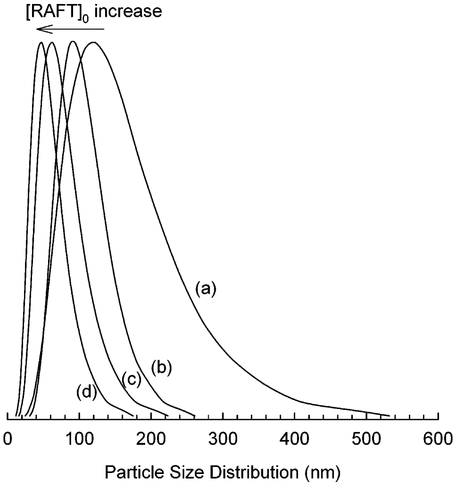
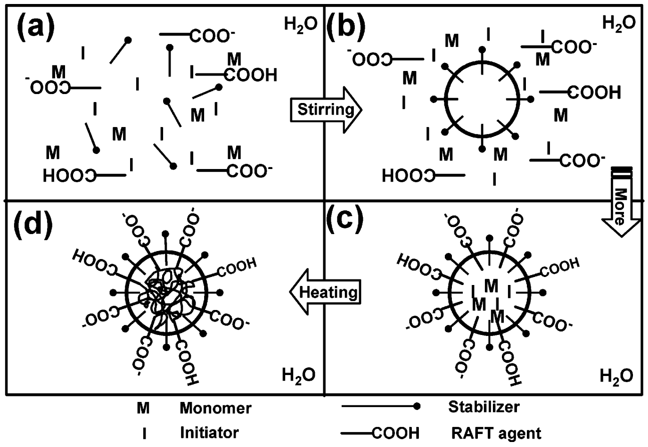


Figure 6. Particle size distribution of the PMMA nanoparticles prepared with various concentrations of RAFT agent at 80 °C.

Scheme 2. Schematic Representation of the Synthetic Mechanism of PMMA Nanoparticles Bearing Carboxyl Group on the Surface via RAFT Miniemulsion Polymerization



functional end group in R moiety (Scheme 1). Before agitation, the pink RAFT agent was observed as a precipitate in the bottom of the reaction vessel since it was not dissolved in the medium. At first, the reaction mixture in DDI water, which contains the polymerization ingredients, is mechanically agitated at 1000 rpm for the preemulsification process. As the agitation step goes further, the precipitated RAFT agent was not observed any longer since the hydrophobic RAFT agent was dissolved in the monomer-containing droplets. To obtain the enhanced emulsification for the miniemulsion process, the reaction vessel was sonicated for 5 min. Since the RAFT agent consists of a relatively hydrophilic carboxyl moiety and hydrophobic moiety bearing phenyl group which strengthens the hydrophobicity, the RAFT agent is expected to present at the interface between the micelles and water medium. The hydrophilic moiety is located outside of the micelles by existing in water phase, but the hydrophobic moiety tends to exist inside the hydrophobic monomer-swollen micelles. This concept is similar to that of the microemulsion polymerization in which the midchain alcohols (usually C4−C8) functioning as costabilizers are aligned with the interface between the micelles and water phase due to the same hydrophilic−hydrophobic nature of the molecules.[50] Upon completion of emulsification, the temperature of the reaction vessel is raised to a desired level, and the polymerization is conducted until the monomer is depleted. The PMMA nanoparticles prepared by this method have functionalities of carboxyl acid and carboxylic anion, and thus the properties of the latex are expected to be quite interesting.

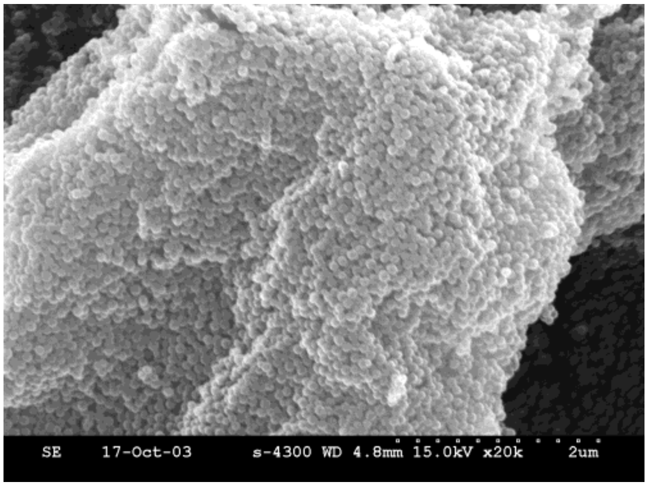


Figure 7. SEM photographs of PMMA nanoparticles prepared by miniemulsion polymerization in the presence of [RAFT]/[AIBN] = 1.0 at 80 °C.

The variation of the size and its distribution of the final PMMA nanoparticles is depicted in Figure 6 in relation to the concentration of the RAFT agent added to the system. It is observed that the concentration of the RAFT agent influences the particle size as well as the distribution. As the amount of the RAFT agent increases, the particle size continuously decreases from 118.8 to 49.5 nm as measured by the Zetasizer 4.

Figure 7 shows a SEM photograph of the monodisperse PMMA nanoparticles carrying carboxyl acid and carboxylic anion on the surface prepared by the aforementioned scheme using 1.0 molar ratio of a RAFT agent to AIBN at 80 °C. It is seen that the particle sizes are approximately 90 nm with a good uniformity, which means that the degradation of the monomer droplets caused by Ostwald ripening is efficiently suppressed. Comparing the SEM photograph of the PMMA prepared by the 1.0 ratio of [RAFT]/[AIBN] as shown in Figure 7, the particle size shows a good agreement between the two measurement techniques. The average particle size is 90 nm by the SEM (in Figure 7) and 91.3 nm by the Zetasizer 4 (Figure 6b). The particle size decreases with the increased overall carboxyl groups on the surface of the nanoparticles caused by the carboxyl group existing in the RAFT agent as shown in Figure 6. The particle size distribution becomes narrower with the concentration of the RAFT agent since the particle size is also controlled by the surface charge. In RAFT living radical (mini)emulsion polymerization of styrene[34] and butyl acrylate,[51] it has been reported that the number-average diameter decreases and the size distribution becomes narrower as the concentration of the RAFT agent increases. This result was postulated by the fact that the active growing radicals produced from the fragmentation of RAFT agent exit the particles and reenter to micelles in order to create new particles during the nucleation period at interval I of the emulsion polymerization mechanism. Gilbert et al. reported that the exit rate coefficient of the radical truly increased with increase of the RAFT agent, resulting in the retardation

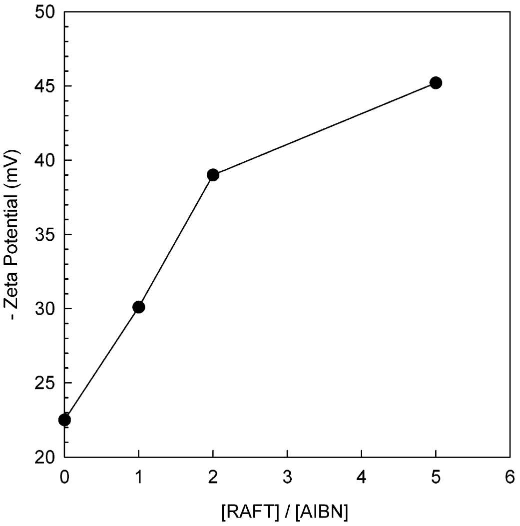


Figure 8. Zeta potential of the PMMA latex prepared with a varying concentration of the RAFT agent at 80 °C.

of the polymerization due to the transfer of the RAFT agent radical to the particles where polymerization reaction is in progress.[36]

The zeta potential is an important indicative of the ionically stabilized colloid systems. The greater magnitude of the zeta potential endows the colloid system with improved stability against coagulation. Figure 8 represents the change of the zeta potential value of the final PMMA latex prepared by the various concentrations of the RAFT agent while all other polymerization parameters were kept at same. Since the SDS surfactant is used to stabilize the colloids, the initial magnitude of the zeta potential has a value of 22.5 mV. As the ratio of [RAFT]/[AIBN] increases up to 5, the absolute value of the zeta potential correspondingly increases up to 45 mV, meaning that the stability of the colloid system is enhanced. If the RAFT agent locates inside of the micelles or polymer particles during or after the polymerization, the zeta potential would remain unchanged since the surface of the micelles or particles is identical. However, if the RAFT agent prefers to locate at the interface of the micelles or particles, the surface properties of the colloid are expected to change in several ways. The augmentation in the zeta potential is thought to be from the carboxylic anion due to a partial dissociation of hydrogen atom from the carboxyl acid moiety in the RAFT agent. Furthermore, the highly developed charge on the surface of the micelles gives rise to a decrease in the size of the micelles, thereby resulting in the smaller size of the final polymer particle.[52]

The variation of the surface properties of the latex nanoparticles stabilized by ionic mechanism also causes electrical property change. Conductivity measurement also provides useful information with high accuracy for the ionically stabilized colloid system. In Figure 9, the conductivity and pH of the PMMA nanoparticle suspending latex medium are measured and illustrated in terms of the RAFT agent. It is noted that the pH of the medium containing water, SDS, and AIBN was 7.13 at 25 °C. After addition of MMA and the emulsification, the pH value decreased to 6.44. With the addition of increasing amount of the RAFT agent, the pH value measured after the polymerization continuously decreases due to the partial ionization of carboxyl groups on the RAFT agent. Correspondingly, the conductivity value steadily increases from 2.35 to 2.68 mS/cm as the ratio of [RAFT]/[AIBN] increases from 0 to 5.0 while all the other polymerization parameters are identical. Since the final particle size is decreased with the RAFT agent, the total surface area of the particles is definitely enlarged. In this case, the SDS concentration in aqueous medium is expected to decrease, which results in reduction in the conductivity. Therefore, the increase in conductivity is suggested to originate from the RAFT agent since it bears the carboxylic group.

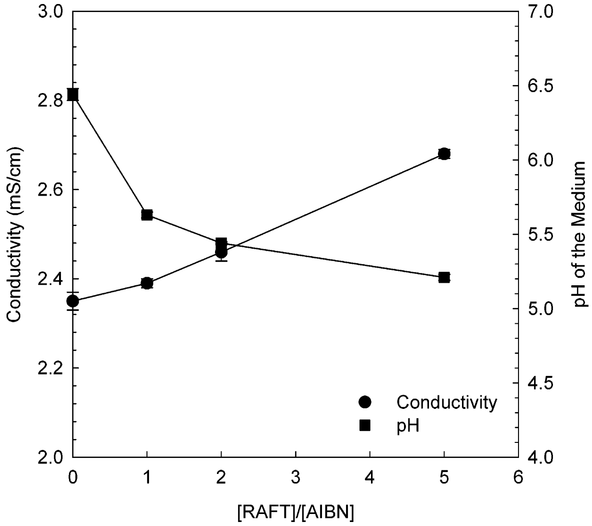


Figure 9. Conductivity and pH of the PMMA suspending medium obtained at the end of the polymerization with various concentrations of RAFT agent at 80 °C.

These results mean that the number of overall surface of carboxyl groups on the PMMA nanoparticles rises with the concentration of the RAFT agent and of the free hydrogen ion in the medium. With respect to the stability issue, it is also noted that no noticeable sign of creaming or destabilization of the PMMA nanoparticles was observed for at least several months by remaining as homogeneous latex. Therefore, the conductivity measured over a span of 2 months remains constant.

Conclusion

We applied a RAFT agent bearing a carboxyl acid in R group to miniemulsion polymerization of methyl methacrylate in order to prepare the stability-enhanced functionalized latex. At the polymerization temperatures of 60, 70, and 80 °C, the pseudo-first-order kinetics are clearly observed with controlled molecular weight and its distribution, which indicates this polymerization system obeys the living radical polymerization. The polymerization kinetics is found to be strongly dependent on the temperature during the living free radical miniemulsion polymerization. The higher the temperature, the faster the polymerization rate, the lower the molecular weight, and the lower the PDI are obtained. This temperature-dependent polymerization rate in living free radical polymerization is ascribed to not only the fast propagation of the free radicals and fast decomposition of the initiator but also the better efficiency of chain transfer agent at elevated temperature. When this RAFT agent is employed to the miniemulsion polymerization, various interesting phenomena are witnessed. It is seen that the increased concentration of the RAFT agent reduces the polymerization rate, since more chain transfer reaction occurs via the reversible addition and fragmentation mechanism at high concentration of the RAFT agent. The number-average molecular weight and the PDI decrease with the RAFT concentration, as expected.

The PMMA nanoparticles prepared by the miniemulsion polymerization using this type of RAFT agent show some interesting characteristics. As the RAFT agent increases up to 5 molar ratio of [RAFT]/[AIBN], the absolute value of the zeta potential correspondingly increases up to 45 mV, meaning that the stability of the colloid system is enhanced probably due to an alignment of the carboxyl end group outward the particles. The augment in the zeta potential is thought to be from the carboxylic anion due to a partial dissociation of hydrogen atom from the carboxylic acid moiety in the RAFT agent. In addition, the particle size continuously decreases from 118.8 to 49.5 nm due to the development of surface carboxyl groups and radical exit/reentry behavior during the polymerization. The variation of the surface properties of the latex stabilized by ionic mechanism also causes the electrical property change. Moreover, the conductivity steadily increases from 2.35 to 2.68 mS/cm as the ratio of [RAFT]/[AIBN] increases from 0 to 5.0 while all the other polymerization parameters are identical. The increase in conductivity may originate from the RAFT agent since it bears carboxyl group. It means that the surface carboxyl groups on the PMMA nanoparticles increases with the increasing RAFT concentration and free hydrogen ion in the medium. With respect to the stability issue, it is also noted that no noticeable sign of creaming or destabilization of the PMMA nanoparticles was observed for at least several months by remaining as homogeneous latex.

Acknowledgment. We thank the Korea Research Foundation for the financial support (Grant KRF-2001-041-E00500) in 2001−2003.

References and Notes

(1) Urban, D.; Takamura, K. *Polymer Dispersions and Their Industrial Applications*; Wiley-VCH: Weinheim, 2002.
(2) Fudouz, H.; Xia, Y. *Adv. Mater.* **2003**, *15*, 892.
(3) Ugelstad, J.; Stenstad, P.; Kilaas, L.; Prestvik, W. S.; Rian, A.; Nustad, K.; Herje, R.; Berge, A. *Macromol. Symp.* **1996**, *101*, 491.
(4) Covolan, V. L.; Mei, L. H. I.; Rossi, C. L. *Polym. Adv. Technol.* **1997**, *8*, 44.
(5) Kim, J. H.; Chainley, M.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 171.
(6) Reese, C. E.; Guerrero, C. D.; Weissman, J. M.; Lee, K.; Asher, S. A. *J. Colloid Interface Sci.* **2000**, *232*, 76.
(7) Sauzzeldde, F.; Ganachaud, F.; Elaissare, A.; Pichot, C. *J. Appl. Polym. Sci.* **1997**, *65*, 2331.
(8) Porcel, R.; Jodar, A. B.; Cabreriozo, M. A.; Hidalgo-Alvarez, R.; Martin-Rodriguez, A. *J. Colloid Interface Sci.* **2001**, *239*, 568.
(9) Hidalgo-Alvarez, R.; de las Nieves, F. A.; van der Linde, A. J.; Bijsterbosch, B. H. *Colloids Surf.* **1986**, *21*, 259.
(10) Bastos-Gonzalez, D.; Ortega-Vinuesa, J. L.; de las Nieves, F. J.; Hidalgo-Alvarez, R. *J. Colloid Interface Sci.* **1995**, *176*, 232.
(11) Peula, J. M.; Santos, R.; Forcada, J.; Hidalgo-Alvarez, R.; de las Nieves, F. J. *Langmuir* **1998**, *14*, 6377.
(12) Guo, X.; Weiss, A.; Ballauff, M. *Macromolecules* **1999**, *32*, 6043.
(13) Yan, C.; Zhang, X.; Sun, Z.; Kitano, H.; Ise, N. *J. Appl. Polym. Sci.* **1990**, *40*, 89.
(14) Charleux, B.; Pichot, C. *Makromol. Chem.* **1992**, *193*, 187.
(15) Sakota, K.; Okaya, T. *J. Appl. Polym. Sci.* **1977**, *21*, 1035.
(16) Ceska, G. W. *J. Appl. Polym. Sci.* **1974**, *18*, 2493.
(17) Okubo, M.; Iwasaki, Y.; Yamamoto, Y. *Colloid Polym. Sci.* **1992**, *270*, 733.
(18) Sarobe, J.; Forcada, J. *Colloid Polym. Sci.* **1996**, *274*, 8.
(19) Delair, T.; Marguet, V.; Pichot, C.; Mandrand, B. *Colloid Polym. Sci.* **1994**, *272*, 962.
(20) Charreyre, M.; Razafindrakoto, V.; Veron, L.; Delari, T.; Pichot, C. *Macromol. Chem. Phys.* **1994**, *195*, 2153.
(21) Okubo, M.; Nakagawa, T. *Colloid Polym. Sci.* **1992**, *270*, 853.
(22) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127.
(23) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Pat. 4,581,429, 1986.
(24) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(25) Kato, M.; Kamingaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(26) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(27) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993.
(28) de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239.
(29) D'Agosto, F.; Hughes, R.; Charreyre, M.; Pichot, C.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 621.
(30) Ladaviere, C.; Dorr, N.; Claverie, J. P. *Macromolecules* **2001**, *34*, 5370.
(31) Sumerlin, B. S.; Donovan, M. S.; Mitsukami, Y.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 6561.
(32) Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570.
(33) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993.
(34) Monteiro, M. J.; de Barbeyrac, J. *Macromolecules* **2001**, *34*, 4416.
(35) Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* **2002**, *35*, 7582.
(36) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417.
(37) Monteiro, J. J.; Hodgson, M.; de Brouwer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3864.
(38) Shim, S. E.; Shin, Y.; Jun, J. W.; Lee, K.; Jung, H.; Choe, S. *Macromolecules* **2003**, *36*, 7994.
(39) *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; Wiley & Sons: New York, 1997; Chapter 20.
(40) Tsavalas, J. G.; Schork, F. J.; de Brouwer, H.; Monteiro, M. J. *Macromolecules* **2001**, *34*, 3938.
(41) Calitz, F. M.; Tonge, M. P.; Sanderson, R. D. *Macromol. Symp.* **2003**, *193*, 277.
(42) Gaynor, S. G.; Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *22*, 201.
(43) Bai, R. K.; You, Y. Z.; Pan, C. Y. *Polym. Int.* **2000**, *49*, 898.
(44) Kanagasabapathy, S.; Sudalai, A.; Bencewicz, B. C. *Macromol. Rapid Commun.* **2001**, *22*, 1076.
(45) Stenzel-Rosenbaum, M.; Davis, T. P.; Chen, V.; Fane, A. G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2777.
(46) Shim, S. E.; Shin, Y.; Lee, H.; Choe, S. *Polym. Bull. (Berlin)* **2003**, *51*, 209.
(47) Shim, S. E.; Jung, H.; Lee, H.; Biswas, J.; Choe, S. *Polymer* **2003**, *44*, 5563.
(48) Matyjaszeski, M. *Controlled Radical Polymerization*; ACS Symposium Series 687; American Chemical Society: Washington, DC, 1998; Chapter 1.
(49) Gilbert, R. G. *Emulsion Polymerization A Mechanistic Approach*; Academic Press: San Diego, 1995; p 60.
(50) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283.
(51) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(52) Rahan, A.; Brown, C. W. *J. Appl. Polym. Sci.* **1982**, *27*, 2563.

MA049930J