

Synthesis of carboxylic acid functionalized nanoparticles by reversible addition–fragmentation chain transfer (RAFT) miniemulsion polymerization of styrene

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Abstract

In this study, an addition–fragmentation chain transfer agent bearing carboxylic acid, 4-toluic acid dithiobenzoate (TADB), was used to synthesize carboxylic acid functionalized PS nanospheres via the miniemulsion polymerization. In addition, non-functionalized RAFT agent, benzyl dithiobenzoate (BDB), was also used to compare the surface properties of the PS nanoparticles. For the TADB system, the rate of polymerization was approximately two-fold faster than the BDB system, while the molecular weights and PDI of PS remain intact.

With increasing the molar ratio of [TADB]/[AIBN] from 0 to 3.0, the average particle diameter is substantially increased from 90 to 126 nm. The absolute value of zeta potential and conductivity also correspondingly increase from 49.1 mV and 3.47 mS/cm to 53.9 mV and 4.21 mS/cm, respectively. The results indicate that the surface of PS nanospheres could be functionalized by means of a carboxylic acid group on the RAFT agent and the stability of the PS miniemulsion latex could be significantly improved.

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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 wide applications for new or advanced materials including surfactants, coatings, adhesives, biomaterials, medical materials and microelectronics.

Several controlled/‘living’ radical polymerization methods have been reported: 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].

Charge-controlled polymer colloids are being considered as important functionalized materials. In order to prepare such functional particles, several methods are adopted such as the (1) co-polymerization with ionic monomers/co-monomers [8–10], (2) polymerization with charge endowing surfactants or initiators [11–13] and (3) multi-step process in which functional groups are incorporated into the polymer particles [14,15]. Such polymer particles are produced by the introduction of highly polar or ionic functional groups including aldehyde [16,17], carboxylate [18,19], chloromethyl [20,21], amino [22,23], and vinyl moiety [24].

Miniemulsion polymerization is the most frequently used in conjunction with the RAFT technique [25–29] among

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several heterogeneous polymerizations since the miniemulsion polymerization is taking place inside the monomer swollen micelles, which is in homogeneous phase. In our previous study, we have reported a novel approach to synthesize carboxylic acid functionalized poly(methylmethacrylate) (PMMA) nanoparticles using a RAFT agent, possessing carboxylic acid end group [30].

In this article, we have synthesized polystyrene (PS) nanospheres having a carboxylic acid functional group on their surfaces using the RAFT miniemulsion polymerization. In addition, the effects of the carboxylic acid on the properties of the PS nanoparticles are investigated in terms of stability by comparing ones prepared with a non-functionalized RAFT agent.

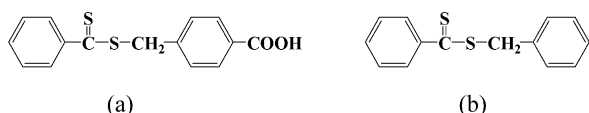
2. Experimental section

2.1. Materials

Reagent grade phenylmagnesium bromide, α -bromo-*p*-toluic acid, and carbon disulfide, used in the 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 the existing impurities and water. Styrene (Samchun Chemical Co., South Korea) were purified using an inhibitor removal column (Aldrich) and stored at $-5\text{ }^{\circ}\text{C}$ prior to use. An initiator, analytical grade of 2,2-azobisisobutyronitrile (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 pH of 6.75 was used as the polymerization medium.

2.2. Polymerization

The RAFT agents, 4-toluic acid dithiobenzoate (TADB) and benzyl dithiobenzoate (BDB) (Scheme 1), were synthesized as reported elsewhere [5,31]. Table 1 shows the recipes used for the miniemulsion polymerization of styrene. The amount of SDS and hexadecane were chosen according to a typical recipe in miniemulsion polymerization [32]. The molar ratio of [RAFT agent]/[AIBN] was varied from 0 to 3. Polymerization ingredients were charged to the reactor. Pre-emulsification was carried out following two steps; first, the polymerization reactor containing the accurate recipe was mechanically stirred at 1000 rpm, and



Scheme 1. RAFT agents used in this study. (a) TADB and (b) BDB.

Table 1
Recipe for the miniemulsion polymerization of styrene at $80\text{ }^{\circ}\text{C}$

Ingredients	Materials used	[RAFT]/ [AIBN]=1.3	[TADB]/ [AIBN]=0–3.0
Water		100 g	100 g
Monomer	Styrene (10 wt% of water)	10 g	10 g
Surfactant	SDS (based on aqueous phase)	0.2884 g (10 mM)	0.4326 g (15 mM)
Costabilizer	Hexadecane (3 wt% of monomer)	0.3 g	0.3 g
RAFT agent	TADB (or BDB)	0.11 g (0.096 g)	0–0.2643 g
Initiator	AIBN	0.02 g	0.05 g

then the ultrasonic homogenization was performed for 5 min. Upon the completion of the pre-emulsification, water-insoluble RAFT agents were not further observed in a separate phase since all the RAFT agent molecules were absorbed into micelles containing the hydrophobe, monomer, and initiator. Polymerization was carried out in a 500 mL three-necked reaction vessel with a mechanical stirrer at $80\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. A mild agitation of 200 rpm was applied throughout the polymerization. During the polymerization for 8 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.

2.3. Characterizations

The molecular weight and PDI were measured using Waters GPC (gel permeation chromatography) equipped with 510 differential refractometer and Viscotex T50 differential viscometer. 10^5 , 10^3 , and $10^2\text{ }\text{\AA}$ μ -styrigel packed high resolution-columns were employed. The calibration was carried out using ten polystyrene standard samples (Polymer Laboratories, UK) with molecular weight ranging 580–7,500,000 g/mol. The latex solution sample withdrawn from the reaction vessel was rinsed with DDI water and centrifuged repeatedly, then the PS powder was dried in vacuum oven for 24 h. The PS 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. Conductivity of the continuous phase was immediately measured by sampling the latex from the reactor using a

conductivity meter (GM-115, KEM Co., Japan) as described elsewhere [33]. Scanning electron microscopy (SEM; Hitachi S-4300) was used to study morphology of the synthesized PS particles.

3. Results and discussion

3.1. Effect of carboxylic acid functional group

Fig. 1 shows the effect of the carboxylic acid functional group of RAFT agents on the polymerization kinetics of the miniemulsion polymerization of styrene at 80 °C. In both cases, pseudo-first order kinetics are well obtained due to a constant number of growing radicals during the polymerization period, which indicates these polymerization systems obey the living free-radical polymerization. For styrene, a temperature-dependent propagation constant, k_p , can be estimated from the following equation [34]:

$$\ln k_p (\text{l/mol s}) = \frac{17.57 - 3909}{T(\text{K})} \quad (1)$$

Since the slope of the kinetic data is directly proportional to k_p value and the number of growing radicals, the number of growing radical can be simply calculated using the k_p value at 80 °C from Eq. (1). The calculated numbers of growing radicals are 8.996×10^{-8} mol/l and 4.385×10^{-8} mol/l for TADB and BDB, respectively. For the TADB system, the number of growing radicals is approximately two-fold greater than the BDB system, implying that a carboxylic acid functional group on the RAFT agent significantly accelerates the rate of polymerization. Since a carboxylic acid moiety attached to a phenyl group acts as a deactivating, i.e. electron-withdrawing, group due to the combined results of a higher electronegativity caused by polar oxygen atoms and resonance effect of carboxylic acid

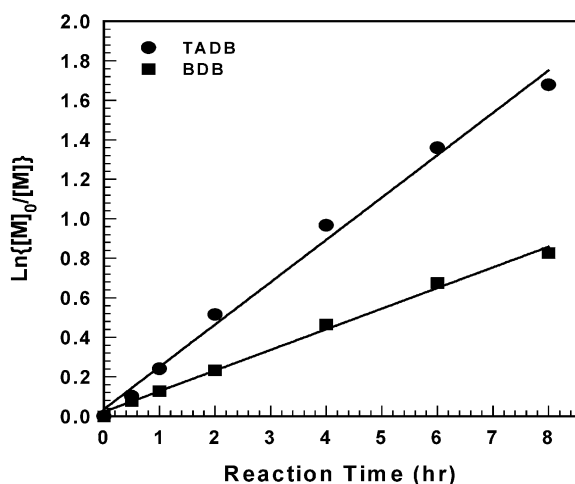


Fig. 1. Polymerization kinetics of the miniemulsion polymerization of styrene using TADB and BDB with 1.3 molar ratio of RAFT agent to AIBN at 80 °C.

[35], radicals from the RAFT agent bearing the carboxylic acid group are more readily generated in the presence of primary radicals decomposed from a thermal initiator.

The evolution of molecular weights of PS prepared in the presence of 1.3 molar ratio of [TADB]/[AIBN] and [BDB]/[AIBN] is compared in Fig. 2. In Fig. 2(a) and (b), it is seen that the number-average molecular weights and PDI values are quite similar for both systems. The results indicate that the existence of a carboxylic acid group on a RAFT agent only influences the rate of polymerization, while the molecular weight properties are not affected. For effective RAFT agents, the final molecular weights of polymer show to be almost identical for the same molar concentration of RAFT agents under the fixed concentrations of a surfactant and an initiator [27]. In their report, three different RAFT agents, cumyl dithiobenzoate (CDB), 1-phenylethyl phenyldithioacetate (PEPDTA) and 1-phenylethyl dithiobenzoate (PEDB) were used in the miniemulsion polymerization of styrene at the same level. The results showed that the variation of RAFT agents caused a substantial difference in the polymerization kinetics, while the final molecular weights of polymer are not affected by the structure of the RAFT agents, which is in line with the theoretical consideration of molecular weight and rate of

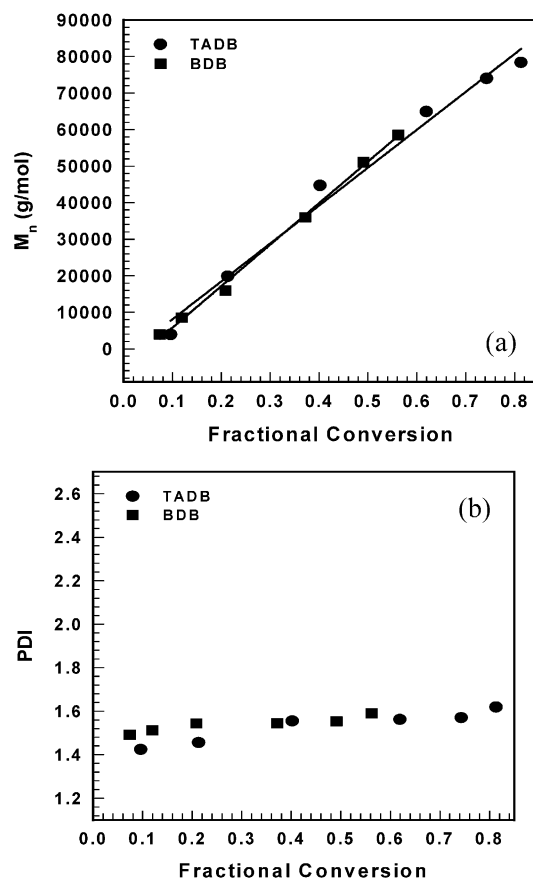


Fig. 2. (a) Number-average molecular weight and (b) polydispersity index of PS prepared by miniemulsion polymerization using TADB and BDB with 1.3 molar ratio of RAFT agent to AIBN at 80 °C.

polymerization in a RAFT system [36]. Our experimental data agree with these phenomena as reported in their publication.

Fig. 3(a) and (b) show the morphology of PS nanospheres prepared by the miniemulsion polymerization using 1.3 molar ratio of [TADB]/[AIBN] and [BDB]/[AIBN] as RAFT agents. The properties of the nanospheres are summarized in Table 2. Importantly, the magnitude of zeta potential and conductivity values are relatively greater for the PS nanospheres prepared with TADB, implying the existence of carboxylic acid group on the surface of PS particles [30].

Scheme 2 illustrates a synthetic mechanism of the functionalized PS latex via the miniemulsion polymerization using a RAFT agent carrying a carboxyl functional end group in R moiety, TADB in Scheme 1. Before agitation, the pink-colored 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 pre-emulsification 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. In order 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 be 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 mid-chain alcohols (usually C4–C8) functioning as co-stabilizers are aligned with the interface between the micelles and water phase due to the same hydrophilic–hydrophobic nature of the molecules [37]. Upon completion of the emulsification, the temperature of the reaction vessel is raised to a desired level and the polymerization is performed until the monomer is depleted. The PS nanospheres prepared by

Table 2

Properties of the PS nanospheres prepared by miniemulsion polymerization using TADB and BDB with 1.3 molar ratio of RAFT agent to AIBN at 80 °C

Properties	RAFT agent	
	TADB	BDB
Particle size (nm)	125.1	135.7
Zeta potential (mV)	−48.2	−44.5
Conductivity (mS/cm)	2.60	2.48

this method have functionalities of carboxyl acid and carboxylic anion, and thus the magnitude of zeta potential and conductivity values of the latex are led to be greater. Although a titration method could be used for a quantitative analysis of carboxylic acid groups on the surface of the polymer colloids, it is technically quite difficult for tiny polymer nanoparticles [38] since the adsorbed surfactant should be removed from the particle surfaces. Therefore, the zeta potential and conductivity values were used to indirectly confirm the existence of carboxylic acid groups on the surface of the PS nanospheres.

3.2. Effect of the TADB concentration

Fig. 4 represents the effect of the TADB concentration on the kinetics of miniemulsion polymerization in synthesizing carboxylic acid-functionalized PS nanospheres at 80 °C, where the molar ratio of [RAFT]/[AIBN] was increased from 0 to 3.0. It is noted that the polymerization recipe in Fig. 4 is different from that in Fig. 1 as listed in Table 1. For example the amounts of surfactant and initiator were increased to find better polymerization conditions for the increased concentration of TADB by conducting a series of polymerizations. In the absence of the RAFT agent, the typical characteristics in radical polymerization are observed and the conversion levels off in ca. 2 h. 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 reversible addition and fragmentation

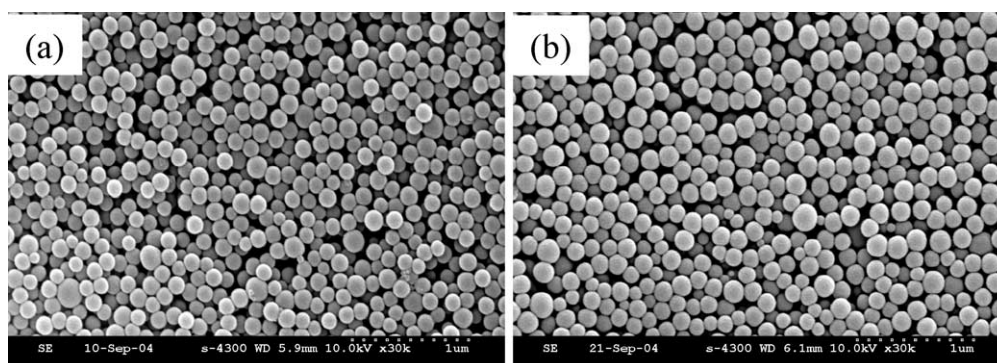
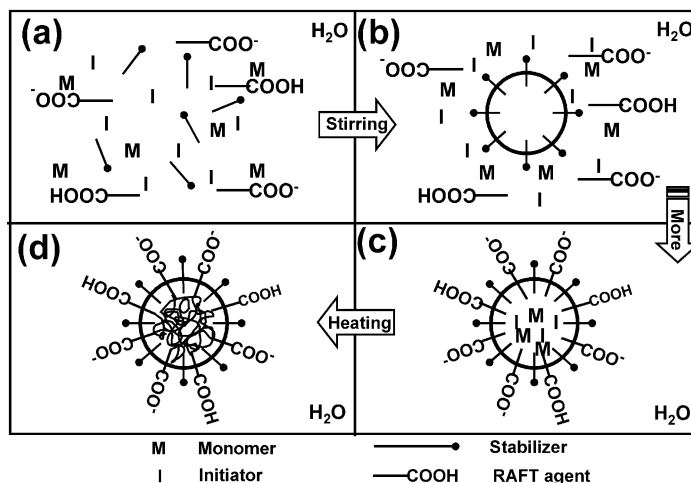


Fig. 3. PS nanospheres prepared by miniemulsion polymerization using (a) TADB and (b) BDB with 1.3 molar ratio of RAFT agent to AIBN at 80 °C.



Scheme 2. Schematic representation of the synthetic mechanism of PS nanospheres bearing carboxyl group on the surface via RAFT miniemulsion polymerization.

mechanism at high concentration of the RAFT agent. Although the polymerization rate seems insensitive to the concentration of RAFT agents in bulk polymerization, significant rate retardation has been reported in miniemulsion and seeded emulsion systems [27,28]. The reason for the retardation of polymerization with an increasing concentration of RAFT agents was explained by the exit of active radicals generated by the addition of an entering radical to the RAFT agent, which causes a reduced number of particles with a corresponding decrease in the rate of polymerization. This phenomenon is also likely to occur in the system observed in Fig. 4.

In Fig. 5, the evolution of molecular weight and PDI during the miniemulsion polymerization of styrene using TADB as the RAFT agent is depicted. The number-average molecular weight increases in a linear fashion with respect to the conversion in the presence of TADB, while a typical growth of molecular weight is observed in the absence of TADB. As expected, the number-average molecular weight decreases with the increasing concentration of TADB. Especially, when 3.0 molar ratio of [TADB]/[AIBN] is

used, the experimental and theoretically estimated [39] molecular weights show a good agreement, which means the polymerization is well controlled above this concentration of TADB. In Fig. 5(b), The PDI of the PS prepared with various concentrations of TADB shows distinctive

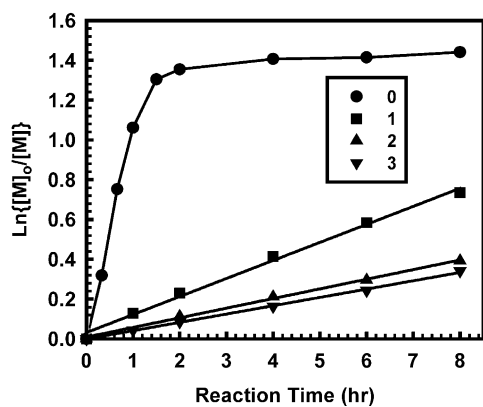


Fig. 4. Polymerization kinetics of miniemulsion polymerization of styrene using an increasing molar ratio of [TADB]/[AIBN] at 80 °C.

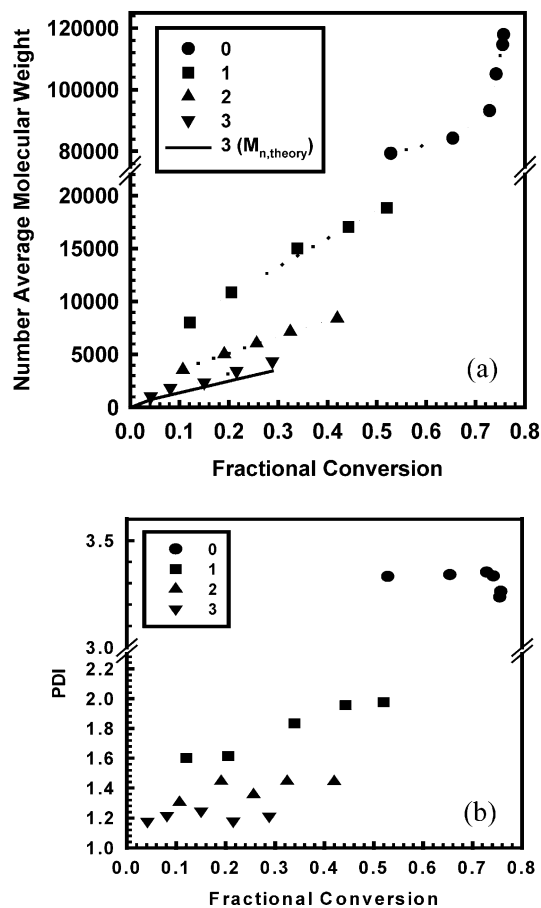


Fig. 5. (a) Number-average molecular weight and (b) polydispersity index of PS prepared by miniemulsion polymerization using an increasing molar ratio of [TADB]/[AIBN] at 80 °C.

difference between the presence and absence of TADB. In the presence of TADB, the PDI is controlled throughout the polymerization and the final PDI's decrease from 1.98 to 1.21 with increasing the molar ratio of [TADB]/[AIBN] from 1.0 to 3.0.

Fig. 6 represents the microphotographs of the PS nanospheres prepared in the absence and 3.0 molar ratio of [TADB]/[BDB] by the mechanism proposed in Scheme 2. It is clearly observed that the size of the PS nanospheres synthesized in the presence of TADB is larger than ones prepared without TADB. The size variation with respect to the concentration of TADB is investigated in Fig. 7. In the absence of TADB, the average particle diameter is 90 nm, while it is substantially increased by the addition of TADB. The average size increased to 126 nm for 3.0 [TADB]/[AIBN]. However, we observed a decrease in particle size with a RAFT concentration in a similar system of the miniemulsion polymerization of methyl methacrylate using TADB as a RAFT agent [30]. We explained the reason for the reduced particle size based on the exit and re-entry of radicals through micelles as proposed by Monteiro [26] and Gilbert [28] et al. On the other hand, Lansalot and co-workers [27] have reported that the size of PS particles prepared by miniemulsion polymerization correspondingly increased with the concentration of a RAFT agent, 1-phenylethyl phenyldithioacetate (PEPDTA) with fixed concentrations of surfactant and initiator. Since those two contradictory phenomena are observed in styrene miniemulsion system, it is now difficult to judge the feasibility of those cases at the present moment.

Since the PS nanospheres synthesized in the presence of TADB carry carboxylic acid and carboxylic anion on the colloid surfaces, the properties of the latex would be related to the amount of surface functional groups.

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. The variation of the surface properties of the latex nano-particles stabilized by ionic mechanism also causes electrical property change. Conductivity measurement also provides useful information with high accuracy for the ionically stabilized colloid system. If the

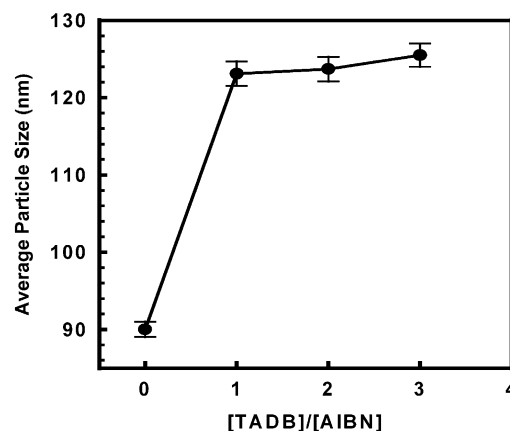


Fig. 7. Effect of an increasing concentration TADB on the size of PS nanospheres prepared by miniemulsion polymerization at 80 °C.

molecules of RAFT agent, TADB, were buried inside of the micelles or polymer particles during or after the polymerization, the zeta potential or conductivity 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.

Fig. 8 represents the change of zeta potential and conductivity values of the final PS latex prepared by the various concentrations of TADB. Since the SDS surfactant is used to stabilize the colloids, the initial magnitude of zeta potential and conductivity have the values of 49.1 mV and 3.47 mS/cm, respectively. As the ratio of [TADB]/[AIBN] increases up to 3.0, the absolute value of zeta potential and conductivity correspondingly increases up to 53.9 mV and 4.21 mS/cm, respectively, meaning that the stability of the colloid system is enhanced. The augmentation in the zeta potential and conductivity 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. Therefore, the surface of PS nanospheres could be functionalized by means of the relatively hydrophilic functional group on the RAFT agent. In addition, the surface functional group could improve the stability of the

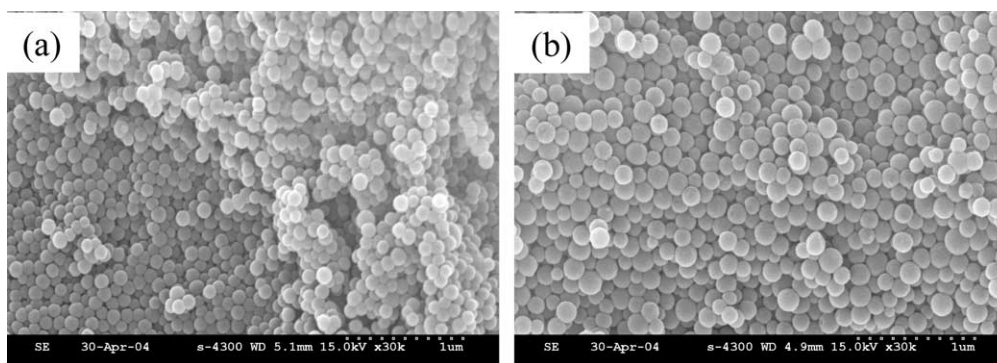


Fig. 6. PS nanospheres prepared by miniemulsion polymerization (a) in the absence and (b) with 3.0 molar ratio of [TADB]/[AIBN] at 80 °C.

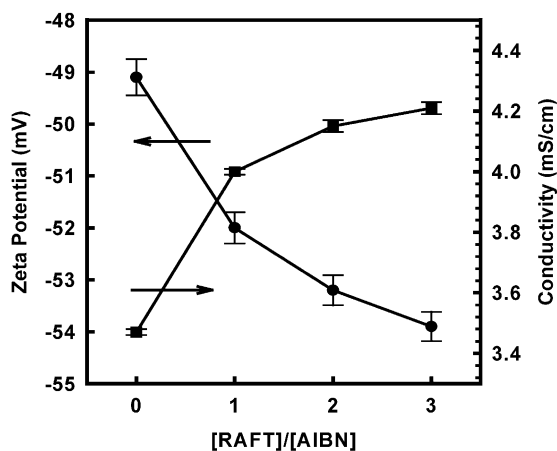


Fig. 8. Effect of an increasing concentration TADB on the zeta potential and conductivity of the PS nanospheres latex prepared by miniemulsion polymerization at 80 °C.

miniemulsion latex by strengthening the electrostatic force between the colloid particles.

4. Conclusions

In this study, an addition–fragmentation chain transfer agent bearing carboxylic acid, TADB, was used to synthesize carboxylic acid functionalized PS nanospheres via the miniemulsion polymerization. In addition, non-functionalized RAFT agent, BDB was also used to compare the surface properties of the PS nanoparticles. For the TADB system, the number of growing radicals is approximately two-fold greater than the BDB system, implying that a carboxylic acid functional group on the RAFT agent significantly accelerates the rate of polymerization while the molecular weights of PS remain intact. This phenomenon was postulated by the fact that radicals from the RAFT agent bearing the carboxylic acid group are more readily generated since a carboxylic acid moiety attached to a phenyl group acts as a deactivating, i.e. electron-withdrawing, group due to the combined results of a higher electronegativity caused by polar oxygen atoms and resonance effect of carboxylic acid.

With increasing the molar ratio of [TADB]/[AIBN] from 0 to 3.0, the average particle diameter is substantially increased from 90 to 126 nm. More importantly, the carboxylic acid functionalized PS nanospheres substantially change the properties of the latex in terms of zeta potential and conductivity. As the ratio of [TADB]/[AIBN] increases up to 3.0, the absolute value of zeta potential and conductivity correspondingly increase from 49.1 mV and 3.47 mS/cm to 53.9 mV and 4.21 mS/cm, respectively. The augmented values indicate that TADB prefers to locate at the interface between the micelles or particles and water phases due to its relatively hydrophilic carboxylic acid group. Therefore, the surface of PS nanospheres could be

functionalized by means of a carboxylic acid group on the RAFT agent and the stability of the PS miniemulsion latex could be significantly improved.

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