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Emulsion Polymerization of Methyl Methacrylate Using a Surface-active RAFT agent: The Role of Surfactant

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Summary

This article deals with the living radical emulsion photopolymerization of methyl methacrylate (MMA) using a RAFT agent which plays the role of an initiator in the absence of an additional thermal initiator, a chain-transfer agent, and a surfactant. The mechanism of the formation of stable spherical polymer beads without coagulation in the absence of a surfactant and the effects of the added surfactant are studied. The molecular weights of the prepared PMMA beads are in the same range (M_n: 10^5 - 10^6 g/mol) as those obtained from a conventional emulsion polymerization. However, the molecular weight distribution (M_w/M_n; polydispersity index; PDI) is controlled to be less than 2.0. The polymer beads in diameter was significantly reduced from 300 nm without a surfactant to decreased to 50 nm upon the addition of sodium dodecyl sulfate (SDS) keeping the molecular weight and the molecular weight distribution constant. Also, the addition of SDS in the preparation of PMMA colloid results in the enhancement of the stability by exhibiting increased ζ-potential values in water

Introduction

Since the emulsion polymerization was first introduced in mid-1930s, the process has been widely used to produce various polymers. And these resultant polymers have been used as in latex or in solid form for a wide range of applications including coatings, paints, adhesives, additives for construction materials, synthetic rubbers, and so forth. The use of water as a reaction medium and the mechanism of its unique particle formation bring several advantageous features of the process.

Recently, living free radical polymerizations such as nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) process have been disclosed to prepare various polymers having a predetermined structure and well-controlled molecular weight distribution, which are hardly achieved in conventional radical polymerization [1].

The current research interests in living radical polymerization are moving towards the use of water as the reaction medium. Therefore, living radical polymerizations in aqueous system such as miniemulsion or emulsion polymerization have received much attention as reviewed by Matyjaszewski [2] and Cunningham [3]. Since the RAFT technique can be easily applied to the conventional emulsion or miniemulsion polymerization for a wide variety of monomers simply by adding a RAFT agent, intensive studies have been carried out in such a field [4,5,6,7].

The constituents for the emulsion polymerization basically consist of monomer, water, surfactant, and initiator, where a surfactant can be omitted if an employed initiator generates a surface-active oligomeric intermediate in the course of polymerization. The surfactant added in the polymerization system gives a better colloidal stability of the formed polymer, however it alters the genuine properties of the polymers. In order to avoid this deleterious drawback caused by a surfactant, an addition-fragmentation reactive surfactant, so-called TRANSURF, which acts as both a chain transfer agent and a surfactant in RAFT emulsion polymerization, has been designed [8].

In this study, a RAFT agent which generates a surface-active agent after decomposition and further reaction with monomers was used to prepare polymer beads in the absence of an additional initiator and a surfactant, and the mechanism of the formation of stable spherical particles is proposed. In addition, the role of a surfactant on the polymerization characteristics was investigated.

Experimental

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 used as received from J. T. Baker Co. (USA). MMA (Junsei Chemicals, Japan) passed through inhibitor removal column packed with a silica gel was stored in a refrigerator prior to use. Double-distilled deionized (DDI) water was used as a reaction medium.

Synthesis of a RAFT agent

A RAFT agent, 4-thiobenzoyl sulfanylmethyl sodium benzoate, was synthesized in this laboratory. 0.03 mol phenylmagnesium bromide (as in 3M solution in ether) and 0.045 mol of carbon disulfide were reacted in dry diethyl ether at 10 °C for 6 hours. After removing unreacted reagents by distillation, 1.7:1 molar ratio of (thiobenzoyl)sulfanyl magnesium bromide to α-bromo-p-toluic acid was added in methanol and the reaction was carried out at 60 °C for 24 hours. COOH end group of the product was replaced by -COONa by 1M of NaOH solution to introduce a water-solubility. Unreacted reagents and methanol were removed by distillation and the product was separated using column chromatography on silica eluting with 8:2 ethyl acetate:*n*-hexane mixture to give 4-thiobenzoyl sulfanylmethyl sodium benzoate as an ivory solid. Yield: 69.3%. ^{1}H NMR, δ: 4.7 (s, 2H, -CH_2-), 7.4-7.5 (m, 5H, Ar*H*), 8.0 (m, 4H, -CH_2-Ar*H*-).

Polymerization

Polymerization was carried out in a 500 mL three-necked reaction vessel with a mechanical stirrer under nitrogen atmosphere. Agitation speed was kept at 150 rpm, and the polymerization temperatures were 60, 70, and 80 °C. 1kW UV lamp with 365 nm wavelength was used to initiate the polymerization. MMA concentration was 10 wt. % (8 g) based on the reaction medium (DDI water, 80 g) and the concentration of the RAFT agent was fixed at 5×10^{-4} mol. During the polymerization for 6 hours, small amount of sample was periodically taken from the reactor for further characterizations. In order to study the effect of additional surfactant, various concentrations of SDS controlled to be above its critical micelle concentration (CMC) were added to the water and pre-emulsified with monomer at 900 rpm for 30 min. After completion of the polymerization, the resultant latex was frozen in a refrigerator and then molten at room temperature. White PMMA beads were obtained by collecting the precipitated phase and followed by drying *in vacuo* at 50 °C for 24 hours.

Analysis

Monomer conversion was measured gravimetrically. A weighed latex sample was diluted with methanol and the precipitated polymer was separated by centrifugation repeatedly. The chemical structure of the synthesized RAFT agent was confirmed by a Varian 400-MHz ^{1}H-NMR using $CDCl_3$ as the solvent. The molecular weight and PDI were characterized using a Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotek T50 differential viscometer. Universal calibration curve was obtained using polystyrene standard samples (Polymer Laboratories, UK) with molecular weights ranging 580 – 7,500,000 g/mole. Scanning Electron Microscopy (SEM; Hitachi S-4300) was used to study the morphology of the synthesized PMMA particles. The particle size and the ζ – potential of the polymer particles were measured using a Malvern Zetasizer 4000.

Results and discussion

Effect of the presence of SDS on polymerization

Figure 1 illustrates a proposed mechanism for the formation of stable spherical polymer colloids by a RAFT agent in the absence of a surfactant and an initiator such as potassium persulfate (KPS) or ammonium persulfate (APS). In Figure 1, the RAFT agent, decomposed by UV, is severed into a dormant and a active species through a homolytic cleavage of the carbon-sulfur bond. The active species carrying carboxyl group undergoes further propagation. In this stage, the RAFT agent plays a role of an initiator and a chain transfer agent. As the hydrophobic monomer reacts with the active species, the length of a hydrophobic aliphatic backbone of oligomer becomes longer, making the intermediate surface-active since it contains both hydrophilic and hydrophobic moieties. Therefore, the intermediate could form micelles which serve as a *locus* of polymerization for the emulsion polymerization. The hydrophilic carboxyl moiety is aligned outwards and the hydrophobic oligomeric chains are placed inside the micelles.

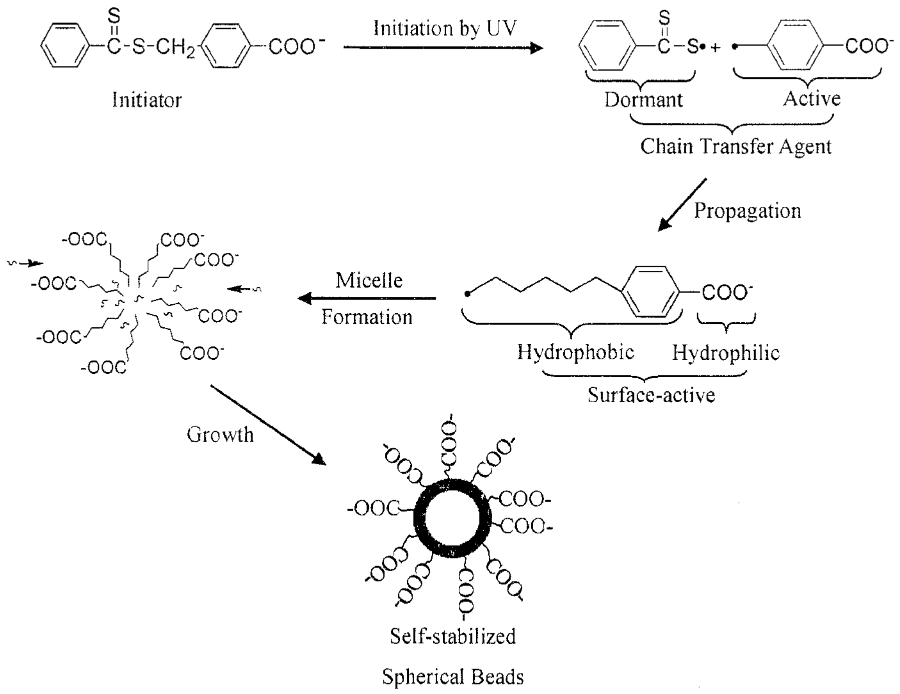

Figure 1: Mechanism of the formation of stable spherical polymer beads using a surface-active RAFT agent in the absence of an additional initiator and a surfactant.

The stabilization, *i.e.* the prevention of coagulation among polymer particles, is achieved by an electrostatic repulsion induced by a negative charge on the beads. In addition, the growth of particles occurs by monomer transportation from monomer droplet to the micelles or monomer-swollen particles. This mechanism is quite similar to the surfactant-free emulsion polymerization where initiators such as KPS or APS generate a surface-active oligomeric intermediate [9]. The level of surface stabilization is therefore dependent on the concentration of carboxyl group on the particles. Finally, stable polymer beads with a controlled molecular weight and a molecular weight distribution can be produced. However, a short polymerization time is recommended for this mechanism since RAFT agents bearing dithioester group are known to undergo a degradation by a UV irradiation for a prolonged time [10]

Figure 2 represents the morphology of the PMMA beads prepared by living radical emulsion polymerization with 5x10^{-4} mol of the RAFT agent at various temperatures in the absence of a surfactant and an initiator for 6 hours. The stable spherical beads are successfully obtained by the mechanism as proposed above. Figure 3 shows the morphology of the PMMA beads synthesized under the same conditions as in Figure 2, but the use of a surfactant. In Figure 3, SDS (8.7 mM) was added to be slightly higher than its CMC (8.1 mM).

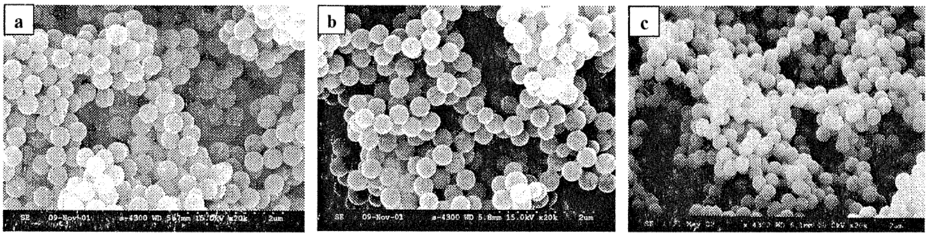

Figure 2: SEM microphotographs of PMMA beads prepared with 5x10^{-4} mol of the RAFT agent at several temperatures (a) 60°C (b) 70°C, and (c) 80°C.

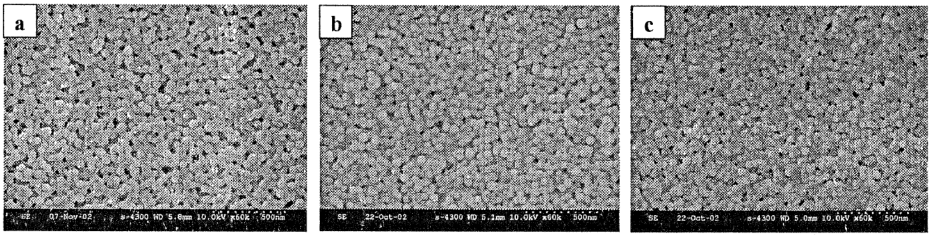

Figure 3: SEM microphotographs of PMMA beads prepared with 5.0×10^{-4}mol of the RAFT agent and 8.7 mM of surfactant (SDS) (a) 60 °C (b) 70 °C, and (c) 80 °C.

Table 1. Characterizations of PMMA beads prepared with and without SDS at various temperatures for 6 hours.

Temperature (°C)	Conversion (%)	SDS (mM)	M_n (g/mol)	PDI	ζ – Potential (mV)	Diameter (nm)
60	84.5	none	338500	1.23	-28.5	407
70	89.0	none	413000	1.29	-23.2	392
80	91.0	none	634101	1.41	-21.1	304
60	87.2	8.7	737984	1.20	-37.8	59.5
70	90.3	8.7	796359	1.23	-34.7	55.6
80	94.0	8.7	757402	1.24	-32.8	47.6

The summarized results in Figure 2 and 3 are given in Table 1. In the absence of SDS, a higher conversion is obtained at a higher temperature due to the fast propagation of the free radicals and possibly due to the fast decomposition and activation of the RAFT agent at elevated temperature. In radical polymerization, it is known that the activation energy for radical propagation is appreciably higher than that of termination at higher temperature [11]. Thus, the increase in k_p/k_t (k_p and k_t represent the rate constants of propagation and termination, respectively) with temperature leads to a fast polymerization rate. The molecular weight increases with the polymerization temperature, which is a general observation in photopolymerization [12]. The PDI tends to slightly increase from 1.23 at 60 °C to 1.42 at 80 °C. The ζ - potential of the prepared PMMA beads shows that the absolute value becomes lower at higher temperature, implying that a lower polymerization temperature leads to more stable latex. In accordance with the temperature increase from 60 to 80 °C, particle size decreases from 407 nm to 304 nm, respectively, which is a common observation in emulsion polymerization.

When 8.7 mM of SDS slightly above its CMC (8.1 mM) is added, the polymerization characteristics vary in several aspects. The conversion for the same period of polymerization time (6 hours) and at the same polymerization temperature increases compared to the case of absence of SDS. This is due to the fact that significant amount of monomer is confined in micelles by emulsification at a high agitation speed of 900 rpm for 30 min prior to starting polymerization. The pre-emulsification can reduce the time needed for a transportation of monomer or oligomeric radical from monomer droplet to micelle through an aqueous medium, which is the most time-consuming, i.e., the polymerization rate determining step [13]. It is seen that the number-average molecular weights in the presence of SDS are higher than those obtained in the absence of SDS, but those are not affected by the polymerization temperature. The PDI value in the presence of SDS is not significantly influenced by the polymerization temperature since the evolution of polymer molecules in (monomer-swollen) micelle is not as complicated as that in the surfactant-free emulsion polymerization. More importantly, the size of the final beads significantly decreases from several hundreds nanometers to approximately 50 nm by addition of SDS. If the monomer transportation to micelle continues to take place throughout the particle growth stage in Smith-Ewart theory, *i.e.*, Interval II, particle diameters in the range of hundreds of nanometer are generally achieved from emulsion polymerization. However, the particle sizes obtained in this study show much smaller than those obtained by conventional method, meaning that polymer particles are prepared from the initially formed monomer-swollen micelles, and that the monomer transportation is not an important phenomenon. In addition, the stability of the polymer beads prepared with SDS is enhanced due to the dense concentration of a negative charge from SDS, so the magnitude of ζ - potential increases.

Effect of the concentration of SDS on polymerization

In order to study the influence of the SDS concentration on polymerization and on the resultant polymer particles, 8.7, 17.3, and 34.7 mM of SDS was added. It is noted that

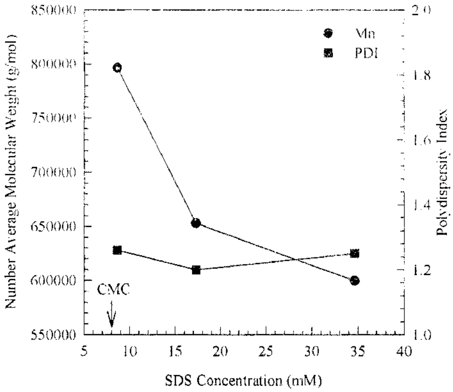

Figure 4: Number-average molecular weight and polydispersity index of the PMMA beads prepared with 5.0×10^{-4} mol RAFT agent by varying concentration of SDS at 70 °C.

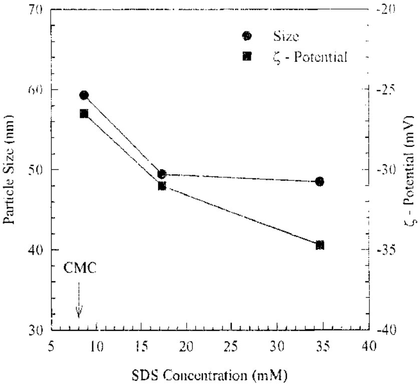

Figure 5: Particle size and ζ - potential of the PMMA beads prepared with 5.0×10^{-4} mol RAFT agent by varying concentration of SDS at 70 °C.

the CMC of SDS in DDI water at room temperature is 8.1 mM [14]. Figure 4 depicts the molecular evolution of the PMMA prepared by 5.0×10^{-4} mol RAFT agent and with various concentrations of SDS at 70 °C. The number-average molecular weight shows a significant decrease with the SDS concentration. It is obvious that the augmentation of SDS concentration generates a greater number of micelles and the amount of monomer trapped in each micelle correspondingly decreases. On the other hand, the PDI is not affected by the concentration of SDS. The number-average molecular weights obtained in this experiment are in the range of 800,000 - 550,000 g/mol which are much higher than those obtained from RAFT (mini)emulsion polymerizations (10,000 - 120,000 g/mol) [5,6,7]. Monteiro and de Barbeyrac [7] founded that an increased SDS concentration expedites the polymerization rate, and reduces particle diameter, however, hardly affects the molecular weight and PDI in the RAFT emulsion polymerization of styrene. The particle size and ζ-potential of the PMMA beads prepared at various concentrations of SDS are shown in Figure 5. Particle sizes are 59.3, 49.4, and 48.5 nm at 8.7, 17.3, and 34.7 mM of SDS. It is seen that the diameter of the particles significantly decreases up to the two-fold SDS concentration than its CMC and varies marginally with further increasing SDS concentration. However, the magnitude of ζ-potential continues to increase with increasing SDS concentration, endowing a higher stability.

Conclusion

Living radical emulsion photopolymerization of MMA using a RAFT agent which plays a role of an initiator, a chain-transfer agent, and a surfactant was conducted and stable spherical beads were successfully obtained without an aid of a surfactant or a thermal initiator. In the absence of SDS, a higher temperature leads to the faster conversion, the higher PDI, and the higher molecular weight, while the smaller particles and the lower magnitude of ζ-potential. In the presence of a constant concentration of SDS, the higher conversion, the higher but consistent molecular weights, the more or less constant PDI are obtained. Upon increasing the SDS concentration, the number-average molecular weights with a marginal change in PDI and the particle size show a significant decrease with increasing SDS concentration. In addition, the stability of the polymer beads was enhanced with increasing SDS concentration.

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