A Novel Estimation Method of the Distribution of Carboxyl Groups Within Copolymer Particles Using Isothermal Titration Calorimeter**

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Summary: A novel quantitative method using isothermal titration calorimeter (ITC) for the estimation of the distribution of carboxyl groups within polymer particles has been proposed. The method has been employed to clarify the difference in the distribution between the particles prepared by batch emulsion copolymerization of styrene and methacrylic acid under inefficient and efficient stirring conditions. At inefficient stirring, monomer was floating as a layer on the aqueous medium, whereas at efficient stirring, the monomer phase was dispersed as droplets. Under inefficient stirring, methacrylic acid (MAA) polymerized faster than styrene (S) due to a slower diffusion rate of S than MAA into the aqueous medium, while under efficient stirring, S and MAA copolymerized at similar rates. ITC measurement showed that under inefficient stirring, the carboxyl groups were distributed mainly in the center of the particles, and their number decreased toward the surface. On the other hand, under efficient stirring, carboxyl groups were distributed homogeneously inside the particle.

Keywords: carboxyl group; emulsion polymerization; isothermal titration calorimeter; polymer particle

Introduction

Carboxyl groups are generally introduced into polymer particles by emulsion copolymerization involving unsaturated acid monomers such as methacrylic acid (MAA) and acrylic acid in order to impart chemical reactivity onto polymer particles and to improve the stability of polymer emulsions.[1–7] There is currently no satisfactory quantitative method to estimate the distribution of carboxyl groups within polymer particles. In our previous research, estimation of the amount of sulfate groups at the polystyrene particle surface prepared by emulsion polymerization was possible even with less than 0.03 g polystyrene particles by isothermal titration calorimeter (ITC),[8] which is a useful microanalytical method based on heat analysis frequently employed in the biochemical field.[9,10] Moreover, semiquantitative estimation of the distribution of carboxyl groups within butyl methacrylate - MAA copolymer particles, which were prepared by emulsion copolymerization with different monomer addition methods (batchwise and continuous-feed), has been successful.[5] The glass transition temperature (T_g) of the copolymer particles ($T_g = 23\,^\circ C$) was lower than the measurement temperature (35 °C). The ITC titration curves indicate that KOH diffused into the interior of the particles.

Recently, we reported that the distribution of carboxyl groups inside the particles, as influenced by the stirring mode during emulsion copolymerization of S and MAA, might strongly affect the formation of the multihollow particles.[11] In that study, the

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emulsion copolymerization was carried out in two stirring modes, which were controlled by changing the position of the stirrer: (a) in aqueous medium below monomer layer or (b) at the interface between the monomer and aqueous layers, as shown in Figure 1. In the former case, the monomer phase was floating on the aqueous medium; this was referred to as ''inefficient'' stirring (Figure 1a). In the latter case, the monomer phase was dispersed as droplets, which was referred to as ''efficient'' stirring (Figure 1b). It was qualitatively suggested on the basis of TEM observation of the ultrathin cross-sections that in the case of inefficient stirring, carboxyl groups were unevenly distributed in the central part of the particle, while in the case of efficient stirring, carboxyl groups were homogeneously distributed within the particle. When these particles were treated by the alkali/cooling method proposed by the authors,[12–17] the multihollow structure was observed in the particles using inefficient stirring, but not with efficient stirring. This seems to be based on the difference in the distribution of carboxyl groups within the particles. Sajjadi et al. have reported on the kinetics of emulsion polymerization in different stirring systems (referred to as ''diffusion-controlled'' and ''kinetics-controlled'').[18,19] They discussed the nanoparticle formation from the perspective of the particle size, their number and surface tension. Only homopolymerizations were examined.

In this article, there is proposed a novel method of estimation of the distribution of carboxyl groups within S-MAA copolymer [P(S-MAA)] particles prepared by batchwise emulsion copolymerization of S and MAA with a nonionic emulsifier using different stirring modes by ITC and the difference in the distributions of carboxyl groups within particles will be clarified.

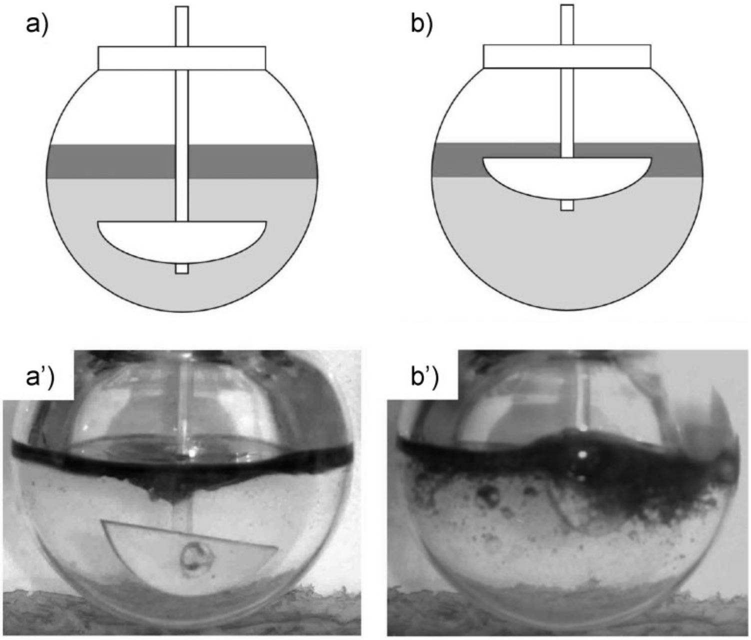


Figure 1.
Models of the stirrer in batchwise emulsion copolymerization (a, a') stirring below the monomer phase (*inefficient stirring*) and (b, b') stirring at the interface between monomer and aqueous phases (*efficient stirring*).

Experimental Part

Materials

S (Mitsubishi Chemical Co, Japan) and MAA (Nacalai Tesque Inc., Kyoto, Japan) were purified by distillation under reduced pressure. Potassium persulfate (KPS, (Nacalai Tesque Inc., Kyoto, Japan)) of analytical grade was purified by recrystallization. A non-ionic emulsifier poly(oxyethylene) nonylphenyl ether (Emulgen 911, Kao Corp, Tokyo, Japan; hydrophilic-lipophilic balance (HLB) = 13.7) and potassium hydroxide (KOH, Nacalai Tesque Inc., Kyoto, Japan) were used as supplied. The water used in all experiments was obtained from a Elix® UV (Millipore Co., Ltd., Japan) purification system; with a resistivity of 18.2 MΩ cm^{-1}.

Emulsion Copolymerization

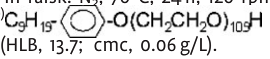
Two kinds of P(S–MAA) particles were prepared by batchwise emulsion copolymerization under the conditions listed in Table 1, using different stirring modes (inefficient or efficient stirring) shown in Figure 1 as well as in the previous article.[11]

During emulsion copolymerization, at regular intervals, samples of polymer emulsions (with a polymer solid content of 1∼2 g) were withdrawn from the bottom of the reactor, after stopping the stirring, to allow formation of an upper monomer layer. The samples were rapidly cooled after adding a few drops of aqueous solution of hydroquinone to stop the polymerization. The overall conversion was determined gravimetrically. The monomer conversions were determined by gas chromatography (GC) (Shimadzu Corporation, GC-18A). The concentration of S in the particles was calculated by subtraction of the saturated S concentration in the water phase (GC). The particle morphology was observed with a transmission electron microscope (TEM) (JEM-1230, JEOL Ltd.; Tokyo, Japan).

Table 1.
Recipe for the preparation of P(S-MAA) particles by batch emulsion copolymerizations[a] under different stirring conditions.

Ingredients		
Styrene	(g)	55.0
MAA	(g)	5.0
KPS	(g)	0.24
Emulgen 910	(g)	4.0
Water	(g)	540

[a] In falsk: N_2; 70°C; 24 h; 120 rpm;

[b] 

$C_9H_{19}-C_6H_4-O(CH_2CH_2O)_{10}-H$

(HLB, 13.7; cmc, 0.06 g/L).

The emulsion samples for ITC measurements were purified by addition of a tenfold amount of methanol (to instantaneously remove the monomer from the particles) and subsequent centrifugal washing with water three times to replace methanol and remove sulfuric acid. The solid content was adjusted to *ca.* 1 wt%.

Quantitative Estimation of MAA Units at the Particles Surface

The amount of MAA units was estimated from the heat of neutralization of the MAA carboxyl groups and KOH by isothermal titration (calorimeter model 4200 ITC, Calorimetry Science Corp., Utah, USA) at 25 °C. 0.05 M aqueous KOH (1 mL) was added to the sample and reference cells and 25 μL of the purified sample emulsion was titrated four times in the sample cell. The amount of MAA units at the particle surface was determined from the peak area using a calibration curve obtained with aqueous solutions of MAA of known concentrations.

Measurement of Glass Transition Temperature of Base Polymer in Emulsion State (Tg_E)

T_{gE} was measured by nano-DSC (nano-DSC6200, Calorimetry Science Corp., Utah, USA) in the range 0 °C–110 °C at a rate of 1 °C/min. The T_{gE} value was obtained from the maximum of the differential curve of the second heating curve.

Results and Discussion

Figure 2 shows TEM photographs of purified P(S-MAA) particles prepared by batch emulsion copolymerizations (see

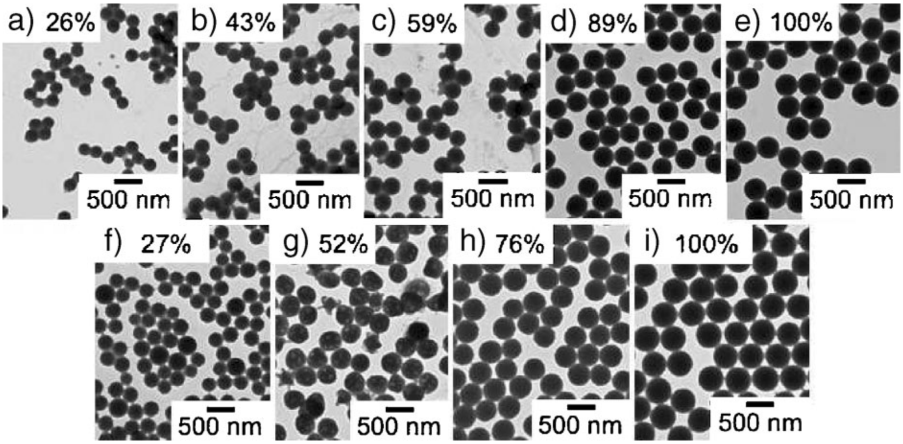


Figure 2.
TEM photographs of P(S-MAA) (MAA: 10 mol%) particles prepared by batch emulsion copolymerizations (see Table 1) with inefficient (a–e) and efficient (f–i) stirring.

Table 1) with inefficient (a–e) and efficient (f–i) stirring. In both stirring systems, close-to-monodisperse particles were prepared without coagulant, although a small amount of by-product particles were obtained in the inefficient stirring system. With efficient stirring (Figure 2g), hollow particles were observed at 52% conversion. The S concentration in the particles obtained at this conversion was 4 mol/L of particles (see Figure 5). The formation of the hollow structure seems to be based on the incorporation of nonionic emulsifier[20] and the remaining monomer. This will be discussed elsewhere.

Figure 3 shows the conversion-time curves for the emulsion copolymerizations of S and MAA (see Table 1) with inefficient (a) and efficient (b) stirring. At the early stage of the polymerization with inefficient stirring (Figure 3a), MAA was consumed preferentially. On the other hand, with efficient stirring (Figure 3b), S and MAA were consumed at almost the same rate.

Figure 4 shows average MAA contents in P(S-MAA) formed in the specific conversion ranges calculated from individual conversion-time data (Figure 3) in both stirring modes. MAA-rich polymer was formed at the early stage of the

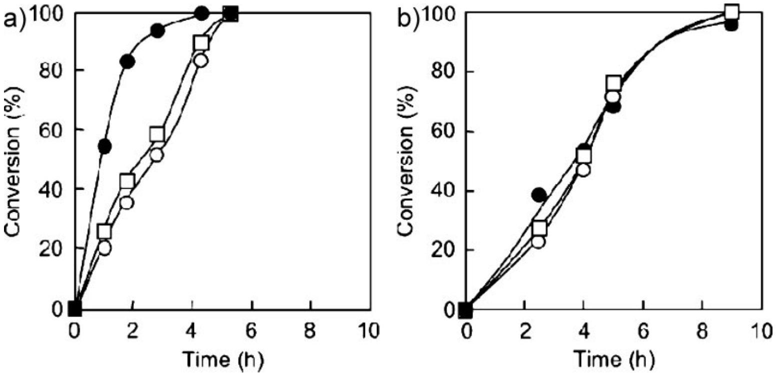


Figure 3.
Conversion-time curves for batch emulsion copolymerizations (see Table 1) showing overall (□), S (○) and MAA (●) conversions with inefficient (a) and efficient (b) stirring.

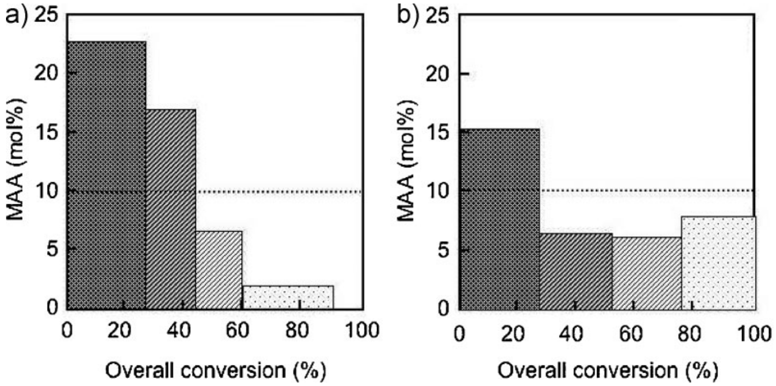


Figure 4.
MAA content of P(S-MAA) (see Table 1) in specific conversion ranges (calculated from conversion-time data in Figure 3) in batch emulsion copolymerizations (see Table 1) with inefficient (a) and efficient (b) stirring.

polymerization with inefficient stirring, the MAA content decreasing with increasing conversion. On the other hand, in the case of efficient stirring, the MAA content remained almost constant except for the early stage. This difference is based on the effect of stirring in agreement with previous studies.[11] In the case of inefficient stirring, S diffuses slowly from the monomer phase to the aqueous medium because the total interface area is much smaller than in the case of efficient stirring. Therefore, the S supply rate to the polymerizing particles via the aqueous medium would be low for inefficient stirring. In order to clarify this point, the S concentration in the polymerizing particles was measured during the polymerization.

Figure 5 shows the relationship of the conversion and S concentration in the particles during the copolymerizations. In the case of inefficient stirring, the concentration was less than 1 mol per L of particles and remained fairly constant during the polymerization. This corresponds to close to 10 vol% of S in the particles. Even at a low conversion of 27%, the S concentration was only 0.72 mol per L of particles. This result indicates that the mobility of copolymer chains in the polymerizing particles seems to be extremely low. Therefore, with inefficient stirring, it seems that the particles would grow in a fashion similar to that in seeded dispersion polymerization,[21] i.e. growth would mainly occur in the particle surface layer. On the other hand, in the case of efficient stirring (open circles), the S concentration at 27% conversion was very similar to the saturated monomer concentration (5.4 mol per L of particles), and then decreased with conversion. Polymer chains would thus be mobile in the particles except at high conversions.

T_{gE} values of monomer swollen P(S-MAA) particles, in which the monomer concentrations were the same as those at the 26% (inefficient stirring) and 27%

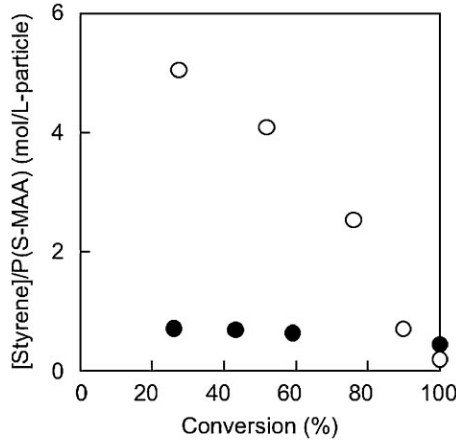


Figure 5.
Styrene concentration in the P(S-MAA) particles as functions of conversion in emulsion copolymerizations (see Table 1) with inefficient (●) and efficient (○) stirring.

(efficient stirring) conversions, were measured with nano-DSC in the emulsion state. In the case of inefficient stirring, T_{gE} was 85 °C, which was above the polymerization temperature (70 °C). On the other hand, with the efficient stirring, T_{gE} was not detected between 0 °C and 110 °C. These results support the above ideas about the mobility of polymer chains in the polymerizing particles.

The above results suggest that the distribution of carboxyl groups within P(S-MAA) particles prepared with inefficient and efficient stirring are different. In order to clarify this point, a novel quantitative analysis for the estimation of distribution of carboxyl groups within the particles utilizing ITC was proposed. First, as described in the experimental part, the monomer remaining in the particles after each conversion was removed without altering the configuration of polymer chains in the particles. Therefore, only the MAA units located at the particle surface would be titrated in the ITC measurements at 25 °C.

Figure 6 shows a typical ITC chart for the heats of neutralization of carboxyl groups whit aqueous 0.05 M KOH; the titration was carried out three times. The neutralization of the sample emulsions was finished within 90 s (also of the aqueous MAA solution). This indicates that only carboxyl groups at the particle surface were detected.[5] However, for purified emulsion samples at 26% and 43% conversions with inefficient stirring, 130 s was required for the complete reaction. This may be due to the penetration of some KOH into the particles because of alkali swelling of the surface layer where numerous carboxyl groups occur.

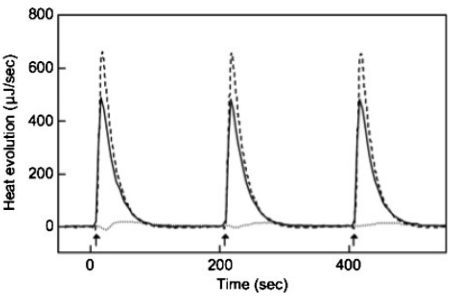


Figure 6.
ITC charts of the reaction of 1 mL of 0.05 M KOH and 25 μL of aqueous MAA solution (——) or P(S-MAA) emulsion (------). $T = 25$ °C. Arrows indicate the sample injection.

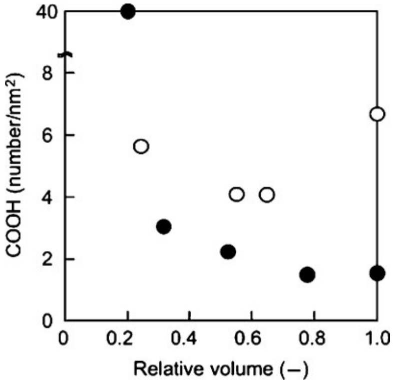


Figure 7.
The number of carboxyl groups at the surface of P(S-MAA) (MAA 10 mol%) particles prepared by batch emulsion copolymerizations with inefficient (●) and efficient (○) stirring as estimated from ITC data at 25 °C.

Figure 7 shows the relationships between the relative volume of P(S-MAA) particles at each conversion and the number of carboxyl groups per unit surface area of the purified P(S-MAA) particles during the emulsion copolymerizations with inefficient and efficient stirring. With inefficient stirring, the carboxyl groups were distributed mainly in the centre of the particles, and their number decreased toward the particle surface. This indicates that MAA-rich copolymer chains formed at the early stages did not diffuse to the particle surface (water phase) during the polymerization. However, in the case of efficient stirring, approximately the same amounts of carboxyl groups were observed regardless of the diameters of the particles.

In order to clarify in more detail the difference in the distributions of carboxyl groups within the particles prepared with inefficient and efficient stirring, both types of P(S-MAA) particles were heated at 70 °C after absorption of the three-fold volume of 4-methylpentan-2-one (MIBK)

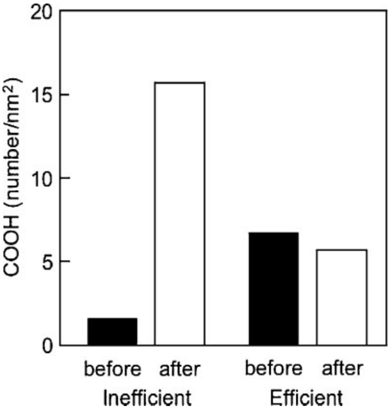


Figure 8.

The number of carboxyl groups at the surface of P(S-MAA) particles measured by ITC at 25 °C. The particles were prepared by batch emulsion copolymerizations with different stirring modes heat treated with MIBK (■ before and ☐ after treatment).

at 25 °C. During the heat treatment, polymer chains should be highly mobile inside the particles, which resulted in rearrangement of chains to reach the thermodynamically stable state. Before the ITC measurement at 25 °C, MIBK was removed from the particles.

As shown in Figure 8, the number of carboxyl groups at the particle surface prepared with inefficient stirring increased remarkably after the treatment. This indicates that the carboxyl groups buried inside the particles were redistributed coming to the surface because of their hydrophilicity.[4,22] With efficient stirring, however little change was observed after the treatment. This suggests that the polymer chains were arranged in a thermodynamically stable state before the treatment.

The two objectives were achieved. A novel method was proposed for the estimation of distribution of carboxyl groups within polymer particles by isothermal titration calorimeter. The effect of stirring in the emulsion copolymerization of S and MAA with nonionic emulsifier on the distribution of carboxyl groups within particles was clarified using the proposed method.

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