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Estimation of distribution state of carboxyl groups within submicron-sized, carboxylated polymer particle with isothermal titration calorimeter

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were titrated by isothermal titration calorimetry with an extremely small amount (ca. 2 mg) of the particles.

Keywords Isothermal titration calorimetry · Carboxyl group · Distribution · Emulsion copolymerization · Particle

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Abstract A novel technique to estimate the distribution state of carboxyl groups within submicron-sized, carboxylated polymer particles was proposed. For the purpose, carboxyl groups in two kinds of butyl methacrylate–methacrylic acid copolymer emulsion, which were prepared by emulsion copolymerizations with different monomer addition methods,

Introduction

To confer chemical reactivity to polymer particles and to improve the colloidal stability of polymer emulsion, carboxyl groups are generally introduced to polymer particles by emulsion copolymerization with such an unsaturated acid monomer as methacrylic acid (MAA) and acrylic acid [1, 2]. In some cases, only carboxyl groups distributed at surface layer were useful [3–6]. A lot of studies have shown that the concentration of carboxyl groups is higher at the surface than in the inside because of high hydrophilicity. However, the absolute amount of carboxyl groups is much more in the inside than at the particle surface because the volume of the inside is much larger than that of surface layer [7, 8]. Recently, we found that the distribution of carboxyl groups inside the particles

was markedly influenced by the stirring state in emulsion polymerization of styrene (S) and MAA [9]. In actual, 93% of carboxyl groups were buried inside the S–MAA copolymer particles.

In most of studies on carboxylated polymer emulsions, potentiometric and conductometric titrations have been used to estimate the amounts of carboxyl groups at particle surfaces and in an aqueous medium [10, 11]. If the total amount of carboxyl groups in the particles or in the polymer emulsion is a known quantity, the amount of carboxyl groups inside the particles can be calculated by subtraction. Muroi [12] estimated the distribution state of carboxyl groups within ethyl acrylate–acrylic acid copolymer particles produced by emulsion polymerization. The estimation was carried out by stepwise conductometric

titrations of carboxyl groups in the copolymers dissolved continuously under the ultracentrifugation at alkaline conditions with a large amount of the samples (ca. 20 g), assuming that they were stripped continuously from the particle surfaces. They obtained a valuable result, but the method cannot be applied for carboxylated polymer particles from which polymer molecules do not dissolve under ultracentrifugation at alkaline conditions. In this way, there has been no satisfactory quantitative method to estimate the distribution state of carboxyl groups within particle.

In the biochemical field, isothermal titration calorimetry (ITC) is one of useful microanalysis. This method offers the potential advantage that a quantitative analysis can be done even with an extremely small amount of sample. In a previous paper, the estimation of sulfate groups as initiator fragments at polystyrene (PS) particle surfaces with ITC was possible even with 30 mg sample [13]. Because T_g of the PS particles at emulsion state was 96 °C, KOH used as titrant did not diffuse inside.

In this article, to estimate the distribution state of carboxyl groups within polymer particle having low T_g , the amounts of carboxyl groups within two kinds of *n*-butyl methacrylate (BMA)–MAA copolymer [P(BMA–MAA)] particles, which were prepared by emulsion polymerization with different monomer addition methods, will be measured with ITC as a function of the reaction time with KOH.

Experimental

Materials

BMA and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere. Deionized water with a specific conductivity of $5 \times 10^6 \Omega \text{ cm}$ was distilled. Potassium hydroxide (Nacalai Tesque, Japan) and 4,4'-Azobis-4-cyanovaleric acid (V-501, Wako Pure Chemical Industries, Japan) were purified by recrystallization as received. Cation-exchange resin (AMBERLITE IR-120B, ORGANO, Japan) was treated with 1 N hydrochloric acid to change to H⁺ form.

Preparation of carboxylated polymer emulsions

Emulsion copolymerizations of BMA and MAA were carried out under the conditions listed in Table 1 utilizing batch and uniform-feed monomer addition methods. The obtained two kinds of P(BMA–MAA) emulsions were purified by ultracentrifugal washing with distilled water five times, and were deionized with cation-exchange resin.

Table 1 Recipes for the preparation of two kinds of P(BMA–MAA) particles by emulsion polymerizations utilizing batch and uniform-feed monomer addition methods (MAA, 5.0 mol%)

Ingredients		Batch ^{a)}	Feed ^{a)}
BMA	(g)	29.1	29.1 ^{b)}
MAA	(g)	0.9	0.9 ^{b)}
V-501	(g)	0.15	0.15
Tween 80	(g)	1.5	1.5
Water	(g)	200	200
Dh ^{c)}	(nm)	260	267
Tg ^{d)}	(°C)	23.5	23

^{a)}N₂; 70 °C; 24 h; stirring rate, 150 rpm

^{b)}Added as mixture solution at the rate of 2.6 g/h for 24 h

^{c)}Hydrodynamic diameter measured by dynamic light scattering

^{d)}Measured by differential scanning calorimeter

Abbreviations: BMA, *n*-butyl methacrylate; MAA, methacrylic acid; P(BMA–MAA); BMA–MAA copolymer, V-501; 4,4'-Azobis-4-cyanovaleric acid; Tween 80, polyoxyethylene sorbitan monooleate

Measurement of the heat of neutralization reaction by ITC

Measurement of the heat of neutralization reaction between carboxyl groups and KOH was carried out with an isothermal titration calorimeter (CSC, Model 4200). The solid content of the emulsion for the ITC measurement was adjusted at 8.6 wt%.

Results and discussions

Figure 1 shows ITC charts at 25 °C for 1 ml of P(BMA–MAA) (a) and PS (b) emulsions, and distilled water (c) with 25 μl of 0.05 N KOH aqueous solution in which the amount of KOH was equivalent to two times that of carboxyl groups in the P(BMA–MAA) emulsions. Heat evolved in the chart (b) for the PS emulsion included the heats of mixing and dilution, which were estimated from the heats evolved in the chart (c) for the distilled water, in addition to that of the neutralization reaction. In comparison with the charts of (b) and (c), the area of the first peak was much larger than that of the distilled water, and their second and third peaks were the same. These indicate that in the first addition of KOH aqueous solution into the PS emulsion that had sulfate groups as initiator end groups at the particle surfaces, the neutralization reaction of surface groups was completely over within 100 s. On the other hand, in the chart (a) of the “batch” P(BMA–MAA) emulsion, which was prepared by batch emulsion copolymerization, the heat evolved still beyond 200 s, and it decreased with the number of the KOH addition. These results suggest that the titration of carboxyl groups by KOH proceeds gradually from the surface to the inside of the P(BMA–MAA) particle.

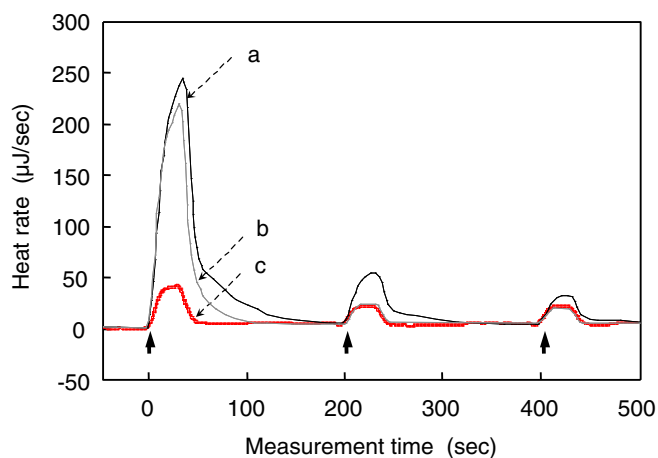


Fig. 1 Titration charts of 1 ml of PS (a) and batch P(BMA-MAA) emulsion (b) with 0.05 N KOH (25 μ l) three times using isothermal titration calorimeter at 25 $^{\circ}$ C. Arrows indicate the injection points of KOH

Figure 2 shows the relationships between the measurement temperature of ITC and the accumulated percentage of the carboxyl groups titrated with the addition frequency of KOH. With an increase in the frequency of KOH addition, the percentage of the neutralized carboxyl groups was almost the same below 25 $^{\circ}$ C, but it was clearly increased above 25 $^{\circ}$ C which corresponds to T_g of the base polymer. These results indicate that at the temperature below the T_g , carboxyl groups at the particle surface layer are only titrated because KOH does not diffuse into the inside of the particles, and above T_g , the neutralization of carboxyl groups proceeds in the inside because excess amount of KOH seems to be necessary to neutralize carboxyl groups inside the particle.

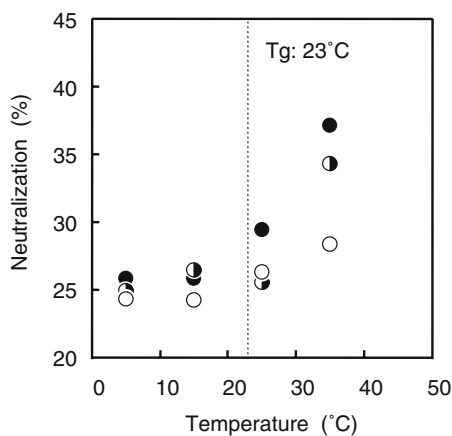


Fig. 2 Percentages of neutralization reaction of carboxyl groups in 1 ml P(BMA-MAA) batch emulsion (MAA content, 5 mol%; solid content, 0.23 wt%) at various temperature with the addition of 25 μ l of 0.05 N KOH: \circ one time; \bullet three times; \bullet five times. Time for each titration, 200 s

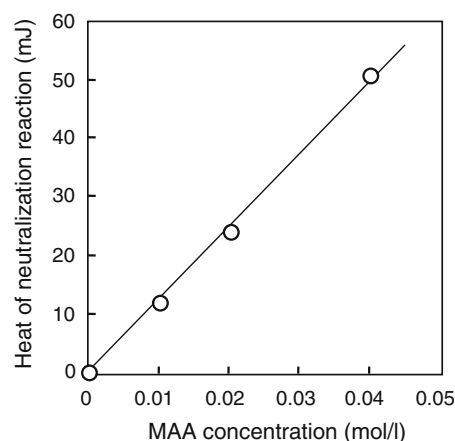


Fig. 3 Relationship between MAA concentration in aqueous solution (25 μ l) in the syringe and the heat of neutralization reaction generated with 0.1 N KOH (1 ml) in the cell at 35 $^{\circ}$ C

KOH and the sample emulsion were, respectively, replaced each other to ITC cell and injection syringe, where 1 ml of 0.1 N KOH in the cell was equivalent to about 90 times amount of carboxyl groups in 25 μ l of P(BMA-MAA) emulsion, of which solid content was around 8 wt%, in the syringe. In this titration system, the ratio of the total heat of mixing and dilution to all the evolved heat was decreased below 0.1. A good liner relationship was established between the concentration of MAA aqueous solution and the heat of neutralization reaction as shown in Fig. 3.

P(BMA-MAA) emulsion was also prepared by emulsion copolymerization with uniform-feed monomer addition method, which were named "feed" P(BMA-

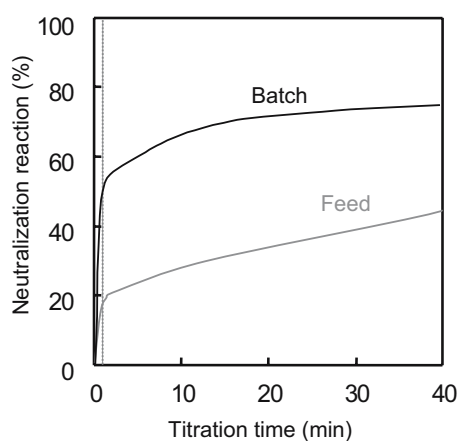


Fig. 4 Neutralization reactions of carboxyl groups of two types of P(BMA-MAA) emulsions (25 μ l) with 1 ml of 0.1 N KOH at 35 $^{\circ}$ C, which were prepared by emulsion polymerization using batch (—) and feed (---) monomer addition methods. KOH/COOH=90

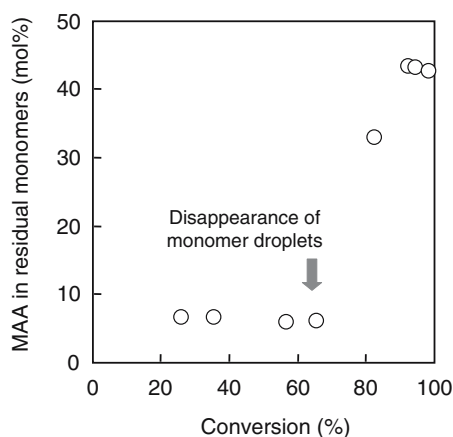


Fig. 5 Relationship between the total conversion and the residual MAA in water and growing particle phases of the batch emulsion polymerization of BMA and MAA (MAA, 5 mol%)

MAA) emulsion, under the same recipe as the “batch” P (BMA–MAA) emulsions. The batch and the feed P(BMA–MAA) emulsions were separately mixed with H^+ form cation-exchange resin for 5 h to change from $-COO^-$ to $-COOH$ after ultracentrifugal washing with distilled water.

Figure 4 shows the relationships between the titration time and the percentages of carboxyl groups titrated with 0.1 N KOH (1 ml) at 35 °C for the batch (a) and the feed (b) P(BMA–MAA) emulsions (25 μ l). In the feed emulsion, only 17% of the total carboxyl groups were titrated in 80 s and then the percentage was increased linearly by 0.5%/min. Because the feed emulsion copolymerization proceeded under a monomer-starved state, it seems that the polymer composition had a sharp distribution, which should result in homogeneous distribution of the carboxyl groups within the particle. On the other hand, in the batch emulsion, 56% of the total carboxyl groups reacted in 80 s, and then 40 min was needed to increase the percentage by 10%. These results suggest that the batch emulsion had many carboxyl groups near the particle surface and the amount decreased toward the center of the particle.

Figure 5 shows variation of the MAA content in residual monomers throughout the batch emulsion copolymerization. In the conversion range of 25 to 65%, the MAA content in the batch emulsion was almost steady at 7 mol% because the monomers supplied constantly from monomer droplets, and then increased markedly, around the conversion of 70% at which the monomer droplets disappeared. P (BMA–MAA) formed at a final stage above 90%, had high MAA contents over 30 mol% as shown in Table 2. This result indicates that in this copolymerization, BMA was

Table 2 Residual BMA and MAA and the MAA content in P (BMA–MAA) prepared at a final stage of the batch emulsion polymerization

Total Conversion (%)	Conversion (%)		MAA content ^{a)} (mol%)
	BMA	MAA	
77	99	65.6	15.2
87	99.4	67.3	
93	99.5	96.5	32.9
96	99.6	97.6	

^{a)} calculated MAA content of P(BMA–MAA) prepared in the conversion ranges between 77–87% 87–93%, and 93–96%

predominantly copolymerized and MAA-rich copolymer was prepared in the final stage.

The reactivity ratio between BMA (monomer 1) and MAA (monomer 2) are as follows: $r_1=1.15$ and $r_2=0.73$ [14]. These values indicate that BMA is predominantly polymerized, resulting in MAA-rich copolymer at the latter stage of the batch emulsion polymerization. That is, these are good agreement with the above ITC data that many carboxyl groups existed near the particles' surface.

In addition, although 75% (based on total MAA polymerized) of carboxyl groups in the batch P(BMA–MAA) particles were titrated for 40 min at 35 °C, it was almost the same as that titrated at 50 °C. The total amount of carboxyl groups included PMAA-rich copolymers and undecomposed V-501 dissolved in the aqueous medium, which was also measured with ITC, corresponded to 15.3% of the carboxyl groups. These results indicate that about 90% of the carboxyl groups within the batch P(BMA–MAA) particle were titrated under the conditions. The copolymer composition was analyzed by 1H NMR, but there was no repeatability in the integration because the amount of fed MAA was small. The composition analysis needs further consideration.

From the above results, it is concluded that the estimation of carboxyl groups of carboxylated particles with ITC gives a useful information about the distribution state of carboxyl groups within the particle even with an extremely small amount of sample.

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