Colloid Polym Sci (2006) 284: 802–806
DOI 10.1007/s00396-005-1445-8

SHORT COMMUNICATION

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Estimation of water absorption state within ionized carboxylated polymer particles with high sensitive differential scanning calorimetry

Received: 17 August 2005
Accepted: 1 October 2005
Published online: 8 February 2006

Part CCLXIX of the series, "Studies on Suspension and Emulsion."

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Abstract Glass transition temperature (*T*g) of submicron-sized, carboxylated polymer particles dispersed in aqueous media, which were prepared by emulsion copolymerization of styrene, *iso*-butyl methacrylate, or methyl methacrylate with methacrylic acid, was measured at alkali or acidic pH region with a power compensation-type high sensitive differential scanning calorimeter. The *T*g of relatively hydrophilic polymer particles was obviously decreased by the neutralization of the carboxyl groups with KOH, whereas that of hydrophobic polymer particles was not changed though water was absorbed therein. These results indicate that water absorption state, which means not only the amount of water absorption but also the heterogeneity of the ionized carboxylated polymer particles, markedly depends on the hydrophilicity of their base polymers. This strongly supports the formation mechanism of multihollow particles by the stepwise alkali/acid or the alkali/cooling treatments of carboxylated polymer particles proposed by the authors.

Keywords Glass transition temperature · Differential scanning calorimeter · Particle · Emulsion polymerization · Plasticization · Carboxyl group · Hollow

Introduction

Carboxylated polymer emulsion, which is produced by emulsion copolymerization with unsaturated acid monomer such as methacrylic and acrylic acids, has been widely applied industrially [1, 2]. In our series of studies about carboxylated polymer particles, it was found that styrene (S)-butyl acrylate-methacrylic acid (MAA) terpolymer particles prepared by emulsion copolymerization were changed to those having many hollows inside the particles by stepwise treatments with alkali and acid [3]; this was named the stepwise alkali/acid method. In following articles, the effects of some factors in each treatment [4, 5] on the formation of the multihollow structure were examined in detail. Moreover, multihollow S-MAA copolymer [P(S-MAA)] particles having a high glass transition temperature (*T*g) were also prepared by the stepwise alkali/acid method [7]. The formation mechanism of the multihollow structure by the stepwise alkali/acid method was discussed from the viewpoints of the interfacial-free energy [8] of aqueous dispersions of P(S-MAA) particles before and after the stepwise alkali/acid treatments as follows. In the alkali treatment process, the ionized P(S-MAA) particle absorbed a certain amount of water as a lot of water pools, of which size is too small to be observed with transmission electron microscope. When acid is added to the alkali treated emulsion, the interfacial tension between the water pool and the polymer drastically increases because of deionization of the carboxyl group. In the acid treatment process, accordingly, the water pools coagulate to reduce the total interfacial-free energy between the water pool and the polymer and result in hollows inside the particles. However, there has been no direct proof showing the existence of the water pools.

In a previous study, the *T*g values of three kinds of poly (methyl methacrylate) (PMMA)-based particles having wide polymer compositions, which were prepared by emulsifier-free emulsion copolymerizations of methyl methacryalate (MMA) with ethyl acrylate, *n*-butyl methacrylate (BMA), or

Table 1 Recipes for the preparation of three kinds of carboxylated polymer emulsions (MAA, 5 mol%) by emulsifier-free emulsion copolymerizations[a] utilizing starved-fed monomer addition method

Ingredients		P(MMA-MAA)	P(*i*BMA-MAA)	P(S-MAA)
MMA[b]	(g)	14.4	–	–
*i*BMA[b]	(g)	–	15.5	–
S[b]	(g)	–	–	14.1
MAA[b]	(g)	0.6	0.5	0.6
KPS	(g)	0.08	0.06	0.20
Water	(g)	285	285	285
Tg[c]	(°C)	109	64	104
Dh[d]	(nm)	310	340	630
Mw[e]	($\times 10^4$)	18	20	12

[a]In flask; 70°C; 24 h; N_2; stirring rate, 200 rpm
[b]The total monomer was added at the rate of 3 g/h for 5 h.
[c]Calculated from Fox's equation
[d]Hydrodynamic diameter measured by DLS
[e]Weight-average molecular weight measured by GPC
Abbreviations: MMA, methyl methacrylate; MAA, methacrylic acid; *i*BMA, *iso*-buthyl methacrylate; S, styrene; KPS, potassium persulfate

MAA, were measured in emulsion and dry states with a power compensation-type high sensitive differential scanning calorimeter (PC-DSC) [9]. They were named as Tg_E and Tg_D. The difference between the Tg_E and the Tg_D values was increased with an increase in the hydrophilicity of the base polymers.

On the basis of the this knowledge, in this article, the absorption state of water inside alkali treated P(S-MAA) particle, which must give a valuable information to clarify the formation mechanism of the multihollow polymer particles described above, will be discussed from the Tg_E measurement in comparison with MMA-MAA copolymer [P(MMA-MAA)] and *iso*-butyl methacrylate (*i*BMA)-MAA copolymer [P(*i*BMA-MAA)] particles.

Experimental

Materials

MMA, *i*BMA, S, and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere. Analytical grade potassium persulfate (KPS) (Nacalai Tesque Inc., Kyoto, Japan) was purified by recrystallization. Commercial grade nonionic polyoxyethylene nonyl phenyl ether nonionic emulsifier with an average of 10.9 ethylene oxides per molecule (Emulgen 911, Kao Co., Tokyo, Japan) was used without further purification. Deionized water was distilled. KOH was used as received from Nacalai Tesque Inc.

Preparation of carboxylated polymer emulsion

P(MMA-MAA), P(*i*BMA-MAA), and P(S-MAA) emulsions (MAA, 5 mol%) were prepared by emulsifier-free emulsion polymerization using starved-fed addition method of a constant monomer composition of a 500-ml four-necked round-bottom flask under the conditions listed in Table 1. The conversions were over 95% by gravimetric measurement. In Table 1, *T*g values of the copolymers were calculated using the Fox's equation with the following *T*g values of homopolymers: poly(MMA) (PMMA), 105°C; poly(*i*BMA) (P*i*BMA), 30°C; polystyrene (PS), 104°C; and poly(MAA) (PMAA), 228°C [10].

Measurement of particle diameter

Each polymer emulsion was diluted to 10 ppm and then the hydrodynamic diameter (D_h) of the particles was measured by dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan) at the light-scattering angle of 90° at room temperature. Expansion of the particle volume by heat treatment at 120°C for 1 h at pH 5 (original emulsion) or 12

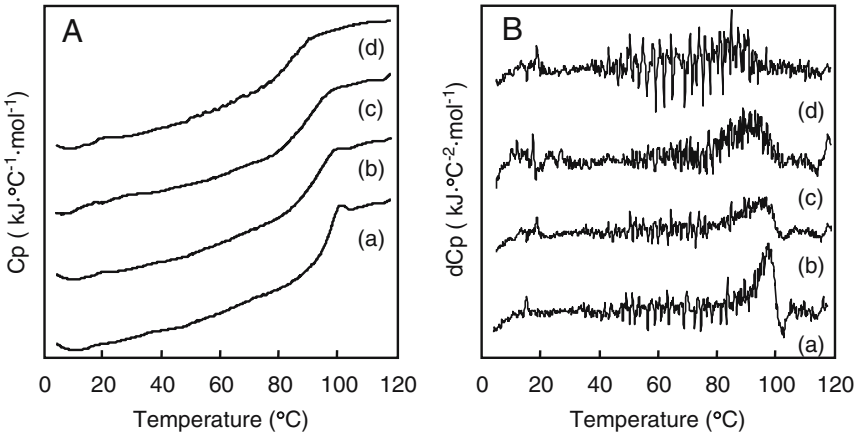

Fig. 1 PC-DSC second heating curves (**a**) and their differential curves (**b**) of P(MMA-MAA) (MAA, 5 mol%) emulsion at pH 5 (**a**) and 12 (**b**–**d**). [KOH]/[MAA] (equivalent ratio): (**a**) 0, (**b**) 0.50, (**c**) 0.75, and (**d**) 1.0

Table 2 Volume expansions of P(MMA-MAA), P(*i*BMA-MAA) and P(S-MAA) particles after alkali treatment ([KOH]/[MAA] (equivalent ration)=1, ph 12, 120°C, 1 h)

	MAA content (mol%)	
	5	10
P(MMA-MAA)	400%	–
P(*i*BMA-MAA)	10%	–
P(S-MAA)	10%	20%

adjusted with KOH aqueous solution was calculated from the following equation:

$$\text{Volume expansion}\ (\%) = \left(\frac{D^3_{\text{h,after}} - D^3_{\text{h,before}}}{D^3_{\text{h,before}}}\right) \times 100$$

where $D_{\text{h,before}}$ and $D_{\text{h,after}}$ mean D_{h} of the particles before and after the heat treatment, respectively.

Measurement of Tg_E

Each polymer emulsion was centrifugally washed three times. The emulsions, of which solid contents were about 3~9 wt%, were adjusted to pH 12 with KOH aqueous solution at various equivalent ratios of KOH to the MAA unit. Tg_E was measured with PC-DSC (nano-DSC 5100, Calorimetry Sciences Co., USA) in the range of 0 to 120°C at the rate of 1°C/min. The measurement was repeated three times. Because the maximum measurement temperature (120°C) is higher than the Tg_E values of the copolymer particles used in this study, the neutralization reaction of carboxyl groups within the polymer particles with KOH would proceed in the first scan. The Tg_E value was obtained as an average value of temperatures (Tg_E^d) indicating at maximum points in second and third differential curves. In the measurement, each emulsion was pressured to 3 atm to prevent water evaporation.

Results and discussion

Figure 1a–d shows PC-DSC second heating curves (a) and their differential curves (b) of P(MMA-MAA) (MAA, 5 mol%) emulsions at pH 5 without KOH (a) and 12 (b–d) adjusted with KOH aqueous solution at various equivalent ratios to the MAA unit. With an increase in the amount of KOH, namely, as the degree of neutralization was increased, Tg_E^d was lowered and the peak became broad below about 85°C.

Volume expansion of the P(MMA-MAA) particles after heat treatment at 120°C for 1 h at pH 12 adjusted with KOH aqueous solution at the same equivalent ratio to the MAA unit is shown in Table 2. The P(MMA-MAA) particles absorbed water as four times as the original particle volume.

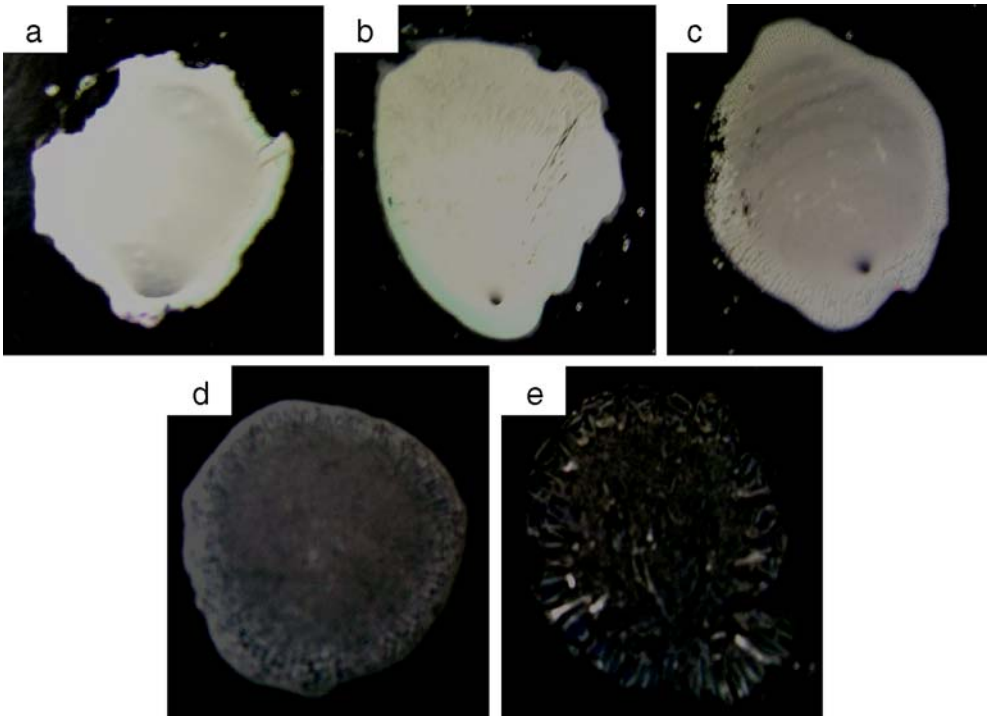

Fig. 2 Photographs of P(MMA-MAA) (MAA, 5 mol%) dried at 4°C on a glass plate cast from the P(MMA-MAA) emulsion after heat treatment [120°C, 1 h, pH 5 (**a**) or 12 (**b**–**e**)]. [KOH]/[MAA] (equivalent ratio): (**a**) 0, (**b**) 0.25, (**c**) 0.50, (**d**) 0.75, and (**e**) 1

Figure 2 shows photographs of P(MMA-MAA) dried at 4°C on a glass plate cast from the P(MMA-MAA) emulsion after the heat treatment at 120°C for 1 h at pH 5 or 12 adjusted with KOH aqueous solution at the various equivalent ratio to the MAA unit. At pH 5, without KOH, the dried polymer was white powder but with the increase in the equivalent ratio of KOH, the polymer formed partially transparent films though it had many cracks.

These results suggest that Tg_E of the P(MMA-MAA) inside the particles was about 85°C while that at the surfaces layer was lower than 4°C. That is, water being absorbed in the particle seems to exist in a heterogeneous state that there is a gradient change of the water content from the surface to the inside.

Figure 3 shows PC-DSC second heating curves of P(*i*BMA-MAA) (MAA, 5 mol%) emulsions at pH 5 without KOH (a) and 12 (b) adjusted with KOH aqueous solution at the same equivalent ratio to the MAA unit. $Tg_E{}^d$ was shifted from 64.2°C of the original particles to 60.4°C by keeping the width of the differential peak by the presence of KOH. This was different from that of the P(MMA-MAA) particles. Volume expansion of the P(*i*BMA-MAA) particles was much lower than that of the P(MMA-MAA) particles because the hydrophilicty of P*i*BMA is lower than PMMA. The P(*i*BMA-MAA) dried at 4°C was white powder regardless of the pH at the heat treatment. These results suggest that the P(*i*BMA-MAA) particles absorbed much less water than that of the P(MMA-MAA) particles and the water existed relatively and uniformly in the P(*i*BMA-MAA) particles.

Figure 4 shows PC-DSC second heating curves of P (S-MAA) (MAA, 5 mol%) emulsion at pH 5 without KOH (a) and 12 (b–e) adjusted with KOH. Tg_E values of the P (S-MAA) emulsion at pH 12 adjusted with KOH aqueous solution at the same (b) and twice (c) equivalent ratios to MAA unit were the same as that of the original emulsion at pH 5 (a). Moreover, although the KOH-added emulsions were kept in an oil bath at 150°C for 1 week, their PC-DSC curves (d,e) were similar to that of the original emulsion (a). As shown in Table 2, volume expansion of the P(S-MAA) particles after the heat treatment was the same as that of the P(*i*BMA-MAA) particles. The Tg_E of the P(*i*BMA-MAA) particles was decreased by the neutralization, on the other hand, that of the P(S-MAA) was not changed. Even if the MAA content was increased to 10 mol%, there was no effect of the neutralization on the Tg_E of the P(S-MAA) (MAA, 10 mol%) particles as shown in Fig. 5, although its volume expansion was clearly increased. These results indicate that the absorbed water molecules do not plasticize PS phase. In other words, they suggest that the water molecules within the alkali-treated P (S-MAA) particles localize only around the ionized carboxyl groups because of high hydrophobicity of PS. This strongly support the formation mechanism of the multi-hollow P(S-MAA) particles by the stepwise alkali/acid [8].

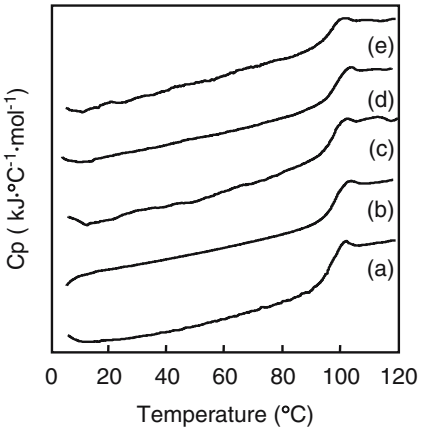

Fig. 4 PC-DSC second heating curves of P(S-MAA) (MAA, 5 mol%) emulsion at pH 5 (**a**) and 12 (**b**–**e**) before (**a**–**c**) and after (**d**, **e**) heat treatment at 150°C for 1 week. [KOH]/[MAA] (equivalent ratio): (**a**) 0, (**b**, **d**) 1, and (**c**, **e**) 2

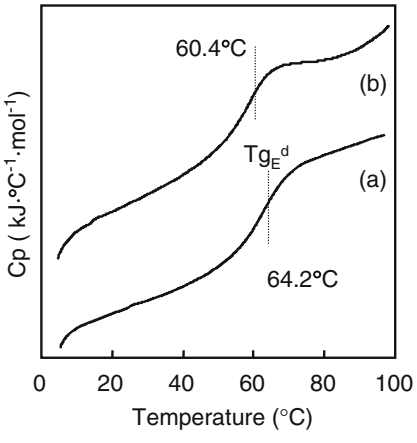

Fig. 3 PC-DSC second heating curves of P(*i*BMA-MAA) (MAA, 5 mol%) emulsion at pH 5 (**a**) and 12 (**b**). [KOH]/[MAA] (equivalent ratio): (**a**) 0 and (**b**) 1

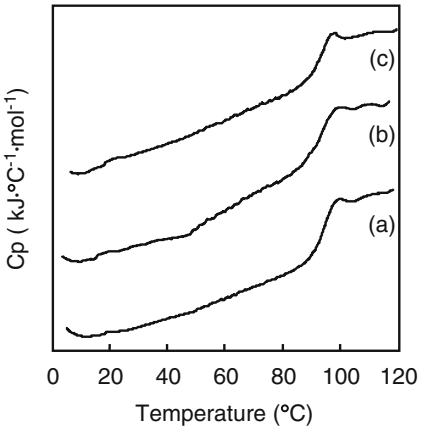

Fig. 5 PC-DSC second heating curves of P(S-MAA) (MAA, 10 mol%) emulsion at pH 5 (**a**) and 12 (**b**, **c**). [KOH]/[MAA] (equivalent ratio): (**a**) 0, (**b**) 1, and (**c**) 2

As described in the introduction, it has been assumed that water molecules around the ionized carboxyl group formed water pools. In addition, the result that multihollow particles were not prepared by the stepwise alkali/acid method using the P(MMA-MAA) and the P(*i*BMA-MAA) particles, also support it.

From the above results, it was concluded that the Tg_E measurement with PC-DSC was useful for the estimation of water absorption state within the carboxylated polymer particles and using this technique, the unclear important problem in the formation mechanism of the multihollow polymer particles by the stepwise alkali/acid method [8] was clarified.

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