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SHORT COMMUNICATION

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Effect of hydrophilicity of polymer particles on their glass transition temperatures in the emulsion state

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Abstract The glass transition temperatures (*Tg*) of three kinds of poly(methyl methacrylate)-based copolymer emulsions having wide polymer compositions, which were prepared by emulsifier-free emulsion copolymerizations of methyl methacryalate with ethyl acrylate, *n*-buthyl methacrylate and methacrylic acid, were measured with a power compensation-type highly sensitive differential scanning calorimeter. The *Tg* values of the copolymers in their emulsion state (Tg_E) were always lower than those in their dry states (Tg_D), and the difference between Tg_E and Tg_D increased with an increase in copolymer hydrophilicities.

Keywords Glass transition temperature · Differential scanning calorimeter · Emulsion polymerization · Plasticization · Hydrophilicity

Introduction

Polymer emulsion produced by emulsion polymerization has wide industrial applications in film form, such as for paints, coatings and adhesives. The polymer emulsion has a minimum film forming temperature (MFT) below which film is not formed. The MFT has been discussed for a while in relation to the glass transition temperature (*Tg*) of the base polymer in a dry state (Tg_D), which is measurable. Although *Tg* in an emulsion state (Tg_E) should be more closely related to the MFT, its measurement had, until recently, not been possible.

Recently, Lee and coworkers reported that Tg_E could be measured with a power compensation-type highly sensitive differential scanning calorimeter (PC-DSC) [1], which has been developed for measuring the thermal behaviors of nucleic acids and proteins. In their report, Tg_E was obviously lower than Tg_D because of the plasticization with water. This result is a great incentive to us, because Tg_E seems to have a strong influence on the preparation of multi-hollow polymer particles by the alkali/acid [2, 3, 4, 5, 6, 7, 8] and alkali/cooling [9, 10, 11] methods, and of nano-sized particles by the particle dissolution method [12, 13, 14, 15, 16] that we proposed. However, most of the polymer emulsions measured by Lee et al. were multi-component polymers (such as terpolymers) having functional groups. This led us to consider the need for further fundamental study.

In this study, fundamental data on Tg_E for three kinds of poly(methyl methacrylate) based-copolymers with different hydrophilicities, which were prepared by emulsion copolymerizations with various amounts of ethyl acrylate, *n*-butyl methacrylate and methacrylic acid, will be shown in order to clarify the effect of polymer hydrophilicity on Tg_E in comparison with Tg_D.

Experimental

Materials

Methyl methacrylate (MMA), ethyl acrylate (EA), *n*-butyl methactylate (*n*-BMA) and methacrylic acid (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.

Preparation of polymer emulsions

Poly(methyl methacrylate) (PMMA) and PMMA-based copolymer emulsions were produced by emulsifier-free emulsion polymerization in a 500 ml four-necked round-bottom flask under the conditions listed in Tables 1, 2, 3 and 4. Only PMMA emulsion was also produced by emulsion polymerization with nonionic emulsifier under the conditions listed in Table 1. The conversions were over 95% by gravimetric measurements. In Tables 2, 3 and 4, the glass transition temperature (*Tg*) values of the copolymers are shown, which were calculated using Fox's equation with the following *Tg* values of the homopolymers: PMMA, 105 °C; poly(ethyl acrylate) (PEA), −24 °C; poly(*n*-butyl methactylate) (P*n*-BMA), 30 °C; poly(methacrylic acid) (PMAA), 228 °C [17].

Measurement of particle diameter

Each polymer emulsion was diluted to 10 ppm, and then the hydrodynamic diameters of the particles were measured by dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan) at a light-scattering angle of 90° at room temperature.

Measurement of Tg_E

Each polymer emulsion was centrifugally washed three times and finally purified with an ion exchange resin. The polymer emulsion was degassed by a desiccator for vacuum with stirring for 20 min.

Table 1 Recipes for the productions of poly(methyl methacrylate) particles by emulsifier-present and emulsifier-free emulsion polymerizations

Ingredient	Emulsifier-present	Emulsifier-free
MMA (g)	20	10
KPS (g)	0.08	0.15
Emulgen 911 (g)	1.3	0
Water (g)	180	90
D_h[a](nm)	370	340
M_w[b](×10^4 g/mol)	40	63
Tg_E[d, c] (°C)	89	102

[a] Hydrodynamic diameter measured by dynamic light scattering (DLS); [b] weight-average molecular weight measured by gel permeation chromatography (GPC); [c] glass transition temperature measured in the emulsion state with a power compensation-differential scanning calorimeter (PC-DSC). Abbreviations: MMA = methyl methacrylate; KPS = potassium persulfate; Emulgen 911 = polyoxethylene nonyl phenyl ether nonionic emulsifier

Table 2 Recipes for the production of poly(methyl methacrylate-ethyl acrylate) particles by emulsifier-free emulsion copolymerizations[a]

EA contents (wt%)	0	11	25	36	52
MMA (g)	10	8.9	7.5	6.4	4.8
EA (g)	0	1.1	2.5	3.6	5.2
KPS[b] (g)	0.15	0.15	0.15	0.15	0.15
Water (g)	95	95	95	95	95
Tg[c](°C)	105	85	62	46	25
D_h[d](nm)	340	430	500	330	310
M_w[e](×10^4 g/mol)	63	63	70	61	35

[a] In flask; N_2; 70 °C; 24 h; stirring rate, 180 rpm; [b] first, 0.1 g of KPS was added and 24 h later the remains (0.05 g) were added; [c] calculated by Fox's equation with reference *Tg* values: PMMA, 105 °C; PEA, −24 °C; [d] hydrodynamic diameter measured by DLS; [e] weight-average molecular weight measured by GPC. Abbreviations: EA = ethyl acrylate

Table 3 Recipes for the production of poly(methyl methacrylate-*n*-butyl methacrylate) particles by emulsifier-free emulsion copolymerizations[a] utilizing the starved-fed monomer addition method

n-BMA contents (wt%)	0	25	50	75	100
MMA[b] (g)	10	22.5	15.0	7.5	0
n-BMA[b] (g)	0	7.5	15.0	22.5	30.0
KPS[c] (g)	0.15	0.40	0.40	0.40	0.40
Water (g)	95	270	270	270	270
Tg[d](°C)	105	83	63	46	30
D_h[e](nm)	340	470	370	380	340
M_w[f](×10^4 g/mol)	63	21	28	25	32

[a] In flask; 70 °C; 24 h; stirring rate, 120 rpm; [b] added at the rate of 3 mg/h for 10 h; [c] first, 0.3 g of KPS was added and 6 h later the remains (0.1 g) were added; [d] calculated by Fox's equation with reference *Tg* values: PMMA, 105 °C; P*n*-BMA, 30 °C; [e] hydrodynamic diameter measured by DLS; [f] weight-average molecular weight measured by GPC. Abbreviations: *n*-BMA = *n*-butyl methylacrylate

Table 4 Recipes for the production of poly(methyl methacrylate-methacrylic acid) particles by emulsifier-free emulsion copolymerizations[a] utilizing the starved-fed monomer addition method

MAA contents (wt%)	0	4.1	8.7
MMA[b] (g)	10	14.4	13.7
MAA[b] (g)	0	0.6	1.3
KPS[c] (g)	0.15	0.20	0.20
Water (g)	95	285	285
Tg[d](°C)	105	109	113
D_h[e](nm)	340	300	320
M_w[f](×10^4 g/mol)	63	17	12

[a] In flask; 70 °C; 24 h; stirring rate, 120 rpm; [b] added at the rate of 3 mg/h for 5 h; [c] first, 0.15 g of KPS was added and 6 h later the remains (0.05 g) were added; [d] calculated by Fox's equation with reference *Tg* values: PMMA, 105 °C; MAA, 228 °C; [e] hydrodynamic diameter measured by DLS; [f] weight-average molecular weight measured by GPC. Abbreviations: MAA = methylacrylic acid

Tg_E was measured with about 1 g of the emulsion, of which solid content was adjusted to 4 wt%, by PC-DSC (nano-DSC 5100, Calorimetry Sciences Co., USA) in the range of 0 °C to 120 °C at the rate of 1 °C/min. In the measurement, the emulsion was pressurized to 3 atm to prevent water evaporation. The Tg_E value was obtained as an average value of temperatures (Tg_E^d) representing the maximum points in three second and third differential curves.

Measurement of Tg_D

Each polymer emulsion was kept at room temperature in a desiccator with silica gel, and then the obtained particles were further dried under reduced pressure for a week. Tg_D was measured, using about 10 mg of the dried particles sealed in an aluminum pan, by a heat flow-type differential scanning calorimeter (HF-DSC) (DSC 120, Seiko Instrument Co. Ltd., Japan) in the range of $Tg \pm 50$ °C, at the rate of 5 °C/min. Tg_D^d was determined in the same way as Tg_E^d.

Results and discussion

Figure 1 shows power compensation-type highly sensitive differential scanning calorimeter (PC-DSC) first and second heating curves of PMMA emulsion prepared by emulsifier-free emulsion polymerization. These curves indicate that the measurements had a good reproducibility. Tg_E^d of the PMMA emulsion was 102 °C.

The diameters and molecular weights of all polymer emulsions used in this study are shown in Tables 1, 2, 3, 4. Because they were similar to each other, their influences on Tg_E were neglected. In a previous article [18], we reported that 75% of Emulgen 911 nonionic emulsifier fed in emulsion copolymerization of styrene (S) and MAA was included inside the copolymer particles produced. As shown in Table 1, the difference in the Tg_D^d value between emulsifier-free and emulsion-containing PMMA particles was 4 °C, and that for the Tg_E^d value between those emulsions was 13 °C. That is, the Tg_D^d and Tg_E^d values of the emulsifier-free PMMA were always higher than those of emulsifier-containing PMMA. These values indicate that the nonionic emulsifier molecules act as plasticizer and accelerate the absorbtion of water into the particles. Therefore, in order to eliminate the influence of emulsifier on Tg, the following Tg_E and Tg_D measurements were carried out with emulsifier-free polymer emulsions produced by emulsifier-free emulsion polymerization.

Figure 2 shows Tg_D^d and Tg_E^d values of MMA-EA copolymer [P(MMA-EA)] particles as a function of EA content. Both Tg^d values linearly decrease with increasing EA content, and Tg_E^d values are always lower than Tg_D^d. The differences between the Tg_D^d and Tg_E^d values are constant, about 10 °C at any EA content. This result indicates that the degree of plasticization with water is independent of the EA content. This may be due to similar hydrophilicities between EA and MMA components. For example, the solubilities of EA and MMA in water are 1.5 and 1.6 g/dL at 20 °C, respectively. This is a reason why the series of the P(MMA-EA) emulsions were produced by batch emulsifier-free emulsion polymerization, as described below.

Figure 3 shows Tg_D^d and Tg_E^d values of MMA-*n*-BMA copolymer [P(MMA-*n*-BMA)] particles as a function of *n*-BMA content. The Tg_D^d and Tg_E^d values and the difference between them linearly decreased with increasing *n*-BMA content. These results suggest that the degree of plasticization with water is decreased with increasing *n*-BMA content in the P(MMA-*n*-BMA) particles, because *n*-BMA is more hydrophobic than MMA. The solubility of *n*-BMA in water is 0.6 g/dL at 20 °C.

The series of P(MMA-*n*-BMA) particles were produced by emulsifier-free emulsion polymerization utilizing a starved-fed monomer addition method in order to prepare copolymers with homogeneous composition, because the solubilities of MMA and *n*-BMA in water are different. In actual fact, as shown in Fig. 4a, in the case of

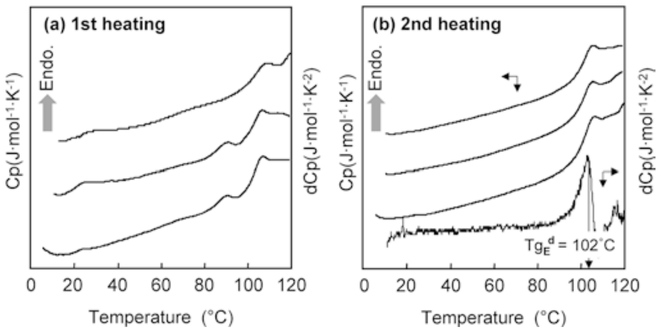

Fig. 1 Power compensation-type highly sensitive differential scanning calorimeter (PC-DSC) first **a** and second **b** heating curves of poly(methyl methacrylate) (PMMA) emulsion prepared by emulsifier-free emulsion polymerization

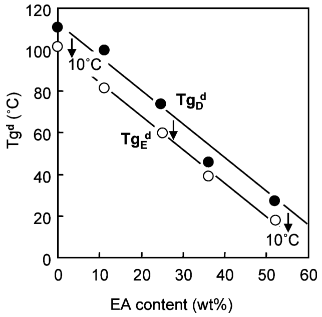

Fig. 2 Relationships between ethyl acrylate (EA) content in MMA-EA copolymer particles and Tg_D^d (filled circles) or Tg_E^d (unfilled circles), which were, respectively, measured at dry and emulsion states with heat flow (HF) and PC-DSC

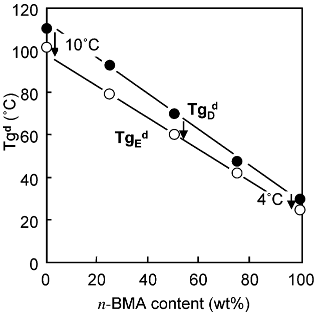

Fig. 3 Relationships between *n*-butyl methacrylate (*n*-BMA) content in methyl methacrylate-*n*-BMA copolymer [P(MMA-*n*-BMA)] particles and $Tg_{\mathrm{D}}^{\mathrm{d}}$ (filled circles) or $Tg_{\mathrm{E}}^{\mathrm{d}}$ (unfilled circles), which were, respectively, measured at dry and emulsion states with HF and PC-DSC

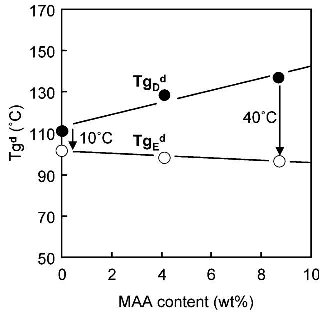

Fig. 5 Relationships between methacrylic acid (MAA) content in methyl methacrylate-MAA copolymer [P(MMA-MAA)] particles and $Tg_{\mathrm{D}}^{\mathrm{d}}$ (filled circles) or $Tg_{\mathrm{E}}^{\mathrm{d}}$ (unfilled circles), which were, respectively, measured at dry and emulsion states with HF and PC-DSC

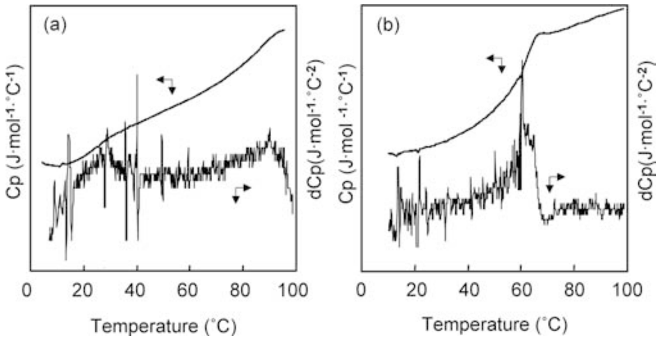

Fig. 4 PC-DSC second heating curves of P(MMA-*n*-BMA) (*n*-BMA content, 50 wt%) emulsions produced by emulsifier-free emulsion copolymerizations utilizing batch **a** and starved-fed **b** monomer additions, and their differential curves

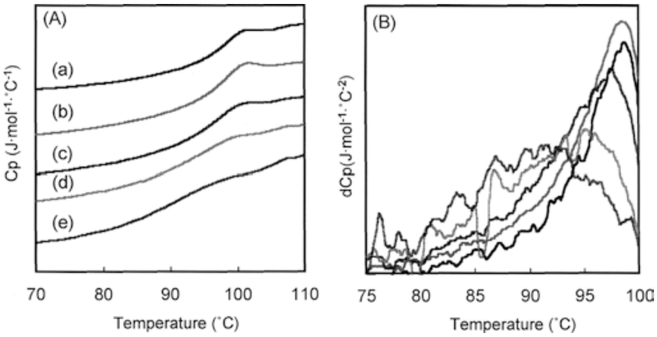

Fig. 6 PC-DSC second heating curves **A** and their differential curves **B** of P(MMA-MAA) (MAA, 4.1 wt%) emulsions with KOH aqueous solution at different neutralizations: [KOH]/[COOH]: **a** 0; **b** 0.21; **c** 0.46; **d** 0.75; **e** 0.99

P(MMA-*n*-BMA) (*n*-BMA, 50 wt%) particles produced by “batch” emulsifier-free emulsion copolymerization, two small broad $Tg_{\mathrm{E}}^{\mathrm{d}}$ peaks were observed at 30 and 90 °C because of wide polymer composition. On the other hand, in the case of those produced utilizing the starved-fed monomer addition method, a sharp $Tg_{\mathrm{E}}^{\mathrm{d}}$ peak was observed, as shown in Fig. 4b. In both cases, similar results were also obtained in $Tg_{\mathrm{D}}^{\mathrm{d}}$ measurements.

Because the difference between the solubilities of MMA and MAA (18 g/dL at 20 °C) in water is large, a series of MMA-MAA copolymer [P(MMA-MAA)] emulsions were also produced by emulsifier-free emulsion copolymerization utilizing a starved-fed monomer addition method. Sharp $Tg_{\mathrm{E}}^{\mathrm{d}}$ peaks were observed in all PC-DSC second heating curves in this system. Variations in $Tg_{\mathrm{D}}^{\mathrm{d}}$ and $Tg_{\mathrm{E}}^{\mathrm{d}}$ values of the P(MMA-MAA) particles as a function of MAA content are shown in Fig. 5. With an increase in the MAA content, the $Tg_{\mathrm{E}}^{\mathrm{d}}$ decreased a little, but $Tg_{\mathrm{D}}^{\mathrm{d}}$ increased. As a result, the difference between the $Tg_{\mathrm{D}}^{\mathrm{d}}$ and $Tg_{\mathrm{E}}^{\mathrm{d}}$ values increased with increasing in MAA content. These results suggest that the P(MMA-MAA) particles were much more hydroplasticized in water as MAA content increased, because MAA is more hydrophilic than MMA.

Figure 6 shows PC-DSC second heating curves and their differential curves for P(MMA-MAA) (MAA, 4.1 wt%) emulsions at different degrees of neutralization with KOH. At a neutralization ratio of 0.21, $Tg_{\mathrm{E}}^{\mathrm{d}}$ and the shape of its differential curve were almost the same as those of the original P(MMA-MAA) particles. The amount of carboxyl groups in the P(MMA-MAA) particles, estimated with an isothermal titration calorimeter at 35 °C at which KOH cannot diffuse into the inside in the short titration time (40 s) because the copolymer in the inside is in a glassy state, was about 20% based on the total amount. This will be reported in detail in a following article [19]. These results indicate that the plasticization with water was not induced inside the P(MMA-MAA) particles below the neutralization ratio of 0.21 because only the carboxyl groups at the particles’ surfaces were ionized with the KOH. Above the neutralization ratio of 0.21, the peaks became broad and shifted towards lower temperature with an increase in the neutralization ratio. This seems to be because plasticization with water was induced in the polymer particles, since the neutralization reaction proceeded in the inside in the first heating measurement in which the temperature of the sample was elevated at a rate of 1 °C/min to 110 °C beyond the Tg_{E}.

From these results, it is clarified that the difference between $Tg_{\mathrm{D}}^{\mathrm{d}}$ and $Tg_{\mathrm{E}}^{\mathrm{d}}$ values depends markedly on the hydrophilicity of the base polymer.

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