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ORIGINAL CONTRIBUTION

Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application

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Abstract From the viewpoint of heat storage application, encapsulation of *n*-hexadecane (HD) was carried out by microsuspension copolymerizations of divinylbenzene (DVB) and acrylic monomers (butyl acrylate, BA; ethyl acrylate, EA) utilizing the self-assembling of phase-separated polymer (SaPSeP) method proposed by the authors. The heat of solidification (H_s) of encapsulated HD in the micron-sized, cross-linked particles was determined by the differential scanning calorimeter (DSC). H_s of the encapsulated HD in poly(DVB) particles was much lower than that of pure HD, but it was increased with BA or EA content copolymerized up to that of pure HD. Such an influence of encapsulation on the H_s was discussed.

Keywords Microsuspension polymerization · Capsule · Particles · Hexadecane · Heat storage material

Introduction

Polymer particles with hollow structures have attractive properties for many industrial applications such as microcapsules, hinding or opacifying agents in coating and molding compositions [1–6]. Recently, we have succeeded in preparing about 5-μm-sized, monodispersed, cross-linked polymer particles with one hollow at the center by seed polymerization of highly divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles [7, 8] prepared by the dynamic swelling method [9, 10]. The formation mechanism of these hollow polymer particles was proposed [11]. On the basis of this mechanism, hollow polymer particles were also prepared by microsuspension polymerization of DVB/toluene droplets dissolving PS and benzoyl peroxide (BPO), although they were polydisperse [12]. The PS dissolved in the DVB/toluene droplets was needed as the accelerator for the phase separation of polydivinylbenzene (PDVB) formed therein during the polymerization [13]. The phase separation in the early stage is the first required point for the formation of the hollow structure because at low conversion the PDVB can move and adsorb at the interface of the droplets due to low viscosity. The second required point is the preferential adsorption of PDVB at the interface of the droplets over PS previously dissolved therein. Therefore, the formation of the hollow structure was named the Self-assembling of Phase-Separated Polymer (SaPSeP) method. Moreover, microsuspension polymerization of DVB droplets including *n*-hexadecane (HD), instead of a polymer, as a nonsolvent was also carried out [14]. The HD capsulated particles were prepared under the conditions where phase separation in the droplets occurred in an early stage of polymerization. The time at which phase separation began depended on both the content of HD and the cross-linking reaction of PDVB. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of chemicals. In the actual preparation, we succeeded in encapsulating hinokitiol, which is abstracted from natural coniferous woods, although the rate of radical polymerization obviously decreased compared with that in the absence of it due to high chain transfer reaction to hinokitiol [15].

Energy storage materials play an important role in conserving available energy and improving its utilization. There are numerous numbers of heat storage materials that

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melt and solidify at a wide range of temperatures, making them attractive for many applications. One group of them is paraffin waxes that are cheap and have moderate thermal energy storage but low thermal conductivity; therefore, it requires large surface areas. The encapsulation of these materials have many advantages that provide large heat transfer area and control the volume change of the storage materials as phase change occurs [16].

We have studied the encapsulation of HD, one of the paraffin waxes used as heat storage materials, in PDVB particle produced by microsuspension polymerization utilizing the SaPSeP method of micron-sized DVB/HD droplets prepared by the Shirasu porous glass (SPG) membrane emulsification technique [17, 18]. The heat capacity of pure HD is about 230 J/g defined as the heat of melting (H_m) and heat of solidification (H_s) while melting (T_m) and solidification (T_s) temperatures are about 15 °C. It was found that the H_s of HD encapsulated by PDVB shell was much lower than that of pure HD. Moreover, the T_s of the encapsulated HD was also lower, about 10 °C, than that of pure HD while T_m still remains at 15 °C [19]. These phenomena are, of course, negative to apply it for heat storage materials.

In this study, to clarify the reason and to improve the thermal properties of encapsulated HD, microsuspension copolymerizations of DVB and acrylic monomer were carried out in droplets containing HD.

Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove polymerization inhibitors before use. Butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) (Nacalai Tesque, Kyoto, Japan; extra pure reagent grade) were purified by distillation under reduced pressure. Poly(vinyl alcohol) (PVA) (Gohsenol GH-17: degree of polymerization, 1,700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical, Osaka, Japan. Reagent grade BPO was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. HD (Nacalai Tesque, Kyoto, Japan; guaranteed reagent grade) was used as received.

SPG membrane emulsification and microsuspension polymerization

The homogeneous solution of monomer, HD, and BPO initiator was dispersed in PVA aqueous solution with SPG membrane (SPG Technology, Japan). Microsuspension polymerization of the monomer dispersions was carried out at 70 °C for 24 h under nitrogen atmosphere in sealed glass tubes under the conditions listed in Tables 1, 2, and 3 for DVB–BA copolymer [P(DVB–BA)], DVB–EA copolymer [P(DVB–EA)], and DVB–MA copolymer [P(DVB–MA)] particles, respectively. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Capsule particles were observed with an optical microscope (MICROPHOT-FXA, Nikon, Tokyo, Japan).

Table 1 Recipes for the preparation of P(DVB–BA) capsule particles with encapsulated HD by microsuspension copolymerization of (DVB–BA)/HD (4/6, *w*/*w*) droplets prepared by the SPG emulsification method

Ingredient (g)	DVB/BA (*w*/*w*)					
	100/0	80/20	65/35	50/50	35/65	20/80
DVB	2.6	2.1	1.7	1.3	0.9	0.5
BA	0.0	0.5	0.9	1.3	1.7	2.1
HD	4.0	4.0	4.0	4.0	4.0	4.0
BPO	0.1	0.1	0.1	0.1	0.1	0.1
PVA	0.5	0.5	0.5	0.5	0.5	0.5
Water	50	50	50	50	50	50

Microsuspension copolymerization: N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes). SPG emulsification method: SPG membrane (pore size=1.1 μm).
DVB: divinylbenzene, *BA*: butyl acrylate, *HD*: *n*-hexadecane, *BPO*: benzoyl peroxide, *PVA*: poly(vinyl alcohol)

Measurement of thermal property

H_s and T_s values of encapsulated HD were measured on an aluminum pan by differential scanning calorimeter (DSC) (DSC 6200, Seiko Instruments, Chiba, Japan) under a N_2 flow with a scanning rate at 5 °C/min. The measurement was also carried out in the presence of acrylic polymer as follows.

Table 2 Recipes for the preparation of P(DVB–EA) capsule particles with encapsulated HD by microsuspension copolymerization of (DVB–EA)/HD (4/6, *w*/*w*) droplets prepared by SPG emulsification method

Ingredient (g)	DVB/EA (*w*/*w*)					
	100/0	80/20	70/30	50/50	35/65	20/80
DVB	2.6	2.1	1.8	1.3	0.9	0.5
EA	0.0	0.5	0.8	1.3	1.7	2.1
HD	4.0	4.0	4.0	4.0	4.0	4.0
BPO	0.1	0.1	0.1	0.1	0.1	0.1
PVA	0.5	0.5	0.5	0.5	0.5	0.5
Water	50	50	50	50	50	50

Microsuspension copolymerization: N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes). SPG emulsification method: SPG membrane (pore size=1.1 μm).
EA: ethyl acrylate

Table 3 Recipes for the preparation of P(DVB–MA) capsule particles with encapsulated HD by microsuspension copolymerization of (DVB–MA)/HD (4/6, *w*/*w*) droplets prepared by SPG emulsification method

Ingredient (g)	DVB/MA (*w*/*w*)	
	100/0	80/20
DVB	2.6	2.1
MA	0.0	0.5
HD	4.0	4.0
BPO	0.1	0.1
PVA	0.5	0.5
Water	50	50

Microsuspension copolymerization: N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes). SPG emulsification method: SPG membrane (pore size=1.1 μm).
MA: methyl acrylate

Polybutyl acrylate (PBA), polyethyl acrylate (PEA), and polymethyl acrylate (PMA), which were prepared by solution polymerization [20], were separately dissolved with HD in toluene. Toluene was evaporated in a capless bottle, and the phase-separated pure HD top layer was removed as much as possible. Each polymer in which HD dissolved or dispersed was put in an aluminum pan for DSC measurement.

Miscibility of HD in polymer particles

Dried PS [21] and poly(*iso*-butyl methacrylate) (P*i*-BMA) [22] particles, which were prepared by emulsifier-free emulsion polymerization with potassium persulfate (KPS) as initiator, were separately dispersed and heated in HD for 24 h at 100 and 70 °C, respectively, which are above their glass transition temperatures (T_g). The miscibilities of HD in the polymer particles were estimated by measuring the T_g values of PS and P*i*-BMA using DSC under a N_2 flow with a scanning rate at 5 °C/min after unabsorbed HD was removed.

Observation of ultrathin cross-sections of particles

Dried capsule particles were dispersed in epoxy matrix, cured at room temperature for 24 h, and then microtomed. The ultrathin cross-sections were observed with a transmission electron microscope (TEM, JEOL JEM-1230 electron microscope).

Results and discussion

Figure 1 shows the optical micrographs of monodisperse, P(DVB–BA) particles with encapsulated HD at various weight ratios of DVB/BA produced by microsuspension copolymerization of (DVB–BA)/HD (4/6, *w*/*w*) droplets prepared by SPG emulsification technique under the conditions listed in Table 1. All particles were nonspherical with smooth outer surface. Because the shell strength was not enough, a part of the shell buckled by shrinkage of HD, which is induced by cooling from the polymerization temperature (70 °C) to room temperature, similarly as discussed in previous articles [23–25]. The densities of HD

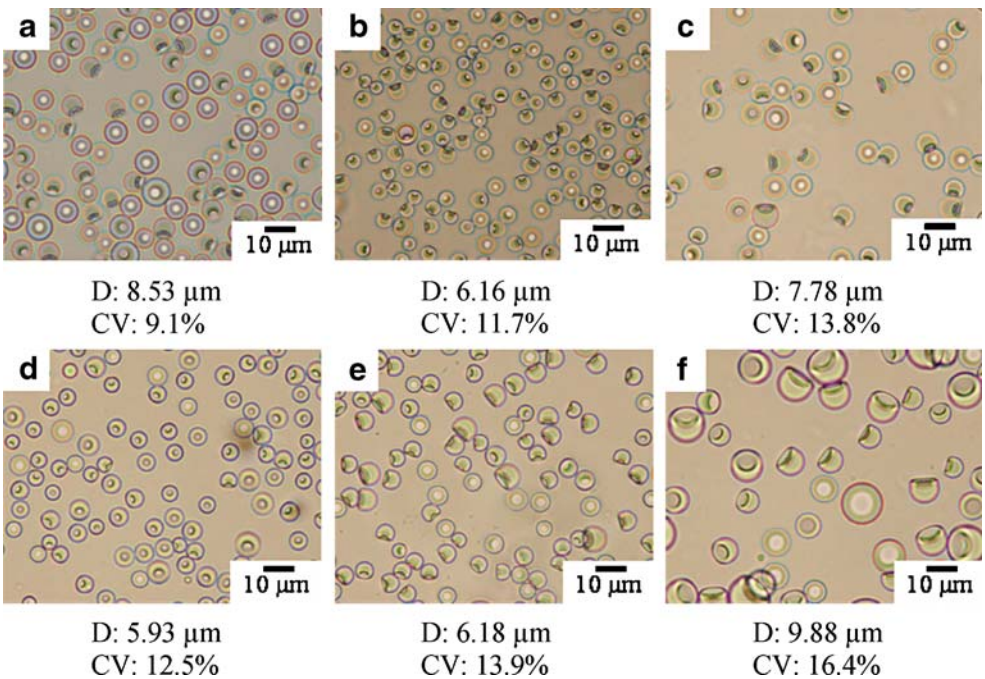

Fig. 1 Optical micrographs of P(DVB–BA) particles prepared by microsuspension copolymerizations utilizing the SaPSeP method of (DVB–BA)/HD (4/6, *w*/*w*) droplets prepared by SPG emulsification technique under the conditions listed in Table 1 at 70 °C. DVB/BA (*w*/*w*): **a** 100/0; **b** 80/20; **c** 65/35; **d** 50/50; **e** 35/65; **f** 20/80

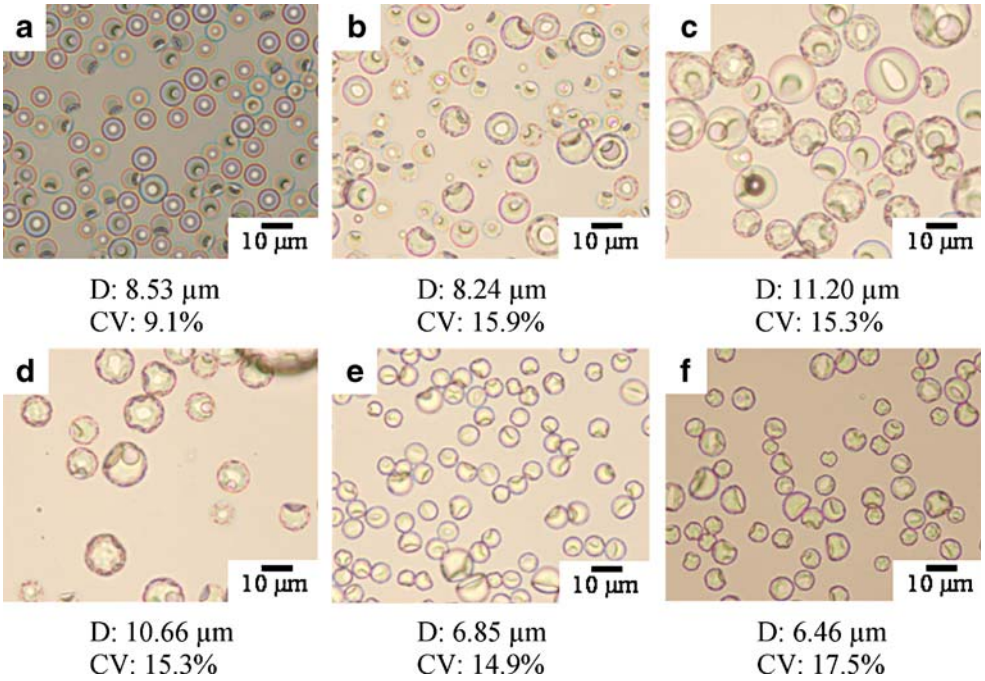

Fig. 2 Optical micrographs of P(DVB–EA) particles prepared by microsuspension copolymerizations utilizing the SaPSeP method of (DVB–EA)/HD (4/6, *w*/*w*) droplets prepared by SPG emulsification technique under the conditions listed in Table 2 at 70 °C. DVB/EA (*w*/*w*): **a** 100/0; **b** 80/20; **c** 70/30; **d** 50/50; **e** 35/65; **f** 20/80

at 20 and 70 °C are 0.773 and 0.739 g/cm^3, respectively [26]. In the case of P(DVB–EA) particles, they were also nonspherical particles, but with rough outer surface (Fig. 2), which is probably due to the adsorption of byproduced particles in an aqueous medium during the polymerization because of higher water solubility of EA. The byproduct particles were observed by dynamic light scattering (FPAR-1000, Otsuka Electronics, Osaka, Japan). The amounts of byproduct particles were measured to be 7.55, 10.84, 10.87, 12.42, and 15.60 wt% of polymer solid for P(DVB–EA) with DVB/EA (*w*/*w*)=80/20, 70/30, 50/50, 35/65, and 20/80, respectively, by centrifugation at 5,000 rpm for 30 min.

The particle diameter (*D*) and coefficient of variation (CV) are shown in Figs. 1 and 2 for P(DVB–BA) and P (DVB–EA) particles, respectively. The particle diameters seem to be affected by the amount of acrylate used. It may be due to the effect on SPG membrane emulsification process. In this experiment, particle size was controlled by SPG membrane pore size used for monomer droplet preparation. Because hydrophilic SPG membrane was used, hydrophilic components easily wet the membrane surface. When acrylate amount was increased, hydrophilicity of dispersed oil phase was also increased. This high hydrophilic dispersed phase apt to wet the membrane surface leading to the difficulty of droplet size and size distribution control. Therefore, different particle sizes were observed even though the same SPG membrane (pore size=1.1 μm) was used. Moreover, in some cases, quite polydisperse particles were obtained.

Figure 3 shows the DSC thermograms of HD encapsulated by P(DVB–BA) shell having various weight ratios of DVB/BA. In all cases, T_s values of the encapsulated HD were about 5 °C, i.e., approximately 10 °C lower than that of pure HD while T_m values still remained at 15 °C. The reason why T_s decrease may be based on a compartmentalization effect is that the impurities located in the capsule particle cannot induce the nucleation of HD encapsulated in the other particles. In the bulk system, it is known that there

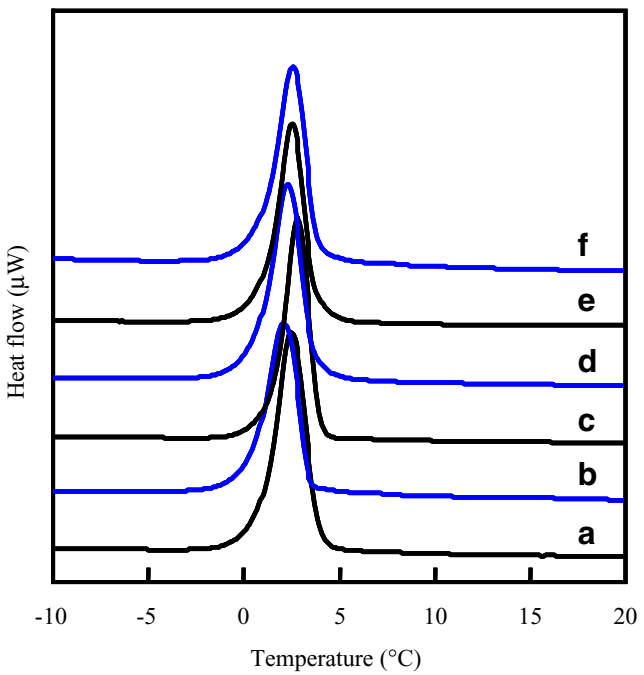

Fig. 3 DSC thermograms of HD encapsulated by P(DVB–BA) shell, prepared by microsuspension copolymerizations utilizing the SaPSeP method of (DVB–BA)/HD (4/6, *w*/*w*) droplets, measured with a cooling rate at 5 °C/min. DVB/BA (*w*/*w*): *a* 100/0; *b* 80/20; *c* 65/35; *d* 50/50; *e* 35/65; *f* 20/80

is an impurity that works as a trigger for the nucleation resulting in heterogeneous nucleation [27]. In emulsion, the numbers of impurity that usually cause heterogeneous nucleation, as in bulk phase, are distributed among a large number of isolated droplets. Therefore, the probability for heterogeneous nucleation for all droplets is drastically reduced. Supercooling was also observed in the case of P (DVB–EA) particles as shown in Fig. 4.

Figure 5 shows the relationships between MA, EA, and BA contents in the copolymer particles and H_s values, which were obtained from the area of solidification curves shown in Figs. 3 and 4 for HD encapsulated by P(DVB–BA) and P(DVB–EA) shells, respectively. The H_s value of encapsulated HD in PDVB particles was the lowest, whereas in the cases of the copolymer particles, they always increase with MA, EA, and BA contents until that of pure HD (around 230 J/g) was reached. On the basis of the mechanism of hollow polymer particle discussed in the previous article [11], the polymer molecules formed in the monomer droplet separate and adsorb at the inner interface, resulting in a cross-linked shell. An increase in the hydrophilicity of P(DVB–BA) chains with increasing BA content should enhance the phase separation between the copolymer chains and HD, possibly resulting in the complete isolation of the HD core from the polymer shell. This HD core seems to be more smoothly solidified than incompletely isolated HD locating in the inner interface of polymer shell, resulting in the increase H_s with the BA content. This is more obvious in the case of P(DVB–EA) capsule particles because of the higher hydrophilicity of EA than BA unit. This seems to be the reason why H_s values of HD encapsulated by the P(DVB–EA) shell were always higher than those by the P(DVB–BA) shell. In the case of P

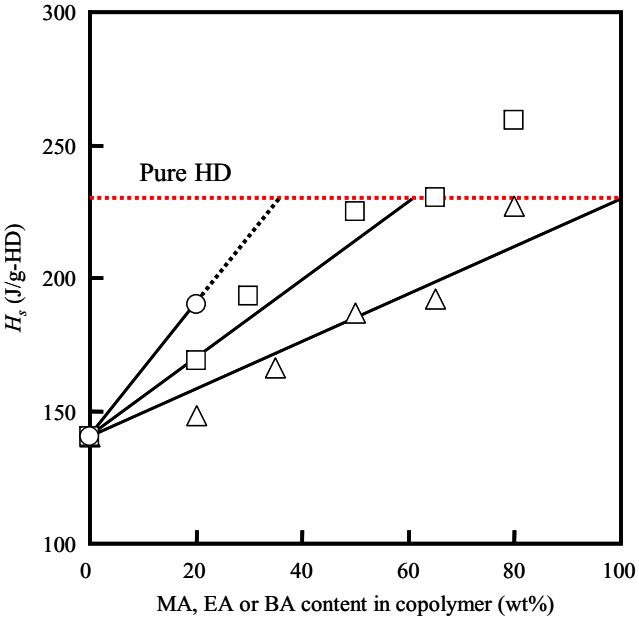

Fig. 5 Relationships between MA (*open circles*), EA (*open squares*) and BA (*open triangles*) contents in P(DVB–MA), P(DVB–EA) and P (DVB–BA) capsule particles, respectively, (polymer/HD, 4/6 by weight) and heats of solidification (H_s) of HD encapsulated by the copolymer shells

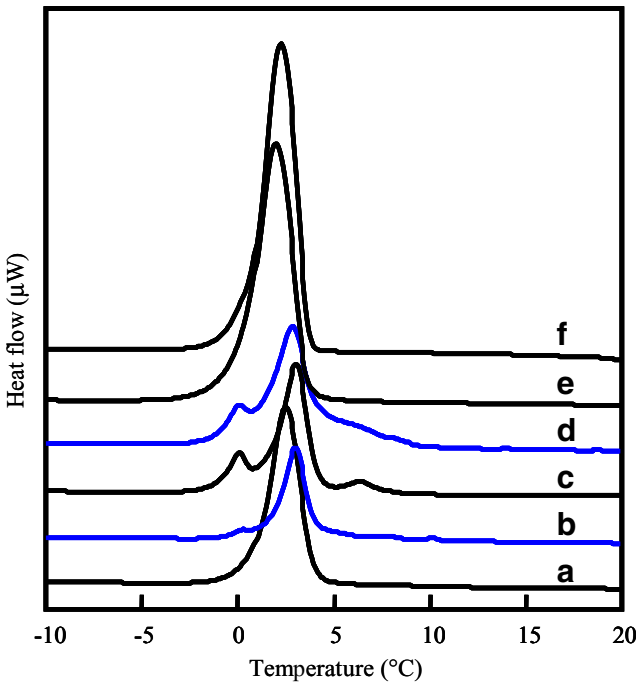

Fig. 4 DSC thermograms of HD encapsulated by P(DVB–EA) shell, prepared by microsuspension polymerizations utilizing the SaPSeP method of (DVB–EA)/HD (4/6, *w*/*w*) droplets, measured with a cooling rate at 5 °C/min. DVB/EA (*w*/*w*): *a* 100/0; *b* 80/20; *c* 70/30; *d* 50/50; *e* 35/65; *f* 20/80

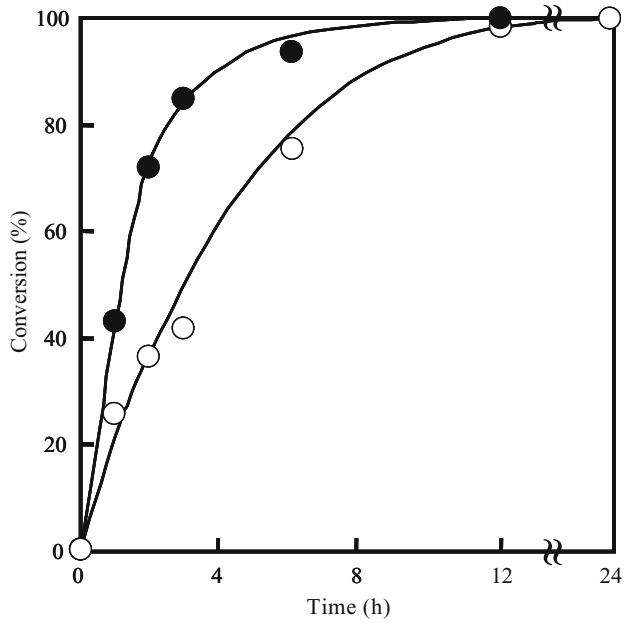

Fig. 6 Time-conversion curves of DVB (*closed circles*) and BA (*open circles*) in microsuspension copolymerization of (DVB–BA)/HD droplets (DVB–BA/HD, 4/6 by weight) at DVB/BA of 50/50 *w*/*w* prepared by SPG membrane under the conditions listed in Table 1

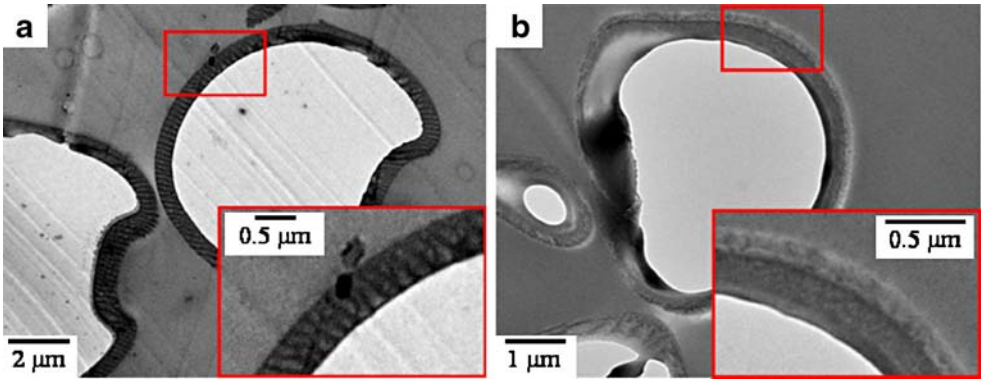

Fig. 7 TEM photographs of cross-sections of **a** PDVB and **b** P(DVB–BA) (DVB/BA=20/80, *w*/*w*) particles prepared by microsuspension polymerizations utilizing the SaPSeP method under the conditions listed in Table 1

(DVB–MA) capsule particles, the highest H_s value was obtained at the same composition as P(DVB–EA) and P(DVB–BA), but the large amount of byproduced particles in an aqueous medium was observed due to the highest water solubility of MA.

Figure 6 shows time-conversion curves of DVB and BA in microsuspension copolymerization of (DVB–BA)/HD (4/6, *w*/*w*) droplets prepared by SPG membrane emulsification at DVB/BA of 50/50 (*w*/*w*). It was found that DVB was polymerized faster than BA, which well accords with presumption based on the significant difference between copolymerization reactivity ratios of DVB and BA, which (r_1 and r_2) are 1.396 and 0.082, respectively [28]. Therefore, it seems that considering the formation mechanism of the capsule particle using the SaPSeP method [11], a cross-linked DVB-rich copolymer shell (outer shell) is formed in the former stage of the copolymerization, and then a BA-rich copolymer inner shell is formed in the latter stage. To confirm this assumption, the observation of ultrathin cross-sections of particles will be carried out.

Figure 7 shows the transmission electron microscope (TEM) photographs of cross-sections of PDVB and P(DVB–BA) (DVB/BA=20/80, *w*/*w*) capsule particles. It was found that a single layer was observed in the shell of PDVB capsule particle, whereas a double-layered structure was formed in the shell of P(DVB–BA) capsule particle. This supports the above assumption that the shell of the latter particles consists of BA-rich inner shell and DVB-rich outer shell. Considering the reactivity ratios in the cases of DVB/EA and DVB/MA, such a two-layer shell might be also formed in the P(DVB–EA) and P(DVB–MA) capsule particles. The acrylate-rich inner shell is expected to contribute to an increase in the H_s value of encapsulated HD due to their hydrophilicity, which will be discussed in the following section.

Table 4 shows the miscibilities of HD in PS and P*i*-BMA particles used as representatives of PDVB and the DVB–acrylic copolymers, respectively. At the temperatures above their T_g, the polymer particles absorbed HD leading to the decrease of the T_g. In the case of PS particle, its T_g was much more decreased than that in the case of P*i*-BMA, indicating that HD was more absorbed in PS than P*i*-BMA particles. That is, the miscibility of HD with PS was higher than that with P*i*-BMA. This suggests that the miscibility of HD with DVB–acrylic copolymer is lower than that with PDVB. Corresponding to Fig. 5, the low miscibility of HD in P(DVB–BA) accelerates the phase separation of the HD core leading to the increase of H_s with the BA content as previously discussed. This influence must be more effective in the case of P(DVB–EA) particles.

Furthermore, the effect of various hydrophilic acrylic polymers on the H_s of HD was studied as shown in Table 5. When toluene was removed by evaporation from homogeneous solutions of polymer/HD/toluene, a mixture of HD with PBA was transparent whereas those with PEA and PMA were turbid. It can be assumed that in the former case, HD dispersed in PBA as monomolecular state or fine domains, which gives high total interfacial area between PBA and HD. In latter cases, large HD domains must be dispersed in each polymer phase. Therefore, the total interfacial area seems to be in the order of PBA>PEA>PMA. These suggest that the decrease in the total interfacial area increases the H_s of HD dispersed in the polymer phase.

Table 4 Glass transition temperature (T_g) of polymer particles dispersed in HD before and after the heat treatment at 10 °C higher than corresponding T_g

Sample	T_g (°C)		
	Before heating	After heating	ΔT_g
PS	89.0	48.5	40.5
P*i*-BMA	60.5	54.0	6.5

Table 5 Heat of solidification (H_s) of incorporated HD in PMA, PEA or PBA, measured by DSC at 5 °C/min cooling rate

	Polymers			
	None	PMA	PEA	PBA
H_s (J/g; HD)	230	220	214	129

Moreover, it seems that the H_s of HD dispersed in the polymer phase also increased with an increase in the hydrophilicity of the polymer in the order of PMA>PEA>PBA. The H_s value for PMA nearly equaled to that of pure HD. Therefore, not only the total interfacial area but also the hydrophilicity of the polymer must affect the H_s of HD contacting the polymer.

Conclusions

Monodispersed DVB copolymer particles with encapsulated HD were prepared by microsuspension copolymerization utilizing the SaPSeP method. The H_s of encapsulated HD in PDVB particles was much decreased from that of pure HD. The problem in the application of the polymer particles with encapsulated HD as heat storage material was improved by the copolymerization of hydrophilic acrylic monomer. This seems to be based on the finding that copolymerizations of hydrophilic monomer enhance the phase separation of copolymer chains and HD, possibly resulting in the complete isolation of the HD core from the polymer shell.

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