

# Production of Polystyrene/Poly(ethylene glycol dimethacrylate) Composite Particles Encapsulating Hinokitiol

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**ABSTRACT:** Polystyrene (PS)/poly(ethylene glycol dimethacrylate) composite polymer particles containing hinokitiol (HT) were produced by suspension polymerization for ethylene glycol dimethacrylate droplets by the dissolution of HT and PS in poly(vinyl alcohol) aqueous solution. The composite particle had a hollow structure in which HT was

included. The evaporation rate of HT from the composite particles became slower than that of pure HT. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 706–710, 2003

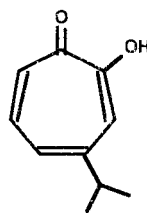
**Key words:** hinokitiol; suspension polymerization; microencapsulation; morphology; colloids

## INTRODUCTION

Polymer particles with hollow structures have gotten a lot of attention in many industrial fields. Such particles are used as microcapsules, weight-saving or thermal insulation agents, and are applied to hiding or opacifying agents in coating and molding compositions because of their high light-scattering ability. For example, submicrometer-sized thermoplastic styrene (S)/acrylic polymer particles containing one hollow at the center were produced by the alkali swelling of carboxylated polymer particles with core-shell structures.<sup>1</sup> We also prepared submicrometer-sized, monodisperse S-butyl acrylate-methacrylic acid terpolymer emulsion particles with many hollows in the inside by stepwise treatments with alkali and acid<sup>2–4</sup> called the stepwise alkali/acid method. Moreover, we succeeded in producing micrometer-sized, monodisperse, crosslinking polymer particles with a single hollow at the center<sup>5,6</sup> by seeded polymerization for highly (divinyl monomer/solvent) swollen particles prepared by the dynamic swelling method, which was proposed for the production of micrometer-sized, monodisperse polymer particles more than 5  $\mu\text{m}$  in diameter.<sup>7,8</sup> The formation mechanism of the hollow structure was discussed in an earlier work.<sup>9</sup> In another previous work, similar hollow polymer particles were produced by suspension polymerization for divinylbenzene (DVB)/toluene droplets by the dissolution of

polystyrene (PS), although they were polydisperse.<sup>10</sup> Suspension polymerization is one polymerization technique that is widely applied in industrial manufacturing. In the polymerization in the study, the PS dissolving in the droplets seemed to be one of the key factors in the formation of the hollow structure because such hollow polymer particles were not obtained without PS. The effect of the PS on the formation of the hollow structure was clarified in detail elsewhere.<sup>11–15</sup>

In this study, suspension polymerization techniques were developed to produce composite particles encapsulating hinokitiol (HT), which is sublimate and has a melting point of 50–52°C.



Hinokitiol

HT is abstracted from natural coniferous woods and has attractive properties such as aromaticity, antibacterial activity, and mildew resistance.

## EXPERIMENTAL

### Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. Ethylene glycol dimethacrylate (EGDM) and DVB (Nippon Steel Chemical Co., Ltd., Tokyo, Japan, DVB96; purity = 96%) were washed with 1N NaOH and deionized water to re-

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move polymerization inhibitors. HT (Osaka Organic Chemical Industry, Ltd., Osaka, Japan, HT-SF; purity = 99.9%) was used as received. Reagent-grade benzoyl peroxide (BPO), 2,2'-azobis(isobutyronitrile) (AIBN), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) were purified by recrystallization. Poly(vinyl alcohol) (PVA; Nippon Synthetic Chemical Ind Co., Ltd., Osaka, Japan, Gohsenol GH-17; degree of polymerization = 1700, degree of saponification = 88%) was used as a colloidal stabilizer. Deionized water was distilled with a Pyrex distillator.

### Preparation of PS

PS, which was dissolved in EGDM droplets, was prepared by the solution polymerization of S (18 g) in toluene (54 g) with AIBN initiator (12 mg) in a sealed glass tube at 60°C for 24 h. The PS was purified by reprecipitation into methanol and was dried under reduced pressure. The weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) were, respectively,  $1.6 \times 10^5$  and  $3.4 \times 10^5$ , which were measured by gel permeation chromatography with the calibration obtained with a PS standard and with tetrahydrofuran as the eluent.

### Suspension polymerization

A typical suspension polymerization was as follows: EGDM (250 mg) dissolving PS (50 mg), HT (25–250 mg), and AIBN (15 mg) were mixed with a 3.80 wt % PVA aqueous solution (7.5 g) and stirred with a Nissei ABM-2 homogenizer (Nihonseiki Kaisha Ltd., Tokyo, Japan) at 1500 rpm for 2 min at room temperature in a glass cylindrical reactor. The suspension polymerization was carried out in sealed glass at 40 or 70°C for 48 h under a nitrogen atmosphere, as listed in Table I. The glass tubes were horizontally shaken at 80 cycles/min (3-cm strokes). The conversion was determined by the gravimetry method with a 100°C oven.

TABLE I  
Suspension Polymerizations for PS/DVB  
Droplets Containing HT<sup>a</sup>

Ingredient	No. 1 <sup>b</sup>	No. 2 <sup>b</sup>	No. 3 <sup>b</sup>	No. 4 <sup>c</sup>
PS <sup>d</sup> (mg)	50	50	50	50
DVB (mg)	250	250	250	250
HT (mg)	25	100	250	100
BPO (mg)	15	15	15	—
V-70 (mg)	—	—	—	15
PVA (mg)	24	24	24	24
Water (g)	7.48	7.48	7.48	7.48
Conversion <sup>e</sup> (%)	75	40	0	41

<sup>a</sup> Purity = 99.9% (by catalog).

<sup>b</sup> N<sub>2</sub>, 70°C, 48 h.

<sup>c</sup> N<sub>2</sub>, 40°C, 48 h.

<sup>d</sup>  $M_w = 3.4 \times 10^5$ ,  $M_n = 1.6 \times 10^5$ , dissolved in DVB.

<sup>e</sup> Determined by gravimetry.

TABLE II  
Transfer Constants<sup>12</sup> to Additives in the Radical  
Polymerization S or MMA

	S	MMA
Phenol	$8.1 \times 10^{-4}$ (50°C)	$2.5 \times 10^{-4}$ (50°C)
Hydroquinone	$3.6 \times 10^{-4}$ (60°C)	$7.0 \times 10^{-4}$ (45°C)
<i>p</i> -Benzoquinone	227 (60°C)	4.5 (60°C)

### Observation of composite particles

The composite particles were observed with a Nikon MICROPHOT-FXA optical microscope (Tokyo, Japan) and a Hitachi S-2500 scanning electron microscope (Tokyo, Japan).

### <sup>1</sup>H-NMR measurement of HT

The <sup>1</sup>H-NMR spectra were obtained with a Bruker DPX250 NMR spectrometer (Karlsruhe, Germany) operating at 250 MHz for protons. Dried PS/poly(ethylene glycol dimethacrylate) (PEGDM)/HT composite particles and pure HT were dispersed in CDCl<sub>3</sub>, which did not dissolve the polymer particle but only HT, with dissolving tetramethylsilane (TMS) as a standard reagent in a 5-mm NMR tube.

### Measurement of weight loss

The release rate of HT from the composite particles, which were placed on a 5-mm aluminum pan, was evaluated by continuous measurement of the weight loss due to the evaporation of HT with thermogravimetry (Seiko Instruments TG/DTA 220U, Chiba, Japan) at 150°C under a N<sub>2</sub> flow.

### Observation of ultrathin cross-sections of the composite particles

The dried composite particles were dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross-sections were observed with transmission electron microscopy (TEM).

TABLE III  
Suspension Polymerizations<sup>a</sup> for PS/EGDM  
Droplets Containing HT<sup>b</sup>

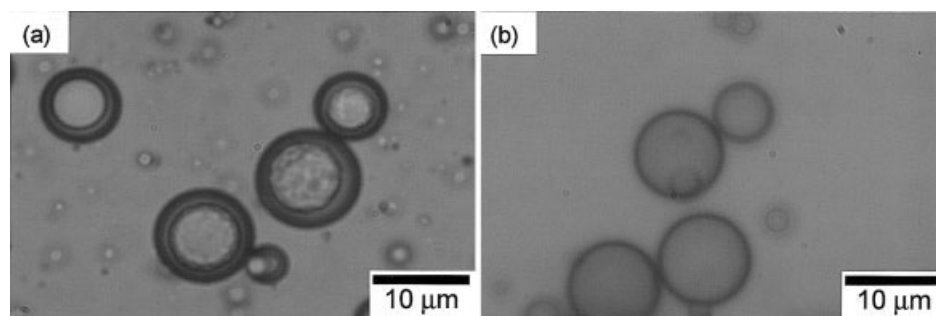
Ingredient	No. 1	No. 2	No. 3	No. 4
PS <sup>c</sup> (mg)	50	50	50	—
EGDM (mg)	250	250	250	250
HT (mg)	25	100	250	100
V-70 (mg)	15	15	15	15
PVA (mg)	24	24	24	24
Water (g)	7.48	7.48	7.48	7.48
Conversion <sup>d</sup> (%)	100	100	94	93

<sup>a</sup> N<sub>2</sub>, 40°C, 48 h.

<sup>b</sup> Purity = 99.9% (by Catalog).

<sup>c</sup>  $M_w = 3.4 \times 10^5$ ,  $M_n = 1.6 \times 10^5$ , dissolved in EGDM.

<sup>d</sup> Determined by gravimetry.



**Figure 1** Optical micrographs of the (a) PS/PEGDM/HT and (b) PEGDM/HT composite particles produced by suspension polymerizations under the conditions of numbers 2 and 4 listed in Table III.

## RESULTS AND DISCUSSION

In a previous study,<sup>10</sup> polymer particles with a single hollow at the center were successfully produced by the suspension polymerization of DVB, with toluene droplets dissolving PS and a BPO initiator. In this study, HT was used in place of toluene.

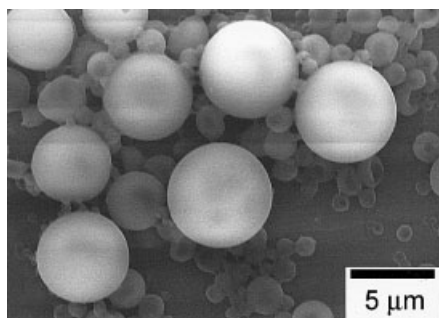
Table I shows the polymerization recipes. In the system of 250 mg of HT (number 3), the polymerization of DVB did not proceed for 48 h at 70°C. The conversion increased with a decrease in HT content, but even in the system of 25 mg of HT (number 1), it was at 75% after 48 h. These results seem to be based on the high-chain-transfer ability of HT, which is a derivative of tropolone. To depress the chain-transfer reaction, V-70 was used as an initiator, which has a

half-life at 30°C of 10 h. However, the polymerization of DVB did not complete for 48 h at 40°C. As shown in Table II, the transfer constants of S, which is similar to DVB in the radical polymerization to *p*-benzoquinone, which has a similar chemical structure to HT, were large in comparison with those of phenol and hydroquinone. However, in the radical polymerization of methyl methacrylate (MMA), the transfer constant to *p*-benzoquinone was much smaller than that in the S system. Accordingly, EGDM, which is a kind of methacrylate monomer, was used as a crosslinking monomer in place of DVB.

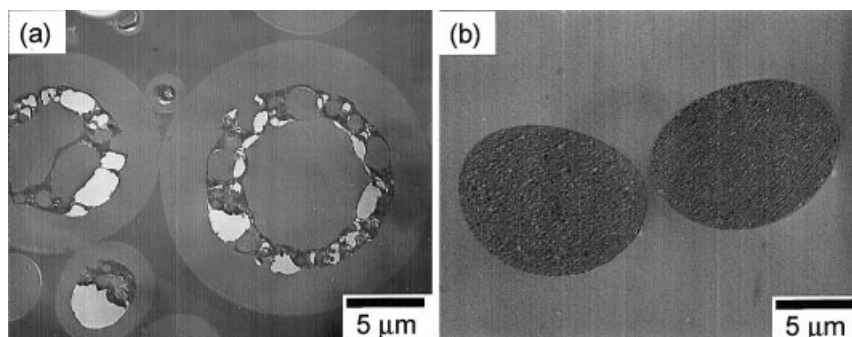
Table III shows the conditions and results. According to our expectations, even with the system that had 250 mg of HT (number 3), the polymerization was almost complete after 48 h at 40°C.

Figure 1 shows the optical micrographs of the PS/PEGDM/HT and PEGDM/HT composite particles produced by suspension polymerization under the conditions of numbers 2 and 4 listed in Table III. The composite particles produced by the suspension polymerization of EGDM, with HT droplets dissolving PS [Fig. 1(a)], seemed to have a heterogeneous structure in the inside. The other composite particles produced in the presence of PS had similar heterogeneous structures. However, for comparison, the PEGDM/HT composite particles produced by the same procedure without PS [Fig. 1(b)] had a homogeneous structure.

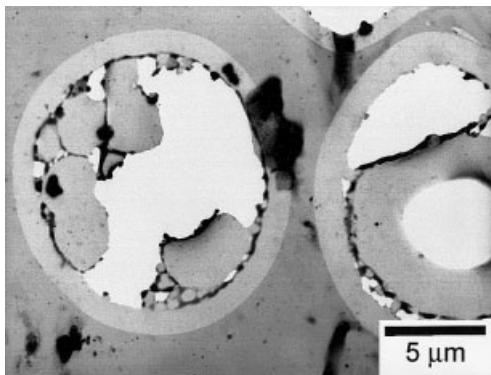
Figure 2 shows a scanning electron microscopy



**Figure 2** SEM photograph of the PS/PEGDM/HT composite particles (number 2 listed in Table III).



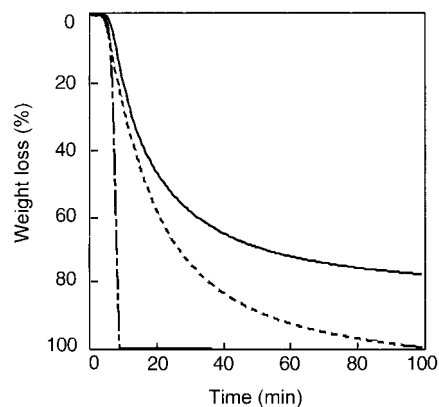
**Figure 3** TEM photographs of ultrathin cross-sections of the (a) PS/PEGDM/HT and (b) PEGDM/HT composite particles produced by suspension polymerization under the conditions of numbers 2 and 4 listed in Table III.



**Figure 4** TEM photograph of ultrathin cross-sections of the PS/PEGDM/HT composite particles (number 2 listed in Table III) after extraction of HT with ethanol on this TEM grid.

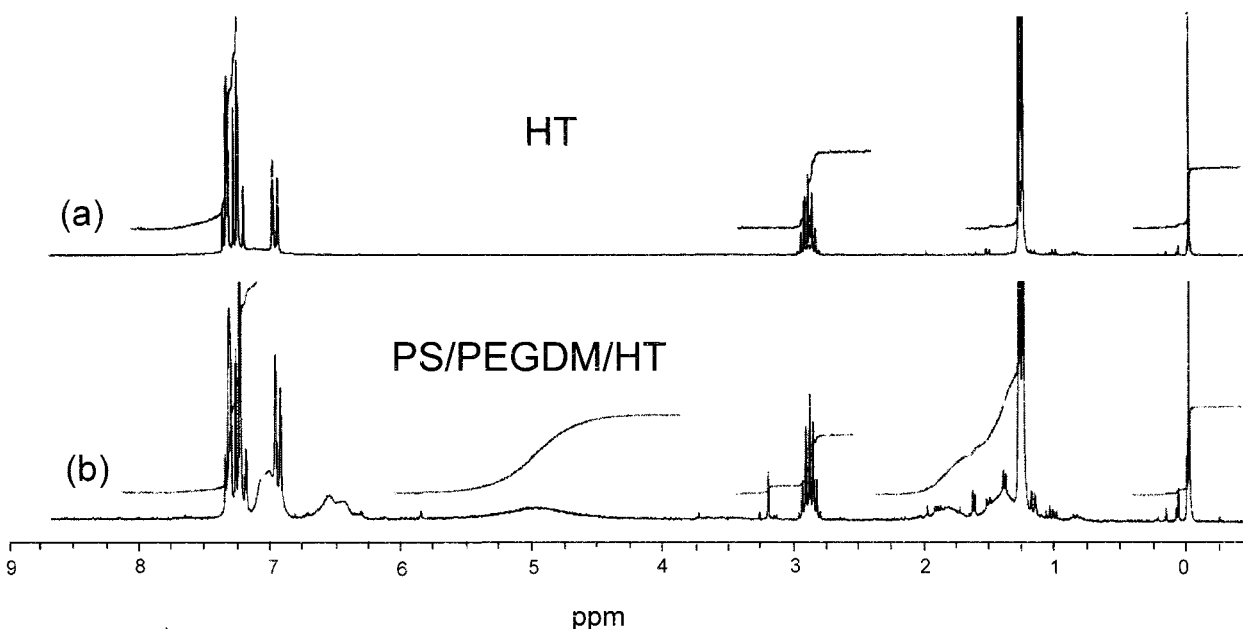
(SEM) photograph of the PS/PEGDM/HT composite particles. The composite particles had smooth surfaces. Therefore, it is clear that the reason the PS/PEGDM/HT composite particles had a heterogeneous structure on the optical micrograph shown in Figure 1 was based on the heterogeneous structure in the inside.

Figure 3 shows the TEM photographs of the ultrathin cross-sections of the PS/PEGDM/HT [Fig. 3(a)] and the PEGDM/HT [Fig. 3(b)] composite particles, which were produced by the suspension polymerizations under the conditions of numbers 2 and 4, respectively, listed in Table III. As shown in Figure 3(a), a shell and hollow structure were observed. The less dark regions indicate a hollow region after the evaporation of HT. The darker regions indicate the remaining HT, which was removed by extraction with ethanol, as shown in Figure 4. A

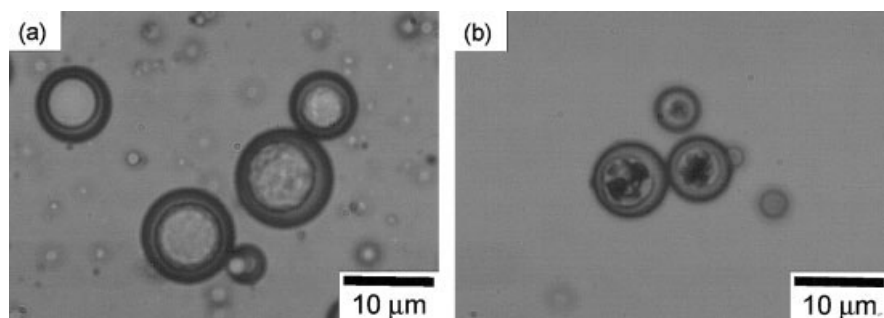


**Figure 6** Weight loss curves due to the evaporation of HT at 150°C under the N<sub>2</sub> flow from the (—) PS/PEGDM/HT and (---) PEGDM/HT composite particles, which were produced by suspension polymerization under the conditions of numbers 2 and 4 listed in Table III and from (- · -) pure HT.

region of similar contrast as the shell was also observed in the core. This was based on the polymers (PEGDM and PS), which were trapped in the crystallized HT during the polymerization. At 40°C, as the EGDM monomer was consumed during the polymerization, HT precipitated in the droplet because the polymerization temperature was below the melting point of HT. Because the viscosity inside the polymerizing droplet became high, the polymers were trapped in the core region. However, such a core-shell structure was not observed in any section of the PEGDM/HT composite particles, and the insides of the sections were observed to be almost homogeneous. This suggests that the HT was dispersed homogeneously in the particles. In this way,



**Figure 5** <sup>1</sup>H-NMR spectra of (a) pure HT and (b) the PS/PEGDM/HT composite particles (number 2 listed in Table III) in CDCl<sub>3</sub> including 0.1 wt % TMS.



**Figure 7** Optical micrographs of the (a) PS/PEGDM/HT composite particles (number 2 listed in Table III) and (b) those redispersed in water after being dried at 100°C for 6 days.

the existence of the PS dissolving in the droplets was important for the encapsulation of the HT by the PEGDM shell.

Figure 5 shows the  $^1\text{H-NMR}$  spectra of the pure HT and the PS/PEGDM/HT composite particles. Most of peaks of HT encapsulated in the hollow PS/PEGDM composite particle were in agreement with those of the pure HT, except for the broad peaks at 1–2, 5, and 6.2–7.2 ppm, which were assigned to PS and PVA. This indicated that HT was not denaturalized during the suspension polymerization. This conclusion was also supported by the fact that the dried composite particle had the same smell as the pure HT.

Figure 6 shows the weight loss curves due to the evaporation of HT at 150°C from pure HT and the PS/PEGDM/HT and PEGDM/HT composite particles. Both composite particles were obtained by drying at room temperature in a desiccator with silica gel for few days to depress the evaporation of the HT. Because PS and PEGDM were not decomposed at 150°C, the weight loss was due to only the evaporation of HT. The weight of pure HT decreased to zero within several minutes at 150°C. However, the rate of weight loss from both composite particles was much slower than that of pure HT. The rate of weight loss of HT from the PS/PEGDM/HT composite particles was slower than that from the PEGDM/HT composite particles. The times needed to evaporate all of the HT from the PS/PEGDM/HT and the PEGDM/HT composite particles were about 220 and 100 min, respectively. This indicated that the shell of the PS/PEGDM composite particle depressed the evaporation of the HT. The amounts of the HT in the composite particles calculated from the weight losses were about 80% based on the polymerization recipe. It seemed that about 20% of the HT was lost by dissolution in the medium during the polymerization.

Figure 7 shows the optical micrographs of the PS/PEGDM/HT composite particles [Fig. 7(a)] and those after drying at 100°C for 6 days [Fig. 7(b)]. In the latter

composite particles from which the HT was completely released, dark regions were observed in the inside because of the evaporation of HT from the inside of the particle. The space was filled with air. This suggested that the PS/PEGDM/HT composite particles had enough of a tough crosslinked shell to retain a spherical shape even when the HT was released at 100°C.

From these results, we concluded that the PS/PEGDM composite particle encapsulating the HT in the hollow was successfully produced by suspension polymerization of EGDM droplets dissolving PS and HT.

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