

# Structural Effect of Emulsifiers on the Emulsion Stability of a Water/Benzene Mixture

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**ABSTRACT:** Core-shell-type microspheres with microphase-separated shells of polystyrene (PS) and poly(ethylene glycol) (PEG) (microsphere<sub>block</sub>; molar ratio: PS/PEG 49.1/45.9 mol %;  $M_w$ : PS chain:  $1.07 \times 10^4$ , PEG chain  $1.0 \times 10^4$ ; the ratio of arm numbers of PEG to PS: 1.0; microsphere<sub>graft</sub>; molar ratio: PS/PEG 33.8/55.9 mol %;  $M_w$ : PS chain:  $1.54 \times 10^4$ , PEG chain  $1.0 \times 10^4$ , the ratio of arm numbers of PEG to PS: 2.55) were synthesized by crosslinking of spherical domains of poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(4-vinyl pyridine) (P4VP) of the microphase-separated films of poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene triblock terpolymer ( $M_n$ :  $2.18 \times 10^4$ ; molar ratio: PS 49.1 mol %, PHEMA 5.0 mol %, PEG 45.9 mol %) and polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethyl-

ene glycol)] *block*-*graft* copolymer ( $M_n$ :  $4.56 \times 10^4$ ; molar ratio: PS 33.8 mol %, P4VP 10.3 mol %, PEG 55.9 mol %; branch number of PEG: 2.55), respectively. The structures of microphase-separated films were investigated by transmission electron microscopy and small-angle X-ray scattering. The effects of the arm number ratio of PS to PEG and the total arm number on the stability of the water/benzene emulsion were investigated. The emulsion stability of oil in water was improved by using the microsphere synthesized with the microsphere<sub>graft</sub>. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 321–331, 2004

**Key words:** microsphere; emulsifier; emulsion stability; polystyrene; poly(ethylene glycol)

## INTRODUCTION

It is well known that block and graft copolymers with incompatible sequences form microphase separation.<sup>1,2</sup> Because of the arrangement of the junction points of sequences of the block and graft copolymers on the interface of incompatible phases, the block and graft copolymers are not only scientifically but also industrially useful emulsifiers.<sup>3–9</sup> Increasing the number of incompatible sequences in the emulsifiers increases the emulsion stability.<sup>6,7</sup> It is possible to vary the number of branches in the graft copolymer. The distance between the branches is decreased by increasing the number of branches. The supermolecules, such as polymer brushes,<sup>10,11</sup> star polymers,<sup>12,13</sup> and Janus-type microspheres<sup>14,15</sup> are composed with linear heteroarms. They formed the microphase separation in selective solvents, which were good solvents for one type of arms and bad solvents for another. With respect to the emulsion stability, they will be good emulsifiers.

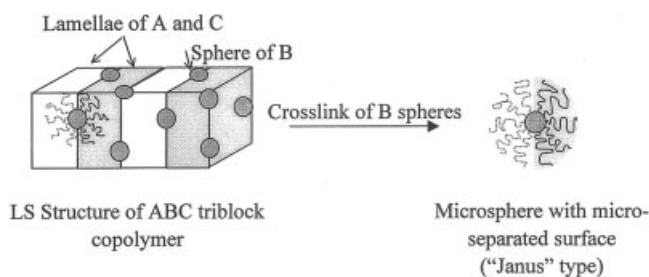
In contrast to the polymer brush with heteroarms, the clear phase separation was expected for the Janus-type microspheres with incompatible arms in good solvents for both arms. The Janus-type microspheres<sup>14,15</sup> were

synthesized by crosslinking of the spherical B microdomains of the A/C lamella–B spherical (LS) structure<sup>16–18</sup> of the microphase-separated films of ABC triblock terpolymers (Fig. 1). The A and C arms were strongly arranged in the film during fixation of the structure of microspheres by crosslinking of the spherical B domains. The linear aggregation of the polymer brushes with a rod structure resulted in the macrogelation of the system.<sup>19–21</sup> The spherical structure is preferable for supermolecular emulsifiers. The Janus-type microspheres were spherical. Thus, the higher stability of the emulsion is expected with the Janus-type microsphere rather than with polymer brushes and star polymers.

When the Janus-type microspheres are synthesized with A/C lamella–B spherical structure with ABC triblock terpolymer, the arm numbers of shells A and C are equal. On the other hand, when the *block*-*graft* copolymer, such as poly(A)-*block*-[poly(B)-*graft*-poly(C)], is used, the arm number ratio of shell C to shell A will be changed. In other words, the arm numbers of shell A and shell C can be independently varied by using the *block*-*graft* copolymer.

The purpose of this work was to investigate the effects of the architecture of the emulsifier, particularly the ratio of arm number of compatible sequences, on the emulsion stability of a benzene/water mixture by using the ABC triblock terpolymer, poly(A)-*block*-[poly(B)-*graft*-poly(C)] *block*-*graft* copolymer, the Janus-type microspheres with the ABC triblock terpoly-

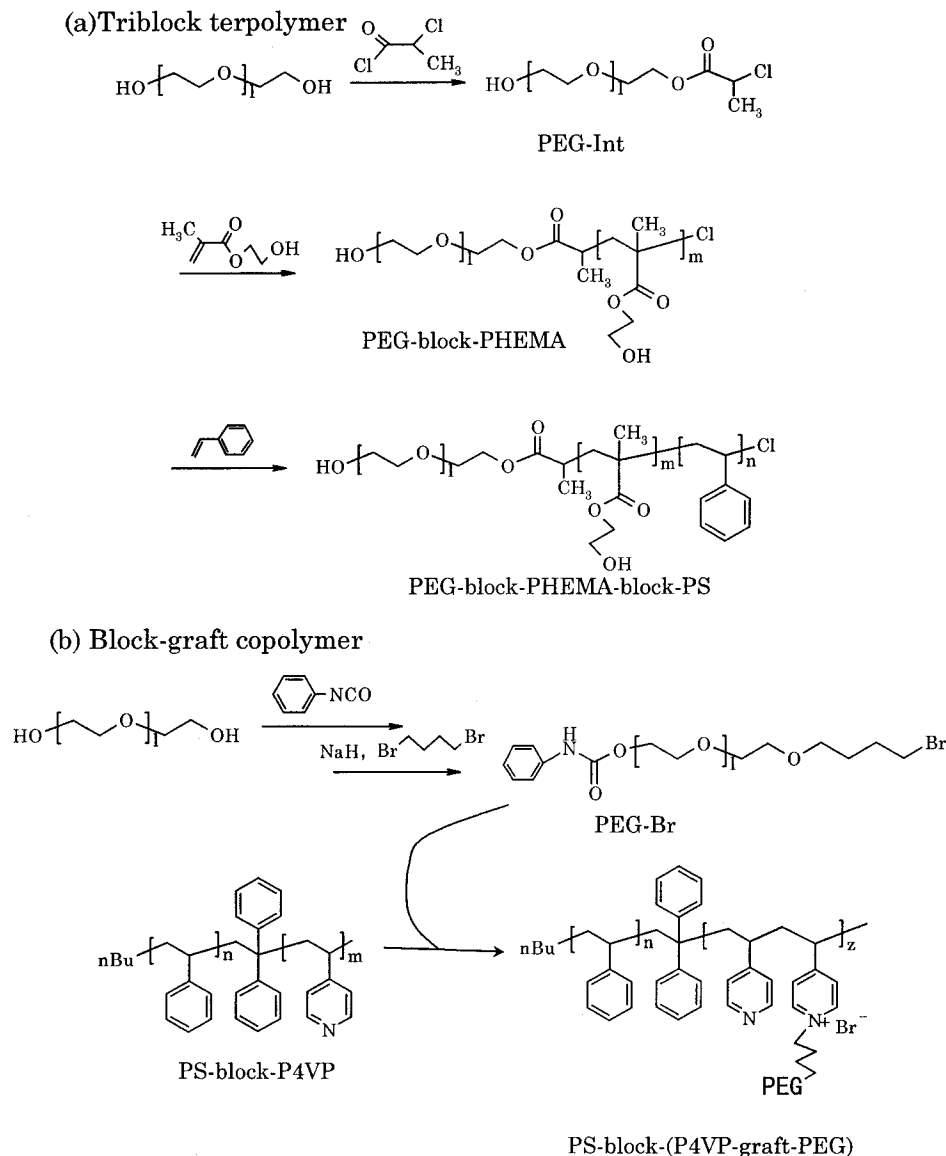
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**Figure 1** Synthetic concept of microgel with microphase-separated shells by crosslinking the spherical microdomains of LS structure.

mer, and the Janus-type microspheres with the poly(C)-*block*-[poly(B)-*graft*-poly(A)] block-*graft* copolymer as the emulsifier. Taking account of the microphase

separation of the block and block-*graft* copolymers, poly(ethylene glycol) (PEG)-*block*-poly(2-hydroxyethyl-methacrylate) (PHEMA)-*block*-polystyrene (PS) synthesized by copper-mediated atom-transfer radical polymerization (ATRP) and PS-*block*-[poly(4-vinyl pyridine) (P4VP)-*graft*-PEG] synthesized by chain coupling of PEG with brominated chain end onto the PS-*block*-P4VP synthesized by an anionic living polymerization technique were chosen as the poly(A)-*block*-poly(B)-*block*-poly(C) triblock terpolymer and the poly(A)-*block*-[poly(B)-*graft*-poly(C)] block-*graft* copolymer, respectively. The synthetic scheme of PEG-*block*-PHEMA-*block*-PS block terpolymer and PS-*block*-(P4VP-*graft*-PEG) block-*graft* terpolymer is shown in Scheme 1. The microphase separation of the block and block-*graft* copolymers was observed by transmission electron microscopy (TEM).



**Scheme 1** Synthesis of poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene and polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)].

Then, the spherical PHEMA and P4VP domains were crosslinked with 1,6-hexane diisocyanate and 1,4-dibromobutane, respectively. The formation of the Janus-type microspheres was confirmed by changing the solubility of the solvents. The stability of the benzene/water emulsion was then measured for the Janus-type microspheres and their raw polymers.

## EXPERIMENTAL

### Materials

2-Hydroxyethyl methacrylate (Tokyo Chemical Industry Co., Japan) and styrene (Kanto, Japan) were purified by distillation under vacuum. Benzene (Kanto), *n*-hexane (Kanto), 2-chloropropionyl chloride (Tokyo Chemical Industry Co.), triethylamine (Kanto), SnCl<sub>4</sub> (Tokyo Chemical Industry Co.), 1,4-dibromobutane (Tokyo Chemical Industry Co.), phenyl isocyanate (Tokyo Chemical Industry Co.), and 1,6-hexamethyl diisocyanate (Tokyo Chemical Industry Co.) were used without purification.

### Synthesis of PEG macroinitiator (PEG-Int)

A PEG macroinitiator (PEG-Int) for ATRP was synthesized by modification of an end of PEG [number-average molecular weight ( $M_n$ ) =  $1.0 \times 10^4$ ; Aldrich, Milwaukee, WI] with 2-chloropropionyl chloride as follows: PEG (1.0 g, 0.1 mmol,  $M_n$  =  $1.0 \times 10^4$ ; Aldrich) and triethylamine (0.010 g, 0.1 mmol) were dissolved in 10 mL of benzene. 2-Chloropropionyl chloride (0.013 g, 0.1 mmol) was added dropwise to the PEG/benzene solution at 0°C and the reaction was carried out at 0°C for 3 h. The PEG-Int was precipitated with 50 mL hexane, and purified by reprecipitation with 10 mL of benzene and 50 mL of *n*-hexane. The modification of the hydroxyl group with 2-chloropropionyl chloride was confirmed by FTIR spectrometry (FT/IR-410, Jasco, Tokyo, Japan) by the KBr method by using peaks at 1750 and 1100 cm<sup>-1</sup> assigned to carbonyl and ether groups, respectively, and <sup>1</sup>H-NMR (GLX-500, 500 MHz, solvent: deuterized dimethyl sulfoxide; JEOL, Tokyo, Japan).

### Synthesis of PEG-*block*-PHEMA-*block*-PS

2-Hydroxyethyl methacrylate (HEMA) and styrene (St) were polymerized stepwise with PEG-Int by an ATRP technique as follows: HEMA (3 mL), PEG-Int (1 g, 0.1 mmol), CuCl (0.001 g, 0.1 mmol) (Wako Pure Chemical Co., Japan), 4,4'-dinonyl-2,2'-dipyridyl (0.082 g, 0.2 mmol) (Aldrich), and 2-butanone (2.1 mL) (Kanto)/1-propanol (0.9 mL) (Kanto) were charged in a tube. The tube was degassed and polymerization was carried out at 70°C for 3 h. Reaction was terminated by cooling the tube in an ice-water bath. PEG-

*block*-PHEMA polymer was purified by precipitation with 100 mL of water and dried under vacuum. St (7 mL), PEG-*block*-PHEMA (1.1 g, 0.1 mmol), CuCl (0.001 g, 0.1 mmol), and 4,4'-dinonyl-2,2'-dipyridyl (0.082 g, 0.2 mmol) were charged in a tube. The tube was degassed and polymerization was carried out at 110°C for 28 h. Reaction was terminated by cooling the tube in an ice-water bath. PEG-*block*-PHEMA-*block*-PS polymer was purified by precipitation with 100 mL of *n*-hexane and dried under vacuum.

### Synthesis of $\alpha$ -phenyl amido- $\omega$ -bromo poly(ethylene glycol) (PEG-Br)

To synthesize a PEG branch (PEG-Br)<sup>1</sup> for grafting with PS-*block*-P4VP, hydroxyl groups of PEG ( $M_n$  =  $1.0 \times 10^4$ ; Aldrich) were modified with phenyl isocyanate and 1,4-dibromobutane as follows: PEG (1.0 g, 0.1 mmol,  $M_n$  =  $1.0 \times 10^4$ ; Aldrich) was dissolved in 10 mL of benzene. Phenyl isocyanate (0.012 g, 0.1 mmol) was added to the solution and the reaction was carried out at room temperature for 72 h. Modified polymer was precipitated with diethyl ether and dried under vacuum. Then, the modified polymer (1.01 g, 0.1 mmol) was dissolved in 10 mL of benzene under a dry nitrogen atmosphere. NaH (0.036 g, 1.5 mmol) (Kanto, Japan) was added to the solution and the reaction was carried out at room temperature for 4 h. 1,4-Dibromobutane (0.324 g, 1.5 mmol) was added dropwise and the reaction was carried out at room temperature for 6 h. After the reaction, the solution was filtered, and the product PEG-Br in the solution was precipitated with 50 mL of diethylether and dried under vacuum. The degree of bromination of the PEG (functionality), determined by Volhart's titration, was 65.4 mol %.

### Synthesis of PS-*block*-[P4VP-*graft*-PEG]

PS-*block*-P4VP ( $M_n$  =  $2.6 \times 10^4$ ; content of styrene 76.9 mol %) was previously synthesized with *n*-butyl lithium in a tetrahydrofuran (THF)/benzene mixture at -78°C by an additional anionic living polymerization technique.<sup>22</sup> The PEG-Br was grafted onto PS-*block*-P4VP as follows: PS-*block*-P4VP (1.0 g, 0.038 mmol) and PEG-Br (2.5 g, 0.25 mmol) were dissolved in benzene (19 mL)/methanol (1 mL). The reaction was carried out for 50°C for 24 h. After the reaction, the product [PS-*block*-(P4VP-*graft*-PEG)] *block*-*graft* copolymer was extracted with THF.

### Preparation and crosslinking of the microphase-separated film

PS-*block*-(P4VP-*graft*-PEG) and PEG-*block*-PHEMA-*block*-PS were dissolved in benzene; the polymer concentration was 1.0 wt %. Then, the solutions were cast

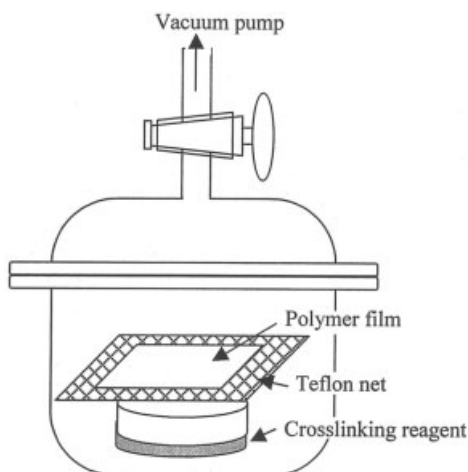


Figure 2 Apparatus used for crosslinking of the films.

onto Teflon dishes and gradually dried at room temperature. To homogeneously crosslink the P4VP and PHEMA domains in *PS-block-(P4VP-graft-PEG)* and *PEG-block-PHEMA-block-PS* films, respectively, the film thickness ranged from 50 to 60  $\mu\text{m}$ . The films and the crosslinking reagents, 1,4-dibromobutane and 1,6-hexamethylene diisocyanate for *PS-block-(P4VP-graft-PEG)* and *PEG-block-PHEMA-block-PS*, respectively, were set in a 300-mL separable flask (Fig. 2). The molar ratios of 1,4-dibromobutane to P4VP for *PS-block-(P4VP-graft-PEG)* and 1,6-hexamethylene diisocyanate to PHEMA for *PEG-block-PHEMA-block-PS* were 1.5. Then the separable flask was degassed and sealed. The reaction was carried out for 24 h at room temperature and 80°C for *PS-block-(P4VP-graft-PEG)* and *PEG-block-PHEMA-block-PS*, respectively. After the reaction, the films were washed three times with excess amounts of hexane and dried under vacuum.

### Preparation of emulsions

Water (50 mL), benzene (50 mL), and polymer (50 mg) were mixed in a cylindrical glass tube ( $\phi = 40$  mm). The solution was irradiated with 28 MHz of ultrasonic wave with an ultrasonic wave irradiator (SV-100III, Iuchi, Japan) for 10 min. Transmittance of upper and

lower layers of the emulsion was measured without wave length control of the light.

### Characteristics

Values of  $M_n$  and  $M_w/M_n$  [polydispersity index (PDI)] of the block and block-graft copolymers were determined by GPC (Tosho HLC-8020, column TSK-GEL G5000-HHR, solvent: chloroform, temperature: 30°C, flow rate: 0.8 mL  $\text{min}^{-1}$ ).

The molar contents of the block and block-graft copolymers were determined by FTIR (Jasco FTIR spectrometer, FT/IR-410) by using specific absorption peaks at 1750, 1100, and 700  $\text{cm}^{-1}$  assigned to the carbonyl, ether, and phenyl groups, respectively, and by  $^1\text{H-NMR}$  (GLX-500, 500 MHz, solvent: deuterized dimethyl sulfoxide; JEOL). Characteristics of the *PS-block-(P4VP-graft-PEG)* and *PEG-block-PHEMA-block-PS* are listed in Table II.

To observe the structure of the microphase separation of the film, the film was microtomed using an Ultracut-N microtome (Reihert). The specimen was stained with ruthenium tetroxide ( $\text{RuO}_4$ ; Soekawa Chemicals), observed under a transmission electron microscope (JEM-200 CX, JEOL) operated at 100 kV. Small-angle X-ray scattering (SAXS) measurements were carried out for the films with a rotating anode X-ray generator (Rotaflex RTP 300 RC; Rigaku Denki, Japan) operated at 40 kV and 100 mA. The X-ray source was monochromatized to  $\text{Cu-K}\alpha$  ( $\lambda = 1.52$  Å) radiation. The SAXS patterns were recorded by using an imaging plate technique.

The hydrodynamic radius of the microgel was measured in benzene at 0.1 wt % of polymer concentration with dynamic light scattering (DLS; TMLS-700HL, Photal) at 25°C.

The contact angle of polymer/benzene solutions on glass was measured in water at 25°C.

## RESULTS AND DISCUSSION

### Synthesis of *PEG-block-PHEMA-block-PS* block terpolymer and *PS-block-(P4VP-graft-PEG)* block-graft terpolymer

First, the target volume fractions of the B sequence,  $\phi_B$ , to form AC lamella-B sphere structures (LS structure)

TABLE I  
Critical Molar Fractions of *PEG-block-PHEMA-block-PS* Block Terpolymer and *PS-block-(P4VP-graft-PEG)* Block-Graft Terpolymer Calculated by Using Eqs. (1) and (2)

Code	$f^a$	Calculated volume fraction (%)			Calculated molar fraction (%)		
		PEG	PHEMA or P4VP	PS	PEG	PHEMA or P4VP	PS
<i>PEG-block-PHEMA-block-PS</i>	1.643	46.9	6.1	46.9	67.0	3.8	29.2
<i>PS-block-(P4VP-graft-PEG)</i>	0.169	47.1	5.8	47.1	67.3	3.5	29.2

<sup>a</sup> Parameter  $f$  described in eq. (2).

TABLE II  
 Characteristics of Poly(ethylene glycol) Macroinitiator (PEG-Int), Poly(ethylene glycol) Branch (PEG-Br), Poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)/(PEG-*block*-PHEMA), Poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene (PEG-*block*-PHEMA-*block*-PS), and Polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)]/(PS-*block*-[P4VP-*graft*-PEG])

Code	$M_n (\times 10^4)^a$			Content (mol %) <sup>b</sup>			Volume fraction (%)			$F^c$	Number of branch <sup>d</sup>
	PEG	PHEMA or P4VP	PS	PEG	PHEMA or P4VP	PS	PEG	PHEMA or P4VP	PS		
PEG-Int	1.00	—	—	100.0	—	—	100	—	—	0.89	—
PEG- <i>block</i> -PHEMA	1.00	0.11	—	96.4	3.6	—	92.0	8.0	—	—	—
PEG- <i>block</i> -PHEMA- <i>block</i> -PS	1.00	0.11	1.07	67.1	2.5	30.4	48.6	4.0	47.4	—	—
PEG-Br	1.0	—	—	100	—	—	100	—	—	0.654	—
PS- <i>block</i> -[P4VP- <i>graft</i> -PEG]	2.55	0.46	1.54	75.2	5.7	19.2	56.6	10.1	33.6	—	2.55

<sup>a</sup> Number-average molecular weight calculated with the data of GPC and the content of each sequence.

<sup>b</sup> Contents of each sequence determined by <sup>1</sup>H-NMR.

<sup>c</sup> Number of 2-chloropropionate group and bromide group introduced in poly(ethylene glycol) determined by Volhart's titration.

<sup>d</sup> Number of PEG branch on PS-*block*-(P4VP-*graft*-PEG).

as a template for Janus-type microgels, were calculated by using the following equations<sup>17</sup> and the results are listed in Table I. It should be noted that  $\phi_A$  and  $\phi_C$  values should be close.

$$\phi_B \leq \frac{\pi(1-f)^2}{(2\pi-f)^2} \quad (1)$$

$$f = \frac{\gamma_{A-C}}{\gamma_{A-B} + \gamma_{B-C}} \quad (2)$$

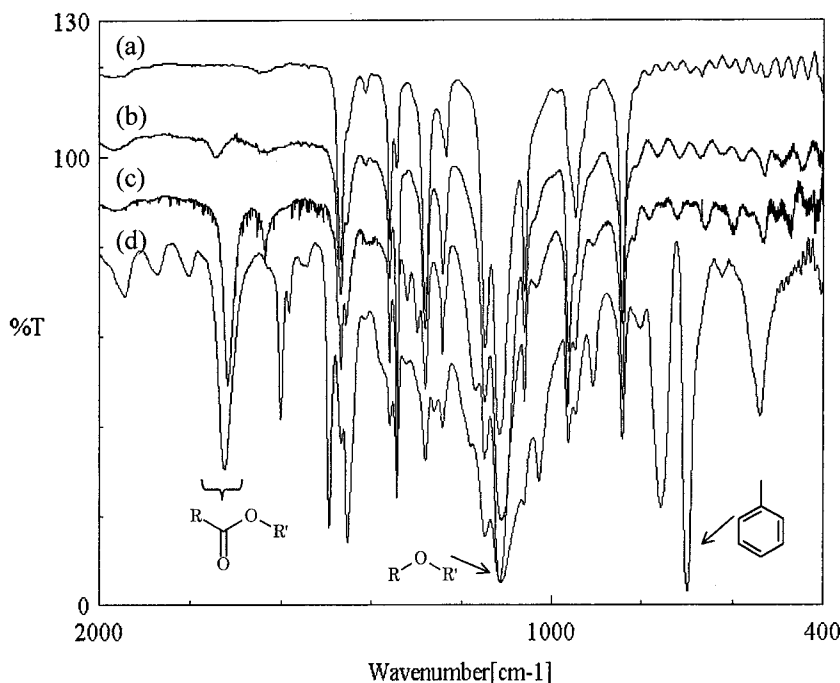
where  $\gamma_{A-C}$  is the interfacial tension between domains A and C. Based on these values, PEG-*block*-PHEMA-*block*-PS and S-*block*-(P4VP-*graft*-PEG) were synthesized.

To synthesize PEG-*block*-PHEMA-*block*-PS block terpolymer, the PEG macroinitiator with one initiation site, 2-chloropropionyl group, PEG-Int, for ATRP was synthesized by esterification of hydroxyl group with 2-chloropropionic chloride. The 2-chloropropionyl group is a popular initiation group of ATRP for methacrylates and styrene.<sup>23,24</sup> Figure 3 shows the FTIR spectra of PEG, PEG-Int, PEG-*block*-PHEMA, and synthesized PEG-*block*-PHEMA-*block*-PS block terpolymer. After esterification of PEG with 2-chloropropionic chloride, a new peak attributed to the carbonyl group of the 2-chloropropionyl group appeared at 1730 cm<sup>-1</sup>, indicating the esterification of PEG with chloro 2-chloropropionate.

Figure 4(a) shows the <sup>1</sup>H-NMR spectra of PEG-Int. After esterification, new signals (b and c) appeared at 1.62 and 4.24 ppm attributed to methyl protons and methylene protons next to the ester group, respectively, even though the signal of OH in PEG in DMSO-*d*<sub>6</sub> at 4.56 ppm was observed. Thus, the introduction of the 2-chloropropionyl group to PEG was

also confirmed by <sup>1</sup>H-NMR. The number of 2-chloropropionyl group introduced in a PEG chain estimated by <sup>1</sup>H-NMR (0.85) showed a good agreement with that measured by Volhart's titration (0.89). The telechelic PEG macroinitiator with two 2-chloropropionyl groups<sup>24</sup> and poly(ethylene oxide) (PEO) macroinitiator with a 2-bromopropionyl group<sup>25</sup> were quantitatively synthesized by esterification of PEG with 2-chloropropionic chloride and PEO with 2-bromopropionic bromide. The polymers with 2-chloropropionyl groups at the ends of the chain were good macroinitiators of ATRP for methacrylates and St.<sup>24,25</sup> In this work, PEG-Int was successfully synthesized by decreasing the amount of 2-chloropropionic chloride. Unreacted PEG can be removed from the PEG-*block*-PHEMA by extraction. Thus, PEG-Int was used for the synthesis of PEG-*block*-PHEMA and PEG-*block*-PHEMA-*block*-PS by ATRP.

After polymerization with HEMA [Fig. 3(c)], absorption of the carbonyl group at 1730 cm<sup>-1</sup> was dramatically increased, attributed to the polymerization of HEMA. Figure 4(b) shows the <sup>1</sup>H-NMR spectra of PEG-*block*-PHEMA. New relatively narrow peaks (e and f), and a broad peak around 0.6 to 1.0 ppm, representing methylene protons next to hydroxyl group, next to the ester group, and in the PHEMA backbone appeared by ATRP of HEMA. After polymerization with St [Fig. 3(d)], a new peak attributed to the phenyl group of St appeared at 720 cm<sup>-1</sup>. Figure 4(c) shows the <sup>1</sup>H-NMR spectra of PEG-*block*-PHEMA-*block*-PS. New narrow peaks (g and h) attributed to aromatic protons and a broad peak around 1.2 to 1.8 ppm attributed to methylene/methine protons in PS appeared, as shown in Figure 4(c), indicating the successful formation of PEG-*block*-PHEMA-*block*-PS. Con-



**Figure 3** FTIR spectra of (a) poly(ethylene glycol), (b) poly(ethylene glycol) macroinitiator, (c) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate), and (d) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene.

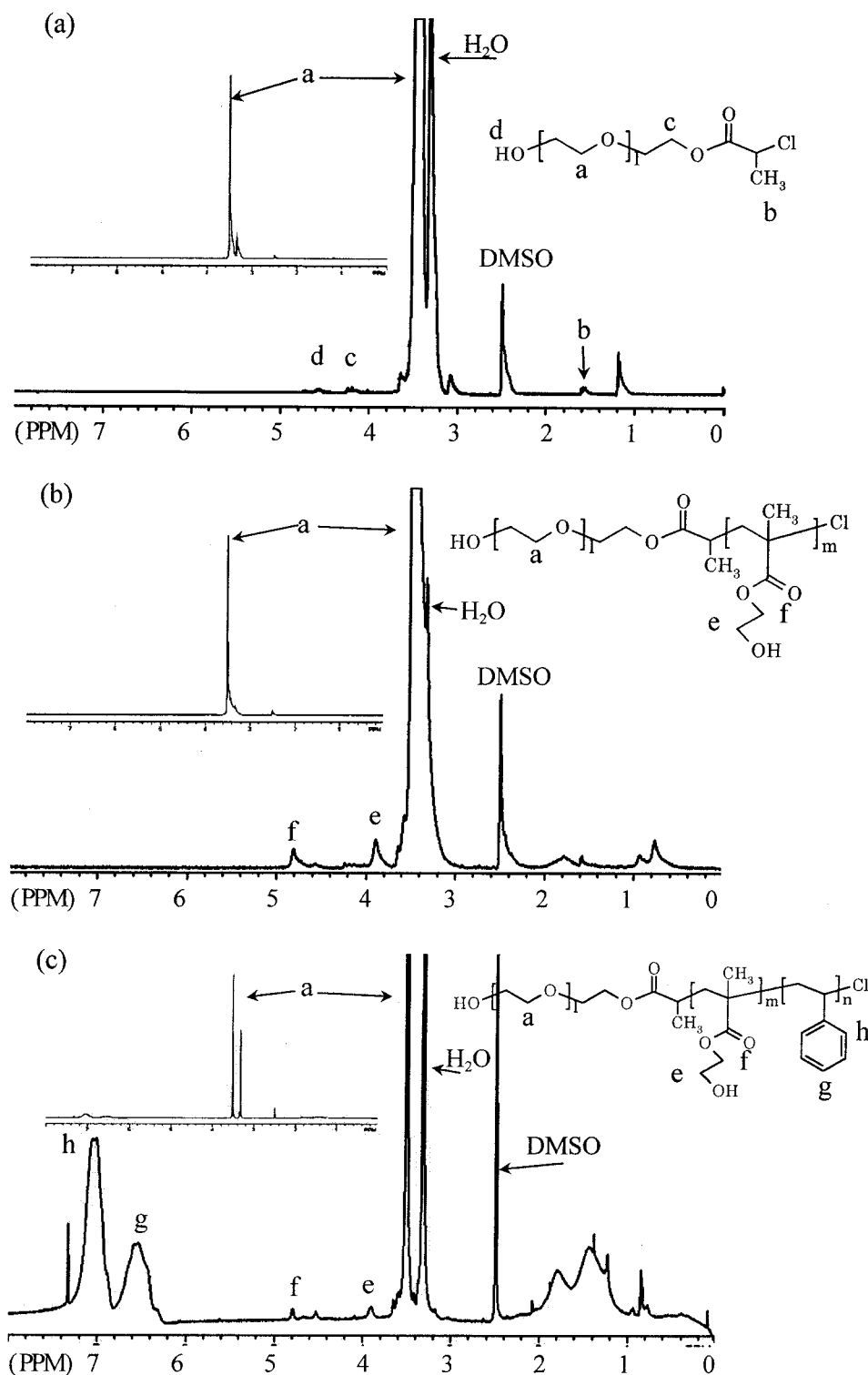
sequently, HEMA and St were continuously polymerized with PEG-Int.

Increasing the molecular weight of the PEG-Int with HEMA and PEG-*block*-PHEMA with St was investigated by GPC. Figure 5 shows the GPC profiles of PEG-Int, PEG-*block*-PHEMA, PEG-*block*-PHEMA-*block*-PS, and PS-*block*-(P4VP-*graft*-PEG). By ATRP of HEMA with the PEG-Int, the entire elution peak of GPC was shifted linearly toward higher molecular weight, indicating that PEG-*block*-PHEMA was synthesized by ATRP of HEMA with PEG-Int. The PDI of PEG-*block*-PHEMA was narrow ( $<1.05$ ). After ATRP of styrene with PEG-*block*-PHEMA, the GPC peak that shifted to higher molecular weight indicates the formation of PEG-*block*-PHEMA-*block*-PS. The molar contents of PEG, PHEMA, and PS were determined by FTIR with peaks at  $1750$ ,  $1100$ , and  $750\text{ cm}^{-1}$  attributed to the carbonyl group in HEMA, the ether group in PEG, and the phenyl group in PS, respectively, and by  $^1\text{H-NMR}$ . The contents determined by FTIR and  $^1\text{H-NMR}$  were in substantial agreement. The molar fractions of the polymers determined by  $^1\text{H-NMR}$  are listed in Table II. The molar fractions of PEG-*block*-PHEMA-*block*-PS were close to the target values for the LS structure listed in Table I. However, the PDI of PEG-*block*-PHEMA-*block*-PS was relatively wide ( $=1.35$ ). An increase in the PDI value was attributed to the higher viscosity of the reaction solution. When the PDI is lower than 1.5, the homogeneous structure of the microphase separation can be obtained. Thus, PEG-*block*-PHEMA-*block*-PS was used as the template polymer for the Janus-type microspheres.

To synthesize PS-*block*-(P4VP-*graft*-PEG), PEG-Br was first synthesized by  $\alpha$ -phenyl- $\omega$ -bromo-PEG. The number of bromide in the PEG, determined by Volhart's titration, was 0.654 (Table II). The GPC peak of PEG-Br without the shift from the PEG indicated the complete inhabitation of the coupling of PEG chains during the bromination. The GPC peak [Fig. 3(d)] was shifted toward higher molecular weight by grafting of PEG-Br onto PS-*block*-P4VP. Because of the absorption of P4VP sequence of PS-*block*-P4VP on the column, PS-*block*-P4VP was not measured by GPC under those conditions. On the other hand, PS-*block*-(P4VP-*graft*-PEG) was measured by GPC. The absorption of the P4VP sequence was hindered by covering with PEG grafted onto the P4VP sequence. The volume fractions of each sequence are listed in Table II. The volume fraction of PEG of PS-*block*-(P4VP-*graft*-PEG) was higher than the target values for the LS structure. The branch number of PEG in PS-*block*-(P4VP-*graft*-PEG) was 2.55. For PS-*block*-(P4VP-*graft*-PEG), the hydrodynamic diameter of the PEG chain is expected to be less than that of PS. Thus, the formation of the LS structure would be expected with PS-*block*-(P4VP-*graft*-PEG) with a larger PEG volume fraction than the target value. Thus, both polymers were used for the synthesis of the Janus-type microspheres.

#### The microphase separation of PEG-*block*-PHEMA-*block*-PS and PS-*block*-(P4VP-*graft*-PEG) films

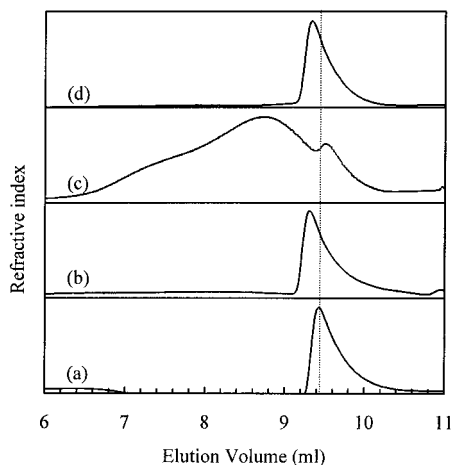
The microphase-separated films were prepared by casting the polymer solutions. The volume fractions of



**Figure 4**  $^1\text{H-NMR}$  spectra of (a) poly(ethylene glycol) macroinitiator, (b) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate), and (c) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene.

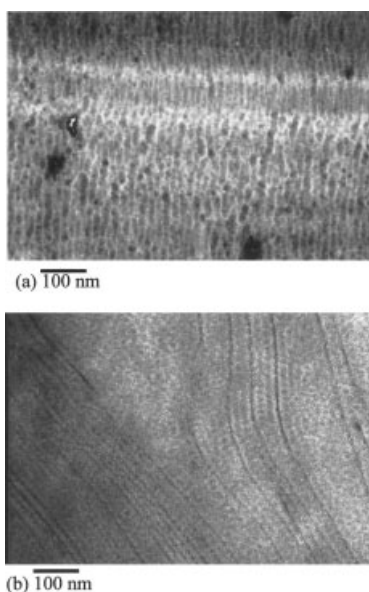
the P4VP were slightly larger than the target values. To decrease the expansion of the middle sequence in the solution, benzene—a good solvent for PS and PEG and a bad solvent for the middle sequences—was used as a cast solvent. The structures of the microphase

separation of PEG-*block*-PHEMA-*block*-PS and PS-*block*-(P4VP-*graft*-PEG) were investigated by TEM (Fig. 6). Dark regions are selectively stained PS, PHEMA, and P4VP with  $\text{RuO}_4$ . The black short rods consisting of PS and PHEMA, and the dark spherical



**Figure 5** GPC profiles of (a) poly(ethylene glycol) macro-initiator, (b) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate), (c) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene, and (d) polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)].

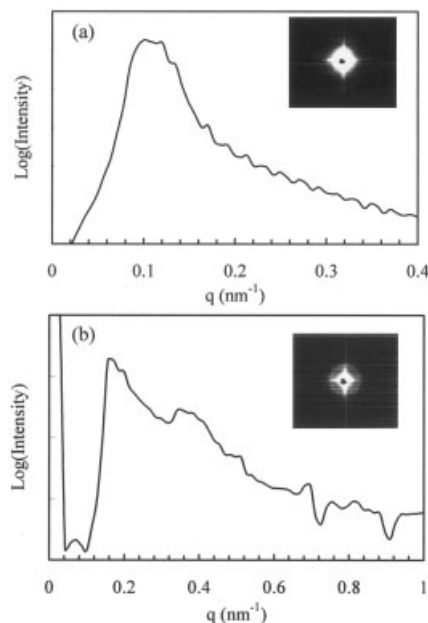
and linear domains consisting of PS and P4VP were observed for PEG-*block*-PHEMA-*block*-PS [Fig. 6(a)] and PS-*block*-(P4VP-*graft*-PEG) [Fig. 6(b)], respectively. The average domain spacing of the dark line was 40 nm. The lamellae and cylinder domains are observed as dark lines by TEM. Thus, the lamellar structure of PS and P4VP was not confirmed by this TEM micrograph. Because the molar fractions of PHEMA and P4VP were much lower than those of PS, the dark regions were assumed to be PS domains.



**Figure 6** TEM micrographs of (a) poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene and (b) polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] stained with  $\text{RuO}_4$ .

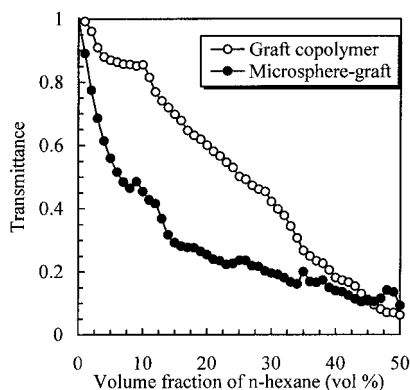
To specify the structure of the microphase separation, SAXS spectra and the scattering patterns were measured (Fig. 7). The clear rings indicate the formation of the ordered structures in the films. The values of  $qn/q_1$  observed for PEG-*block*-PHEMA-*block*-PS were 1.0, 1.225, 1.414, 1.581, 1.732, 1.8708, 2, 2.12, 2.345, 2.645, and 2.739 with  $q_1 = 0.121 \text{ nm}^{-1}$ . This peak pattern agreed with that of the peak pattern for the ordered bicontinuous double diamond (OBDD) with the space group  $\text{Pn}3$  and  $\text{Pn}3m$  [ $=1, (3/2)^{1/2}, 2^{1/2}, (5/2)^{1/2}, 3^{1/2}, (7/2)^{1/2}, 4^{1/2}, (9/2)^{1/2}, (11/2)^{1/2}, 7^{1/2},$  and  $(15/2)^{1/2}$ ].<sup>26,27</sup> Hashimoto and coinvestigators<sup>27</sup> reported TEM morphology of the OBDD structure similar to that shown in Figure 6(a). Thus, the structure of PEG-*block*-PHEMA-*block*-PS was concluded to be the OBDD. The  $d_1$  of this structure was 51 nm. Because the peaks of spherical domains consisting of PHEMA overlapped the peaks of the OBDD, it was impossible to determine the packing structure of the PHEMA domains.

For PS-*block*-(P4VP-*graft*-PEG), the dark lines and spheres were observed by TEM. When  $q_1$  was assumed at  $0.171 \text{ nm}^{-1}$ , the clear peak patterns ( $qn/q_1 = 1, 2, 3,$  and  $4$ ) attributed to the lamellar and cylindrical structures were observed at  $qn = 0.17, 0.34, 0.51,$  and  $0.68$ . However, the peaks attributed to the cylindrical structure ( $qn/q_1 = 1.73$  and  $2.65$ ) were not observed at  $qn = 0.294$  and  $0.45$ , respectively. Thus, the dark lines observed by TEM were lamellae. The domain spacing of lamellae with  $q_1 = 0.171 \text{ nm}^{-1}$  is 36.7 nm. The domain spacing values of lamellae de-



**Figure 7** SAXS profiles of (a) the poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene film and (b) the polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] film.





**Figure 8** Turbidimetric titration of polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene)] and the microsphere<sub>block</sub> synthesized with polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene)] in benzene/*n*-hexane mixture.

terminated by SAXS and TEM were in substantial agreement. The peak pattern of a single crystal with  $q_1 = 0.14 \text{ nm}^{-1}$  was also observed for PS-*block*-(P4VP-*graft*-PEG) at  $q = 0.20, 0.24,$  and  $0.29$ . Not only lamellae but the spherical domains with single-crystal packing patterns existed in the film of PS-*block*-(P4VP-*graft*-PEG). The domain spacing of the spherical domains with single-crystal structure with  $q_1 = 0.14 \text{ nm}^{-1}$  was  $44.9 \text{ nm}$ . If the PS domains were isolated in the film for most cases, the PHEMA domains would also be isolated in the film, which suggests microsphere formation by crosslinking of PHEMA or P4VP. Because of the complex structure, further analysis was not carried out.

### Synthesis of the Janus-type microspheres

The PHEMA and P4VP domains of PEG-*block*-PHEMA-*block*-PS and PS-*block*-(P4VP-*graft*-PEG) microphase-separated films were crosslinked with 1,6-hexane diisocyanate and 1,4-dibromo butane, respectively. After the crosslinking, the crosslinked product of PEG-*block*-PHEMA-*block*-PS, microsphere<sub>block</sub> was not dissolved in benzene, dimethylsulfoxide, and dimethylformamide, but in the water/benzene mixture. The solubility change was attributed to the formation of microspheres with PEG-*block*-PHEMA-*block*-PS. It was impossible to determine the diameter of microspheres and the crosslink density because of its solubility.

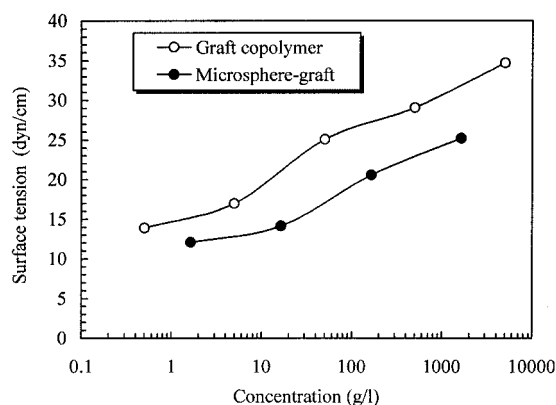
To confirm the crosslinking of PS-*block*-(P4VP-*graft*-PEG), the turbidimetric behaviors of the PS-*block*-(P4VP-*graft*-PEG) series were measured in a benzene/*n*-hexane mixture (Fig. 8). The crosslinked product was precipitated at a lower volume fraction of *n*-hexane attributed to increases of molecular weight of the products by crosslinking. The hydrodynamic di-

ameter of the crosslinked PS-*block*-(P4VP-*graft*-PEG) in benzene measured by DLS at  $90^\circ$  was  $79.5 \text{ nm}$  with a PDI of 1.07. The crosslink density of the P4VP estimated by Volhart's titration was  $38.5 \text{ mol } \%$ , and the P4VP was tightly crosslinked. The microsphere of PS-*block*-(P4VP-*graft*-PEG), microsphere<sub>graft</sub>, with narrow size distribution was formed.

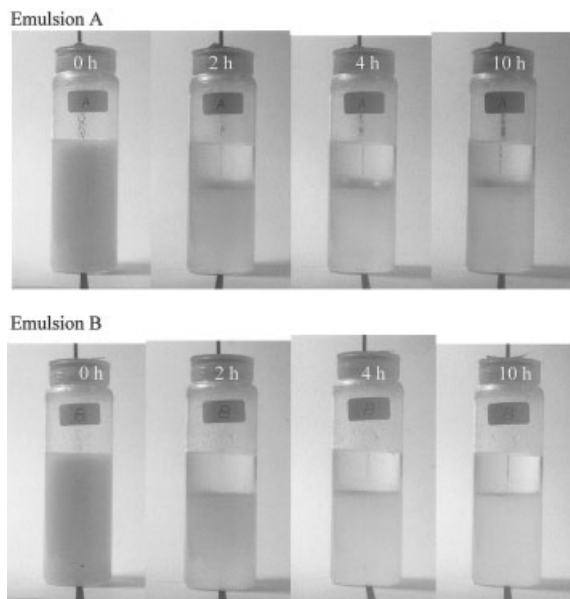
### Emulsion stability of PEG-*block*-PHEMA-*block*-PS, PS-*block*-(P4VP-*graft*-PEG), and their microspheres

The concentration and structural effects of PS-*block*-(P4VP-*graft*-PEG) and the microsphere<sub>graft</sub> on the surface tension between the polymer/benzene and water were measured. Figure 9 shows the surface tension between the polymer/benzene and water. The surface tension of the microsphere<sub>graft</sub> was lower than that of PS-*block*-(P4VP-*graft*-PEG) at the same polymer concentration. As expected, the microsphere<sub>graft</sub>, which was a supermolecule of the aggregates of PS-*block*-(P4VP-*graft*-PEG), was a better emulsifier than PS-*block*-(P4VP-*graft*-PEG). The surface tension of both polymers was increased at 0.1 to 0.01 g/L of the polymer concentration. The critical micelle concentrations of these polymers were in the range from 0.1 to 0.01 g/L. Thus, the stability measurements of the benzene/water mixture were investigated at 0.1 g/L of the polymer concentration.

Figure 10 shows the emulsions of benzene/water with PEG-*block*-PHEMA-*block*-PEG (emulsion A) and with the microsphere<sub>block</sub> (emulsion B). As described above, the microsphere<sub>block</sub> was not dissolved in benzene or water, but in the benzene/water mixture. The homogeneous emulsions were obtained with PEG-*block*-PHEMA-*block*-PEG and the microsphere<sub>block</sub>. After the formation of the emulsion, the emulsions started to phase separate, and transmittance of the upper layer—the benzene layer—was drastically increased. On the other hand, the lower layer—the water layer—was opaque up to 10 h. This indicates that



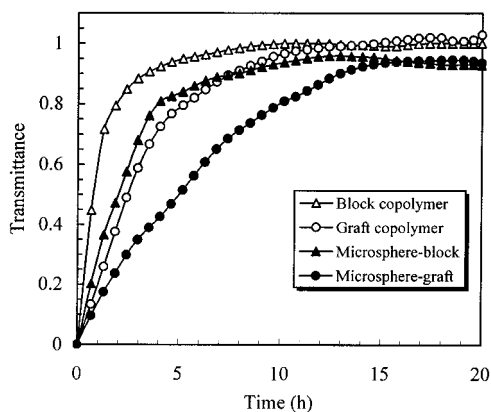
**Figure 9** Surface tension of benzene-polymer solution.



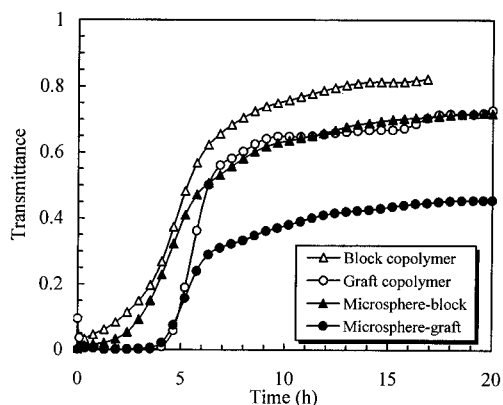
**Figure 10** The benzene/water emulsions with emulsion A [poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene] and emulsion B [microsphere<sub>block</sub> synthesized with poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene].

the oil in water (O/W)-type emulsion was formed with PEG-*block*-PHEMA-*block*-PEG and the microsphere<sub>block</sub>.

For quantitative investigation, the change of transmittance of the upper and lower layers was separately measured. Figure 11 is the transmittance change of emulsions of the upper layer. For all polymers, all emulsions were finally phase-separated. The transmit-



**Figure 11** Transmittance of benzene layer of the benzene/water emulsions with poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene (open triangle); polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] (open circle); the microsphere<sub>block</sub> synthesized with poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene (solid triangle); and the microsphere<sub>graft</sub> synthesized with polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] (solid circle).



**Figure 12** Transmittance of water layer of the benzene/water emulsions with poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene (open triangle); polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] (open circle); the microsphere<sub>block</sub> synthesized with poly(ethylene glycol)-*block*-poly(2-hydroxyethyl methacrylate)-*block*-polystyrene (solid triangle); and the microsphere<sub>graft</sub> synthesized with polystyrene-*block*-[poly(4-vinyl pyridine)-*graft*-poly(ethylene glycol)] (solid circle).

tance of the upper layer was immediately increased after the formation of the emulsion, and it reached over 0.86 with any polymer. The polymers synthesized in this work were not proper emulsifiers for the water in oil (W/O)-type emulsion. The delayed increase of transmittance corresponds to the stability of the emulsion. The better the emulsifier, the slower the increase in transmittance. The efficiency of the emulsifiers was higher for the PS-*block*-(P4VP-*graft*-PEG) series than that for the PEG-*block*-PHEMA-*block*-PEG series. The saturation time of the transmittance of the Janus-type microspheres was longer than that of the precursor polymers. The saturated transmittances of the PS-*block*-(P4VP-*graft*-PEG) and PEG-*block*-PHEMA-*block*-PEG, about 0.95, were higher than those of the microsphere<sub>graft</sub> and microsphere<sub>block</sub>, 0.85. It was found that the efficiency of the emulsifier was improved by forming the Janus-type microspheres even in the upper layer.

Figure 12 shows the transmittance of the lower layer of the emulsion. In contrast to the upper layer, the transmittance of the lower layer increased with an S shape. The saturated values [0.8, 0.7, 0.7, and 0.4 for PEG-*block*-PHEMA-*block*-PS, the microsphere<sub>block</sub>, PS-*block*-(P4VP-*graft*-PEG), and the microsphere<sub>graft</sub>, respectively] were much smaller than those in the upper layer. The polymers synthesized in this work were good emulsifiers to form the O/W-type emulsion. The emulsion stability with PS-*block*-(P4VP-*graft*-PEG) was higher than that with PEG-*block*-PHEMA-*block*-PS. The PEG and PS arms expand to the water layer and benzene droplet, respectively. The higher ratio of arm number of PEG to PS of PS-*block*-(P4VP-*graft*-PEG), 2.55, than that of PEG-*block*-PHEMA-*block*-PS would cause an increase in the stability

of the benzene droplet in water. The formation of the Janus-type microsphere greatly improved the stability of the emulsion of the lower layer. The decrease in the saturated values, by increasing the ratio of the arm number and the total arm number by forming the Janus-type microspheres, in the lower layer was more drastic than that in the upper layer. Thus, the efficiency of the emulsifier in the lower layer was improved by increasing the ratio of arm number of PEG to PS and the total arm number by the formation of the Janus-type microspheres.

### CONCLUSIONS

To investigate the structural effect of emulsifiers, the Janus-type microspheres with microphase-separated shells of PS and PEG, microsphere<sub>block</sub> and microsphere<sub>graft</sub> were synthesized with PEG-*block*-PHEMA-*block*-PS prepared by ATRP and PS-*block*-(P4VP-*graft*-PEG) prepared by a coupling method, respectively. The molecular weight distribution of PEG-*block*-PHEMA-*block*-PS and PS-*block*-(P4VP-*graft*-PEG) was narrow. The microphase-separated films with isolated PS and PHEMA/P4VP domains were obtained. However, details of the structure of the microphase separation of the polymers were not determined by SAXS and TEM because of the complex peaks observed by SAXS. Microspheres were obtained by crosslinking of PHEMA and P4VP. Because of the formation of a superstructure, the surface tension of benzene/microsphere<sub>graft</sub> was lower than that of benzene/PS-*block*-(P4VP-*graft*-PEG). The stability of benzene/water emulsion was investigated with PEG-*block*-PHEMA-*block*-PS, PS-*block*-(P4VP-*graft*-PEG), microsphere<sub>block</sub> and microsphere<sub>graft</sub> as emulsifiers. All polymers formed the oil-in-water-type emulsions. The stability of the oil-in-water emulsion was drastically improved by increasing the ratio of arm number of PEG to PS in the polymer and the formation of supermolecules, that is, the formation of Janus-type microspheres.

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