

Structural Effect of the Microgels with a Core-Shell Morphology Synthesized from Poly(α -methylstyrene-*b*-methyl methacrylate) on the Swelling Behavior of the Microgel

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SYNOPSIS

The swelling behavior of the core-shell microgels [32 mol % poly(methyl methacrylate) (PMMA) core and 68 mol % poly(α -methylstyrene) (PMeSt) shell], the random mixing microgels with 32 mol % PMMA and 68 mol % PMeSt, and the PMMA microgels was investigated in two solvent systems (toluene/*n*-hexane and benzene/*n*-butanol) by turbidimetric titrations from the viewpoint of the structural effect of the microgels. All core-shell microgels did not precipitate in the solvent in which the material block copolymer had perfectly precipitated. For the core-shell microgels, the flat regions appeared on the way to perfect turbidity. From the measurement of the composition of the solvent swollen in the polymers and the microgels, it was determined that these anomalous phenomena were due to the properties of the polymer micelles in the core-shell microgels.

INTRODUCTION

In recent years, many investigations of microgels have been carried out.^{1,2} Of the many kinds of microgels, one of the most interesting observed is the spherical microgel with a core-shell morphology (the core-shell microgel), because it is composed of two different chemical components and it has the microphase separated structure.

In general, this core-shell microgel is synthesized by seed polymerization.³⁻⁵ However, the kinds of feed monomer are limited by the seed particles. Thus, we proposed the new synthetic method of the core-shell microgels as follows: First, the polymer micelle was formed from the block copolymer in the selective solvent. Second, the core part of the polymer micelle was cross-linked. This cross-linked polymer micelle was the microgel with the cross-linked core and soluble shell.⁶ The microgels synthesized by this method could be considered as a fixed polymer mi-

celle. In previous papers,⁶⁻⁸ it was reported that the size and the shape of the microgels could be controlled by changing the selectivity of the solvent and the polymer concentration.

Generally, the microgels showed a lot of interesting properties⁹⁻¹²—especially, strong dependence has been observed between the swelling behavior and the diameter of the particle.¹³ This dependence was usually observed on the microgel without microphase separation. The core-shell microgel was covered with one polymer but its inside structure was not uniform. The anomalous behavior of the core-shell microgel was expected in the swelling behavior; therefore, turbidimetric titrations were carried out.

In this paper, three kinds of the microgels were chosen for turbidimetric titration: the core-shell microgels with the cross-linked poly(methyl methacrylate) (PMMA) core and the poly(α -methylstyrene) (PMeSt) shell, the microgel with a random mixture of PMMA and PMeSt, and the uniform PMMA microgel. Not only the structural effect but also the effect of size of the microgel on the swelling is discussed. The selective adsorption of the good

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solvent (benzene) of the mixed selective solvent in the microgels was measured to determine the turbidimetric behaviors of the microgels.

EXPERIMENTAL

Synthesis of the Microgels

The Core-Shell-Type Microgel

The microgels composed of 32 mol % cross-linked PMMA core and 68 mol % PMeSt shell were prepared from modified poly(α -methylstyrene-*b*-methyl methacrylate) [P(MeSt-*b*-MMA)] no. 6 ($M_n = 6.4 \times 10^4$, methylstyrene = 68 mol %) introduced into the styryl groups in the PMMA sequence (C=C: 10 mol % of PMMA) as reported in the previous paper.⁶ As described in the Introduction, the polymer micelles (PMeSt shell and PMMA core) were formed from block copolymer no. 6 in benzene/cyclohexane solution, then the styryl groups in the PMMA core were cross-linked by radical polymerization with azo-initiator [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), Wako Pure Chemical Industries] at 40°C for 4 h under N₂ gas. The synthetic conditions and the particle sizes are listed in Table I.

The Random Mixing Gel

For the synthesis of the random mixing microgel, the radical polymerization of the 10 g modified block copolymer no. 6 was carried out in 10 mL benzene (a good solvent for both sequences) with 0.1 g azo-initiator [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70)] at 40°C for 4 h under N₂ gas.

Table I Cross-Linking Conditions and Diameters of the Core-Shell Microgels

Run No.	Solvent Composition		Diameter ^a (nm)	D_w/D_n
	Benzene/Cyclohexane (v/v)			
1-1/9	1/9		1000	1.8
1-2/8	2/8		370	1.3
1-3/7	3/7		170	1.1
1-4/6	4/6		100	1.1
1-5/5	5/5		500	2.0

Other cross-linking conditions: temperature, 40°C; polymer concentration, 1 wt %.

^a Determined with transmission electron microscopy.

The PMMA Gel

For the purification of the monomers, methyl methacrylate monomer and divinyl benzene monomer were distilled under *vacuo*. The PMMA gel was synthesized with the purified methyl methacrylate monomer 20 mL, the purified divinylbenzene 2 mL, benzene 10 mL, and 2,2'-azobis-iso-butyronitrile (AIBN) 0.05 g as initiator by radical polymerization at 60°C for 8 h under the N₂ gas. The macrogel was washed with methanol and dried under *vacuo*. The degree of swelling of the macrogel in benzene at 20°C for 2 days was measured.

Separation of the Microgels by Their Sizes

For the synthesis of the microgel from the PMMA macrogel and the random mixing macrogel, the scission of the swollen macrogel in benzene was carried out with an ultrasonic wave generator (Cho-Onpa Kogyo Ltd., USH-300Z20S, 300W, 19 kHz) at room temperature for 1 h. The scissored swollen gel solution was separated by filtration through two Teflon filters stepwise (the pore size: first filter = 3000 nm, second filter = 220 nm).

Homo-PMMA and the Homo-PMeSt

The homo-PMMA and -PMeSt were synthesized as the parent polymers of the block copolymer no. 6 by the anionic polymerization using *n*-butyllithium as an initiator in tetrahydrofuran.⁶ The number-average molecular weights of PMMA and PMeSt were determined with GPC as $M_{n\text{PMMA}} = 2.0 \times 10^4$, $M_{n\text{PMeSt}} = 4.4 \times 10^4$, respectively.

Turbidimetric Titration

Polymer, 0.05 g, was dispersed in 20 mL toluene (or benzene), and then *n*-hexane (or *n*-butanol) was added stepwise under vigorous stirring in a cell (cylindrical Pyrex cell, 200 mL) at 20°C. At each step, the turbidity of the solution was measured with the single-beam HITACHI UV-VIS Spectrophotometer 139 at 600 nm.

Determination of the Solvent Composition in the Polymers

One gram polymer, or microgels were swollen in 100 mL benzene-*n*-butanol mixture (benzene fraction: 40 vol %) at 20°C for 3 days. One gram homo-PMMA was swollen in 100 mL benzene-cyclohexane mixtures at 20°C for 3 days. The surface of the polymer was wiped. The polymer was set immediately

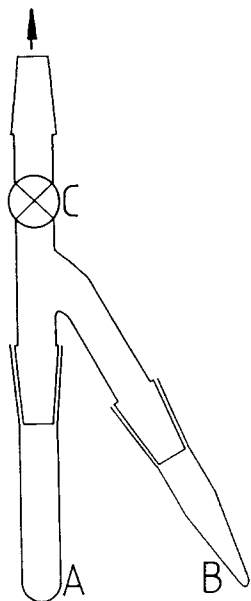


Figure 1 The apparatus used for the determination of the solvent composition in the polymers.

at part A of the apparatus shown in Figure 1. The solvent in the polymer in part A was frozen with liquid nitrogen. The air in this apparatus was evacuated with a vacuum pump, and cock C was closed. Then, part A was heated at 60°C, while at the same time, part B was cooled with liquid nitrogen. The solvent in the polymer was transferred completely by the distillation from part A to part B. The composition of the collected solvent was determined with HPLC (Jasco, TRI ROTOR-II instrument with the fine pack SIL-C₁₈) with methanol at 25°C. The flow rate was 2 mL/min, and the peaks were detected with an UV-spectrophotometer UVIDEK-100 at 254 nm.

RESULTS AND DISCUSSION

Synthesis of the Gels

The core-shell microgels used in this study were synthesized and characterized in the previous work.⁶ Table I shows the cross-linking conditions and the sizes of the core-shell microgels. In Table I, sample 1 is the core-shell microgel and n/m is the composition of the solvent (benzene/cyclohexane) used for the cross-linking. The composition of the block copolymer P(MeSt-*b*-MMA) no. 6 used for the synthesis of microgels was 68 mol % PMeSt, with total molecular weight $M_n = 6.4 \times 10^4$, so that the compositions of all core-shell microgels were 68 mol % PMeSt shell and 32 mol % PMMA core.

Figure 2(a) and (b) shows the transmission electron micrographs of the specific core-shell microgels synthesized in the solvent 3/7 and 1/9, respectively. The dark part of Figure 2(a) shows selectively stained PMeSt sequences with RuO₄. The dark part of Figure 2(b) shows selectively stained styryl groups in PMMA with iodine. The core-shell morphology of the microgel could be confirmed for the small microgel⁶ synthesized in the solvent 3/7 benzene/cyclohexane (v/v). The thickness of PMeSt shells were determined from Figure 2(a) as ca. 8 nm in the solid state. On the other hand, the core of the large particle synthesized in the solvent 1/9 [Fig. 2(b)] would be constructed with many small PMMA cores and the PMeSt mixture. The number-average diameter of the microgel could be controlled from 100 nm to 1000 nm by varying the composition of the solvent used for the cross-linking, because the aggregation number of the polymer micelle used for the synthesis of the microgels could be changed with varying the solvent compositions.

The random mixing gel was synthesized from the block copolymer no. 6, so that the compositions of

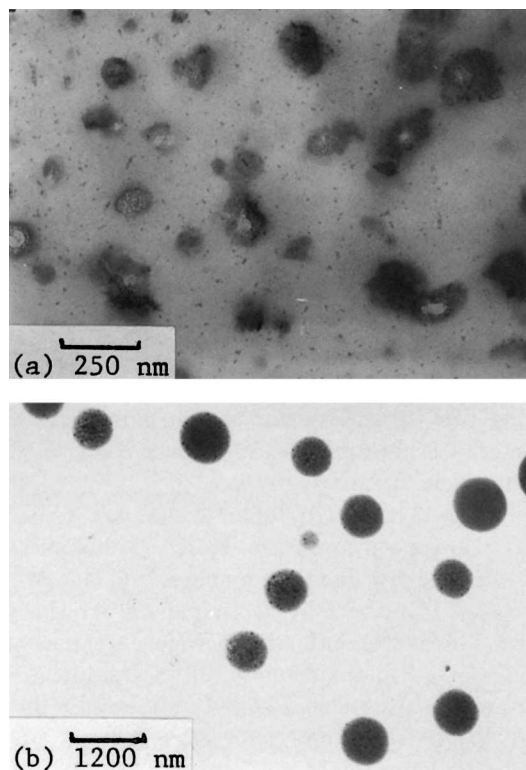


Figure 2 TEM micrographs of core-shell microgels synthesized from block copolymer no. 6: (a) cross-linked in 3/7 benzene/cyclohexane (v/v) stained with RuO₄; (b) cross-linked in 1/9 and stained with I₂.

Table II Swelling of the PMMA Macrogel

Weight of Polymer (g)		Degree of Swelling	
Dry	Swelling	Weight	Volume
0.645	5.005	7.76	10.19

Conditions: in benzene at room temperature for 2 days.

this gel were 68 mol % PMeSt and 32 mol % PMMA. The random mixing gel might not show the microphase-separated morphology, because the microphase separation of the block copolymer (the formation of the polymer micelle) did not occur in benzene, which was a good solvent for both sequences.

The degree of the swelling of PMMA gel in benzene for 2 days at 20°C was measured and is listed in Table II. The molecular weight between the crosslinking points was calculated as 480 from the equation¹⁴ of Flory's interaction parameter between benzene and PMMA, $\chi = 0.429$.¹⁵

The swollen microgels were separated by two different Teflon filters with their diameters (D) in the swelling state as follows: group A, $D < 220$ nm; groups B, $220 \text{ nm} < D < 3000$ nm; and group C, $D > 3000$ nm. From the degree of swelling of PMMA gel in benzene, the diameters (D_{dry}) of the microgels in the solid state were calculated as follows: group a, $D_{\text{dry}} < 102$ nm; group b, $102 \text{ nm} < D_{\text{dry}} < 1380$ nm; and group c, $D_{\text{dry}} > 1380$ nm.

Turbidimetric Titration

The precipitation behavior of the microgel was investigated by turbidimetric titration in the toluene (solvent)/ n -hexane (precipitant) system. The benzene/cyclohexane system used for the crosslinking was unsuitable for the turbidimetric measurement of this study, because the turbidity change was not clear in this system.

In Figure 3, the turbidimetric changes in the toluene/ n -hexane system are shown. Toluene was a good solvent for both sequences. n -Hexane was nonsolvent for the PMMA sequence. At the first stage of measurement, all microgels were swollen and dispersed in the toluene and the solution was clear and the microgels seemed to be soluble in toluene. When n -hexane was added, first, homo-PMMA and the PMMA microgels without PMeSt sequences precipitated, and then the material block copolymer no. 6 and the random mixing microgels precipitated. The random mixing microgels and block copolymer no. 6 precipitated in the solvent

with the same volume fraction, because the composition of the block copolymer no. 6 and the random mixing microgel were the same and there were PMeSt and PMMA sequences on the surface of the random mixing microgel. Then the core-shell microgels and, finally, the homo-PMeSt precipitated with the increase of the n -hexane volume fraction. This order of precipitation suggested that the core-shell microgels could be stabilized by the shell in the solvent with the high precipitant volume fraction. This turbidimetric behavior was similar to the case of the core-shell microgels prepared from the microphase-separated film of the graft copolymer.^{16,17}

Very strange behavior was observed in this titration in that the flat regions with different ranges appeared on the way to perfect turbidity for all of the core-shell microgels. Two reasons for the appearance of these flat regions were proposed: One was that the material block copolymer remained in the microgels and the other was the structural effect of the core-shell morphology.

To make this point clear, turbidimetric titration was carried out in another solvent system: benzene (Bz : solvent)/ n -butanol (BuOH : precipitant). Figure 4 shows that PMeSt precipitated first and PMMA last in the Bz/BuOH system. If the material block copolymer presented in the core-shell micro-

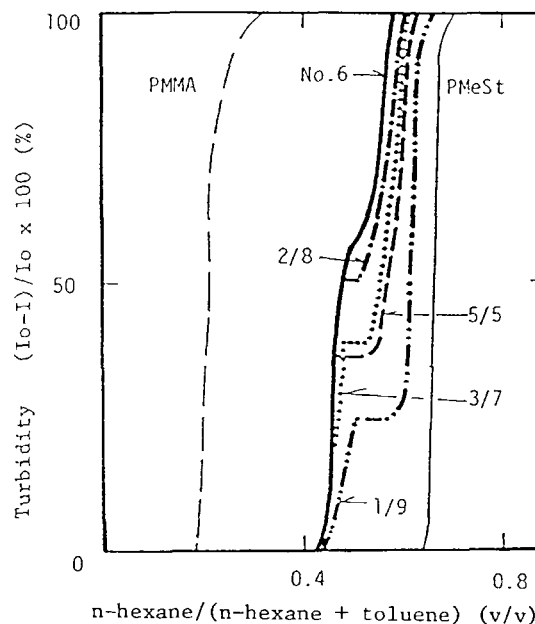


Figure 3 Turbidimetric titration curves in the toluene- n -hexane system: no. 6, the block copolymer; $-n/m$, the core-shell microgel synthesized in the benzene (v)/cyclohexane (v).

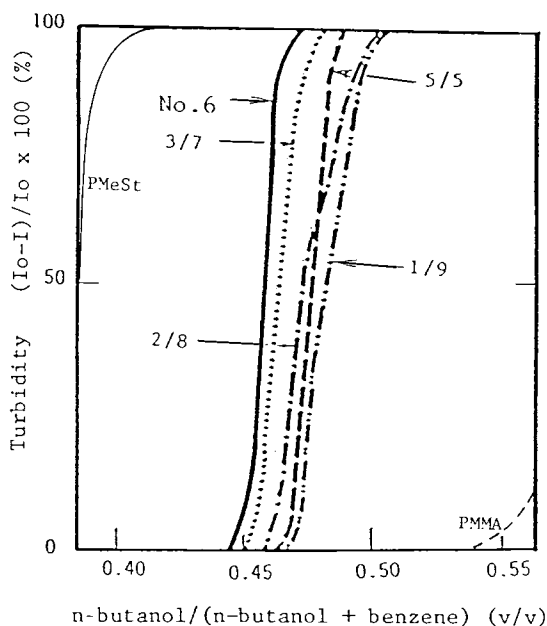


Figure 4 Turbidimetric titration curves in the benzene-*n*-butanol system: no. 6, the block copolymer; $-n/m$, the core-shell microgel synthesized in the benzene (v)/cyclohexane (v).

gels, the flat region could also be observed in the Bz/BuOH system. The flat region on the way to perfect turbidity could not be observed in the Bz/BuOH system. Thus, it was concluded that there was no material block copolymer in the core-shell microgels and these strange behaviors were due to the structural effect of the core-shell microgels. The appearance of the flat regions was explained as follows: The increase of the turbidity until the flat region was certainly due to the precipitation of the inside PMMA core accompanied by the aggregation of the core-shell microgels. Further aggregation did not proceed immediately because of the solubility of the PMeSt chains. Finally, all the microgels precipitated completely as the PMeSt shell precipitated.

To make clear the structural effect of the microgels on the precipitation, the γ_{50} (the solvent composition of the precipitant with turbidity at 50%)^{18,19} against the diameter of the microgel is plotted in Figure 5. The γ_{50} in this figure indicates the dispersion power of PMeSt sequences on the polymer. In other words, the large γ_{50} showed that the microgel was stabilized and did not precipitate by the solubility of the PMeSt sequences. For the gels without microphase separation, i.e., PMMA gels and the random mixing gels, the γ_{50} decreased with the increase of the diameter of the microgel. Contrary to our expectation, for the core-shell microgels, the

volume fraction of the precipitant increased with the diameter of the core-shell microgel.

In Figure 6, the γ_{50} (the solvent composition of butanol as the precipitant with turbidity at 50%)^{18,19} was plotted against the diameter of the microgel. This figure shows the dispersion effect based on the PMMA sequences on the particles. The order of the precipitation was the following: the homo-PMeSt, the PMMA microgels, the random mixing microgels, the material block copolymer, the core-shell microgels, and the homo-PMMA. In general, the solubility of the polymer decreased with the increase of its diameter. The PMMA microgels and the random mixing microgels showed the natural tendency of the precipitation. However, the core-shell microgels showed the opposite tendency. For the core-shell microgels, the volume fraction of the precipitant (BuOH) increased with their diameters. As described before, this opposite tendency was also observed for the core-shell microgels in the toluene/*n*-hexane mixture. These anomalous phenomena of the core-shell microgels, which were the appearance of the flat region on the turbidimetric titration in the toluene/*n*-hexane system and the higher solubility than of the material block copolymer in both solvent systems, would be due to the heterogeneous

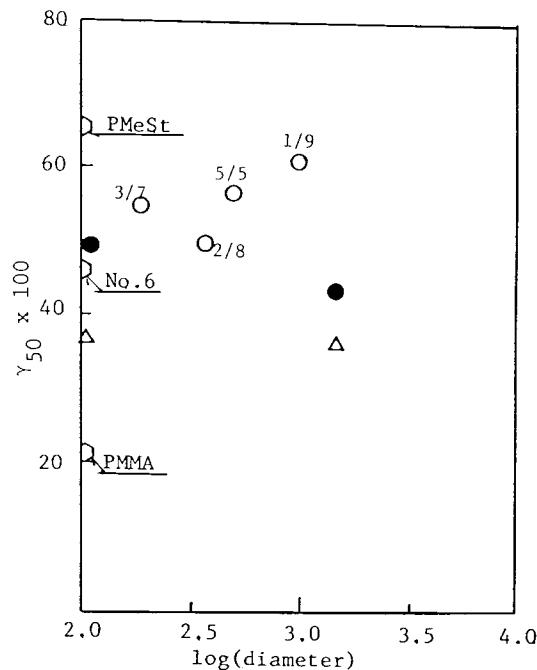


Figure 5 The value of 50% turbidity (γ_{50}) vs. the diameter of microgel in the toluene-*n*-hexane system: (○) core-shell microgel; (●) random mixing microgel; (Δ) PMMA microgel.

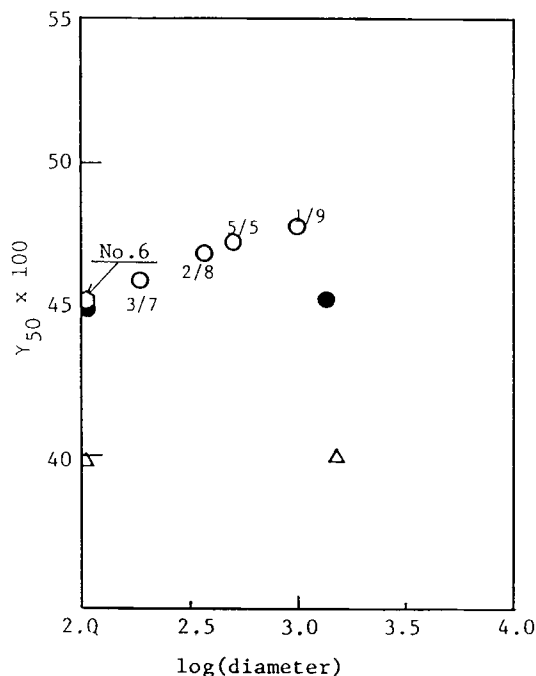


Figure 6 The value of 50% turbidity (γ_{50}) vs. the diameter of the microgel in the benzene-*n*-butanol system: (○) core-shell microgel; (●) random mixing microgel; (△) PMMA microgel.

structure (the core-shell morphology) of the core-shell microgels.

Solvent Compositions in the Swollen Microgels

To investigate the swollen state of the PMMA core in the Bz/BuOH mixture, the solvent composition of the Bz/BuOH mixture in the swollen microgels was measured. The Bz(v)/BuOH(v) = 40/60 mixture, in which the material block copolymer no. 6 and the microgels did not dissolve but swelled well, was used as the solvent for this measurement. The observed values are summarized in Table III. These values corresponded well to the turbidimetric behaviors in the Bz/BuOH system.

It was believed that the thickness of the shell of the core-shell microgel did not change with the diameter of the microgel because the molecular weight of the PMeSt sequence of the material block copolymer was constant. However, the core state of the core-shell microgel depended on the diameter of the microgel. For example, in the large microgel, the inside structure was composed of the small PMMA cores and PMeSt mixture [Fig. 2(b)]. The properties of the polymer micelle before the cross-linking would be the same in the core-shell microgels, so that the nonsolvent volume fraction in the Bz/

Table III Compositions of the Solvents in the Swollen Polymers in the Solvent of Benzene-Butanol [40/60 (v/v)]

Run No.	Polymer ^a	Benzene (%) in the Solvent in Polymer
1	No. 6	35.6
2	1-1/9	50.4
3	1-2/8	43.4
4	1-3/7	44.1
5	1-4/6	59.7
6	1-5/5	74.0
7	Homo-PMMA	Solvent ^b
8	Homo-PMeSt	— ^c

Measurement condition: 20°C.

^a No. 6, the block copolymer no. 6; 1-1/9, microgels prepared from block copolymer no. 6 in solvent 1/9 (benzene/cyclohexane 1/9 [v/v]).

^b The homo-PMMA dissolved in this solvent.

^c The homo-PMeSt was not swollen in this solvent.

BuOH solution could increase with the diameter of the core-shell microgel, similar to the micelle.

For the estimation of the core state of the polymer micelle used for the cross-linking, the solvent composition in the swollen PMMA in the benzene/cyclohexane mixture used for the cross-linking was measured. The observed values are summarized in Table IV. Thus, it was suggested that PMMA was swollen in the solvents for the cross-linking. The PMMA cores of the block copolymer micelles and the core-shell microgels were swollen well in these solvents. The core-shell microgels synthesized from the polymer micelles with a swollen core could adsorb the good solvent component selectively. Consequently, the core-shell microgels precipitated in the solvent with a high nonsolvent volume fraction.

Applications of these core-shell microgels with

Table IV Compositions of the Solvents in the Swollen Homo-PMMA in the Solvent Series of Benzene-Cyclohexane Mixtures

Run No.	Benzene (%) of the Solvent	
	Out of the PMMA	Adsorbed in the PMMA
1	51.3	59.9
2	39.0	39.9
3	32.4	25.6

Measurement condition: temperature, 20°C.

such anomalous properties to the new material are expected.

CONCLUSIONS

The microgels with the core-shell morphology (the 32 mol % PMMA core and the 68 mol % PMeSt shell) synthesized from P(MeSt-*b*-MMA (MeSt = 68 mol %, $M_n = 6.4 \times 10^4$), the microgels with random mixing morphology synthesized from P(MeSt-*b*-MMA), and the PMMA microgel were chosen, and turbidimetric titration was carried out to estimate the structural effect of the microgels on the solubilities of them. Two solvent systems (toluene/*n*-hexane and benzene/*n*-butanol) were chosen for the turbidimetric titrations.

In both systems, the random mixing microgels and the PMMA microgels precipitated in the solvent with a lower volume fraction of the precipitant than that at which the material block copolymer precipitated. Also, the volume fraction of the precipitant decreased with the increase in their diameters. However, the core-shell microgels did not precipitate in the solvent in which the material block copolymer precipitated, and the volume fraction of the precipitant of the microgels increased with their diameters. Moreover, in the toluene-*n*-hexane system, the flat regions appeared on the way to perfect turbidity of the core-shell microgels.

To explain these anomalous turbidimetric behaviors, the composition of the solvent adsorbed in the microgel or the homopolymer was measured. From the measurement of the composition of the solvent adsorbed in PMMA in the benzene-cyclohexane solvents, it was believed that the PMMA cores of the polymer micelles were well swollen with the benzene (good for both sequences) of the solvent used for the cross-linking. In the core-shell microgels, the properties of the polymer micelle remained.

Consequently, the core-shell microgels could show these anomalous turbidimetric behaviors.

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