

# Preparation of Core–Shell Particles by Dispersion Polymerization with a Poly(ethylene oxide) Macroazoinitiator

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**ABSTRACT:** A macroazoinitiator (MAI) containing a poly(ethylene oxide) (PEO) block was used with a methyl methacrylate monomer to prepare polymer particles in ethanol/H<sub>2</sub>O solutions. The effects of the monomer/MAI ratio (RMI) and H<sub>2</sub>O content in the solutions on the molecular weight, particle diameters, and chemical structure of the resulting polymer particles were investigated. The reaction mixtures showed three kinds of states, which were milky colloid solutions, macrogels and/or precipitations, and clear solutions. The colloid solutions were obtained in the solutions with an H<sub>2</sub>O content of about 50–90 vol % and a RMI of 20–400. In the colloid solutions, core–shell nanospheres consisting of PEO shells and poly(methyl methacrylate)

(PMMA) cores were predominantly obtained. In the specific conditions close to the area of gel and/or precipitation formation, particles connected about 0.5–5  $\mu\text{m}$  in length were obtained. Multiblock copolymers nanospheres tended to be obtained with lower RMIs, and PMMA-PEO-PMMA tri-bloc and/or PMMA-PEO di-block copolymer nanospheres were obtained with higher RMIs. The solubility of the monomer and the generated polymer in solutions may have affected the polymerization development and the state of the products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1469–1476, 2008

**Key words:** azo polymers; colloids; core–shell polymers; polyethers; self-assembly

## INTRODUCTION

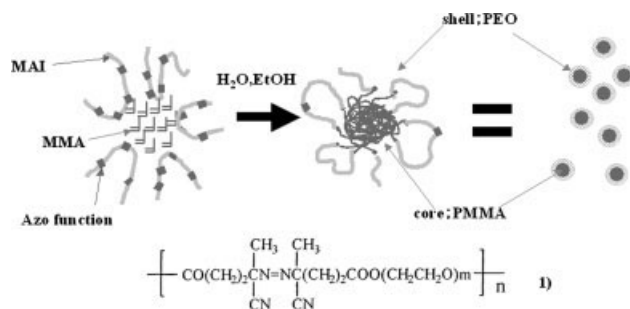
Polymer particles in dispersions, emulsions, and suspensions have been widely used as paints, adhesives, and sealants. Recently, many kinds of nanospheres have been synthesized and used for optical, electrical, and biological applications.<sup>1</sup> With macromonomers as a dispersant in solutions, nanosphere formations in graft copolymerization with monomers have been examined in detail.<sup>2–5</sup> Akashi and coworkers<sup>2–4</sup> reported that core–shell nanospheres consisting of poly(methyl methacrylate) (PMMA) cores and poly(ethylene oxide) (PEO) branches on the surfaces were prepared by the free-radical dispersion copolymerization of methyl methacrylate (MMA) with PEO macromonomers in alcohol/H<sub>2</sub>O mixture solvents. They investigated particle formations by constructing phase diagrams for the monomer/macromonomer ratio and H<sub>2</sub>O fraction in the reaction system.<sup>2</sup> They concluded that the graft copolymers of hydrophilic macromonomers and hydrophobic monomers tended to form various states (gels, clear solutions, and particle formations)

and that particle formation depended on the solvophilic/solvophobic balance of the graft copolymers and the solvents.

The syntheses of block copolymers with the reactivity of azo groups in macroazoinitiators (MAIs) have been investigated by many authors.<sup>6–8</sup> MAIs containing PEO and poly(dimethyl siloxane) have been used to synthesize block copolymers with comonomers of vinyl chloride, styrene, and MMA. Dispersion polymerizations with MAIs containing PEO blocks and comonomers have also been reported;<sup>9,10</sup> however, the formations of polymer particles have not been discussed in detail.

In this study, a MAI containing a PEO block was used with a MMA monomer to prepare polymer nanospheres in ethanol/H<sub>2</sub>O solutions. Because the azoinitiator groups were combined with good dispersive PEO units in the MAI, we expected that the MAI would polymerize with the hydrophobic monomer in hydrophilic solutions and develop polymer nanospheres efficiently (Fig. 1). The products would be block (and/or graft) copolymer particles. The formations of nanoparticles were examined, and the effects of the monomer/MAI ratio (RMI) and H<sub>2</sub>O content in the solution on the particle diameters, molecular weights, and chemical structures were investigated.

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**Figure 1** Schematic representation of core-shell particle formation with MAI: (1) chemical structure of the MAI-containing PEO unit.

## EXPERIMENTAL

### Materials

A MAI containing a PEO unit was purchased from Wako Pure Chemical Co., Ltd. (Osaka, Japan) (VPE-0201). The chemical structure of the MAI is shown in Figure 1. The number-average molecular weight ( $M_n$ ) of the PEO unit in the MAI and the total  $M_n$  were 2000 (Polymerization degree of EO ( $m$ )  $\approx$  45) and 15,000–30,000 (Polymerization degree of PEO and azo unit ( $n$ )  $\sim$  6.6–13.3). The MMA monomer (Tokyo Kasei, Tokyo, Japan) was distilled under reduced pressure before use. The MAI and other chemicals were used without further purification.

### Polymerization

In the dispersion polymerizations, the total volume of the solvents (80 mL) and the amount of MMA monomer (0.1 mol) were fixed; on the other hand, the  $\text{H}_2\text{O}$  fraction in the solvents and the amount of MAI were varied. A typical polymerization method was as follows. After MAI was dissolved ( $2.5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol) in the EtOH/ $\text{H}_2\text{O}$  mixture, the MAI solution and MMA monomer (0.1 mol) were poured into a four-necked, 200-mL flask equipped with a gas inlet, a stirrer, and a condenser. The reaction solution was heated in an oil bath with stirring. After the temperature of the solution reached a fixed temperature (65–75°C),  $\text{N}_2$  gas was introduced, and polymerization was started. Stirring was continued at a constant temperature for 10–20 h. After the polymerization reaction, the obtained solutions were centrifuged and purified by dialysis against  $\text{H}_2\text{O}$  for 1 week. The particles were collected by centrifugation and were dried *in vacuo* at room temperature.

RMI and the solvent compositions ( $\text{H}_2\text{O}$  fraction in EtOH/ $\text{H}_2\text{O}$  mixture) were varied in the preparations. The definition of the RMI was as follows:

$$\text{RMI} = \frac{\text{Monomer (mol)}}{[\text{Weight of MAI (g)} / \text{Polymer unit molecular weight}]}$$

The polymer unit molecular weight was 2262 for VPE-0201.

The conversions of the polymer particles (containing time-dependent conversions) were examined by measurement of the gravity of a small amount (1 mL) of extracted solutions and the solid components. The solid component (polymer particles) was separated by centrifugation and wash cycles (12,000 rpm for 15 min; if a supernatant was still turbid, additional operations were applied), followed by washing with distilled water) and dried under reduced pressure for 24 h. The definition of the conversion of polymer particles was as follows.

$$\text{Conversion (\%)} = \frac{(\text{Measured wt \% of the solid content}) \times 100}{/(\text{Calculated wt \% of the solid content})}$$

In the calculations of the weight percentage of solid content, the densities of the solvents used were as follows:  $\text{H}_2\text{O} = 1.00$  and  $\text{EtOH} = 0.79$ . A small loss of  $\text{N}_2$  in the MAI accompanied by the generation of radicals was neglected.

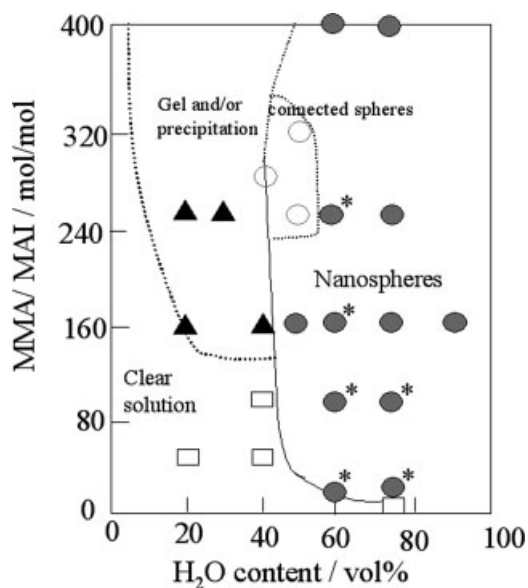
### Characterization

Transmission electron microscopy (TEM; Hitachi FE-TEM HF-2000) (Tokyo, Japan) and scanning electron microscopy (SEM; Hitachi FE-SEM S-4100) were used for observation of the polymer particles. The obtained particles were dissolved in THF, and the solutions were used for the measurement of the weight-average molecular weight ( $M_w$ ) and  $M_n$  distributions with gel permeation chromatography [GPC; LC (Toso, Tokyo, Japan) equipped with a TriSEC model 302W (Viscotek, Houston, TX) detector].  $^1\text{H-NMR}$  spectra were measured by a JNM-LA500 instrument (Jeol, Tokyo, Japan 500, MHz) in  $\text{CDCl}_3$ . The distributions of the particle diameters were measured by dynamic light scattering (DLS; Otsuka-Electric, Osaka, Japan, ELS-8000) in  $\text{H}_2\text{O}$  dispersions.

## RESULTS AND DISCUSSION

### Polymerization and characterization of the polymer particles

At the end of the polymerization, the reaction mixtures showed three kinds of states, which were milky colloid solutions, macrogels and/or precipitations, and clear solutions. These states were related to the solvent composition and RMI in the polymerization and are shown in Figure 2. The MMA concentration (1.25 mol/L), temperature, and duration



**Figure 2** Effect of the H<sub>2</sub>O content and MMA/MAI on nanosphere formation in copolymerization: (●) nanospheres, (○) connected spheres, (□) clear solution, (▲) gel and/or precipitation, (●\*) multiblock copolymer, and (●) ABA- and/or AB-type block copolymer.

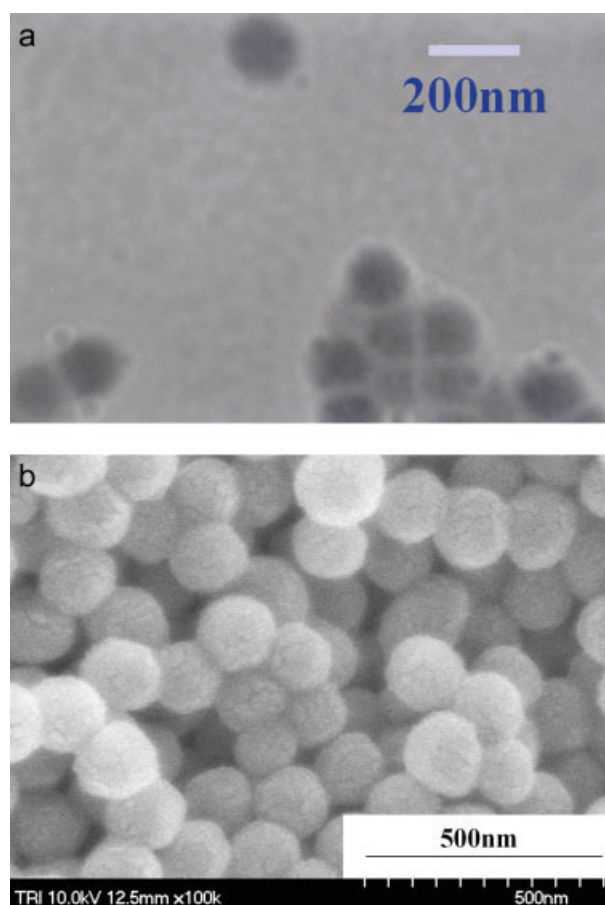
of polymerization (75°C for 15 h) were fixed in these experiments. Colloid solutions were obtained in solutions with an H<sub>2</sub>O content of about 50–90 vol % and a RMI value of 20 to 400. In the region of H<sub>2</sub>O contents below 40 vol % and with large RMIs (ca. >160), macrogels and/or precipitations were obtained. Clear solutions were obtained in the region that excluded the aforementioned ones. Chen et al.<sup>2</sup> investigated the phase diagrams of a MMA/PEO macromonomer reaction system, and their results were similar to those indicated in Figure 2. From the results shown in Figure 2, the state of the product may have been related to the polymer solubility in the solvent.

In the milky colloid solutions, polymer nanospheres were predominantly formed, which was confirmed by TEM and SEM observations. Figure 3 shows the typical TEM and SEM micrographs of the obtained polymer nanospheres. A dark core and thin shell layer around the spheres were observed in the TEM micrograph. Figure 3 indicates that the MAI polymerized and dispersed MMA efficiently. The polymerization started from the cleavage of the azo groups in MAI, and radicals were formed. MAI radicals reacted with MMA, polymer radicals grew larger in molecular weight, and PEO–MMA block (and/or graft) copolymers were prepared. It is well known that EtOH and H<sub>2</sub>O are poor solvents for PMMA; on the other hand, these are good solvents for PEO. PMMA units will form a nucleus in solution, and PEO units will exist on the surface and cover the particles. The steric repulsion of the PEO

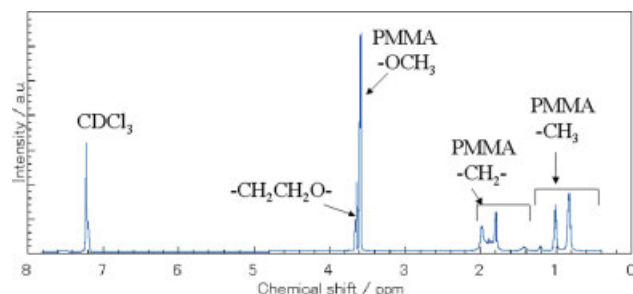
unit can prevent coagulation of the particles (Fig. 1). Okubo et al.<sup>11</sup> prepared PMMA particles with a poly(dimethyl siloxane) MAI as an initiator and a stabilizer (inistab) in supercritical CO<sub>2</sub>.

As shown in Figure 3, the particle diameter distributions were narrow. The number average diameter  $D_n$  and  $D_w/D_n$  values, as measured by DLS, were  $169.3 \pm 20.1$  nm and 1.045, respectively, for the results shown in Figure 3. The dispersion efficiency of the PEO block may have contributed to the narrow distributions of  $D_n$ .

The molecular weight distributions of the polymer particles were measured by GPC, and the results were as follows:  $M_w = 549,000$ ,  $M_n = 215,000$ , and  $M_w/M_n = 2.56$  for the nanospheres shown in Figure 3. Considerably large  $M_w$  values were also measured for the other polymer nanospheres obtained in the different experimental conditions. The large  $M_w$  values may have been related to the decrease in the probability of termination reactions and the relatively stable propagation of the radicals in the nanospheres.<sup>12</sup>



**Figure 3** (a) TEM and (b) SEM photographs of the polymer nanospheres obtained for MMA and MAI in EtOH/H<sub>2</sub>O solution. Polymerization conditions: MMA/MAI = 22.6, H<sub>2</sub>O = 75 vol %, 75°C, and 15 h. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

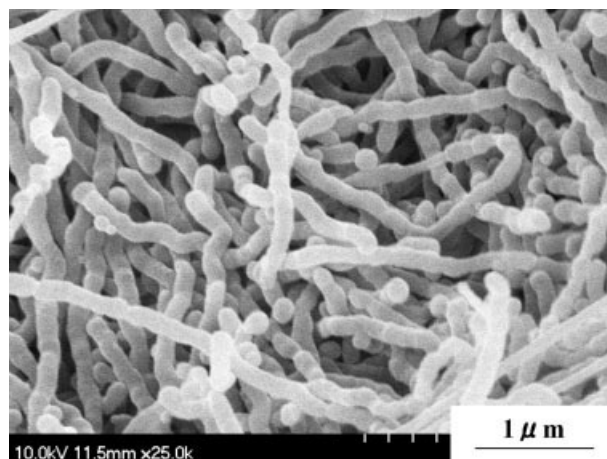


**Figure 4**  $^1\text{H-NMR}$  spectra measured for the nanospheres in  $\text{CDCl}_3$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Figure 4 shows the  $^1\text{H-NMR}$  spectrum measured for the nanospheres shown in Figure 3. The identification of the peaks were as follows: the peaks at 0.84, 1.01, and 1.14 ppm were the PMMA side chain  $-\text{CH}_3$ ; the peaks at 1.42 and 1.80–2.00 ppm were the PMMA main chain  $-\text{CH}_2-$ ; the large peak at 3.60 ppm was the PMMA methyl ester; and the peak at 3.64 ppm was the methylene proton derived from the PEO unit in the MAI. From the peak area ratio of the integration of 0.84, 1.01, and 1.14 ppm (PMMA side chain  $-\text{CH}_3$ ) and 3.64 ppm (PEO  $-\text{CH}_2-$ ) in Figure 4, the molar ratio of the MMA and ethylene oxide (EO) unit was calculated to be 0.1 : 0.0172. As the feed molar ratio of MMA and the EO unit was calculated to be 0.1 : 0.2, the measured one was remarkably low. With total  $M_n$  measured by GPC and the molar ratio obtained by  $^1\text{H-NMR}$  in combination, the number-average molecular weights of the PMMA segment [ $M_n(\text{PMMA})$ ] and PEO segment [ $M_n(\text{PEO})$ ] of the nanospheres shown in Figure 3 were evaluated to be 200,000 and 15,000, respectively. When this is considered with the fact that the  $M_n$  of the PEO unit in the MAI was 2000, the nanospheres shown in Figure 3 were assumed to be composed primarily from PMMA–PEO multiblock copolymers. The relationships between the polymerization conditions ( $\text{H}_2\text{O}$  content in the solvent and RMI) and the properties of the particles (diameters, molecular weights, and chemical structures) are discussed in a later section.

Figure 5 show the SEM micrographs observed for the particles obtained in the specific area indicated by  $\circ$  in Figure 2. The particles connected together in a line about 0.5–5  $\mu\text{m}$  in length and looked like wires. These unique particles also dispersed in the milky colloid solutions after polymerization. The  $M_w$ , as measured by GPC, for the particles shown in Figure 5 was 488,200, and  $M_w/M_n$  was 2.94. Figure 6 shows the SEM micrograph observed for the gels and/or precipitations indicated by  $\blacktriangle$  in Figure 2. The connected particles in three dimensions are shown in Figure 6.

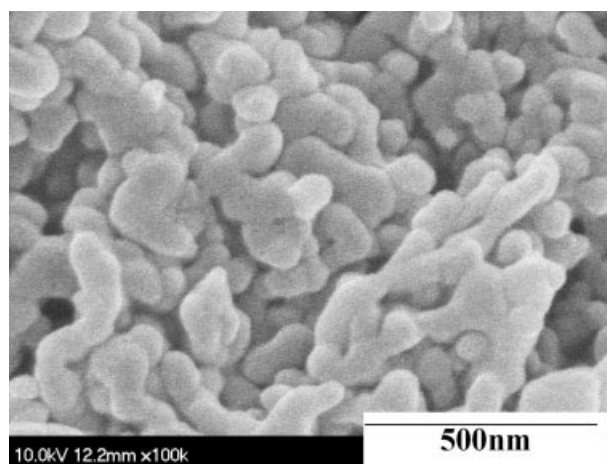
Nanoparticle networks consisting of hydroxypropyl cellulose nanoparticles crosslinked with



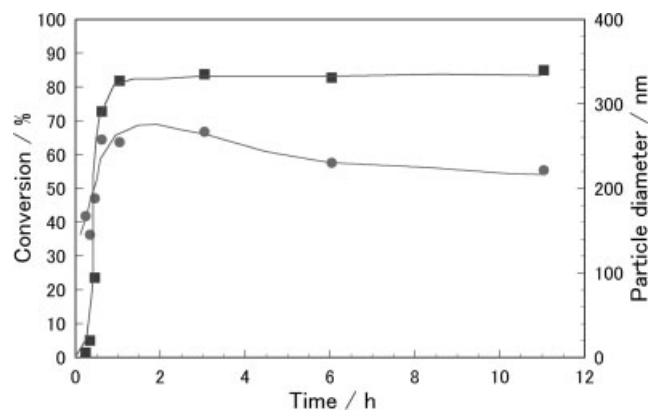
**Figure 5** SEM photograph of the connected spheres obtained for MMA and MAI in  $\text{EtOH}/\text{H}_2\text{O}$  solution. Polymerization conditions: MMA/MAI = 250,  $\text{H}_2\text{O}$  = 50 vol %,  $75^\circ\text{C}$ , and 15 h.

divinyl sulfone have been investigated,<sup>13</sup> and connected particles have been shown in TEM micrographs; however, we have not seen a report on connected particles in line by one-step formation. It seems that interparticle crosslinking by MAI<sup>9</sup> may develop the connected particles shown in Figure 5. We consider the delayed radical formation in MAI after the formation of spheres to be attributable to interparticle crosslinking. We also suppose that the increase in the formation of interparticle crosslinking developed gels and/or precipitations, as shown in Figure 6.

In the case of the obtained nanospheres and connected particles, the reaction mixture was almost dissolved in  $\text{EtOH}/\text{H}_2\text{O}$  at the beginning of the polymerization. The solution turned turbid in about 10 min to 1 h after the polymerization started, which



**Figure 6** SEM photograph of the gels and precipitation obtained for MMA and MAI in  $\text{EtOH}/\text{H}_2\text{O}$  solution. Polymerization conditions: MMA/MAI = 160,  $\text{H}_2\text{O}$  = 40 vol %,  $75^\circ\text{C}$ , and 15 h.



**Figure 7** Conversion of the nanospheres versus time for EtOH/H<sub>2</sub>O. MMA/MAI = 100, MMA = 1.25 mol/L, H<sub>2</sub>O = 75 vol %, and 75°C: (■) conversion and (●) particle diameter ( $D_n$ ).

meant that the polymerization proceeded by dispersion polymerization. Figure 7 shows an example of the time-dependent conversion of the nanospheres at 75°C. The formation and growth of the nanospheres were confirmed by SEM for the centrifuged solid polymers. The variations in the particle diameters measured by DLS and SEM photographs of the nanospheres in the polymerization stages are also presented. The conversion of the nanospheres reached up to 70% about in a few hours, whereas the particle diameter showed a maximum point at about 3 h and then became slightly smaller. Similar results were obtained for other experimental conditions.

The contraction in the particle diameters may have been related to the growth and solubility of the polymer molecules in solution; the polymer particles grew larger in a primary stage. However, an increase in the molecular weight of core PMMA decreased the solubility of the polymer in solution. The solubility of

the polymer may have contributed to the particle diameters, and shrinkage would be measured after a certain stage of the molecular weight growth.

From these results, we concluded that polymer nanospheres composed of PEO shell units and PMMA cores were predominantly prepared with the MAI and MMA monomer in EtOH/H<sub>2</sub>O solutions and appropriate conditions (H<sub>2</sub>O content and RMI).

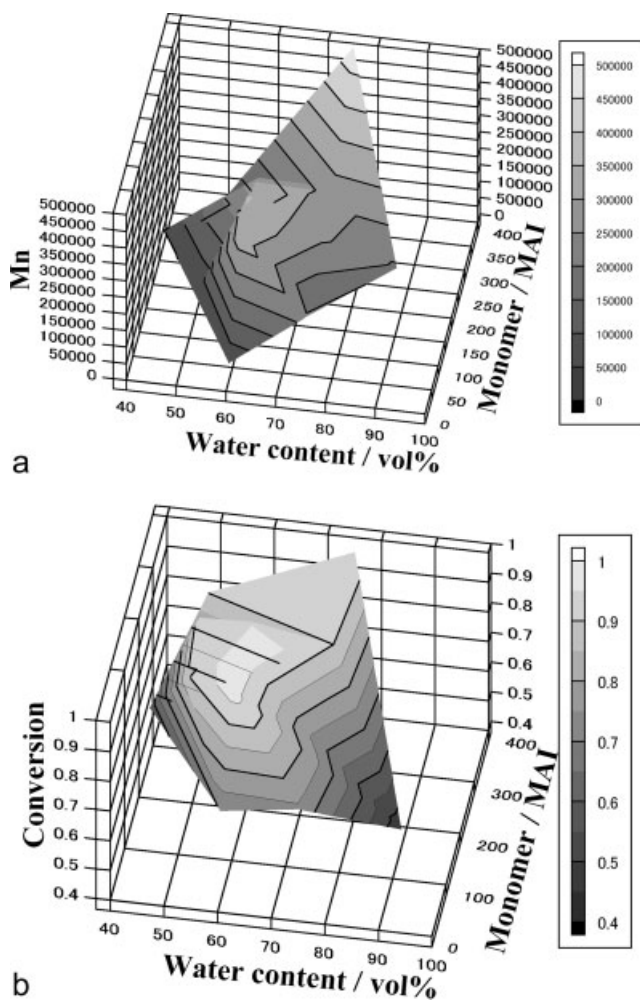
#### Effect of the conditions on the chemical structure of the polymer nanospheres

As mentioned previously, we found that the nanospheres shown in Figure 3 were composed mainly of PMMA-PEO multiblock copolymers. The effects of the H<sub>2</sub>O content in the solvent and RMI on the chemical structures of the nanospheres were investigated. With the results of <sup>1</sup>H-NMR and GPC, the molar ratio of MMA and EO and the  $M_n$ (PMMA) and  $M_n$ (PEO) were obtained, and the results are shown in Table I. The measured molar ratios of EO were lower compared to the feed, extremely so in 75 or 90 vol % H<sub>2</sub>O content solutions. From the results of the obtained  $M_n$ (PEO) shown in Table I, italicized nanospheres [ $M_n$ (PEO) = 2000–3000] were regarded as PMMA-PEO-PMMA tri-block and/or PMMA-PEO di-block copolymers. On the other hand, the other nanospheres [ $M_n$ (PEO)  $\gg$  2000] were supposed to be multiblock copolymers. The results of the type of block copolymers are shown in Figure 2. Grafted PEO may have existed in the obtained copolymer particles; however, the details of the chemical structures were not obtained in this study. There was a tendency for multiblock copolymers to be obtained in with lower RMIs, and ABA- and/or AB-type block copolymers to be obtained with higher RMIs. This trend may have been related to the

**TABLE I**  
Feed and Measured Molar Ratios of MMA and EO and  $M_n$  Values of the PMMA and PEO Blocks Calculated with the <sup>1</sup>H-NMR and GPC Results

RMI	H <sub>2</sub> O content in solvent (vol %)	MMA : EO feed molar ratio	Measured MMA : EO molar ratio	$M_n$			Conversion (%)
				PMMA	PEO	Total $M_n$	
22.6	75	0.1 : 0.2	0.1 : 0.0172	200,000	15,000	215,000	73.8
20	60	0.1 : 0.227	0.1 : 0.1011	40,000	18,000	58,000	70.7
100	75	0.1 : 0.0455	0.1 : 0.0121	151,000	8,000	159,000	77.4
100	60	0.1 : 0.0455	0.1 : 0.0182	310,000	25,000	335,000	97.7
160	90	0.1 : 0.0284	0.1 : 0.0041	190,000	<i>3,000</i>	193,000	46.3
160	75	0.1 : 0.0284	0.1 : 0.0026	256,000	<i>3,000</i>	259,000	72.0
160	60	0.1 : 0.0284	0.1 : 0.0129	335,000	19,000	354,000	97.0
160	50	0.1 : 0.0284	0.1 : 0.0125	51,000	<i>3,000</i>	54,000	59.0
250	75	0.1 : 0.0182	0.1 : 0.0028	279,000	<i>3,000</i>	282,000	90.1
250	60	0.1 : 0.0182	0.1 : 0.0054	278,000	7,000	285,000	94.4
400	75	0.1 : 0.0114	0.1 : 0.0009	485,000	<i>2,000</i>	487,000	95.0
400	60	0.1 : 0.0114	0.1 : 0.0082	86,000	<i>3,000</i>	89,000	57.0

Italicized nanospheres [ $M_n$ (PEO) = 2000–3000] were regarded as PMMA-PEO-PMMA tri-block and/or PMMA-PEO di-block copolymers.



**Figure 8**  $M_n$  and conversion of the polymer particles plotted for  $H_2O$  content in the solvent and RMI.

amount of MAI and the reaction efficiency of the azo unit in MAI. In the lower RMI region, a lot of azo units existed, and there might have been some azo units that did not react, and/or some of the rad-

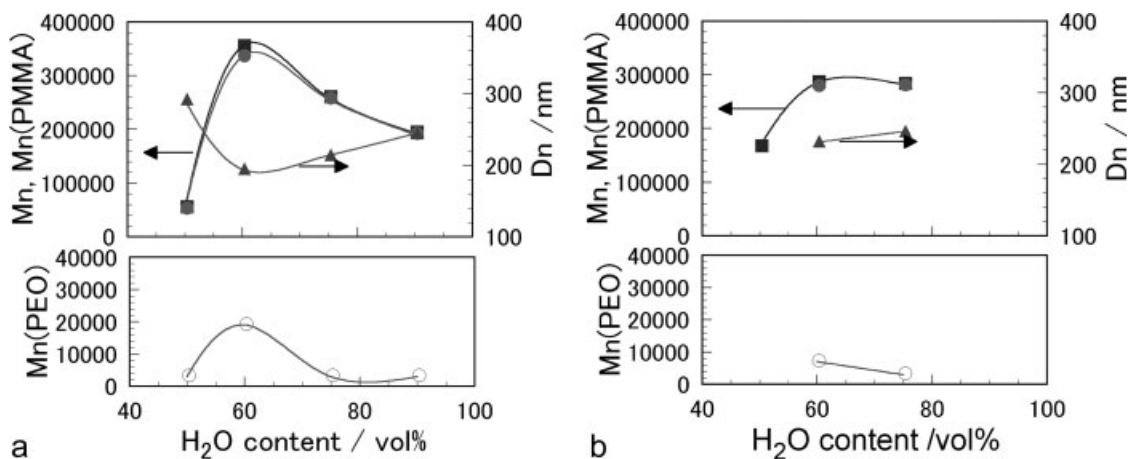
icals might have recombined. On the other hand, in the higher RMI region, small numbers of azo units existed, and these were consumed efficiently in the initiation reaction; namely, the cleavage of the MAI occurred at high efficiency.

The chemical structures of the nanospheres were also affected by the solvent composition; in 60 vol % solutions, multiblock copolymers were obtained at larger RMIs, compared to other solvent compositions. These results were supposed to be related to the solubility and stability of the radicals in solutions. As mentioned previously, the extremely lower molar ratios of EO measured for the nanospheres prepared in 75 and 90 vol %  $H_2O$  content solutions (Table I) may be related. The effect of  $H_2O$  content in the solvent and RMI on the molecular weights and particle diameters are discussed in detail later.

#### Effect of the $H_2O$ content in the solvent on the molecular weights and diameters of the polymer nanospheres

In case of yielding nanoparticles (nanospheres and connected particles),  $M_n$  was plotted against  $H_2O$  content and RMI, and the results are shown in Figure 8(a) in a three-dimensional format. High- $M_n$  (light gray) regions are located almost at the center of the conditions and at larger RMIs at about 75 vol %  $H_2O$  content. On the other hand, low- $M_n$  (dark gray) regions are located at the edge of the experimental conditions, especially for low  $H_2O$  contents. The plots of the conversion of polymer particles versus  $H_2O$  content and RMI [Fig. 8(b)] were similar to the results shown in Figure 8(a).

$M_n$  [total  $M_n$ ,  $M_n(\text{PMMA})$ , and  $M_n(\text{PEO})$ ] and  $D_n$  were plotted as a function of  $H_2O$  content in the solvent at constant RMI values (160 and 250;  $D_n$  was not measured for the connected particles), and the results are shown in Figure 9. An appearance of  $M_w$



**Figure 9** Effect of the  $H_2O$  content in the solvent on  $M_n$  [total  $M_n$ ,  $M_n(\text{PMMA})$ , and  $M_n(\text{PEO})$ ], and  $D_n$ : MMA/MAI = (a) 160 and (b) 250.

variation with H<sub>2</sub>O content resembled that of  $M_n$  in Figure 9(a). The maximum  $M_n$ ,  $M_n(\text{PMMA})$ , and  $M_n(\text{PEO})$  and the minimum  $D_n$  were observed around 60 vol % H<sub>2</sub>O content.  $M_n$  variations were almost determined by  $M_n(\text{PMMA})$  because the  $M_n(\text{PEO})$  values were much smaller than those of  $M_n(\text{PMMA})$ .

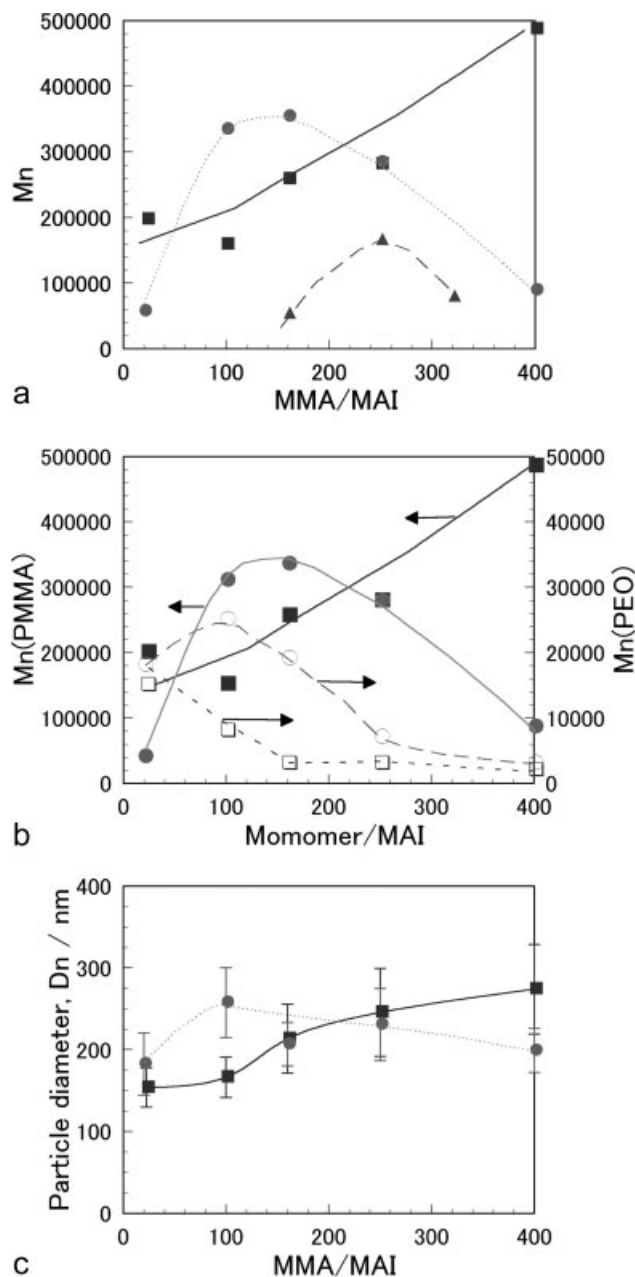
In general, the solvent effects are not remarkable in free-radical polymerizations except when a strong interaction such as a hydrogen bonding influences the monomers and/or solvent. Serizawa et al.<sup>4</sup> showed an unusual size formation of nanospheres synthesized from poly(ethylene glycol) macromonomers and MMA monomer by free-radical dispersion polymerization in EtOH/H<sub>2</sub>O. The particle sizes reached minima or maxima, which were dependent on the molar fraction of MMA used, at an H<sub>2</sub>O content around 70 vol %. They supposed that the self-assembling process of the monomer and macromonomer (like the schematic diagram as shown in Fig. 1) might have been affected by the clustered structure of EtOH in H<sub>2</sub>O. Similar situations to those reported in ref. 4 may have developed in the polymerization process in MAI and MMA in EtOH/H<sub>2</sub>O.

It is well known that polymerization development and the state of the products vary with the solubility of the monomer and the generated polymer in solvents. As shown in Figure 9, below 60 vol % H<sub>2</sub>O content, MMA monomer and MAI dissolved clearly in the solvent before polymerization. Below 40 vol % H<sub>2</sub>O content, solution polymerization mainly developed, and a clear polymer solution or a gel was obtained in a highly soluble media. Dispersion polymerization developed in solvents of rather lower solubility, and polymer dispersion was obtained ( $\geq 50$  vol % H<sub>2</sub>O). Above 75 vol % H<sub>2</sub>O content, the solubility of the MMA monomer was depressed, and a part of the monomer was suspended in the solvent. These facts may be related to the results of very low EO molar ratios measured for the nanospheres prepared in 75 and 90 vol % H<sub>2</sub>O content solutions (Table I).

As shown by the results in Figure 8(a,b), the  $M_n$ 's and conversions were low at the edge of the conditions for the particle formation. We presumed that the polymerization efficiency may have been related to the solubility of the monomer and polymer. Particles with large  $M_n$ 's and high conversions were supposed to be acquired in the appropriate solubility conditions.

#### Effect of RMI on the molecular weights and diameters of the polymer nanospheres

As the RMI parameter meant monomer moles per azo unit and per PEO unit, we expected that RMI would affect the polymerization and dispersion efficiency, namely, the molecular weights and particle



**Figure 10** Effect of RMI on (a) total  $M_n$ , (b)  $M_n(\text{PMMA})$  and  $M_n(\text{PEO})$ , and (c)  $D_n$  for the constant H<sub>2</sub>O content in solvent: (■) 75, (●) 60, and (▲) 50 vol %.

diameters of the resulting polymer particles. To examine the effect of RMI, the polymer particles prepared with different amounts of MAI in fixed conditions (solvents of fixed H<sub>2</sub>O contents; 50, 60, and 75 vol %, MMA concentration; 1.25 mol/L; polymerization temperature = 75°C; duration = 15 h) were compared for  $M_n$ ,  $M_n(\text{PMMA})$ ,  $M_n(\text{PEO})$ , and  $D_n$ . The results are shown in Figure 10. The appearance of a  $M_w$  variation with RMI resembled that of  $M_n$  in Figure 10(a). The  $M_n$  variations were almost determined by  $M_n(\text{PMMA})$  because the  $M_n(\text{PEO})$  values were much smaller than those of  $M_n(\text{PMMA})$ .

In 75 vol % H<sub>2</sub>O content solutions,  $M_n$ ,  $M_n(\text{PMMA})$ , and  $D_n$  increased with increasing RMI within our experimental limits. On the other hand, in 50 and 60 vol % H<sub>2</sub>O content solutions,  $M_n$ ,  $M_n(\text{PMMA})$ , and  $D_n$  increased and reached maxima with increasing RMI. As RMI increased, the concentration of azo groups in the solutions decreased, and the radical concentrations also decreased. Accordingly, the recombination and transfer reactions of the radicals decreased. As a result,  $M_n$  and  $M_n(\text{PMMA})$  increased.  $M_n(\text{PEO})$  decreased with larger RMIs in 60 and 75 vol % H<sub>2</sub>O content solutions, which may have been related to the efficient cleavage of azo units in the MAI with increasing RMI. The RMI was supposed to have an adequate range, and a depression of polymerization efficiency developed with large RMIs. As shown in Figure 8(b), the conversion of polymer particles increased as RMI increased in 75 vol % H<sub>2</sub>O content solutions; however, the conversion increased and reached a maximum in 50 and 60 vol % H<sub>2</sub>O content solutions. Consequently, in 50 and 60 vol % H<sub>2</sub>O content solutions,  $M_n$  showed a maximum with increasing RMI. The characteristics of the solution polymerization may be presented by decreasing H<sub>2</sub>O content in solutions, especially in 50 vol % solutions, and as a result,  $M_n$  and  $M_n(\text{PMMA})$  decreased, as shown in Figures 9(a,b) and 10(a,b).

The concentration of PEO units, which served as a dispersant, decreased with increasing RMI; as a result,  $D_n$  increased with increasing RMI. As shown in Figure 10(c),  $D_n$  increased with RMI in 75 vol % H<sub>2</sub>O content solutions. However, in 60 vol % H<sub>2</sub>O content solutions,  $D_n$  increased and showed a maximum with increasing RMI. The solvent effect for the self-assembling process,<sup>4</sup> as mentioned previously in the discussion of Figure 9, also affected the RMI dependence of  $D_n$  in 75 and 60 vol % H<sub>2</sub>O content solutions.

## CONCLUSIONS

Polymer nanospheres composed of PEO shell units and PMMA cores were predominantly prepared in colloid solutions. The chemical structures of the prepared nanospheres varied with polymerization

conditions (solvent compositions and RMI). The multiblock copolymers tended to be obtained with lower RMIs, and ABA- and/or AB-type block copolymers were obtained with higher RMIs. These results may have been related to the amount and the reaction efficiency of the azo units in the MAI. The chemical structures of the nanospheres were also affected by the solvent compositions; multiblock copolymers tended to be obtained with larger RMIs in 60 vol % solutions, compared to other solvent compositions.  $M_n$  reached a maximum and  $D_n$  showed a minimum at 60 vol % H<sub>2</sub>O content. The dependences of the molecular weight [ $M_n$  and  $M_n(\text{PMMA})$ ] and  $D_n$  on RMI were different for 75 and 60 vol % H<sub>2</sub>O content solutions. The solvents affected a self-assembling process of the MAI and MMA for the nanosphere formation. The efficiency of the dispersion polymerization was also related to the solubility of monomer, MAI, and polymer. Particles with large  $M_n$ 's and high conversions were acquired in appropriate solubility conditions.

## References

1. Caruso, F., Ed. *Colloids and Colloid Assemblies*; Wiley-VCH: Weinheim, 2004.
2. Chen, M. Q.; Kishida, A.; Serizawa, T.; Akashi, M. *J Polym Sci Part A: Polym Chem* 2000, 38, 1811.
3. Chen, M. Q.; Serizawa, T.; Kishida, A.; Akashi, M. *J Polym Sci Part A: Polym Chem* 1999, 37, 2155.
4. Serizawa, T.; Chen, M. Q.; Akashi, M. *Langmuir* 1998, 14, 1278.
5. Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* 1991, 24, 2348.
6. Laverty, J. J.; Gardlund, Z. G. *J Polym Sci Polym Chem Ed* 1977, 15, 2001.
7. Ueda, A.; Nagai, S. *J Polym Sci Part A: Polym Chem* 1986, 24, 405.
8. Hazer, B.; Erdem, B.; Lenz, R. W. *J Polym Sci Part A: Polym Chem* 1994, 32, 1739.
9. Yildiz, U.; Hazer, B.; Capek, I. *Angew Makromol Chem* 1995, 231, 135.
10. Yildiz, U.; Hazer, B. *Polymer* 2000, 41, 539.
11. Okubo, M.; Fujii, S.; Maenaka, H.; Minami, H. *Colloid Polym Sci* 2002, 280, 183.
12. Sato, T.; Matsumoto, Y.; Tanaka, H.; Ota, T. *Makromol Chem* 1987, 188, 769.
13. Hu, Z.; Lu, X.; Gao, J.; Wang, C. *Adv Mater* 2000, 12, 1173.