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Microsphere synthesis by emulsion copolymerization of methyl methacrylate with binary macromonomer blends

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Well-defined poly(vinyl alcohol) (PVA) macromonomer having *c.* two vinylbenzyl groups at the terminal end was prepared by means of free radical polymerization. Polymer microspheres were synthesized by emulsion copolymerization of methyl methacrylate (MMA) with PVA macromonomer in aqueous ethanol solution. In this copolymerization system, the macromonomer acted as not only a comonomer but also a stabilizer. The diameter of the polymer microspheres decreases as the water fraction in mixed solvent increased. The polymer microspheres had a very narrow particle-size distribution. Subsequently, the polymer microspheres were synthesized by emulsion copolymerization of MMA with binary PVA/poly(methacrylic acid) (PMA) macromonomer blends. PMA macromonomer also possessed one vinylbenzyl group per chain. Even in these systems of binary macromonomer blends as the emulsifier, the polymer microspheres formed had a very narrow particle-size distribution. Binary macromonomers formed co-micelles with MMA monomer and acted not only as the comonomer but also as the stabilizer. Copyright © 1996. Published by Elsevier Science Ltd.

(Keywords: macromonomer; emulsion copolymerization; polymer microsphere)

INTRODUCTION

There are reports in the literature on the preparation of monodisperse microspheres in the micrometre range, these microspheres having potential applications in the biomedical field, and in the information and microelectronics industries. Almost all these studies have been concerned with the synthetic method of emulsion and soap-free polymerization.

Recently, there have been several studies on the synthesis of the polymer microspheres by emulsion copolymerization using hydrophilic or amphiphilic macromonomers, such as poly(vinylpyrrolidone)[1,2], poly(2-alkyl-2-oxazoline)[3,4] and poly(ethylene oxide)[5–7], instead of using a homopolymer as a stabilizer. The macromonomer acted not only as stabilizer but also as a comonomer. In previous work[8], we prepared polymer microspheres by the emulsion copolymerization of methyl methacrylate (MMA) with poly(methacrylic acid) (PMA) macromonomers in aqueous ethanol solution. As a result, the particle size (submicrometre to micrometre range) and size distribution could be controlled by selecting the solvent composition, and the feed amount and molecular weight of the PMA macromonomers. In general, binary macromonomer blends can be expected to form co-micelles with low-molecular-weight monomer in the solvent medium. The polymer microspheres produced from this emulsion copolymerization will be stabilized with two kinds of grafted chains. Such microspheres (stabilized with two kinds of grafted chains) can be expected to possess interesting solution properties such as pH-responsive character.

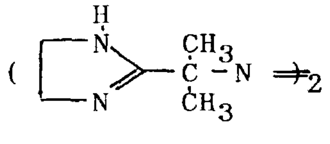
In this work, polymer microspheres were synthesized by emulsion copolymerization of MMA with poly(vinyl alcohol) (PVA) having vinylbenzyl groups at the terminal end, in an aqueous ethanol solution. We studied the control of particle size and size distribution as functions of the solvent composition and the feed amount of PVA macromonomer. On the basis of the data obtained, polymer microspheres were subsequently synthesized by emulsion copolymerization of MMA with binary PVA/PMA macromonomer blends as the emulsifier.

EXPERIMENTAL

Macromonomer syntheses and characterization

The well-defined PMA macromonomers were derived from the hydrolysis of corresponding poly(t-butyl methacrylate) (PBMA) macromonomers. Details of the synthesis and characterization of such macromonomers have been given elsewhere[8].

The PVA macromonomer was prepared following the method reported by the authors[9]. First, poly(vinyl acetate) (PVAc) macromonomer was synthesized by the radical polymerization of vinyl acetate (VAc) initiated by the functional initiator VA-061 [2,2′-azobis(*N*,*N*′-dimethyleneisobutyramidine):



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in the presence of allylmalonic acid diethylester as a degradative chain transfer agent, followed by an end-capping reaction with *p*-chloromethyl styrene (CMS). Under these reaction conditions, the polymerization of VAc is regarded to proceed entirely via the unimolecular termination mechanism. Because the allyl compound leads to degradative chain transfer, the resulting allyl radical is quite stable. This preparation method of the imidazol-terminated prepolymer at one end is applicable to common vinyl monomers[10–12]. Subsequently, PVA macromonomer was derived from its alkaline hydrolysis. Details concerning the synthesis and characterization have been given elsewhere[9,12].

Emulsion copolymerization

Copolymerization was carried out at 60°C under a nitrogen atmosphere in a glass vessel. A mixture of macromonomer (or binary macromonomer blends), MMA and 2,2′-azobisisobutyronitrile (AIBN) was dissolved in a mixed solvent of ethanol and water. The mixture was maintained in a thermostatted bath with shaking (150 shakes per min). After copolymerization, the resulting products were dialysed through a cellulose tube for 1 week. The polymer microspheres were removed by centrifugation.

Measurements

The morphology and particle size of the polymer microspheres were evaluated on a Jeol JSM-T220 scanning electron microscope (SEM) with a tilt angle of 30°. The SEM specimens were prepared by placing a drop of the dispersion solution of microspheres on a glass plate, drying and sputtering with Pt. The number-average diameter ($\bar{D}_n$) and the particle-size distribution ($\bar{D}_w/\bar{D}_n$) were determined by measuring the particle sizes from the SEM micrograph.

RESULTS AND DISCUSSION

Macromonomer syntheses

Imidazoline-terminated PVAc was prepared by free radical polymerization of VAc under a unimolecular termination mechanism. The fraction of imidazoline-terminated PVAc ($\bar{M}_w = 4.7 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.4$) was reacted with an excess of CMS in benzene–water in the presence of sodium carbonate as an acid acceptor. The $\bar{M}_w$ of PVAc macromonomer was determined by gel permeation chromatography (g.p.c.) with the aid of universal calibration[13]. The content of vinylbenzyl groups of PVAc macromonomer was determined by g.p.c. equipped with refractive index (r.i.) and ultraviolet (u.v.; 292 nm) double detectors (*p*-methylstyrene as a model compound). As a result, the functionality of PVAc macromonomer was 1.78 per polymer chain. This result indicated that the CMS reacted not only with −NH− sites (condensation) but also with −N= sites (quaternization) of the terminal imidazoline group. After alkaline hydrolysis using lithium hydroxide, the signal of methyl protons (2.3 ppm) of t-butyl groups disappeared completely in the ^{1}H n.m.r. spectrum. Thus PVA macromonomer was derived from hydrolysis of PVAc macromonomer. The macromonomer possessing several vinylbenzyl groups at the terminal end seems to be favourable as a stabilizer to form micelles with MMA monomer in the various solvent media. The characteristics of PVA macromonomer are listed in *Table 1*.

Table 1 Characteristics of PVA and PMA macromonomers

Code	$10^{-4} \times \bar{M}_w$ [a]	$\bar{M}_w/\bar{M}_n$ [b]	Functionality[c] (number/1-polymer)
PVA-M1	2.4	1.43	1.78
PMA-M1	0.86	1.08	1.00
PMA-M2	4.1	1.05	0.99
PMA-M3	18.8	1.05	0.78

[a] Estimated from the $\bar{M}_w$ of PVAc or PBMA macromonomers determined by g.p.c. (Tosoh high-speed liquid chromatograph HLC-8020 with THF as eluent at 38°C, using a TSK gel GMH$_{XL}$ column and a flow rate of 1.0 ml min^{-1}) using universal calibration

[b] Determined from g.p.c. distributions of PVAc or PBMA macromonomers

[c] Determined from functionality of PVAc or PBMA macromonomers determined by g.p.c. equipped with r.i. and u.v. (292 nm) double detectors

Table 2 Solubility parameters of solvents, monomer and polymers

Reagent	δ (cal cm^{-3})$^{1/2}$
Water	23.4
Methanol	14.5
Ethanol	12.7
Methyl methacrylate	8.8
Poly(methacrylic acid)	12.7–14.5
Poly(vinyl alcohol)	12.6

The well-defined PMA macromonomers were derived from the hydrolysis of PBMA macromonomers, which were prepared by coupling of living PBMA anions initiated by triphenylmethyl sodium with CMS in tetrahydrofuran (THF) at −78°C. Details concerning the synthesis and characterization of such macromonomers have been given elsewhere[8]. The characteristics of the monodisperse PMA macromonomers used in this work are also listed in *Table 1*.

Emulsion copolymerization of MMA with PMA macromonomers

In a previous work[8], we investigated microsphere formation as a function of solvent medium (water/ethanol mixture) and macromonomer concentration. It was found that the diameter of the polymer microspheres (micrometre to submicrometre range) decreased as both the water fraction in mixed solvent and the macromonomer concentration increased. In particular, the particle size depended strongly on the solvent medium. *Table 2* lists the solubility parameters[14] of polymers, monomer and solvents. The closer the cohesive energy density of the solvent medium is to that of MMA monomer, the smaller the size of the monomer droplets (micelles) stabilized by the emulsifier. The polymer is formed as a latex of polymer particles stabilized by the emulsifier during copolymerization. It can be expected therefore that the particle size produced from the water/methanol solvent medium is smaller than that from the water/ethanol one.

We examined the solvent effect on particle size, varying the solvent composition of water/methanol. *Table 3* lists the copolymerization conditions and results for PMA-M1-11 to PMA-M1-14. Typical SEM micrographs of polymerization products are shown in *Figure 1*,

Table 3 Results of emulsion copolymerizations PMA-M1-11 to PMA-M1-14, varying solvent composition[a]

Expt	Water/methanol (v/v)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$
PMA-M1-11	3/7	[c]	[c]
PMA-M1-12	4/6	0.76	1.03
PMA-M1-13	5/5	0.43	1.02
PMA-M1-14	7/3	0.21	1.03

[a] Polymerized at 60°C under conditions: PMA-M1 = 5 wt% for MMA; AIBN = 2 wt% for total monomer

[b] Determined from SEM micrographs

[c] Aggregation behaviour observed

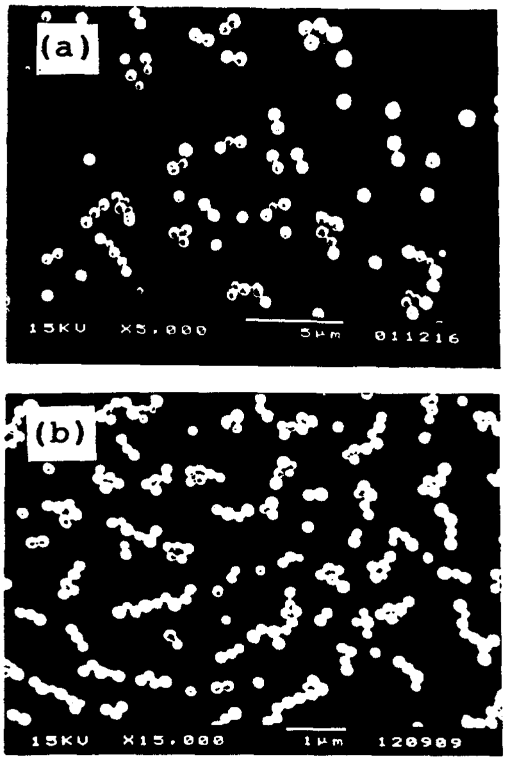

Figure 1 SEM micrographs of PMA-M1-12 (a) and PMA-M1-14 (b)

where micrographs a and b indicate the morphological results of experimental PMA-M1-12 and PMA-M1-14, respectively. These products are spherical particles of poly(methyl methacrylate) (PMMA). It is found from these micrographs that the particle-size distribution ($\bar{D}_w/\bar{D}_n$) of these microspheres is very narrow. The values of particle diameter ($\bar{D}_n$) and $\bar{D}_w/\bar{D}_n$ are collected in *Table 3*. On the other hand, the polymerization product PMA-M1-11 (solvent composition: water/methanol = 3/7 (v/v)) showed a morphology of aggregated PMMA particles. *Figure 2* shows the dependence of particle diameter on solvent composition as a function of the type of alcohol. Data quoted for the water/ethanol emulsion system were obtained in previous work[8]. It is found, as speculated above, that the diameter of microspheres obtained from the water/methanol emulsion system is smaller than that from the water/ethanol emulsion system at the same water content in the medium.

Figure 3 shows the dependence of particle size and particle-size distribution on molecular weight of PMA macromonomers. The diameter of the microspheres decreases gradually with increasing molecular weight of the PMA macromonomers. Micrometre-sized polymer microspheres have a narrow size distribution ($\bar{D}_w/\bar{D}_n \lesssim 1.04$). High-molecular-weight grafted chains are favourable to the steric stability of microspheres formed by copolymerization.

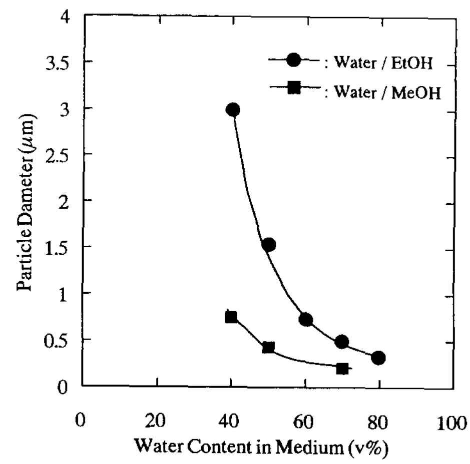

Figure 2 Dependence of particle diameter on the type of alcohols in the solvent medium

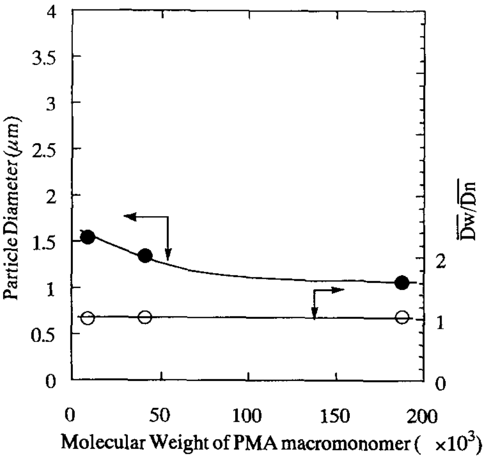

Figure 3 Dependence of particle diameter and particle-size distribution on molecular weights of PMA macromonomers

We examined the effect of the pH of the solvent medium on the particle size of microspheres. These emulsion copolymerizations were carried out at 60°C for 6 h under the conditions: PMA-M1 macromonomer = 5 wt% for MMA; AIBN = 2 wt% for total monomer; solvent composition water/ethanol = 5/5 (v/v). The results of particle diameter and size distribution for products PMA-M1-31 to PMA-M1-34 are listed in *Table 4*. The diameter of the microspheres decreases gradually with increasing pH until pH = 9. However, the particle diameter increases slightly beyond *c*. pH = 10 in the medium. These phenomena can be explained as follows. PMA macromonomer as an emulsifier is an anionic polyelectrolyte. So, the radius of gyration of PMA increases as the pH in the medium increases due to the high degree of dissociation of carboxyl groups. That is to say, high expansion of macroions such as PMA macromonomer is favourable to the steric stability of PMMA microspheres formed by

Table 4 Results of emulsion copolymerizations PMA-M1-31 to PMA-M1-34, varying the pH of the solvent medium[a]

Expt	pH	$\bar{D}_n$ (μm)	$\bar{D}_w/\bar{D}_n$
PMA-M1-31	5	1.70	1.01
PMA-M1-32	7	1.54	1.01
PMA-M1-33	9	1.32	1.03
PMA-M1-34	11	1.54	1.03

[a] Polymerized at 60°C under conditions: PMA-M1 = 5 wt% for MMA; AIBN = 2 wt% for total monomer; solvent composition water/ethanol = 5/5 (v/v)

Table 5 Results of emulsion copolymerizations PVA-M1-11 to PVA-M1-16, varying solvent composition[a]

Expt	Water/ethanol (v/v)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$[b]
PVA-M1-11	3/7	[c]	[c]
PVA-M1-12	4/6	3.78	1.07
PVA-M1-13	5/5	2.51	1.02
PVA-M1-14	6/4	1.12	1.01
PVA-M1-15	7/3	0.65	1.03
PVA-M1-16	8/2	0.60	1.04

[a] Polymerized at 60°C under conditions: PVA-M1 = 5 wt% for MMA; AIBN = 2 wt% for total monomer
[b] Determined from SEM micrographs
[c] Aggregation behaviour observed

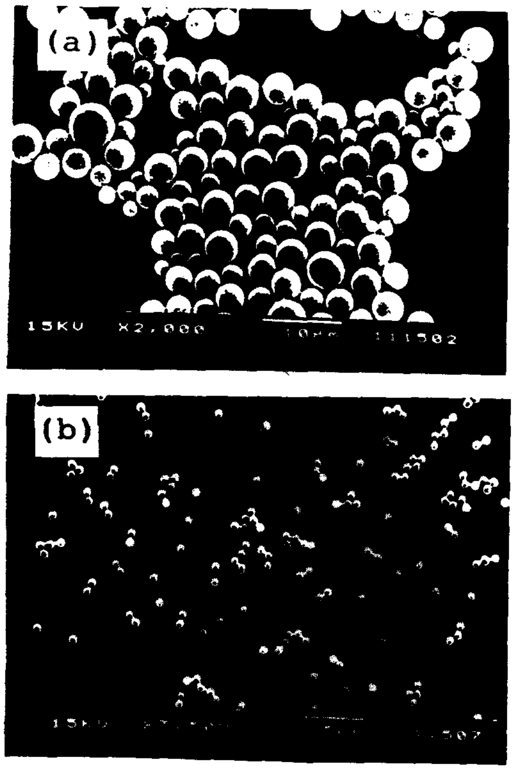

Figure 4 SEM micrographs of PVA-M1-12 (a) and PVA-M1-15 (b)

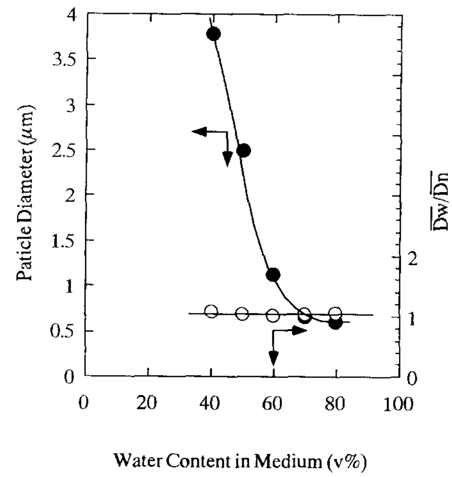

Figure 5 Dependence of particle diameter and particle-size distribution on solvent composition

copolymerization. Beyond *c*. pH = 10, the solubility of PMA macromonomer seems however to decrease due to the hydrophobic nature of the methyl groups in the PMA molecule. The pH effect in the medium will be made clearer by studying on the microsphere formation using poly(acrylic acid) macromonomer as an emulsifier.

Emulsion copolymerization of MMA with PVA macromonomer

In this section, we report the microsphere formation by emulsion copolymerization of MMA with non-ionic PVA macromonomer. We examined first the effect of the solvent composition on particle size. These emulsion copolymerizations (PVA-M1-11–PVA-M1-16) were carried out at 60°C for 6 h under the conditions: PVA-M1 = 5 wt% for MMA; AIBN = 2 wt% for total monomer; varying solvent composition (water/ethanol = 3/7 to 8/2 (v/v)). The results of particle diameter and size distribution for PVA-M1-11 to PVA-M1-16 are listed in *Table 5*. Typical SEM micrographs of polymerization products are shown in *Figure 4*, where micrographs a and b indicate the morphological results of experimental PVA-M1-12 and PVA-M1-15, respectively. These products are spherical particles of PMMA. It is found also from these micrographs that the particle-size distribution of these microspheres is very narrow. On the other hand, the polymerization product of PVA-M1-11 (solvent composition: water/ethanol = 3/7 (v/v)) showed the morphology of aggregated PMMA particles. *Figure 5* shows the dependence of the particle diameter and size distribution on solvent composition. It is found from these plots that the particle diameter decreases (3.8–0.6 μm) with an increase of water content in the medium. Moreover, the particle-size distribution is very narrow ($\bar{D}_w/\bar{D}_n = 1.01$–$1.07$). Thus, we observed a tendency in which the more hydrophilic the medium became, the smaller the particle size. This may be because the critical degree of polymerization, at which the oligomers form the nuclei, decreases in the more hydrophilic solvent, and the number of nuclei increases. Similar phenomena were observed in the dispersion polymerization of styrene in an aqueous ethanol solution[4,15,16].

Figure 6 shows the dependence of the particle diameter and size distribution on PVA-M1 macromonomer concentration as a function of solvent composition. The particle diameter is almost constant for the solvent composition water/ethanol = 7/3 (v/v), regardless of the variation of macromonomer concentration. Submicrometre-sized polymer microspheres have narrow size distribution ($\bar{D}_w/\bar{D}_n \lesssim 1.01$). In this solvent composition, the macromonomer is sufficient to stabilize PMMA

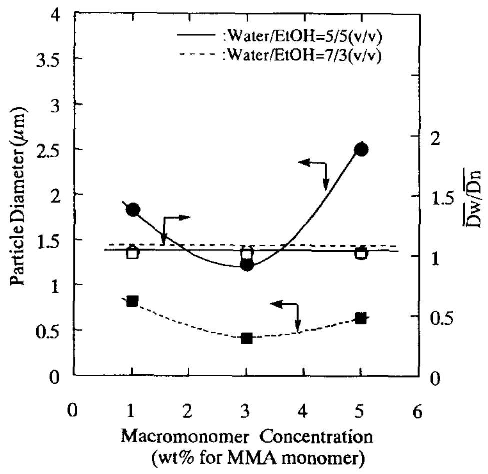

Figure 6 Dependence of particle diameter and particle-size distribution on PVA-M1 macromonomer concentration as a function of solvent composition

particles with 1 wt% of macromonomer concentration. In the solvent composition water/ethanol = 5/5 (v/v), micrometre-sized polymer microspheres are obtained which have a very narrow particle size distribution. However, the particle diameter increases slightly beyond ~3 wt% of macromonomer concentration, regardless of stabilizing PMMA particles. It seems that the solubility of the PVA-M1 macromonomer decreases in this solvent composition, because the medium becomes hydrophobic compared with the solvent composition water/ethanol = 7/3 (v/v).

Emulsion copolymerization of MMA with binary PMA/PVA macromonomer blends

Binary PMA/PVA macromonomer blends can be expected to form co-micelles with MMA monomer in the solvent media. The polymer microspheres produced from this emulsion copolymerization will be stabilized with two kinds of grafted chains (anionic and non-ionic water-soluble polymers). In order to form co-micelles with MMA by binary PMA/PVA macromonomer blends, it is important to choose the conditions of blending. Data concerning the relationship between the particle diameter and solvent composition (water/ethanol) using PMA or PVA macromonomer as a emulsifier were obtained from the former results (see *Figure 7*). The diameters of PMMA microspheres produced from emulsion copolymerization using PMA-M1 macromonomer are more or less identical to those using PVA-M1 macromonomer, regardless of a variation of solvent compositions (curves 1 and 2 in *Figure 7*).

On the basis of the above results, emulsion copolymerizations in co-micelles (MB-1 and MB-2) were carried out at 60°C for 6 h under the following conditions: macromonomers PMA-M1 = 2.5 and PVA-M1 = 2.5 wt% for MMA; AIBN = 2 wt% for total monomer. The results of particle diameter and size distribution for MB-1 and MB-2 are listed in *Table 6*. Typical SEM micrographs of polymerization products MB-1 and MB-2 are shown in *Figure 8*. It is found from these micrographs that the products are microspheres and that their particle-size distributions are very narrow ($\bar{D}_w/\bar{D}_n \lesssim 1.03$). The observed values of particle diameters are plotted in *Figure 7*. Curve 3 for the MB series is located at the intermediate region between curve 1 and curve 2 as shown in *Figure 7*. These facts support the hypothesis that the PMMA particles formed are stabilized by two kinds of grafted chains of binary

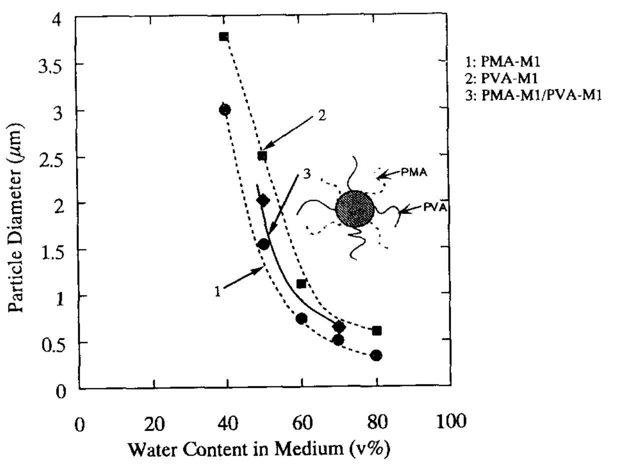

Figure 7 Dependence of particle size on solvent composition as a function of the type of macromonomer

Table 6 Results of emulsion copolymerizations in co-micelles MB-1 and MB-2 as a function of solvent composition[a]

Expt	Water/ethanol (v/v)	$\bar{D}_n$[b] (μm)	$\bar{D}_w/\bar{D}_n$
MB-1	5/5	2.02	1.02
MB-2	7/3	0.65	1.03

[a] Polymerized at 60°C under conditions: PMA-M1 = 2.5 and PVA-M1 = 2.5 wt% for MMA; AIBN = 2 wt% for total monomer
[b] Determined from SEM micrographs

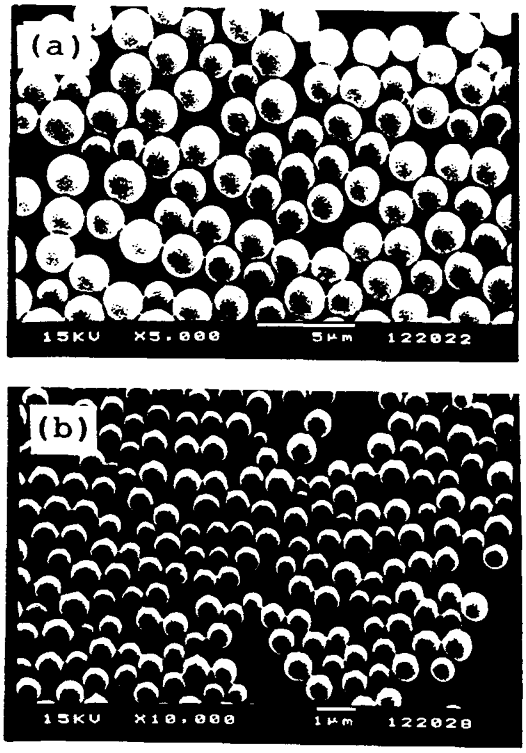

Figure 8 SEM micrographs of MB-1 (a) and MB-2 (b)

PMA/PVA macromonomers in the solvent media. These microspheres are expected to possess interesting solution properties such as pH-responsive character. Results of such investigations will be reported in the near future.

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