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Microsphere synthesis by emulsion copolymerization of methyl methacrylate with poly(methacrylic acid) macromonomers

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Well-defined poly(methacrylic acid) (PMA) macromonomers having one vinylbenzyl group per polymer chain were prepared by the use of the living anionic polymerization technique. The polymer microspheres were synthesized by emulsion copolymerization of methyl methacrylate (MMA) with PMA macromonomers in an aqueous ethanol solution. In this copolymerization system, the macromonomer acted not only as a comonomer but also as a stabilizer. The diameter of the polymer microspheres decreased as the water fraction in the mixed solvent increased. The polymer microspheres that were produced had a very narrow particle size distribution. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PMA macromonomer; emulsion copolymerization; polymer microsphere)

INTRODUCTION

There have been several reports describing the preparation of monodisperse polymer microspheres, because these materials possess several potential applications in areas such as the biomedical field, information technology and microelectronics. These studies have been almost completely concerned with synthetic methods involving emulsion and soap-free polymerizations. In emulsion polymerization, the emulsifier stabilizes the water-insoluble monomer particles.

Since Milkovich and co workers[1–3] first demonstrated the syntheses and applications of a variety of macromonomers, it has been established that the macromonomer technique is one of the best ways for preparing well-defined graft copolymers. The first application of macromonomers was reported by ICI; in this work, a graft copolymer obtained from a lipophile macromonomer was used as a stabilizer for dispersion polymerization in hydrocarbon media[4]. The graft copolymer consisted of a graft segment from the macromonomer which was soluble in the media and a main chain which was insoluble in the media. The steric repulsion of the grafted polymer chain prevented coagulation of the resulting polymer particles. More recently, there have been several studies describing the synthesis of polymer microspheres by emulsion copolymerization using hydrophilic macromonomers, such as poly(*N*-vinylpyrrolidone)[5,6], poly(2-alkyl-2-oxazoline)[7,8], and poly(ethyleneoxide)[6,9–11], instead of using a homopolymer as a stabilizer. The macromonomer that was used acted not only as a stabilizer but also as a comonomer.

We have prepared a variety of macromonomers via the living anionic and radical polymerization techniques[12]. Poly(t-butyl methacrylate) (PBMA) macromonomer[13], having one vinylbenzyl group per polymer chain, was prepared by the coupling of living PBMA, initiated by sodium triphenylmethane, with *p*-chloromethyl styrene (CMS) in tetrahydrofuran (THF) at −78°C. The PBMA segment was able to convert quantitatively to poly(methacrylic acid) (PMA) by hydrolysis, using a mixture of chlorotrimethylsilane and sodium iodide[14,15].

In this present article, polymer microspheres were synthesized by emulsion copolymerization of methyl methacrylate (MMA) with PMA macromonomers in aqueous ethanol solution. We studied the control of particle size and particle size distribution as a function of the solvent composition and the feed amount of emulsifier.

EXPERIMENTAL

Macromonomer synthesis and characterization

The well-defined PBMA macromonomers were prepared by the coupling of living PBMA, initiated by sodium triphenylmethane with CMS in THF at −78°C. The details concerning the synthesis and characterization of such macromonomers have been given elsewhere[13]. In order to obtain the PMA macromonomers, PBMA segments were hydrolysed with iodotrimethylsilane[14,15]. After the hydrolysis, a moiety of the tert-butyl groups ($\delta = 2.1$ ppm) had disappeared in the ^{1}H nuclear magnetic resonance (n.m.r.) spectra. Moreover, we have recognized the existence of the vinylbenzyl group (characteristic absorption at 292 nm) at the terminal end

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of the PMA macromonomer from ultraviolet (u.v.) spectra. Similar results were obtained by other investigators, e.g. Deffieux *et al.*[16] have synthesized α,ω-heterodifunctional polystyrenes with α-acetal and ω-vinylbenzyl groups. It has been shown that iodotrimethylsilane reacts with the acetal group, which is then quantitatively converted into α-iodo ether. The acetal end-groups of the polystyrene precursors were therefore reacted with iodotrimethylsilane in a slight excess in order to generate heterodifunctional polystyrenes with α-iodo ether and vinylbenzyl terminal groups. The characteristics of the PMA macromonomer (M-1) are as follows: number-average molecular weight $(\bar{M}_n) = 8.6 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.08$, vinylbenzyl groups = 1.0 (number per polymer chain).

Emulsion copolymerization

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

Measurements

The morphology and particle size of the polymer microspheres were investigated by the use of a JEOL JSM-T220 scanning electron microscope with a tilt angle of 30°. The particle size distribution was determined from the micrographs that were obtained.

RESULTS AND DISCUSSIONS

In order to determine the yield of the poly(methylmethacrylate) (PMMA) microspheres, we examined first the relationship between conversion and time for emulsion copolymerizations carried out under the following conditions: MMA = 5 ml, M-1 = 0.023 g (5 wt% based on MMA), AIBN = 9.4 mg (2 wt% based on total monomer, and ethanol/water = 5/5 (ml/ml). *Figure 1* shows the time–conversion curve of the emulsion copolymerization. The polymerization rate increased during the time in which the conversion reached a plateau value (ca. 90%), i.e. after 6 h. Therefore we set 6 h as the polymerization time in the following experiments.

We then examined the effect of the solvent composition on particle size. These emulsion copolymerizations were carried out at 60°C for 6 h under the following conditions: macromonomer M-1 = 5 wt% (based on MMA) and AIBN = 2 wt% (based on total monomer), while varying the solvent composition (water/ethanol = 3/7–8/2 (vol/vol). The results obtained for the particle diameters $(\bar{D}_n)$ and particle size distributions $(\bar{D}_w/\bar{D}_n)$ for experiments P11–P16 are listed in *Table 1*. Typical scanning electron micrographs of the polymerization products are shown in *Figure 2*, where micrographs (a), (b), and (c) indicate the morphological results from experiments P13, P15 and P16, respectively.

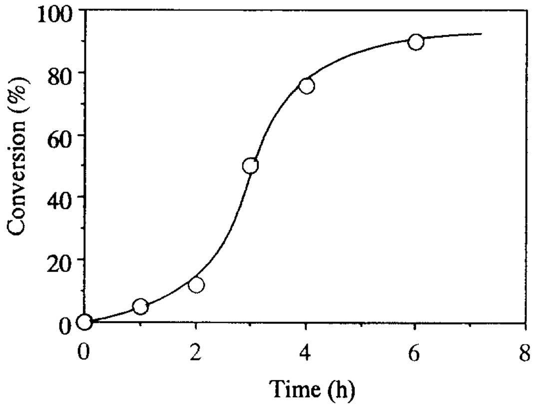

Figure 1 Time–conversion curve of emulsion copolymerization of MMA with macromonomer M-1

Table 1 Results obtained for particle diameters and particle size distributions of systems P11–P16 with varying solvent compositions [a]

System	Water/ethanol (vol/vol)	$\bar{D}_n$ [b] (μm)	$\bar{D}_w/\bar{D}_n$ [b]
P11	3/7	–[c]	[c]
P12	4/6	3.00	1.09
P13	5/5	1.54	1.01
P14	6/4	0.74	1.05
P15	7/3	0.50	1.02
P16	8/2	0.33	1.04

[a] Polymerized at 60°C under conditions where M-1 = 5 wt% (based on MMA) and AIBN = 2 wt% (based on total monomer)
[b] Determined from scanning electron micrographs
[c] Aggregation behaviour observed

All of the products obtained were spherical particles of PMMA. It was found from these micrographs that the particle size distribution of these microspheres was very narrow. On the other hand, the polymerization product obtained from system P11 (solvent composition, water/ethanol = 3/7 (vol/vol) showed a morphology with aggregated PMMA particles. *Figure 3* shows the effects of the solvent composition on the $\bar{D}_n$ and $\bar{D}_w/\bar{D}_n$ values. It was found from these plots that the particle diameter decreased with an increase of water content in the medium (3.00–0.33μm). Moreover, the particle size distribution was very narrow $(\bar{D}_w/\bar{D}_n = 1.01\text{–}1.05)$. Thus, we observed a tendency in which the more hydrophilic the media became, then the smaller was the particle size. This may be because the critical degree of polymerization, i.e. the level at which the oligomers form nuclei, decreases in the more hydrophilic solvent, and thus the number of nuclei increases. Correspondingly, the particle diameter decreases. Similar phenomena were observed in the dispersion polymerization of styrene in an aqueous ethanol solution[8,17,18].

Figure 4 shows the effect of the concentration of macromonomer M-1 on the particle diameter and size distribution as a function of the solvent composition. The particle diameters were almost constant for the solvent composition where water/ethanol = 7/3 (vol/vol), regardless of any variation in the macromonomer concentration. The submicron-size polymer microspheres that were produced had a narrow size distribution $(\bar{D}_w/\bar{D}_n \lesssim 1.03)$. With this solvent composition, the macromonomer was able to stabilize the PMMA

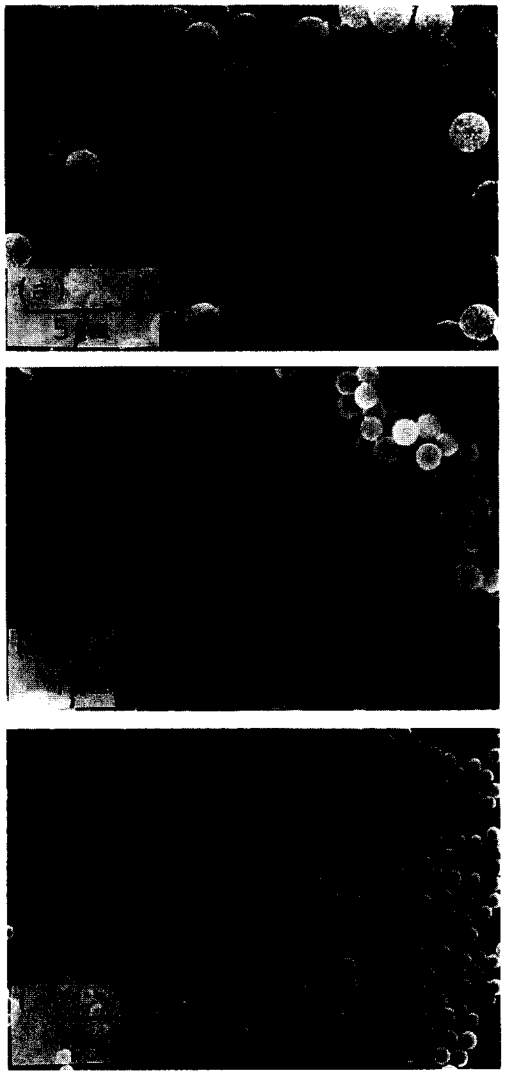

Figure 2 Scanning electron micrographs of PMMA microspheres produced by emulsion copolymerization in ethanol–water media of varying composition: (a) P13; (b) P15; (c) P16

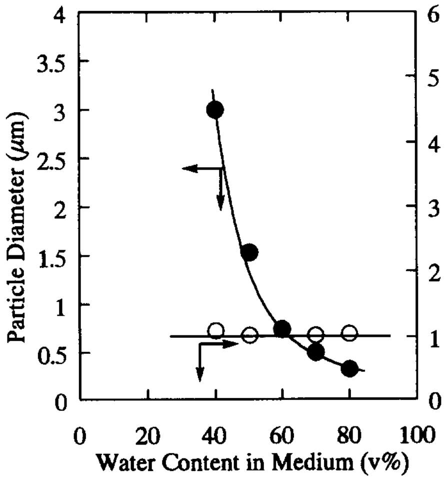

Figure 3 Effect of solvent composition on particle diameter and particle size distribution

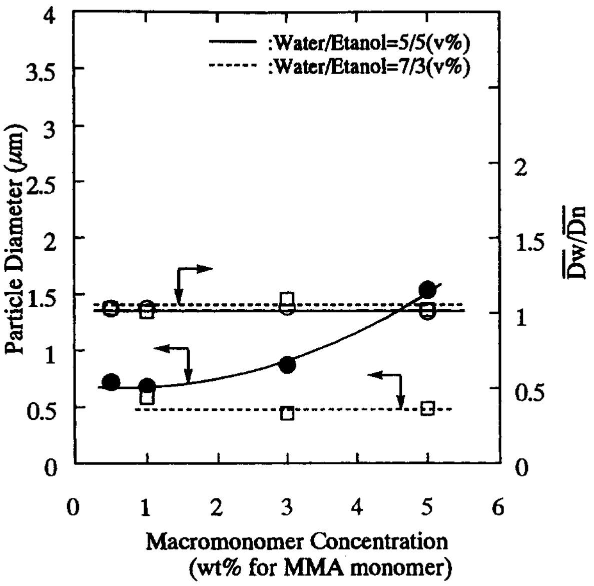

Figure 4 Effect of concentration of the macromonomer M-1 on particle diameter (filled symbols) and particle size distribution (open symbols) as a function of solvent composition: (■ and □) water/ethanol = 7/3; (● and ○) water/ethanol = 5/5 (vol/vol)

particles at a macromonomer concentration of 1 wt%. For the solvent composition where water/ethanol = 5/5 (vol/vol), the macromonomer was able to stabilize the PMMA particles over the concentration range from 0.5 to 3.0 wt%. However, the particle diameter increased slightly beyond a macromonomer concentration of 5.0 wt%, regardless of the stabilizing PMMA particles. It seemed that the solubility of the PMA macromonomer decreased in this solvent system, because the medium became hydrophobic when compared to that of the solvent system where water/ethanol = 7/3 (vol/vol). The particle size distribution was narrow ($\bar{D}_w/\bar{D}_n \leqslant 1.03$) for all of the emulsion copolymerizations examined. It is indicated from these results that the macromonomer with a higher solubility is able to stabilize the polymer particles more efficiently.

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