

NOTES

Graft Copolymers Having Hydrophobic Backbone and Hydrophilic Branches. V. Microspheres Obtained by the Copolymerization of Poly(ethylene Glycol) Macromonomer with Methyl Methacrylate*

INTRODUCTION

In previous papers,¹⁻³ we showed that microspheres consisting of graft copolymers having hydrophobic backbone and hydrophilic branches can be prepared by the free radical copolymerization between hydrophilic oligovinylpyrrolidone macromonomers and hydrophobic monomers such as styrene and methyl methacrylate without any emulsifier. Among macromonomers, amphiphilic poly(ethylene glycol) macromonomers are easily prepared from commercial poly(ethylene glycol) with hydroxy group in the polymer ends and the reactivity has been well understood.^{4,5} When poly(ethylene glycol) macromonomers are used as hydrophilic macromonomers for the preparation of graft copolymers in question by copolymerization with hydrophobic monomers, water-dispersible microspheres are also expected to form and the characteristics of dispersion copolymerization of hydrophilic macromonomers may be clarified. Here we wish to report the characteristics of microsphere formation by the copolymerization of poly(ethylene glycol) macromonomer with methyl methacrylate in ethanol/water mixture.

EXPERIMENTAL

Methacryloyl terminated poly(ethylene glycol) macromonomer was given by Nippon Oil and Fats Co. The number average molecular weight of it was determined as $\overline{M}_n = 1.00 \times 10^3$ by ¹H-NMR spectroscopy according to the method described in the literature.⁴ 2,2'-Azobis[2-(2-imidazoline-2-yl)propane]dihydrochloride (VA-044) (Wako Pure Chemical Ind.) and benzoylperoxide (BPO) were used without further purification. The solvents and commercial methyl methacrylate were purified in the usual way prior to use. ¹H-NMR spectra were measured on JEOL FX-90 (90 MHz) instruments. A scanning electron microscope, Hitachi H-7010A, was used to observe the morphology of the microspheres. Gel permeation chromatographic (GPC) analysis was performed with chloroform as eluent on a Shimadzu LC-6A system equipped with a RI detector (Shodex, SE-51) using a Shodex column (AC-80M, 8 × 500 mm) at room temperature.

RESULTS AND DISCUSSION

Copolymerization of poly(ethylene glycol) macromonomer with methyl methacrylate was carried out in the presence of VA-044 or BPO in ethanol/water (6/4, v/v) mixture or benzene, respectively, at 60°C in a sealed tube after degassing repeatedly. The results are shown in Table I. Conversion was obtained by free gravimetry after dialysis and freeze dry. The content of comonomers in graft copolymer was estimated from ¹H-NMR measurements in CDCl₃ at 45°C. The number average molecular weight of copolymers was determined by GPC.

A typical scanning electron micrograph of microspheres obtained by the copolymerization in ethanol/water mixture is shown in Figure 1. The copolymerization proceeds heterogeneously in ethanol/water mixture to form microspheres as shown in the figure, while in benzene it does homogeneously. In case of homopolymerization of methyl methacrylate in ethanol/water mix-

*For Part IV, see Akashi et al.³

TABLE I
Copolymerization of Poly(ethylene Glycol) Macromonomer (M_1) with Methyl Methacrylate (M_2) at 60°C in Ethanol/ H_2O (6/4,v/v) or Benzene^a

Run	Solvent	Time (h)	Yield (wt %)	\overline{M}_n	M_1 in copolymers (mol %)	Particle size (nm)
1	Ethanol/ H_2O	0.25	53	9.9×10^4	1.28	120
2	Ethanol/ H_2O	0.50	68	6.5×10^4	1.79	160
3	Ethanol/ H_2O	1.0	84	4.3×10^4	1.79	169
4	Ethanol/ H_2O	2.0	91	4.2×10^4	1.92	174
5	Ethanol/ H_2O	8.0	91	9.7×10^4	2.08	178
6	Ethanol/ H_2O	48.0	96	9.4×10^4	2.27	184
7	Benzene	0.25	1.5	—	—	—
8	Benzene	1.0	7.6	3.0×10^4	—	—
9	Benzene	8.0	36	1.9×10^4	2.55	—
10	Benzene	48.0	43	1.8×10^4	2.24	—

^aConditions for copolymerization: 1.66 mol of monomers in total were used in 5 mL of solvent. $[M_1]/[M_2] = 2.28 \times 10^{-2}$; $[\text{initiator}]/[\text{total monomer}] = 1.0 \text{ mol \%}$.

ture, any microsphere was not given but amorphous poly(methyl methacrylate) was precipitated in the bottom of the tube. The result of M_1 in copolymers shows that apparent monomer reactivity of macromonomer is smaller than methyl methacrylate as shown in the literature⁴ and macromonomer-poor graft copolymers were produced in the first stage of copolymerization. The average diameter of the microspheres increased together with the progress of copolymerization and was less than 0.2 μm , which is much smaller than that obtained by the copolymerization of oligovinylpyrrolidone macromonomer with methyl methacrylate.³ As is well known, homopolymer obtained from poly(ethylene glycol) macromonomer is soluble in both ethanol/water mixture and benzene, and poly(methyl methacrylate) is not soluble in ethanol/water mixture but soluble in benzene. Therefore, the copolymerization in ethanol/water mixture becomes a dispersion polymerization system immediately after starting polymerization.

In order to study the mechanism of the microsphere formation, GPC analysis of their copolymerization system was performed and the results are shown in Figure 2. The GPC elution

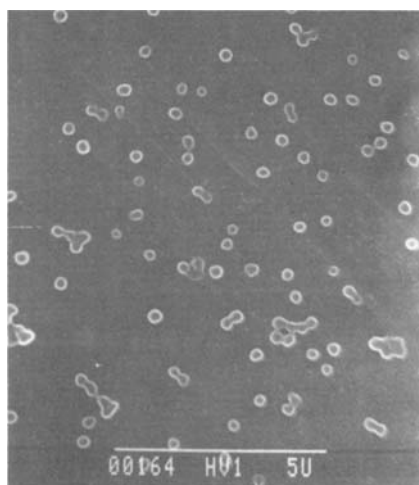


Fig. 1. Scanning electron micrograph of microspheres obtained by copolymerization of poly(ethylene glycol) macromonomer with methyl methacrylate at 60°C in ethanol/water mixture.

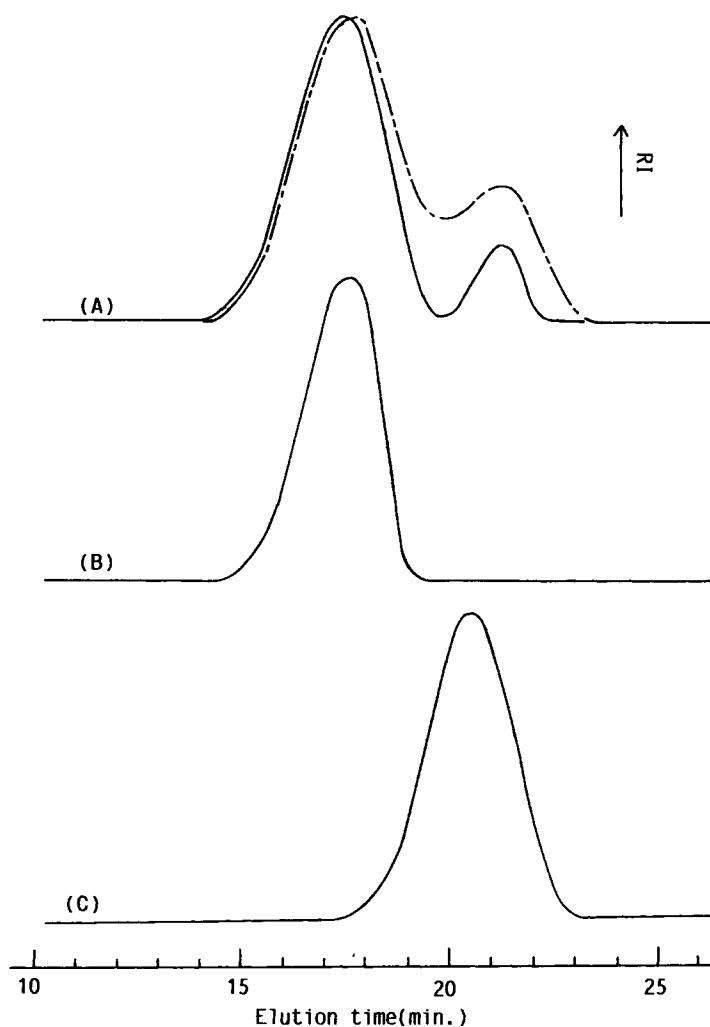


Fig. 2. GPC profiles of graft copolymers by way of copolymerization of poly(ethylene glycol) macromonomer with methyl methacrylate in ethanol/water mixture and benzene. (A): (---) run 4; (—) run 6, (B) Microspheres separated from whole graft copolymers (run 6), (C) Graft copolymers obtained in benzene (run 10).

pattern of the polymers obtained by free radical copolymerization shows generally a single peak. In fact, a single peak was seen for the copolymerization in the benzene [Fig. 2(C)], but graft copolymers prepared in ethanol/water mixture were found to show two peaks [Fig. 2(A)]. Also, the number average molecular weight of the whole graft copolymers decreased once and then increased. The peak corresponding to low molecular weight may be attributed to poly(ethylene glycol) macromonomer-rich graft copolymers, which is soluble in ethanol/water mixture and the main peak is attributed to microspheres. Figure 2(B) shows that GPC profile of microspheres which were separated from the reaction mixture by centrifugation. Evidently it coincides with the main peak of the whole graft copolymers. Moreover, the average molecular weight of graft polymers formed microspheres seems to be considerably higher than that of graft copolymers obtained in benzene, provided that the different initiator was used.

In many cases, the rate of dispersion polymerization is much faster than the corresponding polymerization in solution using the same quantities of reactant.⁶ In this case, the rate of copolymerization in ethanol/water mixture is also much faster than that in benzene though using

a different initiator. As shown in a previous paper,³ first methyl methacrylate-rich graft copolymers are produced to form polymer particles as a nucleus of the microsphere, since methyl methacrylate is more reactive⁵ than poly(ethylene glycol) macromonomer, and then methyl methacrylate is absorbed in particles as similarly as dispersion polymerization.⁶ Because poly(ethylene glycol) branches of graft copolymers are soluble in ethanol/water mixture, they exist in the surface of the polymer particle and may cover it to form the microsphere. Moreover, methyl methacrylate is easy to come in hydrophobic domain of the microsphere and propagate. Propagation polymer radicals in the microspheres are considered to be stable and have a long life time.⁷ Also, the termination rate of the radicals decrease in the microsphere, as the viscosity of the polymerization medium increases.⁶ Consequently, molecular weight of graft polymers can be assumed to increase again in the last stage of copolymerization.

The water dispersibility of obtaining poly(ethylene glycol)-grafted poly(methyl methacrylate) is poor compared to that of oligovinylpyrrolidone- or oligoacrylamide-grafted hydrophobic polymers.^{1-3,8,9} The study on the relationship between the size of microspheres and copolymerization condition is now in progress.

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