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Emulsion Copolymerization of Styrene with Amphiphilic Poly(2-oxazoline) Macromonomer Bearing Ammonio Group at the Chain End

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Synopsis. Emulsion copolymerization of styrene with a block-type amphiphilic poly(2-oxazoline) macromonomer having a quaternary ammonio group at the chain end was performed to produce monodisperse polymer particles in the submicron range. Poly(2-oxazoline) chains and the ammonio group were localized on the particle surface.

Much attention has been paid to functional polymer particles due to their wide use for various purposes. For the functionalization, an emulsion copolymerization of a hydrophobic vinyl monomer with a surface-active monomer, i.e., a surfactant having a polymerizable group, possesses potential advantages such as the control of charge density and the introduction of functional group.[1,2] In some cases, the latex obtained upon using a surface-active monomer is more stable than that in regular emulsion polymerization.[3]

Recently, we have reported emulsion copolymerizations of styrene or vinyl acetate with a block-type amphiphilic poly(2-oxazoline) (PROZO) macromonomer and the effects of the position of the polymerizable group on the copolymerization and the resulting particles have been investigated.[4,5] In these studies, macromonomers possessing the polymerizable group attached to the hydrophobic polymer segment were found to be a good emulsifier; these macromonomers gave monodisperse polymer particles. The resulting particles possessed poly(2-oxazoline) chains on the surface, which are well-known to possess unique properties; poly(2-oxazoline) becomes hydrophilic or hydrophobic by changing the variety of the acyl group and shows high compatibility with various organic polymers.[6,7]

The control of charge density on the particle surface is very important in technical applications. Latexes with high cationic charge density are often used for electrophoretic coating. For preparation of such latexes, ionic-type hydrophilic monomers such as sodium acrylate and sodium 4-styrenesulfonate are normally used as a comonomer. In these systems, however, the extent of the formation of water-soluble polymers was not low.[1] In order to suppress the production of the water-soluble polymer, the emulsion copolymerization using an ionic surface-active monomer is potentially an alternative method. The present paper describes emulsion copolymerization of styrene with a novel cationic surface-active monomer, block-type amphiphilic poly(2-oxazoline) macromonomer **1** bearing quaternary ammonio group at the chain end (Chart 1).

Experimental

Materials. 2-Methyl-2-oxazoline (MeOZO) was purified by distillation over potassium hydroxide. 2-Butyl-2-oxazoline (BuOZO) was synthesized according to the literature.[8] Other reagents and solvents were purified in a usual manner. All operations were performed under argon.

Synthesis of Amphiphilic Poly(2-oxazoline) Macromonomer 1. A typical run was as follows. Under argon, a mixture of 0.76 g (5.0 mmol) of (chloromethyl)-styrene and 1.67 g (6.0 mmol) of silver tosylate in 15 mL of acetonitrile was stirred at 60 °C until silver chloride was completely precipitated. After cooling to room temperature, 1.93 g (15.2 mmol) of BuOZO was added to the mixture and heated at 80 °C for 3 h. 2.91 g (34.2 mmol) of MeOZO was added to the mixture, followed by further heating at 80 °C for 12 h. The mixture was cooled to room temperature and 1.01 g (10 mmol) of triethylamine was added to the mixture. Then, the mixture was kept at 80 °C for 1 h. After filtration of the mixture, the filtrate was evaporated under reduced pressure. The residue was extracted with chloroform, and the organic layer was separated. After evaporation of the solvent and reprecipitation (chloroform–diethyl ether), the polymeric material was collected and dried in vacuo to give 4.37 g of **1a** (yield 65%): ^{1}H NMR (CDCl$_3$) δ=0.9 (m, C$\underline{H}_3$CH$_2$CH$_2$), 1.1—1.7 (m, CH$_3$C$\underline{H}_2$C$\underline{H}_2$CH$_2$ and C$\underline{H}_3$CH$_2$N), 1.9—2.6 (m, CH$_3$C=O and CH$_2$C=O), 3.2—4.0 (br, NCH$_2$ and OCH$_2$), 5.3 and 5.7 (m, C$\underline{H}_2$=CH), 6.7 (m, CH$_2$=C$\underline{H}$), 6.9—7.6 (m, Ph).

Emulsion Copolymerization of Styrene with Amphiphilic Poly(2-oxazoline) Macromonomer 1. A typical run was as follows (Entry 2). Macromonomer **1a**

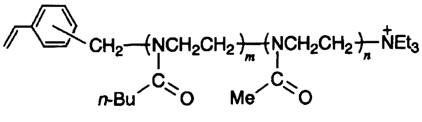

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Chart 1.

Table 1. Composition and Surfactant Property of Macromonomer **1**

Macromonomer	m	n	cmc[a)] × 10^2	γ_{cmc}[a)]
			wt%	dyn cm^{-1}
1a	3.0	7.3	1.3	37
1b	4.4	5.0	2.1	34
1c	6.8	3.2	1.2	36
1d	3.0	0	—[b)]	—[b)]

a) Measured with a Du Noüy tensiometer at an ambient temperature and recalculated to the value at 25 °C.[10)]
b) Insoluble in water.

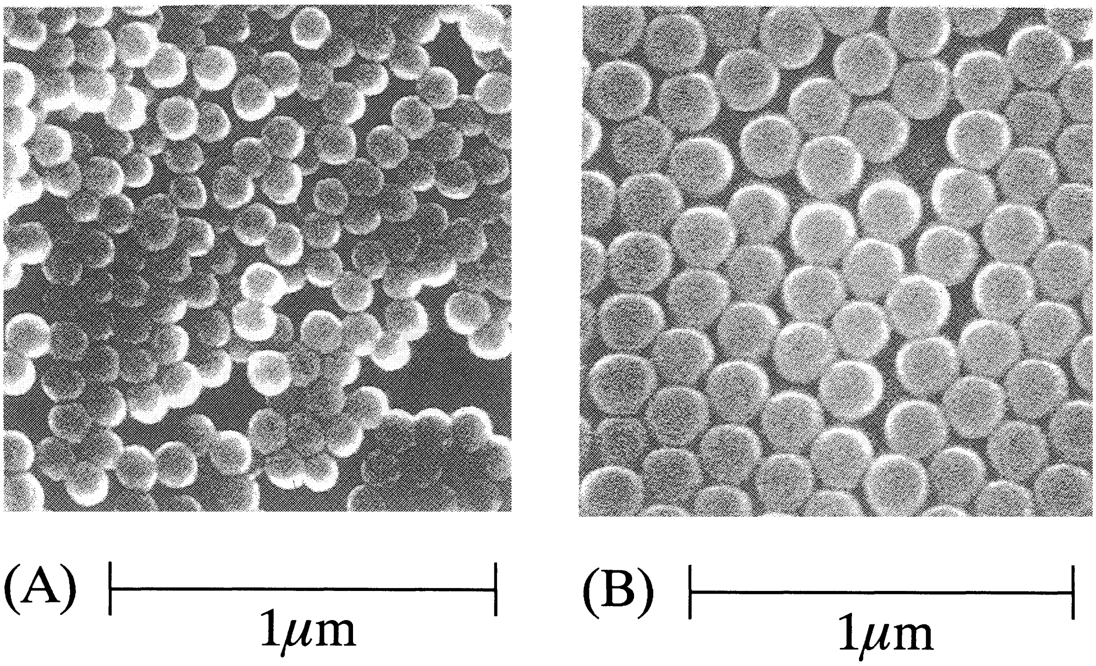

Fig. 1. SEM photographs of copolymer particles obtained by emulsion copolymerization of styrene with weight 5% of: (A) **1a**; (B) **1c**.

Table 2. Preparation of Polymer Particles by Emulsion Copolymerization of Styrene with Amphiphilic Macromonomer **1**

Entry	Preparation		Characterization					
	Macromonomer	Macromonomer concn/wt%	Yield %	Dn$^{a)}$ nm	Dw/Dn$^{a)}$	[Macromonomer]/[Styrene] (mol%)		
						Feed	Statistical$^{b)}$	Surface$^{c)}$
1	**1a**	3	59	120	1.01	0.23	0.41	—$^{d)}$
2	**1a**	5	44	110	1.02	0.38	0.46	2.2
3	**1b**	3	86	160	1.03	0.22	0.27	3.0
4	**1b**	5	79	140	1.02	0.39	0.51	3.6
5	**1c**	3	73	180	1.01	0.21	0.28	—$^{d)}$
6	**1c**	5	87	160	1.01	0.35	0.41	3.3

a) Determined by SEM. b) Determined by ^{1}H NMR. c) Determined by ESCA. d) Not determined.

(0.0375 g) and 0.03 g of 2,2′-azobis(2-propanecarboxyamidine) dihydrochloride were dissolved in 14.2 g of water under argon. The mixture was heated at 56 °C and the copolymerization started by the addition of 0.18 g of styrene. The same amount of styrene was added to the reaction mixture further 3 times at 0.5, 1.0, and 2.0 h. Then the mixture was kept out at 56 °C for 22 h. After separation of coagulum by filtration, the copolymer particles were isolated by centrifugation of the latex. Yield 0.42 g (51%).

Measurements. ^{1}H NMR spectra were recorded on a 250 MHz Bruker AC-250T spectrometer. The surface tension (γ) of the aqueous solutions of **1** was measured by a Shimadzu Du Noüy tensiometer at ambient temperature and the γ values obtained were recalculated to the value at 25 °C. Gel permeation chromatographic analysis was performed with a Toso SC 8010 apparatus with RI detector under following conditions: TSK gel G5000H6 column and chloroform eluent at a flow rate of 1.0 mL per min. The calibration curves for GPC analysis were obtained by using polystyrene standards. Scanning electron micrographic (SEM) analysis was carried out by a Hitachi H-8010 electron microscope. Surface analysis by electron spectroscopy for chemical analysis (ESCA) was carried out with a Shimadzu ESCA 750 apparatus. The measurement was made using Mg–K radiation at 5 kV. The spectra of N_{1s} and C_{1s} were recorded in the binding energy regions, 410—390 and 298—278 eV, respectively. Colloidal titration was performed by the addition of 1/400 N potassium poly(vinyl sulfate) solution to the latex using Toluidine Blue as indicator under argon.

Results and Discussion

By utilizing the living nature of 2-oxazoline (ROZO) polymerization and the quantitative termination of the living polyROZO with amine, block-type amphiphilic macromonomer **1** was synthesized.$^{9,10)}$ The hydrophilic and hydrophobic segments in **1** resulted from the polymerization of MeOZO and BuOZO, respectively. The composition of macromonomers **1a**—**d** used in this study are shown in Table 1.

Macromonomers **1a**—**c** were soluble in water. Macromonomer **1d** having no hydrophilic polymer segment was not soluble in water due to highly hydrophobic nature of **1d**. Surfactant property of **1** was evaluated by measuring the surface tension (γ) of **1** in water. The critical micelle concentration (cmc) of **1** was ca. 0.015 wt% and the γ value at cmc was less than 40 dyn cm^{-1} (Table 1) (1 dyn=10^{-5} N). A homopolymer-type macromonomer consisting only hydrophilic poly-MeOZO segment shows no cmc and its γ value in water is more than 60 dyn cm^{-1}.[11] These date indicate that the present macromonomers exhibit good surfactant properties. The hydrophilic-hydrophobic nature of macromonomers **1a**—**c** depends on the chain lengths (*m* and *n* values); macromonomer **1a** is the most hydrophilic and **1c** the least hydrophilic. The γ and cmc values of these macromonomers were almost the same despite the difference of the chain length of each segment. This may be due to the highly strong hydrophilic nature of the terminal ammonio group.

Emulsion copolymerization of styrene with macromonomer **1** was performed in water at 56 °C for 24 h using 2,2′-azobis(2-amidinopropane) dihydrochloride as a water-soluble initiator. The macromonomer acted as an emulsifier as well as a comonomer.

The polymer particles were analyzed by scanning electron microscope (SEM). Figure 1 shows SEM photographs of polymer particles obtained by using 5 wt% of **1a** (Fig. 1A) and **1c** (Fig. 1B). The resulting particles were relatively monodisperse in the submicron range.

In the range of styrene concentration from 3 to 10% on the total system, and of the macromonomer concentration from 1 to 10% on the total monomer, a stable emulsion was obtained. The copolymerization results are shown in Table 2. In all cases, polymer particles with narrow size distribution were obtained. The size of the resulting polymer particles is dependent upon the hydrophilic nature of the macromonomer as well as various polymerization conditions. When the same concentration of the macromonomer was used, the particle diameter increased with increasing the chain length of the hydrophobic poly(*N*-valerylethylenimine) segment, suggesting that the more hydrophilic the macromonomer examined in this study, the more efficient as an emulsifier. As the concentration of the macromonomer increased, the particle size decreased (Fig. 2). From these data, it was found that the particle size decreased as the content of the hydrophilic polymer chain in the copolymer particles increased, indicating that the more amount of the hydrophilic segment stabilizes the particles more efficiently to produce smaller particles.

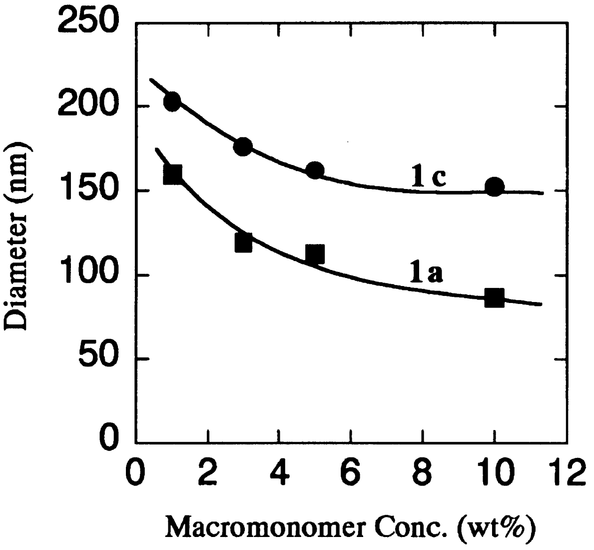

Fig. 2. Effect of macromonomer concentration on the particle size in the emulsion copolymerization using **1**.

The statistical composition of the copolymer particles were determined by ^{1}H NMR spectroscopy from the ratio of integrated values of methylene protons (δ=3.2—3.6) in the main chain of **1** and aromatic protons (δ=6.4—7.4) of polystyrene. The ratio of the macromonomer in the copolymer particles is slightly larger than the feed ratio. From gel permeation chromatographic (GPC) analysis, the copolymer particles did not contain unreacted macromonomer **1**. The molecular weight of the copolymer was determined by GPC as about 10^5.

Recently, we have synthesized amphiphilic poly-(2-oxazoline) macromonomer **2** having a hydroxyl group at the chain end and performed the emulsion copolymerization of styrene with **2** (Chart 2).[4] Macromonomers **1a** and **2** possess segments of almost the same chain lengths and their terminal groups were quaternary ammonio and hydroxyl groups, respectively. The cmc and γ at cmc values of macromonomer **2** are 0.045% and 36 dyn cm^{-1}, respectively. When the macromonomer concentration was 5 wt%, the diameter of the particles obtained by using **2** was 200 nm, which is larger than that by **1a** with the same concentration (Entry 2 in Table 2). These data indicate that macromonomer **1** was more efficient than **2** as an emulsifier.

In order to examine the surface composition of the particles, electron spectroscopy for chemical analysis (ESCA) was performed.[4,12] Generally, ESCA analysis gives information for a solid surface to a depth of

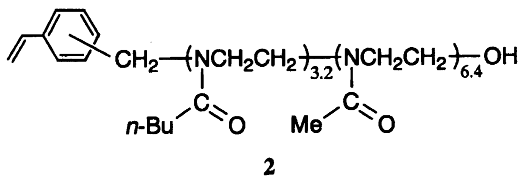

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Chart 2.

5—10 nm. As shown in Table 2, the ratio of the macromonomer by ESCA was much larger than the statistical ratio, indicating that PROZO chains and the quaternary ammonio group were locally present on the particle surface. The amount of cationic species on the surface of the particles (Entry 2) was determined by colloidal titration method as 8.4×10^{-4} mol g^{-1}.[13] This value represents all the cationic species derived from both macromonomer **1** and the initiator, and the value is much higher than that calculated from the statistical ratio (4.2×10^{-5} mol g^{-1}). Furthermore, the data on the surface composition obtained by the colloidal titration was different from that by ESCA analysis. This may be due to the difference of the depth measured from the surface and of the detected species, the total cationic species in the colloidal titration and the total nitrogen content in ESCA.

In conclusion, the emulsion copolymerization of styrene with amphiphilic poly(2-oxazoline) macromonomer **1** having quaternary ammonio group at the chain end gave monodisperse polymer particles in the submicron range. From ESCA analysis, poly(2-oxazoline) chains and the ammonio group were located on the surface. Applications of the present copolymer particles as functional polymers are now under progress in our laboratory.

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