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Emulsion Copolymerization of Styrene with Amphiphilic Poly(2-oxazoline) Macromonomer

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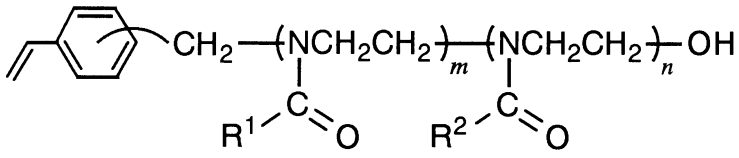
Emulsion copolymerization of styrene with a block-type amphiphilic poly(2-oxazoline) macromonomer having a polymerizable styryl group was performed. The macromonomer possessing the polymerizable group attached to the hydrophobic segment gave monodisperse polymer particles. On the other hand, the macromonomer having polymerizable group linked to the hydrophilic segment produced particles with broad size distribution.

Functionalization of polymer particles has been extensively studied because functionalized particles are widely used for various technical purposes. Among several methods 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; the surface charge density is readily controlled and the level of the resulting water-soluble polymers is low.[1,2] In some cases, the latex obtained by using a surface active monomer was more stable than that by regular emulsion polymerizations.[3]

2-Alkyl-2-oxazolines (ROZOs) are known to polymerize by a cationic (electrophilic) initiator to produce linear poly(N-acylethylenimine)s.[4,5] We found that the product polymers become hydrophilic or hydrophobic, depending upon the nature of the acyl group. Based on these findings, we have recently synthesized novel nonionic polymer surfactants from ROZOs by utilizing the living nature of the polymerization of ROZO.[4-6] For example, AB type block copolymers, in which A and B denote hydrophilic and hydrophobic chains, respectively, were prepared by a one-pot two-stage process.[6] These copolymers have both hydrophilic and hydrophobic segments in the same molecules, and hence, show good surfactant properties, as evaluated by the surface tension (γ) of the copolymer in water. Very recently, block-type amphiphilic polyROZO macromonomers with a styryl, (meth)acryl, or vinyl ester group have been synthesized.[7,8] These macromonomers constitute a new class of surface-active monomers. Furthermore, emulsion copolymerization of vinyl acetate with the amphiphilic macromonomer having a vinyl ester group has given monodisperse polymer latex in the sub-micron range.[8] The macromonomer acted as a polymeric surfactant, and as a comonomer as well. The present paper describes the emulsion copolymerization of styrene with block-type amphiphilic polyROZO macromonomer **1** having a polymerizable styryl group. The effect of the position of the polymerizable group on the resulting particles has been examined.

Block-type amphiphilic macromonomers **1a-1c** were synthesized by utilizing the living nature of ROZO polymerization;[6,7] a one-pot two-stage copolymerization technique using a mixture of (chloromethyl)styrene (a mixture of para and meta isomers in a ratio of 37% : 63%) and sodium iodide as an initiator was employed

for the synthesis of the macromonomer.[9] The hydrophilic segment comes from polymerization of 2-methyl-2-oxazoline (MeOZO). 2-*n*-Butyl- and 2-phenyl-2-oxazolines (BuOZO and PhOZO, respectively) were used for construction of the hydrophobic segment. Macromonomers **1a** and **1b** possess each segment of the almost same chain length, the position of the segments being reversed in **1a** and **1b**. **1c** has a hydrophobic poly(*N*-benzoylethylenimine) segment linked to the polymerizable group. Surfactant property of **1**, as evaluated by measuring the surface tension (γ) in water, was fairly good; the γ values of **1a**, **1b**, and **1c** of 0.5 weight % aqueous solution were 34, 38, and 44 dyns/cm, respectively.



1a: R^1=*n*-Bu, R^2=Me, *m*=3.2, *n*=6.4

1b: R^1=Me, R^2=*n*-Bu, *m*=5.8, *n*=3.2

1c: R^1=Ph, R^2=Me, *m*=3.1, *n*=5.6

Emulsion copolymerization of styrene with macromonomer **1** was carried out in water at 56 °C for 24 h using 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPD) as a water-soluble initiator. The macromonomer acted as an emulsifier as well as a comonomer.[10] The resulting particles were analyzed by scanning electron microscopy (SEM).

Figure 1(A) shows SEM photographs of polymer particles prepared by using **1a** in 5 weight % for the total monomers. The particles were monodisperse in the sub-micron range (*Dn* = 200 nm). Figure 2 shows the effect of the concentration of **1a** on the particle size. In all cases examined, relatively monodisperse polymer particles were obtained. The particle size decreased with increasing the concentration of **1a**. In case of the emulsion copolymerization using macromonomer **1b** in 5 weight % (Fig.1(B)), on the other hand, the resulting particle size was larger than that by **1a** and the size distribution was broader (diameter 150-700 nm).

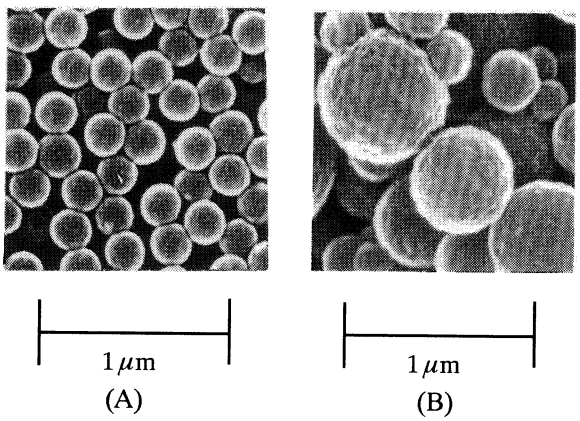


Fig. 1. SEM photographs of polymer particles by using macromonomer (A) **1a** and (B) **1b** (Macromonomer concn. = 5.0 wt % for monomers).

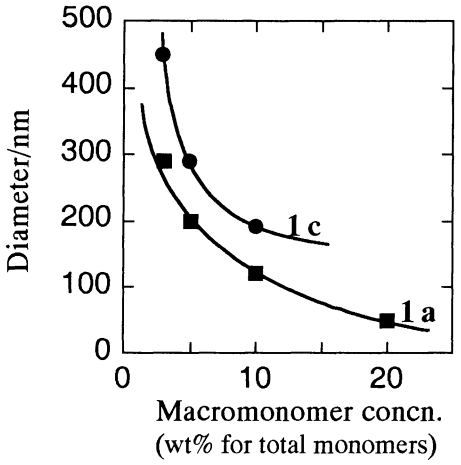


Fig. 2. Macromonomer concentration versus particle size.

These results indicate that the position of styryl group affected the present copolymerization. The reason may be explained as follows. In the micelle of amphiphilic macromonomer **1** before the copolymerization, styryl group of **1a** is inside the micelle as shown in Fig.3(A). Thus, the macromonomer is readily copolymerized with styrene inside the micelle to produce the copolymer particles covalently stabilized by the hydrophilic polyMeOZO chains. In case of macromonomer **1b**, on the other hand, the polymerizable group of the macromonomer is assumed to be located outside the micelle (Fig.3(B)), and hence, is hard to be copolymerized with styrene in the micelle, in the early stage of the copolymerization. Therefore, the weak stabilization by the physically adsorbed macromonomer causes coalescence between the particles to produce larger particles with broad size distribution.

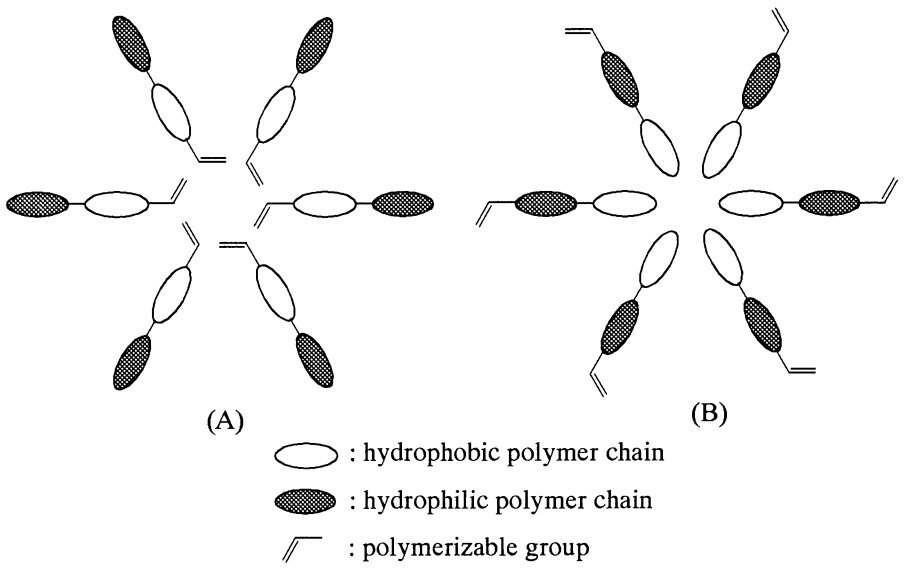


Fig.3. Schematic representations of macromonomer in the micelle : (A) macromonomer **1a**; (B) macromonomer **1b**.

The copolymerization with macromonomer **1c** also gave relatively monodisperse particles and the particle size decreased as the concentration increased (Fig.2). In the same concentration of **1a** and **1c**, the particle diameter obtained by **1a** was smaller than that by **1c**, indicating the less efficiency of **1c** than **1a** as an emulsifier.

Electron spectroscopy for chemical analysis (ESCA) analysis of the copolymer particles was carried out in order to examine the surface composition of the particles.[11] The molar ratio of repeating units of polyROZO and polystyrene was calculated by the peak areas of N_{1s} and C_{1s} in the ESCA spectrum. The sample used was prepared by using macromonomer **1a** in 5 weight % for the total monomers. The ratio determined by ESCA was 0.67, which is much higher than that calculated from the feed ratio ($[polyROZO]_0/[polystyrene]_0=0.045$) or from the statistical ratio ([polyROZO]/[polystyrene]=0.043) determined by ^1H NMR spectrum of the copolymer. These data indicate that polyROZO chains are very much enriched on the surface of the particles.

In conclusion, this study provides a clear-cut example exhibiting the effect of the position of the polymerizable group on the resulting polymer particles obtained in the emulsion copolymerization using

amphiphilic macromonomers. The macromonomer with the hydrophobic segment linked to the polymerizable group gave monodisperse polymer particles possessing polyROZO chains locally on the surface. PolyROZOs possess unique properties,[4,5] and hence, the present copolymer particles may find applications for various purposes as functional particles.

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9) Macromonomer **1a** was synthesized as follows. Under argon, a mixture of (chloromethyl)styrene, 0.90 g (6.0 mmol) of sodium iodide, and 1.93 g (15.2 mmol) of BuOZO in 30 mL of acetonitrile was heated at 80 °C for 3 h. After cooling to room temperature, 3.48 g (40.9 mmol) of MeOZO was added to the mixture. Then, the reaction mixture was kept at 80 °C for 7 h. The mixture was cooled to room temperature and 5.6 mL (5.6 mmol) of 1N NaOH-methanol solution was added to the mixture, followed by stirring for 4 h. The solvents were evaporated under reduced pressure, and the residue was extracted with chloroform. The separated organic layer was evaporated, and the residue was dried *in vacuo* to produce 4.06 g of **1a** (yield 68%).
10) A typical run was as follows. 0.0375 g of macromonomer **1a** and 0.03 g of AAPD were dissolved in 14.2 g of water under argon. The mixture was heated at 56 °C and the copolymerization was started by the addition of 0.18 g of styrene. The same amount of styrene was added to the reaction mixture as further 3 times, after 0.5, 1.0, and 2.0 h. Then, the mixture was kept at 56 °C for 22 h. After removal of coagulum from the latex by filtration, the separation of the copolymer particles using a centrifugation technique gave 0.37 g of the white polymer powder (yield 49%).
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