Preparation of “Confetti” Particles by Dispersion Copolymerization of Acrylonitrile/Styrene with Poly(ethylene glycol) Macromonomer

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The novel spherical particles on which nano-projections were uniformly distributed over the whole surface like “confetti” were prepared by dispersion copolymerization of acrylonitrile with styrene in ethanol/water mixed solvents in the presence of poly(ethylene glycol) (PEG) macromonomer. Transmission electron microscopy and laser light scattering studies showed particles with a narrow size-distribution. The diameter (ca. 150–1000nm) was controlled by changing the solvent composition and concentration of the PEG macromonomer.

In recent years, preparation and characterization of polymeric particles nano- and microscale in diameter have been widely studied. Since the polymeric particles have an extremely large specific surface area, these particles are useful not only in technological studies but also in biomedical fields.[1–5] The formation mechanism,[6] surface functionality[7,8] synthetic methods,[9–11] and morphology[12] of the polymeric particles have been studied. In morphological studies, Okubo et al. prepared hollow particles[13–16] and needle-like crystalline particles by chemical-oxidative dispersion polymerization of xylidine in an aqueous medium.[12]

In our previous work, we synthesized polymeric particles with various functional graft chains on their surface by dispersion copolymerization of functional macromonomers with styrene (St) [6–8,17] or methyl methacrylate (MMA)[18] in a polar solvent. The macromonomer method is very useful for size control and surface modification of the particle. However, no polymeric particles derived from acrylonitrile (AN) have been prepared using the macromonomer method. It is well known that PSt and PMMA are amorphous, while PAN is crystalline. This structural character of PAN is expected to create a unique particle morphology.

In this paper, we extend the macromonomer method to prepare PAN particles in a heterogeneous solution system and investigate the morphology of particles.

Radical copolymerization was carried out as follows. St and AN (Wako Pure Chemical Ind., Ltd.) were purified by distillation under reduced pressure, and 2,2'-azobis(isobutyronitrile) (AIBN; Wako Pure Chemical Ind., Ltd.), which is used as a radical initiator, was purified by recrystallization in ethanol and dried in vacuo before use. Poly(ethylene glycol) monomethacrylate (PEG macromonomer; number-average molecular weight $M_n = 1600$) gifted from Nippon Oil and Fats Co. was used as received.[17] A glass tube containing the solution of monomers and AIBN (1 mol% of total monomers) was sealed under pure nitrogen, and then placed in a water bath at 60 °C for 24 h. The resulting solution diluted with the pure water was centrifuged and the supernatant was extracted three times to remove unreacted chemicals. First, we attempted to perform dispersion copolymerization of AN with PEG macromonomers (1 mol% of AN) with different solvent compositions, monomer concentrations, and monomer compositions but transmission electron microscopy (TEM; Hitachi H-7010A) and laser light scattering (LLS; Colutter N4SD) studies did not show particle formation. This may be attributed to the fact that AN is less hydrophobic than St or MMA. In order to increase the hydrophobicity, a small amount of St (30 mol% of AN) was added into the reaction system. At this time, particle formation was confirmed with TEM and LLS studies. All of particles prepared here were almost quantitatively obtained (yields: 81–90%). Infrared spectroscopy (IR; JASCO FTIR610) confirmed that the particles were composed of AN, St, and PEG, and electron spectroscopy for chemical analysis (ESCA; Shimazu ESCA 1000) confirmed that PEG and AN were present on the surface of the particles. These particles completely dissolved in chloroform.

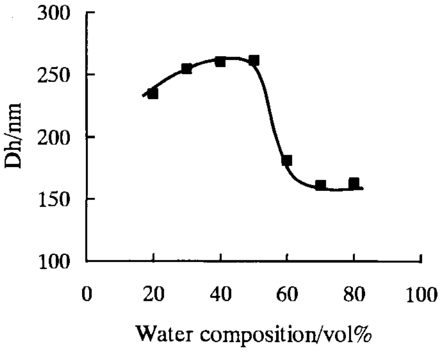

Figure 1. The effects of water composition in ethanol/water (5mL) on the Dh of particles prepared by dispersion copolymerization of AN(3mmol)/St(0.2mmol) with PEG macromonomer (1 mol% to AN and St).

Figure 1 shows the relationship between the hydrodynamic diameter (Dh) of the particles measured by LLS and the water composition in ethanol/water solvents. It was found that Dh increased with an increase in water composition from 20 vol% to 50 vol%. A similar result was obtained in the copolymerization system of the PEG macromonomer with St.[17] However, Dh showed a maximum value (261 nm) when the water composition was increased to 50 vol% and drastically dropped to 181 nm when the water composition was further increased to 60 vol%. Dh values of the particles remained fairly constant when the water composition was increased beyond 60 vol%. One possible reason for the drop in Dh may be a change in reaction system from dispersion polymerization to another polymerization system such as emulsion polymerization when the water composition exceeded 50 vol%.

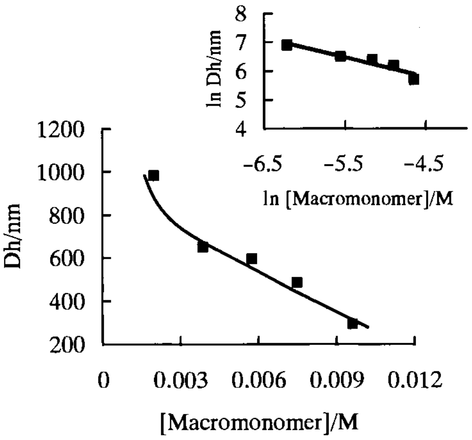

Figure 2. The effects of PEG macromonomer concentration on the Dh of particles prepared by dispersion copolymerization of AN(3mmol)/St(0.9mmol) with PEG macromonomer in ethanol/water (vol/vol = 4/1; 5mL).

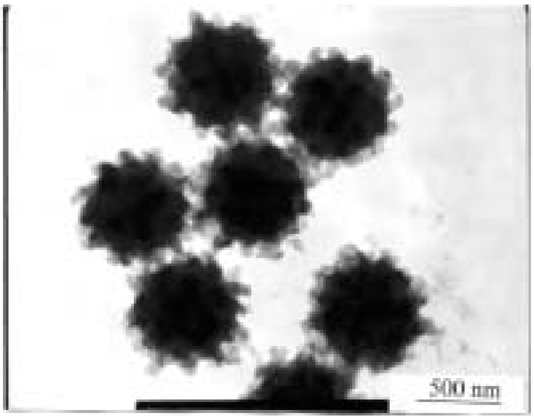

Figure 3. TEM images of particles prepared by dispersion copolymerization of AN(3 mmol)/St(0.9 mmol) with PEG macromonomer (0.7 mol% to AN and St) in ethanol/water (vol/vol = 4/1, 5mL).

The effects of the PEG macromonomer concentration on the Dh of the particles were investigated (Figure 2). The Dh decreased from 980 to 290 nm when the PEG macromonomer concentration increased from 0.002 to 0.010 M. In the system, the PEG macromonomer acts not only as a comonomer but also as a stabilizer of particle dispersion in water by attaching to the particle surfaces. At a higher concentration, the PEG macromonomer is more likely to be adsorbed onto the particle surface, which will increase the dispersion stability and allow smaller particles. As shown in the insert of Figure 2, the following scaling behavior was obtained: Dh = K [Macromonomer]$^{-0.68}$ where K is a constant. The actual value of the exponent (–0.68) was larger than the theoretical value (–0.5) and other results reported previously in dispersion copolymerization systems[18] such as PEG macromonomer with butyl methacrylate (–0.56)[19] or MMA (–0.10)[20]. This means that the Dh of PAN particles is very sensitive to changes in the macromonomer concentration.

The TEM image of a representative sample is shown in Figure 3 where one can clearly see spherical particles with a number of small projections on their surface like “confetti”. From Figure 3, the number-average diameter (Dn) of the particles prepared using PEG macromonomer is estimated to be ca. 810 nm, with the monodispersed size-distribution of particles. In addition, the projections are uniformly distributed over the whole surface at an interval of ca. 100 nm. LLS measurements showed that the Dh and coefficient of variation (CV) of the particles were 980 nm and 13%, respectively. The diameter, measured by TEM photography, is close to that estimated by the LLS study. All other samples prepared here also formed the spherical particles with the “confetti” morphology.

The structure of the freeze-dried particles was investigated by a wide-angle X-ray diffraction (WAXD) system (Rigaku Gygerflex 2013). The WAXD patterns of all of the particles showed a distinct diffraction peak at $2\theta = 22.6°$ (θ = diffraction angle) corresponding to a spacing of 0.39 nm and some small peaks in the 2θ range of 5–30°, indicating that the particles were crystallized. This crystalline structure may be related to the formation of the “confetti” morphology. The presence of many projections on the surface may lead to a dramatically enlarged specific surface area of the particles. The mechanism of formation of the “confetti” shape will require an understanding of the molecular structure.

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