Poly(styrene-co-acrylonitrile) Particles Prepared by Phase Inversion of W/O Emulsions

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Abstract: In this paper, we describe a particle preparation method that combines phase inversion of water in oil (W/O) emulsions with solidification of polymers dissolved in the emulsion droplets, induced by introducing a poor solvent, in order to prepare poly(styrene-co-acrylonitrile) (SAN) particles with a relatively narrow size distribution. W/O emulsions containing SAN are prepared by adding an aqueous solution of polyvinylalcohol (PVA) as a protective colloid into a methylethylketone (MEK) solution of SAN. Sufficient addition of the aqueous solution causes the precipitation of SAN particles from MEK followed by phase inversion from W/O emulsions to oil in water (O/W) emulsions. We also demonstrate that the use of sorbitan fatty acid esters as dispersion agents is effective for controlling size and polydispersity of SAN particles. They depend strongly on the concentrations and kinds of sorbitan fatty acid esters: a low concentration of sorbitan monolaurate resulted in an average particle size of 1.2 μm with a narrow size distribution.

Key words: phase inversion, poly(styrene-co-acrylonitrile), emulsion, particles, sorbitan fatty acid ester

1 INTRODUCTION

Polymer particles with diameters ranging from approximately tens of nanometers to hundreds of micrometers are very promising, having been used as basic materials in various applications such as cosmetic modifiers\textsuperscript{1, 2}, additives for toners\textsuperscript{3} and paint\textsuperscript{31}, diagnostic testing agents for medical treatment\textsuperscript{4}, drug delivery\textsuperscript{5, 6}, and chromatography column packing materials\textsuperscript{7, 8}. For these applications, controlling the particle size distribution is the essential issue, and thus, improvement of the preparation method has been the subject of much research. The typical preparation methods can be categorized into two types. One is a bottom-up process such as suspension polymerization\textsuperscript{9, 10}, emulsion polymerization\textsuperscript{11-14}, dispersion polymerization\textsuperscript{15}, and precipitation polymerization\textsuperscript{16}. The other is a top-down process including mechanical comminution\textsuperscript{17, 18} and emulsion separation methods\textsuperscript{19, 20}.

Emulsion polymerization methods using radical polymerization, which are the most conventional bottom-up preparation methods, require long preparation times. This method generally produces sub-micrometer spherical particles with a narrow size distribution, but it is difficult to obtain larger than micrometer-sized particles. In contrast, mechanical comminution methods, the most common top-down processes, mechanically crush frozen polymer pellets with ball mills or jet mills. This method is unable to control the particle shapes and size distributions, and thus, it produces particles with irregular shapes and a wide size range of several~tens micrometers. Further, besides the top-down and bottom-up methods, one can also obtain polymer particles by using their liquids or solutions. For example, polymer particles can be prepared by dropping polymer solutions or emulsions containing polymers prepared with a high-pressure homogenizer into a poor solvent that precipitates the corresponding polymer from the solution. However, in general it is difficult to control the size and its distribution, and it entails high-energy costs.

In this study, we prepared spherical polymer particles of poly(styrene-co-acrylonitrile) (SAN) with sub-micron sizes and narrow size distributions by a simple and low-energy method without special equipment. In order to prepare SAN particles, we exploited a combination of a phase inversion process of W/O emulsions with solidification of SAN emulsion droplets caused by introducing a poor solvent. W/O emulsions were produced by dropwise addition of a poor solvent, water containing polyvinylalcohol (PVA), as a protective colloid into a methylethylketone (MEK) solution of SAN. Sufficient addition of PVA solution induced the preparation of polymer particles with a narrow size distribution.
cipitation of SAN particles following phase inversion from W/O emulsions to O/W emulsions. We also examined the effects of the concentrations and species of sorbitan fatty acid esters, which are hydrophobic surface-active agents acting as emulsifiers, on the size and size distribution of SAN particles.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Poly(styrene-co-acrylonitrile) (SAN, 25 wt% acrylonitrile, Mw = 165,000; Sigma-Aldrich Co.) was used for the preparation of polymer particles. Copoly(vinyl alcohol-vinyl acetate) (PVA, Kuraray Co. Ltd.) was used as the protective colloid for SAN particles. The degree of polymerization and the hydrolysis of PVA were 500 and 86.5–89.0 mol%, respectively. Methyl ethyl ketone (MEK; Wako Pure Chemical Industries, Ltd.) was used as received as the solvent for SAN. Hydrophobic surface-active agents of sorbitan fatty acid esters (SCn: Kao Co.)—sorbitan monolaurate (SC12), sorbitan monopalmitate (SC16), sorbitan monostearate (SC18), sorbitan distearate (SC218), and sorbitan tristearate (SC318)—were used as emulsifiers for water-in-oil (W/O) emulsions. Oil-soluble dye of C. I. Solvent Red 8 (Orient Chemical Industries Co., Ltd.) was used for staining the oil phase to observe optical microscopy images of emulsions. The dye was composed of four kinds of substances: N,N-di-methylformamide (0.3%), ethoxylated cocoalkylamine (~24%), C. I. Solvent Red 8 (~76%), and a chromium(III) compound (5.3% as Cr). Ion-exchanged water was used in all experiments, and all chemicals were used without further purification.

2.2 Formation of emulsions and solidified SAN particles

A 5.0 wt% SAN stock solution in MEK containing SCn and a 5.0 wt% PVA aqueous solution were used for oil and water phases, respectively. The dissolution of SAN into MEK was performed by ultrasonication with CPX2800H-J sonicator (Branson Ultrasonics Co.). MEK/water emulsions containing SAN and PVA were prepared according to the protocol shown in Fig. 1. The 5.0 wt% PVA aqueous solution (1 mL) was added into 5.0 g MEK solution of SAN, and the resultant mixture was then vigorously stirred for 1–3 min. The procedure for adding the water phase was successively repeated 12 times to obtain emulsions consisting of SAN droplets. For steps 1–4 and 9–12, mixing was for 1–3 min, while the mixing was 5–10 min long for steps 4–8, because of the phase inversion region. This longer mixing time resulted in the formation of stable emulsions. Additional 3 mL water was then added into the mixture four times with a 1–3 min of mixing time for each addition. Phase inversion of the emulsion occurred when the total water volume, which had been added in a stepwise manner, reached the same volume as that of the oil phase.

The mixing was performed using a Mighty Stirrer M-16GX6 (Koike Precision Instruments) or NZ-1100 (Tokyo Rikakikai Co., Ltd.) stirring at 600–1200 rpm.

The SAN particles were collected by centrifugal separation at 3000 rpm for 5 min, after adding the same volume of ethanol (30 mL) into the as-prepared SAN particle dispersion. The collected SAN particles were washed with ethanol three times.

2.3 Measurements

The size and shape of the emulsion droplets were examined with an optical microscope (VHX-2000, Keyence Co.). Solidified SAN particles prepared from the corresponding emulsions were separated by centrifugation, and the particles were then observed with a scanning electron microscope (S-3400N, Hitachi Ltd.). The mean particle size and the particle size distribution of the emulsions and the solidified SAN particles were measured by dynamic light scattering (DLS) using Microtrac 9320-X100 (Nikkiso Co., Ltd.). The electrical conductivities of the emulsions as a function of water content were measured using a
SAN particles prepared by phase inversion

J. Oleo Sci.

desktop water quality analyzer, Laqua Cond Meter DS-72 (Horiba Ltd.) and 3552-10D (Horiba Ltd.) as electrode with platinum black electrode plate, to confirm the phase inversion of the solutions.

3 RESULTS AND DISCUSSION

3.1 Formation and phase inversion of emulsions

In general, the addition of emulsifiers, which lower the interfacial tension, is useful for stabilizing the emulsions. This is called the agent-in-oil method\(^{24,25}\). Hydrophobic surface-active agents having low hydrophilic-lipophilic balance (HLB) were added into the oil phase to decrease the interfacial tension. In this work, sorbitan fatty acid esters such as SC12 were used as the emulsifier. The stability of the emulsions depended on the amount of aqueous solution of PVA, as well as the emulsifier type and concentration, because the thermodynamic destabilization of the emulsions should be accelerated by increasing the surface free energy due to the increase in the interfacial areas\(^{26-28}\).

The effects of the amount of aqueous phase and the concentration of the emulsifiers on the stability of the emulsions were then investigated. Figure 2 shows the optical microscopy images of the resultant emulsions stabilized by a hydrophobic surface-active agent of SC12, and the concentration of surfactants and the volumes of water and oil used for preparation of emulsions were summarized in Table 1. The addition of the aqueous solution of PVA into MEK solutions of SAN caused the formation of emulsion droplets, and the droplets had a multiple structure at high concentrations of water and SC12. Interestingly, phase in-

Fig. 2 Optical micrograph of emulsion droplets. a: SC12 = 0%, PVA = 4 mL; b: SC12 = 0%, PVA = 8 mL; c: SC12 = 0%, PVA = 12 mL; d: SC12 = 0.5%, PVA = 4 mL; e: SC12 = 0.5%, PVA = 8 mL; f: SC12 = 0.5%, PVA = 12 mL; g: SC12 = 1.0%, PVA = 4 mL; h: SC12 = 1.0%, PVA = 8 mL; i: SC12 = 1.0%, PVA = 12 mL; j: SC12 = 3.0%, PVA = 4 mL; k: SC12 = 3.0%, PVA = 8 mL; l: SC12 = 3.0% PVA = 12 mL.
version occurs without SC12 and the amount of water required for phase inversion is independent of SC12 concentration. This result suggests that the phase inversion is induced mainly by PVA dissolved in water. This conclusion is consistent with the fact that the use of pure water without PVA did not induce phase inversion at all. This indicates that PVA plays the role of a protective colloid but not of an emulsifier.

Investigating the effect of SC12 on the emulsion droplets, we found that their sizes depended strongly on the SC12 concentration, as shown by the microscopy images obtained when the water content was 12 mL (Fig. 2). The particle size at [SC12] = 0.5 wt% was as small as 1.2 μm. High surfactant concentrations resulted in the formation of multiple emulsions with a larger size. Therefore, the key role of SC12 as a hydrophobic surface-active agent is to stabilize the emulsion droplets.

In this study, we have no evidence whether the emulsion droplets correspond to the O/W type or W/O type. In general, emulsions formed at high water contents should be O/W type, and vice versa. In this study, emulsion droplets were present at both low and high water contents, as shown in Fig. 2, suggesting that the phase inversion from W/O emulsions to O/W emulsions likely occurs with increasing water content. The conductivity of the emulsions was then measured as a function of the water content to confirm the phase inversion. As shown in Fig. 3, the conductivity increased rapidly when the added water content was approximately 4 mL. The rapid increase is thought to be the result of phase inversion from a W/O emulsion to an O/W emulsion. More direct evidence of the phase inversion was obtained by the optical observation of emulsion droplets using microscopy. The oil phase was stained using an oil-soluble dye of VFR. Figure 4 shows the resultant images of the emulsions stabilized with SC12 at various SC12 and water contents. For systems with lower water content, many colorless droplets dispersed in a reddish continuous phase were observed, indicating the formation of W/O emulsions, while the opposite colored emulsions, i.e., reddish droplets dispersed in a colorless continuous phase, were observed in higher water content systems. Accordingly, the microscopic images of stained emulsions clearly demonstrate the phase inversion from W/O emulsions to O/W emulsions.

Interestingly, there was a dark ring on the rim of each droplet without SC12 and at a low concentration of SC12 (Figs. 4b, f, and h). This means that the hydrophobic VFR dye is concentrated at the rim of the emulsions. Since MEK

| No | SAN / wt% | Oil phase / 5.0 g | SC12 / wt% | MEK / wt% | Water phase / 5 wt% PVA solution / mL |
|----|-----------|------------------|------------|-----------|-------------------------------------|
| a  | 1.0       | 0.0              | 0.0        | 99.0      | 4                                   |
| b  | 1.0       | 0.0              | 0.0        | 99.0      | 8                                   |
| c  | 1.0       | 0.0              | 0.5        | 98.5      | 4                                   |
| d  | 1.0       | 0.0              | 0.5        | 98.5      | 8                                   |
| e  | 1.0       | 0.5              | 0.5        | 98.0      | 4                                   |
| f  | 1.0       | 0.5              | 0.5        | 98.0      | 8                                   |
| g  | 1.0       | 1.0              | 0.5        | 98.0      | 4                                   |
| h  | 1.0       | 1.0              | 1.0        | 98.0      | 8                                   |
| i  | 1.0       | 3.0              | 3.0        | 96.0      | 4                                   |
| j  | 1.0       | 3.0              | 3.0        | 96.0      | 8                                   |
| k  | 1.0       | 3.0              | 3.0        | 96.0      | 12                                  |
| l  | 1.0       | 3.0              | 3.0        | 96.0      | 12                                  |

Fig. 3 Effect of the amount of added water phase on the emulsion conductivity for various concentrations of SC12.
is soluble in water, subsequent addition of water causes MEK to exude from the surface of the emulsion droplets, which causes shrinkage of the droplets. During this process, hydrophobic SAN and VFR dye remain inside the droplets and accordingly are condensed near the rim. In contrast, dark rings were formed in the middle of the droplets, instead of on the rim, for a high SC12 concentration (3.0; Fig. 4l). Although the reason for the formation of the ring in the middle of the droplets is unclear, a possible explanation is that a protective layer consisting of SC12 and PVA formed near the rim, which causes a slow exudation of MEK from the droplet to the bulk water phase. Therefore, the layer between the dark reddish thin film and the rim of the droplet is thought to be a mixed phase of MEK and water.

3.2 Solidification of SAN particles

MEK can be soluble in water but the solubility is not very high. Therefore, the addition of 12 mL water phase was not enough to remove MEK completely from the O/W emulsions of SAN. Sufficient water phase was then added to obtain solidified SAN particles by removing water-soluble MEK completely. Solidified SAN particles dispersed in water were then isolated by centrifugation. The isolated SAN particles were washed with ethanol four times. The average yields of SAN particles were evaluated to be ~70% by weighting dried SAN particles, which were collected by centrifugal separation.

Figures 5 and 6 show representative SEM images of the solidified SAN particles, and the size distribution obtained from DLS measurements of the solidified SAN particles re-dispersed in water, respectively. The resultant SAN parti-
cles prepared without SC12 have a bimodal size distribution at 1.2 μm and 4.2 μm, and a large proportion of the particles have a particle size of 4.2 μm. The addition of 0.5 wt% SC12 greatly inhibited the formation of the larger particles and increased the proportion of the smaller, 1.2 μm, particles. Consequently, the resultant SAN particles have a unimodal size distribution. On the other hand, increasing the concentration of SC12 increases the particle size and the size distribution shifts to a larger size. The concentration dependence of the size is consistent with the results of the O/W emulsion size shown in Fig. 2. Thus, the size and distribution of the emulsion droplets at higher SC12 concentration become larger due to the formation of multiple emulsions, as shown in Fig. 2, indicating that the size of the solidified particles depends on the original O/W emulsion size. We can therefore control the size of solidified polymer particles by that of the O/W emulsions.

3.3 Effect of surfactant type on SAN particles

We demonstrated the effect of the SC12 concentration on the formation and stabilization of emulsions in sections 3.1 and 3.2. In this section, we examine the effect of the alkyl chain length and esterification degree of sorbitan esters on the formation of emulsions. O/W emulsions of SAN were prepared using sorbitan monopalmitate (SC16), sorbitan monostearate (SC18), sorbitan distearate (S2C18), and sorbitan tristearate (S3C18) instead of SC12, as the hydrophobic surface-active agents. It is found that increases in the alkyl chain length and esterification degree, i.e., increases in the hydrophobicity, cause a significant increase

Fig. 5 SEM images of SAN particles.

Fig. 6 Size distribution of SAN particles at different SC12 concentrations.
SAN particles prepared by phase inversion

J. Oleo Sci.

in the emulsion size. Further, the use of highly hydrophobic sorbitan esters causes coalescence of O/W emulsions. Here, we note that the water content required for the phase inversion was independent of the types of sorbitan esters, because the conductivity changes of the emulsions stabilized by SC12, SC16, SC18, S2C18, and S3C18 showed a quite similar manner, as shown in Figs. 3 and 7.

Figures 6 and 8 show the size distributions of solidified SAN particles prepared with each sorbitan ester. As shown in section 3.2, the size of SAN particles prepared with no sorbitan esters had a bimodal distribution. The addition of 0.5 wt% sorbitan esters, except for S3C18, decreased the formation of larger particles, and in particular, the use of SC12 had a marked effect. In addition, the increase in the sorbitan ester concentration caused an increase in the proportion of larger particles or a shift of the size distributions toward a larger size. The shifts were increased by increasing the hydrophobicity of sorbitan esters. Accordingly, SC12 is suitable for the formation of monodisperse SAN particles.

The addition of SC12 hinders the coalescence of W/O emulsion droplets after phase inversion, because PVA-protective W/O emulsion droplets have a high hydrophilicity. On the other hand, for high SC12 concentration, adsorption of SC12 on the O/W emulsions with a sufficiently high concentration stabilizes the O/W emulsions. Thus, the high O/W emulsion stability prevents the phase inversion from O/W emulsions to W/O emulsions. This is in good agreement with the results of the conductivity measurements shown in Fig. 3. The conductivity profiles at a low concentration of 0.5% showed a sharp phase inversion at a water content of ~16 mL, similar to the result obtained in the absence of SC12, while the profiles at higher concentrations showed a gradual phase transition, indicating that the presence of excess SC12 suppresses the phase transition. Similar phenomena were observed in highly hydrophobic surfactant systems, as shown in Fig. 8. The gradual phase inversion is also the reason for the polydispersity of SAN.

4 CONCLUSION

In this study, we demonstrated that SAN particles with a relatively narrow size distribution can be prepared simply by adding an aqueous solution of PVA as a protective colloid into an MEK solution of SAN containing hydrophobic surface-active agents of sorbitan fatty acid esters. The aqueous solution was used for the precipitation of SAN from MEK followed by the phase inversion from a W/O emulsion to an O/W emulsion. Optical microscopic observations of stained emulsions and conductivity measurements were good monitors for the phase inversion, and revealed the role of phase inversion on the properties of the resultant SAN particles. The size and polydisperisty of SAN par-
particles depend strongly on the concentrations and species of sorbitan fatty acid esters. The use of a low concentration of SC12 resulted in the average particle size of 1.2 μm with a narrow size distribution, while increases in the concentration or hydrophobicity of sorbitan fatty acid esters caused the bimodal size distributions due to the formation of larger particles.

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SAN particles prepared by phase inversion

J. Oleo Sci.

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