

Studies on the Characterization of Phase Inversion during Emulsification Process and the Particle Sizes of Water-Borne Microemulsion of Poly(phenylene oxide) Ionomer

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ABSTRACT: In this article, the lightly sulfonated poly(phenylene oxide) (SPPO) ionomers in a series of mixing solvents were emulsified by water to form a series of water-borne microemulsions. The phase inversion during the emulsification process of SPPO ionomer solutions was characterized by measuring the variation of conductivity, viscosity, and surface tension with the addition of water. The effects of properties of solvent systems on the phase inversion procedure, the particle size of emulsions with different solvent systems, and ionic contents of the polymer chain were discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 690–694, 2000

Key words: water-borne emulsion; sulfonated poly(phenylene oxide); phase inversion; emulsification; particle size

INTRODUCTION

Considerable efforts have been dedicated to the studies involving using water to replace organic solvents to reduce air pollution in the coating industry. Water-borne polymer microemulsion is a polymer as microscale (0.01–0.2 μm) particles dispersed in a continuous aqueous medium. It can be prepared from amphiphilic polymer to form a self-emulsification system. This self-emulsification polymer is normally made by incorporating ionic groups or hydrophilic chain segments into the hydrophobic polymer backbone. An ionomer is one of these amphiphilic polymers that consists of macromolecules with a few mol percent ionic groups attached to the hydrophobic backbone.

Most of previous studies on ionomers were concentrated to their bulk properties and rheological properties. Up to now less attention has been paid to ionomers in aqueous solution because they are normally insoluble in water. Recently, Eisenberg et al.¹ prepared a block copolymer with long non-ionic blocks and short ionic blocks, which can form crew-cut micromicells in aqueous medium. Jiang and Wu et al.² reported that a lightly carboxylated SEBS copolymer and a randomly carboxylated polystyrene ionomer can form stable aggregations in water by a special procedure. B. K. Kim studied the water-borne microemulsion of polyurethane ionomer.^{3–6} In our research group, the sulfonated polystyrene ionomer was emulsified to water-borne microemulsion through a phase-inversion procedure.⁷ However, all the above investigations are concentrated on the ionomers with a flexible main chain. In this article, the emulsificability of partial crystalline polymer–sulfonated poly(phenylene oxide) ionomer (SPPO) was studied.

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EXPERIMENTAL

Materials

Poly(phenylene oxide) (PPO) is produced by Beijing Institute of Chemistry Engineering ($M_n = 60,000\text{--}70,000$). It was purified by dissolving it in a hot mixture of tetrahydrofuran (THF) and toluene (90/10, V/V), and water was used as the precipitating agent after filtering; then the precipitate was immersed in methanol and scrubbed by methanol to remove the residual solvent and water in the sample. Finally, the products were dried under vacuum at 65°C for 24 h.

Sulfonated Reaction and Determination of Sulfonated Level

PPO was sulfonated according to the method of Dong-Tsa,⁸ and the sulphonating agent was prepared by adding concentrated sulphuric acid to acetic anhydride. Sulfonated levels were determined by acid-base titration.

Conductivity Measurements

Using a conductometer (model DDS-11A, manufactured by Shanghai Electric Factory, China) to measure the conductivity of the system at 25°C.

Viscosity Measurements

The characteristics of viscosity during the emulsification process were obtained on a RHEOTEST 2.1 rotary cylinder viscometer. The shearing rate was 1312S^{-1} ; test temperature was 25°C.

Surface Tension Measurements

A model JZHY-180 boundary tension meter (products of testing machine factory of Chengde, China) was used to obtain the characteristics of surface tension at 25°C. Particle size and size distribution were measured by a laser light-scattering-type particle size analyzer, a MALVERN Multi-8 Autosizer (UK).

RESULTS AND DISCUSSION

Description of Emulsification Process

The sulfonated PPO (SPPO) with different sulfonated contents were dissolved in proper mixing solvents (e.g., dimethyl sulfoxide (DMSO)/trichloromethane; dimethyl sulfoxide/acetone), to form 2

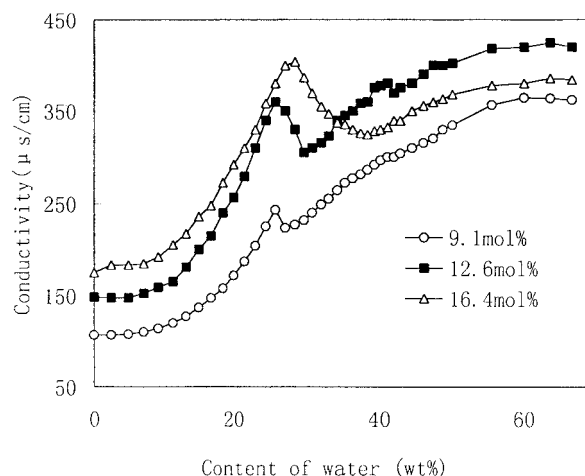


Figure 1 The variation of conductivity of the H^+ -SPPO ionomer in the DMSO/ CHCl_3 (8/2, V/V) mixed solvent during the emulsification process at 25°C.

wt % concentration of SPPO ionomer solutions. Then emulsification was carried out by adding deionized water with constant agitation at room temperature to the ionomer solution. During the addition of water, the conductivity and viscosity of the solution were measured. When the conductivity of emulsion reached a constant level, phase inversion was considered to be complete, and a stable oil-in-water (O/W) emulsion was obtained.

The Variation of Conductivity

There are several structure models for elucidating the association behavior in ionomer solution, such as the microionic lattice model,⁹ the isotropic model,¹⁰ and the two-state structure model.¹¹ Many experimental evidences obtained by SAXS and SANS^{12,13} indicate the coexistence of order and disorder microionic aggregation regions in ionomer solution.

The conductivity varied with the progress of emulsification procedure for the SPPO with different ionic contents in DMSO/ CHCl_3 (8/2, v/v) solutions were shown in Figures 1–2.

Except for the initial stage of conductivity curve in Figure 2, where a sodium hydroxide solution were added to neutralize the sulfonated groups stoichiometrically, the conductivity vs. water contents curves for both the nonneutralized and neutralized SPPO ionomer solutions display about the same characters. That is, the conductivity increased to a maximum value, then it somewhat decreased, then increased again, and then to a constant value. This variation of con-

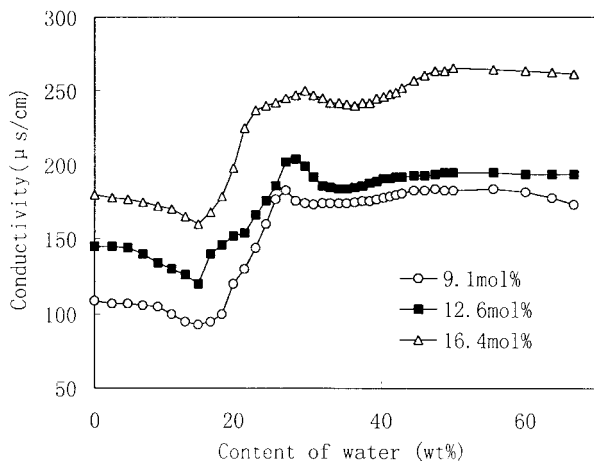


Figure 2 The variation of conductivity of the Na^+ -SPPO ionomer in the $\text{DMSO}/\text{CHCl}_3$ (8/2, V/V) mixed solvent at 25°C during the emulsification process.

ductivity of SPPO ionomer solution may be responsible for the following procedure. The ionic aggregation regions dissociated by adding water; at the same time, some sulfonated groups were unavoidably wrapped into the hydrophobic chain coils because of the hydrophobic main-chain contracting and aggregating by adding water. This led to the conductivity of somewhat of a decrease. With water being continually added to a certain content, the phase inversion procedure was achieved. The hydrophobic main chains further aggregated to form particles, and the ionic groups were moved to the particle surface. This caused the conductivity to increase slowly and then reached constant values. It is obvious that the width of the conductivity peak in the conductivity curves increased with the increase of ionic contents in the polymer chains. These imply that the higher the ionic contents in the polymer chains, the more water was required for completing the phase inversion process. Moreover, the composition of solvent mixture of $\text{DMSO}/\text{CHCl}_3$ also affected the phase inversion process, which were shown in Figures 3 and 4. The lower the polarity, the less water contents were required to initiate the phase-inversion process. Here, the maximum conductivity in the conductivity curves was assigned to indicate the initiation of the phase-inversion process.

Comparing the conductivity curves of nonneutralized (Fig. 1) and neutralized SPPO (Fig. 2), one can find that the conductivity of the first system is greater than that of the second system. This indicated that the ionic migration rate of the

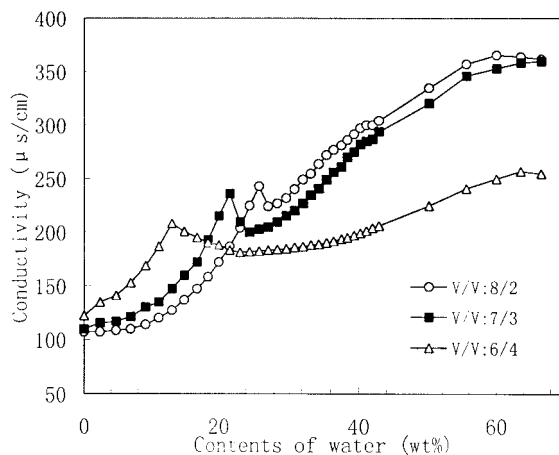


Figure 3 The variation of conductivity of the H^+ -SPPO ionomer in the $\text{DMSO}/\text{CHCl}_3$ (8/2, 7/3 or 6/4, V/V) mixed solvent during the emulsification process; ionic content was 9.1 mol %. Test temperature: 25°C .

Na^+SO_3^- groups was lower than that of the H^+SO_3^- groups. The data are listed in Table I.

The Variation of Viscosity

In a general view, there are some ionic aggregation regions in the ionomer solution that consist of disorder and order ionic aggregations, especially for the middle concentration of the nonpolar solvent systems. The variation of viscosity during the emulsification process will be a comprehensive evidences of hydrophobic segmental aggregation that lead to the viscosity increase, and the dissociation of disorder and order ionic aggrega-

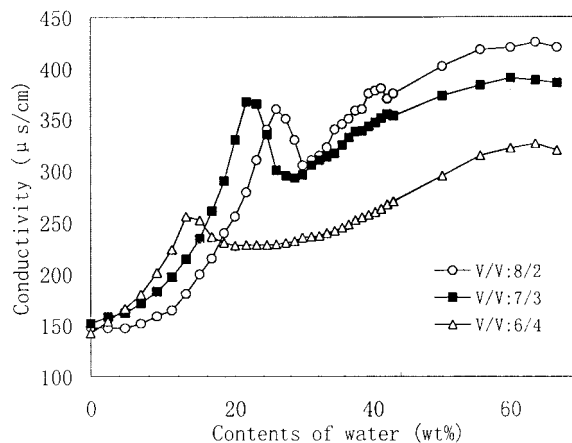


Figure 4 The variation of conductivity of the H^+ -SPPO ionomer in the $\text{DMSO}/\text{CHCl}_3$ (8/2, 7/3 or 6/4, V/V) mixed solvent during the emulsification process; ionic content was 12.6 mol %. Test temperature: 25°C .

Table I The Maximum Conductivity of H⁺-SPPO and Na⁺-SPPO Neutralized by Sodium Hydroxide^a

Ionic Contents (mol %)	Maximum Conductivity of H ⁺ -SPPO Solution ($\mu\text{s}/\text{cm}$)	Maximum Conductivity of Na ⁺ -SPPO Solution ($\mu\text{s}/\text{cm}$)
9.1	365	183
12.6	425	207
16.4	404	266

^a Test temperature: 25°C; in mixing solvents of DMSO/trichloromethane : 8/2 (v/v).

tion regions, which lead to the decrease of viscosity. Figure 5 shows the variation of solutions viscosity of SPPO with different ionic contents during the emulsification process. For a low sulfonated level, such as SPPO with 9.1 mol % of sulfonated groups, once the water was added, the viscosity of the solution increase abruptly, then reach to a constant value, where the water contents was about 23 wt %. After that, the viscosity increased to a maximum with the addition of water, then decreased monotonically with the increase of the water content. However, for relatively high sulfonated content sample, the viscosity decreased at the beginning stage of adding the water. This difference between the samples with lower and higher ionic contents may be considered because the disorder ionic aggregation and order ionic aggregation regions coexisted in the higher ionic contents of the ionomer solutions, while for a low ionic content system only order ionic aggregation regions existed. As the water was dropped into the high ionic content solution, it entered into the disorder ionic regions and

caused the dissociation, so the viscosity decreased at the first emulsifying stage, while for low ionic content system, the dropping water first contacted with the hydrophobic segments and caused the hydrophobic aggregation, which corresponded to the viscosity increase at the initial emulsifying stage. The viscosity plateaus in the second emulsifying stage on all the viscosity curves indicated a phase-inversion process, and it may be considered as a balance of effects of dissociation of order ionic domains, leading to a decrease viscosity and the aggregation of hydrophobic chains leading to an increase viscosity. When the phase inversion was achieved, the system changed from water in oil (W/O) to oil in water (O/W). The polymer particles were dispersed in the water medium, so that the viscosity of the emulsion systems decreased while the water content further increase.

In comparing the viscosity vs. water content curves during the emulsification process for the SPPO ionomer solution and the SPS ionomer solution,⁷ the viscosity of the SPS system monotonously with the addition of water until the phase inversion-procedure was completed. This implies that the effect of the hydrophobic chain aggregations in SPS was more significant than that of in the SPPO system because of more flexible main chains of the SPS ionomer, where the hydrophobic segments aggregation was predominant over the microionic aggregated dissociated domain.

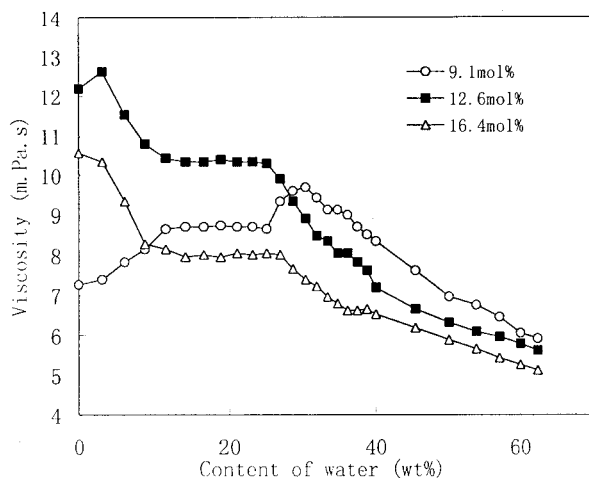


Figure 5 The variation of viscosity of the H⁺-SPPO ionomer in the DMSO/CHCl₃ (8/2, V/V) mixed solvent during the emulsification process at 25°C.

The Variation of Surface Tension

Figure 6 shows the variation of surface tension of SPPO ionomers solutions during the emulsification process. At the initial period of the addition process, water was dispersed as little drops, and was enclosed by organic solvents, so the surface tension showed the characteristic of the organic solvents and changed little. As more of the water content increased, phase inversion occurred and the water became a continuous phase. The surface tension of the system increased rapidly upon further addition of the water because the surface

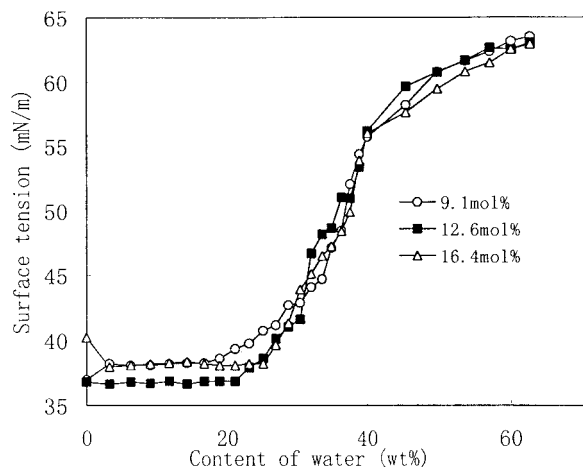


Figure 6 The variation of surface tension of the H^+ -SPPO ionomer in the DMSO/ $CHCl_3$ (8/2, V/V) mixed solvent during the emulsification process at 25°C.

tension of the water was larger than that of the organic solvents. At the last stage, the surface tension of the system reached a constant.

Particle Size and Stability of Emulsion

Figure 7 shows the size distribution of the water-borne emulsion of the SPPO ionomer. Table II shows the effect of the polarity of solvents on the particle size and stability of emulsions. In the solvent system with higher polarity (DMSO/ $CHCl_3$: 8/2, v/v), the ion-containing segments of

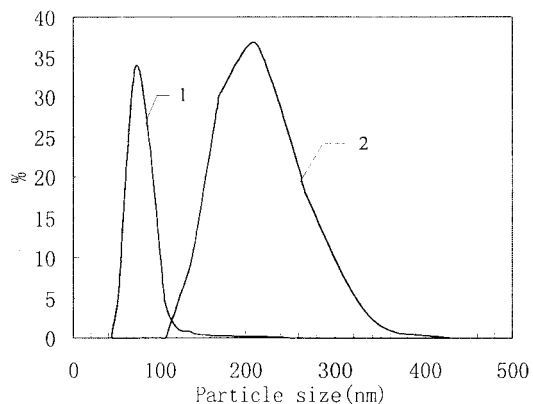


Figure 7 The particle size and size distribution of water-borne emulsion of H^+ -SPPO ionomer; ionic content: 16.4 mol %, mixing solvents were 1: DMSO/ $CHCl_3$ (8/2, V/V) 2: DMSO/ $CHCl_3$ (7/3, V/V).

Table II Effect of the Polarity of Solvents on the Particle Size and Stability of Emulsion^a

DMSO/ $CHCl_3$ (V/V)	Particle Sizes (nm)	Stability (month)
9/1	44,000	0.03
8/2	110.5	5
7/3	479.6	2
6/4	> 10,000	Precipitation

^a Ionic contents: 16.4 mol %; test temperature was 25°C.

the SPPO appeared more evenly distributed, compared to the SPPO in the DMSO/ $CHCl_3$: 6/4 (v/v) system, where the ionic groups were aggregated and probably embedded in hydrophobic segments. Therefore, particle sizes of emulsion in the lower polarity system were larger than that of the higher polarity system. Table II also shows that the smaller the particle sizes, the more stable the emulsion will be.

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