

# Polystyrene Ionomer Aqueous Dispersion. I. Process and Mechanism of the Phase Inversion of Emulsification

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**ABSTRACT:** Aqueous dispersions of lightly sulfonated polystyrene (SPS) that was neutralized by ammonia liquor were prepared. The variations of the conductivity and viscosity of SPS ionomer solution during the emulsification process and the effect of ionic contents on the phase inversion in the emulsification process were studied. The turning points in conductivity curve and the maximum viscosity were considered as the characters of phase inversion in the process of emulsification. The mechanism of phase inversion was inferred. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1671–1675, 1998

**Key words:** aqueous dispersions; sulfonated polystyrene; emulsification; phase inversion

## INTRODUCTION

An aqueous polymer dispersion is a binary colloidal system in which particles of polymer are dispersed in a continuous aqueous phase. Hydrocarbon polymer are incompatible with water. Therefore, a special treatment and/or structural modification is necessary for the polymer to be dispersible in water. This is normally done by incorporating ionic groups into the polymer backbone,<sup>1</sup> and this special type of polymer is called an ionomer.

The ionomers are hydrophilic in nature<sup>2</sup> and, hence, dispersible in aqueous medium. For the presence of ionic groups, the cast film of the ionomers exhibits special physical properties due mainly to the existence of Coulombic forces between the ionic centers,<sup>3</sup> so aqueous dispersions of polymer can be used as a type of waterborne coating. Aqueous dispersion of polymer also has potential applications in the field, such as making ultrafine polymer powder alloys with properties

different from those produced by the more common process of melt blending.

Polyurethane ionomer aqueous dispersions have been widely studied of late.<sup>4–7</sup> In this article, polystyrene ionomers with sulfonic groups are emulsified to aqueous dispersions. The effect of ionic contents on the emulsification process and the mechanism of the phase inversion are determined.

## EXPERIMENTAL

### Materials

Polystyrene (PS), supplied by Yanshan Chemical Ltd., China,  $M_w = 110,000$ , was purified by dissolving it in tetrahydrofuran and precipitated by using water and dried under vacuum at 70°C for 48 h prior to use.

### Sulfonation Reaction

Sulfonations were carried out in 1,2-dichloroethane at 50°C following the procedure described by Weiss and Sen.<sup>8</sup>

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The sulfonation agent was acetyl sulfonate, which was prepared by the reaction of concentrated sulphuric acid with acetic anhydride.

### Emulsification Procedure

The 5% sulfonated PS (SPS) was prepared in a mixed solvent of toluene and methanol. Then the solution was neutralized by equivalents of ammonia liquor.

Emulsification was carried out by adding deionized water, slowly with constant agitation at room temperature, to a solution of SPS ionomer, 5% by weight in a toluene-methanol mixed solvent. During the addition, the conductivity and viscosity of the solution were measured. When the conductivity of the solution reached a constant level, phase inversion was considered to be complete, and addition of water was stopped. After phase inversion, and oil-in-water (O/W) emulsion was formed.

### Measurements and Apparatus

Viscosity change during the emulsification process was monitored using a Rotary Viscosimeter RHEOTEST2.1, manufactured by Co. VEB MLW, Germany. Shear rate was set at  $1312 \text{ s}^{-1}$  throughout the measurement, and test temperature is  $25^\circ\text{C}$ . Electric conductivity during the emulsification process was monitored using a conductometer model DDS-11A, manufactured by the Electric Factory of Shanghai, China. The test temperature is  $25^\circ\text{C}$ .

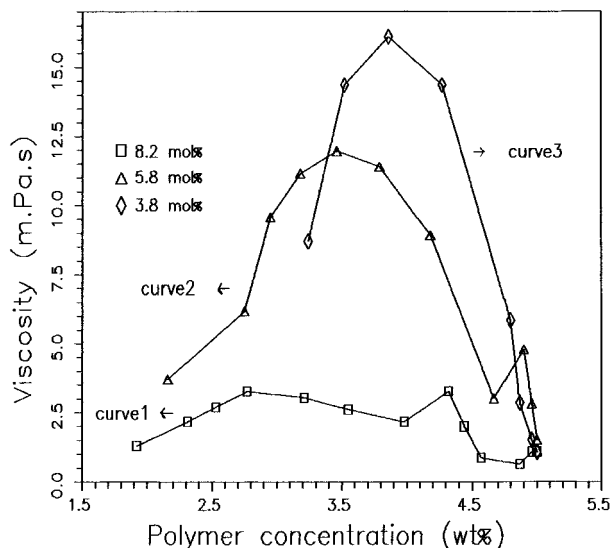
Sulfonation contents of SPS ionomer were measured by titration using a standard sodium hydroxide solution,  $0.1N$ , which was prepared by dissolving 1 g of NaOH in 250 mL of absolute methanol. Phenolphthalein was used as an indicator.

## RESULTS AND DISCUSSION

### The Variation of Viscosity of SPS Ionomer Solution During Emulsification Process

The viscosity varied with the progress of emulsification procedure for the solution of SPS ionomers with different ionic contents, shown in Figure 1.

It is obvious that the viscosity-polymer concentration curves exist for maximum values, with one peak for low ionic contents system (3.8 mol %) and two peaks for middle-level (5.8 mol %)



**Figure 1** The variation of viscosity of SPS ionomer solutions during the emulsification process: start polymer concentration, 5 wt %; test temperature,  $25^\circ\text{C}$ .

and higher-level (8.2 mol %) ionic contents systems. The maximum viscosity ( $\eta_{\max}$ ) and its corresponding polymer concentration are listed in Table I.

### The Variation of Conductivity of SPS Ionomer Solution During Emulsification Process

Table II shows the solution conductivity of SPS ionomer before and after neutralized by ammonia liquor.

From Table II, one can find that the conductivity of the solution decreases markedly after being neutralized by ammonia liquor. This decrease can be attributed to the aggregation of unsolvated salts segments stabilized by Coulombic forces. These forms reduce the transport rate of ionic groups and cause the decrease in the solution conductivity.

The variation of conductivity of 5 wt % SPS ionomer solution with adding water were shown in Figure 2, and the conductivities at turning point were shown in Table III.

In the present study, the turning points in conductivity curve were considered as a character of phase inversion, and the constant conductivity indicated that the complete phase inversion was achieved. It is obvious that the phase inversion behavior was relative to the ionic contents in the SPS chain. The more the ionic contents, the stronger the Coulombic force between the ionic

**Table I Effect of Ionic Contents on Viscosity of SPS Ionomer During Emulsification Process**

| Ionic Contents<br>(mol %) | $\eta_o$<br>(mPa s) | $\eta_{\max 1}$<br>(mPa s) | $\eta_{\max 2}$<br>(mPa s) | $C_0$<br>(wt %) | $C_{\max 1}$<br>(wt %) | $C_{\max 2}$<br>(wt %) |
|---------------------------|---------------------|----------------------------|----------------------------|-----------------|------------------------|------------------------|
| 8.2                       | 1.09                | 3.26                       | 3.25                       | 5               | 4.32                   | 2.77                   |
| 5.8                       | 1.12                | 4.79                       | 11.96                      | 5               | 4.90                   | 3.46                   |
| 3.8                       | 1.08                | 16.10                      | —                          | 5               | 3.86                   | —                      |

Starting polymer solution: 5 wt %; test temperature: 25°C.

groups and the more water was required to reach phase inversion from water in oil (W/O) to oil in water (O/W).

In comparing the results of viscosity and conductivity, one can find that the turning points in the plot of conductivity versus concentration and the peaks in viscosity curve for respective ionic contents systems are corresponding to about the same polymer concentration. This further demonstrated that turning points and  $\eta_{\max}$  are responsible for the phase inversion during emulsifying process.

### The Analysis of Mechanism of Phase Inversion

In general, the apparent viscosity of ionomer solution in low polar organic solvent increases rapidly with the increase of polymer concentration. These usually are attributed to the occurrence of the association of ionic groups in the ion containing polymer. There are several structure models for elucidating the association behavior in ionomer solution, such as the microionic lattice model,<sup>1</sup> the isotropic model,<sup>9</sup> and the two-state structure model.<sup>10</sup> Many kinds of experimental evidence obtained by SAXS and SANS<sup>11,12</sup> indicate the coexistence of ordered and disordered microionic aggregation regions.

Based on the conductivity and viscosity data

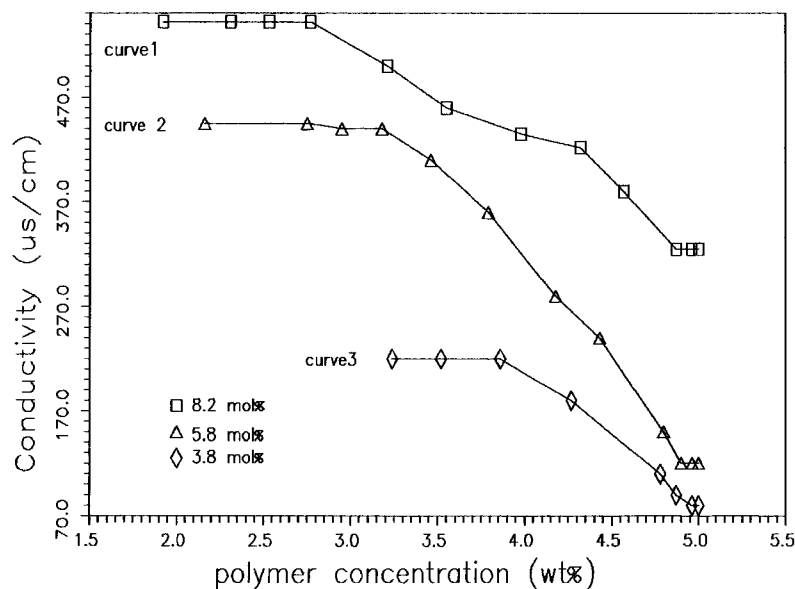
**Table II The Variation of the Solution Conductivity of SPS Ionomer Before and After Neutralized by Ammonia Liquor**

| Ionic Contents<br>(mol %) | Conductivity (us/cm)  |                      |
|---------------------------|-----------------------|----------------------|
|                           | Before<br>Neutralized | After<br>Neutralized |
| 8.2                       | 740                   | 325                  |
| 5.8                       | 340                   | 120                  |
| 3.8                       | 115                   | 38                   |

Starting polymer solution: 5 wt %; test temperature: 25°C.

and their ionic content dependence mentioned above, the phase inversion of emulsification process for the SPS ionomer in toluene–methanol–H<sub>2</sub>O system can be considered as a procedure of the dissociation for both the disordered and ordered microionic aggregation regions and the aggregation of the hydrophobic segments.

From Figure 1 (curves 1 and 2), one can find that two maximum viscosity values exist in an emulsification process for higher ionic contents (8.2 mol %) and middle-level ionic contents (5.8 mol %). It is thought that first maximum viscosity value indicates complete dissociation of the disordered microionic aggregation regions, while the second maximum viscosity value indicates complete dissociation of the ordered microionic aggregation regions. The mechanism of the phase inversion is as follows: when slowly adding water, the water first enters into the interior of the disordered microionic aggregation regions, causing a dissociation of the disordered microionic aggregation regions, and the hydrophobic segments start losing their solvation sheath and subsequently aggregate to form aligned hydrophobic aggregates, which eventually become dispersed phases. The dissociation of disordered microionic aggregation regions makes a increase in the solution conductivity (curves 1 and 2 in Fig. 2), and the association of hydrophobic segments causes an increase in the solution viscosity (curves 1 and 2 in Fig. 1). The viscosity increases with further addition of water for the increased number of hydrophobic aggregates and passes through a maximum that indicates complete dissociation of the disordered microionic aggregation regions. With further addition of water, water starts into the interior of the ordered microionic aggregation regions, accompanied by increased aggregation of hydrophobic segments and causes a sharp increase of the viscosity (curves 1 and 2 in Fig. 1). In this stage, the conductivity of the solution increases with the further addition of water, and the increasing rate of the conductivity is slower than that in the stage



**Figure 2** The variation of conductivity of SPS ionomer solutions during the emulsification process: start polymer concentration, 5 wt %; test temperature, 25°C.

of the dissociation of disordered microionic aggregation regions, indicating that the entrance of water into the ordered microionic aggregation regions is more difficult than into the disordered microionic aggregation regions. When the ordered microionic aggregation regions are completely dissociated, the phase inversion is complete. SPS ionomer molecules form a dispersed phase (the polymer particles) swollen with the organic solvent, dispersed in a continuous water-rich liquid phase. The ionic groups are situated almost on the polymer particle surface after the phase inversion. In this stage, the solution viscosity drops sharply (curves 1 and 2 in Fig. 1), and the conductivity remains almost constant (curves 1 and 2 in Fig. 2).

**Table III** The Conductivity at Turning Point During Emulsifying Process

| Ionic Contents (mol %) | Conductivity (us/cm) |                 | Polymer Concentration (wt %) |                 |
|------------------------|----------------------|-----------------|------------------------------|-----------------|
|                        | Turning Point 1      | Turning Point 2 | Turning Point 1              | Turning Point 2 |
| 8.2                    | 422                  | 542             | 4.32                         | 2.77            |
| 5.8                    | 230                  | 430             | 4.75                         | 3.46            |
| 3.8                    | 220                  | —               | 3.86                         | —               |

Starting polymer solution: 5 wt %; test temperature: 25°C.

For low ionic contents (3.8 mol %) SPS ionomer, only one maximum viscosity value exists in the emulsification process (curve 3 in Fig. 1). This because only a very small amount of the ordered microionic aggregation regions is formed, and the numbers of the microionic aggregation regions also decrease.

From Figures 1 and 2, one can find that the process of emulsification becomes short with the decrease in ionic contents. At higher ionic contents (8.2 mol %), the phase inversion occurs at 2.8% polymer contents compared to 3.5% polymer contents at middle level ionic contents (5.8 mol %) and 3.8% polymer contents at low ionic contents (3.8 mol %). This due to the decrease in the numbers of the microionic aggregation regions with the decrease in ionic contents.

## CONCLUSION

In toluene–methanol mixed solvent, PS ionomer with the sulfonated acid groups neutralized by ammonia liquor can form a microionic aggregation region, which exists as both the disordered microionic aggregation regions and the ordered microionic aggregation regions. With the variation of the ionic contents, the numbers of the microionic aggregation regions and the numbers of the disordered and the ordered microionic aggregation regions also varied, which can affect the

emulsification process. Based on the conductivity and viscosity data and their ionic contents dependence, the phase inversion of emulsification process for the SPS ionomer in toluene–methanol–H<sub>2</sub>O system can be considered as a procedure of the dissociation for both the disordered and ordered microionic aggregation regions and the aggregation of the hydrophobic segments.

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