

# Synthesis and Aqueous Solution Behaviors of Sodium Sulfonate-Terminated Dendritic Poly(ester-amine)

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**ABSTRACT:** Sodium sulfonate-terminated dendritic poly(ester-amine) (SPEA) was synthesized by sulfonation of acrylic double bond-terminated dendritic poly(ester-amine) (APEA) with sodium hydrogen sulfite ( $\text{NaHSO}_3$ ) in mixture of diglycol and 2-butanone under normal pressure. The structure of SPEA was characterized by IR,  $^1\text{H-NMR}$ , and elemental analysis. SPEA was water-soluble. 1.0–40.0% (mass) SPEA aqueous solutions appeared as dilatant fluid. When pH value varied from 1.5 to 12.0, the viscosity of 1–5% (mass) SPEA aqueous solutions changed very small,

and the electric conductivity almost kept stable within pH 3.0–10.0. The relationship between the viscosity and the concentration of SPEA water solutions was similar to that of NaCl water solutions. The surface tension of SPEA water solutions was lower than that of polyethylene glycol 2000 water solutions with the same concentration. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2578–2583, 2008

**Key words:** dendritic; sodium sulfonate; viscosity; electrical conductivity; surface tension

## INTRODUCTION

Sulfonation is a frequently used means for traditional polymer modification because of the negative charge and good water-solubility of sulfonate sodium groups, and macromolecules with multiple sulfonate sodium groups have significant utilities. Yong-Jin et al.<sup>1</sup> reported that the sulfonation step introduced cation exchangeable sites to cation exchange membranes. Yan et al.<sup>2</sup> sulfonated high performance poly(phthalazinones) to improve hydrophilicity and proton conductivities of these proton exchange membrane materials for fuel cell. Young et al.<sup>3</sup> reported that negatively charged sulfonate groups contribute to improve the blood compatibility and to minimize cell adhesion on biomaterials surfaces. Chegel et al.<sup>4</sup> prepared a novel aldehyde dextran sulfonate matrix for affinity biosensors and proved that the negatively charged sulfonate group provided electrostatic attraction of the positively charged biomolecules.

Dendrimers, with a well-defined structure consisting of a core, dendrons and a number of terminal functional groups, are a new class of macromolecules.<sup>5–7</sup> Water-soluble dendrimers are an important member of the dendrimer family, which can be used in the fields of drug delivery, biomimicry, catalysis, sensors, retrieval of heavy metals and rare metals, and preparation of dendrimer-metal nanocomposites.<sup>8–10</sup> The typical water-soluble dendrimers are usually terminated with amino, hydroxyl, and carboxyl groups. For example, the famous poly(amido-amine)<sup>11</sup> and poly(propylene imine)<sup>12</sup> are terminated with amino groups, Arborols<sup>13</sup> are with hydroxyl groups on the periphery. Sebastiano et al.<sup>14</sup> synthesized water-soluble dendritic cyclophanes with terminal carboxylate groups and investigated their molecular recognition properties in aqueous solutions. However, water-soluble dendrimers with peripheral sulfonate sodium groups are less reported. We only found Matthews et al.<sup>15</sup> introduced benzene sodium sulfonate into dendritic Boc-protected poly(aminoamide) and the dendrimer was used to doping of conducting polymers.<sup>16</sup>

In this article, a novel sodium sulfonate-terminated dendritic poly(ester-amine) (SPEA) was prepared by sulfonation of acrylic double bond-terminated dendritic poly(ester-amine) (APEA) using sodium hydrogen sulfite as sulfonating agent, and the aqueous solution behaviors of SPEA were studied.

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## EXPERIMENTAL

### Materials

APEA was prepared following the method of Dongmei et al.<sup>17</sup>; sodium hydrogen sulfite ( $\text{NaHSO}_3$ ), sodium chloride ( $\text{NaCl}$ ), methanol ( $\text{MeOH}$ ), ethanol ( $\text{EtOH}$ ), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), diglycol (DGC), 2-butanone (MEK), and polyethylene glycol 2000 (PEG2000) were purchased from the Third Reagent Company of Shanghai (China).

### Measurements

Infrared (IR) spectra were carried out with a Magna-550 Fourier-transform infrared spectrometer (Nicolet, USA). Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra were recorded on an INOVA 400 MHz using  $\text{D}_2\text{O}$  as a solvent (Varian, USA). Elemental analysis was carried out with a Shimadzu EA-1110 CHNSO (Carlo-Erba, Italia). High efficiency liquid chromatography (HPLC) was performed on a Waters 515 (Waters, USA) using  $\text{C}_{18}$  column ( $4.6 \times 250 \text{ mm}^2$ ) and mixture of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  (volume ratio 0.64:0.16) as an eluent (the total flux 0.8 mL/min, the detection wavelength 254 nm,  $30^\circ\text{C}$ ). Viscosity was performed on a NDJ-1 viscometer (Shanghai Sendi Scientific Instrument, China). The electroconductivity was tested by a DDS-11 electrical conductivity detector with a DJS-10 platinum black electrode (Shanghai Cany Precision Instruments, China). Surface tension was measured by a JZHY-180 interfacial tensimeter (Hebei Chengde Precision Testing Machine, China). The pH value was determined by a PHD-20A acidometer (Shanghai Zhixin Instruments, China).

### Synthesis of SPEA

Dendritic poly(ester-amine) terminated with acrylic double bond (APEA) (3.15 g, 2.53 mmol) was dissolved in 5.30 g 2-butanone in an 100-mL three-necked flask equipped with a mechanic stirrer, then, 2.21 g (21.3 mmol) sodium hydrogen sulfite ( $\text{NaHSO}_3$ ) in 15.9 g DGC was added under vigorously stirring, heated to reflux for 4 h. Then cooled and centrifugalized. The centrifugate containing the product was poured into ethanol. The mixture was filtered and the filter cake was washed with acetone for three times, dried in vacuum at  $50^\circ\text{C}$  to give a white solid SPEA with 71.2% yield (Scheme 1).

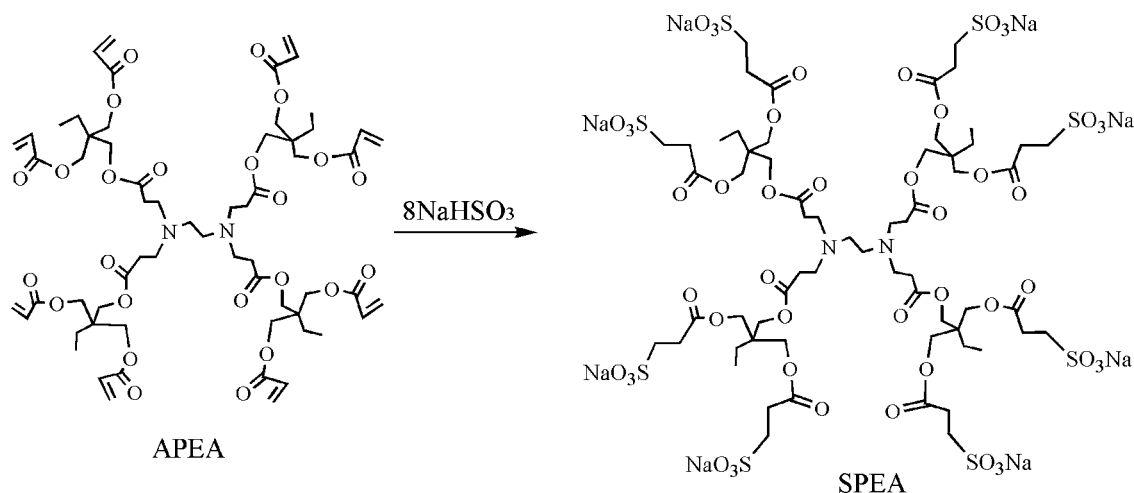
### Test of aqueous solution behaviors

The water solutions of SPEA and  $\text{NaCl}$  with concentration of 1.0%, 2.0%, 3.0%, 4.0%, 5.0%, 10%, 15%, 20%, 25%, 30%, 35%, and 40% (mass) were prepared and their viscosity and electrical conductivity were tested on a NDJ-1 viscometer and a DDS-11 electrical conductivity detector respectively at different pH value. The surface tension of 1.0%, 5.0%, 10%, 15%, 20%, 25%, and 30% (mass) aqueous solutions of SPEA and polyethylene glycol 2000 (PEG2000) were tested by a JZHY-180 interfacial tensimeter. All experiments were carried out at  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Optimization of the reaction conditions

Sulfonation of aliphatic carbon-carbon double bond ( $\text{C}=\text{C}$ ) with sodium hydrogen sulfite ( $\text{NaHSO}_3$ ) was usually carried out under the following conditions: Molar ratio of  $\text{C}=\text{C}$  to  $\text{NaHSO}_3$  was 1 : 1.05, ethanol-water mixture was used as solvent, and the reaction



**Scheme 1** Synthesis of sodium sulfonate-terminated dendritic poly(ester-amine) (SPEA).

**TABLE I**  
The Effects of Solvent on Water Solubility and Content of C=C of the Products

Run	Solvent name (mass ratio)	Reflux temperature (°C)	Name of the products	Water solubility <sup>a</sup> (%)	Content of C=C <sup>b</sup> (%)
1	THF/H <sub>2</sub> O (1.0 : 1.4)	64	P1	10.3	12.9
2	MeOH/H <sub>2</sub> O (1.0 : 1.4)	74	P2	25.1	8.7
3	EtOH/H <sub>2</sub> O (1.0 : 1.4)	79	P3	60.2	9.6
4	DMF/H <sub>2</sub> O (1.0 : 1.8)	103	P4	100	0
5	DMF/H <sub>2</sub> O (1.0 : 1.4)	105	P5	100	0
6	DGC/H <sub>2</sub> O (1.0 : 1.4)	103	P6	100	0
7	DGC/MEK (3.0 : 1.0)	90	P7	100	0

Molar ratio of acrylate double bond to sodium hydrogen sulfite was 1 : 1.05.

<sup>a</sup> Mass percent of soluble parts of 1 g products in 20 mL water.

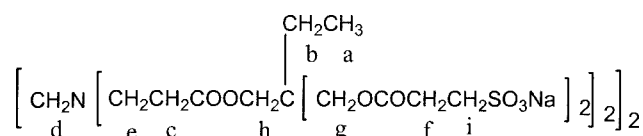
<sup>b</sup> Run 1 to 3 came from chemical titration, run 4 to 7 came from <sup>1</sup>H NMR.

system was refluxed for 2–6 h under the pressure 0.1–0.2 MPa and temperature 85–120°C.<sup>4,18–19</sup>

Herein, APEA and NaHSO<sub>3</sub> (molar ratio 1.0 : 8.4, that is, C=C : NaHSO<sub>3</sub> 1 : 1.05) were refluxed in different solvents for 4 h under normal pressure. The water solubility and content of C=C of the products were listed in Table I.

It was clearly seen that the products (P1, P2, P3) contained non water-soluble parts and remained acrylate double bonds when THF/H<sub>2</sub>O, MeOH/H<sub>2</sub>O, and EtOH/H<sub>2</sub>O mixtures were used as solvents. It may be that the acrylate double bonds could not be completely sulfonated at lower temperature. After using DMF/H<sub>2</sub>O and DGC/H<sub>2</sub>O as solvents, water-soluble products (P4, P5, P6) without C=C were obtained, but, their experimental elementary analysis data were not matched the calculated value (Table II). It may be at higher temperature the sulfonation of acrylate double bonds and the hydrolysis of ester groups in APEA both occurred. To avoid hydrolysis reaction, DGC/MEK mixture was adopted instead of DMF/H<sub>2</sub>O and DGC/H<sub>2</sub>O. At this time, water-soluble product P7 was obtained, and its experimental elementary analysis data was basically consistent with the theoretical ones of the target product SPEA (Table II).

When the structure of SPEA was shown in the following form, (Scheme 2), the chemical shifts (δ/ppm, D<sub>2</sub>O) corresponding to protons from a to i could be found in its <sup>1</sup>H-NMR spectra (Fig. 1), which were 0.71–0.74 (a, 12H), 1.29–1.40 (b, 8H), 2.39–2.44



**Scheme 2**

(c, 8H), 2.50–2.56 (d, 4H), 2.59–2.70 (e, 8H; f, 16H), 3.06 (g, 16H), 3.55 (h, 8H), 3.90–4.00 (i, 16H). The fact that no signals appeared in 5.89–6.38 ppm proved that the acrylate double bonds in APEA were sulfonated completely.

IR spectrum of SPEA, as shown in Figure 2, could be analyzed as follows: 2966.7, 2889.6 cm<sup>-1</sup> (CH<sub>3</sub>, CH<sub>2</sub> stretching vibration peak), 1732.2 cm<sup>-1</sup> (ester carbonyl stretching vibration peak), 1257.7, 1192.1, 1049.4 cm<sup>-1</sup> (stretching vibration peak of S=O bonds in —SO<sub>3</sub><sup>-</sup>).

Elementary analysis, <sup>1</sup>H-NMR spectra and IR spectrum showed that the objective product SPEA was achieved.

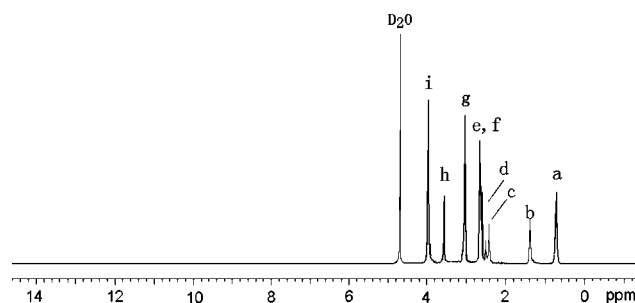
The purity of SPEA was 99.8% evaluated by HPLC (Fig. 3).

Furthermore, the effects of mass ratio of DGC to MEK and reaction time on the yields of SPEA were investigated. The results were shown in Figures 4 and 5. It was easily found that the yields of SPEA were raised when the mass ratio of DGC to MEK increased and the reaction time prolonged. Since the solubility of APEA was better in MEK than in DGC,

**TABLE II**  
Elementary Analysis Data of Sulfonation Products

Name of the products	C (%)	H (%)	N (%)
P4	27.79	6.25	0.97
P5	28.13	5.67	1.11
P6	29.16	4.77	1.28
P7	35.75	4.69	1.25
SPEA	35.84	4.62	1.35

The data of the products P4, P5, P6, and P7 were experimental value, the data of SPEA were calculated value.



**Figure 1** <sup>1</sup>H-NMR spectra of SPEA.

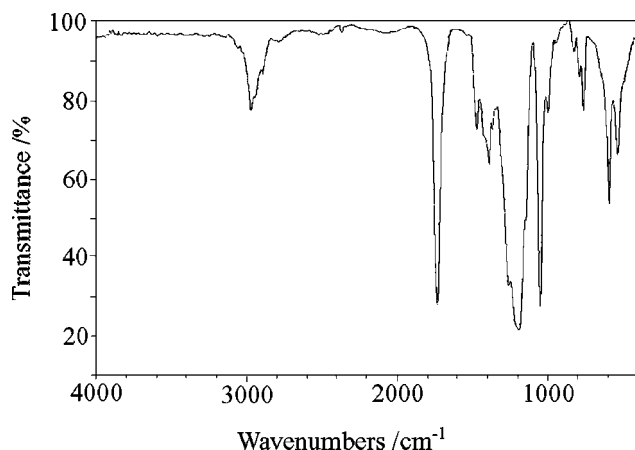


Figure 2 IR spectrum of SPEA.

while  $\text{NaHSO}_3$  could be dispersed better in DGC than in MEK, the yield increased with the increase of DGC content in the DGC and MEK mixture might be that the two raw materials APEA and  $\text{NaHSO}_3$  were better dispersed in the reaction system at the same time when the DGC content in the DGC and MEK mixture increased suitably. When the mass ratio of DGC to MEK exceeded 3.0 and the reaction time was longer than 4 h, the yields of SPEA were raised very small.

### The rheological properties of SPEA solutions

Figure 6 exhibited the relation between the viscosity of 1.0–40% SPEA aqueous solutions and the rotation speed of the rotator of the viscometer. The viscosity

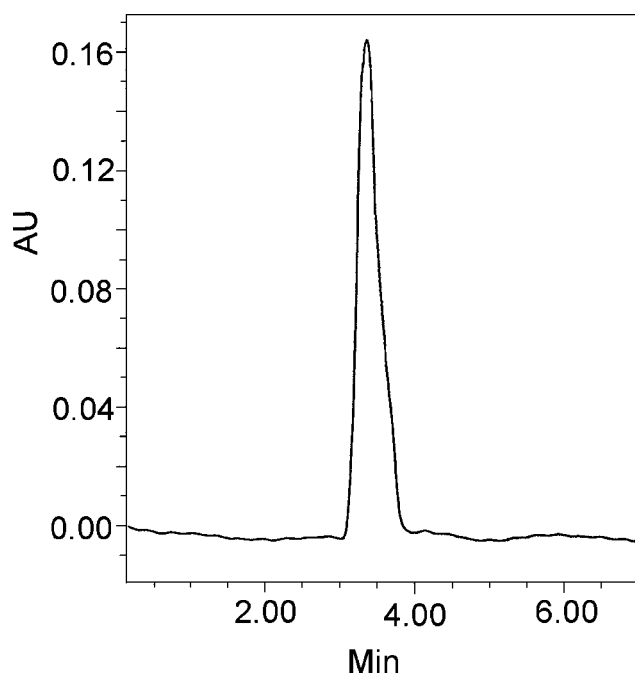


Figure 3 HPLC spectrum of SPEA.

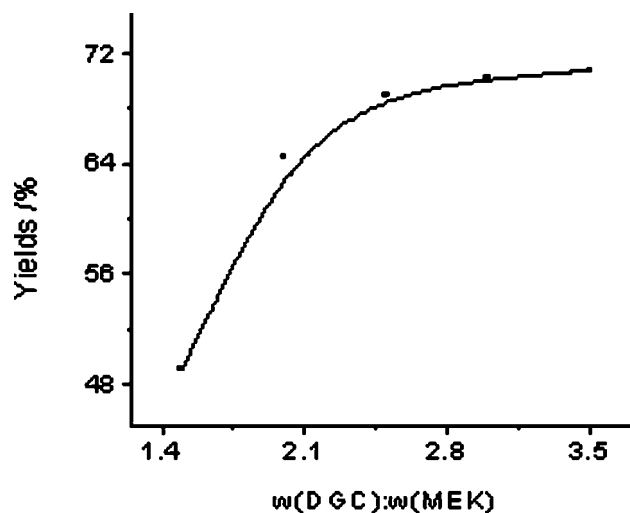


Figure 4 The yields of SPEA vs. mass ratio of DGC to MEK.

of the solutions rose when the rotation speed increased, which indicated that the 1.0–40.0% SPEA aqueous solutions acted as dilatant fluids, while traditional macromolecules water solutions usually appeared as pseudoplastic fluids. It was explained that different from the traditional macromolecules, the increase of shear rate had less effect on the configuration of dendritic SPEA molecules, but created more chances for the collision between the large SPEA molecules, which led to the increase of the friction in the flowing fluid and resulted in the increase of the viscosity.

### Effects of solution concentration on viscosity

Figure 7 exhibited the viscosity of NaCl and SPEA water solutions with a series of concentration. It was

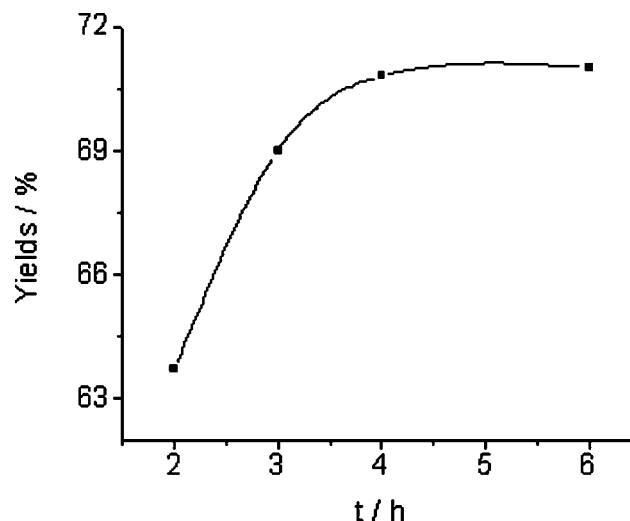
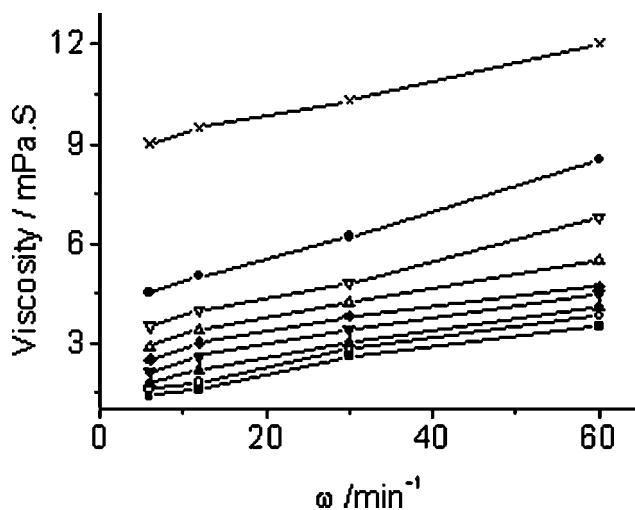


Figure 5 The yields of SPEA vs. reaction time.

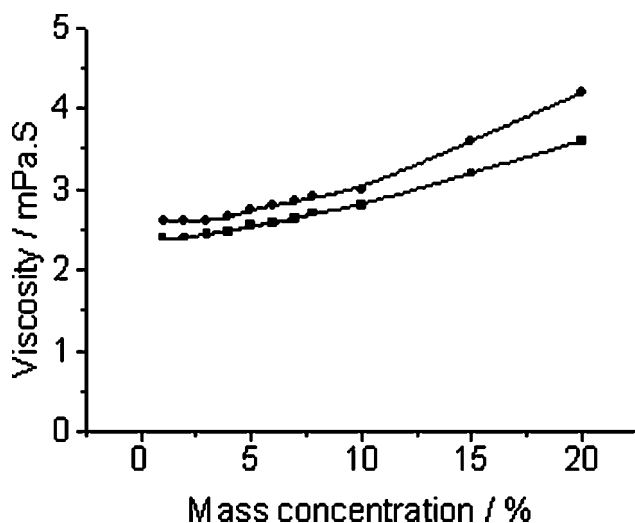


**Figure 6** The relation between viscosity and rotation Speed ( $\omega$ ) of SPEA aqueous (25°C) ■: 1.0%; ○: 5.0%; ▲: 10%; ▼: 15%; ◆: 20%; △: 25%; ▽: 30%; ●: 35%; ×: 40%.

obviously seen that the viscosity of SPEA aqueous gradually rose when the solution-concentration increased, which was similar with the situation of NaCl aqueous. 20% (mass) SPEA solution still had low viscosity.

#### Effects of pH on viscosity and electrical conductivity of SPEA solutions

It can be seen from Table III that the viscosity of the SPEA water solutions with 1.0–5.0% concentrations changed very slightly when the pH value changed from 1.5 to 12.0. This is because the pH value had small effects on the SPEA molecular configuration. This characteristic made SPEA could be used in water solution systems within wide range of pH



**Figure 7** The relationship between viscosity and concentration (25°C, 6 r/min) ■: NaCl; ●: SPEA.

**TABLE III**  
The Relationship Between Viscosity and pH value  
(25°C, 6 r/min)

	pH value				
	1.5	4.0	7.0	9.5	12.0
Viscosity (mPa s)					
A	2.7	2.7	2.7	2.6	2.6
B	2.7	2.7	2.7	2.7	2.6
C	2.7	2.7	2.6	2.7	2.6
D	2.8	2.7	2.6	2.6	2.6
E	2.8	2.7	2.6	2.6	2.6

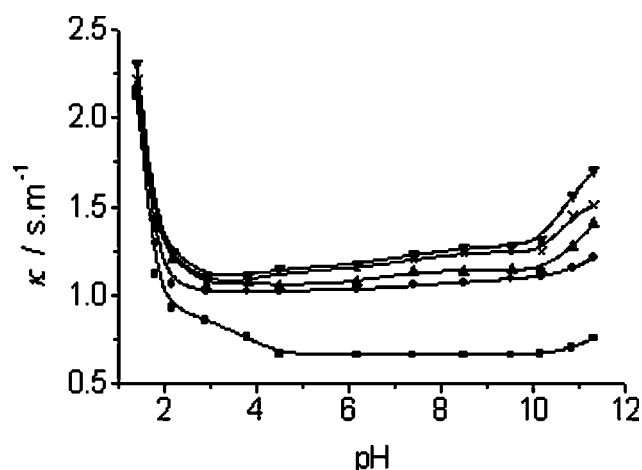
A, B, C, D, and E referred to 1.0%, 2.0%, 3.0%, 4.0%, 5.0% (mass) SPEA aqueous, respectively.

value and less affect the viscosity of the original systems.

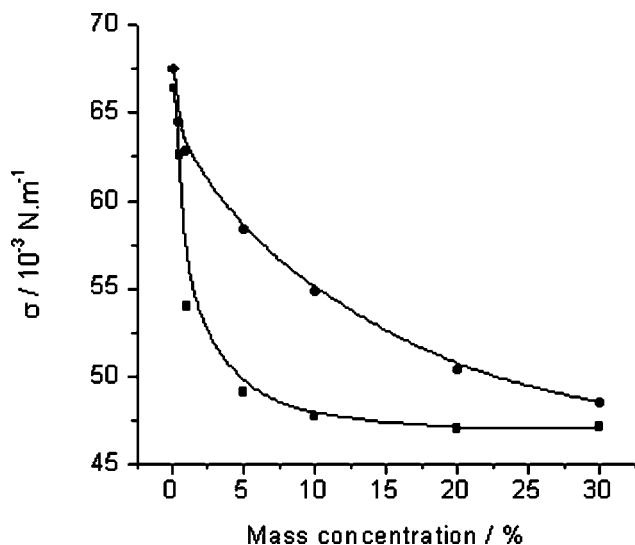
It was exhibited in Figure 8 that the conductivity of SPEA aqueous was basically stable within the pH value 3.0–10.0, except for the 1.0% solution, whose conductivity almost did not changed within the pH value 4.5–10.0. The results indicated that SPEA could be used in water solution systems within wide range pH value and had small effects on the conductivity of the original systems. When the pH value was below 3.0 (4.5) or above 10.0, the conductivity of SPEA aqueous increased, which was caused by free  $H^+$  and  $OH^-$  ions participating electric conduction, respectively.

#### The surface activity of SPEA

Figure 9 showed the relation between the surface tension of SPEA and PEG2000 water solutions and their concentrations. It can be seen that the surface tension of SPEA water solutions was smaller than that of PEG2000 water solutions at the same concen-



**Figure 8** Electric conductivity of SPEA aqueous at different pH value (25°C) ■: 1.0%; ●: 2.0%; ▲: 3.0%; ×: 4.0%; ▼: 5.0%.



**Figure 9** Surface tension *vs* concentration (25°C) ■: SPEA; ●: PEG2000.

tration, especially from 1.0% to 10.0%, the surface tension of SPEA water solutions dropped rapidly.

### CONCLUSIONS

In this work, SPEA was synthesized under mild conditions; that is, the molar ratio of APEA to sodium hydrogen sulfite ( $\text{NaHSO}_3$ ) was 1 : 8.4, the mixture of DGC and 2-butanone (mass ratio 3.0 : 1.0) used as solvent, refluxing for 4 h under normal pressure. The yield of SPEA was 71.2%. The purity of SPEA was 99.8%. SPEA had very good water solubility, and its aqueous solutions appeared as dilatant fluids. When pH value varied from 1.5 to 12.0, the viscosity of 1–5% (mass) SPEA aqueous solutions changed very small, and the electric conductivity almost kept stable from pH 3.0 to 10.0, which indicated that SPEA could be used in water solution sys-

tems within wide range of pH value and had small effects on the viscosity and conductivity of the original systems. The surface activity of SPEA was better than that of polyethylene glycol 2000 (PEG2000).

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