Synthesis and Elastomer Behavior of a Novel Polymer Electrolyte of Acrylic Ester–Salt Copolymer

Jianguo Tang, Dongqing Wang, Yao Wang, Haiyan Liu, Xiaomei Wang

Functional Composite Laboratory, Qingdao Cultivating Base on National Key Laboratory of Novel Fibers and Modern Textile, College of Chemical Engineering, Qingdao University, Qingdao, People's Republic of China

ABSTRACT: This paper studied the synthesis of a novel elastomeric copolymer electrolyte in an aqueous phase. The monomer, sodium allyl sulfonate (SAS), was dissolved in continuous aqueous phase and the second monomer, methyl acrylate (MA), was supplied from MA micelles as dispersed phase. The copolymerization of the two monomers took place in continuous aqueous phase. Confirmed by FTIR and ^{1}H-NMR, a binary copolymer electrolyte of MA and SAS, poly(MA-*co*-SAS), was obtained. The glass transition temperature of the copolymer was indicated as 20.4°C by DSC thermogram, thus, it behaves an elastomer in normal ambient temperature. The mechanical properties of the composite films consisting of both poly(MA-*co*-SAS) and Cu^{2+} ions or reduced copper were affected by the content of ions and reduced copper. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2796–2802, 2006

Key words: elastomer; methyl acrylate; sodium allyl sulfonate; mechanical property; electrolyte

INTRODUCTION

Polymer electrolytes have high molecular weight and ionically conducting property as solid materials. Gray[1] summarized such materials in the following five categories: (1) a liquid solvent-free system where the ionically conducting phase is formed by dissolving salts in a high-molecular weight polar polymer matrix; (2) a gel electrolyte, formed by dissolving a salt in a polar liquid and adding an inactive polymeric material to give the material mechanical stability; (3) a plasticized electrolyte, which is essentially a gel electrolyte but is usually associated with the addition of small amounts of a high dielectric constant solvent to a conducting polymer electrolyte to enhance its conductivity; (4) an ionic rubber, which is essentially a liquid electrolyte comprising a low-temperature molten salt mixture, reduced to a rubbery condition by addition of a small amount of high molecular weight polymer; and (5) a membrane ionomer and, in partic-

ular, a proton-conducting polymer electrolyte used in proton-exchange membrane(PEM) fuel cells. The original sense is localized in the 1st category, and for this reason, most research has been focused on it.

In recent years, new needs for polyelectrolytes have emerged in several fields, such as high-peak brightness polymer light-emitting diodes,[2] actuators,[3] working fuel cells,[4] biosensors, and miniaturization of electronic and optical devices.[5] The skills to prepare these polyelectrolytes concern improvements of ionic conductivity and mechanical properties of polyelectrolytes. Seki Miharu et al.[6] prepared a polymeric solid electrolyte with high-ionic conductivity, by complexing a polyurethane elastomer with $LiClO_4$. The ionic conductivity of these complexes increases with increasing $LiClO_4$ concentration, and reaches a value of 10^{-4} S/cm at 80°C for $[LiClO_4]$ = 1.20 mmol/g polymer. This polyurethane elastomer–$LiClO_4$ complex has good mechanical properties, compared with poly(ethylene oxide)-and poly(propylene oxide)-based complexes. Kim et al.[7] in the center for advanced functional polymers at Hanyang University, Korea, investigated a gel polymer electrolyte, poly(vinylidene-fluoride-*co*-hexafluoropropylene), which has high-ionic conductivity and good mechanical properties. Another example is interpenetrating polymer networks (IPNs),[8] which is applied to dissolve the interface and adhesion problems in the design based on actuators. An IPN was synthesized between poly(3,4-ethylenedioxythiophene) and a polyethylene oxide/elastomer. Its synthetic pathway ensures a gradual dispersion of the electronically conducting polymer

through the thickness of the material. However, some defects of polyelectrolytes need further research to be improved. Hamade and Dillard[9] worked on the bonding effect between elastomer and metal in a cathode. The result indicated the deleterious effect of galvanic activity on the durability of rubber-to-metal adhesive bonds.

Of mechanical properties of polymer electrolytes, elastomeric property is important and necessary somewhere to obtain devices and related applications.[10] The conductive elastomer gasket design is valuable to be evident.[11] Since a gasket is necessary only where an imperfect surface exists, its elastomer imparts its ease of filling defect holes and conductivity. Biosensors, actuators, and stimulation-response devices are like to have, at least in most of cases, elastomeric properties to meet their mechanical deformation and intelligent behaviors, like artificial skins in medical and robot miniatures. Meanwhile, rare example of polymer electrolyte meets (i) to be an ionically conductive polymer, (ii) to have intrinsic ionic group, (iii) most importantly to have lower glass transition temperature that is normally lower than ambient temperature.

For the needs of elastomeric property of polyelectrolytes mentioned earlier, we report a novel elastomeric polymer electrolyte, poly(methyl acrylate-*co*-sodium allyl sulfonate) [poly(MA-*co*-SAS)], synthesized by an aqueous-phase polymerization (APP) in our laboratory. Poly(MA-*co*-SAS) behaves as an elastomer at room temperature. APP method polymerizes monomers in aqueous medium—the continuous phase in the system, differing from traditional emulsion and suspension polymerizations.[12] The monomer concentrations in aqueous medium are controlled by dissolvability of monomers.

EXPERIMENTAL

Materials

Methyl acrylate (MA) was purchased from Yili Fine Chemicals (Beijing, China) and was treated by the following methods. The inhibitor inside was washed out by 0.5 wt % NaOH solution, and the collected MA was neutralized by dilute hydrochloric acid and distilled water. Anhydrous $CaCl_2$ was used to absorb the impurity of rest water inside, before distillation under normal pressure.

Sodium allyl sulfonate (SAS) was purchased from Lufeng Fine Chemicals (Zibo, China) and was recrystallized prior to use. And, reagent-grade, *N,N*-dimethylformamide (DMF), $K_2S_2O_8$ (KPS), anhydrous ethanol, dimethylsulphoxide (DMSO), and NaOH were purchased from Senni Fine Chemicals (Shanghai, China), used as received. Additionally, $CuSO_4·5H_2O$ was purchased from Tian De Institute of fine Chemi-

cals (Linzi, Zibo,China); $CuCl_2·2H_2O$ was purchased from the Fourth Chemicals (Shanghai, China); and chloride acid was purchased from Jiangshan Reagent (Qingdao, China). These chemicals were also used as received.

Copolymerization

The copolymer was synthesized by an aqueous-phase polymerization, using $K_2S_2O_8$ (KPS) as initiator and hydrochloric acid as pH regulator. The SAS aqueous solution was added into a 500-mL flask with a funnel when the flask was purged by nitrogen. Then, MA was dropped into the stirred flask through the funnel. The polymerization was started when the temperature was reached to the settled value, 70°C, and was terminated by adjusting pH of the system, using NaOH solution when polymerization experienced an expected period. Distilling and filtering separated the rest monomers in the system and the product of copolymerization, respectively. Then, the copolymer was washed in anhydrous ethanol. After water washes and filtering, the final product was dried in vacuum.

Preparation of polymer matrix gradient composite films (PMGCF)

The ternary solution of polymer, metal ion, and solvent was prepared in a reactor with reflux condenser, according to the following procedures. First, the polymer was fully dissolved in solvent, and then proportional $CuCl_2·2H_2O$ used as metal ion source was added into the reactor. The system was heated and stirred until the ternary system became even solution. Finally, the solution was coated on a surface of a clean electrode and was dried to a certain degree under room temperature. The film obtained still contains a certain content of solvent and thus is called as swelling cathode film (SCF). The electrolytic system was composed of a copper anode, a graphite cathode that was coated with SCF, and liquid medium between the couple electrodes. The expected electrolysis took place in SCF under constant voltage and temperature. When electrochemical reduction of SCF finished, the cathode was taken out, washed by water, and dried at a temperature of (45 ± 5)°C. The final film was peeled off from the cathode.

Characterization techniques

Infrared spectra of the copolymer were recorded by a MAGNA-IR550 FTIR instrument from Nicolet (Madison, WI, USA), using KBr pellet in which a weight ratio of copolymer to KBr was as 1 : 100. The ^{1}H-NMR measurement was run on an ECP-600 Spectrometer from JEOL (Japan). DMSO-D6 was used as solvent in
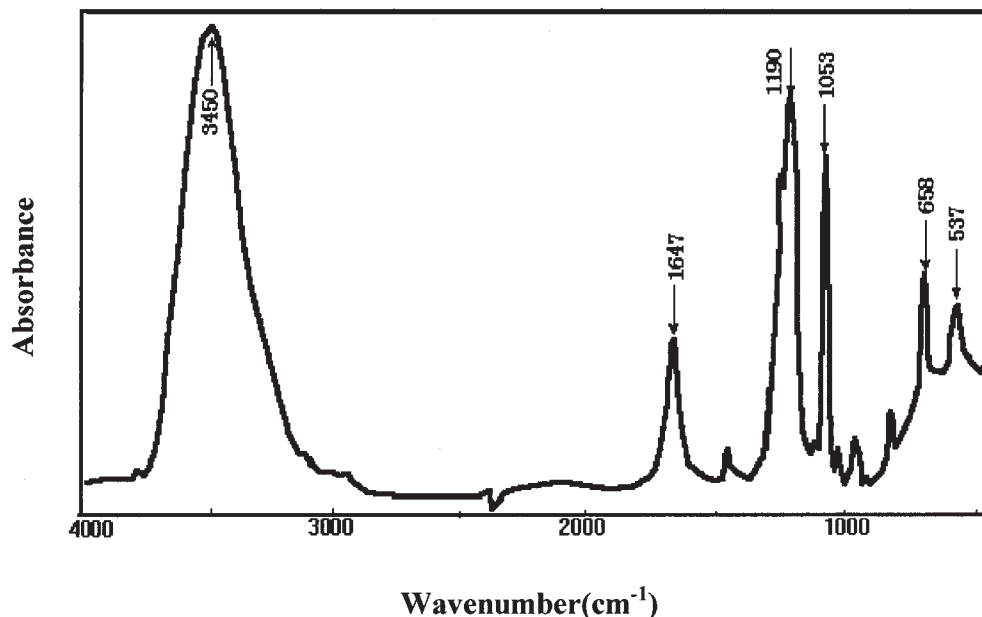
Figure 1 FTIR spectrum of SAS. The sample was the original materials from the supplier mentioned in Experimental section.

measurement. The viscosity of the copolymer was obtained by Ubbelodhe viscometer at $(25 \pm 0.1)°C$ in DMF. DSC measurement was performed on a METTLER TOLEDO STAR^e System from Jeol (Tokyo, Japan). Thermograms were recorded at a heating rate of $10°C/min$. Mechanical properties were instrumented on a Multiple Instron Mechanical Tester, FZY-0102 automated materials testing system (Instron Corporate, Canton, MA 02021), under 10.000 pts/s sample rate, 50% humidity, and 10.000 mm/min crosshead speed at 23°C.

RESULTS AND DISCUSSION

Copolymerization between MA and SAS

The copolymerization between MA and SAS was performed in aqueous phase, according to the solubility of both SAS and MA. SAS dissolved in water, whereas MA only partially (6%) does at the temperature of 25°C. For this reason, most of MA forms micelles as dispersed phase that act as a storehouse offering monomer to aqueous phase. The hydrophilic radicals released by initiator KPS initiate the copolymerization of MA and SAS in aqueous phase. The ratio of two monomers in aqueous phase, f_1, can be calculated according to the molar amount of MA determined by solubility in aqueous phase and the molar amount of SAS initially added into the system.

The reactivity ratios (r_1 and r_2) of MA and SAS in copolymerization can be estimated based on Alfrey–Price eqs. (1) and (2).[13]

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \qquad (1)$$

$$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)] \qquad (2)$$

where the values of Q and e regarding MA and SAS were known as $Q_1 = 0.42$, $e_1 = 0.60$, $Q_2 = 0.089$, and $e_2 = 0.13$.[13,14] The subscript 1 and 2 in the equations refer to MA and SAS, respectively. Thus, the reactivity ratios of MA and SAS were known as $r_1 = 3.6$ and $r_2 = 0.23$, according to eqs. (1) and (2). As $r_1 \gg r_2$ in this copolymerization, the molar ratio of MA to SAS in copolymer, f_{10}, is determinable to be higher than that of MA to SAS in beginning monomer composition f_{10}. Because of the restriction of dissolvability of MA, the saturated concentration of MA in aqueous medium kept constant before dispersed MA micelles consumed up.

The initiator concentration and pH of the system influence the rate of copolymerization between MA and SAS. Initiator, KPS, decomposed by first-order relationship when acid acted as catalyst in copolymerization. The activation energy without catalyst is 33.5 kcal/mol, which is higher than that (26 kcal/mol) under acidic condition. For this reason, the copolymerization system should be adjusted to be in acidity, i.e., pH < 7.

Characterization of the copolymer

The FTIR spectra of monomer SAS[15–17] and the copolymer are shown in Figures 1 and 2. In Figure 1, the characteristic bands of SAS are the stretching vibrations of C=C at 1647 cm^{-1}, S=O at 1190 cm^{-1}, and S—C at 658 cm^{-1}. In Figure 2, the carbonyl group of MA has sharp bands at 1737 cm^{-1}. The methyl sym-
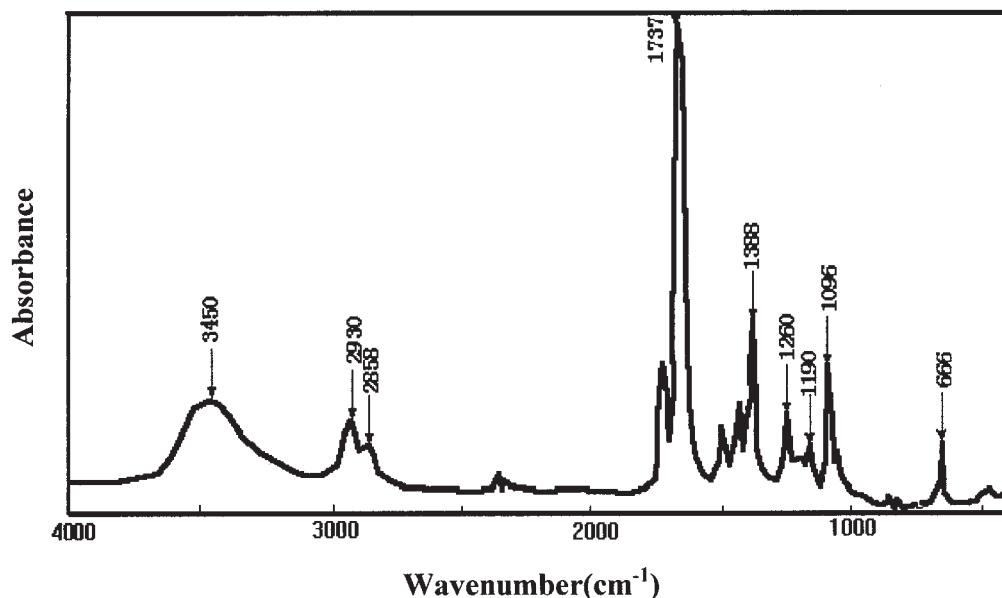
Figure 2 FTIR spectrum of poly(MA-*co*-SAS). The sample was synthesized by the aqueous-phase method in this study. The polymerization conditions are: the molar ratio of MA to SAS, 3 : 1; polymerization temperature, 70°C; and the dosage of KPS, 0.1 wt % over the total weight of two monomers.

metric twisting bands and ester carbonyl stretching bands of MA are at 1388 and 1260 cm^{-1}, respectively. And, the bands at 2930 and 2858 cm^{-1} were assigned to the symmetric and asymmetric stretching vibrations of CH$_2$, respectively. The signals at 3450 cm^{-1} in both spectra (Figs. 1 and 2) correspond to stretching vibrations of O—H in water, which was inevitably absorbed in sample treatment.

^{1}H-NMR spectra of poly (MA-*co*-SAS) and its integral curve are shown in Figures 3 and 4, respectively. Based on literatures,[18,19] the structural information can be known. The signal at 2.50 ppm corresponds to the absorption of solvent-deuterated DMSO-D6. The signal at 3.36 ppm relates to water absorbed by DMSO. The signal at 3.58 ppm is the result of chemical shifts of hydrogen in CH$_2$ groups, which are connected to sulfonic groups (SO$_3^{2+}$). The signal of —CH$_2$ in copolymer backbone is at 3.57 ppm. The strong peak at 1.60 ppm is assigned to the hydrogen proton in —COOCH$_3$. The broad multipeaks (δ = 2.1950–2.3057 ppm) correspond to the hydrogen signal in —CH of polymer backbone. Summarized the structural information discussed earlier, the two structural units of —COOCH$_3$ and —SO$_3$Na were obviously confirmed. According to integral curve (Fig. 4), the molar ratio of MA to SAS in copolymer is (2.09/2): (6.05/6) = 1 : 1.

The Mark–Houwink equation is always helpful to determine the molecular weight of macromolecules. The ratio of specific viscosity (η_{sp}) to concentration (C) in extremely dilute solution of poly(MA-*co*-SAS), η_{sp}/C, can express the intrinsic viscosity. In our experiments, the intrinsic viscosities, [η] and [η]′ were

113 ± 1.2 and 116 ± 3.8, respectively, corresponding to the ratios, 2 : 1 and 3 : 1, of MA to SAS in poly(MA-*co*-SAS). In the principle of the Mark–Houwink equation, the intrinsic viscosities can present comparative magnitudes of the molecular weights. The close values of the intrinsic viscosities above indicated that their molecular weights have no obvious difference.

DSC result indicated that T_g of poly (MA-*co*-SAS) is 20.4°C. It means this polymer electrolyte can behave as an elastomer in normal ambient temperature.
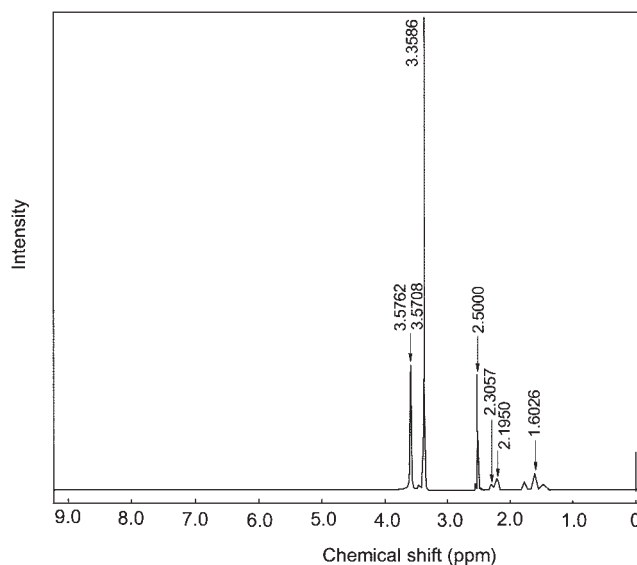

Figure 3 ^{1}H-NMR spectrum of poly(MA-*co*-SAS). The polymerization conditions are: the molar ratio of MA to SAS is 3 : 1, polymerization temperature 70°C, and the dosage of KPS was 0.1 wt % over the total weight of two monomers.
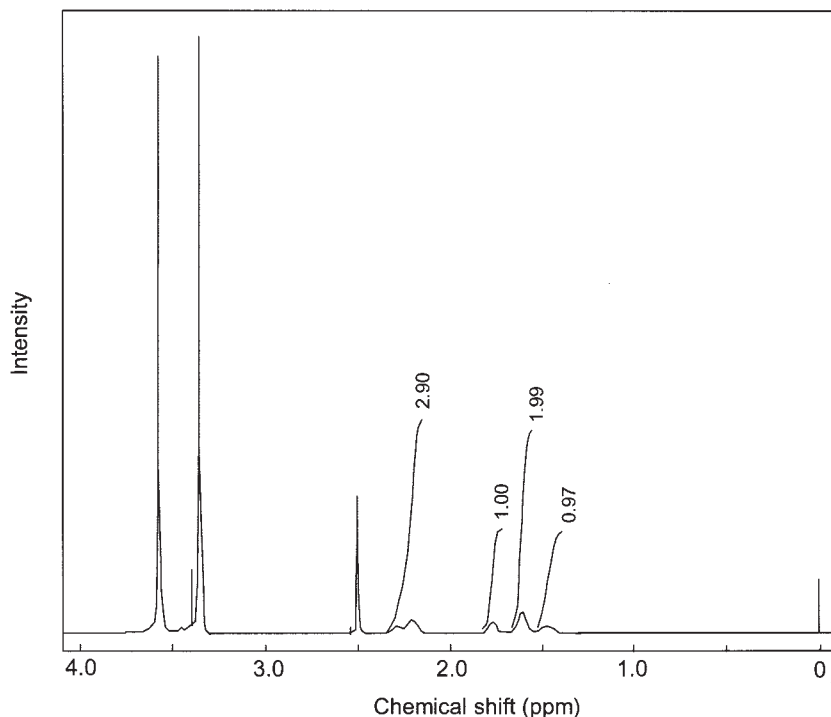
Figure 4 The integral curve of ^{1}H-NMR spectrum of poly(MA-*co*-SAS). The polymerization conditions were the same with Figure 3.

Mechanical properties of PMGCF

In actuality, polymer electrolytes often work together with metal ions, such as transition metals or lanthanides, to prepare functional materials as mentioned in Introduction section. Therefore, it is important to investigate the influence of metal ions on mechanical properties of the copolymer. In this work, copper was investigated as a typical example.

In principle, Cu^{2+} interacts with both carbonyl and sulfonic groups in polymer chain through complex.[20] The mechanical properties of the composites between Cu^{2+} and poly(MA-SAS) are surely affected by Cu^{2+} salt. Referring to the original solution compositions of ternary mixtures of poly(MA-SAS), DMF, and Cu^{2+} salt in Table I, the tensile experimental records of unreduced SCFs of samples 1 and 2 are listed in Table II, and the relationships between tensile stresses and

strains of SCFs (samples 1 and 2) and PMGCFs (samples 3 and 4) are listed in Table III.

In Table III, the difference of the maximum loadings and breakage extensions between SCFs is distinct. The maximum loading increased to 3447 from 1653 cN, corresponding to ratios of Cu^{2+} to copolymer 1 : 10 and 1 : 5, respectively. Therefore, with the increase of copper content, the maximum loading increases. This is due to the complex of the Cu^{2+} with carbonyl and sulfonic groups, whereas, the breaking extensions decreased to 8.31 from 8.89%, correspondingly. The Young's modulus of the two samples was 0.3821 and

TABLE I
Two Samples of Composite Film with Different Contents of Copper Salt

Samples	DMF (mL)	Polymer[a] (g)	$CuCl_2 \cdot 2H_2O$ (g)	Ratio of Cu^{2+}
Sample 1	25	5.0	0.5	10:1
Sample 2	27	5.0	1.0	5:1

[a] Represents that the constitutional unit ratio of MA and SAS in the polymer is 3:1.

TABLE II
Tensile Experiment Data of Samples 1 and 2

	Breaking stress (cN)	Breaking strain (%)	Modulus (MPa)
Sample 1			
1	1750	889	0.3006
2	1256	935	0.4091
3	1952	843	0.4366
Avg.	1853	889	0.3821
Sdv.	358	46	0.0719
Sample 2			
1	3540	821	0.6422
2	3412	830	0.5828
3	3389	842	0.6213
Avg.	3447	831	0.6154
Sdv.	81	10.54	0.03013

TABLE III
Data of Tensile Experiments of SCFs and PMGCFs

| | Stress 0 (cN) | | | |
| | SCFs (unreduced) | | PMGCFs (reduced) | |
Strain ε	1	2	3	4
0	0	0	0	0
1.0	324	593	484	559
2.0	403	788	581	628
3.0	504	1013	678	816
4.0	644	1350	862	1036
5.0	792	1740	1007	1325
6.0	1015	2175	1162	1539
7.0	1289	2663	1355	1689
8.0	1548	3150	1549	1915
8.31*	/	3447*	/	/
8.5	1598		1750	2041
8.89*	1653*		/	/
9.0			1936	2198
9.5			2200	2330
10.0			2323	2569
10.5			2720	2826
10.86*			/	3104*
11.0			3001	
12.0			3824	
13.0			4869	
13.18*			4935*	

Asterisks indicates stresses at the point of breakage.

0.6153 MPa, respectively, which drop in the rubber elastic range of 0.02–0.8 MPa. And so, samples 1 and 2 showed elasticity. This offers a prerequisite for obtaining a polymer–matrix metal composite with good mechanical properties.

It has been for years that PMGCF was investigated by solution reduction synthesis by our group. In this work, PMGCFs are samples 3 and 4 in Table III that were reduced from SCFs. Their mechanical data were listed in 3rd and 4th columns in Table III, in which the orderliness of maximum loadings and breakage extensions are different from unreduced samples (samples 1 and 2).

In Table III, one can find that the maximum loadings of PMGCFs corresponding to samples 3 and 4 are 4935 and 3104 cN. That is, sample 3 has higher tensile strength. In the two PMGCFs, copper was reduced, and the complex between the copolymer and copper was weakened. This indicated that samples 3 and 4 have different determinable factors in these two cases, compared with samples 1 and 2. This would not suggest us to understand the change of mechanical properties according to complex interaction, whereas, the structural factor of the copolymer plays an important role. In samples 3 and 4, the molar ratios of MA to SAS are 2 : 1 and 3 : 1, respectively. Sample 3 contains more sulfonic group, which has stronger polarity that causes higher interaction among macromolecules, and thus the higher tensile strength of the sample. Accompanying it, the rigidity of the sample was

also strengthened. On the other hand, the group of acrylic ester is propitious to elasticity of the copolymer. Therefore, the distinct yield behavior and higher elastic deformation were observed regarding sample 4.

According to the analysis, we can summarize that different status of copper, such as Cu^{2+} or Cu^0, has different influence on mechanical properties of SCFs and PMGCFs.[21]

CONCLUSIONS

Based on the important applications of elastic polymer electrolyte, a binary copolymer of MA and SAS, poly(MA-co-SAS), was synthesized by an aqueous-phase method using KSP as an initiator. The polymerization took place in continuous aqueous phase, in which the monomers were supplied from both dissolved status and micelle drops as dispersed phase. It is different from the traditional emulsion and suspended polymerizations, both of which occur in dispersed phases where micelles and hydrophobic drops of monomers correspond to emulsion and suspended polymerization, respectively.

The content of copper salt influences mechanical properties of composite film. The presence of elasticity in tensile process of the composite film offers a prerequisite for obtaining polymer–matrix metal gradient composite with good mechanical properties.

References

1. Gray, M. F. Polymer Electrolytes; Royal Society of Chemistry: Cambridge, 1997; p 8.
2. Tessler, N.; Harrison, T. N. Friend, H. R. Adv Mater 1998, 10, 64.
3. Carpi, F.; Chiarelli, P.; Mazzoldi, A.; Rossi, D. De. Sens Actuators A 2003, 107, 85.
4. www.azom.com/news.asp?newsID=1353, Azom.com, visited on 23 October 2004.
5. Jager, W. H. E.; Smela, E.; Inganas, O. Science 2000, 290, 1540.
6. Seki, M.; Sato, K.; Yosomiya, R. Die Makromolekulare Chemie 2003, 193, 2971.
7. Kim, H. S.; Choi, J. K.; Bae, Y. C. J Appl Polym Sci 2001, 81, 948.
8. http://atlas-conferences.com/c/a/n/b/44.htm: 2nd European Workshop on Structural Health Monitoring, July 7–9 2004, Amazeum Conference Centre at Deutsches Museum, Munich, Germany.
9. Hamade, R. F. D.; Dillard, A. J Adhes Sci Tech 2003, 17, 1235.
10. Paoli, M.-A. De.; Gazotti, W. A. J Braz Chem Soc 2002, 13, 410.
11. www.parker.com/chomerics/lit/emicat/conductive elastomer design. pdf, Chomerics Company website, visited date: 10 October 2004.
12. Stevens, M. P. Polymer Chemistry: An Introduction; Oxford University Press: New York and Oxford, 1990; p 196.
13. Pan, Z. Polymer Chemistry (in Chinese); Press of Chemical Industry: Beijing, 1997; p 72.

14. Huang, C.; Song, W.; Xu, B.; Gu, W. Synt Fibers (in Chinese) 1993, 22, 15.

15. Williams, D. H.; Fleming, I. Spectroscopic Methods In Organic Chemistry; Elsevier: Amsterdam, 1973; p 210.

16. Potts, J. W. Chemical Infrared Spectroscopy; Wiley: New York, 1963; p 1.

17. Dolphin, D. Tabulation of Infrared Spectral Data; Wiley: New York, 1977.

18. Zhu, M. Instrument Analysis; Higher Education Press: Beijing, 1985; p 332–348, 362–392.

19. Wu, Y Organic Structural Analysis (in Chinese); Press of China University of Science and Technology: Hefei, 1993; p 193.

20. Khandwe, M.; Bajpai, A.; Baipai, U. D. N. Macromolecules 1991, 24, 5203.

21. Tang, J.; Hu, K.; Guo, D.; Liu, H.; Zheng, Z.; Guo, W.; Du, S.; Zhou, Y.; Wu, R. J Appl Polym Sci 1999, 74, 1927.