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Synthesis and characterization of aniline and aniline-*o*-sulfonic acid copolymers

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Abstract

The copolymer of aniline (An) and aniline-*o*-sulfonic acid (AS) is synthesized by chemical oxidation polymerization. The effects of mole ratio of copolymerized monomers on chain structure, thermostability, conductivity, redox properties of copolymer are discussed. It is indicated that if more AS monomers in polymerization system the corresponding structure units will increase, but their relation isn't linear. When An:AS = 1:1, the ratio of structure unit in copolymer is 9:1, and it is only 1:2 for copolymer with An:AS = 1:6. The measurements of conductivity and redox activity also prove that the properties of An-*co*-AS(1:1), (1:3), and (1:4) are similar to polyaniline due to more An units than AS. When An:AS is higher than 1:6, it shows out the properties of copolymer is similar to those of poly(aniline-*o*-sulfonic acid), and their redox route is different. They will transform to follow the route of LH ↔ EH ↔ P. The results of thermo-analysis indicate that the decomposition temperature of AS units is lower than An units because of the electron-withdrawing group substitution. The decomposition temperature of polymer is related to dopant and doping degree. Electron-withdrawing group, $-SO_3H$, substitution and HCl doping will decrease polymer chain decomposition temperature. The mechanism of copolymerization of An and AS is different from homopolymerization. The monomer with low oxidation potential forms free radical cation firstly, which transfers to monomer with higher oxidation potential and initiates its polymerization.

Keywords: Conducting polymers; Polyaniline; Copolymerization; Aniline-*o*-sulfonic acid

1. Introduction

The discover of electro-conductive polymer which exists in a system of π- or σ-bonds opens up a new field for application of organic polymer. Polyaniline (PAN) is one of the most studied conjugated polymers due to its simple synthesis method, high electrical conductivity, good environmental stability and peculiar electrical, optical and magnetic properties. But PAN is difficult to dissolve and melt, especially their doping state. It is possible to improve the processability of PAN incorporating functionalized organic acids doping

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like *p*-toluenesulfonic, camphor sulfonic acids. This approach has the problem of the interaction between those external dopants and the conducting polymer backbone. The structure modification of ring substitution is one of another main methods to improve polyaniline solubility. Unfortunately, introduction of ring-substituted groups is detrimental to polymer's conductivity. In order to lessen the effect of substituted group on polymer electric property, many people pay more and more attention on copolymerization of aniline with other substituted aniline [1–6], such as *o*-toluidine [4], *o*-ethyloxyaniline [5], *o*-aminobenzoic acid [6], and so on. Firstly substituted group on macromolecular chain will increase polymer solubility because of lower rigidity of macromolecular chain. Secondly adjusting substituted group density in chain by changing monomer mole ratio is in favor of control its steric and electron effects on polymer electric properties. Furthermore, copolymers of aniline and substituted aniline have been proved to be more conducting than substituted homopolymers and more soluble than PAN. It is well known that monomer polymerization power is related to ring-substituted group properties and its substituted position [7–9]. Monomer reactivity ratio and charging sequence will influence the product's structure, due to different polymerization mechanism of copolymerized monomers.

The hydrophilic group in chain structure will offer polymer water solubility. Furthermore acidic group such as carboxy and sulfonic group on aromatic ring can react with =N– group to form polaron, which is the charge carrier of doping state PAN. The self-doped effect that different from external doped effect of protonic acid will provide higher electrochemical activities and electric conductivity than conventional PAN in non-aqueous or neutral and basic system, because self-protonation is independent of external protonation in a broad pH range and conductivity does not fall off dramatically with increase in pH as happens with PAN. The properties are very important for PAN applied as broader pH sensor. Usually chlorosulfuric acid or fuming sulphuric acid is used as sulphonating agent for sulfonating PAN in some reports [10,11]. But it is difficult to control sulfonated degree and position by this method. It is more perfect to polymerize sulfonated aniline monomer directly, such as aniline-*o*-sulfonic acid. But it is difficult to homo-polymerize because sulfonic group with strong electron-withdrawing and steric effect will increase monomer oxidizing potential. WEI [12,13] considers that monomer with low oxidized potential will catalyze other monomer polymerization with high oxidized potential. In this paper, we synthesize copolymer by copolymerization of aniline with aniline-*o*-sulfonic acid, and discuss the relation between monomers mole ratio and construction unit ratio of macromolecular chain. It is in favor of the design of PAN with different sulfonated degree. Their influences on the structures and properties of copolymer are also considered.

2. Experimental

2.1. Preparation of copolymer of aniline with aniline-o-sulfonic acid

In a 250 ml Erlenmeyer flask 0.02 mol of mixed monomer was mixed with 140 ml of HCl solution (1.0 mol/l) with stirring in room temperature until solid monomer dissolved completely. The mol ratio of aniline (An) to aniline-*o*-sulfonic acid (AS) in mixed monomer is 1:1, 1:2, 1:4, 1:6, or 1:8. Polymerization was initiated by the addition of ammonium persulfate (APS) in HCl solution (1.0 mol/l), which was added over a period 1 h. The reaction mixture was stirred for 12 h, then keeping at 5 °C freezer for 24 h. Then the reaction solution was kept in room temperature to evaporate excessive water. The polymer precipitate was filtered off and washed with HCl solution (1.0 mol/l) for 3–4 times and then with methanol to remove oligomers until filtrate became colourless. When most of the product precipitated out, black powder was obtained. The black powder was dried in a vacuum oven at 60 °C for 48 h. They were labeled as An-*co*-AS(1:1), An-*co*-AS(1:2), An-*co*-AS(1:4), An-*co*-AS(1:6) and An-*co*-AS(1:8).

2.2. An-co-AS structure characterization and properties measurements

The polymer was dissolved in *N*,*N*-dimethyl formamide (DMF, HPLC, spectro), and its molecular weight and distribution were measured by GPC method in Agilent 1100 GPC chromatograph using polystyrene as standard and DMF as mobile phase. Inca Energy 300 X-ray energy dispersive spectrometer (EDS) of Oxford company (Model 7426) was used to measure the element atom ratio of polymer. The FT-IR spectra of the samples were recorded by Nicolet Avatar 360 Fourier Infrared spectrophotometer (FTIR) with KBr pellet technique. Measurement of the electric conductivity was performed by the method of four points technic (Suzhou Baishen SZ 82) and the samples, PAN pellets were obtained under a pressure of 100 MPa. Before measurements, the pellets were drying in a vacuum oven at 50 °C for 8 h. Thermal stability of copolymer was studied by thermogravimetric analysis (TGA) in a METZSCH STA 409EP thermal analyzer. All thermograms were measured under N_2 atmosphere, and heating from room temperature to 1000 °C (10 min °C min^{-1}).

2.3. Preparation of polymer modified electrodes

Polymer modified electrodes were prepared by depositing 3.0 mg ml^{-1} of An-*co*-AS DMF solution on platinum disk electrodes surface and drying in infrared oven for 15 min. The quantity of polymer fixed on the platinum disk surface was of the order of 0.5 mg cm^{-2} [14].

2.4. Electrochemical experiments

Voltammetric experiments were performed with a CHI660 electrochemical workstation. A three-electrode cell was used with a saturated calomel reference electrode (SCE) and a platinum counter electrode. The polymer modified electrodes were as working electrodes.

3. Results and discussion

3.1. Effect of mol ratio of An to AS on copolymer An-co-AS

Table 1 shows out the effect of mol ratio of An to AS (An:AS) on the yield, molecular weight and construction units ratio of copolymer. By increasing AS content, the yield is higher as well as lower molecular weight. When An:AS is 1:1 or 1:2, the molecular weight of copolymer is similar to PAN. As the ratio lower than 1:4, molecular weight decreases evidently. EDS is used to analyze the elements atom ratio of copolymer. Results of EDS show that the ratio of C atom to S atom is 59.95 in An-*co*-AS(1:1). It is well known that one AS unit contains one S atom and six C atoms. According to EDS results, the ratio of An unit to AS unit in copolymer molecular chain can be calculated by the following formula:

$$\text{An/AS} = (\text{C/S} - 6)/6.$$

The ratio for An-*co*-AS(1:1) is 9:1, and that for An-*co*-AS(1:4) is 5:1. It is indicated that when An:AS is in the range of 1:1 to 1:4, most structure units in copolymer are An. Oppositely, every An unit corresponds to two AS unit in An-*co*-AS (1:6). Evidently, most structure units are AS in An-*co*-AS (1:6) and An-*co*-AS (1:8). So their properties are similar to poly(aniline-*o*-sulfonic acid), showing out low conductivity and molecular weight. It is proved that the structure unit ratio of copolymer can be controlled by adjusting monomer mol ratio during copolymerization. But their relation is not linear, and necessary to be discussed in detail.

Sulfonic group with strong electron-withdrawing and steric effect will increase aniline monomer oxidizing potential. So it is difficult to form free radical cation to initiate polymerization. When there is more aniline in mixed monomer, aniline is easier to polymerize, and tends to homopolymerization. As a result, the product, with most An units in chain will show out properties similar to polyaniline. If there is less An in mixed monomer, aniline monomer will form free radical cation firstly, which will transfer to another monomer, AS. So the homopolymerization of aniline is hindered and the reaction yield is low. When AS content increases to some extent, such as An:AS = 1:6, the transfer of aniline free radical cation will initiate AS polymerization

Table 1
Effects of ratio of An to AS on An-*co*-AS

Mole ratio of An to AS	Yield (%)	Number molecular weight M_n	M_n distribution D	C:S elements atom ratio	C:Cl elements atom ratio	An:AS construction unit ratio
1:0	82.7	9.307×10^5	2.08	–	–	–
1:1	11.47	8.396×10^5	2.12	60	49	9:1
1:2	26.93	8.153×10^5	2.25	–	–	–
1:4	41.56	1.302×10^5	2.41	34	114	5:1
1:6	53.17	9.282×10^4	2.78	9	534	1:2
1:8	58.52	5.831×10^4	3.05	–	–	–

in high yield [15]. The results agree with the theory introduced by WEI [12,13] that monomer with low oxidized potential will initiate the polymerization of monomer with higher oxidized potential. At the same time, the ring-substituted groups decrease the electron spin density of N and C_4 atom, which is unfavour to "head-tail" coupling [16–18], and molecular weight distribution of product widen when AS monomer increasing.

EDS analysis results of atom ratio of C to Cl atom show out that the content of Cl atom is less when more AS constructure units in copolymer. It is indicated that HCl doping content decreases because the self doping reaction of $-SO_3H$ group with =N– group prevents the combination of HCl to molecular chain. But during preparation of sample in vacuum, the volatilization of HCl will reduce element Cl content. So the EDS results can not reflect real HCl doping content.

3.2. *Effect of mole ratio of An to AS on chain structure of copolymer*

FTIR spectra for PAN synthesized in HCl media are shown in Fig. 1. The characteristic IR spectrum absorption bands are around 1588 cm^{-1} and 1498 cm^{-1}, corresponding to stretching of N=Q=N of quinonic rings and N–B–N of benzenic rings respectively. The single peak at 830 cm^{-1} indicates An polymerizes in its para-position. After PAN doped with HCl, the stretching of N=Q=N of quinonic rings and N–B–N of benzenic rings all red shift to 1558 cm^{-1} and 1489 cm^{-1}, because the delocalization of positive charge of $-NH^{+}=$ group deduces electron cloud density of aromatic ring. The red shift degree of N=Q=N absorption band is higher than N–B–N since the effective doping position is on nitrogen atom near quinoid unit.

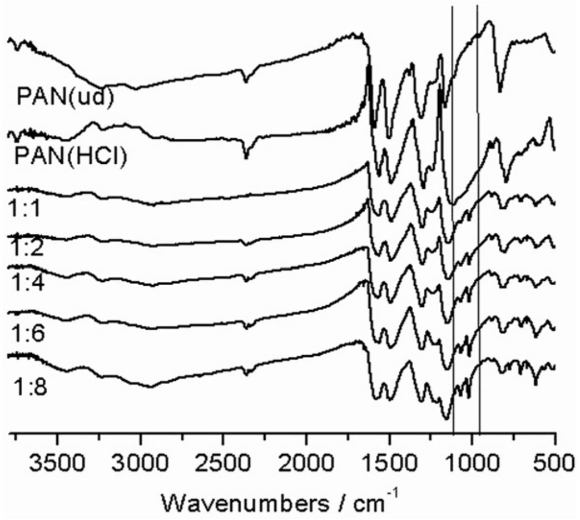

Fig. 1. FTIR spectra of intrinsic and doping state polyanilines and An-*co*-AS with different monomer mole ratio of An to AS.

We also compare FTIR spectra of coploymer in Fig. 1 synthesized in different mole ratio of An to AS condition. In comparison with PAN, the spectra of copolymer show out four new peaks located at 1069, 1020, 614 and 706 cm^{-1}. The peaks of 1069 cm^{-1} and 1020 cm^{-1} are related to symmetric stretching of SO_3 group. Among them, 1069 cm^{-1} is about stretching of Ar–S bond, and 1020 cm^{-1} is about stretching of S=O bond. 614 cm^{-1} and 706 cm^{-1} are related to special stretching of S–O and C–S bond. We also find the strength of the four peaks increase with more AS unit, especially the two peaks of 1069 and 1020 cm^{-1}. It is described that more AS monomer in reaction system will increase sulfonated degree of copolymer.

It is evident that the wavenumber of stretching of N=Q=N of quinonic rings and N–B–N of benzenic rings of copolymer synthesized in HCl media are between that of doping state and intrinsic PAN (Table 2). The steric of sulfonic acid group will hinder HCl from reacting with –N= group, resulting in low HCl doping degree. The results agree with EDS analysis as mentioned above. Although $-SO_3H$ possesses self-doping effect, it will decrease the electron cloud density of quinoid ring and its mechanical constant. In a word, the repulsive interaction of sulfonic acid group and Cl^- and its steric will lead to copolymer less red shift degree than PAN(HCl) and higher blue shift degree than PAN(ud) if more AS unit ratio in copolymer.

Table 2
The characteristic bands of An-*co*-ASs and PAN

Polymer	$V_{N=Q=N}$ (cm^{-1})	V_{N-B-N} (cm^{-1})	N=Q=N characteristic vibration
PAN(HCl)	1558	1488	1113
An-*co*-AS(1:1)	1561	1489	1145
An-*co*-AS(1:2)	1567	1489	1143
An-*co*-AS(1:4)	1568	1491	1150
An-*co*-AS(1:6)	1567	1495	1150
An-*co*-AS(1:8)	1580	1495	1151
PAN(ud)	1588	1498	1162

3.3. Effect of mole ratio of An to AS on conductivities of copolymers

The conductivities of different copolymers are shown in Table 3. Although the conductivities of copolymer decrease in the sequence of An-*co*-AS(1:1), An-*co*-AS(1:2), An-*co*-AS(1:4), their conductivities all locate in the range of 10^{-1}–10^{-2} S cm^{-1}, close to pure PAN synthesized in the same condition. Particularly, the conductivities of An-*co*-AS(1:6) and An-*co*-AS(1:8) are greatly lower than An-*co*-AS(1:4), only about 10^{-4} S cm^{-1}. It is further proved that in the molecular chain of copolymer of An-*co*-AS(1:1), An-*co*-AS (1:2) and An-*co*-AS (1:4) most construction units are aniline. On the contrary there are most AS units in An-*co*-AS(1:6) and An-*co*-AS(1:8), showing out low conductivities similar to poly-*o*-sulfonic aniline.

3.4. Effect of mole ratio of An to AS on thermal stabilities of copolymers

The thermal stabilities of copolymers were studied by TGA. Fig. 2 shows that, An-*co*-AS(1:1) starts to loss weight at the beginning of heating until temperature reaches 106 °C, and the weight loss is 10%, which due to H_2O deprivation. In the range of 106–265 °C, the weight loss is 18.3%, corresponding to doping acid HCl deprivation. From 265 °C polymer chain begins to degrade until 620 °C. The weight loss of An-*co*-AS(1:2) is 8%, corresponding to HCl deprivation in the range of 135–225 °C. Then the polymer begins to degrade. The curve is divided into two parts in 300 °C, and the forepart weight loss is near 15%. It is because the copolymer chain makes up of two kinds of structure unit. In the curve of An-*co*-AS(1:4), there is only 4 wt% loss of HCl, and the forepart before 323 °C of polymer degradation stage loss is 18 wt%. For An-*co*-AS(1:6), in the range of room temperature to 277 °C, the weight loss is only 5%, corresponding to HCl and H_2O volatilize. And the weight losses 46% in 294–370 °C and 47% in 370–620 °C, which all corresponding to polymer degradation. As mentioned above, there is only one step of molecular chain degradation for An-*co*-AS(1:1), and the molecular chain degradations of An-*co*-AS(1:2), An-*co*-AS(1:4) and An-*co*-AS(1:6) are all divided into two steps. Their forepart weight loss increases in the same sequence. As discussion about structure unit ratio of copolymer in §3.1, it is indicated that the forepart weight loss corresponds to AS unit degradation. Electron-withdrawing group substitution will decrease polymer chain decomposition temperature.

Table 3
Effects of ratio of An to AS on the conductivities of An-*co*-AS

Mole ratio of An to AS	Conductivityσ (S cm^{-1})
1:0	0.14–0.18
1:1	0.07–0.15
1:2	0.06–0.11
1:4	0.03–0.095
1:6	0.24×10^{-3}–0.54×10^{-3}
1:8	0.21×10^{-3}–0.42×10^{-3}

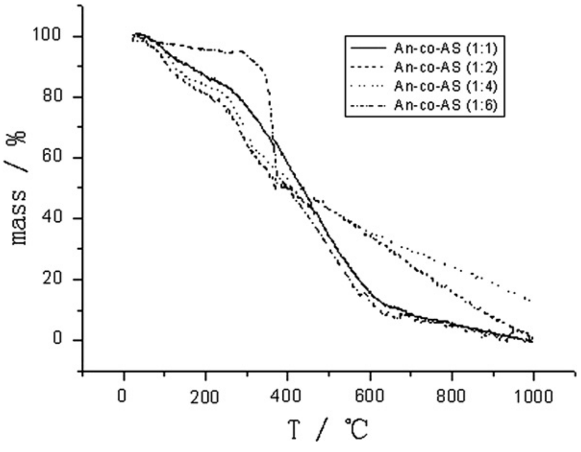

Fig. 2. Thermogravimetric curves of An-*co*-AS with different monomer mole ratio of An to AS.

Furthermore the weight loss of HCl deprivation is less and less by increasing AS units in copolymer, which meets EDS analysis results above. The transition temperature of the two parts of polymer decomposition locates in 300, 323, and 370 °C, respectively for An-*co*-AS(1:2), An-*co*-AS(1:4) and An-*co*-AS(1:6), corresponding to the decomposition temperature of PAN. It is proved that HCl doping will conduce to PAN molecular chain decomposition. As a result, the decomposition temperature decreases.

In TGA and DTA curves of intrinsic state PAN (Fig. 3), polymer starts to loss weight at the beginning of heating until temperature reaches 117 °C, and the weight loss is 9%. There is an endothermic peak of absorbed H_2O deprivation in 102 °C. The polymer chains begin to degrade from 330 to 680 °C. The strong exothermic peak in 550 °C is caused by PAN chain degradation. The degradation of PAN(HCl) is also divided into two parts. The weight loss in the range of 141 to 283 °C is caused by HCl deprivation. And there is a corresponding

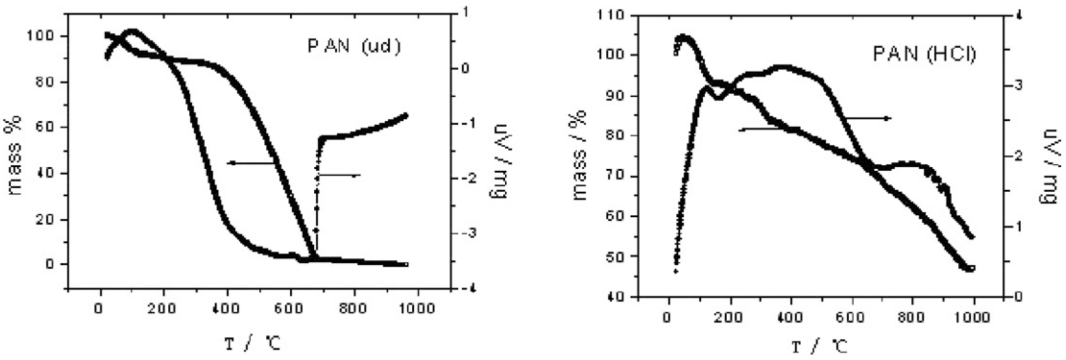

Fig. 3. TGA and DTA curves of mother polyaniline.

endothermic peak in 250 °C. The macromolecular chain begins to degrade from 283 °C. And until 1000 °C it still does not decompose completely. In comparison with intrinsic state PAN, decomposition temperature of PAN(HCl) chain descends 47 °C. The decomposition temperature of PAN is about 300 °C. It conforms the results of An-*co*-AS copolymer, the backpart chain decomposition step is caused by PAN degradation. It has been reported that the decomposition temperature of PAN chain is in the range of 270–370 °C [19–22], which is related to the molecular weight, dopant and doping degree.

3.5. Effect of mole ratio of An to AS on redox behavior of copolymers

It is well established in literature that PAN both in doped as well as intrinsic state can exist in three different discrete oxidation states at the molecular level depending on the relative number of benzinoid and quinoid units in the polymer. These states are known as completely reduced leucoemeraldine (L), intermediate emeraldine (E) and fully oxidized pernigraniline (P) state, which are become LH, EH and PH state after doped, respectively. Their redox processes have two kinds of routes as Fig. 4A and B.

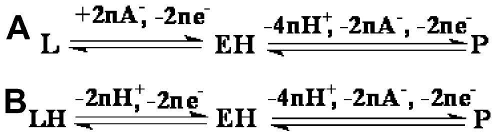

Fig. 4. Redox routes of polyaniline and its derivatives.

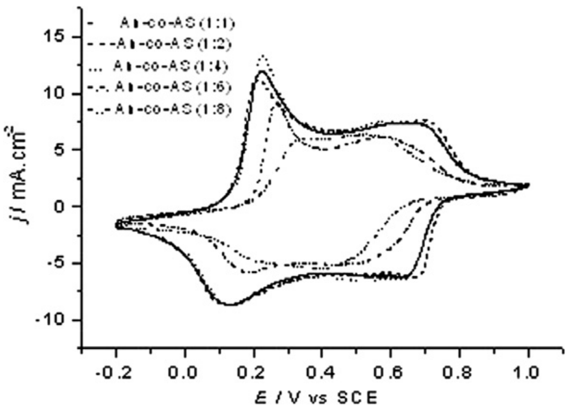

Fig. 5. Redox behavior of different An-*co*-AS modified electrodes in 1.0 mol/l $HClO_4$ media (Scan rate: 50 mV s^{-1}).

Fig. 5 is the CV curves of An-*co*-AS copolymer in 1.0 mol/l of $HClO_4$ media. It shows out that the redox potential of An-*co*-AS(1:1), An-*co*-AS(1:2) and An-*co*-AS(1:4) is similar to PAN, whose L/E transition potential (E_1) is 0.18 V and E/P transition potential (E_2) is 0.7 V. But E_1 of An-*co*-AS(1:6) and An-*co*-AS(1:8) is positive shift and E_2 is negative shift. The steric hindrance and withdrawing electrons from aromatic rings of sulfonic group could lead to an increase in the energy barrier to polaron formation, i.e., difficulty in oxidation of nitrogen atoms, resulting in more positive E_1 values than in PAN. In many cases of the ring-substituted PAN derivatives, E_2 is negative shift, such as poly-*o*-toluidine, poly-2,5-dimethoxyanilie, poly-*m*-choloraniline, aniline and 2-aminoterephthalic acid copolymer [8,23]. The lower positive potential necessary for the formation of the fully oxidized state (P) can be due to its stabilization by the electron donation effect of methyl and methoxy groups [24]. But the substitute group of poly-*m*-choloraniline and sulfonated polyaniline is electron withdrawing. The behavior could be explained by

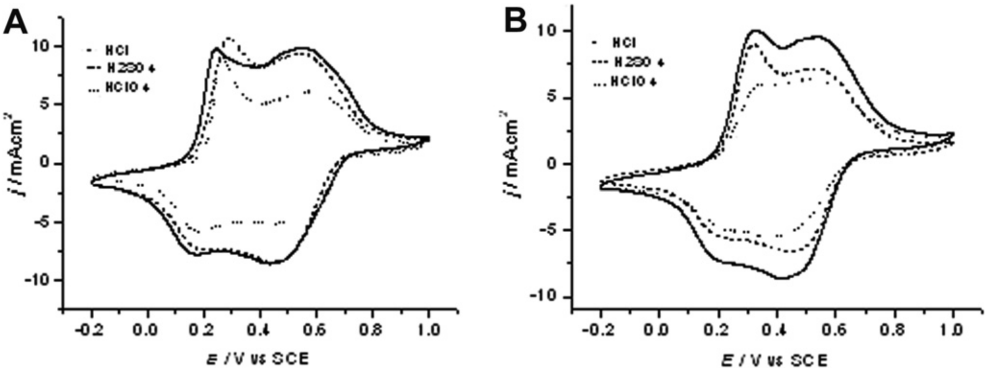

Fig. 6. Redox behavior of An-*co*-AS(1:6) (A) and An-*co*-AS(1:8) (B) modified electrodes in different acid media (Scan rate: 50 mV s^{-1}).

formation of iminic nitrogens with a wider angle to release the steric strain, which discharges the steric tension, leading to a lower E_2 for the second redox process [25]. At the same time their redox currents also decrease. They are also due to the difference of the ratio of two kinds of structure units, An and AS.

Fig. 6 is the CV spectra of An-*co*-AS(1:6) and An-*co*-AS(1:8) in different acid media. In 1.0 mol/l H_2SO_4 media, there are two pair redox peaks of An-*co*-AS(1:6) in 0.29/0.17 V and 0.56/0.45 V, while the two pairs of redox peaks of An-*co*-AS(1:8) are in 0.32/0.23 V and 0.53/0.43 V. L/E transition potential will shift positively and E/P transition potential shift negatively if there are more AS units in copolymer system. The reversibility of E/P transition declines due to the greater differences of oxidation and reduction potential. But the difference of the reversibility of two pair redox peak is less. Their redox process of $L \leftrightarrow EH \leftrightarrow P$ will transform to $LH \leftrightarrow EH \leftrightarrow P$.

We had known that the doped Cl^- content decreased by increasing sulfonic group content. So in low potential, L state in H_2SO_4 media is in favor of H^+ embedding into polymer membrane to form LH state if more sulfonic groups in copolymer. Their redox process will transform to follow the route of $LH \leftrightarrow EH \leftrightarrow P$. But the self-doping effect of sulfonic group shown as Fig. 7 can induce polymer to form doping state even if without proton acid. So the effect of pH on the redox process of copolymer with more sulfonic groups is less and the effect of counter-anion is clearer. As a result two pairs of redox peak are less reversible.

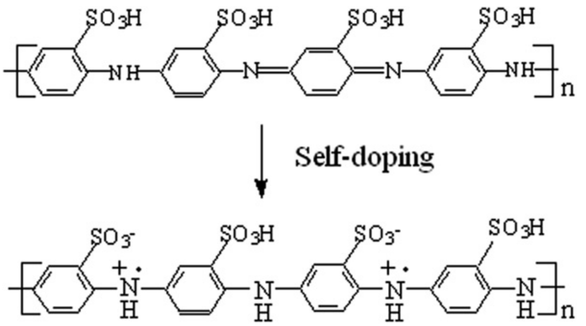

Fig. 7. Schematic plan of the self-doping effect of AS unit in An-*co*-AS copolymer.

By comparison of peak potentials of An-*co*-AS(1:6) and An-*co*-AS(1:8), it is indicated that the redox behavior in HCl media is the same as that in H_2SO_4 media. But in $HClO_4$ media the peak current densities of copolymer are less and peak shape broader. The aggregation state of polymer membrane in acid media is important. The more compact membrane structure polymer in $HClO_4$ is unfavour to anion migration [26].

4. Conclusion

The mole ratio of copolymerized monomers, An and AS will influence chain structure, thermostability, conductivity, redox properties of copolymer. EDS analysis results indicate that when An:AS = 1:1, the ratio of structure unit in copolymer is 9:1, and it is only 1:2 for copolymer with An:AS = 1:6. The measurements of conductivity and redox activity also prove that the properties of An-*co*-AS(1:1), (1:3), and (1:4) are similar to polyaniline due to more An units than AS. When An:AS is higher than 1:6, copolymer shows out properties similar to poly(aniline-*o*-sulfonic acid). The results are related to the mechanism of copolymerization of An and AS, which is different from homopolymerization.

The monomer with low oxidation potential will initiate the polymerization of monomer with higher oxidation potential.

TGA results show out that the decomposition temperature of AS unit is lower than An unit. Electron-withdrawing group, –SO_3H, substitution and HCl doping will decrease polymer chain decomposition temperature.

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