

ELECTRICAL AND MECHANICAL PROPERTIES OF POLYANILINE FILMS —EFFECT OF NEUTRAL SALTS ADDED DURING POLYMERIZATION*

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Abstract The electrical and mechanical properties of polyaniline (PANI) films synthesized by the presence of the selected neutral salts in the polymerization were measured as a function of the properties and the concentration of the selected neutral salts, and the protonation state. It was found that both the electrical and mechanical properties of PANI films were enhanced by adding neutral salts in the polymerization. The adding of the neutral salts in the polymerization resulted in extended conformation of polymer chain and increasing of molecular weight of PANI, which may be the reasons why the electrical and mechanical properties of PANI films were improved by the presence of neutral salts in the polymerization.

Keywords Polyaniline; Electrical and mechanical properties; Neutral salts

INTRODUCTION

Polyaniline (PANI) as the oldest known conducting polymer has attracted attention due to its various structures, unique electrical properties, special doping mechanism, good stability in air and aspect of application in the technology. Recently, Adams et al.^[1] reported that room-temperature conductivity of protonated PANI films has been greatly enhanced by using an improved synthetic method. The improved synthetic method was using lithium chloride (LiCl) as soluble neutral salt to keep the reaction mixture mobile, resulting in lower reaction temperature (such as $\sim -30^{\circ}\text{C}$). They suggested that the enhanced conductivity of PANI films synthesized by the improved method may be due to an increasing of molecular weight of the final polymer. At the same time, Mattoso et al.^[2] reported that the molecular weight of PANI can be substantially increased by the presence of selected soluble neutral salts. These results indicated that the influence of the selected soluble neutral salts added during polymerization is not only on the reaction temperature (down to -30 and -40°C), but also on the molecular weight of the final polymer. Therefore, it is expected that the mechanical properties of PANI films would be improved by the

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presence of selected neutral salts during polymerization. However, no paper concerning neutral salts resulting in improvement of mechanical properties of PANI has been published in the literature.

In this article, the electrical and mechanical properties of free standing film of PANI were measured as a function of concentration of several selected salts, the protonation state and elongation ratio. Results obtained are compared with that of PANI films synthesized by conventional method.

EXPERIMENTAL

Synthetic method for the emeraldine base powder was similar to general method reported by MacDiarmid et al.^[3], but it was modified by adding dissolved neutral salts to the polymerization. Typical synthetic processes of the improved method are as follows: aniline monomer (10 ml, 0.11 mol.) containing the selected neutral salts, such as LiCl, was dissolved in 1.0 mol/L HCl aqueous solution. Then, the above solution reacted with ammonium persulphate (23 g dissolved in 40 ml deionized water) as the oxidant to obtain the emeraldine salt form of PANI. In this experiment, ratio of aniline monomer to ammonium persulphate was kept 1:1 in mol; and the selected neutral salts, such as LiCl, KCl and NaCl, were used. The resulting emeraldine base form of PANI synthesized by the improved method was dedoped with $\text{NH}_3 \cdot \text{H}_2\text{O}$ to the emeraldine base form of PANI. It was found that the freezing point of mixed solution of aniline monomer with neutral salts depends on the kind and concentration of selected neutral salts. A typical temperature variation of mixed solution with the concentration of LiCl salt is shown in Fig. 1. It shows that freezing point decreases with the increase of the concentration of used salt, which is consistent with observations reported by Adams et al.^[1]. In our experiment, the freezing point of mixed solution varied between -6°C and -20°C depending on the concentration and properties of salts used. Moreover, the reaction variation of freezing point was slightly increased after adding oxidant into the mixed solution, but the temperature with the concentration of neutral salts did not change, as shown in Table 1.

Table 1 Effect of selected neutral salts on the temperature of solution before and after adding oxidant

Concentration (mol/L)	Temperature after adding oxidant ($^\circ\text{C}$)			Temperature before adding oxidant ($^\circ\text{C}$)		
	LiCl	NaCl	KCl	LiCl	NaCl	KCl
0.55	-6.0	-7.0	-6.0	-8.2	-7.5	-7.1
1.09	-10.0	-9.0	-10.0	-11.2	-9.4	-11.5
1.65	-11.4	-10.2	-10.0	-13.0	-11.5	-12.0
2.18	-12.0	-15.0	-10.2	-14.0	-16.0	-12.0
5.80	-18.0	-18.0	-16.0	-20.0	-20.4	-18.0

The free standing film of the emeraldine base form of PANI was prepared by evaporating the solution of the emeraldine base form dissolved in NMP at $70 \sim 80^\circ\text{C}$ as described in previous articles^[4]. Oriented PANI film was obtained by a home-made drawing meter at about 80°C . The elongation ratio was determined by l/l_0 , where l_0 and l are the length of samples before and after drawing, respectively. Unoriented and oriented PANI films with different protonation states were obtained by treating their base form with aqueous HCl solution of different acidity. The degree of the protonation state was determined by a pH meter (5—10 A model). The electrical properties of PANI films were measured as a function of the elongation ratio, protonation states, properties and concentration of neutral salts used. The conductivity of PANI films at room temperature was measured by a four-probe method using KEITHLY 196 SYSTEM DMM Digital Multimeter and a R6142 programmable DC Voltage/Current Generator. Conductivity anisotropy for oriented PANI films was determined by a Montgomery method^[5]. Mechanical properties of PANI films were measured by using a model INSTRON 1122. Rectangle samples with 20 mm in length and 4 mm in width were used for measurement of mechanical properties.

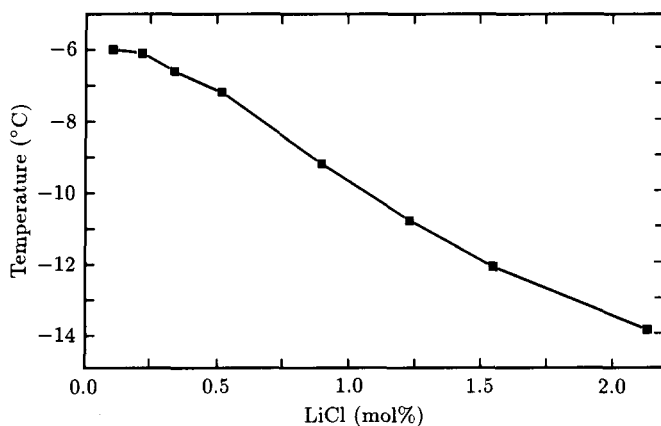


Fig. 1 Dependence of freezing point of aqueous acid solution of aniline monomer mixed with LiCl on the concentration of LiCl

RESULTS AND DISCUSSION

Electrical properties

It is found that the room-temperature conductivity of powder and film of PANI with high protonation state (e.g. $\text{pH}=1$) slightly depends on the properties and concentration of the selected neutral salts as shown in Fig. 2. It shows that the conductivity of PANI films at room temperature is one order of magnitude higher than that of powder samples. This is consistent with the observations obtained from

conventional method^[4]. The dependence of the conductivity of PANI films on the protonation state compared with conventional method is shown in Fig. 3. As we can see that the variation of conductivity with the protonation state for PANI films synthesized by the presence of neutral salts is quite different from the observation without neutral salts^[6-7]. For given concentration of salts (e.g. 2.18 mol), firstly, the variation of conductivity with the protonation for the PANI films is weaker than that of PANI films synthesized by conventional method, and it is independent of variation of selected salts. Secondly, the conductivity of PANI films is enhanced by the addition of neutral salts depending on the protonation state. Compared with conventional method, the conductivity of PANI films is also only enhanced by one order of magnitude in the metallic region (e.g. pH=1 and 0), but it is significantly enhanced by four to five orders of magnitude in the semiconducting region (e.g. pH=3 and 4). In the insulating region (e.g. pH $\geq$ 5), conductivity of PANI films is two orders of magnitude higher than that of conventional method. It was found that the polaron peak at 950 nm in the UV-Vis. absorption for the emeraldine base form of PANI films was shifted to long wavelength with "long tail", which is a metallic behavior^[8], and the position of this peak slightly depends on the neutral salts. Thus, the "long tail" in the absorption indicates not only a higher density of free electrons,

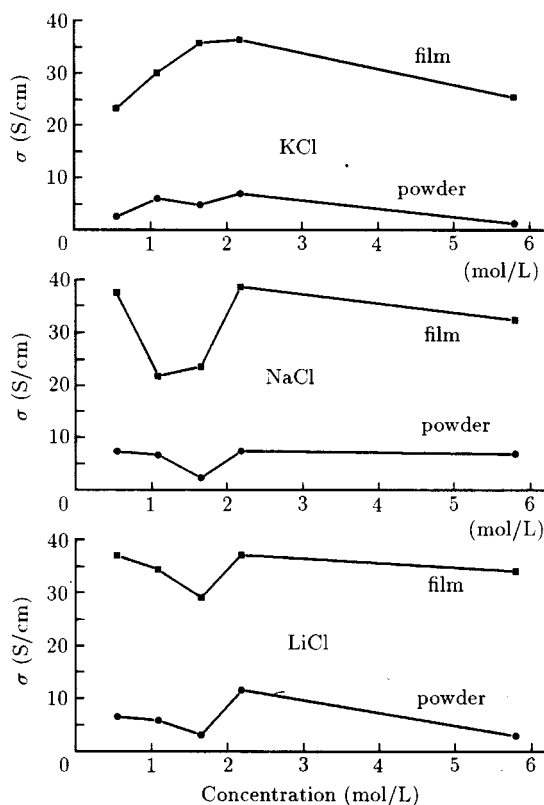


Fig. 2 Influence of selected neutral salts on the conductivity of PANI at room-temperature

but also the change of conformation of PANI film caused by the presence of the selected neutral salts. This may be the reasons why the electrical properties of PANI films are improved by this method.

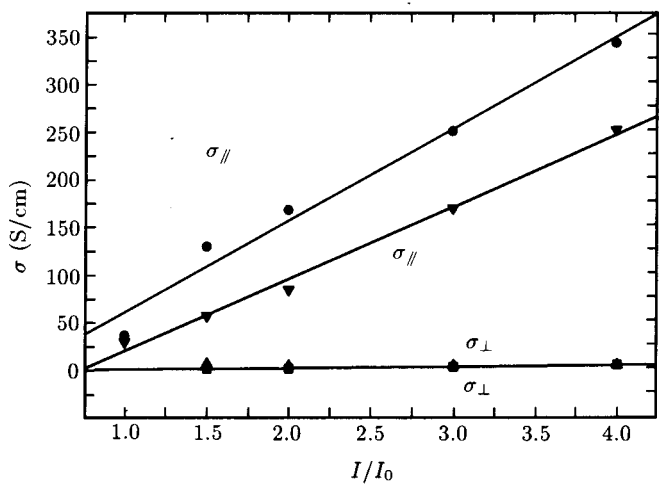


Fig. 3 Dependence of the conductivity of PANI films synthesized by the addition of different neutral salts on the protonation state
● 0.55 mol/L LiCl; ▼ 1.09 mol/L KCl; ▲ 0.55 mol/L LiCl; ■ 1.09 mol/L KCl

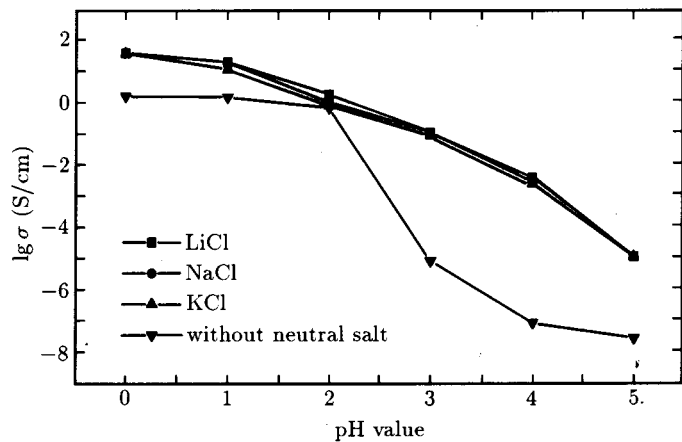


Fig. 4 Conductivity anisotropy of PANI films synthesized by the addition of different neutral salts

Conductivity anisotropy for oriented PANI films synthesized in the presence of neutral salts was observed, as shown in Fig. 4. It is clearly seen that the conductivity along the elongation direction is nearly in a linear relationship to the elongation ratio. However, the conductivity perpendicular to the elongation direction is independent of the elongation ratio. This is consistent with the observations from oriented PANI films synthesized in conventional method^[9]. Moreover, a maximum conductivity at

room temperature is able to achieve up to 350 S/cm with conductivity anisotropy as high as 100:1 for 4:1 stretched samples synthesized by the presence of 0.55 mol/L LiCl salt. The conductivity anisotropy for oriented PANI films synthesized by the improved method is much higher than that of conventional method^[9], although its maximum conductivity is the same as that without neutral salt.

Mechanical properties

As we know, the mechanical properties of PANI films synthesized by conventional method, such as Young's modulus (E), tensile strength (σ) and elongation at break ($\Delta l/l_0$) are estimated to be 1.5 ~ 2.2 GPa, 87.9 ~ 110 MPa and 8 ~ 10.2%, respectively^[10-11]. Compared with PANI films synthesized by conventional method, the Young's modulus and elongation at break are greatly enhanced as shown in Table 2. Moreover, it shows that the mechanical properties, such as Young's modulus, tensile strength and elongation at break strongly depend on the concentrations and properties of selected neutral salts. The presence of neutral salts during polymerization results in improvement of elongation at break of PANI films, this might be due to the extending of polymer chain. As shown in Table 2, the maximum tensile strength, $\sigma = 106.3$ MPa for 0.55 mol/L LiCl salt, the maximum Young's modulus $E = 41.0$ GPa for 1.65 mol. KCl, and the maximum elongation at break, $\Delta l/l_0 = 80\%$ for 1.09 mol/L KCl are observed, respectively. This suggests that the

Table 2 Effect of neutral salts on the mechanic properties of PANI films

Concen- tration	LiCl			NaCl			KCl		
(mol/L)	E^a (GPa)	σ^b (MPa)	$\Delta l/l^c$ (%)	E (GPa)	σ (MPa)	$\Delta l/l$ (%)	E (GPa)	σ (MPa)	$\Delta l/l$ (%)
0.55	36.5	106.3	50	22.5	95.5	48	29.5	65.0	46
1.09	27.0	89.3	50	34.0	98.4	50	26.5	71.1	80
1.65	26.0	86.4	40	28.0	70.0	56	41.0	73.5	46
2.18	28.5	98.4	52	18.0	72.4	60	25.0	75.0	44
2.73	24.0	—	64	—	—	—	—	—	—
5.80	29.0	72.5	44	31.5	73.5	64	33.0	77.2	56

a: Young's modulus; b: Tensile strength; c: Elongation at break, $E = 1.5 \sim 2.2$ GPa, $\sigma = 87.9 \sim 110$ MPa, $\Delta l/l = 8.0 \sim 10.2\%$ for PANI films synthesized by conventional method. (see Reference [10, 11])

mechanical properties of PANI films might be improved by the presence of mixed neutral salts in polymerization. It is very interesting to find that the mechanical properties of PANI films are significantly modified by the presence of mixed salts of LiCl and KCl with 1:1 ratio as shown in Fig. 5. The maximum Young's modulus about 140 GPa was achieved when the 1:1 ratio of LiCl to KCl salt was used in the polymerization. This value is one order of magnitude higher than that of LiCl or KCl used separately. On the other hand, the maximum tensile strength and elongation

at break was observed at the same ratio of LiCl to KCl (1:1). These results indicate that the mechanical properties of PANI films can be adjusted by variation of the properties and the concentration of selected neutral salts. Mattoso et al.^[2] reported that the molecular weight of the PANI can be increased by the improved method. Thus, it is reasonable to believe that high molecular weight resulted from adding neutral salts in the polymerization may be a reason that the mechanical properties of the PANI films was enhanced by the improved method.

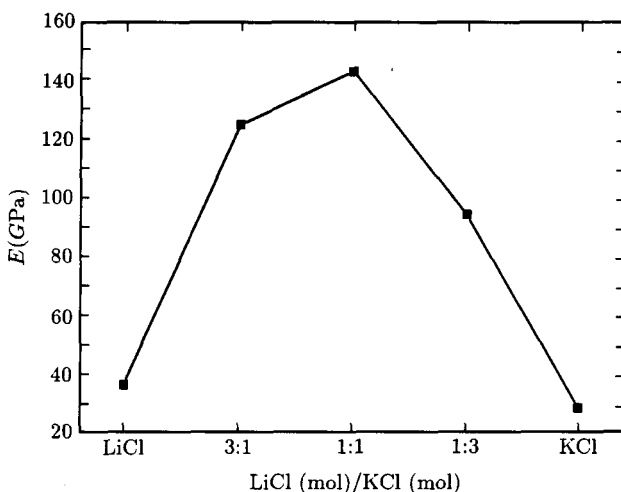


Fig. 5 Effect of mixed neutral salts on the Young's modulus of PANI films

CONCLUSIONS

The electrical and mechanical properties of PANI films synthesized by addition of neutral salts to polymerization were measured as a function of the concentration and properties of selected neutral salts, protonation state and elongation state. The main results obtained are summarized as follows:

1. The conductivity of PANI films at room-temperature can be enhanced by the presence of neutral salts in polymerization. This may be due to an extended conformation of PANI resulted from neutral salts added in the polymerization. As a result, the conductivity along the polymer chain should be increased.
2. Insulator to metal transition caused by proton doping for PANI films synthesized by the presence of neutral salts was observed. The decrease of conductivity with decreasing of doping degree is much slighter than that of PANI films synthesized by conventional method.
3. The mechanical properties of PANI films were enhanced by adding neutral salts in the polymerization. This may be resulted from higher molecular weight of PANI obtained by the improved method.

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