

Preparation of Electrical Conductive Polytoluidine Free-Standing Film

INTRODUCTION

Polyaniline (PAN) and its derivatives with high electrical conductivity and good environmental stability have been studied for more than 20 years.¹⁻⁵ Among these, PAN has been most deeply investigated.^{6,7} Though undissolving in common solvents has limited its investigation and application, PAN promises to have wide uses since Angelopoulos^{7,8} first reported that the free-standing film of the emeraldine base could be obtained by evaporation of a PAN base solution in dimethylsulfoxide, dimethylformamide, or *N*-methyl pyrrolidone (NMP).

Because of its lower conductivity (10^{-1} – 10^{-3} s/cm), poly(*o*-toluidine) (POT) attracted less attention, but it has better solubility than PAN, and this makes it easy to react with other reagents to get composites or copolymers. We have synthesized POT powder with high conductivity and good solubility, and its free-standing film was obtained successfully by evaporation of a solution of POT base powder in NMP. In this work, the characterization of their structure and properties has also been reported.

EXPERIMENTAL

POT salt powder was prepared by chemical oxidative polymerization of toluidine from an aqueous acid solution (1.0M HCl) with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidizing reagent. (The molar ratio of Ox/toluidine is 0.5 at 5–20°C.) Prior to polymerization, toluidine had been purified by vacuum distillation, bp 80°C/15 mmHg. POT base powder was obtained by treating its salt with 5% NH_4OH , then washed in distilled water.

Approximately 2.5 g base fine powder dissolved in 100 mL NMP to produce a dark blue solution and the insoluble material was filtered out. The process using clear POT solution to make film was as reported by M. Wan, etc. Stretching the base film at 70–90°C, $\Delta L/L_0 = 0.3$ – 0.8 , then stretched POT base film was obtained. These films were redoped by treating with 1M HCl to get their salt films.

The electrical conductivity was measured using the conventional four-point probe method. The adsorption

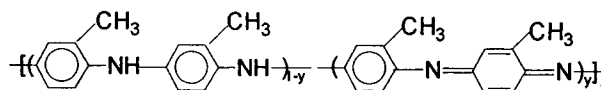
spectra in the ultraviolet (UV) region were taken from a POT solution in NMP with a Nanometrics Nanospec/10 micro spectrophotometer. Infrared (IR) spectra of polymer-KBr pellets were recorded on a Perkin-Elmer Model 683 grating IR spectrometer.

Mechanical properties (including tensile strength and elongation at break) were measured on an Instron 1122 material testing machine at a drawn speed of 10 mm/min and room temperature. Wide-angle X-ray diffraction patterns were taken on a Rigaku (made in Japan) X-ray diffractometer with CuK radiation (40 kV, 30 mA).

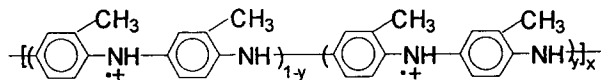
RESULTS AND DISCUSSION

Structural Characterization of POT

Elemental Analysis. POT base form has the following general formula:



Doped by HCl, it forms a polysemiquinone radical cation such as:



and becomes an electrical conductor. Through elemental analysis we can calculate the value of y , which implies the degree of oxidation. The result of elemental analysis of POT are given in Table I.

Whether in base or salt form, the composition of POT free-standing film is similar to its powder. Their degree of oxidation is approximately 0.5, which is the best oxidation state for polymers with high electrical conductivity. The formula of POT obtained by elemental analysis is in good agreement with theoretical formula, POT base powder, for example, its theoretical formula is $\text{C}_7\text{H}_{6.5}\text{N}_{1.0}$ and the experimental result is $\text{C}_7\text{H}_{6.53}\text{N}_{1.00}$. The salt form of POT is about 50% protonated.

Table I Elemental Analysis Data for POT

%	Base Form		Salt Form	
	Powder	Film	Powder	Film
C	76.57	75.60	59.07	59.45
H	6.52	6.50	5.45	5.54
N	12.71	12.65	9.88	9.96
Cl	0.57	< 0.30	12.68	12.98
O ^a	4.50	5.10	12.92	12.07
Formula	$C_7H_{6.53}N_{1.00} \cdot (H_2O)_{0.31}$	$C_7H_{6.52}N_{1.00} \cdot (H_2O)_{0.35}$	$C_7H_{6.5}N_{1.00}(HCl)_{0.51}(H_2O)_{0.37}$	$C_7H_{6.5}N_{1.00}(HCl)_{0.52}(H_2O)_{0.40}$
y value	0.47	0.48	—	—

^a O% = 100% - C% - H% - N% - Cl%.

UV-Visible and IR Spectra. Figure 1 shows the UV-visible spectra for POT. The adsorption peaks for POT base solution are at 330 and 580 nm, due to the excitation of the benzenoid and quinoid ring of POT, respectively. These two peaks change less for POT base film and stretched POT base film. When doped by HCl, the adsorption peak at 330 nm moves to 440 nm and the peak at 580 nm moves to near-IR region, which is usually taken as a characteristic associated with the high conductivity of conducting polymers. This suggests that the protonation of POT is also carried out on quinoid rings like that of PAN.

The IR spectra (Fig. 2) of POT base film is like that of POT base powder. After stretching, the IR spectra of stretched film has nearly no change. And the position of adsorption peaks is in agreement with that in the literature.¹⁰ All results above illustrate that the chemical structure of POT free-standing film has no obvious difference from pristine POT powder in both base and salt forms.

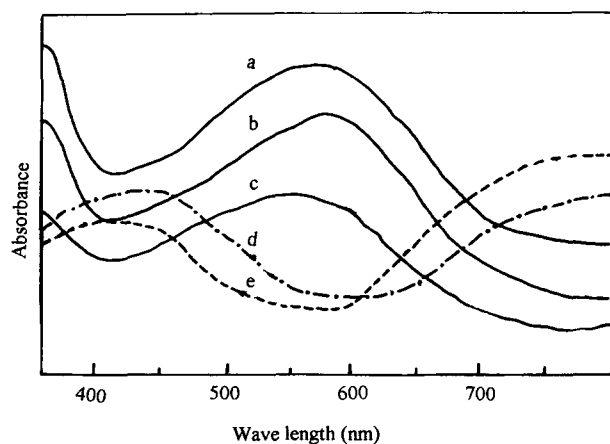


Figure 1 UV-visible adsorption spectra of (a) POT base solution in NMP, (b) POT base film, (c) stretched POT base film, (d) POT salt film, and (e) stretched POT salt film.

Wide-Angle X-ray Diffraction. Wide-angle X-ray diffraction patterns of POT powder and films are shown in Figure 3. The results are quite different from that for PAN.⁹ POT base powder is partly crystalline, and doping changes its crystalline structure. For POT films (base and salt), only broad amorphous peaks appear on their patterns. But on the patterns of stretched films, obviously, the adsorption peaks indicated that microcrystals were generated in the process of stretching.

Electrical Conductivity of POT

The electrical conductivity for POT base form is rather low (about 10^{-8} s/cm), and doping will result in its great increment (Table II). For POT salt powder and film, the electrical conductivity is 0.12 and 0.16 s/cm, respectively. Those are in the same order of magnitude as in the literature.¹¹⁻¹³ But it is interesting that the conductivity of POT stretched salt film can reach 11.2 s/cm, which is bigger than the maximum electrical conductivity of POT in previous reports. We are inclined to explain that the increase of conductivity is due to the chain orientation by the effect of stretching. As a

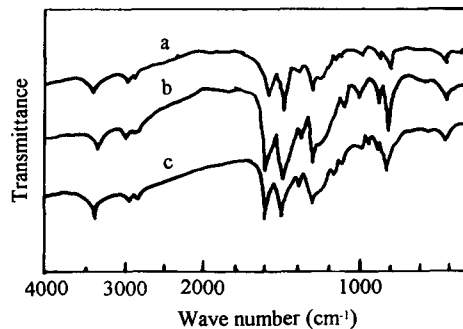


Figure 2 IR spectra of (a) POT base powder, (b) POT base film, and (c) stretched POT base film.

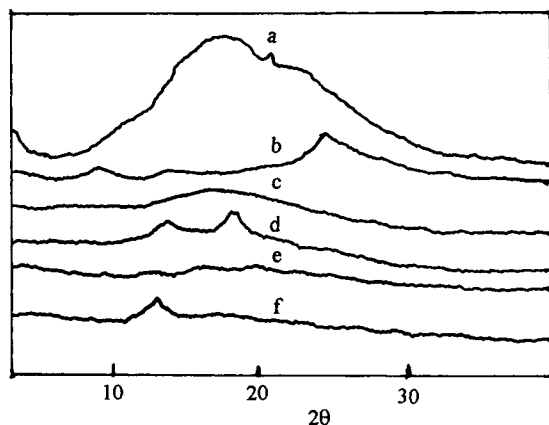


Figure 3 Wide-angle X-ray diffraction patterns of (a) POT base powder, (b) POT base film, (c) POT base film, (d) stretched POT base film, (e) POT salt film, and (f) stretched POT salt film.

matter of fact, this phenomenon can also be viewed in PAn free-standing films.

Mechanical Properties of POT Films

Up to now, no free-standing film of POT with tensile strength has been obtained. The POT film we prepared has good mechanical properties (Table III).

The tensile strength of POT base film is 48.3 N/mm². After protonation its tensile strength is decreased up to one third and its elongation at break decrease 40% and the film becomes brittle. The tensile strength of stretched base film is 57.2 N/mm², which is 18% higher than that of pristine base film, and at the same time its flexibility remains well. This can also be ascribed to the orientation effect by stretching. The stretching only cause 3% increment of tensile strength, and its elongation at break decreases 52% and the film becomes brittle also.

Table II Electrical Conductivity of POT

Sample	Conductivity (s/cm)
POT base powder	3.2×10^{-8}
POT base film	2.6×10^{-8}
Stretched POT base film	1.1×10^{-8}
POT salt powder	0.12
POT salt film	0.16
Stretched POT salt film	11.2

Table III Mechanical Properties of POT Films

Sample	Tensile Strength (N/mm ²)	Elongation at Break (%)
POT base film	48.3	2.6
POT salt film	32.5	1.4
Stretched POT base film	57.2	2.5
Stretched POT salt film	33.5	1.2

CONCLUSIONS

1. The free-standing film polytoluidine with good mechanical properties can be obtained by evaporation of a solution of chemically synthesized POT base powder in NMP. The as-prepared base film can be protonated by HCl to give conductive POT salt film.
2. Stretching POT base film will result in the form of microcrystals. The orientation effect of stretching makes POT base film have better mechanical properties and the electrically conductivity of stretched film can reach to 11.2 s/cm when protonated by HCl.
3. The results of the elemental analysis and the IR and UV-visible spectra show that the composition of the main chain of the POT free-standing film is similar to pristine POT powder. But the crystalline structure of POT has been changed, which is illustrated by X-ray diffraction patterns.

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