Synthesis of Poly(*o*-toluidine) in the Presence of Magnetic Field and Dysprosium Chloride

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ABSTRACT: The poly-*o*-toluidine (POT) was prepared under different magnetization in solution containing 0.5 mol dm⁻³ *o*-toluidine, 1.0 mol dm⁻³ HCl with and without 0.5 mol dm⁻³ DyCl₃, respectively. Their conductivity, UV–vis, FTIR spectra, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscope (SEM) were investigated. The results of conductivity showed that magnetic field and the cooperative effect of Dy³⁺ and magnetic field do obvious effect to conductivity of POT. Meantime, they also can make the energy for the π - π * transitions

and quinoid ring transition in UV–vis spectra smaller. At high magnetization the peaks of POT due to Q–NH⁺–B or B–NH⁺–B and C–H out of plane on 1,4-ring or 1,2,4-ring disappeared in FTIR spectra. Magnetic field and Dy³⁺ can make three dimensions morphologies of the POT clear, but they scarcely affect the crystallinity of POT. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2174–2179, 2007

Key words: poly-*o*-toluidine; dysprosium chloride; conductivity; FTIR spectra; X-ray diffraction; TGA; SEM

INTRODUCTION

Polyaniline (PANI) and its derivatives have good electroactivity¹; PANI has comparatively better electroactivity.² Because of its low solubility in most common solvents, the industrial application of PANI is limited.^{3,4} This problem has been overcome to some extent by using substituted derivatives of aniline such as toluidine, anisidine, N-methyl, N-ethyl anilines, and so on.^{5–7} Poly-o-toluidine (POT) is one of the PANI derivatives that have received focused attention in many technological areas such as rechargeable batteries, sensors, electromagnetic interference (EMI) shielding, electrochromic display devices, smart windows, molecular devices, energy storage systems, membrane gas separation, etc. due to their remarkable physical attributes.^{8–16} In recent years, POT has excited wide interest to study.4,15-18

Rare-earth have special properties because their electronic transitions are relatively insensitive to perturbations in their chemical environment. Interactions of PANI with metal ions give rise to novel chemical and physical properties of the formed macromolecular complex.¹⁹ Rare earth-PANI complexes are important in respect to its possible forefront applications in the areas of research as well as industrial applications.¹ POT has the similar structure with PANI; in the same way, interactions of POT with rare-earth ions may bring rise to novel chemical and physical properties of the formed macromolecular complex, and the POT can be used for emitting elements in organic light-emitting devices (OLEDs) and dopant additions to enhance quantum yield in OLEDs,²⁰ it can also be used as catalyst for some polymer reactions,^{21–22} and so on.

The magnetic field can influence on the chemical reaction containing radicals²³ and can induce orientation of most organic polymer molecules and biological macromolecules due to the magnetic susceptibility anisotropy.²⁴ Some literatures concerning the effect of magnetic field on the properties of electrochemistry and chemistry have been published.^{25,26} The existence of paramagnetic ions (for example, RE³⁺) in solutions can greatly increase the effects of magnetic alignment and improve the properties of a polymer,²⁷ which may lead to the wider application foreground of complex of POT with RE³⁺. POT complex synthesized in the presence of magnetic field may bring some new chemical and physical properties.

In this work, we made tentative exploration to chemically synthesize POT in the presence of DyCl₃ and magnetic field. The effects of magnetic field on properties of POT doped with rare earth cation (Dy³⁺) were presented, conductivity of the POT was done, UV–vis, FTIR spectra were used to characterize the POT, and thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM) of the POT were also described.

EXPERIMENTAL

The *o*-toluidine (reagent grade) was distilled into colorless under reduced pressure before use. Ammonium

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TABLE I Effects of Magnetization on Conductivity					
POT/HCl/Bp Magnetization (mT)		$\sigma \times 10^3/S~cm^{-1}$			
1	0	1.73			
2	500	3.15			
3	800	8.58			
4	935	0.83			

peroxydisulphate ((NH₄)₂S₂O₈), N,N-diamethylcarboxamidine (DMF), and other chemicals were reagent grade and used as-received without further treatment. DyCl₃ was of 99.9% purity. All of the aqueous solutions were prepared with double-distilled water. According to the method described earlier,28 POT was synthesized. A 0.025 or 0.05 mol of purified o-toluidine was dissolved in 50 cm⁻³ of 1.0 mol dm⁻³ HCl aqueous solution with and without DyCl₃. A 0.025 mol of (NH₄)₂S₂O₈ was slowly added into the previous *o*-toluidine solution, and at the same time, the mixture was stirred; the reaction was lasted for 1 h at ambient temperature. The molar ratio of $(NH_4)_2S_2O_8$ as oxidant to o-toluidine is 1:1 unless otherwise stated. POT and POT/DyCl₃ were synthesized in the above-mentioned solution in the absence and presence of magnetic field, respectively, and they were filtrated and washed with 1.0 mol dm⁻³ HCl aqueous solution until the filtrate was colorless. All samples were dried at 110°C for 24 h in vacuum-desiccator.

Conductivity measurements of the resulting products were made using conventional four-probe technique on pressed pellets of the powder samples prepared at 32°C. The UV-vis absorption spectra of all samples were obtained on UV-2550 spectrometer (Shimadzu) in the range of 250–800 nm. DMF was used as the solvent to prepare the sample solutions. FTIR spectra of the samples were performed on a Tensor 27 FTIR spectrometer (Bruker). Pressed pellets were prepared of the powder samples ground with KBr for this purpose. TGA was performed using a (WRT-2P), at a heating rate of 10° C min⁻¹, under nitrogen, from 64° C to 600°C. X-ray diffraction patterns of the powder samples were taken on a (Y-2000), using Cu-Ka radiation $(\lambda = 1.5406 \text{ Å})$, which was used to obtain the degree of crystallinity. The morphologies of POT films were observed using a scanning electron microscope (SEM XL-30 ESEM). The magnetic field was applied by a homemade permanent magnet.

TABLE II Effects of Magnetization and DyCl₃ on Conductivity

Magnetization (mT)	$\sigma \times 10^3/S~cm^{-1}$
0	8.91
500	17.04
800	1.45
935	0.02
	Magnetization (mT) 0 500 800 935



Figure 1 Effect of magnetic field on UV-vis spectra of POT/HCl. (1) 0 mT, (2) 500 mT, (3) 800 mT, (4) 935 mT.

RESULTS AND DISCUSSION

Conductivity of resulting products

Table I gives the effect of magnetization on conductivity of POT doped without $DyCl_3$ at 32°C. Samples 1–4 were synthesized chemically in 1.0 mol dm⁻³ HCl aqueous solutions containing 0.5 mol dm⁻³ *o*-toluidine at different magnetization. It was shown from Table I that the conductivity of resulting products at 500 and 800 mT are bigger than that without magnetization. The reasons for this may be due to the following:



Figure 2 Effect of magnetic field on UV-vis spectra of POT/HCl/Dy. (5) 0 mT, (6) 500 mT, (7) 800 mT, (8) 935 mT.

FILK Band Assignments of Samples 1–4							
	San						
(1) POT/HCl/Bp = 0 mT	(2) POT/HCl/ Bp = 500 mT	(3) POT/HCl/ Bp = 800 mT	(4) POT/HCl/ Bp = 935 mT	Assignment			
800	808	808	810	C-H out of plane on 1,4-ring or 1,2,4-ring			
1104	1107	1106	1106	C–H in plane on 1,4-ring or 1,2,4-ring			
1154	1155	1169	1153	$Q-NH^+-B$ or $B-NH^+-B$			
1257	1259	1258	1258	C-N str in BBB			
1485	1489	1488	1489	Str of N–B–N			
1575	1586	1558	1586	Str of N–Q–N			

TABLE III FTIR Band Assignments of Samples 1–4

Q denotes quinoid units of the POT; B denotes benzenoid.

(i) enhance in conjugation extent, which was supported by a red shift of the peak position in the UV–vis absorption spectra; (ii) enhance in the extent of electron delocalization; and (iii) enhance in the transport speed of charge carriers along and across the POT chain.²⁹ But the conductivity of resulting product at 935 mT is lower than that without magnetization. This may be caused by high magnetization; the POT chain deforms, and the extent of electron delocalization of POT chain decrease, so there is lower conductivity of POT.

Table II gives the effects of magnetization on conductivity of POT with $DyCl_3$ at 32°C. Samples 5–8 were synthesized chemically in 1.0 mol dm⁻³ HCl aqueous solutions containing 0.5 mol dm⁻³ *o*-toluidine and 0.5 mol dm⁻³ $DyCl_3$ at different magnetization. It was shown from Table II that the conductivity of resulting products at 500 mT is bigger than that without magnetization, while the conductivity of resulting products at 800 and 935 mT is lower than that without magnetization. The change is similar with that in Table I; however, the conductivities of the resulting products decrease not only at 935 but also at 800 mT. The reason for this may be due to the cooperate of Dy^{3+} and magnetic.

Comparing sample 1 with sample 5, the conductivity of sample 5 is bigger, that is because the added Dy^{3+} can interact with POT chain,³⁰ it can enhance the extent of electron delocalization, and the transport speed of charge carriers along and across the POT chain.

UV-vis spectra and FTIR spectra

Figures 1 and 2 show the UV–vis absorption spectra of POT/HCl prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 1.0 mol dm^{-3} HCl with and without 0.5 mol dm^{-3} DyCl₃ at different magnetization, respectively.

POT exhibits two marked absorption at 312 nm and at 592 nm in the UV–vis spectra.³¹ Similarly to the spectra of PANI,^{32,33} they can be ascribed to π – π * transitions and quinoid ring transition, respectively.³⁴

By analyzing Figure 1, the two absorption peaks due to π - π * transitions and quinoid ring transition of curves (2)–(4) appears at the longer wavelength compared with that of curve (1). This result indicates that there exists interaction between magnetic field and POT chain, and this interaction makes the energy for the two transitions smaller.

Similar with Figure 1, curves in Figure 2 have the same change. Comparing curve (1) in Figure 1 with curve (5) in Figure 2, the two absorption peaks due to π – π * transitions and quinoid ring transition of curve (5) shifted to longer wavelength than that of curve (1). We suppose that there exists interaction between Dy³⁺

FIIR Band Assignments of Samples 5–8							
San							
(6) POT/HCl/Dy/ Bp = 500 mT	(7) POT/HCl/Dy/ Bp = 800 mT	(8) POT/HCl/Dy/ Bp = 935 mT	Assignment				
809	_	_	C—H out of plane on 1,4-ring or 1,2,4-ring				
1107	1106	1105	C—H in plane on 1,4-ring or 1,2,4-ring				
1167	_	-	$Q-NH^+-B$ or $B-NH^+-B$				
1260	1270	1256	C–N str in BBB				
1489	1489	1490	Str of N–B–N				
1586	1557	1558	Str of N–Q–N				
	San (6) POT/HCl/Dy/ Bp = 500 mT 809 1107 1167 1260 1489 1586	FTIR Band Assignm Sample (6) POT/HCl/Dy/ Bp = 500 mT (7) POT/HCl/Dy/ Bp = 800 mT 809 - 1107 1106 1167 - 1260 1270 1489 1489 1586 1557	FTIR Band Assignments of Samples 5- Sample (6) POT/HCl/Dy/ (7) POT/HCl/Dy/ (8) POT/HCl/Dy/ Bp = 500 mT Bp = 800 mT Bp = 935 mT 809 - - 1107 1106 1105 1167 - - 1260 1270 1256 1489 1489 1490 1586 1557 1558				

TABLE IV FTIR Band Assignments of Samples 5–8

Q denotes quinoid units of the POT; B denotes benzenoid.



Figure 3 Effect of magnetic field and Dy on TGA of POT/HCl. (a) POT/HCl, (b) POT/HCL/Dy³⁺, (c) POT/HCl/Dy³⁺/Bp = 800 mT.

and POT chain, and this interaction also makes the energy for the two transitions smaller.

Tables III and IV show the FTIR spectra of POT/HCl prepared in solution containing 0.5 mol dm⁻³ *o*-toluidine, 1.0 mol dm⁻³ HCl with and without 0.5 mol dm⁻³ DyCl₃ at different magnetization, respectively. The bands assignments of all samples are summarized in Tables III and IV. These bands are in agreement with the literature³⁵ except for a few shifts in the wavenumbers.



Figure 5 Effect of magnetic field on X-ray diffraction patterns of POT/HCl. (1) 0 mT, (2) 500 mT, (3) 800 mT, (4) 935 mT.

It was seen from Table III that the peaks of samples 2–4 due to the stretching vibrations (Str) of N-Q-N shifted obviously and the peaks of sample 3 due to $Q-NH^+-B$ or $B-NH^+-B$ shifted obviously, too. Among the above-mentioned shifts, sample 3 is the most special. The result is that there exists the most obvious interaction between magnetic field and POT chain at 800 mT, and this interaction is favorable to the overlap of the POT chain. It is



Figure 4 Effect of magnetic field and Dy on X-ray diffraction patterns of POT/HCl. (a) POT/HCl, (b) POT/HCL/ Dy^{3+} , (c) POT/HCl/ $Dy^{3+}/Bp = 800$ mT.



Figure 6 Effect of magnetic field on X-ray diffraction patterns of POT/HCl/Dy. (5) 0 mT, (6) 500 mT, (7) 800 mT, (8) 935 mT.



Figure 7 Effect of magnetic field and Dy on SEM of POT/HCl. (a) POT/HCl, (b) POT/HCL/Dy³⁺, (c) POT/HCl/Dy³⁺/ Bp = 800 mT.

also supported by the biggest conductivity of the POT at 800 mT.

From Table IV, the peaks of samples 5–8 due to the stretching vibrations of N—Q—N shifted obviously and the peaks of sample 7, 8 due to Q—NH⁺—B or B—NH⁺—B and C—H out of plane on 1,4-ring or 1,2,4-ring disappeared. The reason for this may be that the paramagnetic ion Dy³⁺ and the radial group formed during the polymerization interact with the imposed magnetic field, especially, at the higher magnetization of 800 and 935 mT, the POT chains took place to rotation or twist leading to the peaks of samples 7, 8 due to Q—NH⁺—B or B—NH⁺—B and C—H out of plane on 1,4-ring or 1,2,4-ring disappeared.

TGA

Figure 3(a–c) shows the TGA curves of POT/HCl, POT/HCl/Dy³⁺, POT/HCl/Dy³⁺/Bp, which were prepared in solution containing 1.0 mol dm⁻³ *o*-toluidine, 1.0 mol dm⁻³ HCl with and without 0.5 mol dm⁻³ DyCl₃, in the absence and presence of magnetic field, respectively.

All samples shown in Figure 3 exhibited a similar thermal behavior except for a small variation in degradation temperature. Similar with PANI, the thermal behavior of the POT-HCl shows a three-step weight loss process, the first weight loss about 100°C is attributed to the loss of water and low-molecular-weight oligomers.³⁶ The second weight loss ranging from 200 to 300°C is believed to be due to the elimination of acid dopant (HCl),³⁷ and the third weight loss starting over 470°C is assigned to the thermal decomposition of POT backbone chains.³⁸ As a comparison, POT/ HCL/Dy³⁺ and POT/HCl/Dy³⁺/Bp have the decomposition temperature of the loss of HCl dopant about 10°C higher than that of POT/HCl, which indicates that the added Dy3+ can dope into POT chain and they may coordinate with nitrogen atoms on POT chains¹⁹. This coordination strengthens the strength of N—H bond on POT chains resulting in the more difficulty to the loss of HCl dopant in POT/Dy³⁺ and POT/HCl/Dy³⁺/Bp polymers.

XRD analysis

Figure 4(a–c) shows the X-ray diffraction patterns of POT/HCl, POT/HCl/Dy³⁺, POT/HCl/Dy³⁺/Bp, which were prepared in solution containing 1.0 mol dm⁻³ *o*-toluidine, 1.0 mol dm⁻³ HCl with and without 0.5 mol dm⁻³ DyCl₃, in the absence and presence of magnetic field, respectively.

Figures 5 and 6 show the X-ray diffraction patterns of POT/HCl prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 1.0 mol dm^{-3} HCl with and without 0.5 mol dm^{-3} DyCl₃ at different magnetization, respectively.

All samples exhibit two broad amorphous reflections near $2\theta = 15^{\circ}$ and $2\theta = 25^{\circ}$; the shape of all curves are similar. The results show that there are hardly influence of POT crystallinity by DyCl₃, magnetic field and cooperative effect of Dy³⁺ and magnetic field.

The morphologies of POT

Figure 7(a–c) shows the SEM morphologies of POT/HCl, POT/HCl/Dy³⁺, POT/HCl/Dy³⁺/Bp prepared in solution containing 1.0 mol dm⁻³ *o*-toluidine, 1.0 mol dm⁻³ HCl with and without 0.5 mol dm⁻³ DyCl₃, in the absence and presence of magnetic field, respectively.

The morphology of POT in Figure 7(a) shows that it is an irregular surface with small and big grains on it. Figure 7(b) shows three dimensions morphologies, which becomes clear when doped in DyCl₃. By imposing magnetic field, three dimensions morphology in Figure 7(c) becomes clearer and more uniform. According to Figure 7, we suppose that Dy³⁺ doped into POT and interacted with POT chain. On the other hand, magnetic field can also make POT chain array directionally. The SEM morphologies are not contradictory to the results of X-ray diffraction because DyCl₃, magnetic field, and cooperative effect of Dy³⁺ and magnetic field scarcely change lattice structure of POT.

CONCLUSIONS

The poly-*o*-toluidine was prepared in 1.0 mol dm^{-3} HCl aqueous solutions containing 0.5 mol dm^{-3}

o-toluidine with and without 0.5 mol dm⁻³ DyCl₃ at different magnetization. The imposed magnetic field can interact with the POT chain with and without paramagnetic ion Dy³⁺. The interaction can affect the conductivity, UV–vis, FTIR spectra, thermostability, and morphologies of the POT. Magnetic field makes the energy of π – π * transitions and quinoid ring transition decrease with and without Dy^{3+.} The FTIR spectra shows that there exists the most obvious interaction between magnetic field and POT chain at 800 mT, and the cooperation effect of Dy³⁺ and magnetic field makes the peaks due to Q–NH⁺–B or B–NH⁺–B and C–H out of plane on 1,4-ring or 1,2,4-ring disappeared at 800 and 935 mT. Magnetic field and Dy³⁺ hardly affect the crystallinity of POT.

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