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Synthesis and Characterization of Poly(*o*-toluidine) in Ionic Liquid and Lanthanum Chloride

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Poly(*o*-toluidine) of high conductivity (10.14 S cm^{-1}) was synthesized by chemical process in a solution containing $LaCl_3$ and ionic liquid. The conductivity, UV-Vis, FTIR spectra, X-ray diffraction and thermogravimetric analysis were investigated. The results of conductivity showed that the cooperative effect of La^{3+} and ionic liquid remarkably improved the conductivity of poly(*o*-toluidine). Meantime, the energy gaps of the π-π* and quinoid ring transitions are affected by the cooperative effect of La^{3+} and ionic liquid in UV-Vis. The peak of Q-NH^+-B or B-NH^+-B in poly(*o*-toluidine) doped with La^{3+} shifts to longer wavelength in FTIR spectra in the presence of ionic liquid. La^{3+} and ionic liquid hardly affect the crystallinity of poly(*o*-toluidine).

Key Words: Poly(*o*-toluidine), Lanthanum chloride, Ionic liquid, Conductivity, Optical spectroscopy, X-ray diffraction, TGA.

INTRODUCTION

Polyaniline has been widely studied[1,2]. However, the industrial applications of polyaniline are restricted[3,4] due to infusibility and insolubility in most common solvents and the poor electroactivity at high pH. The problems have partly been overcome by using substituted derivatives of aniline such as toluidine, anisidine, N-methyl, N-ethyl aniline[5-7]. Poly(*o*-toluidine) is one of polyaniline derivatives that have received focused attention in many technological areas such as rechargeable batteries, sensors, electromagnetic interference shielding, electrochromic display devices, smart windows, molecular devices, energy storage systems, membrane gas separation[8-16]. In recent years, poly(*o*-toluidine) has excited wide interest to study[4,15-18].

Rare-earth have special properties because their f electronic transitions are relatively insensitive to perturbations in their chemical environment. Lv *et al.*[19] reported polyaniline doped with rare-earth Dy^{3+} gave rise to novel chemical and physical properties. The structure of poly(*o*-toluidine) is similar to that of polyaniline[20]. Poly(*o*-toluidine) doped with rare-earth ions may bring the similar effects. Poly(*o*-toluidine) can be used for enhancing quantum yield in organic light-emitting devices[21] or improving the properties of catalyst for some polymer reactions[22-24].

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Ionic liquids are widespread applications in batteries[25], capacitors[26-29], electropolymerization[30-34]. As they are nonvolatile and non-flammable, high thermal stability, relatively inexpensive to manufacture. Synthesis of polyaniline in some ionic liquids has also been studied. Gao and co-workers also fabricated polyaniline nanoparticles in aqueous/ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) interfacial[35]. Wei *et al.*[36] obtained the polyaniline nanotubules in ionic liquid, 1-butyl-3-methyl imidmidazolium hexafluorophosphate and Miao and co-workers[37] prepared polyaniline nanofibrous networks in ionic liquid, 1-hexadecyl-3-methylimidazolium chloride). Innis *et al.*[38] synthesized the polyaniline in the ionic liquid, 1-ethyl-3-methylimidazolium trifluromethanesulfon imides. Zhang *et al.*[39] reported the synthesis of polyaniline in ionic liquid, 1-methyl-3-butylimidazolium hexafluorophosphate and found that the electrochemical activity of the polyaniline can be improved in the ionic liquid with CF_3COOH. They suggested that this might be due to the cooperative effect of CF_3COOH and 1-methyl-3-butylimidazolium hexafluorophosphate. Li *et al.*[40] used ionic liquid, 1-ethylimidazolium trifluoroacetate, as electrolyte for electropolymerization of aniline. poly(*o*-toluidine) has good solubility in many solvents, but the conductivity of poly(*o*-toluidine) is usually far lower than PANI. How to synthesis poly(*o*-toluidine) with high conductivity and good solubility in common organic solutions is a topic of general interest.

In this work, poly(*o*-toluidine) is synthesized in the presence of $LaCl_3$ and ionic liquid. The effects of ionic liquid and La^{3+} on properties of poly(*o*-toluidine) were presented, conductivity of the poly(*o*-toluidine) was measured, UV-Vis, FTIR spectra were used to characterize the poly(*o*-toluidine), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) of the poly(*o*-toluidine) were also described.

EXPERIMENTAL

The *o*-toluidine (Sigma) was distilled into colourless under reduced pressure prior to use. Ammonium peroxydisulphate [$(NH_4)_2S_2O_8$, Sigma], N,N-dimethyl carboxamidine (Sigma) and other chemicals were reagent grade and used as received without further treatment. $LaCl_3\cdot7H_2O$ (Sigma) was of 99.9 % purity. All of the aqueous solutions were prepared with double distilled water.

Based on the literature[41], 1-ethyl-3-methylimidazolium-ethyl sulfate (EMIES) was synthesized. The main prepared progress as follows: first, diethyl sulfate (0.442 mol) was added dropwise to a solution of 1-methylimidazole (0.442 mol) in toluene (200 mL) cooled in an ice-bath at a rate to maintain the reaction temperature below 40 ºC. After addition of the diethyl sulfate, the reaction mixture was stirred at room temperature (*ca.* 30 ºC) for 1 h. Ionic liquid phase was washed with toluene, followed by removed toluene and dried ionic liquid under reduced pressure at 75 ºC.

According to the method described earlier[42], poly(*o*-toluidine) was synthesized. 0.025 mol of *o*-toluidine was dissolved in 50 cm^{-3} of 2.0 mol dm^{-3} HCl aqueous solution containing $LaCl_3$ and different proportions of ionic liquid. Then $(NH_4)_2S_2O_8$ was slowly added into the *o*-toluidine solution and the mixture was stirred. The reaction was lasted for 1 h at ambient temperature (*ca.* 30 ºC). The molar ratio of $(NH_4)_2S_2O_8$ as oxidant to *o*-toluidine is 1:1 or 1:2 unless otherwise stated. The resulting productions were filtrated and washed with 2.0 mol dm^{-3} HCl aqueous solution until the filtrate was colourless. Finally, all samples were dried at 78 ºC for 48 h.

Conductivity of each sample was measured 10 times using conventional four-probe technique on pressed pellets of the powder samples prepared at 32 ºC, the standard error was less than 2 %. The UV-vis absorption spectra of all samples were obtained on UV-2550 spectrometer (Shimadzu) in the range of 250~800 nm. N,N-dimethyl carboxamidine was used as the solvent to prepare the sample solutions. Infrared spectra were recorded on a Tensor 27 FTIR spectrometer (Bruker) in KBr pellet. TGA was performed using a (WRT-2P), at a heating rate of 10 ºC min^{-1}, under nitrogen, from 64 to 500 ºC. X-ray diffraction patterns of the powder samples were taken on a (Y-2000), using Cu-K_α radiation ($\lambda = 1.5406$ Å), which was used to obtain the degree of crystallinity.

RESULTS AND DISCUSSION

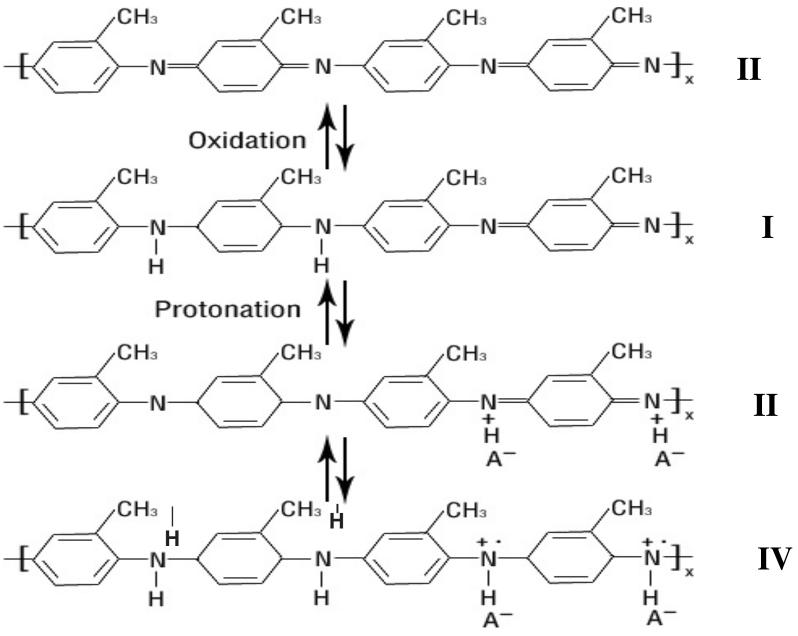
Conductivity of resulting products

Table-1 gives the effect of ionic liquid on conductivity of poly(*o*-toluidine) doped with La^{3+} at 32 ºC. Sample 0-5 in Table-1 were synthesized chemically in 2.0 mol dm^{-3} HCl aqueous solutions containing 0.5 mol dm^{-3} *o*-toluidine, 0.5 mol dm^{-3} $LaCl_3$ and 0.5 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant with different proportion of ionic liquid. It was seen from Table-1 that the conductivity of resulting products at ionic liquid: *o*-toluidine = 2:1 is the highest and it is much higher than the conductivity of poly(*o*-toluidine) reported before[43,44]. This reaction was presented in **Scheme-I**[41,45].

TABLE-1
EFFECTS OF IONIC LIQUID ON CONDUCTIVITY (*o*-TOLUIDINE: $(NH_4)_2S_2O_8$ = 1:1)

No.	0	1	2	3	4	5
Ionic liquid: *o*-toluidine	0	1:4	1:2	1:1	2:1	3:1
σ/S cm^{-1}	0.0378	0.0864	0.1088	0.2292	10.14	0.0533

Protonation of poly(*o*-toluidine) (**I**) results in the formation of a salt (**III**) in which the polymer backbone is positively charged and dopant anions (A^-) are incorporated into the system. Imine nitrogen atoms (=N-) present in the quinoid polymer units are protonated preferentially. An internal redox reaction leads to the transformation of structure (**III**) into the polysemiquinone radical (**IV**), often called 'polaron lattice'. In this reaction benzenoid units of poly(*o*-toluidine) (**I**) containing amine nitrogen atoms (-NH-) are oxidized into the quinoid units with imine nitrogen atoms (=N-). In such a way, fully oxidized poly(*o*-toluidine) (**II**) is formed. Intermediate oxidation states between (**I**) and (**II**) are, however, also possible. The lone-pair electrons of N atom in poly(*o*-toluidine) chain may interact with *d*-orbital of La^{3+} to form coordinate bond due to electron configuration[46] of La^{3+}. The reason for the high conductivity of the samples may be that the synergistic effect of ionic liquid and La^{3+}, which enhance in transport speed of charge carriers along and across the poly(*o*-toluidine) chain.



Scheme-I

Table-2 gives the effect of ionic liquid on conductivity of poly(*o*-toluidine) doped with different proportions of ionic liquid at 32 °C.

TABLE-2
EFFECTS OF IONIC LIQUID ON CONDUCTIVITY (*o*-TOLUIDINE):$(NH_4)_2S_2O_8$ = 2:1)

No.	0	1	2	3	4	5
Ionic liquid: *o*-toluidine	0	1:4	1:2	1:1	2:1	3:1
σ/S cm^{-1}	0.0213	0.0354	0.0362	0.0409	0.0717	0.0202

Sample 0-5 in Table-2 were synthesized chemically in 2.0 mol dm^{-3} HCl aqueous solutions containing 0.5 mol dm^{-3} *o*-toluidine, 0.5 mol dm^{-3} $LaCl_3$ and 0.25 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant with different proportions of ionic liquid. It was shown from Table-2 that the conductivity of resulting products at ionic liquid: *o*-toluidine = 2:1 is the highest. The change is similar to Table-1. The reason for this comes from the cooperation of La^{3+} and ionic liquid.

Comparing Table-1 with Table-2, the conductivity of sample 4 in Table-1 is higher. That is attribute to insufficient $(NH_4)_2S_2O_8$ in Table-2, which may result in forming poly(*o*-toluidine) oligomer and make conductivity of poly(*o*-toluidine) lower.

UV-Vis spectra: Figs. 1 and 2 show the UV-vis absorption spectra of poly(*o*-toluidine) prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl, 0.5 mol dm^{-3} $LaCl_3$ and 0.5 or 0.25 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant with different proportions of ionic liquid, respectively.

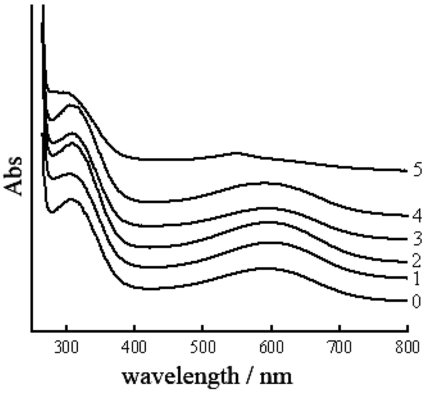


Fig. 1. Effects of ionic liquid on UV-Vis spectra (OT: $(NH_4)_2S_2O_8$ = 1:1)
(0) ionic liquid : OT = 0
(1) ionic liquid : OT = 1:4
(2) ionic liquid : OT = 1:2
(3) ionic liquid : OT = 1:1
(4) ionic liquid : OT = 2:1
(5) ionic liquid : OT = 3:1

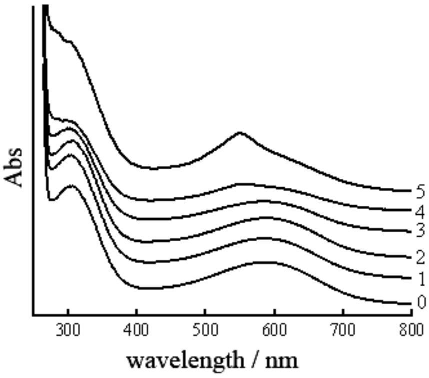


Fig. 2. Effects of ionic liquid on UV-Vis spectra (OT: $(NH_4)_2S_2O_8$ = 2:1)
(0) ionic liquid : OT = 0
(1) ionic liquid : OT = 1:4
(2) ionic liquid : OT = 1:2
(3) ionic liquid : OT = 1:1
(4) ionic liquid : OT = 2:1
(5) ionic liquid : OT = 3:1

Fig. 3 shows the UV-vis absorption spectra of poly(*o*-toluidine), poly(*o*-toluidine)/ionic liquid, poly(*o*-toluidine)/La, poly(*o*-toluidine)/ionic liquid/La prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl and 0.5 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant, respectively.

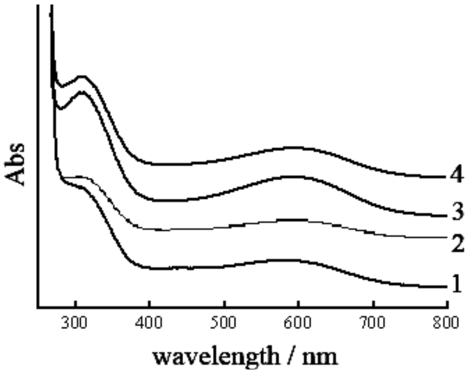


Fig. 3. Effects of ionic liquid and $LaCl_3$ on UV-Vis spectra (OT: $(NH_4)_2S_2O_8$ = 1:1)
(1) POT (2) POT/ionic liquid (3) POT/La (4) POT/ionic liquid/La

Poly(*o*-toluidine) exhibits two-marked absorption at 312 nm and at 592 nm in the UV-Vis spectra[47]. This is similarly to the spectra of polyaniline[48,49], they can be ascribed to π-π* and quinoid ring transitions, respectively[50].

It was seen from Fig. 1 that the two absorption peaks due to π-π* and quinoid ring transitions of curve (1), (2), (3), (4) and (5) appear at the shorter wavelength compared with that of curve (0), this result indicates that there exists interaction between La^{3+}, ionic liquid and poly(*o*-toluidine) chain and the interaction makes the energy gaps of their transitions widen.

Curves in Fig. 2 have the similar change with Fig. 1. Comparing curve (0) in Fig. 1 with curve (0) in Fig. 2, the two absorption peaks due to π-π* and quinoid ring transitions of curve (0) in Fig. 2 shifted to shorter wavelength. It is attributed to insufficient $(NH_4)_2S_2O_8$, which may conjugated chain of poly(*o*-toluidine) shorten and the energy gaps of their transitions widen. This is in agreement with the results of conductivity of poly(*o*-toluidine) mentioned previously.

From Fig. 3, peaks of the π-π* and quinoid ring transitions of curve (3, 4) shift to shorter wavelength than that of curve (1, 2). It indicates that there exists interaction between La^{3+}, ionic liquid and poly(*o*-toluidine) chain. This interaction may make the energy gaps of their transitions widen, too.

FT-IR spectra: Tables 3 and 4 show the FT-IR spectra of poly(*o*-toluidine) prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl, 0.5 mol dm^{-3} $LaCl_3$ and 0.5 or 0.25 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant with different proportions of ionic liquid, respectively.

TABLE-3
FT-IR BAND ASSIGNMENTS OF SAMPLE 0-5/cm^{-1}

Sample (OT: $(NH_4)_2S_2O_8$ = 1:1) (ionic liquid:OT)						Assignment
0.POT (0)	1.POT (1:4)	2.POT (1:2)	3.POT (1:1)	4.POT (2:1)	5.POT (3:1)	
812	811	813	810	807		C-H out of plane on 1,4-ring or 1,2,4-ring
1109	1109	1108	1109	1107	1107	C-H in plane on 1,4-ring or 1,2,4-ring
1158	1171	1172	1171	1170	1170	Q-NH^+-B or B-NH^+-B*
1262	1261	1262	1262	1260	1260	C-N str. in BBB
1491	1487	1489	1488	1484	1485	Str. of N-B-N
1561	1557	1557	1559	1554		Str. of N-Q-N

*Q = Quinoid units of POT = Poly(*o*-toluidine), B denotes benzenoid, OT = *o*-Toluidine

The bands assignments of all samples are summarized in Tables 3 and 4. These bands are in agreement with the literature[51] except for a few shifts in the wavenumber.

It can be seen by comparing sample 1, 2, 3, 4, 5 with sample 0 in Table-3 that the peaks of Q-NH^+-B or B-NH^+-B* of sample 1, 2, 3, 4, 5 shifted obviously based on the precision of TENSOR 27 FTIR spectrometer (4 cm^{-1}). It can be considered from the shifts of peaks of Q-NH^+-B or B-NH^+-B* that there exists obvious interaction between La^{3+}, ionic liquid and POT chain and this interaction is favourable to improving conductivity of poly(*o*-toluidine).

TABLE-4
FTIR BAND ASSIGNMENTS OF SAMPLE 0-5 / cm^{-1}

Sample (OT: $(NH_4)_2S_2O_8$ = 2:1) (ionic liquid:OT)						Assignment
0.POT (0)	1.POT (1:4)	2.POT (1:2)	3.POT (1:1)	4.POT (2:1)	5.POT (3:1)	
816	813	808				C-H out of plane on 1,4-ring or 1,2,4-ring
1107	1108	1107	1107	1106		C-H in plane on 1,4-ring or 1,2,4-ring
1171	1171	1170	1171	1170		Q-NH^+-B or B-NH^+-B*
1261	1261	1260	1261	1259		C-N str in BBB
1488	1488	1486	1486	1488	1490	Str of N-B-N
1558	1559	1560				Str of N-Q-N

*Q = Quinoid units of POT = Poly(*o*-toluidine), B denotes benzenoid, OT = *o*-Toluidine

TG analysis: Fig. 4, (1), (2), (3) show the TGA curves of poly(*o*-toluidine)/HCl, poly(*o*-toluidine)/HCl /La^{3+}, poly(*o*-toluidine)/HCl/La^{3+}/ionic liquid prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl and 0.5 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant in the absence and presence of 0.5 mol dm^{-3} $LaCl_3$ and ionic liquid, respectively.

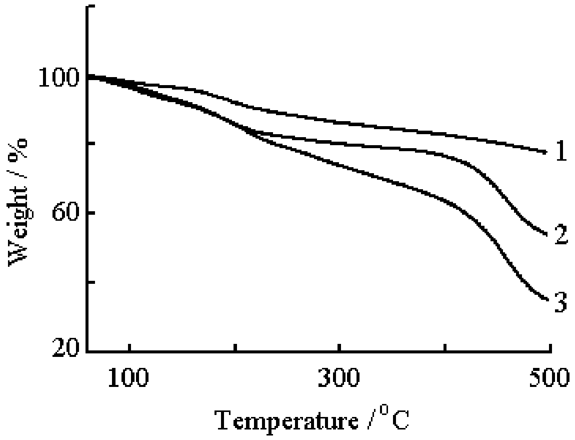


Fig. 4. Effect of ionic liquid and La on TGA of POT/HCl (1) POT/HCl, (2) POT/HCl/La^{3+}, (3) POT/HCl/La^{3+}/ionic liquid

All samples in Fig. 4 have similar thermal behaviour except for a small variation in degradation temperature. The thermal behaviour of the poly(*o*-toluidine)-HCl is similar with polyaniline, the poly(*o*-toluidine)-HCl also shows a three-step weight loss process. The first weight loss about 100 ºC is attributed to the loss of water and low-molecular-weight oligomers[42]. The second weight loss ranging from 200 to 300 ºC is believed to be due to the elimination of acid dopant (HCl)[52] and the third weight loss starting over 470 ºC is assigned to the thermal decomposition of poly(*o*-toluidine) backbone chains[53]. As a comparison, poly(*o*-toluidine)/HCl/La^{3+} and poly(*o*-toluidine)/HCl/La^{3+}/ionic liquid have the decomposition temperature of the loss of HCl dopant *ca.* 20 ºC higher than that of poly(*o*-toluidine)/HCl, which indicates that the added La^{3+} can dope into poly(*o*-toluidine) chain and may coordinate with nitrogen atoms of poly(*o*-toluidine) chains[21]. This coordination result in the more difficulty to the loss of HCl dopant in poly(*o*-toluidine)/HCl/La^{3+} and poly(*o*-toluidine)/HCl/La^{3+}/ionic liquid polymers.

XRD analysis: Figs. 5 and 6 show the X-ray diffraction patterns of poly(*o*-toluidine) (POT) prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl, 0.5 mol dm^{-3} LaCl$_3$ and 0.5 or 0.25 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant with different proportions of ionic liquid, respectively.

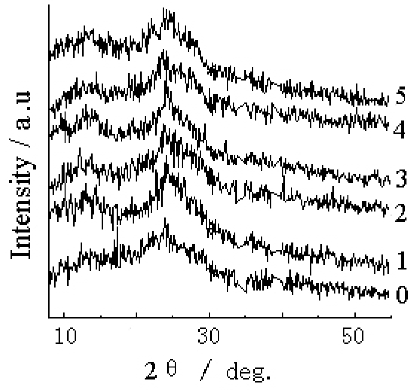


Fig. 5. Effects of ionic liquid on XRD (OT: $(NH_4)_2S_2O_8$ = 1:1)
(0) ionic liquid: OT = 0
(1) ionic liquid: OT = 1:4
(2) ionic liquid: OT = 1:2
(3) ionic liquid: OT = 1:1
(4) ionic liquid: OT = 2:1
(5) ionic liquid: OT = 3:1

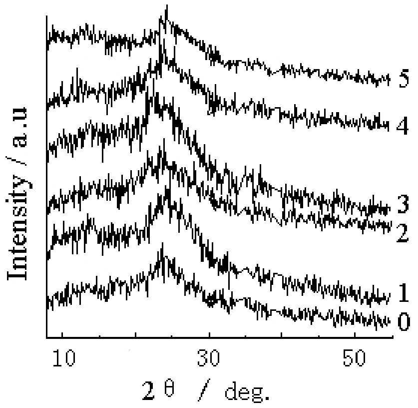


Fig. 6. Effects of ionic liquid on XRD (OT: $(NH_4)_2S_2O_8$ = 2:1)
(0) ionic liquid :OT = 0
(1) ionic liquid :OT = 1 : 4
(2) ionic liquid :OT = 1 : 2
(3) ionic liquid :OT = 1 : 1
(4) ionic liquid :OT = 2 : 1
(5) ionic liquid :OT = 3 : 1

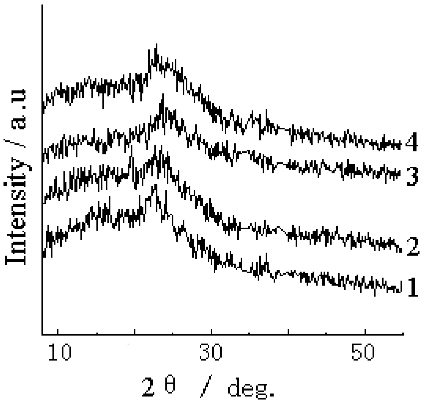


Fig. 7. Effects of ionic liquid and LaCl$_3$ on XRD (OT: $(NH_4)_2S_2O_8$ = 1:1)
(1) POT (2) POT/ionic liquid (3) POT/La (4) POT/ionic liquid/La

Fig. 7 show the X-ray diffraction patterns of poly(*o*-toluidine), poly(*o*-toluidine)/ionic liquid, poly(*o*-toluidine)/La, poly(*o*-toluidine)/ionic liquid/La prepared in solution containing 0.5 mol dm^{-3} *o*-toluidine, 2.0 mol dm^{-3} HCl and 0.5 mol dm^{-3} $(NH_4)_2S_2O_8$ as oxidant in the absence and presence of 0.5 mol dm^{-3} $LaCl_3$ and ionic liquid, respectively.

All samples exhibit two broad amorphous reflections near $2\theta = 15°$ and $2\theta = 25°$, the shape of all curves are similar. The results show that poly(*o*-toluidine) crystallinity is hardly affected by $LaCl_3$, ionic liquid and cooperative effect of La^{3+} and ionic liquid.

Conclusion

The poly(*o*-toluidine) of high conductivity (10.14 S cm^{-1}) was synthesized by traditional chemical process in a new system contained $LaCl_3$ and ionic liquid. La^{3+} and ionic liquid can interact with the poly(*o*-toluidine) chain, the interaction can remarkably improve the conductivity. The optimum synthesized condition of poly(*o*-toluidine) of high conductivity is OT: ionic liquid = 1:2 in the new system. The cooperation of La^{3+} and ionic liquid can also affect UV-Vis, FTIR spectra and thermo-stability of the poly(*o*-toluidine). UV-Vis spectra indicate that the energy gaps of π-π^* and quinoid ring transitions increase due to the cooperation. The FTIR spectra show that there exists the obvious interaction between ionic liquid, La^{3+} and poly(*o*-toluidine) chain and it makes the peaks of Q-NH$^+$-B or B-NH$^+$-B shift to longer wavelength. Poly(*o*-toluidine) crystallinity is hardly affected by $LaCl_3$, ionic liquid and cooperative effect of La^{3+} and ionic liquid.

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