Synthesis and characterization of polyindole with liquid crystalline azobenzene as side chains

Seyed Hossein Hosseini¹* and Maryam Ashjari²

¹Department of Chemistry, Faculty of Science, Islamic Azad University, Islamshahr Branch, Tehran-Iran.
²Department of Chemistry, Faculty of Science and Engineering, Islamic Azad University, Saveh Branch, Saveh-Iran.

Accepted 8 August, 2013

In this study, a series of azobenzene-functionalized liquid crystalline (LC) polyindole derivatives: poly{2-[N-ethyl-N-[4-[4'-(nitrophenyl)azo]phenyl]amino]ethyl-3-indolyl acetate}, poly(In₃AA-RedI), poly{2-[N-ethyl-N-[4-[4'-nitrophenylazo]phenyl]amino]ethyl-3-indolyl acetate-co-indole}, poly(In₃AA-RedI-co-In), poly{2-[N-ethyl-N-[4-[4'-(nitrophenyl)azo]phenyl] amino]ethyl-3-indolyl acetate-co-pyrrole}, and Poly(In₃AA-RedI-co-py) were synthesized. Novel 3-substituted indole with liquid crystalline side chain (In₃AA-RedI) was synthesized by the direct reaction of indole-3-acetic acid with 2-[N-ethyl-N-[4-[4'(nitrophenyl)azo]phenyl] amino]ethanol (RedI). Chemical polymerization of (In₃AA-RedI), and its copolymerization with indole and pyrrole were carried out by using ferric perchlorate as oxidizing agent. The composition, structure and thermal property of these LC polyindole derivatives were fully characterized by FTIR, ¹H,¹³C-NMR and UV-Visible spectroscopic methods, and its LC behavior and photoresponsive property were also investigated by polarized optical microscope and differential scanning calorimetry (DSC). The results show that poly(In₃AA-RedI) exhibited the smectic A (Sₐ) and nematic (N) liquid crystalline behavior. Conclusion shifted phase transition temperatures of the poly(In₃AA-RedI) in the heating process are as follows: C→Sₐ (161°C), Sₐ→N (184°C) and N→I (231°C). Electrical conductivity of polymer [poly(In₃AA-RedI)] and two of its copolymers [poly(In₃AA-RedI-co-In) and poly(In₃AA-RedI-co-Py)], has been studied by four probe methods and produced 8.3×10⁻⁵, 6.4×10⁻⁴ and 4.7×10⁻³ Scm⁻¹ conductivities, respectively.

Key words: Conducting polymers, electrical conductivity, liquid crystalline polymer, optical properties, optical materials, polyindole.

INTRODUCTION

Conjugated polymers are well-known for their excellent electrical conductivities in oxidized (doped) state. The recent development of processable conducting polymers has opened the way for large-scale industrial applications. Conjugated polymers have been used widely in many areas such as rechargeable batteries (Heinze, 1991; Roth and Graupfer, 1993), condensators (Mohammadi et al., 1986), diodes (Turut and Koleli, 1993; Kolelli et al., 1994), and sensors (Hosseini et al., 2005, 2006). Among these classes of polymers, polyaniline, polypyrrole, polythiophene, etc. have been studied extensively because of their favorable processability and relative stability (MacDiarmid, 1997; Hosseini and Entezami, 2001, 2003). Heteroaromatic molecules containing nitrogen have very interesting properties. Polyindole is an electro active polymer, which can be obtained from electrochemical oxidation of indole or chemical oxidation using FeCl₃ or CuCl₂ (Xu et al., 2006). However, only little investigations have been made on chemically synthesized polyindole (John and

*Corresponding author. E-mail: shhosseini@iiau.ac.ir, Tel: +98(9121374816).
The polymerization efficiency and the conductivity of polyindole are lower than the other known hetero atom containing conducting polymers such as polycarbazole, polyfuran, polyisothianapthene, polybithiophene, etc. Therefore, they did not attract much attention as the other types of conducting materials. There are two main procedures for the preparation of soluble conjugated polymers: one is the incorporation of relatively long and flexible side chains; another is the introduction of large counterions (Zaho and Wang, 2006).

Synthesis of three-substituted azobenzene-functionalized polyindoles has attracted much interest both from synthetic considerations as well as from materials science. Polyindoles with azobenzene groups in three-position will not only have better processability and stability, but also may possess novel electronic and optical properties. Thus, the combination of polyindole backbone with photoactive azobenzene groups can provide a new approach to develop other novel materials with unique electronic and optical properties. Azo chromophore has been demonstrated to be good photoisomerizable units (Matsui et al., 2001) for optical switching, image storage and other electrooptic devices. The introduction of photoresponsive moieties into liquid crystalline polymers is a useful method to provide the liquid crystal (LC) materials with photoresponsive properties. Hu and coworkers (Zhao et al., 2005) synthesized a series of novel LC azobenzene-functionalized polythiophenes with the aims of preparing liquid crystalline thiophene derivatives for photonic applications.

In the previous works, we synthesized a new liquid single crystal (Yousefi et al., 2008) and reported liquid crystalline polymer based N-substituted pyrrole (Hosseini and Mohammadi, 2009). This polymer exhibit liquid crystalline and electrically conductivity properties, as well. In this paper, polyindole was selected as a main chain skeleton. The side chain polyindole contains mesogenic group which shows liquid crystalline property. The 3-substituted of the indole ring was prepared and their liquid crystallinity and thermal properties investigated. Figure 1 shows side chain polyindole. So, a series of novel LC azobenzene-functionalized polyindoles synthesized with the aims at preparation of liquid crystalline indole derivatives for photonic applications. The synthesis, characterization, and photoresponsive behavior of these chromophore-based LC polyindole derivatives were fully discussed. Molecular structure of the LC polyindole is illustrated in Figure 2, where LC group is introduced into 3-position of the indole unit. The polymer consists of main chain, flexible methylene spacer, linking group and tailing group, as shown in Figure 2.

EXPERIMENTAL PROCEDURE

Physical measurements

$^1$H, $^{13}$C-NMR spectra were recorded on a BRUKER 250 NMR spectrometer at 400 MHz in deuterated chloroform-d or dimethylsulfoxide-d$_6$ with TMS as an internal standard. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), and integration. Differential Scanning Calorimetry (DSC) analyses were performed at 5°Cmin$^{-1}$ on a TA instruments using STA 625 DSC. FT-IR spectra were recorded on a 8101-M Shimadzu and BRUKER-IF-66.5 spectrometer. Vibrational transition frequencies are reported in wave number (cm$^{-1}$). The UV-Visible spectra were obtained using a UV-Vis recording spectrophotometer (Perkin-Elmer Lambda 15).

Materials

Indole-3-acetic acid (Fluka), indole (Merck) and pyrrole (Fluka, 96%) were distilled prior to use. Tetrahydrofuran (Merck), petroleum ether and ethyl acetate were distilled and dried with molecular sieves (4Å) prior to use. 4-nitroaniline (Merck, 98%), dicyclohexyl carbodiimide (DCC) (Merck, 98%), 4-(dimethylamino)pyridine (DMAP) (Merck, 99%), 2-(N-ethyl aniline)ethanol (Merck, 99%), sodium nitrite (NaNO$_2$) (Merck, 99%), methanol (Fluka) and the other materials used in this work were purchased from Merck chemicals and purified, or prepared according to literature methods.

Preparation of 2-[N-ethyl-N-[4-[(4′-nitrophenyl)azo]-phenyl]amino] ethyl (RedI)

7 g (0.05 mol) of 4-nitroaniline was dissolved in a solution of 25 ml...
of concentrated hydrochloric acid and 150 ml of water. The mixture was cooled to 0°C in an ice-water bath, and then a solution of 3.6 g (0.05 mol) of sodium nitrite in 15 ml of water was added dropwise. The resulting solution of diazonium salt was stirred for 30 min at 0–3°C. Another solution of 5 g (0.03 mol) of N-ethyl-N-hydroxyethyl aniline dissolved in 10 ml of hydrochloric acid (10%) was stirred for 5 min at 0°C. The above solution of diazonium salt was added into this solution within 30 min. The mixture was allowed to stand for 20 min. Then was neutralized with added NaOH solution with slowly and stirring. Reddish crystals were filtered on a Buchner funnel and recrystallised with 2-propanol. Compound 1 was obtained as crimson crystals. Yield 9 g-85%, mp: 170-173°C. UV (THF): λmax=310 nm (0.3 intensity), 470 nm (1.25 intensity). FT-IR (KBr pellets, u in cm⁻¹): 3434 (υOH), 3200 (υN-H, Ar), 2950 (υC-H, Al), 1599 (υN,N), 1515, 1341 (υNO₂), 800-850 (υC-H, OOP) cm⁻¹. ¹H-NMR (CDCl₃): δ 1.26 (2H, d), 1.75 (1H, s), 3.56 (2H, q), 3.62 (2H, t), 3.90 (2H, t). ¹³C-NMR (CDCl₃): δ 12.1, 46.4, 52.8, 60,1, 112.3, 122.5, 124.7, 143.8, 147.2, 151.6, 157.2 ppm.

Preparation of Poly{2-[N-ethyl-N-[4-[(4'-nitrophenyl)azo]phenyl]amino]ethyl-3-indolyl acetate, (In3AA-Redl)}

Polymerization was carried out as follows: 0.5 g (1.06 mmol) of monomer (In3AA-Redl) in 25 ml THF was added dropwise to a suspension 1.126 g, (3.18 mmol) of Fe(ClO₄)₂ in 20 ml of THF under nitrogen atmosphere. The mixture was stirred at 50°C temperature for 24 h. The polymerization mixture was added dropwise into 100 ml of methanol. The precipitates were filtered, dissolved in 5 ml of THF, and precipitated into 100 ml of methanol. This procedure was repeated three times until the unreaceted monomer was completely removed. Finally, the polymer was dried under vacuum at 25°C to constant weight (Compound 3 was obtained). UV (THF): λmax=280 nm (1 intensity), 330 nm (0.3 intensity), 475 nm (0.2 intensity) and 680 nm (0.4 intensity). FT-IR (KBr pellets, u in cm⁻¹): 3384 (υN-H, indole), 3200 (υN-H, aromatic), 2917 (υC-H, aliphatic), 1750 (υC=O), 1627 (υN=O), 1514, 1335 (υNO₂), 1100 (υC=O) cm⁻¹. ¹H-NMR (d6-DMSO): δ 1.09 (3H, t), 1.24 (2H, d), 3.63 (2H, q), 3.72 (2H, t), 4.27 (2H, t), 6.88-7.36 (6H, m), 7.82 (2H, d), 7.95 (2H, d), 8.38 (2H, d), 10.91 (1H, s) ppm. ¹³C-NMR (d6-DMSO): δ 11.8, 30.6, 44.8, 48.2, 61.6, 106.6, 111.3, 111.6, 118.5, 118.4, 121.0, 122.4, 124.1, 124.8, 126.0, 127.0, 136.0, 142.8, 146.8, 151.5, 155.1, 171.5 ppm.

Preparation of Poly{2-[N-ethyl-N-[4-[(4'-nitrophenyl)azo]phenyl]amino]ethyl-3-indolyl acetate-co-indole, Poly(In3AA-Redl-co-In)}

The typical synthesis procedures utilized can be described as follows: 0.1 g (0.2123 mmol) of monomer (In3AA-Redl) and 0.0248 g (0.2123 mmol) of monomer indole in 10 ml of THF was added dropwise to a suspension 0.1503 g (0.4246 mmol) of Fe(ClO₄)₂ in
substituted indole monomer with Fe(CIO₄)₃ always leads to two different types of couplings: head-to-tail and head-to-head. Thus, the α-methylene protons directly attached to the indole ring (β-position) and can be incorporated into a polymer chain with the above two diads. The two peaks located at 1.2-1.5 ppm arise from the methylene protons between the ester group and the indole ring, showing that poly(In3AA-Redl) has a stereo random chain structure with almost equal distribution of head-to-tail and head-to-head linkages along the polymer chain. The ¹³C-NMR spectrum of the poly(In3AA-Redl) is shown in Figure 5. Using INEPT- pulse sequence, we were able to distinguish the proton bonded carbons from all other carbons present in the molecule. On the basis of a comparison with the spectra of poly(In3AA-Redl), the following assignments are proposed: The line at the lowest field (171.5 ppm) corresponds to the carbon of the ester group. The lines at 155.1, 151.5, 146.8, 142.8, 125.0, 124.8, 122.4 and 111.6 ppm are assigned to the aromatic carbons in the Redl moiety. The remaining eight lines at 136.0, 127.0, 124.1, 121, 118.4, 118.3, 111.3 and 106.6 ppm originate from the carbons of the indole ring. In the aliphatic part, the lines of low intensity at 11.2, 30.6, 44.8, 48.2 and 61.6 ppm correspond to the Redl substituent. The peaks are located at 38-40 ppm arise from the d⁵-DMSO solvent.

Figure 6 shows ¹H-NMR spectrum of the polymer poly(In3AA-Redl-co-In) in (d⁵-DMSO) solvent. In this spectrum, peaks of aliphatic protons (-CH₃), (-CH₂-COO-) and (-CH₂-CH₂) observed in 1.1 to 2.2 ppm. Peak of protons (-CH₂-N) and (-O-CH₂) are not observed in spectra, because of overlap with peak of DMSO and water around 2.49 and 3.3 ppm, respectively. Protons of aromatic ring and indole are characterized between 6.5 to 8 ppm. Of course peaks of aromatic ring are not clear precisely because they are blocked copolymer, but they appeared in the area related to aromatic compounds. Copolymer has a low solubility, so ¹H-NMR is not clear. The great adherence of peak is a result of the greater involvement of indole monomers than In3AA-Redl monomer in polymeric chain. The peaks in aromatic region confirm performance of copolymerization.

Figure 7(a) shows UV-Visible spectrum of In3AA-Redl in THF as a solvent. According to Figure 7a, the In3AA-Redl as a monomer has three peaks in 285, 335 and 535 nm. The first absorption band is related to an n-π transition and the second one is associated with a π-π transition. Upon UV irradiation, a trans-cis isomerization is induced, leading to two absorption bands centered near 335 and 535 nm, respectively. The photochemical properties of the poly(In3AA-Redl) were examined also in THF as a solvent (Figure 7b). As can be seen in Figure 7b, the poly(In3AA-Redl) exhibits an absorption band centered at 280 nm which is related to the π-π transition of trans configuration of the azobenzene moieties and a broad absorption bands around 550-750 nm which can be related to the π-π transition of the highly conjugated

RESULTS AND DISCUSSION

All synthetic routes of Redl, In3AA-Redl and poly(In3AA-Redl) shown are in Scheme 1. Therefore, schematic copolymerization of In3AA-Redl with indole and pyrrole has been shown in Scheme 2.

Structural characterization

In order to obtain polymers with higher molecular weights, the polymerization and copolymerization were carried out at 50°C temperature with dropwise addition of monomers. This polymer was found to be soluble in chloroform, THF and methylene chloride, but two copolymers synthesized by chemical oxidative copolymerization using Fe(CIO₄)₃ are not soluble in common organic solvents. Figure 3 illustrates the FT-IR spectra of poly(In3AA-Redl). The peaks of about 3100-3600, 3020 and 2917 cm⁻¹ was related to N-H, C-H (aromatic) and C-H (aliphatic) stretching vibrations, respectively. The peaks at around 1750 and 1100 cm⁻¹ are due to the carbonyl (C=O) stretching vibration and C-O-C stretching vibration respectively.

Figure 4 shows the ¹H-NMR spectrum of poly(In3AA-Redl). On the basis of comparison with the spectrum of monomer, we can assign the following peaks for poly(In3AA-Redl): 1.09 (-CH₃), 1.24 (-CH₂-COO-), 2.52 (DMSO), 3.31 (H₂O), 3.63 (-CH₂-CH₂), 3.72 (-CH₂-N), 4.27 (-O-CH₃), 7.37, 7.82, 7.95 and 8.38 ppm (protons of phenylene groups). The lines refer to the aromatic protons of the indole ring that are located at 6.88-7.36 and 10.85 (H-N) ppm. The oxidative polymerization of β-

Preparation of Poly[2-[N-ethyl-N-[4-[(4'-nitrophenyl)azo]-
phenyl]amino] ethyl-3-indolyl acetate-co-pyrrole], Poly(In3AA-
Redl-co-Py)

Poly(In3AA-Redl-co-Py) was synthesized using the same synthetic procedures as for Poly(In3AA-Redl-co-In). The (In3AA-Redl) monomer (0.1 g, 0.2123 mmol) and pyrrole (0.0142 g, 0.2123 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise to a suspension of Fe(CIO₄)₃ (0.1503 g, 0.4246 mmol) in tetrahydrofuran (10 ml) under nitrogen. The mixture was stirred at 50°C temperature for 24 h. The polymer in solution was precipitated by addition of excess methanol. The precipitate was extracted using boiling absolute ethanol. The precipitate was dried under vacuum. FT-IR (KBr pellets, υ in cm⁻¹): 3429 (υ co-N), 3100 (υ aromatic), 3020 and 2917 cm⁻¹. ¹H-NMR (d⁵-DMSO): 8 1.17-1.3 (broad), 1.3-1.9 (broad), 6.5-9 (broad) ppm.

Structural characterization

In order to obtain polymers with higher molecular weights, the polymerization and copolymerization were carried out at 50°C temperature with dropwise addition of monomers. This polymer was found to be soluble in chloroform, THF and methylene chloride, but two copolymers synthesized by chemical oxidative copolymerization using Fe(CIO₄)₃ are not soluble in common organic solvents. Figure 3 illustrates the FT-IR spectra of poly(In3AA-Redl). The peaks of about 3100-3600, 3020 and 2917 cm⁻¹ was related to N-H, C-H (aromatic) and C-H (aliphatic) stretching vibrations, respectively. The peaks at around 1750 and 1100 cm⁻¹ are due to the carbonyl (C=O) stretching vibration and C-O-C stretching vibration respectively.

Figure 4 shows the ¹H-NMR spectrum of poly(In3AA-Redl). On the basis of comparison with the spectrum of monomer, we can assign the following peaks for poly(In3AA-Redl): 1.09 (-CH₃), 1.24 (-CH₂-COO-), 2.52 (DMSO), 3.31 (H₂O), 3.63 (-CH₂-CH₂), 3.72 (-CH₂-N), 4.27 (-O-CH₃), 7.37, 7.82, 7.95 and 8.38 ppm (protons of phenylene groups). The lines refer to the aromatic protons of the indole ring that are located at 6.88-7.36 and 10.85 (H-N) ppm. The oxidative polymerization of β-

10 ml of THF under nitrogen atmosphere. The mixture was stirred at 50°C temperature for 24 h. The copolymer in solution was precipitated by addition of excess methanol. The precipitate was extracted using boiling absolute ethanol. The precipitate was dried under vacuum. FT-IR (KBr pellets, υ in cm⁻¹): 3429 (υ co-N), 3100 (υ aromatic), 3020 and 2917 cm⁻¹. ¹H-NMR (d⁵-DMSO): 8 1.17-1.3 (broad), 1.3-1.9 (broad), 6.5-9 (broad) ppm.
polyindole units. Because of low solubility of poly(In3AA-Redl-co-In) and poly(In3AA-Redl-co-Py), we were not able to investigate UV-Visible or $^{13}$C-NMR spectra of them.

**Liquid crystalline and thermal properties**

Liquid crystallinity and thermal analysis of the polymer were conducted by optical absorption, optical polarizing...
Scheme 2. Schematic reactions for copolymerization of poly(In3AA-RedI) with pyrrole and indole.

Figure 3. FT-IR Spectrum of poly(In3AA-RedI).
microscope, and differential scanning calorimetry (DSC). Phase transition temperatures were determined by DSC measurement. All DSC runs in this research were made under nitrogen atmosphere with a heating rate of
Figure 6. FT$^1$H-NMR Spectra of poly(In3AA-RedI-co-In).

Figure 7. UV-Visible spectra of a) In3AA-RedI (...) and b) poly(In3AA-Redl) (-).

5°C/min. DSC thermograms of Redl in heating and cooling process are shown in Figures 8(a, b). Figure 8a shows thermogram and endothermic peak at 174.71°C which is related to the melting process of Redl and also a transformation of crystalline phase to isotropic state. Crystalline phase of this compound is changed directly to
isotropic liquid as a result of temperature effect. Therefore, it shows exothermic peak at 272.43°C which is related to the degrading process of RedI. In cooling process no peak is observed probably because the sample decomposition occurs at higher temperature or it does not have clear LC behaviour. By heating the sample again no peak is observed, this confirms probable sample decomposition (Figure 8b).

Transition temperatures for poly(In3AA-RedI) were obtained using DSC shown as in Figure 9. DSC Thermogram of poly(In3AA-RedI) showed 5 glass transition temperature about 59, 91, 151, 181 and 231°C.
Therefore, it has three endothermic peaks. The first endothermic peak at 162°C is an indication of changing of crystalline phase to smectic A liquid crystalline state (C→Sₐ). The second peak at 193°C is related to the changing of smectic A liquid crystalline mesophase to nematic state (Sₐ→N). The last observed endothermic peak in this curve is about 225°C that is related to transition phase of nematic liquid crystalline to isotropic liquid (N→I). In the first and the second transitions, the stability of liquid crystalline mesophases are about 31°C and 32°C, respectively. The images of polarizing optical microscope of poly(In3AA-Redl) demonstrated the smectic A, nematic and isotropic liquid crystalline states. Chemical, structural, thermal and morphological studies indicated that high quality polymer film can be obtained. As-formed polymer film was thoroughly soluble in polar solvent such as DMSO. According to IR and ¹H-NMR spectra, the existence of N–H bond implies that coupling between the monomer units occurred at the C2 and C5 positions.

Figure 9 DSC Thermogram of poly(In3AA-Redl) with rate of 5°C/min.

Conclusion

In this paper, we have described the preparation and investigation of liquid crystalline polyindole with azobenzene group in side chain. The results indicate that these azobenzene-functionalized polyindole derivatives have wide mesophase temperature ranges. DSC thermogram of poly(In3AA-Redl) showed 5 semi glass transition and three endothermic peaks. The endothermic peaks are indicative of changing of C→Sₐ, Sₐ→N and N→I. Images of polarizing optical microscope of poly(In3AA-Redl) demonstrated the smectic A, nematic and isotropic liquid crystalline states. Chemical, structural, thermal and morphological studies indicated that high quality polymer film can be obtained. As-formed polymer film was thoroughly soluble in polar solvent such as DMSO. According to IR and ¹H-NMR spectra, the existence of N–H bond implies that coupling between the monomer units occurred at the C2 and C5 positions.
Figure 10. Cross-polarized optical micrograph of the polymer sample, smectic C phase a) 152°C, b) 160°C, c) 170°C, d) 185°C, e) 195°C and f) 205°C.

References