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Synthesis and characterization of soluble poly(*N*-heptyl indole)

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Abstract

In view of preparing soluble polyindole, indole was *N*-alkylated using bromoheptane and polymerized to poly(*N*-heptyl indole) which is soluble in common organic solvents. This process is being reported for the first time. Poly(*N*-heptyl indole) was characterized by spectral, thermal methods and it shows photoluminescence in liquid state.

Keywords: Conjugated polymer; Poly(*N*-heptyl indole); Photoluminescence

1. Introduction

Conducting polymers have been used widely in many areas such as rechargeable batteries [1,2], condensators [3], diodes [4–6], LEDs [7] and sensors [8]. Among these classes of polymers, polyaniline, polypyrrole, polythiophene, etc. have been studied extensively because of their favorable processibility and relative stability [9]. Nitrogen containing heteroaromatic organic molecules have very interesting properties. Polyindole is an electro active polymer, which can be obtained from electrochemical oxidation of indole or chemical oxidation using $FeCl_3$ or $CuCl_2$ [10]. However, only little investigations have been made on chemically synthesized polyindole. 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, polyphenazine, etc. and hence they did not attract much attention as the other types of conducting materials. One of the reasons for this behavior is the large number of polymerization schemes and large deviations from planarity. Like most of the conjugated polymers such as polythiophenes and polypyrroles, these branching and defects create highly complex structures that are difficult to be analyzed with standard spectroscopic techniques [11].

Polymer LEDs have drawn great attention and been studied extensively in the past one decade. Because polymeric semiconducting materials posses many advantages over inorganic semiconducting materials such as low cost, easy processibility, ease of forming large areas, etc. Solubility of polymer in common organic solvents like $CHCl_3$ and THF will be the preferable feature. Polyindole synthesized by chemical oxidative polymerization using $FeCl_3$ is not soluble in common organic solvents [10]. In order to make soluble polyindole, in this work *N*-heptyl indole was synthesized and polymerized using $FeCl_3$ as oxidizing agent. The resultant polymer material was purified by treating with aqueous ammonia and EDTA solution. Poly(*N*-heptyl indole) may be the promising material in the field of optoelectronics.

2. Experimental part

2.1. General methods and materials

Poly(*N*-heptyl indole) was mixed with KBr powder and compressed into pellet, wherein; the polymer powder was evenly dispersed. Fourier transform infrared spectrum was recorded using GC–FTIR spectrometer (MODEL 670 Thermo Nicolet Nexus,USA spectra). Wide angle X-ray diffraction spectrum for the polymer powder sample was obtained using a Siemens/D-5000 X-ray diffractometer using Cu Kα radiation of wave length 1.54×10^{-10} m and continuous scan speed of 0.045°/min. MALDI-TOF of poly(*N*-heptyl indole) was performed using OMPACT SEQ, KRATOS, UK with 337 nm nitrogen laser, time of flight 1.8 m path length. Thermogravimetric analysis of polymer sample was carried out using 851^e, Mettler Toledo, Switzerland at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetric analysis was carried out using DSC 821^e, Mettler

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Toledo at heating rate of 10 °C/min under nitrogen atmosphere. UV/vis spectra of poly(*N*-heptyl indole) in chloroform solution as well as in solid thin film form were recorded using Labomed. Inc. Spectro UV–vis double beam PC, USA. Photoluminescence spectrum (PL) of polymer sample was recorded in chloroform solvent using SPEX FLUOROLOG 1680 0.22 m double spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ solvent and TMS as internal reference using Avance 300 Bruker NMR instrument, Switzerland.

Indole, NaH, *n*-bromoheptane, $FeCl_3$, EDTA reagent grade materials from E-Merck were used as received. Dry chloroform and THF were prepared by the reported procedure.

2.2. Synthesis

2.2.1. Synthesis of monomer

Four grams of indole and 30 mL THF were taken in 250 mL round bottomed flask. To this solution, 4.08 g NaH was added by batch wise and the reaction mixture was heated upto 60 °C. To this reaction mass 20 mL THF solution containing 12.24 g *n*-bromoheptane was added drop wise. The reaction mass was refluxed for 4 h and the reaction was quenched with 50 mL brine solution. The crude product was extracted with ethyl acetate (3×40 mL), dried over anhydrous sodium sulfate and the solvent was distilled off under vacuum. The pure colorless viscose oil, *N*-heptyl indole (80% yield) was obtained by column chromatography. The structure of the product was confirmed by proton NMR.

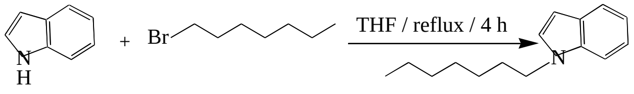
^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.5$ (d, 1H), 7.0–7.3 (m, 4H), 6.4 (d, 1H), 4.0 (t, 2H), 1.8 (t, 2H) and 0.7–1.4 (m, 11H).

2.2.2. Synthesis of polymer

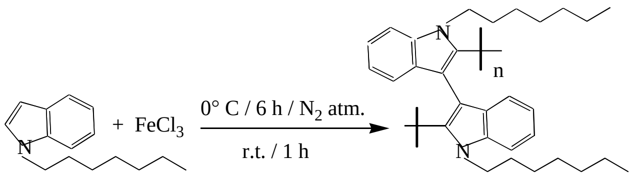
In a typical experiment, 8.5 mmol of *N*-heptyl indole was dissolved in 50 mL dry chloroform in 100 mL round bottomed flask, to this solution 34.2 mmol of $FeCl_3$ was added in lot wise at 0–5 °C for a period of 6 h under N_2 atmosphere. The reaction mass was kept under constant stirring at room temperature for 1 h under N_2 atmosphere. To the above reaction mass 150 mL of methanol was added and the solid was filtered, washed with methanol until the solution becomes colorless. The polymer was dissolved in 25 mL of chloroform and the solution was treated with 20 mL of concentrated ammonia and the mixture was boiled for 30 min. The water phase was separated and fresh ammonia was added. This procedure was repeated for four times and then the chloroform solution was treated with 0.05 M EDTA solution for three times and washed with ample amount of water. Then chloroform layer was separated and the amount of chloroform was reduced under vacuum. The polymer was precipitated by adding 30 mL of methanol, filtered and washed with methanol. The solid was dried at 90 °C till a constant mass. This process yielded 15% polymer with respect to the weight of the monomer used in the reaction.

3. Results and discussion

The monomer was synthesized by *N*-alkylation of indole by refluxing in THF for 4 h with *n*-bromoheptane and NaH, the pure product was isolated by column chromatography (Scheme 1).



Scheme 1. Synthesis of *N*-heptyl indole.



Scheme 2. Synthesis of poly(*N*-heptyl indole).

The polymer was prepared by chemical oxidative coupling using $FeCl_3$ via the dehydrogenation condensation of monomer (Scheme 2). The obtained polymer is soluble in common organic solvents such as chloroform, dichloromethane, acetone, diethyl ether and tetrahydrofuran.

IR spectrum of polymer confirms its structure, the absorption peak at 3030 cm^{-1}is due to C–H (aromatic) stretching, those at 2925 and 2855 cm^{-1} are due to asymmetric and symmetric stretching of the C–H (aliphatic) of the alkyl side chain. The peak observed at 1600 cm^{-1} with the shoulder at 1570 cm^{-1} is attributed to aromatic C$\overset{\text{---}}{-}$C bond in benzene ring. The band at 1350 cm^{-1} is assigned for C=N stretching. The peak located at 735 cm^{-1} reveals the out of plane deformation of the C–H bond. TGA thermogram of poly(*N*-heptyl indole) shows 4.5% weight lose due to moisture present in the polymer sample and the polymer is stable up to 220 °C. Initial degradation of polymer was observed around 220–315 °C with a small weight loss of 2.2% and polymer degradation starts around 315 °C. DSC analysis of poly(*N*-heptyl indole) shows T_g around 85 °C and an exothermic peak at 165 °C may be due to cross linking of the polymer chain. XRD spectrum shows the amorphous nature of polymer. ^{1}H NMR spectrum of the poly(*N*-heptyl indole) showed broad peaks around 1.0 (aliphatic protons), 4.0 (proton attached to nitrogen) and 7.1 (aromatic protons) ppm were observed. UV–

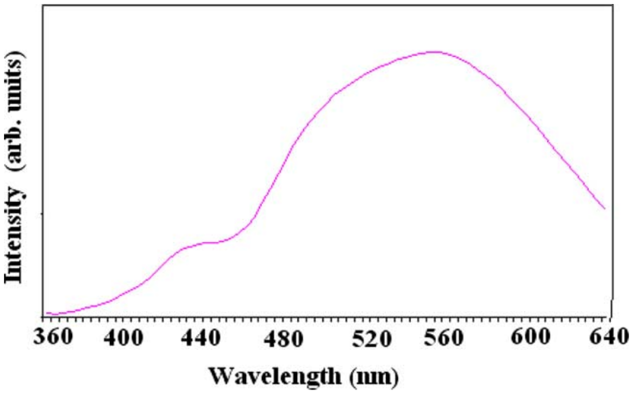


Fig. 1. Photoluminescence spectrum of poly(*N*-heptyl indole) in chloroform excited at 340 nm.

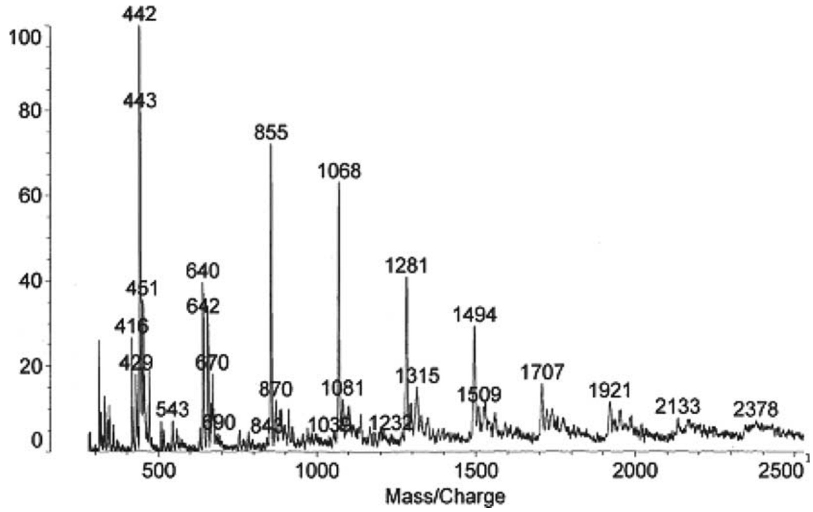


Fig. 2. MALDI-TOF spectrum of poly(*N*-heptyl indole).

vis spectrum of poly(*N*-heptyl indole) in $CHCl_3$ solution and thin solid film showed a broad band around 320 and 310 nm respectively. The PL spectra were recorded in dilute solution in $CHCl_3$ with different excitation wavelength (320, 330 and 340 nm), it gives absorption maximum at 550 nm with a shoulder around 430 nm (Fig. 1).

MALDI-TOF mass analysis was performed to find out the molecular weight of poly(*N*-heptyl indole). The polymer was dissolved in THF and dithranol was used as matrix. The major signal is observed at $m/z = 855$, which agrees well with a value of 856 calculated for four monomer units (Fig. 2). The other signals were observed at 1068, 1281, 1494, 1707, 1921, 2133 and 2346, with regular interval of 213, which is the molecular weight of repeating unit.

4. Conclusion

In summary, soluble poly(*N*-heptyl indole) was synthesized for the first time. Poly(*N*-heptyl indole) is having fluorescence property in solution state. This may be the promising material in the field of optoelectronics.

Acknowledgements

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