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Chemical synthesis and characterization of high molecular weight poly(2,2'-dithiodianiline) (PDTDA)

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Summary

A high molecular weight poly(2,2'-dithiodianiline) (PDTDA) was chemically synthesized by simple solution polymerization method. The weight average molecular weight ($\overline{M}_w$) was observed to be 424,690 by GPC analysis. The chemical structure of the undoped PDTDA was characterized by UV/VIS spectroscopy. It was confirmed that the S-S bonds within repeating units could be conserved well after chemical polymerization by FTIR spectroscopic analysis.

Introduction

Disulfide compounds have been introduced as a new organic/polymer cathode material in lithium batteries [1-5]. A series of compounds having –SH groups within the molecules are being considered as energy storage materials, whereby energy exchange occurs based on the reversible process because the cleavage and recombination of S-S bonds is expected to be easy:

$$2\text{SH-} \leftrightarrow \text{-S-S-}$$

The theoretical capacity and energy density of these materials far exceed those of conventional battery materials as well as those of other candidate materials such as intercalation compounds and current conducting polymers [6, 7]. Among them, poly(2,2'-dithiodianiline) (PDTDA), a new material with polymer chains interconnected with S-S bonds, has been proposed by Naoi et al.. They have shown that PDTDA can be synthesized to form an electroactive thin film by cycling potential electropolymerization method at the glassy carbon electrode surface [8-10]. The discharge capacity and the energy density of the unit cell using the PDTDA as an active material of cathode were 270 Ah/kg and 675Wh/kg, respectively.

In this study, we have tried to obtain high molecular weight PDTDA powders in large quantities using a new and simple chemical synthetic method by oxidation of the monomers, 2,2'-dithiodianiline (DTDA). The molecular weight of the product was investigated and the structure of the chemically synthesized PDTDA was also characterized.

Experimental

Chemical synthesis of poly(2,2'-dithiodianiline) (PDTDA)

2,2'-dithiodianiline (DTDA) monomer (TCI Co.) was used as received. The redox initiator, ammonium persulfate ($(NH_4)_2S_2O_8$, APS) (Aldrich Co.), was used after drying in vacuum at 100 °C for 48 hours. DTDA monomers were dissolved in 1M HCl (aq.) solution at 80 °C. In order to polymerize the DTDA monomers, the 30wt% of initiator solution was slowly added by using a dropping funnel to the reactant solution with vigorous stirring over a period of 4 hours. After the addition, the reaction mixture was agitated continuously for another 12 hours under N_2 atmosphere at 70 °C. As the polymerization proceeded, the color of reacting medium changed to a dark-brown and the minute particles were produced. The precipitated particles were filtered and washed with hot distilled water to remove any impurities such as the residual initiators and the unreacted monomers. The filtered PDTDA were reduced by excess 0.1N NH_4OH (aq.) solution at 70 °C for 24 hours to prepare undoped PDTDA for the various analysis and characterization. The product was collected by filtration and washed three times again with hot distilled water. The filtered product was dried under vacuum at 100 °C for 48 hours. The reaction scheme for the synthesis of the undoped PDTDA is given in Figure 1.

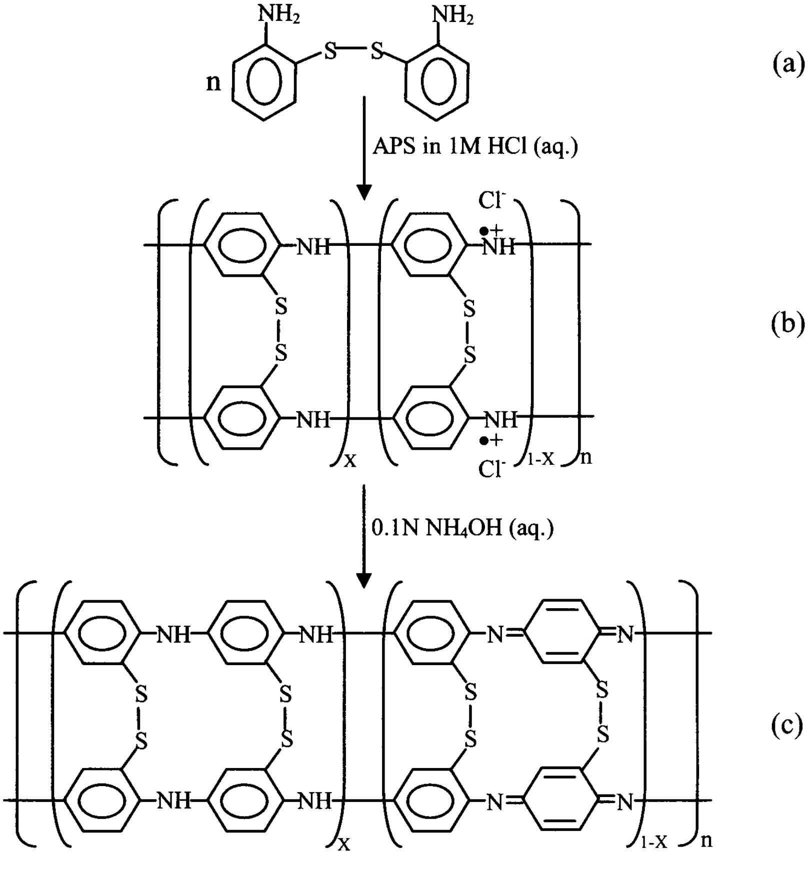

Figure 1. The reaction scheme for chemical synthesis of undoped poly(2,2'-dithiodianiline) (PDTDA): (a) DTDA monomer (b) doped PDTDA (c) undoped PDTDA.

Gel permeation chromatography (GPC) measurements

A Waters 150-CV GPC (Waters Chromatography, Milford, MA) with PS standards (Showa Denko) was used for measurements of molecular weight and polydispersity. The instrument is operated with Ultrastyragel columns of 500, 10^3, 10^4, and 10^5 Å porosities in N,N-dimethylformamide (DMF) solvent.

UV-VIS spectroscopy measurements

The UV-VIS spectra of the polymers were recorded in DMF solvent with a PC driven Shimadzu UV-2101 PC scanning spectrophotometer.

Fourier transform infrared (FTIR) measurements

The FTIR spectra were acquired on a Bomem 102 model fourier transform spectrometer at a resolution of $4cm^{-1}$. A minimum of 30 scans were signal-averaged and the spectra were stored on a magnetic disc for further analysis.

Results and discussion

Molecular weight of the undoped PDTDA

Figure 2 shows the chromatographic characteristic of a 0.5wt% undoped PDTDA solution in DMF. Unlike formerly reported bimodal molecular weight distributions determined in polyaniline (PANI) emeraldine base solutions [11-13], the multimodal distributions were obtained in PDTDA one.

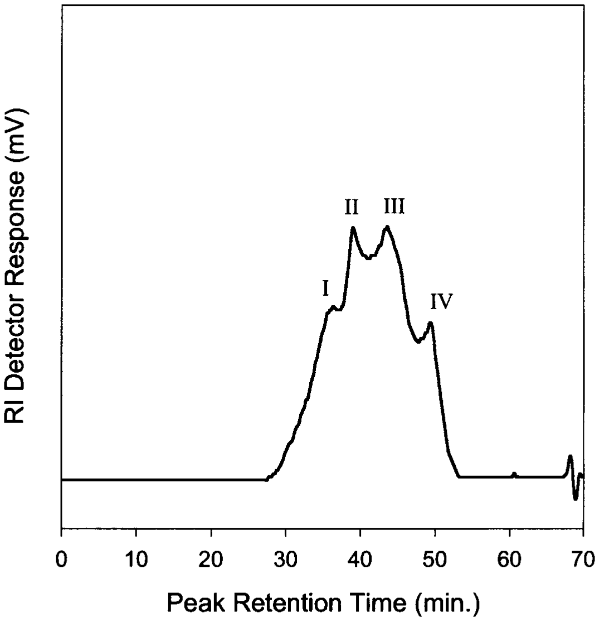

Figure 2. GPC chromatogram of the undoped PDTDA(carrier solvent is DMF and standard polymer is PS).

The chromatogram consists of two major peaks (peak II, III) having weight average molecular weight ($\overline{M}_w$) on the order of 10^5 and two minor peaks of high molecular weight (peak I) on the order of 10^6 and low molecular weight (peak IV) on the order of 10^4. In peak I, various explanations have been offered for this observation. In general, it is believed that some form of aggregation occurs in the base polymer, accounting for the high molecular weight fraction. The aggregation is believed to be due to interchain interactions such as physical entanglements or hydrogen bonding [14, 15]. It is expected that the two major peaks observed (peak II, III) might be related to different structural characteristics, which could affect on the hydrodynamic volume of the PDTDA polymer chain. Full details of this study will be followed and published in the near future. Thus, the chromatogram of PDTDA shows a fairly broad distribution (polydispersity index, PDI = 4.85) of molecular weight, with a calculated $\overline{M}_w$ of 424,690 and a $\overline{M}_n$ of 87,565.

Structural Characterization of the undoped PDTDA

The undoped PDTDA was found to have perfect solubility in N-methy-2-pyrrolidone (NMP), DMF, and dimethyl sulfoxide (DMSO). But, it shows partial solubility in acetonitrile (AN) and tetrahydrofuran (THF).

Figure 3 shows the UV/VIS spectra of the undoped PDTDA (Fig. 3 (a)) and PANI emeraldine base (Fig. 3 (b)) as a reference system. These spectra show bands at 315 nm (band I) and 500 nm (band II) for PDTDA and 325 nm (band I) and 620 nm (band II) for PANI, respectively.

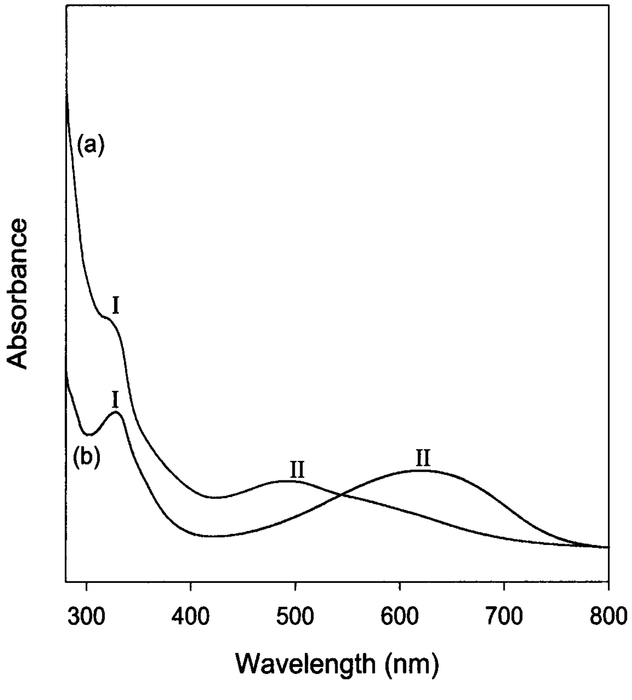

Figure 3. UV/VIS spectra of the undoped polymers in DMF for (a) PDTDA (b) PANI.

Generally, band I is attributed to $\pi \rightarrow \pi^*$ transition of the aniline unit and band II, which is characteristic of undoped emeraldine polymer, arises due to the creation of a localized molecular exciton with the electron on a quinoid moiety and a hole on the two neighboring benzoid moieties based on earlier studies of PANI [16-18].

A hypsochromic shift was observed for the band II of PDTDA (Fig. 3 (a)) in comparison with that of PANI from 620 nm to 500 nm. It could be thought that the –S-S- bonds substituted on the benzene rings can cause an increase in the band gap due to their steric strain increasing the torsional angle between adjacent rings [19]. Another potential explanation of the blue shift is that the spectrum is affected by the further oxidation that occurs during chemical synthesis. Thus, it changed the structure into Pernigraniline form representing Peierls gap transition which indicates that PDTDA is oxidized over 50% [20].

Figure 4 (a) and (b) represents the FTIR spectra of the PDTDA and PANI emeraldine base, respectively. The bands at 3414 and 3326 cm^{-1} as shown in Figure 4 (c), which are assigned to the N-H stretching motion of -NH$_2$ in DTDA monomer, disappeared after formation of base polymer. It could be confirmed that the PDTDA was successfully polymerized without out having any residual monomers in it.

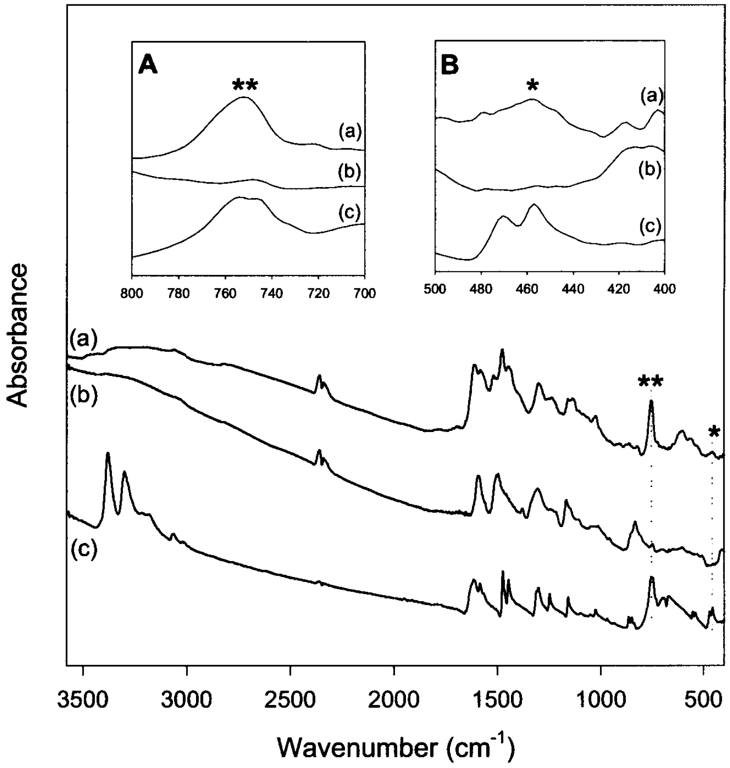

Figure 4. FTIR spectra of the undoped polymers and monomer: (a) PDTDA (b) PANI (c) DTDA monomer.

Both polymers showed bands characteristics of N-H bending and the symmetric component of the C-C (or C-N) stretching modes in the range 1250 – 1300 cm^{-1}. The bands at 1155 and 827 cm^{-1} can be attributed to the in-plane and out-of-plane C-H bending motion of quinoid and benzoid rings, respectively [21, 22]. Bands at 1474 and 1604 cm^{-1} are assigned to the non-symmetric aromatic ring stretching modes. The higher frequency vibration arises from C=C stretching of quinoid rings while the lower frequency vibration from benzoid ring units. In addition, the band at 1604 cm^{-1} can be assigned to the C=N stretching of the quinoid ring, which is overlapped with C=C stretching of the quinoid ring. The occurrence of these two bands clearly shows that these polymers are composed of amine and imine units. For the PDTDA, a band at 750 cm^{-1} corresponding to C-S bending (enlarged region A) and a weak band at 459 cm^{-1} for S-S bending (enlarged region B) are additionally present [23]. It can be noticed that the –S-S- linkages in DTDA monomers are well preserved after polymerization under such a severe reaction condition (acidic medium).

Conclusions

The high molecular weight PDTDA was easily synthesized by chemical method and the weight average molecular weight showed 424,690. The undoped PDTDA was found to have perfect solubility in NMP, DMF, and DMSO and it showed partial solubility in AN and THF. A little different spectroscopic characteristic has been shown in UV/VIS and FTIR spectra from PANI emeraldine base.

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References

1. S.J. Visco, C.C. Mailhe, L.C. De Jonghe, and M.B. Armand (1989) J. Electrochem. Soc., 136:661
2. S.J. Visco and L.C. De Jonghe (1989) Mater. Res. Symp. Proc., 135:553
3. K. Naoi, Y. Oura, Y. Iwamizu, and N. Oyama (1995) J. Electrochem. Soc., 142:354
4. E. Shouji and N. Oyama (1996) J. Electroanal. Chem., 410:229
5. M. Liu, S.J. Visco, and L.C. De Jonghe (1989) J. Electrochem. Soc., 136:2570
6. K. Naoi, M. Menda, H. Ooika, and N. Oyama (1991) J. Electroanal. Chem., 318:395
7. K. Naoi, K.I. Kawase, and Y. Inoue (1997) J. Electrochem. Soc., 144:L170
8. T.C. Wen, L.M. Huang, and A. Gopalan (2001) J. Electrochem. Soc., 148:D9
9. T.C. Wen, L.M. Huang, and A. Gopalan (2001) Syn. Met., 123:451
10. K. Naoi, K. Kawase, M. Mori, and M. Komiyama (1997) J. Electrochem. Soc., 144:L173
11. A. Yasuda and T. Shimidzu (1993) Synth. Met., 61:239
12. A.R. Hopkins, P.G. Rasmussen, and R.A. Basheer (1996) Macromolecules, 29:7838
13. W. Zheng, M. Angelopoulos, A.J. Epstein, and A.G. MacDiarmid (1997) Macromolecules, 30:7634
14. F.S. Wang, X.B. Jing, X.H. Wang, and A.J. Dong (1995) Synth. Met., 69:93
15. P.N. Adams, A.P. Monkman, D.C. Apperley (1993) Synth. Met., 55:725
16. J. Yue, A.J. Epstein, and A.G. Macdiarmid (1990) Mol. Cryst. Liq. Cryst., 189:255
17. M.K. Ram, E. Maccioni, and C. Nicolini (1997) Thin Solid Films, 303:27
18. C.B. Duke, E.M. Conwell, and A. Paton (1986) Chem. Phys. Lett., 131:82
19. J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein, and A.G. MacDiarmid (1991) J.Am. Chem. Soc., 113:2665

20. J.E. Albuquerque, L.H.C. Mattoso, D.T. Balogh, R.M. Faria, J.G. Masters, and A.G. MacDiarmid (2000) 113:19
21. J. Anand, P.S. Rao, S. Palaniappan, and D.N. Sathyanarayana (1998) Synth. Met., 95:57
22. P.S. Rao, J. Anand, S. Palaniappan, and D.N. Sathyanarayana (2000) Eur. Polym. J., 36:915
23. J.B. Lambert, H.F. Shurvell, D.A. Lightner, and R.G. Cooks (1987) Introduction to Organic Spectroscopy, Macmillan Publishing company, New York