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Synthesis and Characterization of a Polyacetylene Derivative Containing Amine Functional Groups

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A monosubstituted polyacetylene having amine functional groups was prepared via the polymerization of 3-ethynylaniline by using transition metal catalysts. The polymerization proceeded well in homogeneous manner to give a relatively high yield of polymer. The polymer structure was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies to have the conjugated backbone system with the designed functional groups. The absorption spectrum starts around 700 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of conjugated polymer system. This polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks.

Keywords 3-ethynylaniline; characterization; conjugated polymer; polyacetylene; transition metal catalyst

Introduction

The carbon-carbon conjugated double bonds in organic polymers endows them with such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability, and so on [1–5]. Considerable progress has been made in the synthesis and applications of organic polymers having a π-conjugated backbone [5–10]. The polyacetylene and its homologues have been promising materials for photovoltaics, displays, lasers, nonlinear optical materials, membranes for gas separation and for liquid-mixture separation and chemical sensors [1,5,6–10].

It was found that the chlorides of W, Mo, Nb, and Ta themselves or in combination with suitable organometallic cocatalysts polymerize various mono- and disubstituted acetylenes [2,3,4,11–15]. Some metal chlorides are known to be converted in situ into metal carbenes which induce metathesis polymerization. These catalysts have also been found to be very effective for the cyclopolymerization of 1,6-heptadiyne and its homologues [15–17].

We have prepared various polyacetylenes with different functionalities, which retain extensive conjugation [1,15,18–20]. A new family of conjugated polymers was prepared through the activated polymerization of ethynylpyridines by using functional alkyl halides [17,21–27]. And also, we have also prepared various conjugated polymers having

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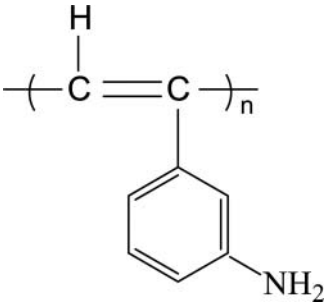

Figure 1. The chemical structure of poly(3-ethynylaniline).

different functionalities from the transition metal-catalyzed polymerization of nitrogen atom-containing acetylenic monomers [28–30].

In this article, we report the synthesis of a new polyacetylene derivative with amine functional groups via the transition-metal catalyzed polymerization of 3-ethynylaniline and the characterization of the resulting poly(3-ethynylaniline) (Fig. 1).

Experimental

3-Ethynylaniline (>98%), $PdCl_2$ (99.9+%), and (bicyclo[2.2.1]hepta-2,5-diene)-dichloropalladium (II) [(NBD)$PdCl_2$] were purchased from Aldrich Chemicals and used as received. $MoCl_5$ (Aldrich Chemicals., 99.9%) and WCl_6 (Aldrich Chemicals., 99.9%) were used as received. $MoCl_5$ and WCl_6 were dissolved in chlorobenzene before use as 0.1 M solution. All procedures for catalyst solution preparation and polymerization were carried out under dry nitrogen atmosphere. Injection of $MoCl_5$ and WCl_6 catalyst solutions was done by hypodermic syringes from air and moisture carefully excluded. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

A general polymerization procedure of 3-ethynylaniline is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (8.54 mmol) of 3-ethynylaniline, 50.5 mg (0.28 mmol, M/C = 30) of $PdCl_2$, and 9.7 mL of DMF ($[M]_0 = 0.8$ M) were added in that order given. Then the polymerization was carried out at 90 °C for 24 hrs under nitrogen atmosphere. As the polymerization proceeded, the reaction solution became into more viscous dark-black solution. After the polymerization time, the polymer solution diluted with 10 mL DMF was precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried in vacuum oven at 40 °C for 24 hrs. The orange-colored polymer powder was obtained in 79% yield.

^{1}H-NMR spectra were obtained in DMSO-d_6 solutions at room temperature using a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) and the chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The inherent viscosities of polymers were determined at a concentration of 0.5g/dL in DMF at 30 °C. Electrochemical measurements were carried out with a KOSENTECH (KST-P1) instrument (Pt disk electrode, CH_3CN, (TBA)PF_6, sweep rate 20 mV/s). The HOMO energy level can be calculated from electrochemical measurements, in particular by using CV with respect to a ferrocene standard.

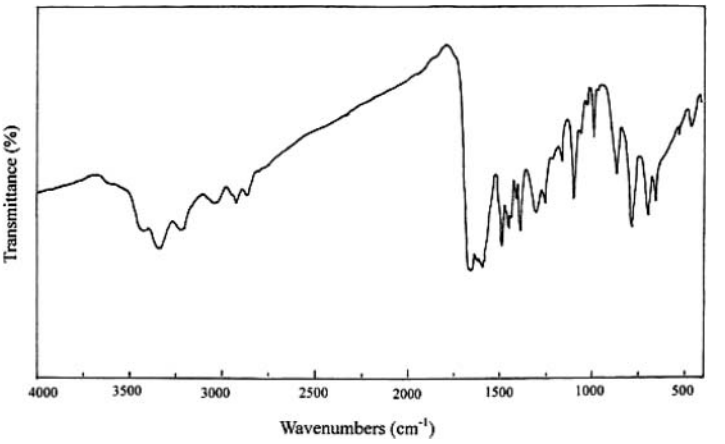

Figure 2. FT-IR spectrum of poly(3-ethynylaniline).

Results And Discussion

Various types of catalysts have been used for the polymerization of substituted acetylenes. Here, we used the palladium and platinum chlorides, which had been known to be very effective for the polymerization of some monosubstituted acetylenes such as propargyl halides [31], propargyl alcohols [32,33] and 9,9-dipropargylfluorenes [17,34], and the Mo- and W-based catalysts, which were found to be effective for the polymerization of some monosubstituted acetylenes [12] and the ring-forming polymerization of dipropargyl monomers [1,34]. In the present polymerization, we can not obtain the polymeric products when $MoCl_5$ and WCl_6 catalysts were used. Only oligomeric products were obtained. However, the Pd- and Pt-based catalysts effectively polymerized 3-ethynylaniline in homogeneous manners to give relatively high yields of polymer. As the reaction proceeded, the color of reaction solution changed from the light brown of initial solution into dark black solution with increased viscosity. $PdCl_2$ was found to effectively polymerize 3-ethynylaniline to give the corresponding polymer in high yield (79%) although this monomer carry the bulky 3-aminophenyl substituents. When (NBD)$PdCl_2$ and $PtCl_2$ were used as catalysts, the polymer yields were 75% and 70%, respectively.

The molecular structure of poly(3-ethynylaniline) was characterized by various instrumental methods such as IR, NMR, and UV-visible spectroscopies. Figure 2 shows the FT-IR spectrum of poly(3-ethynylaniline) measured in KBr pellet. This spectrum of polymer did not show the acetylenic C≡C bond stretching (2107 cm^{-1}) and acetylenic ≡C−H bond stretching (3287 cm^{-1}) frequencies of the monomer. Instead, the C=C stretching

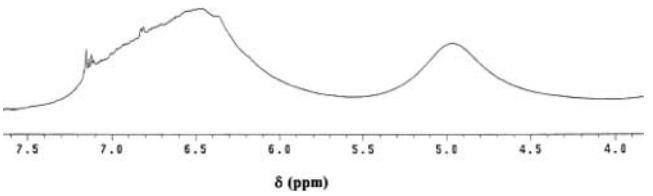

Figure 3. ^{1}H-NMR spectrum of poly(3-ethynylaniline) in DMDO-d_6.

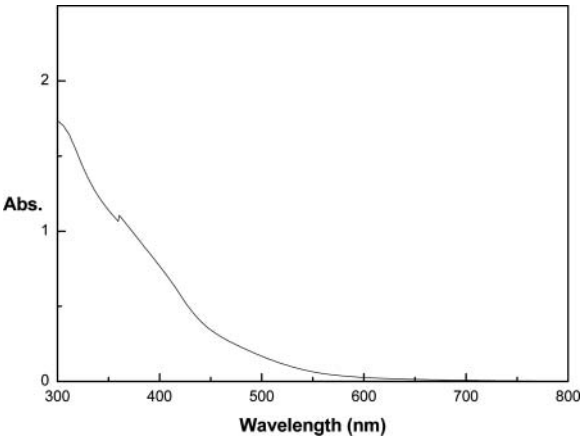

Figure 4. UV-visible spectrum of poly(3-ethynylaniline) in DMF.

frequency peak of conjugated polymer backbone around 1630 cm^{-1} became more intense than that of 3-ethynylaniline. The characteristic broad peaks of primary amine in polymer were observed at 3345 and 3427 cm^{-1}. The peak at 1096 cm^{-1} is due to the C—N stretching frequency. The ^{1}H-NMR spectrum (Fig. 3) of polymer showed the aromatic phenyl protons and the vinylic protons in conjugated polymer backbone in the range of 5.7–7.4 ppm and also showed the amine protons at 4.4–5.5 ppm. The UV-visible spectrum (Fig. 4) of poly(3-ethynylaniline) shows the absorptions at longer wavelength (up to 700 nm) due to the $\pi \rightarrow \pi^*$ interband transition of the conjugated polymer systems. These observations indicate that the present polymer has the conjugated polymer backbone system with the designed 3-aminophenyl substituents.

Poly(3-ethynylaniline) was soluble in such organic solvents as DMF, NMP, and DMSO. The inherent viscosities of the resulting polymers were in the range of 0.11–0.15 dL/g. The morphologies of poly(3-ethynylaniline) were also investigated by X-ray diffraction analysis (Fig. 5). The peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35 [12,30], indicating that the present polymer is mostly amorphous.

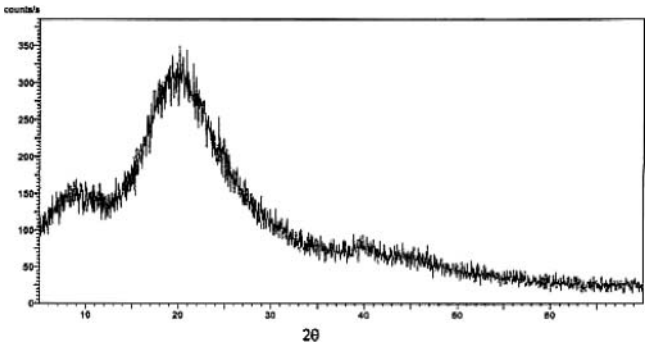

Figure 5. X-ray diffractogram of poly(3-ethynylaniline).

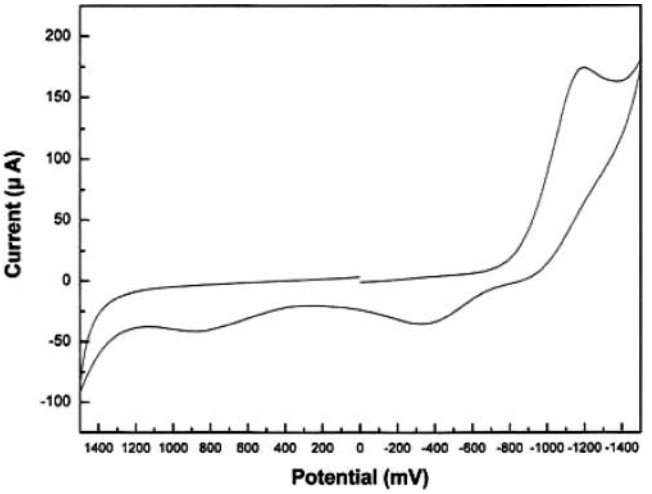

Figure 6. Cyclic voltammogram of poly(3-ethynylaniline) at 100 mV/s (0.1 Et_4NBF_4/DMF).

The electrochemical behavior of poly(3-ethynylaniline) was investigated by cyclic voltammetry (CV) experiment. The potentials were referenced to $Ag/AgNO_3$ and the reduction potential of ferrocene/ferrocenium (FOC) under 0.1M $(t\text{-}Bu)_4NPF_6$/DMF solution. Figure 6 shows the typical CV of poly(3-ethynylaniline). This exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. The HOMO energy level was estimated from the onset oxidation data by means of empirical relationship by Leeuw et al: HOMO $= -(E^{ox} + 4.8$ eV), where the SCE energy level of -4.8 eV below the vacuum level [35]. From the CV measurements, the HOMO energy levels of the present polymer, was calculated to be 5.08 eV.

Conclusions

A new conjugated polyacetylene with 3-aminophenyl substituents was synthesized and characterized. The polymerization of 3-ethynylaniline proceeded well to give relatively high yields of polymer. The molecular structure of polymer was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituents. This polymer was completely soluble in organic solvents. The X-ray diffraction data on poly(3-ethynylaniline) indicated that this polymer is mostly amorphous. The CVs of the polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks.

Acknowledgement

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References

[1] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[2] Lam, J. W. Y. & Tang, B. Z. (2005). *Acc. Chem. Res.*, *38*, 745.
[3] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[4] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). *Chem. Rev.*, *109*, 897.
[5] Liu, J., Lam, J. W. Y., & Tang, B. Z. (2009). *Chem. Rev.*, *109*, 5799.
[6] Arias, A. C., MacKenzie, J. D., MaCulloch, I., Rivnay, J., & Salleo, A. (2010). *Chem. Rev.*, *110*, 3.
[7] Kim, H. C., Park, S. M., & Hinsberg, W. D. (2010). *Chem. Rev.*, *110*, 146.
[8] Raoux, S., Welnic, W., & IeImini, D. (2010). *Chem. Rev.*, *110*, 240.
[9] Yun, S. Y., Wang, K. P., Kim, M., & Lee, D. (2010). *J. Am. Chem. Soc.*, *132*, 8840.
[10] Kang, E. H., Lee, I. S., & Choi, T. L. (2011). *J. Am. Chem. Soc.*, *133*, 11904.
[11] Masuda, T., Hasegawa, K., & Higashimura, T. (1974). *Macromolecules*, *7*, 728.
[12] Masuda, T., & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[13] Gal, Y. S., Cho, H. N., & Choi, S. K. (1985). *Polymer (Korea)*, *9*, 361.
[14] Gal, Y. S., Cho, H. N., & Choi, S. K. (1986). *J. Polym. Sci.: Part A: Polym. Chem.*, *24*, 2021.
[15] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A-Chem.*, *213*, 115.
[16] Gal, Y. S., & Choi, S. K. (1993). *J. Polym. Sci.: Part A: Polym. Chem.*, *31*, 345.
[17] Gal, Y. S., Jin, S. H., Park, J. W., Lee, W. C., Lee, H. S., & Kim, S. Y. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 4101.
[18] Gal, Y. S., Choi, S. K., & Kim, C. Y. (1989). *J. Polym. Sci.: Part A: Polym. Chem.*, *27*, 31.
[19] Gal, Y. S., Jin, S. H., Hyun, A. R., Park, Y. I., Park, J. W., Lim, K. T., & Lee, W. C. (2008). *J. Ind. Eng. Chem.*, *14*, 468.
[20] Gui, T. L., Qiu, J. L., Wang, Y., Shim, S. Y., Jin, S. H., Park, J. W., Lim, K. T., & Gal, Y. S. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 175.
[21] Subramanyam, S., & Blumstein, A. (1992). *Macromolecules*, *25*, 4058.
[22] Balogh, L., Samuelson, L., Alva, K. S., & Blumstein, A. (1998). *J. Polym. Sci.: Part A: Polym. Chem.*, *36*, 703.
[23] Gal, Y. S., Jin, S. H., & Park, J. W. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 5679.
[24] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2009). *J. Polym. Sci.: Part A: Polym. Chem.*, *47*, 6153.
[25] Choi, H. K., Jin, S. H., Park, J. W., Jung, M. J., & Gal, Y. S. (2010). *J. Ind. Eng. Chem.*, *16*, 214.
[26] Gal, Y. S., Kim, M. R., Lim, K. T., Lee, W. C., Lyoo, W. S., Park, Y. I., Park, J. W., Han, S. C., Lee, J. W., & Jin, S. H. (2010). *Mol. Cryst. Liq. Cryst.*, *520*, 75.
[27] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2011). *J. Ind. Eng. Chem.*, *17*, 282.
[28] Gal, Y. S., Jung, B., Lee, W. C., & Choi, S. K. (1992). *J. Polym. Sci.: Part A: Polym. Chem.*, *30*, 2657.
[29] Gal, Y. S., & Choi, S. K. (1995). *Eur. Polym. J.*, *31*, 941.
[30] Gui, T. L., Yin, J. H., Wang, D. X., Jin, S. H., Lee, H. J., Lim, K. T., Lyoo, W. S., & Gal, Y. S. (2006). *Mol. Cryst. Liq. Cryst.*, *459*, 19.
[31] Lee, W. C., Sohn, J. E., Gal, Y. S., & Choi, S. K. (1988). *Polymer (Korea)*, *12*, 720.
[32] Gal, Y. S. (1994). *J. Macromol. Sci.-Pure Appl. Chem.*, *A31*, 703.
[33] Lee, W. C., Gal, Y. S., Kim, S. H., Jin, S. H., Jang, S. H., & Choi, S. K. (1999). *J. Macromol. Sci.-Pure Appl. Chem.*, *A36*, 531.
[34] Gal, Y. S., Jin, S. H., Lee, H. S., & Kim, S. Y. (2005). *Macromol. Res.*, *13*, 491.
[35] Leeuw, D. M., Simenon, M. M. J., Brown, A. R., & Einerhand, R. E. F. (1997). *Syn. Met.*, *87*, 53.