Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Properties of a Polyacetylene Derivative: Poly(17α-Ethynylestradiol)

Won-Chul Lee [a], Sang-Hee Jang [b], Tai-Long Gui [c], Sung-Ho Jin [d] & Yeong-Soon Gal [e]

[a] Department of Textile and Fashion Technology, Kyungil University, Kyungsan, Korea

[b] Department of Food and Nutrition, Kumi College, Gumi, Korea

[c] Department of Electronic Science and Technology, Harbin University of Science and Technology, Harbin, China

[d] Department of Chemistry Education, Pusan National University, Busan, Korea

[e] Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Kyungsan, Korea

Version of record first published: 22 Sep 2010

To cite this article: Won-Chul Lee, Sang-Hee Jang, Tai-Long Gui, Sung-Ho Jin & Yeong-Soon Gal (2008): Synthesis and Properties of a Polyacetylene Derivative: Poly(17α-Ethynylestradiol), Molecular Crystals and Liquid Crystals, 491:1, 270-276

To link to this article: http://dx.doi.org/10.1080/15421400802330911

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 270–276, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330911

Taylor & Francis
Taylor & Francis Group

Synthesis and Properties of a Polyacetylene Derivative: Poly(17α-Ethynylestradiol)

Won-Chul Lee[1], Sang-Hee Jang[2], Tai-Long Gui[3], Sung-Ho Jin[4], and Yeong-Soon Gal[5]

[1]Department of Textile and Fashion Technology, Kyungil University, Kyungsan, Korea.
[2]Department of Food and Nutrition, Kumi College, Gumi, Korea
[3]Department of Electronic Science and Technology, Harbin University of Science and Technology, Harbin, China
[4]Department of Chemistry Education, Pusan National University, Busan, Korea
[5]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Kyungsan, Korea

A new family of mono-substituted polyacetylene having a highly bulky substituents was synthesized and characterized. The polymerization of 17α-ethynylestradiol (EED) was performed by various transition metal catalysts to give the resulting polymer in moderate yield. The polymer structure was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituent. This polymer was completely soluble in organic solvents. The electro-optical and electrochemical properties of poly(EED) were measured and discussed. This exhibited the reversible electrochemical behaviors between the doping and undoping peaks. The HOMO energy level calculated from electrochemical measurements was 5.47 eV.

Keywords: 17α-ethynylestradiol; catalyst; conjugated polymer; cyclovoltamogram photoluminescence; polyacetylene

The authors thank Ms S. E. Chai of Korea Basic Science Institute-Taegu Branch for the measurement of the 500-MHz FT-NMR spectra of the polymers.

This work was supported by the Regional Innovation Center for Automotive Component Test (ACT-RIC of Kyungil University) from Regional Innovation Center Program of the Ministry of Knowledge Economy (MKE).

Address correspondence to Won-Chul Lee, Department of Textile and Fashion Technology, Kyungil University, Gyungsan, Kyungsangbuk-Do 712-701, Korea. E-mail: wclee@kiu.ac.kr

INTRODUCTION

The oligomers and polymers having a π-conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1]. Because of these properties, polyacetylene and its homologues have been promising as organic semiconductors, as chiro-optical materials, as side-chain liquid crystals, and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties [1–8].

The polymerization of substituted acetylenes with hydroxy functional group are of interest because of their unique structures and facile modification of hydroxy groups with other interesting functional groups [9]. The simplest hydroxy-containing polyacetylene, poly(propargyl alcohol), had been polymerized by the various initiator systems such as radical, palladium, nickel, molybdenum, γ-ray, plasma, etc [10–12]. However, the resulting polymers were mostly insoluble in organic solvents as like with polyacetylene. Various substituents have been introduced at α-carbon of propargyl alcohol in order to increase the solubility of polyacetylene derivatives [13–15]. Considerable effort has been devoted to the synthesis of the mono- and di- substituted polyacetylenes and study of their peculiar properties [1–5]. We have also reported on the synthesis of polyacetylene derivatives with highly bulky substituents [16–20]. Now we report on the synthesis of a new family of conjugated polymer with two hydroxy group-containing bulky substituents, poly(17α-ethynylestradiol) [poly(EED)] (Fig. 1), and its electro-optical and electrochemical properties.

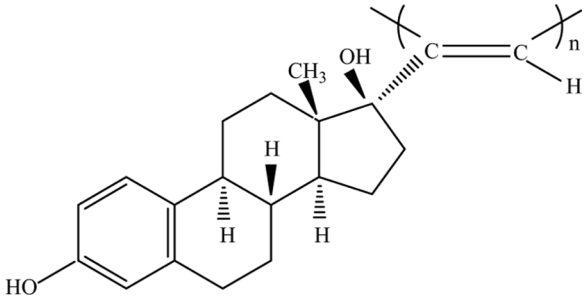

FIGURE 1 The chemical structure of poly(EED).

EXPERIMENTAL

17α-Ethynylestradiol [EED, 17α-ethynyl-1,3,5(10)-estratriene-3,17β-diol, Aldrich Chemicals., 98 + %] was used as received. $PdCl_2$ (Aldrich Chemicals, 99.9 + %), $RuCl_3$ (Aldrich Chemicals), and (bicyclo[2.2.1]-hepta-2,5-diene)-dichloropalladium (II) [(NBD)$PdCl_2$, Aldrich Chemicals] were used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

A typical synthetic procedure of poly(EED) is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (3.37 mmol) of EED, 0.030 g (0.112 mmol, M/C = 30) of (NBD)$PdCl_2$, and 5 mL of DMF ($[M]_0 = 0.56$ M) were added in that order given. Then the polymerization was carried out at 90°C for 24 hrs under nitrogen atmosphere. The polymerization proceeded mostly in homogeneous manner. After the polymerization time, the polymer solution diluted with 10 mL chloroform was precipitated into a large excess of methanol. The precipitated polymer was filtered and dried in vacuum oven at 40°C for 24 hrs. The light-brown powder was obtained in 42 % yield. The molecular weight (Mn) and polydispersity (Mw/Mn) were 7,500 and 2.2, respectively.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed with FISONS EA1110 elemental analyzer. NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in $CDCl_3$. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The molecular weights of the polymers were determined by a gel permeation chromatographer (Waters 150 C) equipped with μ-Styragel columns using THF as an eluent. The optical absorption spectra were measured by a HP 8453 UV-Visible Spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50W voltametric analyzer at a potential scan rate of 50–100 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. The polymer film was coated onto a Pt disc electrode (0.2 cm^2) by dipping the electrode into the polymer solution. A platinum wire was used as the counter electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode. All of the electrochemical experiments were performed in a glove box under an Ar atmosphere at room temperature. The HOMO energy level was calculated from electrochemical measurements, in particular by using CV with respect to a ferrocene standard.

RESULTS AND DISCUSSION

We carried out the polymerization of EED with high bulky substituents having two hydroxy functional groups by transition metal catalysts. We firstly test the polymerization of EED by W- and Mo-based catalysts, which were found to be very effective for the polymerization of some monosubstituted acetylenes and the cyclopolymerization of various dipropargyl monomers [3]. However, W-based catalysts such as WCl_6 and WCl_6-$EtAlCl_2$ failed to polymerize the present monomer. And also $MoCl_5$ gave only a trace amount of oligomeric product.

$PdCl_2$ was found to polymerize EED to give the corresponding polymer in moderate yield (35%) although this monomer carry the highly bulky substituents. $RuCl_3$ showed similar catalytic activity with that of $PdCl_2$. (NBD)$PdCl_2$, which showed good solubility in the polymerization solvent, polymerized EED to give the corresponding polymer in 42% yield. The present polymerizations proceeded mostly in mild manner.

The chemical structure of poly(EED) was characterized by various instrumental methods such as IR, NMR, UV-visible spectroscopies.

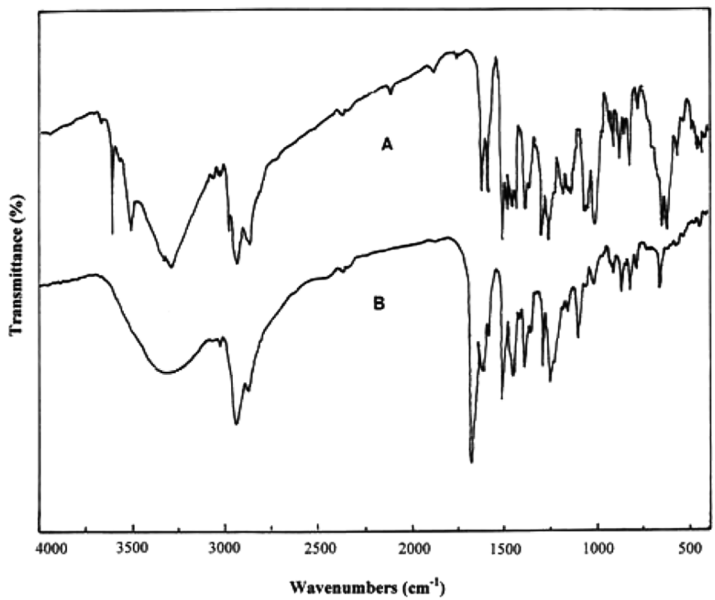

FIGURE 2 FT-IR spectra of EED [A] and poly(EED) [B] in KBr pellet.

Figure 2 shows the FT-IR spectra of EED (A) and poly(EED) [B]. The FT-IR spectrum of the polymer did not show the acetylenic C≡C bond stretching (2105 cm^{-1}) and acetylenic ≡C–H bond stretching (3293 cm^{-1}) frequencies of the monomer. Instead, the C=C stretching frequency peak of conjugated polymer backbone at around 1660 cm^{-1} became more intense than that of the monomer. The elemental analysis data of reprecipitated poly(EED) agreed well with the theoretical value: Calcd for ($C_{20}H_{24}O_2$): C, 81.04%; H, 8.16%; O, 10.80%, Found: C, 80.01%; H, 8.13%; O, 10.86%. The ^{1}H-NMR spectrum of poly(EED) showed the phenyl protons and the vinyl protons of the conjugated polymer backbone at 6.1–7.1 ppm. The characteristic aliphatic proton peaks was also observed at 0.5–3.0 ppm.

In the ^{13}C-NMR spectrum of poly(EED), the acetylenic carbon peaks of monomer at 74.18 and 80.02 ppm were disappeared and the aromatic and vinyl carbon peaks of polymer were observed at the region of 108–164 ppm. In the UV-visible spectra, the absorptions at long wavelength (up to 600 nm) due to the $\pi \rightarrow \pi^*$ interband transition of the conjugated polymer systems were observed. From these spectral data, we concluded that the present polymer have the conjugated polymer backbone system with the designed substituents. We studied the morphology of poly(EED) powder sample by X-ray diffraction analysis. Because the peaks in the diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, the present poly(EED) was mostly amorphous [1,2].

The electro-optical properties of poly(EED) were measured and discussed. The absorption spectrum starts around 600 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of conjugated polymer systems. The photoluminescence spectra of poly(EED) showed that the broad photoluminescence peak is located at 410 nm corresponding to the photon energy of 3.03 eV.

In order to investigate the electrochemical properties of poly(EED), we performed the cyclic voltammetry (CV) experiment. The potentials were referenced to $Ag/AgNO_3$ and the reduction potential of ferrocene/ferrocenium (FOC) under 0.1 M Et_4NBF_4/DMF solution. Figure 3 shows the typical cyclovoltammogram of poly(EED). This exhibited the reversible 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 [21]. From the CV measurements, the HOMO energy levels of the present polymer, was found to be 5.47 eV.

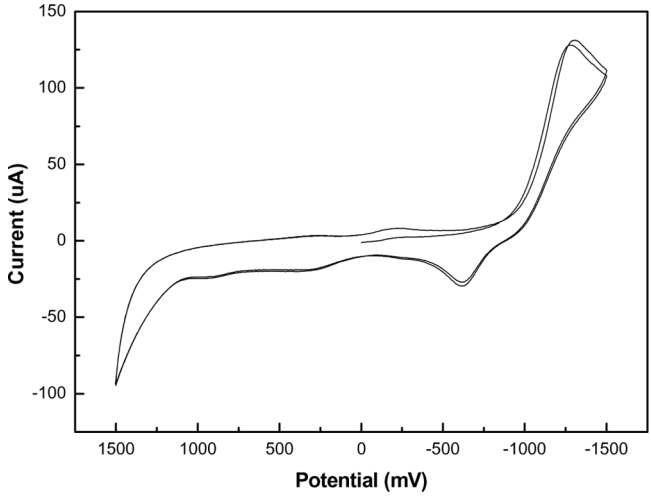

FIGURE 3 Cyclic voltammogram of poly(EED) at 100 mV/s (0.1 M Et4NBF4/DMF).

CONCLUSIONS

A new conjugated polymer with bulky substituent containing two hydroxy groups was synthesized and characterized. The present polymerization of EED proceeded in mild manner to give moderate yield of polymer. The polymer structure 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 and well processible. The photoluminescence peak was located at 410 nm corresponding to the photon energy of 3.03 eV. The HOMO energy level calculated from electrochemical measurements was 5.47 eV.

REFERENCES

[1] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[2] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[3] Bredas, J. L., Beljionne, D., Coropceanu, V., & Cornil, J. (2004). *Chem. Rev.*, *104*, 4971.
[4] Lam, J. W. Y. & Tang, B. Z. (2005). *Acc. Chem. Res.*, *38*, 745.
[5] Sun, A., Lauher, J. W., & Goroff, N. S. (2006). *Science*, *312*, 1030.
[6] Shirota, Y. & Kageyama, H. (2007). *Chem. Rev.*, *107*, 953.
[7] Murphy, A. R. & Frechet, J. M. J. (2007). *Chem. Rev.*, *107*, 1066.
[8] Gunes, S., Neugebauer, H., & Sariciftci, N. S. (2007). *Chem. Rev.*, *107*, 1324.

[9] Chauser, M. G., Rodionov, Yu. M., Misin, V. M., & Cherkashin, M. I. (1976). *Russ. Chem. Rev.*, *45*, 348.
[10] Voronkov, M. G., Pukhnarevich, Sushchinskaya, Annenkova, V. Z., Annenkova, V. M., & Andreeva, N. J. (1980). *J. Polym. Sci.: Part A: Polym. Chem.*, *18*, 53.
[11] Furlani, A., Russo, M. V., Carusi, P., Licoccia, S., Leoni, E., & Valenti, G. (1983). *Gazz. Chim. Ital.*, *113*, 671.
[12] Gal, Y. S., Jung, B., Lee, W. C., & Choi, S. K. (1992). *Polymer (Korea)*, *16*, 597.
[13] Gal, Y. S. (1994). *J. Macromol. Sci.-Pure and Appl. Chem.*, *A31*, 703.
[14] Lee, W. C., Gal, Y. S., Kim, S. H., Jin, S. H., Jang, S. H., & Choi, S. K. (1999). *J. Macromol. Sci.-Pure and Appl. Chem.*, *A36*, 531.
[15] Gal, Y. S., Jin, S. H., Lee, W. C., & Kim, S. Y. (2004). *Macromol. Res.*, *12*, 407.
[16] Gal, Y. S., Jin, S. H., & Kim, S. H. (2006). *J. Ind. Eng. Chem.*, *12*, 235.
[17] Gal, Y. S., Jin, S. H., Lim, K. T., Kim, S. H., Lyoo, W. S., Lee, C. J., Park, J. W., & Kim, S. Y. (2007). *Mol. Cryst. Liq. Cryst.*, *462*, 189.
[18] Gal, Y. S., Lee, W. C., Jin, S. H., Lim, K. T., Jang, S. H., Lyoo, W. S., Han, E., & Kim, S. Y. (2007). *Macromol. Res.*, *53*, 267.
[19] Gal, Y. S., Lee, W. C., Jin, S. H., Lee, J. W., Lyoo, W. S., Kim, S. H., Park, J. W., & Kim, S. Y. (2007). *Mol. Cryst. Liq. Cryst.*, *472*, 267.
[20] Gal, Y. S., Jin, S. H., & Park, J. W. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 5679.
[21] Leeuw, D. M., Simenon, M. M. J., Brown, A. R., & Einerhand, R. E. F. (1997). *Synth. Met.*, *87*, 53.