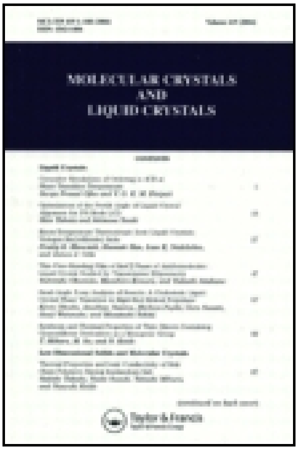

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Synthesis and Electro-Optical Propertiesof a Polyacetylene Derivative: Poly(Ethynylestradiol3-Methyl Ether)

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A new conjugated polymer with bulky substituents was synthesized by the polymerization of ethynylestradiol 3-methyl ether (EEDME) by such transition metal catalysts as $PdCl_2$, $RuCl_3$, and (NBD)$PdCl_2$. The polymerization proceeded well in homogeneous manner to give a moderate yield of polymer. The chemical structure of poly(EEDME) was characterized to have the conjugated polymer backbone with the designed substituents. From the CV measurements, the HOMO energy level of the polymer was calculated to be 5.02 eV. The photoluminescence spectra

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of poly(EEDME) showed that the two photoluminescence peaks are located at 434 and 406 nm corresponding to the photon energy of 2.86 and 3.06 eV, respectively.

Keywords: catalyst; cyclovoltamogram; ethynylestradiol 3-methyl ether; photoluminescence; polyacetylene

INTRODUCTION

Recently, the electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [1–4]. There has been much attention given to conjugated polymers such as polyacetylenes, poly(pyrrole)s, poly(phenylenevinylene)s, and poly(9,9-dialkylfluorene)s as functional materials [5–11]. Among these materials, the polyacetylene is structurally the simplest one and a prototypical conjugated polymer, which exhibits high electrical conductivity upon doping [5–7]. However, it was difficult for practrical applications to opto-electronic devices as an active material because of the insolubility and unstability of polyacetylene itself. Thus various substituted polyacetylenes have been prepared by the linear polymerization of the corresponding acetylene monomers [8–12].

The polymers having a 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 [8]. 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 [7,8,13–16].

Considerable effort has been devoted to the synthesis of the mono- and di-substituted polyacetylenes and study of their peculiar properties. We have also reported on the synthesis of polyacetylene derivatives with highly bulky substituents [17–24]. Now we report on the synthesis of a new conjugated polymer with bulky substituents, poly(ethynylestradiol 3-methyl ether) [poly(EEDME)] and its electro-optical properties.

EXPERIMENTAL

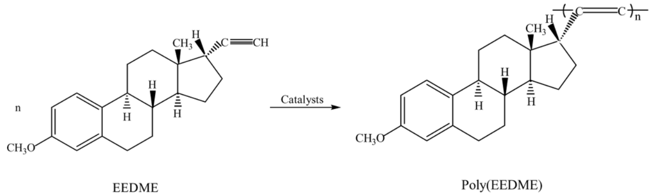
Ethynylestradiol 3-methyl ether (EEDME, Aldrich Chemicals.) was used as received. $PdCl_2$ (Aldrich Chemicals, 99.9 + %), $PtCl_2$ (Strem), and $RuCl_3$ (Aldrich Chemicals), and (NBD)$PdCl_2$ (Aldrich Chemicals) were used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

A typical synthetic procedure of poly(EEDME) is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (3.22 mmol) of EEDME, 0.019 g (0.107 mmol, M/C = 30) of $PdCl_2$, and 5 mL of DMF ($[M]_0 = 0.54$ M) were added in that order given. Then the polymerization was carried out at 100°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 yellow powder was obtained in 95% yield.

NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-$d_6$6. 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 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. 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.

RESULTS AND DISCUSSION

The polymerization of EEDME, an acetylene derivative with highly bulky substituent, was performed by typical transition metal catalysts. We test the polymerization behaviors of EEDME by Pd, Pt, Ru-chlorides (Scheme 1). $PdCl_2$ was found to be very effective for this polymerization to give the corresponding polymer in 95 % yield although the monomer carry the highly bulky substituents. The poly (EEDME) was obtained in yellowdish powder form. $PtCl_2$, $RuCl_3$, and (NBD)$PdCl_2$ were also found to be effective for the polymerization (polymer yield: 72%, 85%, and 78%, respectively). This polymer was completely soluble in aromatic and halogenated hydrocarbons such as chloroform, tetrahydrofuran, chlorobenzene, etc. The



SCHEME 1 Polymerization of EEDME by transition metal catalysts.

number-average molecular weights of the polymers were found to relatively low (Mn: 6,700–11,200).

The polymer structure of poly(EEDME) was characterized by such instrumental methods as NMR, IR, and UV-visible spectroscopies. The ^{1}H-NMR spectrum of poly(EEDME) in $CDCl_3$ showed broadly the phenyl protons and the vinyl proton of the conjugated polymer backbone at 6.2–7.2 ppm. The characteristic aliphatic proton peaks was also observed at 0.3–2.3 ppm. The FT-IR spectra of EEDME and poly(EEDME) were measured in KBr pellet. The IR spectra of poly (EEDME) did not show the acetylenic $C{\equiv}C$ bond stretching (2093 cm^{-1}) and acetylenic $\equiv C{-}H$ bond stretching (3248 cm^{-1}) frequencies of EEDME. Instead, the $C{=}C$ stretching frequency peak of conjugated polymer backbone around 1610–1681 cm^{-1} became more intense than that of the monomer. In the UV-visible spectra, the absorptions at long wavelength 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. The morphology of the polymers was also investigated 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 polymers were mostly amorphous [8].

The electro-optical properties of poly(EEDME) were measured and discussed. Figure 1 shows the UV-visible and photoluminescence (PL) spectra of poly(EEDME). The absorption spectrum starts around 550 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of conjugated polymer systems. The photoluminescence spectra of poly(EEDME) showed that two photoluminescence peaks are located at 434 and 406 nm corresponding to the photon energy of 2.86 and 3.06 eV, respectively.

In order to investigate the electrochemical properties of the polymer, we performed the cyclic voltammetry (CV) experiment. The potentials were referenced to $Ag/AgNO_3$ and the reduction potential

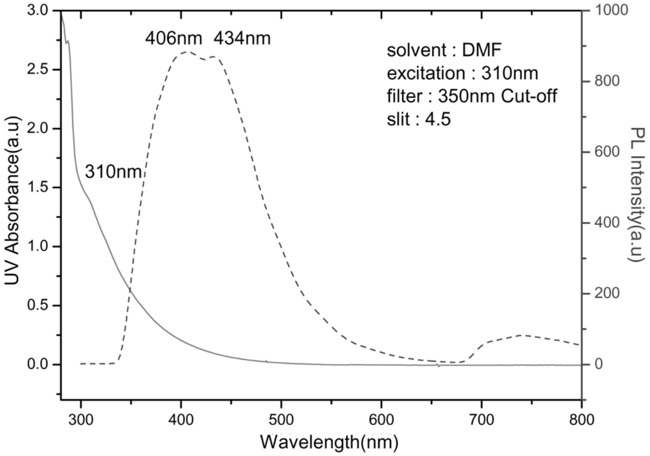


FIGURE 1 Optical absorption and photoluminescence spectra of poly (EEDME) polymer solution.

of ferrocene/ferrocenium (FOC) under 0.1 M Et_4NBF_4/DMF solution. Figure 2 shows the typical cyclovoltammogram of poly(EEDME). 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 $= -(E^{ox} + 4.8\,\text{eV})$, where the SCE energy level of –4.8 eV below

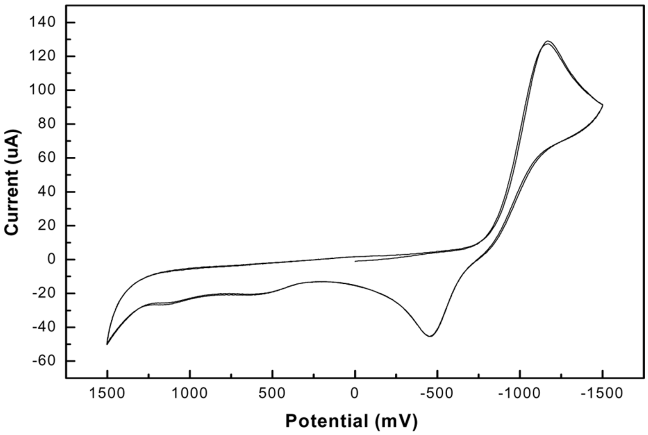


FIGURE 2 Cyclic voltammogram of poly(EEDME) at 100 mV/s (0.1 M Et_4NBF_4/DMF).

the vacuum level [25]. From the CV measurements, the HOMO energy levels of the present polymer, was found to be 5.02 eV.

CONCLUSIONS

New conjugated polymer with bulky substituent was synthesized and characterized. The present polymerization of EEDME proceeded well in homogeneous manner, regardless of the high bulkiness of substituents. 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 aromatic and halogenated hydrocarbons such as chloroform, tetrahydrofuran, chlorobenzene, etc. The HOMO energy level calculated from electrochemical measurements was 5.02 eV. The two photoluminescence peaks were located at at 434 and 406 nm corresponding to the photon energy of 2.86 and 3.06 eV, respectively.

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