

Electro-optical and Electrochemical Properties of Poly(1-hexyne)

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Abstract: Poly(1-hexyne) was prepared by the polymerization of 1-hexyne by using transition metal catalyst. The instrumental analysis data on the polymer structure revealed that the poly(1-hexyne) have the conjugated polyene backbone structure with n-butyl substituents. Poly(1-hexyne) showed UV-visible absorption band at 276 nm and PL spectrum at 415 nm, indicating relatively blue-shifted PL maximum value. From the relationship plot of the oxidation current density ($\log i_{pa}$) as a function of the scan rate ($\log \nu$), it was found that the oxidation current of poly(1-hexyne) versus the scan rate is approximately linear relationship in the range of 30–150 mV/sec and the exponent of scan rate, x value is found to be 0.424. It is explained by that the kinetics of the redox process are close to the diffusion-control process. The band gap energy of poly(1-hexyne) was estimated to be 2.98 eV and HOMO and LUMO level values of poly(1-hexyne) were 5.35 and 2.37 eV, respectively.

Keywords: Poly(1-hexyne), Conjugated polymer, Characterization, Cyclovoltamogram, Photoluminescence

Introduction

The presence of carbon-carbon alternating double bonds in the polymer main chains endows such unique properties as conductivity, nonlinear optical properties, magnetic properties, image patterning, chemical sensing, gas permeability, photoluminescent and electroluminescent properties, and so on [1-11]. An acetylene molecule contains a triple bond, with one more π -bond than in an olefin monomer. This extra π -electrons participates in the polymerization to yield the linear conjugated polymer [1,2].

The structurally simplest conjugated polymer, polyacetylene (PA), is a prototypical conjugated material, which exhibited metallic conductivity upon chemical doping [12]. This finding has spawned an exciting area of research on synthetic metals [4]. Nevertheless, some drawbacks thus far have prevented commercial applications of PA itself. PA does not only suffer from its lack of processibility because of its infusibility and insolubility in common organic solvents, but also from its insufficient stability toward oxygen. In order to improve the processibility and provide interesting functionalities of polyacetylene, various substituted polyacetylenes have been designed and synthesized [1,2,13-20]. The great progress of various transition metal-based polymerization catalysts enabled the synthesis of a wide variety of polymers from acetylene derivatives including monosubstituted and disubstituted acetylenes [2,4,5], and 1,6-heptadiyne derivatives [15,16,21,22].

The Mo- and W- based catalysts have been used as the

catalyst system for the polymerization of acetylene derivatives having various functionalities [2,5,15]. A number of polyacetylenes with aromatic substituents has been prepared and the properties of these conjugated polymers have been elucidated. However, a few study on the synthesis and properties of polyacetylenes with aliphatic substituents has been performed [2,15]. Here, we prepared a monosubstituted polyacetylene, poly(1-hexyne), by the polymerization of 1-hexyne by transition metal catalyst. And the electro-optical and electrochemical properties of the resulting poly(1-hexyne) were measured and discussed.

Experimental

MoCl₅ (Aldrich Chemicals, 99.9+%), WCl₆ (Aldrich Chemicals, 99.9+%), and Me₄Sn (Aldrich Chemicals, 95 %) were used as received. Ph₄Sn (Aldrich Chemicals, 97 %) was purified by recrystallization twice from carbon tetrachloride. PdCl₂ (Aldrich Chemicals, 99.995 %) and PtCl₂ (Strem) were used without further purification. 1-Hexyne (Aldrich Chemicals, 97 %) was distilled after drying with calcium hydride. The polymerization solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

A typical synthetic procedure of poly(1-hexyne) is as follows: In a 20 ml ampule containing 4.52 ml of chlorobenzene ($[M]_0=1.0$ M) were injected the mixture of WCl₆ (0.1 M, 2.43 ml, 0.244 mmol) and Me₄Sn (0.2 M, 2.43 ml, 0.488 mmol). After aging for 15 min at 30 °C, 1-hexyne (1.0 g, 12.17 mmol) was injected to the catalyst solution. After standing at 60 °C for 24 h, the polymer solution diluted with

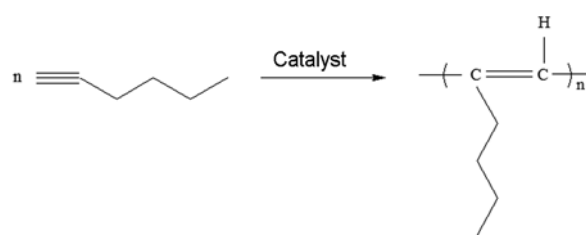
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10 ml chloroform was precipitated into a large excess of methanol. The precipitated polymer was filtered and dried in vacuum oven at 40 °C for 24 h. The light-brown polymer powder was obtained in 42 % yield.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO- d_6 and the chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Elemental analyses were performed with FISON S EA1110 Elemental Analyzer. The optical absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). In order to examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing DMF. ITO, Ag/AgNO₃ and platinum wire were used as a working, reference and counter electrode, respectively. 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.

Results and Discussion

The polymerization of 1-hexyne was carried out by various transition metal catalysts (Scheme 1). Table 1 shows the results for the polymerization of 1-hexyne. We used W- and Mo-based catalysts, which had been known to be very effective for the polymerization of some monosubstituted acetylenes [2] and the cyclopolymerization of 1,6-heptadiyne derivatives [15]. In general, the catalytic activity of WCl₆-based catalysts were greater than those of MoCl₅-based catalysts. WCl₆ alone gave only low yield of polymer (15 %). The higher catalytic activity of WCl₆-based catalysts than that of MoCl₅-based catalysts had been found for the



Scheme 1. Polymerization of 1-hexyne.

polymerization of a monosubstituted aromatic acetylene, phenylacetylene [2,23], whereas the MoCl₅-based catalysts had been found to be very effective for the polymerization of acetylene monomer with polar functional groups [24,25]. The highest polymer yield (45 %) was obtained when the WCl₆-Ph₄Sn catalyst system was used. In general, the polymerization by PdCl₂ and PtCl₂ proceeded slowly to give a relatively low yields of polymer (22 and 15 %, respectively).

The chemical structure of the resulting poly(1-hexyne) was characterized by elemental analyses, NMR, infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(1-hexyne) agreed with the theoretical value: calcd for (C₆H₁₀)_n: C, 87.7 %; H, 12.3 %, found: C, 86.9 %; H, 12.1 %. The ¹H-NMR spectrum of poly(1-hexyne) showed the methyl and methylene proton peaks at 0.8-3.5 ppm, whereas the vinyl protons of conjugated polymer backbone were broadly seen at 4.8-5.7 ppm. In the IR spectrum of poly(1-hexyne), it did not show the acetylenic C≡C bond stretching frequency and the acetylenic ≡C-H stretching frequency. Instead, new C=C stretching frequency peak of conjugated polymer backbone was observed at around 1600 cm⁻¹. The UV-visible spectrum of poly(1-hexyne) prepared by WCl₆-Me₄Sn catalyst also showed a characteristic peak of conjugated polymer, a wide broad π→π* absorption in the visible region. These spectral data indicates that the present poly(1-hexyne) have a conjugated polymer backbone system carrying pendant n-butyl substituents. The

Table 1. Polymerization of 1-hexyne by various transition metal catalysts^a

| No | Catalyst system (mole ratio) ^b | Solvent | M/C ^c | [M] ₀ ^d | Polymer yield (%) ^e | Mn ^f | Mw/Mn ^f |
|----|--|---------------|------------------|-------------------------------|--------------------------------|-----------------|--------------------|
| 1 | WCl ₆ | Chlorobenzene | 50 | 1.0 | 15 | 2,500 | 1.8 |
| 2 | WCl ₆ -Me ₄ Sn(1:2) | Chlorobenzene | 50 | 1.0 | 42 | 3,900 | 2.1 |
| 3 | WCl ₆ -Ph ₄ Sn(1:2) | Chlorobenzene | 50 | 1.0 | 45 | 4,200 | 2.2 |
| 4 | MoCl ₅ | Chlorobenzene | 50 | 1.0 | trace | - | - |
| 5 | MoCl ₅ -Me ₄ Sn(1:2) | Chlorobenzene | 50 | 1.0 | 17 | 2,700 | 1.8 |
| 6 | PdCl ₂ | DMF | 30 | 1.5 | 22 | 2,000 | 2.4 |
| 7 | PtCl ₂ | DMF | 30 | 1.5 | 15 | 2,700 | 2.5 |

^aPolymerization was carried out at 60 °C for 24 h, ^bmixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use, ^cmonomer to catalyst mole ratio, ^dinitial monomer concentration (M), ^emethanol-insoluble polymer yield, and ^fthe molecular weights were determined by GPC.

resulting poly(1-hexyne)s were generally light-brown colored powders. The solubility test was performed for powdery samples in excess solvent. The poly(1-hexyne)s were completely soluble in THF, chloroform, benzene, chlorobenzene, and but insoluble in methanol, ethyl ether, and n-hexane.

The electro-optical properties of poly(1-hexyne) were measured and discussed. The UV-visible spectra and photoluminescence (PL) spectra of poly(1-hexyne) solution (0.1 wt%, DMF) were measured. Figure 1 shows the UV-visible spectra and photoluminescence (PL) spectra of poly(1-hexyne). Poly(1-hexyne) showed UV-visible absorption band at maximum value of 276 nm and broad PL spectrum at maximum value of 415 nm as well as relatively blue-shifted PL spectrum compared to other polyacetylene. The similar homologue, poly(phenyl propargyl sulfide), which included same polyacetylene backbone and inert side group of benzylic sulfide instead of side butyl group of poly(1-hexyne), showed PL maximum value of 460 nm [26]. The blue-shifted PL maximum value of poly(1-hexyne) could be explained by that three dimensional configuration of butyl group is different with planar structure of phenyl group. Also, in our previous report [27] on poly(phenylacetylene) (PPA), PPA showed UV-visible plateau peak at 340 nm and PL peak of 439 nm. PPA includes a different side group of phenyl ring instead of alkyl chain of poly(1-hexyne). As a result, PL peak of poly(1-hexyne) were blue-shifted 24 nm compared to PPA. It can be explained by that the different things between two polymer chemical structures are different side chromophore group and the size of side group. In the case of PPA, conjugated polyene of the main chain may cause to make hybridized chromophore with phenyl ring. However, poly(1-hexyne) does not have this effect and it has only conjugated polyene of main chain with butyl group in side chain. Based on this chemical structure, it can be understood that poly(1-hexyne) spectrum is more blue-shifted. The band gap energy of poly(1-hexyne) was estimated to be 2.98 eV from the analysis of the absorption edge with a plot of $(h\nu)$ vs. $(\alpha h\nu)^2$, where α , h , and ν are the absorbance, Planck's constant, and the frequency of light, respectively.

We studied the electrochemical kinetic behavior of poly(1-hexyne) by using the cyclic voltameter. The measured cyclic voltammograms of poly(1-hexyne) with the various scan rates (30-150 mV/s) are shown in Figure 2(a). The peak potentials are constant as the scan rate is increased. Also we have observed very stable cyclic voltammograms of poly(1-hexyne) from the consecutive scan (up to 30 cycles) in Figure 2(b), which means that this material has relatively stable redox process. In Figure 2, the oxidation of poly(1-hexyne) was started at 0.46 V (vs Ag/AgNO₃) and it also showed the irreversible reduction maximum peak at -0.85 V. The oxidation and reduction current values were gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(1-hexyne) is

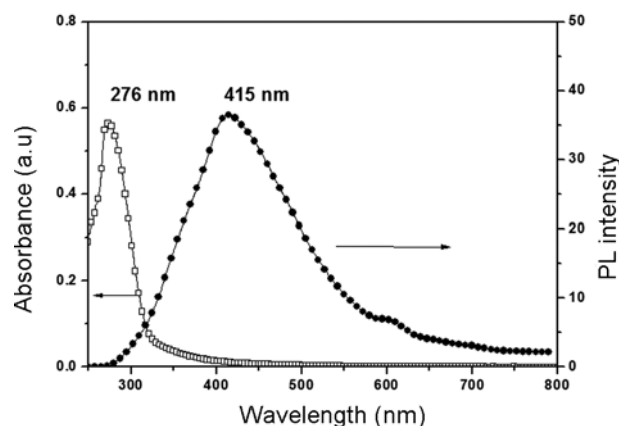


Figure 1. Optical absorption spectrum of poly(1-hexyne) (0.1 wt% DMF solution).

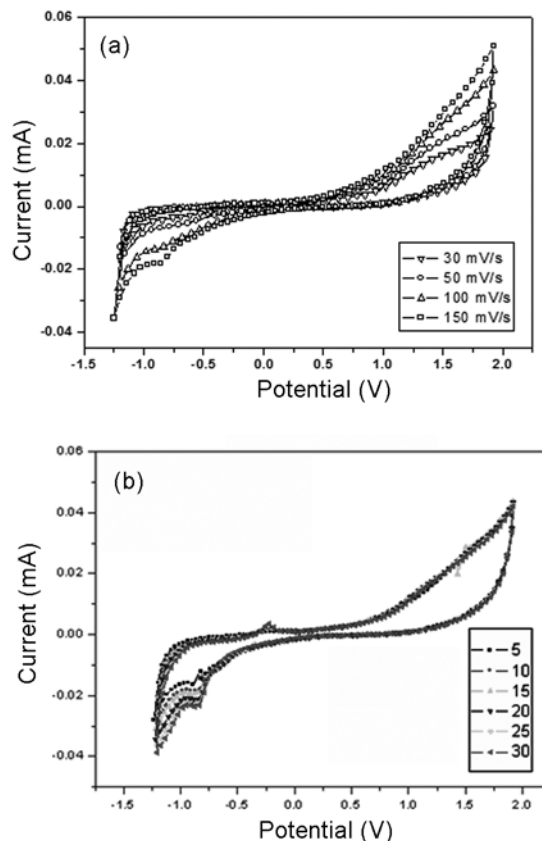


Figure 2. Cyclic voltammograms of poly(1-hexyne) [0.1 M (n-Bu)₄NBF₄/DMF] with various scan rates 30-120 mV/sec (a) and consecutive 30 scans under 100 mV/s (b).

reproducible and stable in the potential range of -1.25 ~ +1.92 V vs Ag/AgNO₃.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [28,29].

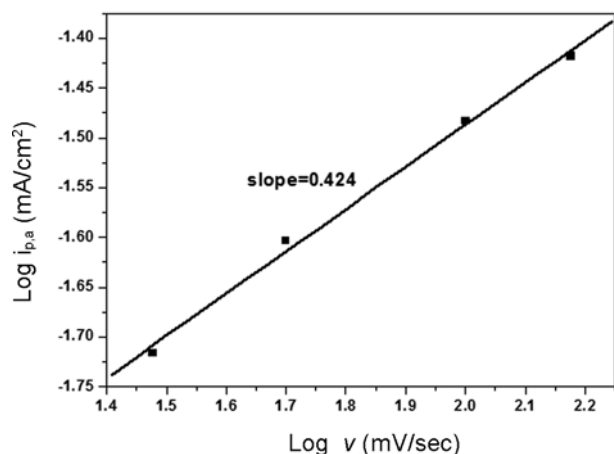


Figure 3. Plot of $\log i_{p,a}$ vs $\log v$ for poly(1-hexyne).

$$i_{p,a} = k v^x \quad (1)$$

$$\text{Log } i_{p,a} = \log k + x \log v \quad (2)$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies equation (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where $x=1$, or the reactant diffusion process, where $x=0.5$. Relations satisfying equation (2) between the oxidation current density ($\log i_{p,a}$) and the scan rate ($\log v$) were obtained. The oxidation current density of poly(1-hexyne) versus the scan rate is approximately linear relationship in the range of 30-150 mV/sec. The exponent of scan rate, x value of poly(1-hexyne), is found to be 0.424. This value means that the redox process may be controlled by the reactant diffusion process [28-30]. For the reference, PPA exhibited x value of 0.236 and it means that the electro-chemical activity of poly(1-hexyne) is superior to PPA because of the replacement of phenyl ring by an alkyl group.

Based on CV data, HOMO and LUMO level values of poly(1-hexyne) were found to be 5.35 and 2.37 eV by through calibration of ferrocene.

Conclusion

In this article, we synthesized poly(1-hexyne) by using various transition metal catalysts. The chemical structure of poly(1-hexyne) was characterized by various instrumental methods to have conjugated polymer backbone system having *n*-butyl substituents. Poly(1-hexyne) showed UV-visible absorption band at 276 nm and PL spectrum at 415 nm, indicating relatively blue-shifted PL maximum value compared to poly(phenyl propargyl sulfide). The band gap energy of poly(1-hexyne) was estimated to be 2.98 eV. The cyclic voltammograms of poly(1-hexyne) exhibited that

the irreversible oxidation and reduction were occurred at around 1.5 V and -0.85 V, respectively (vs Ag/AgNO₃). The redox current value gradually increased as the scan rate increased. HOMO and LUMO level values of poly(1-hexyne) were 5.35 and 2.37 eV, respectively.

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