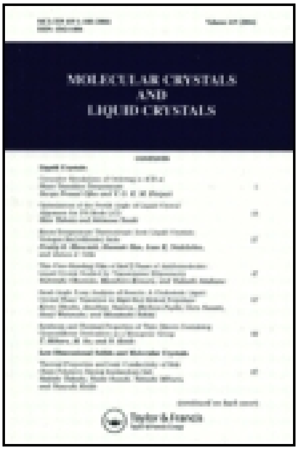

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Preparation, Structural and Spectral Properties of Poly(2-ethynylbenzyl alcohol)

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Preparation, Structural and Spectral Properties of Poly(2-ethynylbenzyl alcohol)

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A hydroxy group-containing polyacetylene, poly(2-ethynylbenzyl alcohol) [poly(EBA)] was prepared by the polymerization of 2-ethynylbenzyl alcohol by using various transition metal catalysts. This polymerization proceeded in somewhat mild manner to give in moderate yield. The instrumental analysis data on the chemical structure of poly(EBA) indicated that the present polymer have a conjugated polymer backbone system with the designed substituents. The photoluminescence peak of polymer was observed at 525 nm, which is corresponded to the photon energy of 2.36 eV and the band gap of poly(EBA) was 2.38 eV. The cyclovoltamograms of the polymer exhibited the irreversible electrochemical behaviors. It was found that the kinetics of the redox process of this conjugated polymer might

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be mainly controlled by the diffusion process from the experiment of the oxidation current density of polymer versus the scan rate.

Keywords: 2-ethynylbenzyl alcohol; electrochemical property; photoluminescence; polyacetylene; polymerization

INTRODUCTION

Conjugated organic polymers are of particular interest in material science because of their extraordinary optical and electronical properties. π-Conjugated materials have demonstrated real promise in such various fields as electric semiconductors, photonics, nonlinear optical applications, gas or liquid separation membranes, chemical sensors, liquid crystals, and organic light-emitting diodes (OLEDs) [1–12].

For more than several decades, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics [5–8]. The initial impetus for the plethora of work on conducting polymers was generated by the discovery of the increase, by nearly 10 orders of magnitude, in the electrical conductivity in the oxidized form of π-conjugated polyacetylene (PA) in 1977 [13,14].

A number of mono- and di-substituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems [1,2,5,15–18]. 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 [19].

The polymerization of acetylene derivatives having hydroxy functional groups are of interests because of their unique structures and facile modification of hydroxy groups with other interesting functional groups. The most simple hydroxy-containing polyacetylene, poly(propargyl alcohol), had been prepared by high pressure with radical initiator, $PdCl_2$, $Ni(CO)_2(PPh)_2$, $NiI_2(PPh_3)_2$, $Ni(NCS)(C{\equiv}C\text{-}R)(PPh_3)_2$, γ-ray, plasma, $MoCl_5$, and $Pd(C{\equiv}CCH_2OH)_2(PPh_3)_2$ [20,21]. However, in most cases, the resulting polymers were insoluble in organic solvents.

In order to increase the solubility of hydroxy-containing polyacetylene, various substituents were introduced at the α-carbon of propargyl alcohol. Soluble poly(1-ethynyl-1-cyclohexanol), poly(3-butyn-2-ol), poly(1-octyn-3-ol), poly(2-phenyl-3-butyn-2-ol), and poly(hydroxyalkyl acetylene)s were prepared and characterized [22,23].

To date, there have been no reports on the synthesis of poly(EBA) (Fig. 1). Here, we report the synthesis and characterization of poly (EBA), a new hydroxy group-containing polyacetylene. And also we

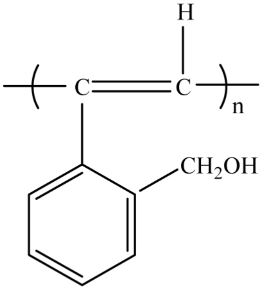


FIGURE 1 The chemical structure of poly(EBA).

studied the electro-optical and electrochemical properties of the resulting poly(EBA).

EXPERIMENTAL

2-EBA (Aldrich Chemicals., 97%) was used as received. The catalysts and polymerization procedures were same with those for polymerization of similar homologues [22,24–26]. A typical synthetic procedure of poly(EBA) is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (7.57 mmol) of 2-EBA, 0.068 g (0.252 mmol, M/C = 30) of (NBD)$PdCl_2$, and 5 mL of DMF ($[M]_0 = 1.26$ 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 DMF 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 52% yield.

NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The electrical conductivity of the sample was determined by using a standard four-point probe measurement without extensive pumping of the doped pellets with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Conductivity was calculated from the measured resistance of the sample. 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). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing DMF. ITO, $Ag/AgNO_3$ 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 2-EBA was performed by various transition metal catalysts. Table 1 shows the results for the polymerization of 2-EBA. $MoCl_5$-based catalyst systems had exhibited high catalytic activity for the polymerization of propargyl alcohol. And also, the polymerization of propargyl alcohol had been known to proceed well in various aromatic and halogenated solvents. However, the resulting polymer was known to be mostly insoluble in organic solvents [21]. The polymerization of 2-EBA, an acetylene derivative having benzyl alcoholic moieties, was also carried out by Mo- and W-based catalysts. $MoCl_5$ alone gives only a low yield of polymer (12%), whereas WCl_6 alone failed to polymerize 2-EBA. A typical organoaluminium cocatalyst, $EtAlCl_2$, slightly increased the polymer yield. Palladium-based catalysts were relatively effective for the present polymerization of 2-EBA. $(NBD)PdCl_2$ was found to be mostly effective for the present polymerization (polymer yield: 52%, Mn = 3,950).

TABLE 1 Polymerization of 2-EBA by Transition Metal Catalysts[a]

No.	Catalyst system[b]	Solvent	$[M]_0$[c]	M/C[d]	Polymer yield (%)[e]	Mn[f]	Mw/Mn
1	$PdCl_2$	DMF	1.5	30	35	2,630	3.2
2	$PtCl_2$	DMF	1.5	30	28	2,330	3.5
3	$(NBD)PdCl_2$	DMF	1.5	30	52	3,950	2.7
4	WCl_6	Chlorobenzene	1.9	50	trace	–	–
5	WCl_6-$EtAlCl_2$	Chlorobenzene	1.9	50	20	2,780	3.2
6	$MoCl_5$	Chlorobenzene	1.9	50	12	–	–
7	$MoCl_5$-$EtAlCl_2$	Chlorobenzene	1.9	50	27	3,120	3.5

[a] Polymerization was carried out at 90°C for 24 hrs.

[b] Mixture of catalyst and cocatalyst solution was aged for 15 min at room temperature before use.

[c] Initial monomer concentration (m).

[d] Monomer to catalyst mole ratio.

[e] Methanol-insoluble polymer.

[f] The molecular weights were determined by GPC.

The chemical structure of the resulting poly(EBA) was characterized by NMR (^{1}H- and ^{13}C-), infrared, and UV-visible spectroscopies. The ^{1}H-NMR spectrum of poly(EBA) prepared by (NBD)$PdCl_2$ catalyst system showed the broad peak at 5.8–7.8 ppm, which is originated from the protons of aromatic phenyl substituent and the vinyl protons of conjugated polymer backbone. The ^{13}C-NMR spectrum of poly(EBA) showed the carbons on the phenyl substituent and the carbons on the conjugated double bond of the polymer backbone in the range of 106–152 ppm. In the IR spectrum of poly(EBA), it did not show the acetylenic C≡C bond stretching frequency (2110 cm^{-1}) and the acetylenic ≡C-H stretching frequency (3262 cm^{-1}). The UV-visible spectrum of poly(EBA) prepared by (NBD)$PdCl_2$ catalyst also showed a characteristic peak of conjugated polymer, a wide broad $\pi \rightarrow \pi^*$ absorption up to 650 nm. From these spectral datas, we concluded that a new conjugated polymer with the designed substituents is formed.

The UV-visible spectra and photoluminescence (PL) spectra of poly(EBA) solution (0.1 wt. %, DMF) were measured (Fig. 2). This polymer showed characteristic UV-visible absorption band at 415 nm and maximum PL peak of 525 nm corresponding to the photon energy of 2.36 eV. We have reported the UV-visible and PL spectra of poly (diethyl dipropargylmalonate), poly(DEDPM) which has similar polyacetylene backbone as well as does not include a charged atom [27].

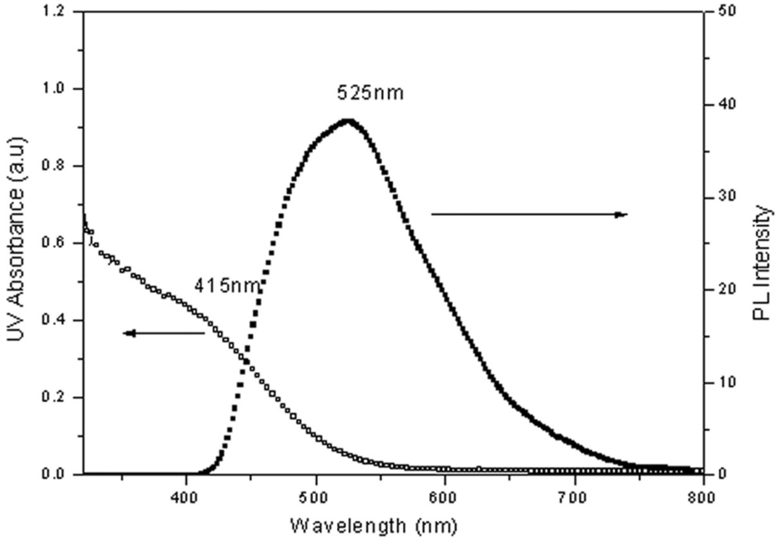


FIGURE 2 Optical absorption and photoluminescence spectra of poly(EBA).

Poly(DEPDM) showed UV-visible maximum value of 442 nm and PL maximum value of 543 nm. Similar polyacetylene backbone showed similar maximum values of optical spectra. A little difference between these spectra is that poly(EBA) exhibited blue-shifted spectra, which may be due to the interaction between vinylene backbone and methylene alcohol of ortho-positioned pendant group. The band gap of poly (EBA) was 2.38 eV.

In order to investigate electrochemical property, we measured various cyclic voltammograms of poly(EBA). As shown in Figure 3(a), we have observed very stable cyclic voltammograms of poly(EBA) from the consecutive scan (up to 30 cycles), which means that this material has relatively stable redox process. The measured cyclic voltammograms of poly(EBA) with the various scan rates (30 mV/s $\sim$ 150 mV/s) are shown in Figure 3(b) to study the electrochemical kinetic behavior. The peak potentials very slightly shifted to higher potentials as the scan rate increased. In Figure 3, the oxidation of poly(EBA) was occurred at 0.58 V (vs. Ag/AgNO$_3$), where the vinylene unit of conjugated polymer backbone might be oxidized in the scan. Poly(EBA) also shows the irreversible reduction at -1.06 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(EBA) is reproducible in the potential range of $-1.8 \sim +1.5$ V vs. Ag/AgNO$_3$.

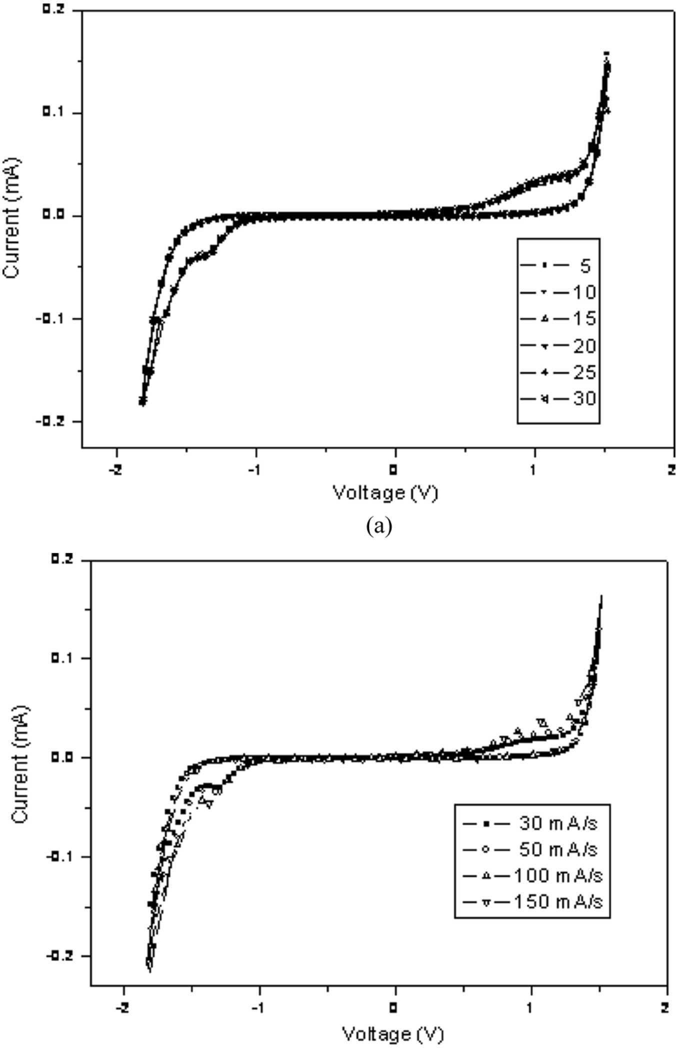
It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [28,29].

$$i_{\mathrm{p,a}} = kv^{x} \tag{1}$$

$$\mathrm{Log}\, i_{\mathrm{p,a}} = \log k + \mathrm{x} \log v \tag{2}$$

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

Assuming that electrode kinetics satisfies Eq. (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 [28]. Relations satisfying Eq. (2) between the oxidation current density (log $i_{\mathrm{p,a}}$) and the scan rate (log v) are shown in Figure 4. The oxidation current density of poly(EBA) versus the scan rate is approximately linear relationship in the range of 30 mV/sec $\sim$ 150 mV/sec. The exponent of scan rate, x value of poly(EBA), is found to be 0.423. This value means that the kinetics of the redox process may be mainly controlled by the diffusion process [28–30].



(a)

(b)

FIGURE 3 Cyclic voltammograms of poly(EBA) [0.1 M $(n\text{-}Bu)_4NBF_4$/DMF] (a) consecutive 30 scans under 100 mV/s and (b) 30 mV/sec ~120 mV/sec with various scan rates.

The electrical conductivity of polymer increased significantly through chemical doping by using an acceptor-type dopant such as iodine. Polymer pellet subjected to vapor-phase iodine doping showed large, irreversible iodine uptakes with no significant decrease in

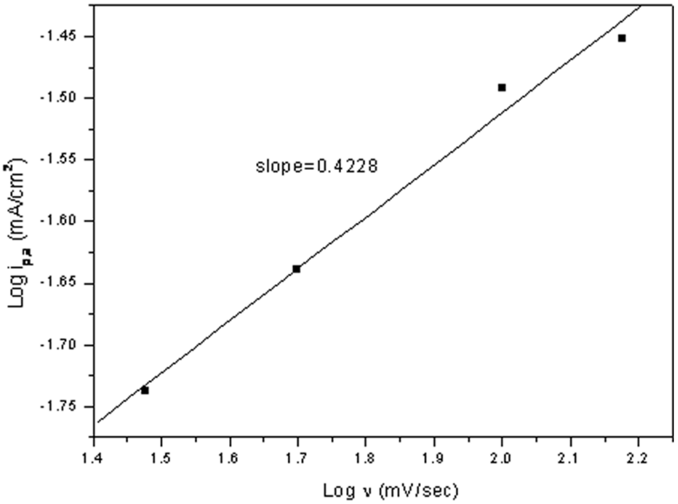


FIGURE 4 Plot of log $i_{p,a}$ vs. log v for poly(EBA).

iodine content even after prolonged vacuum pumping (6 hrs). The polymer pellet was changed eventually into a lustrous, soft, pasty material. The electrical conductivity of the iodine-doped poly(EBA) pellet was 5.50×10^{-4} S/cm. The FT-IR spectra of iodine-doped polymer showed a broad absorption in the range of 3500–1600 cm^{-1}, arising due to electronic transitions from the valence to the conduction bands in conjugated polymer systems.

CONCLUSIONS

We successfully synthesized new conjugated polymer with hydroxybenzyl functional groups through the polymerization of 2-EBA by various transition catalysts. This polymerization proceeded well in polar organic solvents to give the resulting polymer in moderate yield. The photoluminescence (PL) spectra of poly(EBA) indicated that the photoluminescence maximum peak is located at 525 nm, which corresponds to the photon energy of 2.36 eV. The side chains within the polyacetylene derivatives shifted PL maximum values because it made different molecule interaction and arrangement. The cyclovoltamograms of poly(EBA) exhibited the electrochemically stable window. It was found that the kinetics of the redox process of poly(EBA) may be primarily controlled by the reactant diffusion process, based on the experiment of the oxidation current density of poly(EBA) versus the scan rate.

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