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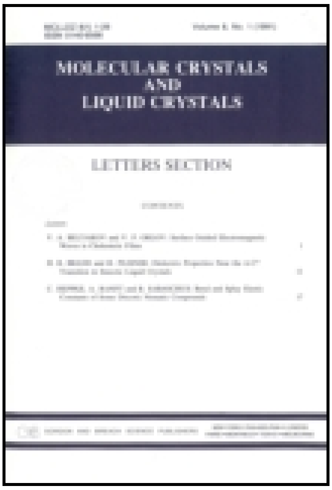

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Synthesis and Optical Properties of a Polyacetylene with Hydroxy Funtional Groups: Poly(4-ethynylbenzyl Alcohol)

Yeong-Soon Gal[a], Sung-Ho Jin[b], Jong Wook Park[c] & Kwon Taek Lim[d]

[a] Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan, Gyeongsangbuk-do, Korea

[b] Department of Chemistry Education, Pusan National University, Pusan, Korea

[c] Department of Chemistry and Center for Display Res., The Catholic University of Korea, Bucheon, Korea

[d] Division of Image and Information Engineering, Pukyong National University, Busan, Korea

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Synthesis and Optical Properties of a Polyacetylene with Hydroxy Funtional Groups: Poly(4-ethynylbenzyl Alcohol)

YEONG-SOON GAL,[1,*] SUNG-HO JIN,[2] JONG WOOK PARK,[3] AND KWON TAEK LIM[4]

[1]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan, Gyeongsangbuk-do, Korea
[2]Department of Chemistry Education, Pusan National University, Pusan, Korea
[3]Department of Chemistry and Center for Display Res., The Catholic University of Korea, Bucheon, Korea
[4]Division of Image and Information Engineering, Pukyong National University, Busan, Korea

A new conjugated polymer with hydroxy functional groups, poly(4-ethynylbenzyl alcohol) [poly(4-EBA)], was synthesized by the polymerization of 4-ethynylbenzyl alcohol (4-EBA) using transition metal catalysts. Such instrumental methods as NMR, IR, and UV-visible spectroscopies revealed that the resulting polymer has a conjugated polymer backbone system having the designed substituents. The photoluminescence maximum peak of poly(4-EBA) was located at 465 nm, which corresponds to the photon energy of 2.67 eV. UV-visible absorption and PL spectra of four similar polyacetylene derivatives were measured and compared.

Keywords Polyacetylene; conjugated polymer; 4-ethynylbenzyl alcohol; photoluminescence; cyclovoltammogram

1. Introduction

Over the past four decades, the electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [1, 2]. The devices using synthetic organic materials are attractive because of they can provide such advantages of organic materials as light weight, low cost, and capability of thin-film, large-area, flexible device fabrication [3–7].

Among these materials, polyacetylene is structurally the simplest one and a prototypical conjugated polymer, which exhibits high electrical conductivity upon doping [8, 9]. This discovery led to the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa [10–12]. Nevertheless, some drawbacks thus far have prevented commercial applications of polyacetylene itself. Polyacetylene does

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[*] Address correspondence to Prof. Yeong-Soon Gal, Chemistry Division, College of Engineering, Kyungil University, Gyeongsan 712-701, Gyeongsangbuk-Do, Korea. Tel.: (+82)53-600-5487; Fax: (+82)53-600-5499. E-mail: ysgal@kiu.ac.kr

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. More processable conjugated polymers had been prepared by the linear polymerization of substituted acetylenes and by the cyclopolymerization of nonconjugated diynes [13–22].

The hydroxy group-containing polymers have received unabated attention in the design and synthesis of multifunctional polymers [13]. Unlike other π-conjugated polymers, they contain hydroxy groups in the side chain that provide the facile modification of hydroxy groups into other interesting functional groups. The simplest polyacetylene with hydroxyl group, poly(propargyl alcohol), was known to be insoluble in any organic solvent and easily susceptible to air oxidation [13, 23]. In order to increase the solubility of hydroxy-containing polyacetylenes, 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), poly(hydroxyalkyl acetylene)s, and poly(2-ethynylbenzyl alcohol) were prepared and characterized [24–27].

In this article, we report the synthesis of a new conjugated polymer with hydroxyl functional groups and the elucidation on the optical properties of the resulting polymer.

2. Experimental

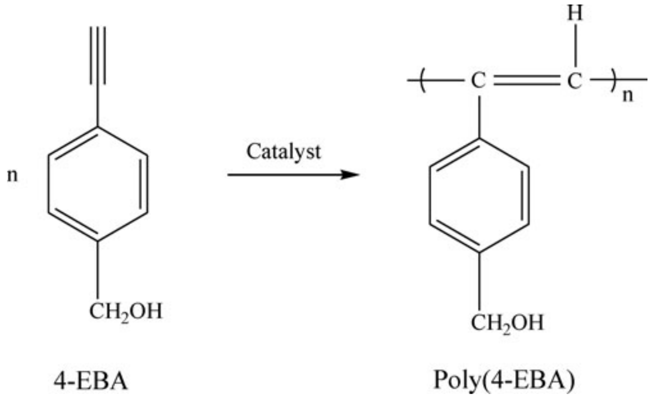
4-Ethynylbenzyl alcohol (Aldrich Chemicals., 97%), $MoCl_5$ (Aldrich Chemicals, 99.9+%), WCl_6 (Aldrich Chemicals., 99.9+%), $EtAlCl_2$ [Aldrich Chemicals, 25 wt.% (1.8 M) solution in toluene], and Me_4Sn (Aldrich Chemicals, 95%) were used without further purification. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

The procedures of catalyst system preparation and polymerization were identical to those for polymerization of similar homologues [25–27]. A typical synthetic procedure for poly(4-EBA) is as follows. In a 30 mL reactor equipped with rubber septum, 1.0 g (7.57 mmol) of 4-EBA, and chlorobenzene (1.01 mL, $[M]_0 = 1.5$ M) were added. Then the catalyst solution of 1.51 mL (0.151 mmol, M/C = 50) of 0.1 M $MoCl_5$ solution and 1.51 mL (0.302 mmol) of 0.2 M $EtAlCl_2$ solution after shaking the catalyst solution at room temperature for 15 min, was injected into the polymerization reactor. After a given time of polymerization at 80°C, 10 mL of DMF was added to the polymerization solution. Then, the polymer solution 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 55% yield.

NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500MHz 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. Molecular weights were determined by a gel permeation chromatographer (Waters 150C) equipped with μ-Styragel columns using THF as an eluent. Monodisperse polystyrene standard samples were used for molecular weight calibration. 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 150Hz.

3. Results and Discussion

Mo- and W-based catalysts, which were found to be very effective for the metathesis polymerization of cycloolefins and the metathesis cyclopolymerization of dipropargyl monomers, were also used for the present polymerization (Scheme 1).



Scheme 1. Polymerization of 4-EBA

WCl_6 alone only gave a trace amount of solid products (<10%). The $EtAlCl_2$ cocatalyst activated the polymerization of 4-EBA by WCl_6 to give 21% yield of polymer. $MoCl_5$ alone and $MoCl_5$-$EtAlCl_2$, which have been found to be very effective for the cyclopolymerization of dipropargyl monomers [15, 16], were also found to be effective for the present polymerization to give a moderate yield of polymer (42%, 55%, respectively). In our previous works, it was found that Mo-based catalysts are very effective for the polymerization of such propargyl monomers as propargyl alcohol, 1-ethynyl-1-cyclohexanol, and hydroxyalkyl acetylene [23, 24, 26]. The Me_4Sn did not show any cocatalytic activity for the polymerization of 4-EBP by WCl_6 or $MoCl_5$.

Palladium-based catalysts were also tested for the polymerization of 4-EBA in DMF solvent. The palladium-based catalyst systems have been known to be effective for the polymerization of nitrogen-containing acetylene derivatives [28, 29]. Palladium-based catalysts were also found to be effective for the polymerization of 4-EBA. The polymer yields for the polymerization of 4-EBA catalyzed by $PdCl_2$ and (NBD)$PdCl_2$ catalysts were 31% and 45%, respectively. The number-average molecular weights were in the range of 2,150–5,720.

The chemical structure of poly(4-EBA) was characterized by NMR (^{1}H- and ^{13}C-), infrared, and UV-visible absorption spectroscopies. Figure 1 shows the ^{1}H-NMR spectrum of poly(4-EBA) in $CDCl_3$. This shows the aromatic phenylene protons and the vinyl protons of the conjugated polymer at 6.0-8.0 ppm, whereas the methylene and hydroxyl proton peaks are observed at 3.6-5.5 ppm. The ^{13}C-NMR spectrum (Figure 2) of poly(4-EBA) shows the phenylene carbon peaks and the vinyl carbons of conjugated polymer backbone in the range of 122–146 ppm. The methylene carbon peak was also observed at 63 ppm. Figure 3 shows the FT-IR spectra of 4-EBA (a) and poly(4-EBA) (b) in KBr pellet. The FT-IR spectrum of poly(4-EBA) did not show the acetylenic $\equiv$C—H and C$\equiv$C bond stretching peaks at 3260 and 2105 cm^{-1}. The strong peak at 1011 cm^{-1} is due to the —CH_2—O—H stretching of primary alcohol. The peak at 816 cm^{-1} is also due to the CH out-of-plane deformation of

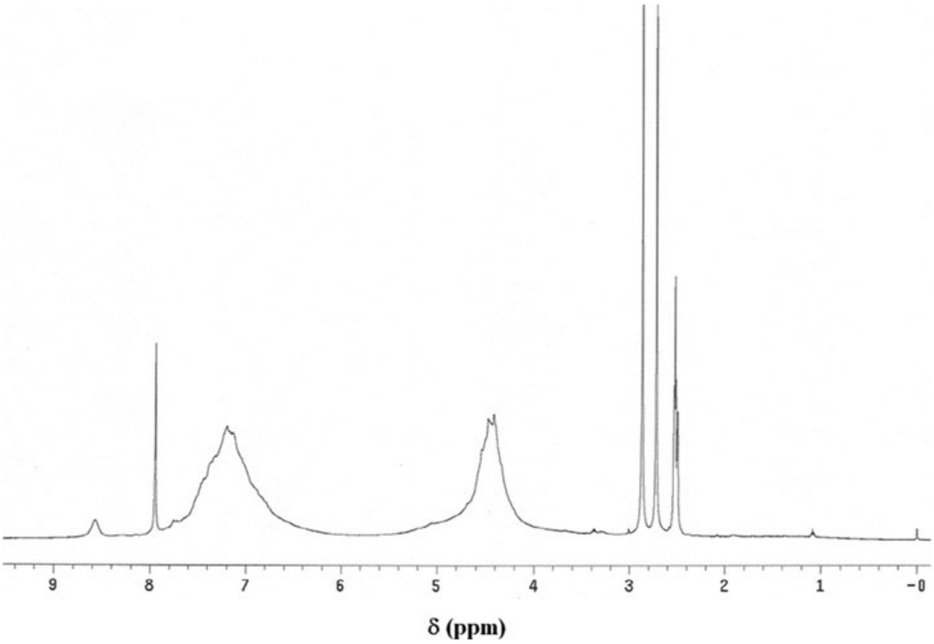


Figure 1. ^{1}H-NMR spectrum of poly(4-EBA) in $CDCl_3$.

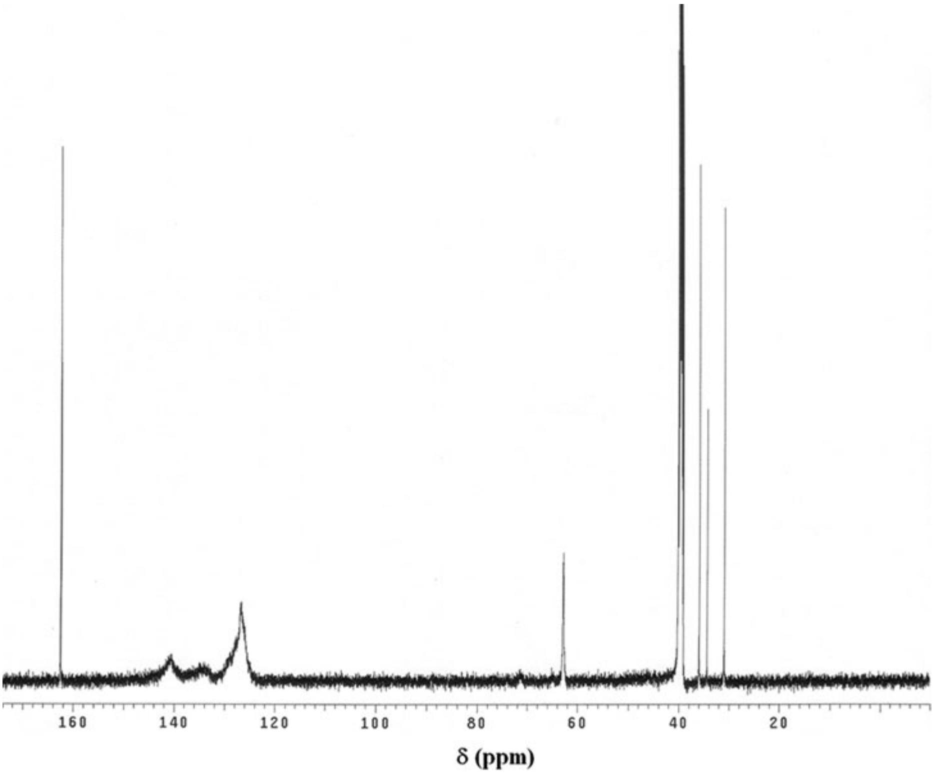


Figure 2. ^{13}C-NMR spectrum of poly(4-EBA) in $CDCl_3$.

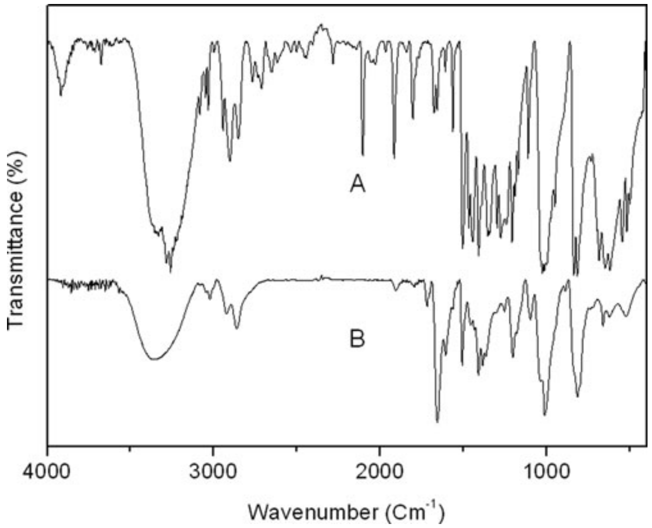


Figure 3. FT-IR spectra of 4-EBA (a) and poly(4-EBA) (b) in KBr pellet.

p-disubstituted benzenes. The aliphatic C—H and aromatic =C—H stretching frequencies were observed at 2850–2950 cm^{-1} and 3010–3030 cm^{-1}, respectively. The UV-visible absorption spectrum of poly(4-EBA) showed a broad absorption peak up to 550 nm, which is a characteristic peak of conjugated systems. These spectral data mean that the present polymer have the conjugated polymer backbone system with the designed substituents.

Our motivation of this study is comparing on UV-visible spectra of polyacetylene derivatives according to the phenyl ring moieties. Recently, there have been many kinds of material examples with conjugated backbone system for organic electronics applications. However, it still remains to solve the problem about the relationship between chemical structure and optical property which is related with electrical property such as band gap, HOMO, and LUMO, etc.

In our previous studies, we reported several kinds of optical data for the similar polyacetylene derivatives as poly(1-hexyne), poly(phenylacetylene), and poly(2-ethynylbenzyl alcohol) [27, 30, 31]. Figure 4 shows the optical absorption and photoluminescence spectra of poly(4-EBA). Four related spectral data are summarized in Table 1. Looking at UV-visible spectra (1.0×10^{-4} M, DMF solution), three compounds including a phenyl ring had a maximum value in the range of 340 nm ~ 415 nm. However, poly(1-hexyne) which does not have a phenyl ring, does not show the long range maximum peak and the edge range was around 330 nm. It can be explained by a phenyl ring which increases conjugation length of polyacetylene main chain. In the case of absorption edge wavelength values, poly(phenylacetyleen) had around 500 nm and poly(2-ethynylbenzyl alcohol) as well as poly(4-EBA) exhibited about 550 nm [27]. Especially, poly(2-ethynylbenzyl alcohol) showed the longest maximum value of 415 nm and the edge value of 550 nm in this series compounds [27]. It means that this absorption optical data not only came from a phenyl ring but also came from the methylene alcohol positioned by ortho site. Comparing with the PL spectra (1.0×10^{-4} M, DMF solution, excited by absorption maximum wavelength) of four conjugated polymers, the tendency was similar with those of UV-visible spectra of polymers. Poly(1-hexyne) showed the shortest maximum value of 415 nm and poly(phenylacetylene) including only a phenyl ring exhibited the PL maximum value at

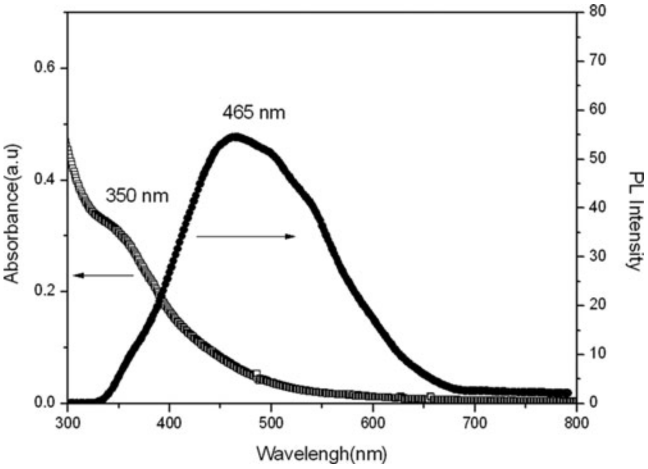
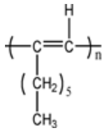
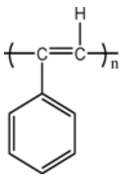
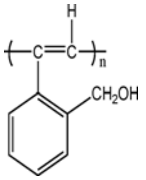
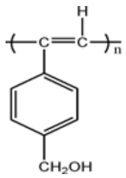


Figure 4. Optical absorption and photoluminescence spectra of poly(4-EBA) in DMF solution.

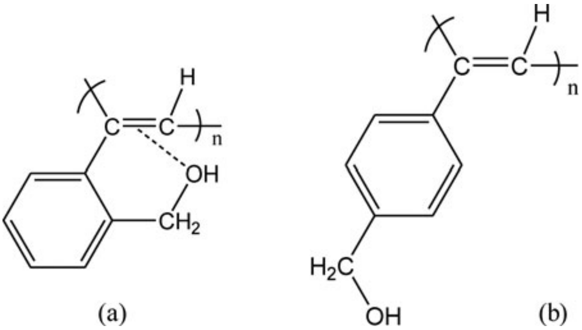
439 nm. When the methylene hydroxyl group was introduced at ortho or para position of phenyl ring, PL peak values were red-shifted to 525 and 465 nm, respectively. It is notable that the polyacetylene with alcohol group extends conjugation length due to hydrogen bonding effect between OH group and conjugated polyene. Comparing ortho OH group with para OH group, para OH group had relatively shorter PL maximum length value compared to ortho OH group. Ortho-positioned methylene alcohols changed peak value more than that with para-positioned methylene alcohols because para-positioned OH group has only intermolecular interaction but ortho-positioned OH group has relatively strong intramolecular interaction due to close distance between OH group and conjugated polyene.

In order to get the specific luminescence color on purpose, it is important factor to tune the PL maximum value. It may be due to that the para-positioned methylene alcohol only interact with intermolecular conjugated polyenes and the ortho-positioned methylene alcohol

Table 1. The summarized optical values of poly(1-hexyne), poly(phenylacetylene), poly(2-ethynylbenzyl alcohol), and poly(4-EBA)

Optical property				
UV-visible absorption maximum value (nm)	276	340	415	350
PL maximum value (nm)	415	439	525	465
PL maximum value (eV)	2.99	2.82	2.36	2.67

can interact with inter- and intramolecular conjugated polyenes as shown in Scheme 2. This additional interaction between methylene alcohol and conjugated polyenes could make red shifted optical maximum values in UV-visible and PL spectra.



Scheme 2. The proposed chemical structures of poly(2-ethynylbenzyl alcohol) (a) and poly(4-EBA) (b).

4. Conclusions

In this article, we reported the synthesis of a hydroxy-containing polyacetylene derivative and the optical properties of the resulting polymer. The polymerization of 4-EBA by transition metal catalysts proceeded in mild homogeneous manner to give a moderate yield of polymer. The chemical structure of poly(4-EBA) was characterized by various instrumental methods to have an ionic conjugated backbonne system bearing the designed substituents. We compared UV-visible absorption and PL spectra of similar polyacetylene derivatives which include a phenyl ring or not. Especially, poly(2-ethynylbenzyl alcohol) and poly(4-EBA) showed the relatively longer maximum peak values compared to other acetylene derivatives in absorption and PL spectra.

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