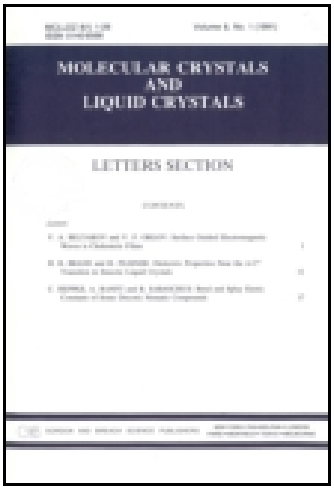

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of a Polyacetylene Derivative with Hydroxy Functional Groups

Sang Hee Jang[a] & Tae-Kwan Son[b]
[a] Department of Wellbeing Food, Gumi University, Gumi, Gyeongsangbuk-do, Korea
[b] School of Mechanical & Automotive Engineering, Keimyung University, Dalseo, Daegu, Korea
Published online: 17 Nov 2014.

To cite this article: Sang Hee Jang & Tae-Kwan Son (2014) Synthesis and Characterization of a Polyacetylene Derivative with Hydroxy Functional Groups, Molecular Crystals and Liquid Crystals, 597:1, 153-158, DOI: 10.1080/15421406.2014.932661

To link to this article: http://dx.doi.org/10.1080/15421406.2014.932661

Mol. Cryst. Liq. Cryst., Vol. 597: pp. 153–158, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.932661

Taylor & Francis
Taylor & Francis Group

Synthesis and Characterization of a Polyacetylene Derivative with Hydroxy Functional Groups

SANG HEE JANG[1] AND TAE-KWAN SON[2]

[1]Department of Wellbeing Food, Gumi University, Gumi, Gyeongsangbuk-do, Korea
[2]School of Mechanical & Automotive Engineering, Keimyung University, Dalseo, Daegu, Korea

A fluorenyl group-containing polyacetylene, poly(9-ethynyl-9-fluorenol) was prepared by the polymerization of 9-ethynyl-9-fluorenol (EF) by [(nbd)RhCl]$_2$. The polymerization proceeded well in homogeneous manner to give in high yield of polymer. The chemical structure of poly(EF) was characterized by such various instrumental methods as NMR, IR, and UV-visible spectroscopies to have the poly(EF) have a conjugated polymer backbone system with the designed fluorene groups. Poly(EF) showed edge range of UV-visible absorption spectrum about 600 nm and the band gap of poly(EF) was 2.20 eV. The maximum photoluminescence peak was observed at 431 nm.

Keywords Conjugated polymer; 9-ethynyl-9-fluorenol; polymerization; cyclovoltammogram; photoluminescence

Introduction

During the past four decades, the remarkable advances have been made in the research area of the polymer syntheses based on the triple-bonded acetylenic monomers Acetylenic triple bonds can be a good candidate to introduce π-conjugated systems due to rich π-electrons and yield the linear conjugated polymer systems [1, 2]. Considerable effort has been devoted to the synthesis of monosubstituted and disubstituted polyacetylenes and poly(1,6-heptadiyne)s and their properties were extensively studied [1, 3–6]. Unlike polyacetylene, substituted polyacetylenes are generally soluble in common organic solvents and stable enough in air for a long period of time. And also they may find a wide range of applications as speciality materials in, e.g., chemical and thermal sensing, optical displays, chiral separation, photovoltaic cells, information storage, fluorescence image patterning, light polarization, and nonlinear optics [7–9].

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,

* Address correspondence to Prof. Sang Hee Jang, Department of Wellbeing Food, Gumi University, Gumi 730-711, Gyeongsangbuk-do, Korea. Tel.: (+82)54-440-1342. Fax: (+82)54-440-1209. E-mail: jangsh@kumi.ac.kr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

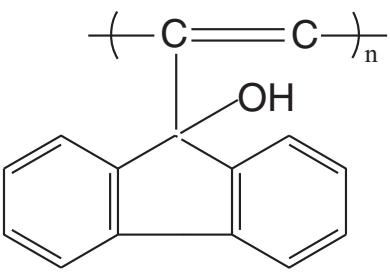

Figure 1. The chemical structure of poly(EF).

$PdCl_2$, $Ni(CO)_2(PPh)_2$, $NiI_2(PPh_3)_2$, $Ni(NCS)(C{\equiv}C\text{-}R)(PPh_3)_2$, γ-ray, plasma, $MoCl_5$, and $Pd(C{\equiv}CCH_2OH)_2(PPh_3)_2$ [1, 10]. However, in most cases, the resulting polymers were insoluble in organic solvents. Soluble polyacetylene derivatives with hydroxy functional groups had been prepared by introducing substituents at the α-carbon of propargyl alcohol. Soluble poly(1-ethynyl-1-cyclohexanol), poly(3-butyn-2-ol), poly(hydroxyalkyl acetylene)s, and poly(2-ethynylbenzyl alcohol) were prepared and characterized [11–13].

Fluorene group-containing poly(phenylene vinylene) derivatives were a good candidate as blue light-emitting organic materials for light-emitting devices for display and other purposes [14, 15]. Fluorene-based low-band gap copolymers were prepared for bulk heterojunction photovoltaic cell applications [16]. The diacetylenic polymer via oxidative coupling of 9,9-dipropargylfluorene was prepared and characterized. The poly(9,9-dipropargylfluorenylene-phenylene) and poly(9,9-dipropargylfluorenylene-biphenylene) were prepared by cross-coupling condensation polymerization [17, 18]. And also, a fluorine-containing spiro-type conjugated polymers were prepared via the cyclopolymerization of dipropargylfluorene and its derivatives [19, 20]. A polyacetylene derivative with electroactive fluorene group and reactive hydroxyl group may be the candidate materials for chemical sensors, permselective membranes, and light-emitting devices. Russo et al reported the synthesis of poly(9-ethynyl-9-fluorenol) [poly(EF)] in the presence of Rh(I), Pt(II), Pd(II), and WCl_6 catalysts, the resulting polymers were generally soluble in organic solvents, but the molecular weights were found to be very low [21].

Now, we report on the synthesis of poly(EF) [Figure 1] by $[(nbd)RhCl]_2$ catalyst, and the characterization of the resulting poly(EF).

Experimental

9-Ethynyl-9-fluorenol (EF, TCI Chemicals) was used as received. (Bicyclo[2.2.1]hepta-2,5-diene)dichloropalladium(II) ($[(nbd)RhCl]_2$, Aldrich Chemicals) was 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(EF) is as follows: In a 50 mL reactor equipped with rubber septum, 1.0 g (4.85 mmol) of EF, 43.55 mg (0.162 mmol, M/C = 30) of $[(nbd)RhCl]_2$, and 8.7 mL of DMF ($[M]_0 = 0.50$ M) were added in that order given. Then the polymerization was carried out at 80 °C for 24 hrs under nitrogen atmosphere. The polymerization mostly proceeded in homogeneous manner. After the polymerization time, the polymer solution diluted with 5 mL DMF was precipitated into a large excess of benzene/petroleum ether. The precipitated polymer was filtered and dried in vacuum oven at 40 °C for 24 hrs. The light-brown powder was obtained in 73% yield.

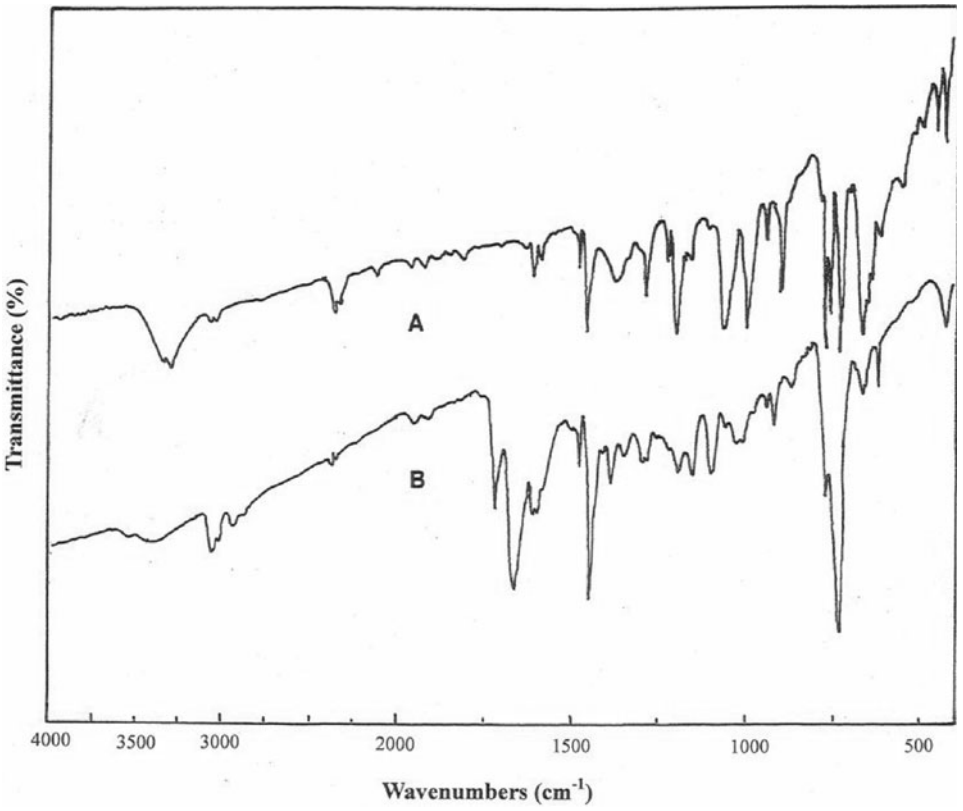

Figure 2. FT-IR spectra of EF (A) and poly(EF) in KBr pellets.

NMR spectra of polymer were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in $CDCl_3$ and the chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. 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 150 Hz.

Results and Discussion

The polymerization of an acetylene derivative containing fluorenol functionalities was carried out by $[(nbd)RhCl]_2$ catalyst, which had been found to be very effective for the polymerization of some monosubstituted acetylenes [6, 22]. This catalyst showed excellent solubility in the polymerization solvent.

The $[(nbd)RhCl]_2$ catalyst polymerized the monomer in mild homogeneous manner to give the relatively high polymer yield (73%). The resulting poly(EF) was completely soluble in such organic solvents as benzene, chlorobenzene, chloroform, DMF, and DMSO,

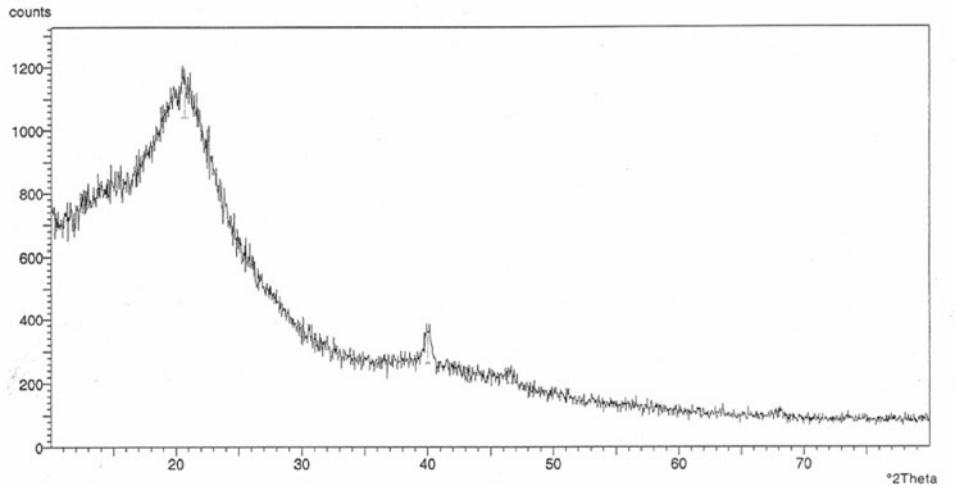

Figure 3. X-ray diffractogram of poly(EF) powder.

but insoluble in methanol and hexane. The good solubility of poly(EF) can be explained that the bulky 9-fluorenyl group at the α-position of propargyl alcohol prevent the cross-linking reaction of allyl protons of polymeric products. The number-average molecular weight (Mn) and the polydispersity (Mw/Mn) of poly(EF) were 5,920 and 1.58, respectively. The relatively low molecular weight of the present polymer was very similar with those of similar polymers with hydroxy functional groups [17].

The chemical structures of the resulting poly(EF) were characterized by NMR (^{1}H- and ^{13}C-), infrared, and UV-visible spectroscopies. The ^{1}H-NMR spectrum of poly(EF) showed the broad peak at 5.4-8.3 ppm, which is originated from the protons of aromatic fluorenyl moieties, and the vinyl protons of conjugated polymer backbone. The ^{13}C-NMR spectrum of poly(EF) showed the carbons on the fluorenyl moieties and the carbons on the conjugated double bond of the polymer backbone in the range of 117-151 ppm. Figure 2 shows the FT-IR spectra of EF and poly(EF) in KBr pellets. The IR spectrum of polymer did not show the acetylenic C≡C bond stretching frequency (2130 cm^{-1}) and the acetylenic ≡C-H stretching frequency (3287 cm^{-1}) of the monomer. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1665 cm^{-1} became more intense than that of the monomer. The characteristic broad peaks of secondary alcohol in polymer was observed at 3370 cm^{-1}. The peaks at 3060 cm^{-1} are due to the aromatic = C−H stretching and the vinylic = C−H stretching frequencies. In the UV-visible spectra, the absorptions at visible regions was observed, which was due to the $\pi \rightarrow \pi^*$ interband transition of the conjugated polymer. From these spectral data, it was concluded that the present polymer have the conjugated polymer backbone system with the designed substituents.

TGA thermogram of poly(EF) prepared by $[(nbd)RhCl]_2$ catalyst was measured under nitrogen atmosphere at a heating rate of 10°C/min. TGA thermogram of poly(EF) showed a slight weight loss around 150°C, which is due to the organic residues and/or moisture absorbed during the process. This polymer shows one abrupt weight loss in the temperature ranges of 180-450°C, which was judged to be originated by the decomposition of conjugated polymer system. This polymer retained 99.1% of its original weight at 100°C, 96.7% at 150°C, 94.1% at 200°C, 70.7% at 400°C 57.5% at 600°C, and 56.5% at 700°C. Figure 3 shows the X-ray diffractogram of poly(EF) powder. As shown in this figure, the peak in

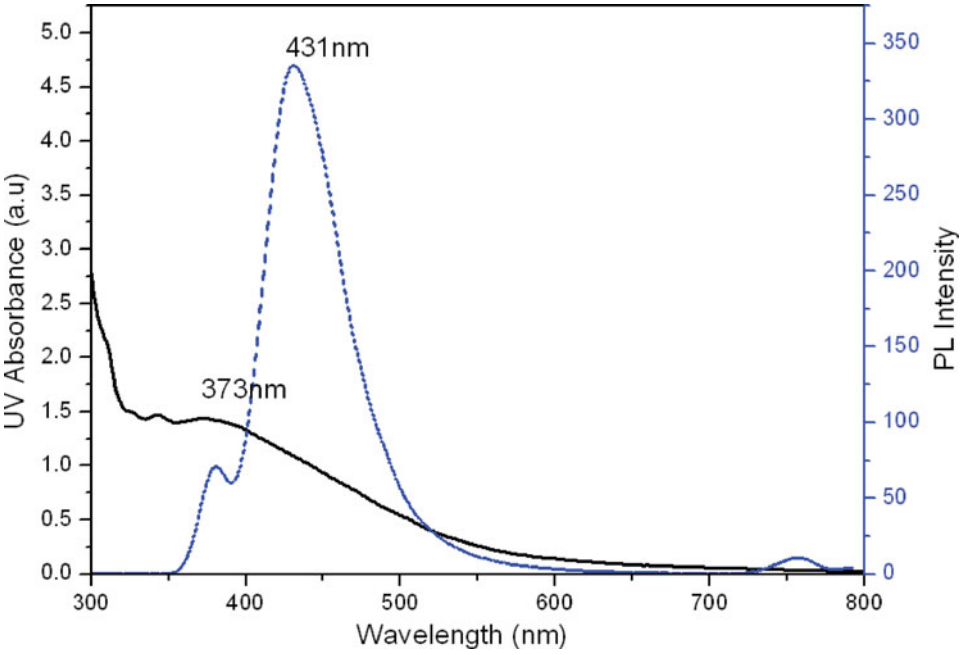

Figure 4. Optical absorption and photoluminescence spectra of poly(EF).

the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35 [3, 4], indicating that the present polymer is amorphous. Figure 4 shows the optical absorption and photoluminescence spectra of poly(EF) solution (0.1 wt.%, DMF). This polymer showed characteristic UV-visible absorption band at 373 nm and edge range of UV-visible absorption spectrum about 600 nm. It means that the band gap of poly(EF) was 2.20 eV. It was reported that the poly(2-ethynylbenzyl alcohol), a similar homologue, showed different edge range of UV-visible absorption spectrum about 525 nm and band gap about 2.38 eV. Comparing edge range of UV absorption spectrum and band gap value, it means that poly(EF) has smaller band gap and relatively extended conjugation length due to interaction between main chain backbone and side pendant group. The photoluminescence spectra of this conjugated polymer showed that the photoluminescence maximum peak is located at 431 nm corresponding to the photon energy of 2.88 eV.

Conclusions

In this paper, the research results for the preparation and characterization of poly(EF) with fluorene functional groups were presented. The polymerization of EF by $[(nbd)RhCl]_2$ catalyst generally proceeded well to give relatively high yield of polymer. The polymer structure was characterized by various instrumental methods to have conjugated polymer backbone system carrying the designed substituents. Poly(EF) showed characteristic UV-visible absorption band at 373 nm and the band gap of 2.20 eV. The X-ray diffraction data on poly(EF) indicated that this polymer is mostly amorphous. The photoluminescence maximum peak of poly(EF) was located at 431 nm corresponding to the photon energy of 2.88 eV.

Acknowledgment

This work was supported by the research fund of Kumi University.

References

[1] Masuda, T., & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[2] Buchmeiser, M. R. (2005). *Adv. Polym. Sci. 176*, 89.
[3] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[4] Gal, Y. S., Lee, W. C., Kim, S. Y., Park, J. W., Jin, S. H., Koh, K. N., & Kim, S. H. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 3151.
[5] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.
[6] Koz, B., Kiskan, B., & Yagci, Y. (2008). *Int. J. Mol. Sci.*, *9*, 383.
[7] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). *Chem. Rev.*, *109*, 897.
[8] Cheng, Y. J., Yang, S. H., & Hsu, C. S. (2009). *Chem. Rev.*, *109*, 5868.
[9] Liu, J., Lam, J. W. Y., & Tang, B. Z. (2009). *Chem. Rev.*, *109*, 6799.
[10] Chauser, M. G., Rodionov, Yu. M., Misin, V. M., & Cherkashin, M. I. (1976). *Russ. Chem. Rev.*, *45*, 348.
[11] Gal, Y. S., Jung, B., Kim, J. H., Lee, W. C., & Choi, S. K. (1994). *J. Macromol. Sci.-Pure Appl. Chem.*, *A31*, 1177.
[12] Gal, Y. S. (1995). *J. Macromol. Sci.-Pure Appl. Chem.*, *A32*, 61.
[13] Lee, W. C., Jin, S. H., Lyoo, W. S., Park, J.W., Lim, K. T., Kim, S. Y., & Gal, Y. S. (2009). *Mol. Cryst. & Liq. Cryst.*, *513*, 196.
[14] Leclerc, M. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 2867.
[15] Zaumseil, J., & Sirringhaus, H. (2007). *Chem. Rev.*, *107*, 1296.
[16] Park, J. S., Ryu, T. I., Song, M., Yoon, K. J., Lee, M. J., Shin, I. A., Lee, G. D., Lee, J. W., Gal, Y. S., & Jin, S. H. (2008). *J. Polym. Sci.: Part A: Polym. Chem.*, *46*, 6175.
[17] Lee, S. G., Kwak, Y. W., Koo, B. K., & Gal, Y. S. (2008). *Mol. Cryst. & Liq. Cryst.*, *491*, 203.
[18] Lee, S. G., Koo, B. K., Gal, Y. S., & Kwak, Y. W. (2009). *Mol. Cryst. & Liq. Cryst.*, *498*, 222.
[19] Gal, Y. S., Jin, S. H., Park, J. W., Lee, W. C., Lee, H. S., & Kim, S. Y. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 4101.
[20] Gal, Y. S., Jin, S. H., Lee, H. S., & Kim, S. Y. (2005). *Macromol. Res.*, *13*, 491.
[21] Russo, M. V., Iucci, G., Polzonetti, G., & Furlani, A. (1992). *Polymer*, *33*, 4401.
[22] Saeed, I., Shiotsuki, M., & Masuda, T. (2006). *Macromolecules*, *39*, 5347.