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Synthesis and Properties of an Ionic Polyacetylene with 3rd Generation Dendritic Moieties

Yeong-Soon Gal [a], Myeong-Ran Kim [a], Kwon-Taek Lim [b], Won-Chul Lee [a], Won Seok Lyoo [c], Young Il Park [d], Jong-Wook Park [d], Seung Choul Han [e], Jae Wook Lee [e] & Sung-Ho Jin [f]

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

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

[c] School of Textiles, Yeungnam University, Gyeongsan, Korea

[d] Department of Chemistry, Center for Nanotech. Res., The Catholic University, Bucheon, Korea

[e] Department of Chemistry, Dong-A University, Busan, Korea

[f] Department of Chemistry Education, Pusan National University, Busan, Korea

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Synthesis and Properties of an Ionic Polyacetylene with 3rd Generation Dendritic Moieties

YEONG-SOON GAL,[1] MYEONG-RAN KIM,[1]
KWON-TAEK LIM,[2] WON-CHUL LEE,[1]
WON SEOK LYOO,[3] YOUNG IL PARK,[4]
JONG-WOOK PARK,[4] SEUNG CHOUL HAN,[5]
JAE WOOK LEE,[5] AND SUNG-HO JIN[6]

[1]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan, Gyeongsangbuk-Do, Korea
[2]Division of Image and Information Engineering, Pukyong National University, Busan, Korea
[3]School of Textiles, Yeungnam University, Gyeongsan, Korea
[4]Department of Chemistry, Center for Nanotech. Res., The Catholic University, Bucheon, Korea
[5]Department of Chemistry, Dong-A University, Busan, Korea
[6]Department of Chemistry Education, Pusan National University, Busan, Korea

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A new ionic conjugated polyacetylene with 3rd generation dendritic benzyl moieties was easily prepared by the activated polymerization of 2-ethynylpyridine by using 3rd generation dendritic benzyl bromide. The chemical structure of polymer was characterized by various instrumental methods to have the ionic conjugated polymer system bearing 3rd generation dendritic benzyl moieties. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 516 nm, corresponding to a photon energy of 2.41 eV. The cyclovoltamograms of this polymer exhibited reversible electrochemical behaviors between the doping and undoping peaks. The kinetics of the redox process of this polymer was found that it is almost controlled by the diffusion process from the experiment of the oxidation current density of polymer versus the scan rate.

Keywords 2-Ethynylpyridine; conjugated polymer; cyclic voltammogram; dendritic benzyl bromide; photoluminescence; polyacetylene

Introduction

Considerable progress has been made in the synthesis and chacterization of conjugated polymers such as polyacetylene, poly(p-phenylenevinylene)s, polythiophenes, polypyrroles, and poly(9,9-dialkylfluorene)s [1–3].

Address correspondence to Yeong-Soon Gal, Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Hayang 712-701, Gyeongsangbuk-Do, Korea. Tel.: (+82)53-850-7115; Fax: (+82)53-850-7628; E-mail: ysgal@kiu.ac.kr

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The polymers having a conjugated backbone show such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [4–6]. Promising materials for electronic devices and molecular electronics can be obtained by the introduction of π-conjugated systems [7]. Acetylenic triple bonds can be a good candidate to introduce π-conjugated systems due to rich pi-electrons and yield the linear conjugate polymer systems [4–6,8–10]

The polyacetylene-based electrolytes such as poly(propiolic salt)s, triethylammonium salt of poly(6-bromo-1-hexyne), and poly(dipropargylammonium salt)s had been reported [5]. In 1991, new class of ionic polyacetylenes has been prepared through the activated polymerization of ethynylpyridines with alkyl halides [11,12]. The presence of a substituted but conjugated backbone combined with the proximity of charge endows such structures practical potential. The electrostatic repulsion between segments favors backbones with extended conformations and hence conjugation lengths are substantially higher than those of some noncharged polyacetylene derivatives [13]. The stability of the electric response, owing to strong dopant binding (ionic bond), is a feature especially useful in energy storage devices [13,14].

In recent years, we have also prepared various ionic conjugated polymers having different functionalities from the activation polymerization of ethynylpyridines by

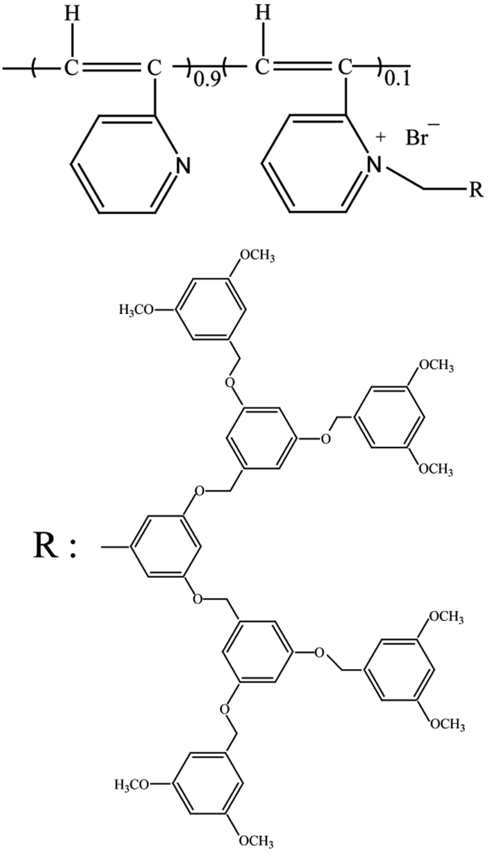

Figure 1. Proposed chemical structure of PEPB-DBM.

using functional alkyl halides [15–17]. Because these conjugated polymers contain extensive conjugation and ionic nature, this ionic polyacetylene family has potentials as material candidates for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices [11,14,18,19].

Dendrimers are highly branched, tree-like macromolecules, which are prepared by repetition of a given set of reactions using either divergent or convergent strategies. Dendrimers are currently attracting the interest of many scientists because of their unique chemical and physical properties and the wide range of potential applications [20,21].

Here, we report the synthesis of a new ionic polyacetylene derivative with 3rd generation dendritic moieties (Fig. 1) via the activated polymerization of 2-ethynylpyridine by using the 3rd generation dendritic benzyl bromide and the characterization of the resulting polymer.

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Experimental

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [22] and vacuum distilled after drying with CaH_2 (85°C/12 mmHg). The 3rd generation dendritic benzyl bromide was preapred according to the reported procedure [23,24]. The analytical grade solvents were dried with an appropriate drying agent and distilled.

An ionic conjugated polymer, poly(2-ethynylpyridinium bromide) with 3rd generation dendritic benzyl moieties (PEPB-DBM), was synthesized by the activated polymerization of 2-ethynylpyridine by using 3rd generation dendritic benzyl bromide. A typical polymerization procedure is as follows. In a 25 mL two-neck flask equipped with rubber septum and purified nitrogen inlet-oulet, 7.0 mL of DMF, 2-ethynylpyridine (0.79 g, 7.7 mmol), and 3rd generation dendritic benzyl bromide (0.80 g, 0.076 mmol, mole ratio of dendritic benzyl bromide to 2-ethynylpyridine 1:10) were added into the reaction flask. Then the reaction solution was warmed to 60°C under nitrogen atmosphere and stirring was continued at this temperature for 24 h. During this time the color of reaction mixture changed from the light brown of the initial mixture into dark brown. After the polymerization time, the resulting polymer solution diluted with additional DMF was precipitated into an excess amount of ethyl ether, followed by filtration. The collected powder was dried under vacuum overnight at 40°C to afford PEPB-DBM (1.28 g) as brown powder.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR (^1H- and ^{13}C) spectra were obtained in DMSO-d_6 solutions at room temperature using a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) and the chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. 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 Potentionstat/Galvanostat Model 273A(Princeton Applied Research). To examine electrochemical properties, the 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.

Results and Discussion

In order to synthesize an ionic conjugated polymer with 3rd generation dendritic benzyl moieties, we used the activation polymerization method of Blumstein, which is a very facile synthetic method of conjugated ionic polymer by using ethynylpyridines and alkyl halides [11–13]. The activated acetylenic groups of N-substituted-2-ethynylpyridinium salt were found to be susceptible to the linear polymerization, yielding the ionic conjugated polymer systems [12]. In general, this polymerization proceeded well without any additional initiator or catalyst.

The polymerization of 2-ethynylpyridine by using 3rd generation dendritic benzyl bromide was carried out in heated oil bath. This polymerization proceeded well at even relatively low temperature of 60°C. As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into viscous dark brown solution. The viscosity of reaction solution was also increased. After the precipitation and drying, the brown polymer powder was obtained. The inherent viscosity of PEPB-DBM was 0.15 dL/g. The polymerization behaviors were found to be very similar with those of the polymerization reaction of 2-ethynylpyridine by using simple alkyl halides such as methyl iodide, propargyl bromide, and 6-azidohexyl iodide [25–27].

The chemical structure of PEPB-DBM was characterized by infrared, NMR, and UV-visible spectroscopies. The polymer obtained by the present quaternarization method was brown in appearance, indicative of the conjugated structures. FT-IR spectra of 2-ethynylpyridine, 3rd generation dendritic benzyl bromide, and PEPB-DBM were measured in KBr pellets. FT-IR spectrum of PEPB-DBM did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) nor acetylenic ≡C-H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1594–1620 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine and 3rd generation dendritic benzyl bromide.

The ^{1}H-NMR spectrum of PEPB-DBM showed the aromatic protons of pyridyl and phenyl moieties and the vinyl proton of the conjugated polymer backbone are observed broadly at 5.6–10.0 ppm. The methoxy protons of 3rd generation dendritic benzyl moieties were seen at 3.2–5.3 ppm, whereas the methylene proton peaks were seen at 0.9–2.3 ppm. The ^{13}C-NMR spectrum of PEPB-DBM showed the aromatic carbon peaks of pyridyl and phenyl moieties and the vinyl carbons of conjugated polymer backbone showed at the range of 100–152 ppm. The carbon peaks of methoxy and methylene moieties were also observed at 52–70 ppm. In the UV-visible spectrum of PEPB-DBM, the absorption spectrum starts around 700 nm and shows a strong absorption band at visible region due to the $\pi \rightarrow \pi^*$ interband transition of the polymer backbone, which is a characteristic peak of the conjugated polyene backbone system.

The electro-optical and electrochemical properties of PEPB-DBM were studied by UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 2 shows the UV-visible and photoluminescence spectra of PEPB-DBM solution (0.1 wt.%, DMF). The absorption spectrum exhibits absorption

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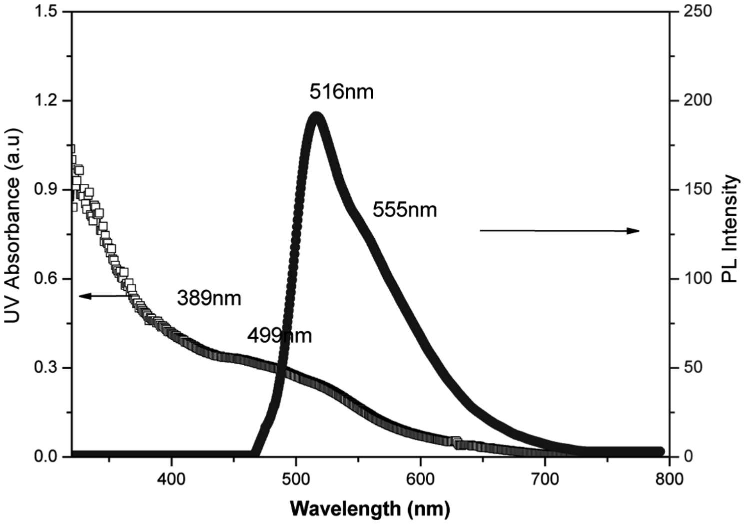
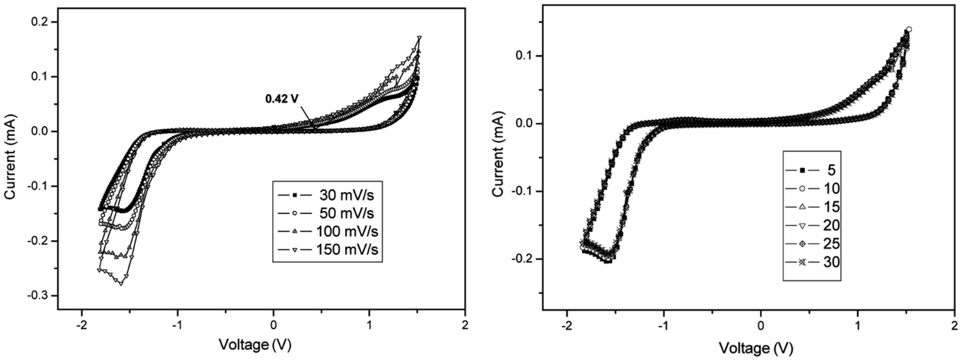


Figure 2. Optical absorption spectrum of PEPB-DBM (0.1 wt.% DMF solution).

maximum value of about 499 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of these conjugated polymer systems. The photoluminescence spectra of this ionic conjugated polymer showed that the photoluminescence peak is located at 516 nm corresponding to the photon energy of 2.41 eV. In our previous paper, we reported the optical properties of poly(2-ethynyl-N-hexylpyridinium bromide) (PEHPB) which has hexyl side group instead of simple pyridine and bulky dendritic groups [28]. PEHPB had UV and PL maximum values of 515 nm and 611 nm. Comparing the maximum wavelength values of UV and PL data, there is blue shift effect in both of UV and PL spectra. It means that the 3rd generation generation dendritic moieties formed the bulky size effect between polymer chains and caused the distorted oriention of polymer main chain.

As shown in Figure 3, we investigated the electrochemical kinetic behavior through the cyclic voltammograms of PEPB-DBM solution with various scan rates



(a) (b)

Figure 3. Cyclic voltammograms of PEPB-DBM [0.1 M (n-Bu)$_4$NBF$_4$/DMF] with various scan rates 30 mV/sec~150 mV/sec (a) and consecutive 30 scans under 100 mV/s (b).

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(30 mV/s~150 mV/s). As the scan rate was increased, the oxidation and reduction potentials were slightly shifted to higher potentials because of higher speed of scan rate. In addition, we have observed stable cyclic voltammograms of PEPB-DBM from the consecutive scan (up to 30 cycles), which means that this material has a stable redox process in tetrabutylammonium tetrafluoroborate/DMF electrolyte solution. In Figure 3, the oxidation of PEPB-DBM occurred at 0.42 V (*vs* Ag/AgNO$_3$), where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan. PEPB-DBM also shows irreversible reduction at -1.20 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of PEPB-DBM is reproducible in the potential range of -1.9~1.5 V *vs* Ag/AgNO$_3$.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [29,30].

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

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

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

On 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. 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 PEPB-DBM *versus* the scan rate is an approximately linear relationship in the range of 30 mV/sec ~ 150 mV/sec. The exponent of the scan rate, the x value of PEPB-DBM, is found to be 0.2145. This value means that the kinetics of the redox process is not so active and is closer to a diffusion process, rather than an electron transfer process [31].

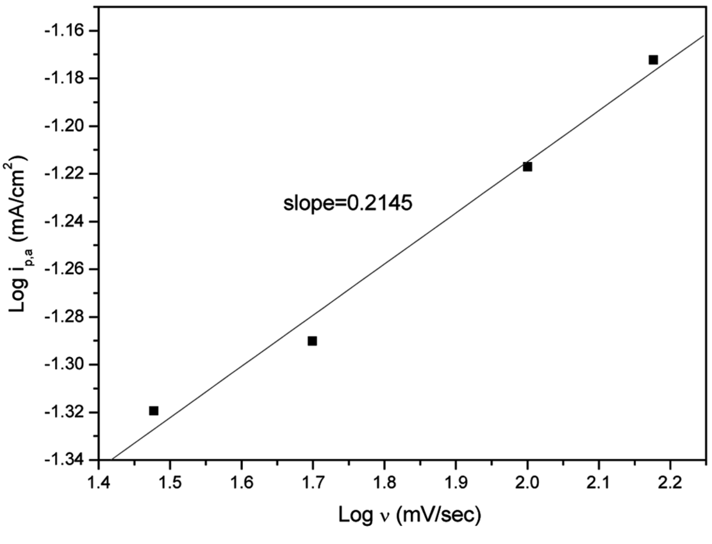

Figure 4. Plot of $\log i_{\mathrm{p,a}}$ *vs* $\log v$ for PEPB-DBM.

Conclusions

A new ionic conjugated polymer with 3rd generation dendritic benzyl moieties was easily prepared by the activated polymerization of 2-ethynylpyridine by using 3rd generation dendritic benzyl bromide. The instrumental analysis data indicated that PEPB-DBM has an ionic conjugated polymer system bearing 3rd generation dendritic moieties. This polymer was completely soluble in such organic solvents as DMF, DMSO, and NMP. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 516 nm, corresponding to a photon energy of 2.41 eV. The cyclic voltammograms of PEPB-DBM exhibited irreversible electrochemical behavior between the oxidation and reduction peaks. The peak potentials were slightly shifted to higher potentials as the scan rate was increased. The kinetics of the redox process of polymer were close to a diffusion process from the experiment plotting the oxidation current density of PEPB-DBM *versus* the scan rate.

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References

[1] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). *Nature*, *347*, 539.
[2] Cho, H. N., Kim, D. Y., Kim, Y. C., Lee, J. Y., & Kim, C. Y. (1997). *Adv. Mater.*, *9*, 326.
[3] Jin, S. H., Jang, M. S., Suh, H. S., Cho, H. N., Lee, J. H., & Gal, Y. S. (2002). *Chem. Mater.*, *14*, 643.
[4] Masuda, T. & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[5] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[6] Lam, J. W. Y. & Tang, B. Z. (2005). *Acc. Chem. Res.*, *38*, 745.
[7] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). *Chem. Rev.*, *109*, 897.
[8] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.
[9] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[10] Koz, B., Kiskan, B., & Yagci, Y. (2008). *Int. J. Mol. Sci.*, *9*, 383.
[11] Subramanyam, S. & Blumstein, A. (1991). *Makromol. Chem., Rapid. Commun.*, *12*, 23.
[12] Subramanyam, S. & Blumstein, A. (1991). *Macromolecules*, *24*, 2668.
[13] Blumstein, A. & Samuelson, L. (1998). *Adv. Mater.*, *10*, 173.
[14] Freund, M. S. & Deore, B. (2007). *Self-Doped Conducting Polymers*, Wiley: England.
[15] Gal, Y. S. & Jin, S. H. (2004). *Bull. Korean Chem. Soc.*, *25*, 777.
[16] 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.
[17] Gal, Y. S., Jin, S. H., & Park, J. W. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 5679.
[18] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2009). *J. Polym. Sci.: Part A: Polym. Chem.*, *47*, 6153.
[19] Subramanyam, S. & Blumstein, A. (1992). *Macromolecules*, *25*, 4058.

[20] Lee, J. W., Kim, B. K., & Jin, S. H. (2005). *Bull. Korean Chem. Soc.*, *26*, 715.

[21] Lee, J. W., Kim, B. K., & Jin, S. H. (2005). *Bull. Korean Chem. Soc.*, *26*, 833.

[22] Gal, Y. S., Cho, H. N., Kwon, S. K., & Choi, S. K. (1988). *Polymer (Korea)*, *12*, 30.

[23] Hawker, C. J. & Frechet, J. M. (1990). *J. Am. Chem. Soc.*, *112*, 7638.

[24] Nantalsksakul, A., Dasari, R. R., Ahn, T. S., Al-Kaysi, R., Bardeen, C. J., & Thayumanavan, S. (2006). *Org. Lett.*, *8*, 2981.

[25] Gal, Y. S., Lee, W. C., & Choi, S. K. (1997). *Bull. Korean Chem. Soc.*, *18*, 265.

[26] Gal, Y. S., Jin, S. H., Lim, K. T., Kim, S. H., & Koh, K. (2005). *Curr. Appl. Phys.*, *5*, 38.

[27] Gal, Y. S., Jin, S. H., Karim, M. A., & Cho, Y. R. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 165.

[28] Gui, T. L., Jin, S. H., Lee, W. C., Park, J. W., Koh, K., Kim, S. H., Lee, S. S., Bae, J. S., Kim, S. Y., & Gal, Y. S. (2005). *Curr. Appl. Phys.*, *5*, 23.

[29] Park, J. W., Lee, J. H., Ko, J. M., Cho, H. N., Choi, S. K. (1994). *J. Polym. Sci.: Part A: Polym. Chem.*, *32*, 2789.

[30] Bard, A. J. & Faulker, L. R. (1980). *Electrochemical Methods*, Wiley: New York, chapter 3, 6 and 10.

[31] Ko, J. M., Rhee, H. W., Park, S. M., & Kim, C. Y. (1990). *J. Electrochem. Soc.*, *137*, 905.

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