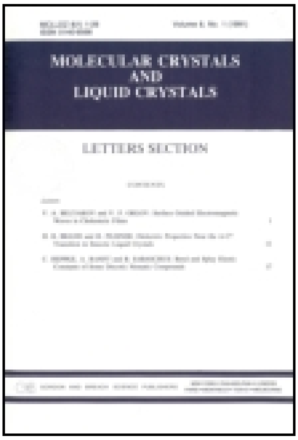

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Synthesis and Characterization of Poly(2-ethynyl-N-perfluorobenzoylpyridinium chloride)

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A new ionic conjugated polymer with pentafluorobenzoyl moieties, poly(2-ethynyl-N-pentafluorobenzoylpyridinium chloride) [PEPBPC], was synthesized via the non-catalyst polymerization of 2-ethynylpyridine using pentafluorobenzoyl chloride. The polymerization proceeded well to provide a high yield of polymer. The chemical structure of PEPBPC was characterized by such instrumental methods as NMR (^1H- and ^{13}C-), IR, and UV-visible spectroscopies to have a conjugated polymer backbone system with N-pentafluorobenzoylpyridinium chloride as substituents. Photoluminescence maximum peak of PEPBPC was located at 627 nm, which corresponds to the photon energy of 1.98 eV. Cyclic voltammograms of polymer exhibited the electrochemically stable window in the range of −1.25 to 1.75V.

Keywords 2-ethynylpyridine; pentafluorobenzoyl chloride; polyacetylene; photoluminescence; cyclic voltammogram.

Introduction

Enormous progresses in organic semiconductors and the knowledge of their corresponding physical and chemical properties have been made [1–5]. The organic semiconductors having a conjugated backbone system shows such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex

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formation ability [6–11]. Applications of organic semiconductors include organic light-emitting diodes (OLEDs) [1,12], photovoltaic cells [13–15], nonvolatile memory devices [16,17], radiofrequency identification (RF-ID) tags [18], and organic thin film transistors (OTFTs) for integration into low-cost, large-area electronics [19, 20].

A facile method for the introduction of π-conjugated systems in organic polymers is by using the polymerization methods of acetylenic monomers with rich π-electrons [6–10]. Polyacetylene (PA), the simplest conjugated polymer, consists of a backbone of carbon atoms, each bonded to one hydrogen atom and connected together by alternating single and double bonds [3,10]. Unfortunately, PA itself is notoriously intractable (insoluble and infusible) and extremely sensitive to air, which has greatly detracted from its potential for real-world technological applications.

Over the past four decades, considerable effort has been devoted to the synthesis of the substituted polyacetylenes and poly(1,6-heptadiyne)s, and their properties were extensively studied [6–11, 21–25]. Unlike PA, substituted PAs 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 [20, 26–31].

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. 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 [6]. A new class of ionic polyacetylenes have been prepared through the activated polymerization of ethynylpyridines with halogens, $FeCl_3$, and alkyl halides [32–34]. This method do not use any additional initiator or catalyst, thereby originally eliminating the contamination of samples by catalyst residues.

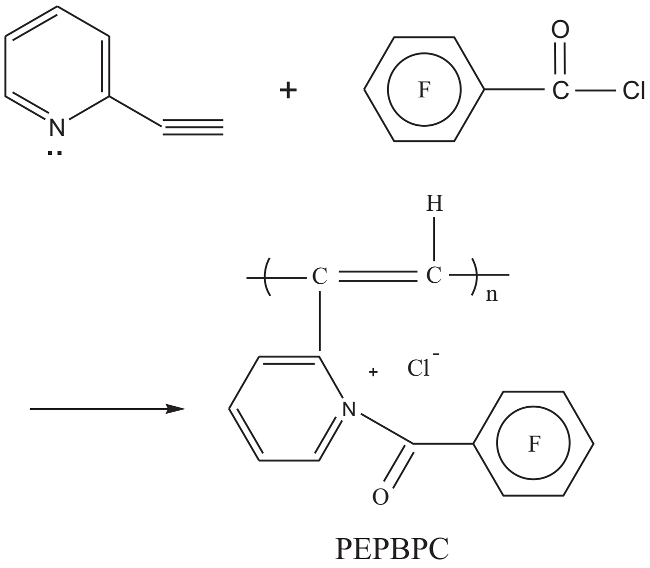
We have also prepared various ionic conjugated polymers with different functionalities from the linear polymerization of acetylenic salt monomers using transition metal catalysts [35,36] and the uncatalyzed polymerization of ethynylpyridines using functional alkyl halides and carbonyl chlorides [37–43]. Because these conjugated polymers contain extensive conjugation and ionic nature, this ionic PA family has potentials as an active candidate materials for the fabrication of intercalated nanocomposite films [44], silver-polymer nanocomposites [45], fluorescence quencher for fluorescent biotin-functionalized Lucifer Yellow dyes [46], hybrid polymer gels [47], and nanocrystalline CdS polymer sensitizer [48].

In this article, we report the synthesis of a new ionic conjugated polymer via the uncatalyzed polymerization of 2-ethynylpyridine using pentafluorobenzoyl chloride (Scheme 1) and the characterization of polymer properties.

Experimental

Pentafluorobenzoyl chloride (Aldrich Chemicals, 99%) was used as received. 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 analytical grade solvents were dried with an appropriate drying agent and distilled.

PEPBPC, an ionic conjugated polymer with pentafluorobenzoyl groups, was synthesized by the activated polymerization of 2-ethynylpyridine by using pentafluorobenzoyl chloride. A typical polymerization procedure is as follows. In a 100 mL two-neck



Scheme 1. Synthesis of PEPBPC.

flask equipped with rubber septum and purified nitrogen inlet-oulet, 25 mL of DMF, 2-ethynylpyridine (2.0 g, 19.40 mmol), and pentafluorobenzoyl chloride (4.47 g, 19.40 mmol) were added into the reaction flask. Then the reaction solution was warmed to 80°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 black. 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 for 24 h to afford PEPBPC in 75% yield.

NMR (^{1}H-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. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 2200 thermogravimetric analyzer. X-ray diffractograms were obtained with PHILIPS X-ray diffractometer (Model: X' Pert-APD). 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). 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

The activated ethynyl groups of N-substituted-2-ethynylpyridinium salt were known to be susceptible to the linear polymerization without any additional initiator or catalyst, yielding the ionic conjugated polymer systems in high yield [32–34]. Here, we used this uncatalyzed polymerization method for the synthesis of a new ionic conjugated polymer with perfluorobenzoyl moieties. The reaction solution of 2-ethynylpyridine and pentafluorobenzoyl chloride was exposed in heated oil bath (80°C). As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into black solution. And the viscosity of reaction solution was also increased. This polymerization proceeded well to give relatively high yield of polymer (75%). In our previous work [43], we performed similar polymerization of 2-ethynylpyridine by using benzoyl chloride. The yield (89%) for the polymerization of 2-ethynylpyridine by using benzoyl chloride was found to be higher than that for the present polymerization of 2-ethynylpyridine using pentafluorobenzoyl chloride (75%).

The molecular structure of PEPBPC was characterized by such various instrumental methods as infrared, NMR, and UV-visible spectroscopies. FT-IR spectra of 2-ethynylpyridine, pentafluorobenzoyl chloride, and PEPBPC were measured and compared. FT-IR spectrum of PEPBPC did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C—H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the C═C stretching frequency peak of conjugated polymer backbone around 1617 cm^{-1} became relatively more intense than those of the C═C and C═N stretching frequencies of 2-ethynylpyridine itself. The aromatic ═C—H stretching frequency of pyridyl substituents and the carbonyl C═O stretching frequency were observed at 3040 cm^{-1} and 1758 cm^{-1}, respectively. The strong peak at 992 cm^{-1} is due to the ring breathing of pyridine moieties.

Figure 1 shows the ^{1}H- and ^{13}C-NMR spectra of PEPBPC in DMSO-d_6. The ^{1}H-NMR spectrum of PEPBPC shows aromatic protons of pyridyl moieties and the vinyl proton of the conjugated polymer backbone broadly at 5.5–10.8 ppm. The ^{13}C-NMR spectrum of PEPBPC spectrum showed the aromatic carbon peaks of pyridyl moieties and the vinyl carbons of conjugated polymer backbone showed at the range of 104–154 ppm. UV-visible absorption spectrum of PEPBPC showed a characteristic absorption band in the visible region (up to 700 nm), which is a strong evidence of the presence of conjugated polyene backbone system. TGA thermogram of PEPBPC shows that this polymer retains 99% of its original weight at 100°C, 90% at 200°C, 78% at 300°C, 69% at 400°C, 63% at 500°C, 58% at 600°C, and 52% at 700°C. The residual weights of present PEPBPC having perfluorobenzoyl groups were found to be much more than those of poly(N-benzoyl-2-ethynylpyridinium chloride) in overall temperature ranges. This polymer was completely soluble in water and such organic solvents as DMF, DMSO, and NMP and the inherent viscosity of PEPBPC was 0.13 dL/g. The X-ray diffractogram of PEPBPC powder was measured (Figure 2). The peak in 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, indicating that the present polymer is amorphous [6, 41].

The electro-optical and electrochemical properties of PEPBPC were investigated by using UV-visible absorption and photoluminescence spectroscopies and cyclic voltammograms (CV). Figure 3 shows UV-visible absorption and photoluminescence spectra of PEPBPC solution (1×10^{-4} M, DMF). Absorption spectrum exhibits absorption maximum values of 333 and 580 nm, and the absorption peaks at the visible region comes from $\pi \rightarrow$

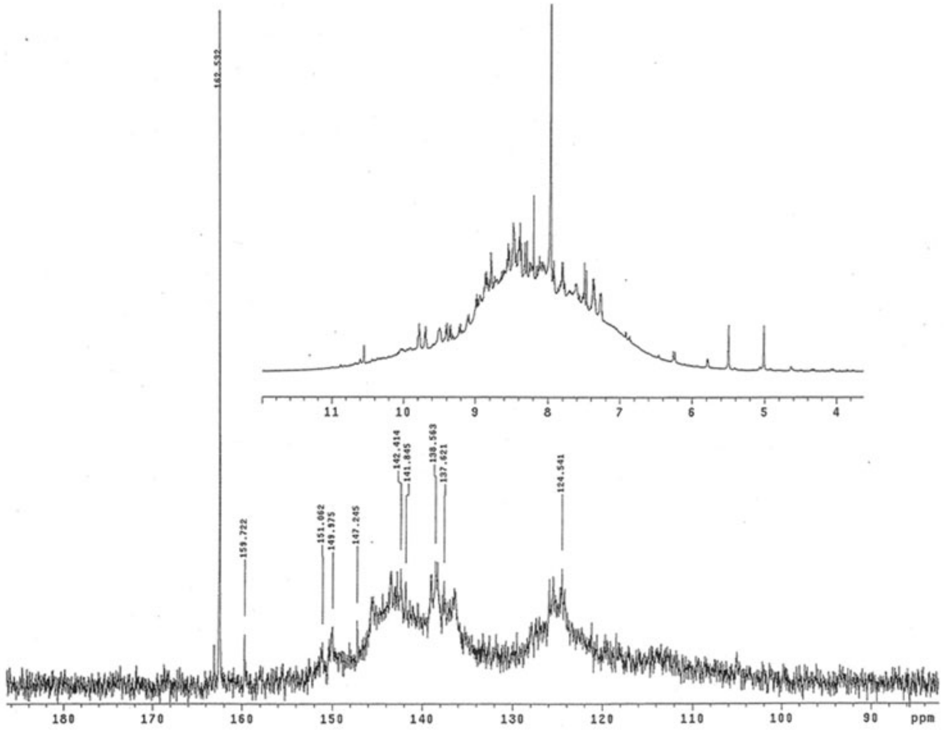


Figure 1. ^{1}H- and ^{13}C-NMR spectra of PEPBPC in DMSO-d$_6$.

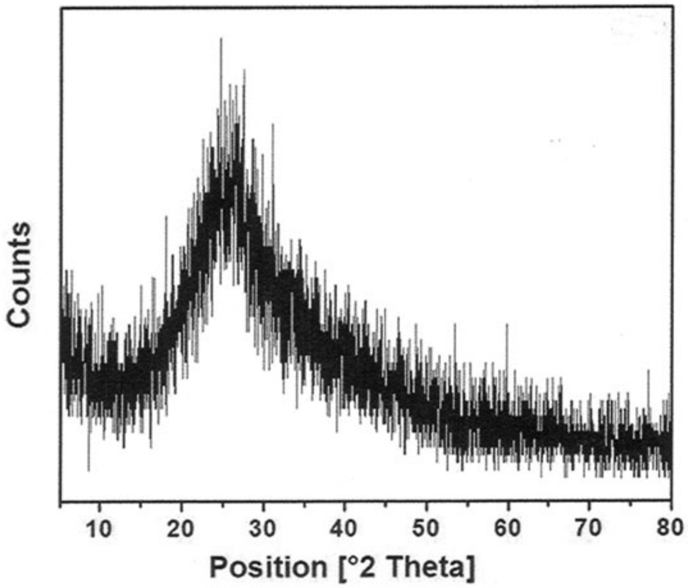


Figure 2. X-ray diffractogram of PEPBPC powder.

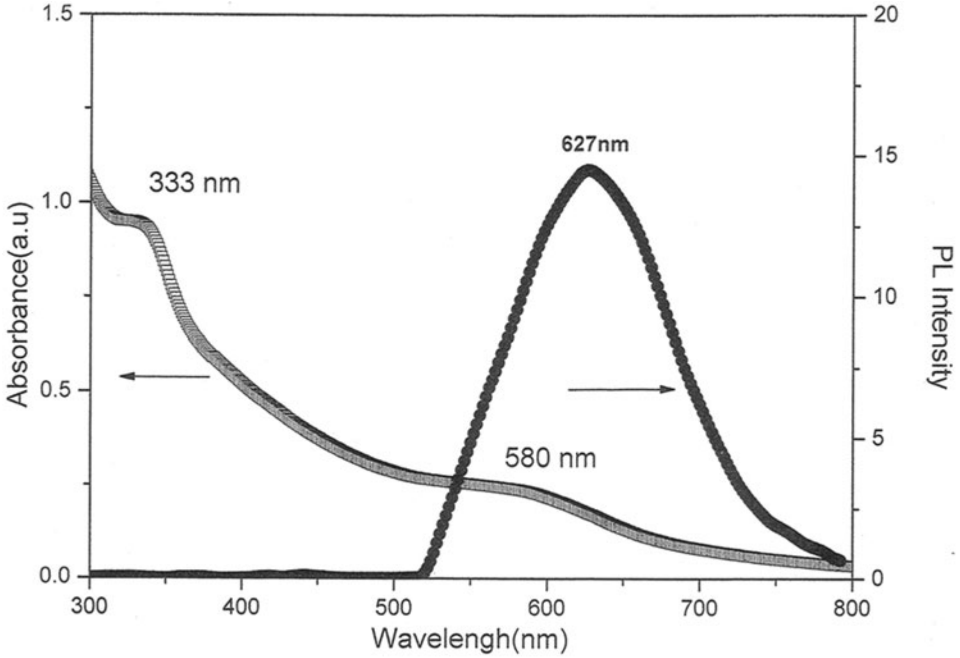


Figure 3. Optical absorption and photoluminescence spectra of PEPBPC (1×10^{-4} M, DMF solution).

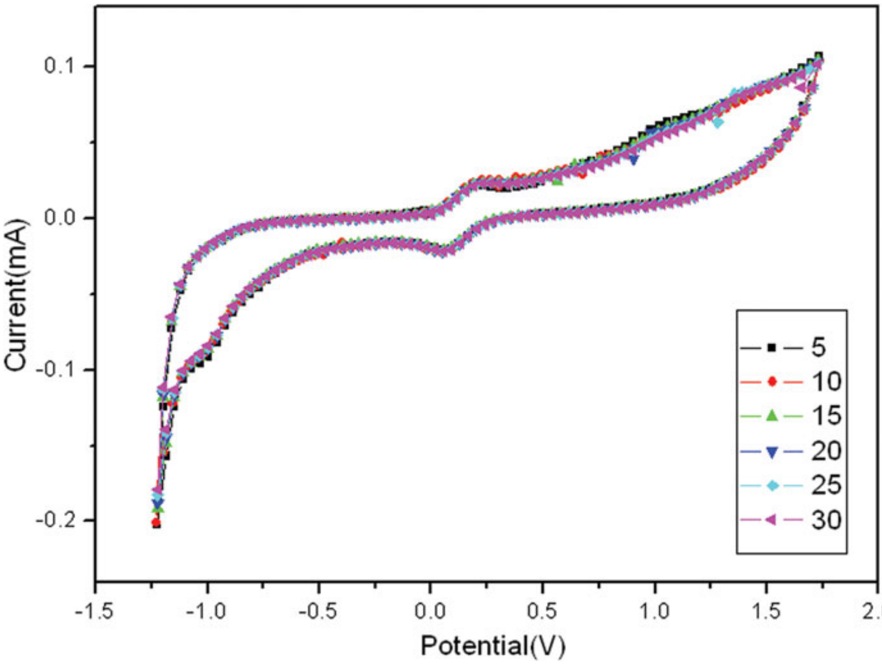


Figure 4. Cyclic voltammograms of PEPBPC with consecutive scans up to 30 cycles: 3.8×10^{-4} M in acetonitrile, 0.1M TBAP electrolyte.

π^* interband transition of PEPBPC. In our previous study, the optical properties of poly(N-benzoyl-2-ethynylpyridinium chloride) (PBEPC) which has similar chemical structure except fluorine atoms of phenyl ring were reported [43]. Poly(N-benzoyl-2-ethynylpyridinium chloride) showed same UV-visible absorption maximum value of 333 nm, but there was weak absorption of 525 nm which is relatively shorter than that of the present PEPBPC. Comparing the maximum wavelength values of absorption data, it is explained by that PEPBPC has longer conjugation length. In the case of photoluminescence (PL) spectrum, PEPBPC showed PL maximum value of 627 nm corresponding to the photon energy of 1.98 eV.

The electrochemical property through the cyclic voltammograms of PEPBPC solution with consecutive scans up to 30 cycles was also investigated (Figure 4). It was observed that PEPBPC had two oxidation and reduction peaks in the range of −1.25 to 1.75V. Especially, the first oxidation and reduction of PEPBPC started to occur at 0.006 and −0.59V (*vs* Ag/AgNO$_3$), where the vinylene or pyridine unit of the conjugated polymer could be oxidized and reduced. Furthermore, stable cyclic voltammograms of PEPBPC from the consecutive scans up to 30 cycles were observed, which means that this material has a stable redox process in tetrabutylammonium perchlorate/DMF electrolyte solution. This result suggests that the electrochemical process of PEPBPC is reproducible in the potential range of $-1.25 \sim 1.75$ V *vs* Ag/AgNO$_3$.

Conclusions

A new ionic conjugated polymer with pentafluorobenzoyl functional groups was easily prepared by the uncatalyzed polymerization of 2-ethynylpyridine using pentafluorobenzoyl chloride. The polymerization proceeded well even at mild reaction condition to give relatively high yield of polymer. The instrumental analysis data revealed that PEPBPC has an ionic conjugated polymer system bearing the pyridyl substituents with N-perfluorobenzoyl moieties. This polymer was completely soluble in water and such organic solvents as DMF, DMSO, and NMP. PEPBPC showed absorption maximum values of 333 and 580 nm, and 580 nm value comes from $\pi \rightarrow \pi^*$ interband transition of PEPBPC. The first oxidation and reduction of PEPBPC started to occur at 0.006 and −0.59V (*vs* Ag/AgNO$_3$). PEPBPC had a stable redox process up to 30 scan cycles in the potential range of $-1.25 \sim 1.75$ V *vs* Ag/AgNO$_3$. Due to its good solubility and electrical properties, this conjugated polymer was expected to have potentials for organic semiconductor devices such as OTFTs, OLEDs, and photovoltaic cells.

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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] Lee, S. J., Park, J. S., Yoon, K. J., Kim, Y. I., Jin, S. H., Kang, S. K., Gal, Y. S., Kang, S., Lee, J. Y., Kang, J. W., Lee, S. H., Park, H. D., & Kim, J. J. (2008). *Adv. Funct. Mater.*, *18*, 3922.

[3] Park, Y. W. (2010). *Chem. Soc. Rev.*, *39*, 2428.

[4] Lee, J., Hong, K. S., Shin, K., & Jho, J. Y. (2012). *J. Ind. Eng. Chem.*, *18*, 19.

[5] Gal, Y. S., Jin, S. H., Park, J. W., Kim, S. H., Lyoo, W. S., & Lim, K. T. (2012). *J. Ind. Eng. Chem.*, *18*, 55.

[6] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.

[7] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.

[8] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.

[9] Liu, J., Lam, J. W. Y., & Tang, B. Z. (2009). *Chem. Rev.*, *109*, 5799.

[10] Goh, M., Matsushita, S., & Akagi, K. (2010). *Chem. Soc. Rev.*, *39*, 2466.

[11] Choi, H. K., Jin, S. H., Park, J. W., Lim, K. T., & Gal, Y. S. (2012). *Mol. Cryst. & Liq. Cryst.*, *563*, 153.

[12] Jin, S. H., Kim, M. Y., Kim, J. Y., Lee, K., & Gal, Y. S. (2004). *J. Am. Chem. Soc.*, *126*, 2474.

[13] Yoon, M., Yoon, H. W., Kim, A. J., Ree, R. S., Gal, Y. S., Lee, J. W., Lee, J. H., & Jin, S. H. (2011). *Mol. Cryst. & Liq. Cryst.*, *550*, 304.

[14] Song, M., Park, J. S., Kim, Y. H., Karim, Md. A., Jin, S. H., Ree, R. S., Cho, Y. R., Gal, Y. S., & Lee, J. W. (2011). *Macromol. Res.*, *19*, 654 2011.

[15] Kim, D. Y., Kim, J., Kim, A. Y., Lee, G., & Kang, M. (2012). *J. Ind. Eng. Chem.*, *18*, 1.

[16] Lee, T. J., Park, S., Hahm, S. G., Kim, D. M., Kim, K., Kim, J., Kwon, W., Kim, Y., Chang, T., & Ree, M. (2009). *J. Phys. Chem. C*, *113*, 3855.

[17] Ko, Y. G., Kwon, W., Kim, D. M., Kim, K., Gal, Y. S., & Ree, M. (2012). *Polym. Chem.*, *3*, 2028.

[18] Crone, B., Dodabalapur, A., Lin, Y. Y., Filas, R. W., Bao, Z., LaDuca, A., Sarpeshkar, R., Katz, H. E., & Li, W. (2000). *Nature*, *403*, 521.

[19] Horowitz, G. (1998). *Adv. Mater.*, *10*, 365.

[20] Murphy, A. R., & Frechet, J. M. J. (2007). *Chem. Rev.*, *107*, 1066.

[21] Gal, Y. S., & Choi, S. K. (1987). *Polymer (Korea)*, *11*, 563.

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

[23] Gal, Y. S., & Choi, S. K. (1993). *J. Appl. Polym. Sci.*, *50*, 601.

[24] 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.

[25] Gal, Y. S., Jin, S. H., Lim, K. T., & Park, J. W. (2011). *J. Appl. Polym. Sci.*, *122*, 987.

[26] Samuel, D. W., Ledoux, I., Dhenaut, C., Zyss, J., Fox, H. H., Schrock, H. H., & Silbey, R. J. (1994). *Science.*, *265*, 1070.

[27] Halvorson, C., Hays, A., Kraabel, B., Wu, R., Wudl, F., & Heeger, A. J. (1994). *Science.*, *265*, 1215.

[28] Potje-Kamloth, K. (2008). *Chem. Rev.*, *108*, 367.

[29] Hatchett, D. W., & Josowicz, M. (2008). *Chem. Rev.*, *108*, 746.

[30] Kwak, G., Lee, W. E., Jeong, H., Sakaguchi, T., & Fujiki, M. (2009). *Macromolecules.*, *42*, 20.

[31] Kang, E. H., Lee, I. S., & Choi, T. L. (2011). *J. Am. Chem. Soc.*, *133*, 11904.

[32] Simionescu, C. I., Dumitrescu, S., Percec, V., & Diaconu, I. (1978). *Materiale Plastice*, *15*, 69.

[33] Subramanyam, S. & Blumstein, A. (1991). *Makromol. Chem., Rapid. Commun.*, *12*, 23.

[34] Subramanyam, S. & Blumstein, A. (1991). *Macromolecules.*, *24*, 2668.

[35] Gal, Y. S. (1994). *J. Chem. Soc., Chem. Commun.*, 327.

[36] Gal, Y. S., Jung, B., Lee, W. C., & Choi, S. K. (1994). *Bull. Korean Chem. Soc.*, *15*, 268.

[37] Gal, Y. S., Lee, W. C., & Choi, S. K. (1995). *Bull. Korean Chem. Soc.*, *18*, 265.

[38] Gal, Y. S. & Jin, S. H. (2004). *Bull. Korean Chem. Soc.*, *25*, 777.

[39] 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.

[40] Gal, Y. S., Jin, S. H., & Park, J. W. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 5679.

[41] Gal, Y. S., Jin, S. H., Park, J. W., & K. T. Lim (2009). *J. Polym. Sci.: Part A: Polym. Chem.*, *47*, 6153.

[42] Gal, Y. S., Jin, S. H., Park, Y. I., Park, J. W., Lyoo, W. S., & Lim, K. T. (2011). *Syn. Met.*, *161*, 445.

[43] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2011). *J. Ind. Eng. Chem.*, *17*, 282.

[44] Liu, H., Kim, D. W., Blumstein, A., Kumar, J., & Tripathy, S. K. (2001). *Chem. Mater.*, *13*, 2756.

[45] Mao, Y., Xu, H. P., Yuan, W. Z., Qin, A., Yu, Y., Faisal, M., Xiao A, Z., Sun, J. Z., & Tang, B. Z. (2011). *J. Mater. Chem.*, *21*, 13627.

[46] Song, X., Wang, H. I., Shi, J., Park, J. W., & Swanson, B. I. (2002). *Chem. Mater.*, *14*, 2342

[47] Kim, K. M., Lim, J. H., Jang, N. Y., & Kim, S. R. (2007). *Macromol. Symp.*, *249–250*, 562.

[48] Lee, W., Mane, R. S., Min, S. K., Yoon, T. H., Han, S. H., & Lee, S. H. (2007). *Appl. Phys. Lett.*, *90*, 263503.