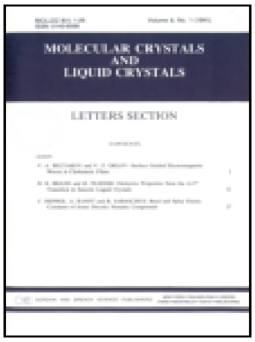

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Yeong-Soon Gal, Sung-Ho Jin, Jong Wook Park, Kwon Taek Lim & Sang Youl Kim (2015) Synthesis of an Ionic Polyacetylene Derivative via the Non-catalyst Polymerization of 2-Ethynylpyridine Using 4-(Bromomethyl)-7-methoxycoumarin, Molecular Crystals and Liquid Crystals, 618:1, 21-29, DOI: 10.1080/15421406.2015.1075838

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1075838

Mol. Cryst. Liq. Cryst., Vol. 618: pp. 21–29, 2015
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ISSN: 1542-1406 print/1563-5287 online
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Synthesis of an Ionic Polyacetylene Derivative via the Non-catalyst Polymerization of 2-Ethynylpyridine Using 4-(Bromomethyl)-7-methoxycoumarin

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A new ionic polyacetylene with coumarin moieties was synthesized via the non-catalyst polymerization of 2-ethynylpyridine using 4-bromomethyl-7-methoxycoumarin in high yield. The polymerization proceeded well in homogeneous manner to give 75% of yield without any additional catalyst or initiator. The polymer structure was identified by such various instrumental methods as NMR, IR, and UV-visible spectroscopies to have a conjugated backbone with the designed coumarin groups. The photoluminescence peak was observed at 512 nm corresponding to a photon energy of 2.42 eV. The cyclovoltamograms of polymer exhibited the electrochemically stable window at the $-1.8 \sim 1.50$ *V region. Oxidation and reduction were started at 0.58 and* -0.8 *V and had stable electrochemical property up to 30 cycles.*

Keywords polyacetylene; non-catalyst; ethynylpyridine; 4-bromomethyl-7-methoxycoumarin; cyclovoltammogram

1. Introduction

The definition of conjugated polyene is that an even number of methyne (=CH—) groups is covalently bonded to form a linear carbon chain bearing one π-electron on each carbon atom [1]. The linear conjugated polymers might have various interesting properties, especially electrical, electronical, magnetic, and optical properties [2–10]. Polyacetylene has been widely studied for both fundamental understanding of its properties and for potential applications [11–13]. However, despite of high conductivity, its poor processibility and insufficient stability constitutes a major obstacle to practical applications. For this reason,

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various substituted polyacetylenes with the improved solubility and stability have been developed [5,6,14–20].

The progress of polymerization catalysts enabled the synthesis of a wide variety of conjugated polymers from monosubstituted and disubstituted acetylenes [14–20], and non-conjugated diynes [5,6,21]. Conjugated polyelectrolytes have been actively investigated for several decades [22,23]. A new class of highly conjugated, substituted polyacetylenes was synthesized by the spontaneous polymerization of monomeric ethynylpyridinium salts without any additional initiator or catalyst [24–26]. The advantage of this polymerization essentially prevents the contamination of polymer sample by residual catalyst or initiator impurities used in the process. In our previous works [27–31], we reported the synthesis of various functional ionic polyacetylenes via the uncatalyzed polymerization of ethynylpyridinium salts produced in the initial quaternization of ethynylpyridines using functional alkyl (carbonyl) halides.

In this article, we report the synthesis of a new ionic polyacetylene with coumarin moieties via the non-catalyst polymerization of 2-ethynylpyridine using 4-bromomethyl-7-methoxycoumarin and the characterization on the polymer structure and properties.

2. Experimental

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [32]. The obtained 2-ethynylpyridine was purified by vacuum distillation after drying with calcium hydride before use (85°C/12 mmHg). 4-Bromomethyl-7-methoxycoumarin (Aldrich Chemicals, 97%) was used as received. The solvents were analytical grade materials and they were dried with an appropriate drying agent and distilled.

Poly{2-ethynyl-[N-(4-methylene-7-methoxycoumarin)pyridinium bromide]} (PEMM CPB) was prepared by the non-catalyst polymerization of 2-ethynylpyridine using 4-bromomethyl-7-methoxycoumarin as follows. In a 50 mL two-neck flask equipped with rubber septum and purified nitrogen inlet-oulet, 15 mL of DMF ($[M]_o = 0.42$ M), 2-ethynylpyridine (0.766 g, 7.43 mmol), and 4-bromomethyl-7-methoxycoumarin (2.0 g, 7.43 mmol) were added into the reaction flask. Then the polymerization was performed in the heated oil bath (80°C) under nitrogen atmosphere and stirring was continued at this temperature for 24 h. During this time, the color of reaction mixture was changed from the light brown of the initial mixture into reddish brown. After the reaction was completed, the polymer solution diluted with additional 10 mL 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 PEMMCPB (2.07 g, 75%) as black powder.

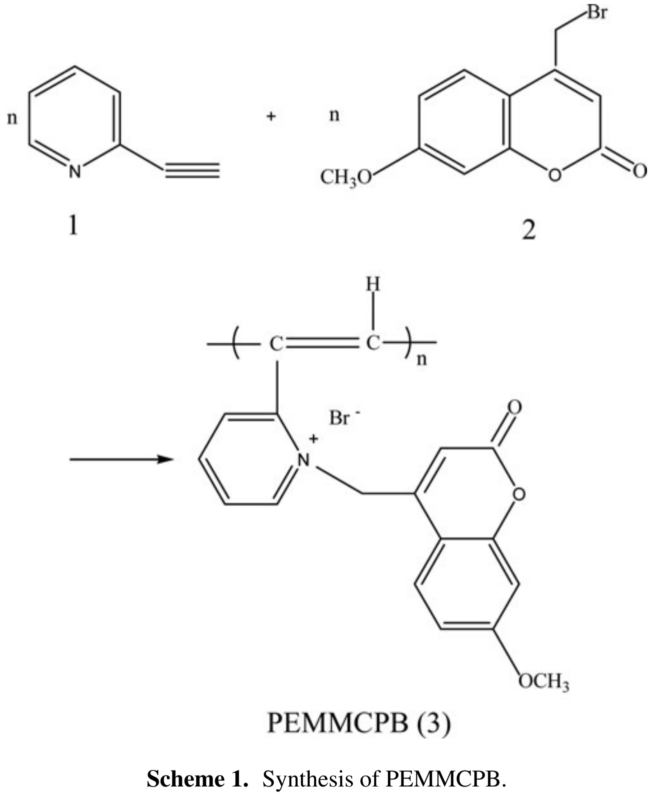
NMR (^{1}H- and ^{13}C-) spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) using DMSO-d_6 solvent and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were recorded using a Bruker EQUINOX 55 spectrometer using pressed KBr plates in the scanning range of 4000 cm^{-1} to 400 cm^{-1}. UV-visible absorption spectra were obtained in DMF (10^{-5} M) using HP 8453 UV-visible spectrophotometer. Photoluminescence spectra were obtained on a Perkin Elmer luminescence Spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. X-ray powder diffraction (XRD) data were collected at 20°C with a PHILLIPS X-ray diffractometer (Model: XPert-APD).

Cyclic voltammetry (CV) was carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research) at a scan rate of 100 mV/s. The polymer solution was prepared in DMF and the electrochemical measurements were performed under 0.1 M tetra-n-butylammonium tetrafluoroborate (TBAT) in anhydrous acetonitrile. A platinum wire was as the counter electrode and an Ag/AgNO_3 electrode was used as the reference electrode. All of the electrochemical experiments were performed in the open air at room temperature.

3. Results and Discussion

The uncatalyzed polymerization method involves providing in which the acetylenic triple bonds is either adjacent to or in conjugation with a quaternized charge-bearing nitrogen atom of ethynylpyridines. These acetylenic monomeric salts have been known to spontaneously polymerize to form charged, highly conjugated polyacetylenes.

Here, we prepared a new ionic polyacetylene (3, PEMMCPB) from the uncatalyzed polymerization of 2-ethynylpyridine (1) using 4-bromomethyl-7-methoxycoumarin (2) (Scheme 1).



Scheme 1. Synthesis of PEMMCPB.

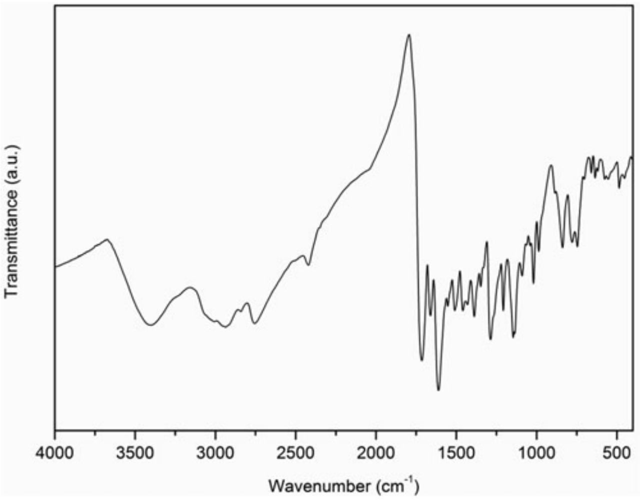


Figure 1. FT-IR spectrum of PEMMCPB in KBr pellet.

The mixture of 2-ethynylpyridine and 4-bromomethyl-7-methoxycoumarin in heated oil bath (80°C) proceeded well in homogeneous manner to give the corresponding polymer. Although the acetylenic monomeric salt, 2-ethynyl-[N-(4-methylene-7-methoxycoumarin)]pyridinium bromide], have very bulky substituent, this polymerization proceeded as like with those of similar polymerizations by using such alkyl halides as 6-(N-carbazolyl)hexyl bromide [33], 3-(6-bromohexyloxy)methylthiophene [28], and 2-(bromomethyl)-3-nitrofuran [34]. As the polymerization proceeded, the color of reaction mixture was changed from the light-brown of the initial mixture into the reddish brown. And also the solution viscosity was increased. After the work-up procedure, the lustrous black polymer was obtained in the yield of 75%.

The chemical structure of PEMMCPB was characterized by NMR, infrared, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectrum of PEMMCPB obtained in KBr pellet. This spectrum 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 1610 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine and 4-bromomethyl-7-methoxycoumarin. The carbonyl stretching and aliphatic C-H stretching peaks are observed at 1705 cm^{-1} and 2939 cm^{-1}, respectively. The peaks at 750 cm^{-1} are originated from CH out-of-plane deformation of pyridyl substituents. In the ^{1}H-NMR spectrum (Figure 2) of PEMMCPB, the aromatic protons of pyridyl and coumarin moieties and the vinyl protons of the conjugated polymer backbone are observed broadly at 5.8–9.4 ppm, whereas the methyl and methylene proton peaks are observed at 3.5–4.5 ppm. The ^{13}C-NMR spectrum (Fiigure 3) of PEMMCPB showed the aromatic carbon peaks of pyridyl and coumarin moieties and the vinyl carbons of conjugated polymer backbone are seen in range of 106–162 ppm. The carbon peaks of the methyl and methylene groups were observed at 16.3 ppm and 55.9 ppm, respectively. In the optical absorption spectrum of PEMMCPB, the absorption spectrum starts around 800 nm and shows a extended absorption band at visible region due to the $\pi \rightarrow \pi^*$ interband transition of the

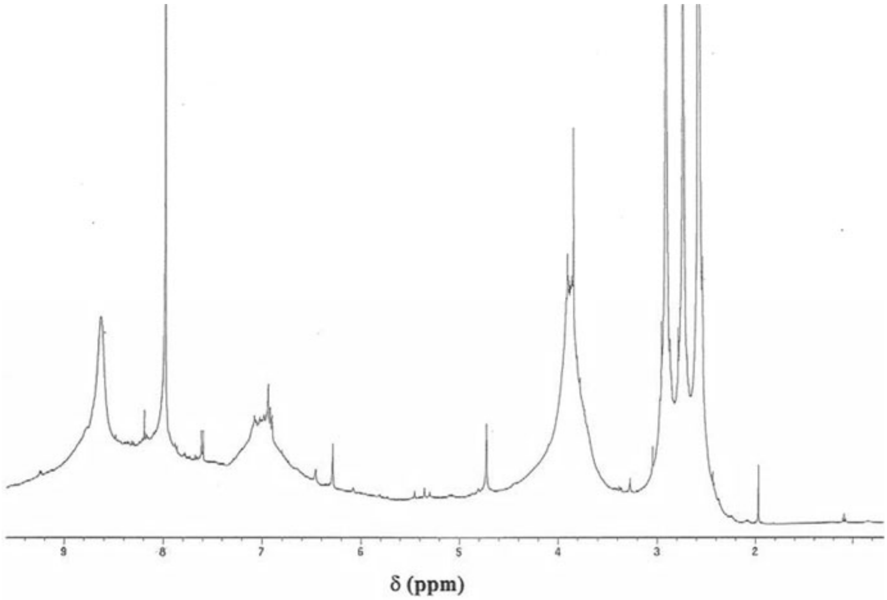


Figure 2. ^{1}H-NMR spectrum of PEMMCPB in DMSO-d_6.

polymer backbone, which is a characteristic peak of the conjugated polyene backbone system.

The X-ray diffractogram (Figure 4) of PEMMCPB showed that 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

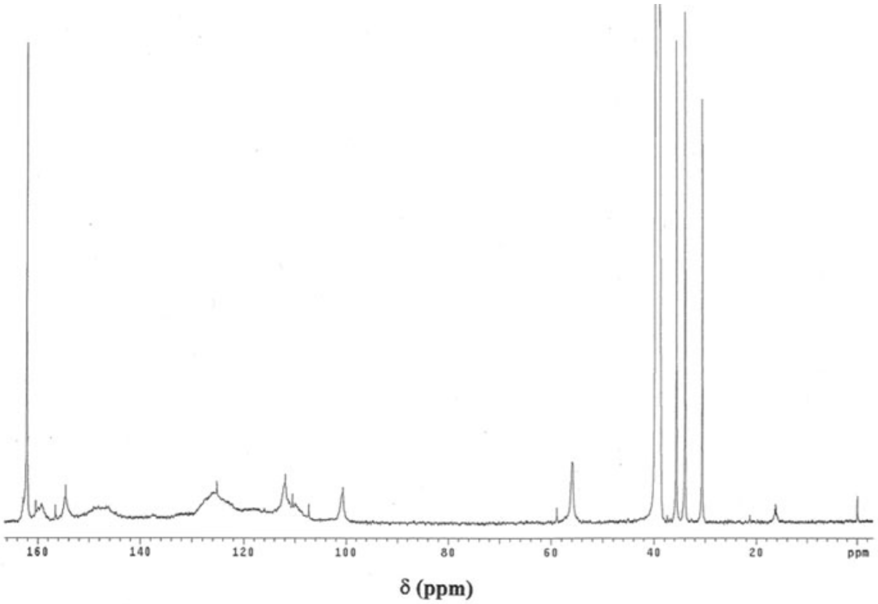


Figure 3. ^{13}C-NMR spectrum of PEMMCPB in DMSO-d_6.

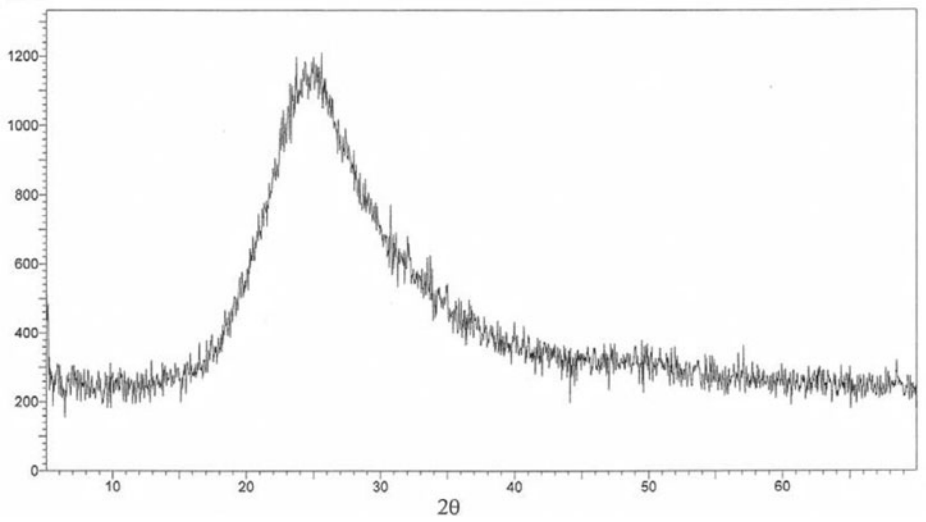


Figure 4. X-ray diffractogram of PEMMCPB powder.

greater than 0.35 [5,28]. This indicated that the present polymer is amorphous. This polymer was completely soluble in such polar organic solvents as methanol, pyridine, DMF, NMP, and DMSO.

The electro-optical and electrochemical properties of PEMMCPB were investigated by using UV-visible absorption and photoluminescence spectroscopies and cyclic

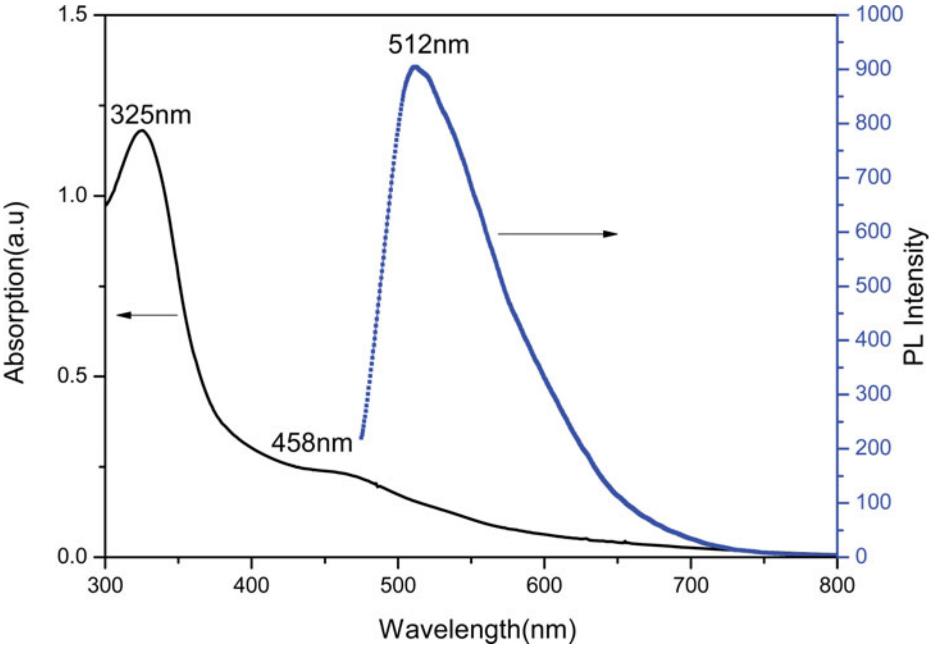


Figure 5. Optical absorption and photoluminescence spectra of PEMMCPB (excitation wavelength: 458 nm, solvent: DMF).

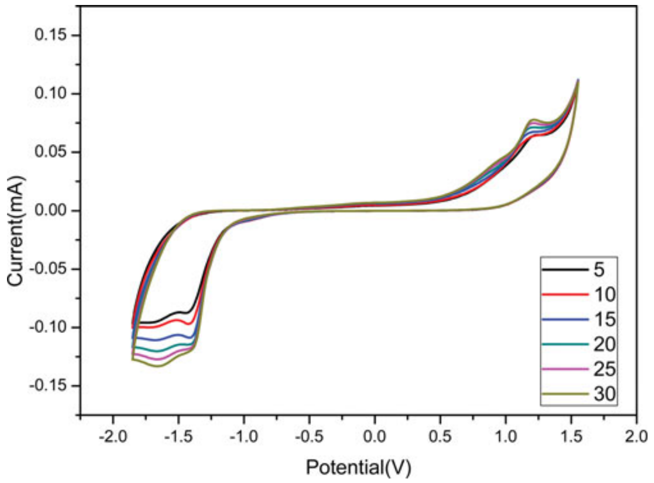


Figure 6. Cyclic voltammograms of PEMMCPB in 4 × 10^{-4} M TBAT/DMF solution: consecutive scans up to 30 cycles.

voltammograms (CV). Figure 5 shows UV-visible absorption and photoluminescence spectra of PEMMCPB solution (1 × 10^{-4} M, DMF). Absorption spectrum exhibits absorption maximum values of 325 and 458 nm, and the absorption peak at the visible region comes from $\pi \rightarrow \pi^*$ interband transition of PEMMCPB. In our previous study, the optical properties of poly(2-ethynyl-N-pentafluorobenzoylpyridinium chloride) (PEPBPC) which has also big-size pendant group were reported [35]. PEPBPC showed similar UV-visible absorption maximum value of 333 nm in ultra-violet region, but there was red-shifted absorption of 580 nm which is relatively longer than that of the present PEMMCPB. Comparing the maximum wavelength values of absorption data, it is explained by that PEMMCPB has shorter conjugation length due to the relatively larger size of side group. In the case of photoluminescence (PL) spectrum, PEMMCPB showed PL maximum value of 512 nm corresponding to the photon energy of 2.42 eV. As a result of PL spectrum maximum wavelength compared to PEPBPC (627nm), PEMMCPB had blue-shifted value.

The electrochemical property was measured by cyclic voltammograms as shown in Figure 6. Oxidation and reduction were checked under consecutive scans up to 30 cycles. As the cycle numbers were increased, the oxidation was maintained and reduction current was slightly increased because of the repeated electrochemical reaction. The reason why it relatively happens at only reduction is not clear, but it may be explained by relatively stable anion such as ester group [19]. Oxidation and reduction were started at 0.58 and −0.8 V and had stable electrochemical property up to 30 cycles. Also, reduction current amount was larger than oxidation. Further studies on electrochemical reaction are underway.

4. Conclusions

Here, a new ionic conjugated polymer (PEMMCPB) was synthesized by the non-catalyst polymerization of 2-ethynylpyridine using 4-bromomethyl-7-methoxycoumarin. This polymerization proceeded well in homogeneous manner to give a relatively high yield of polymer without any additional initiator or catalyst. Spectral analyses data indicated that the obtained

PEMMCPB have the linear conjugated backbone system bearing the N-4-methylene-7-methoxycoumarin pyridinium bromide as substituents. PL spectrum of PEMMCPB showed characteristic maximum peak of 512 nm corresponding to a photon energy of 2.42 eV. The cyclic voltamograms of PEMMCPB exhibited irreversible electrochemical behaviors between the doped and undoped peaks. Oxidation and reduction were started at 0.58 and −0.8 V and had stable electrochemical property up to 30 cycles.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded from the Ministry of Education, Science and Technology (MEST) of Korea (No. 2011-0028320, No. 2012-001846). The authors thank Mrs S. E. Chae of Korea Basic Science Institute-Taegu Branch for the measurement of 500-MHz FT-NMR spectra of polymers.

References

[1] Gibson, H. W., Bailey, F. C., Epstein, A. J., Rommelmann, H., Kaplan, S., Harbour, J., Yang, X. Q., Tanner, D. B., & Pochan, J. M. (1983). *J. Am. Chem. Soc.*, *105*, 4417.
[2] Shirakawa, H. (2001). *Angew. Chem. Int. Ed.*, *40*, 2574.
[3] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[4] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.
[5] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[6] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2013). *Thin Solid Films*, *546*, 128.
[7] Ragupathy, D., Lee, S. C., Al-Deyab, S. S., & Rajendren, A. (2013). *J. Ind. Eng. Chem.*, *19*, 1082.
[8] Ragupathy, D., Lee, S. C., Al-Deyab, S. S., & Rajendren, A. (2014). *J. Ind. Eng. Chem.*, *20*, 930.
[9] Lee, C. W., Kim, O. Y., & Lee, J. Y. (2014). *J. Ind. Eng. Chem.*, *20*, 1198.
[10] Gupta, N. D., Maity, S., & Chattopadhyay, K. K. (2014). *J. Ind. Eng. Chem.*, *20*, 3208.
[11] Shirakawa, H., Louis, F. J., MacDiarmid, A. G., Chiang, C. K., & Heeger, A. J. (1977). *J. Chem. Soc. Chem. Commun.*, 578.
[12] Chiang, C. K., Fincher, Jr., C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, B. J., Gau, S. C., & MacDiarmid, A. G. (1977). *Phys. Rev. Lett.*, *39*, 1098.
[13] Park, Y. W. (2010). *Chem. Soc. Rev.*, *39*, 2428 (2010).
[14] Masuda, T., & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[15] Buchmeiser, M. R. (2005). *Adv. Polym. Sci.*, *176*, 89.
[16] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[17] Liu, J., Lam, J. W. Y., & Tang, B. Z. (2009). *Chem. Rev.*, *109*, 5799.
[18] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2013). *Syn. Met.*, *174*, 19.
[19] Gal, Y. S., Jin, S. H., & Park, J. W. (2014). *J. Nanosci. Nanotech.*, *14*, 6247.
[20] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2014). *Mol. Cryst. Liq. Cryst.*, *601*, 151.
[21] 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.
[22] McCormick, C. L. (Ed), 2001, "Stimuli-Responsive Water-Soluble and Amphiphilic Polymers", ACS Symposium Series 780, Am. Chem. Soc., Washington, DC.
[23] Khan, A. A., Baig, U., & Khalid, M. (2013). *J. Ind. Eng. Chem.*, *19*, 1226.
[24] Subramanyam, S., & Blumstein, A. (1991). *Makromol. Chem., Rapid. Commun.*, *12*, 23.
[25] Subramanyam, S., & Blumstein, A. (1991). *Macromolecules*, *24*, 2668.
[26] Zhou, C., Gao, Y., & Chen, D. (2012). *J. Phys. Chem. B*, *116*, 11552.
[27] 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.

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

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

[30] Gal, Y. S., & Jin, S. H. (2013). *Mol. Cryst. Liq. Cryst.*, *579*, 89.

[31] Gal, Y. S., Jin, S. H., & Park, J. W. (2014). *J. Nanosci. Nanotech.*, *14*, 8028.

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

[33] Gal, Y. S., Lee, S. S., Bae, J. S., Kim, B. S., Jang, S. H., & Jin, S. H. (1999). *Bull. Korean Chem. Soc.*, *20*, 451.

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

[35] Choi, H. K., Jin, S. H., Park, J. W., Lim, K. T., Jang, S. H., Kim, S. Y., & Gal, Y. S. (2013). *Mol. Cryst. Liq. Cryst.*, *584*, 94.