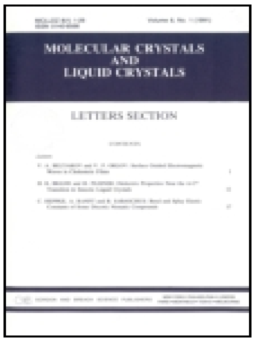


Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

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

A New Poly(aryleneethynylene) from the Cross-Coupling Condensation of 4-[(tert-Butyldimethylsiloxy)methyl]-1,6-heptadiyne and p-Diiodobenzene: Synthesis and Properties

Yeong-Soon Gal, Sung-Ho Jin, Jong Wook Park & Kwon Taek Lim

To cite this article: Yeong-Soon Gal, Sung-Ho Jin, Jong Wook Park & Kwon Taek Lim (2015) A New Poly(aryleneethynylene) from the Cross-Coupling Condensation of 4-[(tert-Butyldimethylsiloxy)methyl]-1,6-heptadiyne and p-Diiodobenzene: Synthesis and Properties, Molecular Crystals and Liquid Crystals, 618:1, 30-37, DOI: 10.1080/15421406.2015.1075839

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1075839

Mol. Cryst. Liq. Cryst., Vol. 618: pp. 30–37, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1075839

A New Poly(aryleneethynylene) from the Cross-Coupling Condensation of 4-[(tert-Butyldimethylsiloxy)methyl]-1,6-heptadiyne and *p*-Diiodobenzene: Synthesis and Properties

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

[1]Department of Fire Safety, Kyungil University, Gyeongsan,
Gyeongsangbuk-Do, Korea
[2]Department of Chemistry Education, Pusan National University, Busan, Korea
[3]Department of Chemistry, The Catholic University of Korea, Bucheon, Korea
[4]Department of Display Engineering, Pukyong National University, Busan,
Korea

*A new poly(aryleneethynylene) was synthesized from the palladium-catalyzed carbon-carbon coupling condensation of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne and* p*-diiodobenzene. This polymerization proceeded well in mild reaction conditions to give a high yield of polymer (92%). The polymer structure was characterized by such instrumental methods as infrared and NMR spectroscopies. This polymer was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The X-ray diffractogram of polymer powder showed that this polymer is amorphous. In the DSC thermogram of polymer, a broad exothermic peak was observed around 205°C (started at 140°C) in the first heating, whereas there was no exothermic peak in the second heating. When this polymer was excited at 272 nm, it gave PL maximum emissions at 327 and 380 nm.*

Keywords conjugated polymer ; 1, 6-heptadiyne; poly(aryleneethynylene); photoluminescence; cyclic voltammogram

Introduction

Conjugated polymers are of particular interest in material science because of their applications in electronic and photonic devices [1–3]. The polymers having a conjugated backbone shows such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [4–8]. Conjugated materials have demonstrated real promise in such various fields as electric semiconductors, photonics, nonlinear optical applications, gas or liquid separation

---

[*] Address correspondence to Yeong-Soon Gal, Department of Fire Safety, Kyungil University, Gyeongsan 712-701, Gyeongsangbuk-Do, Korea. E-mail: ysgal@kiu.ac.kr

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

membranes, chemical sensors, liquid crystals, organic light-emitting diodes (OLEDs), and photovoltaic cells [9–15].

Poly(phenylene-ethynylene)s, a new class of conjugated polymers, have attracted much attention because of their fascinating properties. It was demonstrated that poly(phenylene-ethynylene)s with their unique properties are fantastic materials in such different areas as explosive detection, molecular wires in bridging nanogaps, and polarizers for LC displays [16].

Some ethynylene polymers were also synthesized by palladium-catalyzed coupling reaction between the *p*-diiodobenzene and diethyldipropargyl malonate in high yield [17]. Curing of crystalline polydiacetylenes results in the formation of conjugated networks of alternating double and triple bonds still in crystalline arrays transverse to the polymer backbone [18,19]. Fluorene-based low-band gap copolymers were prepared for bulk heterojunction photovoltaic cell applications [20]. The poly(fluorenyleneethynylene)s were prepared by alkyne metathesis of (9,9-dialkyl)fluoren-2,7-yleneethynylenes [13,21].

The diacetylenic polymer via oxidative coupling of 9,9-dipropargylfluorene was prepared and characterized [22]. And also, various poly(9,9-dipropargylfluorenylene-arylene)s were prepared by cross-coupling condensation polymerization [23–25]. Poly(aryleneethynylene)s with ferrocene unit were also synthesized by the reaction of 1,1′-*bis*(ethynyldimethylsilyl)ferrocene and aromatic dihalides [26].

In this article, we report on the synthesis of a new poly(aryleneethynylene)s from the cross-coupling condensation of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne and *p*-diiodobenzene and its electro-optical and electrochemical properties.

Experimental

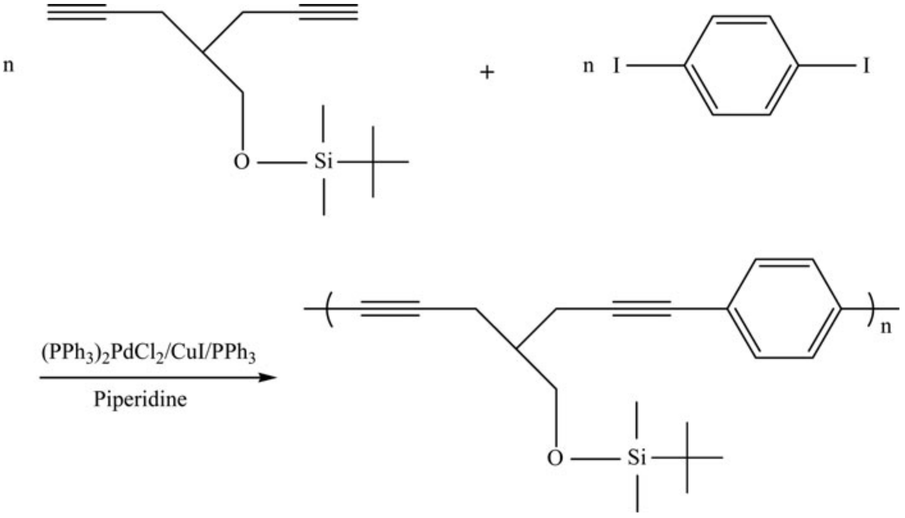
p-Diiodobenzene, *bis*(triphenylphosphine)palladium(II) dichloride, cuprous iodide, piperidine, and benzyltriethylammonium chloride were obtained from Aldrich Chemical Co. and used without further purification. The analytical grade solvents were dried with an appropriate drying agent and distilled. The synthesis of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne was carried out according to the literature method [17]. The palladium-catalyzed reaction of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne and *p*-diiodobenzene was performed in a 100 mL glass pressure vessel with a magnetic stirrer and carried out by the following procedure. After the reactor was charged with 45 mL of piperidine, 2-4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (1.0 g, 4.23 mmol), and *p*-diiodobenzene (1.395 g, 4.23 mmol), 45 mg of $(PPh_3)_2PdCl_2$, and a catalytic amount of CuI was added. Then the reaction was performed at 70°C oil bath under nitrogen atmosphere and stirring was continued at this temperature for 24 h. At the end of reaction, the crude product was isolated by precipitation into methanol. After filtration, the crude polymer was purified with Soxhlet in methanol to remove the residual monomers and oligomers. The collected yellow powder was dried under vacuum overnight at 40°C to afford the corresponding polymer in 92% yield.

NMR (^{1}H-and ^{13}C) spectra were obtained in $CDCl_3$ 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 molecular weights of the polymer were determined by a Shimadzu LC10A gel permeation chromatograph equipped with μ-Styragel columns using THF as an eluent. 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 perchlorate (TBAP) solution containing DMF. ITO, Ag/AgNO$_3$ and platinum wire were used as a working, reference and counter electrode, respectively. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD).

Results and Discussion

The palladium-catalyzed coupling reaction was used for the synthesis of a new poly(aryleneethynylene) with acetylenic and arylene moieties in the polymer main chain (Scheme 1).



Scheme 1. The cross coupling reaction of 4-[(*tert*-butyldimethyl siloxy)methyl]-1,6-heptadiyne and *p*-diiodobenzene

The palladium-catalyzed reaction of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne and *p*-diiodobenzene proceeded well in homogeneous manner under mild reaction condition to give a high yield (92%) of polymer. The reaction mechanism between an aromatic dihalide and a terminal acetylenic comonomer in the presence of copper(I) iodide, base, and palladium catalyst involves the in situ formation of a copper acetylide. In most cases, copper acetylides are insoluble in common organic solvents, which are expected to the reduced with respect to their reactivity and the low molecular weight of the resulting polymer. However, in the present polymerization, insoluble copper salt was not formed during the reaction. The soluble copper salt reacts with palladium aryl complexes produced by the oxidative addition of the aryl iodide to a zero valent palladium intermediate under transfer of acetylide group to palladium. The cross-coupling product is produced by the reductive elimination, regenerating the zero valent palladium species [16,17].

The molecular weight (Mn) and polydispersity (Mw/Mn) of the resulting polymer were 9.3×10^3 and 2.1, respectively. This polymer was completely soluble in common organic solvents such as chloroform, chlorobenzene, toluene, and xylene. In the X-ray diffractogram of polymer powder, the peak in the diffraction pattern is broad and the ratio

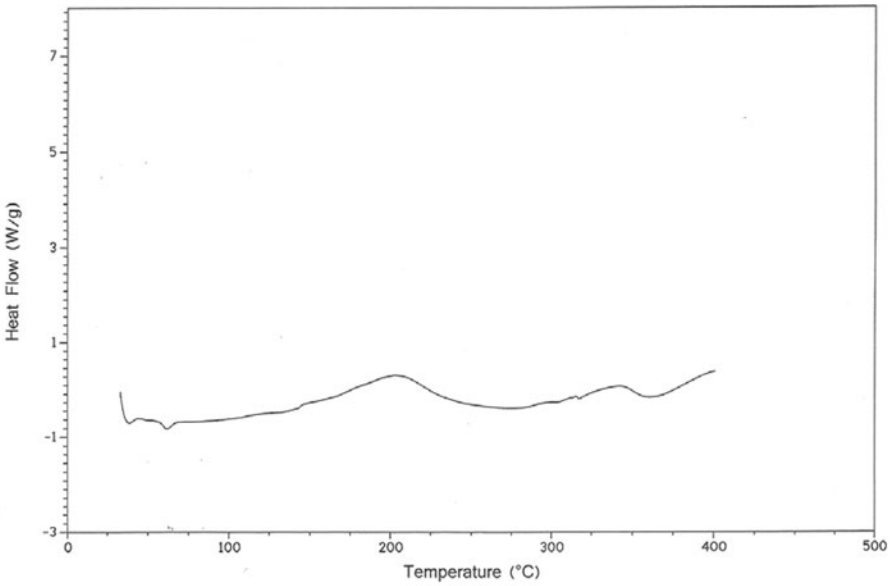


Figure 1. DSC thermogram of polymer under nitrogen atmosphere at a heating rate of 10°C/min.

of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35 [5,17], indicating that the present polymer is amorphous.

The thermal behavior of polymer was examined by differential scanning calorimeter and thermogravimeter. From the DSC thermogram (Figure 1) of polymer, it was found that a broad exothermic peak was observed around 205°C (started at 140°C) in the first heating, whereas there was no exothermic peak in the second heating. The broad exothermic peak is

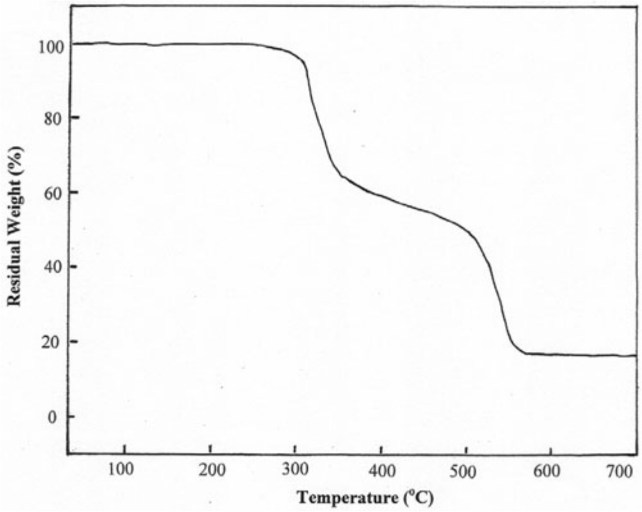


Figure 2. TGA thermogram of polymer under nitrogen atmosphere at a heating rate of 10°C/min.

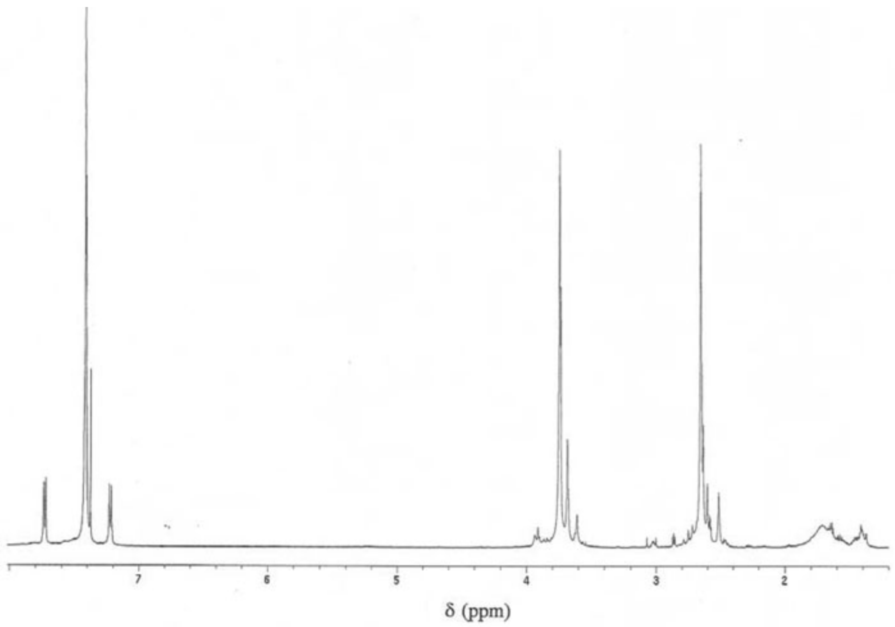


Figure 3. ^{1}H-NMR spectrum of polymer in $CDCl_3$.

probably due to the thermal crosslinking of the internal ethynyl groups in the polymer main chain. The TGA thermogram (Figure 2) of polymer revealed that this polymer is thermally stable up to 250°C. The char yield of this polymer was 16.6% even after heating up to 600°C.

The chemical structure of polymer was characterized by such instrumental methods as infrared and NMR spectroscopies. The IR spectrum of polymer did not show any absorption frequency at 3284 cm^{-1} due to the acetylenic $\equiv$C—H stretching absorption frequency,

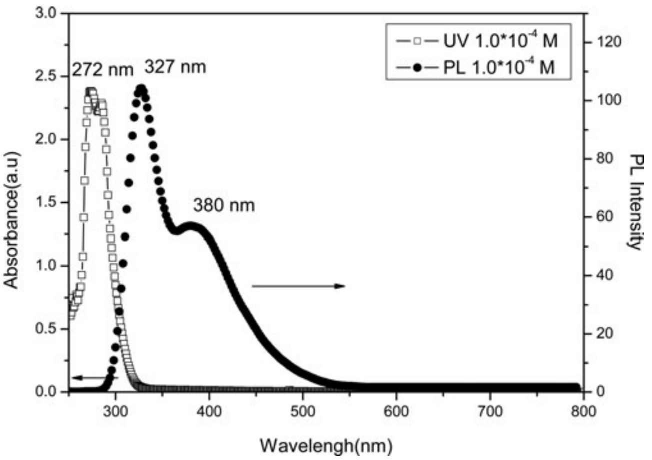
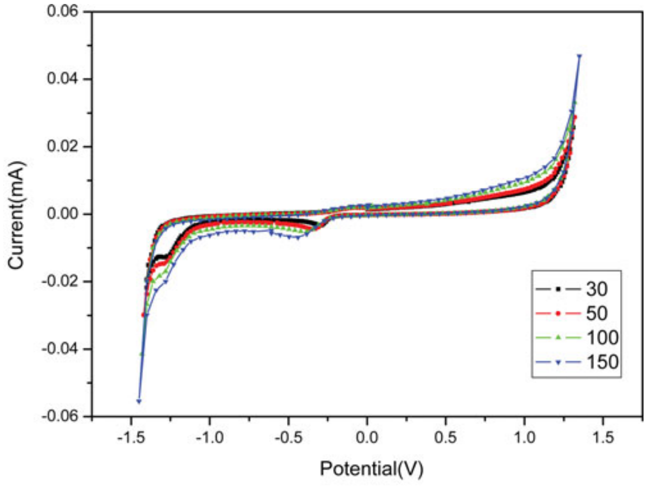
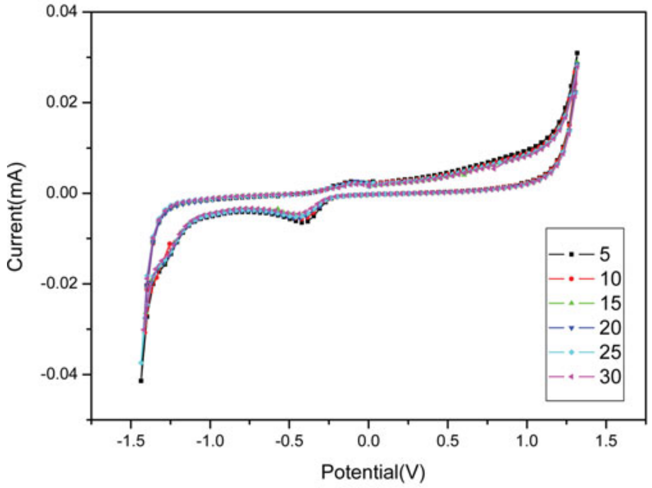


Figure 4. Optical absorption and photoluminescence spectra of polymer (solvent DMF, excitation wavelength: 272 nm).



(a)



(b)

Figure 5. Cyclic voltammograms of polymer under 0.1M TBAP/DMF electrolyte solution: (a) 30 mV/sec ∼150 mV/sec scan rates, (b) consecutive 30 scans under 150 mV/s.

which had been observed in the IR spectrum of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne.

Figure 3 shows the ^{1}H-NMR spectrum of polymer in the range of 1–8 ppm (solvent: $CDCl_3$). The ^{1}H-NMR spectrum of polymer showed the peaks of methylene protons adjacent to ethyne group and methine proton peak at 2.40–3.02 ppm and 3.50–3.98 ppm, respectively. Three methyl proton peaks of t-butyl group and the aromatic proton peaks of phenylene moieties were also observed at 1.38–1.80 ppm and 7.20–7.75 ppm, respectively. On the other hand, the acetylenic proton peak (≡C—H) of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne was disappeared. The proton peaks of dimethylsiloxy groups and trimethyl groups of tert-butyl substituents were observed at 0.18 ppm and 1.02 ppm, respectively.

In the ^{13}C-NMR spectrum of polymer, the signals for both the ethynylene carbons of 4-[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne were disappeared, and the new signals of internal ethynylene carbons were appeared at 82.23 ppm and 88.71 ppm, the first one is assigned to the signal of ethynylene carbon adjacent to phenylene group in the main chain of the polymer.

One of several motivation issues in terms of design and synthesis of poly(aryleneethynylene) is optically clear material in the range of visible light. Optically clear compound is very important in the application of display such as LCD and OLED, because it can be widely used as a coating material to protect device surface. Moreover, optically clear compound is able to expand its application field to not only coating but also optical retardation calibration as well as filling material between display device layers.

Figure 4 shows UV-visible absorption and photoluminescence (PL) spectrum. As shown in Fig. 4, this polymer exhibited no absorption in the range of visible light at all and showed only absorption in 272 nm wavelength. When it was also excited at 272nm, it gave PL maximum emission with 327 and 380 nm. Considering short excitation wavelength, this polymer has vivid advantage for optically clear material. Also, this material includes silicon atom and it is expected that this polymer has superior interface contact property as silicon atom always shows that.

In order to examine the electrochemical property of this polymer, cyclic voltammetry (CV) data was obtained as shown in Fig. 5. This polymer includes a phenyl ring and two triple bonds at each main chain unit, but oxidation and reduction was not appeared largely. Although the scan rate was increased up to 150 mV/sec and maintained by consecutive scans of 30, CV curves were not changed. It means that when this polymer is used for electronic layer, it is inert and stable.

Conclusions

A new conjugated polymer with cyclic recurring unit was synthesized via the ring-forming cyclopolymerization of triyne monomer by transition metal catalyst. The polymerization proceeded in homogeneous manner to give the resulting polymer in 32% yield. Spectral analysis revealed that the present polymer have a conjugated backbone system. The photoluminescence spectrum of polymer showed that the photoluminescence peak is located at 530 nm, corresponding to a photon energy of 2.34 eV. This polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. This polymer can be used as overcoat material on top or inside of LCD and OLED devices in order to protect weak surface of display layer. This polymer has two kinds of advantages such as no absorption at visible wavelength range and two reactive triple bonds at polymer chains. Two triple bonds can provide the second reaction of crosslinking which connects intermolecular chains each other and rapidly increases polymer hardness and it would not make any effect on absorption and optical effect.

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] 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*, 359.
[2] Jin, S. H., Kim, M. Y., Kim, J. Y., Lee, K., & Gal, Y. S. (2004). *J. Am. Chem. Soc.*, *126*, 2474.
[3] Park, Y. W. (2010). *Chem. Soc. Rev.*, *39*, 2428.
[4] Chauser, M. G., Rodionov, Yu. M., Misin, V. M., & Cherkashin, M. I. (1976). *Russ. Chem. Rev.*, *45*, 348.
[5] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[6] Gal, Y. S., Jin, S. H., & Choi, S. K. (2004). *J. Mol. Cat. A: Chem.*, *213*, 115.
[7] Khan, A. A., Baig, U., & Khalid, M. (2013). *J. Ind. Eng. Chem.*, *19*, 1226.
[8] Ragupathy, D., Lee, S. C., Al-Deyab, S. S., Rajendran, A. (2013). *J. Ind. Eng. Chem.*, *19*, 1082.
[9] Torsi, L. & Dodabalapur, A. (2005). *Anal. Chem.*, *77*, 380A.
[10] Chih, C. C., Ouyang, J., Tseng, J. H., & Yang, Y. (2005). *Adv. Mater.*, *17*, 1440.
[11] Wang, L., Fine, D., Sharma, D., Torsi, L., & Dodabalapur, A. (2006). *Anal. Bioanal. Chem.*, *384*, 310.
[12] Ko, Y. G., Kwon, W., Kim, D. M., Kim, K., Gal, Y. S., & Ree, M. (2012). *Polym. Chem.*, *3*, 2028.
[13] Lee, C. W., Kim, O. Y., & Lee, J. Y. (2014). *J. Ind. Eng. Chem.*, *20*, 1198.
[14] Wang, X., & Liu, P. (2014). *J. Ind. Eng. Chem.*, *20*, 1324.
[15] Sattari, S., Reyhani, A., Khanlari, M. R., Khabazian, M., & Heydari, H. (2014). *J. Ind. Eng. Chem.*, *20*, 1761.
[16] Bunz, U. H. F. (2000). *Chem. Rev*., *100*, 1605.
[17] Jin, S. H., Kim, S. H., & Gal, Y. S. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 4025.
[18] Nielsen, M. B. & Diederich, F. (2005). *Chem. Rev*., *105*, 1837.
[19] Baughman, R. H. (2006). *Science*, *312*, 1009.
[20] Park, J. S., Kim, Y. H., Song, M., Kim, C. H., Karim, Md. A., Lee, J. W., Gal, Y. S., Kumar, P., Kang, S. W., & Jin, S. H. (2010). *Macromol. Chem. Phys.*, *211*, 2464.
[21] Pschirer, N. G. & Bunz, U. H. F. (2000). *Macromolecules*, *33*, 9361.
[22] Lee, S. G., Kwak, Y. W., Park, J. W., Jin, S. H., & Gal, Y. S. (2005). *J. Nonlinear Opt. Phys. & Mater.*, *14*, 573.
[23] Lee, S. G., Kwak, Y. W., Koo, B. K., & Gal, Y. S. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 203.
[24] Lee, S. G., Koo, B. K., Gal, Y. S., & Kwak, Y. W. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 222.
[25] Lee, G. Y., Gal, Y. S., & Lee, S. G. (2014). *Mol. Cryst. Liq. Cryst.*, *597*, 95.
[26] Lee, I. S., Lee, C. G., Kwak, Y. W., & Gal, Y. S. (2009). *Bull. Korean Chem. Soc.*, *30*, 309.