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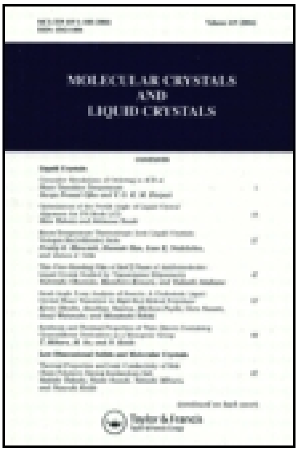

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Synthesis and Characterization of Poly[N-(2-ethyl pyrroyl)-2-ethynylpyridinium Bromide]

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A monosubstituted polyacetylene having two aromatic heterocycles (pyridine and pyrrole) was easily prepared via the uncatalyzed polymerization of 2-ethynylpyridine using 1-(2-bromoethyl)pyrrole. The polymerization proceeded well in homogeneous manner to give a moderate yield of polymer (70%). The chemical structure of resulting polymer was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies to have the conjugated backbone system with the designed N-(2-ethylpyrroyl)pyridinium bromide. The absorption spectrum starts around 800 nm, which is due to the $\pi \rightarrow \pi^*$ *interband transition of conjugated polymer system. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 574 nm, corresponding to a photon energy of 2.16 eV.*

Keywords 1-(2-Bromoethyl)pyrrole; 2-ethynylpyridine; photoluminescence; polyacetylene; uncatalyzed polymerization

Introduction

Polymers with a fully conjugated backbone endows them with such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability, and so on [1–7]. Such materials are of high interest due to their potential as promising materials for photovoltaics, displays, lasers, nonlinear optical materials, membranes for gas separation and for liquid-mixture separation, and chemical sensors [2,3,8–10].

Especially, ionic polymers are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different than the electronic conductivity of metals and conjugated polymers, since current is carried through the movements of ions. Due to their extensive conjugation and ionic nature, these ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices [11–15].

Blumstein and co-workers synthesized several ionic polyacetylenes via the activated polymerization of ethynylpyridines by using the functional alkyl halides [11,12]. They reported that the quaternization of pyridine nitrogen atom with alkyl groups of different sizes

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permitted the formation of monosubstituted ionic polyacetylene with different properties. We have also reported the preparation of various ionic conjugated polymers having different functionalities [16–20].

The ionic poly(ethynylpyridine)s with N-substituents have been used as material candidates for the fabrication of fluorescence quencher for fluorescent biotin-functionalized Lucifer Yellow dyes [21], hybrid polymer gels [22], nanocrystalline CdS polymer sensitizer [23,24], and π-conjugated polymer-nanocomposites [25–27], unipolar write-once-read-many-times (WORM) memory devices [28]. To our knowledge, there had been no report on the synthesis of polyacetylene derivative with pyrrole substituents, which may have the enhanced physical properties by the crosslinking reaction of pendant pyrrole substituents.

In this article, we report the synthesis of a new ionic polyacetylene with two different aromatic heterocycles (pyridine and pyrrole) via the uncatalyzed polymerization of 2-ethynylpyridine using 1-(2-bromoethyl)pyrrole and the characterization of the resulting poly[N-(2-ethylpyrrole)-2-ethynylpyridinium bromide] (PEPEPB).

Experimental

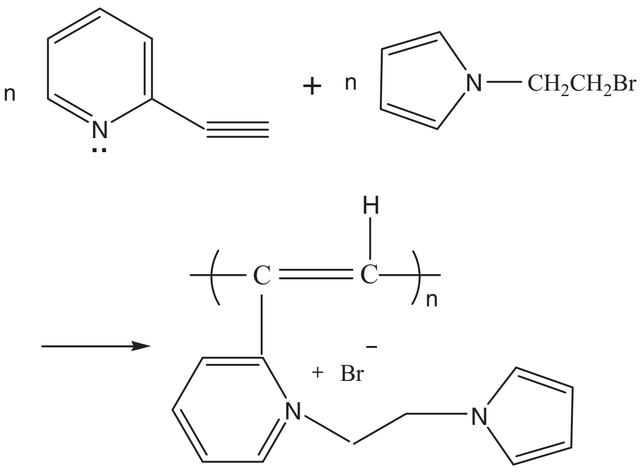
2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85°C/12 mm Hg) [29]. 1-(2-Bromoethyl)pyrrole (Aldrich Chemicals, 97%) was used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

PEPEPB was prepared by the polymerization of 2-ethynylpyridine by using 1-(2-bromoethyl)pyrrole without any additional catalyst or initiator. Polymerization was carries out in a 100 mL round-bottom flask equipped with magnetic stirrer and carried out by the following procedure. After the reactor was charged with 20.0 mL of DMF ($[M]_0 =$ 0.51 M), 2-ethynylpyridine (1.213 g, 11.76 mmol), and 1-(2-bromoethyl)pyrrole (2.00 g, 11.76 mmol). Then the polymerization was carried out at 60 °C for 24 hrs under nitrogen atmosphere. As the polymerization proceeded, the reaction solution became into more viscous reddish brown solution. After the polymerization time, the polymer solution diluted with 10 mL DMF was precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried in vacuum oven at 40 °C for 24 hrs. The brown polymer powder was obtained in 70% yield.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. 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. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200). 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 a PHILLIPS X-ray diffractometer (Model: XPert-APD). 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.

Results and Discussion

The uncatalyzed synthesis of well-defined ionic poly(ethynylpyridine)s was performed through the activated polymerization of ethynylpyridines with alkyl halides. All polymerization reactions involve the quaternization of pyridine nitrogen in ethynylpyridines.



Scheme 1. Synthesis of PEPEPB.

Ethynylpyridinium monomeric species are spontaneously polymerized to form highly conjugated, charged polyacetylenes. Interestingly, this polymerization do not need any additional initiator or catalyst. Thus, this method can essentially eliminate the impurities that can be originated from the catalyst or initiator used during the polymerization.

Thus, we used this uncatalyzed polymerization method for the synthesis of an ionic polyacetylene derivative with two different aromatic heterocycles (Scheme 1). The reaction solution of equal mole ratio of 2-ethynylpyridine and 1-(2-bromoethyl)pyrrole in DMF solvent was exposed in oil bath (60°C). The polymerization proceeded well in mild reaction condition without any additional iniatiator or catalyst to give a moderate yield (70%) of polymer. As the reaction proceed, the solution became viscous and the color of reaction mixture was changed from the light brown of the initial mixture into reddish brown.

This polymerization contains the first quarternarization of 2-ethynylpyridine by 1-(2-bromoethyl)pyrrole. The activated acetylenic functional group that was bonded to the N-(2-ethylpyrroyl)pyridinium ring caused anionic polymerizatiom, initiated by a nucleophilic attack by the nitrogen atom of the unreacted ethynylpyridine and/or the bromide ion.

The molecular structure of PEPEPB was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectrum of PEPEPB measured in KBr pellet. FT-IR spectrum of PEPEPB did not show the acetylenic $C{\equiv}C$ bond stretching (2110 cm^{-1}) and acetylenic $\equiv$C-H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the $C{=}C$ stretching frequency peak of conjugated polymer backbone around 1620 cm^{-1} became relatively more intense than those of the $C{=}C$ and $C{=}N$ stretching frequencies of 2-ethynylpyridine and 1-(2-bromoethyl)pyrrole. The vinyl $=$ C—H stretching frequencies of pyridine and pyrrole moieties were observed at 3031 cm^{-1}. The strong peak at 737 cm^{-1} is due to the CH out-of-plane deformation of pyridyl moieties.

The ^{1}H-NMR spectrum of polymer showed the aromatic pyridyl and pyrroyl protons and the vinylic protons of conjugated polymer backbone in the range of 5.5–9.1 ppm and also showed the methylene proton peaks at 3.2–5.3 ppm. The ^{13}C-NMR spectrum of PEPEPB showed the aromatic carbon peaks of pyridyl and pyrroyl moieties and the vinyl carbons of conjugated polymer backbone showed in the range of 105–144 ppm. The

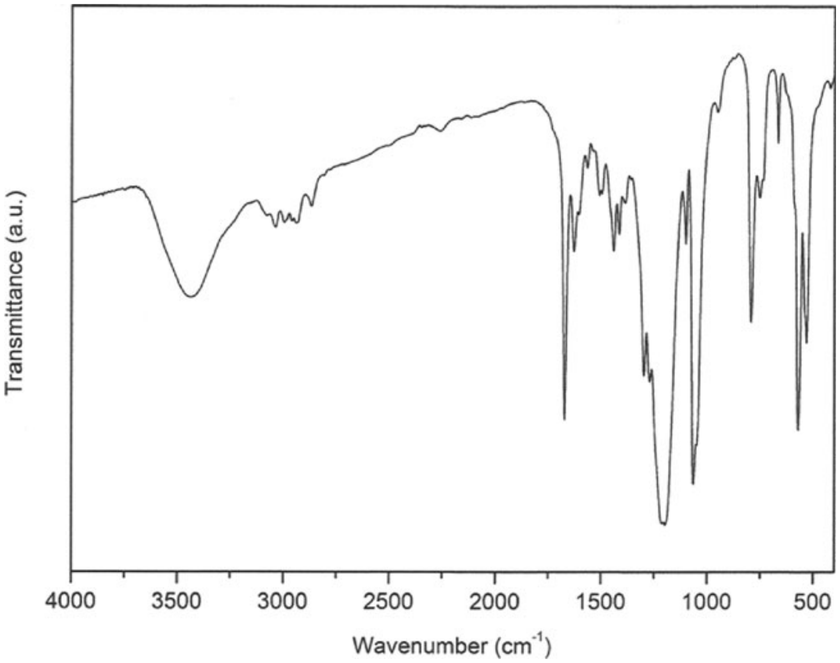


Figure 1. FT-IR spectrum of PEPEPB in KBr pellet.

methylene carbon peaks between two nitrogen atoms were observed at 43–62 ppm. The UV-visible spectrum of PEPEPB showed a characteristic absorption peak in the visible region (up to 800 nm), which is strong evidence for the presence of the polyene backbone system. The results from EDX analysis confirmed the presence of bromide atoms with different environments.

The morphologies of PEPEPB were also investigated by X-ray diffraction analysis. 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 [1,2], indicating that the present polymer is mostly amorphous. This polymer was soluble in such organic solvents as DMF, NMP, and DMSO. The inherent viscosity of PEPEPB was 0.14 dL/g. The thermal properties of PEPEPB were studied by TGA thermometry. This polymer showed slightly weight loss at relatively low temperature (even below 200°C), which is mainly due to the absorbed moisture and/or organic resudues in the polymer. PEPEPB exhibited an abrupt weight loss from 242°C. TGA thermogram shows that the polymer retains 98.1% of its original weight at 100°C, 96.5% at 200°C, 86.2% at 300°C, 64.1% at 400°C, 44.8% at 600°C, and 6.2% at 800°C.

Figure 2 shows the UV-visible and photoluminescence (PL) spectra of PEPEPB solution (1.0×10^{-4} M in DMF). The photoluminescence spectra of PEPEPB showed that the photoluminescence maximum peak is located at 574 nm corresponding to the photon energy of 2.16 eV. When PL was checked with excitation of 529 nm wavelength, excitation peak was removed by using cut-off filter in PL detection. In our previous study [18], the photoluminescence maximum peak of similar ionic polyacetylene with two aromatic heterocycles (pyridine and thiophene) was observed at very similar wavelength (573 nm).

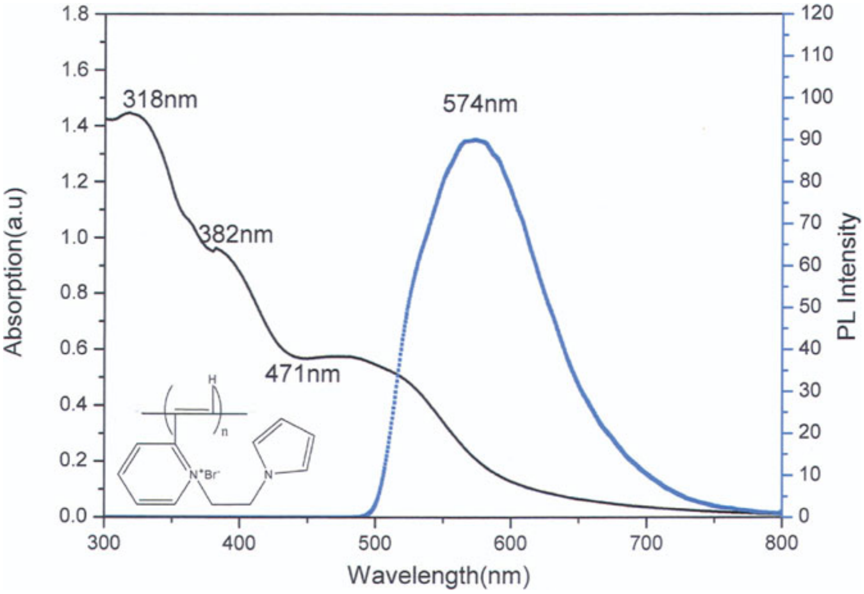


Figure 2. UV-visible and photoluminescence spectra of PEPEPB.

Conclusions

A new ionic conjugated polyacetylene with two different aromatic heterocycles was easily synthesized by the uncatalyzed polymerization of 2-ethynylpyridine using 1-(2-bromoethyl)pyrrole. The activated triple bond of N-(2-ethylpyrroyl)-2-ethynylpyridinium bromide formed at the initial reaction time was susceptible to the linear polymerization, followed by an identical propagation step that contains the produced macroanion and the quaternized monomeric species. The polymer structure was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed aromatic substituents. This polymer was completely soluble in such organic solvents as DMF, NMP, and DMSO. The X-ray diffraction data on PEPEPB powder indicated that this polymer is mostly amorphous. The photoluminescence maximum peak of polymer was located at 574 nm corresponding to the photon energy of 2.16 eV.

Further works on the gel-forming properties and the physical properties of modified thin films are now in progress.

Acknowledgments

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References

[1] Masuda, T., & Higashimura, T. (1984). *Acc. Chem. Res.*, 17, 51.
[2] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, 100, 1645.
[3] 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.

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

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

[6] Lim, C. W., Song, K., & Kim, S. H. (2012). *J. Ind. Eng. Chem.*, 18, 24.

[7] 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.

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

[9] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). *Chem. Rev.*, 109, 897.

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

[11] Subramanyam, S., & Blumstein, A. (1992). *Macromolecules*, 25, 4058.

[12] Balogh, L., Samuelson, L., Alva, K. S., & Blumstein, A. (1998). *J. Polym. Sci.: Part A: Polym. Chem.*, 36, 703.

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

[14] Choi, H. K., Jin, S. H., Park, J. W., Kim, S. Y., & Gal, Y. S. (2012). *J. Ind. Eng. Chem.*, 18, 814.

[15] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2012). *Mol. Cryst. Liq. Cryst.*, 565, 1.

[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] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2012). *J. Nanosci. Nanotech.*, 12, 4361.

[20] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2012). *Mol. Cryst. Liq. Cryst.*, 568, 52.

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

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

[23] Lee, W., Min, S. K., Cai, G., Mane, R. S., Ganesh, T., Koo, G., Chang, J., Baek, S. J., Lee, S. H., & Han, S. H. (2008). *Electrochim. Acta*, 54, 714.

[24] Kwak, W. C., Kim, T. G., Lee, W., Han, S. H., & Sung, Y. M. (2009). *J. Phys. Chem. C*, 113, 1615.

[25] Kim, D. W., Blumstein, A., Kumar, J., Samuelson, L. A., Kang, B., & Sung, C. (2002). *Chem. Mater.*, 14, 3925.

[26] Kim, D. W., Kumar, J., & Blumstein, A. (2005). *Appl. Clay Sci.*, 30, 134.

[27] 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.

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

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