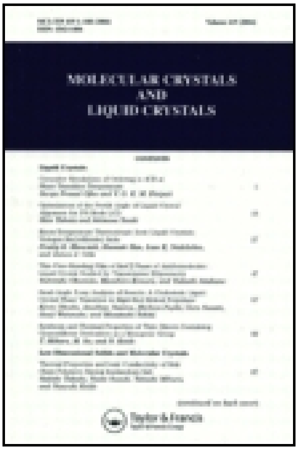

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrochemical properties of poly(2-ethynylpyridinium bromide) having propargyl side chains

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To cite this article: Tai-Long Gui, Sung-Ho Jin, Jong-Wook Park, Kwangnak Koh, Sung-Hoon Kim, Kwon Lim & Yeong-Soon Gal (2004): Electrochemical properties of poly(2-ethynylpyridinium bromide) having propargyl side chains, Molecular Crystals and Liquid Crystals, 425:1, 237-242

To link to this article: http://dx.doi.org/10.1080/15421400490506874

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 237/[515]–242/[520], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506874

ELECTROCHEMICAL PROPERTIES OF POLY(2-ETHYNYLPYRIDINIUM BROMIDE) HAVING PROPARGYL SIDE CHAINS

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Received 1 October 2003; accepted 3 January 2004.
This work was supported by Korea Research Foundation Grant KRF-2002-015-CP0269.

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An ionic conjugated polymer, poly(2-ethynylpyridinium bromide) having propargyl side chain (PEPB-P), was prepared by the activated polymerization of 2-ethynylpyridine with propargyl bromide in high yield. The electrochemical properties of PEPB-P were studied by using cyclic voltammograms. PEPB-P showed the well-defined and stable redox process at −0.1 to +1.6 V. The oxidation and reduction occurred at 0.84 and 0.69 V, respectively. The redox current value increased as the increased scan rate and the exponent of scan rate, x value was found to be 0.75, which means that the redox kinetics is mainly controlled by both electron transfer and diffusion process.

Keywords: 2-ethynylpyridine; conjugated polymer; cyclic voltammograms; poly (2-ethynylpyridinium bromide)

INTRODUCTION

For the past three decades, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics [1–3]. This considerable interest was triggered by the discovery of high electric conductivity in molecular crystals of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) in 1973 [4] and in the oxidized form of π-conjugated polyacetylene (PA), a few years later [5]. The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [6–8].

A number of mono- and di-substituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems [6–11]. The ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices [8], due to their extensive conjugation and ionic nature.

Acetylenic compounds such as 2- and 3-ethynylpyridines, dipyridyl-acetylene, and dipyridyl-diacetylene are known to be spontaneously polymerized by the alkyl halide treatment in polar solvents such as acetonitrile, methanol, DMF, etc. without the simple N-alkyl products [12–14], which is similar to the vinyl polymer formation from 4-vinylpyridine including cation radical. In recent years, we reported on the synthesis of an series of conjugated ionic polymers by the activated polymerization of 2-ethynylpyridine with functionalised alkyl halides [15–17]. In our previous paper [18], we reported on the synthesis and its electro-optical properties of poly(2-ethynylpyridinium bromide) having propargyl side chain (PEPB-P). Now we report on the electrochemical properties of PEPB-P.

EXPERIMENTAL

PEPB-P sample was prepared by the activation polymerization of the 1:1 mixture of 2-ethynylpyridine and propargyl bromide at MeOH reflux condition for 24 hrs without any additional initiator or catalysts. The polymer yield and inherent viscosity were 95% and 0.21 dL/g, respectively. Details of preparation and purification procedures have already been reported in the previous paper [18]. Because of solubility of PEPB-P in polar solvents such as water, methanol, ethanol, acetonitrile, DMF, DMSO, etc., the electrochemical characteristics were studied in solution and also by utilizing Nafion film which is a perfluorinated ion exchange membrane having sulfonate groups, as a solid electrolyte.

To examine the electrochemical properties, the polymer was coated with solution-coating method onto platinum foil as a working electrode with the area of 1 cm^2. After coating, the films adhered to the electrode were dried in a vacuum oven for 30 min. The thickness of the polymer film was 5 μm. The electrochemical measurements were performed in 0.1 M tetraethylammonium tetrafluoroborate [$(\text{t-Et})_4\text{NBF}_4$] containing DMF solution. Ag wire and platinum foil were used as a reference and a counter electrode, respectively. Cyclic voltammetric waves were produced by using a Hokuto Denko HA-301 potentiostat/galvanostat (AUTOLAB/PG-STAT12) equipped with a HA-301 functional generator and a X-Y reorder.

RESULTS AND DISCUSSION

The cyclic voltammograms of PEPB-P with the consecutive scan are shown in Figure 1. As the cycling number increased up to 250 cycles at the potential range of -0.1 to $+1.6$ V, PEPB showed the well-defined and stable redox process and there was no characteristic change such as the increase of current density in cyclic voltammograms. On the other hand, the oxidation and reduction occurred at 0.84 and 0.69 V, where the pendant pyridinium units were oxidized and reduced.

We also observed the variation of the redox peak current density as the various scan rates (20 mV/s ~ 120 mV/s) to investigate electrochemical kinetic behavior. The peak potential shifts were almost independent of scan rate. Also, the redox current value was typically increased as the scan rate is increased. This result suggests that the electrochemical process is reproducible in the potential range of $-0.1 \sim 1.6\,\text{V}$ *vs.* Ag/Ag. It has been reported that the relationship between redox peak current and the scan rate can be expressed as a power law type as follows [19]

$$i_{\text{p,a}} = kv^x \qquad [1]$$

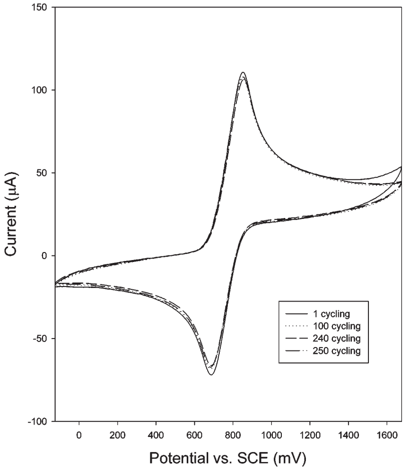

FIGURE 1 Cyclic voltammograms of PEPB with consecutive scan at 100 mV/s (0.1 M Et_4NBF_4/DMF).

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 [20]. The value of x can be calculated by using Eq. [2], obtained by rearranging Eq. [1].

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

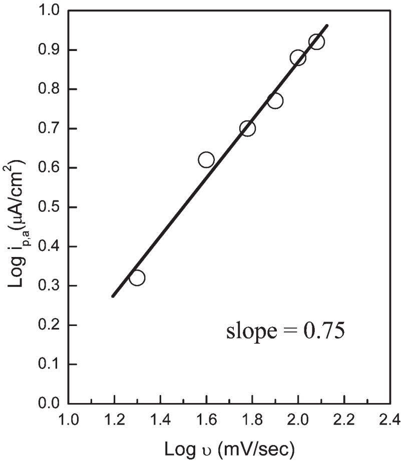

FIGURE 2 Plot of log $i_{\mathrm{p,a}}$ *vs.* log v for PEPB-P.

Relations between the oxidation current density (log $i_{p,a}$) and the scan rate (log v) are shown in Figure 2. The oxidation current density *vs.* the scan rate is approximately linear relationship in the range of 20–120 mV/s. The exponent of scan rate, x value was found to be 0.75. It was concluded that the kinetics of the redox process is mainly controlled by both electron transfer and diffusion process. This means that insertion/desertion of BF_4^- ions is responsible for the charge electron neutrality during the redox process of PEPB-P.

CONCLUSIONS

In this article, we presented the electrochemical properties of a water-soluble ionic conjugated polymer, PEPB-P, which was prepared by the activated polymerisation of 2-ethynylpyridine and propargyl bromide. This polymer showed the well-defined and stable redox process in the range of -0.1 to $+1.6$ V. The oxidation and reduction occurred at 0.84 and 0.69 V, respectively. The redox current value was increased as the scan rate was increased. The exponent of scan rate, x value was found to be 0.75, which means that the redox kinetics is mainly controlled by both electron transfer and diffusion process.

REFERENCES

[1] Chien, J. C. W. (1984). *Polyacetylene*, Academic Press: New York.

[2] Toshima, N. & Hara, S. (1995) *Prog. Polym. Sci.*, *20*, 155.

[3] McQuade, D. T., Pullen, A. E., & Swager, T. M. (2000). *Chem. Rev.*, *100*, 2537.

[4] Ferraris, J. P., Cowan, D. O., Walatka, V. J., & Perlstein, J. H. (1973). *J. Am. Chem. Soc.*, *95*, 948.

[5] Chiang, C. K., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., & MacDiarmid, A. G. (1977). *Phys. Rev. Lett.*, *39*, 1098.

[6] Masuda, T. & Higashimura, T. (1981). *Acc. Chem. Res.*, *17*, 51.

[7] Choi, S. K., Lee, J. H., Kang, S. J., & Jin, S. H. (1997). *Prog. Polym. Sci.*, *22*, 693.

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

[9] Nagai, K., Masuda, T., Nakagawa, T., Freeman, B. D., & Finnau, I. (2001). *Prog. Polym. Sci.*, *26*, 721.

[10] Gal, Y. S., Jin, S. H., Lee, H. J., Kim, S. H., Lee, W. C., & Choi, S. K. (2003). *Macromol. Res.*, *11*, 80.

[11] Tretiak, S. & Mukamel, S. *Chem. Rev.*, (2002). *102*, 3171.

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

[13] Balogh, L. & Blumstein, A. (1995). *Macromolecules*, *28*, 5691.

[14] Blumstein, A. & Samuelson, L. (1998). *Adv. Mater.*, *10*, 173.

[15] 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.

[16] Gal, Y. S., Lee, W. C., Lee, S. J., Park, J. W., Ko, J. M., & Chun, J. H. (1999). *J. Macromol. Sci.-Pure Appl. Chem.*, *A36*, 1503.

[17] Gal, Y. S., Lee, W. C., Lee, S. S., Bae, J. S., Kim, B. S., Jang, S. H., Jin, S. H., & Park, J. W. (2000). *Kor. Polym. J.*, *8*, 131.

[18] 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.

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

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