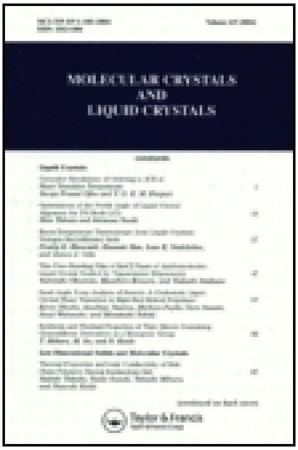

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Electrochemical Properties of Poly(α-methylbenzyl dipropargylamine) Prepared by the Cyclopolymerization of α-Methylbenzyl dipropargylamine

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The electrochemical properties of poly(α-methylbenzyl dipropargylamine) was studied by cyclic voltametry. Poly(α-methylbenzyl dipropargylamine) was prepared by the cyclopolymerization of α-methylbenzyl dipropargylamine in high yield. The photoluminescence peaks of the present polymer was observed at 443 nm corresponding to the photon energy of 2.80 eV. The cyclovoltamograms of the polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of poly(MBDPA) might be mainly controlled by the electron transfer process from the experiment of the oxidation current density of poly(MBDPA) versus the scan rate.

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Keywords: catalyst; conjugated polymer; cyclopolymerization; polyacetylene; α-methylbenzyl dipropargylamine

1. INTRODUCTION

In recent years, the electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [1]. The technological developments in plastic electronics and photonics have been required to gain a much fundamental understanding of the nature of electronic excitations, charge carriers, and transport phenomena in ordered and disordered conjugated organic materials [1–3].

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. It can be made free-standing thin film by using Shirakawa catalysts [$Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$] [4]. However, the drawbacks are that PA is thermally unstable and insoluble, making it unsuitable for general use. More processable conjugated polymers can be prepared by the linear polymerization of substituted acetylene monomers and by the cyclopolymerization of nonconjugated diynes [5–14].

Cyclopolymerization of nonconjugated diynes is very interesting method for the synthesis of conjugated polymer system via an alternating intramolecular–intermolecular chain propagation [6,8,9]. The simplest conjugated cyclopolymer, poly(1,6-heptadiyne), was prepared by the polymerization of 1,6-Heptadiyne by various transition metal catalysts in high yield [15,16]. However, the resulting poly(1,6-heptadiyne)s were also insoluble in any organic solvent and unstable to air oxidation as like with that of PA. Introduction of substituents at 4-position of 1,6-heptadiyne can help enhance the processibility and stability of the polyene systems, thus a variety of substituted poly(1,6-heptadiyne)s were designed and synthesized [6,17–23].

Nitrogen-containing polymers have received unabated attention in the design and synthesis of multifunctional polymers [6]. Unlike other π-conjugated polymers, they contain nitrogen heteroatom either in the main chains or in the side chains that provide facile quaternarization reaction and protonation of the nitrogen sites [5,6]. In our previous paper, we reported the studies on the synthesis and characterization of new conjugated cyclopolymer by the cyclopolymerization of a dipropargylamine derivative [22].

Now, we report the electro-optical and electrochemical properties of poly(α-methylbenzyldipropargylamine) [poly(MBDPA)] prepared by the cyclopolymerization of α-methylbenzyl dipropargylamine.

2. EXPERIMENTAL

The poly(MBDPA) was prepared by the polymerization of MBDPA by using the catalyst of $MoCl_5$-$EtAlCl_2$ (1:2) under nitrogen atmosphere for 24 hrs at 90°C. The diluted polymer solution was precipitated into an large excess of ethyl ether, filtered from the solution, and then dried under vacuum at 40°C for 12 hrs. The polymer yield was 61% and the number-average molecular weight was 9,300. The spectroscopic studies on the microstructures of this cyclopolymer indicated that the polymer contains the mixture of five and six-membered ring moieties [22]. The polymers were generally soluble in halogenated and aromatic hydrocarbons such as chloroform, chlorobenzene, DMF, DMSO etc.

NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. 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). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. ITO, Ag/$AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

3. RESULTS AND DISCUSSION

We prepared a new conjugated cyclopolymer by the cyclopolymerization of α -methylbenzyl dipropargylamine by using transition metal catalysts and elucidated the polymer structure by NMR, IR, and UV-visible spectroscopies [22]. The present poly(MBDPA) sample was prepared by using the $MoCl_5$-$EtAlCl_2$ catalyst system. The polymer yield and number-average molecular weight were 61% and 9,300, respectively. The polymers were generally soluble in halogenated and aromatic hydrocarbons such as chloroform, chlorobenzene, DMF, DMSO etc. Figure 1 shows the chemical structure of poly(MBDPA).

The electro-optical properties of poly(MBDPA) were measured and discussed. Figure 2 shows the UV-visible spectra and photoluminescence (PL) spectra of poly(MBDPA) solution (0.1 wt.%, DMF). In our

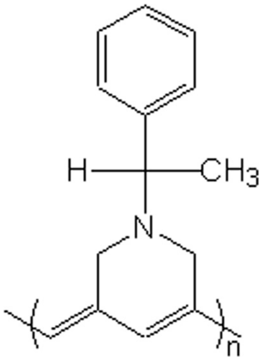


FIGURE 1 The chemical structure of poly(MBDPA).

previous papers [24,25], we had reported the PL spectra of 9,9-dipropargyl fluorene and poly(2-ethynyl-N-propagylpyridinium bromide), they showed 432 nm and 510 nm PL maximum values at each excitation wavelength of UV maximum value. Poly(MBDPA) showed characteristic UV-visible absorption band at 310 nm and blue PL spectrum at 443 nm corresponding to the photon energy of 2.80 eV.

To investigate the electrochemical kinetic behavior, the measured cyclic voltammograms of poly(MBDPA) with the various scan rates

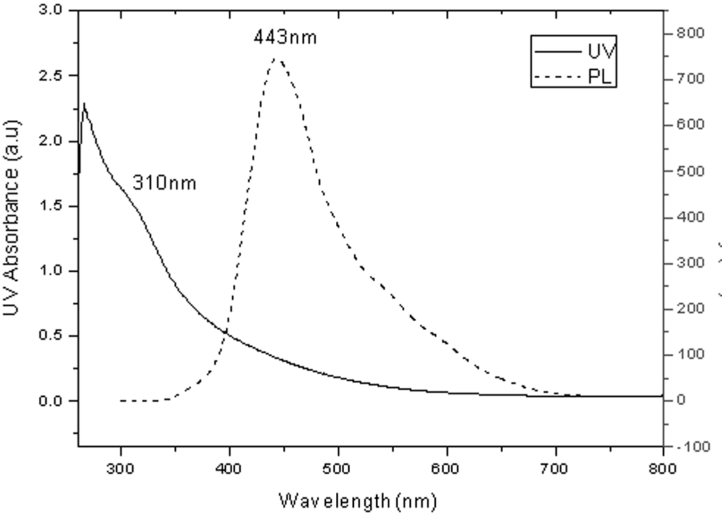
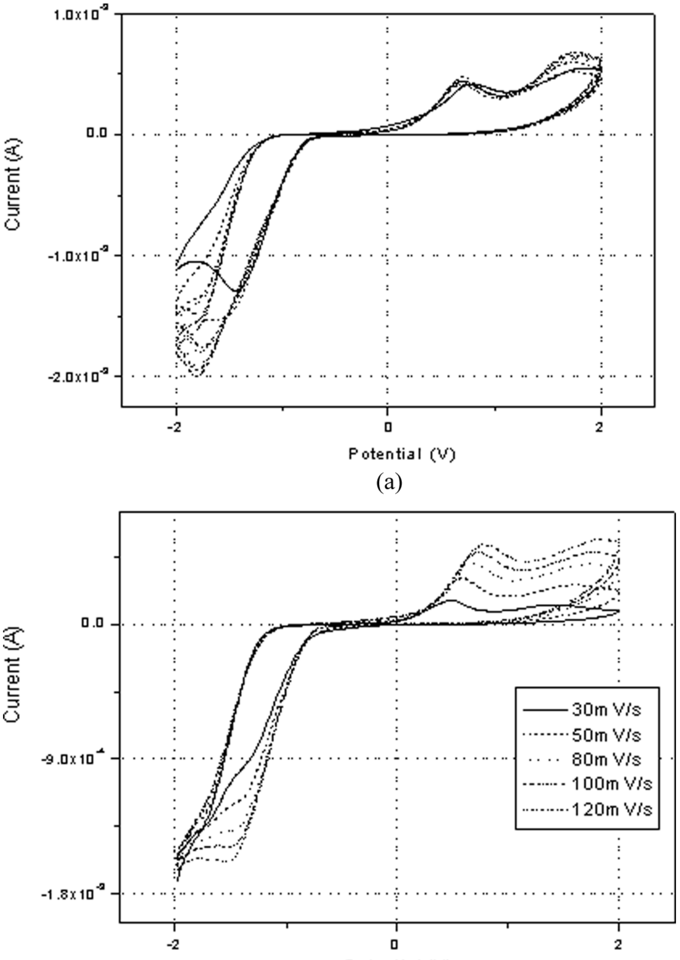


FIGURE 2 Optical absorption and photoluminescence spectra of poly(MBDPA) solution.

(30 mV/s ~ 120 mV/s) are shown in Figure 3(b). The peak potentials are gradually shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of poly (MBDPA) from the consecutive scan (up to 30 cycles) in Figure 3(a), which means that this material has relatively stable redox process.



(a)

(b)

FIGURE 3 Cyclic voltammograms of poly(MBDPA) [0.1 M(n-Bu)$_4$NBF$_4$/DMF] (a) consecutive 30 scans under 100 mV/s and (b) 30 mV/sec ~ 120 mV/sec with various scan rates.

In Figure 3, the oxidation of poly(MBDPA) was occurred at 0.7 V (vs Ag/AgNO$_3$), where vinylene unit of conjugated polymer backbone might be oxidized in the scan. Poly(MBDPA) also shows the irreversible reduction at -1.5 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(MBDPA) is reproducible in the potential range of $-2.0\sim+2.0$ V vs Ag/AgNO$_3$.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [26,27].

$$i_{\mathrm{p,a}} = k\nu^{x} \tag{1}$$

$$\log i_{\mathrm{p,a}=\log k+\mathrm{x}\log\nu} \tag{2}$$

where $i_{\mathrm{p,a}}$ = oxidation peak current density, ν = scan rate, k = proportional constant, and x = exponent of scan rate.

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 [26,28]. Relations satisfying Eq. (2) between the oxidation current density ($\log i_{\mathrm{p,a}}$) and the scan rate ($\log\nu$) are shown in Figure 4. The oxidation current density of poly(MBDPA) versus the scan rate is approximately linear relationship in the range of 30 mV/sec ~ 120 mV/sec.

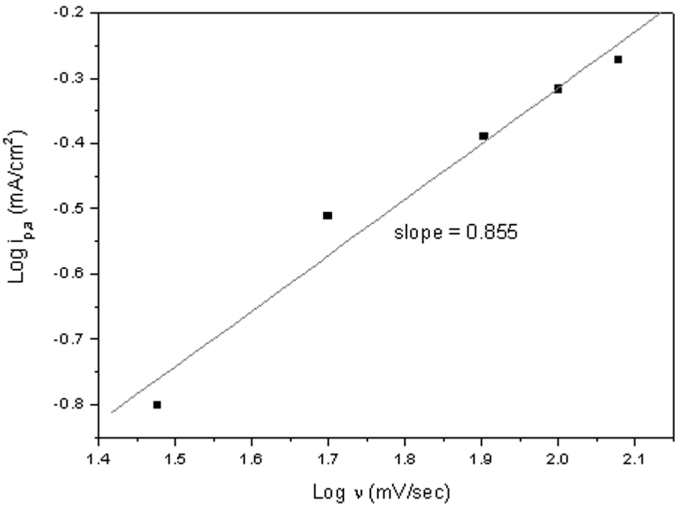


FIGURE 4 Plot of $\log i_{\mathrm{p,a}}$ vs $\log\nu$ for poly(MBDPA).

The exponent of scan rate, x value of poly(MBDPA), is found to be 0.855. This value means that the kinetics of the redox process may be mainly controlled by the electron transfer process [26–28].

4. CONCLUSIONS

In this article, we presented the research results on the electro-optical and electrochemical properties of a new conjugated cyclopolymer prepared by the cyclopolymerization of MBDPA. The photoluminescence (PL) spectra of poly(MBDPA) showed that the photoluminescence peak is located at 443 nm corresponding to the photon energy of 2.80 eV. The cyclovoltamograms of the polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of poly (MBDPA) might be mainly controlled by the electron transfer process from the experiment of the oxidation current density of poly(MBDPA) versus the scan rate. This conjugated polymer may be a candidate material for organic semiconductor, chemical sensor, fluorescence quencher, permselective membrane, and nanocomposites.

REFERENCES

[1] Bredas, J.-L., Beljonne, D., Coropceanu, V., & Cornil, J. (2004). *Chem. Rev.*, *104*, 4971.

[2] Shirota, Y. & Kageyama, H. (2007). *Chem. Rev.*, *107*, 953.

[3] Lo, S. C. & Burn, P. L. (2007). *Chem. Rev.*, *107*, 1097.

[4] Ito, T., Shirakawa, H., & Ikeda, S. (1974). *J. Polym. Sci.: Part A: Polym. Chem.*, *12*, 11.

[5] Masuda, T. & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.

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

[7] Lam, J. W. Y. & Tang, B. Z. (2003). *J. Polym. Sci.: Part A: Polym. Chem.*, *41*, 2607.

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

[9] Buchmeiser, M. R. (2005). *Adv. Polym. Sci.*, *176*, 89.

[10] Mayershofer, M. & Nuyken, O. (2005). *J. Polym. Sci.: Part A: Polym. Chem.*, *43*, 5723.

[11] Gui, T. L., Yin, J. H., Wang, D. X., Jin, S. H., Lee, H. J., Lim, K. T., Lyoo, W. S., & Gal, Y. S. (2006). *Mol. Cryst. &. Liq. Cryst.*, *459*, 19.

[12] Gal, Y. S., Jin, S. H., Lim, K. T., Kim, S. H., Lyoo, W. S., Lee, C. J., Park, J. W., & Kim, S. Y. (2007). *Mol. Cryst. &. Liq. Cryst.*, *462*, 189.

[13] Gal, Y. S., Park, J. H., Jin, S. H., Lim, K. T., Lee, C. J., Park, J. W., Lee, W. C., & Kim, S. Y. (2007). *Curr. Appl. Phys.*, *7*, 480.

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

[15] 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.

[16] Gal, Y. S., Lee, W. C., Gui, T. L., Jin, S. H., Koh, K., Kim, S. H., Kim, D. W., Ko, J. M., & Chun, J. H. (2001). *Korea Polymer J.*, *9*, 220.

[17] Lee, H. J., Gal, Y. S., Lee, W. C., Oh, J. M., Jin, S. H., & Choi, S. K. (1995). *Macromolecules*, *28*, 1208.

[18] Gal, Y. S., Jung, B., Lee, W. C., Lee, H. J., & Choi, S. K. (1995). *Macromolecules*, *28*, 2086.

[19] Gal, Y. S., Jin, S. H., Lee, H. S., & Kim, S. Y. (2005). *Macromol. Res.*, *13*, 491.

[20] Naidu, B. V. K., Oh, B. H., Nam, D. H., Hwang, C. K., Jin, S. H., Lim, K. T., Hwang, H. S., Lee, J. W., & Gal, Y. S. (2006). *J. Polym. Sci.: Part A: Polym. Chem.*, *44*, 1555.

[21] Czekelius, C., Hafer, J., Tonzetich, Z. J., Schrock, R. R., Christensen, R. L., & Muller, P. (2006). *J. Am. Chem. Soc.*, *128*, 16664.

[22] Gal, Y. S., Lee, W. C., Jin, S. H., Lim, K. T., Jang, S. H., Lyoo, W. S., Han, E., & Kim, S. Y. (2007). *Macromol. Res.*, *15*, 267.

[23] Gal, Y. S., Lee, I. S., Chang, E. H., Jeong, Y. C., & Kwak, Y. W. (2007). *Bull. Korean Chem. Soc.*, *28*, 1305.

[24] Gal, Y. S., Jin, S. H., Gui, T. L., Chun, J. H., Koh, K. N., Kim, S. H., Lee, W. C., & Park, J. W. (2004). *Mat. Sci. & Eng. C*, *24*, 173.

[25] Gal, Y. S., Gui, T. L., Jin, S. H., Park, J. W., Koh, K. N., Lee, W. C., Kim, S. H., & Kim, S. Y. (2003). *Synthetic Metals*, *353*, 135–136.

[26] Park, J. W., Lee, J. H., Ko, J. M., Cho, H. N., & Choi, S. K. (1994). *J. Polym. Sci.: Part A: Polym. Chem.*, *32*, 2789.

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

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