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A monosubstituted ionic polyacetylene having a quaternary ammonium salt was synthesized and characterized. The polymerization of dimethylphenylpropargylammonium bromide (DMPPAB) was performed by various transition metal catalysts to give the resulting polymer in high yield. The polymer structure was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituent. This polymer was mostly soluble in organic solvents. The electrochemical properties of poly(DMPPAB) were measured and discussed.

Keywords Conjugated polymer; cyclovoltamogram; dimethylphenylpropargylammonium bromide; polyacetylene; transition metal catalyst

Introduction

Considerable progress has been made in the synthesis and applications of oligomers and polymers having a π-conjugated backbone [1–7]. These conjugated organic materials are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1,8]. Because of these properties, polyacetylene

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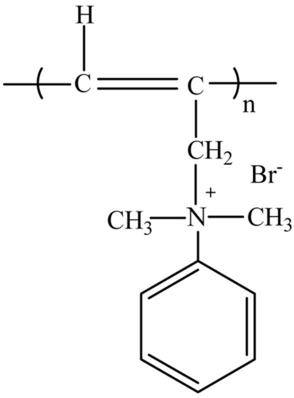


Figure 1. The chemical structure of poly(DMPPAB).

and its homologues have been promising materials for photovoltaics, displays, lasers, nonlinear optical materials, membranes for gas separation and for liquid-mixture separation and chemical sensors [4–7,9–13].

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. The natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building blocks of life, the nucleic acids and proteins, are polyelectrolytes. Synthetic polyelectrolyte have been and continue to be a very active of scientific research and commercial growth [14].

Such ionic polyacetylenes as poly(propiolic salt)s [15], triethylammonium salt of poly(6-bromo-1-hexyne) [16], poly(propargylammonium salt)s and poly(dipropargylammonium salt)s [17–19] were reported. We have prepared a new family of substituted polyacetylenes that retain extensive conjugation. They were prepared through the activated polymerization of ethynylpyridines by using the functional alkyl halides [13,20–23]. And also, we have also prepared various ionic conjugated polymers having different functionalities from the transition metal-catalyzed polymerization of ionic acetylenic monomers [24,25]. Because the conjugated polymers contain extensive conjugation and ionic nature, this ionic polyacetylene family has potentials as material candidates for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices [1,26,27].

Now, we report the synthesis of a new ionic polyacetylene derivative with quaternary ammonium salt via the transition-metal catalyzed polymerization of DMPPAB and the characterization of the resulting poly(DMPPAB)] (Fig. 1).

Experimental

$PdCl_2$ (99.9+%), $RuCl_3$, and (bicyclo[2.2.1]hepta-2,5-diene)-dichloropalladium (II) [(NBD)$PdCl_2$] were purchased from Aldrich Chemicals and used as received. DMPPAB was prepared by the reaction of propargyl bromide and dimethylphenylamine in acetonitrile as reported method (yield: 81%) [18]. DMPPAB was purified by the recrystallization from ethanol-ether. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

A typical synthetic procedure of poly(DMPPAB) is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (4.16 mmol) of DMPPAB, 0.037 g

(0.139 mmol, M/C = 30) of (NBD)PdCl$_2$, and 7 mL of DMF were added in that order given. Then the polymerization was carried out at 80°C for 24 hrs under nitrogen atmosphere. As the polymerization proceeds, the reaction solution became into viscous dark-red 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 black polymer powder was obtained in 83% 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. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: Xpert-APD). The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR spectrometer. Redox potential of the polymer was determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 100 mV/s or various scan rate from 30 to 150 mV/s. The synthesized polymer was dissolved in acetonitrile (AN) with 0.1 M tetrabutylammonium perchlorate (TBAP) as an electrolyte. We used a platinum working electrode and a saturated Ag/AgNO$_3$ reference electrode. Ferrocene was used for potential calibration (all reported potentials are reference against ferrocene/ferrocenium, FOC) and for reversibility criteria.

Results and Discussion

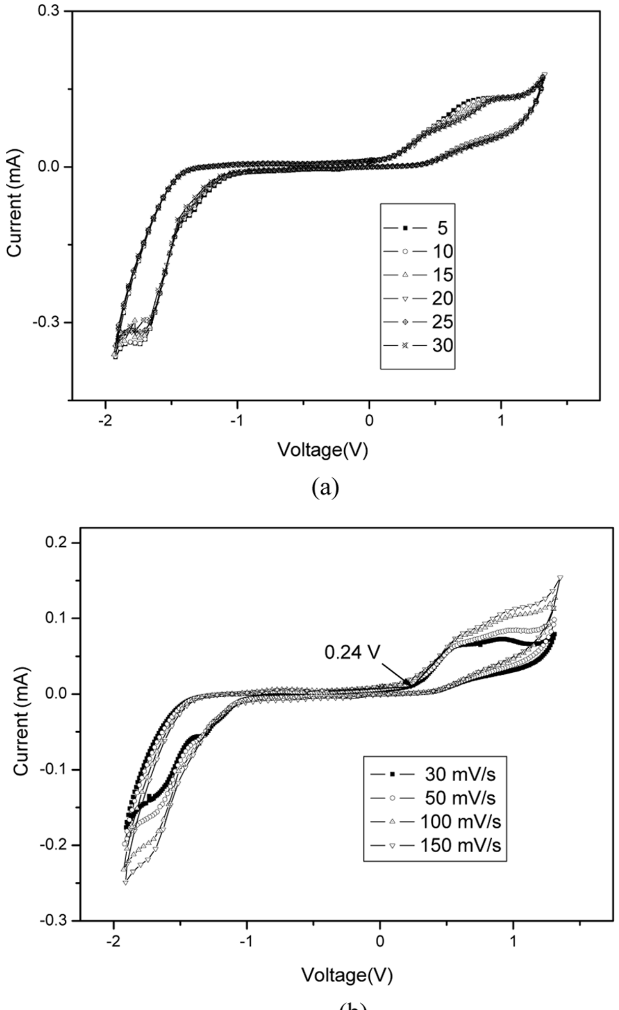
We performed the polymerization of DMPPAB by using transition metal catalysts. We firstly test the polymerization of DMPPAB by W- and Mo-based catalysts, which were found to be very effective for the polymerization of some monosubstituted acetylenes and the cyclopolymerization of various dipropargyl monomers [1–3,28]. However, W-based catalysts such as WCl$_6$ and WCl$_6$-EtAlCl$_2$ failed to polymerize the present monomer. And also MoCl$_5$ gave only a trace amount of oligomeric product.

PdCl$_2$ was found to effectively polymerize DMPPAB to give the corresponding polymer in high yield (85%) although this monomer carry the bulky quaternary ammonium salts. The polymer yields were slightly decreased when PtCl$_2$ and RuCl$_3$ were used as catalyst (62% and 75%, respectively). (NBD)PdCl$_2$, which showed good solubility in the polymerization solvent, polymerized DMPPAB to give the corresponding polymer in 83% yield. The present polymerizations proceeded mostly in mild manner.

The polymer structure was characterized by various instrumental methods such as IR, NMR, UV-visible spectroscopies. The FT-IR spectrum of DMPPAB did not show the acetylenic C$\equiv$C bond stretching and acetylenic $\equiv$C$-$H bond stretching frequencies of the monomer. Instead, the C=C stretching frequency peak of conjugated polymer backbone at 1580–1660 cm^{-1} became more intense than that of the monomer. The ^{1}H-NMR spectrum of poly(DMPPAB) showed the phenyl protons and the vinyl protons of the conjugated polymer backbone at 6.5–8.4 ppm. The characteristic aliphatic methyl and methylene proton peaks was also observed at 2.4–5.0 ppm.

In the ^{13}C-NMR spectrum of poly(DMPPAB), the acetylenic carbon peaks of monomer at 72.68 and 82.72 ppm were disappeared and the aromatic and vinyl carbon peaks of polymer were observed at the region of 110–155 ppm. The methyl and methylene carbon peaks were seen at 44.5 and 55.2 ppm, respectively. In the UV-visible spectra, the absorptions at long wavelength (up to 650 nm) due to the $\pi \rightarrow \pi^*$ interband transition of the conjugated polymer systems were observed. From these spectral data, we concluded that the present polymer have the conjugated polymer backbone system with the designed substituents. The morphology of poly(DMPPAB) powder sample was studied by X-ray diffraction analysis. Because the peaks in the diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, the present poly(DMPPAB) was mostly amorphous [1,2]. The inherent viscosities of poly (DMPPAB)s were in the range of 0.10–0.15 dL/g.

In order to characterize the electrochemical kinetic behavior and an electrochemically stable window, the cyclic voltammograms (CVs) of poly(DMPPAB)



(a)

(b)

Figure 2. Cyclic voltammograms of poly(DMPPAB) in 0.1 M TBAP/acetonitrile solution: (a) consecutive scans under 100 mV/sec, (b) various scan rates of 30 mV/sec~150 mV/sec.

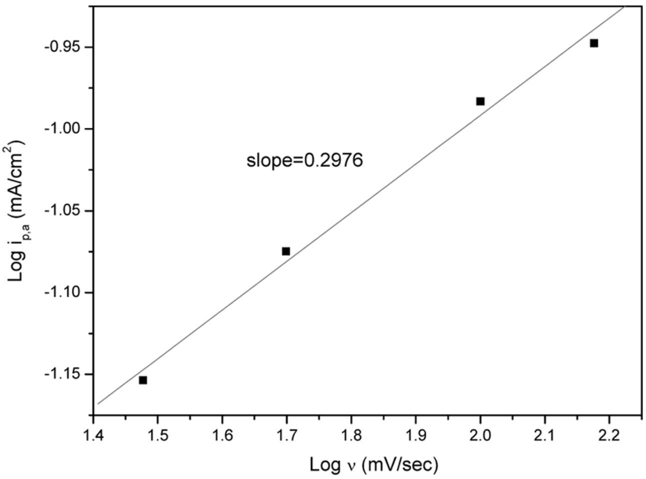


Figure 3. Plot of log $i_{p,a}$ *vs* log v for poly(DMPPAB) cyclic voltammograms.

including a consecutive scan and various scan rates (30 mV/s∼150 mV/s) were recorded as shown in Figure 2. Typical CVs obtained at the scan rate of 100 mV/s for poly(DMPPAB) solution are presented in Figure 2(a). We have observed that the shape of CVs is almost unchanged, concluding that poly(DMPPAB) is fairly stable without any severe degradation up to 30 cycles of the consecutive scan. In Figure 2(b), as the speed of scan rate was increased, the peak potentials were gradually shifted to higher potentials and the current values were increased. Finally, the oxidation of poly(DMPPAB) was occurred at 0.24 V (vs Ag/AgNO$_3$), where vinylene group of conjugated polymer backbone might be oxidized in the scan. Poly(DMPPAB) also shows the irreversible reduction at −1.90 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(DMPPAB) is reproducible in the potential range of −2.0∼+1.5 V vs Ag/AgNO$_3$ (Fig. 2).

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 [29–31].

$$i_{p,a} = kv^{x} \tag{1}$$

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

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

Considering that electrode kinetics satisfy Eq (1), the electrochemical redox reaction is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5. The relationship plot of the oxidation current density (log $i_{p,a}$) as a function of the scan rate (log v) is shown in Figure 3. The oxidation current of poly(DMPPAB) versus the scan rate is approximately linear relationship in the range of 30 mV/sec∼150 mV/sec and the exponent of scan rate, x value is found to be 0.2976. This value means that the kinetics of the redox process is not so active and is controlled by the diffusion process.

Conclusions

A new conjugated polymer with bulky quaternary ammonium salts was synthesized and characterized. The polymerization of DMPPAB catalyzed by transition metal catalysts proceeded well to give high yield of polymer. The polymer structure was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituents. This polymer was mostly soluble in organic solvents. The CVs 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(DMPPAB) might be controlled by the diffusion process from the experiment of the oxidation current density of poly(DMPPAB) versus the scan rate.

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References

[1] Kang, K. L., Kim, S. H., Cho, H. N., Choi, K. Y., & Choi, S. K. (1993). *Macromolecules*, *26*, 4539.
[2] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[3] Lam, J. W. Y. & Tang, B. Z. (2005). *Acc. Chem. Res.*, *38*, 745.
[4] Masuda, T. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 165.
[5] Potje-Kamloth, K. (2008). *Chem. Rev.*, *108*, 367.
[6] Joo, S. & Brown, R. B. (2008). *Chem. Rev.*, *108*, 638.
[7] Hatchett, D. W. & Josowicz, M. (2008). *Chem. Rev.*, *108*, 746.
[8] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., & Holmes, A. B. (2009). *Chem. Rev.*, *109*, 897.
[9] Kwak, G., Jin, S. H., Park, J. W., & Gal, Y. S. (2008). *Macromol. Chem. Phys.*, *209*, 1769.
[10] Gal, Y. S., Lee, W. C., Jin, S. H., Lim, K. T., Park, J. W., & Kim, S. Y. (2008). *Mol. Cryst. Liq. Cryst.*, *492*, 229.
[11] Gal, Y. S., Jin, S. H., Hyun, A. R., Park, Y. I., Park, J. W., Lim, K. T., & Lee, W. C. (2008). *J. Ind. Eng. Chem.*, *14*, 468.
[12] Lee, S. J., Park, J. S., Yoon, K. J., Kim, Y. I., Jin, S. H., Kang, S. K., Gal, Y. S., Kang, S., Lee, J. Y., Kang, J. W., Lee, S. H., Park, H. D., & Kim, J. J. (2008). *Adv. Funct. Mater.*, *18*, 3922.
[13] Gal, Y. S., Jin, S. H., Park, J. W., & Lim, K. T. (2009). *J. Polym. Sci.: Part A: Polym. Chem.*, *47*, 6153.
[14] Yang, S. Y. & Rubner, M. F. (2002). *J. Am. Chem. Soc.*, *124*, 2100.
[15] Davidov, B. E., Krentsel, B. A., & Kchutareva, G. V. (1967). *J. Polym. Sci.: Part C*, *16*, 1365.
[16] Kawasaki, M., Masuda, T., & Higashimura, T. (1983). *Polymer J.*, *15*, 767.
[17] Kim, S. H., Choi, S. J., Park, J. W., Cho, H. N., & Choi, S. K. (1994). *Macromolecules*, *27*, 2339.
[18] Gal, Y. S., Lee, W. C., Jang, S. H., Lee, H. J., & Jin, S. H. (1997). *Polymer (Korea)*, *21*, 737.

[19] Vygodskii, Y. S., Shaplov, A. S., Lozinskaya, E. L., Vlasov, P. S., Malyshkina, I. A., Gavrilova, N. D., Kumar, P. S., & Buchmeiser, N. R. (2008). *Macromolecules*, *41*, 1919.

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

[21] Gal, Y. S., Jin, S. H., & Kim, S. H. (2006). *J. Ind. Eng. Chem.*, *12*, 235.

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

[23] Gal, Y. S., Jin, S. H., Karim, M. A., & Cho, Y. R. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 165.

[24] Gal, Y. S. (1994). *J. Chem. Soc., Chem. Commun.*, 327.

[25] Gal, Y. S., Jung, B., Lee, W. C., & Choi, S. K. (1995). *Synth. Met.*, *69*, 549.

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

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

[28] 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.

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

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

[31] Kim, Y. E., Kwon, Y. S., Lee, K. S., Park, J. W., Seo, H. J., & Kim, T. W. (2004). *Mol. Cryst. Liq. Cryst.*, *424*, 153.