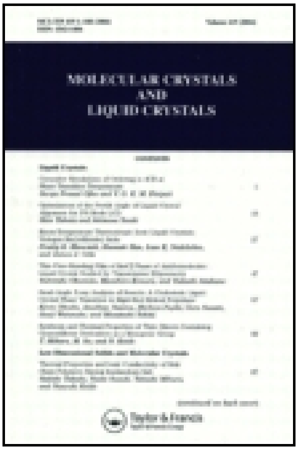

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Electro-Optical and Electrochemical Properties of Poly(phenylacetylene)

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Electro-Optical and Electrochemical Properties of Poly(phenylacetylene)

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Poly(phenylacetylene)[Poly(PA)] was prepared by the polymerization of phenylacetylene with the catalyst of (NBD)$PdCl_2$. The instrumental analysis data on the polymer structure revealed that the poly(PA) have the conjugated polyene backbone structure with phenyl substituents. The band gap energy of poly(PA) was estimated to be 2.51 eV and the photoluminescence spectra of poly(PA) showed that the photoluminescence peak is located at 439 nm, corresponding to a photon energy of 2.82 eV. The cyclovoltamograms of poly(PA) exhibited that the irreversible oxidation and reduction were occurred at 0.38 V and −0.93 V, respectively (vs Ag/$AgNO_3$). The redox current value gradually increased as the scan rate increased.

Keywords: characterization; conjugated polymer; cyclovoltamogram; photoluminescence; poly(phenylacetylene)

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INTRODUCTION

Considerable progress has been made in the synthesis and characterization of various types of conjugated polymers because of their extraordinary electronic and optical properties [1–3]. In recent years, the examined applications of conjugated polymers include organic light-emitting diodes (OLEDs), chemical sensors, photovoltaic cells, field-effect transistors, and so on [4–8]. The acetylenic triple bonds have rich π-electrons, which can be easily polymerized to yield the linear conjugated polymer systems [2].

The Mo- and W-based catalysts have been used as the catalyst system for the polymerization of acetylene derivatives having various functionalities [9–14]. Especially Mo-based catalyst systems have been known to be effective for the polymerization of substituted acetylenes containing some polar functional groups such as hydroxy, carboxylic acid and ester, amines and ethers [15–19]. And also, it was reported that a novel molybdenum oxytetrachloride ($MoOCl_4$)-based catalyst ($MoOCl_4$-Et_3Al-EtOH, $MoOCl_4$-Et_2Zn-EtOH) induces the living polymerization of *o*-(trifluoromethyl)phenylacetylene [20].

The polymerization of phenylacetylene, a typical acetylene derivative, have been carried out by various initiator systems [15,21,22]. We have also reported the polymerization of phenylacetylene by $MoCl_5$/2-propyn-1-ol homologues [23,24] and $Mo(OEt)_5$-$EtAlCl_2$ catalyst system [25]. Group IV metallocene catalysts such as Cp_2TiCl_2, Cp_2ZrCl_2, Cp_2HfCl_2/R_xAlCl_{3-x}, $Cp_2MoCl_2/EtAlCl_2$ have been applied for the polymerization of acetylene derivatives [22,26,27]. To our knowledge, there have been no reports on the studies for the polymerization of phenylacetylene using (bicyclo[2.2.1]hepta-2,5-diene) dichloro palladium(II) [(NBD)$PdCl_2$]. And also, the systemmatic studies on the electro-optical and electrochemical properties of the resulting poly(PA) did not carried out.

Here, we report the polymerization behaviors of PA by using (NBD)$PdCl_2$. And the electro-optical and electrochemical properties of poly(PA) were measured and discussed.

EXPERIMENTAL

PA (Aldrich Chemicals., 98%) was vacuum distilled after drying with calcium hydride. (NBD)$PdCl_2$ (Aldrich Chemicals) was used as received. The polymerization solvent, chlorobenzene, was dried with calcium hydride and distilled. A typical synthetic procedure of poly(PA) is as follows:

In a 50 mL reactor equipped with rubber septum, 0.175 g of (NBD)PdCl$_2$, (M/C = 30) and 10 mL DMF ($[M]_0 = 1.63$ M) were added. And PA (2.0 g, 19.58 mmol) was added into the polymerization reactor. After 24 hrs at 80°C, the polymer solution diluted with 10 mL chloroform was precipitated into a large excess of methanol. The precipitated polymer was filtered and dried in vacuum oven at 40°C for 24 hrs. The orange-colored powder was obtained in 41% yield.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR (^{1}H- and ^{13}C-)spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d$_6$ and the chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Elemental analyses were performed with FISONS EA1110 Elemental Analyzer. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 2200 thermogravimetric analyzer. The optical absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. 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 DMF. ITO, Ag/AgNO$_3$ and platinum wire were used as a working, reference and counter electrode, respectively. 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

We used the homogeneous (NBD)PdCl$_2$ catalyst, which shows excellent solubility in the polymerization solvent (DMF). To date, this catalyst has not been used for the polymerization of phenylacetylene. This catalyst polymerized PA in mild homogeneous manner to give a moderate yield of polymer (41%). The number-average molecular weight of this polymer was relatively low (Mn = 3,650) and the polydispersity (Mw/Mn) was 2.31.

The polymer structure of the resulting poly(PA) was characterized by elemental analyses, NMR (^{1}H- and ^{13}C-), infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(PA) agreed with the theoretical value: calcd for $(C_8H_6)n$: C, 94.08%; H, 5.90% found: C, 93.23%; H, 5.60%.

Figure 1 shows the ^{1}H-NMR spectrum of poly(PA) prepared by (NBD)PdCl$_2$ catalyst. It shows the broad peak at 5.8–8.2 ppm, which

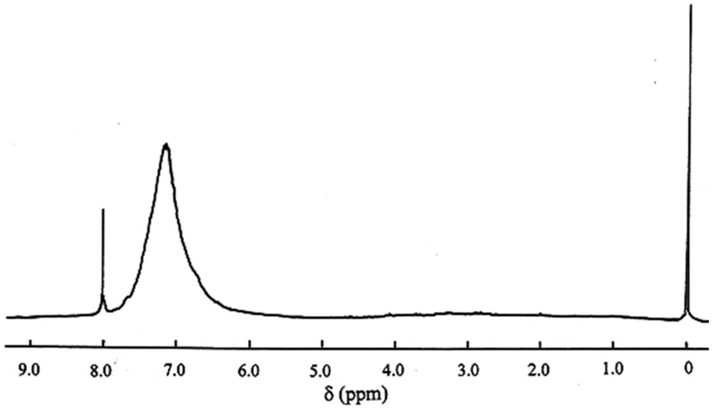

FIGURE 1 ^{1}H-NMR spectrum of poly(PA).

is originated from the protons of aromatic phenyl substituent and the vinyl protons of conjugated polymer backbone. Figure 2 shows the ^{13}C-NMR spectrum of poly(PA) in $CDCl_3$. The chemical shift of the carbons on the phenyl substituent and the carbons on the conjugated double bond of the polymer backbone were observed at 124–146 ppm.

In the IR spectrum of poly(PA), it did not show the acetylenic C≡C bond stretching frequency and the acetylenic ≡C−H stretching frequency. Instead, the C=C stretching frequency peak of conjugated polymer backbone at 1600 cm^{-1} became more intense than those of

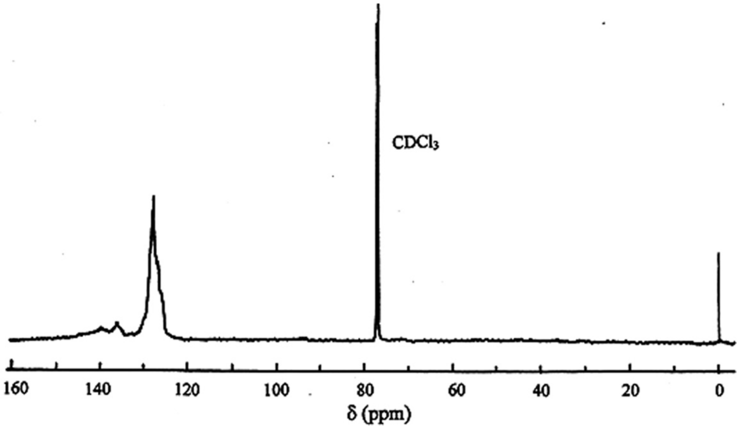

FIGURE 2 ^{13}C-NMR spectrum of poly(PA).

PA. It shows the aromatic =C–H stretching frequencies of phenyl substituents at 3021 and 3055 cm^{-1}. The absorption frequencies at 757 and 698 cm^{-1} are due the C–H out-of-plane deformation of mono-substituted benzene. The UV-visible spectrum of poly(PA) prepared by (NBD)$PdCl_2$ catalyst also showed a characteristic peak of conjugated polymer, a wide broad $\pi \rightarrow \pi^*$ absorption up to 550 nm. These spectral data indicates that the resulting poly(PA) have a conjugated polymer backbone system carrying pendant phenyl substituents.

The resulting poly(PA)s were generally orange-colored powders. The solubility test was performed for powdery samples in excess solvent. The poly(PA)s were completely soluble in THF, chloroform, benzene, chlorobenzene, and but insoluble in methanol, ethyl ether, and n-hexane.

Figure 3 shows the TGA thermogram of poly(PA), which was measured under nitrogen atmosphere at a heating rate of 10°C/min. This thermogram shows an abrupt weight loss after 250°C, which is originated from the thermal decomposition and the cross-linking of the present polymer system. The slight weight loss at relatively low temperature (around 100°C) is due to the moisture and/or organic residues absorbed during the process.

The electro-optical properties of poly(PA) were measured and discussed. The UV-visible spectra and photoluminescence (PL) spectra of poly(PA) solution (0.1 wt.%, DMF) were measured. Figure 4 shows

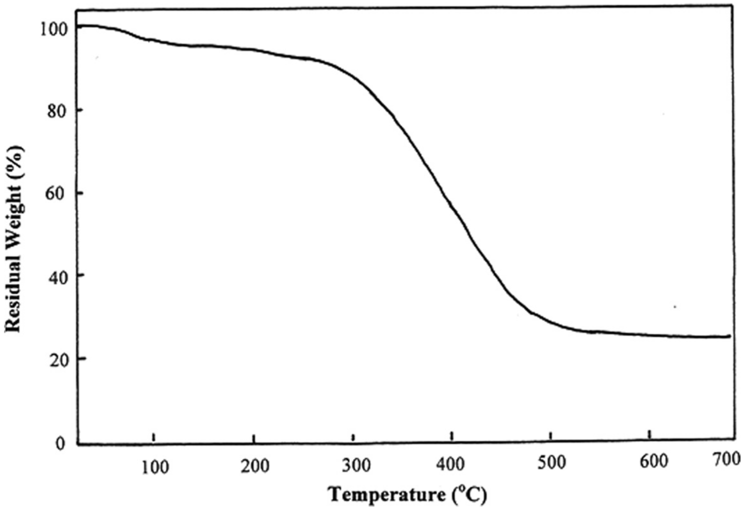

FIGURE 3 TGA thermogram of poly(PA).

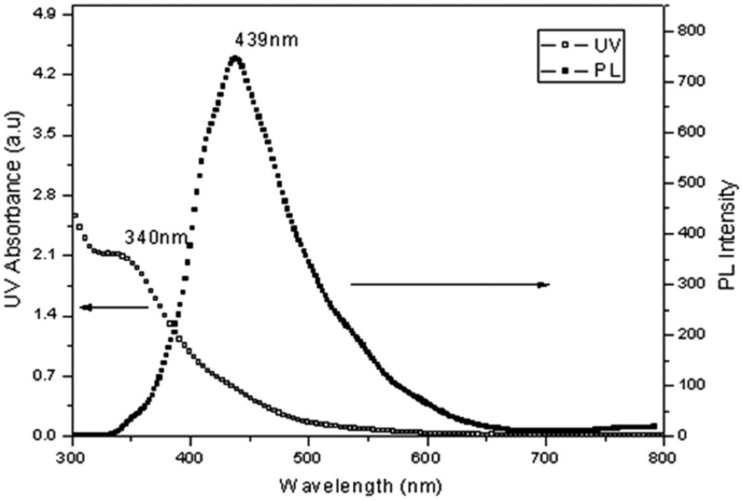

FIGURE 4 Optical absorption and photoluminescence spectra of poly(PA).

the UV-visible spectra and photoluminescence (PL) spectra of poly(PA). Poly(PA) showed characteristic UV-visible absorption band at 340 nm and PL spectrum at 439 nm, indicating relatively blue-shifted PL maximum value. The similar homologue, poly(phenyl propargyl sulfide), which included same polyacetylene backbone and similar side group of benzylic sulfide instead of side phenyl group of poly(PA), showed PL maximum value of 460 nm [28]. The blue-shifted PL maximum value of poly(PA) could be explained by that the adjacent side group of phenyl ring makes steric interaction to conjugated polyacetylene backbone. The band gap energy of poly(PA) was estimated to be 2.51 eV from the analysis of the absorption edge with a plot of $(h\upsilon)$ vs. $(\alpha h\nu)^2$, where α, h, and ν are the absorbance, Planck's constant, and the frequency of light, respectively.

The electrochemical kinetic behavior of poly(PA) was also studied by the cyclic voltammograms measuring with the various scan rates (30 mV/s ~ 150 mV/s) as well as consecutive scans of 30 cycles. The peak potentials are very slighty shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of poly(PA) under the 30 consecutive cycles, suggesting that this material has relatively stable redox process in the potential range of $-2.4 \sim +1.6$ V vs $Ag/AgNO_3$. The irreversible oxidation and reduction of poly(PA) were occurred at 0.38 V and -0.93 V, respectively (vs $Ag/AgNO_3$). The redox current value gradually increased as the scan rate increased.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type [29,30].

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

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

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

Based on the Eq. (2), we reported the related data in previous papers [31,32]. By calculating the slope x of the Eq. (2), we found that x is 0.236 and it follows the linear relationship in the Eq. (2). This result means that the kinetics of this redox process may not reach to the diffusion-control process and not be so fast electro-active although it has very stable durability for electrochemical process and linear relationship according to scan rate.

CONCLUSIONS

In this article, we synthesized poly(PA) by using (NBD)$PdCl_2$ catalyst. The chemical structure of the resulting poly(PA) was characterized by various instrumental methods to have conjugated polymer backbone system having phenyl substituents. Poly(PA) showed characteristic UV-visible absorption band at 340 nm and PL spectrum at 439 nm, indicating relatively blue-shifted PL maximum value compared to poly(phenyl propargyl sulfide). The band gap energy of poly(PA) was estimated to be 2.51 eV. The cyclovoltamograms of poly(PA) exhibited that the irreversible oxidation and reduction were occurred at 0.38 V and −0.93 V, respectively (vs Ag/$AgNO_3$). The redox current value gradually increased as the scan rate increased.

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