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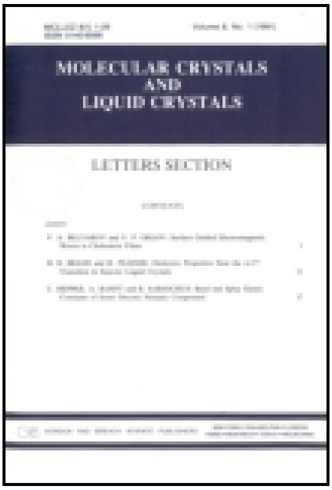

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Synthesis and Characterization of a Polyacetylene Derivative: Poly(2-ethynyl-N-methylpyridinium Tetraphenylborate)

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A monosubstituted ionic polyacetylene with bulky counter anions was prepared via the ion-exchange reaction of precursor polymer by using sodium tetraphenylborate. The chemical structure of the resultiing polymer was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies to have the conjugated backbone system with the designed functional groups. The absorption spectrum starts around 770 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of conjugated polymer system. The photoluminescence maximum peak of polymer was located at 576 nm, which corresponds to the photon energy of 2.16 eV. This polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks.

Keywords Polyacetylene; conjugated polymer; 2-ethynylpyridine; ion-exchange; characterization

Introduction

The organic semiconductors having a conjugated backbone system shows such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1–5]. Applications of organic semiconductors include organic light-emitting diodes (OLEDs) [4, 6, 7], photovoltaic cells [8–10], nonvolatile memory devices [11–13], and organic thin film transistors (OTFTs) [14, 15] for integration into low-cost, large-area electronics.

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. The conjugated polymer-based electrolytes such as poly(propiolic salt)s, triethylammonium salt of poly(6-bromo-1-hexyne), and poly(dipropargylammonium salt)s had been reported [1]. A new class of ionic polyacetylenes have been prepared through the activated polymerization of ethynylpyridines with halogens, $FeCl_3$, and alkyl halides [16, 17].

We have also prepared various polyacetylenes with different functionalities, which retain extensive conjugation [1, 18–28] by the transition metal-catalyzed polymerization of

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*Address correspondence to Prof. Yeong-Soon Gal, Chemistry Division, College of Engineering, Kyungil University, Gyeongsan 712-701, Gyeongsangbuk-Do, Korea. Tel.: (+82)53-600-5487; Fax: (+82)53-600-5499. E-mail: ysgal@kiu.ac.kr functional acetylenic monomers and the uncatalyzed polymerization of ethynylpyridines by using functional alkyl halides.

In our previous work, we prepared a new ionic polyacetylene, poly(2-ethynyl-N-methylpyridinium iodide) [PEMPI], via the uncatalyzed polymerization of 2-ethynylpyridine by using iodomethane [29, 30]. Here, we prepared an ionic conjugated polymer with a bulky substituent (N-methylpyridinium tetraphenylborate), poly(2-ethynyl-N-methylpyridinium tetraphenylborate) [PEMP-TPB,Figure 1] via the ion-exchange reaction of precursor polymer, PEMPI. Further, we characterized the electro-optical and electrochemical properties of the resulting PEMP-TPB.

Experimental

Iodomethane (Aldrich Chemicals, 99.5%) and sodium tetraphenylborate (Aldrich Chemicals, 99.5%) were used as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [31] and vacuum distilled after drying with CaH_2 (85 °C/12 mmHg). The precursor polymer, PEMPI was prepared by the uncatalyzed polymerization of 2-ethynylpyridine with iodomethane in DMF solvent without any additional initiator or catalyst (polymer yield: 78 %) [29].

PEMP-TPB, an ionic conjugated polymer having bulky counter–anion (tetraphenylborate), was prepared by the ion-exchange reaction of PEMPI by using sodium tetraphenylborate. The typical ion-exchange reaction was performed as follows: In 50 mL methanol solution of 1.0 g PEMPI (4.08 mmol in monomeric repeating unit), the 50 mL methanol solution of sodium tetraphenylborate (1.70 g, 5.26 mmol) was dropped with stirring. The brown product was precipitated into the bottom as soon as the two homogeneous solutions contact each other. The precipitated polymer was filtered and dried under vacuum at 40°C for 24 hrs. 1.35 g (yield: 76 %) of PEMP-TPB was obtained in brown power. The polymer was purified by the reprecipitation of the polymer solution diluted with DMF solvent into a large excess of methanol, and filtered and dried under vacuum at 40°C for 24 hrs.

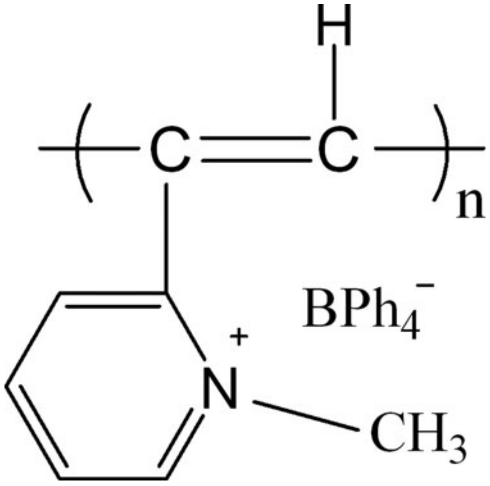

Figure 1. The chemical structure of PEMP-TPB.

NMR (^{1}H-, ^{13}C-) spectra 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 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 utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Xenon lamp was used as the excitation source, and the incident beam took the maximum absorption peak of the polymers. The electrochemical measurements were performed in 0.1M tetraethylammonium tetrafluoroborate [$(t\text{-Et})_4NBF_4$] 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. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The electrical conductivity of the sample was determined by using a standard four-point probe measurement without extensive pumping of the doped pellets with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Conductivity was calculated from the measured resistance of the sample [32].

Results and Discussion

PEMPI, a precursor ionic polymer of PEMP-TPB, was easily prepared by the uncatalyzed polymerization of 2-ethynylpyridine by using 1-iodomethane [29]. The polymerization proceeded well in homogeneous manner to give PEMPI in 78 % yield.

The ion-exchange reaction of the precursor ionic polymers with counter anion is very facile synthetic method for the modification of polymer properties. The modification of water-soluble PEMPI was performed by the simple ion-exchange reaction of PEMPI by using sodium tetraphenylborate in methanol. The brown product was precipitated into the bottom as soon as the two homogeneous methanol solution of PEMPI and sodium tetraphenylborate contact each other. The brown PEMP-TPB power was obtained in 76 % yield. PEMP-TPB was completely soluble in such organic solvents as DMF, DMSO, and NMP. However, this product was found to be insoluble in water, methanol, whereas the precursor polymer, PEMPI, was completely soluble in these solvents.

The molecular structure of PEMP-TPB was characterized by various instrumental methods such as IR, NMR, and UV-visible spectroscopies. The FT-IR spectrum (Figure 2) of PEMP-TPB did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C—H bond stretching (3293 cm^{-1}) frequencies of the monomer. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1630 cm^{-1} became more intense than that of 2-ethynylpyridine. More intense peaks of aromatic =C—H stretching frequencies at 3050 cm^{-1} were observed in the IR spectrum of PEMP-TPB because of tetraphenylborate counter anions.

The ^{1}H-NMR spectrum (Figure 3) of PEMP-TPB shows the aromatic proton peaks of pyridyl and phenyl protons and the vinylic protons in conjugated polymer backbone in the range of 5.7–9.5 ppm. Especially a characteristic strong three peaks of tetraphenylborate counter anions were observed in the range of 6.7–7.5 ppm. The ^{13}C-NMR spectrum of PEMP-TPB showed the multiple peaks at the region of 113–159 ppm, which are originated from the aromatic carbons of pyridyl and phenyl moieties and the vinyl carbons of conjugated polymer backbone. The UV-visible spectrum of PEMP-TPB shows the absorptions at longer wavelength (up to 770 nm) due to the $\pi \rightarrow \pi^*$ interband transition of the conjugated

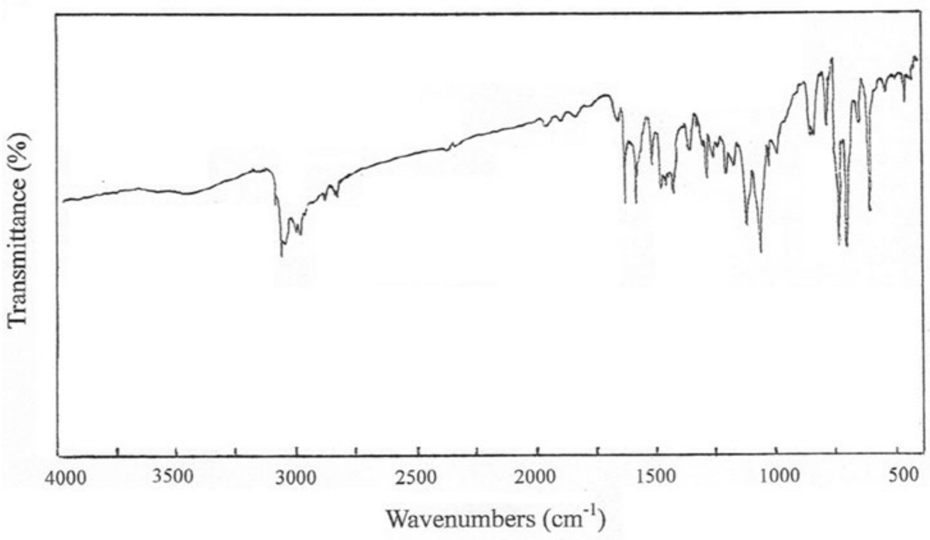

Figure 2. FT-IR spectrum of PEMP-TPB in KBr pellet.

polymer backbone. These results indicate that the present PEMP-TPB has the conjugated polymer backbone system with the designed bulky substituents.

The inherent viscosity of PEMP-TPB was 0.13 dL/g. The morphologies of PEMP-TPB 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. It is indicated that the present polymer is mostly amorphous [1, 33]. The TGA thermogram

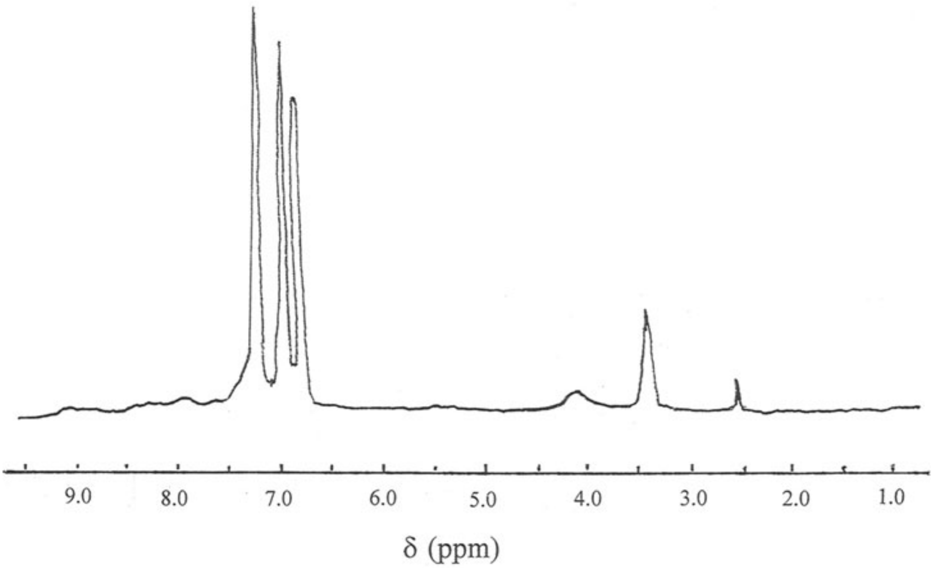

Figure 3. ^{1}H-NMR spectrum of PEMP-TPB in DMSO-d$_6$.

(Figure 4) of PEMP-TPB shows an abrupt weight loss after 180°C. This polymer retained 99.5% of its original weight at 170°C, 94.2% at 200°C, 37.5% at 300°C, and 24.5% at 500°C. The residual weight percentage after heating up to 700°C was 10.5%. It was found that the present polymer with a highly bulky substituents is thermally more stable than that of precursor polymer, PEMPI. The DSC thermogram of PEMP-TPB showed an exothermic peak in the temperature range of 282–350°C (peak temperature: 328°C). The electrical conductivity of iodine-doped PEMPI pellet [composition: $(\text{EMP-TPB})_1(\text{I}_2)_{0.15}$] was 3.20×10^{-4} S/cm.

The UV-visible and photoluminescence (PL) spectra (Figure 5) on PEMP-TPB were measured and discussed. The absorption spectrum of PEMP-TPB exhibits absorption maximum peaks at 379 nm and 486 nm. The photoluminescence spectra of PEMP-TPB polymer showed that the photoluminescence maximum peak is located at 576 nm corresponding to the photon energy of 2.16 eV, whereas the photoluminescence maximum peak of precursor PEMPI was located at 568 nm, corresponding to the photon energy of 2.19 eV.

The electrochemical properties of PEMP-TPB were studied by cyclic voltammometry. Figure 6 shows the cyclic voltammogram of the PEMP-TPB film, which was measured at 0.1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) in DMF solution at a scan rate of 100 mV/s at the potential range of –0.1 to +1.7 V. This ionic polymer exhibited p-doping and undoping peaks at about 0.89 and 0.63 V, respectively (vs Ag/AgCl). As the cycling number increased up to 250 cycles, this polymer showed the well-defined and stable redox process and there was no characteristic change such as the increase of current density in cyclic voltammograms.

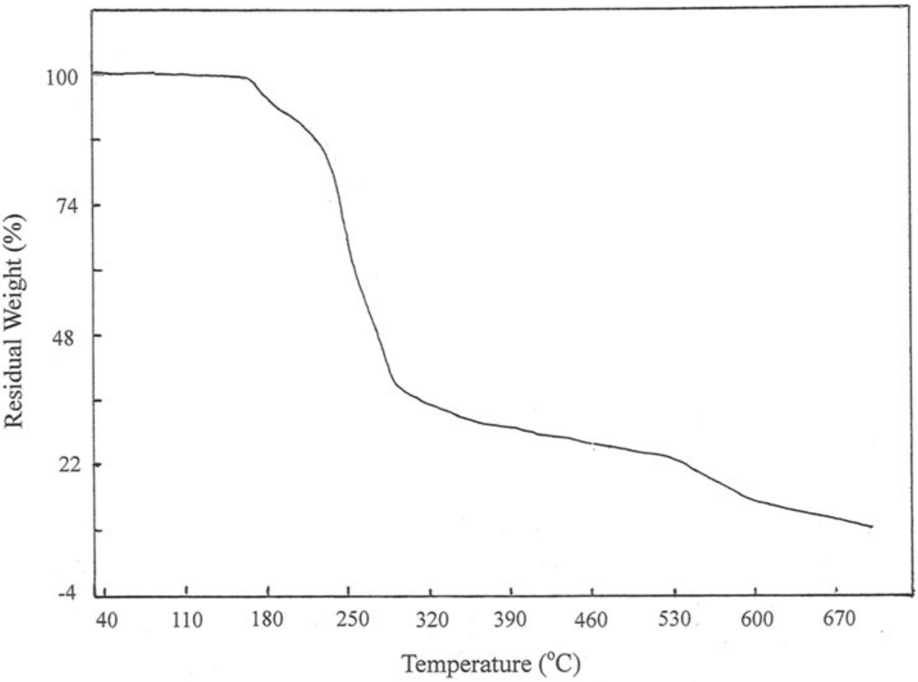

Figure 4. TGA thermogram of PEMP-TPB at a heating rate of 10°C/min under nitrogen atmosphere.

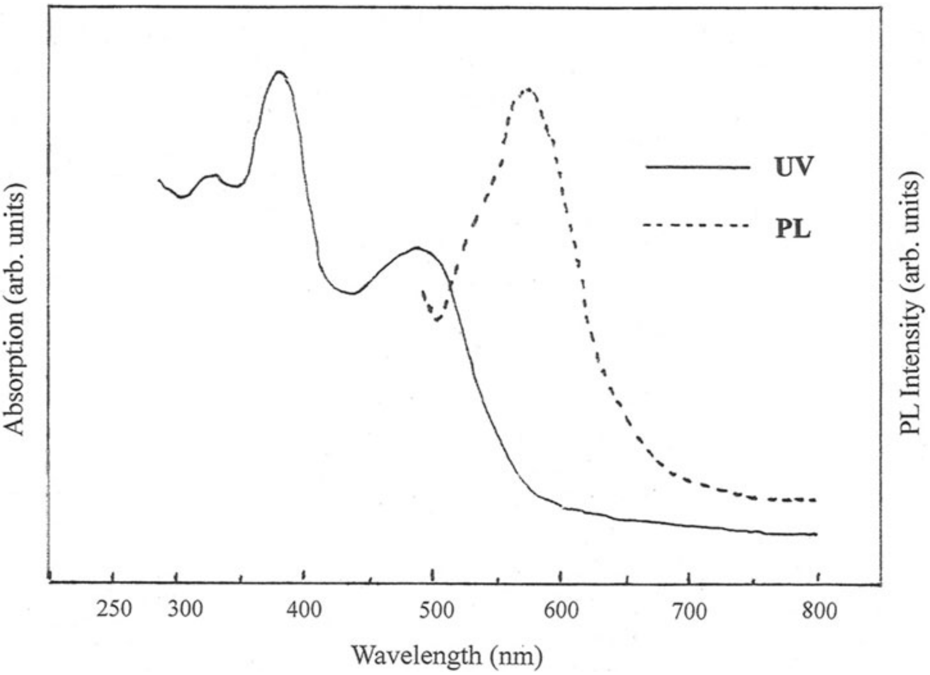

Figure 5. Optical absorption and photoluminescence spectra of PEMP-TPB in DMF solution.

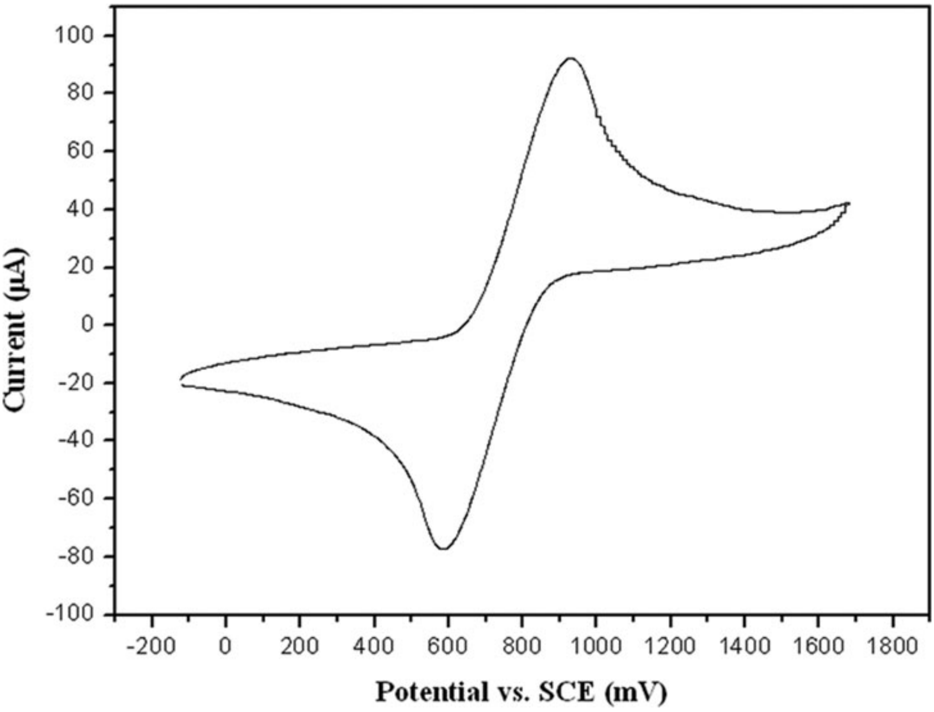

Figure 6. Cyclic voltammogram of PEMP-TPB at 100 mV/s (0.1 Et_4NBF_4/DMF).

Conclusions

A new conjugated polyacetylene with a highly bulky substituents was prepared by the ion-exchange reaction of precursor polymer PEMPI by using sodium tetraphenylborate. The polymer properties was easily modified by changing the counter ion of precursor polymer. The X-ray diffraction data on PEMP-TPB powder revealed that this polymer is mostly amorphous. The molecular structure of polymer was characterized by various instrumental methods to have a conjugated polymer backbone system having the designed substituents. The photoluminescence maximum peak of polymer was located at 576 nm corresponding to the photon energy of 2.16 eV. The CVs of the polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks.

Funding

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