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Synthesis and Characterization of Water-Soluble Ionic Conjugated Polyacetylene

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A water-soluble ionic conjugated polymer with pyridyl functional groups, poly(2-ethynyl-N-pentylpyridinium iodide)[PEPPI] was synthesized via the activated polymerization of 2-ethynylpyridine using 1-iodopentane without any additional initiator or catalyst. The polymerization proceeded well to provide a high yield of polymer. The polymer structure was characterized by such instrumental methods as NMR (^{1}H- and ^{13}C-), IR, and UV-visible spectroscopies to have a conjugated polymer backbone system having N-pentylpyridinium iodide as substituents. The photoluminescence maximum peak of PEPPI was located at 583 nm, which corresponds to the photon energy of 2.13 eV. The cyclovoltamograms of polymer exhibited the electrochemically stable window at the $-1.54{\sim}1.54$ V region. It was found that the kinetics of the redox process of PEPPI are mainly controlled by the reactant diffusion process based on the experiment of the oxidation current density of polymer versus the scan rate.

Keywords Conjugated polymer; cyclic voltammogram; 2-ethynylpyridine; 1-iodopentane; photoluminescence; polyacetylene

Introduction

Considerable progress has been made by the introduction of π-conjugated systems in electronic devices and molecular electronics [1–8]. The polymers having a conjugated backbone shows such unique properties as electrical conductivity, paramagnetism,

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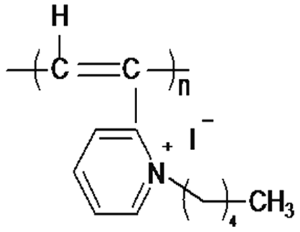

Figure 1. The chemical structure of PEPPI.

migration and transfer of energy, color, and chemical reactivity and complex formation ability [9–11]. Acetylenic triple bonds can be a good candidate to introduce π-conjugated systems due to rich π-electrons and yield the linear conjugated polymer systems [9–11,12–14]. Considerable effort has been devoted to the synthesis of the monosubstituted and disubstituted polyacetylenes and poly(1,6-heptadiyne)s and their properties were extensively studied [9–11]. Unlike polyacetylene, substituted polyacetylenes are generally soluble in common organic solvents and stable enough in air for a long period of time [12,13]. And also they may find a wide range of applications as speciality materials in, e.g., chemical and thermal sensing, optical displays, chiral separation, photovoltaic cells, information storage, fluorescence image patterning, light polarization, and nonlinear optics [11,15–20].

The polyacetylene-based electrolytes such as poly(propiolic salt)s, triethylammonium salt of poly(6-bromo-1-hexyne), and poly(dipropargylammonium salt)s had been reported [10]. In 1991, a new class of ionic polyacetylenes have been prepared through the activated polymerization of ethynylpyridines with alkyl halides [21–23].

We have also prepared various ionic conjugated polymers having different functionalities from the linear polymerization of acetylenic salt monomers by using transition metal catalysts [24–26] and the activation polymerization of ethynylpyridines by using functional alkyl halides [27–32]. Because these conjugated polymers contain extensive conjugation and ionic nature, this ionic PA family has potentials as material candidates for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices [10,33].

Here, we report the synthesis of a new water-soluble ionic polyacetylene derivative (Fig. 1) via the activated polymerization of 2-ethynylpyridine by using 1-iodopentane and the characterization of the polymer properties.

Experimental

1-Iodopentane (Aldrich Chemicals, 98%) was used as received. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [34] and vacuum distilled after drying with CaH_2 (85°C/12 mmHg). The analytical grade solvents were dried with an appropriate drying agent and distilled.

PEPPI, an ionic conjugated polymer, was synthesized by the activated polymerization of 2-ethynylpyridine by using 1-iodopentane. A typical polymerization procedure is as follows. In a 50 mL two-neck flask equipped with rubber septum and purified nitrogen inlet-oulet, 15 mL of DMF, 2-ethynylpyridine (1.0 g, 9.70 mmol), and 1-iodopentane (1.92 g, 9.70 mmol) were added into the reaction flask. Then the reaction solution was warmed to 80°C under nitrogen atmosphere and stirring was continued at this temperature for 24 h. During this time the color of reaction mixture changed from the light brown of the initial mixture into dark red-brown. After the polymerization time, the resulting polymer solution diluted with additional DMF was precipitated into an excess amount of ethyl ether, followed by filtration. The collected powder was dried under vacuum overnight at 40°C for 24 h to afford PEPPI in 87% 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. 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). The 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.

Results and Discussion

The activated acetylenic functional groups of N-substituted-2-ethynylpyridinium salt were known to be susceptible to the linear polymerization, yielding the ionic conjugated polymer systems [21,22]. In general, this polymerization proceeded well without any additional initiator or catalyst. Here, we used this activation polymerization method for the synthesis of water-soluble ionic conjugated polymer. The reaction solution of 2-ethynylpyridine and 1-iodopentane was exposed in heated oil bath (80°C). As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into dark red solution. And the viscosity of reaction solution was also increased. This polymerization proceeded well to give high yield of polymer (87%).

The molecular structure of PEPPI was characterized by such various instrumental methods as infrared, NMR, and UV-visible spectroscopies. FT-IR spectra of 2-ethynylpyridine, 1-iodopentane, and PEPPI were measured and compared. FT-IR spectrum of PEPPI did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C−H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1570–1665 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine. The aromatic =C-H stretching frequency of pyridyl substituents was observed at 3031 cm^{-1}.

The ^{1}H-NMR spectrum of PEPPI was measured in DMSO-d_6. The aromatic protons of pyridyl moieties and the vinyl proton of the conjugated polymer backbone are observed broadly at 6.2–9.6 ppm. The methyl and methylene proton peaks of pentyl substituents are observed at 0.3–1.9 ppm, whereas the proton peaks of methylene groups adjacent to nitrogen atom of pyridine moieties are seen at 3.6–4.9 ppm. Figure 2 shows the ^{13}C-NMR spectrum of PEPPI in DMSO-d_6.

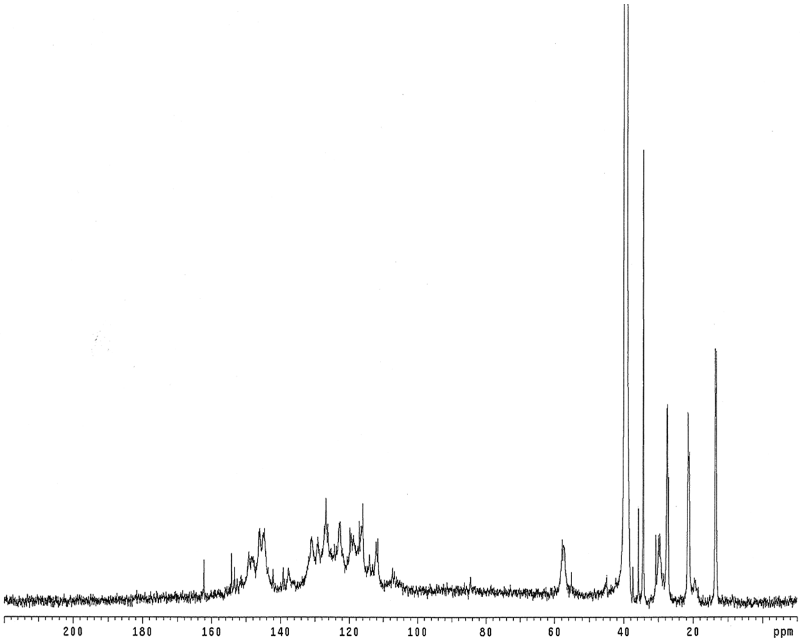

Figure 2. ^{13}C-NMR spectrum of PEPPI in DMSO-d_6.

This spectrum showed the aromatic carbon peaks of pyridyl moieties and the vinyl carbons of conjugated polymer backbone showed at the range of 105.4–153.4 ppm. The five carbon peaks of n-pentyl substituent were also observed at 13.4, 21.2, 27.6, 29.7, and 57.8 ppm. The UV-visible spectrum of PEPPI showed a characteristic absorption band in the visible region, which is strong evidence of the presence of the conjugated polyene backbone system. The thermal properties of PEPPI were studied by TGA thermometry. Figure 3 shows the TGA thermogram of PEPPI measured at a heating rate of 10°C/min under nitrogen atmosphere. This polymer exhibited an abrupt weight loss from 190°C. This shows that the polymer retains 97.5% of its original weight at 100°C, 95.1% at 200°C, 57.5% at 300°C, 38.9% at 400°C, 32.9% at 500°C, 27.6% at 600°C, and 25.0% at 700°C. This polymer was completely soluble in water and such organic solvents as DMF, DMSO, and NMP and the inherent viscosity of PEPPI was 0.14 dL/g.

The electro-optical and electrochemical properties of PEPPI were studied by using UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 4 shows the UV-visible and photoluminescence spectra of PEPPI solution (0.1 wt.%, DMF). The absorption spectrum exhibits absorption maximum value of 337 and 515 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of these conjugated polymer. The photoluminescence spectra of this ionic conjugated polymer showed that the photoluminescence maximum peak is located at 583 nm corresponding to the photon energy of 2.13 eV. When PL was checked with excitation of 515 nm wavelength, excitation peak was removed by using cut-off filter in PL detection. In our previous study, the optical properties of poly(2-ethynyl-N-hexylpyridinium iodide) (PEHPI) which has hexyl side group instead of pentyl side group were reported [35]. PEHPI showed same UV maximum value of 515 nm and longer

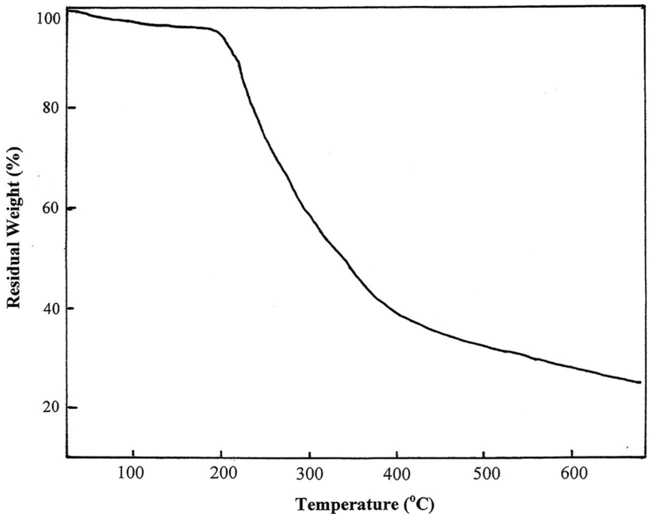

Figure 3. TGA thermogram of PEPPI measured under nitrogen atmosphere at a heating rate of 10°C/min.

shifted PL maximum value of 611 nm. Comparing the maximum wavelength values of PL data, PL maximum value of PEPPI was blue-shifted 28 nm compared to PEHPI. Pentyl side group which is relatively shorter than hexyl group causes blue shift in PL. It is explained by that the planarity of conjugation chromophore was effectively decreased by pentyl side group. The decreased planarity made the relatively distorted conjugation structure. The band gap of PEHPI was 2.17 eV.

The electrochemical kinetic behavior through the cyclic voltammograms of PEPPI solution with various scan rates (30 mV/s~150 mV/s) was also investigated (Fig. 5). As the scan rate was increased, the oxidation and reduction potentials are

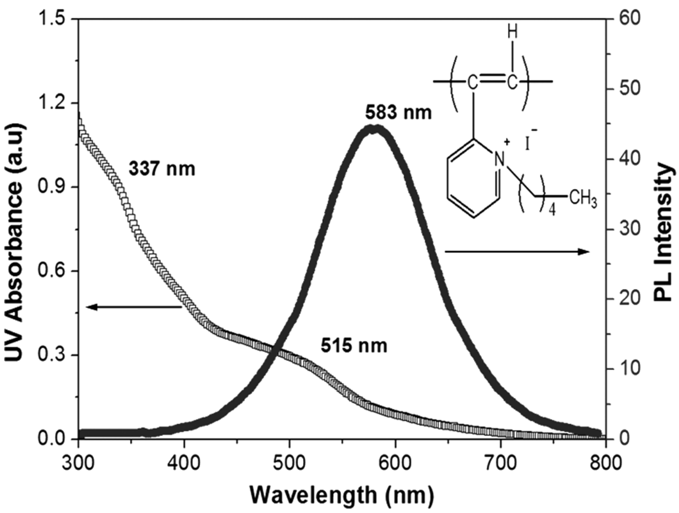

Figure 4. Optical absorption and PL spectrum of PEPPI (0.1 wt% DMF solution).

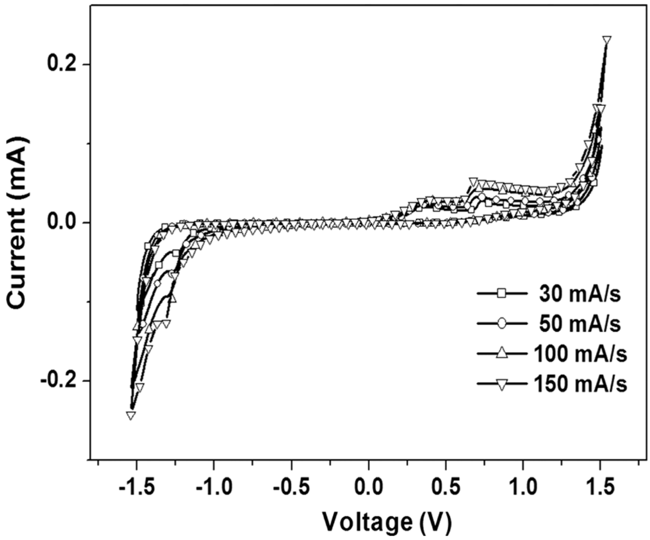

Figure 5. Cyclic voltammograms of PEPPI [0.1 M $(n\text{-Bu})_4NBF_4$/DMF] with various scan rates (30 mV/sec~120 mV/sec).

very slightly shifted to higher potentials because of higher speed of scan rate. Additionally, we have observed stable cyclic voltammograms of PEPPI from the consecutive scan (up to 30 cycles), which means that this material has a stable redox process in tetrabutylammonium tetrafluoroborate/DMF electrolyte solution. In Figure 5, the oxidation of PEPPI occurred at 0.11 and 0.63 V (*vs* Ag/$AgNO_3$), where the vinylene and pyridine units of the conjugated polymer could be oxidized in the scan. PEPPI also shows reduction at −0.95 and −1.35 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of PEPPI is reproducible in the potential range of −1.54~1.54 V *vs* Ag/$AgNO_3$. and there are two vivid redox peaks.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [36,37].

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

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

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

On 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. Relations satisfying Eq. (2) between the oxidation current density ($\log i_{p,a}$) and the scan rate ($\log v$) are shown in Figure 6. The exponent of the scan rate, the x value of PEPPI, is found to be 0.5044. This means that the kinetics of the redox process is very close to a diffusion process [38].

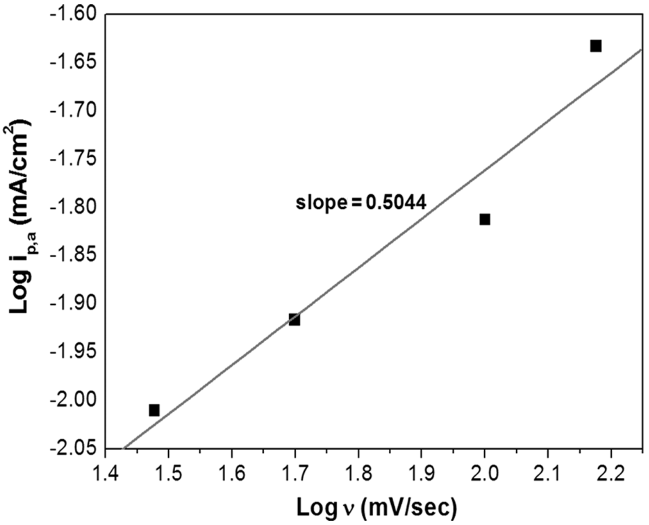

Figure 6. Plot of log $i_{p,a}$ *vs* log v for PEPPI.

Conclusions

The pyridine-containing ionic conjugated polymer was easily prepared by the activated polymerization of 2-ethynylpyridine by using 1-iodopentane. The instrumental analysis data revealed that PEPPI has an ionic conjugated polymer system bearing the designed substituents. This polymer was completely soluble in water and such organic solvents as DMF, DMSO, and NMP. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 583 nm, corresponding to a photon energy of 2.13 eV. The cyclic voltamogram of PEPPI exhibited irreversible electrochemical behavior between the oxidation and reduction peaks, but it showed two vivid redox peaks. The kinetics of the redox process of polymer was very close to a diffusion process from the experiment plotting the oxidation current density of PEPPI *versus* the scan rate.

Acknowledgments

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