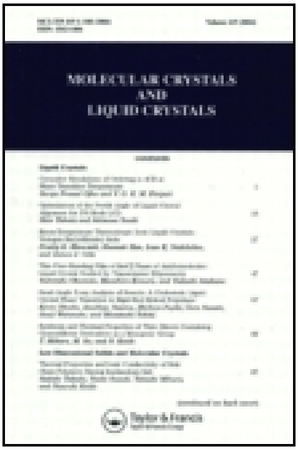

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Synthesis and Properties of Conjugated Polymer with Carboxylic Acids

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Synthesis and Properties of Conjugated Polymer with Carboxylic Acids

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An ionic conjugated polymer was prepared by the spontaneous polymerization reaction of ethynylpyridines by using 11-bromoundecanoic acid in high yield without any additional initiator or catalyst. The activated acetylenic triple bond of

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N-substituted-2-ethynylpyridinium bromide, formed at the initial quaternarization process, was susceptible to linear polymerization. The polymer structure was characterized by various instrumental methods such as NMR, IR, and UV-visible spectroscopies. The photoluminescence peak is located at 593 nm corresponding to a photon energy of 2.09 eV. The electrochemical properties of this ionic polyacetylene were also measured and discussed.

Keywords: 2-ethynylpyridine; carboxylic acid; conjugated polymer; photoluminescence; polyacetylene

1. INTRODUCTION

Recently, the electronics and photonics technologies have opened their materials base to organics, in particular π-conjugated oligomers and polymers [1–3]. There has been much attention given to conjugated polymers such as polyacetylenes, poly(pyrrole)s, poly(phenylenevinylene)s, and poly(9,9-dialkylfluorene)s as functional materials. Among these materials, the polyacetylene (PA) is structurally the simplest one and a prototypical conjugated polymer, which exhibits high electrical conductivity upon doping [4]. Nevertheless, some drawbacks thus far have prevented commercial applications of PA itself. PA does not only suffer from its lack of processibility because of its infusibility and insolubility in common organic solvents, but also from its insufficient stability toward oxygen.

Thus, various substituted polyacetylenes have been prepared by the linear polymerization of the corresponding acetylene monomers [5–11]. Conjugated polymer systems have been used as candidate materials such as organic semiconductors, chemical sensors, light-emitting diodes, nonlinear optical materials, liquid crystalline materials, membranes for optical resolution of racemic mixtures, and membranea for gas separation and for liquid-mixture separation.

Conjugated polyelectrolytes are charged conducting macromolecules containing a large number of ionizable or ionic groups [6,12]. In 1990, Blumstein *et al.* prepared the well-defined ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides [13]. We have also reported the synthesis of various ionic conjugated polymers having different functionalities [14–20]. Due to their extensive conjugation and ionic nature, these ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices [12].

Now, we report the synthesis of a new ionic conjugated polymer with carboxylic acid moieties, by the activated polymerization of

2-ethynylpyridine with 11-bromoundecanoic acid and, the electro-optical and electrochemical properties of the resulting polymer.

2. EXPERIMENTAL

2.1. Materials

2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85° C/12 mmHg). 11-Bromoundecanoic acid (Aldrich Chemicals) was used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled. Poly[2-ethynyl-N-(ω-undecylic acid)pyridinium bromide] (PEUPB) was prepared by the activated polymerization of 2-ethynylpyridine with 11-bromoundecanoic acid without any additional initiator or catalyst in DMF solvent as follows. The 1:1 mixture of 2-ethynylpyridine (1.0 g, 9.70 mmol) and 11-bromoundecanoic acid (2.57 g, 9.70 mmol) in DMF solvent (5 mL, $[M]_0 = 1.13\,M$) was stirred for 24 hrs at 100°C under nitrogen atmosphere. As the reaction proceeded, the color of reaction mixture changed from the light brown of the initial mixture into dark black. After the polymerization time, the resulting polymer solution was precipitated into a large excess amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at 40°C for 24 hrs. The polymer yield was 82%.

NMR (^1H- 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. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 25°C. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The photoluminescence spectra were obtained by a 456 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube). The emission signal was collected by using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A displex), a monochromator (Spex 750 M), and a photomultiplier (Hamamatsu R943-02). The signal from the photomultiplier was amplified by an EG&G 5101 lock-in amplifier with the chopping frequency of 170 Hz, and converted to the digital signal in the autoscan system. A multi-channel photodiode detector (MCPD, Otsuka Electronics., Co., Japan) was used to obtain visible absorption spectra.

To examine the electrochemical properties, the 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

The activated acetylenic groups of N-substituted-2-ethynylpyridinium halides were found to be susceptible to the linear polymerization, yielding the ionic conjugated polymer systems [13,21]. We used this method to prepare the ionic conjugated polymer with carboxylic acid groups in the polymer side chain. The PEUPB (Fig. 1) was prepared by the activated polymerization of 2-ethynylpyridine by using 11-bromoundecanoic acid in DMF without any additional initiator or catalyst.

As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into viscous dark black solution. The black polymer powder was obtained in 82% yield. This polymerization behaviors were found to be very similar with that of the polymerization reaction of 2-ethynylpyridine with 6-(N-carbazolyl)hexyl bromide [22]. The present polymerization process contains the first quarternarization of 2-ethynylpyridine by 11-bromoundecanoic acid at the elevated temperature. The activated acetylenic triple bond of N-substituted-2-ethynylpyridinium bromide is susceptible to the linear polymerization. The activated monomeric species can be initiated by the non-bonding electron pair of 2-ethynylpyridine and/or or bromide counter anion.

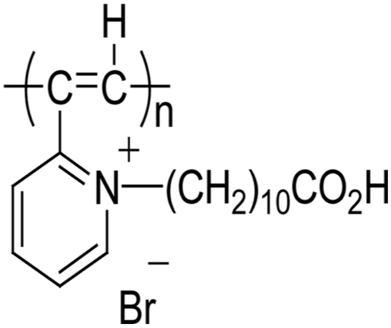

FIGURE 1 Chemical structure of PEUPB.

The polymer structure was characterized by NMR, infrared, and UV-visible spectroscopies. Figure 2 shows the FT-IR spectra of 2-ethynylpyridine (A), 11-bromoundecanoic acid (B), and polymer (C) in KBr pellets. The FT-IR spectrum of polymer 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 1620 cm^{-1} became more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine itself. The peak at 1719 cm^{-1} is due to the carbonyl C=O stretching frequencies of polymer. And the peaks at 2852 and 2924 cm^{-1} are characteristics of the aliphatic C−H stretching frequencies.

The ^{1}H-NMR spectrum of polymer shows the aromatic protons of pyridyl moieties and the vinyl protons of the conjugated polymer backbone at 6.4–9.6 ppm. The peaks of the two methylene protons adjacent to nitrogen and carboxylic acid are observed at 3.2–4.7 ppm and the internal eight methylene protons are also observed at 0.5–2.4 ppm.

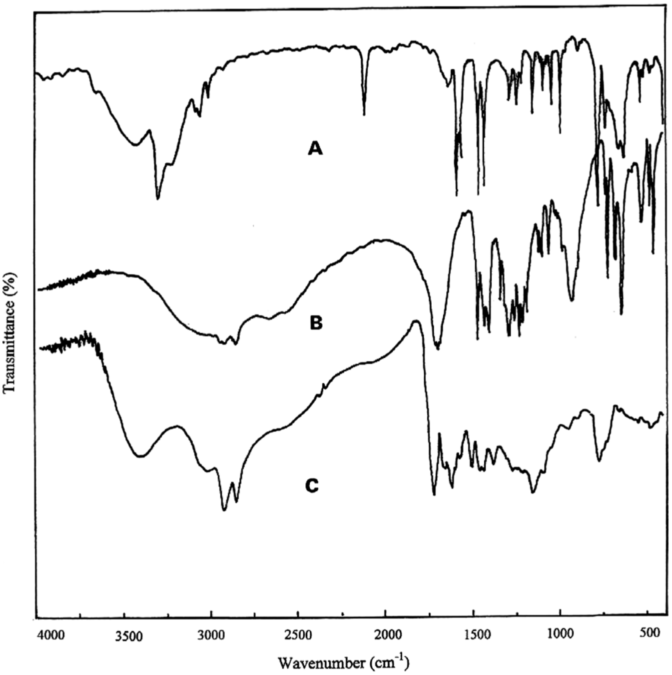

FIGURE 2 FT-IR spectra of 2-ethynylpyridine (A), 11-bromoundeconic acid (B), and PEUPB (C) in KBr pellets.

The ^{13}C-NMR spectrum of polymer showed the multiple and complicated peaks at the region of 110–155 ppm, which are originated from the aromatic carbons of pyridyl moieties and the vinyl carbons of conjugated polymer backbone. The two methylene carbon peaks adjacent to nitrogen and carboxylic acid are observed at 56–59 ppm. And the internal eight methylene carbons are also observed at 24–36 ppm. The carbonyl carbon peak was observed at 174 ppm. The other methylene carbon peaks are observed at the region of 20–60 ppm. From these spectral data, we concluded that this polymer has a ionic conjugated polymer system bearing the designed substituents. This polymer was completely soluble in such organic solvents as DMF, DMSO, NMP, but insoluble in hexanes and ethyl ether. 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, this polymer was amorphous [5]. The inherent viscosity of PEUPB was 0.17 dL/g.

Figure 3 shows the UV-visible spectra and photoluminescence (PL) spectra of polymer in DMF solution. The UV-visible spectrum of polymer showed a characteristic peak at the visible region (400–800 nm), which is a characteristic peak of the conjugated polyene backbone system. The photoluminescence peak is located at 593 nm corresponding to the photon energy of 2.09 eV.

To investigate the electrochemical kinetic behavior, we measured the cyclic voltammograms (CV) of polymer with the various scan rates (30 mV/s $\sim$ 120 mV/s). The solution could be stirred during CV experiment for getting more accurate CV result, but we checked

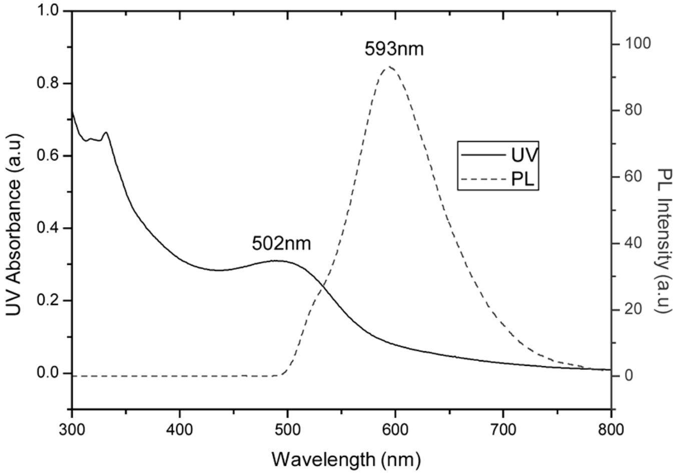

FIGURE 3 Optical absorption and photoluminescence spectra of PEUPB.

electrochemical property without stirring because the polymer solution was well homogenized. PEUPB exhibited oxidation and reduction potentials at 0.9 V and -0.58 V in this electrochemical system. The peak potentials are gradually shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of polymer from the consecutive scan (up to 30 cycles), which means that this material has relatively stable redox process.

4. CONCLUSIONS

In this article, we dealed with the synthesis and properties of a new conjugated ionic polymer with carboxylic acids. This ionic conjugated polymer was easily prepared in high yield by the activated polymerization of 2-ethynylpyridine by using 11-bromoundecanoic acid. This polymer was completely soluble in such organic solvents as DMF, DMSO, and NMP. The instrumental analyses on the polymer structure indicated that the present polymer have a conjugated backbone system with the designed functional substituents. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 593 nm, corresponding to a photon energy of 2.09 eV. The cyclic voltammograms of polymer revealed that this polymer has the stable redox process.

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