

Synthesis and Optical Properties of Poly(2-ethynylpyridinium bromide) Having Glycidyl Functionality

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Abstract : The synthesis of poly(2-ethynylpyridine) having glycidyl functionality was performed by the direct polymerization of 2-ethynylpyridine and epibromohydrin under mild reaction conditions without any initiator and catalysts. The polymerization proceeded well to give the resulting poly(2-ethynylpyridinium bromide) with a glycidyl functionality having relatively high molecular weight in high yields. The polymer structure was characterized by various instrumental methods to have the conjugated polymer backbone structure having glycidyl functionality. This ionic polymer was completely soluble in water, methanol, DMF, DMSO, and N,N-dimethylacetamide, but insoluble in THF, toluene, acetone, nitrobenzene, and n-hexane. This polymer system exhibited the UV-visible absorption around 300 and 520 nm and red photoluminescence spectrum around 725 nm.

Introduction

Conjugated polymer systems obtained from acetylene derivatives have been studied as organic semiconductors,¹⁻³ as membranes for gas separation and for liquid-mixture separation,⁴⁻¹⁰ as materials

for enantioseparation for racemates by high performance liquid chromatography,^{11,12} as a side-chain liquid crystal,¹³⁻¹⁶ as materials for chemical sensors,^{17,18} and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties.¹⁹⁻²⁴

Conjugated ionic polymer systems have potential as materials for mixed ionic and electronic con-

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ductivity, energy storage devices such as batteries and permselective membrane, and light-emitting devices, due to their extensive conjugation and various functionalities.²⁵⁻²⁷

The cyclopolymerization of 2-ethynyl-N-propargylpyridinium bromide having two different triple bond functionalities (acetylene and propargyl) yielded an interesting conjugated cyclopolymer having cumulated pyridine moiety.²⁸ The synthesis of simple mono- and disubstituted ionic polyethynylpyridines had been carried out with the activation of the acetylene bond in ethynylpyridines.^{26,29,30} We have studied the polyacetylene materials having pyridine moiety such as poly(2-ethynylpyridine),³¹ poly(N-propargylpyridinium bromide),³² poly(2-ethynyl-N-propargylpyridinium bromide),²⁸ and poly(2-ethynylpyridinium bromide) having a pendant propargyl moiety.^{33,34} The incorporation of cross-linkable functional group such as glycidyl, allyl, and others was thought to be very interesting in the viewpoints of improvement of thermal and aging properties of processed polymeric materials.

In this article, we report the studies on the synthesis of a novel conjugated ionic polymer having reactive functionality, poly(2-ethynylpyridinium bromide) having epoxy group in the side chain and the characterization of the resulting conjugated ionic polymer.

Experimental

Materials. 2-Vinylpyridine (Aldrich Chemicals., 97%), bromine (Aldrich Chemical., A.C.S. reagent, 99.5+%), and sodium amide (NaNH₂, Aldrich Chemicals., tech., 90%) were used as received. Epibromohydrin (Aldrich Chemicals., 98%) was dried with CaSO₄ and fractionally distilled. The solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

Preparation of 2-ethynylpyridine. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method.³¹

Synthesis of Poly(2-ethynylpyridinium bromide) Having Glycidyl Functionality (PEPBG).

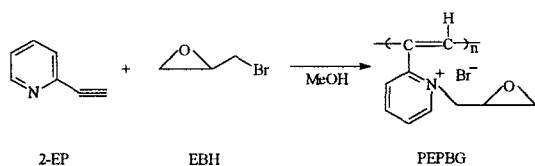
In a 250 mL three-neck flask equipped with reflux condenser, thermometer, and rubber septum, methanol (200 mL), 2-ethynylpyridine (3.0 g, 29.12 mmol, [M]₀=0.146 M), and epibromohydrin (4.10 g, 29.93 mmol) were introduced in the given order. And the reaction was carried out under methanol reflux condition. In order to check the polymer yield and polymer viscosity according to the reaction time during the polymerization, each 10 mL reaction solution was taken from the polymerization mixture at the pre-scheduled polymerization time (1, 3, 6, 12, 24 hrs). As the reaction proceeded, the color of reaction mixture was changed from light-brown of initial mixture into deep purple. After a given 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.

Instruments and Measurement. NMR (¹H- and ¹³C-) spectra of polymers were recorded on a Bruker AM-200 spectrometer in DMSO-*d*₆, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed with Perkin-Elmer 240DS Elemental Analyzer. UV-visible spectra were taken in THF on a JASCO V-530 spectrophotometer. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. 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 Shimadzu UV-3100 UV-VIS-NIR spectrophotometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photoluminescence spectroscopy. Solid-state emission measurement was achieved using films supported on glass substrate and mounted with front-face excitation at an angle of <45°.

Results and Discussion

The direct polymerization of 2-ethynylpyridine by alkyl halides is very facile synthetic method for the conjugated ionic polymer in one step. The

Poly(2-ethynylpyridinium bromide) Having Glycidyl Functionality



synthesis of PEPBG via the reaction of 2-ethynylpyridine (2-EP) and epibromohydrin (EBH) at a moderate reaction condition was carried out as follows.

The polymerization of ethynylpyridines by using simple alkyl halides such as ethyl iodide,³⁴ 1-octyl bromide,²⁹ and lauryl bromide,³⁴ had been known to proceed even at mild reaction conditions of low temperature (50°C). The activated acetylenic triple bond of N-alkyl-2-ethynylpyridinium halide was known to be susceptible to the polymerization under mild reaction conditions. In this polymerization of 2-ethynylpyridine with epibromohydrin having epoxide moiety, the polymerization behavior was found to be similar to those of the polymerization reaction of 2-ethynylpyridine with simple alkyl halides and propargyl bromide.^{29,33,34} This polymerization proceeded well under methanol reflux condition to give the resulting polymer in high yield. The reaction state and polymer yield according to the polymerization time were consecutively checked from the precipitation of the solution taken from the polymerization reactor. The color of the reaction solution changed from light brown of the initial mixture of 2-EP and epibromohydrin into light purple after 1 hr, and finally into dark purple. The polymer yield calculated from the precipitation according to the polymerization time revealed that this polymerization proceeded well at early 3 hrs, reaching about 50% polymer yield, and then final 82% after 24 hrs. The absorption spectra of the polymerization solution according to the polymerization time were also checked. The UV-visible spectrum of initial mixture of 2-EP and epibromohydrin does not show any absorbance upto 450 nm, which can be originated from the absorbance of conjugated polymer backbone. The absorption peak of polymer reaction solution as the polymerization proceeds extended upto around 800 nm, though the intensity of absorption was weak. These peaks at the wide visible regions indicated that the con-

jugated polymer system was formed. However, a characteristic absorption peak at the wavelength (>500 nm), which had been observed in the visible spectrum of the polymer solution of poly(2-ethynylpyridinium bromide) having simple alkyl or propargyl group, was not observed. The weak absorption peak tailed to around 800 nm was observed. This is perhaps indicative of a wide distribution of conjugated polyene segments coupled with the ionic nature of side groups.

This polymerization was carried out in polar solvents such as methanol, acetonitrile, and DMF. The polymer yields were in the range of 79-85%. The polymerization of 2-EP and epibromohydrin at 100°C in DMF solvent yielded similar polymerization results in the viewpoints of polymer yield and molecular weights. The inherent viscosities of the resulting polymers were in the range of 0.10-0.25 dL/g, depending on the polymerization conditions.

The polymer structure of PEPBG was characterized by elemental analysis, NMR (¹H- and ¹³C-), infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated PEPBG agreed with the theoretical value: Calcd for (C₁₀H₁₀NOBr): C, 50.03%; H, 4.20%; N, 5.84%; O, 6.66%; Br, 33.28%, Found: C, 52.13%; H, 4.10%; N, 6.65%; O, 7.20%.

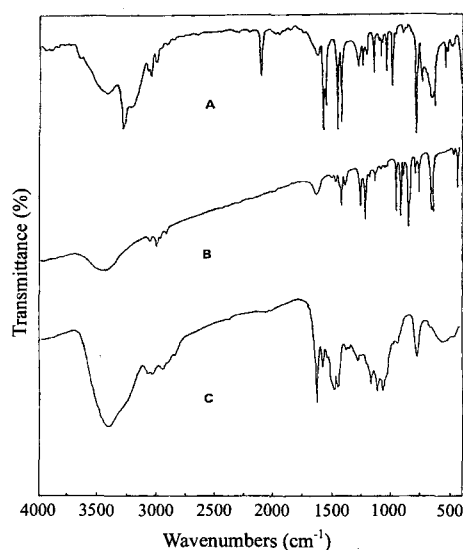


Figure 1. FT-IR spectra of 2-ethynylpyridine (A), epibromohydrin (B), and PEPBG (C) in KBr pellet.

Figure 1 shows the IR spectra of 2-EP (A), epibromohydrin (B), and PEPBG (C) in KBr pellets. In the IR spectrum of PEPBG (C), it did not show the peaks for acetylenic $C\equiv C$ bond stretching (2110 cm^{-1}) and the acetylenic $\equiv C-H$ stretching (3293 cm^{-1}). Instead, the $C=C$ stretching frequency peak of conjugated polymer backbone at 1623 cm^{-1} became more intense than those ($C=C$ and $C=N$ stretching frequency) of 2-EP. A characteristic peak of pendant epoxide moiety appeared at 1277 cm^{-1} . The peaks at 1582 and 775 cm^{-1} originated from the CH_2 scissor vibration frequencies and $C-H$ out-of-plane deformation frequencies, respectively. The peak at 2835 cm^{-1} is a characteristic one of $N-CH_2-$. The broad absorption peak around 3414 cm^{-1} is due to the moisture and organic residue absorbed by ionic PEPBG during the treatment.

The ^1H-NMR spectrum of PEPBG showed the aromatic proton peaks at 7.0-9.5 ppm. The vinyl proton of conjugated polymer backbone was also observed broadly at around 6.6 ppm. The protons of epoxide rings and methylene groups were observed at 4.80-5.42 and 3.80-4.25 ppm, respectively.

The $^{13}C-NMR$ spectrum of PEPBG showed the olefinic carbon peaks of highly conjugated polymer backbone at the region of 151.5-155.0 ppm. The carbon peaks of aromatic carbons of pyridines were seen at 125.1-148.2 ppm. The peaks of the methylene and the methine carbons of glycidyl functional group were also observed at around 54.2 and 58.4 ppm, respectively. The small peak at around 102.5 ppm was thought to be the olefinic carbon peak of some oligomeric products.

The resulting PEPBGs were generally brown or black powders. The solubility test was performed for powdery samples in excess solvent. The PEPBGs were completely soluble in DMF, DMSO, MeOH, N,N-dimethylacetamide, formic acid, and water, but insoluble in THF, toluene, nitrobenzene, acetone, and n-hexane.

Figure 2 shows the TG thermogram of PEPBG under nitrogen atmosphere. It is seen that the polymer retains 99% of its original weight at 100°C , 95% at 173°C , 90% at 204°C , 80% at 258°C , 40% at 472°C , and 27% at 700°C . The slight weight loss at low temperature ($\leq 150^\circ\text{C}$)

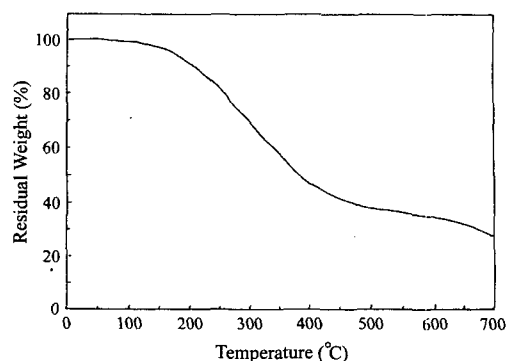


Figure 2. TGA thermogram of PEPBG under nitrogen atmosphere (heating rate: $10^\circ\text{C}/\text{min}$).

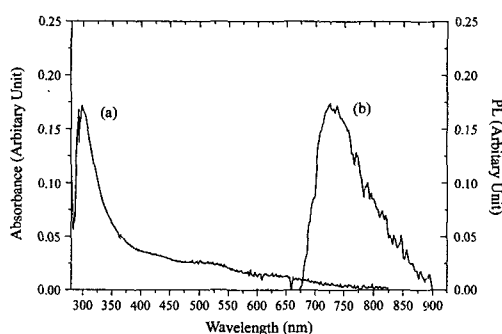


Figure 3. Optical absorption (a) and photoluminescence spectra (b) of PEPBG thin film on quartz substrate.

is due to the absorbed moisture and/or organic residues in the polymer.³³

Figure 3 shows the UV-visible absorption and photoluminescence spectra of spin-coated PEPBG film (thickness: less than 100 nm) on quartz substrate. All measurements were carried out in air at room temperature. In Figure 3(a), PEPBG shows two absorption bands around 300 and 520 nm. The former strong band is due to the side chained pyridinium groups. The latter band is relatively weak and might be based on the $\pi \rightarrow \pi^*$ conjugation band transition of the polyene main chain. This band was relatively weaker than that of poly(2-ethynylpyridinium tosylate) having propargyl side chain.³⁴

The band gap energy of this polymer was estimated to be 2.1 eV from the analysis of the absorption edge with a plot of $(h\nu)$ vs. $(\alpha h\nu)^2$, where α , h , and ν are the absorbance, Planck's constant, and the frequency of light, respectively.³⁵ This band gap energy is larger than that of trans-

polyacetylene by about 0.4 eV.³⁶ Because the backbone of PEPBG is the same as that of trans-polyacetylene, this might be due to the steric hindrance between pendant N-glycidyl-2-pyridinium groups in PEPBG. The photoluminescence spectrum of the film shows that the photoluminescence peak is located at 725 nm corresponding to the photon energy of 1.71 eV as shown in Figure 3(b). So there is the Stokes' shift between the maximum in emission and the absorption edge. This indicates that emission is due to the exciton states rather than the interband transition.

Conclusions

The direct polymerization of 2-EP and epibromohydrin under mild reaction conditions gave a soluble and easily processable ionic conjugated polymer, PEPBG, in high yields. The polymerization was found to proceed by the propagation mechanism of activated acetylene functions of 2-ethynylpyridinium derivatives by quaternization by epibromohydrin. The polymer structure of resulting PEPBG was characterized by various instrumental methods to have conjugated polymer backbone system having epoxide moiety as pendant side chain. The resulting PEPBGs were soluble in polar organic solvents such as DMF, DMSO, methanol, water, N,N-dimethylacetamide, but insoluble in THF, toluene, nitrobenzene, and n-hexane. This polymer exhibited the UV-visible absorption around 300 and 520 nm and red photoluminescence spectrum around 725 nm.

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