Synthesis and Properties of Poly[2-ethynyl-*N*-(*p*-hydroxyphenylethyl) pyridinium bromide] and Poly[2-ethynyl-*N*-(*p*-hydroxyphenylethyl) pyridinium tetraphenylborate]

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Abstract: A new hydroxyl group-containing conjugated ionic polymer, poly[2-ethynyl-*N*-(*p*-hydroxyphenyl-ethyl)pyridinium bromide], was synthesized by the activated polymerization of 2-ethynylpyridine with *p*-(2-bromoethyl) phenol without any additional initiator or catalyst. The polymerization proceeded well to give a moderate yield (65%) of polymer at a reaction temparature of 90 °C. Another polymer, poly[2-ethynyl-*N*-(*p*-hydroxyphenyl-ethyl)pyridinium tetraphenylborate], was readily prepared by the ion-exchange reaction of poly[2-ethynyl-*N*-(*p*-hydroxyphenylethyl)pyridinium bromide] with sodium tetraphenylborate. These polymers were completely soluble in organic solvents such as DMF, DMSO, and acetone, but insoluble in water and ether. Instrumental analyses, such as NMR, IR, and UV-Vis spectroscopies, indicated that the new materials have conjugated polymer backbone systems with the designed substituents and counter anions. X-Ray diffraction analyses of the polymers indicated that they were mostly amorphous.

Keywords: conjugated polymer, 2-ethynylpyridine, characterization, ion-exchange reaction, sodium tetraphenylborate.

Introduction

Polymers have been traditionally used as insulators-after all, metal cables are coated in plastic to insulate them. In 1977, however, Shirakawa *et al.* discovered that the conductivity of polyacetylene (PA) increases significantly upon doping with various electron acceptors or electron donors.[1-3] Among the π-conjugated polymers, the PA is structurally the simplest one, and it can be made free-standing thin film by using Shrakawa catalysts [Ti(OC$_4$H$_9$)$_4$-Al(C$_2$H$_5$)$_3$].[4,5] However, the drawbacks are that PA is insoluble, infusible, and unstable to air oxidation. Thus it was difficult for practrical applications to opto-electronic devices as an active material. To overcome these problems of PA itself, more stable het-

erocycle-based polymers such as polypyrrole[6,7] and polythiophene[8,9] were prepared, and these materials can be easily obtained in their oxidized conducting form by means of one-step electrochemical synthesis.

And also, a number of mono- and di- substituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.[10-18] The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability.[10] Because of these properties, PA and its homologues have been promising as organic semiconductors,[1,2,19] as membranes for gas separation and for liquid-mixture separation,[20] as chiro-optical materials,[21,22] as side-chain liquid crystals,[11] as materials for chemical sensors,[23] and as materials for nonlinear optical property[24,25] and for photolumines-

cence and electroluminescence properties.[26-29]

The polymerization of acetylene monomers having hydroxy functional group are of interest because of their unique structures and facile modification of hydroxy groups into other interesting functional groups. To date, the following polyacetylenes with hydroxy group were synthesized and characterized: poly(propargyl alcohol),[30] poly(1-ethynyl-1-cyclohexanol),[31] poly(9-ethynyl-9-fluorenol),[32] poly(3-butyn-2-ol),[33] poly(2-phenyl-3-butyn-2-ol),[34] and poly(3-ethynyl-phenol).[35]

The ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices[36] because of their extensive conjugation and ionic nature. Poly(propiolic salt)s were prepared by the solid-state polymerization of propiolic salts with γ-irradiation.[37] Water-soluble ionic conjugated polymers were prepared by the quarterization of poly(6-bromo-1-hexyne)[38] or the activated polymerization of ethynylpyridines with alkyl halides.[39,40] We have also prepared various ionic conjugated polymers having different functionalities by the simple linear polymerization of corresponding ionic monomers or the activated polymerization of ethynylpyridines with functionalized alkyl halides.[12,27,41-45] However, there have been no reports on the ionic polyacetylene derivatives with the hydroxy functional group.

Now we report the synthesis of two new ionic conjugated polymers having hydroxy functional groups, poly[2-ethynyl-N-(p-hydroxyphenylethyl)pyridinium bromide] (PEHPB) and poly[2-ethynyl-N-(p-hydroxyphenylethyl)pyridinium tetraphenylborate] (PEHP-TPB) and the characterization of the resulting ionic conjugated polymers.

Experimental

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method.[46] Sodium tetraphenylborate (Aldrich Chemicals, NaBPh₄, 99.5+%) was used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled.

PEHPB was prepared by the activated polymerization of 2-ethynylpyridine with p-(2-bromoethyl)phenol without any additional initiator or catalyst in DMF solvent as follows. The 1:1 mixture of 2-ethynylpyridine (1.0 g, 9.7 mmol) and p-(2-bromoethyl)phenol (1.95 g, 9.7 mmol) in 10 mL DMF solvent was stirred for 24 hrs at 90 °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 an excess amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at 40 °C for 24 hrs. The polymer yield was 65%.

PEHP-TPB, a similar conjugated ionic polymer having bulky counter anion (tetraphenylborate), was preapared by the ion-exchange reaction of PEHPB by using sodium tetraphenylborate. The typical ion-exchange reaction was performed as follows: In 20 mL methanol solution of 0.5 g PEHPB (4.8 mmol in monomeric repeating unit), the 20 mL methanol solution of sodium tetraphenylborate (2.00 g, 5.84 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. 0.52 g (yield: 57.7%) of PEHP-TPB was obtained in light-brown power.

NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d₆, 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 UV-visible absorption spectra were measured by a JASCO V-530 spectrophotometer. 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). Thermal properties of polymers were measured under nitrogen atmosphere at a heating rate of 10 °C/min up to 700 °C with Rheometric Thermal Analyzer.

Results and Discussion

The ethynylpyridines were known to be polymerized by alkyl halides to give the corresponding poly(2-ethynyl-N-alkylpyridinium halide)s by self-polymerization method without any additional initiator or catalyst. In previous works, various bulky functionalized alkyl halides had been used for the activated polymerization of ethynylpyridines. Here, we synthesized two ionic conjugated polymers having hydroxy functional groups by the activated polymerization of 2-ethynylpyridine by using p-(2-bromoethyl)phenol and the consecutive ion-exchange reaction of poly[2-ethynyl-N-(p-hydroxyphenylethyl)pyridinium bromide] (PEHPB) with sodium tetraphenylborate (Scheme I).

The polymerization of ethynylpyridines by using simple alkyl halides such as methyl iodide, 1-octyl bromide, lauryl bromide, etc had been known to proceed even at the mild reaction condition of low temperature (< 50 °C).[36,39,40,44] The activated acetylenic triple bond of N-alkyl-2-ethynylpyridinium halides was found to be susceptible to the linear polymerization even under mild reaction conditions. However, the present polymerization did not proceed at the somewhat low temperatures. Thus the present polymerizations were carried out at the more elevated temperature (90 °C). As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into dark black. The polymer yield according to the polymerization time
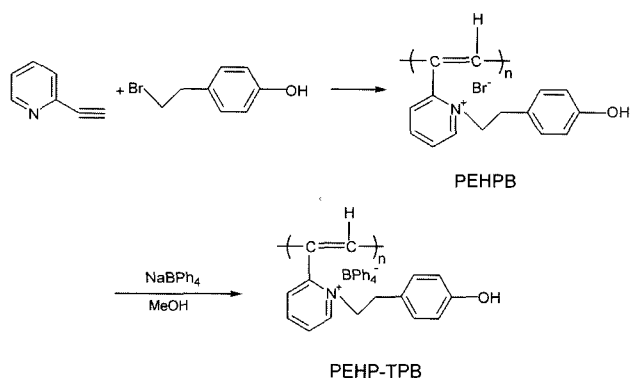
Scheme I. Synthesis of poly[2-ethynyl-N-(p-hydroxyphenylethyl) pyridinium bromide] (PEHPB) and poly[2-ethynyl-N-(p-hydroxy-phenylethyl)pyridinium tetraphenylborate] (PEHP-TPB).

revealed that this polymerization proceeded gradually up to 24 hrs and the polymer yield after 24 hrs reaches 65% and then plateau. This polymerization also proceeded well in such organic solvents as DMSO and NMP. The polymerization behavior of 2-ethynylpyridine with p-(2-bromoethyl)phenol was found to be similar with that of the polymerization reaction of 2-ethynylpyridine with 6-(N-carbazolyl)hexyl bromide.[47]

Two different polymerization mechanisms were proposed for the formation of the present poly(ethynylpyridine)s. One, proposed by Kabanov et al. for the polymerization of quar-terinized vinylpyridines, involves the initiation step by the counter anion followed by propagation by the created anionic species. The alternative mechanism involves an initiation step involving a nucleophilic attack by the unquarterinized amine of ethynylpyridines on the electrophilic triple bond of the quarterinized ethynylpyridines. The latter mechanism was proposed to be more favorable based on the inetresting findings by Katritzky et al. They succeeded in isolating the quarterinized pyridinium salt in reactions of propargyl halides (halide = bromide, chloride). They found that the polymeri-zation of propargylpyridinium monomers can be initiated by addition of such nucleophiles as pyridines and tertiary amines. We had also isolated the acetylenic pyridinium salts such as propargylpyridinium bromide and 2-ethynyl-N-pro-pargylpyridinium bromide. In our previous works, the simi-lar polymerization of 2-ethynylpyridine by using propargyl bromide[11] and propargyl tosylate[12] were also found to pro-ceed well to give high yields of polymer, regardless of the counter anions (bromide, tosylate). These observations means that the latter mechanism is more possible for the present polymerization. The polymerization mechanism was assumed to include the initial formation of 2-ethynyl-N-(p-hydroxy-phenylethyl)pyridinium bromide and the initiation step for the polymerization of 2-ethynyl-N-(p-hydroxyphenylethyl) pyridinium bromide by the non-bonding electron pair of 2-ethynylpyridine and/or bromide counter anion.

The ion-exchange reaction of the precursor polymer is very facile synthetic method for the modification of poly-mer properties. The modification of PEHPB was performed by the simple ion-exchange reaction of PEHPB by using sodium tetraphenylborate (Scheme I). The brown product was precipitated into the bottom as soon as the two homoge-neous methanol solution of PEHPB and sodium tetraphe-nylborate contact each other. The light-brown powder was easily obtained in relatively high yield.

The chemical structures of PEHPB and PEHP-TPB were characterized by NMR, infrared, and UV-visible spectro-scopies. The ^{1}H-NMR spectrum of PEHPB in DMSO-d_6 showed the aromatic (pyridyl and phenyl) protons and the vinyl proton of the conjugated polymer backbone at 6.6-9.5 ppm. The methylene protons of p-hydroxyphenylethyl sub-stituents were also observed at around 3.0 ppm. Figure 1 shows the ^{1}H-NMR spectrum of PEHP-TPB in DMSO-d_6. It shows three type aromatic (pyridyl, phenyl, and tetraphenyl-borate) protons at the region of 6.4-9.4 ppm. Especially a characteristic strong peaks of tetraphenylborate counter anions were observed at 6.7, 6.9, and 7.2 ppm. The integra-tion ratio of the pyridyl protons and the phenyl protons of tetraphenylborate was 1 : 4.7 (1:5 for ideal structure). The methylene proton peaks of p-hydroxyphenylethyl substituents were also observed at 2.4-3.5 ppm. Figure 2 shows the ^{13}C-NMR spectrum of PEHP-TPB in DMSO-d_6. It shows the multiple peaks at the region of 115-158 ppm, which are originated from the aromatic carbons of pyridyl and phenyl moieties and the vinyl carbons of conjugated polymer back-bone. The two methylene carbon peaks were also observed at around 58 ppm.

Figure 3 shows the FT-IR spectra of two ionic conjugated polymers, PEHPB and PEHP-TPB, in KBr pellet. The characteristic O-H stretching frequency peaks of PEHPB and PEHP-TPB were observed around 3422 cm^{-1}. The FT-
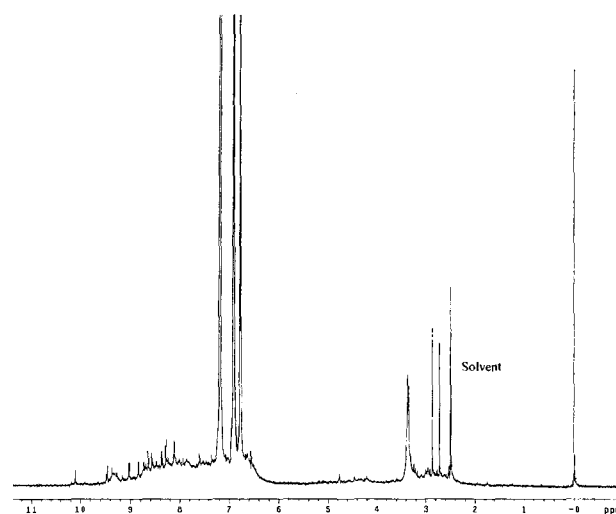
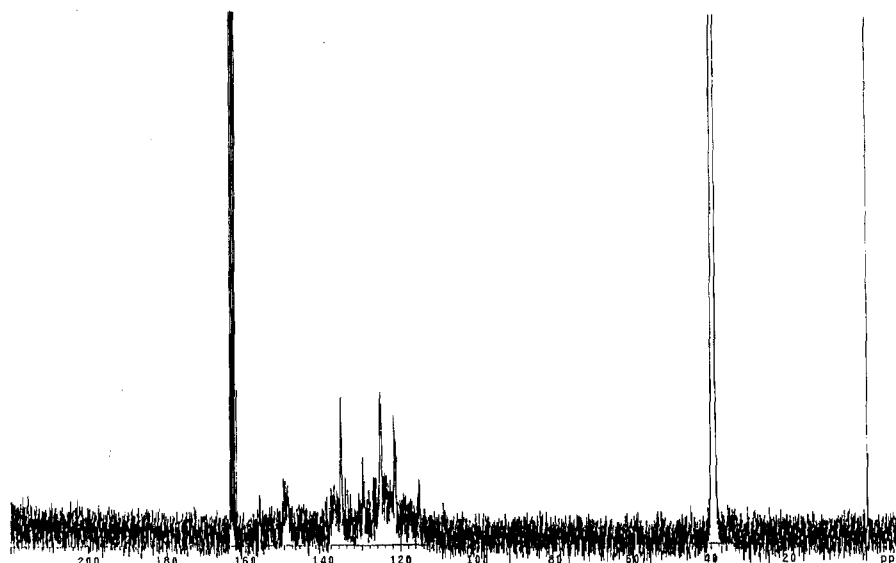**Figure 1.** ^{1}H-NMR spectrum of PEHP-TPB in DMSO-d_6.

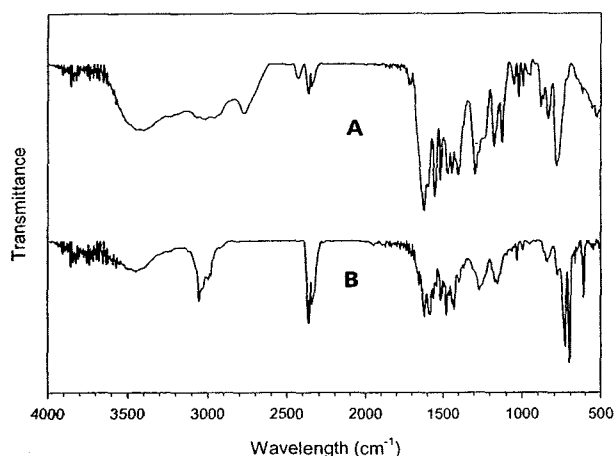Figure 2. ^{13}C-NMR spectrum of PEHP-TPB in DMSO-d$_6$.

Figure 3. FT-IR spectra of (A) PEHPB and (B) PEHP-TPB in KBr pellet.

Figure 4. UV-visible spectra of PEHPB (—) and PEHP-TPB (...) in DMF solvent.

IR spectra of the polymers 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 at 1618 cm^{-1} became more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine itself. More intense peaks of aromatic =C-H stretching frequencies at 3053 cm^{-1} were observed in the IR spectrum of PEHP-TPB (B) because of tetraphenylborate counter anions. The Ar-O stretching peaks were also observed around 1289 cm^{-1}. Figure 4 shows the UV-visible spectrum of PEHPB and PEHP-TPB in DMF solvent. It showed an interesting peak at the visible region (400-800 nm), which is a characteristic peak of the conjugated
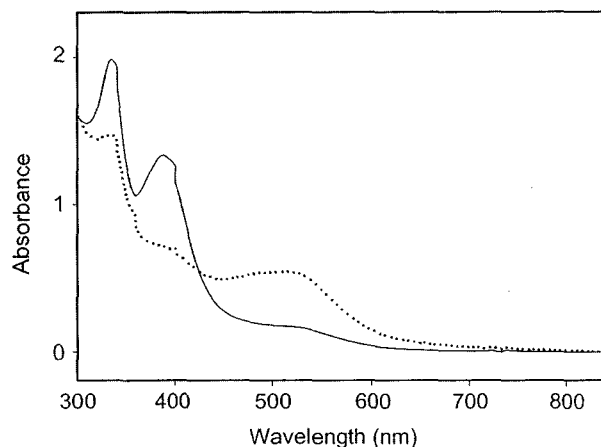
polyene backbone system. The UV-visible spectrum of PEHP-TPB showed a characteristic λ_{max} at 512 nm, whereas the UV-visible spectrum of PEHPB only showed shoulder at the same wavelength. From these spectral data, we concluded that the present two polymers has an ionic conjugated polymer backbone system bearing the designed functional groups.

The PEHPB was found to be very hygroscopic at atmospheric conditions because of the ionic character and the hydroxy group in polymer structure, whereas the ion-exchanged product, PEHP-TPB was found to be less hygroscopic. The hygroscopic nature of PEHPB was also evidenced by the broad and intense peaks at around 3450 cm^{-1} in the infrared spectrum of PEHPB. These polymers were completely soluble in such organic solvents as DMF, DMSO,

and acetone, but insoluble in water and ether. PEHPB was completely soluble in methanol, whereas the similar polymer (PEHP-TPB) having tetraphenylborate as counter anion was insoluble in methanol. The inherent viscosities of PEHPB and PEHP-TPB were 0.18 and 0.20 dL/g, respectively. The morphology of PEHPB and PEHP-TPB was also investigated by X-ray diffraction analysis. The X-ray diffractograms of the resulting polymers are shown on Figure 5. 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,[10,43] the polymers were mostly amorphous.

Figure 6 shows the TGA thermogram of PEHPB under nitrogen atmosphere at a heating rate of 10 °C/min. The TG thermogram of PEHPB indicated that this polymer start to
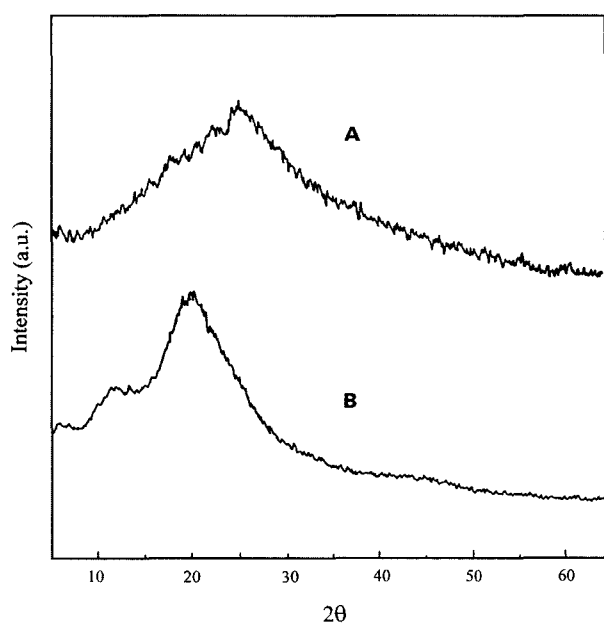

Figure 5. X-ray diffractograms of (A) PEHPB and (B) PEHP-TPB.
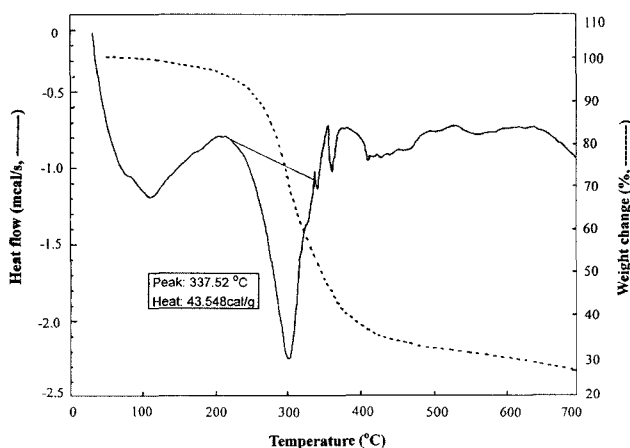

Figure 6. TGA thermogram of PEHPB under nitrogen atmosphere at heating rate of 10 °C/min.

decompose above 200 °C. PEHPB retains 95% of its original weight at 232 °C, 80% at 283 °C, 60% at 321 °C, and 40% at 379 °C. The TG thermogram of PEHP-TPB was very similar with that of PPEHPB. The char yields of PEHPB and PEHP-TPB after heating up to 700 °C were 27 and 31%, respectively.

Conclusions

Two ionic conjugated polymers were prepared by the activated polymerization of 2-ethynylpyridine by using *p*-(2-bromoethyl)phenol without any additional initiator or catalyst and the consecutive ion-exchange reaction of PEHPB by using sodium tetraphenylborate. The polymerization mechanism was assumed to include the initial formation of 2-ethynyl-*N*-(*p*-hydroxyphenylethyl)pyridinium bromide and the initiation step for the polymerization of 2-ethynyl-*N*-(*p*-hydroxyphenylethyl)pyridinium bromide by the non-bonding electron pair of 2-ethynylpyridine and/or bromide counter anion. These polymers were completely soluble in such organic solvents as DMF, DMSO, and acetone. The inherent viscosities of PEHPB and PEHP-TPB were 0.18 and 0.20 dL/g, respectively. The polymer structure was characterized by various instrumental analysis to have the conjugated polymer backbone system with the designed substituents. The X-ray diffraction analyses of PEHPB and PEHP-TPB indicated that the polymers were mostly amorphous.

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