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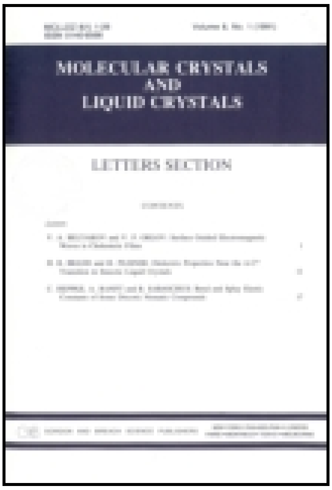

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Synthesis and Characterization of Poly[p-(N-ethylbenzenesulfonate sodium)-2-ethynylpyridinium Bromide]

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Synthesis and Characterization of Poly [*p*-(N-ethylbenzenesulfonate sodium)-2-ethynylpyridinium Bromide]

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A substituted polyacetylene with benzenesulfonate functional groups was synthesized from the non-catalyst polymerization of 2-ethynylpyridine using sodium 4-(2-bromoethyl)benzenesulfonate. The activated acetylenic triple bond of monomeric N-substituted-2- ethynylpyridinium bromide, formed at first quaternarization process of 2-ethynylpyridine by sodium 4-(2-bromoethyl)benzenesulfonate was susceptible to linear polymerization. Instrumental analysis datas revealed that the polymer had the fully conjugated backbone system with the designed substituents. The photoluminescence spectrum of polymer showed that the photoluminescence peak is located at 545 nm, corresponding to a photon energy of 2.28 eV.

Keywords Polyacetylene; 2-ethynylpyridine, sodium 4-(2-bromoethyl)benzenesulfonate, non-catalyst polymerization; photoluminescence

Introduction

Substituted polyacetylenes (PAs) with a fully conjugated backbone have attracted considerable attention due to their unique properties such as semiconductivity, paramagnetism, photoluminescence, photoconductivity, high nonlinear optical susceptibility, high gas permeability and so on [1–12].

Ionic PAs were described as a conjugated polymer where a significant fraction of monomeric unit contained a covalently attached ionic and/or ionizable groups acting as a stable/immobile dopant anion [13]. Due to their extensive conjugation and ionic nature, these ionic PAs have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices [14–18]. Sodium salts and acid forms of such conducting polymers as poly(3-thiophene ethanesulfonate) and poly(3-thiopphene butanesulfonate) were the first examples of self-doped conducting polymers to show water solubility in neutral and doped states [19]. Following these initial reports, there had been a number of report concerning the synthesis

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of conjugated polymers with various sulfonate groups [20, 21]. In 1978, Simionescu et al firstly reported the synthesis of 2- or 3-ethynylpyridine homopolymer with MeI or EtI and the preparation of conducting complexs by mixing the quaternized ethynylpyridine polymers with LiTCNQ or TCNQ in acetonitrile [22]. Blumstein et al reported the uncatalyzed synthesis of several well-defined ionic PAs through the activated polymerization of ethynylpyridines using alkyl halides [14, 16]. They reported that the quaternization of ethynylpyridine nitrogen atom with alkyl groups permitted the formation of monosubstituted ionic PAs with different functionalities. We have also prepared various ionic PAs by the non-catalyst polymerization of ethynylpyridines using functional alkyl halides or cyclic compounds [23–28].

The pyridine-contaioning ionic PAs have been used as material candidates for hybrid polymer gels [29], nanocrystalline CdS polymer sensitizer [30, 31], π-conjugated polymer-nanocomposites [32–34], fluorescence enhancer [35], and unipolar write-once-read-many-times (WORM) memory devices [36].

Herein, we report the synthesis of a new ionic PA with benzenesulfonate groups through the uncatalyzed polymerization of 2-ethynylpyridine using sodium 4-(2-bromoethyl)benzenesulfonate and the characterization of the resulting poly[N-(2-ethylbenzenesulfonate sodium)-2-ethynylpyridinium bromide] (PESEPB).

Experimental

Solvents were analytical grade materials. They were dried with an appropriate drying agent, distilled and stored under nitrogen. The bromination of 2-vinylpyridine and the followed dehydrobromination of brominated product were used for the synthesis of 2-ethynylpyridine according to the literature method [37]. 2-Vinylpyridine (Aldrich Chemicals., 97%), bromine (Aldrich Chemicals., 99.99 + %), sodium amide (Aldrich Chemicals., 95%), and sodium 4-(2-bromoethyl)benzenesulfonate (TCI, >98%) were used without further purification.

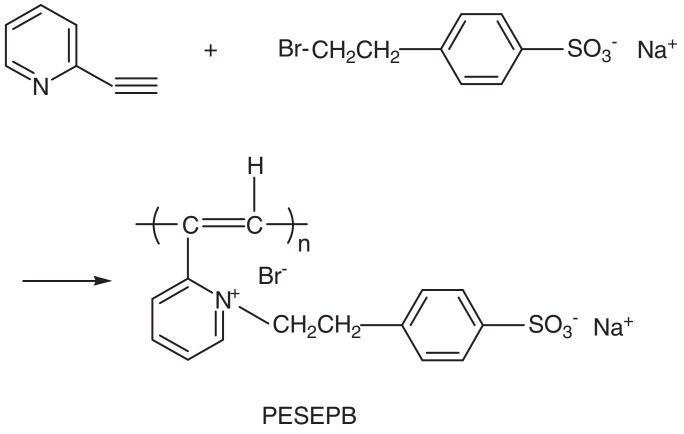
PESEPB was prepared via the non-catalyst polymerization of 2-ethynylpyridine using sodium 4-(2-bromoethyl)benzenesulfonate. Polymerization was carried out in a 100 mL round-bottom flask equipped with magnetic stirrer and carried out by the following procedure. Sodium 4-(2-bromoethyl)benzenesulfonate (2.78 g, 9.7 mmol) was dissolved in N,N-dimethylformamide (DMF, 20.5 mL, $[M]_0 = 0.40$ M) at 90°C. Then, 2-ethynylpyridine (1.0 g, 9.7 mmol) was injected to the DMF solution of sodium 4-(2-bromoethyl)benzenesulfonate. The polymerization was carried out at 90°C for 24 hrs under nitrogen atmosphere. As the polymerization proceeded, the initial light-brown reaction solution became into more viscous dark reddish brown solution. The polymer solution diluted with 10 mL DMF was precipitated into a large excess of ethyl ether. The precipitated polymer was easily filtered and the resulting solid was dried in vacuo at 40°C. The black polymer powder was obtained in 87% yield.

IR and NMR spectra were recorded on a Bruker EQUINOX 55 spectrometer and a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA), respectively. UV-visible spectra were obtained on a HP 8453 UV-visible spectrophotometer. Photoluminescence spectra were obtained on a Perkin Elmer luminescence Spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. X-ray diffractograms were recorded on a PHILLIPS X-ray diffractometer (Model: XPert-APD). Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 2200 thermogravimetric analyzer. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200).

Results and Discussion

The non-catalyst synthetic method for ionic PAs has significant benefit because it essentially exclude the contamination of polymer sample which can be originated from the catalyst or initiator used during the process. Many of these ionic PAs exhibit an enhanced solubility in organic solvents including especially water owing to the presence of ionic moieties. Ethynylpyridinium monomeric species, which was formed at the initial reaction step, are spontaneously polymerized to form highly conjugated, charged PAs.

Here, we used the non-catalyst polymerization method for the synthesis of an ionic PA with benzenesulfonate groups (Scheme 1). The reaction solution of 2-ethynylpyridine and sodium 4-(2-bromoethyl)benzenesulfonate in DMF solvent was exposed in oil bath (90°C). The polymerization proceeded well without any additional iniatiator or catalyst. As the reaction proceed, the solution became viscous and the color of reaction mixture was changed from the light brown of the initial mixture into dark reddish brown. The balck polymer powder was obtained in 87% yield. The reaction contains the first quarternarization of 2-ethynylpyridine by sodium 4-(2-bromoethyl)benzenesulfonate. The activated acetylenic functional group of monomeric salt was susceptible to the anionic polymerization, initiated by a nucleophilic attack by the nitrogen atom of the unreacted ethynylpyridine and/or the bromide ion [26, 27].



Scheme 1. Synthesis of PESEPB.

In order to evaluate the chemical structure of PESEPB, various instrumental methods such as IR, NMR, and UV-visible spectroscopies were used. Figure 1 shows the FT-IR spectrum of PESEPB measured in KBr pellet. FT-IR spectrum reveals the disappearance of the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C-H bond stretching (3293 cm^{-1}) frequencies of ethynyl group. Instead, the $C = C$ stretching frequency peaks of conjugated polymer backbone and aromatic rings around 1625 cm^{-1} became relatively more intense than those of the $C = C$ stretching frequencies of 2-ethynylpyridine and 4-(2-bromoethyl)benzenesulfonate. The strong peak at 1215 cm^{-1} is due to the $S = O$ stretching frequencies of sulfonate salts. The strong peak at 747 cm^{-1} is due to the CH out-of-plane deformation of pyridyl moieties.

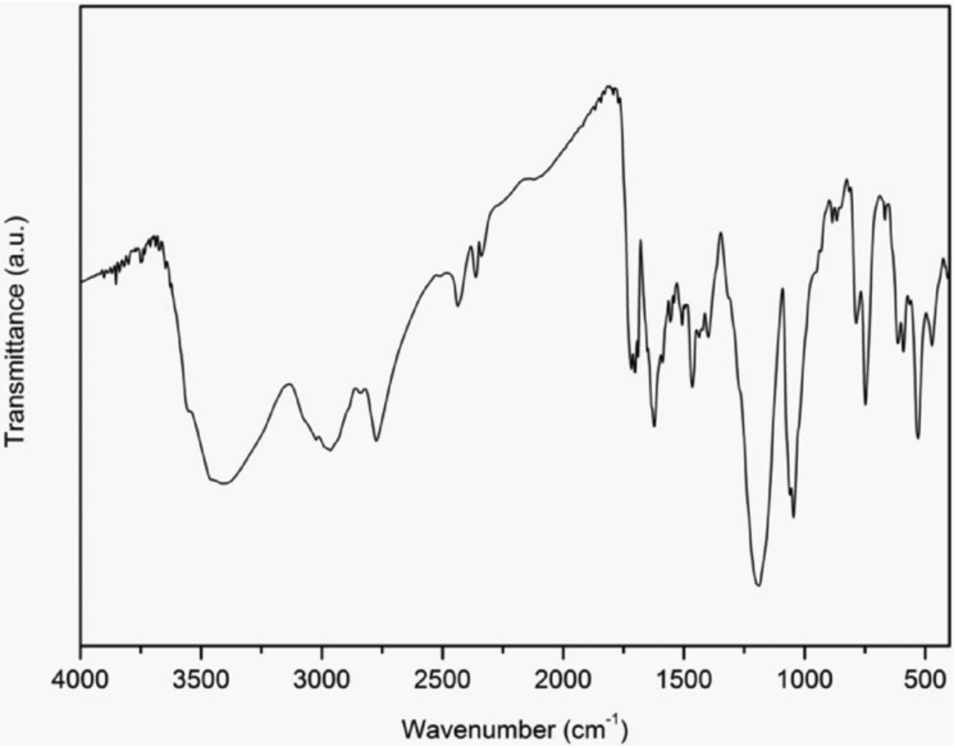


Figure 1. FT-IR spectrum of PESEPB in KBr pellet.

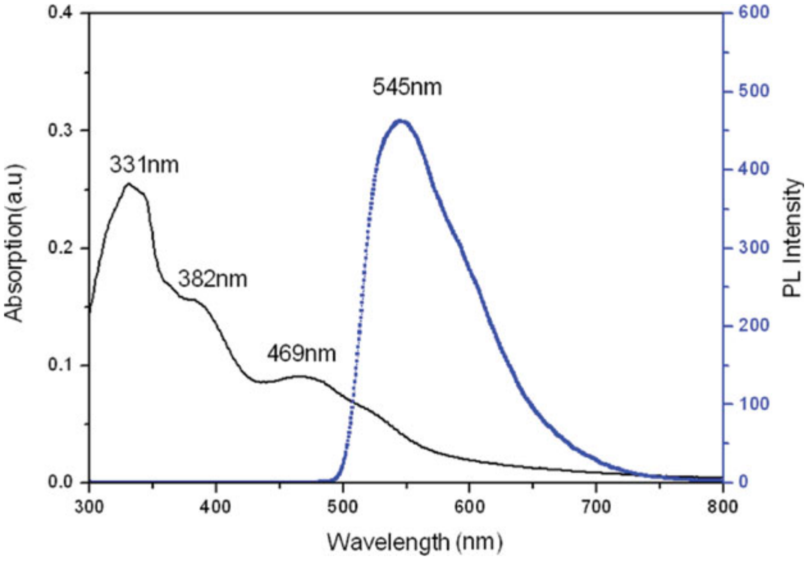


Figure 2. UV-visible and photoluminescence spectra of PESEPB.

The ^{1}H-NMR spectrum of polymer showed the aromatic pyridyl and phenylene protons and the vinylic protons of conjugated polymer backbone in the range of 6.2–9.7 ppm and also showed the methylene proton peaks at 3.4–4.6 ppm. The ^{13}C-NMR spectrum of PESEPB showed the aromatic carbon peaks of pyridyl and phenylene moieties and the vinyl carbons of conjugated polymer backbone showed in the range of 108–158 ppm. The methylene carbon peaks were observed at 47–54 ppm. The UV-visible spectrum (Figure 2) of PESEPB in DMF exhibits a very broad absorption in the range of 300–750 nm with three λmax at 331, 382, and 469 nm. The newly observed absorption peaks in the visible region (up to 750 nm) are strong evidence that the present polymer have an expanded -conjugation system along the polymer chain. The photoluminescence spectra of PESEPB showed that the photoluminescence maximum peak is located at 545 nm corresponding to the photon energy of 2.28 eV.

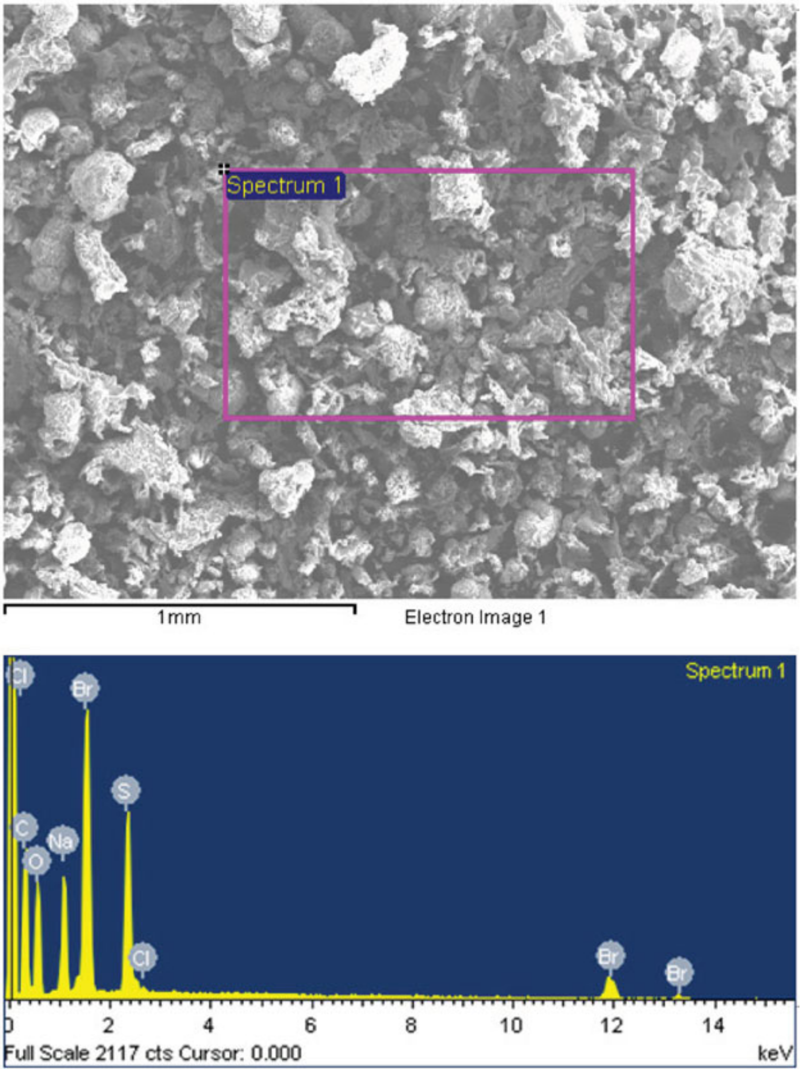


Figure 3. EDX spectrum of PESEPB powder.

When PL was checked with excitation of 469 nm wavelength, excitation peak was removed by using cut-off filter in PL detection. In our previous work [38], the optical properties of poly[2-ethynyl-N-(4-(methylthio)benzylpyridinium bromide] which has methylthiobenzyl side group were studied. Poly[2-ethynyl-N-(4-(methylthio)benzylpyridinium bromide] showed similar edge range of UV-visible absorption spectrum about 600–750 nm, but UV and PL maximum values were red-shifted to 532 nm and 508 nm, respectively. Comparing UV absorption spectra and PL maximum values of two similar polymers, it means that the highly charged sulfonate group of conjugated polymer makes relatively red-shifted maximum values.

This polymer was soluble in such polar organic solvents as DMF and dimethylsulfoxide (DMSO) and was insoluble in chloroform and benzene.The solubility of polymer in aqueous solutions can be due to the hydrophilic interactions between the covalently attached ionic group on the polymer main chain and polar water molecules [13]. The inherent viscosity of PESEPB was 0.13 dL/g. The morphologies of PESEPB 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 [1, 2], indicating that PESEPB is mostly amorphous. The EDX spectrum of PESEPB (Figure 3) clearly depicts the presence of C, O, Na, Br, and S elements. The thermal properties of PESEPB were studied by TGA thermometry. This polymer showed slightly weight loss at relatively low temperature (about 5% at 200°C), which is mainly due to the absorbed moisture and/or organic resudues in the polymer. PESEPB exhibited an abrupt weight loss from 225°C. TGA thermogram shows that the polymer retains 98.0% of its original weight at 100°C, 95.8% at 200°C, 70.0% at 300°C, 52.5% at 400°C, 49.5% at 500°C, 36.9% at 600°C, and 16.7% at 700°C.

Conclusions

A new ionic PA with benzenesulfonate moieties was easily synthesized by the non-catalyst polymerization of 2-ethynylpyridine using sodium 4-(2-bromoethyl)benzenesulfonate. The first reaction of 2-ethynylpyridine and sodium 4-(2-bromoethyl)benzenesulfonate yields a monomeric species with activated terminal acetylene group. The acetylene groups of monomeric were susceptible to the linear polymerization, followed by an identical propagation step that contains the produced macroanion and the quaternized monomeric species. The spectral data on polymer structure revealed that the polymer had an expanded -conjugation system along the polymer chain. The solubility of polymer in aqueous solutions was due to the hydrophilic interactions between the ionic polymer and the polar water molecules. The X-ray diffraction data on polymer indicated that this polymer is mostly amorphous. The photoluminescence maximum peak of polymer was located at 545 nm corresponding to the photon energy of 2.28 eV.

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