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Synthesis and properties of ionic conjugated polymer with spiroxazine moiety

Sung-Hoon Kim[a,*], Soo-Jong Lee[a,1], So-Yeon Park[a], Hee-Jung Suh[a], Sung-Ho Jin[b], Yeong-Soon Gal[c]

[a] *Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, South Korea*
[b] *Department of Chemistry Education, Pusan National University, Pusan 609-735, South Korea*
[c] *Polymer Chemistry Laboratory, College of General Education, Kyungil University, Kyungsan 712-701, South Korea*

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Abstract

A noble conjugated ionic polymer with photochromic spiroxazine moiety, poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] (PEHSPB) **6** was prepared by the activated polymerization of 2-ethynylpyridine **5** with 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** without any additional initiator or catalyst. The polymerization reaction was performed in DMF solvent at the temperature of 120 °C. As the polymerization proceeded, the reaction solution became more viscous and black in colour. The polymer yield and inherent viscosity were 75% and 0.15 dL/g, respectively. The instrumental analysis data on the chemical structure of PEHSPB **6** indicated that the present PEHSPB **6** have a conjugated polymer backbone system with the spiroxazine-hexyl substituents. X-ray diffraction analyses of the polymers indicated that the present polymers are mostly amorphous. The photoluminescence peak is located at 515 nm corresponding to the photon energy of 2.41 eV. Upon UV irradiation, closed spiroxazine form is transformed into the open merocyanine form that reverts back to the colourless spiro form in dark.

Keywords: Ionic polymer; Conjugated polymer; 2-Ethynylpyridine; Spiroxazine; Photochromism; Luminescence

1. Introduction

Conjugated organic polymers are of particular interest in material science because of their extraordinary optical and electronical properties. For more than several decades, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics [1,2]. The initial impetus for the plethora of work on conducting polymers was generated by the discovery of the increase, by nearly 10 orders of magnitude, in the electrical conductivity in the oxidized form of π-conjugated polyacetylene (PA) in 1977 [3].

Among the π-conjugated polymers, the polyacetylene is structurally the simplest one, and it can be made as free-standing thin film by using Shrakawa catalysts [$Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$] [4–6]. 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.

To overcome these problems of PA itself, 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 [7–11]. The polymers having a conjugated backbone are

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* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

[1] Present address: FITI Testing and Research Institute, Seoul 892-64, South Korea.

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expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, colour, and chemical reactivity and complex formation ability [7,12–21].

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. The polyelectrolytes include proteins, nucleic acids, pectins, polyacrylic acid, and polystyrene sulfonate. A few examples of conjugated polyelectrolytes include poly(propiolic salt)s [22], triethylammonium salt of poly(6-bromo-1-hexyne) [23], and poly(ethynylpyridine)s [24–28]. In 1990, Blumstein et al. prepared the well-defined ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides. We have also reported on the preparation of various ionic conjugated polymers having different functionalities [29–32]. 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 [25].

Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and their potential applications in the areas of linear and nonlinear optics [33]. Although spiroheterocyclic compounds have attracted significant attention because of their potential use, they still await major commercial exploitation. One of the prime reasons for the lack of industrial applications for photo- and thermochromic materials, particularly organic compounds, is their poor durability. Although the thermo- and photochromism of spiropyran has been extensively studied [34–37], only little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects, but the replacement of benzopyran ring by a naphthoxazine ring, which results in spironaphthoxazine, greatly improves resistance to prolonged UV irradiation, which confers greatly commercial importance [38].

Now, we report the synthesis of new ionic conjugated polymer, poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] by the activated polymerization of 2-ethynylpyridine with 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine, and the electro-optical properties of the resulting polymer.

2. Experimental

2.1. Materials

1,3,3-Trimethyl-2-methyleneindolin, 1-nitroso-2,7-dihydroxynaphthalene, 1,6-dibromohexane, 2-vinylpyridine, bromine (99%), and sodium amide (tech., 90%) were purchased from Aldrich Chemicals and were used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled.

2.2. Synthesis of 2-ethynylpyridine **5**

2-Ethynylpyridine **5** was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [15].

2.3. Synthesis of 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-b][1,4]oxazine **4**

1,3,3-Trimethyl-6′-hydroxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxynaphthalene **2** according to the method described in Refs. [39,40]. 50% yield: m.p. 212–214 °C; Anal. cald. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.89; H, 4.97; N, 8.59.

A stirred solution of **3** (1 g, 2.9 mmol) and 1,6-dibromohexane (1.47 g, 2.9 mmol) in acetone (150 ml) containing suspended powdered potassium carbonate (0.32 g) was refluxed for 24 h. The solution was filtered and then the filtrate was evaporated under reduced pressure. The product obtained was washed with methanol several times and recrystallized from hexane. 63% yield: mp 147 °C; MS *m*/*z* M^+ 507; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6H), 1.57 (m, 5H), 1.91 (m, 4H), 3.44(t, $J = 6.52$ Hz, 2H), 4.18 (t, $J = 6.52$ Hz, 2H), 6.57 (d, $J = 7.52$ Hz, 1H), 6.84 (d, $J = 9$ Hz, 1H), 6.89 (t, $J = 8.04$ Hz, 1H), 7.03 d, $J = 9.1$ Hz, 1H), 7.08 (d, $J = 6.52$ Hz, 1H), 7.20 (t, $J = 7.16$ Hz, 1H), 7.56 (d, $J = 9.04$ Hz, 1H), 7.63 (d, $J = 9.04$ Hz, 1H), 7.71 (s, 1H), 7.84 (s, 1H); Anal. cald. for $C_{28}H_{31}N_2O_2Br$: C, 66.27; H, 6.16; N, 5.52; O, 6.31. Found: C, 66.95; H, 6.43; N, 6.07; O, 6.27.

2.4. Synthesis of poly(2-ethynyl-N-hexyloxyspiroxazine pyridinium bromide) [PEHSPB] **6**

PEHSPB **6** was prepared by the activated polymerization of 2-ethynylpyridine **5** with 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** without any additional initiator or catalyst in DMF solvent as follows. The 1:1 mixture of 2-ethynylpyridine **5** (0.203 g, 19.7 mmol) and 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** (1.00 g, 19.7 mmol) in DMF solvent (5 mL $[M]_0 = 0.318$ M) was stirred for 24 h at 120 °C under nitrogen atmosphere. As the reaction proceeded, the colour 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 h. The polymer yield was 75%.

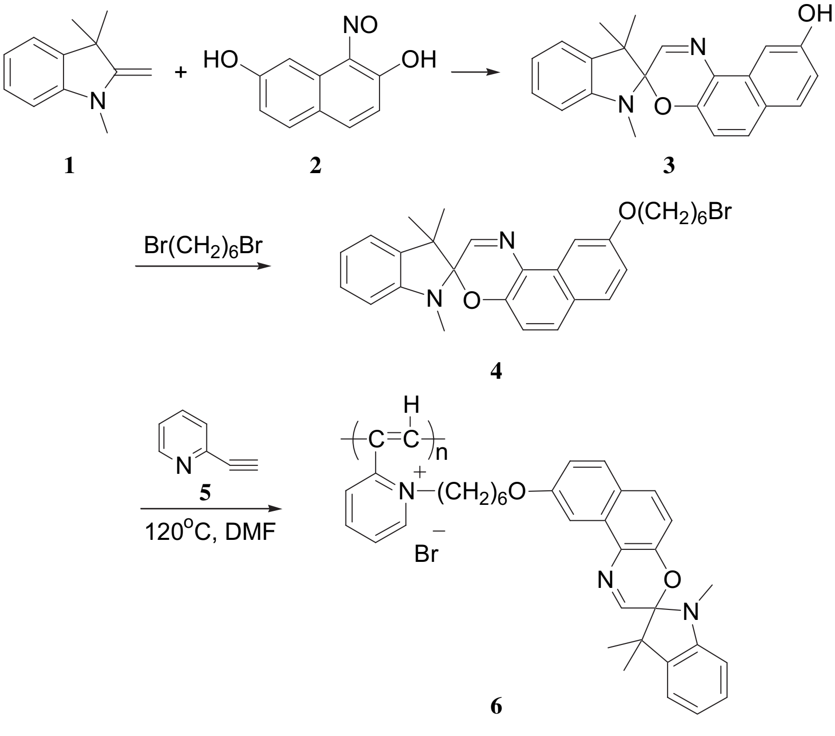
2.5. Instruments and measurement

NMR (^{1}H 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. ^{1}H NMR spectra of intermediates were recorded on the Bruker, Avance Digital 400. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Melting points were determined using an Electrothermal IA 900 and are uncorrected. CHN analyses were carried out with a Carlo Elba model 1106 analyzer. Mass spectra were recorded on a Shimadzu OP-1000 spectrometer using electron energy of 70 eV and direct probe EI method. 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 750M), 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.

3. Results and discussion

A functional alkyl bromide, 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4**, was prepared by the reaction of 1,3,3-trimethyl-6′-hydroxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **3** and 1,6-dibromohexane as described in Scheme 1. 1,3,3-Trimethyl-6′-hydroxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxynaphthalene **2** according to the method described in Refs. [39,40].

The activated acetylenic functional groups of *N*-substituted-2-ethynylpyridinium halides were found to be susceptible to the linear polymerization, yielding the ionic conjugated polymer systems. We used this synthetic method to prepare the ionic conjugated



Scheme 1. Synthesis of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] (PEHSPB).

polymer with photo-responsive spiroxazine moieties in the polymer side chain. The PEHSPB was prepared by the activated polymerization of 2-ethynylpyridine **5** with 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** in DMF solvent without any initiator and catalyst (Scheme 1).

It was known that the polymerization of ethynylpyridines by using such simple alkyl halides as methyl iodide, 1-octyl bromide, lauryl bromide, etc. proceed even at the mild reaction condition of low temperature (<50 °C) [25–27,30]. The activated acetylenic triple bonds of *N*-alkyl-2-ethynylpyridinium halide was found to be susceptible to the polymerization under mild conditions. However, the present polymerization did not proceed at relatively low temperature. Thus, the polymerizations were carried out at the elevated temperature (120 °C). As the reaction proceeded, the colour of reaction mixture changed from the light brown of the initial mixture into dark black. The black polymer powder was obtained in 75% yield. These polymerization behaviors were found to be very similar to that of the polymerization reaction of 2-ethynylpyridine with 6-(*N*-carbazolyl)hexyl bromide [41].

The presence of oxygen did not influence the present polymerization. And the quarternarized ethynylpyridines were found to participate the polymerization reaction. 2-Ethynylpyridine **5** itself can be thermally polymerized to give only low yield of polymer. Thus, the present polymerization process may contain the first quarternarization of 2-ethynylpyridine **5** by spiroxazine-hexyl bromide **4** at the elevated temperature. The inactivity at low temperatures may be due to the very low quarternarization reactivity. The activated acetylenic triple bond of *N*-substituted-2-ethynylpyridinium bromide formed at the elevated temperature is susceptible to the linear polymerization. The activated monomer can be initiated by the nonbonding electron pair of 2-ethynylpyridine and/or bromide counter anion, which is very similar mechanism for the spontaneous polymerization of 3- and 4-vinylpyridines on quarternarization of the pyridine nitrogen by alkyl halides [42,43] and ethynylpyridines by simple alkyl halides [25–27].

The chemical structure of PEHSPB was characterized by NMR, infrared, and UV–visible spectroscopies. Fig. 1 shows the FT-IR spectra of 2-ethynylpyridine **5**, 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4**, and PESHPB **6** in KBr pellets. The FT-IR spectrum of PEHSPB **6** 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 **5**. Instead, the C=C stretching frequency peak of conjugated polymer backbone at 1600–1620 cm^{-1} became more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine **5** and spiroxazine-hexyl bromide **4**. The peak at 1085 cm^{-1} is due to the C–O–C linkages of PEHSPB **6**. And the peaks at 2862 and 2931 cm^{-1} are characteristics of the aliphatic C–H stretching frequencies.

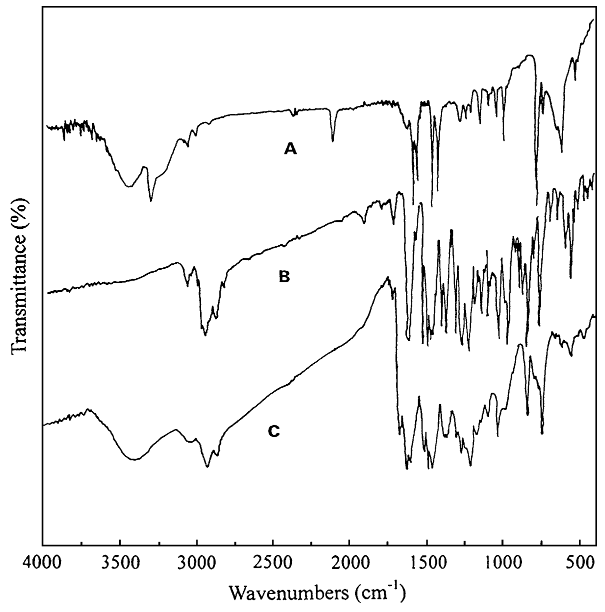


Fig. 1. FT-IR spectra of 2-ethynylpyridine **5** (A), 1,3,3-trimethyl-6′-bromohexyloxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-*b*][1,4]oxazine **4** (B), and poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** (C) in KBr pellets.

Fig. 2 shows the ^{1}H NMR spectrum of PEHSPB **6** in DMSO–d_6. It shows that the aromatic protons of pyridyl and spiroxazine moieties and the vinyl proton of the conjugated polymer backbone at 6.5–8.6 ppm. The peaks of the internal four methylene protons of hexyl linkage and the two methyl protons of spiroxazine moieties are observed broadly at high field region of 0.4–2.0 ppm. And the methylene adjacent to oxygen atom (of ether linkages) was observed broadly at 3.2–4.2 ppm. The methyl and methylene protons adjacent to the N-atom were observed at 2.4–3.0 ppm.

Fig. 3 shows the ^{13}C NMR spectrum of PEHSPB **6** in DMSO–d_6. The multiple and complicated peaks at the region of 98–164 ppm, which are originated from the

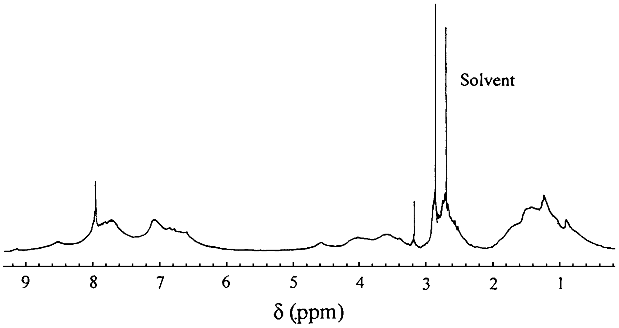


Fig. 2. ^{1}H NMR spectrum of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** in DMSO–d_6.

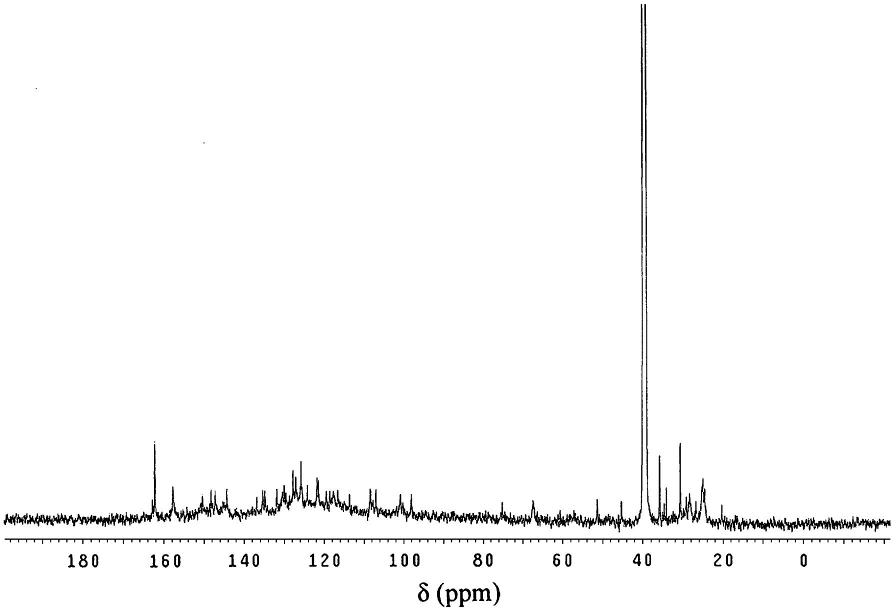


Fig. 3. ^{13}C NMR spectrum of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** in DMSO–d_6.

aromatic carbons of pyridyl and spiroxazine moieties and the vinyl carbons of conjugated polymer backbone. The methylene carbon peaks adjacent to the oxygen atom are observed at 75 ppm. And the quaternary carbon peaks of spiroxazine moieties are seen at 68 ppm. The other methylene and methylene carbon peaks are observed at the region of 20–60 ppm. From these spectral data, we concluded that PEHSPB **6** has a ionic conjugated polymer system bearing the designed spiroxazine substituents.

Fig. 4 shows the UV–visible spectra and photoluminescence (PL) spectra of PEHSPB **6** in DMF solution. The UV–visible spectrum of PEHSPB **6** 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 515 nm corresponding to the photon energy of 2.41 eV.

In order to evaluate the thermal properties of PEHSPB **6**, we measured the TGA and DSC thermograms of PEHSPB **6** under nitrogen atmosphere. Fig. 5 shows the TGA thermogram of PEHSPB. As shown in this figure, this polymer was found to be stable up to 230 °C. The DSC thermogram exhibited the glass transition temperature at 171.6 °C. 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, the polymers were mostly amorphous [7,8].

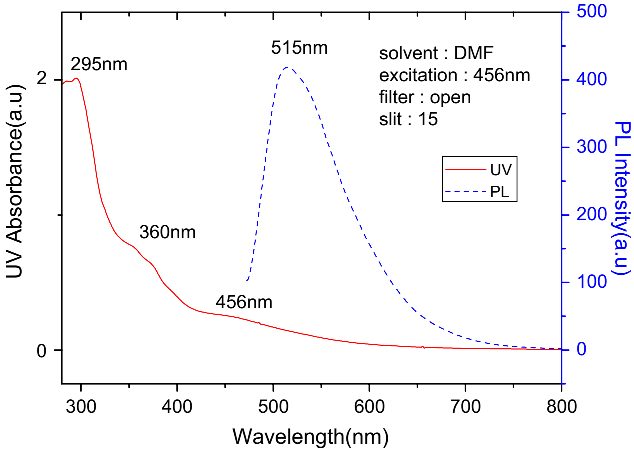


Fig. 4. Optical absorption and photoluminescence spectra of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6**.

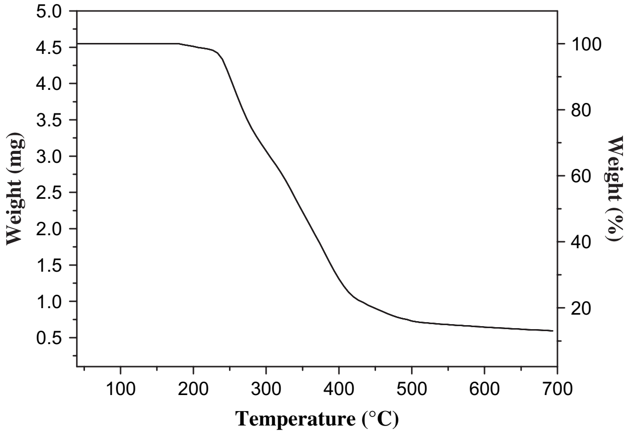


Fig. 5. TGA thermogram of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** under nitrogen atmosphere.

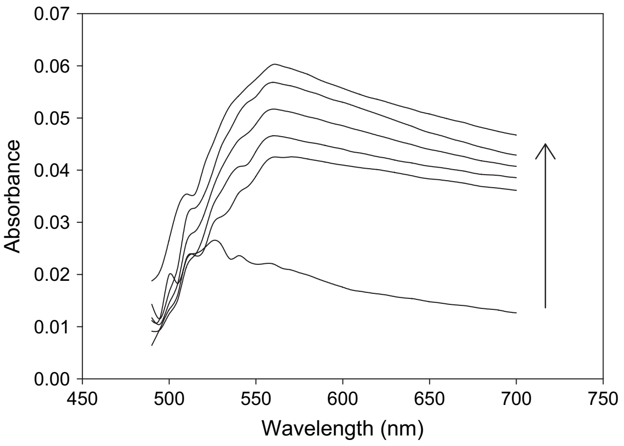


Fig. 6. Visible spectral changes of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** in DMF upon UV irradiation.

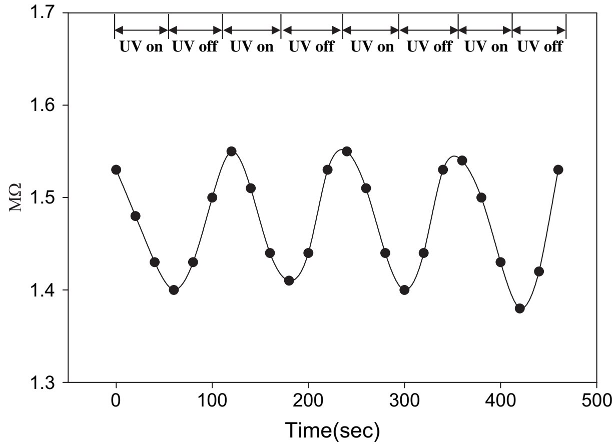


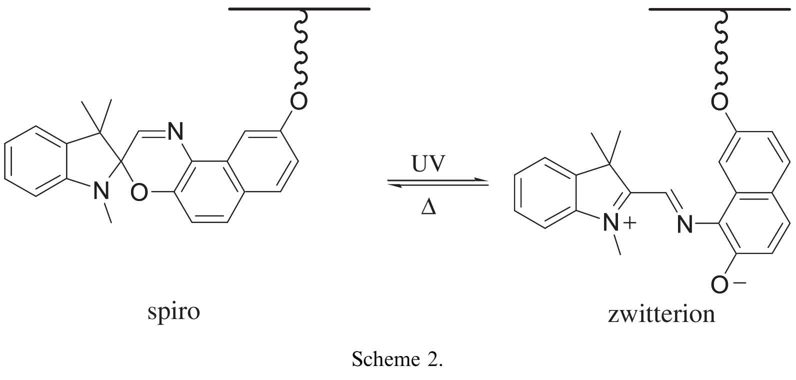
Fig. 7. Resistance charges of poly[2-ethynyl-*N*-hexyloxyspiroxazine pyridinium bromide] **6** in DMF following periodic UV irradiation.

The photochromic reaction in question is caused by the reversible heterolytic cleavage of the C(spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closure under visible light irradiation or in dark. Electronic absorption spectral changes of polymer upon UV irradiation in DMF are depicted in Fig. 6. The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. The original spectral pattern was reversibly recovered within 3 min.

The photoinduced ionic conductivity response was also analyzed at 150 °C and is shown in Fig. 7. The ionic conductivity increased upon UV irradiation, which brought about the generation of zwitterion form, and subsequently decreased in dark, which brought about the generation of closed spiro form (Scheme 2). Sufficient reversibility was found in this polymer and this response was completely synchronized with that in the absorbance charges.

4. Conclusions

In this article, we dealt with the synthesis and properties of a new conjugated ionic polymer with spiroxazine moiety, PEHSPB **6**. We prepared PEHSPB **6** in high yield by the activated polymerization of 2-ethynylpyridine **5** and spiroxazine-hexyl bromide **4** without any additional initiator or catalyst. 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 has a conjugated backbone system with the designed spiroxazine moieties. The photoluminescence spectra of PEHSPB **6** showed that the photoluminescence peak is located at 515 nm corresponding to the photon energy of 2.41 eV. This polymer was found to be stable up to 230 °C and the glass transition temperature was 171.6 °C. The closed spiroxazine form is transformed into the open



Scheme 2.

merocyanine form that reverts back to the colourless spiro form in dark, upon UV irradiation.

Acknowledgement

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