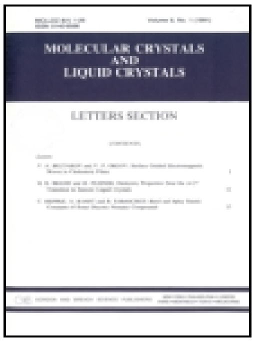

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Synthesis of Poly(2-Ethynylpyridinium Trifluoroacetate) by Spontaneous Polymerization

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Poly (2-ethynylpyridinium trifluoroacetate) (P2EPF) was synthesized by the spontaneous polymerization of 2-ethynylpyridine (2-EP) and trifluoroacetic acid (TFA). TFA, as a strong acid for sufficient activation of the acetylenic triple bond, was used in the spontaneous polymerization of 2-EP producing conjugated and ionic polyacetylenes. P2EPF was soluble in polar organic solvents due to inherent characteristics of ionic polymers. The chemical structure and composition of P2EPF were characterized by ^{1}*H-NMR,* ^{13}*C-NMR, FT-IR, and UV-Vis spectrometer. The fluorescence spectra of P2EPF suggested that P2EPF were successfully synthesized as potential conducting materials.*

Keywords 2-Ethynylpyridine; trifluoroacetic acid; ionic conjugated polymer

Introduction

Conducting polymers have great potential application in various fields such as solar cell, sensor, semiconductor, energy-storage device, light emitting device and permselective membrane [1–3]. Polyacetylene is a simplest conjugated polymer, consists of a backbone of carbon atom, each bonded to one hydrogen atom and connected together by alternating single and double bonds. This simplest carbon-carbon conjugated structure has not only big potential but also drawbacks such as infusible and unstable to air oxidation [4,5]. Many researchers have studied on the synthesis of substituted polyacetylenes to tackle these drawbacks. Unlikely, mono and di-substituted polyacetylenes are soluble in aqueous and organic solvents, even stable in air for a long time. Successful polymerization of a substituted acetylene was achieved by Masuda [6]. In the polymerization of substituted polyacetylenes, numerous catalyst has been used such as Mo-, W-, Nb-, Ta- and Rh- based transition metals. A series of previous studies have reported a new family of mono and disubstituted polyacetylenes that possess an ionic nature and extensive backbone conjugation. Kang *et al.* reported cyclopolymerization of dihexyldipropargylammonium salts having bromine and tosylate as counter ions by $MoCl_5$- based metathesis catalysts [7]. Blumstein and coworkers reported the preparation of ionic polyacetylenes by using ethynylpyridine

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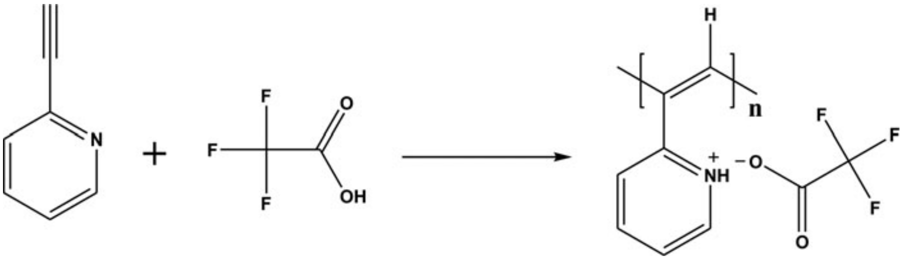

Figure 1. Synthesis of poly (2-ethynylpyridinium trifluoroacetate).

an alkyl halide, via activated polymerization without initiators or catalysts [8] which involve the initial formation of alkylpyridinium salts via the Menschutkin reaction. Gal *et al.* reported synthesis of poly(ethynylpyridine) with diverse alkyl halide by activated polymerization and studied the electro optical properties of the resulting conjugated ionic polymers [9–11]. Blumstein *et. al* reported spontaneous polymerization of 2-ethynylpyridine (2-EP) with strong acid which showed fast and exothermic reaction without solvent [12].

In this work, the activated polymerization of 2-EP with trifluoroacetic acid is attempted. Figure 1 shows the structures of poly(2-ethynylpyridinium trifluoroacetate) (P2EPF).

Experimental Details

Materials

2-EP (Sigma-Aldrich, 98%), trifluoroacetic acid (Sigma-Aldrich, 99%) and N,N-dimethylformamide (Sigma-Aldrich, 99.8%) was used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled.

Synthesis of poly(2-ethynylpyridinium trifluoroacetate)

P2EPF were synthesized by the spontaneous (activated) polymerization of 2-EP with trifluoroacetic acid. P2EPF was prepared as follows: 2-EP (0.11 g, 1.0 mmol) and DMF (0.1g) were placed in a 50mL round flask. The reaction mixture was cooled below 0 °C. TFA (0.12 g, 0.1 mmol) was slowly added to the cooled solution. The solution was warmed to 65 °C with stirring for 3 h under nitrogen atmosphere. During the reaction, the color of the solution changed from light brown into dark red-brown. The resulting polymer was precipitated into an excess amount of ethyl ether. The red precipitate was collected and dried in a vacuum oven at 40 °C overnight (yield: 72 %, $M_n = 2821$ g/mol).

Result and Discussion

P2EPF of conjugated ionic polyacetylene was obtained by spontaneous polymerization of 2-EP and TFA in mild condition without any initiator, catalyst and alkyl halide. The spontaneous polymerization mechanism was proposed by Blumstein [4, 8]. In the proposed mechanism, the triple bond is activated by an electron withdrawing group such as a quaterinzed pyridinium group via the Menschutkin reaction, when it is susceptible to nucleophilic addition of unquaterinzed monomers. Propagation step involves nucleophilic attack of the resulting carbanion on the triple bond of quaternized monomer molecules. This reaction is

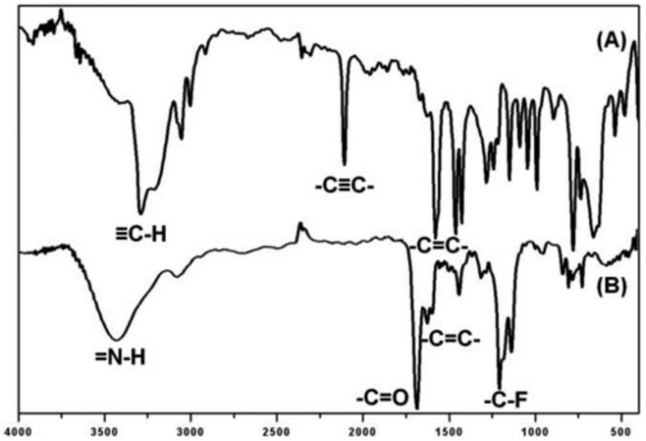

Figure 2. The infrared spectrum of (A) 2-EP and (B) P2EPF in KBr pellet.

dependent on the rate of generation of the quaternized monomers [8]. For the reaction with 2- ethynylpyridine, TFA was compared with acetic acid. In contrast with TFA, acetic acid did not induce the activation of 2-ethynylpyridine. This result suggected that the activation of 2- ethynylpyridine had relevance to acidity. TFA is more acidic than acetic acid due to the inductive effect from fluorine atoms, which caused activation of 2- ethynylpyridine. The spontaneous polymerization of 2- ethynylpyridine with HCl is evident with the reference of the acidifying effect [12]. TFA offered a faster rate of generation of quaternized monomers than alkyl halides in the spontaneous polymerization, which showed fast exothermic reaction in the initial stage. P2EPF was highly soluble in polar solvents such as water, acetone, DMF and DMSO due to its ionic nature. P2EPF was also soluble in some nonpolar solvent such as chloroform and benzene.

The infrared spectrum result showed alteration of functional groups after polymerization. Figure 2 depicts the infrared spectrum of 2-EP (A) and P2EPF (B). The infrared spectrum of 2-EP shows specific bands at 2100 cm^{-1} and 3290 cm^{-1} which are caused by the –C≡C– stretching band and the ≡C–H stretching band, respectively. TFA peaks in P2EPF are shown around at 1200 cm^{-1} and 1700 cm^{-1} attributable to the -C-F band and the -C = O band, respectively. The highly intense new peak of P2EPF around 3400cm^{-1} is assigned to = NH stretch of the side group pyridinium rings and indicative of the hydrogen bonding effect [12]. The specific peaks of 2-EP disappeared in P2EPF.

Figure 3 shows NMR spectra of P2EPF in DMSO-d_6. In general, the NMR spectrum of conjugated polymers having pyridyl moieties shows a poor quality because of the line-broadening effect. The ^{1}H-NMR spectrum of P2EPF showed the aromatic protons of pyridyl moieties and the vinyl protons of conjugated polymer backbones broadly at 6.5-9.7 ppm. The ^{13}C-NMR spectrum of P2EPF showed the aromatic carbon peak of pyridyl moieties and conjugated polymer backbones in the range of 115-155 ppm. The carbon peaks of trifluoroacetate counterion were also observed at 113, 115, 118, 121 (-CF_3) and 163 (-COO) ppm. The *cis* and *trans* content in the P2EPF backbone was confirmed by FT-IR and ^{13}C-NMR analysis [8,13]. The peak in the X-ray diffraction pattern (data not shown) is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, indicating that the present polymer is amorphous [5].

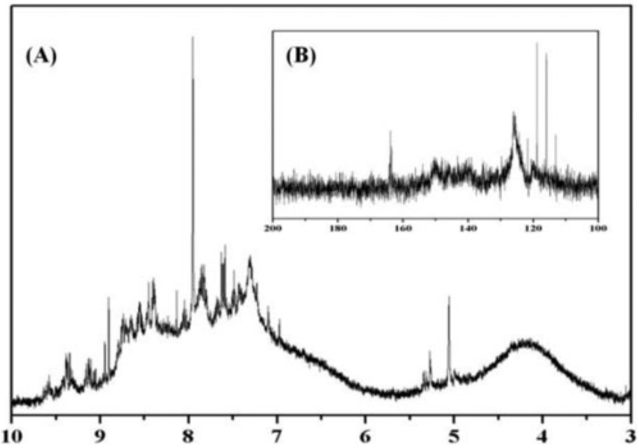

Figure 3. NMR spectrum of P2EPF (A) ^{1}H-NMR, (B) ^{13}C-NMR in DMSO d_6.

Figure 4 shows the UV-Vis spectrum and photoluminescence (PL) spectra of the P2EPF solution (0.1 wt%, DMF). P2EPF showed a characteristic wide a UV-Vis absorption band in the range of 300-700 nm, which is due to that the polymer possesses possibly a high degree of conjugation. This UV-Vis absorption band was attributed to π-π^* transition on the conjugated backbone. The PL spectra of P2EPF showed two kinds of overlapped fluorescence bands centered at 513 nm and 550 nm. On the other hand, the polymerization between 2-EP and alkyl halides gave only one peak in the PL spectrum. This result is attributed to the intramolecular excimer formation by the pyridyl side group chromophores. Similar observations were evidenced for protonated poly(2-vinylpyridine), which exhibits a "dimer-like excimer" due to interaction between protonated pyridyl side-groups adjacent to one another [14]. It is believed that the difference is attributed to the activated polymerization mechanism. The propagation mechanism involves a nucleophilic attack by quaternized monomer molecules. The stacking of the quaternized side group in the propagation step may be affected from steric hindrance between quaternized side groups. Perhaps, steric

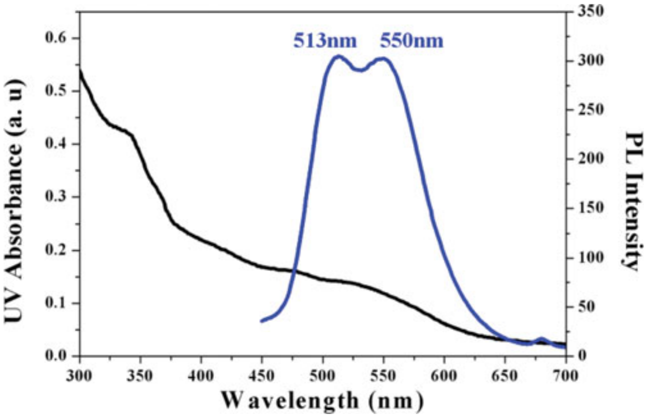

Figure 4. UV-vis and PL spectrum of P2EPF in DMF.

hindrance can form specific orientation of side groups in the polymer backbone. However, the side group of P2EPF has less steric hindrance than the alkyl group in the previous report, which may allow free orientation. Therefore, the P2EPF has a larger probability of disorientation in stacking side groups, and then results in both peaks of normal excimer and dimer-like excimer formation.

Conclusion

An ionic conjugated polyacetylene of P2EPF was prepared by spontaneous polymerization without any additional initiator, catalyst or alkyl halide. The polymerization of 2-EP with TFA showed faster and greater reactivity than alkyl halides, which is due to the faster rate of generation of quaternized monomers. P2EPF was soluble not only in polar solvents but also in some nonpolar solvents such as chloroform and benzene. The infrared and NMR spectrum results confirmed polymer configuration, existence of ionic nature and conjugated backbones. The P2EPF showed a wide UV-Vis absorption band in the range of 300-700 nm from π-π^* transition on the conjugated backbones. The PL spectrum consisted of two broad bands of normal excimer and dimer-like excimer. This result suggested the steric hindrance effect of side groups in the polymer backbone.

Acknowledgment

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