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## Synthesis and Electro-Optical Properties of an Ionic Polyacetylene with N-glycidylpyridinium Tosylate

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*An ionic conjugated polymer with a reactive glycidyl functionalities, poly(2-ethynyl-N-glycidylpyridinium tosylate), was synthesized by the activated polymerization of 2-ethynylpyridine with glycidyl tosylate. The instrumental analyses on the polymer structure revealed that the present polymer have a conjugated polymer backbone system with the designed substituents. The photoluminescence peak is located at 710 nm corresponding to the photon energy of 1.75 eV. The cyclic voltammogram of this conjugated polyelectrolyte revealed that it show the well-defined and stable redox process.*

**Keywords:** 2-ethynylpyridine; conjugated polymer; cyclic voltammogram; gel-forming; photoluminescence; polyacetylene

## INTRODUCTION

The acetylenic triple bonds have rich  $\pi$ -electrons, which can be used to polymerize to yield the linear conjugated polymer systems [1–8]. Among the various types of  $\pi$ -conjugated polymers, the polyacetylene (PA) is structurally the simplest one, and it can be made free-standing

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thin film by using Shrakawa catalysts [9,10]. PA is the best-known conjugated polymer, whose doped form shows high conductivity that stands comparison with that of copper [11]. Unfortunately, applications of this promising material have remained limited because the polymer is insoluble, infusible, and electrically unstable. To overcome these problems of polyacetylene, a number of mono- and di-substituted polyacetylenes has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems [2–8,12]. The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration, energy transfer, color, chemical reactivity and complex formation ability [3].

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. The conjugated polyelectrolytes such as poly(propionic salt)s [13], triethylammonium salt of poly(6-bromo-1-hexyne) [14], and poly(ethynylpyridine)s [15,16] were reported. In 1991, Blumstein *et al.* prepared very interesting ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides [17,18]. We have also reported on the preparation of various ionic conjugated polymers having different functionalities [19–24]. 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, and light-emitting devices [25].

Now, in a series of synthesis of conjugated polymers, we report the synthesis of a new gel-formable ionic conjugated polymer via the activated polymerization of 2-ethynylpyridine by using glycidyl tosylate, and the characterization of the resulting polymer.

## EXPERIMENTAL

2-Vinylpyridine, bromine (99.5+%), sodium amide (tech., 90%), and glycidyl tosylate (99%) were purchased from Aldrich Chemicals and were used as received. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [16]. The analytical grade solvents were dried with an appropriate drying agent and distilled.

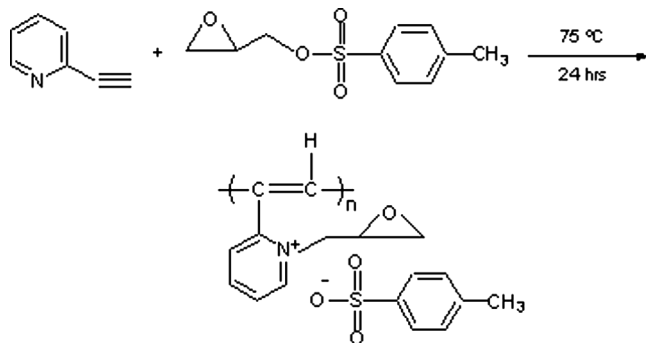
Poly(2-ethynyl-N-glycidylpyridinium tosylate) (PEGPT) was prepared by the activated polymerization of 2-ethynylpyridine with glycidyl tosylate in methanol solvent without any additional initiator or

catalyst as follows. 2-Ethynylpyridine (0.5 g, 48.5 mmol) was added into the methanol solution (8 mL,  $[M]_0 = 0.5$  M) of glycidyl tosylate (1.106 g, 48.5 mmol). Then the reaction solution was stirred for 24 hrs at 75°C under nitrogen atmosphere. As the reaction proceeded, the color of reaction mixture changed from the light brown of the initial mixture into dark purple. After the polymerization time, the resulting polymer solution was precipitated into an excess amount of ethyl ether. The precipitated polymer was easily filtered and dried under vacuum at 40°C for 24 hrs. The black polymeric powder was obtained in 52% yield.

NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO- $d_6$ . FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. 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 30°C. The electrical conductivity of the sample was determined by using a standard four-point probe measurement without extensive pumping of the doped pellets with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Conductivity was calculated from the measured resistance of the sample [26]. The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS50 (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 750 M), and a photomultiplier (Hamamatsu R943-02). To examine the electrochemical properties, the polymer was coated with solution-coating method onto platinum foil as a working electrode with the area of 1 cm<sup>2</sup>. After coating, the films adhered to the electrode were dried in a vacuum oven for 30 min. The thickness of the polymer film was 5  $\mu$ m. The electrochemical measurements were performed in 0.1 M tetraethylammonium tetrafluoroborate [(t-Et)<sub>4</sub>NBF<sub>4</sub>] containing DMF solution. Ag wire and platinum foil were used as a reference and a counter electrode, respectively. Cyclic voltammetric waves were produced by using a Hokuto Denko HA-301 potentiostat/galvanostat (AUTOLAB/PG-STAT12) equipped with a HA-301 functional generator and a X-Y reorder.

## RESULTS AND DISCUSSION

The PEGPT was prepared by the activated polymerization of 2-ethynylpyridine with glycidyl tosylate in methanol solvent without any initiator and catalyst (Scheme 1).

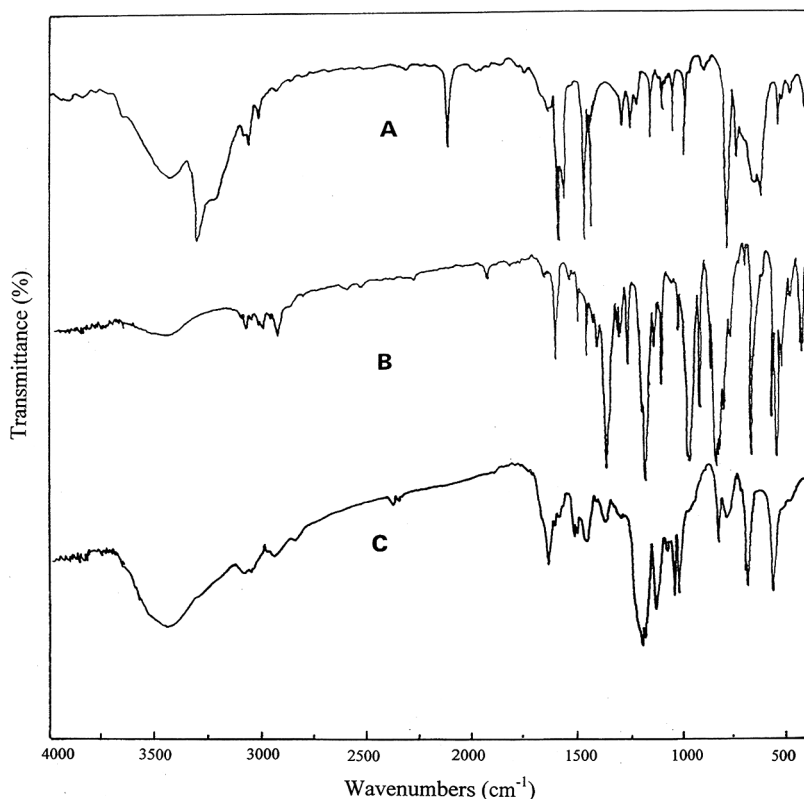


**SCHEME 1** Synthesis of PEGPT.

The present polymerization of 2-ethynylpyridine with glycidyl tosylate proceeded smoothly in homogeneous manner to give the corresponding polymer in 52% yield. The color of reaction mixture was changed from the light brown of the initial mixture into dark purple as the polymerization proceeded. The black polymer powder exhibited somewhat hygroscopic character. This polymer was soluble in such polar organic solvents as methanol, pyridine, DMF, NMP, and DMSO, but insoluble in ethyl ether, THF, toluene, and acetone. The inherent viscosity of the resulting polymer was 0.15 dL/g.

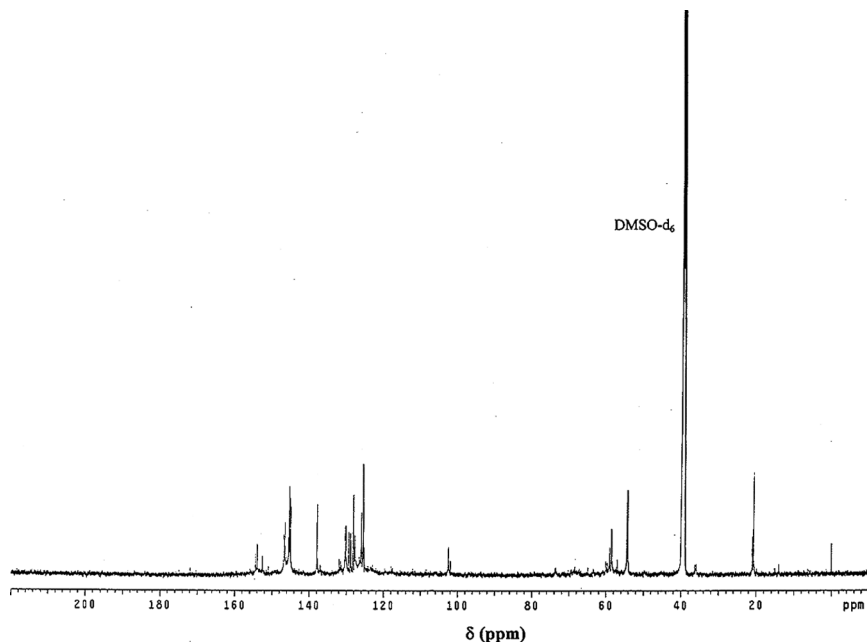
It was found that the present polymerization is not influenced by the presence of oxygen or strong acidic cocatalysts. Thus, we ruled out the possibility of free-radical mechanism for the formation of conjugated polyacetylenes. Katritzky *et al.* succeeded in isolating the quaternarized acetylenic pyridinium salts in the reactions of propargyl bromide and propargyl chloride with pyridine [26]. They found that the polymerization could be initiated in these species by addition of nucleophiles such as pyridines and tertiary amines. Thus, the present polymerization seems to proceed in anionic mechanism. It contains the first quaternarization of 2-ethynylpyridine by glycidyl tosylate. The activated acetylenic triple bond of 2-ethynyl-N-glycidylpyridinium bromide is susceptible to the linear polymerization. The quaternarized monomeric species can be initiated by the non-bonding electron pair of 2-ethynylpyridine and/or tosylate anion.

Figure 1 shows the FT-IR spectra of 2-ethynylpyridine, glycidyl tosylate, and PEGPT in KBr pellets. The FT-IR spectrum of PEGPT did not show the acetylenic  $\text{C}\equiv\text{C}$  bond stretching ( $2110\text{ cm}^{-1}$ ) and acetylenic  $\equiv\text{CH}$  bond stretching ( $3293\text{ cm}^{-1}$ ) frequencies of 2-ethynylpyridine. Instead, the  $\text{C}=\text{C}$  stretching frequency peak of conjugated polymer backbone around  $1627\text{ cm}^{-1}$  became relatively more intense



**FIGURE 1** FT-IR spectra of 2-ethynylpyridine (A), glycidyl tosylate (B), and poly(2-ethynyl-N-glycidylpyridinium tosylate) (C) in KBr pellets.

than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine and glycidyl tosylate. The peak at  $1191\text{ cm}^{-1}$  and  $1362\text{ cm}^{-1}$  are due to the C-O-C stretching of epoxides and the  $\text{SO}_2$  stretching of sulfone functional groups. The  $^1\text{H}$ -NMR spectrum of PEGPT showed that the aromatic protons of pyridyl and tosylate moieties and the vinyl proton of the conjugated polymer backbone at 6.4–9.6 ppm. The peaks of the methylene and methine protons of glycidyl groups and the methyl protons of tosylate were observed broadly at the region of 3.7–5.7 ppm and 2.6–3.7 ppm, respectively. Figure 2 shows the  $^{13}\text{C}$ -NMR spectrum of PEGPT in  $\text{DMSO-d}_6$ . It exhibited the multiple and complicated peaks at the region of 117–155 ppm, which are originated from the aromatic carbons of pyridyl and tosylate moieties and the vinyl carbons of conjugated polymer backbone. The sharp peak at

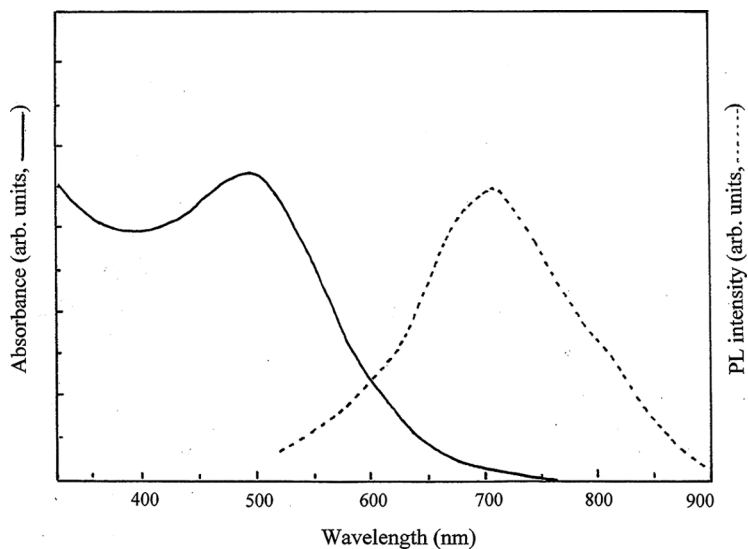


**FIGURE 2**  $^{13}\text{C}$ -NMR spectrum of poly(2-ethynyl-N-glycidylpyridinium tosylate) in  $\text{DMSO-d}_6$ .

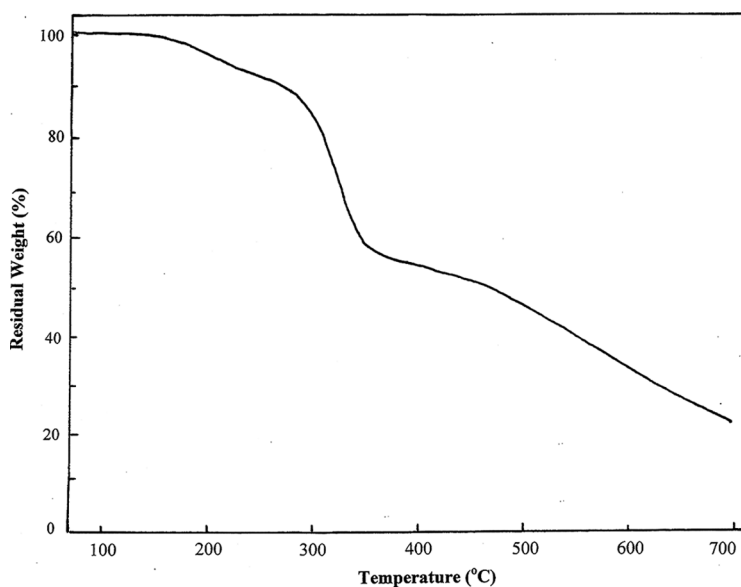
20.58 ppm is attributed to the methyl carbons of tosylate moieties. Figure 3 shows the optical absorption and photoluminescence spectra of PEGPT in DMF solvent. The UV-visible spectrum of PEGPT showed that the absorption spectrum starts around 750 nm and shows a strong absorption band at visible region due to the  $\pi \rightarrow \pi^*$  interband transition of the polymer backbone, which is a characteristic peak of the conjugated polyene backbone system. From these spectral data, we concluded that PEGPT has an ionic conjugated polymer system bearing the pyridinium tosylate in its side chains.

The TGA thermogram (Fig. 4) of PEGPT showed a slight weight loss after 170°C and second abrupt weight loss after 280°C. This polymer retained 99% of its original weight at 165°C, 95% at 223°C, 90% at 277°C, 70% at 334°C, 50% at 470°C. The percentage of residual weight after heating up to 700°C was 22%. In DSC thermogram (Fig. 5), it was found that some exothermic reaction starts at 125°C (peak temperature: 175), which is originated by the gel-forming reaction of the glycidyl functional groups. 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

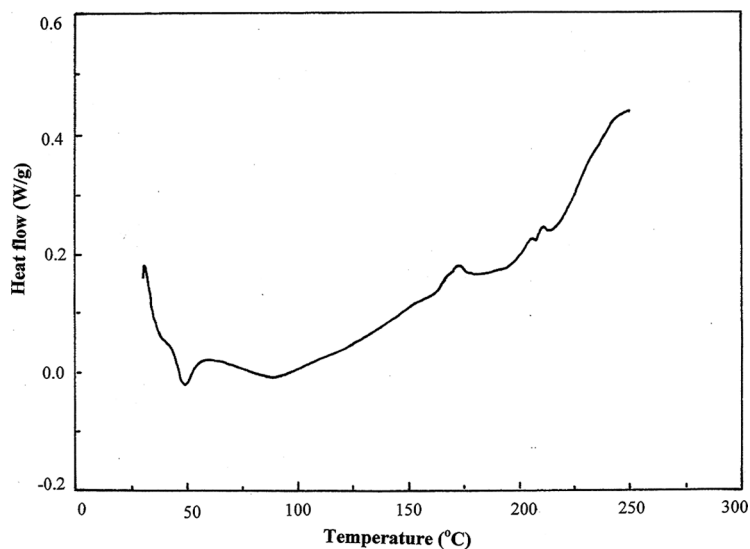




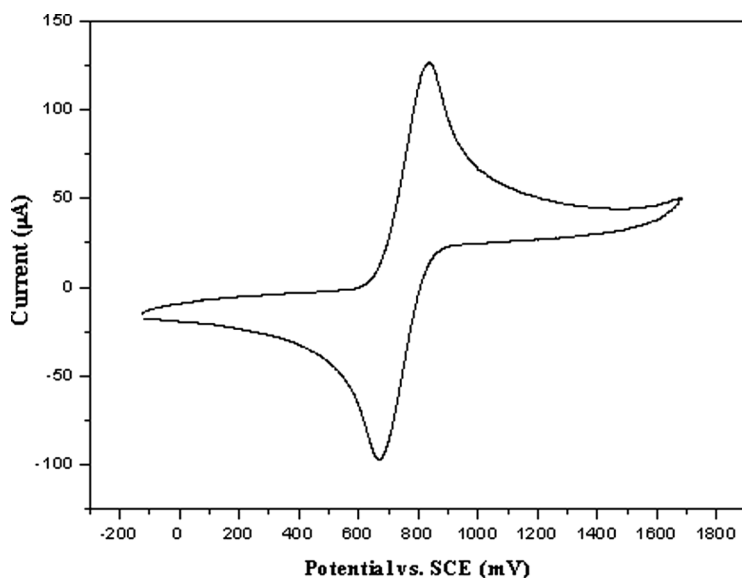
**FIGURE 3** Optical absorption and photoluminescence spectra of poly(2-ethynyl-N-glycidylpyridinium tosylate) in DMF.



**FIGURE 4** TGA thermogram of poly(2-ethynyl-N-glycidylpyridinium tosylate) under nitrogen atmosphere in a heating rate of 10°C/min.



**FIGURE 5** DSC thermogram of poly(2-ethynyl-N-glycidylpyridinium tosylate) under nitrogen atmosphere in a heating rate of 10°C/min.



**FIGURE 6** Cyclic voltammogram of poly(2-ethynyl-N-glycidylpyridinium tosylate) in 0.1M tetraethylammonium tetrafluoroborate in DMF solution with scan rate of 100 mV/s in the range of -0.1~1.7 V.

greater than 0.35 [3], indicating that the present polymer is amorphous. The electrical conductivity of iodine-doped PEGPT pellet [composition: (EGPT)<sub>1</sub>(I<sub>2</sub>)<sub>0.31</sub>] was  $2.80 \times 10^{-4}$  S/cm. The photoluminescence spectrum (Fig. 3) showed that the PL peak is located at 710 nm corresponding to the photon energy of 1.75 eV.

Figure 6 indicates the cyclic voltamogram of the polymer film in 0.1 M tetraethylammonium tetrafluoroborate (Et<sub>4</sub> NBF<sub>4</sub>) in DMF solution at a scan rate of 100 mV/s at the potential range of -0.1 to +1.7 V. It shows the typical cyclic voltammogram of PEGPT. This polymer exhibited *p*-doping and undoping peaks at about 0.83 and 0.68 V, respectively (vs Ag/AgCl). As the cycling number increased up to 250 cycles, this polymer showed the well-defined and stable redox process and there was no characteristic change such as the increase of current density in cyclic voltammograms.

## CONCLUSIONS

A new ionic conjugated polymer, PEGPT, was prepared by the activated polymerization of 2-EP by using glycidyl tosylate in moderate yield. The analytical spectral datas on the chemical structure indicated that the present polymer has an ionic conjugated polymer system bearing the pyridinium tosylate in the side chains. The electrical conductivity of iodine-doped PEGPT pellet was  $2.80 \times 10^{-4}$  S/cm. The photoluminescence spectra of this ionic conjugated polymer showed that the photoluminescence peak is located at 710 nm corresponding to the photon energy of 1.75 eV. The cyclic voltamogram indicated that the oxidation and reduction occurred at 0.83 and 0.68 V, respectively. This gel-forming conjugated polyelectrolyte with broad absorption spectra can meet the requirements to efficiently quench fluorescence of multiple probes in a broad spectral range through overlap-dependent energy transfer. Further works on the gel-forming properties and the mechanical properties of cured thin films are now in progress.

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