

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### SYNTHESIS AND ELECTRO-OPTICAL PROPERTIES OF POLY(2-ETHYNYLPYRIDINIUMTOSYLATE) HAVING PROPAGYL SIDE CHAIN

Yeong-Soon Gal<sup>a</sup>; Won-Chul Lee<sup>b</sup>; Seok-Joo Lee<sup>c</sup>; Jong-Wook Park<sup>d</sup>; Jang-Myoun Ko<sup>e</sup>; Jong-Han Chun<sup>f</sup>

<sup>a</sup> Polymer Chemistry Laboratory College of General Education, Kyungil University, Kyungsangbuk-

Do, Korea <sup>b</sup> Department of Textile Engineering, Kyungil University, Kyungsangbuk-Do, Korea <sup>c</sup>

Department of Physics, Korea Advanced Institute of Science and Technology, Taejon, Korea <sup>d</sup>

Department of Polymer Engineering, Chungju National University, Chung-Buk, Korea <sup>e</sup> Department of

Industrial Chemistry, Taejon National University of Technology, Taejon, Korea

Online publication date: 20 September 1999

**To cite this Article** Gal, Yeong-Soon , Lee, Won-Chul , Lee, Seok-Joo , Park, Jong-Wook , Ko, Jang-Myoun and Chun, Jong-Han(1999) 'SYNTHESIS AND ELECTRO-OPTICAL PROPERTIES OF POLY(2-ETHYNYLPYRIDINIUMTOSYLATE) HAVING PROPAGYL SIDE CHAIN', Journal of Macromolecular Science, Part A, 36: 10, 1503 – 1519

**To link to this Article:** DOI: 10.1081/MA-100101611

**URL:** <http://dx.doi.org/10.1081/MA-100101611>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **SYNTHESIS AND ELECTRO-OPTICAL PROPERTIES OF POLY(2-ETHYNYLPYRIDINIUM TOSYLATE) HAVING PROPAGYL SIDE CHAIN**

**Yeong-Soon Gal and Won-Chul Lee\***

Polymer Chemistry Laboratory  
College of General Education  
\*Department of Textile Engineering  
Kyungil University  
Hayang 712-701, Kyungsangbuk-Do, Korea

**Seok-Joo Lee**

Department of Physics  
Korea Advanced Institute of Science and Technology  
373-1 Kusung-Dong, Yusung-Gu, Taejon 305-701, Korea

**Jong-Wook Park**

Department of Polymer Engineering  
Chungju National University  
Chungju 380-702, Chung-Buk, Korea

**Jang-Myoun Ko and Jong-Han Chun**

Department of Industrial Chemistry  
Taejon National University of Technology  
305 Samsung-Dong  
Dong-Gu, Taejon 300-717, Korea

**Key Words:** Ionic Polymers, Poly(2-ethynylpyridinium Salts), Propargyl Tosylate, Photoluminescence

---

\* Author to whom correspondence should be addressed.

## ABSTRACT

Novel conjugated ionic polymer was prepared by the polymerization of 2-ethynylpyridine with propargyl tosylate in refluxing methyl alcohol. The polymerization proceeded well in homogeneous manner to give a relatively high yield of polymer. The resulting poly(2-ethynylpyridinium tosylate) having propargyl side chain [poly(EPT-P)] were hygroscopic and soluble in water, methyl alcohol, DMF, and DMSO. The inherent viscosities of the polymers were in the range of 0.08-0.29dL/g. Instrumental analyses using NMR, IR, and UV-visible spectroscopies and elemental analyses indicated that the resulting poly(EPT-P) have a conjugated ionic polymer backbone carrying N-propargyl-2-pyridinium tosylate. Thermal and electro-optical properties of the polymers were also studied.

## INTRODUCTION

Conjugated polymers have been the subject of intensive research due to their interesting properties such as electrical conductivity [1-3], gas and liquid mixture separation [4-8], side-chain liquid crystal [9, 10], radiation degradation [11, 12], and nonlinear optical (NLO) susceptibilities [13-17].

A large effort in synthetic chemistry has produced a wide range of mono- and di-substituted polyacetylenes with various functional groups such as alcohol [18-20], ether [21-23], amine [24], thioalkane [25, 26], and carboxylic acid [27] and ester [28], etc.

The examples of ionic polymers having conjugated backbone were scarce and restricted to some cases as follows: poly(propionic acid) salt [29], water soluble polyene polymers by the quaternization of poly(6-bromo-1-hexyne) [30], and the synthesis of mono- and di-substituted ionic polyacetylene by the activation of the acetylene bond in ethynylpyridines by alkyl halides or methane sulfonates [31-33]. Due to their extensive conjugation and ionic nature, these polymers have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, chemical sensors, and permselective membrane [32].

In the series of our recent studies, we have synthesized the ionic polymers from mono-, di-, and tri-propargylammonium salts by the use of transition metal catalysts [34-40]. The nature of counter ion appeared to make an important effect on the polymerization behavior and the physical properties of resulting polymers.

The polymerization of 2-ethynylpyridine was carried out to give a water-soluble conjugated polymer having a moderate molecular weight [41]. And, we also reported the activated polymerization of 2-ethynylpyridine by propargyl bromide under methyl alcohol reflux condition [42].

Now we report the synthesis of a water-soluble, thus a well processible conjugated polyelectrolyte by the facile one-step polymerization in methanol reflux condition of 2-ethynylpyridine and propargyl tosylate. Furthermore, the characterization and electro-optical properties of the resulting polymer will also be discussed.

## EXPERIMENTAL

### Materials

Propargyl bromide (Aldrich Chemicals., 80 wt% solution of toluene) was dried with calcium hydride and fractionally distilled. Propargyl alcohol was dried with  $K_2CO_3$  and distilled under reduced pressure. *p*-Toluene sulfonyl chloride was recrystallized from toluene/petroleum ether in the cold. 2-Vinylpyridine (Aldrich Chemicals., 97%) was used after distillation under reduced pressure. Sodium amide ( $NaNH_2$ , Aldrich Chemicals., 95%) was used as received. The solvents were analytical grade materials, and they were dried with an appropriate drying agent and fractionally distilled.

### Preparation of Propargyl Tosylate

Propargyl alcohol (10.6 g, 0.19 mol) and *p*-toluene sulfonyl chloride (20 g, 0.10 mol) were placed in a 500 mL three-neck flask equipped with thermometer, a water-bath containing a small amount of ice, and a 250 mL dropping funnel. 32 mL of 5N NaOH solution was added dropwise at a rate that did not cause the temperature of the reaction mixture to exceed 15°C. Another portion of *p*-toluene sulfonyl chloride (20 g, 0.10 mmol) was added, and then 32 mL of 5 N NaOH solution was slowly introduced. Stirring was continued for an additional 4 hours, and the oily layer was separated from the water layer by extraction with diethyl ether and then the ether layer was washed thoroughly with 50 mL of 10% NaOH solution, and dried by standing overnight over 20 g anhydrous  $K_2CO_3$ . After the solvent was removed, the residue was distilled under reduced pressure. Propargyl tosylate was obtained in 55% yield, b.p. 107-110°C/1mmHg.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.4 (s,  $\text{CH}_3^-$ ), 2.5 (t, C-H), 4.6 (d,  $-\text{O}-\text{CH}_2-\text{C}\equiv$ ), 7.3-7.9 (m, phenyl ring).

FT-IR (KBr pellet, wavenumbers,  $\text{cm}^{-1}$ ): 3290, 3067, 2954, 2927, 2133, 1597, 1362, 1175, 1096, 979, 930, 814, 665.

### Preparation of 2-Ethynylpyridine

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination according to the literature method [41].

### Synthesis of Poly(2-Ethynylpyridinium Tosylate) Having Propargyl Side Chain

In a 250 mL three-neck flask equipped with reflux condenser, thermometer, and rubber septum, methyl alcohol (90 mL), 2-ethynylpyridine (2.00 g, 19.392 mmol), and propargyl tosylate (4.60 g, 19.634 mmol) were introduced in the given order and then, the reaction mixture were refluxed in methanol. In order to check the polymerization behaviors and the polymer properties during the polymerization according to the polymerization time, each 10 mL reaction solution was taken from the reaction mixture at the scheduled polymerization time (0.5, 1, 3, 6, 12, 24 hours). As the reaction proceeded, the color of the reaction mixture was consecutively changed into dark-red. After a given polymerization time, the resulting polymer solution was precipitated into a large amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at  $40^\circ\text{C}$  for 24 hours. The polymer yield was calculated by gravimetry.

### Instruments and Measurement

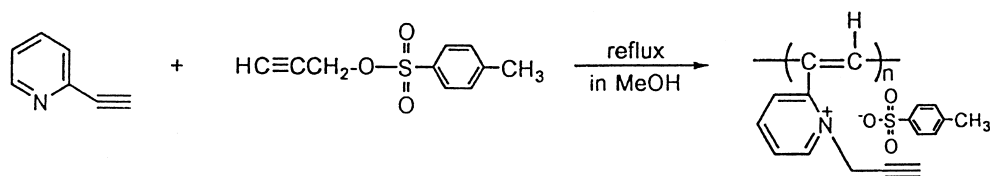
NMR spectra were recorded on a Bruker AM-200 spectrometer in  $\text{DMSO}-d_6$ . IR spectra were obtained with a Bomem MB-100 spectrometer using a KBr pellet. Elemental analyses were performed with Perkin-Elmer 240C Elemental Analyzer. The inherent viscosities ( $\eta_{\text{inh}}$ ) were determined at a concentration of 0.5 g/dL in DMF solvent at  $30^\circ\text{C}$ . Thermogravimetry (TGA) was performed under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . Up to  $600^\circ\text{C}$  with a DuPont 2100 Analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of  $10^\circ\text{C}/\text{min}$ . X-ray diffraction patterns of polymer samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered  $\text{CuK}\alpha$  radiation at a scan speed of  $4^\circ/\text{min}$ . The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR

Spectrometer. The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation source. The emission signal was collected using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A dispex), 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 170Hz, and converted to the digital signal in the autoscan system.

## RESULTS AND DISCUSSION

### Polymerization

The polymerization of 2-ethynylpyridine activated by propargyl tosylate was carried out under methyl alcohol reflux conditions without any catalyst or initiator as follows.

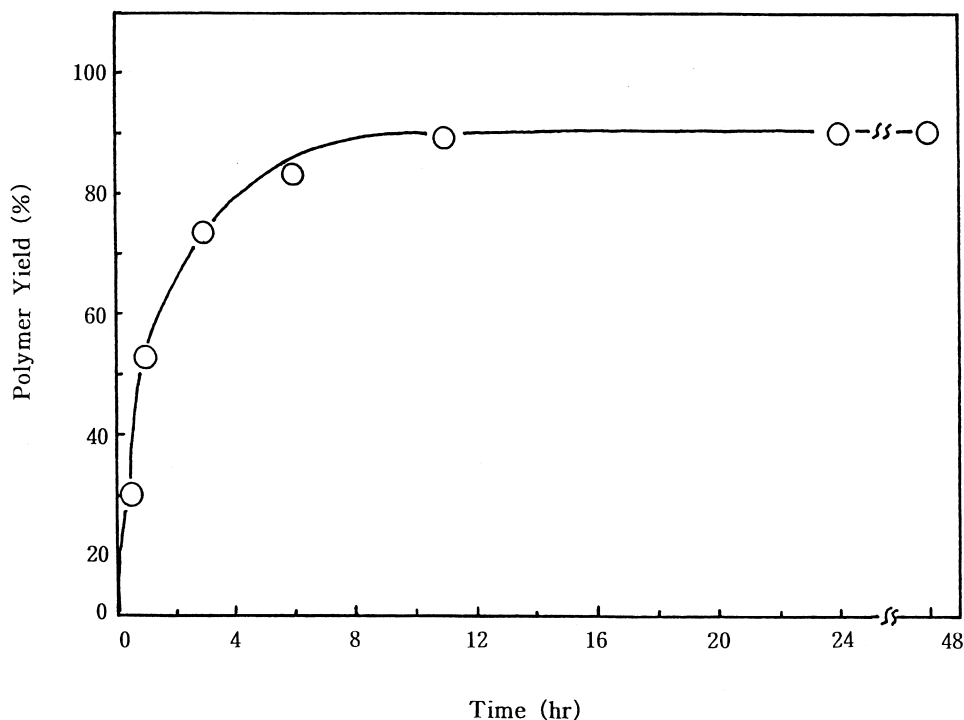


**Scheme 1.** Synthesis of Poly(2-ethynylpyridinium tosylate) having Propargyl Side Chain.

As the reaction proceeds, the color of the reaction mixture was consecutively changed into dark-red. The polymerization solution was homogeneous during all the polymerization times. The polymer yield was calculated and the UV-visible spectroscopies were measured from the polymer solution taken in the polymerization reactor according to the reaction time.

Figure 1 shows the time-dependence curve of polymer yield according to the reaction time. This polymerization was found to proceed quickly in early time. The polymer yield, even after 1 hour, was 43% and the polymer yield reached about 80% after 12 hours.

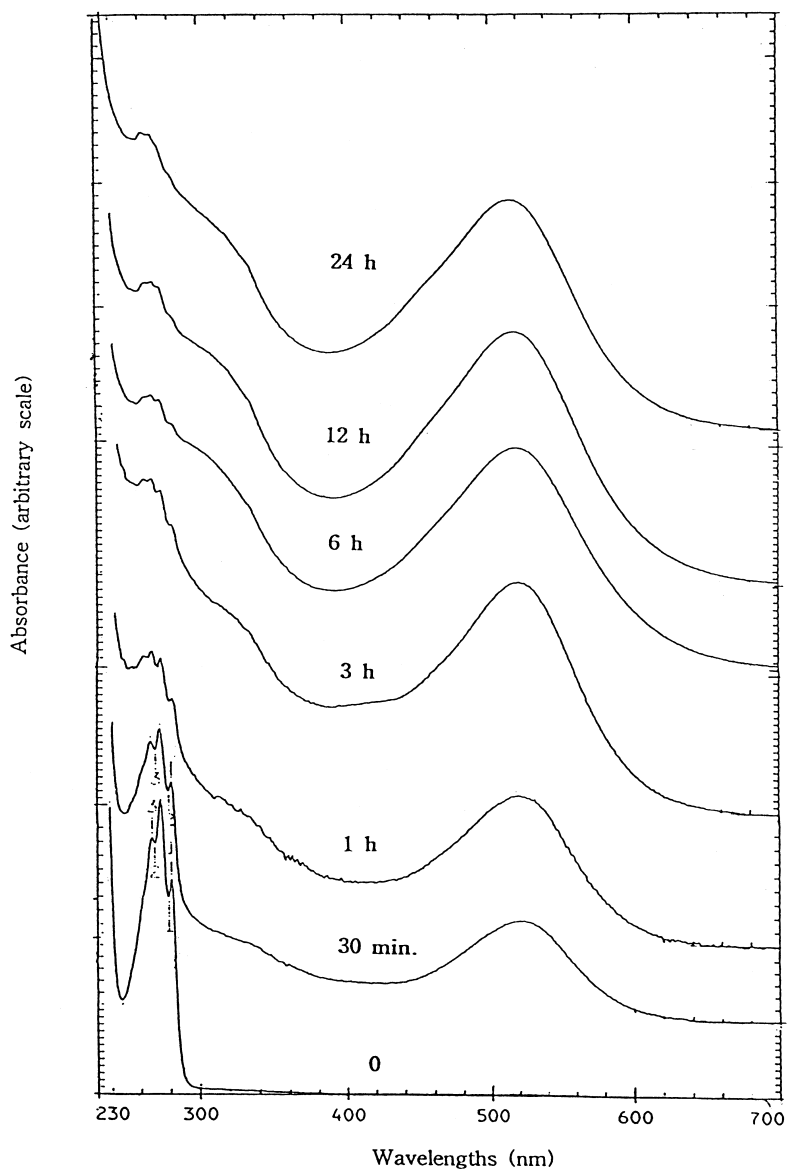
Figure 2 shows the UV-visible spectra of the initial mixture of 2-ethynylpyridine and propargyl tosylate and the polymerization solution according to the reaction time. The spectrum of the initial mixture of 2-ethynylpyridine



**Figure 1.** The polymer yield according to the polymerization time in the polymerization of 2-ethynylpyridine activated by propargyl tosylate under methyl alcoholreflux condition.

and propargyl tosylate did not show any absorbance peak in the visible region. However, an peculiar absorption band at 519 nm, which is originated from the  $\pi \rightarrow \pi^*$  transition of conjugated polymer backbone, was newly observed even after the polymerization time of 30 minutes. As the polymerization time is increased, the initial sharp peaks of monomeric mixture became more broad. On the other hand, the peak of conjugated polymer backbone ( $\lambda_{\max}$ : 519 nm) became stronger.

The attempted reaction of pyridine and propargyl tosylate in the methanol reflux condition did not give any polymeric products, but gave only propargyl pyridinium tosylate. This means that the propargyl functional group do not undergo polymerization reaction by the simple attack of pyridine nitrogen atom. And also the reaction of 2-ethynylpyridine alone in the methyl alcohol



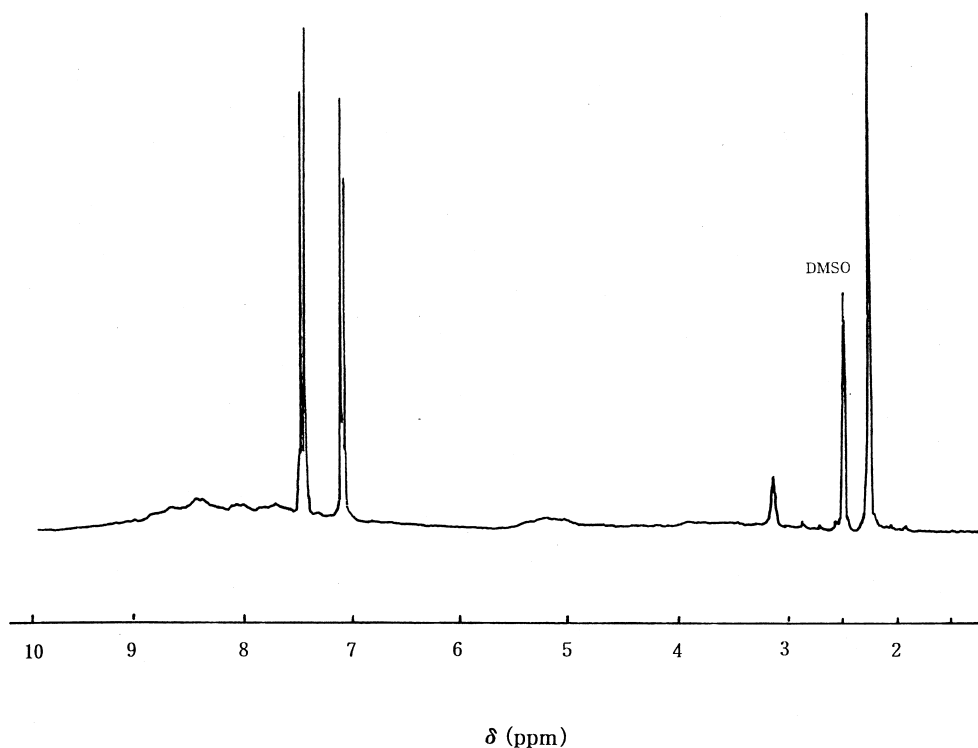
**Figure 2.** UV-visible spectra of the initial mixture of 2-ethynylpyridine and propargyl tosylate and the reaction mixtures taken from the reactor during the polymerization according to the polymerization time.



reflux condition did not yield any tractable polymeric products besides somewhat color changes. Thus, this polymerization was thought to be activated by the quarterization of 2-ethynylpyridine with propargyl tosylate. And the polymerization mechanism was deduced to be similar to that for the spontaneous polymerization of 3- and 4-vinylpyridines on quarterization of the pyridine nitrogen by alkyl halides [43, 44].

### Polymer Structure

The polymer structure of poly(EPT-P) was characterized by elemental analyses, NMR, infrared, and UV-visible spectroscopies. The elemental analysis data of reprecipitated poly(EPT-P) agreed with the theoretical value: Calcd for  $(C_{17}H_{15}NO_3S)_n$ : C, 65.14%; H, 4.84%; N, 4.47%; S, 10.23%; O, 15.32%. Found: C, 64.95%; H, 4.80%; N, 5.11%; S, 10.21%; O, 14.93%. Figure 3 shows the  $^1H$ -



**Figure 3.**  $^1H$ -NMR spectrum of poly(2-ethynylpyridinium tosylate) having propargyl side chain in  $DMSO-d_6$ .

NMR spectrum of poly(EPT-P) in DMSO-d. The aromatic proton peaks of pyridine moiety and vinyl proton of polymer backbone are broadly observed at the region of 6.5-9.3 ppm. On the other hand, the peaks of tosylate moiety are observed more strongly at 7.1 and 7.4 ppm. The methylene proton peak and acetylenic proton peak of propargyl functional group is also observed at 5.2 and 3.53 ppm, respectively. Also, the methyl protons of tosylate were also observed at 2.25 ppm. On the other hand, the acetylenic proton peak of 2-ethynylpyridine at 3.03 ppm disappeared.

Figure 4 shows the FT-IR spectra of 2-ethynylpyridine, propargyl tosylate, and poly(EPT-P) in a KBr pellet. The IR spectra of 2-ethynylpyridine and propargyl tosylate showed a characteristic acetylenic C≡C bond stretching frequencies at 2110 and 2133 cm<sup>-1</sup>, respectively. However, in the IR spectrum of poly(EPT-P), it did not show the acetylenic C-H bond stretching frequencies at 3293 and 3290 cm<sup>-1</sup> and the acetylenic C≡C bond stretching frequency of 2-ethynylpyridine at 2210 cm<sup>-1</sup>. Instead the peak at 1610 cm<sup>-1</sup> became more intense. The acetylenic C≡C stretching frequency of propargyl functional group on poly(EPT-P) was observed at 2125 cm<sup>-1</sup>.

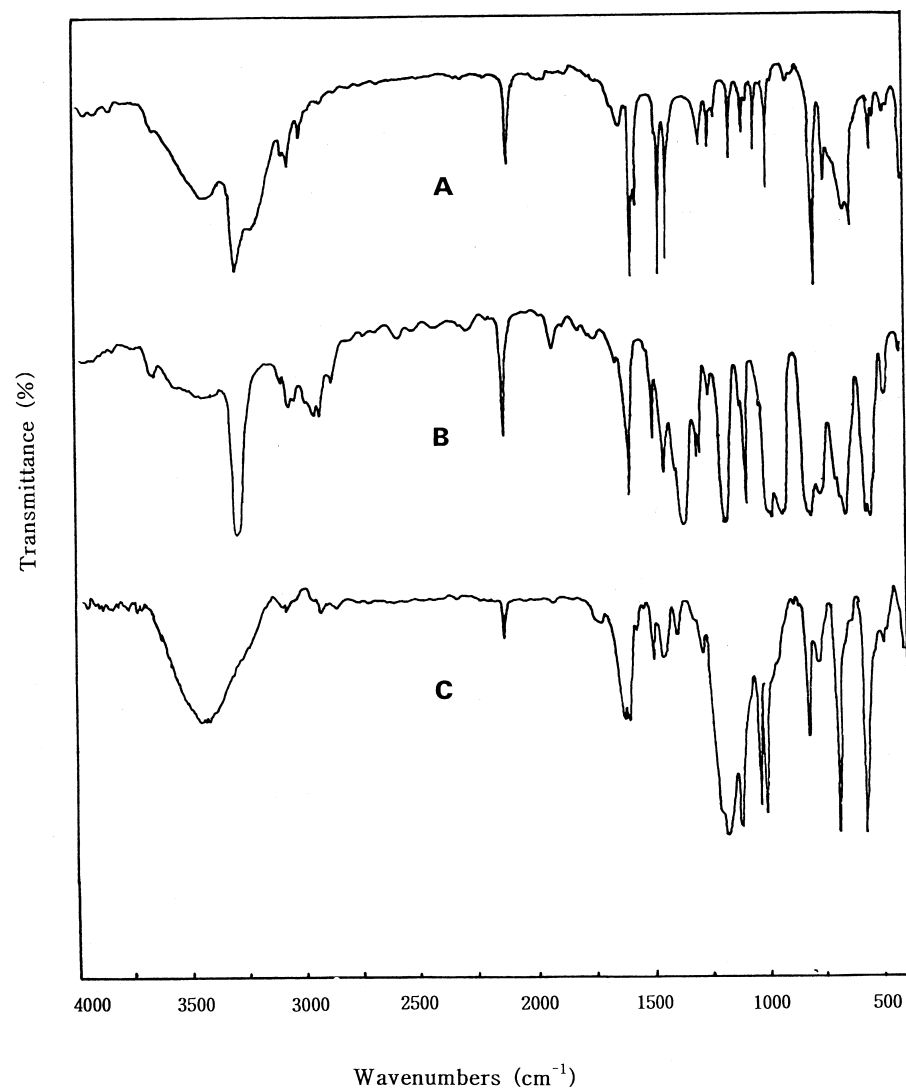
The UV-visible spectra (Figure 2) of Poly(EPT-P)s exhibited an absorption peak at longer wavelength upto 700nm ( $\lambda_{\max}$ : 519 nm), which is originated from the  $\pi \rightarrow \pi^*$  absorption peak of conjugated polymer backbone.

These spectral data indicate that the resulting poly(EPT-P) have a conjugated polymer backbone structure carrying N-propargyl pyridinium tosylate as substituent.

### Polymer Properties

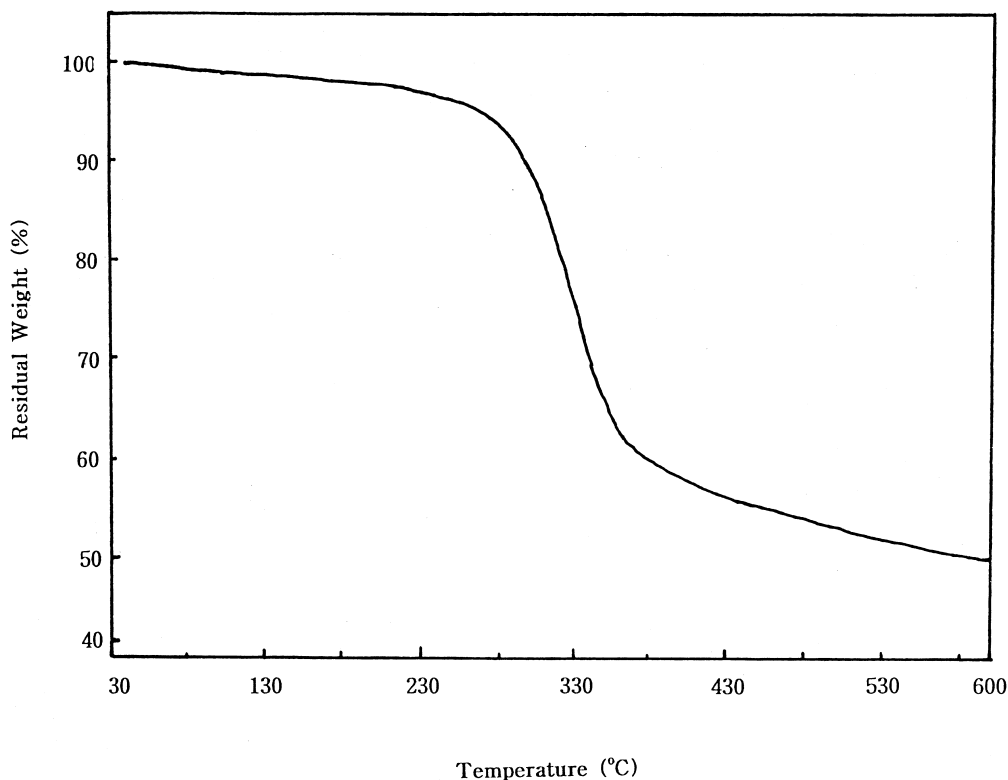
The resulting poly(EPT-P)s were dark-red hygroscopic powders. The solubility test was performed for powdery samples in excess solvent. The poly(EPT-P) was completely soluble in water, methyl alcohol, formic acid, DMF, DMSO, and nitrobenzene, but insoluble in benzene, toluene, carbon tetrachloride, and n-hexane. The inherent viscosities of the resulting poly(EPT-P) was in the range of 0.08-0.29dL/g. The viscosity gradually increased as the polymerization time increased. These values were found to be relatively higher in comparison to those of polymers from acetylenic salt monomers such as dihexyldipropargylammonium salts [37] and propargyltriphenylphosphonium bromide [34].

The TGA thermogram of poly(EPT-P) was also tested under nitrogen atmosphere (Figure 5). This polymer system was found to be more thermally



**Figure 4.** IR spectra of 2-ethynylpyridine (A), propargyl tosylate (B), and poly(EPT-P) (C) in a KBr pellet.

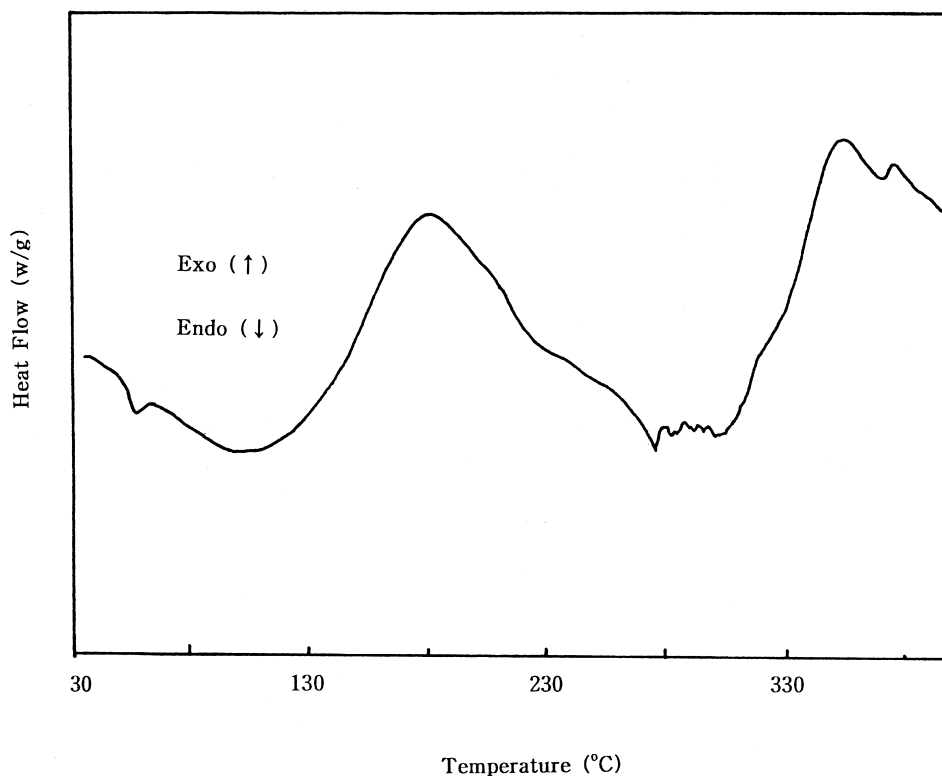
stable than those of similar poly(2-ethynylpyridinium) derivatives having bromide as counter ion [42]. The poly(EPT-P) retains 99% of its original weight at 105°C, 95% at 267°C, 90% at 302°C, 70% at 342°C, and 50% at 600°C. Figure 6 shows the DSC thermogram of poly(EPT-P) under nitrogen atmosphere in the range of 30–400°C. This polymer shows two exothermic peaks at 180 and 353°C.



**Figure 5.** TGA thermogram of poly(2-ethynylpyridinium tosylate) having propargyl side chain.

The first peak at 180°C originated from the thermal crosslinking of conjugated polymer backbone and propargyl side chain. On the other hand, the second peak at 353°C is due to the thermal decomposition of the polymer system. This polymer did not show the glass-transition temperature as with those of other similar conjugated polymers [42, 45].

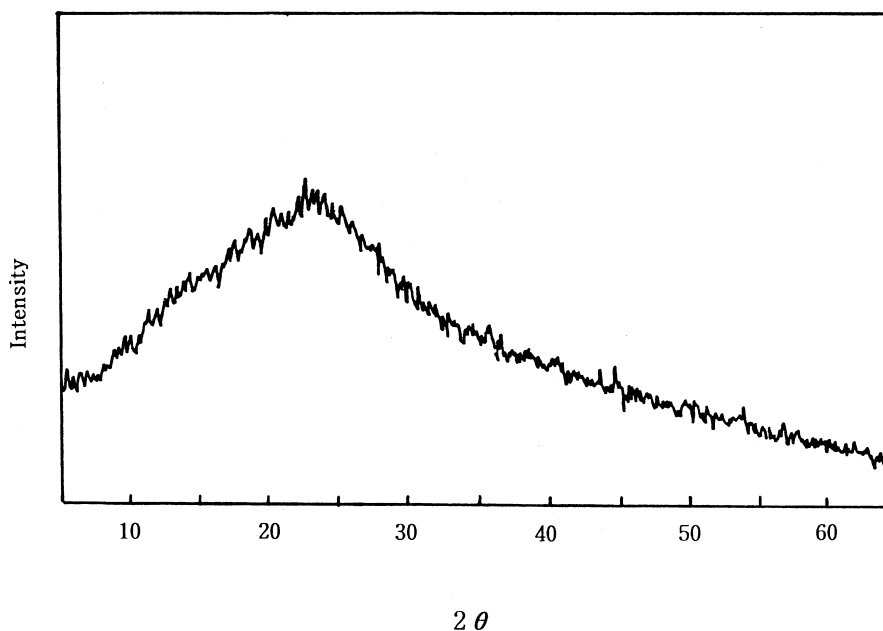
The morphology of poly(EPT-P) was also investigated by X-ray diffraction analysis (Figure 7). Because the peak in diffraction pattern is broad and the ratio of the half-height width to diffraction angle ( $\Delta 2\theta/2\theta$ ) is greater than 0.35 [46], the poly(EPT-P) was found to be amorphous.



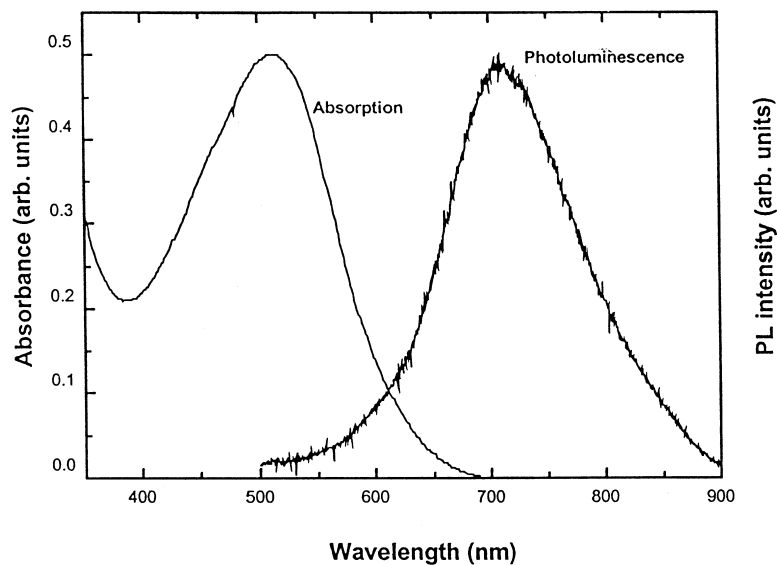
**Figure 6.** DSC thermogram of poly(2-ethynylpyridinium tosylate) having propargyl side chain.

### Optical Absorption and Photoluminescence Properties

Figure 8 shows the optical absorption and photoluminescence spectra of poly(EPT-P) film (thickness 1  $\mu\text{m}$ ) on quartz substrate. All measurements were carried out in air at room temperature. The absorption spectrum starts around 700 nm, and shows a strong absorption band at around 519 nm due to the  $\pi \rightarrow \pi^*$  inter-band transition of the polyene main chain. The band gap energy of this polymer was estimated to be 2.1 eV from the analysis of the absorption edge with a plot of  $(h\nu)$  vs.  $(\alpha h\nu)^2$ , where  $\alpha$ ,  $h$ , and  $\nu$  are the absorbance, Planck's constant, and the frequency of light, respectively [47]. This band gap energy is larger than that of *trans*-polyacetylene by about 0.4 eV [48]. Because the backbone of poly(EPT-P) is the same as that of *trans*-polyacetylene, this might be due to the



**Figure 7.** X-ray diffractogram of poly(2-ethynylpyridinium tosylate) having propargyl side chain.



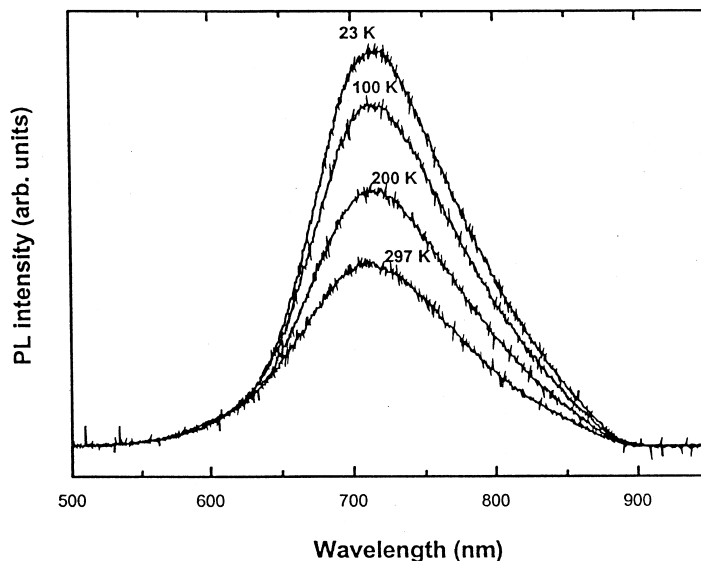
**Figure 8.** Optical absorption and photoluminescence spectra of poly(EPT-P) thin film on quartz substrate.

steric hindrance between pendant N-propargyl-2-pyridinium tosylate groups in poly(EPT-P). The photoluminescence spectrum of the film shows that the photoluminescence peak is located at 710 nm corresponding to the photon energy of 1.7 eV. So there is the Stokes' shift between the maximum in emission and the absorption edge. This indicates that the emission is due to the exciton states rather than the interband transition.

The temperature-dependent photoluminescence spectra of poly(EPT-P) film are shown in Figure 9. As the temperature was increased, the photoluminescence intensity decreased. This is because the non-radiative decay channels are increased as the temperature increased. But there were no changes in the location of the peak and the line shape of the spectrum as the temperature was varied. Thus the temperature does not affect exciton states of poly(EPT-P).

## CONCLUSION

The polymerization of 2-ethynylpyridine activated by propargyl tosylate under methyl alcohol reflux conditions gave a conjugated polymer, poly(2-



**Figure 9.** Temperature-dependent photoluminescence spectra of poly(EPT-P) thin films on quartz substrate.

ethynylpyridinium tosylate) having propargyl side chain in high yields. This polymerization was found to be activated by the quaternization of 2-ethynylpyridine with propargyl tosylate. The resulting poly(EPT-P) was completely soluble in polar solvents such as water, methyl alcohol, DMSO, and DMF, but insoluble in nonpolar hydrocarbon solvents such as chlorobenzene, toluene, and chloroform. The polymerization mechanism was deduced to similar to that for the spontaneous polymerization of 3- and 4-vinylpyridines on quaternization of the pyridine nitrogen by alkyl halides. The resulting polymer structure was identified to have a conjugated ionic polymer backbone carrying N-propargyl-2-pyridinium tosylate as substituent. The photoluminescence properties of poly(EPT-P) revealed that the emission is originated from the exciton states rather than the interband transition. And also, it was found that the temperature does not affect the exciton states of polymer.

### ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundations (KOSEF) through the Advanced Material Research Center for Better Environment at Taejon National University of Technology.

### REFERENCES

- [1] H. W. Gibson, *Handbook of Conducting Polymers*, T. A. Skotheim, Ed., Dekker, New York, 1986, Vol. 1, p. 405.
- [2] P. Cukor, J. I. Krugler, and M. F. Rubner, *Makromol. Chem.*, **182**, 165 (1981).
- [3] Y. S. Gal and S. K. Choi, *J. Appl. Polym. Sci.*, **50**, 601 (1993).
- [4] H. Kita, T. Takamoto, K. Tanaka, and K-I. Okamoto, *Polym. Bull.*, **20**, 349 (1988).
- [5] Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, *J. Appl. Polym. Sci.*, **43**, 1227 (1991).
- [6] S. H. Han, E. Y. Kim, Y. S. Kang, and S. K. Choi, *Macromolecules*, **24**, 973 (1990).
- [7] T. Aoki, K.-I. Shinohara, T. Kaneko, and E. Oikawa, *Macromolecules*, **29**, 4192 (1996).



- [8] J. S. Yang and G. H. Hsiue, *J. Memb. Sci.*, **120**, 69 (1996).
- [9] H. S. Jin, S. H. Kim, H. N. Cho, and S. K. Choi, *Macromolecules*, **24**, 6050 (1991).
- [10] S. J. Choi, S. H. Jin, W. S. Ahn, H. N. Cho, and S. K. Choi, *Macromolecules*, **27**, 309 (1994).
- [11] B-Z. Tang, T. Masuda, T. Higashimura, and H. Yamaoka, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 1197 (1989).
- [12] Y. Mujie, Z. Jian, L. Aibing, S. Zhiquan, Z. Mingjian, and L. Senhao, *J. Polym. Sci. Polym. Chem. Ed.*, **27**, 3829 (1989).
- [13] J. L. Moigne, A. Hilberer, and F. Kajzar, *Makromol. Chem.*, **192**, 515 (1991).
- [14] M. Jang and J. Liu, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 3155 (1993).
- [15] H. J. Lee, J. M. Oh, S. J. Choi, H. K. Kim, and S. K. Choi, *Polym. Bull.*, **32**, 433 (1994).
- [16] D. W. Samuel, I. Ledoux, C. Dhenaut, J. Zyss, H. H. Fox, R. R. Schrock, and R. J. Silbey, *Science*, **265**, 1070 (1994).
- [17] C. Halvorson, A. Hays, B. Kraabel, R. Wu, F. Wudl, and A. J. Heeger, *Science*, **265**, 1215 (1994).
- [18] A. Usanmaz and N. Kizilirmak, *J. Macromol. Sci.-Pure and Appl. Chem.*, **A29**, 1175 (1992).
- [19] Y. S. Gal, *J. Macromol. Sci.-Pure and Appl. Chem.*, **A31**, 703 (1994).
- [20] Y. S. Gal, B. Jung, J. H. Kim, W. C. Lee, and S. K. Choi, *J. Macromol. Sci.-Pure and Appl. Chem.*, **A31**, 1177 (1994).
- [21] W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Polymer (Korea)*, **13**, 520 (1989).
- [22] W. C. Lee, J. H. Seo, Y. S. Gal, S. H. Jin, and S. K. Choi, *Bull. Korean Chem. Soc.*, **14**, 708 (1993).
- [23] H. J. Lee, Y. S. Gal, W. C. Lee, J. M. Oh, S. H. Kim, and S. K. Choi, *Macromolecules*, **28**, 1208 (1995).
- [24] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 2657 (1992).
- [25] Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 115 (1988).
- [26] T. Masuda, T. Matsumoto, T. Yoshimura, and T. Higashimura, *Macromolecules*, **23**, 4092 (1990).
- [27] T. Masuda, M. Kawai, and T. Higashimura, *Polymer*, **23**, 744 (1982).
- [28] M. S. Ryoo, W. C. Lee, and S. K. Choi, *Macromolecules*, **23**, 3029 (1990).

- [29] B. E. Davidov, B. A. Krentsel and G. V. Kchutareva, *J. Polym. Sci.: Part C. 16*, 1365 (1967).
- [30] M. Kawasaki, T. Masuda, and T. Higashimura, *Polymer J.*, *15*, 767 (1983).
- [31] A. Subramanyam and A. Blumstein, *Macromolecules*, *24*, 2668 (1991).
- [32] A. Subramanyam and A. Blumstein, U. S. Patent, 5037916 (1991).
- [33] A. Subramanyam, A. Blumstein, and K-P. Li, *Macromolecules*, *24*, 2668 (1991).
- [35] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Bull. Korean Chem. Soc.*, *15*, 267 (1994).
- [36] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Korea Polymer J.*, *2*, 104 (1994).
- [37] K. L. Kang, S. H. Kim, H. N. Cho, K. Y. Choi, and S. K. Choi, *Macromolecules*, *26*, 4539 (1993).
- [38] S. H. Kim, S. J. Choi, J. W. Park, H. N. Cho, and S. K. Choi, *Macromolecules*, *27*, 2339 (1994).
- [39] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Macromolecular Reports*, *A31*, 271 (1994).
- [40] Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *European Polymer J.*, *32*, 579 (1996).
- [41] Y. S. Gal, H.N. Cho, S. K. Kwon, and S. K. Choi, *Polymer (Korea)*, *12*, 30 (1998).
- [42] Y. S. Gal, W. C. Lee, and S. K. Choi, *Bull. Korean Chem. Soc.*, *18*, 265 (1997).
- [43] V. A. Kabanov, T. I. Patrikeeva, and V. A. Kargin, *Proc. Acad. Sci., U.S.S.R.*, *166*, 1350 (1966).
- [44] I. Mielke and H. Ringsdorf, *J. Polym. Sci., Part C.*, *31*, 107 (1970).
- [45] Y. S. Gal, *Eur. Polymer J.*, *33*, 169 (1997).
- [46] T. Masuda and T. Higashimura, *Acc. Chem. Res.*, *17*, 51 (1984).
- [47] O. Madelung, "Introduction to Solid State Theory", Springer-Verlag, Berlin, 1978.
- [48] N. C. Greenham and R. H. Friend, *Solid State Physics*, Vol. 49, Academic Press, Inc., Boston, 1996.

Received October 10, 1998

Revision received June 1, 1999