

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>

### Chemical and Electrochemical Syntheses of Soluble Electroconducting Poly(2,5-Thienylene) Derivatives

Hideki Shirakawa<sup>a</sup>; Sho'Ichi Fukumoto<sup>a</sup>; Hiroyuki Tanaka<sup>a</sup>; Yukio Ugawa<sup>a</sup>; Kazuo Akagi<sup>a</sup>; Kyoji Kaeriyama<sup>b</sup>; Hideyuki Masuda<sup>c</sup>

<sup>a</sup> Institute of Materials Science University of Tsukuba, Tsukuba, Ibaraki, Japan <sup>b</sup> Research Institute for Polymers and Textiles, Tsukuba, Ibaraki, Japan <sup>c</sup> Industrial Research Institute of Kanagawa Prefecture, Kanazawa-ku, Yokohama, Japan

**To cite this Article** Shirakawa, Hideki , Fukumoto, Sho'Ichi , Tanaka, Hiroyuki , Ugawa, Yukio , Akagi, Kazuo , Kaeriyama, Kyoji and Masuda, Hideyuki(1991) 'Chemical and Electrochemical Syntheses of Soluble Electroconducting Poly(2,5-Thienylene) Derivatives', *Journal of Macromolecular Science, Part A*, 28: 11, 1245 – 1254

**To link to this Article:** DOI: 10.1080/00222339108054097

**URL:** <http://dx.doi.org/10.1080/00222339108054097>

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.

## **CHEMICAL AND ELECTROCHEMICAL SYNTHESSES OF SOLUBLE ELECTROCONDUCTING POLY(2,5-THIENYLENE) DERIVATIVES**

HIDEKI SHIRAKAWA,\* SHO'ICHI FUKUMOTO,  
HIROYUKI TANAKA, YUKIO UGAWA, and KAZUO AKAGI

Institute of Materials Science  
University of Tsukuba  
Tsukuba, Ibaraki 305, Japan

KYOJI KAERIYAMA

Research Institute for Polymers and Textiles  
Tsukuba, Ibaraki 305, Japan

HIDEYUKI MASUDA

Industrial Research Institute of Kanagawa Prefecture  
Kanazawa-ku, Yokohama 236, Japan

### **ABSTRACT**

Soluble electroconducting poly[3-( $\omega$ -phenylalkyl)-2,5-thienylene]s are synthesized by electrochemical and chemical polymerizations of 3-(2-phenylethyl)thiophene and 3-(3-phenylpropyl)thiophene, which are synthesized by a Grignard cross-coupling reaction of 1-bromo-3-phenylalkane with 3-bromothiophene in the presence of dichloro[1,3-bis(diphenylphosphino)propane]-nickel(II). The chemical, electrochemical, and electrical properties of these polymers

are reported, including initial characterization, spectroscopy, and electrochemical cyclic voltammetry.

## INTRODUCTION

Functionalized soluble poly(2,5-thienylene) derivatives with alkyl or alkoxy groups at the 3- and/or 4-positions have recently attracted much attention [1–6]. Alkyl substituents bearing phenyl moiety at the end of the alkyl chain ( $\omega$ -phenylalkyl group) should be more functional and are more suitable for further modification than are *n*-alkyl groups. We report here preliminary results on a new series of poly(2,5-thienylene) derivatives in which an  $\omega$ -phenylalkyl group is substituted at the 3-position. Thus, 3-(2-phenylethyl)thiophene [PET] and 3-(2-phenylpropyl)thiophene [PPT] were synthesized and polymerized by chemical and electrochemical methods. Chemical polymerization yielded soluble poly[3-(2-phenylethyl)-2,5-thienylene] [PPET] and poly[3-(3-phenylpropyl)-2,5-thienylene] [PPPT] in some organic solvents. The chemical structures, electrochemical properties, and electrical properties of these polymers are also discussed.

## EXPERIMENTAL

Two kinds of monomer, PET and PPT, were synthesized by a Grignard cross-coupling reaction of 1-bromo-2-phenylethane and 1-bromo-3-phenylpropane, respectively, with 3-bromothiophene in the presence of dichloro[1,3-bis(diphenylphosphino)propane]-nickel(II) [Ni(dppp)Cl<sub>2</sub>]. Electrochemical polymerization of PPT was carried out galvanostatically at 5 to  $-32^{\circ}\text{C}$  in a one-compartment cell by using propylene carbonate as a solvent and Et<sub>4</sub>NPF<sub>6</sub> as an electrolyte unless otherwise specified. An ITO glass and a platinum plate were used as the anode and the cathode, respectively. The monomer and electrolyte concentrations were 0.2 and 0.03 mol/L, respectively. The charge density was 1.2 C/cm<sup>2</sup> with a current density of 2.0 mA/cm<sup>2</sup>.

Chemical polymerization of PET and PPT was carried out in such organic solvents as toluene, chloroform, and nitromethane catalyzed by FeCl<sub>3</sub> at room temperature. The reaction mixture was added into an excess amount of methanol with stirring to precipitate the neutral (undoped) polymer.

Molecular weight distribution and UV-visible spectra were measured by using a JASCO HPLC system equipped with a multi-channel detector (MULTI-340) and a GPC column (Shodex A-804). Molecular weights were calibrated by using polystyrene standards. Proton and  $^{13}\text{C}$ -NMR spectra were obtained in  $\text{CDCl}_3$  solution on a JEOL JNM-GSX270. Infrared spectra were recorded by using a JASCO FT/IR-8000. Electrical conductivity of doped films prepared by the electrochemical method was measured by a pressure-contacted four-probe method. *In-situ* measurements of electrical conductivity during vapor-phase iodine doping of chemically synthesized polymers were performed by a conventional four-probe method. A thin polymer film coated on a polyester film was attached onto platinum wires by using conducting carbon paste (Acheson Electrodag 502).

## RESULTS AND DISCUSSION

### Electrochemical Polymerization of PPT

In order to get optimal conditions for the electrochemical polymerization of PPT, the effect of current density upon electrical conductivity of the polymer films was examined during polymerization at  $-20^\circ\text{C}$ . As shown in Fig. 1, the optimal current density was  $2.5\text{ mA/cm}^2$ . At this condition, self-standing films with good mechanical properties were obtained. When the current density was higher than  $3.0\text{ mA/cm}^2$ , the films were generally brittle with poor conductivity. Figure 2 shows the relationship between polymerization temperature and electrical conductivity of the films. The electrical conductivities as high as  $15\text{--}20\text{ S/cm}$  were obtained for films prepared at  $-26$  to  $-27^\circ\text{C}$ . It is worth noting that the quality of the films is also improved at such low temperatures.

Figure 3 shows the infrared spectra of PPT monomer (M), electrochemically (Pec) and chemically (Pc) synthesized undoped PPPT polymers. Three C—H out-of-plane vibrations of the monomer, a strong band at  $773\text{ cm}^{-1}$  and two weak bands at  $835$  and  $862\text{ cm}^{-1}$ , characteristic of a monosubstituted thiophene ring at the 3-position, disappear in the polymer spectra. Instead, a new band appears at  $828\text{ cm}^{-1}$ , assignable to C—H out-of-plane vibration of 2,3,5-trisubstituted thiophene rings in the polymers.

Cyclic voltammogram of PPPT gives one anodic (acceptor doping) peak at  $0.6\text{ V}$  (vs Ag) and one cathodic (undoping) peak at  $0.57\text{ V}$ . The

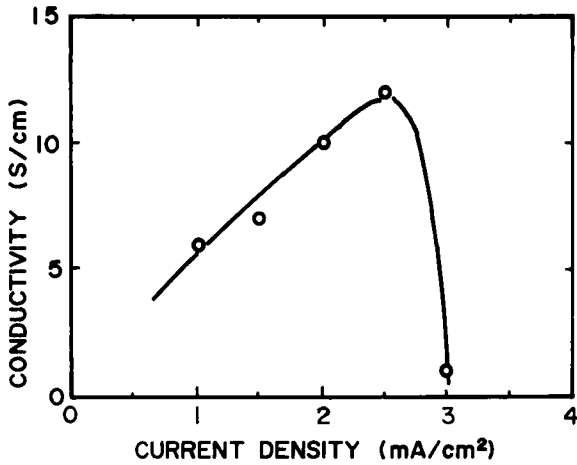


FIG 1. Effect of current density upon the electrical conductivity of as-prepared doped PPPT films.

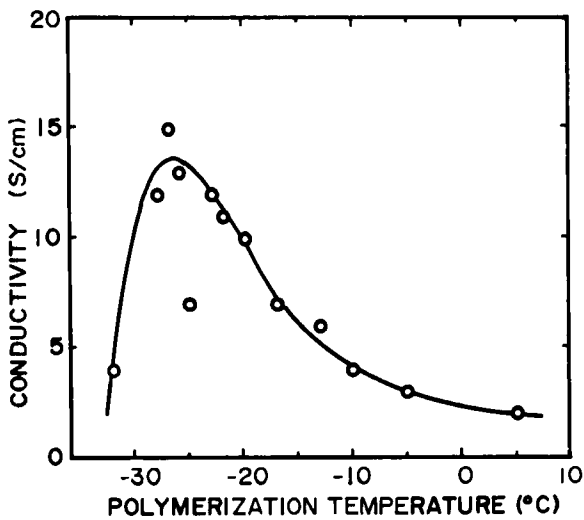


FIG 2. Effect of polymerization temperature upon the electrical conductivity of as-prepared doped PPPT films.

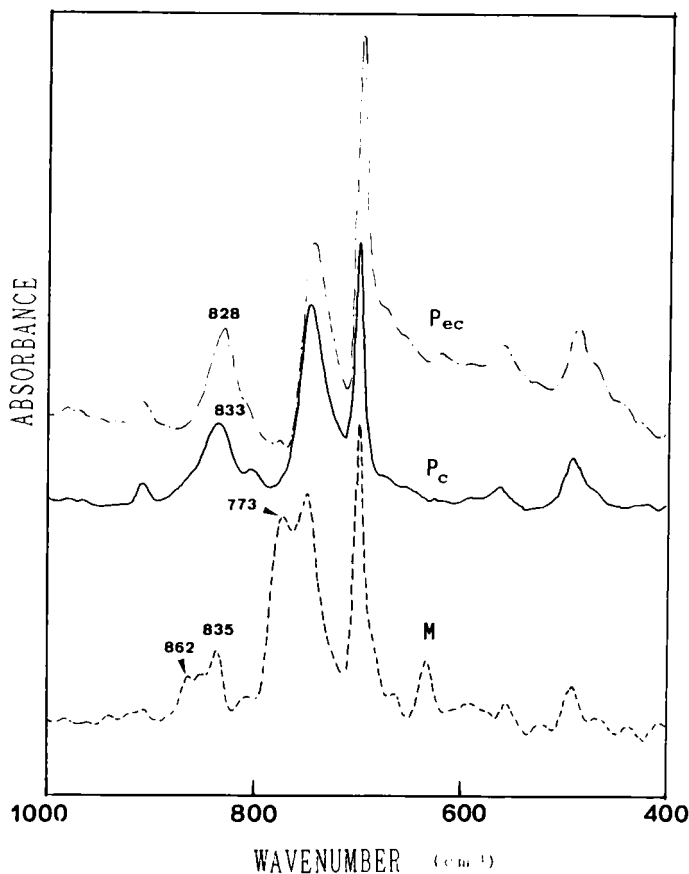


FIG 3. FT-IR spectra of PPT monomer (M) and PPPTs prepared by the electrochemical method (Pec) and by the chemical method (Pc).

color of a thin PPPT film changes from blue (anion doped) to light orange (undoped) during a doping-undoping cycle. The change of absorption spectra during electrochemical doping is shown in Fig. 4. A weak absorption peak at 1.1 eV at zero potential is due to insufficient undoping of the as-prepared doped film. When applied potential is higher than 0.6 V, two peaks at 0.8 and 1.7 eV appear with increasing applied potential and a  $\pi \rightarrow \pi^*$  transition at 3.1 eV decreases concomitantly. Neither doped polymer nor undoped polymer was soluble in such organic solvents as THF, chloroform, and toluene. Since chemically

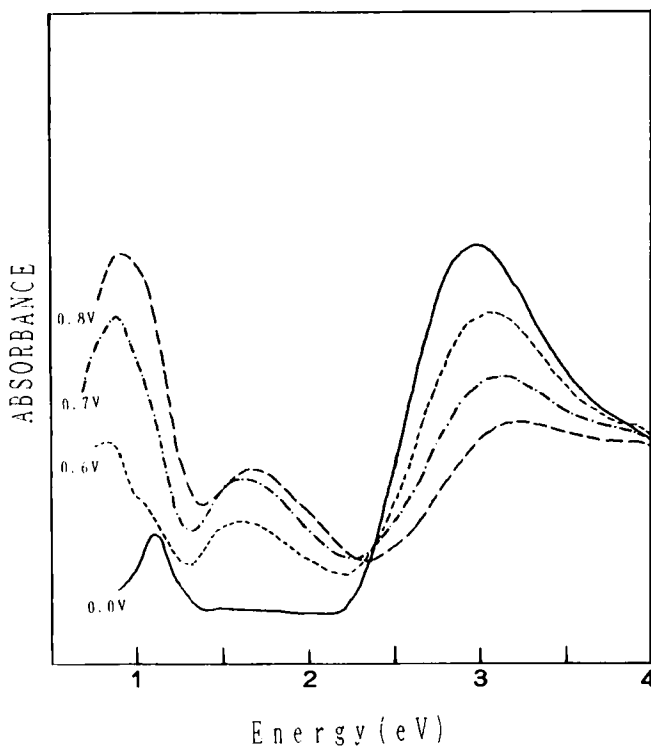


FIG 4. Absorption spectra of thin PPPT film during the electro-chemical doping.

synthesized polymers are soluble in some organic solvents, as described in the next section, electrochemical polymerization on the electrode must accompany crosslinking reaction.

### Chemical Polymerization of PPT and PET

Neutral polymers of PPT and PET prepared by chemical polymerization were soluble in THF, chloroform, carbon tetrachloride, benzene, and nitrobenzene. Figure 5 shows two- and three-dimensional GPC of PPPT as a function of degree of polymerization ( $DP$ ) calibrated by standard polystyrenes. As can be seen from the two-dimensional chromatogram (Fig. 5, top), the maximum wavelength ( $\lambda_{\max}$ ) of PPPT depends upon the degree of polymerization. Thus,  $\lambda_{\max}$  of PPPT in THF

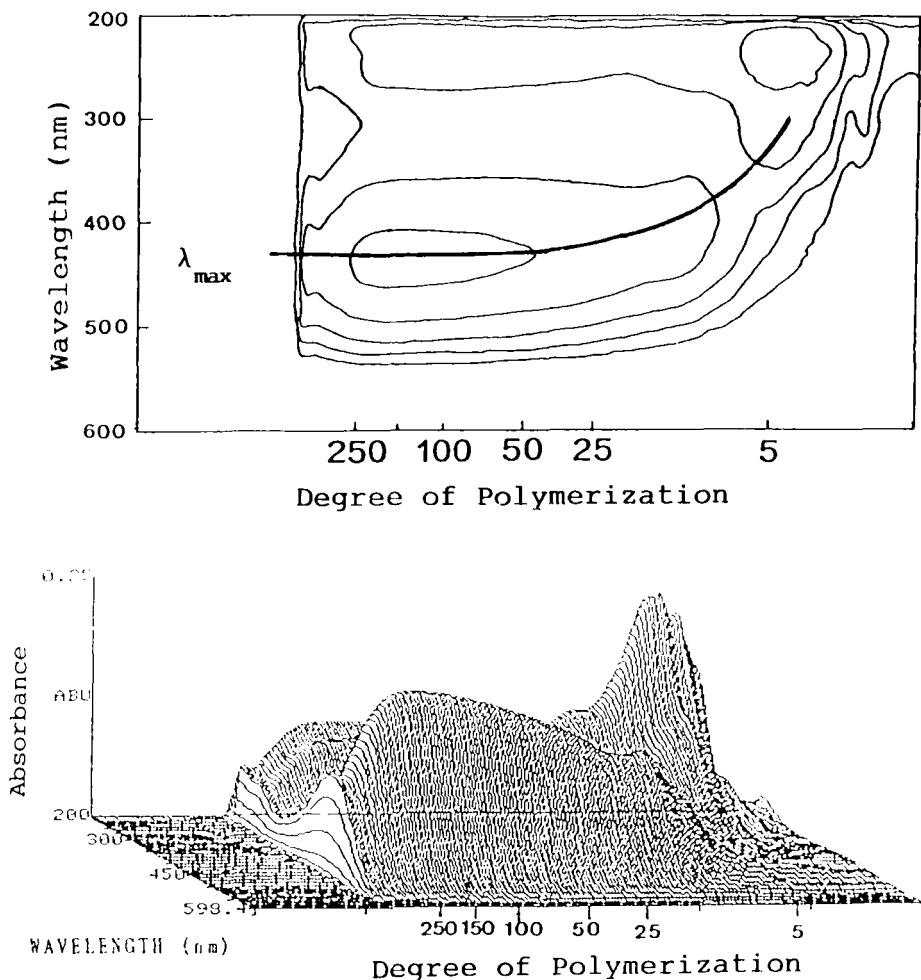


FIG 5. Two-dimensional (top) and three-dimensional (bottom) GPC of soluble PPPT prepared by the chemical method.

solution changes continuously from 300 nm for an oligomer ( $DP = 5$ ) and saturates to 436 nm for polymers having a  $DP$  of more than 50. This observation suggests that PPPT has an effective conjugation length of at least 50 monomer units in THF solution. The same tendency was also observed for PPET with a saturated  $\lambda_{\max}$  of 426 nm. As shown in Fig. 3, the infrared spectrum of PPPT was in good agreement with that



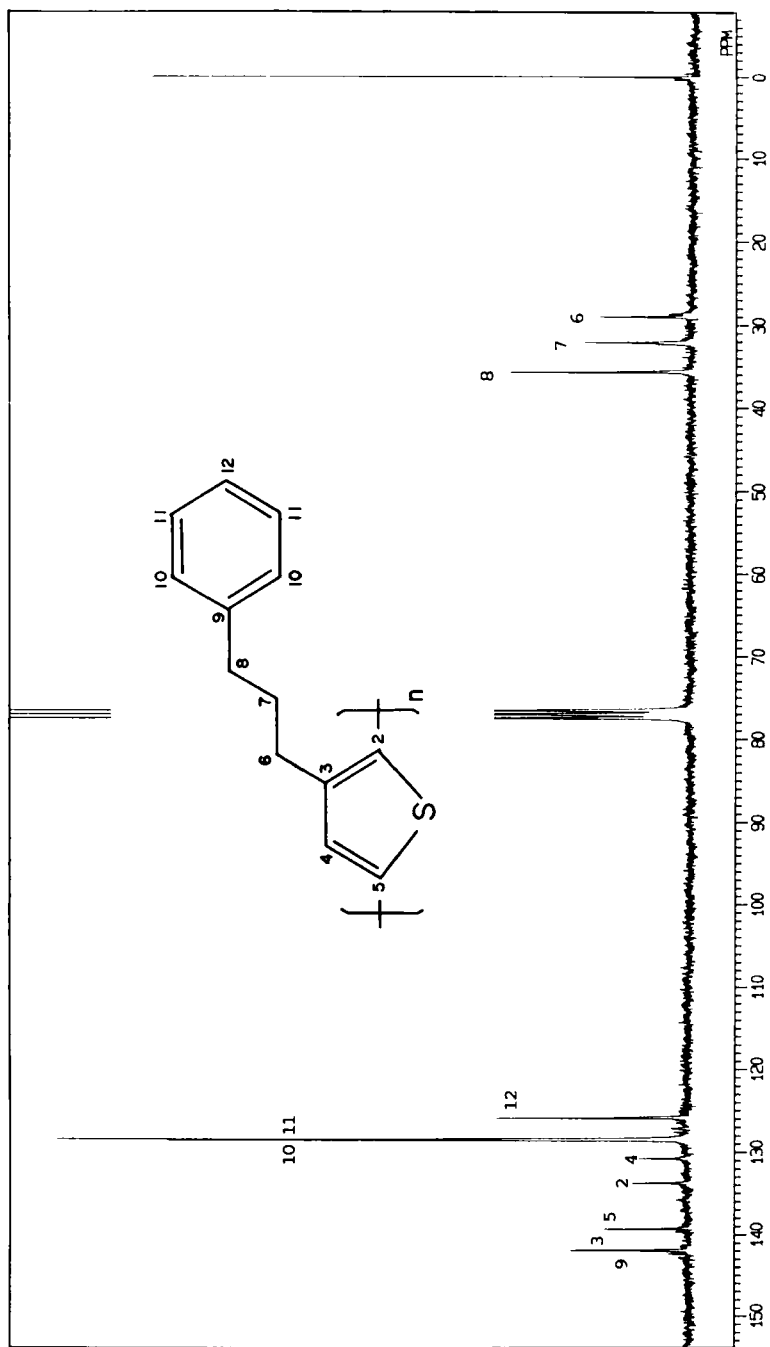


FIG 6.  $^{13}\text{C}$ -NMR spectrum of chemically synthesized PPPT in  $\text{CDCl}_3$  solution.

of PPPT prepared by electrochemical polymerization, indicating that both polymers, prepared by different methods, have the same fundamental structure of 2,5-thienylene, except that the polymer prepared by the electrochemical method has an undetectable amount of intermolecular bondings which cause insolubility in organic solvents.

Figure 6 shows the  $^{13}\text{C}$ -NMR spectrum of PPPT in  $\text{CDCl}_3$  solution. Four intense peaks at 125.9, 128.6, 128.4, and 142.1 ppm are assignable to carbon atoms of the phenyl ring at the 12, 11, 10, and 9 positions, respectively, and four intense, well-defined peaks at 133.7, 142.0, 130.8, and 139.3 ppm in the aromatic region are assigned to carbon atoms of the thiophene ring at the 2, 3, 4, and 5 positions, respectively. No other peaks are observed in the aromatic region. On the other hand, Wegner et al. reported that more than 10 additional peaks were observed between 125 and 150 ppm in addition to four major peaks in  $^{13}\text{C}$  spectrum of poly(3-dodecylthiophene) [5]. Although no assignments of these minor peaks were reported, Wegner et al. considered that the polymer contains not only the regular 2,5'-linkage but also a linkage of adjacent units in the 2,4'-position or branched structures. Wudl et al. observed 12 well-defined peaks along with four strong peaks in the aromatic region of the NMR spectrum of poly(3-hexylthiophene) [6]. They assigned the four strong peaks to the carbon atoms of thiophene rings entirely involved in head-to-tail linkages, and four of the 12 weaker aromatic resonances to carbon atoms within the thiophene rings involved in head-to-head linkage. In view of the simple and well-defined solution  $^{13}\text{C}$ -NMR spectra of PPPT and PPET, we conclude that both polymers have regular head-to-tail 2,5'-linkages.

Electrical conductivity of cast films doped with  $\text{I}_2$  was  $1.5 \times 10^{-1}$  to  $1.0 \times 10^{-3}$  S/cm for both PPPT and PPET, depending on the preparative conditions.

In conclusion, we have demonstrated that stereoregular soluble conducting polythiophene derivatives can be prepared by introducing a  $\omega$ -phenylalkyl group into thiophene at the 3-position. Although the electrochemically synthesized polymer was not soluble in organic solvents, its electrical conductivity was as high as 15 S/cm.

## REFERENCES

- [1] M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, p. 837 (1986).

- [2] K. Y. Jen, G. G. Miller, and R. Elsenbaumer, *Ibid.*, p. 1346 (1986).
- [3] R. Sugimoto, S. Takeda, H. B. Gu, and K. Yoshino, *Chem. Express*, *1*, 635 (1986).
- [4] S. Hotta, S. D. D. V. Rughooputh, A. J. Heeger, and F. Wudl, *Macromolecules*, *20*, 212 (1987).
- [5] M. Leclerc, F. M. Diaz, and G. Wegner, *Makromol. Chem.*, *190*, 3105 (1989).
- [6] R. M. Souto Maior, K. Hinkelmann, H. Eckert, and F. Wudl, *Macromolecules*, *23*, 1268 (1990).