Electrochemical Doping of Poly(3-vinylperylene) and Electrical Properties of Doped Polymers

Il-Ryon JEON, Naoki NOMA, Rodney F. C. CLARIDGE[†],
and Yasuhiko SHIROTA*

*Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadaoka, Suita, Osaka 565, Japan*

ABSTRACT: Poly(3-vinylperylene) has been prepared by radical polymerization of 3-vinylperylene, and characterized by spectroscopic methods, mol. wt. determination, and differential scanning calorimetry. Electrochemical doping of poly(3-vinylperylene), and characterization and electrical properties of doped polymers have been studied. Electrochemically-doped poly(3-vinylperylene) is identified as a partially oxidized radical-cation salt with ClO_4^- as a dopant. The polymer with a doping degree of 86% exhibits a room-temperature conductivity of $1 \times 10^{-5} \, S \, cm^{-1}$ and an activation energy of *ca.* 0.4 eV. The presence of hole charge carriers is shown from the electron spin resonance spectrum.

KEY WORDS Poly(3-vinylperylene) / Electrochemical Doping / Electrochemically-Doped Polymer / Radical Cation / Electrical Conductivity / Activation Energy /

Electrically conducting polymers, including both semiconducting polymers and polymers with metallic conduction, have been a subject of recent extensive studies. They have drawn attention for both academic interest and potential technological applications.[1,2]

Wholly π-conjugated linear polymers, *e.g.*, polyacetylene,[3,4] poly(*p*-phenylene),[5,6] poly(*p*-phenylene vinylene),[7,8] polypyrrole,[9,10] polythiophene,[11] and polyaniline,[12-14] have been studied intensively for their highly conductive properties.

For the purpose of developing a new class of electrically conducting polymers, we have been studying electrochemical doping of vinyl-type polymers containing pendant π-electron systems, and properties and applications of doped polymers.[15-24] Non-conjugated polymers containing pendant π-electron systems are of interest for the following reasons: the variety of possible pendant molecules, chemical stability, ease of processability, photoconducting properties, and invariance of the standard oxidation/reduction potential irrespective of the doping degree. We have shown that non-conjugated vinyl polymers bearing pendant π-electron systems, *e.g.*, poly(*N*-vinylcarbazole) and poly(1-vinylpyrene), are transformed into electrically conducting polymers by electrochemical doping,[15-18] and that electrically conducting polymers are also obtained by electrolytic polymerization of vinyl monomers, *e.g.*, *N*-vinylcarbazole, 1-vinylpyrene, and 3-vinylperylene.[17,19,20] Electrochemically-doped polymers function as positive electrode materials for secondary batteries,[21,22] and as photoactive materials for photovoltaic devices.[23,24]

As a part of our studies on electrochemical doping of non-conjugated pendant polymers,

---

† On leave from Chemistry Department, University of Canterbury, Christchurch 1, New Zealand.

we have investigated electrochemical doping of poly(3-vinylperylene) in the present study. Since perylene, which has a larger π-electron system than pyrene, is known to produce conductive charge-transfer complexes with bromine or iodine,[25,26] and highly conductive radical-cation salts by electrocrystallization,[27] it is of interest to study electrochemical doping of poly(3-vinylperylene). This paper describes preparation of poly(3-vinylperylene), its electrochemical doping and characterization and electrical properties of a doped polymer.

EXPERIMENTAL

Materials

Perylene (Nacalai Tesque, Inc., guaranteed reagent) was purified by recrystallization from toluene. 3-Vinylperylene was prepared according to the method of Buckley and Teuscher.[28] 3-Perylenecarboxaldehyde was synthesized from perylene by Vilsmeier reaction, and then converted to 3-vinylperylene using Wittig reaction. Methylenetriphenylphosphorane was prepared *in situ* by the reaction of methyltriphenylphosphonium bromide with *n*-butyllithium. The phosphorane was reacted with 3-perylenecarboxaldehyde in dry tetrahydrofuran at room temperature for 24 h to give 3-vinylperylene. It was purified twice by silica gel column chromatography, mp 154—155°C. MS *m/z*: 278 (M^+), 251 ($M^+ - CH = CH_2$). Found: C, 94.59%; H, 5.12%. Calcd for $C_{22}H_{14}$: C, 94.96%; H, 5.04%. ^1H NMR (CS_2) δ (ppm): 5.42 (dd, 1H, $=CH_2$), 5.76 (dd, 1H, $=CH_2$), 7.95 (dd, 1H, $-CH=$), 7.25—8.15 (m, 11H, ArH). VIS (THF), λ_{max} (nm) (log ε): 426 (4.4) and 452 (4.5). IR (KBr) (cm^{-1}): 990 and 910 ($\delta_{C=C}$).

2,2'-Azobisisobutyronitrile (AIBN) (Wako Pure Chemical Industries, Ltd., guaranteed reagent) was purified by recrystallization from methanol. Tetra-*n*-butylammonium perchlorate (Tokyo Kasei Kogyo Co., Ltd., guaranteed reagent) was recrystallized from ethanol three times, dried at 70°C for 24 h, stored in a desiccator, and redried *in vacuo* at room temperature immediately before use. Dichloromethane was treated with conc. sulfuric acid, washed with water, dried, and distilled over calcium hydride immediately before use. Benzene and tetrahydrofuran were purified and dried by ordinary methods.

Polymerization of 3-Vinylperylene

Polymerization of 3-vinylperylene was carried out in a benzene solution at 70°C with AIBN as an initiator. The monomer and initiator concentrations were 5×10^{-2} mol dm^{-3} and 5×10^{-4} mol dm^{-3}, respectively. A solution containing the monomer and AIBN in benzene was placed in a glass tube (4 cm in diameter and 5 cm in height), and evaculated at *ca.* 10^{-4} Torr by several freeze-pump-thaw cycles, sealed off, and allowed to stand with constant stirring in a thermostat maintained at 70°C. After an appropriate time (3 days), the reaction solution was poured into a large volume of methanol to precipitate polymers. The polymers were purified by repeated reprecipitation from chloroform/methanol, collected by filtration, dried *in vacuo*, and weighed (polymer yield 32%). Found: C, 94.04; H, 4.98%. Calcd for $C_{22}H_{14}$: C, 94.96%; H, 5.04%. ^1H NMR (CS_2) δ (ppm): 1.70—1.85 (m, 2H, CH_2), 3.45—3.60 (m, 1H, CH), 7.20—8.10 (m, 11H, ArH). VIS (THF), λ_{max} (nm) (log ε): 447 (4.3) and 420 (4.2). IR (KBr) (cm^{-1}): 2950 (ν_{CH}) and 2850 (ν_{CH_2}).

Electrochemical Oxidation

Cyclic voltammetry was carried out for a dichloromethane solution of poly(3-vinylperylene) (1×10^{-3} mol dm^{-3}) containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}) as a supporting electrolyte with Ag/Ag$^+$ 0.01 mol dm^{-3} reference electrode. Electrochemical doping of poly(3-vinylperylene) was carried out potentiostatically for a dichloromethane solution of poly(3-vinylperylene) (2.5×10^{-3} mol dm^{-3}) containing tetra-*n*-butylammonium perchlorate (0.1 mol dm^{-3}) in a two-compart-

ment cell with three electrodes. Platinum plates ($1.5 \times 2.5\,cm^2$ and $2.0 \times 2.0\,cm^2$) were used as working and counter electrodes.

When controlled-potential anodic oxidation of poly(3-vinylperylene) was carried out at 0.8 V *vs.* Ag/Ag$^+$ 0.01 mol dm^{-3} reference electrode, green-colored polymers were deposited onto the surface of the working electrode. They were washed with purified dichloromethane, dried *in vacuo*, and collected. For example, when the electrolysis of poly(3-vinylperylene) (17.4 mg, 2.5×10^{-3} mol dm^{-3}) started, a current of *ca.* 1.4 mA flowed, and it gradually decreased to 0.4 mA during the electrolysis. After the electrolysis for 5 h, during which time *ca.* 10 coulombs of electricity flowed, 16.0 mg of electrochemically-doped polymers were obtained. The degree of doping for resulting polymers was determined from the chlorine content of the dopant.

Electron Spin Resonance Spectroscopy

Electron spin resonance measurements in the solid state were made using *ca.* 30 mg of the green-colored, electrochemically-doped polymer in a thin glass tube. A sample of powdered magnesium oxide containing manganese 2$^+$ in a similar tube was used as reference. The two tubes were placed together in a larger ESR tube (4 mm) in the cavity. The position of the samples was changed several times to ensure a reliable determination of g-value.

Conductivity Measurements

Electrical conductivity was measured by a two-probe d.c. method for samples of pressed pellets, both on which gold was vacuum-deposited to make the electrode. The activation energy for electrical conduction was determined from Arrhenius plots of electrical conductivities measured in a temperature range from 20 to 80°C.

Apparatus

Electrochemical measurements were performed with a Model HA-501 potentiostat (Hokuto Denko, Ltd.), a model HB-104 function generator (Hokuto Denko, Ltd.), and a Model RW-21 recorder (Rikadenki Kogyo Co., Ltd.). Infrared and electronic absorption spectra were measured with a Model A-102 diffraction grating infrared spectrophotometer (Japan Spectroscopic Co., Ltd.) and a Model U-3200 double beam spectrophotometer (Hitachi, Ltd.), respectively. Electron spin resonance spectra were measured with a bruker ESP-300 spectrometer. The glass-transition temperature of the polymer was measured with a Model SSC-5000 differential scanning calorimetry (Seiko Instruments Inc.).

RESULTS AND DISCUSSION

Preparation and Characterization of Poly(3-vinylperylene)

To our knowledge, synthesis and characterization of poly(3-vinylperylene) has not been reported. It has recently been reported that 3-vinylperylene is neither polymerized nor copolymerized with styrene or maleic anhydride under normal free radical conditions, and that it strongly retards or inhibits the radical polymerization of reactive monomers such as styrene, methyl methacrylate or vinyl acetate.[29]

However, radical polymerization of 3-vinylperylene in the presence of AIBN as an initiator in benzene yielded polymers as yellow powder. The molecular weight of the resulting polymers was determined to be $M_n = 1300$, $M_w = 1600$ by gel permeation chromatography with polystyrene as a standard. Thus, they are oligomers with a degree of polymerization of about five or six. Here we call them polymers or poly(3-vinylperylene) for the sake of convenience. As Figure 1 shows, poly(3-vinylperylene) prepared in the present study exhibits a glass transition at *ca.* 166°C as determined by differential scanning calorimetry. The polymer is not readily soluble in many ordinary solvents, but sufficiently soluble in carbon disulfide, chloroform and benzene to make spectroscopic measurements and to carry
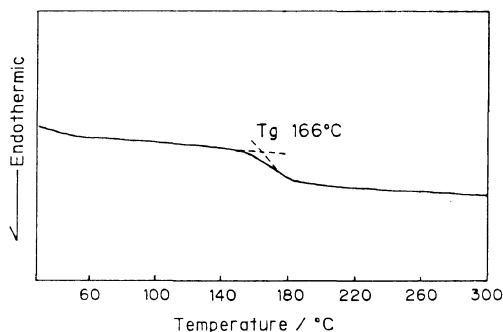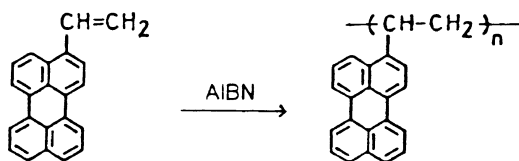
Figure 1. DSC trace of poly(3-vinylperylene). Heating rate, $10°C$ min^{-1}.

Figure 2. Electronic absorption spectra of (a) perylene
(— — —), (b) 3-vinylperylene (— — — —), and (c) poly(3-vinyl-
perylene) (———) in THF. Concentration, 1.1×10^{-5} mol
dm^{-3}.

out electrochemical doping. Transparent polymer films can be formed by casting from a solution.

The characteristic infrared absorption bands at 990 and 910 cm^{-1} observed for 3-vinylperylene, which are due to the C–H out-of-plane deformation vibration of the vinyl group, are absent in the spectrum of poly(3-vinylperylene). Instead, the polymer shows weak infrared absorption bands at 2950 and 2850 cm^{-1} due to the stretching vibration of the methylene and methine groups of the polymer backbone. These results indicate that the polymerization of the monomer took place at the vinyl group to give the polymer.

Figure 2 shows the electronic absorption spectrum of a dilute solution of poly(3-vinylperylene) in tetrahydrofuran, together with those of perylene and 3-vinylperylene. The polymer shows the absorption band due to the perylene chromophore in the wavelength region from 400 to 500 nm; the spectrum resembles that of perylene, but the absorption band of the polymer is *ca.* 10 nm red-shifted relative to perylene. The absorption band of 3-vinylperylene is *ca.* 15 nm red-shifted relative
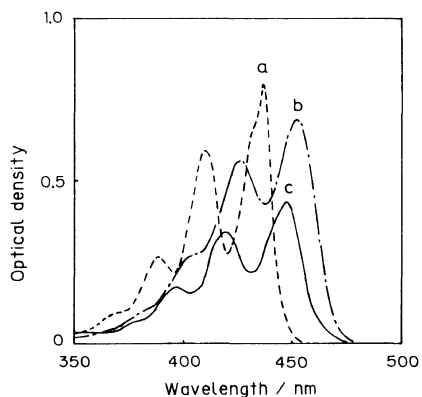
to perylene. It is suggested that the polymer chain alkyl group causes the red shift of the electronic absorption band of the perylene chromophore, and that the vinyl group in 3-vinylperylene is conjugated with the perylene chromophore to cause the red shift of the absorption band. The molar extinction coefficient of the absorption maximum in THF is slightly lower for the polymer (log $\varepsilon = 4.3$) than for 3-vinylperylene (log $\varepsilon = 4.5$) and perylene (log $\varepsilon = 4.6$).

Electrochemical Doping of Poly(3-vinylperylene) and Characterization of the Doped Polymer

Figure 3 shows cyclic voltammograms for the anodic oxidation of poly(3-vinylperylene) in dichloromethane. The anodic oxidation process of poly(3-vinylperylene) is irreversible. The current of anodic and cathodic waves gradually increases when the sweep is repeated. This is suggested to result from the accumulation of electroactive polymers deposited onto the surface of the electrode. The peak potential for the anodic oxidation of the pendant perylene chromophore is *ca.* 0.81 V *vs.* Ag/Ag$^+$ 0.01 mol dm^{-3}. The cathodic waves are observed at *ca.* 0.68 and 0.57 V. When the sweep was repeated, the cyclic voltammogram exhibits another anodic wave at a potential more
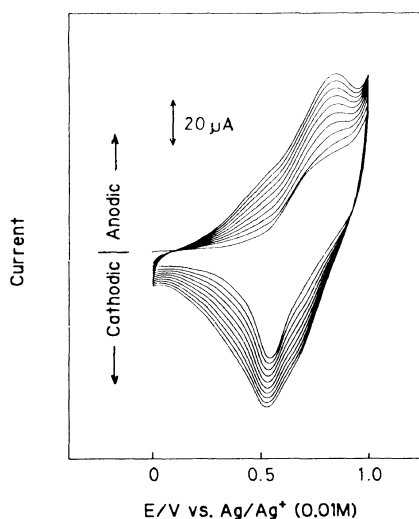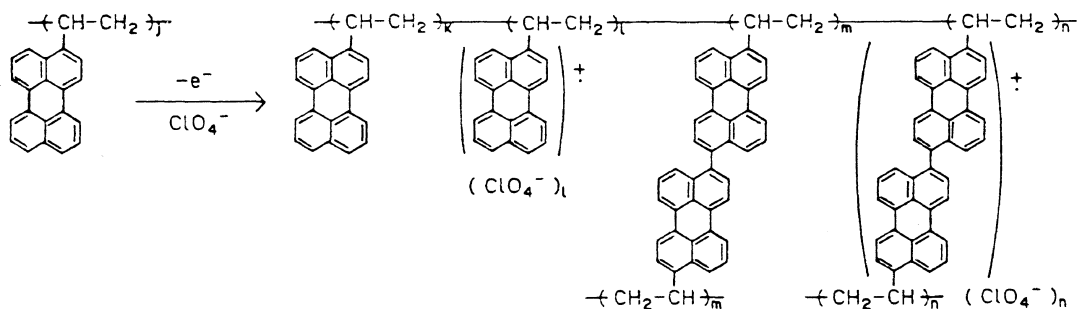
Figure 3. Cyclic voltammograms of poly(3-vinylperylene) in CH_2Cl_2. [poly(3-vinylperylene)] $= 1 \times 10^{-3}$ mol dm^{-3}; [Bu_4NClO_4] $= 0.1$ mol dm^{-3}; sweep rate, 100 mV s^{-1}.

coupling reaction of pendant perylene radical cations.

Based on the information obtained from the cyclic voltammetry, electrochemical doping of poly(3-vinylperylene) was carried out by controlled-potential anodic oxidation. Poly(3-vinylperylene) dissolved in dichloromethane containing 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate was anodically oxidized at 0.8 V $vs.$ Ag/Ag$^+$ 0.01 mol dm^{-3} reference electrode. Deep green-colored polymers were deposited onto the surface of the working electrode. The polymer exhibits electrochromic behavior; the color of the polymer changes reversibly from yellow to green when the polymer is doped, and from green to yellow when dedoped. The electrochemically-doped polymer was identified as a partially oxidized radical-cation salt with $ClO_4{}^-$ as a counter anion from the electronic and infrared absorption spectra, and elemental analysis. The cyclic voltammograms suggest that the polymer contains a biperylene chromophore due to the coupling reaction of perylene radical cations.

negative than 0.5 V in addition to the wave at 0.81 V $vs.$ Ag/Ag$^+$ 0.01 mol dm^{-3}. This anodic wave is suggested to be due to the oxidation of the biperylene moiety generated by the

The incorporation of $ClO_4{}^-$ as a dopant in the electrochemically-doped polymer is shown from its infrared absorption spectrum; it exhibits strong absorption bands at 1140, 1110, and 1080 cm^{-1} due to $ClO_4{}^-$.

Figure 4 shows the solid-state electronic absorption spectra of doped and dedoped polymers deposited onto the ITO coated glass. The principal features of the absorption spectrum of the doped polymer are a new band with maximum at $ca.$ 613 nm together

with a shoulder band at $ca.$ 760 nm and the band in the region from 400 to 500 nm. The latter band is characteristic of the neutral perylene chromophore. The bands with a maximum at 613 nm and a shoulder at 760 nm are ascribed to the radical cation of the pendant perylene chromophore in the doped polymer, because these bands diminish when the electrochemically-doped polymer is partially dedoped. The radical cation of perylene generated by a variety of methods shows a
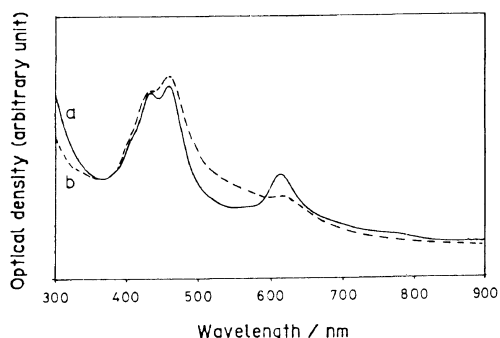
Figure 4. Electronic absorption spectra of (a) doped (———) and (b) dedoped (———) poly(3-vinylperylene) in the solid state. The doped polymer was obtained by controlled-potential anodic oxidation of poly(3-vinylper-ylene) in dichloromethane ($1 \times 10^{-3} \, \text{mol dm}^{-3}$) for 3 min. The dedoped polymer was obtained by reducing the doped polymer at $-0.5 \, \text{V}$ *vs.* Ag/Ag^+ $0.01 \, \text{mol dm}^{-3}$ reference electrode for 10 min.

Figure 5. Electron spin resonance spectrum of doped poly(3-vinylperylene) in the solid state. The doped polymer was obtained by electrochemical doping of poly(3-vinylperylene) in dichloromethane ($2.5 \times 10^{-3} \, \text{mol dm}^{-3}$) for 5 h.

sharp band maximum in the 540—560 nm region in a dilute solution.[30] On the other hand, the absorption spectrum of the perylene–SbCl_5 complex in the solid state has been reported to show broad absorption bands with peaks at 600 and 760 nm due to the perylene radical cation, which is red-shifted by *ca.* 40—60 nm relative to those reported for the perylene radical cation in solutions.[31]

That the electrochemically-doped polymer is a radical-cation salt is also evidenced by ESR spectroscopy. Figure 5 shows the ESR spectrum of the doped polymer. A strong single line ($g = 2.0035$, line width $= 1.5$ Gauss) was observed, but no hyperfine features were observable. The g-value is close to that of the free electron. The result provides the evidence for the presence of hole charge carriers.

The green-colored, electrochemically-doped poly(3-vinylperylene) is fairly stable in air. Table I lists room-temperature conductivities and activation energies for electrical conduction of electrochemically-doped polymers prepared by electrochemical oxidation of poly(3-vinylperylene). Electrochemically-doped poly(3-vinylperylene) with a doping degree of *ca.* 86% exhibits a room-temperature
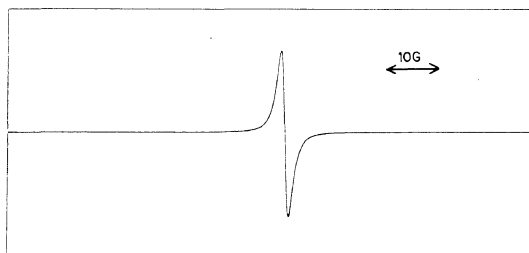
conductivity (σ_{rt}) of $1 \times 10^{-5} \, \text{S cm}^{-1}$. In this case, the mobility of charge carriers is estimated to be *ca.* $5 \times 10^{-8} \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ based on the doping degree and the specific gravity (ρ) of the doped-sample ($\rho = 1.4$). Electrolytic polymerization of 3-vinylperylene also gives electrically conducting polymers with comparable room-temperature conductivities.[20] Electrochemically-doped poly(3-vinylperyl-ene) is found to exhibit much higher electrical conductivities than electrochemically-doped poly(1-vinylpyrene) ($\sigma_{rt} = 4 \times 10^{-7} \, \text{S cm}^{-1}$; doping degree 21%).[17] This is probably due to higher doping degree and higher mobility of charge carriers for poly(3-vinylperyl-ene) than for poly(1-vinylpyrene). The electrical conduction is of thermally activated process, following the equation:

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

The activation energies for electrical conduction in electrochemically-doped poly(3-vinylperylene) were 0.4—0.6 eV. The activation energy is thought to be mainly associated with the hopping transport process of charge carriers.

The electrical conductivities of electrochemically-doped poly(3-vinylperylene) are lower than those of radical cation salts or charge-transfer complexes of low-molecular-weight compound, perylene. This may be attributed to a lower mobility of charge carriers for the

Table I. Room-temperature conductivities of electrochemically-doped poly(3-vinylperylene)[a]

Exp. No.	Degree of doping/%[b]	Conductivity σ_{rt}/S cm^{-1}	Activation energy/eV
1	86	1×10^{-5}	0.4
2	77	9×10^{-6}	0.6

[a] Doped polymers were obtained by electrochemical doping of poly(3-vinylperylene) (2.5×10^{-3} mol dm^{-3}) in dichloromethane containing Bu$_4$NClO$_4$ (0.1 mol dm^{-3}) at 0.8 V *vs.* Ag/Ag$^+$ 0.01 mol dm^{-3} for 5 h.
[b] Determined from chlorine content.

polymer than for the low-molecular-weight materials probably because of the lower order of the arrangement of pendant perylene chromophores in the polymer. Poly(3-vinylperylene) functions as a positive electrode material for secondary batteries[32].

REFERENCES

1. J. S. Miller, "Extended Linear Chain Compounds," Vols. 1—3, Plenum Publishing Co., New York, 1982.
2. T. Shimidzu, *Mol. Cryst. Liq. Cryst.*, **190**, 75 (1990).
3. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
4. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, *J. Chem. Phys.*, **69**, 5098 (1978).
5. D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, **71**, 1506 (1979).
6. L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Met.*, **1**, 307 (1979).
7. G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polymer*, **20**, 1441 (1979).
8. I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.*, **25**, 327 (1984).
9. A. F. Diaz and K. K. Kanazawa, *J. Chem. Soc., Chem. Commun.*, 635 (1979).
10. K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synth. Met.*, **1**, 329 (1979/80).
11. G. Tourillon and F. Garnier, *J. Phys. Chem.*, **87**, 2289 (1983).
12. A. Kitani, J. Izumi, J. Yano, Y. Hiromoto, and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **57**, 2254 (1984).
13. A. G. MacDiarmid, J. C. Chiang, M. Halpern, W.-S. Huang, S.-L. Mu, N. L. D. Somasiri, W. Wu, and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.*, **121**, 173 (1985).
14. E. M. Genies, A. A. Syed, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, **121**, 181 (1985).
15. H. Kanega, Y. Shirota, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 158 (1984).
16. Y. Shirota, T. Kakuta, and H. Mikawa, *Makromol. Chem., Rapid Commun.*, **5**, 337 (1984).
17. N. Noma, Y. Shirota, and H. Mikawa, *J. Chem. Soc. Jpn.*, 312 (1986).
18. Y. Shirota, N. Noma, Y. Shimizu, H. Kanega, I.-R. Jeon, K. Nawa, T. Kakuta, H. Yasui, and K. Namba, *Synth. Met.*, **41—43**, 3031 (1991).
19. Y. Shirota, N. Noma, H. Kanega, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 470 (1984).
20. I.-R. Jeon, N. Noma, and Y. Shirota, *Mol. Cryst. Liq. Cryst.*, **190**, 1 (1990).
21. T. Kakuta, Y. Shirota, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 553 (1985).
22. Y. Shirota, T. Nogami, N. Noma, T. Kakuta, and H. Saito, *Synth. Met.*, **41—43**, 1169 (1991).
23. Y. Shirota, T. Kakuta, H. Kanega, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 1201 (1985).
24. Y. Shirota, N. Noma, and H. Mikawa, *Synth. Met.*, **18**, 399 (1987).
25. H. Akamatsu, H. Inokuchi, and Y. Matsunaga, *Nature*, **173**, 168 (1954).
26. T. Uchida and H. Akamatsu, *Bull. Chem. Soc. Jpn.*, **34**, 1015 (1961).
27. H. J. Keller, D. Nothe, H. Pritzkow, D. Wehe, and M. Werner, *Mol. Cryst. Liq. Cryst.*, **62**, 181 (1980).
28. D. A. Buckley and L. A. Teuscher, *Br. Polym. J.*, **12**, 55 (1980).
29. A. R. Katritzky and D-W. Zhu, *Macromolecules*, **22**, 3495 (1989).
30. H. Kurota, T. Sakurai, and H. Akamaru, *Bull. Chem. Soc. Jpn.*, **39**, 1893 (1966).
31. G. E. Blomgren and J. Kommanreur, *J. Chem. Phys.*, **35**, 1636 (1961).
32. I.-R. Jeon, N. Noma, and Y. Shirota, *Bull. Chem. Soc. Jpn.*, to be published.