Formation of Adducts of Poly(thienylene)s with Electron Acceptors and Electric Conductivities of the Adducts

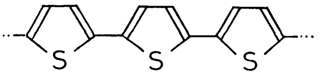
Takakazu YAMAMOTO,* Ken-ichi SANECHIKA, and Akio YAMAMOTO
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

(Received November 20, 1982)

Affinities of poly(thienylene) type polymers toward electron acceptors (iodine and SO_3) and electric conductivities of the polymer–electron acceptor adducts have been investigated. π-Conjugated poly(2,5-thienylene) has a high affinity toward iodine to absorb 60 wt% of iodine per the polymer. Poly(3-methyl-2,5-thienylene) has a higher affinity toward iodine and absorbs 136 wt% of iodine per the polymer. In the case of copolymer composed of 2,5- and 2,4-thienylene units the affinity against iodine increases with increase in the proportion of the 2,5-thienylene unit in the copolymer. The poly(2,5-thienylene)–iodine and poly(3-methyl-2,5-thienylene)–iodine adducts show electric conductivities of 5×10^{-2} S cm^{-1} and 4×10^{-1} S cm^{-1}, respectively, at room temperature. The activation energies of the electric conduction are 10 kJ/mol and 7.6 kJ/mol for the poly(2,5-thienylene)–iodine adduct (wt% of iodine=60) and poly(3-methyl-2,5-thienylene)–iodine adduct (wt% of iodine=136), respectively. The electric conductivity of the copolymer–iodine adduct sharply decreases on introduction of the 2,4-thienylene unit into the copolymer. The electric conductivity of the iodine adduct of the copolymer containing only 6% of 2,4-thienylene unit drops to *ca.* 1/100 of that of the iodine adduct of pure poly(2,5-thienylene). The activation energy of the electric conduction of the polymer-iodine adducts decreases with increase in the content of the 2,5-thienylene unit as well as with the increase in the amount of iodine absorbed. Every poly(thienylene) type polymer has a high affinity toward SO_3, a stronger electron acceptor than iodine, to absorb about 70 wt% of SO_3 per the polymer. The SO_3–polymer adducts have electric conductivities of *ca.* 10^{-4} S cm^{-1}.

Synthesizing electric conducting π-conjugated polymers and revealing the mechanism of the electric conduction are subjects of recent interest. Several polymers including poly(acetylene),[1] poly(*p*-phenylene),[2] poly(pyrrolylene),[3] and poly(phenylene sulfide)[4] have been found to have high electric conductivities when they form adducts with electron acceptors or electron donors.

In the preceding paper[5] we reported preparation of poly(2,5-thienylene) having conjugated thiophene



rings and compared its properties with those of poly(2,4-thienylene). It was revealed that the π-electrons in poly(2,5-thienylene) are extensively delocalized whereas the conjugation in poly(2,4-thienylene) is very limited. The difference in the electron delocalization is expected to be reflected in the chemical reactivities of these polymers toward electron acceptors and hence in their development of electric conductivities. In the present paper we wish to report on the reactions of these polymers with electron acceptors such as iodine and SO_3 and on the enhancement of electric conductivities on their adduct formation. Since the polymers employed in the present study are structurally better defined than electrochemically prepared polymers having similar π-conjugation systems (poly(pyrrole),[3] poly(thiophene),[6] and poly(furan)[6]), one can investigate effects of the structure of the polymers (*e.g.*, effect of the bonding between the thienylene units in the polymer chain, effect of the CH_3-substituent, and effect of the composition of the copolymer) on the affinity toward electron acceptors and electric conductivities of the adducts. This is taken as one of advantages of the present study.

Results and Discussion

Formation of Adducts with Electron Acceptors. As described in the preceding paper, poly(2,5-thienylene) is colored dark reddish brown with its λ_{max} in $CHCl_3$ at 418 nm. When exposed to the vapor of I_2, the color of poly(2,5-thienylene) changes from deep brown to black, indicating the formation of an adduct between the polymer and iodine. Figure 1 shows time course of the absorption of iodine by $CHCl_3$-unextractable poly(2,5-thienylene), and copolymers composed of 2,5- and 2,4-thienylene units on exposure to the vapor of I_2 at room temperature (29—31 °C). Pure poly(2,5-thienylene) has a high affinity toward iodine and it absorbs about 60 wt% of iodine on its prolonged exposure to the iodine vapor. Most of the iodine once absorbed by poly(2,5-thienylene) are not removed by evacuation at room temperature. A copolymer composed of 94% of 2,5-thienylene and 6% of 2,4-thienylene units has almost the same affinity toward iodine as the 2,5-thienylene homopolymer, whereas further increase in the fraction of 2,4-thienylene unit in the copolymer strongly decreases the affinity toward iodine. Thus, the final amount of iodine absorbed by a copolymer containing 13% of 2,4-thienylene unit ((3) in Fig. 1) decreases to about 30 wt%.

The delocalization of π-electrons along the recurring 2,5-thienylene units is expected to raise the energy level of HOMO as shown in Fig. 5 of our preceding paper[5] and this makes poly(2,5-thienylene) strongly interact with an electron acceptor, iodine in this case. On the other hand such delocalization is absent in poly(2,4-thienylene) as we observed in the electronic spectra. Thus, intervention of the 2,4-thienylene unit into the 2,5-thienylene polymer will break the delocalization and the interaction between the polymer and iodine then decreases in accord with the data

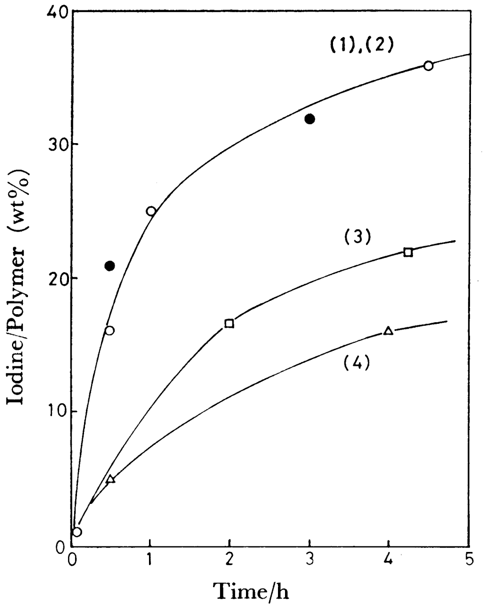


Fig. 1. Time course of absorption of iodine by poly-(2,5-thienylene) and copolymers composed of 2,5- and 2,4-thienylene units. Exposed to vapor of I_2 in a vacuum line at room temperature. 2,5-Thienylene: 2,4-thienylene=100:0 (○, (1)); 94:6 (●, (2)); 87:13 (□, (3)); 62:38 (△, (4)). In Figs. 1, 3, 4, and 5 the number attached to a curve or line corresponds to the number of Run in Table 2 of our preceding paper.[5]

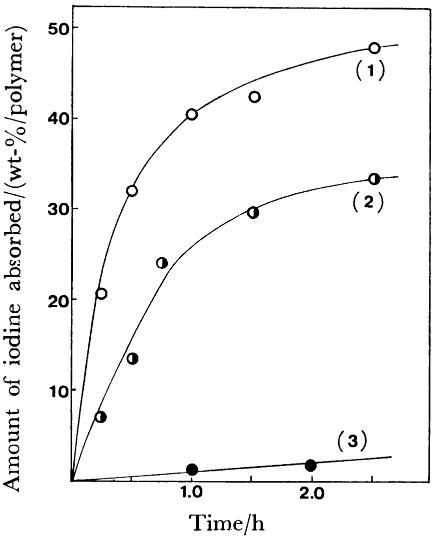


Fig. 2. Time course of absorption of iodine by poly-(2,5-thienylene). ○: $CHCl_3$-unextractable fraction, ◑: $CHCl_3$-soluble fraction (M_w=1370), ●: CH_3OH-soluble fraction (M_w=600).

shown in Fig. 1.

Although the $CHCl_3$-unextractable poly(2,5-thienylene) has a strong affinity toward iodine, $CHCl_3$-soluble (M_w=1370) and methanol-soluble (M_w=600) fractions have considerably weaker affinities (especially in the case of the methanol-soluble fraction) toward iodine (Fig. 2), indicating that the extent of delocalization in the polymers is not sufficient to lend the polymer strong affinity toward iodine.

The methyl-substituted polymer, poly(3-methyl-2,5-thienylene), has a higher affinity toward iodine than poly(2,5-thienylene). Thus, $CHCl_3$-soluble and $CHCl_3$-unextractable poly(3-methyl-2,5-thienylene) absorb 116 and 136 wt% of iodine, respectively, after exposure to the vapor of iodine for 10 h, the amounts being more than twice of the amounts of iodine absorbed by the $CHCl_3$-soluble and $CHCl_3$-unextractable unsubstituted poly(2,5-thienylene), respectively. Enhancement of electron-donating ability of poly(2,5-thienylene) by the methyl substitution accounts for the higher affinity of poly(3-methyl-2,5-thienylene) toward iodine. The iodine adducts of the poly(thienylene) type polymers have high stabilities in air, which provide an advantage in using the iodine adducts as semiconductors or positive electrodes in galvanic cells.[7]

In IR spectra of the polymers, the absorption bands are generally broadened on the complex formation with iodine. The IR spectra of the adducts generally show four major peaks in a region of 1000—1400 cm^{-1} which are assignable to skeletal deformation vibration of the thienylene group. The poly(2,5-thienylene)-iodine adduct has an apparent specific gravity of 2.2. An ESR spectrum of the adduct shows an absorption signal at g=2.008.

When the polymers are exposed to a vapor of SO_3, a stronger electron acceptor, every poly(thienylene) type polymer absorbs about 50—60 wt% of SO_3. Since thiophene itself has donor properties, such a strong acceptor as SO_3 seems to be able to interact even with nonconjugated poly(2,4-thienylene). The $CHCl_3$-soluble poly(2,5-thienylene) is soluble in concd H_2SO_4 and the fluorescing blue solution gives rise to an absorption band at 850 nm ($\varepsilon_{max}=6\times10^3$) which may be assigned to a CT band.

In contrast to the facile formation of adducts with iodine and SO_3, poly(2,5-thienylene) and its related polymer did not form adducts with tetracyanoquinodimethan, a typical organic electron acceptor. Since it is known that tetracyanoquinodimethan forms a stable 1:1 adduct with thiophene,[8] the low affinity of the polymers against tetracyanoquinodimethan seems to be due to difficulty in entry of the electron acceptor into microcrystals of the polymers or due to sterical non-fitting of tetracyanoquinodimethan with the polymers. Kossmehl and Chatzitheodorou reported formation of adducts of poly(2,5-thienylene) prepared by our method with AsF_5, one of the strongest electron acceptors, and electric conductivity of the adducts.[9]

When poly(2,5-thienylene) was dipped into a THF solution of potassium naphthalenide, color of the polymer changed from deep reddish brown to black, suggesting formation of an adduct of the polymer with potassium similar to the reported adduct of poly(acetylene) with alkali metals.[1,10] However, characterization of the adduct was not feasible due to the high air-sensitivity of the adduct (explosive in air).

Electric Conductivity. *Iodine Adduct*: All the poly(thienylene) type polymers are insulators having electric conductivity of 10^{-14}—10^{-11} S cm^{-1}. The electric conductivity, however, increases markedly on the ad-

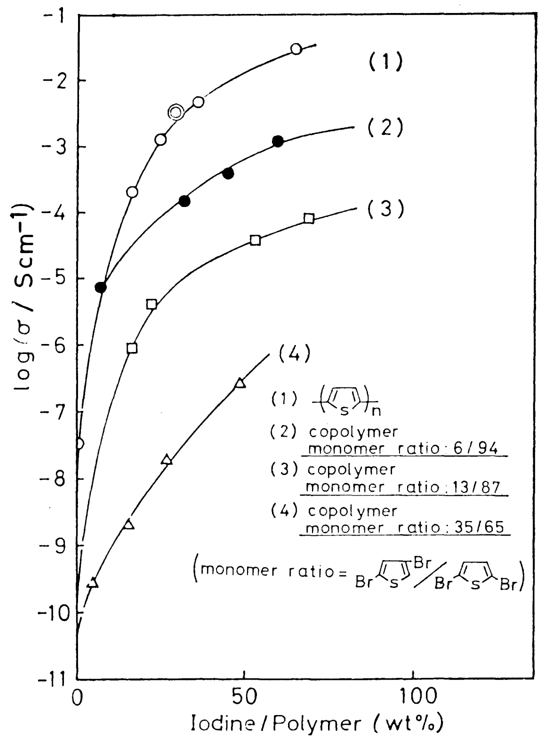


Fig. 3. Electric conductivities of the iodine adducts of poly(2,5-thienylene) and the copolymers *vs.* amount of iodine absorbed. The numbering of the curve corresponds to that in Fig. 1.

duct formation with the electron acceptors as observed in the other π-conjugated polymers such as poly(acetylene)[1] and poly(p-phenylene).[2] Figure 3 shows the increase of the electric conductivities of poly(2,5-thienylene) and the copolymers on interaction with iodine.

The following observations are made from experiments related to Fig. 3.

(1) The electric conductivity, σ, increases with increase in the amount of iodine absorbed. The electric conductivity of the poly(2,5-thienylene)–iodine adduct is comparable to those of commercially used inorganic semiconductors such as doped Si and Ge ($\sigma=10^{-4}$—10^{1} S cm^{-1}).

(2) The composition of the copolymer strongly influences the electric conductivity, incorporation of only 6% of 2,4-thienylene unit causes decrease in the electric conductivity by a factor of 10^2 ((2) in Fig. 3), although the incorporation of only 6% of 2,4-thienylene unit does not affect the electronic spectrum[5] and the affinity of the polymer toward iodine. The steep decrease in the electric conductivity by the contamination with only a small amount of 2,4-thienylene unit indicates that the electric conductivity is strongly influenced by the extent of the delocalization of π-electrons along the polymer chain. However, it is inferred from these results that the random incorporation of considerable proportion of insulating 2,4-thienylene unit, roughly one part per two parts of the 2,5-thienylene units, still leaves appreciable conductivity in the polymer ((4) in Fig. 3).

(3) A 1:1 mixture of poly(2,5-thienylene) and poly(2,4-thienylene) on treatment with iodine shows much higher electric conductivity (see a double circle in Fig. 3) than the copolymer containing 2,5- and 2,4-thienylene units in about 1:1 ratio. Although the electronic spectral data reported in our preceding paper have afforded evidence that the polymer obtained by the dehalogenative polycondensation of a mixture of 2,5- and 2,4-dibromothiophene is not a mixture of two homopolymers, the present result renders additional evidence for the formation of the copolymer. In the absorption of iodine by the 1: 1 mixture of pure poly(2,5-thienylene) and poly(2,4-thienylene), iodine is absorbed only by poly(2,5-thienylene). Therefore, the 1:1:0.27 mixture of poly(2,5-thienylene), poly(2,4-thienylene), and iodine shown by the double circle in Fig. 3 is considered to be a mixture of poly(2,5-thienylene) absorbing 54 wt% of iodine and pure poly(2,4-thienylene). On this basis it may be concluded that electric conductivity of 2×10^{-2} S cm^{-1} of poly(2,5-thienylene) containing 54 wt% of iodine has decreased to 4×10^{-3} S cm^{-1} (datum shown by the double circle) by mixing with the insulating poly(2,4-thienylene).

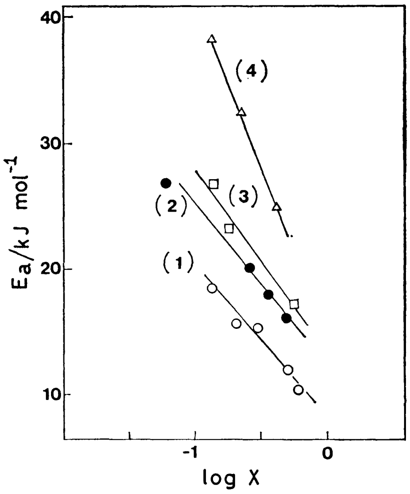


Fig. 4. Activation energy of the electric conduction of the iodine adducts of poly(2,5-thienylene) and copolymers *vs.* logarism of the amount of iodine absorbed (X=mass of iodine/mass of polymer). For numbering of the line, see a caption of Fig. 1.

Poly(3-methyl-2,5-thienylene)–iodine adducts show somewhat higher electric conductivities than the poly(2,5-thienylene)–iodine adducts: for example, poly(3-methyl-2,5-thienylene) absorbing 136 wt% of iodine has an electric conductivity of 4×10^{-1} S cm^{-1}.

The electric conductivities, σ, of the iodine-adducts varies with temperature according to the following equation,

$$\sigma = \sigma_0\exp(-E_a/RT). \qquad (1)$$

Figure 4 shows plots of the activation energy, E_a, of the electric conduction against logarithm of the amount iodine absorbed, $\log X$. As shown in Fig. 4 a linear correlation holds between E_a and $\log X$ for each polymer. A similar linear correlation between E_a and $\log X$ has been observed concerning the electric conduction of poly(acetylene) absorbing moderate amounts of iodine (3—30 wt% per poly(acetylene)). This de-

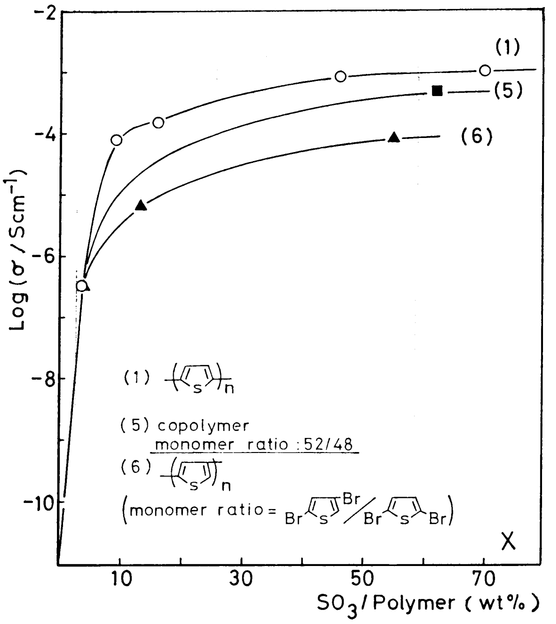


Fig. 5. Electric conductivities of the SO_3 adducts of poly(2,5-thienylene) (1), poly(2,4-thienylene) (6), and a copolymer composed of 52% of 2,5-thienylene and 48% of 2,4-thienylene units (5).

crease in E_a with the increase in the amount of iodine absorbed by poly(acetylene) is called "semiconductor-metal transition" since further increase in the amount of iodine absorbed gives the poly(acetylene)–iodine adduct a metallic conductivity ($\sigma > 10^3$ S cm^{-1}) with small E_a.[1b,d] However, in cases of poly(2,5-thienylene) and the copolymers the iodine adducts still show appreciable activation energies even at a high concentration of iodine and metal-like conductivity has not been attained, although a recent paper reported that electrochemically prepared poly(thienylene-$0.25BF_4$) have electric conductivity of 10^1—10^2 S cm^{-1}.[6b]

E_a increases with increase in the proportion of 2,4-thienylene unit in the copolymer. The iodine adduct of the $CHCl_3$-unextractable poly(3-methyl-2,5-thienylene) (iodine=136 wt%) shows somewhat lower activation energy of the electric conduction (E_a=7.6 kJ/mol) than the iodine adduct of poly(2,5-thienylene).

SO_3 Adduct: Figure 5 shows the electric conductivities of the SO_3 adducts of poly(2,5-thienylene), poly(2,4-thienylene), and a copolymer containing 2,5- and 2,4-thienylene units in about 1:1 ratio. Although π-conjugated poly(2,5-thienylene), among the polymers, shows the highest electric conductivity on the adduct formation with SO_3, the structure of the polymer affects the electric conductivity to a much less extent, compared with the iodine adducts of the polymers. The activation energy for the electric conduction of the SO_3 adducts decreases with increase in the amount of SO_3 absorbed (Fig. 6), but such a linear correlation observed for the iodine adducts (Fig. 5) is not observed for the SO_3 adducts. An ESR spectrum of the SO_3–poly(2,5-thienylene) shows an absorption signal at g= 1.962.

Mechanism of the Electric Conduction. It is known that a part of iodine absorbed by poly(acetylene) exists in the form of I_3^- and it is generally accepted that the counter cation (hole) formed in poly(acetylene) participates in the electric conduction.[1b–c] Since poly(thiophene) reportedly has ionization potential of 0.7 V[6c] comparable to that of poly(acetylene) (0.7 V), it will be reasonable to assume that iodine can abstract an electron from poly(2,5-thienylene) to form an ion pair and the electron conduction originates from the migration of the cation center along the π-conjugated chain.[11] If the 2,4-thienylene unit is incorporated into the polymer chain, the migration of the cation center will stop at the 2,4-thienylene unit and thus the electric conduction will be hindered in accord with the results described above.

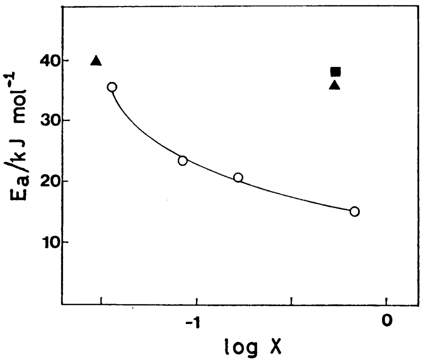


Fig. 6. Activation energy of the electric conduction of the SO_3 adducts of poly(2,5-thienylene) (○), poly(2,4-thienylene) (▲), and a copolymer composed of 52% of 2,5-thienylene and 48% of 2,4-thienylene units (■). X=mass of SO_3/mass of polymer.

The electric conductivity of the SO_3–poly(2,4-thienylene) adduct, however, is not explained by such a simple mechanism and thinking of special mechanisms of the electric conduction (for example, SO_3^- assisted migration of the cationic center or tunnel effect) seems to be necessary.

Experimental

Materials. Poly(thienylene) type polymers were prepared according to methods described in our preceding paper.[5] Commercially available I_2 and SO_3 were used without purification. Tetracyanoquinodimethan was purified by recrystallization before use. The THF solution of potassium naphthalenide was prepared by a reaction of naphthalene (2.0 g, 16 mmol) and potassium metal (1.5 g, 38 mmol) in THF (15 cm^3) for 21 h at room temperature. Remaining potassium was filtered off.

Absorption of Electron Acceptors. Powdery poly(thienylene) type polymer placed in a glass vessel was exposed to vapor of iodine at room temperature by using a vacuum line. The amount of iodine absorbed was measured by weighing the polymer–iodine adduct and halogen analysis of the adduct. Both data coincided within an experimental error. The reactions of the polymers with SO_3 (vapor) were carried out analogously. When a pellet prepared by pressing the powdery polymer at 600 kg/cm^2 was used, the rate of absorption of iodine was considerably slower.

Measurement of the Electric Conductivity. The powdery polymer–electron acceptor adduct was molded into a pellet (diameter = 1.3 cm) by pressing it at 600 kg/cm^2. From the pellet a bar was obtained by cutting off other parts of the pellet, and the electric conductivity was measured with the bar using the four-point method. A Takeda Riken TR-8651 electrometer was used to measure the electric conductivity.

Measurement of Spectra. Electronic and IR spectra were recorded on Hitachi model 200-20 and Hitachi model 295 spectrometers, respectively.

References

1) a) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, **1977**, 578; b) Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, *J. Chem. Phys.*, **73**, 946 (1980); c) W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979); d) H. Shirakawa and T. Yamabe, "Synthetic Metal", Kagaku-Dojin, Kyoto (1980) and references therein; e) Y. Furukawa, I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, *Chem. Lett.*, **1981**, 1489; f) J. C. W. Chien, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 249 (1981).

2) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughmann, *J. Chem. Phys.*, **71**, 1506 (1979); L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Metals.*, **1**, 307 (1979); M. Tanaka, A. Watanabe, H. Fujimoto, and J. Tanaka, *Chem. Lett.*, **1980**, 907.

3) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, **1979**, 635; K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, *Synth. Metals*, **1**, 329 (1979/80); A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, **1980**, 397.

4) J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, **1980**, 347; R. R. Chance, L. W. Schacklette, G. G. Miller, D. M. Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughmann, *ibid.*, **1980**, 348.

5) T. Yamamoto, K. Sanechika, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 1497 (1983).

6) a) V. L. Afanas'ev, I. B. Nazarova, and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser, Khim.*, **1980**, 1687; b) Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982); c) A. F. Diaz, J. Crowley, J. Bargon, G. P. Gardini, and J. B. Torrance, *ibid.*, **121**, 355 (1981).

7) T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1981**, 187; D. MacInnes, Jr., M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDirmid, and A. J. Heeger, *ibid.*, **1981**, 317; Japan Kokai, 56-136469 (1981).

8) B. P. Bespalov, A. A. Pankratov, and V. V. Titov, *Zh. Org. Khim.*, **10**, 134 (1974).

9) G. Kossmehl and G. Chatzitheodorou, *Makromol. Chem. Rapid Commun.*, **2**, 551 (1981).

10) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, **100**, 1013 (1978).

11) This explains chemical concept of the electric conduction. Physical treatment of the electric conduction of poly(acetylene)-acceptor (or donor) adducts have revealed that positive (or negative) solitons play important roles in the electric conduction (Refs. 1c and 1d as well as H. Takayama, Y. R. Lin-Lin, and K. Maki, *Phys. Rev. B*, **21**, 21 (1980)).