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ELECTROCHEMICAL POLYMERIZATION OF DITHIENYLBENZENE AND DITHIENYLPYRIDINE

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ABSTRACT

1,4-Bis(2-thienyl)benzene (T14B), 2,5-bis(2-thienyl)pyridine (T25P), and 2,6-bis(2-thienyl)pyridine (T26P) were electrochemically polymerized. The conductivity of poly-T14B, poly-T25P, and poly-T26P was 1.7×10^{-1} , 2.6×10^{-8} , and 1.2×10^{-7} S/cm, respectively. A poly-T26P film has a very even surface and is composed of fibrils growing on a thin, dense layer. Infrared spectra showed the monomer units to be linked through the 5,5'-positions of the thiophene rings. On electrochemical oxidation, poly-T26P became a quaternary ammonium salt. Visible/near-infrared spectra of poly-T14B showed that bipolaron states were formed. The conductivities of poly-T25P and poly-T26P rose to about 10^{-2} S/cm by iodine doping, irrespective of the bonding sites of pyridine.

INTRODUCTION

Films of polythiophene and polypyrrole were obtained by the electrochemical polymerization of thiophene and pyrrole, respectively [1, 2]. They were highly conducting with unique absorption spectra that changed on oxidation or reduction. These films are of interest from the standpoint of industrial applications and their electronic structures [3]. Although benzene and pyridine form 6- π -electron systems similar to thiophene and pyrrole, only a few reports have appeared on the electrochemical polymerization of benzene [4].

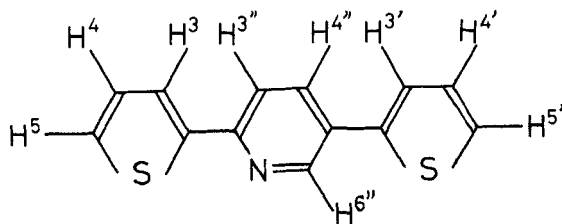
We conducted a study of the electrochemical polymerization of thiophene and its derivatives [5]. Our previous paper indicated that α,ω -dithienylpolyenes were electrochemically polymerized and that copolymers containing thiophene and butadienylene or hexatrienylene group were obtained [6]. This proved to be a convenient method for the electrochemical preparation of conjugated copolymers containing thiophene rings in their main chains. In the present paper this method has been applied to dithienyl-substituted benzene and pyridine, with the result that new conjugated copolymers were obtained. From 2,6-bis(2-thienyl)pyridine a very smooth film occurring as a thin, dense layer and fibrillar structure was obtained.

EXPERIMENTAL

Materials

1,4-Bis(2-thienyl)benzene (T14B) was prepared by the reaction of 1,4-dibromobenzene with 2-thienylmagnesium bromide in the presence of a nickel catalyst, and recrystallized from chloroform; mp 209-210°C (Ref. 7: 208°C). 2,6-Bis(2-thienyl)pyridine (T26P) was prepared by the previously reported method and recrystallized from methyl alcohol; mp 79.5-80.0°C (Ref. 8: 78-79°C). 2,5-Bis(2-thienyl)pyridine (T25P) was prepared by the reaction of 2,5-dibromopyridine with 2-thienylmagnesium bromide in the presence of a nickel catalyst and twice recrystallized from ethyl alcohol; mp 149.5-150.5°C. NMR; δ 7.11 (m, 2H, H⁴, and H^{4'}): δ 7.35 (m, 2H, H⁵, and H^{5'}): δ 7.40 (dd, J(3'-4') 4.8 Hz, J(3'-5') 0.7 Hz, 1H, H^{3'}): δ 7.58 (dd, J(3-4) 3.5 Hz, J(3-5) 0.7 Hz, 1H, H³): δ 7.64 (d, J(3''-4'') 8.6 Hz, 1H, H^{3''}): δ 7.85 (dd, J(4''-6'') 1.9 Hz, 1H, H^{4''}): δ 8.83 (d, 1H, H^{6''}).

Results of elemental analysis. T14B, calculated for C₁₄H₁₀S₂ (242.4): C, 69.38; H, 4.16; S, 26.46%. Found: C, 69.13; H, 4.08; S, 26.46%. T25P, calculated for C₁₃H₉NS₂ (243.3): C, 64.17; H, 3.73; N, 5.76; S, 26.35%. Found: C, 64.19; H, 3.49; N, 5.70; S, 26.30%. T26P, calculated for C₁₃H₉NS₂ (243.3): C, 64.17; H, 3.73; N, 5.76; S, 26.35%. Found: C, 64.10; H, 3.68; N, 5.72; S, 26.26%.



The solvents used were nitrobenzene (PhNO_2), benzonitrile (PhCN), nitromethane (MeNO_2), propylene carbonate (PC), and acetonitrile (MeCN), purified as previously reported [5, 6]. Tetrabutylammonium (Bu_4N) salts were examined for their capacity to serve as electrolytes.

Electrochemical Polymerization and Measurements

Electrochemical polymerization was carried out galvanostatically. The reaction vessel was a one-compartment cell equipped with two electrodes. In order to avoid contamination of the polymerization solution, no reference electrode was used. A platinum plate or indium tin oxide conducting glass (ITO) was used as the anode and a platinum plate as the cathode. Monomer and electrolyte concentrations were 0.05-0.1 and 0.05 mol/L, respectively. Prior to polymerization, argon was bubbled through the solution, and bubbling was continued up to the end of polymerization. The current density was 1 mA/cm² and the polymerization time was 2 h. Applied voltages were 2.4-3.9 V for the polymerization of T14B and 2.6-5.3 V for T25P and T26P. Since the voltage rose from 3.1 to higher than 50 V in Exp. 8 in Table 2, the electrochemical polymerization was interrupted at 0.33 h.

In the polymerization of T14B, a charge of 12.2 C yielded 11.3 mg of poly-T14B. Since the BF_4^- content was 0.34 mol per T14B unit, the transfer of 2.34 electrons was theoretically necessary for the polymerization reaction of one monomer unit. Current efficiency was calculated as 77%.

NMR spectra were measured on a Nicolet NT-360 spectrometer. UV/near-infrared spectra were measured on Hitachi U-3400 and Cary-17D spectrometers. ESCA spectra were measured on a Shimadzu ESCA 750 spectrometer. The reference used in the ESCA measurements was the C_{1s} signal at 285.00 eV. The F_{1s} signal was corrected for the relative cross section. The correction factor was 4.3.

RESULTS AND DISCUSSION

Electrochemical Polymerization

The results of polymerization of T14B are summarized in Table 1. Since the solubility of T14B in MeNO_2 , MeCN , and PC was low, PhNO_2 and PhCN were used as polymerization solvents. Films were obtained only under certain conditions, but pressed pellets from powdery products showed higher conductivity than the films, possibly due to their bulkiness. Though the films' densities were lower than 1 g/cm³, those of pellets ranged from 1.2 to

TABLE I. Results of Electrochemical Polymerization of T14B^a

Exp.	Solvent	Electrolyte	Anode	Conductivity, S/cm
1	PhNO ₂	Bu ₄ NBF ₄	Pt	9.6 × 10 ⁻³ (pellet)
2	PhNO ₂	Bu ₄ NCIO ₄	Pt	3.0 × 10 ⁻² (pellet)
3	PhCN	Bu ₄ NBF ₄	Pt	3.0 × 10 ⁻² (pellet)
4	PhCN	Bu ₄ NCIO ₄	Pt	5.0 × 10 ⁻⁴ (film)
5	PhNO ₂	Bu ₄ NBF ₄	ITO	1.7 × 10 ⁻¹ (pellet)
6	PhNO ₂	Bu ₄ NCIO ₄	ITO	2.4 × 10 ⁻³ (film)
7	PhCN	Bu ₄ NBF ₄	ITO	4.0 × 10 ⁻² (pellet)
8	PhCN	Bu ₄ NCIO ₄	ITO	8.8 × 10 ⁻³ (film)

^aThe concentration of T14B = 0.05 mol/L; polymerization temperature, 25°C; current density, 1 mA/cm²; time, 2 h.

1.3 g/cm³. When the film of Exp. 4 was pulverized and pressed into a pellet, its conductivity was as high as 3.3 mS/cm. Product conductivity depended on the type of anode used. ITO gave higher conductivity than a platinum plate. This dependence was not observed in the electrochemical polymerization of thiophene and 3-methylthiophene. Good results were not obtained using Bu₄NPF₆ and Bu₄NI.

In the electrochemical polymerization of pyrrole, film conductivity increased with decreasing temperature to -30°C. In the case of 3-methylthiophene, the conductivity was highest at 5°C. With T14B, conductivity was highest for the PhNO₂/Bu₄NBF₄ system. Film quality was best for the PhCN/Bu₄NCIO₄ system. The dependence of conductivity on polymerization temperature was examined for both systems, and the results are shown in Fig. 1. In the PhNO₂/Bu₄NBF₄ system, filmlike products were obtained in the temperature range 35-45°C. At other temperatures, powdery products were obtained. Temperature range interpolation indicated conductivity possibly to be highest at about 40°C, but, indeed, less conductive bulky films were produced. In the PhCN/Bu₄NCIO₄ system, conductivity increased with decreasing temperature, as was found to be the case in the electrochemical polymerization of pyrrole. Below 5°C, the solubility of T14B was so low that no polymerization occurred. Poly-T14B films obtained at 35°C in the

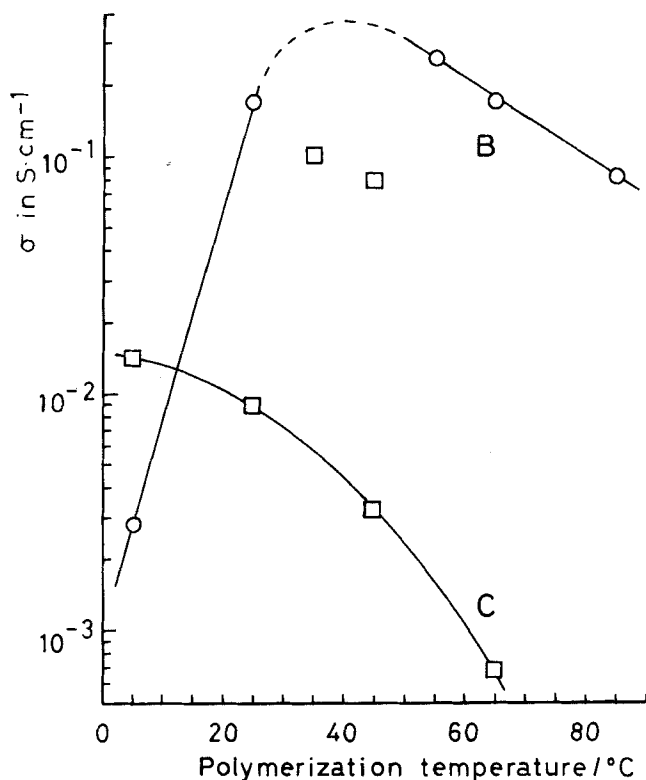


FIG. 1. Dependence of conductivity of poly-T14B on polymerization temperature. Electrolyte: (B) Bu_4NBF_4 , (C) Bu_4NClO_4 . Product: (○) powder, (□) film.

$PhNO_2/Bu_4NBF_4$ system were used in the following spectroscopic studies.

The results of the electrochemical polymerization of T25P and T26P are summarized in Table 2. T25P was only slightly soluble in MeCN and PC. $PhNO_2$ and $MeNO_2$ were tested as solvents. Film products were obtained, but with rough surfaces and low conductivities. T26P was soluble in all solvents listed in the Experimental section. High-quality films with smooth surfaces were obtained in $PhNO_2$. Films were obtained in PC and $MeNO_2$, but they were brittle. High-quality films were obtained in MeCN but with surfaces not as smooth as those obtained in $PhNO_2$ and very low conductivity.

TABLE 2. Results of Electrochemical Polymerization of T25P and T26P^a

Exp.	Monomer	Solvent	Anode	Time, h	Conductivity, S/cm
1	T25P	PhNO ₂	Pt	2	3.6×10^{-9}
2	T25P	MeNO ₂	Pt	2	1.7×10^{-9}
3	T25P	PhNO ₂	ITO	2	2.6×10^{-8}
4	T26P	PhNO ₂	Pt	2	$<1.8 \times 10^{-8}$
5	T26P	PC	Pt	2	$<1.7 \times 10^{-8}$
6	T26P	MeNO ₂	Pt	2	$<1.0 \times 10^{-8}$
7	T26P	MeCN	Pt	2	$<5.0 \times 10^{-9}$
8	T26P	PhNO ₂	ITO	0.33	1.2×10^{-7}

^aConcentration of monomers = 0.1 mol/L; electrolyte, Bu₄NBF₄; polymerization temperature, 25°C; current density, 1 mA/cm².

Films of poly-T25P and poly-T26P obtained, respectively, in Exp. 3 and 8 were used in the spectroscopic studies.

Polymer Yield

The ESCA spectra indicated carbon, sulfur, boron, and fluorine to be present in oxidized poly-T14B. The content of BF₄⁻ was 0.34 mol per T14B unit. On the basis of content and polymer yield, the current efficiency was calculated as 77%. Similarly, for poly-T25P the content of BF₄⁻ was 0.21 mol per monomer unit and the current efficiency was 73%; for poly-T26P, these values were 0.16 mol and 56%, close to those of polythiophenediyl. Since BF₄⁻ associated with quaternary ammonium charges in the polymer was included as shown below, the content of BF₄⁻ associated with cationic charges in the pi system was lower than 0.16 mol per monomer unit.

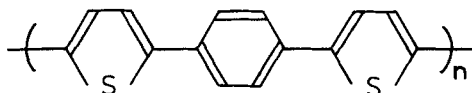
Scanning-Electron-Microscope (SEM) Observation

The electrode-side surface of poly-T26P is apparently glossy and even, while the solution-side surface is even but not glossy. These surfaces and cross section were observed by SEM (Fig. 2). The electrode-side surface was complete-

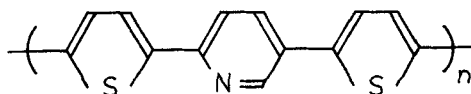
ly even, but the solution-side surface was less so. The electrode-side surfaces of many films have been shown to be more even than the solution-side surfaces [9], but the present film had the most even surface. The photograph of the cross section shows the film to consist of fibrils growing on a thin, dense layer.

Infrared Spectra

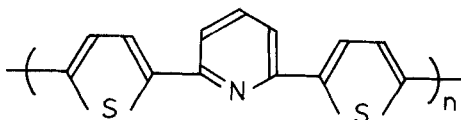
The infrared spectra of neutral polymers are shown in Fig. 3. The spectrum of poly-T26P was measured for a thin film, and the spectra of poly-T14B and poly-T25P in a KBr disk because thin films could not be peeled off the anode. In these three spectra, two sharp bands appeared at around 800 and 700 cm^{-1} , assignable to 2,5-disubstituted thiophene [10]. In the spectra of poly-T25P and poly-T26P, no bands were detected at 820 and 730 cm^{-1} , possibly due to 2,4-disubstituted thiophene [11]. In the spectrum of poly-T14B, a moderate band was found at 820 cm^{-1} , assignable to 1,4-disubstituted benzene. There were no bands at 2800-3000 cm^{-1} possibly because of C-H stretching vibration. Based on these findings the polymers may have the following structures:



Poly-T14B

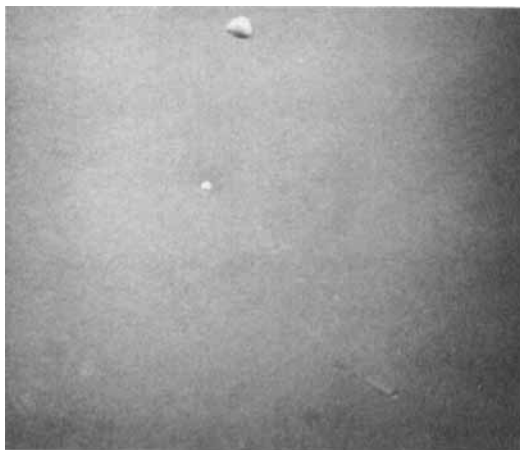


Poly-T25P



Poly-T26P

New bands not observable in neutral polymers appeared for oxidized polymers. For oxidized poly-T14B, bands were noted at 1400, 1350, 1150, 1040, and 940 cm^{-1} , and in oxidized poly-T25P at 1420, 1340, 1260, 1090, and

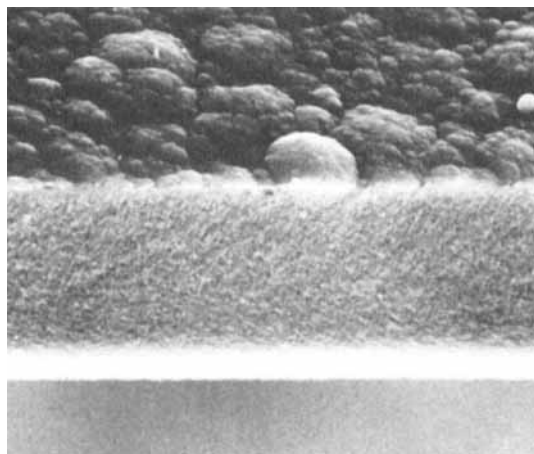


(a)



(b)

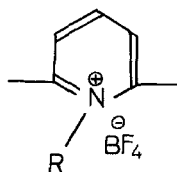
FIG. 2. SEM photographs of the poly-T26P film. (a): Electrode side (3000X). (b): Solution side (3000X). (c): Cross section (4000X). Thickness: 10 μm .



(c)

FIG. 2. (continued)

1030 cm^{-1} . These bands could also be observed in oxidized polythiophenes and were due to molecular vibrations along oxidized conjugated double bonds. For oxidized poly-T26P, there were bands at 2970, 2870, 1620, 1180, and 1060 cm^{-1} . The first two bands were assigned to aliphatic hydrocarbon. Since some bands of Bu_4NBF_4 could not be seen in oxidized poly-T26P, these five bands were not attributable to Bu_4NBF_4 . Some pyridine units may possibly become quaternary ammonium salts on electrochemical oxidation, as follows:



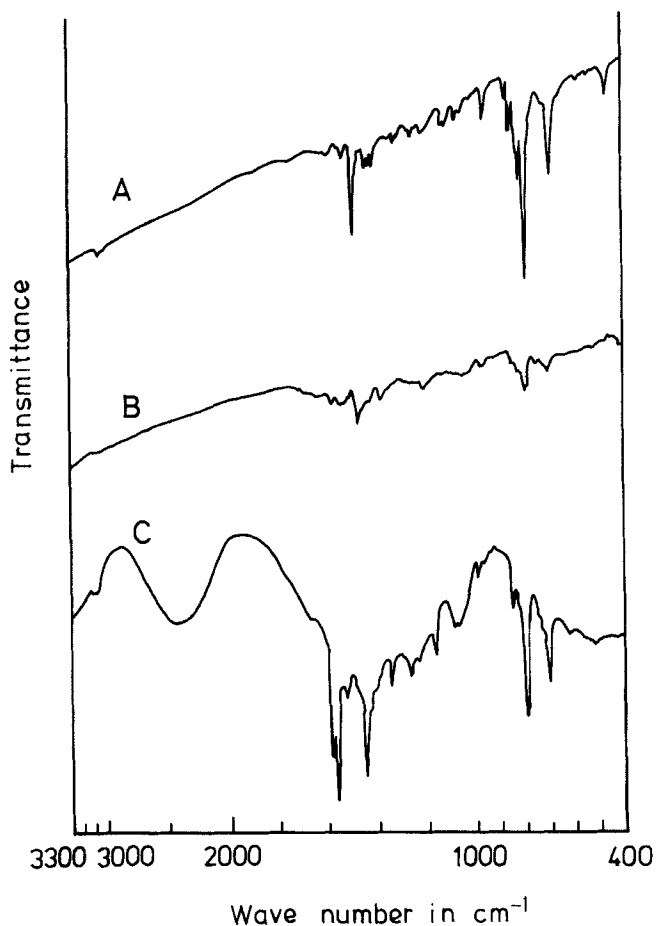


FIG. 3. Infrared spectra of neutral polymers. (A) Poly-T14B in KBr disk. (B) Poly-T25P in KBr disk. (C) Poly-T26P film.

Visible-Near-Infrared Spectra

Figure 4 shows the absorption spectra of dry poly-T14B films on ITO. A neutral film had a peak at 400 nm and an oxidized film three peaks at 335, 420, and 940 nm. The peaks at 400 and 335 nm corresponded to the transitions between valence and conduction bands. The peaks at 420 and 940 nm may perhaps be the transition between valence and bipolaron bands. A neu-

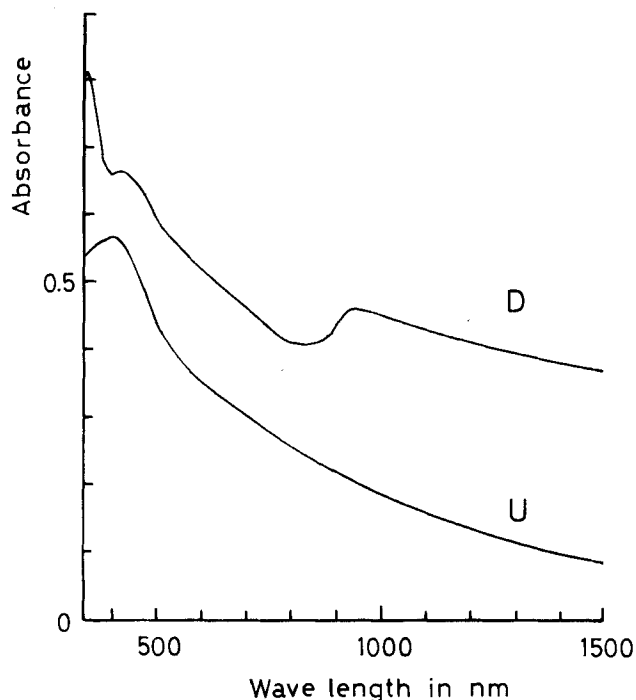


FIG. 4. Visible/near-infrared spectra of poly-T14B on ITO. (D) Oxidized. (U) Neutral. Electrolyte: Bu_4NBF_4 . Polymerization time: 1 min.

tral poly-T25P film had a peak at 420 nm, corresponding to the transition between valence and conduction bands, and an oxidized film had three peaks at 355, 450 (shoulder), and ~ 1300 (broad) nm. The last peak rapidly decreased and disappeared in 30 min in air. The shoulder at 450 nm remained unchanged. Thus, these two peaks may not be interrelated as in a bipolaron. As for poly-T26P, no new peaks appeared on oxidation. Some pyridine units of poly-T26P became quaternary salts in which positive charge was localized. Thus, conductivity was low.

Doping of Poly-T25P and Poly-T26P with Iodine

Poly-T25P and poly-T26P films reduced electrochemically were doped by exposure to iodine vapor. Their conductivities were measured in situ during

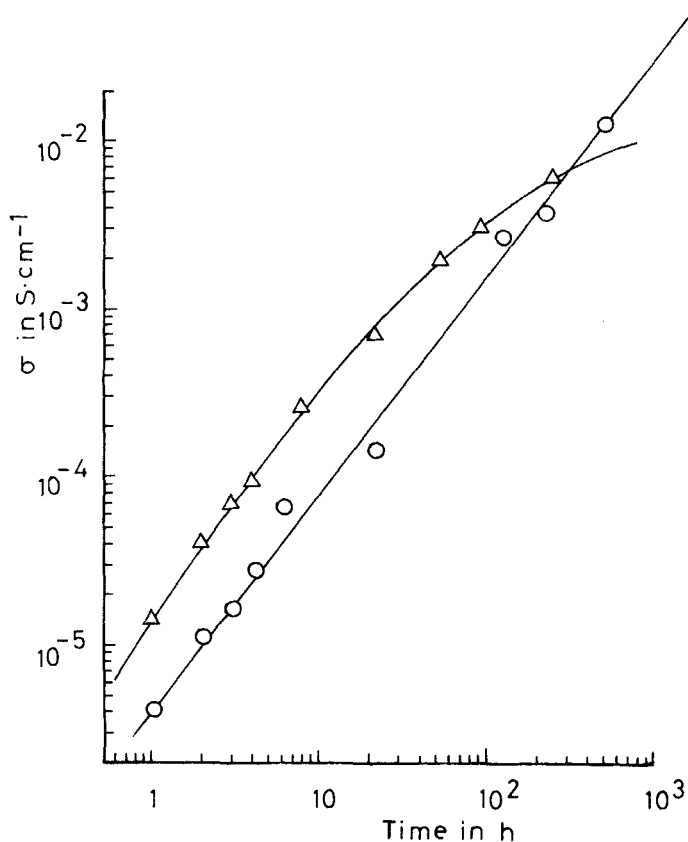


FIG. 5. Dependence of conductivity on doping time. Dopant: iodine. (○) Poly-T26P. (△) Poly-T25P.

vapor-phase doping and rose to 6 and 13 mS/cm, respectively, as shown in Fig. 5. Thus, iodine-doped states may possibly be quite different from electrochemically oxidized states.

The conductivity of poly-T25P was essentially the same as that of poly-T26P. Bonding sites on pyridine had no significant effect on conductivity, in contrast to those of polyphenylene where 1,4-bonding resulted in greater conductivity than 1,3-bonding. The conductivity of polypyridinediyl has been reported to be essentially independent of bonding sites [12].

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