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PREPARATION OF POLY(2,4-THIENYLENE) AND COMPARISON OF ITS OPTICAL AND ELECTRICAL PROPERTIES WITH THOSE OF POLY(2,5-THIENYLENE)

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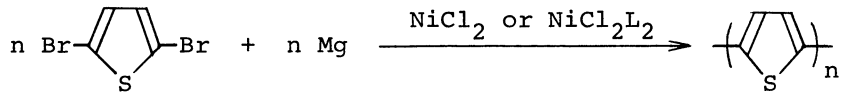
Poly(2,4-thienylene) is prepared by Ni-catalyzed dehalogenation polymerization of 2,4-dibromothiophene with Mg. Comparison of chemical and physical properties of poly(2,4-thienylene) with those of Poly(2,5-thienylene) indicates that π-electrons of the latter polymer are delocalized along the polymer chain, whereas those of the former polymer are not. Poly(2,4-thienylene) is converted into a semiconductor by doping with SO_3.

Previously we reported[1] preparation of poly(2,5-thienylene) having a conjugated polymer system by utilizing transition metal-catalyzed dehalogenation polymerization of dihalogenated organic compounds with magnesium;[2,3]

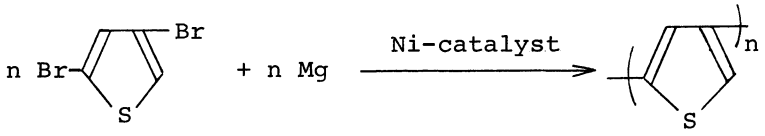


(1)

poly(2,5-thienylene)

Later Lin and Dudek also reported preparation of the same polymer by a similar method using $Ni(acac)_2$ as the catalyst.[4a] More recently Afanas'ev and his coworkers reported preparation of poly(2,5-thienylene) by an electrochemical method.[4b] Poly(2,5-thienylene) has very high affinity toward electron acceptors such as I_2, and the polymer becomes a semiconductor when it is doped with the electron acceptors.[1,4,5] Among the poly(2,5-thienylene)-electron acceptor adducts the one with iodine has been utilized to make electronic cells and batteries.[5]

The electric conducting properties of the poly(2,5-thienylene)-electron acceptor adducts seem to be related to the presence of delocalized π-electrons along the polymer chain, but details of the electric conduction has not been clarified yet. In order to get further information about the electronic state of the polymer we have prepared a polymer having a different type of recurring thienylene units (2,4-thienylene) and compared chemical and physical properties of the two polymers;



(2)

poly(2,4-thienylene)

Procedure for the Preparation of Poly(2,4-thienylene). Treatment of 2,4-dibromothiophene (4.66 g, 19.3 mmol) with 469 mg (19.3 mmol) of magnesium in dry THF (10 cm^3) for 1 h gave a homogeneous solution. Di-n-butyl ether (40 cm^3) and 20 mg of $NiCl_2$(bpy) were added to the reaction mixture, and after carrying out the polymerization for 5 h under reflux the reaction mixture was poured into methyl alcohol (200 cm^3). The polymer precipitated was collected over a glass filter and dried in vacuum to yield 760 mg (58 %) of brown poly(2,4-thienylene). Extraction of the polymer by $CHCl_3$ with a Soxhlet extractor for 15 h gave 210 mg of a $CHCl_3$-extractable fraction. The molecular weight of the $CHCl_3$-extractable fraction is ca. 2050 (degree of polymerization = ca. 25) as determined by vapour pressure osmometry. The $CHCl_3$-unextractable fraction is considered to have a higher molecular weight. Polymerization at boiling point of THF (66°C) without adding di-n-butyl ether gave lower yield of polymer (17 %) and lower proportion (31 %) of the $CHCl_3$-unextractable fraction. IR: 820, 740 cm^{-1} (δ(C-H)).

Properties. Table 1 shows comparison of chemical and physical properties of poly(2,4-thienylene) with those of poly(2,5-thienylene). Both polymers are not crystalline and they have almost the same thermal stabilities, but they differ in optical and electric properties.

Table 1. Properties of Poly(2,4-thienylene) and Poly(2,5-thienylene)[a)]

		Poly(2,5-thienylene)	Poly(2,4-thienylene)
1	Crystallinity	Amorphous	Amorphous
2	Residual Wt. at 900°C	52 %	48 %
3	Color	black	light brown
4	UV-Visible	λ_{max} = 410 nm (Mw = 1100-1400)	λ_{max} = 280 nm (Mw = 2050)
5	Fluorescence	Strong fluorescence	No fluorescence
6	Affinity toward I_2	High (ca. 50%/polymer)[b)]	Low
7	Affinity toward SO_3	High (ca. 65 wt %/polymer)[b)]	High (ca. 70%/polymer)[b)]
8	Electric Conductivity (σ)		
	Non-doped	5×10^{-11} S·cm^{-1}	5×10^{-13} S·cm^{-1}
	Doped with I_2 (at 24°C)	4×10^{-2} S·cm^{-1} (E_a = 3.7kcal/mol)	7×10^{-11} S·cm^{-1}
	Doped with SO_3 (at 24°C)	1×10^{-4} S·cm^{-1} (E_a = 3.2 kcal/mol)	9×10^{-5} S·cm^{-1} (E_a = 8.5 kcal.mol)

a) Data for the $CHCl_3$-unextractable fraction except for the UV-Visible and Fluorescence data, which were obtained for the $CHCl_3$-unextractable fraction.

b) Absorbed amount.

Optical Properties. Poly(2,5-thienylene) is black, whereas poly(2,4-thienylene) is light brown. Electronic spectrum of $CHCl_3$-soluble poly(2,5-thienylene) shows a large bathochromic shift of the π-π^* absorption band from the λ_{max} of thiophene (230 nm) to 410 nm, whereas that of $CHCl_3$-extractable poly(2,4-thienylene) shows only a small shift. The bathochromic shift of poly(2,5-thienylene) depends on the degree of polymerization as shown in Fig. 1. When exposed to UV-light (365 or 253.7 nm) poly(2,5-thienylene) fluoresces a light green color, whereas poly(2,4-thienylene) does not show the fluorescence. These results suggest that the π-electrons in poly-(2,5-thienylene) are extensively delocalized along the polymer chain, whereas those in poly(2,4-thienylene) are not (Fig. 2). The difference in the optical properties between the two polymers is consistent with difference in affinity toward I_2 between the two polymers (vide infra).

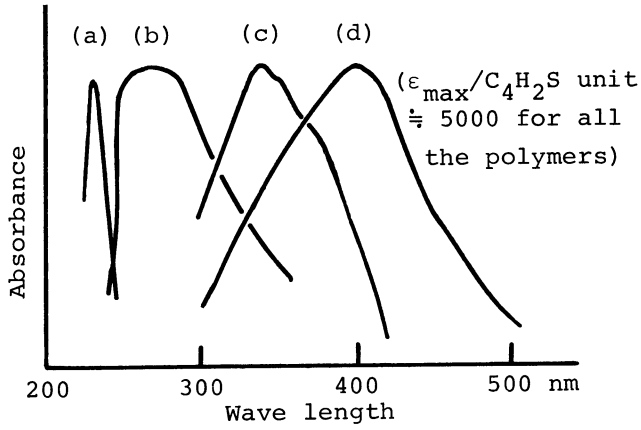


Fig. 1. UV-Visible Specta of (a) Thiophene, (b) Poly(2,4-thienylene) (Mw = ca. 2000), (c) Poly(2,5-thienylene) (Mw = ca. 500), & (d) Poly(2,5-thienylene) (Mw = ca. 1300).

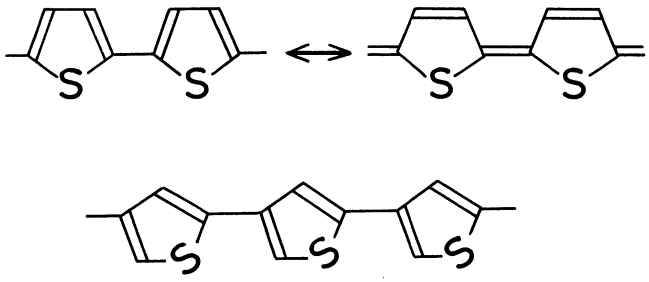


Fig. 2. Delocalization of π-electrons along the poly(2,5-thienylen) chain (upper). Poly(2,4-thienylene) does not have extensively delocalized π-electrons (lower).

Affinity toward Electron Acceptors. Poly(2,5-thienylene) has high affinity toward iodine. When exposed to vapor of I_2, it absorbs iodine. The polymer fraction having higher molecular weight absorbs iodine more smoothly: the $CHCl_3$-unextractable fraction absorbs 47 wt-% of iodine per polymer in 2.5 h at room temperature, whereas the $CHCl_3$-extractable and CH_3OH-extractable fractions incorporate 35 wt-% and 2 wt-% of iodine, respectively, under the same conditions. The poly(2,5-thienylene)-iodine interaction is so strong that iodine once absorbed can not be liberated even in vacuum.

Poly(2,4-thienylene) absorbs 15 wt-% of iodine on exposure to the vapor of I_2, but the polymer-iodine interaction is weak in this case, and iodine once absorbed is easily removed when the adduct is placed in vacuum. For this reason the poly(2,4-thienylene)-iodine adduct is not suitable for a positive electrode of a cell.[5] The strong absorption of iodine by poly(2,5-thienylene) is attributable to a strong charge-transfer interaction between iodine and the polymer which is considered to have high electron-donating properties due to the delocalization of π-electrons. On the contrary, the weak absorption of iodine by poly(2,4-thienylene) indicates absence

of such a strong charge-transfer interaction due to lack of the extensive delocalization of π-electrons.

When treated with SO_3, a stronger electron acceptor than iodine,[6] both polymers absorb SO_3 strongly: SO_3 once absorbed can not be removed in both cases. Since thiophene itself has donor properties, such a strong electron acceptor as SO_3 seems to be able to interact with poly(2,4-thienylene) having no extensively delocalized π-electrons. The polymers doped with the electron acceptors have considerably high stability in air.

Electric Conductivity. Poly(2,5-thienylene) and poly(2,4-thienylene) themselves are insulators, but they are converted into semiconductors by doping with suitable electron acceptors. As reported in our previous paper,[1] electric conductivity of poly(2,5-thienylene) increases by a factor of 10^9 on doping with iodine (Table 1). On the contrary, electron conductivity of poly(2,4-thienylene) slightly increases on doping with iodine. Doping with SO_3, on the other hand, raises the electric conductivities of both poly(2,5-thienylene) and poly(2,4-thienylene). Since the magnitude of increase in the electron conductivity is almost equal for the both polymers (Table 1), the increase in the electric conductivity is attributable mainly to the formation of the charge transfer complex and the presence or absence of the extensively delocalized π-electrons in the starting polymers seems to affect the electric conductivity of the polymer-SO_3 adducts only slightly.

It is generally accepted that presence of extensively delocalized π-electrons along a polymer chain is essential for high (or metallic) electric conduction of the polymer.[8] The present results, however, suggest possibility that in some cases formation of the charge transfer complex is more important for a polymer to have the semiconducting properties and delocalization of π-electrons contributes mainly to the formation of the charge transfer complex.

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