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Preparation and Characterization of Poly(thienylene)s

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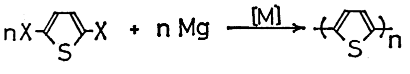
Nickel compounds ($NiCl_2$ and $NiCl_2$(2,2′-bipyridine)) catalyze polycondensation of dihalothiophenes (2,5-dihalothiophenes, 2,4-dibromothiophene, and 3-methyl-2,5-dibromothiophene) by dehalogenation with magnesium to give the corresponding poly(thienylene) type polymers (poly(2,5-thienylene), poly(2,4-thienylene), and poly(3-methyl-2,5-thienylene)). Copolymerization of 2,5-dibromothiophene and 2,4-dibromothiophene affords copolymers formulated as $\{2,5\text{-}C_4H_2S\}_m\{2,4\text{-}C_4H_2S\}_n$. About 15 wt% of poly(2,5-thienylene) prepared in THF at 66 °C is soluble in $CHCl_3$ at room temperature and the $CHCl_3$-soluble fraction has a molecular weight of 1370. The remaining fraction is considered to have a higher molecular weight as judged from its physical properties. IR and ^{1}H-NMR spectra of the polymers are consistent with the structures described above. The electronic spectra of poly(2,5-thienylene) and poly(3-methyl-2,5-thienylene) show large bathochromic shifts of the π-π^* absorption bands from those of thiophene and 3-methylthiophene, respectively, indicating that π-electrons in these polymers are extensively delocalized along the polymer chains. In contrast to the electronic spectra of these polymers, that of poly(2,4-thienylene) shows only a minor shift of the π-π^* absorption band from that of thiophene reflecting the less extensive π-electron delocalization along the polymer chain in the poly(2,4-thienylene). All the polymers are nonsensitive to air and have high thermal stabilities.

Preparation of polymers having π-conjugation systems along the polymer chains is a subject of recent interest in connection with their potential utility as polymer conductors or semiconductors.1) A previous paper2) from our group revealed that the transition metal catalyzed C–C coupling reaction between RMgX and R′X3) was applicable to the preparation of poly(phenylene) type polymers from dihaloaromatic compounds, X–Ar–X,

$$n\,X\text{-}Ar\text{-}X + n\,Mg \longrightarrow [X\text{-}Ar\text{-}MgX] \xrightarrow{[M]} \{Ar\}_n \qquad (1)$$

$$M = Ni, Pd, etc.$$

We have applied this transition metal-catalyzed dehalogenative polycondensation to the preparation of poly(2,5-thienylene) from 2,5-dihalothiophene,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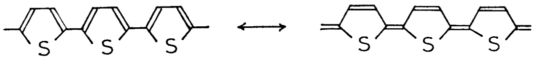
The polymer has a π-conjugation system similar to that of poly(acetylene) which shows high electric conductivities when doped with electron acceptors such as I_2 and AsF_5 or electron donors such as Li and Na,1)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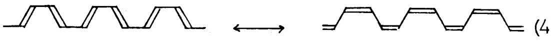
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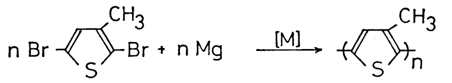
This paper deals with the preparation and characterization of poly(2,5-thienylene) and its related polymers including its methylated analogue (poly(3-methyl-2,5-thienylene)), its isomer (poly(2,4-thienylene)), and copolymers of 2,5-dibromothiophene and 2,4-dibromothiophene,

Part of the results were briefly reported in communication form.4) After publication of our first communication, Lin and Dudek5) also reported preparation of poly(2,5-thienylene) using a similar technique, and more recently preparation of polymers having similar π-conjugation systems to that of poly(2,5-thienylene), poly(2,5-pyrrolylene) derivatives6) and poly(2,5-selenienylene),7) by using the dehalogenative polycondensation technique has been reported. Electrochemical polymerization of thiophene in an $[N(Et)_4][BF_4]$ solution was also reported.8)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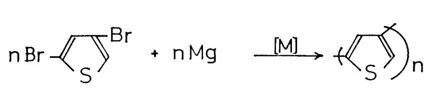
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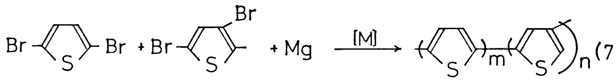
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Results and Discussion

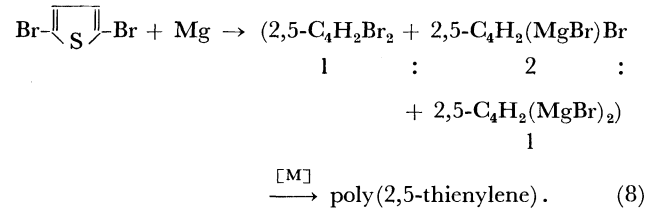
Preparation of Polymers. *Poly(2,5-thienylene)*: Table 1 shows results of the dehalogenative polycondensation of dihalothiophenes. As shown in Table 1, 2,5-dibromothiophene and 2,5-dichlorothiophene are polymerized at reflux temperature of THF (66 °C) to give poly(2,5-thienylene) according to Eq. 2. 2,5-Dibromothiophene and 2,5-dichlorothiophene seem to have almost the same reactivities in the polymerization.

Gas chromatographic analysis of compounds obtained by hydrolysis of the reaction product of 2,5-dibromothiophene and magnesium (1:1) before addition of the catalyst revealed that the 1:1 reaction of 2,5-dibromothiophene and magnesium afforded a mixture containing 2,5-C_4H_2S(MgBr)Br and 2,5-$C_4H_2S(MgBr)_2$ as well as intact 2,5-dibromothiophene in about 2:1:1 ratio. Thus, the polymerization is considered to proceed through the C–C coupling between these compounds,

TABLE 1. PREPARATION OF POLY(THIENYLENE)S

Expt	Monomer[a)]	Catalyst[b)]	Solvent[c)]	Temp °C	Time h	Yield %	CHCl$_3$-extractable fraction / CHCl$_3$-unextractable fraction[d)]
1	2,5-$C_4H_2SBr_2$	None	THF	66	5	0	
2	2,5-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF	66	3	61	22/78
3	2,5-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF	66	5	78	Not measured
4	2,5-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF	25	21	7	37/63
5	2,5-$C_4H_2SBr_2$	$NiCl_2$	THF	66	5	54	Not measured
6	2,5-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF+n-Bu_2O	110	1	48	2/98
7	2,5-$C_4H_2SBr_2$	$NiCl_2$(bpy)	Et_2O	35	4	8	70/30
8	2,5-$C_4H_2SBr_2$	$NiCl_2$(dppp)	THF	66	3	49	Not measured
9	2,5-$C_4H_2SBr_2$	$PdCl_2$(bpy)	THF	66	5	0	
10	2,5-$C_4H_2SBr_2$	$FeCl_3$	THF	66	5	14	Not measured
11	2,5-$C_4H_2SBr_2$	Fe(acac)$_3$	THF	66	5	12	Not measured
12	2,5-$C_4H_2SBr_2$	$CoCl_2$	THF	66	5	5	Not measured
13	2,5-$C_4H_2SCl_2$	$NiCl_2$(bpy)	THF	66	4	40	27/73
14	2,4-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF	66	5	17	69/31
15	2,4-$C_4H_2SBr_2$	$NiCl_2$(bpy)	THF+n-Bu_2O	110	5	58	29/71
16	3-Me-2,5-C_4HSBr_2	$NiCl_2$(bpy)	THF	66	3	55	83/17
17	3-Me-2,5-C_4HSBr_2	$NiCl_2$(bpy)	THF+n-Br_2O	110	3	40	95/5

a) $C_4H_2SX_2$ = Dihalothiophene. 3-Me-C_4HSBr_2 = 3-Methyl-2,5-dibromothiophene. b) bpy = 2,2′-Bipyridine. dppp = 1,3-Bis(diphenylphosphino)propane. 0.003 mol% of the catalyst per monomer was added. c) THF+n-Bu_2O = 1:4 mixture of THF and dibutyl ether. d) See text.



$$\text{Br-}\langle S \rangle\text{-Br} + Mg \rightarrow \underset{1}{(2,5\text{-}C_4H_2Br_2} : \underset{2}{+\ 2,5\text{-}C_4H_2(MgBr)Br} : \underset{1}{+\ 2,5\text{-}C_4H_2(MgBr)_2)} \xrightarrow{[M]} \text{poly(2,5-thienylene)}. \qquad (8)$$

It is seen in Table 1 that nickel catalysts are effective for the polymerization, whereas $PdCl_2$(bpy), which has high activities in the preparation of the poly(phenylene) type polymers, is not. $FeCl_3$, Fe(2,4-pentanedionato)$_3$, and $CoCl_2$ showed feeble catalytic activities. When the polymerization was carried out at lower temperatures (Expts 4 and 7), the yield of the polymer as well as the proportion of the $CHCl_3$-unextractable fraction (*vide infra*) decreased. The polymerization at 110 °C by using a 1:4 mixture of THF and dibutyl ether (Expt 6) proceeded smoothly and most of the polymer obtained was not extractable by hot $CHCl_3$.

When the ratio of Mg to 2,5-dibromothiophene deviates from unity, yield of the polymer and the proportion of the $CHCl_3$-unextractable fraction considerably decrease in accord with the theory of polycondensation. Addition of a monofunctional compound, 2-bromothiophene, also causes decrease in the yield and the proportion of the $CHCl_3$-unextractable fraction.

Poly(2,4-thienylene) and Poly(3-methyl-2,5-thienylene): Polymerization of 2,4-dibromothiophene and 3-methyl-2,5-dibromothiophene can be carried out analogously. However, as for the polymerization of 2,4-dibromothiophene, polymerization at the reflux temperature of THF did not give a satisfactory yield and the polymerization at higher temperature by using a 1:4 mixture of THF and dibutyl ether (Expt 15) was required to get a reasonably high yield.

Copolymers: Table 2 summarizes results of copolymerization of 2,5-dibromothiophene and 2,4-dibromothiophene according to Eq. 7. In Table 2 the ratio of the 2,5- and 2,4-thienylene units in the polymer was calculated from relative intensities of absorption bands in IR spectra characteristic of 2,5-thienylene and 2,4-thienylene units (*vide infra*). The calibration line for the calculation was obtained by taking IR spectra of samples containing pure poly(2,5-thienylene) and poly(2,4-thienylene) in various ratios.

It is seen from Table 2 that the ratio between 2,5- and 2,4-thienylene units in the copolymers is almost the same as the ratio of the two monomers employed for the copolymerization (Runs 4 and 5). This indicates that both monomers have almost the same reactivities in the copolymerization (2,4-dibromothiophene seems to have a slightly higher reactivity), and consequently the polymer is considered to have a random sequence with respect to the two thienylene units. The compositions of the copolymers obtained in Runs 2 and 3 could not be determined from their IR spectra, since the proportions of 2,4-thienylene units were too small. The data obtained in Runs 4 and 5, however, suggest that the copolymers obtained in Runs 2 and 3 contain *ca.* 6 and 13% of 2,4-thienylene units, respectively.

Properties of Polymers: Poly(2,5-thienylene) prepared in Expt 2 in Table 1 was fractionated into two parts by extraction with hot $CHCl_3$. The brown $CHCl_3$-extract (22 wt%) softens at 116 °C. About 2/3 of the $CHCl_3$-extract (about 14 wt% of the crude polymer) was soluble in $CHCl_3$ at room temperature and had number-average molecular weight of 1370 as de-

Table 2. Copolymerization of 2,5-dibromothiophene and 2,4-dibromothiophene[a)]

Run	Monomer ratio		Time	Yield[b)]	Ratio of monomer unit in the polymer	
	2,5-Dibromothiophene	2,4-Dibromothiophene	h	%	2,5-Thienylene	2,4-Thienylene
1	100	0	3	81	100	0
2[c)]	94	6	3	61	d)	
3	87	13	2	54	d)	
4	65	35	3	65	62	38
5	48	52	2	42	44	56
6	0	100	5	58	0	100

a) Catalyst: $NiCl_2$(bpy) (0.003 mol/monomer). Solvent: THF for Runs 1 and 2, and an 1:4 mixture of THF and $(n\text{-}Bu)_2O$ for Runs 3—6. b) Calculated from the weight and carbon content of the crude polymer. c) Data from Ref. 2a using commercially available (from Merck Co. Ltd.) 2,5-dibromothiophene without purification. d) The proportion of 2,4-thienylene is too small to be determined from IR.

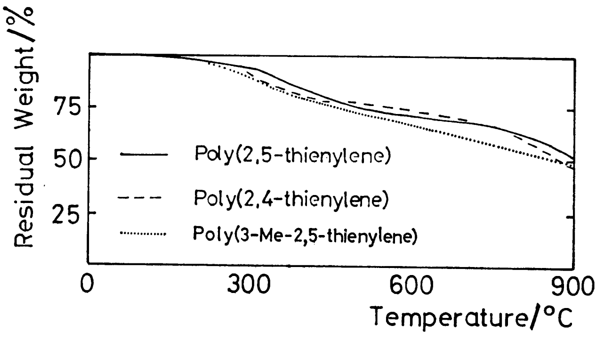


Fig. 1. Thermogravimetric analyses of poly(thienylene)s.

termined by VPO. The molecular weight corresponds to a formula of $\mathrm{Br(C_4H_2S)_{14.8}Br}$ and analytical data roughly agrees with the formulation (Found: C, 51.6; H, 2.8. Calcd: C, 51.7; H, 2.8). The remaining $CHCl_3$-unextractable polymer (78 wt%) is insoluble in most organic solvents and seems to have a higher molecular weight than the $CHCl_3$-soluble fraction as judged from its higher thermal stability, lower solubility, and analytical data which show higher carbon content (C, 53.7; H, 2.7).[9)]

Thermogravimetric analyses of poly(2,5-thienylene) and related polymers are shown in Fig. 1. Poly(2,5-thienylene)s prepared in experiments other than Expt 2 were also separated into the $CHCl_3$-extractable and -unextractable fractions and the fractions were found to have similar properties described above.

Poly(2,4-thienylene) and the copolymers of 2,5- and 2,4-dibromothiophenes have similar thermal stabilities to that of poly(2,5-thienylene), but there is a trend that both the proportion and molecular weight of the $CHCl_3$-soluble fraction extracted at room temperature increase with increase in the proportion of the 2,4-thienylene unit in the polymer chain. In the case of pure poly(2,4-thienylene) 23 wt% of the crude polymer was soluble in $CHCl_3$ at room temperature, and the $CHCl_3$-soluble fraction had a number average molecular weight of 2100, which corresponds to a formula of $\mathrm{Br(C_4H_2S)_{23.7}Br}$.

A larger part of poly(3-methyl-2,5-thienylene) is extractable by hot $CHCl_3$ and a fraction soluble in $CHCl_3$ at room temperature had a higher molecular weight ($M_w=2300$) than poly(2,5-thienylene) prepared under similar conditions, indicating that solubility of poly(2,5-thienylene) is enhanced by substitution of the 3-hydrogen of the thienylene ring with the CH_3 group. Poly(3-methyl-2,5-thienylene) has similar thermal stability to that of poly(2,5-thienylene) as shown in Fig. 1. Poly(2,5-thienylene), poly(2,4-thienylene), and the copolymers have apparent specific gravities of 1.3—1.4 as measured by weighing pellets of the polymers obtained by pressing them at 600 kg/cm². Poly(3-methyl-2,5-thienylene) had a somewhat smaller apparent specific gravity, 1.2.

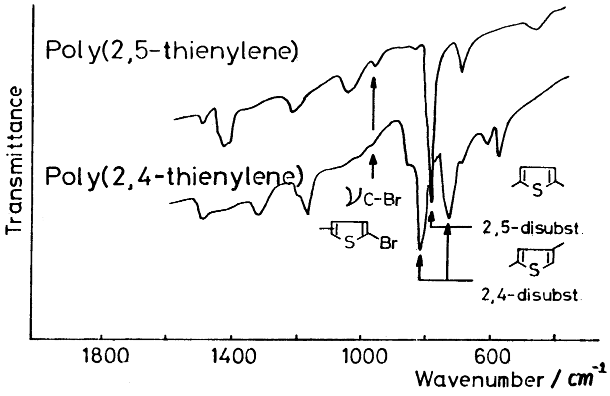


Fig. 2. IR spectrum of poly(2,5-thienylene) and poly(2,4-thienylene).

IR and NMR Spectra. The IR spectra of the polymers are consistent with the structures of the polymers shown in Eqs. 2, 5, 6, and 7. Figure 2 shows the IR spectra of poly(2,5-thienylene) and poly(2,4-thienylene). The IR spectrum of poly(2,5-thienylene) shows one sharp out-of-plane δ(C–H) vibration band characteristic of 2,5-disubstituted thienylene[10)] at 788 cm⁻¹, whereas that of poly(2,4-thienylene) shows two out-of-plane δ(C–H) vibration bands at 730 and 820 cm⁻¹. The out-of-plane δ(C–H) vibration band of poly(3-methyl-2,5-thienylene) appears at 810 cm⁻¹. The IR spectra of the copolymers show both bands assignable to the 2,5-thienylene and 2,4-thienylene units and the composition of the copolymers were determined from their relative intensities as described before.

ν(C–Br) and ν(C–Cl) bands of the terminal halo-

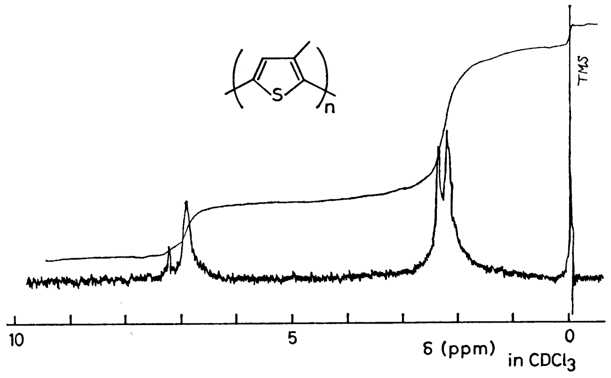
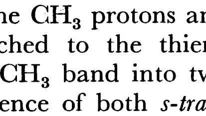


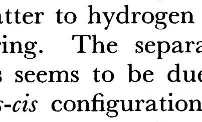
Fig. 3. ^{1}H-NMR spectrum of Poly(3-methyl-2,5-thienylene) in $CDCl_3$. 100 MHz.

thienyl groups are sometimes observable at 980 and 1000 cm^{-1}, respectively, but the intensities of the bands were very weak.

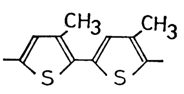
The ^{1}H-NMR spectra of the $CHCl_3$-soluble poly(2,5-thienylene) and poly(2,4-thienylene) show complex bands in a range of δ 6.5—7.5 assignable to hydrogens of the thienylene unit, whereas that of the $CHCl_3$-soluble poly(3-methyl-2,5-thienylene) (Figure 3) shows two absorption bands at δ 2.0—2.5 and δ 6.5—7.1 in an intensity ratio of 3:1, the former being assignable to the CH_3 protons and the latter to hydrogen directly attached to the thienylene ring. The separation of the CH_3 band into two peaks seems to be due to the presence of both *s-trans* and *s-cis* configuration and/or head-to-tail and head-to-head units in the polymer chain,



s-trans(head-to-tail)



s-trans(head-to-head)



s-cis(head-to-tail)

It is known[11] that 2,2′-bithiophene derivatives exist as mixtures of *s-trans* and *s-cis* isomers in solution.

Optical Properties. The extent of π-conjugation in the polythienylenes is reflected in their colors and electronic spectra. Poly(2,5-thienylene) and poly(3-methyl-2,5-thienylene) are dark reddish brown, whereas poly(2,4-thienylene) is light brown. The electronic spectrum of the $CHCl_3$-soluble poly(2,5-thienylene) shows a large bathochromic shift of the π-π^* absorption band from the λ_{max} of thiophene at 230 nm to 418 nm (Fig. 4), but that of the $CHCl_3$-soluble poly(2,4-thienylene) shows only a small shift. When exposed to UV-light (365 or 253.7 nm) poly(2,5-thienylene) fluorecses a light green color, whereas poly(2,4-thienylene) does not show the fluorescence. These results indicate that the π-electrons in poly(2,5-thienylene) are extensively delocalized along the polymer chain (Eq. 3), whereas those in poly(2,4-thienylene) are not.

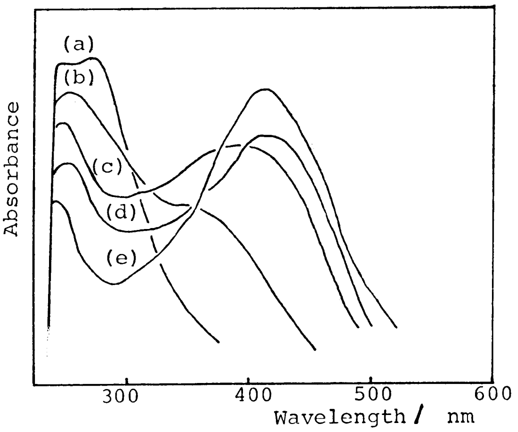


Fig. 4. Electronic spectra of $CHCl_3$-soluble (a) poly(2,4-thienylene) (M_w=2100), (b) copolymer obtained in Run 5 in Table 2, (c) copolymer obtained in Run 4 in Table 2, (d) copolymer obtained in Run 3 in Table 2, and (e) poly(2,5-thienylene) (M_w=1370). $\varepsilon_{max}/C_4H_2S$=about 5000 for all polymers.

If a simplified molecular orbital theory proposed by Hückel[12] for conjugated polyens can be applied to other π-conjugated polymers $H{\leftarrow}A{\rightarrow}_nH$ (A=π-electron-system containing unit such as *p*-phenylene and 2,5-thienylene), the energies of the orbitals of the polymer are given by the following equation,

$$E_i = \alpha + 2\beta \cos\frac{i\pi}{n+1} \quad (i=1,2,\cdots,n), \tag{9}$$

where α and β represent energy of an orbital of isolated unit, A, and exchange integral between the two orbitals in the adjacent two A's, respectively. Application of this equation to HOMO of A gives the following energies of the polymer $H{\leftarrow}A{\rightarrow}_nH$

$$E_i(\text{occupied}) = \alpha_1 + 2\beta_1 \cos\frac{i\pi}{n+1} \quad (i=1,2,\cdots,n), \tag{10}$$

where α_1 and β_1 represent the energy of HOMO of A and exchange integral between the HOMO's in the adjacent two A's, respectively. Application to LUMO gives an analogous equation,

$$E_i(\text{unoccupied}) = \alpha_2 + 2\beta_2 \cos\frac{i\pi}{n+1} \quad (i=1,2,\cdots,n), \tag{11}$$

E_i(occupied) and E_i(unoccupied) given by Eqs. 10 and 11 are depicted in Fig. 5.

Equations 10 and 11 afford the following highest occupied energy ε_1 and the lowest π-π^* transition energy $\Delta\varepsilon$

$$\varepsilon_1 = \alpha_1 - 2\beta_1 \cos\frac{\pi}{n+1} \tag{12}$$

$$\Delta\varepsilon = (\alpha_2-\alpha_1) + 2(\beta_1+\beta_2) \cos\frac{\pi}{n+1} \tag{13}$$

and cosequently a plot of ε_1 against $\Delta\varepsilon$ is expected to give a linear line with a slope of $-2\beta_1/2(\beta_1+\beta_2)$. By using data of peak anode potential which corresponds to $-\varepsilon_1$ and the lowest π-π^* transition energy which

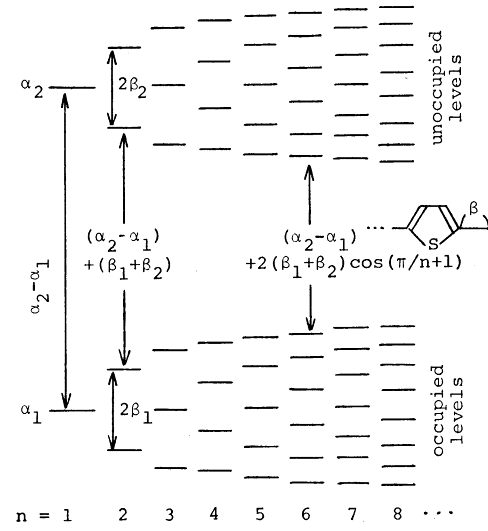


Fig. 5. Energy levels in $H\{A\}_nH$.

corresponds to $\Delta\varepsilon$, Diaz and his coworkers showed[1g] that the plot of $-\varepsilon_1$ against $\Delta\varepsilon$ actually gives straight lines with a slope of *ca.* 0.5 for oligo(*p*-phenylene), oligo(2,5-thienylene), and oligo(2,5-pyrrolylene). The value of the slope indicates that β_1 and β_2 equal to each other in these oligomers. The β_1 (or β_2) estimated using the data of Diaz is −0.63 eV for oligo(2,5-thienylene) and −0.58 eV for oligo(*p*-penylene).

Since poly(*p*-phenylene) is known to be converted into a good electric conductor with an electric conductivity of 10^4 S cm^{-1} when doped with AsF_5,[1c] the present result that the absolute value of β in oligo(2,5-thienylene) is larger than that in oligo(*p*-phenylene) implies a possibility that poly(2,5-thienylene) can be converted into similar or better electric conductors when doped with suitable acceptors. The observed values of $\Delta\varepsilon$ of oligo- or poly(2,5-thienylene), $H\{2,5\text{-}C_4H_2S\}_n$ (n=3, 4, ∞), agree well with values calculated by using Eq. 13 and the $(\alpha_2-\alpha_1)$ and $(\beta_1+\beta_2)$ values estimated from the λ_{max}'s of thiophene and 2,2′-bithiophene.

Figure 4 indicates the electronic spectra of the copolymers. It is seen that the λ_{max} shifts to longer wavelength with increase in the content of the 2,5-thienylene unit reaching 418 nm where the pure poly(2,5-thienylene) shows the absorption peak. This indicates that the π-electrons in the sequence composed of 2,5-thienylene units are delocalized along the polymer chain, whereas the delocalization is broken by intervention of the 2,4-thienylene unit. These results clearly indicate that the polymer obtained in the copolymerization is not a mixture of the two homopolymers but it contains both the 2,5- and 2,4-thienylene units in a polymer chain.

The electronic spectrum of poly(3-methyl-2,5-thienylene) also shows a large bathochromic shift of the π-π^* absorption band from λ_{max} of 3-methylthiophene at 230 nm to 420 nm, the magnitude of the bathochromic shift (190 nm) being almost the same as that observed for nonsubstituted poly(2,5-thienylene). This indicates that π-electrons in poly(3-methyl-2,5-thienylene) are also extensively delocalized along the polymer chain, similarly to those in poly(2,5-thienylene). It is reported[13] that optical properties of substituted poly(acetylene)s, $\{CH{=}CR\}_n$, are much different from $\{CH{=}CH\}_n$ because of difficulties in forming a planar π-electron-conjugated polymer chain due to the steric repulsion between R and H or two R's. The finding obtained with poly(3-methyl-2,5-thienylene) is in contrast to the finding obtained with $\{CH{=}CR\}_n$, and the examination with the CPK molecular model indicates that there exists no special steric repulsion in forming a planar, conjugated polymer chain in the case of poly(3-methyl-2,5-thienylene) composed of recurring 5-membered rings.

As revealed by the electronic spectra of the polymers, the degree of delocalization of π-electrons along the polymer chain is affected by the mode of joining the thienylene units as well as by the composition of the two kinds of thienylene units in the copolymer. The degree of delocalization of π-electrons determines reactivities and electric conducting properties of the polymers as will be reported in the succeeding paper.

Stability in Air. All the poly(thienylene)s described above have high stabilitities in air in contrast to the sensitivity of poly(acetylene) against oxygen in air. The IR spectra of poly(thienylene)s showed no change after exposure of the polymer to air more than 1 year. Their high stabilities in air provide a great advantage in using them in various possible application.

Comparison with Electrochemically Prepared Poly(thiophene). Recently it has been reported that electrochemical oxidation of thiophene gives an electric conducting polymer film[8] and it has been proposed that the polymer has a structure similar to above-mentioned poly(2,5-thienylene).[8b] However, the IR spectrum of the electrochemically prepared polymer[8b] is somewhat different from that of poly(2,5-thienylene) prepared in the present study. Particularly notable in the IR spectrum of the polymer prepared by the electrochemical method is that the characteristic band of the 2,5-thienylene unit around 788 cm^{-1} due to the δ(C–H) absorption is considerably weaker in the IR spectrum.[18] It may be argued that the electrochemically prepared polymer of thiophene has a structure somewhat different from that of poly(2,5-thienylene).

Experimental

Materials. Commercially available 2,5-dibromothiophene was recrystallized from hexane. 2,4-Dibromothiophene,[14] 3-methyl-2,5-dibromothiophene,[15] $NiCl_2(bpy)$,[16] and $NiCl_2(dppp)$[17] were prepared according to methods in literature. Solvents for polymerization were dried over Na, distilled under dry N_2, and stored under dry N_2. Granular magnesium was activated by stirring under N_2 for 1 d.

Preparation of Polymers. *Expt 2 in Table 1*: 2,5-Dibomothiophene (22.7 g, 94.0 mmol) was added dropwisely into a vessel containing 2.29 g (94.0 mmol) of Mg and dry THF (60 ml). After consumption of all magnesium (1—2 h) at room temperature a small amount of the solution taken by a micro syringe was hydrolyzed with water, and gas chromatography indicated the hydrolyzed product contained thiophene, 2-bromothiophene, and 2,5-dibromothiophene in a 1:2:1 ratio. When $NiCl_2(bpy)$ (90 mg, 3.1×10^{-1} mmol) was added to the remaining THF solution of the product of the reaction of 2,5-dibromothiophene and magnesium, a smooth polymerization started. After carrying out the reaction for 5 h under reflux, the polymerization solution was poured into an HCl–acidic methanol mixture to obtain a dark brown precipitate. From the methanol solution a yellow solid (0.10 g, low-molecular weight poly(2,5-thienylene)) was recovered. The dark brown precipitate was collected over a glass filter, washed with methanol repeatedly, and dried in vacuum to yield 7.0 g (78%) of crude poly(2,5-thienylene), which was fractionated into $CHCl_3$-extractable (78 wt%) and $CHCl_3$-unextractable (22 wt%) fractions by extracting it with $CHCl_3$ by using a Soxhlet extractor. About 2/3 of the $CHCl_3$-extract was soluble in $CHCl_3$ at room temperature. The other polymerization in THF or diethyl ether was carried out analogously.

Expt 6 in Table 1: A similar reaction between 2,5-dibromothiophene and magnesium (1:1) was carried out in dry THF (10 cm^3). After completion of the reaction, dibutyl ether (40 cm^3) and $NiCl_2(bpy)$ were added. After carrying out the polymerization for 1 h under reflux (100 °C), the reaction mixture was poured into the HCl-acidic methanol and polymer obtained was treated as in the case of Expt 2 described above. The other polymerizations in the mixture of THF and dibutyl ether were carried out analogously.

Analysis and Measurements. Microanalysis of C and H was performed by Mr. T. Saito of our laboratory by using Yanagimoto CHN Autocorder Type MT-2. IR and ^1H-NMR spectra were recorded on a Hitachi Model 295 spectrometer and a Japan Electron Optics Laboratory PS-100 NMR spectrometer, respectively. Thermogravimetric analysis was performed with a Shimadzu thermoanalyzer TGA-30. Glc analysis was carried out with a Shimadzu GC-6A or GC-3BT gas chromatograph. Molecular weight was determined by a Corona 117 vapor pressure osmometer.

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9) Although the $CHCl_3$-extractable fraction did not contain magnesium, the $CHCl_3$-unextractable fraction contained magnesium (2.5—3.0 wt%) as proved by macroanalysis. $MgBr_2$ captured by poly(2,5-thienylene) through coordination to sulfur may be the origin of the magnesium component. For this reason, the true carbon content of the $CHCl_3$-unextractable poly(2,5-thienylene) is regarded to be higher than the found value. It was difficult to remove magnesium from the $CHCl_3$-extractable fraction.

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