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Synthesis of functional polymers containing distyrylthiophene moiety using the Heck reaction

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Summary

Polymers containing a *trans,trans*-2,5-thienylenevinylene-1,4-phenylenevinylene moiety were prepared by palladium-catalyzed polycondensation. Couples of 2,5-divinylthiophene derivatives **1** with *p*-dihalobenzenes **2** successfully produced the expected polymers **5**, whereas couples of 2,5-dihalothiophene derivatives **3** with *p*-divinylbenzene **4** gave only oligomers due to the homo-coupling reaction of **3**. Synthesis of a thermotropic liquid crystalline polymer having *trans,trans*-2,5-distyrylthiophene skeletons as mesogen was also investigated by use of the polycondensation between **1** and bis(*p*-iodophenyl) compounds **6** that concurrently have flexible segments.

Introduction

A Palladium-catalyzed substitution reaction at a vinylic position, namely the Heck reaction, is one of the useful methods for C–C bond formation. Its effectiveness for polymer synthesis has been demonstrated by several reports including ours (1, 2). By means of the polycondensation using the Heck reaction, we prepared novel polymers having cinnamoyl or distrylbenzene skeletons. Some of these polymers showed thermotropic liquid crystallinity. `Here is described the extension of these previous works of us to the polycondensation of thiophene derivatives, which produced wholly conjugated and liquid crystalline polymers having thienylenevinylene-phenylenevinylene units. Poly(2,5-thienylenevinylene-1,4-phenylenevinylene) has been prepared by use of the Wittig reaction, however, which produces a mixture of *trans*- and *cis*-vinylene skeletons (3, 4). By contrast, as mentioned in our previous papers (1, 2), the polymer prepared by the Heck reaction exclusively consists of *trans*-vinylene units.

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Experimental

Materials. Monomers **3a**~**3c** were prepared by the iodation or bromination of the corresponding thiophene derivatives according to the literature methods (5, 6) and purified by silica gel column chromatography (hexane as eluent). One of the starting materials, 3-*n*-butylthiophene, was synthesized by the nickel-catalyzed coupling reaction of 3-bromothiophene with *n*-butylmagnesium chloride (7), while the other, 3-methylthiophene, was commercially available. *p*-Divinylbenzene **4** was prepared according to the literature method (8). Preparation of **6a** and **6b** has been described in our previous paper (2). p-Diiodo- and p-dibromobenzene **2a** and **2b** were purified by recrystallization. Palladium acetate, tri-*o*-toylphosphine (Tol_3P), and phenothiazine were used as purchased. Triethylamine, tributylamine, and solvents were dried and purified under a nitrogen atmosphere according to conventional methods.

3-*n*-Butyl-2,5-divinylthiophene 1a To a 50-mL autoclave containing $Pd(OAc)_2$ (44.8 mg, 0.2 mmol), Tol_3P (122 mg, 0.4 mmol), phenothiazine (25 mg, 0.12 mmol), and a Teflon-coated magnetic stirrer bar were added **3b** (2.98 g, 10 mmol), triethylamine (2.43 g, 24 mmol), and DMF (25 mL) under a nitrogen atmosphere. Ethylene was introduced to the autoclave with stirring until the pressure became 30 Kg/cm^2. While the mixture was stirred at 100°C in an oil bath for 8 h, ethylene was occasionally added and the pressure was kept at 40 Kg/cm^2. Afterwards the autoclave was cooled to room temperature and unreacted ethylene was subsequently vented out. Then, diethyl ether (20 mL), water (30 mL), and hexane (30 mL) were added to the reaction mixture. The organic phase separated was washed with 5% HCl aq. and subsequently with water, and then dried over anhydrous magnesium sulfate. The residue after the evaporation under reduced pressure was purified by silica gel column chromatography (hexane as eluent; R_f=0.7) to give 3-*n*-butyl-2,5-divinylthiophene **1a** (1.04 g, 54 %): ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H, -CH_3), 1.10-1.25 (m, 4H, -$CH_2CH_2CH_3$), 2.54 (t, J = 7.2 Hz, 2H, -$CH_2C_3H_7$), 5.10 (d, J = 10.2 Hz, 2H, -CH=CH_2), 5.49 (br d, J = 17.4 Hz, 2H, -CH=CH_2), 6.49-7.07 (m, 2H, -CH=CH_2), 6.69 (s, 1H, a proton on C4 of the thiophene ring).

In the same manner, 3-methyl-2,5-divinylthiophene **1b** and 2,5-divinylthiophene **1c** were prepared.

1b: 66% yield; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, -CH_3), 5.10 (d, J = 10.2 Hz, 2H, -CH=CH_2), 5.43 (d, J = 17.4 Hz, 1H, -CH=CH_2), 5.47 (d, J = 17.4 Hz, 1H, -CH=CH_2), 6.70 (dd, 1H, -CH=CH_2), 6.80 (dd, 1H, -CH=CH_2), 6.77 (s, 1 H, a proton on C_4 of the thiophene ring).

1c: 50% yield; ^{1}H NMR ($CDCl_3$) δ 5.10 (d, J = 10.8 Hz, 2H, -CH=CH_2), 5.51 (d, J = 17.4 Hz, 2H, -CH=CH_2), 6.77 (dd, 2H, -CH=CH_2), 6.79 (s, 2H, protons of the thiophene ring).

A Typical Procedure for The Polymerization To a solution of *p*-diiodobenzene (330 mg, 1 mmol), $Pd(OAc)_2$ (4.48 mg, 0.02 mmol), Tol_3P (12.2 mg, 0.04 mmol), and phenothiazine (2.5 mg, 0.012 mmol) in DMF (2 mL) were added **1a** (192 mg, 1 mmol) and *n*-Bu_3N (446 mg, 2.4 mmol) under a nitrogen atmosphere. After heated with stirring at 50 °C for 24 h, the reaction mixture was poured into methanol (50 mL). The reddish polymer precipitated was filtered and dried in vacuo (245 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 0.87~1.02 (m, 3H, -CH_3), 1.28~1.68 (m, 4H, -CH_2C$H_2$$CH_3$), 2.52~2.74 (m, 2H, -C$H_2$$C_3H_7$), 6.72~6.95 (m, 3H, -$C_6H_4$-CH=C$H$- and a proton on C4 of the thiophene ring), 7.08-7.20 (m, 2H, -C_6H_4-CH=CH-), 7.41 (s, 4H, -C_6H_4-); FT-IR (KBr, cm^{-1}) 3023, 2955, 2927, 2857, 1675, 1619, 1594, 1457, 1297, 1158, 942, 832, 802, 561.

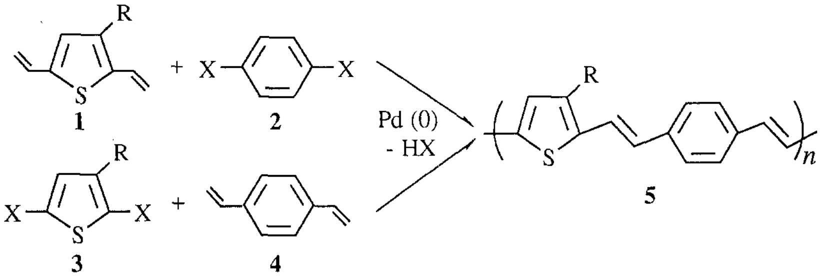
Measurements. ^{1}H NMR spectra were obtained on a JEOL GX-400 or Hitachi R600 spectrometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR 1600 series spectrophotometer. DSC analyses were conducted by a SEIKO DSC 200 system at a heating and cooling rate of 10 °C/min. Molecular weights of polymers were determined by VPO at 40°C in $CHCl_3$ as well as GPC with Shodex® A803 as column, $CHCl_3$ as eluent (1 mL/min), and calibration plots based on polystyrene standards.

Results and Discussion

Synthesis of Poly(2,5-thienylenevinylene-1,4-phenylenevinylene)

For the preparation of poly(2,5-thienylenevinylene-1,4-phenylenevinylene) by the Heck reaction, two pathways were undertaken as shown in Scheme I. One is the polycondensation between 2,5-divinylthiophene derivatives **1** and *p*-dihalobenzenes **2**, and the other is that between 2,5-dihalothiophene derivatives **3** and *p*-divinylbenzene **4**. In result, the former couples successfully produced the expected polymers **5**, but the latter gave only oligomers (Table 1). The polymerizations were carried out in DMF including $Pd(OAc)_2$/2Tol_3P as catalyst, *n*-Bu_3N or Et_3N as quencher for hydrogen halide generated, and phenothiazine as radical inhibitor.

Scheme I



1a, R = *n*-Butyl
1b, R = CH_3
1c, R = H

2a, X = I
2b, X = Br

3a: R = *n*-Butyl, X = I
3b: R = *n*-Butyl, X = Br
3c: R = CH_3, X = Br

Table I. Polycondenzation between **1** (or **3**) and **2** (or **4**) Catalyzed by Palladium Complex in DMF.[a]

Run	Monomers		Temp. (°C)	Time (h)	Polymer Yield(%)[b]	$CHCl_3$-insoluble fraction		$CHCl_3$-soluble fraction		
						wt%	X content(%)[c]	wt%	M_n[d]	X content(%)[c]
1	**1a**	**2a**	50	24	91	10		90	3200	
2	**1a**	**2a**	90	8	96	51	0.94	49		3.77
3	**1a**	**2b**	120	30	96	50		50	2300	
4	**1b**	**2a**	50	24	95	86	4.11	14		
5	**1c**	**2a**	50	24	114	97	15.38	3		
6	**3a**	**4**	100	10	43	0		100		
7	**3b**	**4**	100	40	82	0		100	930	0.48
8	**3b**	**4**	130	20	79	0		100		
9	**3c**	**4**	100	30	76	49	2.48	51	800	

[a] Catalyst: $Pd(OAc)_2/2Tol_3P$ = 2 mol% for **2** (or **4**) except for run 3 (4 mol% for **2**); base: *n*-Bu_3N or Et_3N = 1.2 equiv for a halogen group; radical inhibitor: phenothiazine = 1 mol% for **1** (runs.1-5); [**1** (or **3**)] = [**2** (or **4**)] = 0.5 mol/L.

[b] The weight percent yield of methanol-insoluble polymer: the value was evaluated on the assumption that HX was completely released. Thus the yield of the oligomeric oroduct was over 100% (run 5).

[c] Halogen content determined by elemental analysis. [d] Determined by VPO at 40°C in $CHCl_3$.

In the polycondensation between **1** and **2**, the product polymers, which precipitated with the progress of the polymerization, were fractionated into chloroform-soluble and -insoluble parts. The IR and ^1H NMR spectra identified the polymer structures. It must be remarked that the chloroform-insoluble part showed the identical IR spectra with the soluble one. Typical absorption peaks were observed at 942~946, 832, and 802 cm^{-1} due to out-of-plane bending vibrations of C-H bonds of *trans*-vinylene groups, phenylene rings, and thienylene ones, respectively. On the other hand, the iodine content, which was given by the elemental analysis, in the product polymer showed much difference between two fractionated parts; the chloroform-insoluble polymer contained the smaller amount of iodine than the soluble polymer (Table 1, run 2). Since iodine exists on the polymer terminal as iodophenyl group, the lower content of it signifies the higher molecular weight of the polymer; the degrees of polymerization calculated on the basis of the iodine contents (0.94 and 3.77) were 50 and 12 for the chloroform-insoluble and -soluble polymers, respectively. Thus it is concluded that the chloroform-insoluble polymer had the same unit structure as the soluble polymer but had the higher molecular weight. Introduction of the longer alkyl group into the thiophene ring presented the higher solubility and hence the higher molecular weight to the product polymer. This is apparently indicated by the proportion of the chloroform-soluble polymer as well as by the iodine content (runs 2, 4, and 5). The degrees of polymerization of the polymers derived from **1b** and **1c** were estimated to be 13 and 3.3, respectively, even for the chloroform-insoluble portion. Although *p*-dibromobenzene **2b** also acted as the monomer in place of **2a**, the higher reaction temperature was reasonably required (run 3).

In contrast to the couples of **1** with **2**, the polycondensation between **3** and **4** yielded only oligomeric products. This behavior probably resulted from a dehalogenative coupling reaction of two halothiophene groups (9), which deviated the mole ratio of the functional groups from 1:1. Indeed, as seen in run 7, the bromine content (0.48%) of the product polymer was much lower than the calculated value (8.58%), which was based on the molecular weight determined by VPO with assuming that the polymer had a bromothienyl group as one terminal.

Synthesis of Liquid Crystalline Polymers Having 2,5-Distyrylthiophene Units as Mesogen

A 2,5-distyrylthiophene skeleton prepared by the above-mentioned polycondensation is rigid enough to be expected to act as mesogen. Thus the polycondensations between **1** and bis(p-iodophenyl) compounds **6** having flexible segments were carried out (Scheme II, Table II).

The introduction of flexible segments increased the solubility of the product polymers; **7a**, **7b**, and **7d** were completely soluble in organic solvents such as DMF, DMSO, and $CHCl_3$, whereas **7c** and **7e** were not. The *trans*-vinylene structure was identified by IR and ^1H NMR spectra; the out-of-plane bending vibration of a C-H bond was observed at 944~950 cm^{-1} and the coupling constant between vinylene protons was within a range of 15.45~15.65 Hz.

Scheme II

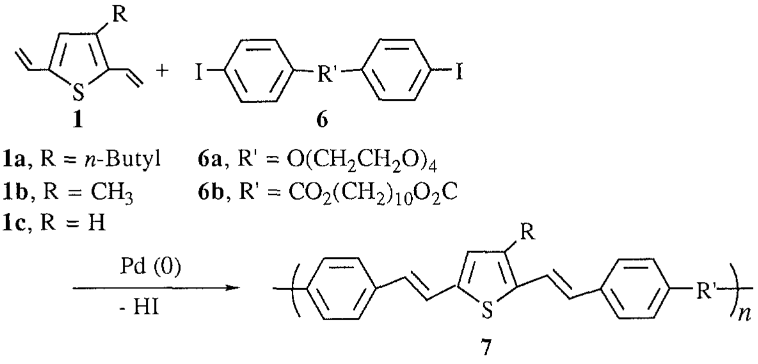


Table II. Pd-Catalyzed Polycondensation between **1** and **6** at 80 °C[a]

Run	Polymer	Monomers		Time (h)	Yield[b] (%)	M_w[c]	$\frac{M_w}{M_n}$[c]
1	**7a**	**1a**	**6a**	20	92	14300	1.72
2	**7b**	**1b**	**6a**	20	93	10900	1.80
3	**7c**	**1c**	**6a**	20	97	9200[d]	1.68[d]
4[e]	**7d**	**1b**	**6b**	40	90	3500	1.45
5	**7e**	**1b**	**6b**	24	96	10300[d]	1.84[d]

[a] Catalyst: $Pd(OAc)_2/2Tol_3P$ = 2 mol% for **1** except for run 4 (4 mol% for **1**); base: $n\text{-}Bu_3N$ = 1.2 equiv for an iodophenyl group; radical inhibitor: phenothiazine = 1 mol% for **1**; solvent: DMF unless otherwise noted. [**1**] = [**6**] = 0.25 mol/L.

[b] The weight percent yield of methanol-insoluble polymer: the value was evaluated on the assumption that HX was completely released.

[c] GPC(polystyrene standards); eluent, $CHCl_3$.

[d] Measured for the $CHCl_3$-soluble portion (74 and 55wt% of the polymer obtained on run 3 and 5, repectively).

[e] Reaction solvent: pyridine.

As discussed in our previous paper (2), a homo-coupling reaction of iodophenyl groups occurred also in the polycondensation between **1b** and **6b** in DMF. The ^1H NMR spectra of product polymer **7e** showed two doublet peaks due to a biphenyl group at δ 8.10 and 7.52 (J = 8.54 Hz) in addition to signals due to distyrylthiophene units (Figure 1 (b)). The relative intensity of the corresponding signals indicated that the ratio of the biphenyl unit to the distyrylthiophene one in **7e** was 40:60. This homo-coupling reaction did not occur in the polymerization of **1** with **6a** and also in the polymerization carried out in pyridine even if **6b** was reacted. However, the polymerization in pyridine was much slower than that in DMF. The ^1H NMR spectra of **7d** prepared in pyridine showed no signals due to the biphenyl group but those due to the iodophenyl group existing as the polymer terminal (Figure 1 (a)).

Thermotropic liquid crystallinity of the product polymers was examined by using DSC and an optical microscope with cross-polarizers. Among **7a**~**7d**, only **7c** had liquid crystallinity. The DSC thermograms of **7c** showed two reproducible transition peaks at 142°C and 161°C on the heating scan. Polarizing microscopy indicated that the first and second peaks were due to the transitions from solid to liquid crystal and from liquid crystal to isotropic liquid, respectively. Between these transitions, **7c** was completely anisotropic liquid, but no classification of the mesophase could be made from the texture observed. As compared with the related polyether containing *m*-distyrylbenzene units as mesogen, **7c** showed a mesophase in the narrower range of

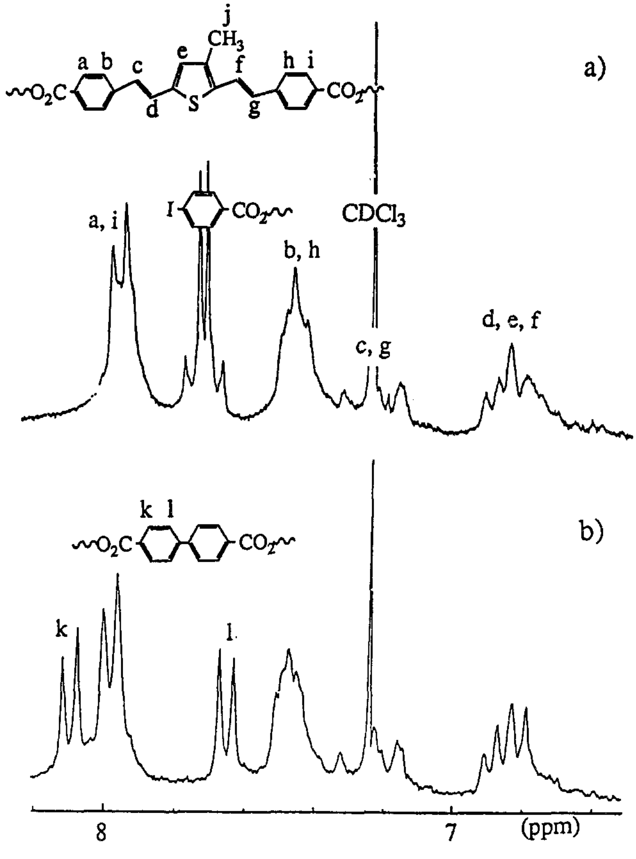


Figure 1. The low field parts (δ 6.6~8.2) of the ^{1}H NMR spectra of **7d** (a) and **7e** (b) (400 MHz, CDCl$_3$).

temperature; the mesophase of the former was observed between 132°C and 167°C (2). This means that the 2,5-distyrylthiophene moiety is the weaker mesogen than the *m*-distyrylbenzene one. In contrast to **7c**, DSC thermograms of other three polymers having side alkyl chains showed no peak (**7a**) or only one peak due to melt at 49°C (**7b**) and at 53°C (**7d**). It appears that the side alkyl chain disturbs the formation of ordered structures, i.e., liquid-crystallinity and also crystallinity.

References and Notes

1. Suzuki M, Sho K, Lim J-C, Saegusa T (1989) Polym Bull 21: 415, and references therein
2. Suzuki M, Lim J-C, Saegusa T (1990) Macromolecules 23: 1574
3. Kossmehl G, Härtel M, Manecke G (1970) Makromol Chem 131: 37
4. There are several papers dealing with the preparation of polythienylenevinylenes and their copolymers: Kossmehl G, Härtel M, Manecke G (1970) Makromol Chem 131: 15; Kossmehl G, Yaridjanian A (1981) Makromol Chem 182: 3419; Jen K-Y, Eckhart H, Jow T R, Shacklette L W, Elsenbaumer R L (1988) J Chem Soc, Chem Commun : 215; Yamada S, Tokito S, Tsutsui T, Saito S (1987) J Chem Soc, Chem Commun : 1448; Murase I, Ohnishi T, Noguchi T, Hirooka M (1987) Polym Commun: 277; Jen K-Y, Lawrence M M, Shacklette L W, Elsenbaumer R L (1987) J Chem Soc, Chem Commun: 309; Berlin A, Branamante S, Ferraccioli R, Pagani G A, Sannicolo' F (1987) Synthetic Metals 18: 117; Shim H-K, Lenz R W, Jin J-I (1989) Makromol Chem 190: 389; Blohm M L, Pickett J E, Van Dort P C (1993) Macromolecules 26: 2704
5 Tamaru Y, Yamada Y, Yoshida Z-I (1979) Tetrahedron 35: 329
6 Barker J, Huddleston P R, Wood M L (1975) Synth Commum 5: 59
7 Tamao K, Nakajima I, Kumada M, Minato A, Suzuki K (1982) Tetrahedron 38: 3347
8 Strey B T (1965) J Polym Sci, A3: 265.
9 Spectroscopic analyses were not informative to reveal the production of the bithiophene moiety; e.g. the ^{1}H NMR spectra showed so complicated signals that it was impossible to specify the signal due to the bithiophene structure. However, palladium-catalyzed dehalogenative coupling reactions of bromo-thiophene derivatives have been known: see ref. 5

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