CHEMISTRY LETTERS, pp. 985-988, 1994.

Preparation of Long Alkyl-substituted Oligothiophenes

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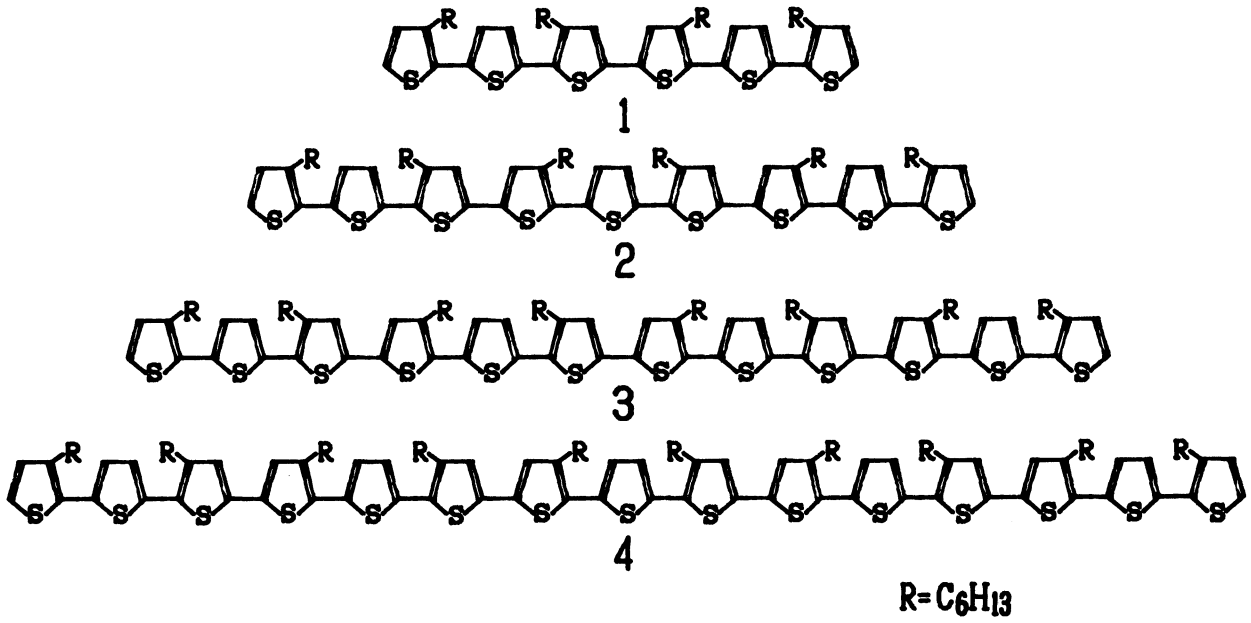
New hexyl-substituted oligothiophenes (sexi-, novi-, duodeci-, and quindeci-thiophenes) were prepared by a Ni(0)-catalyzed coupling reaction of a 5,5''-dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene. The structures were determined by ^{1}H NMR spectra, GPC data, and elemental analyses. Their $\pi-\pi^*$ transitions were compared with those of poly(alkylthiophenes).

A large amount of work has been devoted to the study of π-conjugated polymers, because those polymers show high electric conductivities in oxidized states, nonlinear optical susceptibilities and so on. Among those polymers, polythiophene and its derivatives have attracted a great deal of attention owing to their high stability toward oxygen and moisture in both oxidized and neutral states.[1] Recently, several researchers have prepared poly[3-(long alkyl)thiophenes] which have not only considerable conductivities ranging from 10 to 95 S/cm in oxidized states but also good solubility in usual solvents.[2] NMR measurements of the poly(alkylthiophenes) showed that the polymers contained approximately 25 mole-% head-to-head configuration, indicating that the effective conjugation length is limited by twists of the polymer chain.[3] α-Oligothiophenes having well-defined structures are good models for studying charge storage in conducting (oxidized) polymer chains[4] and candidates for new functional materials.[5] Thus far α-oligothiophenes from terthiophene to octithiophene have been prepared.[6] The solubilities of the oligothiophenes decreased when the chain became longer. In practice, unsubstituted octithiophene was

insoluble in any solvents. Yassar et al. have prepared an alkyl-substituted duodecithiophene containing 12 thiophene rings, but the position of the alkyl groups in the oligothiophene was uncertain.[7] In this report, we show the preparation of new hexyl-substituted oligothiophenes: sexithiophene (**1**), novithiophene (**2**), duodecithiophene (**3**), and quindecithiophene (**4**).



Oligothiophenes **1**, **2**, **3**, and **4** were prepared by a reductive coupling reaction of 5,5''-dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene (**5**) according to a similar procedure described for the preparation of α-octithiophenes.[6] The dibromide **5** was synthesized by bromination of the corresponding dihexylterthiophene[8] with N-bromosuccinimide in a 1:1 mixture of chloroform and acetic acid at ambient temperature in 94.8% yield. The dibromide **5** (3.00 g, 5.22 mmol) in 20 ml of hexane was added dropwise to an activated nickel(0) reagent prepared from anhydrous $NiCl_2$ (109 mg, 0.84 mmol), Zn (2.53 g, 38.7 mg-atoms), triphenylphosphine (850 mg, 3.2 mmol), and 2,2'-bipyridine (126 mg, 0.85 mmol) in 75 cm^3 of N,N-dimethylformamide. The mixture was heated at 70 ^oC for 5 h. The resulting mixture was poured into 500 cm^3 of 15% HCl methanol solution and the obtained precipitate was filtered off. Liquid chromatography of the residue (hexane-benzene/ silica gel) afforded **1** (40 mg, 1.8%), **2** (60 mg, 2.8%), **3** (30 mg, 1.4%), and **4** (40 mg, 1.8%).

The structures of the isolated hexyl-substituted oligothiophenes were determined based on ^1H NMR spectra and GPC data described below. Figure 1 shows the 270 MHz

^{1}H NMR spectra for aromatic protons of the hexyl-substituted oligothiophenes at 27 ^{o}C. The peaks at δ=7.26 are due to $CHCl_3$ as impurity in $CDCl_3$. The all spectra shows two moderate doublet peaks at δ=6.94 and 7.18. The coupling constant (J=5.0 Hz) and the chemical shifts were consistent with ^{1}H NMR data of 3,3'-dimethyl-2,2'-bithiophene.[9] Therefore, these doublet peaks are assigned to the 4- and 5-positions on the terminal 2-substituted 3-alkylthiophene. The peaks in the region of δ=7.00-7.02 and 7.05-7.10 would be ascribed to the aromatic protons of the alkylthiophene units and the thiophene units, respectively. From these splitting pattern and intensity ratio of peaks demonstrated that the isolated oligothiophenes were identified with **1**, **2**, **3**, and **4**. Furthermore, GPC data summarized in Table 1 suggest that the oligomers were

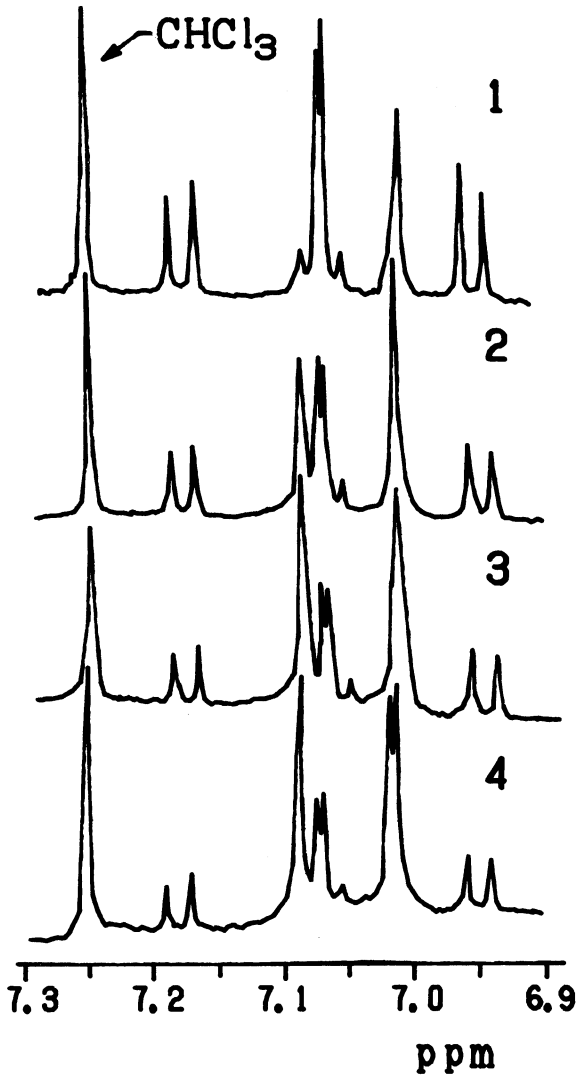


Fig.1. ^{1}H NMR spectra for aromatic protons of hexyl-substituted oligothiohenes.

Table 1. GPC data and elemental analyses of hexyl-substituted oligothiophenes

Oligomer	M(Calcd)	GPC data [a]			Analyses (%) Found (Calcd)	
		Mn	Mw	Mn/Mw	C	H
1	831	1.05×10^3	1.10×10^3	1.05	68.76 (69.34)	7.52 (7.51)
2	1246	1.55×10^3	1.71×10^3	1.10	69.12 (69.40)	7.54 (7.44)
3	1660	1.78×10^3	1.97×10^3	1.11	69.25 (69.43)	7.48 (7.40)
4	2075	2.27×10^3	2.57×10^3	1.13	68.96 (69.44)	7.39 (7.38)

a) Number-average molecular weight (Mn) and weight-average molecular weight (Mw) were determined with polystyrene as a standard.

monodispersion and each average molecular weight estimated by GPC is compatible with each one calculated. These GPC data and elemental analyses corroborate the identification of the oligomers described above.

The absorption spectra of **1**, **2**, **3**, and **4** in chloroform had $\pi-\pi^*$ transitions at 3.02, 2.82, 2.77, and 2.72 eV, respectively. Poly(3-dodecylthiophene)[10] and poly(3-hexylthiophene)[11] which contained about 25 mole-% head-to-head configuration had shown a $\pi-\pi^*$ transition at 2.83 eV. The value of the polymers close to that of **2**, indicating those poly(3-alkylthiophenes) have a similar effective conjugation length to **2** (hexyl-substituted novithiophene). Gallazzi et al. reported that poly(3,3''-dihexyl-2,2':5',2''-terthiophene) had shown a $\pi-\pi^*$ transition at 2.72 eV,[8] which was the same value as **4** surprisingly. Consequently, it seems reasonable to consider that the poly(dihexyl-terthiophene) is assembly of **4** from the viewpoint of their electric structures. Works is in progress in order to characterize electrical and nonlinear optical properties.

The authors are grateful to Dr. S. Okada (Institute for Chemical Reaction Science, Tohoku University) for GPC measurement and Ms. M. Nishinaka (Faculty of Science, Kobe University), Ms. K. Hayashi, and Ms. T. Ikeuchi (Faculty of Science, Osaka University) for elemental analysis.

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(Received February 14, 1994)