Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Sep 2010

To cite this article: Schoichi Gondo, Yasuyuki Goto & Masanao Era (2007): Preparation of Regioregular Alkylthiophene Oligomers and Their Optical Properties, Molecular Crystals and Liquid Crystals, 470:1, 353-358

To link to this article: http://dx.doi.org/10.1080/15421400701503600

Mol. Cryst. Liq. Cryst., Vol. 470, pp. 353–358, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701503600

Preparation of Regioregular Alkylthiophene Oligomers and Their Optical Properties

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We successfully prepared regioregular hexylthiophene oligomers, dimmer to seximer of hexylthiophene, by using the Suzuki coupling. Introduction of hexyl chain provided excellent solubility to the oligothiophenes; even in seximer, the oligomer was soluble in conventional organic solvents such as toluene and chloroform. Additionally, the oligomer formed thin film with good uniformity by spin-coating from chloroform solution. In this article, we also report optical properties of the oligomer.

Keywords: oligothiophene; optical properties; regioregular

Polymer and oligomer consisting of alkylthiophene have received attention as an organic semiconducting material because of not only their potential of high career mobility and an optical nonlinearity but excellent film-processability [1–7]. In the thiophene materials, introducing regioregularity into molecular skeleton is a promising approach to prepare high performance organic semiconductor. Regioregularity of conjugated molecular chains improves the planarity of a main chain and enhances stacking of π-conjugated system in the solid thin. As a result, one expects the improvement of electric and optical properties in the thiophene materials. In fact, very high carrier mobility of $0.1\,cm^2/Vs$ was demonstrated to be attained in a regioregular poly(3-hexylthiophene) [2]. In this study, we successfully prepared

This work is partly supported by Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Sports, Science and Culture of Japan (No.18550168).

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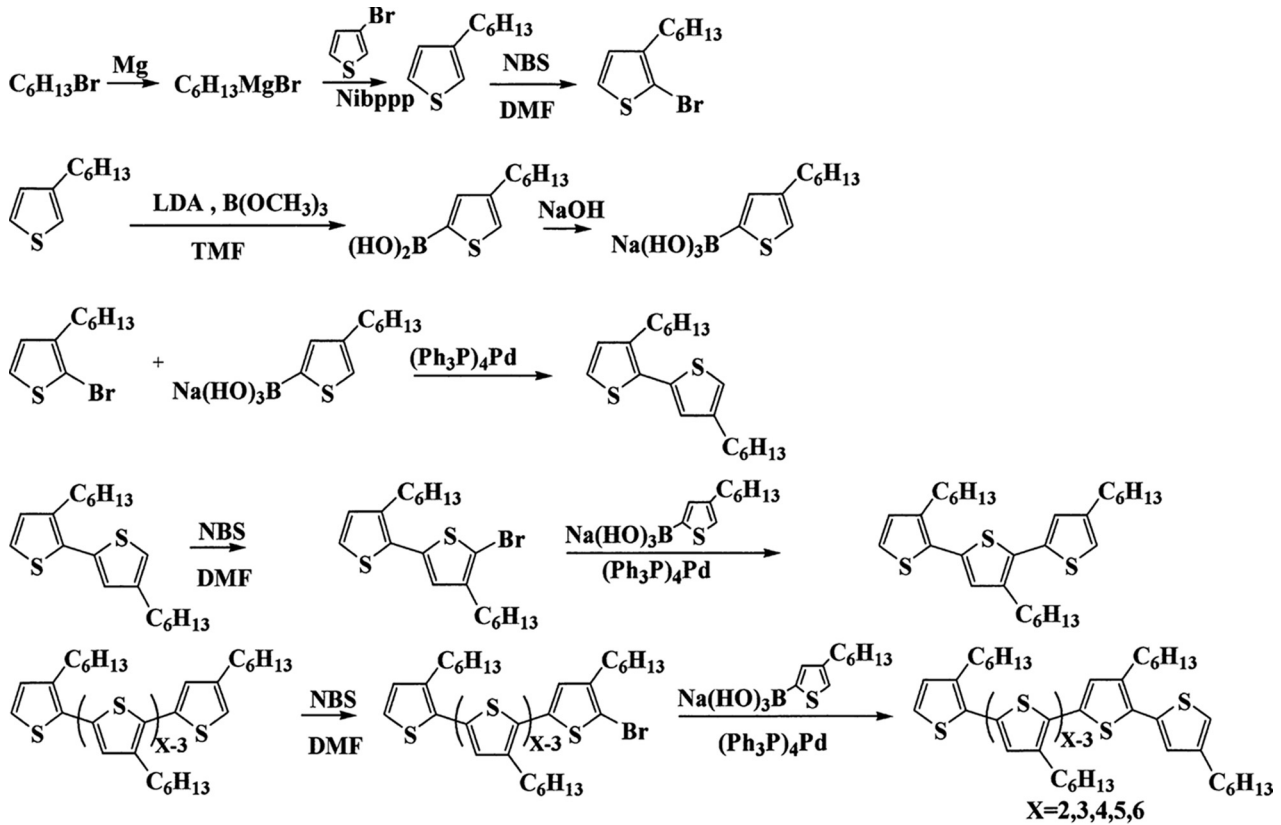
regioregular hexylthiophene oligomers having the head-to-tail sequence. In this article, we reports preparation and optical properties of the regioregular alkylthiophene oligomers.

Regioregular thiophene oligomers were prepared according to ref.8 (synthetic route is shown in Scheme 1). Sodium 4-hexyl-2-thienylboronate (**1**) was obtained by a conventional procedure using butyl lithium and trimethylborate. NBS bromination of 3-hexylthiophene provided 4-hexyl-2-bromothiophene (**2**). The NBS bromination selectively substitutes bromine on α-position of thiophene ring. By the Suzuki coupling of **1** and **2**, then, head-to-tail regioregular bithiophene (dimmer, $X = 2$) was prepared. By repeating the NBD bromination and the Suzuki coupling of α-bromo-substituted thiophene oligomer and **1**, we can prepare head-to-tail regioregular thiophene oligomer with various length. In this study, five regioregular alkylthiophene oligomers ($X = 2$, 3, 4, 5, and 6) were successfully prepared.

Obtained oligomers possess excellent solubility and film processability due to incorporation of alkyl chain; the oligomers were soluble in conventional organic solvents such as chloroform and toluene. By spin-coating from the solutions, the relatively long oligomers ($X \geqq 4$) provided yellow or orange transparent film with good uniformity whereas dimmer and trimer were liquid at room temperature. Figures 1a and b show absorption and fluorescence spectra of the oligomers in chloroform, respectively. For comparison, absorption spectra of thiophene oligomer having no alkyl chain (nT; $n = 2$–6) are also shown in Figure 1a [7]. Absorption peak λ^A_{max}, fluorescence peak λ^f_{max} of the oligomers is red-shifted as number of thiophene ring (in other words, elongation of π-conjugation). Extinction coefficient at absorption peak wavelength, ε_{max}, also increases with thiophene chain length. In comparison with absorption peaks of oligothiophenes having no alkyl chain, the value of λ^A_{max} of the regioregular thiophene oligomers is lower. The relatively lower λ^A_{max} value of the regioregular thiophene oligomer is most likely to be due to conformational defect induced by incorporation of alkyl chain.

Absorption spectra of the regioregular thiophene oligomer in chloroform and in film state are compared in Figure 2. Absorption band in film state is red-shifted in comparison with those in chloroform, demonstrating the mean π-conjugation length of the oligothiophenes is elongated in film state. The result is most likely to be due to decreasing conformational defects in film state.

From the absorption spectra, we estimated fluorescence quantum of fluorescence Φ_F of the oligomers [9]. The Einstein's A coefficient A_{21} was obtained by the following equation,



SCHEME 1 Synthetic route of head-to-tail regioregular hexylthiophene oligomers employed in this study.

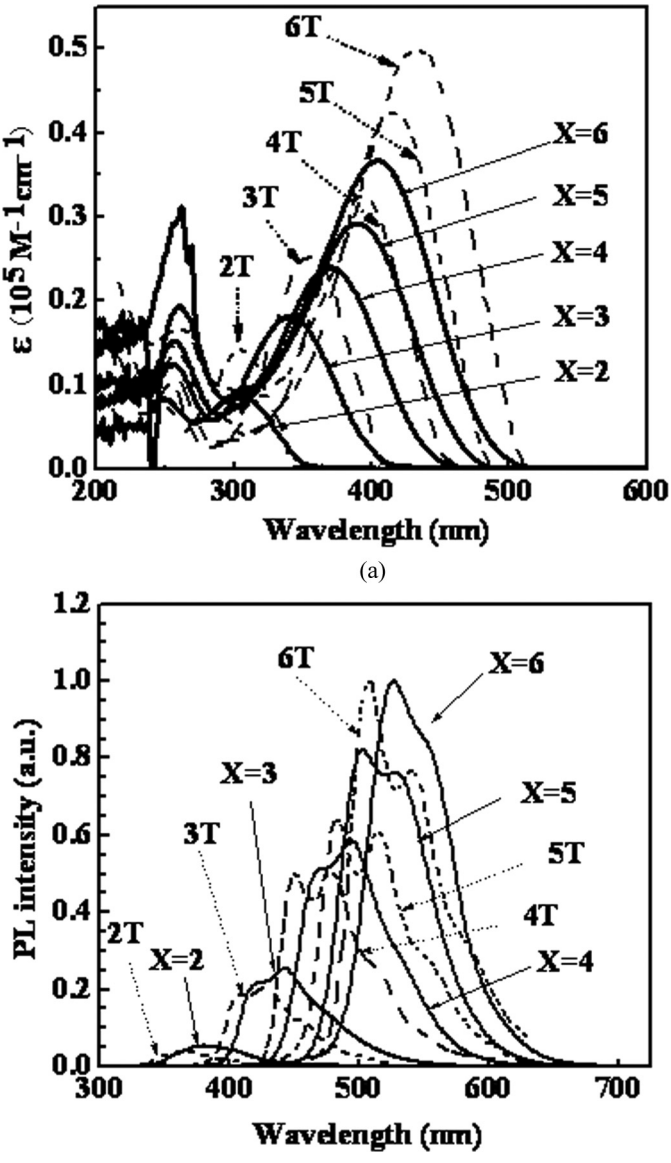


FIGURE 1 Absorption (a) and fluorescence (b) spectra of the oligomers (X = 2–6) in chloroform. Broken lines show absorption and fluorescence spectra of parent thiophene oligomers in dioxane [7].

$$A_{21} = 2.9 \times 10^{-9} \tilde{\nu}_{21}^2 \int_0^\infty \varepsilon d\tilde{\nu}, \tag{1}$$

where $\tilde{\nu}_{21}$ is absorption peak wavenumber, and ε extinction coefficient. The natural radiative life time τ_0 is given by reciprocal A_{21}.

$$\tau_0 = \frac{1}{A_{21}}. \tag{2}$$

When total rate of non-radiative process from excited state to ground state is k_{NR}, fluorescent life time of excited state τ is represented by

$$\tau = \frac{1}{(A_{21} + k_{NR})}. \tag{3}$$

Then, fluorescence quantum efficiency is given by

$$\Phi_F = \frac{\tau_0}{\tau} = \frac{A_{21}}{(A_{21} + k_{NR})}. \tag{4}$$

Accordingly, we can estimate Φ_F from the values of fluorescence life and integrated extinction coefficient.

Fluorescence life time τ of the regioregular oligomers in chloroform and in film state was measured by a fluorescence life time

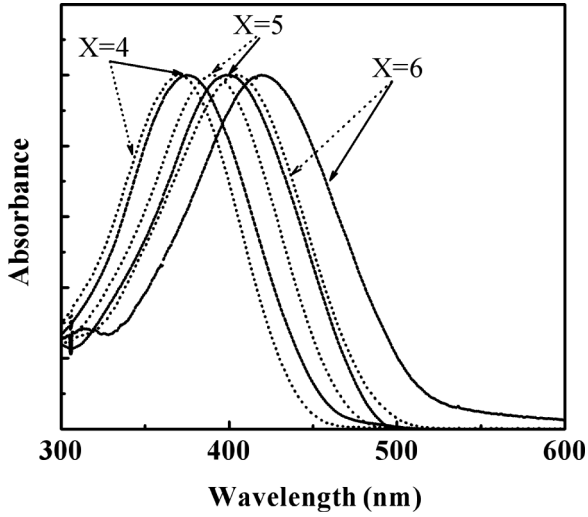


FIGURE 2 Comparison between absorption spectra of the regioregular thiophene oligomers in film state and in chloroform: solid lines; in film and dotted lines; in chloroform.

TABLE 1 Absorption Peak λ^A_{max} and Fluorescence Peak λ^f_{max} in Chloroform, Fluorescence Quantum Efficiency Φ_F, Natural Radiative Life Time τ_0, Fluorescence Life Time τ of Head-To-Tail Regioregular Thiophene Oligomers

X	λ^A_{max} (nm)	λ^f_{max} (nm)	Φ_F in $CHCl_3$	Φ_F in film state	τ in $CHCl_3$ (nsec)	τ in film state (nsec)	τ_0 (nsec)
2	303	380	–	–	–	–	5.62
3	339	442	0.04	–	0.14	–	3.53
4	372	494	0.09	0.07	0.29	0.24	3.38
5	391	503	0.18	0.09	0.50	0.26	2.72
6	405	527	0.29	0.09	0.68	0.27	2.36

spectrometer using time correlated single photon counting (Edinburgh Instruments, Lifespec-ps). The values of absorption peak λ^A_{max} and fluorescence peak λ^f_{max} in chloroform, fluorescence quantum efficiency Φ_F, natural radiative life time τ_0, fluorescence life time τ are summarized in Table 1.

In chloroform, fluorescence quantum efficiency Φ_F of the oligothiophenes increases with thiophene chain length, demonstrating that π-electron mobility is enhanced by elongation of π-conjugation. The value of Φ_F of the oligothiophene films is drastically decreased, comparing with those in chloroform. The drastic reduction of Φ_F may be caused by enhancement of encounter probability of excited state with quenching sites such as conformational and chemical defects through rapid energy migration between thiophene oligomers in film state.

In this work, we successfully prepared head-to-tail regioregular thiophene oligomers. The oligomer possessed good solubility to conventional organic solvents and good film processability. The study on regulation of aggregation structure of the oligothiophenes and relation between aggregation structure and electric properties, in particular, carrier mobility is now in progress.

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