

Note

SYNTHESIS AND OPTICAL PROPERTIES OF POLY(THIENYLACETYLENES)*

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Abstract 3-Ethynyl-4-(trimethylsilyl)thiophene (**1a**) and 3-ethynyl-4-bromothiophene (**1b**) selectively undergo acetylene polymerizations in the presence of the MoCl_5 - and WCl_6 - Ph_3SiH catalysts to give soluble, high-molecular-weight poly(thienylacetylenes) (**2**) (M_w up to 602000) in high yields (up to 100%). Light transmission spectra of THF solutions of **2** continuously red-shift with increasing concentration. The concentratochromism shows a logarithmic concentration dependence; that is, the optical transitions of **2** are predictably tunable by simply changing their concentrations.

Keywords Polyacetylenes, Poly(thienylacetylenes), Conjugated polymers, Optical materials, π - π interaction, Light transmission, Chromic effects

INTRODUCTION

Polyacetylene and polythiophene are two prototypical conjugated polymers and their electrical conductivity^[1], photoconductivity^[2], photo- and electroluminescence^[3], and nonlinear optical properties^[4] have attracted much attention. Certain substituted polythiophenes have been found to exhibit thermochromism and solvatochromism^[5]. Schrock et al. have found that electronic absorption spectra of THF solutions of a living polyacetylene red-shift when stored in the absence of air for some time^[6]. Design of macromolecules consisting of both acetylene and thiophene moieties is of interest because such polymers may exhibit unique electrical, optical, and optoelectronic properties. Materials properties are commonly utilized in the solid states, but optical transitions of molecules are usually studied in dilute solutions. Investigation into the optical transitions in concentrated solutions should help in gaining an insight into "real" transition events and molecular interactions in the solid states, where the materials are actually used. Such studies, however, have been a virtually unexplored research area. In this study, we synthesized

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poly(thienylacetylenes) (**2**) and studied their optical transitions in concentrated solutions. We found that the light transmission spectra of the THF solutions of **2** continuously red-shift with increasing concentration and that the novel concentratochromism observes a simple logarithmic concentration dependence.

EXPERIMENTAL

The thienylacetylene monomers (**1**) were prepared according to the published procedures^[7] and purified on a silica-gel chromatographic column (eluent: *n*-pentane) followed by simple distillation at atmospheric pressure. Both monomers gave satisfactory analysis data. Selected spectroscopic data for **1a**: ¹H-NMR (300 MHz, CDCl₃) δ (TMS) 7.59 (1H, *d*, *J* = 2.8 Hz, H of C-2), 7.32 (1H, *d*, *J* = 3.0 Hz, H of C-5), 3.10 (1H, *s*, CH $\equiv$), 0.25 (9H, *s*, Me₃Si); ¹³C-NMR (75 MHz, CDCl₃) δ (TMS) 143.25 (C-4), 131.93 (C-2), 131.67 (C-5), 125.54 (C-3), 80.25 (C $\equiv$), 78.15 (CH $\equiv$), -1.13 (Me₃Si). For **1b**: ¹H-NMR δ 7.51 (1H, *d*, *J* = 3.4 Hz, H of C-2), 7.23 (1H, *d*, *J* = 3.4 Hz, H of C-5), 3.25 (1H, *s*, CH $\equiv$); ¹³C-NMR δ 130.54 (C-2), 123.36 (C-3), 123.01 (C-5), 113.40 (C-4), 80.29 (CH $\equiv$), 77.42 (C $\equiv$).

The polymerizations of **1** were carried out under an atmosphere of dry nitrogen at room temperature. In a typical run, MoCl₅ (12.1 mg, 0.044 mmol) and Ph₃SiH (11.5 mg, 0.044 mmol) were admixed with freshly distilled toluene (0.7 mL) in a baked 20-mL Erlenmeyer flask and stirred at 80 °C for a few minutes. To this catalyst mixture was added a toluene solution (1.5 mL) of **1a** (0.4 g, 2.22 mmol). After stirring at 80 °C for 24 h, the polymerization reaction was terminated with a mixture (10 mL) of methanol and toluene (5:100 by volume). The reaction mixture was added via a cotton filter into a large amount of methanol (300 mL) with stirring. The precipitated polymer was filtered through a Gooch-type crucible and dried under vacuum to a constant weight. Purple fibrous solid; yield: 72%. *M_w* (GPC, polystyrene calibration): 168000; *M_w*/*M_n*: 3.4. Selected spectroscopic data for **2a**: ¹H-NMR (300 MHz, CDCl₃) δ (TMS) 6.91 (H of C-2), 6.08 (H of C-5), 5.79 and 5.40 (*trans* and *cis* CH=, respectively), 0.13 (9H, Me₃Si) [the peaks in the aromatic and olefinic absorption regions (7.5–5.0) are broad and overlap with each other, which makes the accurate integration of the individual peaks rather difficult]; ¹³C-NMR (75 MHz, CDCl₃) δ (TMS) 139.8 (C-2), 132.85 (C-5), 123.85 (—CH=), 1.01 (Me₃Si).

RESULTS AND DISCUSSION

The thienylacetylenes or ethynylthiophenes **1** were prepared by palladium-catalyzed coupling reactions between alkynes and 3-halogenated thiophenes^[7]. Compounds **1** are attractive monomers, because they may, under appropriate polymerization conditions, yield poly(thienylacetylenes) (**2**) and/or poly(ethynylthiophenes) (**3**), which may be further polymerized to give polyacetylene-polythiophene ladder polymers (**4**). The transition-metal halides such as MoCl₅ are well-known catalysts for both acetylene^[8] and thiophene polymerizations^[9]. Because the thiophene polymerization is via an oxidative coupling mechanism, to avoid possible complication of producing crosslinking products, we used a reducing agent Ph₃SiH as a cocatalyst to reduce the oxidation power of the metal halides in the hope of synthesizing soluble poly(thienylacetylenes). Thus, when a MoCl₅–Ph₃SiH mixture is used to initiate the polymerization of **1a**, a soluble polymer is obtained in high yield (Table 1, no. 1). GPC curves of the polymer recorded on both RI and UV detectors are monomodal with *M_w* as high as 168000. WCl₆–Ph₃SiH mixture is also an effective polymerization catalyst for **1a**, giving a soluble polymer at 89% yield. However, when WCl₆ alone is used to polymerize **1b**, the GPC curve of the resulting polymer is bimodal, giving a polydispersity index as high as 72.6 (Table 1, No. 4).

Table 1. Polymerization of thienylacetylenes^{a)}

No.	Monomer	Catalyst	Yield (%)	Polymer	
				$M_w^{b)}$	$M_w/M_n^{b)}$
1	1a	MoCl ₅ -Ph ₃ SiH	72	168000	3.4
2	1a	WCl ₆ -Ph ₃ SiH	89	108800	3.6
3	1b	MoCl ₅ -Ph ₃ SiH	100	584200	1.8
4	1b	WCl ₆	100	602100	72.6

a) Polymerized in toluene at 80°C for 24 h, $[M]_0 = 1.0$ mol/L, $[\text{cat.}] = [\text{cocat.}] = 20$ mmol/L; b) By GPC (polystyrene calibration)

The molecular structure of the polymers is characterized spectroscopically. The ¹H-NMR spectrum of the polymer from **1a** shows no absorption peaks from the acetylenic proton. Instead, two new peaks appear at $\delta = 5.79$ and 5.40, which are assignable to the *trans* and *cis* olefin protons, respectively, according to Shoolery's rules^[10]. Integration of the peaks in the unsaturated ($\delta = 7.5\sim 5.0$) and saturated ($\delta = -0.5\sim 0.5$) absorption regions gives a ratio of 3:9, confirming that only the acetylene triple bonds had undergone the polymerization reaction. If the thiophene moiety had undergone the coupling polymerization, the integration in the aromatic and olefinic regions would be less than 3. Furthermore, if only the thiophene moiety had undergone the coupling polymerization, there would be no absorption peaks in the aromatic and olefinic absorption regions at all. The ¹³C-NMR spectrum further supports the molecular structure of the polymer from **1a** as **2a**, possessing a backbone consisting of alternating double bonds. For the polymers obtained from **1b**, their polyacetylene backbone structure is also confirmed by the NMR analysis.

Figure 1 shows the light transmission spectra of THF solutions of **2a**. Interestingly, when the concentration (*C*) of **2a** changes, its transmission spectrum shifts. A concentration increase from 0.3 to 22.6 mg/mL causes a red-shift of the transmission spectrum as large as 126.1 nm. A cutoff wavelength (λ_c) may be defined as the wavelength at which light transmittance is 0.1%. When λ_c is plotted against $\lg C$, a straight line is obtained (Fig.2); that is, the light transmission in the polymer solutions observes a semilogarithmic relation of

$$\lambda_c = \alpha \lg C + k \quad (1)$$

where α and k are constants. As can be seen from Fig.2, the same λ_c -*C* relation holds for the THF solutions of **2b**.

To gain an insight into the possible causes and mechanisms of the concentratochromism, we further investigated optical transmission properties of THF solutions of other substituted polyacetylenes^[11, 12]. Transmission behavior of all the polyacetylene solutions follows eq. (1) and the slopes (α) of their λ_c -*C* plots are summarized in the inset of Fig.2. The α values for the two poly(thienylacetylenes) are quite high. The α value decreases when the thiophene group is replaced by a phenyl ring. Further decrease in α is observed when *t*-butyl groups are attached to the polyacetylene backbone. In the case of phenylacetylene (monomer), a 32-fold increase in concentration brings about a mere 12.2 nm red-shift in λ_c and accordingly its α value is negligibly small.

On the basis of the experimental results and taking into account that the polyacetylene backbone is rather rigid^[13], it seems reasonable to assume that the concentratochromism is derived from interchain π - π interactions in the conjugated polymer systems. The fact that the transmission spectra of the acetylene monomer solutions hardly red-shift with increasing concentration suggests that the alternating-double-bond backbones of the polyacetylenes are necessary for causing the concentratochromism. When the polyacetylene main chains are surrounded by the *t*-butyl side chains, the shielding effect of the bulky aliphatic groups would hinder the π - π interactions of the alternating-double-bond backbones, thus only limited concentratochromic effects were observed in

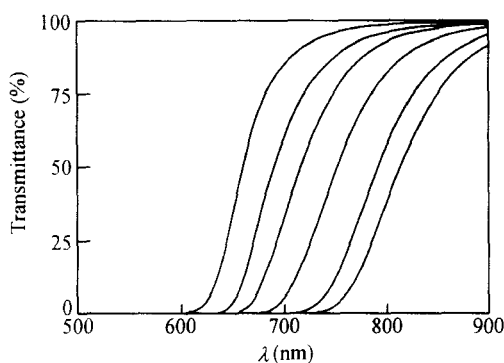


Fig. 1 Light transmission spectra of THF solutions of **2a**

Concentration of **2a** (from left to right): 0.3, 0.8, 1.9, 4.7, 12.8, 22.6 mg/mL

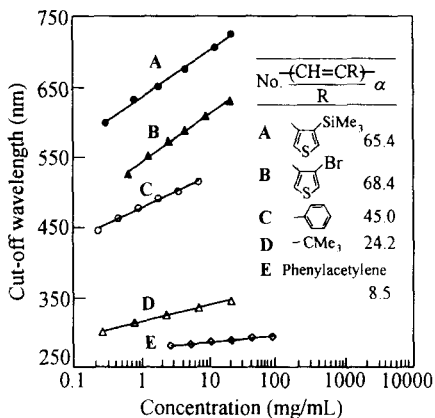


Fig. 2 Concentration dependence of cutoff wavelength of THF solutions of substituted polyacetylenes

Data for an acetylene monomer (phenylacetylene) is also shown for comparison.

the poly(*t*-butylacetylene) system. When conjugated aromatic groups like phenyl or thienyl are attached to the polyacetylene backbones, the increase in polymer concentration would facilitate the "contact" of the aromatic rings and thus intensify interchain π - π interactions via the aromatic side chains. Such interactions may effectively increase the conjugation length of the polymer systems, hence red-shifting the transmission spectra. Electron-donating and -withdrawing groups attached to the thienyl moieties may cause partial polarization of the ring systems, and interaction between such polarized ring systems would be stronger, thus inducing the pronounced concentratochromic effects.

We envision that the concentratochromism may be solvent-dependent because different solvents may have different effects on the interchain π - π interactions. An example of such solvatochromism is given in Fig.3. The λ_c - C plots for both the toluene and 1, 2-tetrachloroethane solutions of poly(phenylacetylene), observe eq. (1). However, compared with the toluene solution, the transmission spectrum in the tetrachloroethane solution was blue-shifted and its concentratochromic effect was more noticeable, as evidenced by its higher α value.

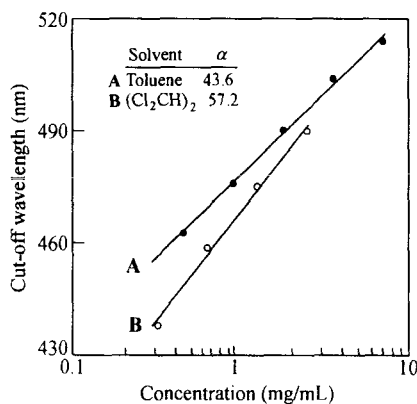


Fig. 3 Solvatochromism of poly(phenylacetylene) solutions

Attractive interactions between π -systems control such diverse phenomena as the vertical base-base interactions which stabilize the double helical structure of DNA^[14], the geometries of the interactions between aromatic residues in proteins which may be an important force in determining how proteins fold^[15], the intercalation of drugs into DNA^[16], the molecular recognition in chiral separation^[17], the complexation in host-guest systems^[18], the electron transfer in photoconductive polymers^[19], the packing of aromatic molecules in crystals^[20], and porphyrin aggregation^[21]. Because of the immense significance in chemistry, physics, and biology, a large amount of theoretical work has been done^[22], but experimental evaluation of the π - π interactions has been a nontrivial task. We demonstrate here that such interactions may be evaluated by a simple UV analysis. Comparison of the data in Fig.2 suggests that the stronger the π - π interactions, the steeper the slope of the λ_c - C plot or the higher the α value^[23]. Thus, the α value may serve as a sensitive indicator of the degree of the π - π interaction.

In summary, in this study, we synthesized novel conjugated polymers **2** whose repeating units consist of both acetylene and thiophene moieties, and discovered that the light transmission spectra of **2** are predictably tunable by a simple change in concentration. We found a simple rule, eq.(1), for light transmission in concentrated solutions, which may serve as a "spectroscopic ruler" for measuring the π - π interactions in conjugated polymer systems. The poly(thienylacetylenes) with tunable optical properties may find potential applications as optical filters, optical switches, optical limiters, etc^[24]. Further studies on synthesizing two-dimensional conjugated polyacetylene-polythiophene ladder polymers **4** using **2** as precursor polymers are under way. Our preliminary results indicate that the thiophene moieties in **2** undergo rapid polymerization in the presence of FeCl₃. Thus, when a fibrous **2a** sample is added to a chloroform solution of FeCl₃, the purple solid instantly changes to a black gel. Insoluble polymers also form in a concentrated solution of **2a**. However, when a dilute polymer solution is used, a black but soluble product is obtained. Obviously, the formation of the crosslinking products in the solid state and in the concentrated solution are due to the interchain thiophene polymerization. This further supports our hypothesis for the existence of the interchain π - π interactions between the thiophene groups in the poly(thienylacetylene) systems.

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