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Optical Properties of a Novel Carbon–Carbon Chain Polymer with Pendent Poly(thiophene)s

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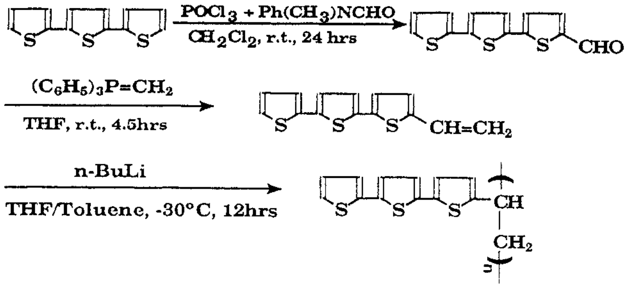
ABSTRACT: The synthesis of a novel soluble carbon–carbon chain polymer with pendent terthiophene groups, poly(5-vinyl-2,2′:5′,2″-terthiophene) (PVT), is described. The solvent-cast thin films of PVT display strong blue-green photoluminescence and, thus, PVT is expected to show electroluminescence in this region. The terthiophene side chains in PVT cross-link when the polymer is oxidized in solution or as thin films with $FeCl_3$ or $SbCl_5$. Based on model studies we have proposed that terthiophene radical cations, initially generated upon doping, slowly couple with neighboring neutral species to yield the radical cations of sexithiophene. The neutralization of the doped polymer with triethylamine yielded an insoluble, cross-linked material. The UV irradiation of thin films of PVT results in cross-linking and insolubilization of the polymer. The mechanism of the photoinitiated cross-linking reaction is discussed.

Conjugated polymers such as poly(arylenevinylene)s, poly(thiophene)s, and poly(*p*-phenylene) have received considerable attention recently mainly due to their interesting electrical and nonlinear optical properties which makes them good candidates for applications in rechargeable batteries and microelectronic devices.[1,2] For example, polythiophene and even thiophene oligomers have been utilized as semiconductors in prototype devices such as Schottky diodes,[3] metal-insulator-semiconductor field effect transistors,[4] and light emitting diodes.[5] Unfortunately, several of these rodlike macromolecules are intractable and thus are not amenable to conventional plastic processing technology. In recent years, considerable effort has been devoted by several researchers to design and synthesize new soluble electroactive polymers using different approaches,[1b,6] but very little has been done to produce side-chain polymers with pendent conjugated groups.[7] Furthermore, due to the growing interest in electroluminescent (EL) devices, comprised of plastics, several main-chain polymers with intermittent sequences of conjugated and nonconjugated segments have recently been prepared to gain control of color and efficiency of light emission.[8] Since the color of luminescence depends upon the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), we believe that the color of light emission can be controlled efficiently by producing polymers with a variety of pendent polyphenyls and poly(thiophene)s. Thus, we are attempting to synthesize several carbon–carbon chain polymers with pendent polyphenyls and poly(thiophene)s.[9] In this communication we report the synthesis and optical properties of a soluble carbon–carbon chain polymer with pendent terthiophene groups, poly(5-vinyl-2,2′:5′,2″-terthiophene) (PVT). The polymer displays strong blue-green photoluminescence (PL). Our studies demonstrate that UV irradiation of thin films of PVT results in cross-linking and insolubilization of the polymer. Furthermore, we have shown that the terthiophene residues of PVT cross-link when the polymer is oxidized with $FeCl_3$ or $SbCl_5$. The mechanisms of oxidative cross-linking and photoinitiated cross-linking reactions are discussed. The polymer was prepared according to Scheme I.

Scheme I



5-Formyl-2,2′:5′,2″-terthiophene[10] (FT) was prepared from terthiophene by a literature procedure.[11] The monomer, 5-vinyl-2,2′:5′,2″-terthiophene (VT),[12] was synthesized from FT by a Wittig reaction.[13] Our initial attempts to polymerize VT by either free radical methods (AIBN or dibenzoyl peroxide initiators) or anionic polymerization with *n*-butyllithium in THF were unsuccessful. Since the anionic polymerization is expected to be very slow in toluene,[14] polymerization was carried out in a mixture of THF and toluene (1:1) at −30 °C. The number-average molecular weight (M_n) of poly(5-vinyl-2,2′:5′,2″-terthiophene) (PVT) obtained by this method (estimated by GPC using polystyrene standard) is ca. 9100 (M_w/M_n = 1.21) which corresponds to about 33 repeat units. The ^1H NMR, ^{13}C solid-state NMR (cross-polarization, magic angle spinning), and elemental analysis of the polymer are consistent with the structure: ^1H NMR δ ($CDCl_3$) 1.55 (2H, $-CH_2$), 2.36 (1H, CH), 6.8–7.3 (7H, aromatic protons); ^{13}C NMR (CP/MAS) δ 37.00 (CH_2), 48.10 (CH), 124.86 (unsubstituted thiophene C's), 136.80 (substituted thiophene C's). Anal. Calcd for $C_{14}H_{10}S_3$ (repeat unit): C, 61.28; H, 3.67; S, 35.05. Found for polymer: C, 61.83; H, 3.73; S, 35.51.

The UV–vis spectrum of PVT in THF shows an absorption maximum at 361 nm, which is blue-shifted by about 20 nm compared to the monomer due to the loss of conjugation of the vinyl group with the terthiophene moiety.[15] The polymer, spin-cast from tetrahydrofuran (THF) on quartz plates, gave uniform, light-yellow films. The UV–vis spectrum of the polymer films shows a band at λ_{max} 366 nm at room temperature.

The emission spectrum of PVT in CH_2Cl_2 (λ_{ex} = 350 nm) displays a broad band from 410 to ca. 650 nm, centered at ca. 490 nm. The photoluminescence (PL) spectrum (λ_{ex} = 360 nm) of the polymer films shows a similar band

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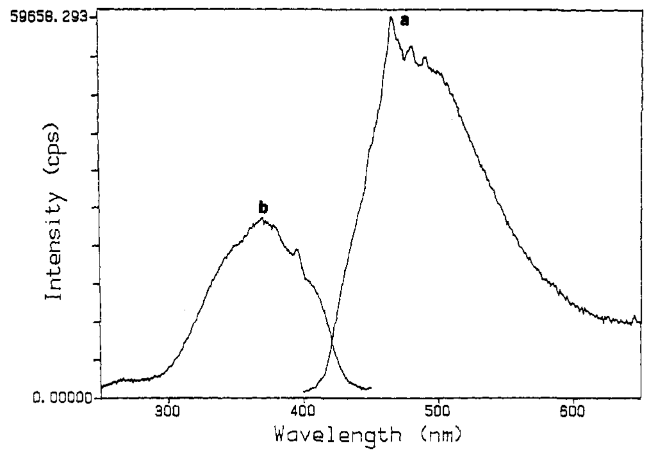

Figure 1. Photoluminescence ($\lambda_{excitation}$ = 360 nm) (curve a) and excitation ($\lambda_{emission}$ = 490 nm) (curve b) spectra of spin-cast thin-film of PVT.

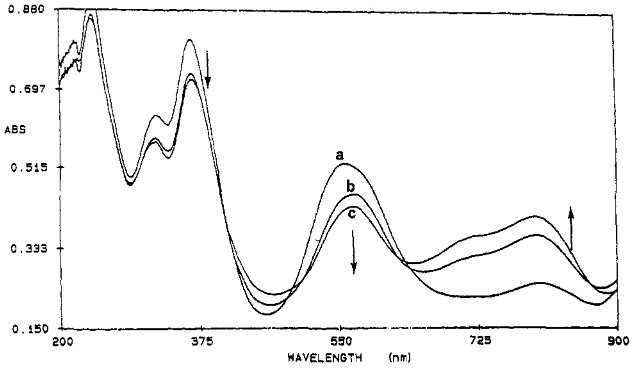

Figure 2. Absorption spectra of $FeCl_3$ doped (in CH_2Cl_2) PVT after 2 (a), 10 (b), and 30 (c) min of doping.

which is well within the blue and extends into the green (Figure 1). This luminescence is strong, and even under a bench top lamp (366 nm) the polymer films have an intense blue-green glow. Since the EL and PL emissions in the conjugated polymers examined thus far are very similar, we anticipate PVT to show electroluminescence in the blue-green region. Studies involving the fabrication of the electroluminescent diode and the measurements of the quantum yield in the polymer thin films are in progress. The excitation spectra (emission monochromator at 490 nm) of the polymer in solution and film are very similar to the respective absorption spectra. The excitation spectrum of the polymer film is shown in Figure 1.

The absorption spectrum of $FeCl_3$ doped PVT in CH_2Cl_2 at room temperature shows a strong new band at ca. 560 nm (2.14 eV). The intensities of the new band and the band at 366 nm (due to neutral terthiophenes) decrease over a period of 30 min with concomitant appearance of an additional absorption at ca. 810 nm (1.54 eV) (Figure 2). The spectral changes were minimal after 30 min. We have observed that the radical cation of α,α-dimethylterthiophene generated in CH_2Cl_2 by oxidation with $FeCl_3$ shows a strong band at ca. 580 nm.[16] Fichou et al.[17] recently reported a strong band at 1.59 eV in the absorption spectrum of the radical cation of sexithiophene in CH_2Cl_2. Apparently, terthiophene radical cations, initially generated upon doping of PVT, slowly couple with neighboring neutral species to yield the radical cations of sexithiophene.[18] The neutralization of the doped polymer with triethylamine yielded an insoluble, cross-linked material. We recently observed a similar oxidative cross-linking reaction in poly(2-thienylmethyl methacrylate).[9b]

The light-yellow films of PVT, upon exposure to $SbCl_5$ vapors under argon atmosphere, turned purple-blue. The UV–vis spectrum of the doped films displays a strong band at ca. 578 nm and a very weak band at ca. 835 nm, which indicates that oxidative cross-linking does not occur very efficiently in polymer films. The intensities of these bands do not change over several hours. Since in the solid state the movement of polymer chains is restricted, only those terthiophene side chains that are aligned head-to-head couple to give sexithiophene cation radicals.

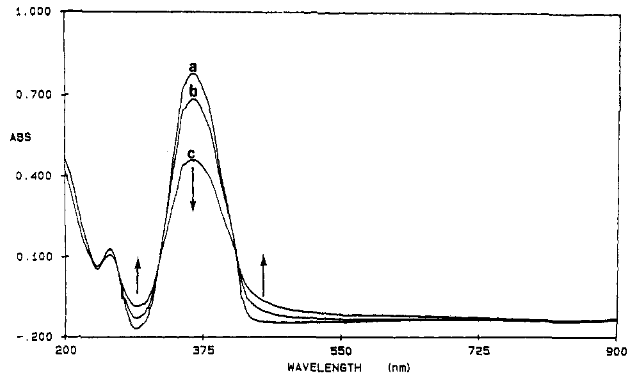

Figure 3. Absorption spectra of PVT before (a) and after 1 h (b) and 5 h (c) of irradiation at 366 nm.

Irradiation (366 nm) of thin films of PVT in ambient air causes the optical density of the band at 366 nm to decrease while two new weak absorptions appear to the blue and to the red of the original band with clean isosbestic points at 318 and 416 nm (Figure 3). The irradiated films became insoluble, indicating a significant amount of cross-linking. The polymer films, upon irradiation in argon atmosphere, remained soluble and the changes in the UV–vis spectrum were minimal. It is now well established that oligomeric and polymeric thiophenes are efficient photosensitizers of singlet oxygen.[19] Recently, Holdcroft et al.[20] demonstrated that solid-state photochemistry of poly(3-hexylthiophene) is dominated by two mechanisms: Diels–Alder addition of singlet oxygen to thienyl residues and photooxidation of the alkyl side chain. They have suggested that the latter reaction, mediated by $^{\bullet}OH$ and other oxygen centered radicals, is responsible for cross-linking and photoinsolubilization of the polymer. Similar pathways may explain the photochemistry of PVT. The photodegradation of the terthiophene residues by the Diels–Alder addition of the singlet oxygen to the thienyl rings and subsequent ring opening could explain the new bands at 1651 ($-C{=}C{-}C{=}O$) and 1047 ($C{=}S^{+}{-}O^{-}$) cm^{-1} in the infrared spectrum and the blue-shifted absorption in the UV–vis spectrum of irradiated PVT. A new band at 3427 ($-OH$) cm^{-1} in the IR spectrum of the irradiated PVT is consistent with photooxidation of the alkyl main chain by initial formation of hydroperoxide and its subsequent photolysis to give alkoxy radicals and $^{\bullet}OH$. Interestingly, in contrast to observations by Holdcroft et al.[20] in poly(3-hexylthiophene), we observe the growth of a longer wavelength absorption (ca. 440–725 nm) upon irradiation of PVT films. In addition, we find that the ratio of the intensity of the band at 835 nm (due to sexithiophene radical cation) to that at 578 nm (due to terthiophene radical cation) in thin films of PVT which have been irradiated for 30 min prior to doping with $SbCl_5$ is larger ($A_{835}/A_{578} \sim 1.0$) compared to that of unirradiated doped films ($A_{835}/A_{578} \sim 0.8$). Although this evidence is not conclusive, these results suggest the formation of sexithienyl residues, presumably by cross-linking of the terthiophene side chains, upon photolysis of polymer films. We are further investigating this photoinitiated cross-linking reaction.

The synthesis of other carbon–carbon chain polymers with pendent polythiophenes and polyphenyls is in progress.

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of 5-vinyl-2,2′:5′,2″-terthiophene and poly(5-vinyl-2,2′:5′,2″-terthiophene) (PVT), absorption spectra of doped and undoped THF cast PVT films, excitation ($\lambda_{emission}$ = 490 nm) and emission ($\lambda_{excitation}$ = 350 nm) spectra of PVT in CH_2Cl_2, absorption spectrum of doped UV-irradiated PVT film, and IR spectra (KBr pellets) of irradiated and unirradiated PVT films (9 pages). Ordering information is given on any current masthead page.

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