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Unusual solvatochromism in phosphonylated polythiophenes. Poly[3-(11-diethylphosphorylundecyl)thiophene]†‡§

Janusz Kowalik and Laren M. Tolbert

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA.
E-mail: janusz.kowalik@chemistry.gatech.edu

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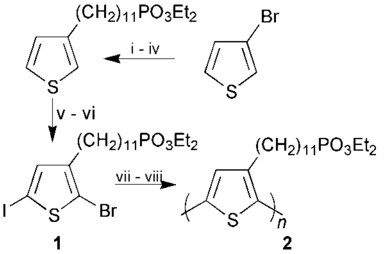
Highly stereoregular poly[3-(11-diethylphosphorylundecyl)thiophene] 2 is soluble in both aprotic and protic solvents, yet displays a remarkable solvatochromism involving a hydrogen bond network with the phosphonate moiety.

Since their discovery and synthesis two decades ago, polythiophenes (pT) have progressed swiftly to applications.[1] A promising area for conducting polymers includes development of sensors by using macromolecules with specific receptor groups.[1b,2] The search for functional groups influencing the properties of pTs as well as allowing the design of multidimensional, supramolecular systems for truly molecular applications is well underway. Among the most important properties of polythiophenes are thermochromism and solvatochromism. The origin of both phenomena is the optical response to a conformon formation, twists in which the planarity of the backbone has been disrupted. Both features are believed to be single chain phenomena, that is, the coexistence of two separate phases in different ratios during the process is responsible for the chromic behavior.[3] Given the diverse conformational chemistry produced in nature by organophosphorus moieties, the use of a phosphonate group in the polythiophene structure provides an attractive approach to developing higher orders of organization (supramolecular systems). Here, we offer the first example of a polythiophene containing the dialkylphosphonate functionality.[4] The polymer belongs to a limited group of polythiophenes soluble in both protic and aprotic solvents, yet exhibits remarkably divergent behavior in the two solvents. Polymer **2** was synthesized in a stereocontrolled process involving nickel-mediated Negishi-type condensation of **1**[5a] obtained in a series of reactions illustrated in Scheme 1.

The resulting polymer was *ca.* 90% stereoregular, with a predominantly head-to-tail (HT–HT) connectivity.[5a,6] The polymer displayed a high degree of conjugation in the solid state, as indicated by the presence of a vibrational structure in the UV–VIS spectrum and a λ_{max} value at 558 nm with a shoulder at 606 nm.[5] In aprotic solvents (THF, $CHCl_3$) the absorption spectrum became featureless and the absorption maximum shifted to 440 nm ($\Delta\lambda_{max}$ = 118 nm). Remarkably, in protic solvents (ethanol, methanol) the shape of the absorption spectrum remained similar to that in the solid state with only a small higher-energy shift in the absorption maxima, Fig.1(*a*) and (*b*).



Scheme 1 *Reagents and conditions*: i, $BrMg(CH_2)_{11}OMOM$, Ni(dppe)Cl_2, Et_2O, r.t. → reflux, 2 h, 70%; ii, HCl(aq)/MeOH, reflux, 6 h, 100%; iii, MsCl, Py, CH_2Cl_2, 0–5 °C, 5 h, 85%; iv, $NaPO_3Et_2$, THF, reflux, 30 h, 89%; v, NBS, DMF, r.t., 3 h, 88%; vi, I_2, HgO, PhH, 12 h, 80%; vii, Zn*,[5a] THF; viii, Ni(dppe)Cl_2, THF, r.t., 3 d.

The solvatochromic properties of **2** were observed in a mixed CH_2Cl_2–MeOH system, with the results shown in Fig. 1. Increasing the concentration of the CH_2Cl_2 caused a reduction in the intensity of the absorption in the 550–650 nm region, with concomitant increase in the higher energy region with a maximum at *ca*. 440 nm. The presence of a pseudo-isosbestic point[7] suggested two separate species (conformons) existing in equilibrium at ratios which depended on the concentration of the protic and aprotic solvents. Interestingly, the vibrational structure of the absorption is maintained at 10% CH_2Cl_2 in MeOH, which suggests the extended conjugation within the polyaromatic backbone was rapidly lost beyond that point, owing to the enhanced freedom of rotation. There are at least three possible self-organization mechanisms to be considered: self-assembly *via* alkyl chain association, phosphoryl group dipole–dipole interaction and hydrogen bonding. Owing to exceptionally good vibrational characteristics and the sensitivity of the phosphonate moiety to its microenvironment, IR spectroscopy has long been an attractive technique in studying its hydrogen bond interactions. The highly polarized P=O bond in organophosphorus compounds is an excellent hydrogen bond acceptor, yielding complexes ranging from weak (< 1 kcal mol^{-1})[8] to strong (> 10 kcal mol^{-1})[9] as a function of the hydrogen bond donor. Fig. 2 illustrates the dependence of the wavenumber shift of the ν(P=O) vibration on the solvent used.

As expected by analogy with adsorption of phosphonates on transition metal surfaces,[10] the major interaction with the hydrogen donor involves bonding *via* the lone pair orbitals of

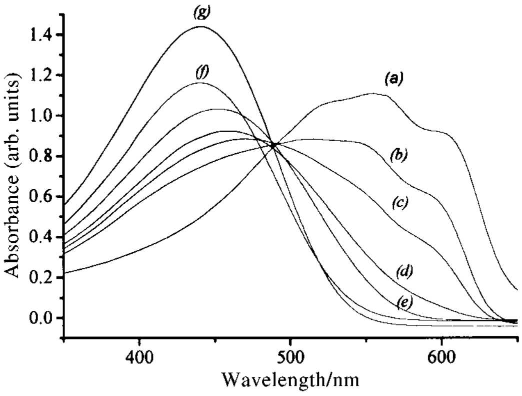


Fig. 1 Absorption spectra and solvatochromism of **2**: (*a*) solid film and (*b*)–(*g*) 10^{-4} M solutions in CH_2Cl_2–MeOH, v/v = *(b)* 0 : 10, (*c*) 1 : 9, (*d*) 2 : 8, (*e*) 3 : 7, (*f*) 8 : 2, (*g*) 10 : 0.

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† Dedicated to Professor Przemysław Mastalerz on the occasion of his 75th birthday.

‡ First presented in part at *The Fifth Chemical Congress of North America*, Cancun, Quintana Roo, Mexico, November 11–15, 1997, p. 123.

§ Electronic supplementary information (ESI) available: solutions of **2** in CH_2Cl_2 (left) and MeOH (right). See http: www.rsc.org/suppdata/cc/b0/b001621g/

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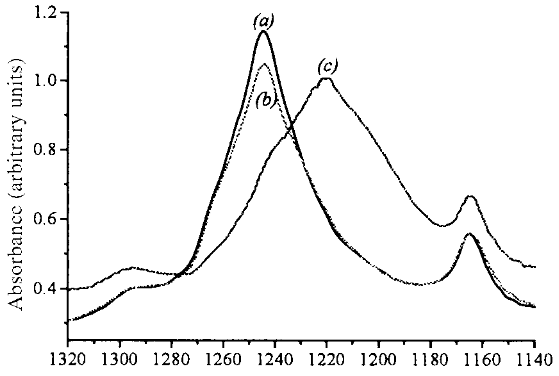

Fig. 2 IR spectra of **2** (P=O vibration): (*a*) solid film, (*b*) solid film saturated with CCl_4, (*c*) solid film saturated with MeOH.

the P=O oxygen atom. This leads to a weakening of the P=O bond and to a lowering of the corresponding mode frequency. In the gas phase, where the molecule is considered free, this peak has a maximum at 1276 cm^{-1}.[8] In our solid polymer film and the sample saturated with CCl_4 the P=O stretch appears at 1244 cm^{-1}. In the absence of a hydrogen donor it is likely that a dipole–dipole interaction between the phosphonate groups leads to aggregation[8,10a,11] and is responsible for the shift. Saturation of the polymer film with methanol leads to a shift of the P=O vibration to 1216 cm^{-1}. This absorption displays a shoulder at 1208 cm^{-1}. We suggest that the presence of two vibrational modes relates to the presence of two modes of interaction of the phosphoryl oxygen atom with the hydrogen bond donor, the 1208 cm^{-1} peak corresponding to interaction of the P=O group using both lone electron pairs.[8] The frequency shift of 28 cm^{-1} is considered indicative of a strong hydrogen-bonding interaction.[12] Hydrogen bond interactions were tested by NMR spectroscopy. ^1H NMR spectra for solutions of the polymer **2** in THF-d_8 and CD_3OD are shown in Fig. 3(*a*) and (*b*).

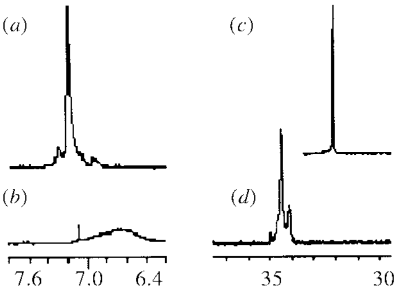

Fig. 3 ^1H NMR spectra of **2** (aromatic region) in: (*a*) THF-d_8, (*b*) CD_3OD (δ relative to TMS). ^{31}P NMR spectra of **2** in: (*c*) THF-d_8, (*d*) CD_3OD (δ relative to 85% H_3PO_4 (external)).

While the aromatic proton resonance of **2** in deuterated THF solution appeared as a sharp singlet at δ 7.08 (fast spin–spin relaxation), the corresponding resonance in CD_3OD solution showed line broadening characteristic of a spectrum of a highly associated species. The breadth of the aromatic proton signal in the range δ 6.3–7.1 could also arise from paramagnetic line broadening,[13] which is related to the observed extension of the effective conjugation in the polyheterocyclic chain. This is in agreement with the results of the UV–VIS spectroscopy. Fig. 3(*c*) and (*d*) illustrate ^{31}P NMR spectra of **2** in THF-d_8 and CD_3OD. The observed chemical shifts of δ *ca.* 32–34 (*vs.* 85% H_3PO_4, external) are consistent with the dialkyl phosphonate moiety.[14] A sharp, narrow signal at δ 32.11 due to an averaged species appeared in the THF-d_8 solution, whereas in CD_3OD solution broader, multiple resonances were observed in the range δ 34.97–34.12 ppm, with the most intense feature at δ 34.48. In contrast to the THF solution, for which delocalization of rapid spin diffusion resulted in a single averaged ^{31}P resonance, in CD_3OD solution the protonated segments of solvated phosphonate remained distinct on the NMR time scale giving rise to a multiplet of signals. The downfield shift of the resonance peak in methanol solution, $\Delta\delta$ = 2.4 ppm, is most likely a result of the deshielding effect due to hydrogen-bonding interactions. For interactions of diethyl 4-vinylphenylphosphonate with 1,1,1,3,3,3-hexafluoroisopropyl alcohol the $\Delta\delta$ value at 0.7 ppm corresponds to an enthalpy of hydrogen bond formation of $-\Delta H$ = 8.6 kcal mol^{-1}.[12b] Our considerably larger value of $\Delta\delta$ seems to indicate cooperative interaction of several factors, leading to a very efficient self-organization of **2** in a protic solvent.

In summary, we describe the first synthesis of a polythiophene containing a phosphonate function. The energy gap difference of *ca.* 0.4 eV between the polymer dissolved in a protic *vs.* aprotic solvent results in a remarkable solvatochromic effect. We suggest that a combination of London forces, dipole–dipole interactions and a hydrogen-bond network involving a protic solvent and the phosphonate moiety cooperate in stabilizing an extended conjugated form of the polymer.

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