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Synthesis and optical properties of water-soluble poly(*p*-phenylenevinylene)s

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A novel conjugated polymer containing carboxylic acid and 2-[2-(2-methoxyethoxy)ethoxy]ethoxy substituents which is soluble in both organic solvents and aqueous bases is synthesized.

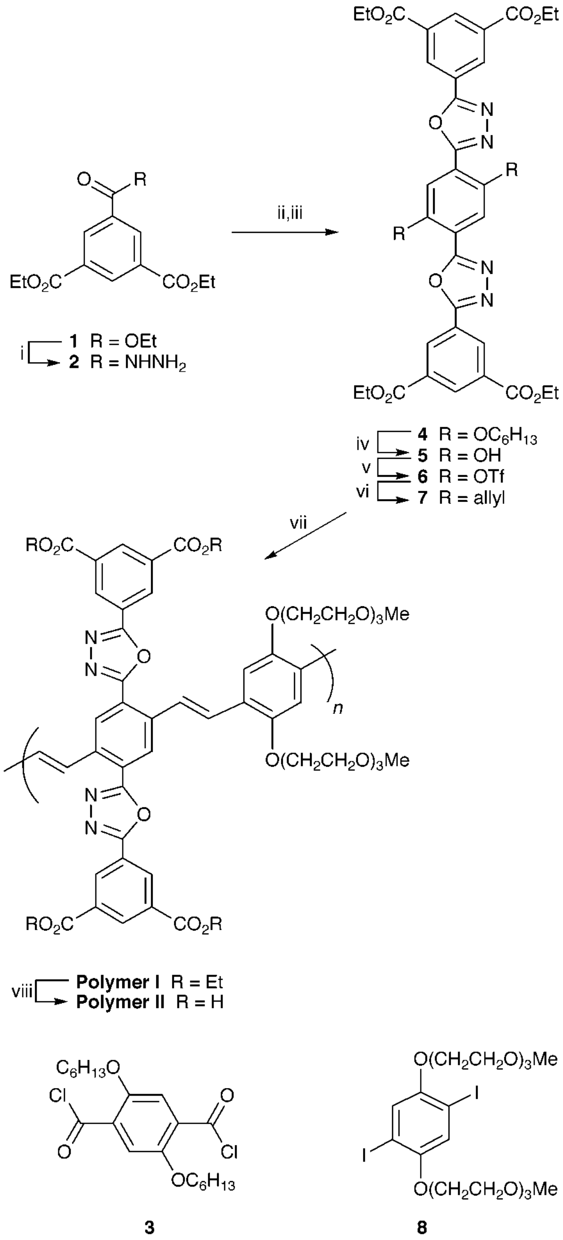
The most common driving force for the self-assembly of conjugated polymers is aromatic π–π interaction.[1,2] The resulting π–π stacking of conjugated polymers has a profound effect on the electronic and optical properties of the bulk polymers.[3,4] Controlling the self-assembly of conjugated polymers is thus of great importance for optimizing materials properties and producing novel new materials.[3–6] Conjugated polymers with polar functional groups such as hydroxy or carboxylic acid moieties may serve this purpose.[7,8] The controllable hydrogen bonding among hydroxy or carboxylic acid group allows modification of interchain interactions, thus altering the properties of the polymer. One such example is the regioregular polythiophenes with pendent carboxylic acid side chains, which have been demonstrated to be polymer chemoselective sensors.[8]

We are interested in designing hydrogen-bonded shape-persistent polymer networks. Our ultimate goal is to achieve stable, nanoporous polymer networks with controllable and uniform pore sizes. For this purpose, the polar functional groups have to be anchored in geometrically-fixed positions, rather than on flexible side chains.[7,8] Here we report the synthesis and optical properties of a water-soluble poly(phenylenevinylene) (PPV)-based polymer, shown in Scheme 1 as Polymer II. PPV, the most extensively studied electroluminescent polymer, was chosen as the polymer backbone.[9] The hydrogen-bonding anchors, isophthalic acids,[10] are covalently bonded to the PPV backbone through oxadiazole rings arranged orthogonally to the polymer backbone, a structure which assures shape persistence during self-assembly. The rigid arm and the polymer backbone are electronically cross-conjugated to enable the electronic and optical properties of the polymer backbone to change in response to the self-assembly process.

Polymer II was synthesized by the approach outlined in Scheme 1. Starting from triethyl benzene-1,3,5-tricarboxylate **1**, oxadiazole derivative **4** was synthesized in three steps. The two alkoxy groups in **4** were converted to vinyl groups (**7**) in an approach previously reported.[11] The precursor polymer (Polymer **I**) was synthesized by the Pd-catalyzed Heck coupling reaction of **7** with dihalide **8**,[12] which was synthesized by the reaction of 2,5-diiodohydroquinone with 3,6,9-trioxadecyl toluene-*p*-sulfonate.[13]

Polymer I is soluble in THF, $CHCl_3$ and CH_2Cl_2, and insoluble in DMSO, water and aqueous bases. Its weight-average molecular weight, measured by gel-permeation chromatography (GPC) at 30 °C with polystyrene as the standard, is 91 kDa with a polydispersity of 3.2. The hydrolysis of Polymer I was performed in THF with $KOBu^t$ as the base.[14] After hydrolysis, Polymer II shows opposite solubility characteristics to that of Polymer I. For example, Polymer II is insoluble in $CHCl_3$, slightly soluble in THF, and soluble in DMSO and dilute aqueous bases such as NaOH, NH_4OH *etc*. The structures of both polymers were confirmed by spectroscopic studies and elemental analysis.

Polymer II shows unusual solubility behavior in aqueous bases. For example, Polymer II is only soluble in aqueous NaOH solutions with limited NaOH concentration (between 2 and 0.01 M). It is insoluble in solutions with NaOH concentrations that are too high (> 3 M) or too low (< 0.001 M). The decreased solubility of Polymer II in concentrated NaOH solutions may be related to the crown ether–metal ion type of bonding between ethylene oxide side chains of different polymer chains and metal ions. Such interaction results in a less soluble polymer network.



Scheme 1 *Reagents and conditions*: i, NH_2NH_2, EtOH, 52%; ii, **3**, Et_3N, $CHCl_3$, 87%; iii, $POCl_3$, 78%; iv, BBr_3, CH_2Cl_2, 93%; v, Tf_2O, pyridine, 86%; vi, tributylvinyltin, $Pd(PPh_3)_4$, 45%; vii, **8**, $Pd(OAc)_2$, $P(o\text{-}Tol)_3$, DMF, 90%; viii, $KOBu^t$. THF, quant.

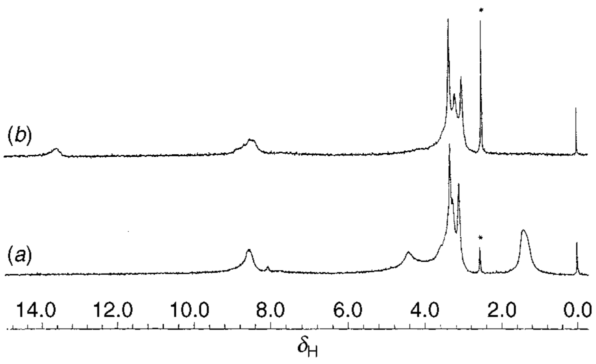


Fig. 1 ^{1}H NMR spectra of polymers (*a*) I and (*b*) II.

Fig. 1 shows the ^{1}H NMR spectra of both polymers. Before hydrolysis, Polymer I shows chemical shifts due to ester moieties at δ 4.40 and 1.5. The chemical shifts due to the ethylene oxide moieties appear between δ 3.0 and 3.7 as broad multiple peaks. The aromatic and vinyl protons are totally overlapped; only one broad peak at δ 8.6 is observed. After hydrolysis, a new peak at δ 13.5, corresponding to the carboxylic acid protons, appeared in the spectrum of Polymer II. The chemical shifts due to the ester moieties in Polymer I disappeared, indicating complete hydrolysis. Attempts to carry out the hydrolysis in acidic media such as TFA were unsuccessful.[15] It was found that, under acidic conditions, the conjugated polymer backbone was destroyed, resulting in a yellow polymer. Apparently, the acidic protons attacked the vinyl bond in the PPV backbone. The vulnerability of the vinyl bond to proton attack may be due to the partial polarization induced by the alternate electron-withdrawing and electron-donating substitution pattern of the backbones.

Polymer II also possesses good thermal stability. Differential scanning calorimetry (DSC) measurement and thermal gravimetric analysis (TGA) show that Polymer II has a decomposition temperature above 325 °C. No crosslinking process, common to the PPV backbone, is observed in the temperature range of 50–350 °C, indicating that the vinyl bonds on different polymer chains are well separated.

Fig. 2 shows the UV/Vis and fluorescence spectra of both polymers. Polymer I has two absorption peaks: *ca.* 506 nm is the absorption peak of the PPV backbone, *ca.* 310 nm can be assigned to the conjugated oxadiazole unit. After hydrolysis, the absorption of the PPV backbone is slightly blue-shifted, especially in aqueous base solutions. The maximum absorption wavelength in 1% NaOH is 484 nm.

Polymer I shows red fluorescence with an emission maximum at 615 nm. The photoluminescence quantum efficiency of Polymer I in dilute THF solutions is 3.7%. The fluorescence of Polymer II is significantly blue-shifted compared to that of Polymer I and is dependent on the choice of solvents. When a dilute DMSO solution of Polymer II was excited at 510 nm, a maximum emission at 555 nm with a shoulder at around 595 nm was observed. Polymer II in dilute NaOH solution, however, has an emission maximum at 593 nm, nearly 40 nm red-shifted compared to that of its DMSO solutions, and has a photoluminescence quantum efficiency of 4.2%.

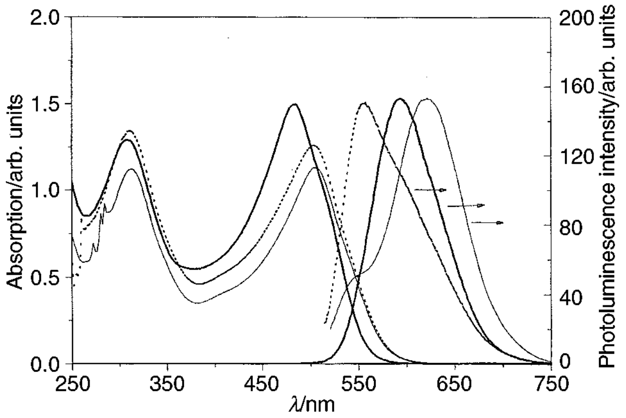


Fig. 2 Fluorescence and UV/Vis spectra of polymers I and II in solution. (*a*) I in THF, (*b*) II in 1% NaOH, (*c*) II in DMSO.

In summary, we have synthesized a novel PPV polymer containing carboxylic acid functional groups. This polymer possesses solubility in both organic solvents (DMSO) and aqueous bases (such as NaOH, NH_4OH *etc.*). The unique structure of this polymer makes it an attractive system for self-assembly studies. Its high electron affinity[11] and photoluminescence properties also warrant further study of this polymer for light-emitting diode applications, particularly as an electron-transporting layer in multilayer devices.

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Notes and references

1 *Conjugated Polymers*, ed. J. L. Bredas and R. Silbey, Kluwer, The Netherlands, 1991.
2 T. A. Skotheim, Ed. *Handbook of Conducting Polymers I & II*, ed. T. A. Skotheim, Marcel Dekker, New York, 1986.
3 N. C. Greenham and R. H. Friend, *Solid State Phys.*, 1995, **49**, 1.
4 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.
5 T. Bjørnholm, D. R. Greve, N. Reitzel, T. Hassenkam, K. Kjaer, P. B. Howes, N. B. Larsen, J. Bøgelund, M. Jayaraman, P. C. Ewbank and R. D. McCullough, *J. Am. Chem. Soc.*, 1998, **120**, 7643.
6 V. V. Tsukruk, *Prog. Polym. Sci.*, 1997, **22**, 247.
7 R. D. McCullough, P. C. Ewbank and R. S. Loewe, *J. Am. Chem. Soc.*, 1997, **119**, 633.
8 I. Benjamin, H. Hong, Y. Avny, D. Davidov and R. Neumann, *J. Mater. Chem.*, 1998, **8**, 919.
9 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
10 K. Eichhorst-Gerner, A. Stabel, G. Moessner, D. Declerq, S. Valiyaveettil, V. Enkelmann, K. Müllen and J. P. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1492.
11 Z. Peng and J. Zhang, *Chem. Mater.*, 1999, **11**, 1138.
12 R. F. Heck, *Org. React.*, 1982, **27**, 345.
13 B. Winkler, L. Dai and A. W. H. Mau, *Chem. Mater.*, 1999, **11**, 704.
14 F. C. Chang and N. F. Wood, *Tetrahedron. Lett.*, 1964, 2969.
15 D. J. Pesak, J. S. Moore and T. E. Wheat, *Macromolecules*, 1997, **30**, 6467.

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