

Increased Alignment of Electronic Polymers in Liquid Crystals via Hydrogen Bonding Extension

Johan Hoogboom and Timothy M. Swager*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Received August 4, 2006; E-mail: tswager@mit.edu

Generating highly anisotropic materials is central to achieving enhanced performance in organic electrooptic materials.^{1,2} We have been interested in making use of the facile ability of nematic liquid crystals to display macroscopic order to control the chain conformation and alignment of poly(phenylene ethynylene)s (PPEs).^{3,4} In previous studies, we have established the role of pendant itpycene units to create sufficient solubility and a strong coupling to the molecular directors of nematic liquid crystals.^{3–7} These methods produce electronic polymers with chain-extended planar conformations for improved transport properties. Enhanced transport promises superior performance in electronics, photovoltaics, and sensor applications. However, just as the polymer's alignment can be influenced by the liquid crystal, the director of the liquid crystal can also be influenced by the presence of an extended rigid polymer. As a result, it is attractive to consider shape-persistent polymers in networks or as ultrahigh molecular weight forms that can span the gaps between critical features (e.g., electrodes) in electrooptic devices and thereby produce a homogeneous anchoring element for alignment of liquid crystals.

Here, we show that the dichroic ratio (DR) and polymer ordering, determined from the polarized absorption of the PPE, increase dramatically when *interchain* interactions of the polymer are increased by introducing hydrogen bonding end groups (Figure 1). To accomplish this goal, we have appended PPEs previously shown to exhibit high dichroic ratios with ureidopyrimidinone (Upy) end groups. UPys have been extensively studied by Meijer and co-workers and exhibit self-association constants of 10^7 in organic solvents.^{8,9} Furthermore, it has been shown that the incorporation of hydrogen bonding groups into polymers can give rise to enhanced polymer properties and very interesting structures.^{10–13} In this paper, we demonstrate that hydrogen bonding interactions between PPEs dramatically improve their alignment in and the stability of liquid crystal solutions.

The end capping hydrogen bonding unit **2** (Chart 1) was synthesized in a four-step reaction adapted from literature procedures,¹⁴ in 39% isolated yield (see Supporting Information). The synthesis of the triptycene compounds has been described elsewhere.⁴

The dimerization of **1** was studied with NMR spectroscopy. The monomer and dimer exchange slowly on the NMR time scale, and distinct signals are observed for both species, thereby allowing a dimerization constant to be determined by integration.^{15,16} In pure chloroform, the monomer concentration was below the NMR detection limit. However, by using hydrogen bonding cosolvent mixtures (CDCl₃ with DMSO-*d*₆ or MeOD), the dimerization constants could be measured and K_{dim} can be estimated by extrapolation to 0% cosolvent. This method is only approximate because of the loss of correlation for very low concentrations of

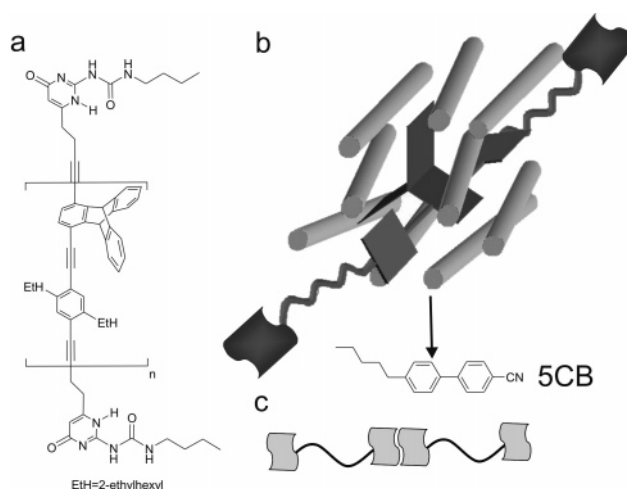
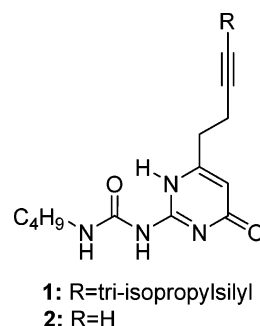


Figure 1. (a) PPE end capped with UPy groups. (b) Schematic representation of the alignment of PPEs by a nematic LC. (c) Schematic representation of interpolymer interactions mediated by hydrogen bonding.

Chart 1



cosolvent, as observed before by Meijer (see Supporting Information),¹⁵ but indicate a lower limit for the dimerization constant of 10^6 .

The end-capped polymer was synthesized by first allowing diethynyltriptycene (1 equiv) and di-2,5-(2-ethylhexyl)-1,6-diiodobenzene (1 equiv) to react under Sonogashira conditions. After a period of time, half of the reaction mixture was worked up to serve as a blank (**P1a**: 18 h and **P2a**: 4 h) and then 0.05 equiv of **2** was added to the other half and allowed to react for 2 more hours to yield end-capped **P1b** and **P2b**. Variations in the reaction times allowed for polymer growth before the addition of **2** (Table 1), with longer reaction times (more than 4 h) giving higher molecular weight polymers with a relatively low percentage of hydrogen bonding units, which were isolated as powders that formed gels in common solvents. Shorter reaction times (less than 4 h) provided lower molecular weight polymers with a higher percentage of

Table 1. Physical and Spectral Data of Polymers **P1** and **P2**

polymer ^a	M_n (KDa)	PDI	λ_{\max} sol (nm)	λ_{\max} LC (nm)	dichroic ratio
P1a	15	2.5	385	405	8.7
P1b	18	2.6	385	405	13.2
P2a	3	2.0	385	407	8.5
P2b	3	2.0	385	407	14.2

^a **a** denotes the blank; **b** is end capped with **2**.

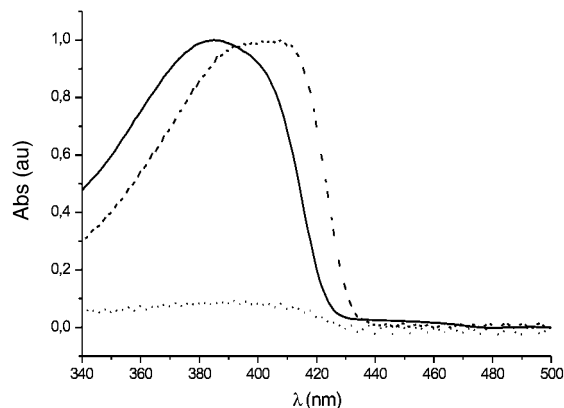


Figure 2. Normalized absorption spectra of **P2b**: in chloroform solution (solid), polarized absorption in an LC cell with parallel (dashed lines) and perpendicular (dotted lines) polarizer with respect to the LC director.

hydrogen bonding units. The latter gave materials that are more useful for our studies, forming elastomers and gels.

Polymer characterization with FTIR clearly showed the formation of hydrogen bonds in solid state and an extensive hydrogen bonding network upon gel formation. Upon going from methanol solution to a gel phase, the NH peaks of the polymer sharpened up considerably and shifted to lower wavenumber. In addition, a splitting of the main broad NH peak into two sharper peaks indicated that strong hydrogen bonding takes place upon formation of the gel phase (see Supporting Information).

Absorption spectroscopy showed a characteristic peak at 385 nm for chloroform solutions of the PPEs (Figure 2). Upon dissolving the polymer in 5CB and transferring it into a parallel rubbed liquid crystal cell, the absorption maximum shifted to 407 nm, indicative of the increased conjugation length of the polymer.^{2–4}

Polarized absorption of the liquid crystal solutions in parallel aligned test cells showed that the polymers end capped with **2** display much higher dichroic ratios than their nonfunctionalized counterparts (Figure 2, Table 1, Supporting Information). This indicates that end capping the PPE with **2** dramatically increases the polymer ordering, even at the low concentration of polymers used in these experiments (0.6 wt % **P1** and 0.78 wt % **P2**).

The direct involvement of hydrogen bonding in the increased dichroic ratio was shown by adding an excess of **1** to **P1b** and **P2b**. The dichroic ratio decreased in time (Figure 3) and leveled off around the dichroic ratio values obtained for **P1a** and **P2a**. We also conducted control experiments with **P1a** and **P2a** and found no change in dichroic ratio upon addition of similar amounts of **1**. This clearly supports that extended PPEs, created by intermolecular hydrogen bonding, have increased ordering, and that the materials are still able to equilibrate with other hydrogen bonding donors (Figure 3, inset).

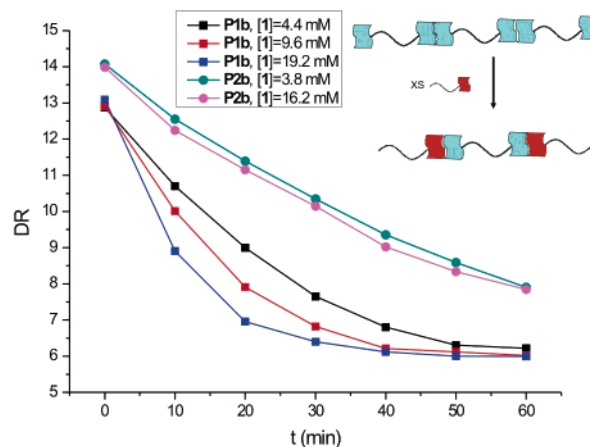


Figure 3. Plot of the dichroic ratio versus time of compounds **P1b** and **P2b** upon addition of various concentrations of **1**. Inset: schematic depiction of the effect of **1** on hydrogen bonding interactions.

In conclusion, PPEs end capped with hydrogen bonding moieties can be readily synthesized in high yield, with the polymer properties depending on the reaction time for polymer growth. The hydrogen bonding interactions between the polymer chains dramatically increase the dichroic ratio of the system.

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Supporting Information Available: Synthetic procedures and characterization, dimerization studies and FTIR, morphology of the polymers and polarized absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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