

## Conjugated Polymer Liquid Crystal Solutions: Control of Conformation and Alignment

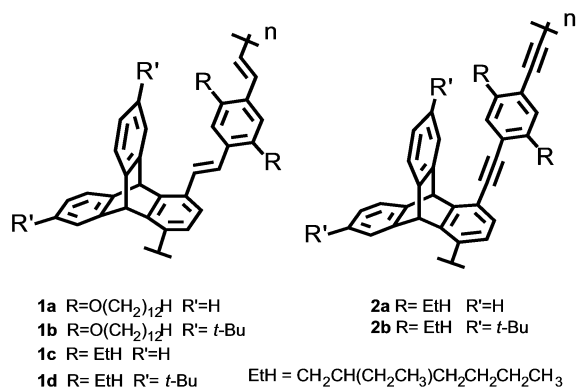
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The ability to control the orientation and electronic structure of molecules with extended electronic structure is the key to producing materials with optimized properties and to ultimately assembling molecular circuitry. Liquid crystals represent an ideal means to produce arrays of molecular wires; columnar liquid crystals with extended aromatic cores have long been considered as one-dimensional conductors.<sup>1</sup> Although these systems have shown promise, particularly as photoconductors, there is limited electronic coupling between the aromatic cores due to limited overlap of the  $\pi$ -orbitals, particularly in the liquid crystalline state. We have been interested in developing an alternative liquid crystal strategy for assembly of electronic materials whereby electronic polymers with very strong intramolecular electronic coupling (delocalization) are dissolved into a liquid crystal host. We have begun these studies with nematic liquid crystals because they are readily oriented over long distances and are easily reoriented (switched) by electric fields. We report herein switchable nematic solutions containing conjugated polymers and show that the conjugation length is extended over that observed in isotropic solutions.

To produce stable nematic solutions we synthesized fluorescent poly(phenylene vinylene)s, **1**, and poly(phenylene ethynylene)s, **2**,



containing rigid triptycene groups using Suzuki and Sonagishira protocols.<sup>2</sup> We have previously shown the triptycene groups to impart extraordinary solubility and have found that conjugated polymers containing these groups are soluble even without any flexible side chains.<sup>3</sup> This desirable solubility results from the fact that the rigid three-dimensional nature of the triptycene groups prevents strong interpolymer interactions (aggregation)<sup>4</sup> that cause the low solubility that typically plague conjugated polymers. The three-dimensional nature of the triptycene also has important organizational influences, and we have most recently established that the addition of triptycene structures can either be used to redirect<sup>5</sup> or enhance<sup>6</sup> molecular alignment in liquid crystals and

**Table 1.** Summary of Polymer Properties

| polymer                             | $M_n^e$<br>(kDa) | PDI | absorption <sup>a</sup><br>$\lambda_{max}$ (nm) | fluorescence <sup>a</sup><br>$\lambda_{max}$ (nm) | S in<br>LC <sup>b</sup> |
|-------------------------------------|------------------|-----|---|---|-------------------------|
| <b>1a</b> <sup>c</sup>              | 10.4             | 3.0 | 435   | 510   | NA                      |
| <b>1b</b>                           | 8.3              | 2.3 | 424 (428)                                       | 506 (519)   | 0.43                    |
| <b>1c</b>                           | 12.2             | 2.2 | 417 (424)                                       | 484 (499)   | 0.62                    |
| <b>1d</b>                           | 12.6             | 2.5 | 416 (437)                                       | 487 (491)   | 0.69                    |
| <b>2a</b>                           | 22.9             | 2.9 | 384 (412)                                       | 419 (428)   | 0.73                    |
| <b>2a</b> (low $M_n$ ) <sup>d</sup> | 8.55             | 2.3 | 383 (413)                                       | 418 (428)   | 0.73                    |
| <b>2b</b>                           | 26.2             | 2.3 | 385 (413)                                       | 419 (427)   | 0.75                    |
| <b>2b</b> (low $M_n$ ) <sup>d</sup> | 8.07             | 2.0 | 382 (413)                                       | 419 (427)   | 0.79                    |

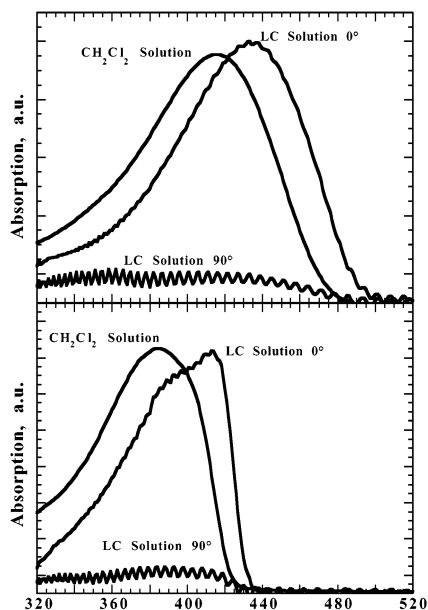
<sup>a</sup> Values in CH<sub>2</sub>Cl<sub>2</sub> solution and the corresponding values in a 6CHBT solution are shown in parentheses. <sup>b</sup> Calculated from the absorption spectra recorded on a 10-mm cell loaded with 1% polymers in 6CHBT, through a polarizer parallel and perpendicular to the director of the polyimide on the surface. <sup>c</sup> This polymer was not totally soluble in 6CHBT. <sup>d</sup> Synthesized in a polymerization mixture containing 0.1 equiv phenylacetylene endcapping agent in place of 0.05 equiv of dialkyne monomer. <sup>e</sup> Relative to polystyrene standards (GPC), which overestimates  $M_n$  for low-molecular weight PPEs and gives closer correlations with absolute molecular weights for higher-molecular weight materials.<sup>8</sup>

stretched polymers. This property results from the natural tendency of host-guest mixtures to lower their energy by minimizing the amount of free volume.

A cursory examination of polymers from our own laboratory shows that polymers that are completely soluble in typical organic solvents (CHCl<sub>3</sub>, toluene), but that lack triptycenes, were not soluble in the nematic liquid crystal phases of 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CHBT,  $T_m = 12.4$  °C,  $T_{NI} = 42.4$  °C), and 4-(*trans*-4-pentyl-cyclohexyl)benzotrile (5PCH,  $T_m = 30$  °C,  $T_{NI} = 55$  °C). As a result, the triptycenes in **1** and **2** appear to be critical elements for the creation of homogeneous conjugated polymer nematic solutions. To further enhance solubility, *tert*-butyl groups were added to **1b**, **1d**, and **2b**, and we found that these materials dissolved even more readily in the liquid crystals.

To test the alignment of the polymer in LCs, solutions of **1** and **2** in 6CHBT were loaded into liquid crystal cells with rubbed internal polyimide surfaces that give a homogeneous alignment of the nematic liquid crystal. Polarized absorption spectroscopy of these test cells with the polarizers aligned parallel (0°) or perpendicular (90°) to the nematic director were used to calculate the order parameters. These measurements and other properties are summarized in Table 1. Representative spectra for **1d** and **2a** are given in Figure 1.<sup>7</sup> In most cases the optical order parameter, *S*, is high, and in all cases the polymer long axes align with the director of the nematic liquid crystal. On the basis of the high-order parameters we can safely assume that the polymer chains are in a highly extended conformation as opposed to a typical random coil present in isotropic solution. Polymer **1a** is only partially soluble and thereby complicated analysis of the alignment. The addition of *tert*-butyl groups to **1b** produces homogeneous solutions in the liquid crystals. The lower-order parameter in **1b** relative to the other

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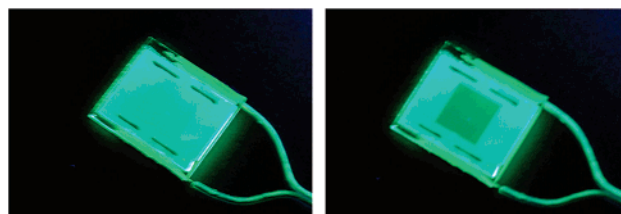


**Figure 1.** Absorption spectra taken at rt of **1d** (top) and **2a** bottom in  $\text{CH}_2\text{Cl}_2$  and 6CHBT. The red-shift in the liquid crystal solution is clearly apparent, and the alignment is apparent from the ratio of the spectra taken at  $0^\circ$  and  $90^\circ$  to the nematic director. The periodic signal at  $90^\circ$  is due to interference effects from the rubbed polyimide coatings.

polymers is likely related to the dodecyloxy side chains that have a preferred conformation that extends them from the polymer's backbone, thereby disrupting the surrounding liquid crystals. In the case of the ethylhexyl (EtH) side chains the branched structure facilitates conformations that align the side chains with the polymer backbone and consequently coincident with the liquid crystal director.

Further proof that the polymers form true solutions is revealed by demonstrating that the polymers realign with the nematic director when a voltage (9 V) was applied across the cell. Under an applied field the nematic director and the polymer backbones align normal to the surface of the cells. This results in a dramatic reduction (75–85%) in the polymer absorption and complete loss of polarization. These results are due to the realignment of the polymer, and consequently its transition dipole, in the direction of the electric field (normal to the test cell surfaces), which minimizes the projection of the transition dipole along the electric vector of the incident light beam. The reorientation of the polymer is also readily apparent by visualizing the polymer's fluorescence in the presence and absence of an applied voltage as shown in Figure 2. In all cases the polarized fluorescence is rapidly recovered upon removal of the voltage.

A particularly important aspect of conjugated polymer liquid crystal solutions is the fact that we observe an enhancement in the effective conjugation length of the polymers.<sup>9</sup> This is readily seen in Figure 1 wherein the liquid crystal solutions absorb further to the red than isotropic solutions in methylene chloride. The red-shift in the polymers is not simply a solvatochromic effect as the absorptions of the polymers blue-shift upon heating these solutions above the liquid crystal's isotropic transition. Hence, it appears that



**Figure 2.** Fluorescent image of a test cell containing **1d** in 6CHBT. At the left a test cell is shown with no applied voltage, and the nematic director and polymer are aligned with the short axis of the cell. At the right, 9 V is applied between ITO pads on the top and bottom of the test cell that realigns the liquid crystal and polymer normal to the glass slides.

the nematic liquid crystalline state promotes an extension of the conjugation length of the polymers. Such effects are highly desirable to optimize the transport properties of these materials.

In the case of polymers **2** we also examined the effect of molecular weight and purposely produced low-molecular weight materials by polymerizing in the presence of small amount of phenylacetylene (2–10% by mole), which serves as an endcapping agent. High-molecular weight materials ( $M_n > 30$  kDa) were too insoluble to form homogeneous solutions; however, the moderate- and low-molecular weight samples detailed in Table 1 were well behaved. The lower-molecular weight PPEs most readily formed homogeneous solutions; however, only **2b** gave an improvement in  $S$  at lower molecular weight.

In summary, we have shown that specially designed conjugated polymers form well-aligned, highly conjugated, chain-extended structures in nematic liquid crystals that may be redirected with electric fields. The ability to organize polymers in this fashion can be used to create new molecular electronic devices wherein polymers are extended between electrodes. Furthermore nematic solutions may be useful in processing polymers into highly organized states for optimization of transport properties in sensors, electroluminescent devices, and field effect transistors.

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**Supporting Information Available:** Additional data and synthetic preparations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

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- (2) For details see the Supporting Information.
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