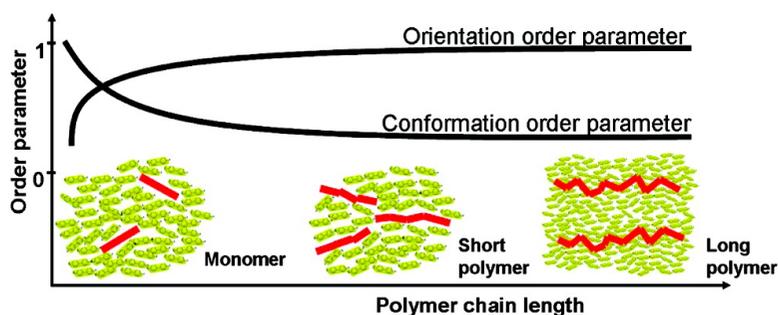


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J. Am. Chem. Soc., **2008**, 130 (37), 12262-12263 • DOI: 10.1021/ja805017m • Publication Date (Web): 19 August 2008

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Chain-Length Dependent Nematic Ordering of Conjugated Polymers in a Liquid Crystal Solvent

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The nanoscale ordering of conjugated polymers plays an important role in enhancing the performance of organic electronic devices.^{1–5} Key to this effort is the use of long-range supramolecular interactions to create organized self-assembled structures.^{6–8} In particular, liquid crystalline (LC) solvents are ideal templates for inducing the large-scale nematic ordering of conjugated polymers.^{9,10} According to Onsager,¹¹ the degree of alignment in a nematic mixture is enhanced for rodlike solutes that are longer than the LC solvent molecules. This prediction has recently been verified for a conjugated polymer solute in an LC solvent using single molecule spectroscopy.^{12,13} Correlated long-range anisotropic solvation forces are thought to be responsible for a nearly perfect polymer alignment—an effect termed “cooperative anisotropic solvation” (CAS).¹² However, it is not well established how much longer the polymer solute has to be to experience an enhanced ordering.

In this communication, we demonstrate the dependence of the solute order parameter on the solute molecular weight (M_n). Using ensemble absorption polarization spectroscopy together with single molecule fluorescence polarization measurements, we have determined the order parameter of the conjugated polymer MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]) in 5CB (4-cyano-4-n-pentylbiphenyl) as a function of chain length. For comparison to the solvent order¹⁴ and to approximate an oligomer, we also show results for the dye R6G.

The degree of solute alignment for five MEH-PPV samples and R6G was characterized using absorption spectroscopy. Figure 1 shows the polarized absorption spectra for MEH-PPV with $M_n = 12\,100$ in the nematic and isotropic phases. The absorption intensity in the isotropic phase A_{iso} agrees well with the isotropic average, $\langle A \rangle = A_{||} + 2A_{\perp}$, verifying the homogeneous solvation of the MEH-PPV. The dichroic ratio, $D = A_{||}/A_{\perp}$, is larger than 1, indicating a parallel alignment of the conjugated polymer backbone with the LC director.^{15,16} The dichroic ratios determined at the absorption maximum increase with increasing M_n (inset) due to a better alignment of the longer polymer chains.

The weight-dependent ordering of MEH-PPV was further confirmed using single molecule fluorescence polarization spectroscopy. Figure 2 shows single molecule fluorescence polarization distributions for two MEH-PPV samples with $M_n = 53\,000$ and $M_n = 3\,900$. The mean polarization increases with increasing M_n as further illustrated in the inset.

The alignment and conformation of an uncollapsed polymer chain containing a small number of defects can be quantitatively expressed by two coupled order parameters, the orientation and conformation order parameters, S_o and S_c .^{12,13} By analogy to the solvent order parameter describing the orientation of the LC solvent molecules with respect to the LC director, $S_o = 1/2(3 \cos^2 \alpha - 1)$ gives the

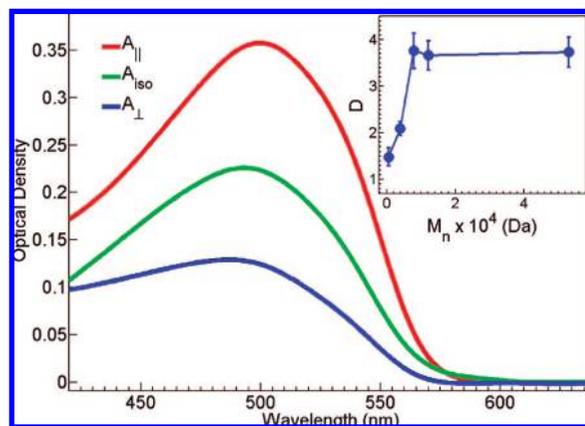


Figure 1. UV-vis absorption spectra of MEH-PPV ($M_n = 12\,100$) in the nematic and isotropic phases of 5CB. Inset: Dichroic ratio D as a function of M_n . Lines are given as guides to the eyes.

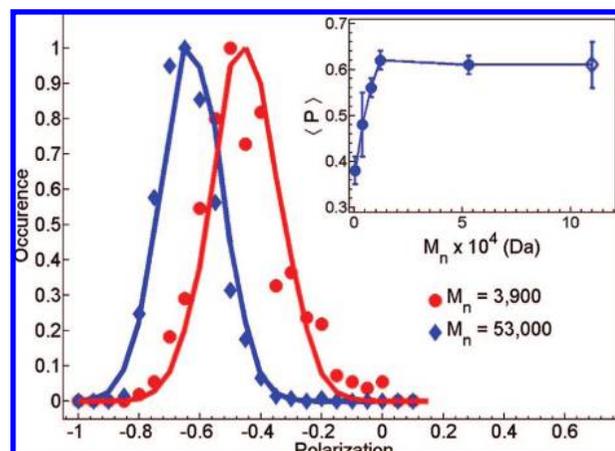


Figure 2. Single molecule fluorescence polarization distributions for MEH-PPV samples with $M_n = 53\,000$ and $M_n = 3\,900$. Inset: Mean polarization as a function of M_n . Results of a previously measured sample with $M_n = 110\,000$ are included for comparison (open symbol).¹² Lines are given as guides to the eyes.

alignment of the main internal polymer axis relative to the LC director expressed by the angle α . S_c is a measure of the orientation of the chain segments with respect to the main polymer axis defined as $S_c = 1/2(3 \cos^2 \beta - 1)$, where β is the angle between the individual segments and the main polymer axis (Figure 3). Experimentally, the conformation order parameter is related to the mean polarization of the molecular transition dipoles of a single polymer chain that is composed of multiple chromophores orientated along the chain segments.

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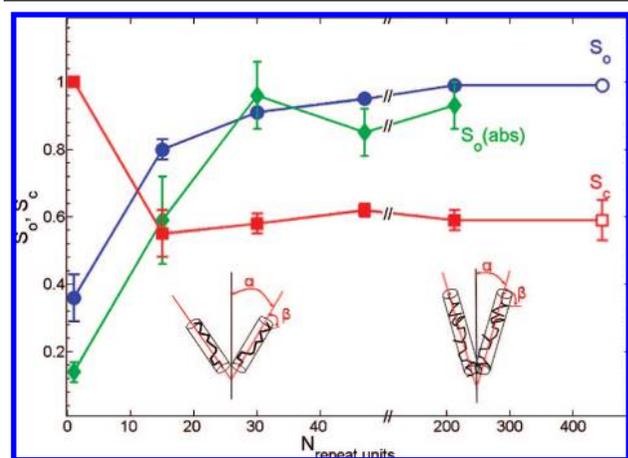


Figure 3. Orientation S_O and conformation S_C order parameters as a function of repeat units. Results of a previously measured sample with 423 repeat units are included for comparison (open symbols).¹² Green diamonds are data points from ensemble absorption measurements. Lines are given as guides to the eyes. The cartoon (not to scale) shows qualitatively how the ordering of a polymer in an LC is enhanced with increasing polymer chain length.

By fitting the experimental fluorescence polarization distributions (solid lines in Figure 2), we obtain the chain orientation order parameter S_O for a rod-shaped polymer solute in an anisotropic LC solvation potential. The solvation potential depends linearly on the number of repeat units,^{13,17} which were calculated from the measured M_n , leaving the distribution of segment orientations (i.e., S_C) as the only adjustable variable in this model. The results of this analysis for the two order parameters are presented in Figure 3 for all investigated samples.

Analysis of the order parameter shows that the alignment increases with increasing length, confirming the concept of CAS. The conformation order parameter decreases from 1 for the single chromophore R6G to 0.59 for MEH-PPV, independent of the MEH-PPV chain length. The latter is in good agreement with the fact that the percentage of tetrahedral defects ($\sim 1\text{--}11\%$) is independent of M_n as deduced from absorption and NMR spectra. While the total anisotropic solvation energy increases with increasing chain length, the total number of defects also increases, requiring more energy to stretch a longer polymer chain. The competition between anisotropic solvation and internal chain bending energy leads therefore to the observed invariance of the conformation order parameter. Nevertheless, all polymer chains are stretched in the LC solvent compared to isotropic solution,^{10,15,18} as shown previously by Monte Carlo simulation^{12,13} and verified here by an up to 20 nm red shift of the absorption maxima in 5CB.

The advantage of using an LC solvent for ordering conjugated polymers is that the alignment can be achieved over large length scales,⁹ which is confirmed by the orientation order parameters obtained from the polarized absorption spectra (green diamonds in Figure 3). The order parameter of an absorbing solute is given by the polarization anisotropy, $P_A = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$, corrected by the angle ξ between the transition dipole moment and the aligned molecular axis.^{15,16} For $\xi = 0$, $S_O = P_A$, while for $\xi > 0$, $S_O = P_A \cdot \{2 / (3 \cos \xi - 1)\}$. Because the conformation order parameter is a measure of the chain segment orientation and thus chromophore alignment for nearly perfectly aligned chains, we used the angle associated with the conformation order parameter in our analysis (i.e., $\xi = \beta$). This approach gives excellent agreement between the single molecule and ensemble experiments.^{13,15} The MEH-PPV sample with $M_n = 3900$ shows a difference for the two methods, which can be rationalized by the photoselection of longer, straighter, and thus better aligned chains

when exciting at 532 nm for the fluorescence polarization experiments.¹⁸ Better agreement is indeed achieved if one calculates the order parameter from the absorption intensities at 532 nm instead of the absorption maximum, which gives 0.75 compared to 0.80 obtained from the single molecule experiments.

It is worth considering the experimental M_n dependence in light of possible practical applications of polymer-doped LC devices.¹⁹ A saturation of the absorption and fluorescence anisotropy occurs at a polymer chain length of only 30 to 45 repeat units (~ 10 to 15 times the length of a solvent molecule), giving a practical limit for the size of the MEH-PPV solute because larger MEH-PPV polymer chains show a significant decrease in solubility but do not increase the polarization anisotropy. In contrast, stiffer poly(phenylene ethylene)s with iptycene scaffolds designed to increase ordering and solubility give a continuous increase of the order parameter with M_n of 10K to over 200K.²⁰

In summary, we have provided experimental verification of the concept of CAS by showing how the order parameter for conjugated polymers dissolved in a nematic LC scales with M_n . Ensemble absorption polarization measurements agree well with results obtained by single molecule fluorescence polarization spectroscopy, indicating a large-scale ordering of the MEH-PPV solute in 5CB. These results demonstrate that the increasing number of defects for larger polymer weights inherently limits the polarization anisotropy of the polymer solute. For applications in colored LC displays, a further increase in the dichroic ratio could, in principle, be achieved with a stiffer macromolecular solute.

Acknowledgment. Support was provided by the Robert A. Welch Foundation (C-1664 to S.L., E-1320 to T.R.L.) and the National Aeronautics and Space Administration (NCC-1-02038 to T.R.L.). S.L. thanks 3M for a Non-Tenured Faculty Grant. D.S. thanks the NSF and DoD for an REU fellowship (PHY-0453365).

Supporting Information Available: Sample preparations, chemical structures, experimental setups, data analysis, NMR data, and absorption spectra of MEH-PPV. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA805017M