Orthogonal Orientations for Solvation of Polymer Molecules in Smectic Solvents

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We explore the solvation of single conjugated polymer molecules in a smectic liquid crystal using single molecule spectroscopy. We find evidence for two distinct orientations for solvation: the majority of polymers are narrowly orientated parallel to the nematic director, as expected, but, unexpectedly, a second population is aligned perpendicular to the director. These molecules reside in the gaps between the layers. This latter type of solvation has not been previously observed and is not expected when the density variation along the director is sinusoidal.

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The nature of the solvent plays an important role in the conformational properties and structure of stiff polymers in solution. Depending on the solvent quality and intramolecular interactions, the polymer molecules can be extended (rodlike), collapsed, toroidal, or even in a nanonematic state where the segments of the locally rodlike polymer pack together like flower stems in a bouquet [1,2]. A particularly interesting case is when the solvent itself possesses order, as is the case of a nematic liquid crystalline solvent [3,4]. In this case long rodlike polymer molecules align along the nematic director to a much greater degree than the solvent molecules themselves because longer rods experience the local nematic field over much larger distances than the solvent nematogens. This striking effect, previously inferred from small angle neutron scattering [5] and viscosity measurements [6], was recently measured directly, using single molecule spectroscopy, for solutions of conjugated polymers [3,4] and colloidal virus particles [7].

In this work we investigate, using single molecule spectroscopy, the solvation of a polymer molecule in a *smectic* liquid crystal (LC). In an ideal smectic A phase, the solvent molecules are aligned preferentially along a particular direction (called the director) as in a nematic phase, but in addition there are layers. Within each layer the arrangement of molecules is liquidlike, but the layers stack above each other in a one-dimensional crystalline array [8]. This is clearly an idealization; however, x-ray scattering experiments [9–11] have demonstrated quite convincingly that the variation of the average density along the director is *sinusoidal* in thermotropic smectics, in agreement with theory [12]. Very little is known regarding the effect of smectic solvation on the properties of single polymer molecules. We study this phenomenon using single molecule polarization spectroscopy of the rodlike polymer poly(2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) dissolved in the smectic phase of a solvent composed of 8CB molecules. MEH-PPV is readily soluble in 8CB (1×10^{-3} g/ml), indicating that 8CB is a "good solvent" for this polymer.

We discover that there are two distinct, orthogonal orientations for the polymer solute (Fig. 1, top). In the majority of cases, the polymer molecules are aligned parallel to the director as is seen when the solvent is in the nematic phase. Surprisingly about 10% of the polymer molecules are aligned *perpendicular* to the director. Such an orientation seems possible in an ideal smectic material where the polymers might fit into the "empty spaces" between layers. But how is this possible in a material with only a sinusoidal density variation and no real "gaps"? It may be that the insertion of MEH-PPV into the low-density interlayer region is induced by specific molecular interactions between the alkyl side chains of MEH-PPV with the alkyl tail of the 8CB. The single molecule measurements therefore reveal interesting information regarding the local structure that is not accessible in ensemble x-ray measurements. The experiments suggest the intriguing possibility of using long chains as a molecular scaffold for creating a new class of tunable nanostructured materials.

Isolated MEH-PPV polymer chains, dissolved in a single domain LC that is mounted inside a temperature-controlled cell, are studied by confocal microscopy [4]. The microscope is equipped with two orthogonally polarized detector systems allowing us to measure the polarization ratio P for each single polymer molecule diffusing through the excitation volume according to $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities polarized parallel and perpendicular to the LC director. The sign of P expresses the relative orientation of the main polymer axis: positive values indicate parallel alignment of the polymer chain and negative values indicate perpendicular alignment.

Figure 1 shows P histograms for MEH-PPV in the nematic (left) and smectic (right) phase of 8CB as well as two typical intensity trajectories (insets). For the nematic phase, all polymer molecules are aligned parallel to the director (left scheme on top of Fig. 1). For the smectic LC phase, two orthogonal polymer orientations are observed, indicated by the reversal of intensity ratios for different fluorescence bursts and the appearance of an

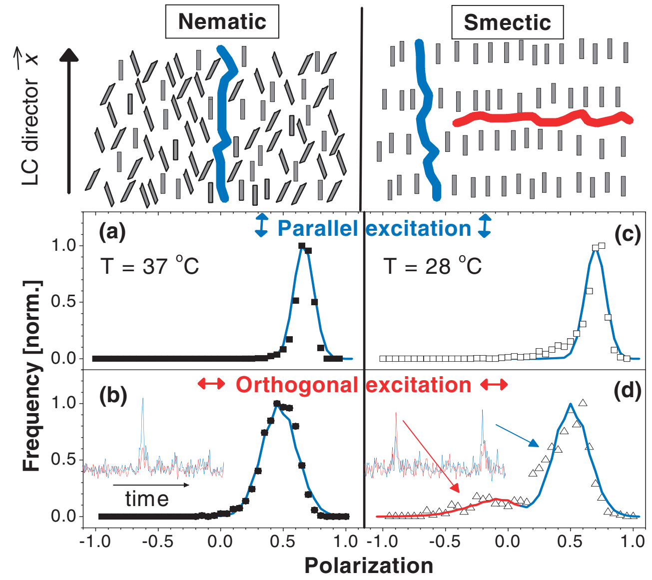

FIG. 1 (color). Orthogonal orientations for solvation of MEH-PPV in a smectic LC. Top: schematic picture of the nematic (left) and ideal smectic (right) LC phase. In the nematic phase, the solvent molecules (indicated by cylinders) have an orientational order with an alignment of the main molecular axis parallel to the LC director. In the ideal smectic phase, the solvent molecules possess positional order along the director forming two-dimensional layers. Solvation of larger polymers (not scaled) is indicated by the blue and red chains. Bottom: *P* histograms measured with excitation polarized parallel (a), (c) and orthogonal (b), (d) to the director. The insets show a typical fluorescence burst from a single polymer molecule diffusing through the excitation volume. Positive *P* is consistent with parallel alignment to the director (blue chain). For orthogonal excitation in the smectic phase (d), the fluorescence transient reveals the presence of molecules with an opposite *P*. These molecules are orientated perpendicular to the director (red chain). The corresponding *P* histogram shows that a small fraction (~10%) of polymer molecules is aligned perpendicular with a larger degree of disorder. The solid lines are theoretical fits to the histograms using a previously described anisotropic mean-field solvation model which also includes optical effects due to photon shot noise and the high numerical aperture of the objective [4].

additional broad distribution in the *P* histogram peaked at negative *P* values [Fig. 1(d)]. Similar diffusion constants for MEH-PPV in both orientations as obtained from autocorrelation analysis (not shown) confirm the concept of a second solvation site.

We hypothesize that the perpendicular aligned polymer molecules occupy gaps in between the solvent layers formed in the smectic phase (right scheme on top of Fig. 1). The perpendicular solvation site is emphasized in the *P* histogram by using orthogonal excitation, which selectively excites the chromophores orientated perpendicular to the director. For orthogonal excitation [Figs. 1(b) and 1(d)], the peak of the positive *P* is shifted towards smaller values due to the selective excitation of chromophores tilted away from the director. This is consistent with independent observations that energy transfer is insignificant for extended MEH-PPV conformations solvated in a LC [4].

The perpendicular alignment inferred from the negative *P* values is assigned to a local minimum in the smectic solvation potential. The absence of a change of the polarization ratio during a fluorescence burst implies a large energy barrier for the interconversion between the solvation sites. Using parallel excitation, the histogram for the smectic phase also exhibits a tail towards smaller *P* [Fig. 1(c)]. This tail can be attributed to polymer molecules aligned with a main part of their chain parallel to the director and a shorter segment bent perpendicular into interlayer channels. Such bends in the polymer chain have been observed in beads-on-a-chain simulations where MEH-PPV is represented by stiff segments interrupted by tetrahedral defects [2]. With roughly 8 defects per chain for our MEH-PPV sample, these bends should be energetically favorable over more severe hairpinlike turns found for nematic solvation of MEH-PPV [4]. Such "L-shaped" conformations can also contribute to the negative *P* distribution when using orthogonal excitation. It should be emphasized that the basic phenomenon reported herein of distinguishable parallel and perpendicular polymer chain orientations is not itself a consequence of photoselection, since circularly polarized excitation experiments for the smectic phase also exhibit distinguishable bursts with either positive or negative polarization.

Computer simulations of small bent molecules (azobenzene derivatives) dissolved in smectics show that these molecules segregate to the interlayer region [13,14], a segregation that is accompanied by an increase in the interlayer spacing [15–17]. It is possible that this effect plays a role in the perpendicular solvation of the MEH-PPV polymers as well. A big difference between the solvation of polymers and small molecules, of course, is that the polymers interact with the solvent on length scales that are 2 orders of magnitude larger. Local effects are therefore expected to be less important for polymers than small molecule solutes.

The ordering of the polymer along the director increases with decreasing temperature without a discontinuous change at the smectic-nematic phase transition (see Figs. 2 and 3). The absence of a pronounced phase transition for *P* is consistent with a second [18] or weak first [19] order phase transition reported for the solvent order parameter and is further obscured by the stiffness and length of the individual polymer segments (~50 monomers). Possible local fluctuations of the layers could also be responsible for the observed insensitivity [8]. The observed *P* histograms and fractional population of the orthogonal solvation sites are reproducible for repeated temperature cycling between different LC phases, including the isotropic phase (not shown), indicating that the

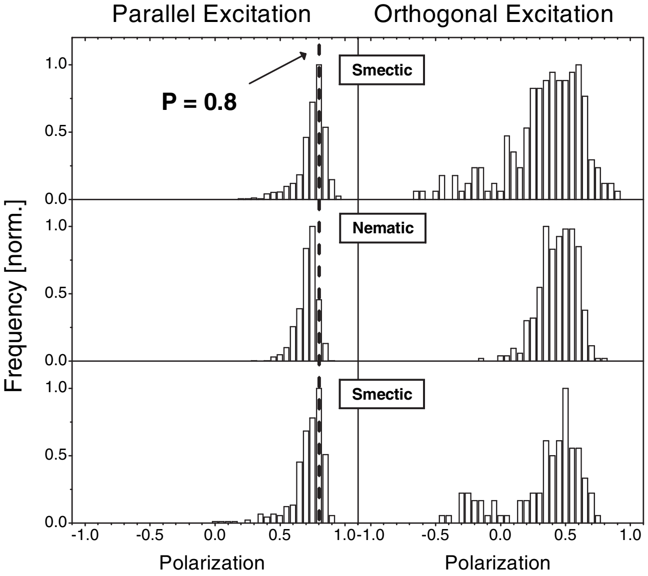

FIG. 2. P histograms using parallel (left) and orthogonal excitation (right). The temperature is varied from 28 to 37 and back to 28 °C (top to bottom) cycling between the smectic and nematic LC phases. The P histograms on the right show a second distribution with negative P values indicating polymer molecules aligned perpendicular to the director in the smectic phase (top and bottom), which is absent in the nematic phase (middle) and for a sample containing only 8CB (not shown). For parallel excitation (left, 488 nm, 1 kW/cm^2), the maximum of the P histogram shifts to smaller values in the nematic compared to the smectic phase (see line for $P = 0.8$). This is due to the increased stretching of the polymer chain with increasing order of the LC solvent molecules (see Fig. 3).

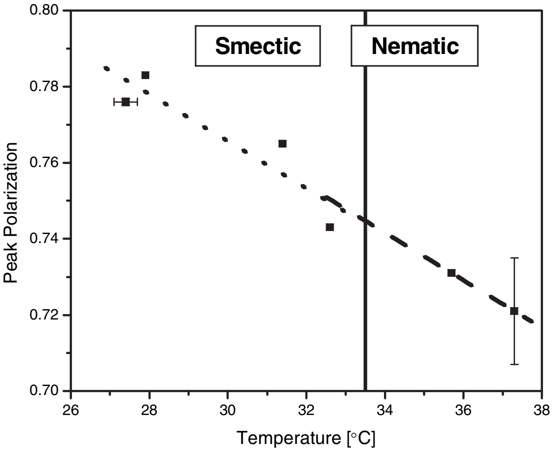

FIG. 3. Peak P as a function of temperature. P increases roughly linearly with temperature in the studied temperature range from 27 to 37 °C across the smectic-nematic phase transition. The lines are independent linear fits to P in the smectic and nematic LC phases demonstrating the lack of a strongly discontinuous phase transition for P. The decrease of P with increasing temperature can be explained by a decrease in conformational order of the polymer chain due to a lower solvation energy counteracting the intrinsic bending energy and conformational entropy of the chain. (The shown error bars are representative for all data points.)

observed distributions reflect the equilibrium state of the systems (see Fig. 2).

We have shown previously [4] that the measured P values for single conjugated polymer molecules dissolved in a nematic LC can be quantitatively modeled to determine the orientational distribution of polymer segments with respect to the director of a LC, allowing for information on how anisotropic solvation impacts the orientation and conformation of polymer chain solutes. The large positive P values in all the histograms shown in Fig. 1 indicate a high degree of order of the MEH-PPV molecules parallel to the director that far exceeds the order parameter of the 8CB solvent (i.e., $S_O = \langle \frac{3}{2}\cos^2\alpha - \frac{1}{2} \rangle \sim 1$ where α is the tilt angle between the major axis of the chain and the LC director). An analysis of the single molecule P values herein shows that for the parallel site in the smectic solvent, the MEH-PPV chain segments are aligned with the director to a much greater degree than in the nematic phase with molecular polarization values of $P_{\text{chain}} \sim 0.75$. P_{chain} is defined as

$$P_{\text{chain}} = \Big(\sum_i \mu_{ix'}^2 - \frac{1}{2}\sum_i (\mu_{iz'}^2 + \mu_{iy'}^2)\Big)\Big/\Big(\sum_i \mu_{ix'}^2 + \frac{1}{2}\sum_i (\mu_{iz'}^2 + \mu_{iy'}^2)\Big),$$

where $\vec{\mu}_i$ is the transition dipole of the ith polymer segment, and is related to the internal conformational order parameter $S_C = \langle P_2(\cos\beta) \rangle = \langle \frac{3}{2}\cos^2\beta - \frac{1}{2} \rangle$ according to $P_{\text{chain}} = 3S_C/(2 + S_C)$. β is the angle between each segment and the polymer principle axis (x' axis). These model calculations also give the experimentally determined orientational probability distribution function $f(\beta)$ for the segments of the polymer molecules in the parallel and perpendicular solvation sites, which are shown in Figs. 4(a) and 4(b) together with two representative polymer conformations [Figs. 4(c) and 4(d)] [2,4]. Using a mean-field potential, $f(\beta)$ is calculated from the fitted value of P_{chain} with the self-consistent definition of the order parameter $\langle P_2(\cos\beta) \rangle = \int d\beta \sin\beta f(\beta) P_2(\cos\beta)$. These results emphasize that there are orthogonal solvation sites for polymer chains in a single smectic LC. The average molecular polarization P_{chain} of the perpendicularly orientated polymer chains is decreased from 0.75 to ≤ 0.5. The broad distribution and smaller P_{chain} of the perpendicularly oriented polymers [Fig. 4(b)] reflect a greater degree of disorder. The lower P_{chain} for the perpendicular solvation site may be due to various factors, including a disordered polymer conformation, a broad orientational distribution, and/or fast molecular rotation

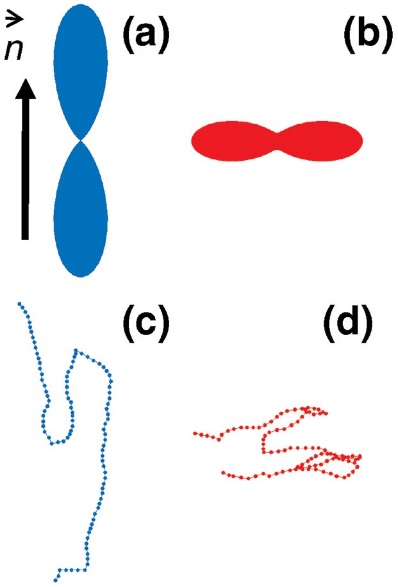

FIG. 4 (color). Graphical representation of the experimentally determined orientational probability distribution functions for the segments of the polymer molecules in the parallel (a) and perpendicular (b) solvation sites. The average molecular polarizations P_{chain} of the polymer chains are 0.75 and 0.4 for the parallel and perpendicular solvation site, respectively. (c),(d) Corresponding conformations of a 100-segment homopolymer generated by beads-on-a-chain simulations [2,4]. The arrow indicates the direction of the LC director.

in the y-z plane on the time scale of the ~50 ms transit time. All three effects are qualitatively consistent with expectations for polymer molecules solvated between layers in a smectic LC.

The experimentally observed perpendicular alignment of MEH-PPV implies the presence of significantly larger interlayer gaps than in neat 8CB and can be qualitatively understood from a generalization of mean-field theory of the nematic-smectic transition. In the theory of thermotropic LCs the nematic phase becomes stable relative to the isotropic phase (as the temperature is lowered) because the favorable attractive interactions between aligned molecules becomes more significant than the loss of configuration entropy. Similarly, the smectic phase becomes stable relative to the nematic phase because the gain in favorable attractive interactions (when molecules are layered) overcomes the entropic cost of creating these layers. One would expect the entropic cost of creating layers to be reduced if the polymer molecules inhabit the interlayer region. The presence of polymers therefore stabilizes the layers at a larger separation than in the neat solvent.

In conclusion, we present evidence for two orthogonal solvation sites for the conjugated polymer MEH-PPV dissolved in the smectic LC 8CB. The majority of polymers are aligned parallel to the director with an order parameter approaching unity, while a small fraction (~10%) of molecules with a larger degree of disorder fits into interlayer channels. Our results demonstrate that single molecule spectroscopic data on dilute polymer chain solutes can probe the three-dimensional structure of smectic LCs otherwise inaccessible by other techniques.

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