

Ordering of Single Conjugated Polymers in a Nematic Liquid Crystal Host

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We describe molecule-by-molecule observations, using single molecule fluorescence spectroscopy, of the ordering of the components in a nematic phase formed by a binary mixture of short and long rods. A stiff conjugated polymer, MEH-PPV (poly[2-methoxy-5-((2-ethylhexyl)oxy)-1,4-phenylenevinylene]), present at very low concentrations in a binary nematic–nematic phase with the mesogen 5CB (4-*n*-pentyl-4'-cyanobiphenyl) is investigated. We observe near-perfect orientational order of the stiff, rodlike conjugated polymers translating through a planar nematic phase. This represents striking experimental evidence for the predicted enhanced alignment of long rods in the nematic phase of a binary mixture of rods.

Introduction

It is well-known that rodlike molecules can exist in ordered, liquid crystalline phases.¹ The transition from an isotropic to an anisotropic phase was explained by Onsager as an interplay between loss of orientation entropy and decrease in excluded volume.² More complex multiphase systems, such as polydisperse rodlike polymers³ and stiff-chain polymer–lyotropic liquid crystal mixtures,⁴ are also known to exhibit various ordered phases, as can be described in the context of Flory theory.⁵ The rich phase behaviors of mixtures of colloidal rodlike and spherulike particles have been reported recently.⁶ In the present work we describe molecule-by-molecule observations of the ordering of the components in a nematic phase formed by a binary mixture of short and long rods. We observe near-perfect orientational order of the stiff, rodlike conjugated polymers translating through a planar nematic phase. This represents striking experimental evidence for the predicted enhanced alignment of long rods in the nematic phase of a binary mixture of rods.

Onsager's intuitive prediction that long rods would be more perfectly ordered than short rods in an anisotropic phase of a polydisperse solution has been substantiated by a wide variety of theoretical studies.^{7,8} However, no compelling experimental distinction of the order parameters for the components in such a mixture has yet been reported. Here we report a measurement of the order parameter of a stiff conjugated polymer, MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]), present at very low concentrations in a binary nematic–nematic phase with the mesogen 5CB (4-*n*-pentyl-4'-cyanobiphenyl) (structures shown in Figure 1A). We consider this system to be a binary mixture of long and short rods, because previous work has suggested that MEH-PPV adopts a "defect cylinder" conformation in good solvents.⁹ We have employed single-molecule fluorescence spectroscopy to measure the alignment of the MEH-PPV molecules relative to the director of the nematic phase—molecule by molecule as the

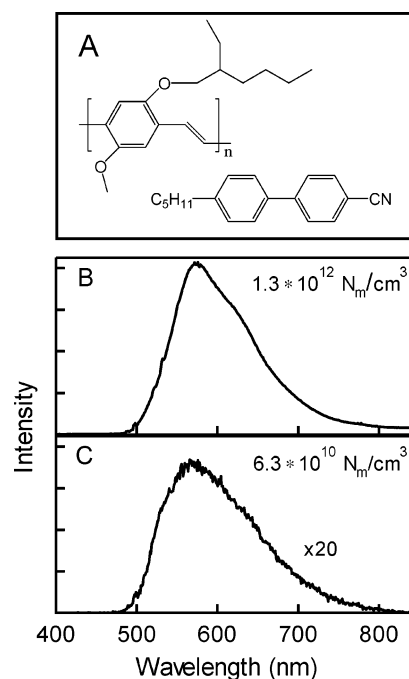


Figure 1. (A) Structures of MEH-PPV ($M_w \sim 110\,000$ g/mol) and 5CB. (B) and (C) Spectra of MEH-PPV for different polymer concentrations in the liquid crystal, normalized for concentration, and plotted on the same intensity scale.

cylindrical polymers diffuse through the focal volume. In other words, we have elucidated the alignment distribution, rather than an ensemble average order parameter. This procedure has enabled us to deconvolve the intrinsic anisotropy of the polymer's electronic transitions from the anisotropy due to orientational disorder of the polymer rods. We report the striking observation that the polymer is substantially more aligned with respect to the liquid crystal director than is the host mesogen.

Experimental Section

Nematic liquid crystal films of MEH-PPV-doped 5CB (10^{-5} – 10^{-8} percent by weight) with planar alignment were prepared between a quartz slide and a glass coverslip, starting from a polymer–mesogen–chlorobenzene triphase system, as

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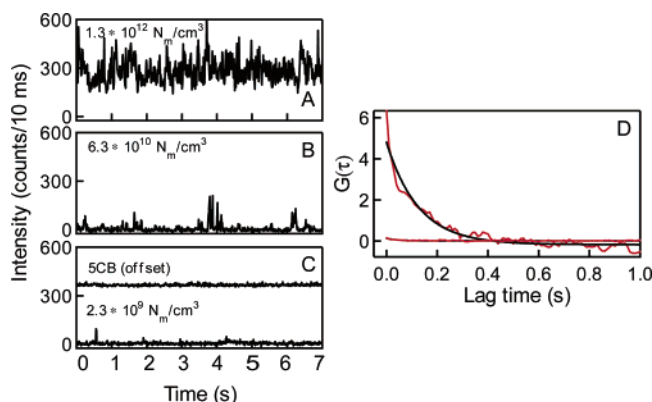


Figure 2. (A)–(C) Single-channel intensity trajectories for different polymer concentrations. (C) also shows a trajectory for 5CB with no polymer present. (D) Normalized circular intensity autocorrelations and single-exponential fits for 5CB and MEHPPV-doped 5CB (6.3×10^{10} molecules/cm³).

described previously.^{10,11} MEH–PPV/5CB (1–2 drops) was sandwiched between the unidirectionally rubbed PVA alignment layers of a quartz slide and glass coverslip separated by a 76 μm Mylar spacer. Samples were placed between crossed polarizers; the observation of birefringence signaled formation of a nematic phase.

Samples were excited at 488 nm by a cw Ar⁺ laser, focused to a 300 nm diameter, diffusion-limited spot by a 100X oil immersion objective. Emission was collected by the same objective and filtered (with notch and colored glass filters) to remove scattered light. Intensity trajectories were acquired with avalanche photodiode detectors (using a polarizing cube beam splitter to detect *x*- and *y*-polarized emission); spectra were collected with a back-illuminated liquid nitrogen cooled CCD camera. Diffusing polymer molecules in the *x*–*y* plane ($\sim 1 \mu\text{m}$ from the surface) were optically excited with focused, circularly polarized light propagating in the *z* direction using an oil immersion objective located on the coverslip side of the sample. Bursts of polymer emission and background from 5CB were collected by the same objective and filtered to remove scattered excitation light.

Histograms of single-molecule polarizations were generated using an automated routine. Dual-channel intensity data were processed into background-corrected, burst-size bins. The polarization ratio, *P*, was determined for bursts above a total-intensity threshold of 250 counts. Results were nearly identical to histograms constructed in a manual, burst-by-burst fashion; however, the latter histograms tended to have smaller standard deviations (0.03–0.07), likely due to an improvement in (local) background subtraction.

Results and Discussion

Emission spectra of MEH–PPV, obtained via subtraction of the 5CB signal, are shown in Figure 1. Each spectrum represents the signal accumulated from hundreds of polymers diffusing through the focal volume during a 300 s acquisition window. Intensity data acquired at fixed positions in the sample and detected with an avalanche photodiode (APD) detector confirm that MEH–PPV fluorescence is collected in bursts from the diffusing polymers, and that the number of bursts increases with polymer concentration, as shown in Figure 2 (panels A–C). By autocorrelating intensity trajectories and fitting the decays with a model for 3-dimensional diffusion¹² (Figure 2D), we estimated an average diffusion time of 80 ± 30 ms for MEH–PPV molecules leaving the focal volume. Assuming a diffusion

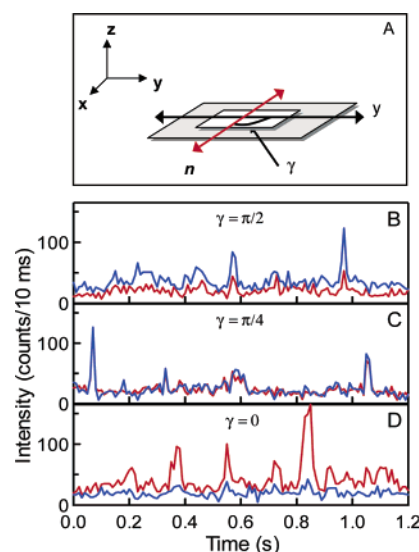


Figure 3. (A) Schematic of sample orientation. The bulk alignment direction or director, *n*, is oriented at an angle γ with respect to the *y*-axis. (B)–(D) Portions of dual-channel intensity trajectories for different sample orientations. Data were collected for many seconds in each (fixed) position in the sample.

distance of $\sim 1 \mu\text{m}$, we infer that the diffusion constant $D = \langle x^2 \rangle / 2t \sim 10^{-11} \text{ m}^2 \text{ s}^{-1}$. This value is in agreement with previously reported ensemble values, determined by using forced Rayleigh scattering to retrieve the binary mass diffusion constant of tracer molecules along the director of 5CB.¹³ Also, in fluorescence polarization measurements discussed below (see Figure 3), we observed that molecules retain their characteristic polarization ratios throughout their diffusion times, suggesting that translation through the focal volume occurs with little or no rotational reorientation.

A combination of experiment and simulation was employed to investigate (1) the degree of alignment between the MEH–PPV molecules and the liquid crystal director in the nematic phase and (2) the distribution of intrinsic anisotropies exhibited by the polymers in the aligned environment versus an unaligned, “isotropic” phase consisting of a polymer/5CB/chlorobenzene solution. Fluorescence anisotropy measurements were performed, employing a polarizing cube beam splitter to direct the *x*- and *y*-polarized emission (*I_x* and *I_y*) from individual diffusing polymers to two APDs. Single-molecule polarizations were determined according to

$$P \equiv \frac{I_y - I_x}{I_y + I_x} \quad (1)$$

Polarization histograms were generated to investigate distributions of anisotropies. In simulations of these data, polymers were approximated by cylinders in a three-dimensional, spherical coordinate system of overall cylindrical symmetry (to approximate a uniaxial liquid crystal). Single-polymer polarizations were calculated according to the cylinders’ orientations,^{14,15} defined by the azimuthal and polar angles, ϕ and θ , incorporating a parameter, *A*, for the intrinsic molecular anisotropy (*A* = 0 for spheres and 1 for dipoles). Probability distributions of single-molecule polarizations were simulated assuming a mean potential that depends on the orientation angles (α) between the molecules’ long axes and the liquid crystal director. By obtaining the best fit to the experimental data, we were able to calculate the distributions (assumed to be Gaussian) of intrinsic anisotropies and orientation angles from which we determined

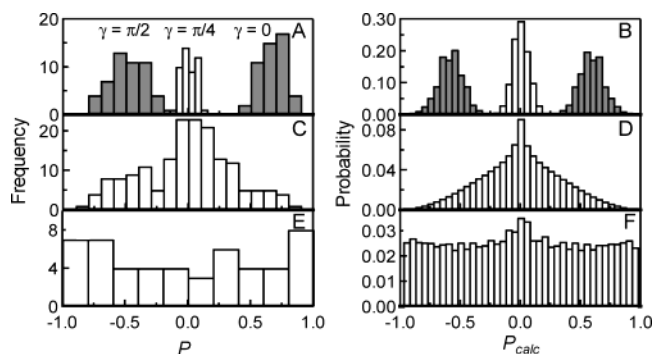


Figure 4. Histograms of experimental single-molecule polarizations and probability distributions obtained from simulations. (A) Data for MEH-PPV molecules in nematic samples with $\gamma = 0, \pi/4$, and $\pi/2$. Mean polarizations and standard deviations for the three histograms are 0.64 ± 0.11 , 0.01 ± 0.06 , and -0.54 ± 0.12 , respectively. (B) Simulation of rods aligned in the nematic phase. Molecular anisotropy, $A = 0.65 \pm 0.10$; standard deviation of orientational order = 3° , corresponding to an order parameter of 0.99. (C) Experimental results for MEH-PPV molecules in an “isotropic” sample, consisting of a polymer/5CB/chlorobenzene solution. The mean polarization is 0.01 ± 0.37 . (D) Simulation for an isotropic distribution of polymer molecules. $A = 0.65 \pm 0.25$; standard deviation of orientational order = 3° . (E) Measured polarization data for dye molecules (DiI, simple dipoles) immobilized in a 1.15 mm thick PMMA film. The mean value is 0.00 ± 0.64 . (F) Simulation for an isotropic distribution of dye molecules (dipoles); $A = 1.00 \pm 0.01$.

the ensemble order parameter,¹ $S = (1/2)\langle 3 \cos^2 \alpha - 1 \rangle$, of the aligned polymers.

Investigations of nematic samples employed three different orientations of the director with respect to the two detectors, as shown in Figure 3, where γ is the angle between the director and the y-axis in the laboratory frame. When the director lies along either axis ($\gamma = \pi/2$ or 0), the measured MEH-PPV bursts in the dual-channel intensity trajectories exhibit significant polarization bias in that direction (Figure 3B,D). This behavior suggests that polymer molecules are both highly aligned along the director and highly polarized. Polarization histograms in Figure 4A confirm these observations, displaying relatively narrow distributions of molecular anisotropies (standard deviation $\sigma_P \sim 0.12$)¹⁶ with a mean polarization of $\langle P \rangle \sim 0.6$. With the director at 45° to both APDs ($\gamma = \pi/4$, Figure 3C), intrinsic anisotropy is obscured: no polarization bias is evident in the intensity data, and the histogram in Figure 4A is peaked at 0.0.

Because it is insensitive to molecular shape, the very narrow ($\sigma_P \sim 0.06$) histogram for $\gamma = \pi/4$ permits direct assessment of the orientational order, which can then be used to deduce the distribution of intrinsic anisotropies contributing to the widths of the experimental $\gamma = 0, \pi/2$ polarization histograms. Simulations conducted in this manner (Figure 4B) returned a mean anisotropy $A = 0.65$ with a standard deviation of 0.1 and a very narrow distribution of orientation angles (α) with a standard deviation of 3° . The order parameter calculated from this distribution is $S = 0.99$, representing nearly perfect alignment of polymer molecules with the liquid crystal director! This result is especially startling when compared to literature values for the order parameter of 5CB,^{17,18} which range from $S = 0.4$ – 0.6 and correspond to a spread in α of $\sim 20^\circ$.

In the “isotropic” (polymer/5CB/chlorobenzene) phase, MEH-PPV molecules were observed to exhibit a wide range of polarizations, consistent with a truly random distribution in three dimensions. The polarization histogram in Figure 4C contains values ranging from -0.9 to $+0.9$, with a standard deviation $\sigma_P = 0.4$. Simulations performed by assuming an isotropic distribution yielded a mean intrinsic anisotropy of 0.65, as in

the nematic samples, but a broader distribution of anisotropies, with a standard deviation of 0.25. For comparison, we investigated a sample of single dye molecules (simple dipoles) randomly distributed in a thick, optically transparent polymer film. The experimental polarization histogram is shown in Figure 4E, beside the probability distribution simulated with a mean molecular anisotropy of 1.00 ± 0.01 (Figure 4F). These data confirm that our instrument is capable of measuring high polarizations and support our assertion that, though the MEH-PPV molecules are highly anisotropic, they are not dipoles.

Our system may be envisioned as a binary mixture of long (polymer) and short (5CB) rods in the nematic phase. According to a macroscopic interpretation based on mean field theory, simulations of the experimental results suggest that the short 5CB rods experience a small orientation energy of $\sim 4 kT$ and consequently exhibit a rather broad distribution of orientation angles. In contrast, the long polymer rods experience an orientation energy on the order of $100 kT$ and are constrained to lie almost perfectly parallel to the director.

For a microscopic interpretation, we estimated aspect ratios for 5CB and MEH-PPV from their order parameters (0.6 and 0.99, respectively) and mole fractions, using a simple statistical mechanical lattice model adapted previously for a binary mixture of hard rods.^{19–21} The interaction between the rods is determined entirely in the “hard core” requirement that no two rods occupy the same lattice site. As such, our calculation considers a tradeoff between the entropy of mixing and that associated with packing the rods onto the lattice. By minimizing the configurational Helmholtz free energy contributions to the orientation entropy and excluded volume at a specific pressure and temperature, we obtained the aspect ratios of the rods and the lattice occupation density. The model makes the unlikely assumption that the rods have equal diameters; however, it reveals that our experimental observations are reasonable when the MEH-PPV cylinder has a length at least five times that of the 5CB host. Physically, we expect the polymer to be at least 25 times as long as 5CB, with a substantially larger diameter. Interestingly, it has been suggested that thick rods, analogous to MEH-PPV, can destabilize the nematic phase.²²

Conclusion

We have observed near-perfect orientational order of stiff, rodlike conjugated polymers translating through a planar nematic phase. To our knowledge, this represents the first experimental evidence for the improved alignment of long versus short rods in an anisotropic phase. It also provides the means and incentive for detailed optical investigation of more complicated liquid crystalline systems.

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