

Conjugated Polymers Confined and Sheared: Photoluminescence and Absorption Dichroism in a Surface Forces Apparatus

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ABSTRACT: Within a surface forces apparatus newly equipped for spectroscopic measurements, the photoluminescence and absorption spectra were studied of conjugated polymer films confined to less than the random coil dimension. A dilute solution of MEH-PPV, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene), was exposed to atomically smooth surfaces of muscovite mica and allowed to adsorb from toluene, and then the surface spacing was reduced to ≈ 2 nm, which is less than the unperturbed radius of gyration of the polymer chains. Subsequent unidirectional shear with amplitude ≈ 20 times the surface spacing provided preferential alignment while the solvent evaporated. Chain alignment was quantified from both photoluminescence and absorption spectra. Curiously, a bimodal distribution of chain alignment was observed, parallel to the shear direction in $\frac{2}{3}$ of the cases but perpendicular to the shear direction in $\frac{1}{3}$ of the cases. On the basis of analysis of the photoluminescence spectra, confinement and shear-induced changes of the electronic structure are also discussed. This is considered to be the first study of polymer absorption and photoluminescence spectra within the contact area of a surface forces apparatus.

Introduction

The structure and dynamics of polymers have been observed to change fundamentally when the system becomes geometrically confined.^{1–4} Physical properties that change with confinement include the effective viscosity, the diffusion constant, the melting point, and the structure. Here we are concerned with confinement between single crystals of mica in a surface forces apparatus (SFA), such that the spacing is well-defined within subnanometer accuracy and directional alignment might, in principle, result from shear. Because of its capacity for constraining the intersurface separation at close distances while measuring shear forces, the surface forces apparatus, SFA (and its cousin, the AFM, atomic force microscope), has been widely applied in polymer science. One of the most general findings is that because extremely large deformations are easily generated in these thin films, it easily happens that molecules are deformed more rapidly than they can reequilibrate.

Force measurement carries no direct information, however, regarding molecular composition, structure, conformation, or mobility. With this in mind, this laboratory has been working to integrate the surface forces apparatus with spectroscopic probes. Previously we reported a fluorescence-based method⁵ and ensuing studies using that method^{6,7} to investigate the translational diffusion of dye molecules embedded at nanomolar concentration within confined liquids. But although single-molecule sensitivity is attractive, this approach presents the drawback that the fluorescent probe molecule might itself potentially modify the structure and dynamics of the matrix within which it is embedded. Furthermore, fluorescence dyes do not give direct information about molecular conformations of the chains to which they are attached.

For these reasons, it is also desirable to develop methods to visualize molecular conformations directly

and in situ. Recently, we reported a method of chemical imaging using confocal Raman spectroscopy.⁸ Here we present our first experiments using absorption and photoemission. For study, a conjugated polymer was selected because by comparing the absorption and photoemission spectra in orthogonal directions parallel to the plane of the surface, the direction of chain alignment can be inferred.

The significance of this study is twofold. First, it introduces in-situ spectroscopic methods to quantify polymer conformations in a confined geometry. On the practical side, this study shows that confinement combined with sliding friction provides a simple, generalizable method to produce new kinds of electronic structures in a conjugated polymer and hence its optoelectronic properties.

Experimental Section

The conjugated polymer was MEH-PPV, poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene), end-capped with dimethylphenyl. Orange-colored dilute solutions of this were prepared in toluene (Figure 1a), and a drop was loaded between crossed cylinders of freshly cleaved mica in a home-built surface forces apparatus adapted for photoluminescence measurements (Figure 1b). To prepare the sample, step-free single crystals of mica were cleaved to thickness 2–4 μm , silvered, draped over crossed cylinders placed at right angles to one another and glued in place, and finally were pressed together under a large load with liquid in between. The surface separation was reduced with simultaneous shear, eventually reaching a thickness 5 times less than the unperturbed coil diameter of 10 nm, and under the action of periodic shear the polymer film was allowed to dry slowly by evaporation in a sealed chamber (Figure 1c). Under the applied load of ≈ 1 MPa, the crossed cylinders deformed at the apex, producing a circular region of ≈ 50 μm diameter where the mica plates were parallel with fluid confined in between. For interferometric measurements of film thickness, an image of the sample was focused to the entrance slit of a spectrometer, and lines sectioned through the contact area were dispersed and recorded by a CCD camera. We mounted the mica sheets to align one of the optical axes of mica parallel to the shear direction. Chain conformations and light-emitting properties of the resulting films, 2.0 ± 0.2 nm thick, were characterized.

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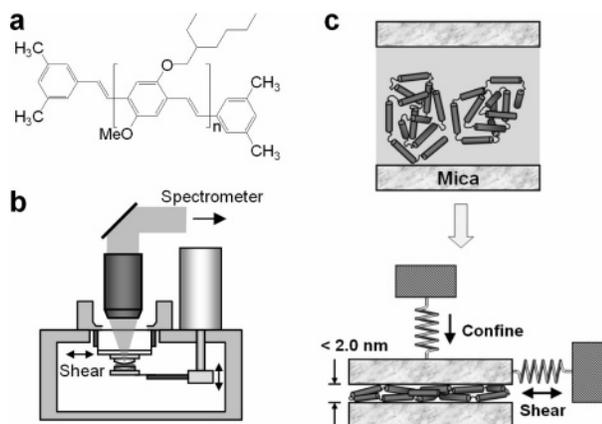


Figure 1. Experimental scheme. The conjugated polymer, MEH-PPV (a), was dissolved in dilute toluene solution at concentration 0.5 mg mL^{-1} . After loading into a surface forces apparatus adapted for photoluminescence studies (b), the solution was squeezed under an applied load to nanometer thickness, sheared, and dried (c). The shear perturbations were sinusoidal at 1.3 Hz with large amplitude, 15 times the final film thickness (33 nm rms amplitude). This caused the electronic structure of the ultrathin film, denoted in the diagram by red cylinders, to align preferentially perpendicular to the shear direction. The average molecular weight of the polymer was stated by the manufacturer to be $50\text{--}300\text{ kg mol}^{-1}$ (American Dye Source).

Shear was applied in the method used by this laboratory for a number of years,⁹ but some modification of the traditional surface forces technique was needed to enable photoluminescence measurements. Normally, surface spacing in a surface forces apparatus is measured using interferometry between silver films coated onto the backside of mica sheets, but for photoluminescence studies it is necessary that laser light be able to enter the thin film and that emitted light be able to leave it.

Therefore, we have replaced silver with multilayer dielectric coatings. Electron-beam deposition was used to coat 13 alter-

nating layers of TiO_x and Al_2O_3 with high reflectivity in the region $700\text{--}800\text{ nm}$ and transparent below 700 nm , thus enabling not only determination of film thickness by interferometry but also detection of photoluminescence at wavelengths where the coating was transparent. To minimize photodamage, the power of the incident light from the argon ion laser (488 nm) was kept below $1\text{ }\mu\text{W}$ at the sample stage. The use of low power was critical because MEH-PPV was found to be prone to photobleach.

In the absorption experiments, the spatial resolution was the pixel size, $3.3\text{ }\mu\text{m}$. In the photoluminescence experiments, the spatial resolution was $\approx 0.3\text{ }\mu\text{m}$, and the data were acquired using the same optical setup as for confocal Raman experiments that was described by us recently elsewhere.⁸

Absorption Spectra

Unlike the study of discrete dye molecules at surfaces, in the case of a conjugated polymer the entire polymer chain comprises the dye whose optical properties are measured. To quantify how sliding caused the polymer chains to orient, first we analyzed with polarized light the optical absorbance of these thin films. Figure 2a illustrates the raw data, ~ 10 orders of fringes produced by multiple optical interference between silver coated on the backsides of the mica sheets. From diminished fringe intensity as a function of wavelength, the optical absorbance at those discrete wavelengths was deduced by methods introduced by Helm,¹⁰ and the data for the bulk polymer solution (Figure 2b) was compared to that in the thin films (Figure 2c). These conclusions were confirmed from separate analysis (not shown) of bandwidth and spectral changes. One sees that the polymer backbone was isotropic when first confined but became increasingly anisotropic with elapsed time.

For quantification, the absorption anisotropy (A) was defined as $A = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + A_{\perp})$, where A_{\parallel} and A_{\perp} represent the integrated areas under the absorption peaks parallel and perpendicular to the shear direction,

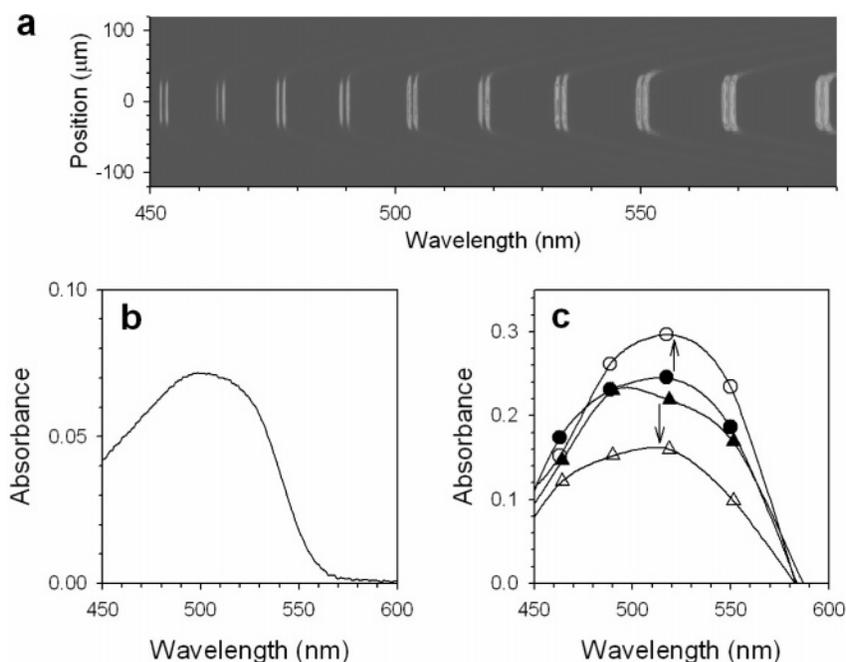


Figure 2. Absorbance measurements illustrating shear-induced alignment perpendicular to shear. Panel a shows 10 fringes of multiple optical interference. They form doublets because mica is birefringent. Panel b shows optical absorbance vs wavelength for MEH-PPV in toluene solution. Panel c contrasts optical absorbance just after confinement to 2.0 nm thickness (filled symbols) and after confinement and shear for 1 h (open symbols). Circles and triangles denote polarized absorption perpendicular and parallel to the shear direction, respectively. Detailed inspection showed that the implied chain anisotropy was identical everywhere in the thin film within the pixel resolution of $3.3\text{ }\mu\text{m}$ with absorption anisotropy 0.35 .

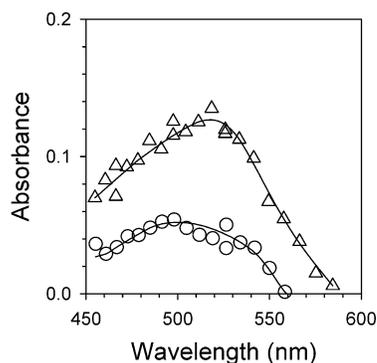


Figure 3. Absorbance measurements illustrating shear-induced alignment parallel to shear. Optical absorbance is plotted against wavelength for MEH-PPV films 2.0 nm thick. Circles and triangles denote polarized absorption perpendicular and parallel to the shear direction, respectively. The absorption anisotropy is +0.5.

respectively. For the MEH-PPV molecule, calculations by Barbara and co-workers show that perfect alignment gives $A = 0.65$ due to the cylindrical shape of the molecule.^{11,12} In the experiments in Figure 2, $A = -0.24 \pm 0.03$; the negative sign indicates alignment perpendicular to the shear direction. Detailed investigation of the data, pixel by pixel, confirmed that not only the film thickness but also the absorption anisotropy was homogeneous across the contact area within the pixel resolution of $3.3 \mu\text{m}$.

As discussed in more detail below, this spatial homogeneity contrasts notably with the optoelectronic response of conjugated polymers obtained from conventional room temperature methods, which is well-known to differ from spot to spot along a sample;¹³ in the present experiments the same orientation was observed everywhere within the contact area. In this respect, the spatial homogeneity that we observed resembles that normally obtained only from high-temperature processing of conjugated polymers.

The direction of chain alignment, perpendicular or parallel to the shear direction, was found to vary stochastically from experiment to experiment (more on this below). An example of orientation preferentially parallel to the shear direction is shown in Figure 3. To explore the distribution of response, Figure 4 summarizes the findings from 17 independent experiments. One observes that perpendicular orientation was observed in ca. $1/3$ of occurrences and parallel orientation in ca. $2/3$ of the occurrences.

Photoluminescence

Of more practical potential importance is photoluminescence (PL); this, the light emitted when the sample is illuminated, is most sensitive to those structures of lowest electronic energy to which absorbed light is funneled. The conjugation length in dilute solution is estimated to be $\approx 6 \text{ nm}$,¹⁴ but the films studied here were thinner (2 nm), so clearly one should expect potentially interesting differences from photoluminescence spectra characteristic of the bulk solution. In these experiments we employed the Frantz–Salmeron method to cleave the mica¹⁵ for technical reasons discussed elsewhere.¹⁶

Figure 5a shows the photoluminescence (PL) spectrum of this polymer in bulk dilute toluene solution. Next, Figure 5b–d shows the PL intensity as a function of wavelength at various times while the film was sheared and dried. In the field of optoelectronics, it is

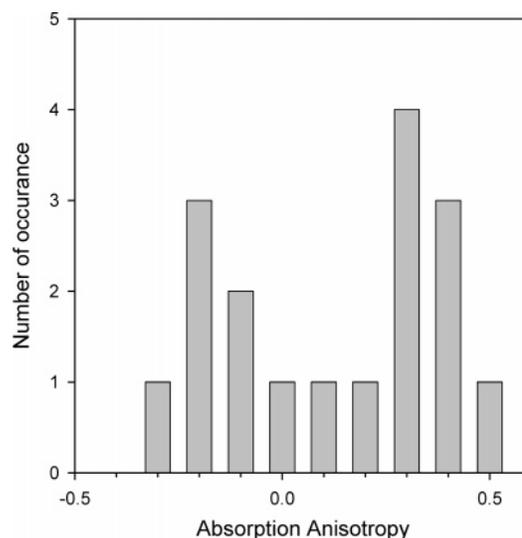


Figure 4. Histogram of absorption anisotropy in 17 independent experiments. The bimodal distribution shows peaks with alignment both perpendicular to shear (negative absorption anisotropy) and parallel to shear (positive absorption anisotropy). Possible reasons are discussed in the text.

known that as the electronic states of conjugated polymers become increasingly coupled, the quantum yield decreases.¹³ From this perspective, it is significant that the total PL intensity decreased markedly after drying, as quantified in Figure 5e; the lower quantum yield indicates coupling of the electronic states after solvent evaporated.

Even more intriguing is the time dependence. At the beginning of the shear process, the intensity parallel to the polarization of the excitation was strongest, as must be expected for a sample that had not yet reoriented, yet this trend reversed as shear continued. The ratio of PL intensity, perpendicular relative to parallel, required 1 h to reach steady state (Figure 5e).

The final ratio of roughly 3 indicates that the lowest electronic energy levels, those that generated the PL, had evolved to become oriented preferentially perpendicular to the shear direction. It is noteworthy that reorientation proceeded so slowly—about 10 orders of magnitude slower than the relaxation time of these same chains in bulk solution, where the longest relaxation time of chains of this length is on the order of microseconds.¹⁷ In the literature, slow equilibration of confined fluid films is usually measured indirectly by friction, a mechanical property. It is fascinating to see this also directly in the optical properties.

In the field of conjugated polymers, films so thin are not normally studied because uniform films so thin cannot be produced. Concerning thicker samples, NSOM and other studies by Van den Bout and co-workers^{13,18} find evidence that some kind of mesostructure develops, usually attributed to “molecular aggregation”. Yet the present experiments, conducted at room temperature, were measured to be the same throughout the contact area. Apart from the diminished aggregation peak, the spectral bands in these molecularly thin films are similar to those when a conjugated polymer is annealed at high temperature.²⁰

Inspecting more closely the PL spectra in Figure 5, we note that they contain three characteristic bands whose assignment is known in the field of conjugated polymers.¹³ These are the $0 \rightarrow 0$ transition, $0 \rightarrow 1$ transition and aggregation peak. In their details, these

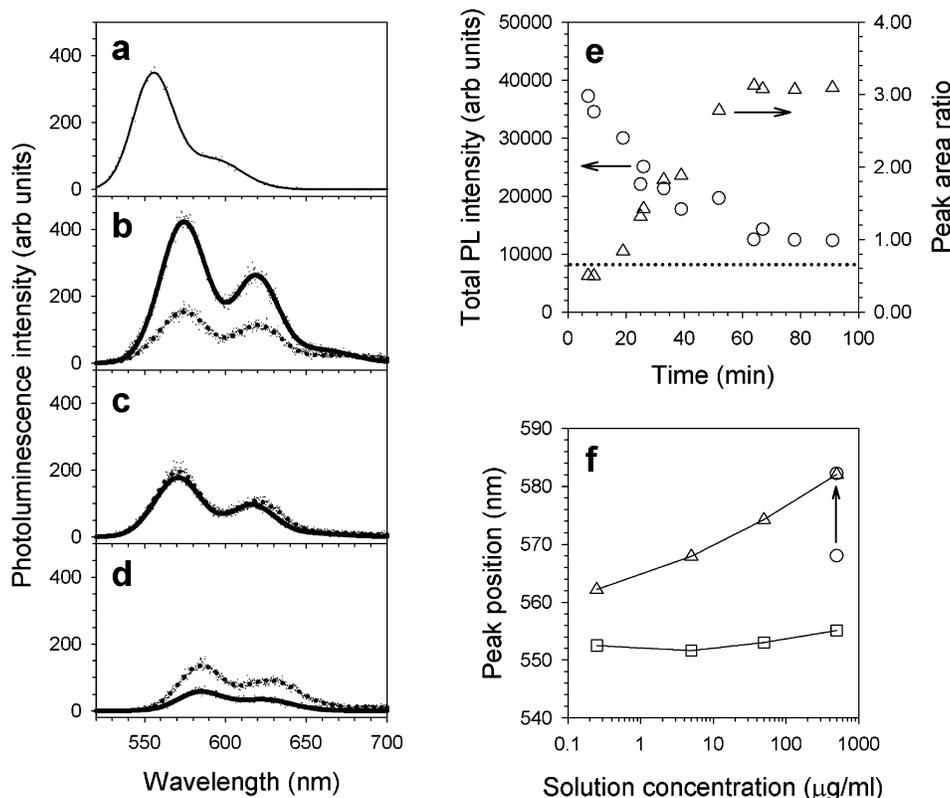


Figure 5. Photoluminescence spectra of films 2.0 ± 0.2 nm thick. Panel a shows PL spectra of bulk solution for comparison. Illustrative PL data, polarized parallel and perpendicular to incident light, which was also the shear direction (bold and dotted lines, respectively) are plotted after 7, 25, and 130 min (b, c, and d, respectively). In (d), the film is dry. Panel e shows integrated intensity (circles) and intensity ratio, perpendicular to parallel (triangles) plotted against time sheared; the dotted line characterizes the latter in bulk solution. Panel f shows concentration dependence of the peak wavelength of the $0 \rightarrow 0$ transition for MEH-PPV solutions of various concentrations in solution (squares), in films dried without shear (triangles), a film 2 nm thick sheared in solvent (circle), and this same film dried after shear (at end of the vertical arrow).

bands display intriguing differences from those characteristic of conventional thicker films, whose properties have been studied extensively. Specifically, the bands in Figure 5 are somewhat narrower on the frequency scale; by well-known arguments, this frequency narrowing shows that the environment was less heterogeneous than in the usual bulk samples. Furthermore, the band at highest wavelength (~ 680 nm) is smaller in relative amplitude than in conventional bulk films, indicating less aggregation.

Additional information about the influence of chain packing on electronic states comes from analysis of the leftmost peak, the $0 \rightarrow 0$ transition. Analyzed in terms of the wavelength at peak maximum, the significance is that the larger the red shift (i.e., the larger the wavelength), the greater the electronic delocalization. This can be interpreted loosely as a more extended conjugation length.

Exploring the quantitative aspect of this idea, Figure 5f shows that although insensitive to concentration in bulk solution, in dried films this red shift was larger, the larger the solution concentration from which the films were prepared. The origins of electronic delocalization are controversial in the large literature on conjugated polymers, however. Without wishing to comment here on this subtle matter, we note that by controlling chain conformations by confinement and shear, and the degree to which chains are intertwined by solution concentration, the data in Figure 5 show the capability to manipulate the polymer conformations that underlie the lowest electronic energy states that govern PL properties.

What was the effect of shear? The two data points separated by an arrow in Figure 5f show that the consequence of shearing a wet film was in the opposite direction; it reduced the red shift relative to dried films. Although systematic experiments in this direction are still at an early stage, this underscores the main practical finding presented in this paper, at the combination of confinement and shear can be used to tailor optical properties of the material.

Prospects

First, we comment speculatively on the surprising observation that chain alignment in Figures 2 and 5 was often perpendicular to the shear direction, not parallel to it as is generally supposed to occur when fluids flow. Our attempts to date seeking to standardize the experimental protocol in order to understand the experimental conditions leading to perpendicular or parallel alignment have not, to date, been successful. In principle, the reason for the bimodal distribution may involve small differences in evaporation rate or in the rate at which the thin film was formed, but as the observed bimodal distribution of findings has persisted despite our careful attempts to standardize the experimental protocols, the controlling distinction which determines the direction of shear alignment is clearly extremely sensitive to seemingly small changes in the initial conditions.

Also in the study of block copolymer melts,^{21,22} either perpendicular or parallel alignment is observed, depending on a tradeoff between external deformation rate

and internal relaxation rate of the film. At present, we do not know whether this is a deep or coincidental analogy. In principle, it might be connected to the ribbonlike mesostructure observed in NSOM (near-field scanning optical microscopy) studies of thicker films of another conjugated polymer,¹⁸ but the PL spectra obtained in this study provide no direct evidence in favor. Alternatively, there may be some tradeoff between sliding (which would favor alignment in the flow direction) and rolling (which would favor alignment perpendicular to the flow direction).²³

From another point of view, there is the interesting possibility (in future work) to build upon the sensitive optical responses of conjugated polymers to study fundamental aspects of polymers when adsorbed from solution, rather than confined as was done in the present study. This rich family of questions can be studied experimentally in the same instrument described here; the only modification needed is that the light incident from the argon ion laser be directed outside the location where the crossed mica cylinders of the surface forces apparatus are closest together. Then the photoluminescence spectrum is characteristic of a single adsorbed polymer layer. Preliminary experiments have already been performed, showing the feasibility of such studies. In the context of the present study, the significance was to show that the confinement effects reported above did result from confinement, not merely from adsorption and optical interactions with the mica surfaces. In future studies, it would be interesting to extend studies of this kind to include polarization and concentration dependence to explore how polymer segment alignment parallel to the adsorbing surface depends on solution concentration and other relevant variables.

In conclusion, this study describes a simple, generalizable approach by which to capitalize on friction of molecularly thin films to control a materials properties that carries possible functionality. This was illustrated by showing how optoelectronic properties were modified by combined alignment of chain conformations by shear and confinement to slits thinner than random-coil dimensions. Looking to the future, we also conjecture that novel chemical reactions may transpire after reactant molecules have been confined and oriented by frictional sliding.

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