Reflectance anisotropy spectroscopy of oriented films of semiconducting polymers

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We present reflectance anisotropy spectroscopy (RAS) data for aligned films of luminescent conjugated polymers. Ultrathin films (5–10 nm) spin-cast onto friction-deposited poly-tetrafluoroethylene (PTFE) show birefringence and dichroism indicating alignment of the polymer chains with the PTFE axis. The observed dichroism agrees very well with recently published polarized ultraviolet absorption spectra. In particular, the spectrum of a derivative of poly (*para*-phenylene) shows the onset of a perpendicular-polarized absorption feature at 5 eV, consistent with recent theoretical predictions. Thick films, prepared by gel-processing in polyethylene (PE), also show characteristic optical anisotropy, and the RAS results are interpreted in terms of the ellipsometric functions, Ψ and Δ. © *2000 American Institute of Physics.*
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I. INTRODUCTION

Semiconducting and metallic conjugated polymers have attracted much attention because of their applications in thin-film devices such as light-emitting diodes[1,2] and electrochemical cells,[3] field-effect transistors and photovoltaic devices.[4] In particular, much research has focused on light-emitting polymers such as poly (*para*-phenylene vinylene) (PPV), poly (*para*-phenylene) (PPP) and their soluble derivatives. The most instructive optical studies of the fundamental electronic structure of these polymers are polarized spectroscopies of uniaxially oriented samples such as those produced by gel-processing in polyethylene.[5,6]

In this work, we present fabrication and optical characterization of ultrathin, oriented films of a polyfluorene derivative, poly (9-hexyl-9-(2′-ethyl-hexyl)-fluorene-2, 7-diyl) (HEH-PF, see inset of Fig. 1). Films spin-cast onto substrates coated with friction-deposited poly-tetrafluoroethylene (PTFE) show measurable optical anisotropy, including dichroism of the lowest $\pi-\pi^*$ absorption feature and birefringence below and above the band gap. These films are only a few monolayers thick, significantly thinner than those prepared by Pichler *et al.*[7] The optical anisotropy is measured by reflectance difference spectroscopy (RAS), which has been shown to be sensitive even for sub-monolayer coverage.[8] We anticipate, therefore, that this nondestructive technique will become popular for characterization of ultrathin organic films.

We also extend this method to study tensile-drawn films of a PPV derivative, poly(2-butyl, 5-(2′-ethyl)-hexyl) *para*-phenylene vinylene (BuEH-PPV) gel-processed in polyethylene. The physical thickness and high anisotropy of stretched films requires a different quantitative analysis, but the qualitative observations are similar to those for the ultrathin films. The BuEH-PPV chains are aligned with the PE fibrils during the drawing process, leading to high-structural order and molecular alignment.

II. EXPERIMENT

Substrates for the ultrathin films were glass microscope slides coated with friction-deposited PTFE as described in the literature.[9] Deposition was done with both the substrate and the PTFE source held at 290 °C, and a loading of 4 kg/cm^2 of contact area. The substrate was fed at ~1 mm/s. The resulting films were barely visible by eye but showed strong birefringence under a cross-polarized microscope. Semiconducting polymers were spin-cast from dilute solution (typically 0.01%–0.1%) onto the substrates at typical

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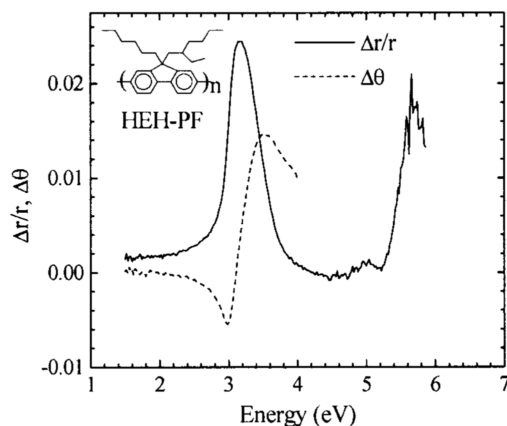

FIG. 1. RAS data for an ultrathin film of HEH-PF/PTFE. The raw RAS data, $\Delta r/r$ and $\Delta\theta$, show the clear dichroism and birefringence near the absorption edge due to alignment of the HEH-PF molecules with the PTFE template. The inset shows the molecular structure of HEH-PF.

spin rates of 2000 RPM. The HEH-PF was spin cast from toluene solution; dichroism was also observed for a polythiophene derivative spin-cast from chloroform solution and for MEH-PPV spin-cast from ODCB solution. The resulting films showed no noticeable dichroism under the microscope, and typical optical densities were ~0.05.

Gel-processed films were prepared as described by Hagler *et al.*[10] The RAS data shown are for a gel-film of BuEH-PPV, 17 wt % in PE, drawn to a ratio of 100. This film gave particularly good data because it is only ~1 μm thick compared to more typical values of 5–10 μm for other films studied. As a result, the sample is optically thin (max O.D. ~0.3) throughout the spectral range measured. Free-standing films were mounted on a silica plate at the focus of the RAS spectrometer's optics. Ultraviolet (UV) dichroism data on HEH-PF for comparison with the RAS spectra of the ultrathin films were taken for a gel-film of HEH-PF, 15 wt % in PE, drawn to a ratio of 50.

The RAS spectrometer, manufactured by ISA-Jobin-Yvon, utilizes a Xenon lamp and a photomultiplier tube (PMT) to achieve a broad spectral range. The design and operating principles of RAS spectrometers are described in detail in the literature.[11] In RAS, the measured quantity is the difference between the normal-incidence reflectance for two orthogonal polarization directions in the surface plane. The results are displayed as $\Delta\tilde{r}/\tilde{r}\approx\Delta r/r+i\Delta\theta$ (to first order in Δr and $\Delta\theta$) with $\tilde{r}=r\exp(i\theta)$. We define $\Delta\tilde{r}$ as $\tilde{r}_y-\tilde{r}_x$ where the subscripts denote the incident polarization vectors along the optical eigenaxes.

In RAS, light incident on the sample is polarized at (±)45° to the optical eigenaxis; the reflected light is then modulated by a photoelastic modulator (PEM) and analyzed by a second polarizer. A lock-in amplifier detects the signal from the PMT, modulated at the first and the second harmonic of the PEM drive frequency. These signals are, as a fraction of the dc (direct current) signal, related to the difference in magnitude and in phase, respectively, between the 0° and 90° components. Rotating the polarization (or the sample) by 90° simply reverses the sign of the magnitude and phase differences; rotating so that the polarization is parallel to an optical axis reduces the difference signal to zero. Both of these checks were routinely made to ensure reliable data.

III. RESULTS AND DISCUSSION

A. Optical formalism

Reflectance anisotropy (RA) data are the difference in magnitude and phase of the complex reflection coefficient for light polarized along two orthogonal axes. The formal definition of RA in terms of the reflection coefficient $\tilde{r}=re^{i\theta}$ is

$$\frac{\Delta\tilde{r}}{\tilde{r}}\equiv 2\,\frac{\tilde{r}_y-\tilde{r}_x}{\tilde{r}_y+\tilde{r}_x}\approx\frac{\Delta r}{r}+i\Delta\theta, \tag{1}$$

with $\Delta r=r_y-r_x$ and $\Delta\theta=\theta_y-\theta_x$. In the case of thin films, the real and imaginary parts of the RA is related to the anisotropy of the dielectric tensor, $\tilde{\varepsilon}=\varepsilon_1+i\varepsilon_2$, as follows:

$$\frac{\Delta r}{r}+i\Delta\theta=i\,\frac{4\pi d}{\lambda(\tilde{\varepsilon}_b-1)}(\tilde{\varepsilon}_y-\tilde{\varepsilon}_x)$$
$$=\frac{4\pi d}{\lambda(\tilde{\varepsilon}_b-1)}[(\varepsilon_{2,x}-\varepsilon_{2,y})+i(\varepsilon_{1,y}-\varepsilon_{1,x})], \tag{2}$$

where ε_b is the dielectric function of the substrate and is taken real (glass) in the second equality sign. The reflectance, $\tilde{r}$, is dominated by the substrate which is assumed to have thickness much greater than the wavelength of the light. Hence, for thin films on isotropic substrates, $\Delta r/r$ gives the dichroism, and $\Delta\theta$ gives the negative birefringence.

B. Ultrathin films of HEH-PF

The RAS spectra for a 10 nm thick HEH-PF/PTFE film is shown in Fig. 1. The $\Delta r/r$ signal clearly shows the dichroism of the lowest $\pi-\pi^*$ absorption, and the $\Delta\theta$ signal shows the dispersion and birefringence near the absorption edge. Above 4 eV, the $\Delta\theta$ signal is dominated by a weak optical anisotropy of the glass substrate, but no effect was seen in the $\Delta r/r$ signal for the glass. The effects on $\Delta\theta$ and $\Delta r/r$ due to the PTFE layer are much smaller than those from the conjugated polymer.

Polarized UV absorption measurements on highly oriented free-standing films of HEH-PF/PE[12] provide complementary data by directly probing the absorption coefficient parallel and perpendicular to the chain axis. In Fig. 2, we show the dichroism ($\alpha_\parallel-\alpha_\perp$) for a highly oriented, free-standing HEH-PF/PE film, together with the corresponding data from the RAS measurement on the ultrathin film on PTFE. The lowest energy peaks are slightly offset because $\Delta\varepsilon_2$ (measured by $\Delta r/r$) includes a contribution from the dispersion of the anisotropic index of refraction in addition to the (dominant) contribution from the absorption. Of particular note in Fig. 2 is the faithful reproduction in the RAS data of the dip at 5.2 eV in the dichroism spectrum. This feature corresponds to the perpendicular-polarized shoulder to the high-energy absorption features, which has been studied theoretically[13] and recently reported experimentally[12] for PPP derivatives. The parallel- and perpendicular-polarized spectra are shown in the inset of Fig. 2.

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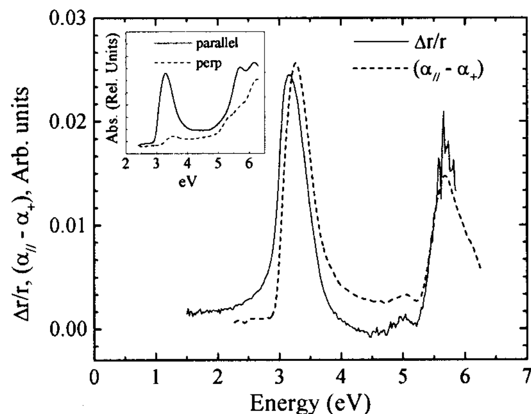

FIG. 2. The $\Delta r/r$ data shown together with the UV dichroism spectrum for highly oriented HEH-PF/PE blends. The onset at 5 eV of the perpendicular-polarized absorption band is clearly evident in both spectra as a downturn in the dichroism. The inset shows the polarized UV absorption spectra used to generate the dichroism spectrum.

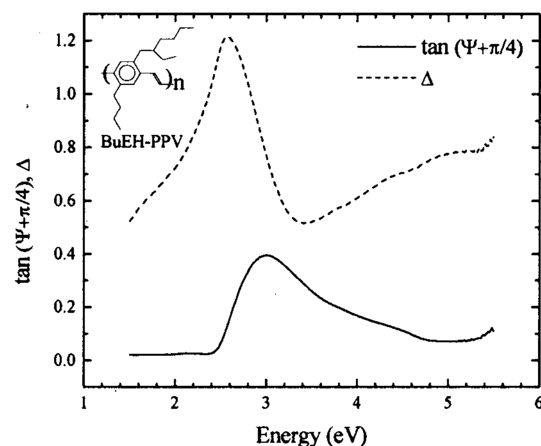

FIG. 3. The ellipsometric functions tan($\Psi+\pi/4$) and Δ for a free-standing film of BuEH-PPV/PE, as computed from the RAS spectra. The inset shows the molecular structure of BuEH-PPV.

The two simple models for explaining the optical anisotropy of the HEH-PF chains on the PTFE substrate are (1) a highly aligned layer at the interface with an isotropic layer above, or (2) a uniformly anisotropic film. Calculations for these models follow from Eq. (2), in which the RAS signal is proportional to the magnitude of the anisotropy multiplied by the layer thickness. The absorption coefficient for HEH-PF in spin-cast films is $\sim 1.7\times 10^5\ \text{cm}^{-1}$, so a highly oriented layer (1) would have to be ~3 Å thick to yield this anisotropy. Alternatively, a uniform layer (2) with modest anisotropy would have $\Delta\varepsilon_2 \sim 0.1$ at the absorption maximum where ε_2 is ~1.8 in unoriented samples. We observed similar values of the anisotropy in ultrathin films of PPV derivatives and polythiophene derivatives studied by RAS. Clearly, the anisotropy is modest but measurable, indicating that further processing steps, such as melting to exploit the liquid crystallinity of the polymers[14] may enhance orientation at the molecular level.

C. Free-standing films of BuEH-PPV/PE

In the case of thick, free-standing films, the modulated signal from the detector is no longer small compared to the maximum possible modulation by the PEM-analyzer combination. The formal definition of these limits can be derived from the discussion by Acher *et al.*[15] The proper interpretation of the data is in terms of the ellipsometric variables Ψ and Δ where $\rho=\tilde{r}_x/\tilde{r}_y=\tan\Psi e^{i\Delta}$. By definition, normal-incidence reflection from a perfectly isotropic material gives $\rho=-1$, so in the limit of small anisotropy, $\Psi\approx-\pi/4$ and $\Delta \ll 1$. The ellipsometric angles in this limit correspond to the RAS values as follows:

$$2(\Psi+\pi/4)=\Delta r/r, \quad (3a)$$

$$\pi-\Delta=\Delta\theta. \quad (3b)$$

To compute the ellipsometric angles, we must consider the detected signal and the numerical output of the spectrometer. The time-varying signal at the detector is given by

$$I(t)=I_0\{1+I_S\sin\delta(t)+I_C\cos\delta(t)\}, \quad (4a)$$

$$\delta(t)=A\sin\omega t, \quad (4b)$$

where A is the magnitude of the piezo-optic modulation by the PEM (typically $\sim 10^{-3}$), and ω is the modulation frequency (in this case, 50 kHz). Then the general expression for the ellipsometric angles is

$$I_S=\sin 2\Psi\sin\Delta, \quad (5a)$$

$$I_C=\cos 2\Psi. \quad (5b)$$

Solving these equations for Ψ and Δ gives

$$\text{Sin}\,\Delta=I_S/(1-I_C^2)^{1/2}, \quad (6a)$$

$$\text{Sin}\,2\Psi=(1-I_C^2)^{1/2}. \quad (6b)$$

Finally, we note that, due to the small-signal expansion, the recorded values for $\Delta r/r$ and $\Delta\theta$ from the spectrometer are simply $(-I_C)$ and $(-I_S)$,[15] respectively.

The spectra of Δ and tan($\Psi+\pi/4$) for the free-standing film of BuEH-PPV are shown in Fig. 3. Since the film is optically thin ($T\approx 0.75$), the spectra represent absorption and refraction of the incident beam as it passes through the film, reflects off of the silica plate and passes through the film again. Refraction and absorption in the bulk dominate the RAS signal rather than anisotropic reflections at the air-film and film-substrate interfaces. Due to the physical thickness of the film the polarization state of the light will change significantly on a single pass; the off-axis linear polarization will become elliptically polarized with a leading-order eccentricity. This is in contrast to the ultrathin films for which the phase thickness is very small and the reflected polarization is nearly linear. The simple numerical relations between dielectric function and RAS signal, then, are not strictly valid in the case of highly anisotropic, thick films. Analytical relations for RAS were deduced also for thick layers, but they cannot be used in our case for data evaluation, since the absolute values of ϵ are not known.[16] Nonetheless, the data provide a qualitative measurement of the dielectric anisotropy of the oriented BuEH-PPV films. Birefringence in spin-cast films of BuEH-PPV was shown[17,18] to limit waveguide modes in thin films to purely TE modes. Hence, the birefrin-

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gence below the absorption edge in luminescent polymers will have a significant role in the design of solid-state lasers.

IV. CONCLUSION

We have shown that oriented, ultrathin films of conjugated polymers can be readily fabricated by spin-coating onto friction-deposited PTFE. Films that are only a few monolayers thick can be quickly and nondestructively characterized by RAS to ascertain the birefringence and dichroism due to molecular orientation. In addition, thick films oriented by gel-processing in PE show high degrees of anisotropy, in agreement with polarized UV absorption measurements on the same film. RAS is a promising candidate for characterization and *in situ* monitoring of ultrathin films of molecular conductors and semiconductors, which may form the basis for molecular electronics.

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