Large Photoinduced Circular Dichroism in Chiral Polyfluorene

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At 77 K, thermally annealed films of chiral poly[9,9-bis((3*S*)-3,7-dimethyloctyl)-2,7-fluorene] show a photoinduced absorption (PIA) band near 1.5 eV due to a transition from the lowest triplet state to a higher triplet state. This photoinduced absorption is found to show circular dichroism (CD). Dividing this CD by the magnitude of the PIA, we find that the selectivity for absorption of left circular polarized light over right circularly polarized light is remarkably high and characterized by a dissymmetry ratio $g = +0.2$. The unusual magnitude of g is interpreted as arising from extrinsic CD, i.e., from the interaction of the local linear polarization of the triplet−triplet absorption with the linear birefringence of the surrounding polymer matrix.

Introduction

Circular dichroism is a difference in absorbance between left and right circular polarized light by chiral molecules or materials in their *electronic ground state*. In the last decades, this method has been extended to cover circularly polarized absorption from excited states. The associated effect can be termed photoinduced circular dichroism (PICD) and provides information on the structure and dynamics of the chiral molecules in their *excited state*. The first reports described circular dichroism in photostationary triplet−triplet absorption,[1] later developments involved time-resolved methods using short light pulses.[2] PICD has been used to study light induced conformational changes in, e.g., small molecules[3,4] and proteins[5] in solution. Here we apply PICD to solid films of chiral poly[9,9-bis((3*S*)-3,7-dimethyloctyl)-2,7-fluorene] (**1**, Figure 1).

Chiral polyfluorenes have been used as the active layer in polymer light emitting diodes. After thermal annealing, the layers show a surprisingly large degree of circular polarization in absorption and (electro-)luminescence. This is believed to be related to long-range molecular order induced by annealing.[6]

Here we investigate the circular dichroism in the photoinduced absorption of a thermally annealed layer of *chiral* polyfluorene **1**. A main question is whether the large degree of circular polarization observed in ground state chiroptical measurements, also transfers to the excited state absorption. Results are of importance in understanding the chiroptical response and long-range molecular order in solid films of π-conjugated polymer.

Experimental Section

Materials and Sample Preparation. The films were prepared by spincoating a solution (22.5 mg/mL) of chiral polyfluorene (poly[9,9-bis((3*S*)-3,7-dimethyloctyl)-2,7-fluorene], **1**) at 1000 rpm. The synthesis of the polymer has been described.[7] The thickness of the film was measured by the Veeco surface profilometer and was found to be ∼290 nm. Thermal annealing of the films was done in air at 120 °C for 10 min. UV−vis measurements were done on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. The CD effect in this particular annealed film with ellipticity >2000 mdeg, was measured using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer and a circular sheet polarizer (Oriel).

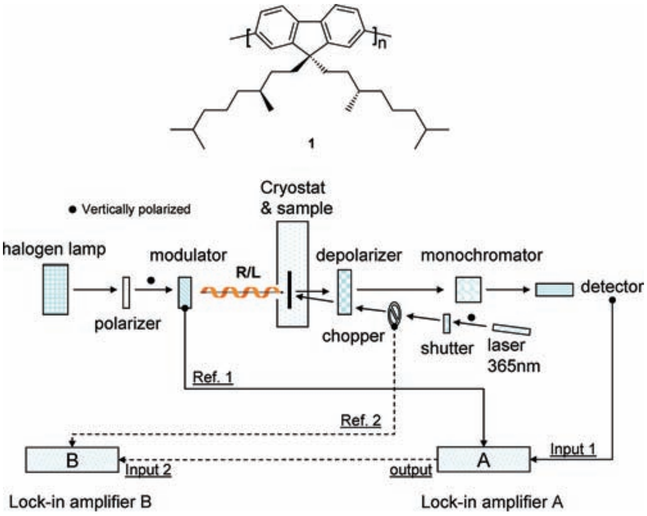

Figure 1. Chemical structure and PICD setup.

Detection of Photoinduced Circular Dichroism (PICD). To measure photoinduced absorbance effects, a tailor-made set up was installed as shown in Figure 1. The sample was held in an N_2 flow cryostat at $T = 77$ K. The incident laser light (Argon ion laser, Spectra-Physics type 2020, 365 nm, 60 mW) was allowed to pass through a chopper at 75 Hz. White light (halogen lamp) was used as probe. The intensity of the white light transmitted through the sample (T) was determined first by modulating it at a known frequency. To probe the PIA signal, the white light intensity was kept constant, whereas the laser light was modulated at 75 Hz. Fluorescence corrections were made to the PIA signal. However, not entire fluorescence could be rectified. The setup measures PIA and fluorescence in separate scans and takes a difference in the values to obtain the corrected PIA. Owing to very high fluorescence from these thick annealed films, 100% corrections are not achieved. Some residual fluorescence signal appears in the high-energy region around 2.8 eV.

When the modulated laser light illuminates the sample during one-half of the modulation period, the photoinduced absorption

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associated with the triplet−triplet transition gives rise to a reduction of the transmission ($\Delta T = T^{\mathrm{ON}} - T^{\mathrm{OFF}}$) at wavelength of the probe light. The associated PIA signal is proportional to the normalized differential transmission ($\Delta T/T$).

Defining absorbance A in the traditional way we write

$$A = -\log\left(\frac{T}{T_0}\right) \tag{1}$$

where T_0 is the transmitted light intensity and T is the intensity of the incident light.

The differential absorbance (PIA) recorded between on and off laser modes can now be expressed as

$$\mathrm{PIA} = \Delta A = A^{\mathrm{ON}} - A^{\mathrm{OFF}} = -\log\left(\frac{T^{\mathrm{ON}}}{T^{\mathrm{OFF}}}\right) \cong \frac{-1}{\ln 10}\left(\frac{\Delta T}{T_0}\right) \tag{2}$$

where we have used the Taylor series to approximate the logarithmic function:

$$-\ln\left(\frac{T^{\mathrm{ON}}}{T^{\mathrm{OFF}}}\right) \cong 1 - \frac{T^{\mathrm{ON}}}{T^{\mathrm{OFF}}} \cong \frac{T^{\mathrm{OFF}} - T^{\mathrm{ON}}}{T_0} = -\frac{\Delta T}{T_0} \tag{3}$$

The PIA signal was recorded by feeding the detector output directly into a lock-in amplifier (Stanford research systems SR830) and monitoring the intensity of transmitted light with chopper frequency as the reference (Figure 1). The detector signal was fed in directly to lock-in amplifier (B) bypassing (A).

To measure PICD, the probe light has to be circularly polarized. This was achieved by passing the probe light through a linear calcite polarizer and subsequently through a photoelastic modulator (PEM, Morvue) held at $\lambda/4$ retardation wavelength and rotated by 45° from the vertical axis. The PEM operates at 50 kHz. After passing through the sample, the probe light is depolarized using a Rochon prism or alternatively a multicrystalline sapphire plate. The laser light used to excite the sample was also depolarized to avoid photoselective excitation of polymer chains with a particular orientation.

To measure the PICD, a double lock-in method was used. The signal from the detector is first analyzed for components at 50 kHz using lock-in amplifier (A). This records the circular differential transmission by the sample. Illuminating the sample with time-modulated laser light, the circular differential transmission signal picked up by amplifier (A) will now oscillate between two values. One corresponds to the ground state CD and the other to the ground state CD plus the PICD. This modulation occurs at the same frequency as the modulation of the laser light and can be recorded by feeding the output of lock-in amplifier (A) into a second lock-in amplifier (B) with the frequency of the chopper (modulating the laser light) as reference. Here it is important that the time constant for the first lock-in amplifier (A) is set short enough for its output to follow the second modulation. Here we used a time constant of 10 μs. The lock-in amplifier is autophased during the measurement of scattered laser light through the sample. The phase angle recorded for PIA and PICD measurements is relative to this measurement.

In summary, the output signal of lock-in amplifier (A) corresponds the circular differential transmission ($\Delta T_{\mathrm{LR}} = T_{\mathrm{L}} - T_{\mathrm{R}}$) and oscillates between $\Delta T_{\mathrm{LR}}{}^{\mathrm{ON}}$ and $\Delta T_{\mathrm{LR}}{}^{\mathrm{OFF}}$. These latter values are related to the circular dichroism in the dark and light period of the modulation cycle:

$$\Delta A_{\mathrm{CD}}^{\mathrm{OFF}} = A_{\mathrm{L}}^{\mathrm{OFF}} - A_{\mathrm{R}}^{\mathrm{OFF}} = -\log\left(\frac{T_{\mathrm{L}}^{\mathrm{OFF}}}{T_{\mathrm{R}}^{\mathrm{OFF}}}\right) \cong -\frac{-1}{\ln 10}\left(\frac{\Delta T_{\mathrm{LR}}^{\mathrm{OFF}}}{T^{\mathrm{OFF}}}\right) \tag{4}$$

$$\Delta A_{\mathrm{CD}}^{\mathrm{ON}} = A_{\mathrm{L}}^{\mathrm{OFF}} - A_{\mathrm{R}}^{\mathrm{OFF}} = -\log\left(\frac{T_{\mathrm{L}}^{\mathrm{ON}}}{T_{\mathrm{R}}^{\mathrm{ON}}}\right) \cong -\frac{-1}{\ln 10}\left(\frac{\Delta T_{\mathrm{LR}}^{\mathrm{ON}}}{T^{\mathrm{ON}}}\right) \tag{5}$$

Lock-in amplifier (B) is used to record the amplitude of this oscillation ($\Delta T_{\mathrm{LR}}{}^{\mathrm{ON}}$ and $\Delta T_{\mathrm{LR}}{}^{\mathrm{OFF}}$) and the PICD can now be obtained by dividing this output by the white light intensity T using the relation.

$$\mathrm{PICD} = \Delta A_{\mathrm{CD}}^{\mathrm{ON}} - \Delta A_{\mathrm{CD}}^{\mathrm{OFF}} \cong \frac{-1}{\ln 10}\left[\frac{\Delta T_{\mathrm{LR}}^{\mathrm{ON}} - \Delta T_{\mathrm{LR}}^{\mathrm{OFF}}}{T_0}\right] \tag{6}$$

The PICD is expected to be linearly dependent on the magnitude of the photoinduced absorption. Therefore, this quantity itself is not very characteristic of the material. If we divide the PICD by the PIA, we obtain a quantity, g_{PICD}, that would describe the degree of circular polarization in the photoinduced CD. g_{PICD} is expected to be independent of the experimental parameters controlling the magnitude of the PIA signal.

$$g_{\mathrm{PICD}} = \frac{\mathrm{PICD}}{\mathrm{PIA}} \tag{7}$$

In this case we study only pure photoinduced absorption and not bleaching so that the PIA > 0.

Photoinduced linear dichroism (PILD) can be recorded using the same setup after changing the retardation of the PEM to $\lambda/2$ instead of $\lambda/4$ and detecting the second harmonic of the modulation frequency (i.e., 100 kHz) using a lock-in amplifier (A).

Results and Discussion

Films of **1** are fully transparent in the visible and near-infrared region of the spectrum and feature a dipole allowed optical transition to the lowest excited singlet state with an onset of at 2.9 eV. This transition can be used to photoexcite the material (Figure 2a). Upon excitation at 3.55 eV, the film shows photoinduced absorption (PIA) in the near-infrared region of the spectrum with a maximum around 1.53 eV (Figure 2b). The modulation technique used here is sensitive to photoinduced absorption from long-lived excited states. The signal at 1.53 has been assigned to an allowed transition from the lowest excited triplet state (T_1) to a higher lying triplet state (T_n).[8−11] At high photon energies (>2.5 eV), the fluorescence from the polyfluorene can be observed, showing a vibronic progression that is characteristic for this transition.

For the thermally annealed films of **1** we observe PICD with a magnitude up to 1×10^{-4} (expressed in optical density) at 1.53 eV (Figure 2c). The maximum in PICD coincides with that of the PIA. Upon dividing the PICD by the magnitude of

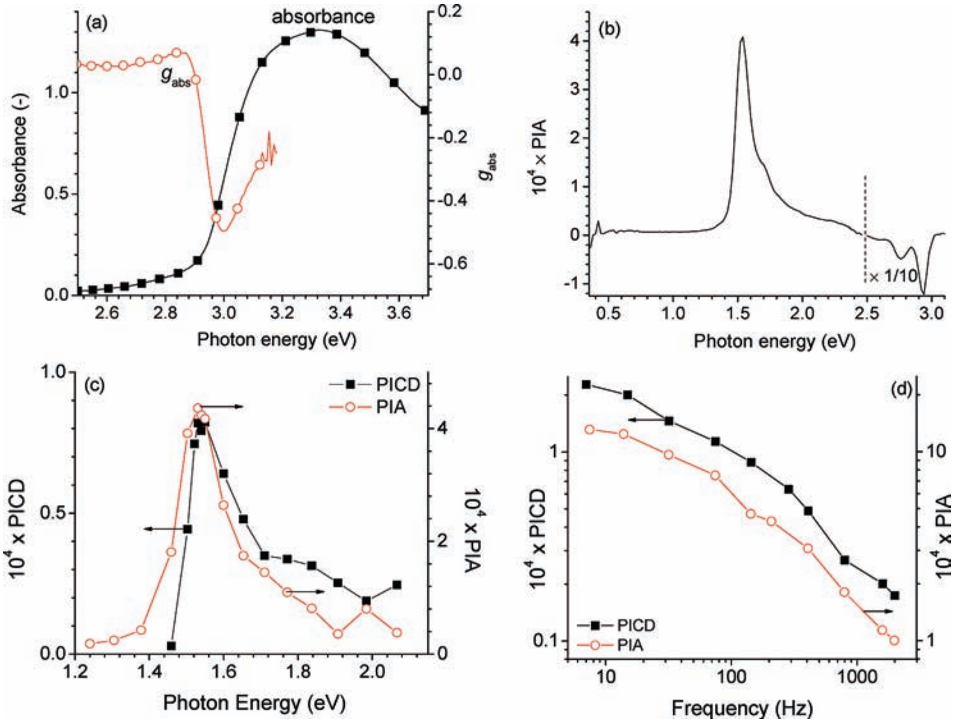

Figure 2. (a) Absorbance and g_{abs}. (b) PIA spectrum of a 290 nm thick, annealed film of **1** (power 50 mW, modulation frequency 275 Hz). The structure of **1** is shown in Figure 1. PICD and PIA spectrum of the same film with respect to (c) photon energy (power 60mW, modulation frequency 75 Hz), and (d) modulation frequency (power 60 mW). The lines joining the points in (c) and (d) are to guide the eye. Experiments are done at a temperature of 77 K and a laser excitation of 3.55 eV. The signal is monitored at 1.53 eV.

the PIA, we obtain a degree of circular polarization $g_{PICD} = +0.2$ at 1.53 eV. This surprisingly large polarization is of the same order of magnitude as the degree of circular polarization in ground state absorption $g_{abs} = (A_L - A_R)/(A_R)$, which reaches +0.5 at 3.0 eV.

Here the PICD is measured using a double modulation technique, using a photoelastic modulator for fast (50 kHz) modulation of the circular polarization of the probe light and slow mechanical modulation of the pump beam (75 Hz). Importantly, under the conditions of the experiment, photoinduced linear dichroism (PILD) is found to be much smaller than the PICD. We measure a degree of linear polarization g_{PILD} = PILD/PIA) smaller than 0.006 in an absolute sense at 1.53 eV. Hence artificial contributions to the PICD resulting from instrument imperfections in the form of linear birefringence are unlikely.[12]

The PICD and PIA signals follow practically the same band shape and feature the same peak position. Therefore, we assign the PICD to the triplet−triplet transition of the material. This assignment is further supported by the similar dependences of the two signals on the frequency of modulation of the primary UV excitation beam (Figure 2d). The intensity of both the PIA and PICD decays with increasing frequency with a dependence that may be described by a power law. This indicates a broad distribution of lifetimes for the triplet state with some triplets having a lifetime exceeding 10 ms.

The dependences of the PICD and PIA signals on the intensity of incident light are also very similar (Figure 3). When the power of the incident laser light (I) is low (<30 mW), the PIA and PICD vary approximately linearly with I ($\propto I^{0.9}$). At higher power, the dependence of the PIA and PICD signal is clearly sublinear in I. The change in power dependence is accompanied by a change in the phase angle of the PIA and PICD signals. This phase angle is virtually the same for both signals, which further supports the assignment of both signals to a triplet−triplet transition. At low power, the phase angle is close to −37, which indicates that the triplet state has an average lifetime comparable in magnitude to the period of the UV modulation (13 ms). At higher power, the phase angle becomes smaller in absolute magnitude, indicating a decrease in the average lifetime of the long-lived excited states. This can be interpreted in terms of bimolecular triplet−triplet annihilation as the main decay mechanism for the triplet excitations decay at high excitation density. At low excitation density the triplets decay mainly monomolecularly. This type of behavior is characteristic for triplet excitations in π-conjugated polymers.[13]

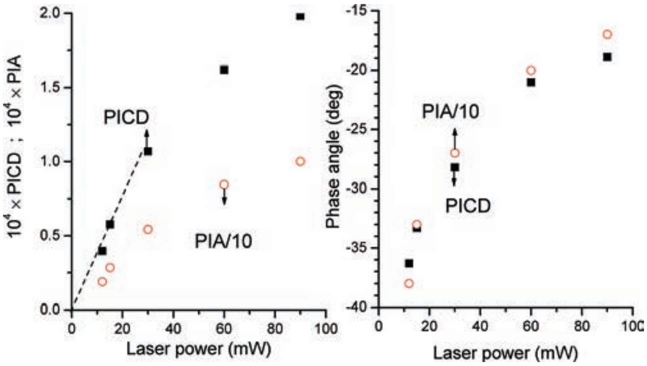

Figure 3. (a) Amplitude and (b) phase angle of the PICD and PIA signals of the **1** (film thickness 290 nm). Experiments are done at a modulation frequency of 75 Hz, a temperature of 77 K, and a laser excitation of 3.55 eV. The signal is monitored at 1.53 eV.

With the modulation technique used, the long lifetime τ of the triplet excitations allows us to detect the PIA and PICD with high sensitivity at a relatively low modulation frequency of the excitation beam (ω). In the simplified case of exponential decay of the excited state with a single, sharply defined lifetime τ, the amplitudes of the PIA and PICD are proportional to $\tau/1^{1/2} + \omega^2\tau^2$. This proportionality factor rises with increasing τ and approaches unity for $\tau \geq \omega$. Thus the modulation scheme could be applied with equal sensitivity to photoinduced species with a shorter lifetime, provided that higher modulation frequencies ω are used. Although the absolute magnitude of the PIA and PICD signals depend on the ratio ω/τ as explained above, these dependencies cancel out when g_{PICD} is calculated.

As discussed above, the PICD and PIA spectra in the neighborhood of the triplet−triplet absorption show very similar band shapes. The band shape of a CD spectrum often gives an indication of the origin of the circular differential absorption. Systems with identical chromophoric groups held in a chiral arrangement usually give rise to a bisignate CD spectrum.[14] This bisignate band shape can be explained by the coupled oscillator model. The monosignate band shape observed in the PICD indicates that the coupled oscillator model does not apply to the PICD. To rationalize this, we first note that the density of triplet excitations is very low. Therefore, direct interactions between transition dipole moments for the triplet−triplet transition of two triplet excitations are negligible because of the large distance between the triplet excitations. Second, even for a single isolated triplet excitation, electronic coupling between chromophoric sites can still give rise to exciton coupled CD effects, but for triplet−triplet transitions this requires interchromophoric electron exchange.[1] In contrast, for a singlet excitation electron exchange is not necessary and electromagnetic coupling between chromophoric site is sufficient to induce exciton coupled CD. In the case of π-conjugated polymers, the required interchromophoric coupling is most likely of interchain nature, and because the probability for electron exchange between chains is relatively low, only weak exciton coupled CD effects are expected for the triplet−triplet transitions.

An important indication on the origin of the observed PICD comes from considering the magnitude of $g_{\mathrm{PICD}} = +0.2$ at 1.53 eV. This value of g_{PICD} found here is considerably larger than reported for the triplet−triplet absorption in binaphtyl derivatives ($g \approx 10^{-3}$)[1] or for heme proteins ($g \approx 10^{-4}$).[15] Furthermore, it is also much larger than g_{abs} for dipole allowed transitions in helically folded polymers or chiral small molecules in dilute solutions ($g_{\mathrm{abs}} = 10^{-2}$ to 10^{-3}). Because of this discrepancy in magnitude, it seems unlikely that the PICD arises from the helical conformation of the polyfluorene chain that carries the triplet excitation.

The large PICD observed here most likely arises from interaction of the linearly polarized photoinduced transition T_1-T_n with the surrounding birefringent matrix of thermally annealed polymer. The feasibility of such a mechanism has been demonstrated by studies on cholesteric liquid crystals.[16] Here it could be shown that an isolated electronic transition can acquire appreciable CD depending on the orientation of their transition dipole moment with respect to the local director of the LC host and its helicity and pitch. In our case, the orientation of the T_1-T_n transition dipole moment is directly linked to the director of the LC phase and parallel to the chain direction.[17] The positive sign of the observed PICD for **1** implies that the photon energy associated with the selective reflection band of the cholesteric arrangement is lower than that of the probe light in the PICD, provided that the cholesteric arrangement is left handed.[16] So far, it has not yet been possible to determine the handedness of chiral polyfluorene by circular selective reflection measurements.[18] However, correlation of the sign of the CD at 3.0 eV with the handedness of cholesteric ordering established for chiral oligofluorenes,[19] supports a left handed helical arrangement for annealed films of **1**.

Conclusion

In summary, modulation spectroscopy has been used to detect photoinduced CD. The PICD associated with the T_1-T_n transition in thermally annealed films of chiral polyfluorene is very large, displaying a degree of circular polarization $g_{\mathrm{PICD}} = +0.2$. The sign and magnitude of the PICD can provide information on the handedness and pitch of the chiral nematic molecular order in the film.

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