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Optically probing structure and organization : single-molecule spectroscopy on polyethylene films and a resonance Raman study of a carotenoid

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3 Spincoated Polyethylene Films Probed by Single Molecules

abstract – We have studied ultra-thin spincoated high-density polyethylene films by means of single-molecule spectroscopy and microscopy at 1.8 K. The films have been doped with 2,3,8,9-dibenzanthanthrene (DBATT) molecules, which function as local reporters of their immediate environment. The orientation distributions of single DBATT probe molecules in 100 to 200 nm thin films of high-density polyethylene differ markedly from those in low-density films. We have found a preferential orientation of dopant molecules along two well-defined, mutually perpendicular directions. These directions are preserved over at least a 2 mm distance. The strong orientation preference of the probe molecules requires the presence of abundant lateral crystal faces and is therefore not consistent with a spherulitic morphology. Instead, a shish-kebab crystal structure is invoked to explain our results.

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3.1 Introduction

The omnipresent polymer polyethylene has so far been of interest to molecular spectroscopists mainly as an inert host to chromophores being studied. Single-molecule optics offers the possibility to investigate how PE chains are organized on a molecular level. We report on an unexpected observation for a novel type of sample of spincoated high-density polyethylene (HDPE) films, doped with 2,3,8,9-dibenzanthanthrene (DBATT) chromophores. These highly fluorescent molecules function as local probes of the PE matrix when studied with polarization-dependent single-molecule spectroscopy and microscopy. As such, they may be used to reveal both highly local dynamics and structural properties of their immediate environment [20, 24, 25, 32].

Our investigation of the local organization of polyethylene chains by means of single-molecule optics has involved several kinds of PE samples. Thin films have been prepared, both by pressing (LDPE) and by spincoating from a hot decalin solution (both LDPE and HDPE) at 100°C. The characterization of all these polyethylene samples doped with DBATT, revealed unexpected orientation distributions for spincoated HDPE films. Where DBATT guest molecules in doped LDPE films, both spincoated and pressed [75], were randomly oriented, the dopant chromophores in spincoated HDPE displayed preferential orientation. This chapter concerns the investigation of the DBATT alignment in spincoated HDPE, and the simultaneous effort to characterize the organization of these uniquely thin films.

Polyethylene crystallized from a melt or solution commonly forms a lamellar crystal structure. The lamellae consist of folded PE chains and are typically only tens of nanometers thick and may be tens of micrometers long. PE chains are incorporated into the lamellae with the chain axis perpendicular to the extended lamellar surfaces (001) called the fold-planes. The lamellae form spherically approximately symmetric structures called spherulites, in which they are oriented radially outward [42, 76]. This morphology is called spherulitic. Under conditions of shear flow in the melt or solution, PE chains are known to orient along the flow direction. Crystallization subsequently occurs in the so-called ‘shish-kebab’ form [77–85]. This consists of highly extended-chain crystals of the heavier fraction of PE chains, on which folded-chain crystals (lamellae) are formed. These lamellae are oriented with their fold-surfaces perpendicular to the flow direction.

We studied the local organization of the PE chains in spincoated HDPE films by determining both the orientations of molecular transition-dipole moments ($\vec{\mu}$) and lateral positions of embedded chromophores with great accuracy. The use of single-molecules for probing the local structure of PE requires that as

many photons be collected from every individual molecule as possible. In the absence of softeners, polyethylene samples are usually rather opaque, which inhibits accurate position determination with optical methods. In a previous Letter [86], we described a novel method of producing thin (100–200 nm) and perfectly clear films of pure PE, by means of spincoating. We demonstrated the possibility of determining both the in-plane projections of the molecular transition-dipole moments ($\vec{\mu}_{ip}$) of dopant DBATT molecules and their lateral positions. It is possible to obtain the lateral position with a sub-wavelength accuracy of approximately 20 nm.

Probing the spincoated HDPE films with single DBATT molecules has revealed a long-range order in their orientations. The orientation distributions for embedded DBATT molecules are preserved over a distance of 2 mm. The in-plane projections of the transition-dipole moments of the dopant molecules are aligned along two preferred, mutually perpendicular directions. The induced alignments of the local probes rule out that the 180 nm thin HDPE films are spherulitic in nature. In fact, the measured orientation distributions can be explained on the basis of a shish-kebab crystal structure.

3.2 Experimental

The sample preparation procedures, the samples and the setup have been described in detail in Chapter 2 and in [86]. A short description follows: Perfectly clear low- and high-density PE (LDPE and HDPE) films were prepared by spincoating at elevated temperatures (100 °C), from viscous hot (125 °C, initially heated to 145 °C) solution of PE in 1:1 cis,trans-decalin (Aldrich, 99+ % pure). We used PE pellets from Wacker, with a crystallinity of about 20–40 % (LDPE) and 80 % (HDPE) after washing these in p.a. chloroform (Biosolve AR) to remove any impurities. The concentrations of LDPE and HDPE in decalin were $2.7 \times 10^{-2} \text{ g ml}^{-1}$ and $2.0 \times 10^{-2} \text{ g ml}^{-1}$ respectively. Glass cover slides (Marienfeld, thickness 0.13 – 0.16 mm, diameter 10 mm) served as substrates for spincoating. The substrates were extensively ozone-cleaned and subsequently silanized using 1,1,1,3,3,3-hexamethyldisilazane (Aldrich, HMDS, 99+ % pure) in order to make them hydrophobic and obtain uniform wetting by the spincoating solution. We obtained PE samples of uniform and reproducible thickness in a range of 100 to 200 nm. After spincoating, a certain amount of decalin is still present in the films [86]. In order to remove part of the excess decalin, the films were stored under vacuum in an exsiccator for about one week. After the initial period in the exsiccator, the partially dried PE films were doped with 2,3,8,9-dibenzanthanthrene (DBATT), by infusion

from a 1×10^{-6} M solution in p.a. chloroform. As chloroform is a good solvent for decalin, the infusion process probably also leads to the removal of most of the remaining decalin. The soaked samples were finally rinsed with clean chloroform and stored in the exsiccator for at least a month before use.

The optical quality using our procedure was such that the produced films were invisible to the naked eye. In order to obtain transparent films, it is crucial that film deposition occurs gradually. The substrate was spun at 2500 rpm for about 90 seconds. The temperature of the substrate of 100 ± 5 °C was critical for obtaining clear films. Any local cooling, for example due to air flow, or excessive heating of the sample substrate inevitably produced partially or entirely opaque films. Samples older than about eleven months display a slight opacity, which is barely visible. Upon inspection under a conventional light microscope these slightly opaque samples displayed no tears or other visible macroscopic features.

All single-molecule experiments were performed at 1.8 K in a helium bath cryostat. We used a standard, home-built low-temperature confocal microscope. The insert for the cryostat allows for coarse horizontal displacement of the sample over about 2 mm. Fine adjustments of the lateral excitation coordinates (smaller than $50 \mu\text{m}$) are possible with a scanning mirror. Our excitation source, used to excite around 592 nm, is a narrow bandwidth continuous-wave single-mode dye laser (Coherent 899-21, Rhodamine 6G, linewidth 1 MHz), pumped with an Ar-ion laser (Coherent Innova 300, 6 W). The laser can be detuned continuously over a range of about 30 GHz. The diffraction-limited confocal volume probed in 180 nm films is about $0.1 \mu\text{m}^3$. The propagation direction of the excitation light is perpendicular to the sample plane and will hence be referred to as the z-axis. Excitation spectra are recorded by detecting fluorescence photons on a single-photon counting Avalanche Photo-Diode (EG&G, SPCM-AQ-161). At 1.8 K the $0 - 0$ transitions of the dopant molecules in spincoated films of PE are sufficiently narrow (80 – 200 MHz) to be individually resolved. By stepwise incrementation of the excitation polarization angle after each 30 GHz sweep, using a variable $\frac{\lambda}{2}$ -retarder plate, we determine the projection of the molecular transition-dipole moment ($\vec{\mu}$) of the relevant $\pi^* \leftarrow \pi$ transition of DBATT onto the lateral (sample) plane ($\vec{\mu}_{ip}$). To this end an excitation spectrum is recorded at each excitation polarization angle. The resulting stack of spectra, or spectral trace, shows the fluorescence intensity of individual molecules as a function of the excitation polarization and detuning frequency. The emission of a single molecule displays a \cos^2 -dependence on the excitation polarization [87], which yields the orientation of the corresponding $\vec{\mu}_{ip}$. The orientation angle of a dopant molecule's $\vec{\mu}_{ip}$ is typically determined with an accuracy of better than 5° . Having measured

the orientations of $\vec{\mu}_{ip}$ for all molecules within a 30 GHz range, it is possible to subsequently acquire diffraction-limited images (magnification factor 208) of the same molecules by selectively exciting them at their individual resonance frequencies. For this we excited with circularly polarized light and used a back-illuminated CCD camera (Princeton Instruments Spec-10:400B) as a detector. The resulting photon-distributions allow the determination of each molecule's lateral position with an accuracy of about 20 nm. Such distributions could only be acquired, because the sample displays almost no scattering of the exciting laser light.

3.3 Results

An orientation distribution of the in-plane components of the transition-dipole moments ($\vec{\mu}_{ip}$) of single DBATT molecules in spincoated HDPE is displayed in Figure 3.1(a). This distribution was measured within one confocal volume. It is evident from this Figure that the orientations are not randomly distributed. Clearly visible above the inevitable statistical fluctuations, the histogram displays two distinct maxima separated by 90° , one at 96° and one at 188° . The two oriented parts of the distribution in Figure 3.1(a) have widths (standard deviations) of σ equal to 12° and 15° respectively. There are almost no unoriented molecules forming a constant offset to the oriented fractions in this distribution. The chromophore orientations were also measured at other sample positions roughly 0.5 mm apart along a line on the horizontal scanning axis of the insert, as indicated in the insets of each histogram. Figure 3.1 summarizes the dependence of the $\vec{\mu}_{ip}$ -orientations of the dopant molecules on the macroscopic position in this sample. Only a few representative histograms are shown in this Figure. The distance between the sample positions indicated in the insets of Figures 3.1(a) and (c) corresponds to roughly 2 mm. Similar distributions were measured in this sample, after rotating it by 45° as well as 90° , at points along the line of the horizontal scanning axis. At most positions the measured distributions were found to be bimodal, with the laboratory angle values for the maxima conserved. The measurement shown in Figure 3.1(d) is an exception to these findings. It shows no clear preferential chromophore orientation. As we will discuss later, the cause for the randomization of the orientations turns out to be related to an aging effect evident in all our measurements on spincoated HDPE films. In passing we note that both the distribution in Figure 3.1(d) and our observations for spincoated LDPE films, rule out the possibility that the bimodal distributions are due to an experimental bias.

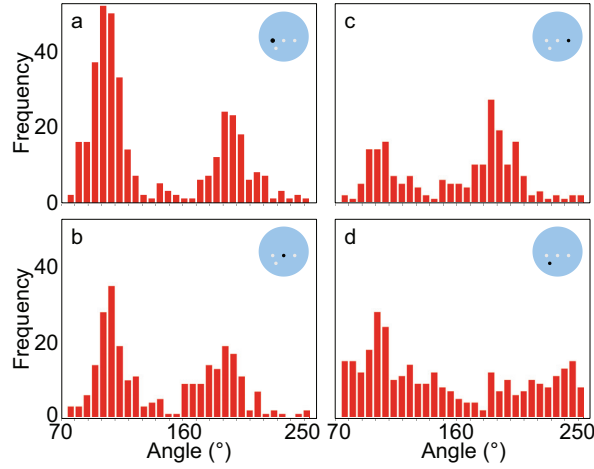


Figure 3.1: Orientation distributions of molecular $\vec{\mu}_{ips}$ in single confocal volumes at various positions on the same sample, as indicated on the schematic drawings of the circular substrate (not drawn to scale). The angles are in the laboratory frame, where 90° corresponds to the vertical. The line on which the first three points lie ((a) – (c)), does not pass through the center of the sample substrate. The distance between the sample positions indicated in (a) and (c) corresponds to about 2 mm. The standard deviations of the oriented peaks at 96° and 188° in (a) are $\sigma = 12$ and 15° respectively. No clear trend was found in the change of the relative numbers of molecules in each oriented peak with sample position. The total number of molecules N represented in each histogram is: (a) $N = 361$, (b) $N = 260$, (c) $N = 210$, and (d) $N = 323$. The distribution indicated in (d) was measured at a sample position along a horizontal scan after turning the sample by 45° .

We have so far considered the $\vec{\mu}_{ip}$ -orientations of embedded DBATT molecules, irrespective of their spatial positions within the confocal volume. Single-molecule microscopy enables us to also investigate whether a relation exists between orientation and microscopic lateral position in the confocal volume. Figure 3.2 shows the positions and orientations of 259 molecular $\vec{\mu}_{ips}$ at a sample position roughly $600 \mu\text{m}$ from the center. The peculiar shape of the spot in the scatter-plot is due to the fact that molecules excited by the first diffraction ring of the excitation spot were also detected. Hence, the lack of molecules between the central spot and the outer ring is caused by the near absence of exciting light, not by a local absence of dopant molecules. As can be seen in the inset, the corresponding orientation distribution is again bimodal, with the two maxima approximately at 90° and 180° in the laboratory frame. The data in this Figure are from a different sample than the data in Figure 3.1. The dots and lines in the scatter plot have been colored to indicate to which

part of the orientation distribution in the inset they belong. Combining the information from the scatter-plot and the histogram in the inset, no obvious relation between the microscopic lateral position of a single dopant molecule and the orientation of its $\vec{\mu}_{ip}$ is evident. Similar orientation distributions were measured at other positions, again showing the same preferred orientations, but revealing no relation between lateral position and orientation.

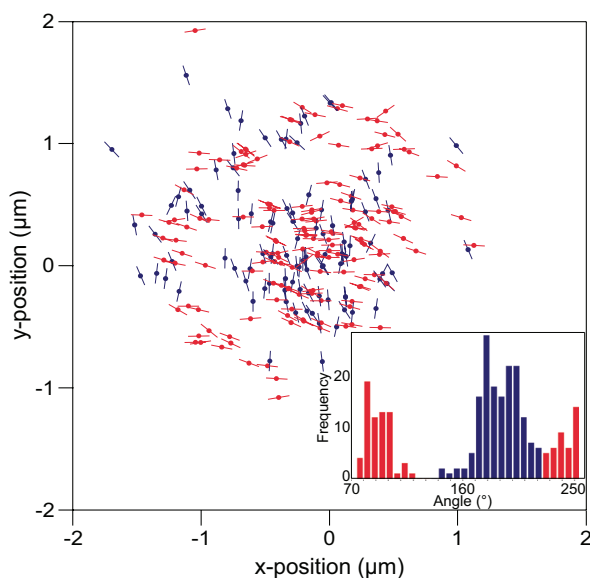


Figure 3.2: In plane orientations (lines) of single molecules ($\vec{\mu}_{ip}$) and their lateral positions (dots) within one confocal volume. The outer ring in the scatter-plot is formed by molecules that were excited by the first diffraction fringe of the excitation laser. The empty ring between this outer ring and the central spot is due to the near absence of excitation light in this region. The fact that the scatter-plot is not completely symmetric, is caused by optical aberrations of our objective at 1.8 K and the imperfect alignment of the detection pinhole. The number of molecules displayed is 259. A color code is used to indicate which position corresponds to which part of the orientation distribution shown in the inset.

3.4 Discussion

3.4.1 Order in spincoated films of HDPE

In contrast to our measurements on LDPE films, there appear to be two strongly preferred directions of orientation for guest molecules in spincoated

HDPE. Our results, moreover, clearly reveal the persistence of the bimodal distributions at a macroscopic length-scale. Even across a distance of 2 mm (between (a) and (c) in Figure 3.1), the laboratory-frame orientations of $\vec{\mu}_{ip}$ are distributed about the same values. The phenomenon of long-range order is not limited to a single sample either, as was mentioned in the discussion of Figure 3.2.

For now we would like to focus on the cause of the long-range persistence of the two preferred orientation directions. First we consider how the PE matrix induces the embedded probe molecules to align along two directions throughout the sample. Before speculating on possible causes we need to consider where the chromophores are most likely to be situated. We expect oriented guest molecules to be embedded in oriented regions of the highly crystalline matrix and somehow reproduce any existing order in the matrix. The matrix appears to be strongly ordered indeed. If we compare the $\vec{\mu}_{ip}$ -orientations of dopant DBATT molecules for spincoated HDPE, to those for pressed and subsequently stretched LDPE films ($\sigma = 19^\circ$) discussed in Chapter 4 [75], we see that in Figure 3.1(a) the $\vec{\mu}_{ip}$ are more narrowly distributed in the former than in the latter, whereas the latter technique is commonly used for orienting embedded chromophores along a single direction. The bimodal nature of the orientation distributions for our samples, the widths of the two peaks and the long-range order, are in fact more reminiscent of the results for flash-frozen n-tetradecane (Shpol'skii) matrices [24, 25]. The widths in Figure 3.1(a) are slightly smaller than widths for DBATT embedded in the polycrystalline Shpol'skii matrix of n-tetradecane ($\sigma = 17^\circ$). The situation for the thin HDPE films is estimated to be different from that for the Shpol'skii systems, where DBATT probe molecules were trapped inside the crystals by the rapidly crystallizing matrix. We contend that the planar DBATT molecules are primarily deposited on the various accessible crystal surfaces. It is unlikely that a substantial fraction of the large aromatic DBATT molecules is incorporated inside the PE crystals, since the probe molecules are introduced into the matrix after spincoating. Penetration of the already formed crystals is prohibitively slow for large dopant molecules [42]. At the time the chromophores are introduced, however, some solvent is still present, and hence crystallization of the matrix need not be complete. Infusion of our chromophore also involves further removal of the solvent. There is a possibility that some embedded DBATT molecules are caught in the subsequently formed crystal regions. Even for these regions, however, we expect that most dopant molecules are expelled during crystallization if it occurs slowly enough. Most oriented chromophores should therefore be deposited on the crystals and we furthermore expect the molecular planes to be coplanar with the crystal faces.

The most obvious possible cause of orientation in the PE matrix is flow orientation. Considering the fact that the sample is prepared by spincoating, one might expect that any orientational preference would be along radial directions of the circular sample substrate. During the initial spincoating phase, excess solution is cast off radially and the thickness of the layer of solution is determined by an equilibrium between its viscous forces and the centrifugal force. In general, the flow of both semi-crystalline polymer melts [82, 83, 85] and viscous solutions [78, 79] is known to have an orienting effect on polymer chains. It is also known that the crystalline order of flow-oriented PE is determined by the flow direction. A radial orientation preference might well occur in spincoated polymer films in general, but our results do not reveal radial orientations for spincoated HDPE. At different lateral sample positions, the laboratory-frame orientations in a sample oriented by radial flow should change. Figure 3.1 indicates that the opposite is the case. The values of the preferred orientation angles of embedded DBATT molecules do not depend on the lateral position in the sample. The long-range order in our data cannot be explained, therefore, as simply resulting from a radial flow-oriented crystal structure.

The fact that LDPE samples displayed random orientation distributions, whereas they were prepared according to the same procedure as HDPE films, points to the factor of crystallinity as being crucial for explaining the results in HDPE. After the uniform layer of hot PE solution has been created during the initial phase of the spincoating process, it is possible that some measure of radial ordering exists for extended PE chains. Perhaps due to the elevated temperature of the spincoating solution and substrate (100 °C), however, oriented chains can partly randomize if the solvent phase persists long enough. After all, the boiling point of 1:1 cis,trans-decalin lies at about 190 °. Of all common solvents used for spincoating, only water has a larger temperature difference between spincoating conditions and the boiling point. Nonetheless, if the extended, heavier PE chains deposit along a random direction, this could still result in crystallization leading to long-range order in the PE matrix. The continued presence of solvent in the matrix after spincoating would slow down the formation of crystals, enabling the growth of more extended crystal regions and leading to longer range order.

What causes the direction of initial deposition of heavier chains remains unknown. This could possibly be the result of some sort of template effect. High resolution Atomic Force Microscopy (AFM) images of our silanized sample substrates, however, have not revealed any topographic features that might result in preferential nucleation of PE crystals along a certain direction.

Having concerned ourselves with the long-range order of DBATT guest

molecules in spincoated HDPE, we now turn to the microscopic ordering within the confocal volume. The single-molecule microscopy results in Figure 3.2, showing both the orientation of guest molecules and their microscopic lateral position, do not reveal an obvious relation between the two. Molecules distributed around both preferred directions can be found with equal probability at any lateral position.

We have also tried to determine whether increased order exists on a smaller length-scale using single-molecule microscopy. To this end we have analyzed the intermolecular orientation-angle difference $\Delta\alpha$ as a function of intermolecular separation in the lateral plane. Since the film in question is about 180 nm thick, certain molecules will lie behind others and the actual distance between two molecules might well be larger than the lateral separation. Determination of a chromophore’s axial position, however, requires the detection of considerably more photons than needed for the measurement of its lateral position [74]. Under the present conditions it is not possible to obtain accurate information on each chromophore’s depth in the sample and still construct a statistically relevant data set for PE samples. The lateral intermolecular separation is therefore taken as an approximation of the actual intermolecular distance.

For distributions like those in Figures 3.1 and 3.2, showing two orientation peaks with their maxima separated by 90° , the $\Delta\alpha$ distributions will have maxima at 0° and 90° . The angle differences between 0° and 45° will mostly correspond to the ‘intra-peak’ intermolecular differences and those from 45° to 90° to ‘inter-peak’ differences in orientation. We are interested in determining whether molecules that are closer together are also more likely to have the same orientation. Such a correlation may be expected if chromophores are located in the same region of locally increased order, *i.e.*, adsorbed on the same lateral ((110) or (100)) crystal surface. For this purpose we calculate the standard deviation of the ‘intra-peak’ angle-difference distribution, since obviously only molecules distributed about the same preferred direction are likely to show such increased order. Figure 3.3 is a plot of the standard deviation of the $0-45^\circ$ angle differences between pairs of $\vec{\mu}_{ip}$ s versus the lateral distance between the corresponding molecules. A decrease in this standard deviation, *i.e.*, a narrowing of the angle-difference distribution, below a certain intermolecular separation, would reveal the approximate size of a region of increased order. Figure 3.3 makes clear that we can see no increasing likelihood of molecular alignment with decreasing intermolecular separation. The initial sharp rise in σ from 0 nm is of course caused by an initial lack of molecular pairs at 0 nm separation and can therefore be ignored.

Figure 3.4 reveals that there is a limit to using single-molecule optics for probing increased local order. It shows the distribution of all lateral inter-

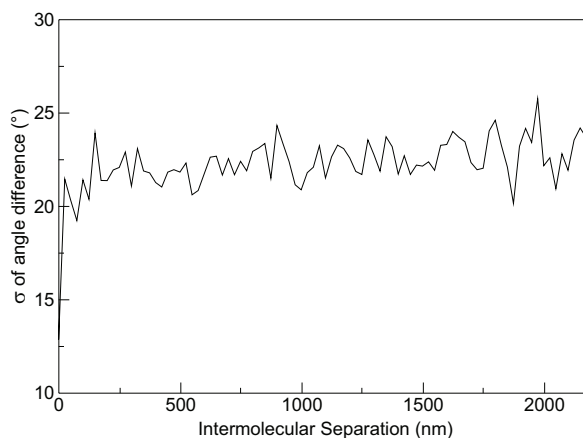


Figure 3.3: The standard deviation (σ) of all $0 - 45^\circ$ angle differences between pairs of molecular $\vec{\mu}_{ip}$ versus the corresponding in-plane intermolecular separation.

molecular separations. The number of molecules at a separation of 0 nm is negligible, and rises sharply towards a separation of 500 nm. Most molecules are somewhere between 400 and 1400 nm apart. We are not sensitive at intermolecular separations smaller than about 150 nm, since there are too few molecules separated by that distance or less to sample a meaningful number. Below this separation, therefore, the data for the standard deviation in Fig-

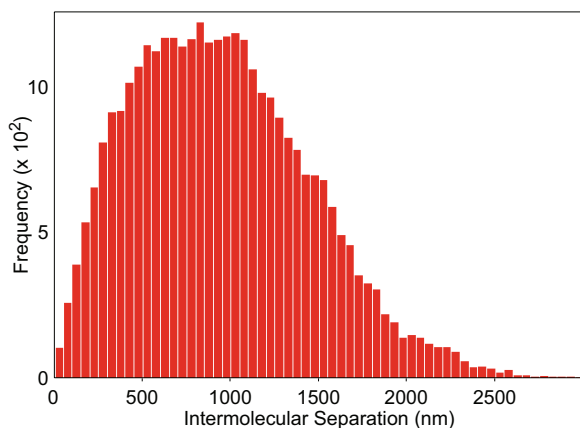


Figure 3.4: Histogram showing the frequency of lateral intermolecular separations. The low number of molecules separated less than 150 nm rules out any conclusion concerning an increased likeliness that these molecules also have the same orientation.

ure 3.3 are not statistically significant. Nonetheless, the standard deviation in Figure 3.3 does not increase within the range of sensitivity. This shows that down to a separation of 150 nm, in this confocal volume molecules are not more likely to be oriented alike, with decreasing intermolecular distance. Note that the limit to our method is intrinsic, due to the requirements for adequate samples for single-molecule optics. Too high a concentration of dopant molecules might result in intermolecular excitation energy transfer between molecules lying close together, which would of course invalidate their use as local probes: the orientations and locations of the excited molecule and the fluorescent molecule are not necessarily the same.

3.4.2 Polyethylene Morphology

We have already mentioned that the unexpected bimodal distributions of the in-plane projections of the molecular transition-dipole moments are connected to the crystallinity of the PE matrix. The strong preference for two orientation directions found in our results, becomes all the more surprising if we consider on which crystal faces the probe molecules of DBATT might reside. If we wish to draw any conclusions about the length scale of regions of order in the PE matrix it is important that we ponder the chromophore whereabouts. The lateral (110) and (100) crystal surfaces, with the PE chains forming the crystal face, are the most likely to induce a particular orientation for adsorbed chromophores. In the most common morphology of semi-crystalline PE, called spherulitic, there is little lateral surface available for chromophore deposition [42, 88]. The largest surface area is made up by (001) fold planes, to which the long axis of the folded PE chains are nearly perpendicular [76]. As these faces tend to be rather irregular, they are unlikely to impose a particular orientation on deposited guest molecules. Our orientation results, therefore, showing narrow distributions about two preferred directions, seem to indicate that in the spincoated films of HDPE, the polymer crystal structure is not made up of spherically symmetric spherulites.

Although we have already dismissed the notion that the spincoated HDPE films display simple flow-oriented long-range order, there is one aspect of flow-oriented PE crystal structure that presents itself as a convenient explanation for the 90° difference found between the two preferential chromophore orientations: it possesses abundant lateral crystal faces, which are moreover perpendicular to the (001) fold planes. The crystal structure of flow-oriented crystals is commonly of the shish-kebab form. Shish-kebab crystal forms have occasionally also been observed in the crystallization from unoriented melt of semi-crystalline polymers [89]. Moreover, confined crystallization in ex-

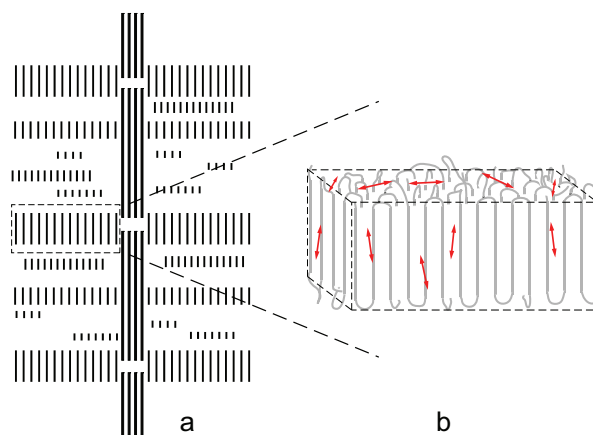


Figure 3.5: (a) Schematic shish-kebab crystal structure. The long axis of the shish-kebab and the PE chains coincide. The white regions in between the various kebab lamellae represent the amorphous regions in the PE matrix. (b) Three dimensional blow-up of part of a 'kebab' lamella, showing how single molecules might be adsorbed on the lateral and fold-plane surfaces (not to scale). Adsorbed chromophores are drawn as dipoles.

tremely thin films is known to occur differently than under the standard circumstances [90,91] that produce a spherulitic morphology. For this reason, the shish-kebab structure is invoked as a source of inspiration for interpreting our results (see Figure 3.5). This structure is formed when high molecular weight chains deposit (from melt or solution) in highly extended-chain crystals along a direction of preference. Subsequently, folded-chain crystal lamellae or 'kebabs' are formed on the shish's lateral surfaces. Close to the shish, the lamellae forming the kebabs have extended surfaces perpendicular to the long axis of the shish [82] and are typically separated from one another by several nanometers, depending on the crystallinity of the sample [80,84]. Dopant molecules might deposit on the lateral faces of the shishs and kebabs or on the perpendicular fold-surfaces of the kebabs.

By itself, chromophore deposition on the perpendicular crystal faces does not suffice to explain the measured bimodal distributions, in which the two maxima are 90° apart. After all, the presence of two perpendicularly oriented crystal faces in the PE matrix does not guarantee that the projections of the alignments of adsorbed dopant molecules onto the sample plane are also distributed about the same directions. In the end, the manner in which DBATT molecules deposit on each crystal face, is determined by the specific interactions between DBATT and the relevant surface. Our probe molecule is a

planar (cata-condensed) aromatic chromophore and for the isolated molecule, $\vec{\mu}$ was calculated to lie in the molecular plane (see Chapter 4) [75]. On deposition the dopant molecule will be co-planar with the crystal face. It is important to realize that one expects to find isolated DBATT molecules on each crystal surface, since the interactions to be taken into account are not the same as for epitaxial crystallization. The latter phenomenon cannot occur on the fold-surfaces, because of the irregular surface properties and the resulting unfavorable interaction between crystals of the dopant molecules and PE [42]. Isolated molecules, however, could perfectly well be found on fold planes of the kebabs, perpendicular to the long axis of the shish. Due to the erratic nature of the fold-planes, they are unlikely to orient the guest molecules to a large extent, other than inducing approximate co-planarity of the molecular and fold-plane.

The heavier, extended PE fraction is most likely to deposit parallel to the sample substrate, due to space restrictions in our thin spincoated HDPE films. Shish-kebab structures will then grow in the sample plane. They would contain fold-surfaces perpendicular to this plane (see Figure 3.5). The molecular planes of dopant molecules deposited on this plane are hence expected to be roughly parallel with the propagation direction of the exciting laser light (z -axis). Consequently, those chromophores whose $\vec{\mu}$ does not point precisely along the z -axis, will be detectable in our experiment. The projections of all detectable $\vec{\mu}$ s in the sample plane, will be oriented along a single direction, which is perpendicular to the long axis of the shish and parallel to the kebabs. In the end, therefore, the width of the orientation distribution of the fraction of dopant molecules situated on the fold-planes would be determined by the planarity of the fold-planes. As opposed to those on the fold-surfaces, dopant molecules adsorbed on the lateral faces are expected to have a certain preferred orientation, which is determined by the specific interactions of the planar DBATT molecules and the crystal surface. All lateral faces are in principle accessible to the dopant molecules. Possible manners of chromophore deposition have been represented in Figure 3.5(b). The molecules on the fold-plane of the kebab are arbitrarily rotated, but approximately co-planar with the surface. The orientations of probe molecules on the lateral surfaces are distributed about a preferred direction with respect to the PE chains. We cannot distinguish the situations in which we regard the shish-kebab from above, below or from the side. This results in a globally cylindrically symmetric distribution of transition-dipole moments, which is centered around the long-axis of the shish-kebabs. This means the preferred direction of chromophores adsorbed on the lateral faces would be perpendicular to those deposited on the fold-surfaces. The width of the resulting distribution corresponding to the

former fraction, would be determined by both the angle between the transition-dipole moments and the crystal's long axis, and the orientation distribution of the DBATT molecules with respect to the PE chains in the lateral surface. Deposition of DBATT molecules on the faces of an oriented shish-kebab crystal structure would therefore explain the two preferred $\vec{\mu}_{ip}$ -orientations found.

We have established that chromophores embedded on both the lateral faces and fold-surfaces of PE crystals in a shish-kebab crystal structure, would probably result in a bimodal distribution of the in-plane projections of their transition-dipole moments. Furthermore, the distributions of $\vec{\mu}_{ip}$ s of those molecules adsorbed on the lateral faces, will always be centered around directions perpendicular to the center of the distributions of $\vec{\mu}_{ip}$ s belonging to chromophores adsorbed on the fold-surfaces. In the end, due to the fact that we observe the orientations and positions of the DBATT probe molecules, we have no direct information on the nature of the PE crystal structures. The reported distributions are not consistent with a spherulitic morphology, however, and may be explained by a shish-kebab crystal structure. It would be most interesting to perform an X-ray analysis, to establish whether such a structure does in fact exist in spincoated ultra-thin HDPE films.

3.4.3 Aging of single-molecule distributions

The appearance of the histogram in Figure 3.1(d) is exceptional in that it shows no strongly preferred chromophore orientations. It seems that this is due to an aging effect in the PE film, related to the temperature cycles in the cryostat. In fact, each successive day of measuring on this sample, we found distributions in which the peaks at 96° and 188° were slightly broader and less pronounced. Before recording the data in Figure 3.1(a), the sample had been through two temperature cycles from room temperature (RT) to 1.8 K. Before recording Figure 3.1(b) it had cycled once more from 80 K to 1.8 K and once again the same before 3.1(c). By the time Figure 3.1(d) was recorded, however, the sample had been through four cycles from RT to 1.8 K and three from 80 K to 1.8 K. The gradual disappearance of the bimodal character of the measured distributions has been made more apparent in Figures 3.6 and 3.7. The former shows the angle-difference histograms for the distributions shown in Figure 3.1. As was explained before, for a bimodal distribution of orientations in which the two maxima lie about 90° apart, the corresponding distribution of $\Delta\alpha$ will have clear maxima at both 0° and 90° . The distributions in Figures 3.6(a) to (c) display an increasingly less pronounced minimum, whereas Figure 3.6(d) shows no minimum at $\Delta\alpha = 45^\circ$ at all. As the measured orientation distributions in Figure 3.1 become less bimodal, the ratio of

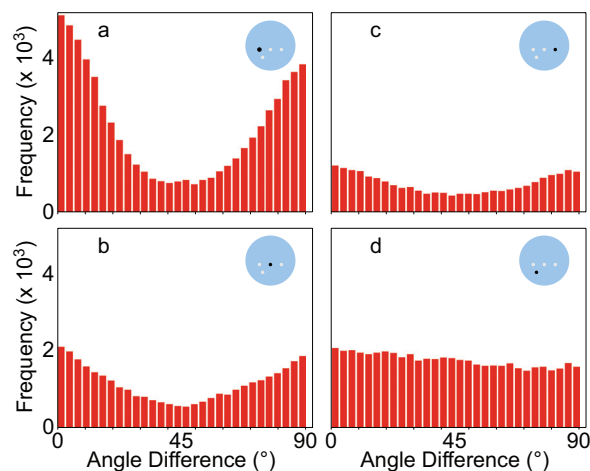


Figure 3.6: Histograms of the intermolecular angle differences, for the $\vec{\mu}_{ip}$ orientation distributions of DBATT in spincoated HDPE at the sample positions indicated in the schematic drawing. The histograms in (a) to (d) correspond to those shown in Figure 3.1 (a) to (d).

maximum to minimum decreases in the angle-difference histograms. We can take the ratio of the maximum value at 0° to the minimum value at 45° as a measure for the loss of bimodality. Figure 3.7 shows how this ratio decreases with each consecutive day of measuring (and therefore with increasing number of temperature cycles). Note that we found the ratio to be similar for distributions measured on the same day.

Although this trend in itself does not prove the deleterious effect of extreme cooling on the sample structure, we have found that storage in the dark at room temperature under dry nitrogen, helium or under vacuum, keeps samples and corresponding orientation distributions stable for many months. This is evidence that experimental conditions induce or accelerate a process that causes the orientations of embedded DBATT molecules to randomize. Our method and our experiments were not aimed at clarifying this effect and we can only speculate as to its cause. As the observed (spectral) density of chromophores in one confocal volume did not decrease with time, we are certain that the changing nature of the orientation distributions is not related to a selective bleaching of certain well-oriented guest molecules. A more likely explanation is that different thermal expansions of the thin and fragile HDPE film and the glass coverslide, lead to extensive microscopic tearing of the sample.

Eventually, the bimodal distributions also disappear in the dark under vacuum. Fresh spincoated HDPE samples all displayed the sort of bimodal distri-

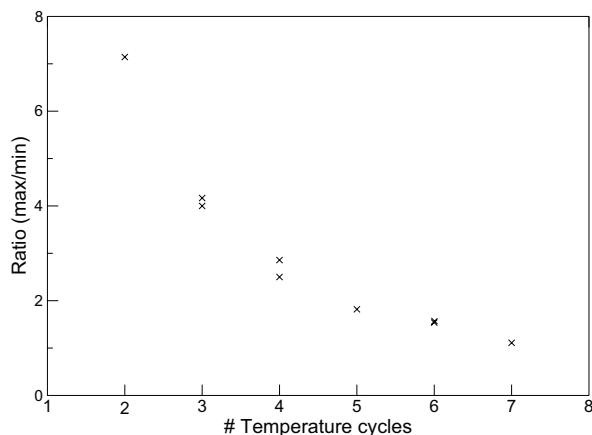


Figure 3.7: This figure shows the decrease of the bimodality of the orientation distributions of $\vec{\mu}_{ip}$ with time. We have calculated the ratio of the maximum values at $\Delta\alpha = 0^\circ$ and the minimum values at 45° for all angle-difference histograms measured, versus the number of temperature cycles the sample described in Figures 3.1 and 3.6 had been subjected to.

butions of chromophore orientations shown in Figures 3.1(a)–(c), while samples stored for over eleven months under vacuum in the absence of light did not. It is unlikely that the deterioration at room temperature occurs by the same mechanism as that aggravated by extreme cooling. The trend towards random chromophore orientations at room temperature could be the consequence of a slow transition to a spherulitic morphology in the spincoated PE matrix. We would expect such a process to be accelerated at higher temperatures and not by cooling to cryogenic temperatures.

3.5 Conclusions

This chapter has reported unexpected orientation distributions of single DBATT molecules in spincoated HDPE films. Molecular orientations are distributed about two mutually perpendicular preferred directions, which are constant throughout the sample. This indicated the presence of a long-range order in the sample. We contend that the PE morphology in our thin films cannot be spherulitic, as the lack of available lateral crystal surfaces, could not induce the dopant molecules to align along two preferred directions. Extended shish-kebab crystal structures would be more suited to explain the measured distributions. This suggests that these structures, commonly observed in flow-

oriented semi-crystalline polymers, might also occur in ultra-thin spincoated HDPE samples. The origin of the actual values of the preferred orientation directions is not known.

Acknowledgments

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