

Following single diffusing conjugated polymers in swollen plastic

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Introduction

In our experiments we follow the dynamics of single fluorescent conjugated polymer chains embedded in a non-fluorescent swollen polymer film. In general, a single conjugated polymer chain can be described as a chain of distinct spectroscopic units, namely chromophores. Chromophores are defined by the undisturbed conjugation of several repeat units and have an absorption dipole related to the backbone orientation of a given polymer chain. However, this conjugation can be interrupted by defects (e.g., cis-trans isomerizations, keto or alkyl defects), twisted repeat units or interactions with the environment, leading to several chromophores with different conjugation lengths.

The spin-coated polymer film with incorporated conjugated polymers is swollen by the addition of a solvent saturated gas. This post-processing technique is also known as solvent vapor annealing (SVA) and is an important and widely used technique to equilibrate polymer films, which are employed in organic devices, e.g. light-emitting diodes or organic photo-voltaics.^{1, 2} By watching the dynamics of conjugated polymers during the SVA process, a fundamental picture at the single molecule level can be obtained, which will help to understand and design improved post-processing schemes for organic based devices.^{3, 4}

Experimental setup

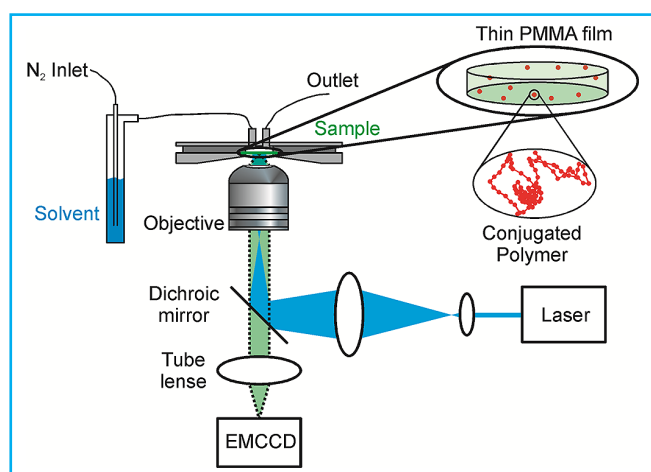


Figure 1. Scheme of the setup for wide-field single-molecule spectroscopy (EMCCD electron multiplying charged coupled device, PMMA poly(methyl methacrylate)).

Application Note

An inverted microscope was used for wide-field excitation and detection as schematically drawn in Figure 1. The excitation source was provided by a fiber-coupled diode laser with a wavelength of 488 nm in continuous wave mode. The laser beam was expanded and focused via a lens system onto the back-focal plane of the 1.35 NA oil immersion objective through the back port and a dichroic mirror in the microscope. An excitation area of $\sim 80 \times 80 \mu\text{m}^2$ was generated in the focal plane and the fluorescence of the sample is collected by the same objective and passes through the dichroic mirror. The fluorescence signal was imaged on an EMCCD camera from Andor (iXon3 DU897-DCS-BV) after an additional magnification of 1.6x and after passing a fluorescence filter. The excitation intensity was set to $100 \text{ mW}/\text{cm}^2$ and the overall magnification results in a resolution of 160 nm per pixel leading to diffraction limited spots of $\sim 2 \times 2$ pixels for a single molecule.

Experiment

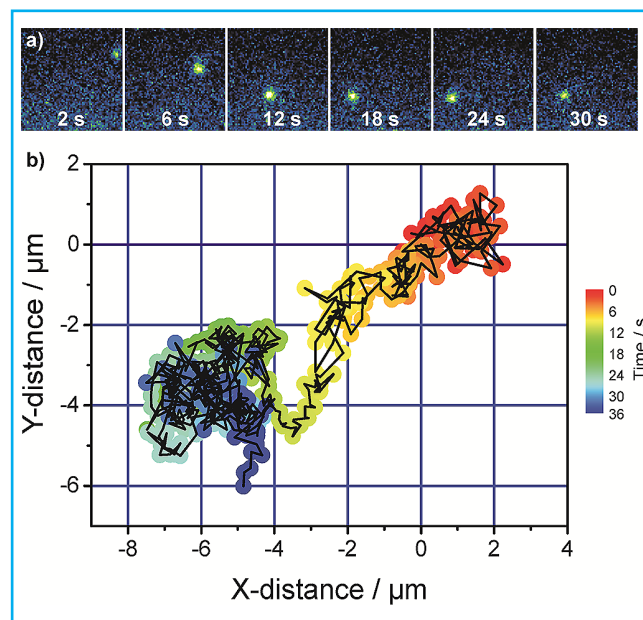


Figure 2. Tracking the position of a single conjugated polymer chain embedded in a poly(methyl methacrylate) host matrix during solvent vapor annealing (SVA). (a) Wide-field fluorescence images of a diffusing conjugated polymer chain during SVA at the times indicated below (size is $10 \times 10 \mu\text{m}^2$). (b) The position tracked over time at each individual frame. The color encodes the time at which the diffraction limited spot was localized with respect to the start of the experiment with a precision of about 20 – 30 nm and a time resolution of 60 ms, depending on the brightness.



Application Note

The sample consists of a roughly 50 – 100 nm thick poly(methyl methacrylate) film on top of a glass substrate in which the analyte molecules are embedded at single molecule concentrations. This leads to a spot density in the fluorescence microscope of roughly one spot (corresponding to one molecule) at $10 \times 10 \mu\text{m}^2$ as shown in Figure 2a. The sample is incorporated in a home-built SVA chamber to apply a solvent saturated gas to the polymer film, which leads to swelling of the polymer film and diffusion of the analyte molecules. The fluorescence intensity of single molecules, here fluorescent conjugated polymer chains, can be recorded during the SVA process by the EMCCD camera to track the position of the chain and study its diffusion dynamics as shown in Figure 2. The diffusion dynamics correspond to the amount of swelling of the polymer film as well as unfolding and folding events of the conjugated polymer itself. Therefore, a detailed analysis of the diffusion dynamics can provide us with molecular details of the equilibration process during SVA.

Performance

Besides the brightness of the molecules, the detection efficiency and signal to noise ratio of the camera limits the possible achievable position and time resolution in these experiments. In other words, a better detection efficiency and signal to noise ratio, especially at low integration times, provides more details for a diffusing single conjugated polymer chain. In this regard we obtained the latest back-illuminated EMCCD camera from Andor, iXon3 DU897-DCS-BV, with which the tracking of a single conjugated polymer chain during SVA can be conducted as shown in Figure 2.

References

- (1) Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* 2005, 87, (8), 083506.
- (2) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S.; Ree, M. *Nat. Mater.* 2006, 5, (3), 197-203.
- (3) Vogelsang, J.; Brazard, J.; Adachi, T.; Bolinger, J. C.; Barbara, P. F. *Angew. Chem.-Int. Edit.* 2011, 50, (10), 2257-2261.
- (4) Vogelsang, J.; Adachi, T.; Brazard, J.; Bout, D. A. V.; Barbara, P. F. *Nat. Mater.* 2011, 10, (12), 942-946.

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