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Molecular rearrangements observed by single-molecule microscopy

W. Trabesinger[a,*], A. Renn[a], B. Hecht[a], U.P. Wild[a], A. Montali[b], P. Smith[b], Ch. Weder[b]

[a]Institute for Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland
[b]Institute of Polymers, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland

Abstract

We have applied quantitative single-molecule photoluminescence microscopy for directly observing molecular rearrangements in a polymeric material subjected to tensile deformation. The system examined is a blend of fluorescent conjugated polymer molecules embedded in polyethylene, known to exhibit strong phase separation. Statistical analysis of the sizes of phase-separated domains reveals that during tensile deformation large domains of fluorescent molecules are transformed into smaller clusters and ultimately isolated single molecules. In addition to elucidating the nature of the stretch-induced morphology change, our work underscores the fundamental value of single-molecule techniques for material analysis [1]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Single-molecule microscopy; Conjugated polymers; Material science

1. Introduction

The ability to tailor-make semiconducting polymers with well-defined molecular properties has entailed a variety of device applications, which were previously solely feasible with inorganic semiconductors. To name only a few examples, there are polymer light-emitting devices [2], transistors [3] and lasers [4]. Since the functionality of such polymeric devices is highly dependent on their supramolecular structure, control over the morphology of materials at the molecular level is essential. Very often, low entropies of mixing and unwanted molecular interactions lead to aggregation phenomena during the preparation of polymeric blends. In recent work concerning the fabrication of photoluminescent polarizing materials [5], we have shown that tensile deformation of initially phase-separated blends of a poly(2,5-dialkoxy-*p*-phenyleneethynylene) derivative (EHO-OPPE, Fig. 1) and ultrahigh molecular weight polyethylene (UHMW-PE) induces an apparent molecular dispersion of the rod-like conjugated fluorescent polymer within the matrix. However, this conclusion could only be inferred from luminescence spectra of the undeformed and the deformed polymer blend, respectively. We introduce the methodology of single-molecule photoluminescence microscopy for the direct observation of morphology changes at the single-molecular level occurring during the deformation processes [1]. The key advantage, arising from this approach, is that ensemble averaging, which is intrinsic to conventional techniques, is completely removed, allowing for the full statistical characterization of distributions of parameters. With respect to the present application, this means that molecular scale information about the distribution of chromophores within a host can be obtained.

2. Experimental

2.1. Sample preparation

Samples were prepared by casting a solution of EHO-OPPE (average molecular weight $\sim 1 \times 10^4$ g mol^{-1}; 10.5×10^{-4}, 1×10^{-4} and 0 mg), and UHMW-PE (Hostalen Gur 412, Hoechst AG, average molecular weight $\sim 4 \times 10^6$ g mol^{-1}; 500 mg) in *p*-xylene (Fluka p.p.a., 50 g; dissolution at 130°C after degassing the mixture in vacuum at 25°C for 15 min) into a petri dish. The films obtained after drying under ambient conditions for 24 h were uniaxially deformed at 120°C to well-defined ratios λ ($\lambda =$ final length/initial length) of up to 80, yielding transparent films of 1–2 μm thickness. The temperature of 120°C, which is above the glass transition temperature of EHO-OPPE allowed for higher mobility of the guest molecules, while no melting of the polyethylene matrix occurred. For examination using confocal microscopy, the deformed polymer films were immersed in index-matching oil between a microscopy slide and a cover slip.

* Corresponding author. Tel.: +41-1-632-7905; fax: +41-1-632-1021.
E-mail address: wtrabe@phys.chem.ethz.ch (W. Trabesinger).

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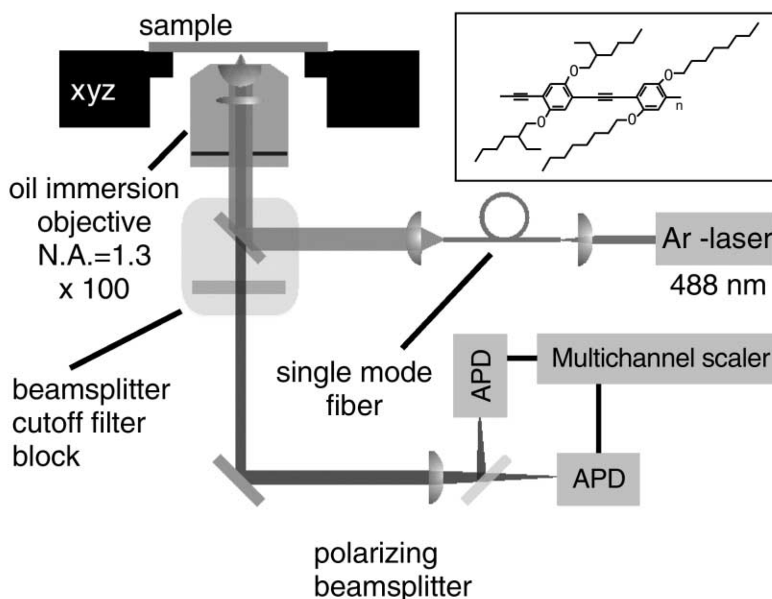

Fig. 1. Setup used for scanning confocal optical microscopy (SCOM). The inset shows the chemical structure of EHO-OPPE.

2.2. Confocal microscopy

The samples were imaged using a scanning confocal optical microscopy (SCOM) setup, depicted in Fig. 1. Illumination of the sample was performed with circularly polarized light using the 488 nm line of an Ar^+ laser, which was focused onto a diffraction-limited spot on the sample. The luminescence emitted by the sample was filtered by a combination of a dichroic mirror and a cut-off filter, split into two polarization directions, parallel and perpendicular to the direction of deformation, respectively, and detected on two avalanche photodiodes. A linearized *xyz* piezo-scanner allowed for positioning the sample relative to the laser focus for sequential acquisition of the fluorescence signal and subsequent image formation by means of a computer. In order to measure the time course of the emitted luminescence, a multichannel scaler was connected to either of the two photodetectors.

2.3. Results and discussion

Fig. 2(a) and (b) show SCOM images obtained for an undeformed film containing 10^{-4}% (w/w) EHO-OPPE. Note that (a) and (b) show the same spot on the sample recorded with orthogonal polarization. Both micrographs indicate the presence of large aggregates of chromophores without any distinguishable order. As is evident from comparing the average luminescence intensities for the two polarization images, no preferential orientation of the chromophores can be detected. After subjecting the identical sample to tensile deformation (Fig. 2(b) and (c)) up to a draw ratio of $\lambda = 80$ ($\lambda =$ final length/initial length), a striking change in the pattern of luminescence occurs. In Fig. 2(b) and (c) spatially separated luminescence spots are found in rows that coincide with the direction of tensile deformation (top and bottom). In contrast to Fig. 2(a) and (b), the spots in the deformed samples are diffraction-limited, indicating small molecular aggregates, in accord with the generally lower photon count rates. In order to check, whether some of the luminescent spots originate from isolated molecular emitters, they were positioned within the laser focus and their luminescence signal was monitored as a function of time using a multichannel scaler. Typical indications for the presence of isolated single emitters, such as sudden photo bleaching in unitary intensity steps, were found. For more detailed analysis, all isolated spots in the luminescence images were fit to Gaussians, yielding the integrated luminescence intensities and the respective errors. Combination of all individual observations into probability distributions of intensities (histograms) quantifies the relative occurrence of a certain number of photons, when picking an arbitrary luminescent spot. A series of samples with varying draw ratio was prepared and the histograms described above generated for each. As anticipated from the stepwise photobleaching observed in the time traces, integer multiples of a fundamental luminescence intensity were found, indicating stoichiometric accuracy for the determination of aggregate sizes. In addition, these results confirm that a single photophysically indistinguishable species accounts for the luminescence signal observed in our measurements. The most important finding of this analysis is that the relative statistical weight of different aggregate sizes changes dramatically, as the draw ratio is increased. In the low draw-ratio samples, large clusters dominate, whereas an increase of the draw ratio enhances the statistical weight of small clusters, until mostly very small aggregates (two to three chromophores) and isolated single molecules are observed. The linear arrangement of isolated fluorescence spots in Fig. 2(b) and (c) can therefore be attributed to origin from

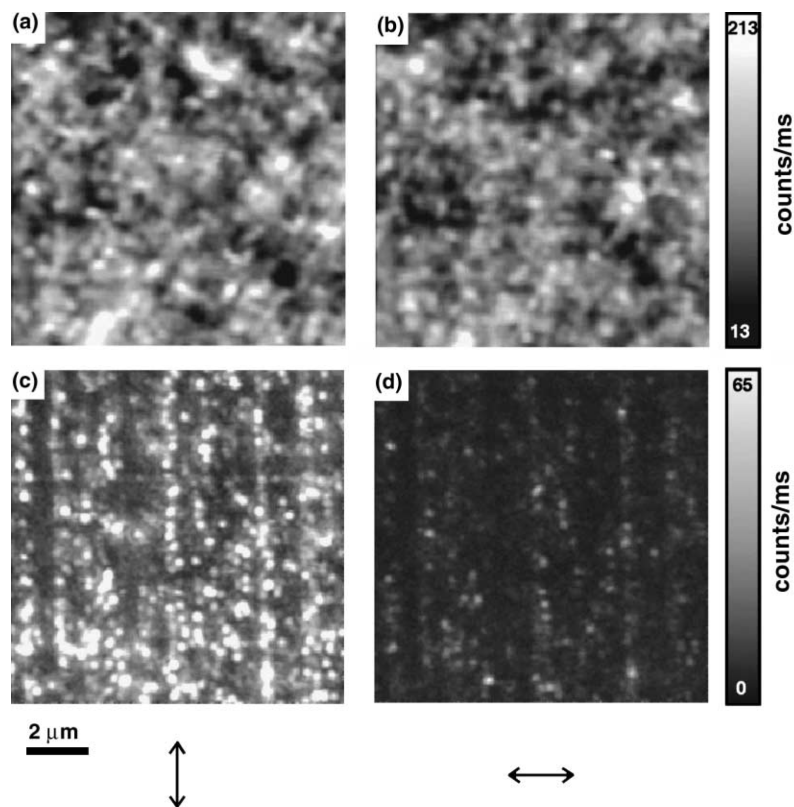

Fig. 2. Comparison of orthogonally polarized luminescence micrographs obtained on the same sample spot for (a), (b) an undeformed film and (c), (d) for a $\lambda = 80$ film. (Left panel) Polarization direction coincides with the direction of tensile deformation. (Right panel) Orthogonal polarization. Note that larger aggregates in (c) show disorder, as indicated by the residual luminescence of spots in image (d).

the dissolution of large clusters into smaller ones and finally into single chromophores.

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