Polymer Processing

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The Folding of Individual Conjugated Polymer Chains during Annealing

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In memory of Paul F. Barbara

The intensive study of conjugated polymers during the last two decades has been fueled by their potential application in organic light-emitting diodes (OLEDs), photovoltaic cells, and organic lasers. For these applications the polymer molecules are typically processed into thin solid films by spin-casting. The way the conjugated polymer chains arrange in film formation depends on the preparation conditions and critically influences the photophysical and electrical properties of the film.[1] Thus, film morphology has a prominent effect on the performance of technical devices (e.g. OLEDs). In order to create more homogeneous films with improved performance, film casting is often followed by annealing: above the glass transition temperature T_g, polymer chains are able to disentangle into lower-energy arrangements. This can be achieved in two ways: by heating the polymer above its T_g (thermal annealing) or by lowering T_g below the ambient temperature by exposure to a solvent-saturated atmosphere (solvent vapor annealing, SVA). The latter route seems to be more promising for the processing of polymer films for organic electronics since one can avoid the risk of thermal damage. However, much remains to be learned about the mechanism of SVA.

Like the morphology of pristine films, the conformation of individual chains of a conjugated polymer is a crucial parameter since the conformation and photophysical properties of the polymer chains are intimately connected. The question of how information about chain conformation can be derived from spectroscopic measurements and, subsequently, what factors determine the conformation has been addressed in single-molecule studies over the past ten years. Conformation affects the efficiency of intramolecular energy transfer and thus the fluorescence emission properties such as transient fluorescence intensity as well as emission spectra and emission polarization.[2] Studies based on these effects have mainly provided qualitative information in the comparison of different samples, for example under which conditions the chains are more or less collapsed. In contrast, investigations based on the absorption anisotropy, which is probed by varying the polarization of the excitation light and is not limited to the emitting segments of the chain, have generated quantitative information about chain conformations that have been compared to numerical simulations. For example, Barbara and co-workers examined the extensively investigated conjugated polymer (poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV); taking into account chemical defects, they proposed structures such as a defect cylinder and a defect coil conformation.[3] By now we have learned that in single-molecule samples prepared by spin-casting, owing to the fast evaporation of the solvent, conjugated polymer chains can be trapped in non-equilibrium conformations (“memory effect”); thus experimental conditions like the solvent[2] exert a significant influence.

Wouldn’t it be extremely interesting to apply the powerful techniques of single-molecule spectroscopy to study the conformational changes and dynamics during SVA on a truly molecular level? This challenge has recently been taken on by Vogelsang et al.[4] They have studied the conjugated polymer MEH-PPV embedded in poly[methylmethacrylate] (PMMA) with single-molecule spectroscopy, and have demonstrated its usefulness for an improved molecular understanding of SVA. After the samples have been spin-cast, the single conjugated polymer chains adopt heterogeneous, collapsed conformations that are (at least partly) kinetically trapped in non-equilibrium states. The swelling of the host matrix upon solvent vapor absorption triggers two major reactions by the embedded conjugated polymer chains:

a) Translational diffusion: This response was investigated with series of fluorescence images acquired by wide-field microscopy and by fluorescence correlation spectroscopy (FCS). Large fluctuations of the apparent diffusion coefficients were revealed and sorted into three time regimes: 1) stationary positions on the time scale of seconds, 2) translocations occurring between 100 ms and 1 s, and 3) rapid diffusion on the 1–100 ms time scale. These experiments indicate a profound spatial heterogeneity of the swelling process.
b) Conformational reorganization. Single MEH-PPV chains that moved sufficiently slowly could be tracked in consecutive fluorescence images. When the samples were exposed alternately to solvent vapor and pure N_2, their fluorescence intensity of single polymer chains reproducibly proved 1) to be on average significantly increased and 2) to exhibit large fluctuations under SVA conditions.

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Higher fluorescence intensity, reflecting an increase in the fluorescence quantum yield, was attributed to an extended conformation of the MEH-PPV chains, in accordance with studies on the ensemble level.[5] In principle, changes in fluorescence intensity could also be induced by differences in oxygen concentration, since the absence of oxygen will lengthen the triplet lifetime. The authors therefore carefully tried to avoid residual oxygen in their samples. Thus, it was demonstrated that conjugated polymer chains undergo folding/unfolding events between collapsed and extended conformations during SVA.

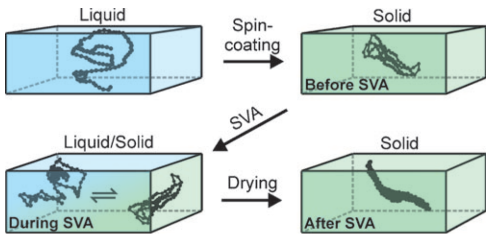

Figure 1. MEH-PPV chain conformations from sample preparation until after solvent vapor annealing (SVA). From Ref. [4].

As a result of the degrees of freedom of their flexibility during SVA, the MEH-PPV chains equilibrate and adopt an ordered, low-energy collapsed conformation when the solvent vapor is finally removed from the system. This overall effect of SVA was investigated by Vogelsang et al. using fluorescence excitation spectroscopy with polarized light. Here, the modulation depth M of the fluorescence signal of single MEH-PPV chains upon rotation of linearly polarized excitation light is used to determine the excitation anisotropy A (a direct measure of the conformational order) with a clever method previously introduced by the same group.[6] Comparing results before and after exposure to toluene vapor, the authors demonstrate that SVA leads to significantly sharper distributions of A values—a quantitative criterion for the transition into homogeneous low-energy conformations.

The "memory" of the MEH-PPV chains concerning the solvent from which the samples were cast also is lost during SVA. While films spin-cast from toluene did show a monomodal distribution of A values (before SVA), in case of chloroform the corresponding distribution had to be approximated by a bimodal function whose origin is not clear at present. The differences between films spin-cast from toluene and chloroform have been attributed to the different boiling points of the solvents. Briefly, in this picture toluene leads to relatively ordered conformations, while chloroform gives rise to a higher conformational heterogeneity. After SVA the "memory" is erased, resulting in very similar collapsed conformations.

Moreover, it was shown that the equilibration effect is largely independent of the choice of the solvent used for SVA as long as the solubility of MEH-PPV/PMMA is sufficient (demonstrated for toluene and chloroform). In contrast, hexane-saturated gas did not lead to conformational changes. The proposed course of the polymer conformations, from sample preparation until after SVA, is summarized in Figure 1.

The study by Vogelsang et al. represents an important step forward in the spectroscopic investigation of conjugated polymers. Using a variety of state-of-the-art experimental techniques, they demonstrated the capability of single-molecule spectroscopy to extract real-time information about the conformational dynamics of individual conjugated polymer chains. This study goes beyond previous work on conjugated polymers embedded in inert polymer hosts, which were basically confined to static conditions, by following translational and conformational dynamics in situ. It most probably will stimulate a multitude of future investigations on how conformations of conjugated polymer chains can be varied and controlled, and on the impact of other sample characteristics, like the choice of the host matrix.[7] Finally, and most importantly, the authors have ventured out of the "ivory tower" of single-molecule spectroscopy and have paved the way to a detailed mechanistic understanding of polymer reorganization during solvent vapor annealing—a process of significant industrial importance.

Single-molecule spectroscopy of conjugated polymers was pioneered by Paul F. Barbara and his co-workers.[8] In their first ground-breaking contribution collective behavior like single-step photobleaching and discrete fluorescence intensity jumps were observed in single conjugated polymer chains, giving evidence for the strong communication between individual chromophores along the polymer backbone. In another seminal report polarization-dependent single-molecule measurements gave information on the conformations adopted by single polymer chains.[3] Moreover, in recent years Barbara and his group have studied single conjugated polymer molecules under realistic device conditions, establishing a direct link between advanced microscopy/spectroscopy and the function of a material.[9] A recent example along this promising line of research has been highlighted here. Sadly, Paul Barbara passed away on October 31, 2010; he and his ingenious contributions to the field will be deeply missed.

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