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A closer look at polymer annealing

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Abstract

Solvent vapour annealing processes are used to optimize the material properties of thin films of semiconducting polymers used in electronic devices. One such process has now been examined at the molecular level.

Single-molecule spectroscopy and microscopy (SMS) techniques have had a tremendous impact in biophysics — in studies of the motion of individual protein molecules, for example. SMS techniques are also suitable for investigating the underlying heterogeneity in complex liquids and solids, such as that associated with different molecular conformations, and for directly observing dynamic changes in materials at the molecular level. Polymeric materials would therefore seem a natural fit for single-molecule studies, as they are, by definition, structurally heterogeneous. Yet SMS has so far not been widely used in polymer science, apart from in studies of certain fluorescent polymers^{1–4}.

Reporting in *Angewandte Chemie*, Vogelsang *et al.*⁵ now describe the use of SMS techniques to reveal the conformational dynamics of single polymer chains during solvent vapour annealing (SVA) — an industrially important process in which the exposure of polymer films to solvent vapour enables the polymer molecules to reach conformational equilibrium, thus optimizing the films' useful properties. An understanding of SVA at the molecular level should lead to improvements in this widely used process.

Annealing processes are attractive techniques for improving the material properties of organic semiconductors (such as conductive polymers) for use in transistors, solar cells and other devices⁶. SVA induces translocations and folding/unfolding of molecules in polymer films at ambient temperatures, eventually leading to the formation of macrostructures featuring equilibrated, long-range molecular order^{7,8}. But so far, our understanding of the morphological transformations — the changes in polymer-chain conformations — that occur during SVA has been sketchy.

Vogelsang *et al.*⁵ are the first to use SMS to study real-time conformational changes in single conductive polymer chains during SVA. They investigated a prototype conductive polymer (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]; MEH-PPV) isolated as single molecules in a host matrix (a non-conductive polymer, poly(methyl methacrylate); PMMA). The authors observed clear differences in the translational diffusion of single

MEH-PPV chains before, during and after SVA. Before and after annealing, single chains were visible as sharp, stationary fluorescent spots, but during annealing, the spots were blurred and danced around freely (Fig. 1).

From these results, Vogelsang *et al.* concluded that MEH-PPV/PMMA films absorb solvent and swell during SVA, and that the annealing process lowers the glass-transition temperature of the film to below ambient temperature, which increases chain mobility. The film therefore exists as a heterogeneous mixture of solid and liquid-like phases during annealing. Crucially, the authors were able to monitor the translational motion of single MEH-PPV chains in the solid and liquid-like phases by simply tracking the movement of the fluorescence spots. Some of the single-chain diffusion was, however, too rapid to be observed using microscopy, but the authors were able to detect this using a technique known as fluorescence correlation spectroscopy. The authors' results also showed that SVA generates different kinds of swelling processes in the host matrix, and causes single MEH-PPV polymer chains to diffuse in several different ways.

In the past few years, various studies¹⁻³ have provided evidence that MEH-PPV molecules adopt numerous configurations within a PMMA host, ranging from complex disordered structures that are roughly cylindrical, to highly ordered ones such as toroids and rods. The three-dimensional shape of MEH-PPV polymer chains is expected to have a profound impact on the electronic properties of the molecules and on their individual fluorescence quantum yields — a measure of how much light the chains produce in response to excitation by incoming photons. Vogelsang and colleagues⁵ found that MEH-PPV polymer chains undergo folding and unfolding events between collapsed and extended conformations during SVA. The transition between these conformations correlates with fluctuations in the fluorescence intensity of single chains, which occur because the fluorescence quantum yield of MEH-PPV is lower in collapsed conformations.

The authors also characterized the conformational order of single MEH-PPV chains using fluorescence excitation polarization spectroscopy, which measures variations in fluorescence in different directions. From these data, Vogelsang *et al.* concluded that SVA equilibrates MEH-PPV single chains in the matrix towards lower-energy conformations, which ultimately leads to the production of highly ordered conformations after annealing. The authors used the same technique to analyse vapour-annealed MEH-PPV/PMMA films that had been prepared in different solvents. They observed that, as long as SVA was performed using a good solvent (one in which the film is soluble), then single chains could be reorganized into low-energy, high-order conformations regardless of the solvents in which the film was prepared.

The ability to follow annealing effects at the molecular level will undoubtedly improve our understanding of polymer reorganization processes, and offers a complementary approach to microscopy methods that monitor the surface features and textures of thin films. Insights into how single-chain morphology changes in thin films, block co-polymers, or even in highly ordered self-assembled structures, will help to direct molecular-design strategies for making improved conductive polymers for device applications. Vogelsang and colleagues' findings are obviously of relevance to industrially important processes for assembling

conductive polymer thin films, but in the longer term, they might also be applicable to the control of morphological order in other polymeric functional materials. We expect that surprising discoveries will be made as single-molecule methods are used to explore other subjects in polymer science. ■

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Figure 11. Monitoring single polymeric chains.

Vogelsang *et al.*⁵ have used single-molecule spectroscopy and microscopy to study the conformational changes of individual MEH-PPV polymer molecules isolated in a thin film of PMMA (another polymer) before, during and after solvent vapour annealing. Each of the panels **a** to **c** shows accumulated images, taken over 60 seconds, of the same MEH-PPV chain embedded within an 8×8-micrometre region of PMMA film. **a**, Before annealing, single MEH-PPV chains are visible as static fluorescent spots, which correspond to collapsed, disordered polymeric conformations (such as the structure shown beneath the fluorescence data). **b**, During annealing, the spots are mobile and the background fluorescence increases. Here, the fluorescent spot is extended and blurred because of the motion of the single chain as it moves from left to right. **c**, After annealing, static spots are again visible, but these now correspond to extended, highly ordered polymer conformations, such as the one shown. (Figure adapted from ref. 5.)