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Reversibly Slowing Dewetting of Conjugated Polymers by Light

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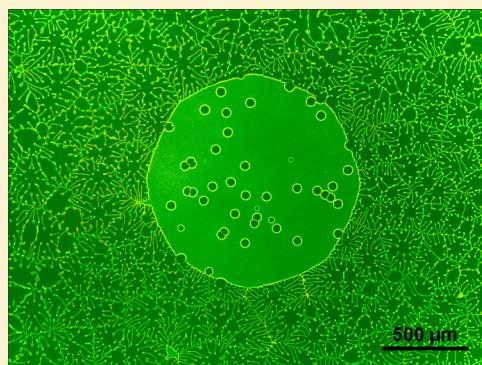
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S Supporting Information

ABSTRACT: Dewetting, i.e., the retraction of a fluid from a surface it “dislikes”, is a macroscopic phenomenon controlled through parameters like viscosity and surface tension on length-scales much larger than the size of the molecules. So far, dewetting was known to proceed in the same manner, independent of the dewetting film being illuminated by light or not, e.g., through an optical microscope. Here, we demonstrate that the velocity of dewetting of conjugated polymers can be reversibly tuned through appropriate exposure to light. We relate this observation to the absorption of photons of suitable energy resulting in the generation of excitons which may partially delocalize along and across polymer chains and so induce changes in polymer chain conformation. Such changes, in turn, may cause stiffening or overlap of polymer chains and thus lead to macroscopically detectable differences in behavior of an ensemble of conjugated molecules expressed via material properties like viscosity.



INTRODUCTION

Like all polymers, conjugated polymers can adopt a multitude of molecular conformations. Through a variation of parameters like solvent quality, molecular architecture, polymer concentration, temperature or due to various types of inter- and intramolecular interactions, chain conformations and the dynamics of conformational changes can be controlled.^{1,2} Optoelectronic properties of conjugated polymers,^{3–6} on the other hand, are strongly influenced by alterations in molecular conformations.^{3,4} In a highly simplified conformation-property picture, photons are absorbed by quasi-localized⁷ subunits (chromophores) on a conjugated polymer chain,^{8,9} resulting in excited electronic states. The corresponding optoelectronic properties vary depending on the packing adopted by the chromophores.¹⁰

Absorption of a photon can (temporarily) change the conformation or physical shape of chromophores, probably also over some distance along the polymer chain as suggested by simulations.¹¹ Photoexcited states (excitons) may to some extent delocalize along a conjugated polymer chain, i.e., spread across several chromophores. Delocalization of an excitonic state along a conjugated polymer chain may be related to the local chain rigidity;¹² i.e., the more delocalized the exciton the more rigid the polymer. Furthermore, chain rigidity itself is related to polymer viscosity; rigid polymers are often highly viscous.¹³ This brings up the interesting question: could light be used to predictably manipulate chain conformations and to control macroscopic (mechanical) properties of conjugated materials, for example its viscosity?

In this paper, we show that light is slowing dewetting in thin films containing conjugated polymers and this effect of light on dewetting velocity is a reversible phenomenon. This supports a mechanism of conformational changes in conjugated polymers induced by photoexcitation. Furthermore, we show that the here observed phenomenon is of generic nature as several conjugated polymer systems responded in a similar way to illumination by light.

EXPERIMENTAL METHODS

Poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylenvinylene] (MEH-PPV) was purchased from Sigma-Aldrich, with a weight-average molecular weight (M_w) of 150 000–250 000 g/mol and with a polydispersity index (PDI) around 5. MEH-PPV was used without further purification. Low molecular weight polystyrene (PS) was bought from Polymer Standards Service with M_w = 3250 g/mol and PDI \leq 1.05. Poly(3-hexylthiophene) (P3HT) with number-average molecular weight (M_n) of 26400 g/mol (contour length \approx 59 nm obtained by gel permeation chromatography), with PDI = 1.79 and a regioregularity of 96.2% was purchased from Merck Chemicals. The 6 mg/mL mixture of MEH-PPV and PS was dissolved in a solvent blend of equal amounts of toluene, tetrahydrofuran and cyclohexanone. Poly[[9-(1-octynonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzo-thiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), and P3HT were both dissolved in chloroform only. All vials used for solution preparation were at all times wrapped in aluminum foil for protection against light. Hydroxy terminated polydimethylsiloxane

Received: January 18, 2013

Revised: March 1, 2013

Published: March 15, 2013

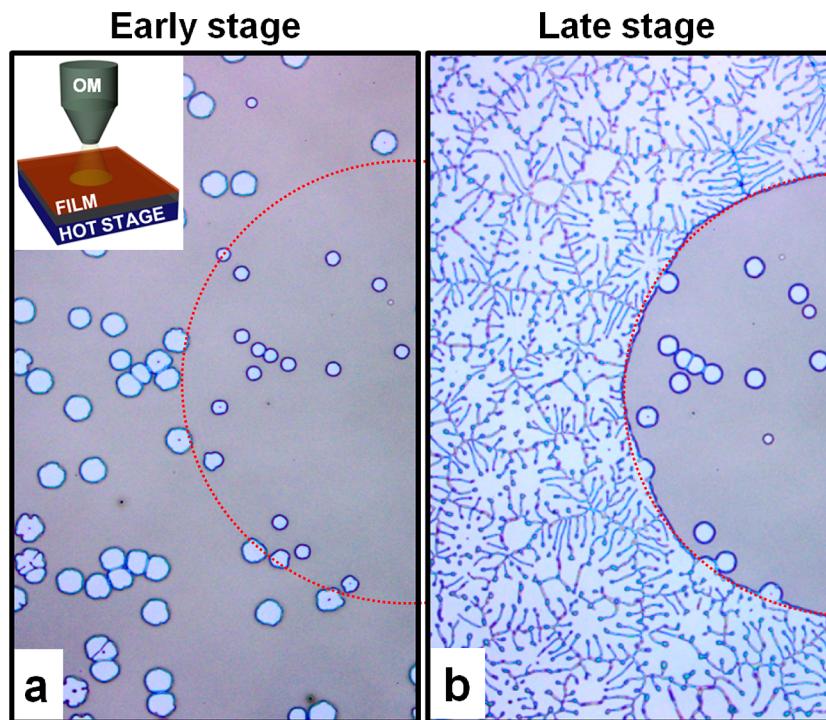


Figure 1. Optical micrographs depicting the morphology of a 50 nm thick MEH–PPV/PS (10%/90%) film after (a) 12 h and (b) 25 h of dewetting at 115 °C on a silicon wafer coated with \approx 2 nm thick PDMS layer. Inner regions delimited by the dotted semicircles were exposed to white light while the complementary regions outside were not exposed to light. Size of images is 1070 \times 1880 μm^2 . Inset in part a shows the schematics of the experimental setup.

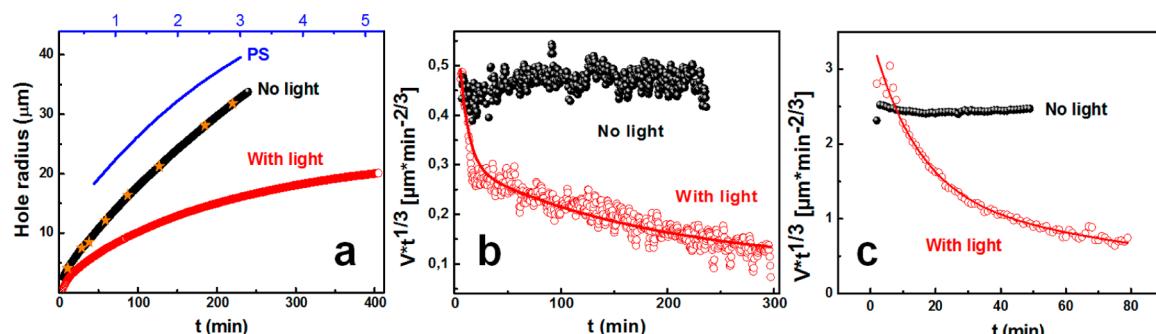


Figure 2. (a) Typical evolution of the radius of two randomly chosen dewetting holes as a function of dewetting time, measured at 125 °C. Each hole was located in a 35 nm thick film of MEH–PPV/PS (15%/85%) deposited on a silicon wafer coated with \approx 2 nm of PDMS. One hole was exposed (empty circles) while the other hole was not exposed to white light (filled circles). For comparison, dewetting of an 88 nm thick PS film at 100 °C is represented by the blue line in part a. Various holes in the same sample as the one represented by the filled circles, which up to the time of observation were never exposed to any light (“zero light”) have been recorded as control measurements (stars). (b) Dewetting velocities (V) corresponding to the holes measured in part a, multiplied by dewetting time (t) to the power of $1/3$ ($=V \cdot t^{1/3}$). (c) $V \cdot t^{1/3}$ of two randomly selected dewetting holes as a function of t measured at 100 °C in a 40 nm thick film of PCDTBT/PS (15%/85%) deposited on a silicon wafer coated with a 15 nm thick PDMS layer. One hole was not exposed (filled circles) while the other hole, located on the same film, was exposed to light (empty circles). Red lines in parts b and c are fits obtained using a double exponential decay function.

(PDMS) of $M_w = 139\,000$ g/mol was purchased from ABCR and dissolved in *n*-heptane. Solutions of both MEH–PPV/PS and PDMS were stirred at 60 °C overnight and then filtered using 0.2 μm polyvinylidene difluoride (PVDF) pore size filters.

UV-cleaned silicon wafers were coated either with an ultrathin layer of \approx 2 nm PDMS spin-cast at 2000 rpm for 30 s from a 5×10^{-9} M (or 5×10^{-7} M) solution in *n*-heptane or with a 15 nm thick layer of PDMS spin-cast at 2000 rpm for 30 s from a solution containing 1 wt % PDMS in *n*-heptane. PDMS films were then annealed in an oven at 160 °C for 4 h and then washed in *n*-heptane for 1 h. A layer of only irreversibly adsorbed PDMS molecules remained after washing.

Thin solid films of MEH–PPV/PS, PCDTBT/PS or P3HT/PS with a thickness of a few tens of nanometers were obtained by spin-

cast from solutions of MEH–PPV/PS (10%/90%, 15%/85% or 20%/80% weight ratio), PCDTBT/PS (15%/85%) or P3HT/PS (5%/95%) onto PDMS coated silicon wafers. Wafers were coated with a thin PDMS layer to act as a highly reproducible nonwettable substrate enabling slippage and so facilitating dewetting.¹⁴ The obtained films were subsequently annealed at temperatures above the glass transition of the PS matrix (\approx 90 °C) in order to induce dewetting. Annealing at temperatures ranging between 100 and 125 °C was done using a Linkam hot stage. All dewetting experiments were performed in an inert nitrogen atmosphere (under continuous nitrogen flow).

Films were used as spin-cast or after 24 h of aging in vacuum and at room temperature. Dewetting was followed using a Zeiss optical microscope. Dewetting experiments were performed in the dark or

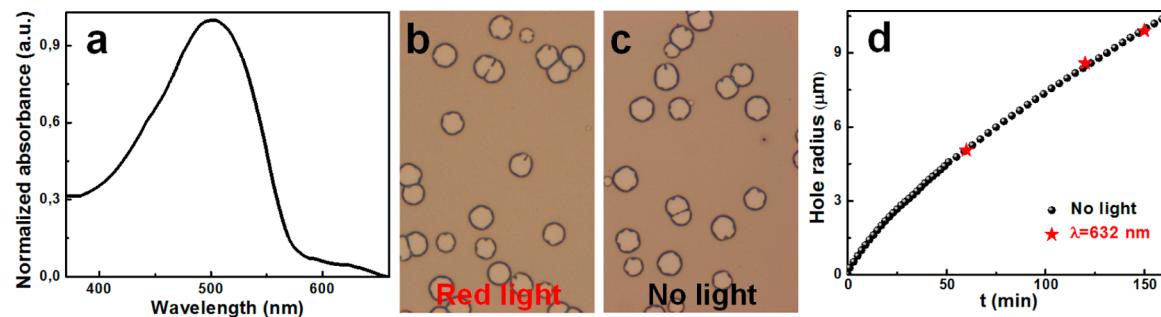


Figure 3. (a) UV-vis absorption spectrum recorded from an as prepared MEH-PPV/PS film (20%/80%) on silicon wafer (no PDMS). (b, c) Optical micrographs ($162 \times 242 \mu\text{m}^2$) showing the morphology of two identical thin MEH-PPV/PS (10%/90%) polymer films (35 nm thickness) after simultaneous dewetting at 125°C for 2 h. The first film was exposed to red light during dewetting (b) while the second film was dewetting in the dark (c). (d) Evolution of the radius of a dewetting hole for films similar to part c dewetting at 125°C in the dark. Stars represent experimental points for the film in part b that was exposed to red light. Films in parts b-d were spin-cast on silicon wafers coated with $\approx 2 \text{ nm}$ of PDMS.

observed under illumination with light as used in optical microscopy. Identical films dewetting on the same hot stage (Figure 3) were separated from each other by an aluminum foil in order to avoid scattering of light from one film to the other. For the film in Figure 3c, half of the hot stage window was covered so that no light of any kind could go in. Experiments were performed on many dewetting holes located either on the same film or on different films. Good reproducibility was achieved both for exposed and not exposed films. For illumination of the thin film during dewetting, white light (from a Zeiss light emitting diode source VIS-LED producing $1.4 \times 10^{11} \text{ photons}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$) coming through the optical microscope objective or red light from a helium-neon laser (633 nm, power of 2.55 mW producing $4.5 \times 10^{14} \text{ photons}\cdot\text{mm}^{-2}\cdot\text{s}^{-1}$, Spindler & Hoyer) were used. UV-vis absorption spectra were acquired using a Lambda 650S spectrometer from Perkin-Elmer.

RESULTS AND DISCUSSION

A simple dewetting experiment allows to probe polymer viscosity.^{15,16} As can be seen in Figure 1a dewetting in a thin film spin-cast from a solution of MEH-PPV and PS proceeded much faster in the nonilluminated region located outside the red dotted semicircle than inside this encircled “exposed” region. At a later stage (Figure 1b), the dewetting process was already complete in the not exposed region (the final dewetting pattern consisted of stable droplets) while dewetting in the exposed region was still continuing. We thus conclude that exposure to white light, here coming from the optical microscope, slowed down dewetting in MEH-PPV/PS films significantly.

A quantitative analysis of the temporal evolution of dewetting is shown in Figure 2. As an example for the degree of deceleration of the dewetting process by light, we point out that after ca. 3.5 h of dewetting at 125°C the radius of a hole in the exposed region was about 2 times smaller than in the not exposed region. Short exposure to white light required for recording the optical micrographs was not able to slow down dewetting measurably.

The opening velocities V of holes dewetting at a constant temperature in the two regions are shown in Figure 2b. Without exposure to light, dewetting followed the characteristic time (t) dependence $V(t) \sim t^{-1/3}$ for dewetting of viscous films on a slippery substrate,^{16,17} dominated by viscous dissipation in the rims surrounding the dewetting holes.¹⁸ As a control experiment, we verified that dewetting of neat PS did not show any influence of light: the same results were obtained with and without exposure to light. Thus, when not illuminated by white light, dewetting of a PS film with added MEH-PPV is

qualitatively the same as for a neat PS film (see Figure 2a). In order to highlight deviations from such behavior, we multiplied $V(t)$ curves by $t^{+1/3}$. Consequently, without the influence of light the value of $V \cdot t^{+1/3}$ was found to be constant in time. In contrast, a significant drop was found when dewetting was observed under illumination with white light. A strong initial reduction in dewetting velocity was followed by a slower process of deceleration. Assuming the existence of two distinct exponential decay processes, we would obtain characteristic relaxation times of $14 \pm 6 \text{ min}$ and $150 \pm 35 \text{ min}$, respectively.

Deceleration of dewetting was clearly due to the presence of conjugated polymers (MEH-PPV) in the films. Varying the amount of MEH-PPV in the blend films from 2% to 15% demonstrated that deceleration by light was more pronounced for higher amounts of MEH-PPV. Nonetheless, even for 2% to 5% of MEH-PPV this effect, although small, was still observable (see Figure S1 in the Supporting Information). All the above experiments indicated that light was able to slow down the dewetting process when the polymer films contained MEH-PPV.

In order to verify if the observed phenomenon of slowing down dewetting is related to the absorption of a photon, we have illuminated the films with light of a wavelength too long to be absorbed by the studied polymers. We exposed thin films containing MEH-PPV to red light (633 nm) while dewetting. MEH-PPV does not absorb light above 600 nm (see Figure 3a). As can be seen in Figure 3b, even after 2 h of exposure no difference in the diameter of dewetting holes was detectable when compared to holes in a not exposed film. Thus, in contrast to white light, red light was not able to decelerate dewetting. Only when photons get absorbed by the polymer, a noticeable influence on the dewetting velocity was observed.

Dewetting can be slowed down by increasing the viscosity of the polymer.¹⁸ A reduction in $V \cdot t^{+1/3}$ by a factor of 2 (see Figure 2b) thus can be represented by a more than 2-fold increase in viscosity (assuming that contact angle and slippage length stayed constant).¹⁶ Viscosity of a polymer can be increased by a stiffening at the segmental level. Therefore, we tentatively propose that absorption of light by MEH-PPV led to changes in molecular conformations of the conjugated polymer chains which effectively rigidified the chains. Tretiak et al. have shown in their simulations that conformations of phenylene-vinylene oligomers tend to become planar when molecules are excited by absorption of light, i.e., photo-excitation is reducing torsional disorder¹¹ and thus may cause stiffening of the molecule. Such stiffening of MEH-PPV chains,

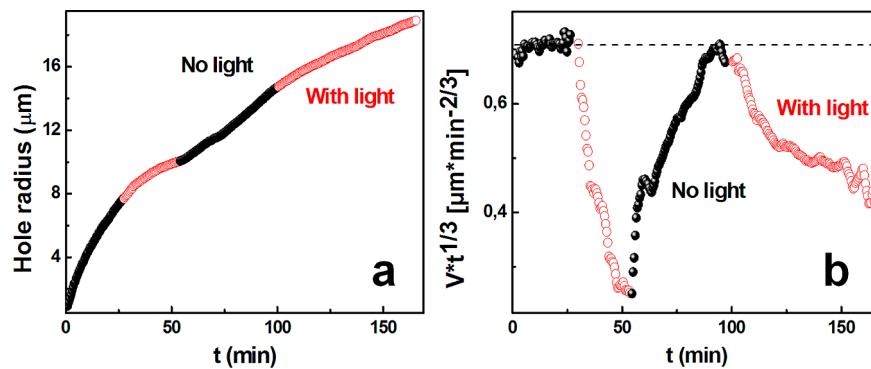


Figure 4. Temporal evolution of (a) the radius and (b) dewetting velocity of a randomly chosen dewetting hole, measured in a thin film of MEH–PPV/PS (40 nm thickness; 10%/90%) at 110 °C. Filled circles are representing experimental points taken without illumination, while empty circles were measured with exposure to white light. The eye-guiding horizontal line in part b represents the expected $V \cdot t^{1/3}$ for dewetting with no light.

in turn, may be responsible for an increase in viscosity and thus a decrease of dewetting velocity.

We may ask if the interaction of light with any conjugated polymer will lead to similar consequences. In other words, is the mechanism responsible for slowing of dewetting by light operative also in other conjugated polymer systems? Therefore, we have performed similar dewetting experiments also for two other conjugated polymer systems: poly[[9-(1-octynonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) and poly(3-hexylthiophene) (P3HT). In Figure 2c, the temporal evolution of the dewetting velocity in a film of PCDTBT/PS is shown. Again, consistent with a general phenomenon, a hole exposed to light dewetted progressively slower than one growing in a region which was not exposed to light. However, the rate of deceleration by light in films containing PCDTBT was not as pronounced as for films containing MEH–PPV, possibly due to an intrinsically higher chain rigidity of the former polymer. A similar light induced slowing of dewetting was observed also for thin films of P3HT/PS (see Figure S2 in the Supporting Information). Thus, it appears that slowing of dewetting is a generic feature of conjugated polymers. Light has a direct influence on a polymer property detected on a macroscopic length scale: the viscosity of the conjugated polymer.

In order to exclude any degradation of the polymer during exposure to light as an explanation of the observed behavior, we checked if the induced changes revert back when stopping exposure to light. Can conjugated chains return to their initial conformation? In other words, is the light-induced slowing down of dewetting a (fully) reversible phenomenon? To scrutinize for reversibility, we followed the growth of a single, randomly chosen hole dewetting for alternating periods with and without exposure to white light (see Figure 4). As expected, the film initially dewetting in the dark behaved like a viscous fluid on a slippery substrate,^{16,17} with a constant value of $V \cdot t^{1/3}$ (Figure 4b). Once the film was exposed to light, dewetting slowed down continuously. However, after switching off the light again, $V \cdot t^{1/3}$ increased back to its initial value. Switching on light once more led again to a slowing down of dewetting. The relatively long period of time (ca. 35 min) required for returning to the initial state may be due to illumination-induced metastable polaron-supporting states, as previously observed in MEH–PPV films.¹⁹ Alternatively, slow relaxations may be attributed to the formation of localized, metastable triions in conjugated polymer films upon photoexcitation.²⁰

CONCLUSIONS

Our experimental results clearly show that the effect of light on dewetting velocity is a reversible phenomenon. This supports a mechanism of (temporary) conformational changes in conjugated polymers induced by photoexcitation. Caused by absorption of light, conjugated polymers may adopt more rigid/planarized conformations. The energy of absorbed photons, partially delocalizing along the conjugated polymer chain, seems to be sufficient to lead to changes in molecular conformation, expressed through a higher effective polymer viscosity. Thus, exposing a thin film of conjugated MEH–PPV molecules embedded in an optically inert PS matrix to white light can cause slowing of dewetting. Being a reversible but slow process, it is possible to tune the dewetting velocity by appropriate periods of illumination. As several other conjugated polymer systems responded in a similar way to illumination by light, we believe that the here observed phenomenon is of generic nature.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Authors thank David Vanden Bout, Ullrich Steiner, Carlos Silva, Werner Stille, Falko Ziebert for fruitful discussions. I. B., N. S., and G. R. acknowledge financial support by the Deutsche Forschungsgemeinschaft through the Freiburg Institute for Advanced Studies (FRIAS).

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