Macromolecules

Article

pubs.acs.org/Macromolecules

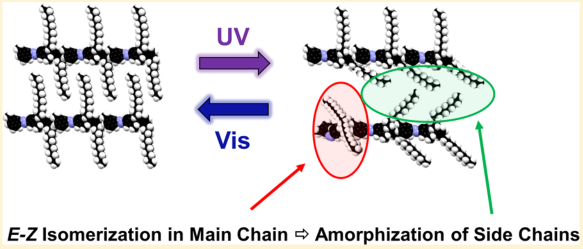
Light-Controlled “Molecular Zippers” Based on Azobenzene Main Chain Polymers

Christopher Weber,[†] Tobias Liebig,[†] Manuel Gensler,[†] Linus Pithan,[†] Sebastian Bommel,[†,∥]
David Bléger,[‡] Jürgen P. Rabe,[†,§] Stefan Hecht,[‡,§] and Stefan Kowarik*,[†]

[†]Department of Physics and [‡]Department of Chemistry and [§]IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
[∥]Deutsches Elektronen-Synchrotron, 22607 Hamburg, Germany

Supporting Information

ABSTRACT: Single strands of azobenzene main chain polymers exhibiting alkyl side chains can be largely and reversibly contracted and extended with light. We show that upon self-assembly in a thin layered film they act as “molecular zippers” that can be opened and closed with UV- and blue light, respectively. Simultaneously *in situ* recorded time-resolved X-ray diffraction and optical spectroscopy measurements, together with scanning force microscopy show that upon the light-induced $E \rightarrow Z$ isomerization of the main chain azobenzenes the layered film morphology remains, while the initially highly ordered alkyl side chains become disordered. Already the $E \rightarrow Z$ isomerization of about 20% of all azobenzene chromophores triggers a complete disorder of the alkyl chains. The kinetics of this partial amorphization of the film is about 18 times slower than the ensemble kinetics of the initial azobenzene photoisomerization. This is the first demonstration of a rigid main chain polymer film with reversibly photoswitchable side chain crystallinity.



INTRODUCTION

Photoresponsive materials based on molecular switches[1] such as stilbenes, azobenzenes, diarylethenes, or spiropyrans have attracted increasing attention recently, because of their possible use in data storage,[2] self-healing materials,[3] molecular electronics,[4] energy storage,[5] and micromechanics.[6−11] In contrast to other stimuli, temperature, electric fields, or solution composition, light possesses many advantages as a primary energy source, in particular its fast, clean, precise and remotely controlled application.

Today, arguably the best studied molecular switch is azobenzene, which can be switched from the thermally stable planar *E*-isomer (*E*) to the metastable 3D *Z*-isomer (*Z*) via irradiation with UV-light.[12] The back-reaction from *Z* to *E* proceeds via thermal relaxation or can be induced by irradiation with blue light. In 2001, Finkelmann et al. showed that large reversible shape changes of azobenzene functionalized elastomers in solids can be generated optically.[13] Also in 2001, McGrath reported the direct observation of light-induced structural reorganization within a solid monolayer of azobenzene-containing functionalized dendrimers.[14,15] During the following years a large variety of photomechanical responses has been found for polymers with azobenzene chromophores in the side chains.[16−20] Application ideas make use of the fact that light-induced collective or cooperative motions of azobenzenes at a molecular level can be amplified to macroscopic scales, often via a photoinduced phase transition within the polymer film. For example, Ikeda and co-workers have used liquid crystalline thin films of azobenzene polymers to build light-driven motors, in which an isothermal transition from a liquid-crystalline to an isotropic state caused by $E \rightarrow Z$ photoisomerization of the azobenzene moieties acts as the driving force.[21,22]

All of these systems are based on polymers with azobenzene in the side chains, which allows one to control the molecular structure of a polymer film indirectly via modifying the interaction between adjacent polymers with light. However, polymers with molecular switches in the main chain allow for a more direct optical control over the molecular structure.[23−30] Recently Bléger et al. developed polymers with azobenzenes in the main chain and dodecyl side chains that enable a maximized photodeformation in solution[31] and allow for crawling motion on surfaces.[32] The rigid-rod polymer **P1** (see Figure 1) incorporates azobenzene chromophores in a poly(*p*-phenylene) backbone with two dodecyl side chains per repeat unit. A

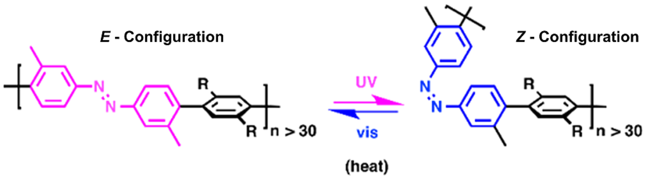


Figure 1. Chemical structure of **P1** (R = n-$C_{12}H_{25}$).

Received: December 18, 2014
Revised: January 23, 2015
Published: February 26, 2015

DOI: 10.1021/ma502551b

crucial aspect of the design is the presence of *o*-methyl groups and therefore introduction of large dihedral angles between the azobenzene units in order to decouple these units and break the electronic conjugation. This point ensures that a *Z*-rich photostationary state (PSS) can be reached upon irradiation with UV-light.[33] The azobenzene polymers can be switched from a thermodynamically stable linear and elongated conformation where the azobenzenes are in the so-called *E*-configuration to a compact and kinked conformation with azobenzenes in the *Z*-configuration. An important remaining question is, whether in an ordered thin film the polymer can still switch and whether molecular switching of the chromophores may trigger larger structural changes through coupling to neighboring polymers.

In this work, we show that in thin films **P1** self-assembles into "molecular zippers". Molecular zippers are common in biological systems like DNA or proteins and can be defined as molecular structures where molecules are interlocked in two directions through noncovalent interactions, along the length of the zip and across it.[34,35] We find that thin films of **P1** can be reversibly switched between a highly ordered state (closed zippers) and a less ordered state (open zippers). We use real-time and *in situ* grazing incidence X-ray diffraction (GIXD) and UV–vis differential reflectance spectroscopy (DRS) simultaneously to obtain information on both the photoisomerization of the azobenzene chromophores and the significant photoresponse of the molecular zippers. Our findings suggest that the observed complete amorphization of the film is induced by *E* → *Z* isomerization of about 20% of the azobenzene chromophores and that the ensemble kinetics of the *E* → *Z* isomerization is about 18 times faster than the kinetics of the amorphization.

EXPERIMENTAL SECTION

Materials. The **P1** polymers were synthesized as previously reported with molecular weight of $M_n \approx 46\,000$ g mol^{-1} (corresponding to 72 repeat units) and a polydispersity of 1.3, as determined by GPC vs polystyrene standards (owing to the rigid-rod character of poly(*p*-phenylene)s, this molecular weight is most likely overestimated by a factor of 1.5–2).[36] The synthesis and switching behavior of **P1** in solution has been described elsewhere.[36] Azobenzene polymer thin films were cast from 25 mg/mL solution in toluene onto freshly cleaved muscovite mica substrates (Plano GmbH Wetzlar, Germany). After the dispense step (5 s), the samples were accelerated to 1500 rpm and the rotation was stopped after 5 s. The films had a nominal thickness of 20 nm as determined with AFM.

Methods. The sample morphology was characterized with atomic force microscopy (AFM) (NanoWizard III, JPK Instruments AG, Germany). The microscope was operated in tapping mode, using silicon cantilevers (AC240TS, Olympus Corporation, Japan, 2 N/m). The AFM micrographs were imaged in air at room temperature.

We performed further structural characterization with grazing incidence X-ray diffraction (GIXD). Switching measurements with high temporal resolution (<10 s) were carried out at the Swiss Light Source (Beamline MS-X04 SA) at the Paul Scherrer Institute with a X-ray energy of 16 keV and a Pilatus 100k detector.[37] The beam width was 144 μm and the beam height was 17 μm. For the remaining X-ray diffraction measurements a laboratory rotating Cu Kα 8 keV source (Rigaku, EFG, beam size = 2 × 2 mm) with a point detector was used. The angle of incidence in GIXD measurements was chosen to be $\alpha_i = 0.8 \times \theta_{critical}$ with $\theta_{critical}$ being the angle of the total reflection edge of the mica substrate. Since the angle of incidence exceeds the critical angle of the polymer film, our GIXD measurements are sampling the full depth of the film.

For differential reflectance spectroscopy (DRS) we used a setup consisting of a 75 W xenon Lamp (LOT-QuantumDesign), a fiber with a reflectance probe and a reference leg to monitor intensity fluctuations of the lamp (Ocean Optics) and two Mini-spectrometers (Thorlabs). All GIXD and DRS measurements presented in this paper have been performed at room temperature (25 °C) under high-vacuum conditions ($p \sim 10^{-7}$ mbar) in a vacuum chamber, equipped with beryllium window for X-ray access and several quartz-glass windows for optical access. *E* → *Z* isomerization of the samples was induced with an unpolarized 365 nm high power UV-LED (Thorlabs). The light-intensity on the sample surface was 91 mW/cm^2. The fwhm of the light-spot of 11.3 mm was chosen to be slightly larger than the sample diameter of 10 mm. In the simultaneous GIXD and DRS measurements GIXD samples the whole footprint area of 2 mm × 10 mm, while DRS was chosen to sample a spot within the GIXD footprint, not in the peak of the UV-light intensity but in a region with an intensity comparable to the average UV-intensity in the GIXD sampling area. Additional UV–vis absorption spectroscopy was measured with a Shimadzu UV–vis scanning spectrophotometer.

RESULTS

Layered Island Structure As Revealed by Microscopy. AFM images of the main chain azobenzene polymer films show a homogeneous sample morphology, characterized by large islands with diameters >1 μm and several clearly distinguishable layers (Figure 2a). Large terraces with round step edges allow for further evaluation. A histogram of the step-height distribution is plotted in Figure 2b. The most frequently occurring step-height of 3.0–3.5 nm suggests a predominant edge-on orientation of the polymers with respect to the mica substrate.

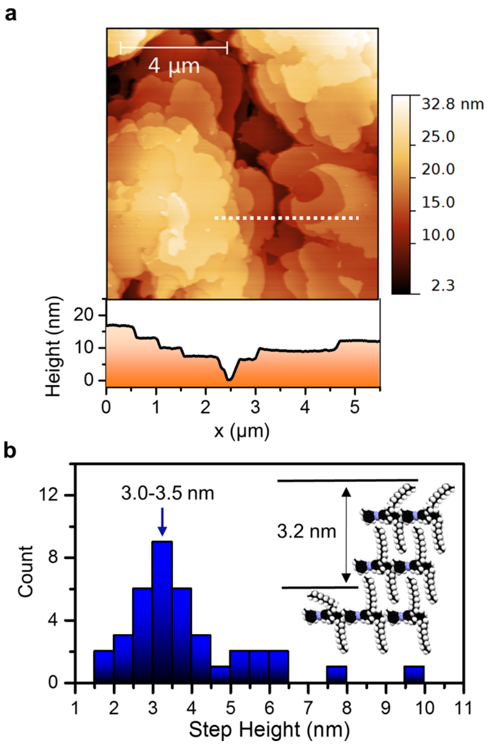


Figure 2. (a) AFM Image of a spin-casted **P1** film with height profile and (b) step height distribution.

The inset of Figure 2b shows an illustration of a stacking model involving interdigitation of dodecyl side chains that would be in agreement with the AFM data. Irradiating the sample for 10 min with UV-light (91 mW/cm^2) did not have a significant effect on the overall sample morphology (Supporting Information, Figure S1). Only locally some island shapes change slightly. X-ray reflectivity (XRR) measurements show no out-of-plane Bragg reflections of the polymer film (see Supporting Information, Figure S2), which is in agreement with AFM, where the varying step heights also indicate the absence of a coherently ordered periodic structure perpendicular to the substrate surface.

Light-Controlled Molecular Interdigitation As Shown by X-ray Diffraction. To investigate the initial molecular structure within the film and the UV light induced structural changes we used time-resolved grazing incidence X-ray diffraction (GIXD). X-ray diffraction is sensitive to coherently ordered molecular crystals and thus presents a powerful technique to address the isomerization of molecular switches in domains with long-range ordering.[38−40] The black curve in Figure 3a shows a GIXD scan of a **P1** thin film before the very first UV-irradiation. Plotted is the scattered X-ray intensity as a function of the in-plane wavevector transfer $q_{\|} = (4\pi/\lambda) \sin \theta$, where 2θ denotes the angle between primary and diffracted beam. There are three main diffraction features. The first in-plane scattering feature appears at a wavevector transfer $q_{\|} = 0.42$ Å^{-1}, corresponding to an in-plane lattice spacing $d_{\|} = (2\pi/q_{\|})$ of 1.5 nm. Referring to earlier X-ray diffraction studies of rigid rod polymers with long alkyl side chains we tentatively assign this peak to the packing structure of the polymer main chain.[41]

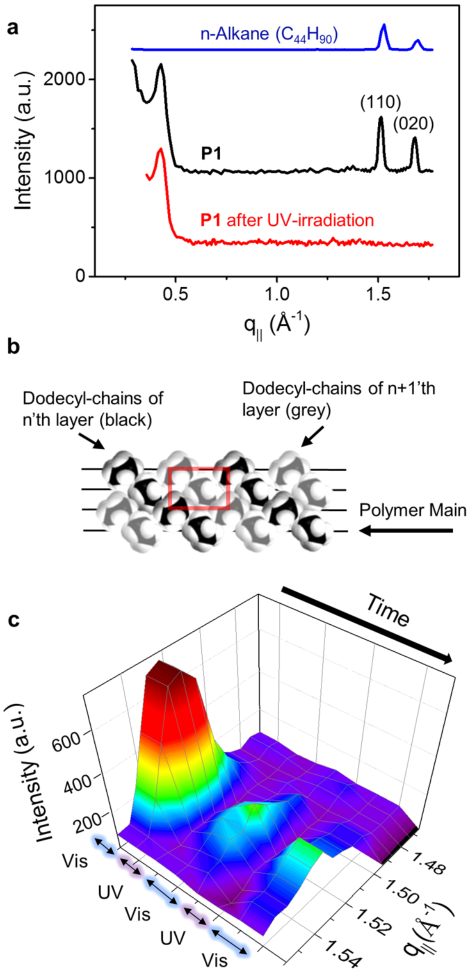


Figure 3. (a) GIXD scan of a **P1** thin film before (black) and after (red) UV-irradiation. For comparison the scattering signal of n-$C_{44}H_{90}$ (blue) is also shown (curves shifted for clarity). (b) Illustration of the proposed in-plane unit cell of dodecyl side-chains (top view). (c) GIXD scans of the (110) Bragg peak of the sample before the very first UV-irradiation and during two irradiation cycles with UV light and visible light.

In Figure 3a, the position and relative strength of two in-plane Bragg reflections at $q_{\|} = 1.52$ Å^{-1} ($d_{\|} = 4.13$ Å) and $q_{\|} = 1.69$ Å^{-1} ($d_{\|} = 3.72$ Å) resemble the in-plane scattering features of the thin film structure of long n-alkanes like $C_{44}H_{90}$ (blue curve), where the n-alkane chains align nearly perpendicular to the substrate surface.[42−44] The large spacing of 1.5 nm between two dodecyl-chains along the polymeric backbone in the stretched out E-rich conformation prevents that a single layer of **P1** can mimic the n-alkane thin film structure (see Figure 3b). However, if the dodecyl side-chains of the nth layer are allowed to interdigitate with dodecyl-chains from the $(n + 1)$th and $(n - 1)$th layer, the **P1** polymers can easily adopt the n-alkane thin film structure, since the interchain spacing of 1.5 nm along the polymeric backbone happens to be almost exactly twice as long as the longer axis of the n-alkane in-plane unit cell (0.74 nm). In fact, interdigitating dodecyl side-chains have been found in the case of comparable polymers with long dodecyl side chains such as poly(3-dodecylthiophene), poly[5,5′-bis(3-dodecyl-2-thienyl)-2,2′-bithiophene)] (PQT), poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene) (pBTTT) or poly(n-dodecyl acrylates).[45−48]

We checked for light-induced changes in the crystal structure with time-resolved GIXD. The red curve in Figure 3a shows the GIXD signal after the sample was exposed to UV-light with an intensity of 91 mW/cm^2 for 10 min. UV-irradiation leads to a comparatively small decrease of (10 ± 1)% of the intensity of the Bragg peak at $q_{\|} = 0.42$ Å^{-1} which we attribute to the main chain of the polymer. If most of the ordered azobenzenes within the film would switch, a stronger decrease or a shift of the scattering feature at $q_{\|} = 0.42$ Å^{-1} would be expected. On the other hand, the in-plane Bragg reflections at $q_{\|} = 1.52$ Å^{-1} and $q_{\|} = 1.69$ Å^{-1} vanish after around 4 min of UV-light exposure (91 mW/cm^2 at 3.4 eV), indicating amorphization of the initially crystalline dodecyl side chains since no new Bragg reflections appear.

We observed a slight temperature increase from 22 to 24 °C due to UV-light absorption of the substrate or the film. However, heating the sample up to 100 °C did not significantly influence the crystal structure, so that the structural transition is indeed light-induced (and not due to local heating effects). From the thermal stability up to 100 °C we also conclude that the experiments were carried out far below the melting temperature of the (unswitched) azobenzene polymer thin film. Figure 3c provides a 3D plot showing GIXD scans of a **P1** thin film that were measured during 3 irradiation cycles. The GIXD measurement of the freshly prepared sample before the very first UV-irradiation shows a Bragg peak at $q_{\|} = 1.52$ Å^{-1}. After 10 min of UV-irradiation the peak vanishes, but it reappears if the sample is irradiated with visible light. While the structural recovery in the first switching cycle is not complete, we find that from the second irradiation cycle on the light-induced structural transition is almost completely reversible.

Kinetics of the $E \rightarrow Z$ Isomerization As Judged by Optical Spectroscopy. To investigate how the observed light-induced changes within the film are related to $E \rightarrow Z$ isomerization of azobenzenes we performed UV−vis spectroscopy in transmission and reflection geometry. A comparison of the optical absorbance of the sample before and after irradiation with UV-light is shown in Figure 4a. Upon UV-irradiation, the

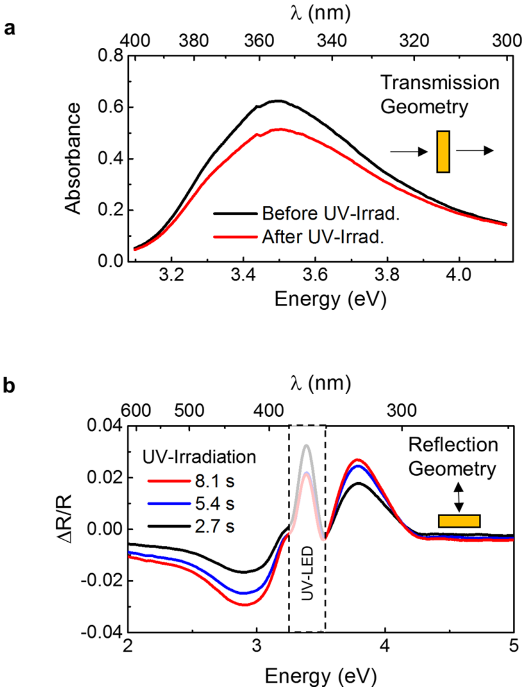


Figure 4. (a) Thin film absorbance at 3.5 eV before and after 5 min irradiation with UV-light (3.4 eV, 91 mW/cm^2). (b) DRS spectra during UV-irradiation showing the relative change of reflectivity due to $E \rightarrow Z$ isomerization of azobenzene chromophores.

film absorbance between 3.2 and 4 eV corresponding to the absorption maximum of the *E*-isomer increases by 7%. We find that from the second switching cycle on the spectral changes are almost completely reversible. Assuming that the optical absorption of the polymer film in the region around 3.5 eV is dominated by the azobenzene moieties we can estimate how many azobenzenes switch. This assumption is reasonable because neither the dodecyl nor the phenyl groups absorb in the region around 3.5 eV. From earlier ^{1}H NMR and optical absorbance measurements in solution we know that the absorbance of *Z*-isomers at 3.5 eV is about 14 times weaker than the absorbance of *E*-isomers at 3.5 eV.[36] Under the assumption that the ratio between *E*-isomer absorbance and *Z*-isomer absorbance at 3.5 eV does not significantly change when the polymers are in a thin film, we can give an estimation of the fraction of *Z*-isomers in the thin film after UV-irradiation. Figure 4a shows that the absorbance of a **P1** thin film at 3.5 eV decreases by (19 ± 1)% upon UV-irradiation with respect to the dark state where all azobenzenes are in the *E*-conformation. A simple calculation gives that about (20 ± 2)% of all azobenzenes within the film are switched from *E* to *Z* (see Supporting Information for the detailed calculation). It has to be noted, though, that this number might change over the course of many switching cycles. We also prepared films with a different nominal thicknesses (1–25 nm); however, no significant effect of the film thickness on the relative amount of switched azobenzenes has been found in this range.

It is important to note that the kinetics of the observed amorphization of the initially highly ordered dodecyl side chains differs from the ensemble kinetics of the $E \rightarrow Z$ isomerization, which can be measured with differential reflectance spectroscopy (DRS). Figure 4b shows the relative change of the optical reflectivity during UV-irradiation. It increases in the region between 3.5 and 4.2 eV corresponding to the energy gap of the π–π^* transition of *E*-azobenzene, while it decreases in the visible region between 2.5 and 3.2 eV, corresponding to the energy gap of the n-π^* transition of the *Z*-azobenzene. Note that due to interference effects, the peak positions in DRS (Figure 4b) are slightly shifted with respect to the peak positions in the measurements in transmission geometry (Figure 4a). This behavior proves that $E \rightarrow Z$ isomerization is indeed occurring within the polymer film. The sharp feature at 3.4 eV can be attributed to diffusely scattered light from the UV-LED that is used to induce $E \rightarrow Z$ isomerization.

We performed simultaneously *in situ* GIXD and DRS measurements to study the relation between the partial disordering of the initially highly ordered film and the $E \rightarrow Z$ isomerization of **P1**. As can be seen in Figure 5a, both the optical reflectivity at 2.75 eV and the GIXD intensity at $q_{\|}$ = 1.53 Å^{-1} decrease upon UV-irradiation and increase again after the UV-light is switched off. Both the DRS and the GIXD intensity signals show a general decline after several switching cycles, possibly caused by drifts in room temperature that can lead to a slight misalignment in the optical and X-ray reflection

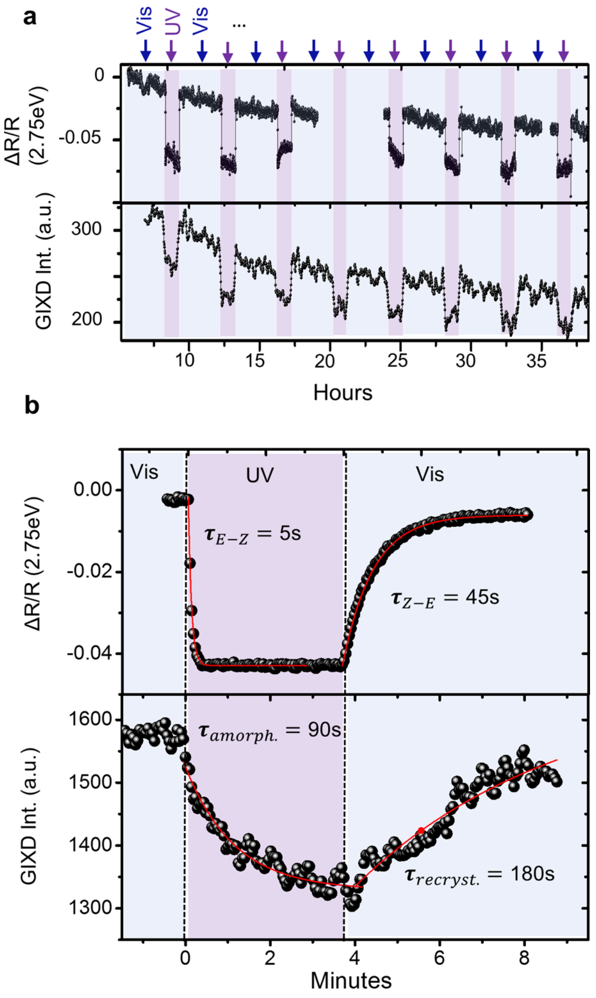


Figure 5. (a) Simultaneous DRS (above) and GIXD (below) during 9 switching cycles. UV irradiation induces $E \rightarrow Z$ isomerization of **P1** and amorphization. The $Z \rightarrow E$ isomerization and recrystallization is induced by the Xe lamp. (b) Comparison of the switching kinetics as determined by time-resolved DRS and GIXD under identical conditions but not simultaneously measured.

geometry. Also a physical process within the sample like photoinduced chromophore reorientation[49] could lead to a reduction in DRS and GIXD signals. Further, a gradient in the intensity of the UV-light could cause mass transport within an azobenzene containing thin film[50] reducing the number of molecules in the sampled area.

GIXD measurements with higher temporal resolution, taken at the SLS synchrotron source show that the time to reach the photostationary state (PSS) differs drastically between DRS and GIXD measurements (see Figure 5b). In DRS the PSS is reached with a time constant of τ = 5 s. The red line is a monoexponential fit to the data. In the GIXD measurement the PSS is reached with a time constant of τ = 90 s under the same conditions. After the UV-light is switched off, the optical reflectivity returns back to its initial state with a time constant of τ = 45 s, while the time constant of the recrystallization as monitored with GIXD is τ = 180 s. Note that the *Z* → *E* isomerization is induced by visible light (<3 eV) since the time-resolved optical measurements within a wide spectral range require constant irradiation with white light from a Xe-lamp. We found that the UV-intensity of the Xe-light had only a minor effect ($\Delta R/R$ at 3.5 eV = 0.05%) on the *E* → *Z* isomerization compared to our UV-LED ($\Delta R/R$ at 3.5 eV ~ 4%). Therefore, we can exclude that most azobenzenes were already in the *Z*-configuration before the UV-LED was switched on.

■ DISCUSSION

Combining our results from GIXD and DRS, we can understand the switching mechanism in the layered thin films of the main chain azobenzene polymers. With GIXD we find an interdigitating molecular zipper structure, in which UV-light induces amorphization of the dodecyl side-chains, corresponding to an opening of the molecular zippers. A comparison of the time-resolved GIXD and DRS measurements shows that the kinetics of this amorphization is more than 1 order of magnitude slower than the ensemble kinetics of the *E* → *Z* isomerization. Interestingly, we observe a fast monoexponential decay in the time-resolved DRS data. If the reason behind the slower kinetics of the amorphization was a slower switching mechanism of constrained azobenzenes in highly ordered domains coexisting with less ordered domains, one would expect a double exponential decay of the DRS data, because optical spectroscopy is sensitive to all azobenzene chromophores within the film. If a double exponential fit based on the two different time constants that were obtained with DRS and GIXD is applied to the DRS data, one finds that less than 0.6% of all azobenzene chromophores within the film could switch with a slower time constant. From this we conclude that a monoexponential decay describes the time-resolved DRS data with adequate accuracy and that the time constant of the amorphization is not primarily governed by the kinetics of the *E* → *Z* isomerization.

UV–vis spectroscopy measurements of the optical absorbance of the polymer film showed that in the polymer film only a fraction (around 20%) of all azobenzenes undergo *E* → *Z* isomerization. This is supported by GIXD measurements, where the Bragg peak at $q_{\parallel}$ = 0.42 Å^{-1}, which we attribute to the ordering of the polymer main chain, decreases only slightly upon UV-irradiation, indicating that most of the ordered polymer main chains remain stretched out even after the side chains lost their coherent long-range order. A scenario that could explain all of our experimental findings is illustrated in Figure 6. Strain and disorder generated by fast isomerization (τ = 5 s) of a single azobenzene moiety, possibly close to a defect site or domain boundary slowly spreads throughout the film (τ = 90 s), thereby disrupting the coherent ordering of the initially crystalline dodecyl side chains and ultimately leading to an amorphous structure of the film. After the UV-light is switched off, *Z* → *E* isomerization of the switched azobenzene moiety occurs (τ = 45 s, triggered by the visible light of the Xe lamp), followed by a slower recrystallization process of the dodecyl side chains (τ = 180 s). Therefore, light-induced switching occurs rapidly at the local molecular level by *E* → *Z* and *Z* → *E* photoisomerization, and subsequent structural changes in the thin films are associated with longer time scales. A similar behavior has been observed for thin films of side chain azobenzene polymers, where the photochemically induced isomerization of azobenzene chromophores triggers a photoexpansion of the film.[51] The time constants of the photoexpansion and the mechanical relaxation were found to be considerably slower than the corresponding time constants of the azobenzene photoisomerization and the thermal back-reaction. The time constants of the amorphization and the recrystallization of the polymer film are primarily not governed by switching but by structural and topological constraints, such as chain stiffness, pinning of amorphous chains, and the thickness distribution of lamellae.[52]

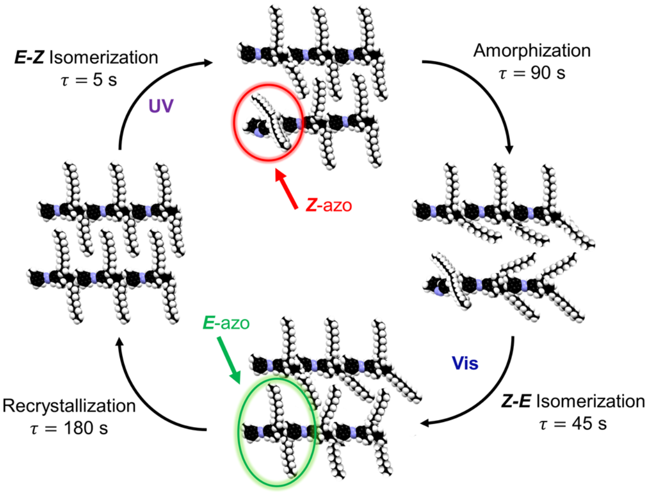


Figure 6. Sketch of the proposed switching scenario. Light-induced *E* → *Z* isomerization of azobenzene chromophores in the polymer main chain disrupts the coherent ordering of dodecyl side chains.

■ CONCLUSION

We have shown that it is possible to switch layered thin films of main chain azobenzene polymers reversibly between a highly ordered state involving interdigitating dodecyl side chains (closed zippers) and a significantly less ordered state with disordered side chains (open zippers). To our knowledge this is the first demonstration of a rigid main chain polymer-based molecular zipper undergoing reversible light-controlled opening and closing. It is a remarkable result that fast *E* → *Z* isomerization (τ = 5 s) of a small fraction (~20%) of all azobenzene chromophores within the polymer film is sufficient to disrupt the long-range ordering of the protruding dodecyl side chains and to induce amorphization of the film. This amorphization occurs on a much larger time scale (τ = 90 s), determined by structural and topological constraints. Our findings of a delay between azobenzene switching and the structural effects are important for optomechanically active or self-healing materials that make use of a reversible light-controlled phase transition.

ASSOCIATED CONTENT

Supporting Information

Figures S1 (AFM), S2 (XRR data), and S3 (^{1}H NMR) and calculation of E/Z ratio in thin film. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*(S.K.) E-mail: stefan.kowarik@physik.hu-berlin.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Generous support by the German Research Foundation (DFG via SFB 658, SFB 765, BL 1269/1-1 and the International Graduate Research Training Group 1524) is gratefully acknowledged. We acknowledge the Paul Scherrer Institut, Villigen, Switzerland for provision of synchrotron radiation beamtime at beamline X04 of the SLS and would like to thank Philip Wilmott and Steven Leake for their assistance. We also thank Stefan Kirstein for helpful discussions.

REFERENCES

(1) *Molecular Switches*; 2nd ed.; Feringa, B. L., Browne, W. R., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2011; Vol. *51*, pp 2281−2281.

(2) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658−660.

(3) Amamoto, Y.; Kamada, J.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 1660−1663.

(4) Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2011**, *133*, 20009−20029.

(5) Kucharski, T. J.; Ferralis, N.; Kolpak, A. M.; Zheng, J. O.; Nocera, D. G.; Grossman, J. C. *Nat. Chem.* **2014**, *6*, 441−447.

(6) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25−35.

(7) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612−5613.

(8) Mirfakhrai, T.; Madden, J. D. W.; Baughman, R. H. *Mater. Today* **2007**, *10*, 30−38.

(9) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.

(10) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307−310.

(11) Van Oosten, C. L.; Bastiaansen, C. W. M.; Broer, D. J. *Nat. Mater.* **2009**, *8*, 677−682.

(12) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. *J. Am. Chem. Soc.* **1958**, *80*, 3528−3531.

(13) Finkelmann, H.; Nishikawa, E.; Pereira, G.; Warner, M. *Phys. Rev. Lett.* **2001**, *87*, 015501.

(14) Tsukruk, V. V.; Luzinov, I.; Larson, K.; Li, S.; Mcgrath, D. V. *J. Mater. Sci. Lett.* **2001**, *20*, 873−876.

(15) Junge, D. M.; McGrath, D. V. *J. Am. Chem. Soc.* **1999**, *121*, 4912−4913.

(16) *Smart Light-Responsive Materials*; Zhao, Y.; Ikeda, T., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 2009.

(17) Yager, K. G.; Barrett, C. J. *J. Photochem. Photobiol. A: Chem.* **2006**, *182*, 250−261.

(18) Kim, H.-K.; Wang, X.-S.; Fujita, Y.; Sudo, A.; Nishida, H.; Fujii, M.; Endo, T. *Macromol. Rapid Commun.* **2005**, *26*, 1032−1036.

(19) Karageorgiev, P.; Neher, D.; Schulz, B.; Stiller, B.; Pietsch, U.; Giersig, M.; Brehmer, L. *Nat. Mater.* **2005**, *4*, 699−703.

(20) Lomadze, N.; Kopyshev, A.; Rühe, J.; Santer, S. *Macromolecules* **2011**, *44*, 7372−7377.

(21) Yamada, M.; Kondo, M.; Miyasato, R.; Naka, Y.; Mamiya, J.; Kinoshita, M.; Shishido, A.; Yu, Y.; Barrett, C. J.; Ikeda, T. *J. Mater. Chem.* **2009**, *19*, 60.

(22) Ikeda, T.; Ube, T. *Mater. Today* **2011**, *14*, 480−487.

(23) Irie, M.; Schnabel, W. *Macromolecules* **1981**, *14*, 1246−1249.

(24) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Macromolecules* **1981**, *14*, 262−267.

(25) Hugel, T.; Holland, N. B.; Cattani, A.; Moroder, L.; Seitz, M.; Gaub, H. E. *Science* **2002**, *296*, 1103−1106.

(26) Sapich, B.; Vix, A. B. E.; Rabe, J. P.; Stumpe, J. *Macromolecules* **2005**, *38*, 10480−10486.

(27) Hosono, N.; Yoshikawa, M.; Furukawa, H.; Totani, K.; Yamada, K.; Watanabe, T.; Horie, K. *Macromolecules* **2013**, *46*, 1017−1026.

(28) Shankar, M. R.; Smith, M. L.; Tondiglia, V. P.; Lee, K. M.; McConney, M. E.; Wang, D. H.; Tan, L.-S.; White, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 18792−18797.

(29) Wang, D. H.; Wie, J. J.; Lee, K. M.; White, T. J.; Tan, L.-S. *Macromolecules* **2014**, *47*, 659−667.

(30) Wie, J. J.; Wang, D. H.; Lee, K. M.; Tan, L.-S.; White, T. J. *Chem. Mater.* **2014**, *26*, 5223−5230.

(31) Bléger, D.; Liebig, T.; Thiermann, R.; Maskos, M.; Rabe, J. P.; Hecht, S. *Angew. Chem.* **2011**, *50*, 12559−12563.

(32) Lee, C.; Liebig, T.; Hecht, S.; Bléger, D.; Rabe, J. P. *ACS Nano* **2014**, *8*, 11987−11993.

(33) Bléger, D.; Dokić, J.; Peters, M. V.; Grubert, L.; Saalfrank, P.; Hecht, S. *J. Phys. Chem. B* **2011**, *115*, 9930−9940.

(34) Bisson, A. P.; Carver, F. J.; Hunter, C. A.; Waltho, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 10292−10293.

(35) Bhosale, R.; Perez-Velasco, A.; Ravikumar, V.; Kishore, R. S. K.; Kel, O.; Gomez-Casado, A.; Jonkheijm, P.; Huskens, J.; Maroni, P.; Borkovec, M.; Sawada, T.; Vauthey, E.; Sakai, N.; Matile, S. *Angew. Chem.* **2009**, *48*, 6461−6464.

(36) Bléger, D.; Liebig, T.; Thiermann, R.; Maskos, M.; Rabe, J. P.; Hecht, S. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 12559−12563.

(37) Willmott, P. R.; Meister, D.; Leake, S. J.; Lange, M.; Bergamaschi, a; Böge, M.; Calvi, M.; Cancellieri, C.; Casati, N.; Cervellino, a; Chen, Q.; David, C.; Flechsig, U.; Gozzo, F.; Henrich, B.; Jäggi-Spielmann, S.; Jakob, B.; Kalichava, I.; Karvinen, P.; Krempasky, J.; Lüdeke, a; Lüscher, R.; Maag, S.; Quitmann, C.; Reinle-Schmitt, M. L.; Schmidt, T.; Schmitt, B.; Streun, a; Vartiainen, I.; Vitins, M.; Wang, X.; Wullschleger, R. *J. Synchrotron Radiat.* **2013**, *20*, 667−682.

(38) Hoshino, M.; Uchida, E.; Norikane, Y.; Azumi, R.; Nozawa, S.; Tomita, A.; Sato, T.; Adachi, S.; Koshihara, S. *J. Am. Chem. Soc.* **2014**, *136*, 9158−9164.

(39) De Loera, D.; Stopin, A.; Garcia-Garibay, M. a. *J. Am. Chem. Soc.* **2013**, *135*, 6626−6632.

(40) Koshima, H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, *131*, 6890−6891.

(41) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253−267.

(42) Gorce, J.; Spells, S. J.; Zeng, X.; Ungar, G. *J. Phys. Chem. B* **2004**, *108*, 3130−3139.

(43) Craig, S. R.; Hastie, G. P.; Roberts, K. J.; Sherwood, J. N. *J. Mater. Chem.* **1994**, *4*, 977.

(44) Weber, C.; Frank, C.; Bommel, S.; Rukat, T.; Leitenberger, W.; Schäfer, P.; Schreiber, F.; Kowarik, S. *J. Chem. Phys.* **2012**, *136*, 204709.

(45) Tsao, H. N.; Müllen, K. *Chem. Soc. Rev.* **2010**, *39*, 2372−2386.

(46) Kline, R. J.; DeLongchamp, D. M.; Fischer, D. A.; Lin, E. K.; Richter, L. J.; Chabinyc, M. L.; Toney, M. F.; Heeney, M.; McCulloch, I. *Macromolecules* **2007**, *40*, 7960−7965.

(47) Keg, P.; Lohani, A.; Fichou, D.; Lam, Y. M.; Wu, Y.; Ong, B. S.; Mhaisalkar, S. G. *Macromol. Rapid Commun.* **2008**, *29*, 1197−1202.

(48) Ballauff, M. *Integration of Fundamental Polymer Science and Technology—2*; Lemstra, P. J.; Kleintjens, L. A., Eds.; Springer Netherlands: Dordrecht, The Netherlands, 1988; pp 391−394.

(49) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.

(50) Bian, S.; Williams, J. M.; Kim, D. Y.; Li, L.; Balasubramanian, S.; Kumar, J.; Tripathy, S. *J. Appl. Phys.* **1999**, *86*, 4498.

(51) Tanchak, O. M.; Barrett, C. J. *Macromolecules* **2005**, *38*, 10566–10570.

(52) Lippits, D.; Rastogi, S.; Höhne, G. *Phys. Rev. Lett.* **2006**, *96*, 218303.