Light-Induced Contraction and Extension of Single Macromolecules on a Modified Graphite Surface

Chien-Li Lee,† Tobias Liebig,† Stefan Hecht,‡,§ David Bléger,*‡ and Jürgen P. Rabe*,†,§

†Department of Physics, ‡Department of Chemistry, and §IRIS Adlershof, Humboldt-Universität zu Berlin, 12489, Berlin, Germany

ABSTRACT Synthesis rigid-rod polymers incorporating multiple azobenzene photoswitches in the backbone were deposited from solution onto a monolayer of octadecylamine covering the basal plane of graphite. Large contractions and extensions of the single macromolecules on the surface were induced by irradiation with UV and visible light, respectively, as visualized by scanning force microscopy. Upon contraction, the single polymer chains form more compact nanostructures and also may move across the surface, resembling a crawling movement. We attribute the efficiency of these processes to the low mechanical and electronic coupling between the surface and polymers, the high density of azobenzenes in their backbones, and their rigidity, allowing for maximized photodeformations. The visualization of on-surface motions of single macromolecules directly induced by light, as reported herein, could help promote the development of optomechanical nanosystems.

KEYWORDS: azobenzene · single macromolecule · photoisomerization · graphene · molecular workbench · scanning force microscopy

Control over the motion of single molecules is a fundamental challenge in the field of nanotechnology, in particular for the development of artificial molecular machines,1−3 and typically requires converting external energy—either chemical fuels or physical stimuli—into movement through concerted conformational changes. Ingenious systems have been developed, sometimes inspired by Nature, such as artificial muscles4,5 and DNA/molecular walkers,6−9 or by our macroscopic surroundings, such as molecules resembling wheels,10 pinions,11 and even cars,12−14 for which the most sophisticated example to date is a system equipped with four rotary motors fueled by electrons via voltage pulses.15 Physical stimuli, which are particularly attractive, as they allow for noninvasive control with typically high spatial precision, include electrons,15−17 mechanical manipulation via the tip of a scanning probe microscope,10,11 and light.18

In that context, molecules able to undergo reversible conformational changes leading to large contraction and extension of their structures are of potential great interest. Small molecules, such as azobenzene photoswitches,19 usually exhibit contractions and extensions of low amplitudes due to their limited size,20−22 while macromolecules are more promising for obtaining mechanical movements over larger distances.24−26 Recently, we have shown that drastic contraction/extension cycles can be induced on command in rigid-rod polymers incorporating many azobenzene photoswitches in the main-chain (see P1, Figure 1).27 The embedded photoswitches act as hinges, which upon light-induced isomerization lead to reversible shrinking and stretching of the polymer backbone. One key element of the molecular design is the rigidity of the backbone, in that case, a poly(paraphenylene), which maximizes the photodeformation and should eventually allow for enabling large mechanical motion. Another crucial aspect of the design is the introduction of large twist angles between the azobenzene units in order to break the conjugation. This point ensures attainment of a cis-rich photostationary state (PSS) upon irradiation with UV light, since azobenzenes directly connected at their para-positions display rather cis-poor PSSs.28

* Address correspondence to rabe@physik.hu-berlin.de, david.bleger@chemie.hu-berlin.de.

Received for review September 19, 2014 and accepted October 26, 2014.
Published online October 26, 2014 10.1021/nn505325w

© 2014 American Chemical Society
Rigid-rod polymers P1 were shown to perform in solution, exhibiting conformational rigid-rod → random-coil transitions accompanied by changes in hydrodynamic volume of ca. 75%, as determined by static and dynamic light-scattering measurements. Nevertheless, in order for linear chains to eventually act as molecular machines, i.e., able to transport/manipulate other objects or perform mechanical work, they arguably have to be interfaced with robust scaffolds such as nanotubes, particles, or planar surfaces.

In this article, we present the immobilization and orientation of the photoshrinkable linear polymer P1 on a modified graphite surface and provide a direct visualization of dramatic extensions, contractions, and crawling movements of single macromolecules induced by a physical, noninvasive stimulus, i.e., light. A “molecular workbench” was employed, consisting of a graphene surface of highly oriented pyrolytic graphite (HOPG) covered by an ordered monolayer of flat-lying octadecylamine (ODA), which has been used to both orient single macromolecules and manipulate them by scanning force microscopy (SFM) techniques. Indeed, the ODA monolayer decouples the polymers—both mechanically and electronically—from the surface, a point of prime importance since a strong mechanical coupling would prevent the polymers from moving at all, while an electronic coupling with the semimetallic surface could impede the photoswitches from isomerizing fast via quenching of the photoinduced excited states.

RESULTS AND DISCUSSION

Alignment of Single Rigid-Rod Polymers on Modified Graphite. Rigid-rod polymers P1 deposited on a graphite surface coated with an ODA monolayer were imaged by SFM (Figure 2a). Some rather high protruding defects serve as markers to ascertain that all SFM images were taken at the same location. Two different aligning directions with 60° orientation difference of the rod-like polymers P1 mark a clear grain boundary at the top left corner, reflecting the 3-fold symmetry of the ODA lamellae under the P1 polymers. Many straight rod-like conformations confirm that the initial configuration of the polymer is trans-rich, as received from the synthesis and corresponding to the thermodynamically most stable form of azobenzene. Occasionally, some kinks within a chain as well as overlapping of different polymers were found, but overall P1 macromolecules are aligned along the ODA lamellae located underneath. These lamellae serve as soft nanoscopic “rails”, with the chemical nature of the hydrophilic head groups and the length of the alkyl chains defining a surface potential ripple, thus orienting the single polymer molecules on the surface.

Interestingly, deposited P1 polymers exhibit a rather homogeneous height of \( h = 0.7 \pm 0.1 \text{ nm} \), as indicated by a cross section profile (Figure 2e, along the white line in Figure 2a). The experimental height approximately matches the expected molecular width of the backbone of P1, as estimated by the distance between two methyl groups placed in meta-position on one phenyl ring: \( d_{\text{methyl-methyl}} \approx 0.5 \text{ nm} \). The first two rods (numbered 1 and 2 in Figure 2e) have a characteristic width of 10 nm, which is defined as the thinnest apparent width among P1 rods, and the distance between them is ca. 18 nm (about three lamellae). Nevertheless, the measured widths are broadened due to the finite SFM tip radius (see discussion below for more details). The third and fourth rods (3 and 4) are separated by only 12 nm (about two lamellae), where the tip of the cantilever cannot go down to the surface due to the finite radius of the SFM tip apex, explaining why these two peaks are only partially resolved. The fifth polymer has a kinked spot, resulting in a slightly larger width. Although many closely aligned parallel polymers cannot be fully

Figure 1. Chemical structure and schematic representation of P1 in the extended (trans-rich) and contracted (cis-rich) state on graphite modified with an octadecylamine (ODA) monolayer. Isolated single P1 can shrink and stretch upon exposure to UV (\( \lambda = 365 \text{ nm} \)) and visible (\( \lambda = 436 \text{ nm} \)) light, respectively. The three layers are labeled: 1, HOPG; 2, ODA monolayer; 3, polymer P1.
resolved by the SFM tip, some completely isolated rods can be identified.

Both P1 polymers and ODA lamellar structures can be clearly seen in zoomed-in images (see Figure 2b). The blue line shows that the cross section of the lamellae (blue line in Figure 2f) exhibits periodic peaks and valleys (peaks are marked by vertical lines in Figure 2f) with the characteristic lamellae width of 6 ± 0.2 nm, which is very similar to the width prior to the deposition of P1 (see Figure S1), indicating that the ODA monolayer was not altered by the deposition of the polymers. The red line in Figure 2b shows the cross section of a single P1 polymer located above a valley of the lamella (see also red line in Figure 2f) with a width of ca. 10 nm.

The sample was irradiated with UV light (λ = 365 nm) for 8 min (Figure 2c). The color saturation (white) was set to 1.5 nm. One can observe that before irradiation nearly all P1 polymers are under 1.5 nm height, whereas after irradiation, several parts of P1 polymers exceed 1.5 nm height. Besides the increase of the height, most of the rods were also shortened. Zoom-in images in Figure 2b and d highlight a polymer chain, which was shortened after irradiation and concomitantly exhibits an increase in height from 0.7 nm to 0.9 nm (see green dashed line in Figure 2f). The increase in height accompanied by the shortening of the rods indicates a shrinking process, which should be attributed to the trans → cis photoisomerization of the embedded azobenzenes.

In order to quantify this process to some extent, the level of contraction was estimated on a large-scale image as the change in the area occupied by the polymers, which amounts to a 23% decrease (see Figure S2). Due to the finite radius of the SFM tip apex, lateral dimensions of objects are generally overestimated, since the tip starts to interact with the imaged object before the tip apex encounters it. In order to know if the measured characteristic width could be the actual width of single polymer, the process of deconvolution was applied by using the following model (Figure 2g).

We assume the cross section of a single P1 polymer to be rectangular with a width w and height h. By assuming further that the tip is capped with a semisphere with radius R, the apparent width of a single P1 polymer can be estimated to be $L = w + 2Rh - \frac{h^2}{R}$, Here, we took h from the apparent height, h = 0.7 nm, and assumed the real width to be w = 3.3 nm (assuming that dodecyl chains of P1 are fully stretched, possibly on the alkyl chains of the ODA molecules). Taking $R = 8$ nm, i.e., a typical tip radius, we obtained an apparent width of a single P1 polymer to be $L = 9.8$ nm (black line in Figure 2f), which correlates well with the measured apparent width. Therefore, we attribute the P1 rods with characteristic width to the width of single polymers. The formation of P1 dimers and higher aggregates is in any case not likely due to the bulky, highly twisted tetramethyl biphenyl linkers present in the backbone of the polymer. In summary, based on the width, the height, and the geometry of the polymers,
we can conclude that the measured rods are single (macro)molecules. This conclusion was further verified by the behavior of P1 upon irradiation.

Light-Induced Motion of Single Macromolecules at the Surface. In a more systematic study, another sample was irradiated at $\lambda = 365$ nm for 30 s, 2 min, 4 min, 9 min, and 19 min and then at $\lambda = 436$ nm for 10 min to induce the trans $\rightarrow$ cis and back cis $\rightarrow$ trans isomerization, respectively (see Movie S1 for snapshots of P1 polymers undergoing contractions and extensions). The width of the ODA lamellae seems to be unchanged after switching the P1 polymers (see Figure S1), indicating that the ODA lamellae were not affected by the photoirradiation.

Figure 3a shows selected SFM zoom-in images of two different locations, following the contraction of two single rigid-rod P1 polymers (I and II) upon UV-light irradiation. For I the apparent length changed from 60 nm (ca. 25 repeat units) to 22 nm (see Figure 3b, I), while the width increased from 13 nm to 24 nm and the height from 0.7 nm to 1.4 nm. After 19 min of irradiation, no further change in size was observed, indicating that the polymer reached a PSS. Both length and width attained nearly equal values, suggesting that the single chain has adopted a more compact, disk-like shape. Considering that the geometry of a single rigid-rod P1 polymer is cylindrical, the aspect ratio can be defined as the ratio of the width to its length. Using the apparent widths and lengths, the aspect ratio was evaluated to change drastically, from 1/4.6 to 1/1, i.e., from a rod-like to a disk-like morphology. This particular change in aspect ratio was also observed in solution by light-scattering measurements.27 Drastic contraction of $\Delta L = 38$ nm (from 60 to 22 nm) was measured in that particular case, whereas for II, which is longer, this value reached $\Delta L = 48$ nm (from 83 nm to 35 nm; see Figure 3b, II). Similar measurements performed on several other well-isolated single polymers confirm this trend; that is, upon UV-light irradiation lengths are typically reduced by about 60%, while heights and widths nearly double (see Figure 3c). The direct visualization of such high levels of directly light-induced contractions in single (macro)molecules is quite remarkable. It should be noted that another example of this kind, reported by Baigl and co-workers,37 details the indirect light-fueled compaction of DNA, with azobenzene-containing polyamine aqueous solution acting as the photoswitchable medium; that is, the motion of the DNA at the surface was induced by structural changes of the surrounding molecules.

Besides the light-induced formation of disk-shaped single-chain polymeric nanostructures associated with the high levels of contraction, we also observed crawling movements of some polymers during UV-light irradiation. Figure 4 shows SFM snapshots of the same location (extracted from Movie S1, green frame), where a polymer, which was initially fully stretched (Figure 4a), is contracted and, at the same time, shifts...
MATERIALS AND METHODS

Preparation and Characterization of P1 Polymers in Solution. For the purpose of reaching large-scale molecular contractions and extensions, the rigid-rod polymer P1 (Figure 1),\textsuperscript{27} which incorporates azobenzene photoswitches in a poly(paraphenylene) (PPP) backbone functionalized with dodecyl solubilizing groups, has been recently prepared by Suzuki polycondensation and characterized in solution.\textsuperscript{27} Large twist angles were introduced between the chromophores to break the conjugation of the \(\pi\)-system.\textsuperscript{28} This electronic decoupling leads to a relatively high cis content in the polymeric backbone (81\% upon UV-light (360 nm) irradiation in solution).\textsuperscript{27} The molecular weight of the sample used in this study is \(M_w \approx 40,000\) g/mol, with a polydispersity index of 1.7.\textsuperscript{29} The width of P1 determined by the dodecyl chains (assumed stretched) is \(\sim 3.3\) nm, and its height determined by the methyl groups attached to the azobenzene moieties is \(d_{\text{methyl}} \sim 0.5\) nm.

Sample Preparation and SFM Measurements. In order to isolate single rod-like P1 polymers, the graphite surface has been modified with a SAM of octadecylamine, which has been previously demonstrated to be able to isolate and orient single macromolecules such as DNA and polyelectrolytes.\textsuperscript{33,35} First, a droplet of octadecylamine (0.1 g/L in chloroform) was spin-coated onto freshly cleaved HOPG (ZYH grade, Materials Quartz, Inc.) at 40 rounds per second. The resulting SAM was equilibrated in water: a droplet of Milli-Q water was deposited on the surface for 15 s and removed by spinning it off. SFM images of ODA SAM reveal a lamellar structure with a width of \(w \approx 6 \pm 0.2\) nm (see Figure S1). In a second step, a droplet of P1 (1 g/L in dichloromethane) was spin-cast onto the ODA monolayer. The sample was then stored in ambient conditions (white light) to allow the polymers to reach an equilibrium with the ODA monolayer. Imaging was performed by SFM in tapping mode using a multimode head (Digital Instruments Inc., Santa Barbara, CA, USA) and Olympus microcantilevers with a resonance frequency of 70 kHz and a spring constant of 2 N/m.
Photoirradiation. UV light (365 ± 10 nm, LEDs, Nitride Semiconductors Co., Ltd.) with an estimated intensity of \( I \approx 50 \text{ mW/cm}^2 \) was used for the \( \text{trans} \rightarrow \text{cis} \) photoisomerization, and blue light (436 ± 5 nm, filtered from a mercury lamp, Carl Zeiss HBO 50), with an estimated intensity of \( I \approx 40 \text{ mW/cm}^2 \), was used for the \( \text{cis} \rightarrow \text{trans} \) photoisomerization. The incident light was guided and focused onto the sample surface at 45° incident angle, generating a light spot of 1 cm diameter on the sample. During irradiation, the cantilever was lifted up to avoid blocking the incident light.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. Generous support by the German Research Foundation (DFG via IGRTG 1524, SFB 658 and BL 1269/1-1) and the European Research Council through ERC-2012-STG_308117 (Light4Function) is gratefully acknowledged.

Supporting Information Available: Additional information on the light-induced motion of polymers \( \text{P1} \) on graphite (Figures S1 and S2 and Movie S1). This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


38. As measured by GPC in THF vs polystyrene (PS) standards; nevertheless, owing to the rigid-rod character of PPPs, their molecular weight is most likely overestimated by a factor of 1.5–2 using GPC calibrated with flexible PS standards. See ref 39.