Smart Polymers

Light-Orchestrated Macromolecular "Accordions": Reversible Photoinduced Shrinking of Rigid-Rod Polymers**

David Bléger, Tobias Liebig, Raphael Thiermann, Michael Maskos,* Jürgen P. Rabe,* and Stefan Hecht**

Synthetic molecular systems undergoing structure and property changes as a response to external stimuli offer a series of relevant functions. Their direct use in solution, immobilized at surfaces, or integrated into adequate matrices, allow for the elaboration of nano-carriers,[1] molecular electronic memory circuits,[2] adaptive systems,[3] artificial muscles,[4] or healable materials,[5] among others. Reversible systems are commonly generated by utilizing molecular switches[6] as responsive bistable molecules. Of particular interest are switches controlled by non-invasive triggers, especially light, which can display high spatial and temporal resolution. Photoswitches[7] were used to change properties, such as conductance[8] and basicity,[9] based on light-induced alteration of the molecular geometry, that is, their dimensions and shape. In nature, light-induced geometrical modifications of molecular systems[10] lead to primary biological functions, such as the visual perception in vertebrates,[11] or proton pumping in some bacteria,[12] two examples that nicely illustrate the potential of photo-inducing structural modifications in organic systems.

Changing the geometry of macromolecules can be exploited for the elaboration of guest-encapsulation structures,[13] and opto-mechanical materials,[14] which enable direct conversion of photon energy into mechanical work. To prepare efficient structures and materials however, it is

desirable to design macromolecules apt to dramatically change shape and dimensions upon exposure to light.[15] Azobenzenes[16] are ideal candidates, since upon UV and visible light irradiation, they reversibly undergo a large geometrical modification, isomerizing from their linear and flat *E* isomer to a more compact and kinked *Z* form. The groups of Aida,[17] and in particular McGrath,[18] later on also Müllen and co-workers,[19] introduced azobenzene photochromes into the core of rather spherical dendrimers, resulting in (quasi)isotropic nano-objects that display significant changes in hydrodynamic volume upon photoirradiation, with contractions as high as $\Delta V_h = 37\%$,[19] as evaluated by gel permeation chromatography (GPC). It is reasonable to expect that volume contractions of larger magnitude can be realized in anisotropic architectures, for example, cylindrical objects with high aspect ratio (defined as the ratio of a cylinder's length to its diameter). Herein we report on the synthesis of such rigid-rod polymers consisting of azobenzene photochromes in the main chain and the dramatic change of their shape induced upon irradiation. The embedded photoswitches act as hinges, which upon light-induced isomerization lead to reversible shrinking and stretching of the polymer backbone.

Rigid-rod polymer **P1** (Figure 1) incorporates azobenzene photoswitches in a poly(*para*-phenylene) (PPP) backbone. The critical step to achieve large shrinkage of the rods is to

[*] Dr. D. Bléger, Prof. Dr. S. Hecht
Department of Chemistry, Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
E-mail: david.bleger@staff.hu-berlin.de
          sh@chemie.hu-berlin.de
Homepage: http://www.hechtlab.de

T. Liebig, Prof. Dr. J. P. Rabe
Department of Physics, Humboldt-Universität zu Berlin
Newtonstrasse 15, 12489 Berlin (Germany)
E-mail: rabe@physik.hu-berlin.de

R. Thiermann, Prof. Dr. M. Maskos
BAM Bundesanstalt für Materialforschung und -prüfung
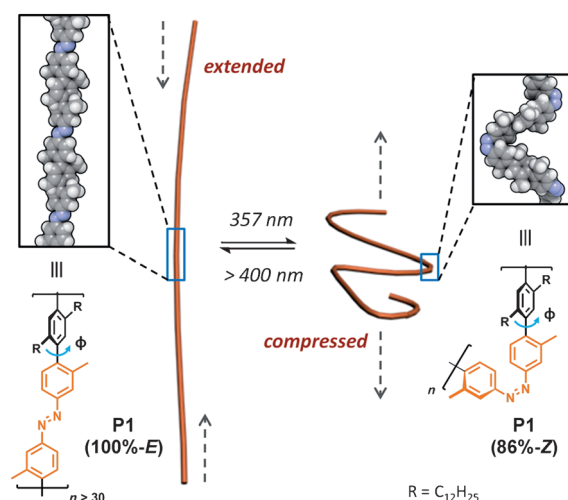Unter den Eichen 87, 12205 Berlin (Germany)
E-mail: michael.maskos@bam.de

Figure 1. Chemical structure and schematic representation of **P1** ($R = C_{12}H_{25}$) in the extended (100%-*E*) and compressed (86%-*Z*) state. Molecularly dissolved **P1** can reversibly shrink and stretch upon exposure to UV ($\lambda = 357$ nm) and visible ($\lambda > 400$ nm) light, respectively.

attain a *Z*-rich photostationary state (PSS), in which a large amount of azobenzenes are in their *Z*-configuration. This point is not straightforward since azobenzenes directly connected at their *para*-positions display rather *Z*-poor PSS.[20,21] However, we recently developed an electronic decoupling approach allowing for quantitative photoswitching in linear bisazobenzenes.[21] It was shown that introducing large twist angles between the chromophores and therefore breaking the conjugation, lead to systems with restored photoswitching efficiency. Rigid rod **P1** displays large twist angles (Φ)[22] along its polyaromatic backbone leading to a 86% overall *Z* content[23] in the PSS. To our knowledge, this is the first time that such a high amount of *Z* forms has been observed in rigid multi-azobenzene architectures.[24]

Polymer **P1** was synthesized by Suzuki polycondensation[25] using [Pd$_2$dba$_3$] (dba = dibenzylideneacetone) in combination with Buchwald's SPhos ligand,[26] a catalytic system developed to couple sterically hindered substrates (for details see the Supporting Information). The use of the SPhos ligand was essential for reaching high molecular weight polymers because **P1** is sterically crowded at its coupling positions by methyl groups and dodecyl chains, introduced in the backbone to confer large twist angles and good solubility, respectively. The sample studied herein has a molecular weight of $M_n \approx 46000 \text{ g mol}^{-1}$ [27] (theoretically corresponding to 72 repeat units), with a polydispersity index of 1.3.

Irradiating solutions of all-*E* **P1** (extended state) with UV light[28] induces modifications in the UV/Vis absorption spectra (Figure 2a), typically observed for single azobenzenes. As the embedded photochromes isomerize, the band corresponding to the π–π* transition (at 357 nm) decreases and the band attributed to the n–π* transition (centered at 450 nm) increases, in agreement with the large amount of *Z*-configured azobenzenes in the backbone. In addition, shrinkage of the **P1** rods is readily determined from the GPC curves (Figure 2b). By virtue of the large twist angles (Φ) UV irradiation leads to a *Z*-rich PSS with a significantly increased retention volume, corresponding to a change of hydrodynamic volume $\Delta V_h = -75\%$, (based on the GPC data).[29]

Static and dynamic light-scattering (SLS/DLS) measurements were performed to measure the accurate dimensions and conformations of **P1** in the two states.[28] At concentrations of approximately 1 g L^{-1} in THF, both the radius of gyration (R_g) and the hydrodynamic radius (R_h) of **P1** decrease upon UV light irradiation, from $R_h = 10$ nm for 100% *E*-**P1** to $R_h = 5.3$ nm for 86% *Z*-**P1**. This change corresponds to a significant drop of the hydrodynamic volume ($\Delta V_h = -72\%$, in good agreement with the change determined by GPC), as illustrated by the increase of the apparent diffusion coefficient (D_{app}, see Figure 2c). Light-scattering data additionally allow the change in shape to be determined, by calculating the so-called ρ ratio.[30] The ρ ratio decreases from 2.3–2.9 (for a rod-like molecule of this size—length $l > 40$ nm, diameter $D = 2$ nm—the ρ-ratio should be > 2) to 1.5–1.9 (for random coil structures, $\rho = 1.505$).[31] Therefore, shrinkage of **P1** is accompanied by a conformational rod→coil transition, as a consequence of the *E*→*Z* isomerization of the embedded azobenzenes. Moreover, the process was found
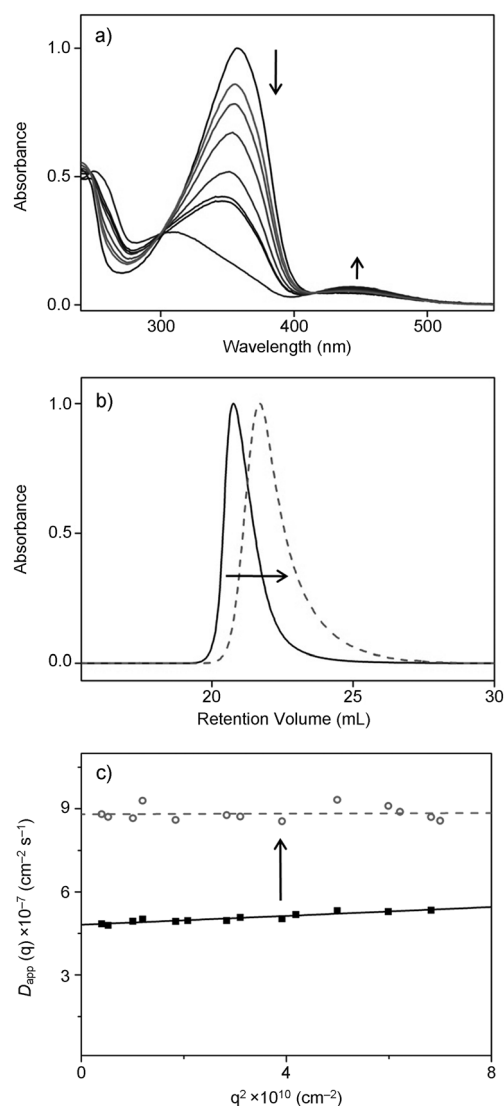

Figure 2. Monitoring **P1** shrinking upon UV irradiation ($\lambda = 357$ nm). a) Time evolution of the UV/Vis absorption spectra of a solution of **P1** in CH$_2$Cl$_2$ until the PSS was reached (in ca. 45 s), b) GPC curves of **P1** in the extended all-*E* (before irradiation, solid line) and compressed *Z*-rich state (after irradiation, broken line) in THF, and c) angular dependence of the apparent diffusion coefficient (D_{app}) in THF (0.7 g L^{-1}) before (filled squares/solid line) and after (open circles/dashed line) irradiation. Arrows indicate changes on UV irradiation.

to be reversible (as shown by UV/Vis absorption spectroscopy, ^{1}H NMR spectroscopy, GPC, and light scattering measurements), that is, irradiation with visible light ($\lambda > 400$ nm)[28] triggers reverse *Z*→*E* isomerizations leading to the recovery of the rod-like geometry.[32]

The possibility to exploit the rod→coil transition in an ensemble of molecules was further examined by synthesizing a polymer homologue of **P1**. It is anticipated that *Z*-rich polymers will display a diminished ability to stack, when compared to all-*E* rigid rods, owing to the kinked configuration of *Z*-azobenzenes. A variation in the stacking propensity should enable the elaboration of photoswitchable assemblies. Similar to polymer **P1**, PPP derivative **P2** (see
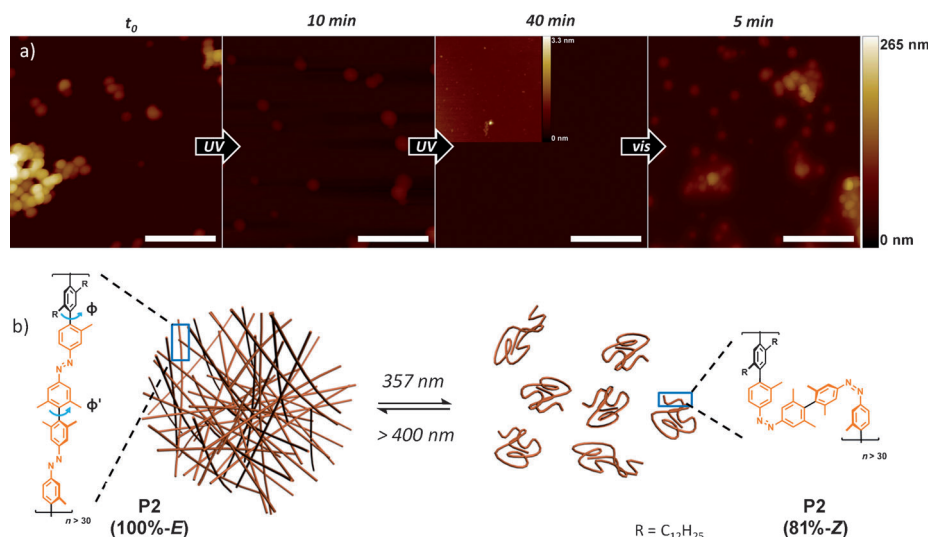
Figure 3. Light induced reversible disruption of molecular aggregates of **P2** (R = C$_{12}$H$_{25}$). a) Selected snapshots of the disruption process (SFM), scale bar: 1 μm. The inset (*t* = 40 min) shows a z-expansion (z-scale: 3.3 nm) of the surface, emphasizing the absence of aggregates after UV-light irradiation. The aggregates were spin-coated on mica from a 1 g L^{-1} solution of **P2** in THF. b) Polymer **P2** contains a few solubilizing groups and therefore aggregates in the extended (100%-*E*) state. In the compressed (81%-*Z*) state, the intermolecular aggregates are disrupted.

Figure 3) features large twist angles (Φ,Φ')[33] leading to a *Z*-rich PSS with a 81% overall *Z* content, as determined by ^{1}H NMR spectroscopy (see Supporting Information, Figure S3). However, **P2** is functionalized with only two dodecyl chains per 2.4 nm long repeat unit (vs. two dodecyl chains per 1.4 nm long repeat unit in **P1**). As a result, all-*E* **P2** has a slightly reduced solubility and is consequently able to form aggregates in apolar solvents.[34] The sample studied here (for synthesis and characterization, see the supporting information) displays a molecular weight of $M_{n} \approx 56\,000$ g mol^{-1} [27] (theoretically corresponding to 66 repeat units), with a polydispersity index of 1.7. Light scattering measurements indicate that clear solutions of **P2** in THF (ca. 1 g L^{-1}) contain nano-sized spherical ($\rho \approx 1$) aggregates, with hydrodynamic radii of $R_{h} \approx 45$ nm.[28] A visualization of the spherical aggregates on mica surfaces by scanning force microscopy (SFM) is shown in Figure 3a. The distribution of the aggregates is rather narrow, with an average height of 80 nm (see Figure S12 in the Supporting Information).

When solutions of **P2** are exposed to UV light, the rod → coil transition takes place, as indicated by the GPC curves of molecularly dissolved **P2** in THF (see Supporting Information, Figure S1). Remarkably, this conformational transition induces a disruption of the sphere-like aggregates, according to SFM as well as SLS/DLS measurements. Selected SFM snapshots of samples precipitated during a disruption–reaggregation cycle are shown in Figure 3a. Upon ex situ photo-irradiation over 40 min, the dimensions of the sphere-like aggregates continuously decrease from almost 80 nm height (corresponding roughly to the diameter) to a residual approximately 3 nm height (see inset Figure 3a). We did not observe any large deformations of the aggregates which remain rather spherical until complete disruption. The

spheres were reformed within a few minutes upon irradiation with visible light (> 400 nm). Analogous observations were made by light-scattering measurements: Upon UV-light irradiation, the R_{h} decreases from 45 nm for the aggregates to 25 nm for the presumably molecularly dissolved polymer and the ρ-ratio increases from 0.9–1 ($\rho = 0.775$ for monodisperse homogeneous spheres) to 1.2–1.5 (for random coil structures, $\rho = 1.505$).[31] The disruption was additionally observed by monitoring the ^{1}H NMR spectra, where a very broad peak, centered around 6.2 ppm and attributed to the aggregated areas, completely vanishes upon UV-light irradiation (see Figure S4). In the literature, triggered disassembly of sphere-like nano-objects is almost exclusively realized in water using switchable amphiphiles.[35] From this perspective, our **P2** system, which relies on the ability of the polyaromatic rods to stack in one switching state but not the other, is rather unique and should generally be operating in most common non-polar solvents.

In summary, this study shows a unique approach for maximizing the photodeformation of individual molecules, using azobenzene-containing anistropic molecular architectures. Reversible and efficient shrinkage of rod-like polymers, such as **P1**, demonstrated and quantified by SLS/DLS measurements, is accompanied with an unprecedented decrease in hydrodynamic volume. Furthermore, designing multi-azobenzene rods with reduced solubility, such as **P2**, leads to the formation of spherical aggregates in organic solvents, which could reversibly be disrupted by alternating irradiation with UV and visible light. Based on this work, we aim to use the optimized shrinkable polymers for the bottom-up construction of efficient opto-mechanical materials.[14] Furthermore, the transfer of this concept to aqueous solution promises possible applications as "smart" carriers.

[1] S. S. Agasti, A. Chompoosor, C. C. You, P. Ghosh, C. K. Kim, V. M. Rotello, *J. Am. Chem. Soc.* **2009**, *131*, 5728–5729, and references therein.

[2] J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. DeIonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H. R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414–417.

[3] R. Vaia, J. Baur, *Science* **2008**, *319*, 420–421.

[4] a) R. H. Baughman, *Science* **2005**, *308*, 63–65; b) J. D. W. Madden, T. Mirfakhrai, R. H. Baughman, *Mater. Today* **2007**, *10*, 30–38; c) J. D. Madden, *Science* **2007**, *318*, 1094–1097.

[5] For a general Review on self-healing materials, see: a) S. R. White, B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, *Annu. Rev. Mater. Res.* **2010**, *40*, 179–211. For an example of optically healable polymer, see: b) S. J. Rowan, M. B. Burnworth, L. M. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, C. Weder, *Nature* **2011**, *472*, 334–338.

[6] *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**.

[7] For comprehensive accounts on photoswitches, see: a) Special issue: *Photochromism: Memories and Switches* (Ed.: M. Irie), *Chem. Rev.* **2000**, *100*, 1683; b) *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**. For the utilization of photoswitches in material sciences, see: c) M. M. Russew, S. Hecht, *Adv. Mater.* **2010**, *22*, 3348–3360, and references therein.

[8] V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samori, M. Mayor, M. A. Rampi, *Angew. Chem.* **2008**, *120*, 3455–3457; *Angew. Chem. Int. Ed.* **2008**, *47*, 3407–3409.

[9] a) M. V. Peters, R. S. Stoll, A. Kühn, S. Hecht, *Angew. Chem.* **2008**, *120*, 6056–6060; *Angew. Chem. Int. Ed.* **2008**, *47*, 5968–5972; b) R. S. Stoll, M. V. Peters, A. Kühn, S. Heiles, R. Goddard, M. Bühl, C. M. Thiele, S. Hecht, *J. Am. Chem. Soc.* **2009**, *131*, 357–367.

[10] A. Sgarbossa, G. Checcucci, F. Lenci, *Photochem. Photobiol. Sci.* **2002**, *1*, 459–467.

[11] Absorbed photons isomerize the chromophore of the light-sensitive pigment rhodopsin, leading to a series of structural changes in the G-protein scaffold. This constitutes the first events of the visual perception, see: T. Ebrey, Y. Koutalos, *Prog. Retinal Eye Res.* **2001**, *20*, 49–94, and references therein.

[12] For an overview on the so-called Bacteriorhodopsin, see: a) H. Luecke, B. Schobert, H. T. Richter, J. P. Cartailler, J. K. Lanyi, *Science* **1999**, *286*, 255–260; b) W. Kühlbrandt, *Nature* **2000**, *406*, 569–570.

[13] Encapsulation of guests into a so-called dendritic box was initially reported by Meijer and co-workers, see: a) J. F. G. A. Jansen, E. M. M. Debrabandervandenberg, E. W. Meijer, *Science* **1994**, *266*, 1226–1229. Guest encapsulation into azobenzene-containing dendritic box was pioneered by Balzani, Vögtle, and co-workers, see: b) V. Balzani, A. Archut, G. C. Azzellini, L. De Cola, F. Vogtle, *J. Am. Chem. Soc.* **1998**, *120*, 12187–12191, and reported more recently by Müllen and co-workers, see: c) T. T. Nguyen, D. Turp, D. Wang, B. Nolscher, F. Laquai, K. Müllen, *J. Am. Chem. Soc.* **2011**, *133*, 11194–11204.

[14] For an outstanding example at the single-molecule level, see: a) T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, H. E. Gaub, *Science* **2002**, *296*, 1103–1106. For a selected example of opto-mechanical crystals, see: b) M. Irie, M. Morimoto, *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178. For selected examples of opto-mechanical liquid crystals and liquid crystalline elastomers, see: c) Y. L. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145–145; d) K. D. Harris, R. Cuypers, P. Scheibe, C. L. van Oosten, C. W. M. Bastiaansen, J. Lub, D. J. Broer, *J. Mater. Chem.* **2005**, *15*, 5043–5048. For a selected example of opto-mechanical free-standing films, see e) N. Hosono, T. Kajitani, T. Fukushima, K. Ito, S. Sasaki, M. Takata, T. Aida, *Science* **2010**, *330*, 808–811.

[15] D. Bléger, Z. Yu, S. Hecht, *Chem. Commun.* **2011**, *47*, 12260–12266.

[16] For comprehensive Reviews on azobenzenes, see: a) *Organic Photochromes* (Ed.: A. V. El'tsov, Consultants Bureau, New York, **1990**, chap. 3; b) *Smart Light-Responsive Materials* (Eds.:

Y. Zhao, T. Ikeda, Wiley, Hoboken, **2009**, chap. 1; c) *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**, chap. 4.

[17] D. L. Jiang, T. Aida, *Nature* **1997**, *388*, 454–456.

[18] a) D. M. Junge, D. V. McGrath, *Chem. Commun.* **1997**, 857–858; b) D. M. Junge, D. V. McGrath, *J. Am. Chem. Soc.* **1999**, *121*, 4912–4913; c) S. Li, D. V. McGrath, *J. Am. Chem. Soc.* **2000**, *122*, 6795–6796; d) L. X. Liao, F. Stellacci, D. V. McGrath, *J. Am. Chem. Soc.* **2004**, *126*, 2181–2185.

[19] D. Grebel-Koehler, D. J. Liu, S. De Feyter, V. Enkelmann, T. Weil, C. Engels, C. Samyn, K. Müllen, F. C. De Schryver, *Macromolecules* **2003**, *36*, 578–590.

[20] F. Cisnetti, R. Ballardini, A. Credi, M. T. Gandolfi, S. Masiero, F. Negri, S. Pieraccini, G. P. Spada, *Chem. Eur. J.* **2004**, *10*, 2011–2021.

[21] D. Bléger, J. Dokić, M. Peters, L. Grubert, P. Saalfrank, S. Hecht, *J. Phys. Chem. B* **2011**, *115*, 9930–9940.

[22] $\Phi = 89.9°$ according to DFT calculations performed on the corresponding bisazobenzenes, see Ref. [21].

[23] As determined by ^{1}H NMR spectroscopy, see Figure S2 in the Supporting Information.

[24] For comparison, a PSS with 33% Z-content was reported in a) Z. Yu, S. Hecht, *Angew. Chem.* **2011**, *123*, 1678–1681; *Angew. Chem. Int. Ed.* **2011**, *50*, 1640–1643; 55% Z-content in b) T. Masuda, A. Izumi, M. Teraguchi, R. Nomura, *Macromolecules* **2000**, *33*, 5347–5352; 62% Z-content in Ref. [13c].

[25] J. Sakamoto, M. Rehahn, G. Wegner, A. D. Schlüter, *Macromol. Rapid Commun.* **2009**, *30*, 653–687.

[26] T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696.

[27] 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. [25].

[28] See Supporting Information for details.

[29] Using the relation $V = 0.4\,KM_n^{a+1}$ where $K = 0.01363$ and $a = 0.7$ are the Mark–Houwink parameters for PS in THF, see: H. L. Wagner, *J. Phys. Chem. Ref. Data* **1985**, *14*, 1101–1106.

[30] It is defined as $\rho = R_g/R_h$, see: *Light scattering from polymer solutions and nanoparticle dispersions* (Ed.: W. Schärtl), Springer, Heidelberg, **2007**.

[31] Deviation of ρ from ideal values is due to the polydisperisty of the sample.

[32] Note that after irradiation with visible light, a small amount of azobenzene moieties remain in the Z-form, as typically encountered for PSSs; however, 100% E-**P1** was recovered by subsequent heating.

[33] $\Phi = 89.9°$ and $\Phi' = 90.0°$, according to DFT calculations performed on the corresponding bisazobenzenes, see Ref. [21].

[34] For the aggregation behavior of conjugated polymers, see: a) T. Q. Nguyen, V. Doan, B. J. Schwartz, *J. Chem. Phys.* **1999**, *110*, 4068–4078; b) J. H. Chen, Y. C. Li, C. Y. Chen, Y. X. Chang, P. Y. Chuang, H. L. Chen, C. S. Hsu, V. A. Ivanov, P. G. Khalatur, S. A. Chen, *Langmuir* **2009**, *25*, 4668–4677, and references therein.

[35] For selected examples on photoresponsive micelles, see: a) H. I. Lee, K. Matyjaszewski, W. Wu, J. K. Oh, L. Mueller, G. Sherwood, L. Peteanu, T. Kowalewski, *Angew. Chem.* **2007**, *119*, 2505–2509; *Angew. Chem. Int. Ed.* **2007**, *46*, 2453–2457; b) X. Zhang, Y. P. Wang, P. Han, H. P. Xu, Z. Q. Wang, A. V. Kabanov, *Langmuir* **2010**, *26*, 709–715; c) R. Haag, C. Kordel, C. S. Popeney, *Chem. Commun.* **2011**, *47*, 6584–6586; d) Ref. [16b], chap. 6. For the light-induced aggregation and micromanipulation of vesicles, see: e) G. C. Dol, K. Tsuda, J. W. Weener, M. J. Bartels, T. Asavei, T. Gensch, J. Hofkens, L. Latterini, A. P. H. J. Schenning, B. W. Meijer, F. C. De Schryver, *Angew. Chem.* **2001**, *113*, 1760–1764; *Angew. Chem. Int. Ed.*

2001, *40*, 1710–1714. For a recent example on the light-induced disassembly of self-assembled vesicle-capped nanotubes, see: f) A. C. Coleman, J. M. Beierle, M. C. A. Stuart, B. Macia, G. Caroli, J. T. Mika, D. J. van Dijken, J. Chen, W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* **2011**, *6*, 547–552. For pH responsive micelles, see: g) R. Nguyen, N. Giuseppone, L. Allouche, E. Buhler, *Angew. Chem.* **2009**, *121*, 1113–1116; *Angew. Chem. Int. Ed.* **2009**, *48*, 1093–1096; h) J. H. van Esch, C. B. Minkenberg, L. Florusse, R. Eelkema, G. J. M. Koper, *J. Am. Chem. Soc.* **2009**, *131*, 11274–11275. For micelles responsive to CO_2/argon bubbling cycles, see: i) P. G. Jessop, Y. X. Liu, M. Cunningham, C. A. Eckert, C. L. Liotta, *Science* **2006**, *313*, 958–960.