

Influence of Linkage Chemistry on Folding, Self-Assembly, and Photoresponse of Amphiphilic Azobenzene Main Chain Polymers

This manuscript is dedicated to Prof. Jean Fréchet on the occasion of his 70th birthday and to his extraordinary contributions to polymer science.

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ABSTRACT: Two types of amphiphilic polymers composed of azobenzene repeat units in the main chain connected either via ethynylene (acetylene) or butadiynylene (diacetylene) linkages and carrying oligo(ethylene glycol) side chains were reported. Synthesis was accomplished by polycondensation involving Sonogashira–Hagihara cross coupling and Glaser coupling, respectively. Solvent titration experiments revealed that both polymers fold into stable helices in a polar environment. While the ethynylene-bridged polymer resembled the behavior of its oligomeric counterparts, introduction of the extended diacetylene unit strengthened π,π -stacking interactions in case of the

butadiynylene-bridged polymer leading to a pronounced aggregation tendency and suppressing photoisomerization in the folded state. Our study demonstrates the importance of backbone connectivity to balance intra- and intermolecular forces for the successful design of photoresponsive polymers. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 313–318

KEYWORDS: azobenzene; foldamers; photochromism; self-assembly; π,π -stacking

INTRODUCTION In recent years increasing research efforts have been devoted toward developing new photoresponsive soft materials,¹ which have great promise ranging from electronics, for example, in data storage, over energy-related applications, for example, in photovoltaics, all the way to medicine, for example, in photodynamic therapy. In such systems light is absorbed and triggers either an irreversible or reversible change of the materials' physicochemical properties. For this reason, synthetic chemists have been introducing photosensitive units—here we focus on (reversible) photochromic moieties^{2–4}—into larger macromolecular and supramolecular systems.^{1,5} With regard to photoswitchable macromolecules, there have been various approaches followed to maximize the light-induced property changes. One promising approach exploits cooperativity as a means to amplify the incoming light signal either in an intramolecular fashion via cooperative helical folding or in an intermolecular fashion by cooperative aggregation.⁶

Focusing on the first concept and trying to realize large conformational changes within individual macromolecules,⁶ we have been designing^{7,8} and improving^{9–12} photoswitchable foldamers. In our design, we have been connecting photochromic azobenzene repeat units via linear ethynylene bridges attached in the

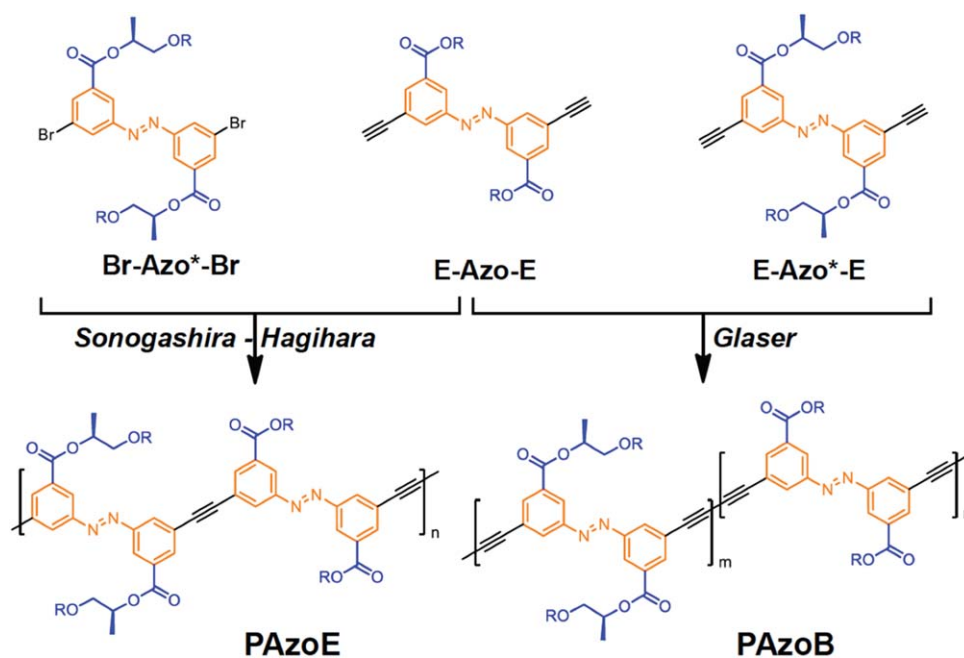
meta-positions of each phenyl ring of the azobenzenes. Attachment of polar oligo(ethylene glycol) side chains to this hydrophobic backbone leads to an amphiphilic macromolecule, which in a good solvent for both compartments adopts a random coil structure consisting of *transoid* (“zig-zag”) and *cisoid* (“zig-zig”) local conformations while in a polar solvent it folds into a helix with local *cisoid* conformations.¹³ Introduction of the azobenzene moieties provides an additional means to reversibly fold and unfold the backbone in one and the same polar solvent. In several studies using well-defined oligomers we were able to establish structure–property relationships (or more precisely: sequence–folding–switch relationships), deciphering the effect of chain length,⁹ number, and relative orientation of azobenzene moieties in the backbone.¹¹ In some of our more advanced foldamers, we were able to couple switching events in a cooperative fashion¹⁰ and to localize the excitation by incorporating an energy gradient.¹²

Based on these studies of well-defined oligomers we were interested in extending the established concept to elongated polymeric systems. Such systems could either be derived by covalent polymerization to yield helical polymers¹⁴ or alternatively by supramolecular polymerization¹⁵ to provide self-assembled helical aggregates.¹⁶ Here we report the design

Additional Supporting Information may be found in the online version of this article.

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SCHEME 1 Investigated polymers **PAzoE** and **PAzoB** and their synthesis via polycondensation ($R = -(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$; azobenzene photochromes and ethynylene/butadiynylene linkages are shown in *orange* and *black*, respectively, while (a)chiral oligo(ethylene glycol) side chains are depicted in *blue*).

and synthesis as well as the folding and photoresponsive behavior of two types of azobenzene main chain polymers (Scheme 1). One of them, that is, poly(azobenzene ethynylene), **PAzoE**, is a mere extension of already investigated oligomers based on an acetylene bridge,⁹ while the other, that is, poly(azobenzene butadiynylene), **PAzoB**, includes diacetylene bridges. The latter are expected to enhance the π,π -stacking interactions as known from aggregation of topologically related macrocycles.¹⁷ Furthermore diacetylenes could potentially allow for intramolecular topochemical crosslinking¹⁸ to covalently lock the helical structures.¹⁹

EXPERIMENTAL

General Methods and Materials

The three relevant monomers, that is, azobenzene dibromide with chiral side chains (**Br-Azo*-Br**) as well as twofold ethynyl-terminated azobenzene either with achiral (**E-Azo-E**) or chiral side chains (**E-Azo*-E**), were prepared as described by us previously.⁷ Chemicals and solvents were used as received from commercial suppliers. Dry solvents were obtained from an Innovative Technologies solvent purification system. ¹H-NMR (¹H-nuclear magnetic resonance) spectra were recorded on a 400 MHz Bruker AV 400 spectrometer at 27 °C using residual protonated solvent signals as internal standard [$\delta(\text{CHCl}_3) = 7.26$ ppm]. Gel permeation chromatography (GPC) measurements were performed on a WGE Dr. Bures system equipped with both ultraviolet (UV) (300 nm) and refractive index (RI) detection using tetrahydrofuran (THF) as the eluent on SDV Linear M 8×300 mm 5- μm columns using a flow rate of 1 mL/min at 30 °C. Calibration was done with several narrow polydispersity polystyrene samples

and 2,4-di-*tert*-butyl-4-methoxyphenol was employed as an internal standard in the samples.

Optical Spectroscopy

UV/vis absorption spectra were recorded in the given solvents of spectroscopic grade using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer, equipped with Peltier thermostated cell holders ($\Delta T = \pm 0.05$ °C). Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C. Circular dichroism (CD) spectra were recorded on a JASCO 700 spectrometer using quartz cuvettes of 1 cm path length, equipped with Peltier thermostated cell holders, at 25 ± 0.05 °C. Fresh samples of polymer **PAzoB** for CD spectroscopy in acetonitrile were prepared from a chloroform stock solution, in which no aggregates are present.

Irradiation Experiments

Irradiation was performed using a LOT-Oriel 1000 W (set to 900 W during course of irradiation) medium pressure Xe lamp, equipped with either an interference filter providing $\lambda_{\text{irr}} = 357$ nm at 35% *T* and FWHM = 42 nm (to induce *E* → *Z* photoisomerization) or a cut-off filter giving $\lambda_{\text{irr}} > 405$ nm at *T* = 65% (to induce *Z* → *E* photoisomerization).

Synthesis

Poly(azobenzene ethynylene), **PAzoE**

In a dried flask flushed with argon, a mixture of **Br-Azo*-Br** (210 mg, 0.25 mmol), **E-Azo-E** (153 mg, 0.25 mmol), Pd(PPh₃)₄ (22 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol), and PPh₃ (11 mg, 0.04 mmol) was added to a mixture of diisopropylamine (5 mL) and toluene (5 mL). After stirring for 20 h at 80 °C, the reaction mixture was concentrated *in vacuo*, the crude residue was redissolved in a minimum

amount of methylene chloride, and precipitated in excess petroleum ether to remove the unreacted monomers and short oligomers. The desired polymer was obtained in 50% yield as an orange powder. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 8.64 (broad s, 4H, Ar-H), 8.29–8.42 (m, 8H, Ar-H), 5.45 (m, 2H, OCH), 4.58 (broad s, 4H, OCH_2), 3.91 (broad s, 4H, OCH_2), 3.6–3.8 (m, 36H, CH_2), 3.55 (broad s, 8H, CH_2), 3.35 (broads, 12H, CH_3), 1.43 (broad s, 6H, CCH_3). GPC (THF, 30 °C): $M_w = 12,500$; PDI (M_w/M_n) = 1.9.

Poly(azobenzene butadiynylene), PAzoB

In a dried flask equipped with a guard tube filled with CaCl_2 , a mixture of **E-Azo*-E** (210 mg, 0.25 mmol), **E-Azo-E** (153 mg, 0.25 mmol), and CuBr (35 mg, 0.2 mmol) was added together to dry methylene chloride (10 mL). After stirring for 21 h at room temperature, the reaction mixture was concentrated *in vacuo*, the crude residue was redissolved in a minimum amount of methylene chloride, and precipitated in excess methanol to remove the unreacted monomers and short oligomers. The desired polymer was obtained in 70% yield as an orange solid. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 8.58–8.68 (m, 4H, Ar-H), 8.26–8.46 (m, 8H, Ar-H), 5.38–5.51 (m, 2H, OCH), 4.58 (broad s, 4H, OCH_2), 3.92 (broad s, 4H, OCH_2), 3.58–3.82 (m, 36H, CH_2), 3.57 (broad s, 8H, CH_2), 3.35 (broads, 12H, CH_3), 1.45 (broad s, 6H, CCH_3). GPC (THF, 30 °C): $M_w = 12,000$; PDI (M_w/M_n) = 1.7.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Both target polymers were prepared using mild and functional group tolerant transition metal-catalyzed polycondensation reactions. On the one hand, palladium-catalyzed Sonogashira-Hagihara cross coupling²⁰ in an $A_2 + B_2$ format provided **PAzoE** from dibromide **Br-Azo*-Br** and bisacetylene **E-Azo-E** (Scheme 1, left). On the other hand, copper-catalyzed Glaser coupling,²¹ employing both a chiral and an achiral bisacetylene monomer in equimolar ratio, yielded **PAzoB** (Scheme 1, right). Note that while the first route gives a strictly alternating copolymer in which a chiral azobenzene repeat unit is always attached to an achiral one, the second route leads to a random copolymer with regard to placement of the chiral side chains. The attachment of these polar oligo(ethylene glycol) side chains to all monomers imparts to the resulting polymers an amphiphilicity, which drives helical folding in polar solvents. Furthermore, introduction of chirality in (at least some of) these oligo(ethylene glycol) side chains is used to bias the twist sense of the helical conformation thereby enabling the use of CD spectroscopy to monitor conformational transitions.²² The structural composition of both polymers was confirmed by $^1\text{H-NMR}$ spectroscopy (Supporting Information Figs. S1 and S2²³) while their molecular weights and weight distribution was determined by GPC calibrated with polystyrene standards in THF, a denaturing solvent in which the polymers are supposed to adopt a random coil structure (Supporting Information Figs. S3 and S4^{23,24}).

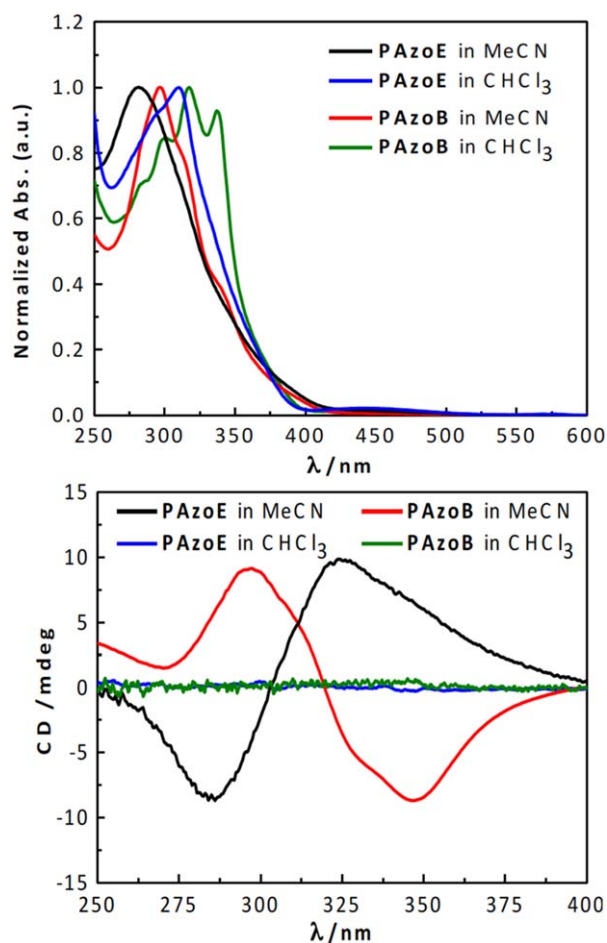


FIGURE 1 UV/vis absorption (top) and CD (bottom) spectra of polymers **PAzoE** (2.2 $\mu\text{g/mL}$) and **PAzoB** (2.5 $\mu\text{g/mL}$) in acetonitrile and chloroform at 25 °C.

Folding Behavior of Polymers

To investigate the backbone conformation of the prepared polymers, UV/vis absorption as well as CD spectroscopy were employed to monitor the diagnostic change in vibronic transitions of the *transoid* versus *cisoid* conformation and the Cotton effect related to a twist sense bias caused by chirality transfer from the enantiomerically pure side chains, respectively.¹³

In the case of polymer **PAzoE**, a standard solvent denaturation experiment involving a change from neat acetonitrile solution to a neat chloroform solution gave rise to a bathochromic shift of its absorption maximum from 290 to 310 nm due to a transition from predominantly *cisoid* to mainly *transoid* local conformations. This spectral change is indicating that **PAzoE** adopts a helical conformation in the polar acetonitrile while existing as a random coil in the less polar chloroform (Fig. 1, top, black and blue lines).²⁵ In acetonitrile polymer **PAzoB** displays an absorption spectrum reminiscent of **PAzoE** in the helical conformation and only with a slight bathochromic shift (Fig. 1, top, red line), presumably due to the extended π -conjugation of each chromophore repeat unit. On the contrary, in chloroform the absorption spectrum of **PAzoE** is comprised of multiple vibronic

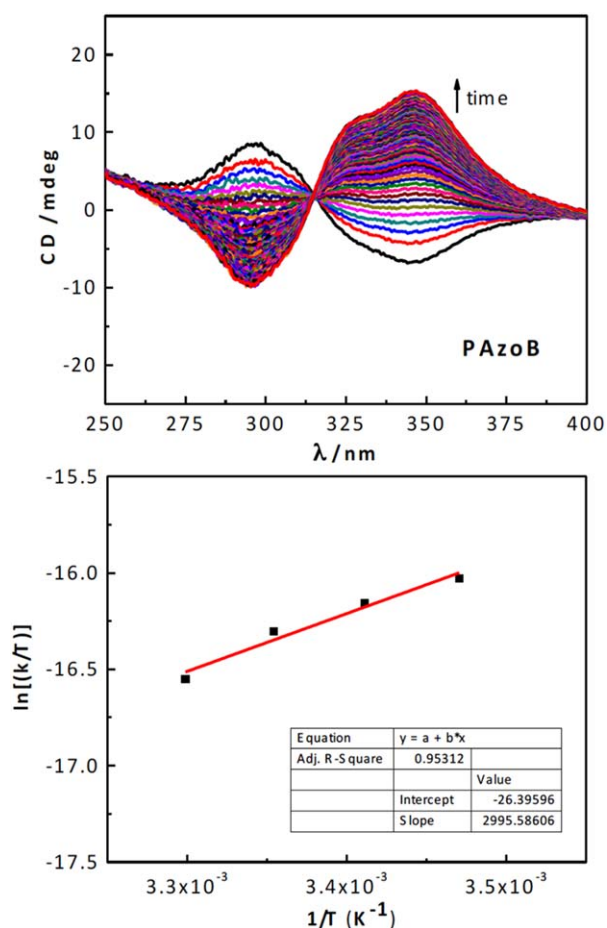


FIGURE 2 Temporal evolution of CD spectra of polymer **PAzoB** (2.5 $\mu\text{g/mL}$) in acetonitrile at 25 $^{\circ}\text{C}$ (**top**) and the Eyring plot resulting from kinetic measurements of the self-assembly of polymer **PAzoB** at different temperatures in acetonitrile (**bottom**).

transitions, which correspond to the conventional *transoid*, that is, zig-zag, conformation for a poly(*meta*-phenylene butadiynylene) backbone,²⁶ once again indicating a random coil structure in the less polar solvent (Fig. 1, top, green).

The results from absorption measurements were complemented by CD spectroscopy. In acetonitrile, the observation of Cotton effects for both **PAzoE** and **PAzoB** supports their folding into helical conformations in the polar solvents. Interestingly, the sign of the Cotton effect is the opposite for both polymers, suggesting that **PAzoE** prefers to adopt a right-handed helical conformation (as its oligomers⁹), while **PAzoB** exists predominantly as left-handed helix in polar solution (Fig. 1, bottom, black and red lines). Furthermore, the CD spectrum of **PAzoB** reproduces some of the features of the absorption spectrum, namely the bathochromic shift as well as the two slight shoulders. Upon changing the solvent to chloroform, the CD signals of both polymers vanish completely, implying the loss of the helical conformations and population of random coil structures (Fig. 1, bottom, blue and green lines).

Helicity Change of PAzoB Polymer

As mentioned earlier, the incorporation of the extended butadiyne linkages into the polymer backbone of **PAzoB** should lead to a decrease of the electron density as compared with **PAzoE** that should further strengthen the already abundant π,π -stacking interactions within the helix backbone but also between helices. Based on this assumption, CD spectroscopy was used to investigate the existence of such latter intermolecular interactions in the folding-promoting solvent acetonitrile. In contrast to the conventional static Cotton effect for polymer **PAzoE**, the initially negative Cotton effect for polymer **PAzoB** converted to a positive one in the dark over time (Fig. 2, top).

This observed helicity change indicates the inversion of the twist sense bias of the helical structures. As the CD spectra of the two oppositely handed forms are not exact mirror images and an initial formation of a meta-stable helix, which would then convert into its exact oppositely twisted counterpart, appears implausible, we suppose that temporal CD signal changes in the case of **PAzoB** are the result of aggregation. In this process, which has been observed in related oligomers²⁷ as well as supramolecular polymer systems,^{15,16} individual left-handed **PAzoB** helices assemble into right-handed aggregates. Interestingly, the formed aggregates seem to exhibit considerable stability since comparison of the fresh and aged samples of **PAzoB** in acetonitrile by means of GPC showed a clear decrease in retention time/elution volume (Supporting Information Fig. S5²³), pointing to a significantly increased hydrodynamic volume even in the less polar eluent THF. Unfortunately, more detailed dynamic light scattering measurements were not successful due to the aggregates' low solubility in polar solvents.

To gain further insight, concentration-dependent CD experiments were carried out and revealed that in acetonitrile the helicity inversion of **PAzoB** occurs over a large concentration range, that is, from 0.45 to 5.0 $\mu\text{g/mL}$ (Supporting Information Figs. S6 and S7²³). These measurements show that **PAzoB** aggregates even in relatively diluted conditions thereby pointing to a rather low critical aggregation concentration below 0.45 $\mu\text{g/mL}$.²⁸ Furthermore, the measurements support the aggregation hypothesis as the population of the initial left-handed isolated helical conformation is much less pronounced at higher concentration, which favors aggregation. Analysis of the observed kinetics provided an estimate of the rate constants of the aggregation process, which increase with increasing concentration until reaching a constant value at a concentration of about 1.7 $\mu\text{g/mL}$ (Supporting Information Figs. S6 and S7²³).

Finally, temperature-dependent experiments (Supporting Information Fig. S8²³) were used to derive the respective activation parameters for the self-assembly of **PAzoB** (Fig. 2, bottom) using Eyring's equation.²⁹ While both the enthalpy of activation ΔH^{\ddagger} (-5.95 kcal/mol) as well as the entropy of activation ΔS^{\ddagger} (-99.7 cal/mol) are negative, entropy contributes mainly to the activation energy ΔG^{\ddagger} (28.8 kcal/mol) for self-assembly. This finding illustrates the entropic penalty

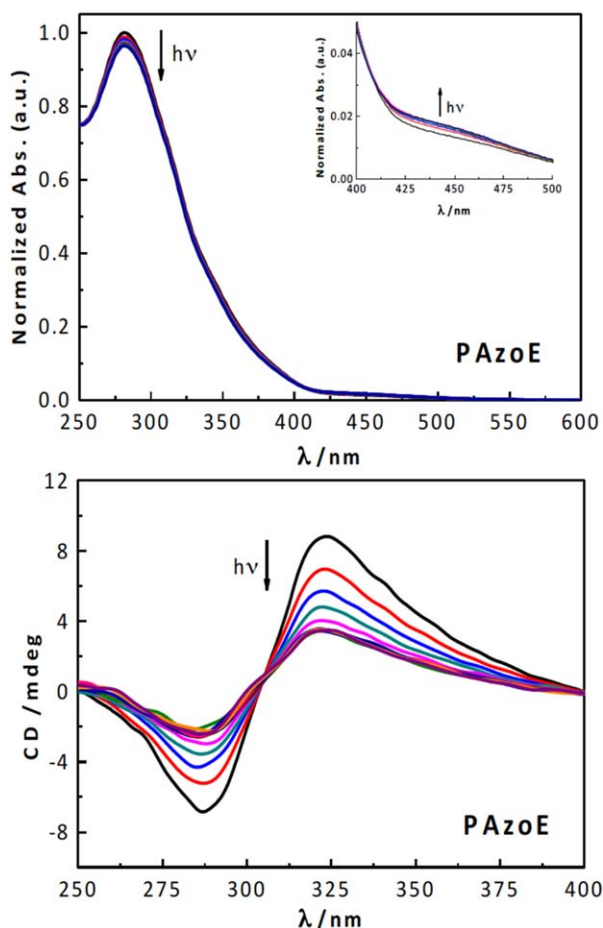


FIGURE 3 UV/vis absorption (top) and CD (bottom) spectra of $E \rightarrow Z$ photoisomerization of polymer **PAzoE** (2.2 $\mu\text{g/mL}$) during the course of irradiation at $\lambda_{\text{irr}} = 358$ nm in acetonitrile at 25 $^{\circ}\text{C}$. The insets in the UV/vis spectra show a magnification of the increasing $n \rightarrow \pi^*$ absorption band of the azobenzene units.

imparted by supramolecular—and in fact most—polymerization processes.^{15,30}

Photoresponsive Behavior of Polymers

The photoresponsive behavior of the polymers was studied by monitoring both UV/vis and CD spectra upon irradiation with 358 nm UV-light to induce $E \rightarrow Z$ photoisomerization of the azobenzene moieties. In the case of **PAzoE** in the folding promoting solvent acetonitrile (as well as in denaturing CHCl_3) the expected $E \rightarrow Z$ photoisomerization takes place as evident by the characteristic decrease of the $\pi \rightarrow \pi^*$ band at 290 nm accompanied with an increasing $n \rightarrow \pi^*$ transition at 450 nm (Fig. 3, top). Concomitantly, the intensity of the Cotton effect in the CD spectra of **PAzoE** decreased by approximately 60% (Fig. 3, bottom), illustrating that photoconversion to Z -configured azobenzene repeat units leads to (partial) unfolding.

On the contrary, when irradiating **PAzoB** in acetonitrile no change in the optical spectra was detected. This observed

complete inhibition of photoisomerization could potentially be attributed to either conceivable photoinduced topochemical crosslinking of stacked diacetylene units,¹⁸ deactivation of the excited azobenzene photochromes by energy transfer or strong π, π -stacking interactions between the E -configured azobenzene moieties precluding rotation/inversion to the Z -isomer. However, topochemical crosslinking of the diacetylene units was ruled out as no residual Cotton effect appeared in the CD spectra for **PAzoB** after irradiation in acetonitrile followed by transfer into chloroform (Supporting Information Fig. S9²³). This is most likely due to the unfavorable relative orientation of the diacetylene fragments.¹⁸ Energy transfer from the photoexcited azobenzene units to the diphenylbutadiyne units is most likely taking place yet depending on the distance and relative orientation of the donor and acceptor moieties. In an important control experiment, formation of 45% Z -configured azobenzene repeat units within the **PAzoB** backbone was found upon irradiation in chloroform (Supporting Information Fig. S10²³), suggesting that the disappearance of the strong π, π -stacking interactions in the unfolded random coil structure allows for the photoisomerization events to occur. Therefore, it is reasonable to assume that the strong π, π -stacking interactions within the backbone of **PAzoB**—also enabling more efficient deactivation via energy transfer—are responsible for the polymer's photostatic behavior in acetonitrile.³¹ Note that the phenomenon of the helicity inversion of polymer **PAzoB** discussed earlier is not affected upon exposure to UV-light.

CONCLUSIONS

In summary, we have designed and synthesized two helical polymers composed of azobenzene moieties connected via either ethynylene or butadiynylene units in the main chain. Relying on their similar geometries (due to the *meta*-connectivity) and non-covalent interactions, both polymers form stable helical conformations in polar media while adopting random coil structures in apolar environments. However, the difference in the linkage chemistry is reflected in the polymers' different self-assembly as well as photochemical behavior. On the one hand, **PAzoE** displays no noticeable aggregation at low concentrations, typically employed in absorption and CD spectroscopy, and undergoes photoinduced $E \rightarrow Z$ isomerization, similar to its shorter oligomeric counterparts.⁹ On the other hand, **PAzoB** exhibits a strong aggregation tendency (even at rather low concentrations), leading to supramolecular aggregates with opposite handedness as compared with individual helices. Furthermore, **PAzoB** does not undergo $E \rightarrow Z$ photoisomerization in the folded (aggregated) state. We explain these two distinguishing features of **PAzoB** by the strongly enhanced π, π -stacking interactions due to the introduction of the additional electron-withdrawing acetylene units. Our present study reveals the critical role of the linkage chemistry in the design of helical architectures with specific optical properties, potentially useful for the generation of smart photoresponsive materials.^{1,5,6,32}

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