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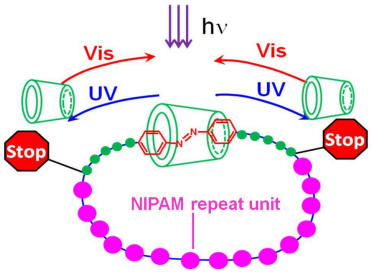

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ARTICLE

Synthesis of a poly(*N*-isopropylacrylamide) charm bracelet decorated with a photomobile α-cyclodextrin charm

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Cyclic poly(N-isopropylacrylamide) with an azobenzene inserted in the main chain (azo-c-PNIPAM, M_n 8,800 g/mol) was synthesized by 'click' ring closure of an α-azobenzene, ω-azido poly(N-isopropylacrylamide) obtained by reverse addition fragmentation transfer (RAFT) polymerization of NIPAM with an azobenzenyl-substituted chain transfer agent. Taking advantage of the azobenzene/α-cyclodextrin inclusion complex and conducting the ring closure in the presence of excess α-cyclodextrin (α-CD), we prepared an azo-c-PNIPAM with an interlocked α-CD of topology reminiscent of a single-charm bracelet, The polymers were characterized by gel permeation chromatography, ^{1}H NMR spectroscopy, UV-visible absorption spectroscopy, and FTIR spectroscopy. 2D NOESY spectroscopy confirmed that the azobenzene group of the ring was inserted into the α-CD cavity. Trans to cis isomerization of the azobenzene group was induced by irradiation at 365 nm. The cis-azobenzene moiety was expelled from the α-CD cavity, as indicated by a hypsochromic shift of the π-π* electronic transition, corroborated by circular induced dichroism (CD) spectroscopy, ^{1}H NMR and 2D NOESY spectroscopy. The reverse cis to trans isomerization induced by irradiation at 440 nm triggered the re-insertion of the azobenzene group in the α-CD cavity.

Introduction

The synthesis of cyclic polymers and the impact of the cyclic topology on the properties of polymer solutions and films have generated fascinating research ideas in polymer science and technology for many decades. The connection of the two ends of a polymer chain exerts significant conformational restrictions to the chain movement, which affect a variety of macroscopic physical properties.[1-3] For example, compared to their linear precursors, cyclic polymers exhibit lower solution viscosity, smaller hydrodynamic volume, higher glass transition temperature, and higher thermal stability. Furthermore, recent studies have demonstrated that cyclic polymers have longer *in-vivo* circulation half-lives, compared to their linear counterparts, displaying a favorable feature for bio-medical applications.[4] Important advances in this field became possible thanks, on the one hand, to the advent of new polymerization methods, such as ring-expansion metathesis polymerization[5] and controlled radical polymerizations[6, 7] and, on the other hand, to the availability of "click reactions", such as the Huisgen 1,3-dipolar cycloaddition between an alkyne and an azide that allow highly efficient end-to-end ligation of heterotelechelic polymers.[8-10] Cyclic polymers can be tailored to create a variety of architectures, such as cyclic amphiphilic homopolymers,[11] cyclic polymer brushes,[12, 13] cyclic gels,[13, 14] liquid crystalline cyclic polymers,[15] and cyclic block copolymers.[16-20]

There are still challenging areas in the field of cyclic polymers. Mechanically interlocked rings, for instance, remain difficult to prepare[21]. Such structures consist of two or more rings that do not contain any covalent bond between them yet cannot be separated from each other without covalent bond cleavage. In the realm of organic and organometallic chemistry, complex interlocked molecular architectures have been obtained based on a combination of supramolecular chemistry[22-24] and dynamic covalent chemistry.[25, 26] In polymer science, this topology remains poorly represented. An early example was reported by Okada and Harada, who achieved the photocyclization of a dianthracene-capped poly(ethylene glycol) threaded with cyclodextrins (polyrotaxane).[27] More

recently, Grubbs's group reported the synthesis of "molecular charm bracelets" using ring-opening metathesis polymerization of a Boc-amine macromer used as a clip for the cyclization of diolefin polyether "charms" around the larger ring.[28]

We report here the first synthesis of *responsive* macromolecular charm bracelets, as an entry into new addressable nanomaterials and nanosystems that would take advantage of the unique properties of the cyclic polymer topology. Light was selected as the stimulus and azobenzene was the photoresponsive moiety. Azobenzene undergoes a light-induced trans to cis isomerization upon UV irradiation and the reverse cis to trans isomerization upon illumination by visible light.[29] The photoisomerization brings about changes in the physical properties of azobenzene that can be manipulated to trigger macroscopic changes[30-33]. From the view point of our targeted responsive macromolecular charm bracelet, azobenzene possesses a strikingly interesting feature: in the trans configuration, it forms an inclusion complex with α-cyclodextrin, (α-CD), a cyclic oligosaccharide of toroidal topography consisting of six α-1,4-glucopyranoside units.[34] The supramolecular trans-azobenzene/α-CD complex was used here as a clip to position an α-CD "charm" on a polymer chain. Subsequent light irradiation triggered a slight shuttle motion of the α-CD along the main ring, since the cis azobenzene moiety produced by UV light does not-fit in the α-CD cavity. [34]

The synthetic approach to the targeted charm bracelet, is represented schematically in Figure 1. An azobenzene group linked to the end of polymer chain served as a lure to capture an α-CD on the polymer chain end prior to cyclization. Excess α-CD was employed in order to ensure that every chain carries an azobenzene/α-CD inclusion complex. Subsequently, we closed the ring permanently via a standard "click" azide/alkyne cycloaddition. Poly(*N*-isopropylacrylamide) (PNIPAM) was selected as the ring main chain, since it is amenable to controlled radical polymerization, reasonably flexible to facilitate end-to-end coupling, [35] and more importantly it does not form an inclusion complex with α-CD.[36]

Due to the complexity of the mechanically linked structures, confirmation of the interlocked nature of the products could prove difficult. The use of 2D-NMR (NOESY) spectroscopy and induced circular dichroism (ICD) facilitated the analysis, as they are sensitive tools to detect the formation of azobenzene/α-CD inclusion complexes, as demonstrated in various systems.[37-39] Further support for the successful preparation of polymers consisting of two mechanically linked rings was obtained by comparing their spectral characteristics and solution properties to those of a cyclic polymer prepared under identical conditions, but in the absence of α-CD. Furthermore, photochemical manipulations uncovered the light-induced shuttle motion of the α-CD ring in the vicinity of the azobenzene moiety. This motion affects the spectral properties of the mechanically interlocked structure in water, in particular its induced circular dichroism, without affecting the solution phase transition temperature.

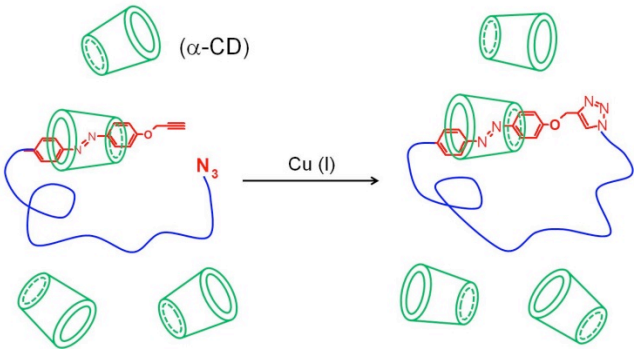


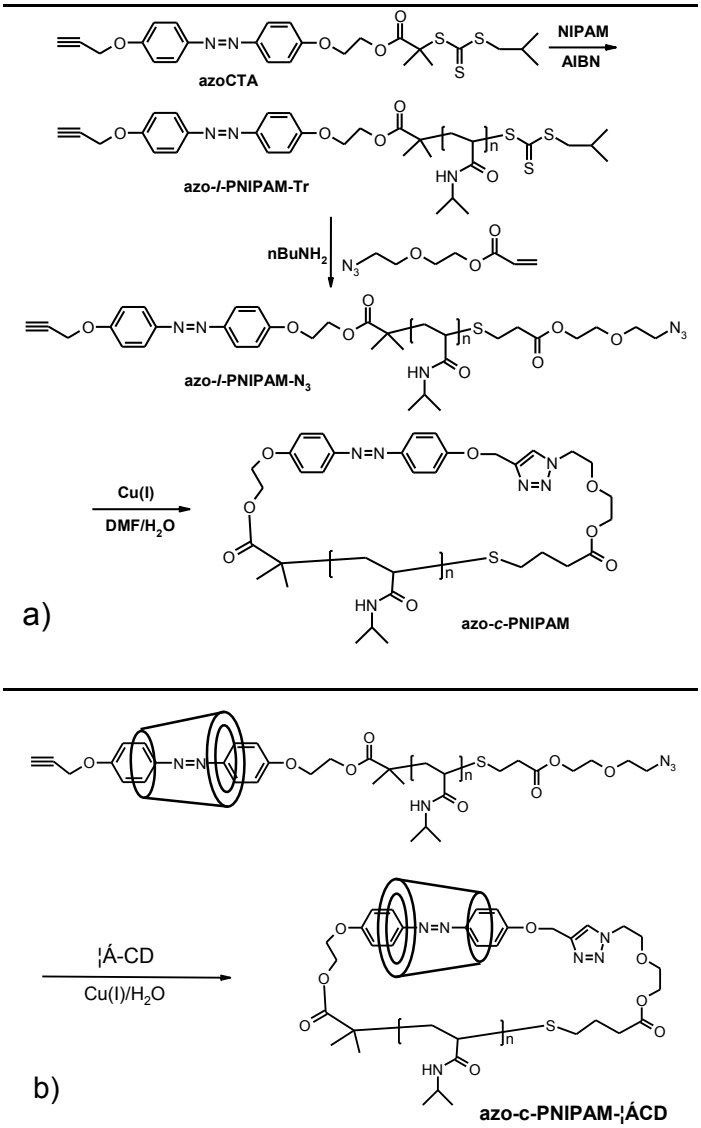
Fig. 1 Schematic representations of the capture of α-cyclodextrin (α-CD, green) by the terminal azobenzene group (red) of the polymer and subsequent cyclization.

Results and discussion

Preparation and cyclisation of azobenzene-modified-PNIPAM

Scheme 1a presents the detailed preparation of the cyclic azobenzene-substituted PNIPAM sample (azo-c-PNIPAM) prepared in the absence of α-CD. The mechanically interlocked polymer (azo-c-PNIPAM-αCD) was obtained by the same route, but the cyclisation step was carried out in the presence of α-CD (Scheme 1b), as described in the following section. In order to ensure that each polymer possesses an azobenzene group along the main chain and to introduce a terminal alkyne group, we prepared the linear precursor (azo-*l*-PNIPAM-Tr) by RAFT polymerization of NIPAM in the presence of a chain transfer agent (azoCTA, Scheme 1a) substituted with a 4-propargyloxyazobenzenyl moiety. The polymerization was conducted in dry dioxane at 65 ^{o}C for 4 hr with a monomer (NIPAM) to azoCTA molar ratio of 100:1, leading to α-propargyloxyazobenzene, ω-isobutyltrithiocarbonate PNIPAM (azo-*l*-PNIPAM-Tr) of molecular weight M_n = 8.8 kDa and polydispersity index PDI = 1.04, as determined by GPC analysis with MALLS detection (see Figure S1). The degree of polymerization of the polymer, obtained by end-group analysis of the ^{1}H NMR spectrum of azo-*l*-PNIPAM-Tr (see Figure S2), was DPn ~70. Subsequently, the trithiocarbonate end group of azo-*l*-PNIPAM-Tr was substituted with an azide group by a one-pot reaction involving aminolysis of the ω-isobutyltrithiocarbonate group with *n*-butylamine and Michael addition of the resulting thiol with 2-(2-azidoethoxy)ethyl acrylate. The ^{1}H NMR spectrum of α-propargyloxyazobenzene, ω-azido PNIPAM (azo-*l*-PNIPAM-N_3) (Figure 2, bottom) displays a resonance at 3.40 ppm, assigned to the methylene protons α to the terminal azide group. The isobutyltrithiocarbonate protons signals at 1.02 and 3.28 ppm of azo-*l*-PNIPAM-Tr (Figure S2) cannot be detected, confirming that the transformation was successful. The GPC elution band of azo-*l*-PNIPAM-N_3 coincides with that of azo-*l*-PNIPAM-Tr, but it has a small shoulder on the high molecular weight side that signals the presence of a small fraction of dimers formed

via thiol-thiol oxidative coupling. The dimers could not be removed from the main polymer component prior to cyclization.



Scheme 1. Synthetic route for the preparation of interlocked α-CD and cyclic poly(*N*-ispropylacrylamide) containing an azobenzene moiety.

The cyclization of azo-*l*-PNIPAM-N_3 was performed in a DMF/Water (1:1 v:v) mixture under conditions of high-dilution to minimize the formation of dimers and higher oligomers. The high dilution conditions ([azo-l-PNIPAM-N_3] ~ 2.0 x 10^{-7}) were achieved by dropwise addition of azo-l-PNIPAM-N_3 to the reaction mixture (see experimental conditions). The success of the alkyne-azide coupling was confirmed by the emergence of the characteristic resonance of the 1,2,3-triazole ring proton at 7.84 ppm (peak a, Figure 2, top) in the ^{1}H NMR spectrum of the recovered polymer and concomitant vanishing of the resonance due to the terminal alkyne proton (2.58 ppm, peak 1 in Figure 2, bottom). The signals due to the methylene protons α to the alkyne and to the azide groups in azo-*l*-PNIPAM-N_3 underwent downfield shifts from 4.80 to 5.30 and from 3.40 to 4.50 ppm, respectively, which can be ascribed to effects of the newly-formed adjacent 1,2,3-triazole ring. The azide stretching band at 2113 cm^{-1} observed in the FTIR spectrum of azo-*l*-PNIPAM-N_3 (Figure 3) cannot be detected in the spectrum of azo-*c*-PNIPAM, bringing further support to the successful outcome of the cyclization. The GPC trace of azo-*c*-PNIPAM exhibited a significant shift to longer elution time, compared to the linear precursor, azo-*l*-PNIPAM-N_3 (Figure S1), as a consequence of the hydrodynamically more compact topology of azo-*c*-PNIPAM, as observed previously.[35]

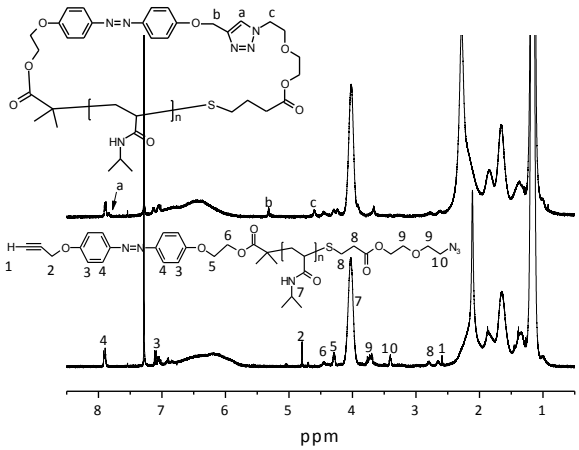


Fig. 2 ^{1}H NMR spectra of azo-*l*-PNIPAM-N_3 (bottom) and azo-*c*-PNIPAM (top) in $CDCl_3$.

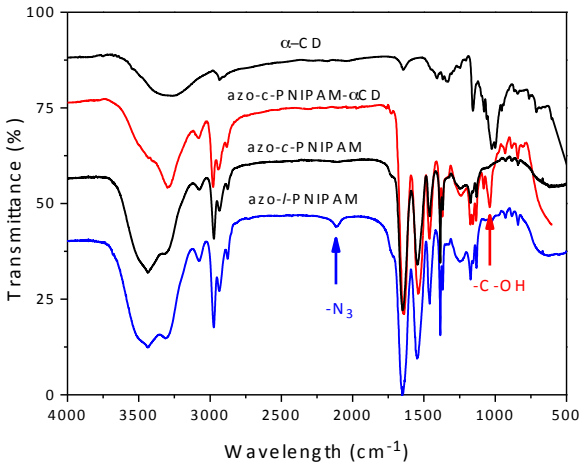


Fig. 3. FTIR spectra of azo-*l*-PNIPAM, azo-*c*-PNIPAM, azo-*c*-PNIPAM-αCD, and α-cyclodextrin (from bottom to top).

Preparation, purification, and characterization of mechanically interlocked azobenzenyl-PNIPAM/α-CD (azo-c-PNIPAM-αCD) (Scheme 1b)

In this case, prior to cyclisation, α-CD was added in large excess to an azo-*l*-PNIPAM-N_3 aqueous solution in order to link α-CD via supramolecular interaction with the azobenzene moiety to one end of the polymer chain to be cyclized (Scheme 1b). We considered a possible problem inherent to this scheme,

which may complicate spectra interpretation: the linear polymer could be end-capped by an α-CD torus placed with its wide rim either facing the main chain or pointing towards the chain end, as depicted in Figure 4. Evidence from experimental data and theoretical considerations indicate that the primary and secondary hydroxyl groups of α-CD are located, respectively, on the narrow and wide rims of the torus.[40]. The primary (wide) rim, with the primary hydroxyl groups directed towards the exterior of α-CD, is slightly hydrophobic. Molecular dynamics simulations indicate that it is surrounded by seven or eight bound water molecules.[41] The secondary (narrow) rim is relatively rigid and hydrophilic and it is surrounded by fifteen to seventeen water molecules. Compared with the primary rim, the secondary rim has more water molecules around it and they form a network of hydrogen bound. Hence, it is not easy for a guest molecule to enter the α-CD cavity from the side of the secondary rim. Molecular dynamic simulations of the formation an inclusion complex between α-CD and azobenzene surfactant confirmed that in this case, which is relevant to our study, the azobenzene group preferentially enters the cavity from the primary rim.[42] By analogy, we assume that in our case too, the guest will enter the cavity from this side, so that the α-CD wide rim faces the main chain.

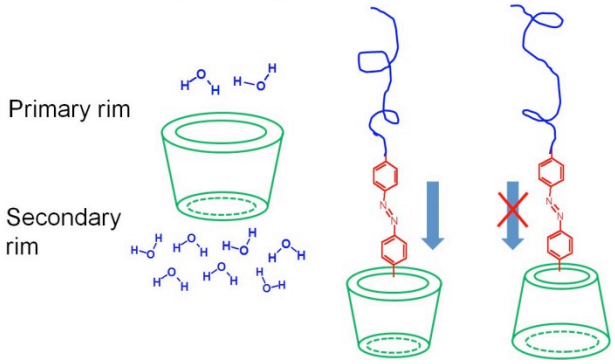


Fig. 4. Schematic representations of the preferential mode of entry of the azobenzene moiety into the α-CD cavity.

A 10-fold molar excess of α-CD, with respect to azobenzene solution was added dropwise to a Cu(I) solution supplemented with the same concentration of α-CD. At the end of the addition of azo-*l*-PNIPAM-αCD to the Cu(I) solution, the catalyst was removed by filtration from the cyclization mixture. The filtrate was subjected to ultrafiltration and extensive dialysis using membranes (MWCO 3 kDa and MWCO 6-8 kDa) permeable to α-CD. Preliminary analyses by ^{1}H NMR and FTIR spectroscopy indicated that the clipping of the α-CD onto the PNIPAM cycle was successful. Unfortunately, the GPC elution profile of the sample recovered via freeze-drying of the filtrate was subjected to ultrafiltration and extensive dialysis using membranes (MWCO 3 kDa and MWCO 6-8 kDa) permeable to α-CD. Preliminary analyses by ^{1}H NMR and FTIR spectroscopy indicated that the clipping of the α-CD onto the PNIPAM cycle was successful. Unfortunately, the GPC elution profile of the sample recovered via freeze-drying of the dialyzed solution presented a fast eluting band accounting for ~20 % of the total polymer in addition to the major band positioned at an eluting time very close to that of azo-c-PNIPAM (Figure 5a).

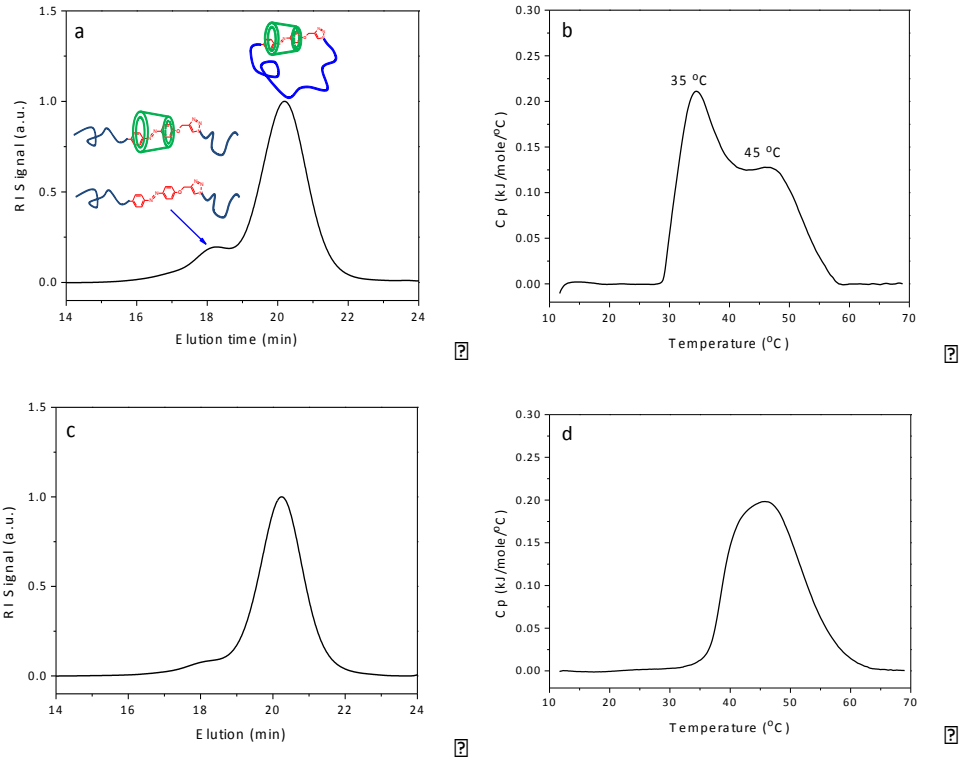


Fig. 5. GPC traces of azo-*c*-PNIPAM-αCD as-prepared (a) and purified (c) and HS-DSC endotherms of azo-*c*-PNIPAM-αCD as-prepared (b) and purified (d); eluent: DMF, temperature: 40 °C.

The faster eluting band is attributed to linear dimers or oligomers formed as by-products of the cyclization. When the cyclization was conducted in the absence of α-CD, the amount of linear contaminants was negligible. Obviously, the presence of the rigid and bulky α-CD close to one chain end significantly hinders the end-to-end ligation of the PNIPAM chain. It was imperative to remove the linear chains from the mixture, but separation by techniques such as dialysis or chromatography did not seem feasible in view of the similarity in size and chemical composition of the components. The selection of PNIPAM turned out to be providential, since we were able to devise a purification protocol using its well-established thermosensitivity in water[43]. As shown in Figure 5b, the high sensitivity differential scanning calorimetry (HS-DSC) trace of the crude cyclization mixture consisted of two endotherms with well-separated maxima at 35 and 45 °C. The endotherm centered at the higher temperature was tentatively attributed to the cyclic polymer, based on our previous observation that the phase transition temperature of cyclic PNIPAM is higher than that of the linear precursor, and that the endotherm is broader,[35] as observed also in the DSC trace of the mixture. The linear side product was removed from the crude cyclization mixture by centrifugation at 36 °C, a temperature for which it is insoluble. The cyclic azo-c-PNPAM-αCD, which is soluble at 36 °C was recovered from the supernatant by lyophilization. The GPC trace of the recovered product provides excellent evidence that the separation was successful (Figure 5c): the slower eluting band dominates the elution profile. The band due to the linear polymers is hardly detectable. Moreover the retention time of the main component is similar to that of azo-c-PNIPAM. Furthermore, the DSC trace of the recovered product presented a single and broad endotherm centered at 45 °C (Figure 5d).

In Figure 3, we present the FT-IR spectrum of azo-c-PNIPAM-αCD (red trace) and, for comparison, the spectra of azo-l-PNIPAM-N_3, azo-c-PNIPAM, and α-CD. The C-OH stretching bands around 1035 cm^{-1}, characteristic of α-CD, are present in the spectrum of azo-c-PNIPAM-αCD (red arrow), but not in the spectra of either azo-c-PNIPAM or azo-l-PNIPAM-N3. ^{1}H NMR studies were carried out next in order to ascertain that the azo-c-PNIPAM and the α-CD rings are interlocked.

The ^{1}H NMR spectrum of azo(trans)-c-PNIPAM-αCD is presented in Figure 6 (spectrum a). It has all the signals characteristic of the PNIPAM cycle, such as a singlet at 3.80 ppm attributed to the isopropyl methine proton. It also possesses signals due to the α-CD protons: a sharp singlet at 4.91 ppm attributed to the resonance of the α-CD anomeric protons (C1H) and multiplets around 3.50 (C2H and C4H) and 3.65 ppm (C3H, C5H, and C6H).[44] The resonances of the azobenzene protons at the ortho (α) and meta (β) positions of the azo bond appear at 8.2 and 7.2 ppm, respectively. They are shifted downfield, compared to the corresponding signals in the spectrum of azo(trans)-c-PNIPAM (Figure 6, spectrum c). Similar shifts were reported in studies of azobenzene/αCD inclusion complexes. They are attributed to interactions of the azobenzene protons with the inner protons of α-CD.[45] The 2D NOESY spectrum of azo-c-PNIPAM-αCD in D_2O (25 °C), presented in Figure 7, clearly displays correlation peaks (circled areas) between the α-CD cavity inner protons (C3H and C5H) and the azobenzene protons.

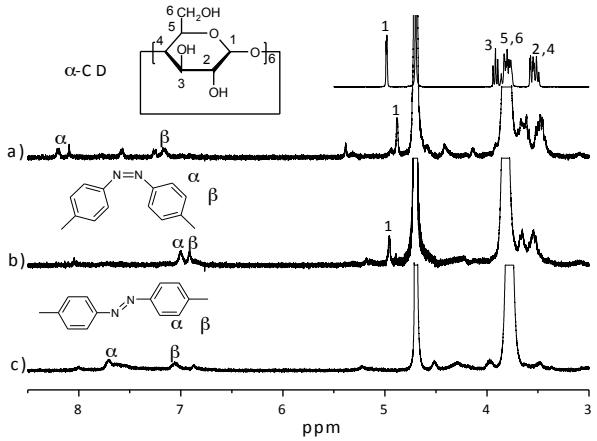


Fig. 6 ^{1}H NMR spectra of azo(trans)-c-PNIPAM-αCD (a), azo(cis)-c-PNIPAM-αCD (b), and azo(trans)-c-PNIPAM (c). The ^{1}H NMR spectrum of α-CD is inserted on the top of the figure for reference; azo(cis)-c-PNIPAM-αCD was prepared by irradiation of azo(trans)-c-PNIPAM-αCD with a light of λ = 365 nm for 10 min; solvent: D_2O.

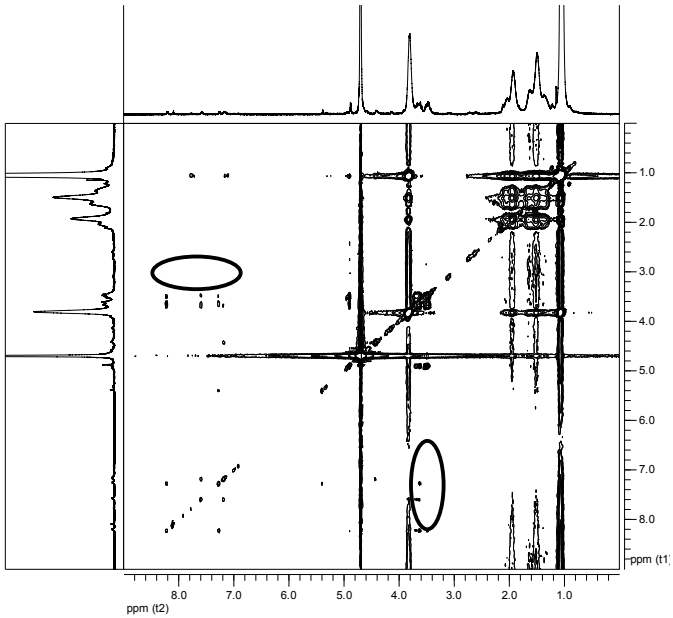


Fig. 7 NOESY spectrum of azo(trans)-c-PNIPAM-αCD; correlation peaks are circled; solvent: D_2O.

The general features of the ^{1}H NMR spectrum of azo-c-PNIPAM-αCD and the presence of NOE correlation peaks indicate that the azobenzene is deeply inserted within the hydrophobic cavity of the α-CD. From the ratio of the area of the C1H signal of α-CD to that of the PNIPAM isopropyl methine proton, we estimate that the molar ratio of α-CD to azo-c-PNIPAM is greater than 90 %. The spectral data do not

give information on the orientation of the α-CD torus along the ring. In the structure of azo-c-PNIPAM-αCD represented in Scheme 1b the secondary (small) ring of α-CD points towards the1,2,3-triazole ring. This orientation is believed to be predominant, based on considerations on the preferred mode of α-CD docking on the azobenzenyl endgroup of the linear precursor azo-l-PNIPAM-N_3.

Photophysical properties of azo-c-PNIPAM-αCD in water.

Figure 8 presents the UV-Vis absorption spectra of azo-l-PNIPAM-N_3, azo-c-PNIPAM, and azo-c-PNIPAM-αCD in water with the azobenzene group in the trans form and in the photostationary state reached after a 10 min irradiation at 365 nm. The spectra recorded prior to irradiation (trans azobenzene) present a strong π-π* transition with maximum absorbance at λ = 356 nm, 358 nm, and 364 nm, respectively, for azo-l-PNIPAM-N_3, azo-c-PNIPAM, and azo-c-PNIPAM-αCD. The hypsochromic shift of the π-π* band upon catenation of the PNIPAM and α-CD rings is attributed to the change in polarity sensed by the azobenzene moiety upon entrapment in the hydrophobic cavity of α-CD. The n-π* band appears as a weak and poorly resolved shoulder on the long-wavelengths side of the π-π* band. Upon irradiation at 365 nm, the π-π* and n-π* transitions shift to 316 nm and ~ 440 nm, respectively. Importantly, the spectra of azo(cis)-c-PNIPAM and azo(cis)-c-PNIPAM-αCD are identical. This spectral coincidence implies that the environment of the cis-azobenzene moiety is the same in both polymers. Hence, it confirms that the cis-azobenzene, due to its size, has escaped from the α-CD cavity upon irradiation, pushing the α-CD towards the PNIPAM section of the ring.

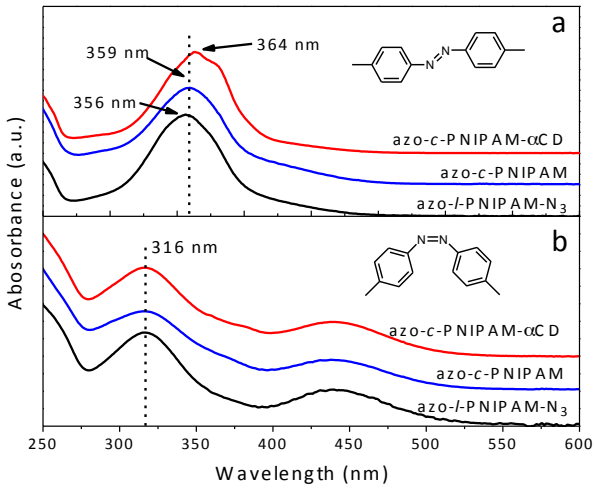


Fig. 8 UV-absorption spectra of azo-*l*-PNIPAM-N_3, azo-*c*-PNIPAM and azo-*c*-PNIPAM-αCD before (a) and after (b) irradiation at λ = 365 nm for 10 min; polymer concentration: 0.5 g/L; room temperature.

We also estimated the effect of spontaneous cis-to-trans transition after reaching the photostationary state (10 min irradiation at 365 nm). In 5 min absorbance intensity corresponding to the position of the π-π* transition peak increased by ~5%. This time scale covers most experiments performed, hence the contribution of the cis/trans isomerization was neglected in the frame of this study.

The induced circular dichroism (ICD) spectrum of azo(trans)-c-PNIPAM-αCD (Figure 9 black curve) displays a strong positive band centered around 364 nm and a weak negative band at 440 nm corresponding, respectively to the π-π* and n-π* transitions [46, 47]. Theoretical predictions indicate that for chromophores inserted within the α-CD cavity, electronic transition moments parallel to the α-CD axis give rise to positive ICD signals, whereas electronic transition moments perpendicular to the α-CD axis give rise to negative signals.[48] When electronic transition moments lay outside the α-CD cavity, the moments parallel give negative signals and the perpendicular moments have positive signals. Hence the ICD spectrum of azo(trans)-c-PNIPAM-αCD gives further evidence that the trans azobenzene moiety along the cyclic PNIPAM backbone is inserted in the α-CD cavity with its π-π* transition moment oriented parallel to the CD axis. In the ICD spectrum of the (predominantly cis) photostationary state, the positive band at 364 nm (π-π* transition) is much weaker than prior to UV irradiation. These observations confirm that the cis azo-benzene is located in close proximity to α-CD, but outside the cavity.

The α-CD/azobenzene complexation status along the azo-c-PNIPAM-αCD ring after UV irradiation was studied also by ^{1}H NMR spectroscopy (Figure 6, spectrum b). The trans-cis isomerization is accompanied by a significant upfield shift, from 8.2 ppm to 7.0 ppm, of the resonance of the proton α to the azo group (ortho position). This effect was observed in previous studies of the trans-cis photoisomerization of azobenzene derivatives.[49]

It was attributed to steric constraints experienced by the α protons in the cis-azobenzene isomer. Furthermore, the 2D NOESY spectrum of azo(cis)-c-PNIPAM-αCD does not display correlation peaks between the aromatic azobenzene protons and the inner cavity α-CD protons (see Figure S4), confirming the UV-Vis and ICD data described in the previous sections.

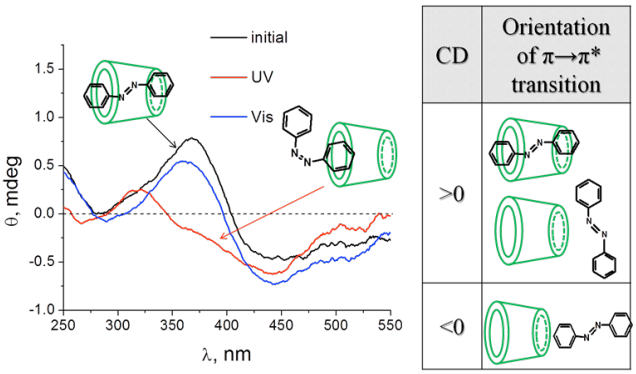


Fig. 9 Induced circular dichroism spectra of an aqueous azo-c-PNIPAM-αCD solution before (black curve) and after (red curve) irradiation at 365 nm for 10 min, and (blue curve) after irradiation at 460 nm of the azo(cis) isomer; polymer concentration: 9.0 g/L; room temperature.

The trans-cis photoisomerization of azobenzene is accompanied by a change in the dipole moment of the chromophore. In the case of the azobenzene moiety used here, the cis-conformation is more polar than the trans configuration, Consequently, the trans-cis photoisomerization is accompanied by an increase in the hydrophilicity of the azo-PNIPAM samples. Macroscopically, this effect can be detected by an increase in the cloud point of azo-PNIPAM aqueous solutions. Figure 10 presents the temperature-dependent transmittance of aqueous solutions (1.0 g/L) of azo-*l*-PNIPAM-N_3, azo-*c*-PNIPAM, and azo-*c*-PNIPAM-αCD before and after exposure to UV 365 nm irradiation. The light-triggered azobenzene polarity increase results in a 1.1°C increase of the solution phase transition temperature for the linear azo-l-PNIPAM-N_3 and an even higher increase, 1.7 °C, for the cyclic homolog azo-c-PNIPAM. Surprisingly, the trans-cis photoisomerization has no effect on the phase transition of azo-*c*-PNIPAM-αCD.

The data reported in the previous sections indicate that trans-azobenzene is entrapped in the cavity of α-CD, which screens the water/azobenzene interactions. Upon UV irradiation, the relatively more polar cis-azobenzene is expelled from the α-CD cavity and brought in contact with water molecules. This should have affected the phase transition temperature. This effect is expected to be small in view of the enhanced polarity of the cis azobenzene isomer, compared to the trans isomer. It is overshadowed by the strong hydrophilicity of the α-CD moiety constrained along the polymer ring. Unusual polymer solubility properties as a consequence of supramolecular interactions with CD have been observed previously[50].

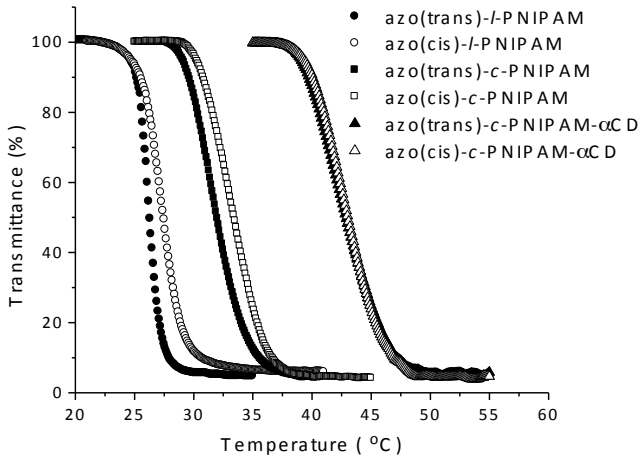


Fig. 10 Changes with temperature of the transmittance of solutions in water of azo-*l*-PNIPAM, azo-*c*-PNIPAM, and azo-c-PNIPAM-αCD before exposure to irradiation at 365 nm (open symbols) and after irradiation (full symbols); polymer concentration: 1.0 g/L.

Experimental

Materials

All chemicals were purchased from Sigma-Aldrich Chemicals Co. unless otherwise specified. Azobisisobutyronitrile (AIBN, 98%) was recrystallized from methanol prior to use. *N*-Isopropylacrylamide (NIPAM, 99%) was obtained from Acros Organics and recrystallized from an acetone/hexanes (4/6, v/v) mixture. Sodium borohydride, potassium nitrite, potassium carbonate, tetrafluoroboric acid, *p*-nitrophenol, phenol, 2-bromoethanol, and 10 % palladium on carbon were used as received. 1,4-Dioxane, *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were purified by a solvent purification system with two packed columns of activated alumina provided by Innovative Technology Inc. 2-(2-Azidoethoxy)ethyl acrylate was synthesized according to a standard method, starting with 2-(2-azidoethoxy)ethanol and acryloyl chloride.[51] All other solvents were of reagent grade and used as received. Water was deionized using a Millipore MilliQ system.

Synthesis of the azobenzene-containing chain transfer agent (AzoCTA, see structure in Scheme 1)

Oxalyl chloride (8.0 mL, 100.0 mmol) was added while stirring to 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid[52] (3.3 g, 13.0 mmol) kept under a nitrogen atmosphere at room temperature. At the end of addition, the mixture was heated to 50 °C and stirred for 2 hrs. The excess oxalyl chloride was removed in vacuo to yield 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methyl propionyl chloride. Subsequently, a solution of 4-propargyl-4'-(4-hydroxy-ethoxy)-azobenzene (compound *4* in Scheme S1 prepared as described in SI*)* (2.0 g, 6.6 mmol) in methylene chloride (20.0 mL) was added dropwise to 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methyl propionyl chloride. The resulting solution was stirred at 60 °C for 6 hrs. At the end of reaction, the solution was cooled to room temperature and ethanol was added to quench the remaining acyl chloride. The excess ethanol was removed by rotary-evaporation. The product was purified by flash column chromatography on silica gel using dichloromethane/hexane (3/1 v/v) as eluent. Yield: 1.5 g, 50 %. ^{1}H NMR ($CDCl_3$) ppm, δ 0.98 (d, 6H, -CH(C*H*$_3$)$_2$), 1.73 (s, 6H, -SC(C*H*$_3$)$_2$C(=O)), 1.90 (septet, 1H, -C*H*(CH$_3$)$_2$), 2.58 (s, 1H, ≡C*H*), 3.10 (d, 2H, -SC*H*$_2$), 4.26 (t, 4H, -C(=O)OC*H*2), 4.52 (t, 4H, -C*H*2OAr), 4.80 (s, 2H, ≡C-C*H*$_2$-), 7.02 (d, 1H, Ar-*H*), 7.12 (d, 1H, Ar-*H*), 7.89 (d, 2H, Ar-*H*); MS (MH·), found: 531.14638 *m*/*z*, calcd for $C_{26}H_{30}N_2O_4S_3$: 531.14405 *m*/*z*. The MS data, ^{1}H NMR and ^{13}C NMR spectra of AzoCTA are presented on Figures S5, S6, and S7, respectively.

α-Azobenzene ω-trithiocarbonate poly(N-isopropyl-acrylamide) (azo-PNIPAM-Tr)

The polymer was synthesized by RAFT polymerization performed in a septa-sealed round bottom flask with magnetic stirring. The chain transfer agent (*Azo*CTA, 106.0 mg, 0.2 mmol), the initiator (AIBN, 3.3 mg, 0.02 mmol), and the monomer (NIPAM, 2.26 g, 20.0 mmol) were dissolved in purified 1,4-dioxane (15.0 mL). The solution was de-oxygenated by bubbling nitrogen for 30 min at room temperature. After that, the flask was placed in an oil bath preheated to 65 °C. The polymerization was allowed to proceed for ~4 hrs under constant magnetic stirring. At the end of the polymerization, the solution was cooled to room temperature. The polymer was isolated by precipitation in diethyl ether. It was purified by two consecutive reprecipitations from THF into diethyl ether. Yield 1.60 g, 70%. GPC, M_n = 8.8 kDa and M_w/M_n = 1.04. ^{1}H NMR ($CDCl_3$) ppm, δ 1.02 (d, -$CH_2CH(CH_3)_2$), 1.16 (s, -NHCH(CH_3)$_2$), 1.20-2.40 (multiplets, polymer backbone protons), 2.58 (s, ≡C*H*), 3.28 (s, -C(=S)SCH_2), 4.02 (s, -NHC*H*), 4.28 (t, 4H, -C(=O)OC*H*2), 4.45 (t, 4H, -C*H*2OAr), 4.80 (s, 2H, ≡C-CH_2-), 6.40 (bs, -C(=O)N*H*), 7.02 (d, Ar-*H*), 7.12 (d, Ar-*H*), 7.89 (d, Ar-*H*); FTIR ν 3293, 2970, 2113, 1640, 1538, 1458, 1367, 1171, 1130, 736 cm^{-1}.

α-Azobenzene ω-azido poly(N-isopropylacrylamide) (azo-l-PNIPAM-N_3)

The polymer was synthesized by a one-pot aminolysis/Michael-addition sequential end-group transformation starting from *azo-l*-PNIPAM-*Tr* (0.9 g, 0.1 mmol) dissolved in THF (10 mL). After complete dissolution of the polymer, the solution was degassed by bubbling N_2 for 15 min. 2-(2-Azidoethoxy)ethyl acrylate (185.0 mg, 1.0 mmol, 10 equiv) and n-butylamine (73.0 mg, 1.0 mmol, 10 equiv) were added to the solution. The reaction mixture was stirred for 2 hrs at room temperature under N_2 atmosphere. The polymer, α-(2-(2-azidoethoxy)ethyl-2-methylpropionyl) ω-propargyl acrylate PNIPAM (*azo-l*-PNIPAM-N_3), was recovered by precipitation in diethyl ether and purified by two consecutive reprecipitations from THF into diethyl ether. Yield 0.8 g, 88%. GPC, M_n = 9.1 kDa and M_w/M_n = 1.07. ^{1}H NMR ($CDCl_3$) ppm, δ 1.16 (s, -NHCH(CH_3)$_2$), 1.20-2.40 (multipeaks, polymer backbone protons), 2.58 (s, ≡C*H*), 2.68 (s, -SCH_2CH_2C(=O)), 2.82 (s, -SCH_2CH_2C(=O)), 3.40 (s, -$CH_2CH_2N_3$), 3.70 (s, -$CH_2CH_2OCH_2CH_2N_3$), 4.02 (s, -NHC*H*(CH_3)$_2$), 4.28 (t, -C(=O)OCH_2), 4.45 (t, -CH_2OAr), 4.80 (s, 2H, ≡C-CH_2-), 6.40 (bs, -C(=O)N*H*), 7.02 (d, Ar-2*H*), 7.12 (d, Ar-2*H*), 7.89 (d, Ar-4*H*); FTIR ν 3293, 2970, 2113, 1640, 1538, 1458, 1367, 1171, 1130, 736 cm^{-1}.

Cyclization of azo-*l*-PNIPAM-N_3

A DMF/water mixture (1:1 v:v, 1.0 L) was placed in a round bottom flask and degassed by bubbling N_2 for 30 min. Sodium ascorbate (2.0 g, 10.0 mmol, 200 equiv) was added to the aqueous solution followed by dropwise addition of $CuSO_4$ (0.8 g, 5.0 mmol, 100 equiv) in water (5.0 mL), yielding a turbid brown Cu(I) suspension. A solution of azo-*l*-PNIPAM-N_3 (450.0 mg, 0.05 mmol, 1 equiv relative to the propargyl-azobenzene concentration) in 40.0 mL of DMF/water (1:1) mixture (feed solution) was added to the Cu(I) suspension via a syringe pump at a rate of 2.0 mL/hr. The reaction was carried out at 50 °C under N_2 atmosphere for 20 hrs. At the end of the addition, the reaction solution was allowed to stir for another 60 min. The brown catalyst precipitate was removed by filtration. The filtrate was concentrated and purified by ultrafiltration using a membrane with MWCO of 3 kDa. The cyclic polymer (azo-*c*-PNIPAM) was then recovered by freeze-drying. Yield 300.0 mg, 66%. GPC, M_n = 9.2 kDa and M_w/M_n = 1.08. ^{1}H NMR ($CDCl_3$) ppm, δ 1.16 (s, -NHCH(CH_3)$_2$), 1.20-2.40 (multiple peaks, polymer backbone protons), 2.68 (s, -SCH_2CH_2C(=O)), 2.82 (s, -SCH_2CH_2C(=O)), 3.68 (t, -OCH_2CH_2OC(=O)-), 4.02 (s, -NHC*H*(CH_3)$_2$), 4.18 (t, -OCH_2CH_2OC(=O)-), 4.60 (t, =NCH_2CH_2O-), 5.25 (t, -C(=O)OCH_2C), 6.40 (bs, -C(=O)N*H*), 7.02 (d, Ar-2*H*), 7.12 (d, Ar-2*H*), 7.85 (s, 1H of triazole), 7.89 (d, Ar-4*H*); FTIR ν 3302, 2970, 2112, 1639, 1537, 1458, 1367, 1267, 1172, 1130, 735 cm^{-1}.

Cyclization of azo-*l*-PNIPAM-N_3 in the presence of α-CD

Water (250.0 mL) was placed in a round bottom flask and degassed by bubbling N_2 for 30 min. Sodium ascorbate (0.5 g, 2.5 mmol, 200 equiv) was added to the aqueous solution followed by dropwise addition of $CuSO_4$ (0.2 g, 1.25 mmol, 100 equiv) in water (5.0 mL), yielding a turbid brown Cu(I) suspension. α-Cyclodextrin (2.0 g, 2.0 mmol) was added to the Cu(I) suspension. A solution of azo-*l*-PNIPAM-N_3 (120.0 mg, 0.013 mmol of polymer, 1 equiv compared to propargyl-azobenzene) and α-cyclodextrin (128.0 mg, 0.13 mmol, 10 equiv compared to azobenzene) in water (20 mL) (feed solution) was added to the Cu(I) suspension via a syringe pump at a rate of 2 mL/hr. Assuming fast diffusion of the polymer and fast click reaction, we estimate that the concentration of azo-l-PNIPAM-N_3 in the cyclisation does not exceed 2.0 x 10^{-7} M. This dilution of azo-l-PNIPAM-N_3 may cause dissociation of the inclusion complex. The reaction was carried out at 25 °C under N_2 atmosphere for 10 hrs. At the end of the addition, the reaction solution was allowed to stir for another 60 min. The brown catalyst precipitate was removed by filtration. The filtrate was concentrated and purified by ultrafiltration using a membrane with MWCO of 3 kDa. The cyclic azo-PNIPAM with interlocked α-cyclodextrin (α-CD) was further dialyzed against water for 3 days with a membrane of MWCO of 6 - 8 kDa to remove all free α-CD. The dialysate was subjected to centrifugation (35 °C, 6,000 rpm) for 1 hr to remove the residual linear polymer (pellet). The cyclic polymer (azo-c-PNIPAM-αCD) was then recovered from the supernatant by freeze-drying. Yield: 60 mg, 50%. GPC, M_n = 9.4 kDa and M_w/M_n = 1.05. ^{1}H NMR (D_2O) ppm, δ 1.06 (s, -NHCH(CH_3)$_2$), 1.20-2.20 (multipeaks, polymer backbone protons), 2.60 (s, -SCH_2CH_2C(=O)), 2.72 (s, -SCH_2CH_2C(=O)), 3.45 (multiple, C2H and C4H of α-CD), 3.65 (multiple, C3H C5H, and C6H of

α-CD), 3.81 (s, -NHC*H*$(CH_3)_2$), 4.12 (t, -OCH_2CH_2OC(=O)-), 4.88 (s, C1H of α-CD), 5.38 (t, ArOCH_2C), 7.2-7.3 (s, Ar-4*H*), 8.2 (s, Ar-4*H*); FTIR ν 3302, 2970, 2112, 1639, 1537, 1458, 1367, 1267, 1172, 1130, 735 cm^{-1}.

NMR spectroscopy

^{1}H, **^{13}C** NMR spectra and 2-dimensional NOESY NMR spectra were recorded on a Bruker AMX-400 (400 MHz) instrument. The chemical shifts are referenced to tetramethylsilane (TMS). Sample solutions were prepared by dissolving 10 mg of polymer in 1 mL of solvent ($CDCl_3$ or D_2O). For cis-azobenzene NMR spectra, the polymer solution was irradiated with a Prizmatix LED light source at selecting light of λ = 365 nm (at 30% of its output power) for 10 min at room temperature immediately before measurement.

Mass spectroscopy

Mass spectrum was recorded on a Micromass Autospec TOF instrument equipped with a LSIM source (Centre Regional de Spectrometrie de Masse, Universite de Montreal, Montreal, QC, Canada).

FTIR spectroscopy

FTIR spectra were recorded on a Bruker Vector-22 spectrometer by using KBr as matrix pellets. The spectrum was scanned from 4000 to 450 cm^{-1} with a resolution of 2 cm^{-1}.

GPC-MALLS measurements

Gel permeation chromatography (GPC) was performed with a GPC system consisting of an Agilent 1100 isocratic pump, a set of TSK-gel α-M (particle size 13 μ, exclusion limit 1×10^7 Da for polystyrene in DMF) and a TSK-gel α-3000 (particle size 7 μ, exclusion limit 1×10^5 Da for polystyrene in DMF) (Tosoh Biosep) columns, a Dawn EOS multi-angle laser light scattering detector λ = 690 nm (Wyatt Technology Co.) and an Optilab DSP interferometric refractometer λ = 690 nm (Wyatt Technology Co.) under the following conditions: injection volume, 100 μL; flow rate, 0.5 mL/min; eluent, DMF; temperature, 40 °C. The dn/dc value of PNIPAM was determined to be 0.074 mL/g at 690 nm in DMF at 40 °C using an Optilab DSP interferometric refractometer (Wyatt Technology Corp).

High-Sensitivity Differential Scanning Calorimetry (HS-DSC)

HS-DSC measurements were performed on a VP-DSC microcalorimeter (MicroCal Inc.) with a cell volume of 0.520 mL and under an external pressure of ca. 180 kPa. The heating rate was set constant at 1.0 °C/min in the range of 10 - 70 °C. The experimental data were analyzed using the Origin based software supplied by the manufacturer. The temperature of the phase transition (T_M) was taken at the maximum of the transition peak. The enthalpy of the transition (Δ*H*) was determined from the area of the endotherm. For each experiment, the solutions for analysis (polymer concentration: 1.0 g/L) were kept at room temperature for 12 hours prior to measurement. Three heating and cooling scans were recorded under the same conditions and the values of T_M and Δ*H* were averaged on the three scans.

Induced circular dichroism spectroscopy (ICD)

ICD measurements were recorded at room temperature from 250 nm to 550 nm on a Chirascan CD spectrometer (Applied Photophysics, Leatherhead, United Kingdom) using a 0.2-mm optical path length quartz cell. Data were acquired every 1 nm with an integration time of 0.5 s. Values measured for the solvent (water) were subtracted from the sample spectra. Data were smoothed using the software supplied by the manufacturer.

Photoisomerization experiments

Photoisomerization was carried out with a Prizmatix LED light source selecting light of λ = 365 nm (output 50 mW) or of λ = 460 nm (output 22 mW). The photoisomerization kinetics were conducted at room temperature. A polymer solution (2 mL, 0.5 g/L) was placed in a 10-mm cuvette. It was irradiated at λ = 365 nm (30% power output, for trans-to-cis isomerization) or at λ = 460 nm (40% power output, cis-to-trans isomerization) under magnetic stirring. Absorption spectra of the samples were measured at intervals of 10 s for 200 s. For turbidity measurements under irradiation, a polymer (azobenzene in the trans configuration) solution (1.0 g/L) was irradiated at λ = 365 nm (20 % power output) for 5 min to reach the photo-stationary state. The sample was placed in the sample compartment of the UV-Vis spectrometer for turbidity measurements. Throughout the measurement, the sample was kept under irradiation (λ = 365 nm, 20 % power) with a light beam perpendicular to the spectrometer beam to prevent thermal relaxation of azobenzene from the cis to the trans configuration. For CD measurements, polymer solutions (9.0 g/L) were irradiated at λ = 365 nm (100 % power output) for 5 min to reach the photo-stationary state and then placed in the sample compartment of the CD spectrometer. Spontaneous cis-trans thermal transition during the CD scanning time (5 min). was negligible.

Conclusions

We prepared a new type of charm bracelet consisting of interlocked α-cyclodextrin and PNIPAM rings. The synthesis of this copolymer was facilitated by linking to the end of the linear PNIPAM precursor an azobenzene group that lured the α-CD towards the PNIPAM chain via supramolecular interactions. The α-CD remained clipped to the azobenzene group after closure of the PNIPAM ring via click ligation.

However it shifted away from the azobenzene group upon UV irradiation as a consequence of the trans to cis isomerization of the azo chromophore. The light-triggered motion of the α-CD was reversed upon visible irradiation. The shuttle motion experienced by α-CD upon trans/cis isomerization of the azobenzene is represented in Figure 11. The figure stresses the fact that, in principle, the α-CD ring can move either towards the 1,2,3-triazole ring or in the opposite direction. From the data presented we cannot determine if both routes are taken or if one is favoured over the other. Previous work indicates that the 1,2,3-triazole ring can form an inclusion complex with α-CD.[53, 54] It is certain however that the motion of α-CD is short-ranged, since the NIPAM repeat units are too bulky to fit in the α-CD cavity. We are currently exploring methods to amplify the light-triggered motion of α-CD, either in solution or in thin films.

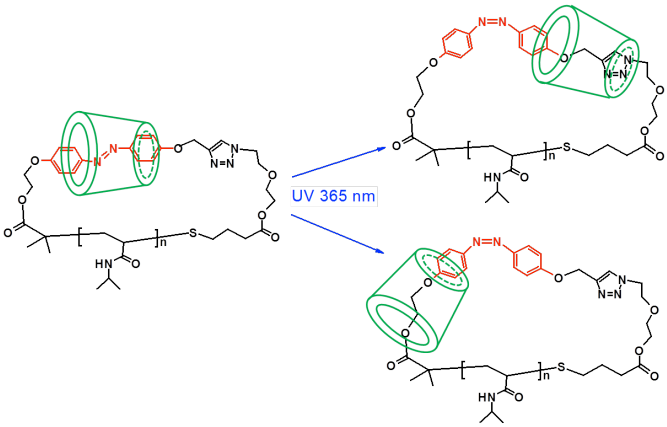


Fig. 11 Schematic representation of the shuttle motion experienced by α-cyclodextrin upon trans −cis photo-isomerization of azo-c-PNIPAM-αCD.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [Experimental procedures for the preparation of 4-propargyloxy-4'-(2-hydroxyethoxy)-azobenzene, GPC traces of azo-l-PNIPAM and azo-c-PNIPAM, ^{1}H NMR spectrum of azo-l-PNIPAM-Tr, FTIR spectra of azo-l-PNIPAM-Tr and azo-l-PNIPAM-N_3 ^{1}H NMR spectrum, ^{13}C NMR spectrum, and high resolution mass spectrum of azoCTA, 2D NOESY spectrum of azo-*c*-PNIPAM-αCD after irradiation at 365 nm for 10 min in D_2O at 25 °C.] . See DOI: 10.1039/b000000x/

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