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Counter-intuitive photo-modulation of the aqueous phase behavior of azo dye-functionalized polyacrylamides†

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Three sets of water-soluble non-ionic polymers, which are thermo- as well as photo-responsive, are synthesized by statistical copolymerization of hydrophilic substituted acrylamides with varying amounts of a polymerizable azobenzene dye. Their coil-to-globule phase transition of the lower critical solution (LCST) type in aqueous solution is investigated with respect to the nature of the *N*-substituents and the content of azo dye. The phase transition temperatures T_{CP} drop from >100 °C to <0 °C with increasing dye content. Irradiation of the copolymers with UV-vis light at 365 nm induces the *E*-to-*Z* ("*trans–cis*") isomerization of the azobenzenes, reaching an *E* : *Z* ratio of 21 : 79 in the photo stationary state, while three isosbestic points in the spectra suggest a clean interconversion. The thermal back reaction to the *E*-isomer is relatively slow, with a half-life of the order of 12 h. For the copolymers with a small azo dye content, the *E*-to-*Z* photo-isomerization induces an increase of the phase transition temperature T_{CP}, as it is expected due to the enhanced dipole moment of the *Z*-isomer. In contrast, the copolymers with higher azo dye contents behave counter-intuitively, *i.e.*, their T_{CP} values markedly lower upon UV-irradiation. Possible reasons, *e.g.* chromophore aggregation, are discussed. In addition, DLS reveals that, at all temperatures and in both the *E*- and the *Z*-state, small clusters are formed by the polymer chains, probably mediated by the hydrophobic azobenzene side groups. These coexist with large associates.

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Introduction

Stimuli-responsive polymers are characterized by their ability to undergo marked and reversible property changes, prompted by a small stimulus ("trigger").[1] Well-established effective stimuli are small changes of the temperature,[2] the pH,[3] the ionic strength,[4] or the irradiation by light.[5] Such stimuli-responsive or "smart" behaviors have attracted particular attention in aqueous media, where the induced changes of their hydrophilicity can be translated into a coil-to-globule collapse phase transition and the subsequent association of the macromolecules. This behavior has been exploited for various applications, such as sensors, actuators, artificial muscles, or the controlled release of active agents.[5–8] Useful stimuli can be discerned into non-invasive and invasive ones. Changes of the salt concentration or pH represent invasive stimuli as they require the addition or removal of another compound, *e.g.* of salts, acids, or bases to the system. In contrast, temperature and light are non-invasive stimuli. The latter are often advantageous since the back and forth switching is not complicated by addition and/or separation procedures, such as dialysis, in particular when enduring systems capable of numerous switching cycles are envisaged.

Changing the temperature, or more precisely the crossing of a phase transition temperature, is a well-established effective trigger. The polyacrylamides studied here feature a phase transition of the lower critical solution temperature (LCST) type in aqueous solution, *i.e.*, the polymer chains undergo a coil-to-globule transition upon heating above a specific temperature.[8,9] Typically, such a transition can easily be observed in the form of a cloud point, which is observed at a specific temperature, the cloud point temperature T_{CP}. While the occurrence of an LCST is known for a plethora of non-ionic polymers in aqueous media and has been largely used to implement thermo-responsive systems,[10] light has been much less studied as a stimulus for reversible smart systems. Only few highly reversible photo-switches that are useful in aqueous media are known, and their photo-induced isothermal changes of polymer hydrophilicity have been typically small.[11–14] Arguably, the most common photo-responsive polymer systems in the past were based on spiropyranes,[15] on

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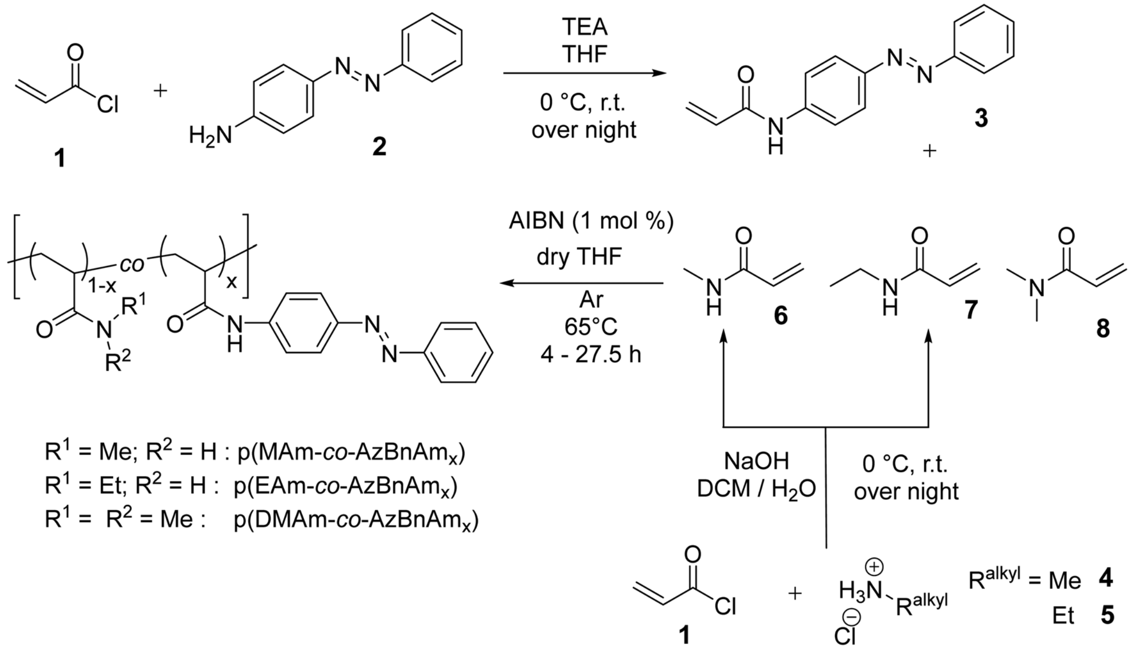
cinnamates,[16] and above all, on azobenzenes.[17] In the case of azobenzenes, the structural change is achieved through the photo-isomerization of the thermodynamically preferred *E*- ("*trans*") to the metastable *Z*-isomer ("*cis*") by near UV-light exposure. Since the *Z*-isomer disposes of a notable dipole moment in contrast to the *E*-form,[18] it is assumed that the polarity of the chromophore, and thus also the polymer as a whole, is increased as well. This is generally expected to reduce the hydrophobicity of the chromophore and thereby to result in increased transition temperatures after irradiation.[17,19–21]

One of the advantages of azobenzenes as photo-active moiety is that their *E*–*Z* isomerization is virtually free of side reactions and therefore fully reversible and without fatigue.[22] Yet in the past, the photo-induced shifts achieved were small, being typically in the order of 5 °C or even less,[17,20,21,23–30] with few exceptions, as *e.g.* 14 °C were reported by Menzel and coworkers.[31] The temperature shift is generally too small for a practical implementation of these systems. Moreover, the substantial spectral overlap of the absorption bands of the *E*-and *Z*-isomers of the dye at around 350 nm only allows for a partial *E*-to-*Z* isomerization in the photo-stationary state.[32] Obviously, this hindrance can aggravate the problem of the commonly observed small leverage effect of the azobenzene photo-switch. Still, incomplete *E*-to-*Z* isomerization cannot be the major factor as evidenced in recent studies using both thermo- and photo-responsive copolymers of *N*,*N*-dimethylacrylamide (DMAm) functionalized with 4-acryloyl-2,5,2′,5′-tetramethoxyazobenzene, whose *Z*- and *E*-isomers exhibit UV-vis spectra with distinct absorbance bands in the visible range. Although both isomers can be selectively excited, the changes of the photo-induced shifts of the phase transition temperature that could be realized were still well below 10 °C.[33] Another limitation of the azobenzene photo-switch results from the mostly quite fast thermal relaxation of the metastable *Z*-isomer to the thermodynamically preferred *E*-isomer.[34,35] Hence, for applications where bi-stable states of the chromophore are needed, azo dyes with prolonged half-lives ($t_{1/2}$) above several hours must be selected.

Anyhow, the effect of the azobenzene moiety in its different isomeric states on the solubility changes has not been fully understood so far, since even a counter-intuitive decrease of the T_{CP} in the *Z*-state was observed occasionally.[36–39] In fact, such an unexpected decrease of the T_{CP} upon irradiation was noted already more than two decades ago by Menzel and coworkers.[36] They reported that polyacrylamide copolymers with low (around 1.5–5 mol%) azobenzene contents showed the expected increase of T_{CP} after irradiation with UV-light, while the analogous copolymers with higher dye contents (5–8 mol%) underwent a decrease of T_{CP} after irradiation.[36] A similar observation was reported for water-soluble non-ionic polyacrylates bearing oligo(ethyleneoxide) side chains as hydrophilic moieties.[37] Again, the copolymers with low contents of azobenzene underwent the expected increase of T_{CP} after irradiation and subsequent *E*–*Z* isomerization, while those with higher dye contents suffered a decrease of T_{CP}. Still, the effects in this copolymer series were small, with photo-induced T_{CP} changes of less than 2 °C.[37] Also, Kaberov and coworkers reported counter-intuitive changes of T_{CP} upon irradiation for poly(2-oxazoline)s that were functionalized with azobenzenes, reaching from changes of a few degrees to almost none, with increasing azobenzene content.[38] Tribet and coworkers also reported a non-monotonous variation of T_{CP} for a set of azobenzene-functionalized polyacrylamides when increasing the dye content.[39] They attributed this behavior to the



Scheme 1 Monomer synthesis *via* acylation by acryloyl chloride **1** in THF, exemplified for azo dye aniline yellow **2** producing acrylamide AzBnAm **3**. Use of methyl or ethyl ammonium chloride **4** or **5** in a two-phase solvent mixture of CH_2Cl_2/H_2O yields acrylamides MAm **6** and EAm **7**, respectively.

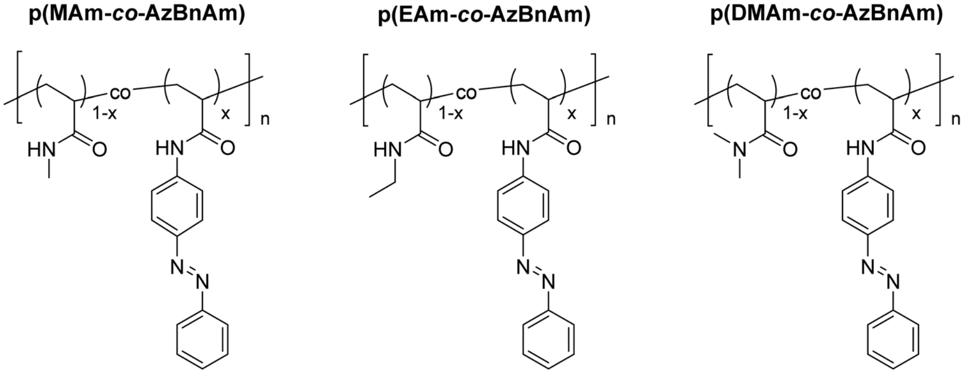


Fig. 1 Chemical structure of the investigated acrylamide copolymers ($0 \leq x \leq 0.2$).

partial shielding of the azobenzene residues in the *E*-form by aggregation, thereby (over)compensating the polarity difference of shielded azobenzenes in the *E*-form *vs.* the non-aggregated *Z*-form.[39]

In this context, we synthesize three series of azobenzene-functionalized water-soluble non-ionic polymers from the azo dye-functionalized monomer 4-acrylamido azobenzene (AzBnAm **3**, *cf.* Scheme 1) and comonomers *N*-methyl acrylamide (MAm), *N*-ethyl acrylamide (EAm), or *N*,*N*-dimethyl acrylamide (DMAm) (Fig. 1), and investigate their photo-modulated solubility in aqueous solution with turbidimetry, spectroscopically, and with dynamic light scattering. A single copolymer p(DMAm-*co*-AzBnAm) was reported in an early study for photo-switching the activity of a conjugated enzyme,[40] for which a counter-intuitive decrease of the LCST-transition in the *Z*-state was described. Remarkably, the analogous copolymers p(DMAm-*co*-AzBnA) made from DMAm and 4-acryloyloxy azobenzene (AzBnA), *i.e.* of the acrylic ester analog of AzBnAm, however, showed an increase of the LCST-transition in the *Z*-state, as expected.[31,40]

Experimental

Materials and methods

Materials. Tetrahydrofuran (THF, stabilized by 2,6-di-*tert*-butyl-*p*-cresol (BHT), purity >98.0%) was treated by CaH_2 for simultaneous drying and removing the antioxidant stabilizer as well as any hydroperoxide possibly formed. Shortly before use, it was distilled and kept in the dark under an argon atmosphere. *N*,*N*-Dimethyl acrylamide (DMAm, >98.0%, stabilised with 4-methoxyphenol, TCI) was filtered through aluminium oxide (AlOx, activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å, Sigma-Aldrich) to remove the inhibitor. Acryloyl chloride (>96.0%, stabilised with phenothiazine, Merck Millipore) was distilled to remove the inhibitor. Azobisisobutyronitrile (AIBN, >98%, Fluka) was recrystallized from methanol. Methyl ammonium chloride (>98.0%, Fluka), ethyl ammonium chloride (>98.0%, Sigma-Aldrich), triethylamine (TEA, >99.7%, Acros), 4-amino azobenzene (aniline yellow, >98.0%, TCI), and sodium hydroxide (>98.8%, Chemsolute) were used as received. Methanol (technical grade) and dichloromethane (DCM, CH_2Cl_2, technical grade) were distilled prior to use. Water for purification and sample preparation was deionized *via* reverse osmosis (electrical conductivity <1 μS cm^{-1}).

Nuclear magnetic resonance (NMR) spectra were recorded on the spectrometer Bruker Avance Neo 400 MHz. The spectra were evaluated with the software Topspin, version 4.07. The chemical shifts δ are given in ppm. Spectra were recorded in deuterated water (D_2O), methanol (CD_3OD), dimethyl sulfoxide (DMSO-d_6), or chloroform ($CDCl_3$), purchased from VWR Chemicals (99.8% D) and used as received. The residual proton signal of the used solvent or, respectively, its ^{13}C signal was used to calibrate the ^1H and ^{13}C NMR spectra. The ^{13}C NMR spectra were recorded proton decoupled.

UV-vis and turbidimetry measurements were made on a dual beam spectrometer model Carry 500 (Agilent). Samples for turbidimetry (concentration = 1 g L^{-1} in deionized water) were prepared at least 1 day before the measurements and stored at ambient temperature in the dark. Samples were heated at a rate of 0.5 K min^{-1}, and the transmission at 600 nm was recorded every 0.25 K. The cloud point temperature (T_{CP}) is defined as the onset temperature of the decay of the transmission.

Irradiations set-ups: all UV-irradiations were carried out with a UV flashlight Alonefire SV47 12 W 365 nm (Shenzhen Shiwang Technology Co. Ltd, Shenzhen/China). The samples were irradiated with an irradiance of 200 mW cm^{-2} as determined by an optical power meter PM100D with a sensor S170C (Thorlabs, Newton/USA). Green light irradiations were performed on a home assembled set-up with a high-power LED (3 W, type 700 mA) on an aluminum heat sink connected with to the power socket *via* a step down converter to regulate the current for the LED. The set-up was acquired from led-and-more.de (Berlin/Germany).

Dynamic light scattering (DLS) measurements were carried out using an LS spectrometer (LS Instruments, Fribourg, Switzerland) consisting of a solid state laser (Thorlabs, Dachau, Germany) with a wavelength of 660 nm and a maximum power of 100 mW, a goniometer and two avalanche photodiode detectors, where the wavelength of 660 nm is not expected to induce the *E*–*Z* switch using the absorption spectra in Fig. 3. Modulated 3D cross-correlation mode was used to reduce possible multiple scattering effects.[41] The solutions were placed in cylindrical glass cuvettes with an outer diameter of

5 mm and a wall thickness of 0.4 mm, and the cuvettes were located in an index matching bath, filled with decalin and connected to a JULABO F32 thermostat (JULABO Labortechnik GmbH, Seelbach, Germany). Temperature-dependent DLS measurements were performed at a scattering angle of 130° from 15 °C to 45 °C, with 1 °C intervals for both copolymers, both before and after irradiation, respectively. The temperature was equilibrated for 3 min before each measurement. Each measurement lasted 30 s and was repeated 5 times at each temperature.

The intensity autocorrelation functions $G_2(\tau) - 1$ were analyzed using the REPES algorithm in the Gendist software,[42,43] calculating the intensity-weighted distribution functions of hydrodynamic radii R_h. They are given in the equal area representation, $R_hA(R_h)$ *vs.* log R_h.[42]

Size exclusion chromatography (SEC) was conducted with a home-assembled apparatus equipped with an isocratic pump (Thermo Fischer Scientific, Dreieich/Germany) and a refractive index detector (Shimadzu RID-6A, Shimadzu Corporation, Kyoto/Japan), a GRAM-precolumn (10 μm 8 × 50) and a main column GRAM-linear (7 μm 8 × 300 mm) from Polymer Standard Solutions PSS (Mainz/Germany). *N*-Methyl-2-pyrrolidone (with 0.5% LiBr) was the eluent, calibration by narrowly molar mass distributed polystyrene.

SEC with water as eluent was conducted with the addition of 0.1 M NaCl and 0.3 vol% of formic acid. Measurements were performed at a flow rate of 1 mL min^{-1} at 40 °C. The stationary phase was a 300 × 8 mm^2 PSS NOVEMA Max column. Measurements were executed with synchronous UV and RI detection. Samples were filtered through 0.45 μm polytetrafluoroethylene filters (Carl Roth, Karlsruhe/Germany) with an injected volume of 100 μL. Polyvinylpyrrolidone standards (PSS, Mainz/Germany) were used for calibration.

Synthesis of 4-acrylamido azobenzene (AzBnAm, **3**): in a 500 mL round bottom flask 8.01 g (40.6 mmol, 1.00 eq.) of 4-amino azobenzene **2** and 4.93 g (48.7 mmol, 1.20 eq.) of TEA were dissolved in 300 mL of THF and cooled with an ice bath. 4.43 g of acryloyl chloride **1** (48.95 mmol, 1.20 eq.) in 40 mL of THF were added dropwise over 45 min. Then the reaction mixture was allowed to warm to room temperature and stirred overnight. The precipitated TEA hydrochloride was filtered off, and the filtrate concentrated under reduced pressure. The crude product was purified by recrystallization from CH_2Cl_2 to yield monomer AzBnAm **3** as an orange solid (5.19 g, 51%). ^{1}H NMR (400 MHz), deuterated (DMSO-d$_6$, 298 K): δ = 10.52 (1H, NH), 7.90–7.84 (6H, m, H$_{aryl}$ *ortho*-position), 7.57 (3H, m, H$_{aryl}$ *meta* + *para* positions), 6.53 (1H, m, ═CH–), 6.35 (1H, m, ═CH$_Z$), 5.82 (1H, m, ═CH$_E$) ppm. ^{13}C NMR (400 MHz, DMSO-d$_6$, 298 K): δ = 163.59, 152.08, 147.79, 142.16, 131.63, 131.11, 129.45, 127.75, 123.77, 122.41, 119.69 ppm (Fig. S2 and S3, ESI†).

Synthesis of *N*-methyl acrylamide (MAm, **6**): In a 1 L Erlenmeyer flask, 10.0 g (148.1 mmol, 1.00 eq.) of methyl ammonium chloride **4** in 40 mL of distilled water were mixed with 370 mL of CH_2Cl_2 and stirred vigorously. After adding 12.4 g (318 mmol, 2.15 eq.) of NaOH dissolved in 80 mL of distilled water, the mixture was placed in an ice bath. 13.81 g of acryloyl chloride **1** (152.6 mmol, 1.03 eq.) in 130 mL of CH_2Cl_2 were added dropwise over 30 min. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. The phases were separated, and the aqueous phase extracted with CH_2Cl_2 (4 times with 40 mL portions). The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure. MAm **6** is obtained as colorless viscous liquid (9.85 g, 78%). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ = 6.69 (1H, br, NH), 6.1–6.3 (2H, m, ═CH$_E$ + ═CH–), 5.59 (1H, m, ═CH$_Z$), 2.85 (3H, m, –CH$_3$) ppm. ^{13}C NMR (400 MHz, CDCl$_3$, 298 K): δ = 166.65, 130.92, 125.84, 26.26 ppm (Fig. S4 and S5, ESI†).

Synthesis of *N*-ethyl acrylamide (EAm, **7**): in a 1L Erlenmeyer flask, 10.01 g (122.76 mmol, 1.00 eq.) of ethyl ammonium chloride **5** in 135 mL of distilled water were mixed with 300 mL of CH_2Cl_2 and stirred vigorously. Then, 10.56 g (263.93 mmol, 2.15 eq.) of NaOH in 140 mL of distilled water were added and the mixture cooled down with an ice bath. 11.58 g of acryloyl chloride **1** (128 mmol, 1.04 eq.), in 100 mL of CH_2Cl_2, were added dropwise over 1 h. The ice bath was removed, the reaction mixture allowed to warm up to ambient temperature, and stirred overnight. The phases were separated and the aqueous phase extracted with CH_2Cl_2 (thrice with 150 mL portions). The combined organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by vacuum distillation at 140 °C. To prevent premature polymerization, 60 mg of hydroquinone were added to the crude product prior to the distillation. Monomer EAm **7** is obtained as colorless viscous liquid (9.61 g, 79%). ^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K): δ = 8.08 (1H, br, NH); 6.15 + 6.07 (2H, m, H$_2$C═); 5.56 (1H, m, ═CH–); 3.14 (2H, m, –CH$_2$–), 1.03 (3H, t, –CH$_3$) ppm. ^{13}C NMR (400 MHz, DMSO-d$_6$, 298 K): δ = 164.45, 131.93, 124.81, 33.48, 14.65 ppm (Fig. S6 and S7, ESI†).

General procedure for the copolymerization of *N*-alkyl acrylamides with AzBnAm **3**: in a typical procedure, the specific *N*-alkyl acrylamide, varying amounts of the functional comonomer AzBnAm **3**, and 1 mol% of AIBN (regarding the sum of both monomers) were placed in a dry 10 mL Schlenk tube with septum, and dissolved in purified THF to produce a 2 mol L^{-1} solution. The solutions were purged by argon to remove oxygen, and the vessel was immersed into a preheated oil bath of 65 °C for a specified amount of time while continuous stirring the reaction mixture. The conversion was checked regularly by taking samples from the active polymerization and measuring the consumption of the monomers by ^{1}H NMR spectroscopy *via* the signal decay of the acrylic protons. After the polymerization, a last NMR sample was taken to quantify the final conversion. Then, air was allowed to enter the reaction vessel, and the mixture was cooled to ambient temperature. The polymerization mixture was precipitated into the 10-fold volume of diethyl ether or *n*-pentane. The precipitated crude polymer was isolated by filtration. It was purified by repeated dissolution in THF and precipitation into the non-solvent until no more acrylic proton signals from residual monomers were detected in the ^{1}H NMR spectra. Table 1 compiles the polymers synthesized.

Results and discussion

Monomer and polymer synthesis

The monomers *N*-methyl acrylamide (MAm, **6**), *N*-ethyl acrylamide (EAm, **7**), and 4-acrylamido azobenzene (AzBnAm, **3**) were prepared in one step from commercially available chemicals (*cf.* Scheme 1). Their ^{1}H and ^{13}C NMR spectra were in agreement with the ones reported in literature.[44–46]

All polymers were produced *via* free radical polymerization in purified dry THF at 65 °C, using AIBN as initiator. Their key molecular data are summarized in Table 1. For the copolymer series made, we observe that the polymerization rates decrease with increasing content of azobenzene monomer in the reaction mixture. This is illustrated exemplarily for the conversion of the three copolymerizations of EAm with varying amounts of AzBnAm (Fig. 2). Similar retardation effects have been often noted when copolymerizing azobenzene-functionalized monomers, but the causes of this phenomenon are not yet fully understood.[31,47–49]

While the homopolymerization of EAm **7** reached a conversion of 90% within 2 h, only 1 mol% of AzBnAm **3** in the monomer feed increased the needed time to over 6 h, and 5 mol% of **3** even further to over 22 h. This effect drastically prolongs the necessary reaction time. However, the resulting molar masses of the polymers and their dispersity seem to be mostly not affected. Even a slightly increased apparent molar mass for azobenzene-enriched polymers is observed (*cf.* Table 1). Still, this trend might be an apparent one, resulting from the changing solvent quality of the eluent when the content of the hydrophobic azodye in the copolymers increases.

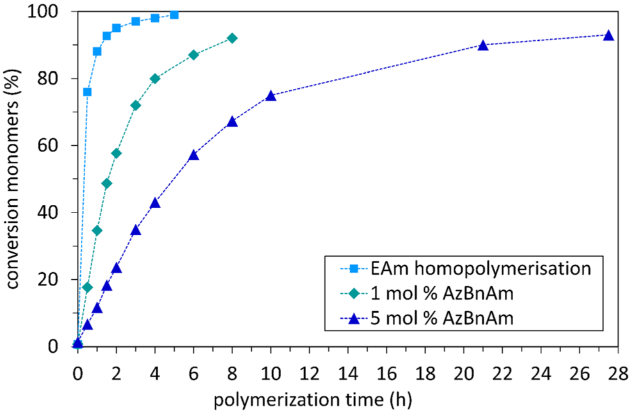


Fig. 2 Conversion over time for homo- and copolymerization of EAm **7** with varying molar amounts of AzBnAm **3**: reaction mixture devoid of **3** (■), containing 1 mol% of **3** (♦), and containing 5 mol% of **3** (▲). Conversions are determined *via* the decay of the acrylic proton signal intensity in the ^{1}H NMR spectra. The dotted lines are meant to guide the eye.

Spectral properties of the copolymers in solution

Crucial features of a photo-switch based on azo chromophores are the ratio the *E*-isomer (*trans*) to the *Z*-isomer (*cis*) ($E:Z$) achieved after irradiation with UV-light, as well as the half-life of the metastable *Z*-isomer. The $E:Z$ ratio defines the extent to which the system can be switched and is a measure for the magnitude of the polarity change that can be induced, which is assumed to modulate the water solubility. The half-life ($t_{1/2}$) of the *Z*-isomer is another key parameter of such photo-responsive polymers, as it defines the timescale for which the photo-induced isomerization enables the implementation of a bi-stable switching system, or whether photo-switching to the *Z*-isomer is only possible under permanent irradiation. From an application point of view, the former scenario has been the most attractive. Yet, the thermal relaxation of the *Z*-state of most azobenzenes is relatively fast. The half-lives in solution are often shorter than 1 h, often only in the order of minutes or

Table 1 Overview on the homopolymers and copolymers made from the azobenzene-functionalized acrylamide **3** (AzBnAm), and *N*-methyl acrylamide (MAm, **6**), *N*-ethyl acrylamide (EAm, **7**), or *N*,*N*-dimethyl acrylamide (DMAm **8**). The polymer names follow a systematic scheme, coded as p(YAm) and p(YAm-*co*-AzBnAm$_x$), where Y indicates the *N*-substitutent of the *N*-alkyl acrylamides (M = methyl, E = ethyl, DM = dimethyl), and *x* indicates the mol% of azo dye (AzBnAm **3**) incorporated. Copolymerizations were conducted in 2 mol L^{-1} solutions in THF at 65 °C, using 1 mol% of AIBN as initiator. The table summarizes the apparent number average molar mass M_n^{app}, polymer dispersity *Đ*, and average molar content *x* of AzBnAm incorporated in the copolymers

Code	AzBnAm in feed [mol%]	Polymerization time [h]	Monomer conversion[a] [%]	M_n^{app}[b] [kg mol^{-1}]	*Đ*[b]	Dye content in copolymer[c] [mol%]
p(MAm)	0	4	100	2.3[d]	3.0[d]	—
p(MAm-*co*-AzBnAm$_{4.5}$)	4	4	n.d.[e]	18	1.9	4.5 ± 0.5
p(MAm-*co*-AzBnAm$_{8.0}$)	7	4	n.d.[e]	16	1.8	8.0 ± 0.8
p(MAm-*co*-AzBnAm$_{11.5}$)	10	4	34	15	1.9	11.5 ± 1.2[f]
p(EAm)	0	5	98	13	2.5	—
p(EAm-*co*-AzBnAm$_{1.0}$)	1	8	92	32	1.7	1.0 ± 0.5
p(EAm-*co*-AzBnAm$_{5.0}$)	5	27.5	93	30	1.9	5.0 ± 0.5
p(DMAm)	0	4.5	100	19	2.0	—
p(DMAm-*co*-AzBnAm$_{2.0}$)	2	5	89	17	2.3	2.0 ± 0.5
p(DMAm-*co*-AzBnAm$_{5.0}$)	5	5	82	17	2.3	5.0 ± 0.5
p(DMAm-*co*-AzBnAm$_{9.0}$)	9	6.5	46	21	1.7	9.0 ± 0.9
p(DMAm-*co*-AzBnAm$_{11.5}$)	13	6.5	52	21	1.5	11.5 ± 1.2
p(DMAm-*co*-AzBnAm$_{15.5}$)	15	6.5	48	23	1.6	15.5 ± 1.6[f]

[a] Determined by ^{1}H NMR in the reaction mixture (decay of the signal of the acrylic protons). [b] Determined for the purified copolymers by SEC in *N*-methyl-2-pyrrolidone, calibration by polystyrene standards. [c] Precision ± 10 rel%, but not better than ±0.5 mol% for low contents of azo dye (determined by ^{1}H NMR). [d] Determined by aqueous SEC, calibration with poly(*N*-vinylpyrrolidone) standards. [e] Not determined. [f] Copolymer is not soluble at a concentration of 1 g L^{-1} in water.

even less, and depend sensitively on the chemical nature of the substituents and their substitution pattern.[32]

For the monomer dye AzBnAm **3**, both characteristics were studied *via* ^{1}H NMR. While storage in the dark in DMSO for several days allows for achieving the clean *E*-isomer, *i.e.*, an *E*:*Z* ratio of 100:0 before irradiation, the ratio *E*:*Z* changes to 21:79 in the photo-stationary state after UV irradiation at 365 nm. Although the *Z*-state is reached in majority, the system cannot be fully switched from *E* to *Z*. Similarly, the irradiation with green light (λ = 525 nm) induces an *E*:*Z* ratio of 75:25 in the photo-stationary state. Thus, for the reverse isomerization from the *Z*- to the *E*-form, again, the isomer is formed in the majority, but not completely. According to this qualitatively expected finding, the only partial *E*–*Z* switching of the dye leaves an appreciable percentage of the potential of the polarity switch unutilized. This limitation is due to the spectral overlap of the *E*- and *Z*-isomer absorption maxima at around 350 nm, rendering a selective excitation of one of the states impossible (*cf.* Fig. S27, ESI†). The corresponding NMR spectra are displayed in the ESI† (*cf.* Fig. S2, S8 and S9, ESI†). The half-life of the chromophore in the water-insoluble dye monomer **3** is determined as $t_{1/2}$ = 38 h at 20 °C in DMSO-d$_6$, which had to be used because of the low solubility of the monomer in water or methanol (*cf.* Fig. S1, ESI†).

In the case of the water-soluble copolymers, the *Z*-to-*E* thermal relaxation is accelerated, and the half-life of the chromophore is reduced to about 12 h, as illustrated in Fig. 3.

The recovery of the *E*-state of the azo chromophore is shown exemplarily for copolymer p(DMAm-*co*-AzBnAm$_{9.0}$). Being around 12 h, the half-life falls below the value determined for the low molar mass dye but is still sufficiently high to serve as a photo-switch for many purposes. The faster relaxation of the *Z*-state may be caused either by water being the more polar solvent than DMSO, or by the anchoring of the dye to a polymer chain. Nevertheless, the half-life in the polymers is still sufficiently long for single irradiation experiments over several hours, such as measurements of the T_{CP}. Note that Fig. 3 suggests that the photo-isomerization between the *E*- and *Z*-isomers occurs cleanly without side reactions, according to the three isosbestic points seen at 244, 300 and 410 nm. Also, no differences in the absorption spectra are observed between the azobenzene bearing polymer in water and the azobenzene bearing monomer in methanol (*cf.* Fig. S27, ESI†).

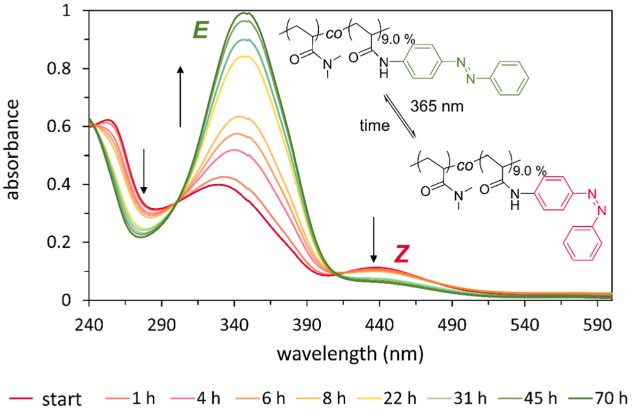


Fig. 3 Evolution of UV-vis-spectra of p(DMAm-*co*-AzBnAm$_{9.0}$) in water (0.03 g L^{-1}) after irradiation at 365 nm (LED) for 15 min, when annealing in the dark at 20 °C. The band marked by the red "*Z*" indicates the majority *Z*-state system present directly after irradiation. The band labeled by the red "*Z*" indicates the absorption of the majority *Z*-state system present directly after irradiation. The band labeled by the green "*E*" indicates the system in the *E*-state, which evolves gradually over time due to the thermal back isomerization. The arrows highlight the accompanying changes in the absorbance spectra, *i.e.*, the reduction of the absorption bands at *ca.* 250 and *ca.* 440 nm of the *Z*-state, and the increase of the main absorption peak of the *E*-isomer at about 350 nm over time.

Aqueous phase behavior followed by turbidimetry

The specific *N*-alkyl acrylamide monomers **6**–**8** were chosen since their homopolymers show high lying LCSTs, in the case of DMAm and MAm far above 100 °C,[10] as the bulky hydrophobic azo dye to be incorporated is expected to markedly reduce the T_{CP} of the copolymers. For instance, copolymers of AzBnAm **3** with *N*-isopropyl acrylamide were only water-soluble for dye contents below 5 mol%.[17] The cloud point temperature T_{CP} of the various copolymers (*cf.* Fig. 1), measured after storage in the dark for one day (majority *E*-state), confirm our expectations (Fig. 4). While the high T_{CP}-values of the p(MAm) and p(DMAm) homopolymers imply that also their copolymers with a low chromophore content (here below 5 mol%) do not exhibit a cloud point below 85 °C, this behavior changes for low-to-moderate azobenzene contents. In fact, the decrease of the T_{CP} with increasing content of AzBnAm **3** is so steep that when copolymerizing the dye monomer with the highly hydrophilic **6** or **8**, copolymers with contents of 13 mol% or more of **3** are no longer soluble in water. In the case of copolymers derived from EAm **7**, even lower azo dye contents (>6 mol%) yield water-insoluble polymers. In agreement with the literature discussed,[19,21] this reduces the useful compositional spread of the copolymers, and reveals how narrow the window of opportunity is for incorporating such a type of photo-switch.

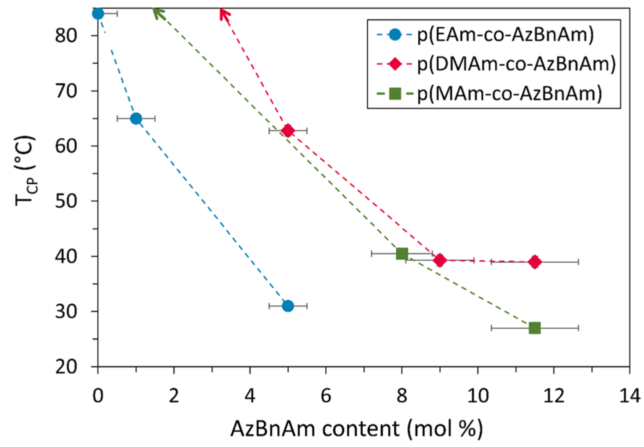


Fig. 4 Evolution of the cloud points of *N*-alkyl acrylamide copolymers functionalized with AzBnAm **3** before irradiation in water (1 g L^{-1}): reduction of the T_{CP} with increasing amounts of azodye monomer in the copolymers with EAm **7** (●), DMAm **8** (♦), or MAm **6** (■). The arrows for the DMAm and MAm copolymer sets indicate T_{CP} values over 85 °C.

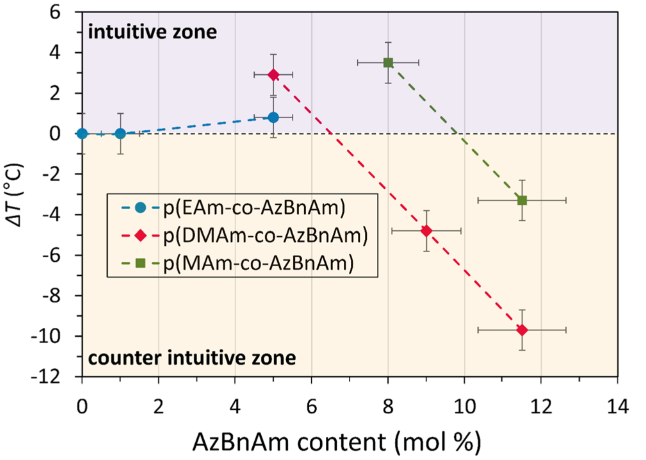


Fig. 5 Shifts of the cloud point temperatures ΔT of azodye functionalized *N*-alkyl acrylamide copolymers in water (1 g L^{-1}) upon irradiation by 365 nm light for 15 min for copolymer series p(EAm-*co*-AzBnAm$_x$) (●), p(DMAm-*co*-AzBnAm$_x$) (♦), and p(MAm-*co*-AzBnAm$_x$) (■). The shift of the cloud points ΔT shown is defined as the difference between T_{CP} after irradiation at 365 nm (*i.e.*, majority *Z*-isomer) and T_{CP} before irradiation (*i.e.*, majority *E*-isomer), and is plotted as function of the AzBnAm content in the polymers. The broken lines are meant to guide the eye.

When irradiating the polymers in aqueous solution by near UV-light, the three copolymer series exhibit characteristic differences in their phase behavior (Fig. 5). While for the copolymers p(EAm-*co*-AzBnAm), hardly any effect of the irradiation on the T_{CP} is observed, the copolymers of MAm and DMAm undergo marked irradiation effects that follow the same qualitative behavior. Low amounts of incorporated azobenzene induce a small increase of the T_{CP} (ΔT), by around +3 °C upon irradiation and concomitant *E*-to-*Z* photo-isomerization, thus showing the expected direction of the shift of the T_{CP}. Yet, for both the copolymers with higher azobenzene contents, the shift direction of the T_{CP} is inverted, *i.e.*, T_{CP} decreases after the *E*-to-*Z* photo-isomerization took place. Most interestingly, in the case of p(DMAm-*co*-AzBnAm$_{11.5}$), we achieve the biggest change of ΔT of up to -10 °C (Fig. 5), far bigger than the common T_{CP} changes reported in the literature when irradiating water-soluble polymers that bear various types and amounts of azobenzenes.

The observed inversion of the shift direction upon irradiation suggests that the generally accepted polarity change of the chromophore in the *E*- *vs.* the *Z*-state can be neither the only, nor necessarily the dominating driving force for the photo-modulated water-solubility of the copolymers. Tribet and coworkers for instance also reported a change from an intuitive to a counter-intuitive evolution of ΔT for copolymers with increasing contents of azobenzenes upon irradiation.[39] From the analysis of their UV-vis spectra, they deduced an aggregation of the chromophores in the *E*-state for the polymers with relatively high dye contents, that may minimize the azobenzene's exposure to the surrounding water.[39] This behavior (as sketched in Fig. 6) may reduce the hydrophobic impact of the *E*-isomer, so that when aggregated, the *E*-isomer effectively lowers the LCST transition of the polymer less than the *Z*-isomer does in the isolated state. Nevertheless, the *E*-isomer is less polar and thus more hydrophobic than the *Z*-isomer as individual moiety.

In fact, similar arguments were put forward to explain that T_{CP} of hydrophobically end-capped poly(*N*-isopropyl-acrylamide), poly(NIPAM) passes through a minimum with increasing hydrophobicity of the end group(s), but eventually reaches again the value of the unmodified homopolymer for strongly hydrophobic ends.[50,51] Since such an aggregation influences the energetic state of the chromophores, aggregate formation is typically reflected by new absorbance bands or at least by characteristic shoulders in the UV-vis spectra.[39,52] Following this reasoning, we superpose the normalized main absorption peaks from the UV-vis spectra of the various copolymers of the p(DMAm-*co*-AzBnAm) series when isomerized in majority to the *E*-state. In contrast to the systems studied by Tribet and coworkers,[39] we observe only marginal differences between the shapes of the bands with increasing chromophore content (Fig. 7), *i.e.*, between the copolymers with a $T_{CP} > 85$ °C (2.0 mol%) and those showing intuitive (5.0 mol%) or counter-intuitive (9.0 and 11.5 mol%) changes of the T_{CP} upon *E*-to-*Z*-isomerization.

This suggests that the aggregation of the chromophores, if there is any, is virtually the same for all these polymers, even though the photo-modulation of the solubility within the copolymer series changes from an intuitive to a counter-intuitive behavior (*cf.* Fig. 5). While we cannot rigorously rule out an aggregation of the chromophores in the *E*-state -be it intermolecularly or intramolecularly- for our copolymers as well, it seems probable that, yet another mechanism/effect contributes to the unconventional modulation of the cloud points upon irradiation.

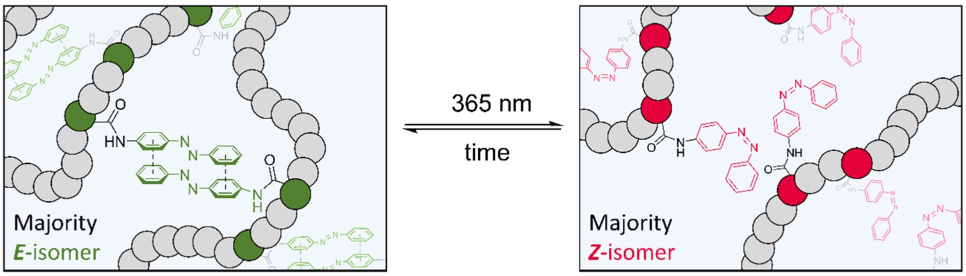


Fig. 6 Hypothetical explanation of the counter-intuitive cloud point modulation by aggregation of the azobenzene moieties in water in the *E*-, but not in the *Z*-state, *e.g.* due to π–π-stacking.

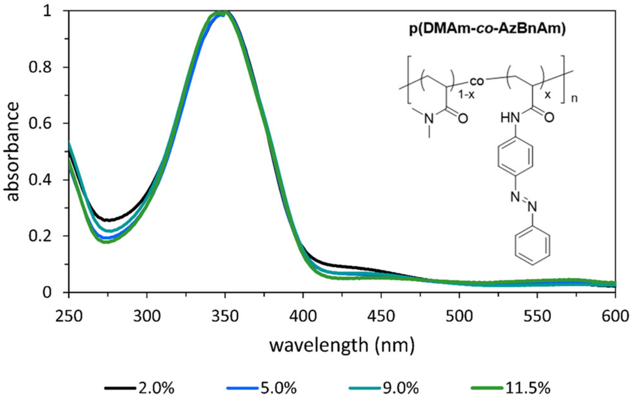


Fig. 7 Normalized UV-vis spectra of the copolymers of the p(DMAm-*co*-AzBnAm) series in water (0.03 g L^{-1}) before irradiation: p(DMAm-*co*-AzBnAm$_{2.0}$) (—, $T_{CP} > 85$ °C), p(DMAm-*co*-AzBnAm$_{5.0}$) (—) with intuitive change, and p(DMAm-*co*-AzBnAm$_{9.0}$) (—) and p(DMAm-*co*-AzBnAm$_{11.5}$) (—) both with counter-intuitive changes of T_{CP} upon *E*-to-*Z*-isomerization.

Self-assembly behavior analyzed by temperature-resolved dynamic light scattering (DLS)

To further clarify the postulated shielded aggregation of the chromophores, we perform DLS measurements to determine the hydrodynamic radii of the chains, R_h, and to detect possible association of the polymer chains. The DLS studies were exemplarily performed for a pair of water-soluble copolymers based on MAm **4**, namely p(MAm-*co*-AzBnAm$_{8.0}$) and p(MAm-*co*-AzBnAm$_{11.5}$). These copolymers have a similar cloud point shift, but with either an intuitive shift ΔT of +3.5 °C of T_{CP} for p(MAm-*co*-AzBnAm$_{8.0}$), or a counter-intuitive shift ΔT of −3.3 °C for p(MAm-*co*-AzBnAm$_{11.5}$). Furthermore, these two copolymers have comparable apparent molar masses (16 and 15 kg mol^{-1}), dispersities (1.8 and 1.9) and degrees of polymerization (164 and 144). Also, estimating the radius of gyration R_g using the equation of $R_g = a\sqrt{N/6}$,[53] where a is the monomer length and N is the number average degree of polymerization, both copolymers have similar R_g values of 1.3 nm and 1.2 nm, respectively. Hence, they are well-suited to analyze differences regarding the temperature-dependent behavior in aqueous solution.

The temperature-dependent DLS measurements for both copolymers are carried out both before and after UV irradiation. The intensity autocorrelation functions are shown in Fig. S28 in the ESI.† They exhibit two decays for all samples and at all temperatures, which we tentatively attribute to the diffusion of single chains (fast mode) and to large associates (slow mode). At certain temperatures, *i.e.*, 40.5 and 43.5 °C for the *E*- and *Z*-states of p(MAm-*co*-AzBnAm$_{8.0}$), respectively, and 29.5 and 23.5 °C for the *E*- and *Z*-states of p(MAm-*co*-AzBnAm$_{11.5}$), the amplitude of the slow mode increases abruptly. These temperatures are similar to the T_{CP} values from turbidimetry (*cf.* Fig. 4 and 5). A significant fraction of large associates is at the origin of the turbidity above T_{CP}. Below the transition temperature, the slow mode is rather weak for p(MAm-*co*-AzBnAm$_{8.0}$) in both, the *E*- and the *Z*-states. In contrast, while it is also very weak for p(MAm-*co*-AzBnAm$_{11.5}$) in the *E*-state, it is stronger in the *Z*-state. *I.e.*, for this copolymer, irradiation affects the aggregation behavior.

The distribution functions of R_h obtained from the autocorrelation functions by numerical inverse Laplace transformation are displayed in Fig. 8. They show consistently two peaks in the range of a few nm and a few 100 nm. Their areas reflect the behavior observed for the amplitudes of the decays in the autocorrelation functions.

The resulting average R_h-values determined from the two peaks are shown in Fig. 9. For both states of p(MAm-*co*-AzBnAm$_{8.0}$), the system shows smaller particles of R_h around 7 nm. After the temperature was increased to 40.5 °C for the *E*-state and to 43.5 °C for the *Z*-state, the R_h values get smaller ($R_h \sim 6$ nm) due to the contraction of the single chains. Meanwhile, both states exhibit larger particles at around 150–200 nm below 40.5 °C, hinting at the formation of large associates. For the *E*-state, they grow gradually from 200 nm to 450 nm when the temperature is further increased above 40.5 °C, while the large associates stay almost unchanged for the *Z*-state until 45 °C. In contrast, for p(MAm-*co*-AzBnAm$_{11.5}$), both in the *E*- and *Z*-state, the smaller particles have an R_h value of 5.5 to 6 nm, which is smaller than for p(MAm-*co*-AzBnAm$_{8.0}$). The larger associates have sizes in the range of 200 to 400 nm for the *E*- and of 200–300 nm for the *Z*-state. Large associates are not observed for p(MAm-*co*-AzBnAm$_{11.5}$) up to 27 °C, which suggests that at such a high content of hydrophobic azobenzene, intramolecular association of the polymer chains prevails over their intermolecular association.[54] Comparing the R_h values of the small particles of both copolymers with the estimated R_g values of 1.3 nm and 1.2 nm for the single chains, the former are much larger than the latter by a factor of 4–5. The resulting low R_g/R_h ratios can be attributed to a self-assembled core–shell structure, where the azobenzene chromophores form compact cores due to hydrophobic interactions, while the copolymer backbones form a loosely packed shell.

The observed coexistence of single chains/small clusters and large associates even below T_{CP} and under dilute conditions is reminiscent of the one observed by DLS in dilute aqueous solutions of poly(*N*-isopropyl methacrylamide).[55] In contrast, only the diffusion of single chains was not observed in its analogue poly(NIPAM) lacking the hydrophobic methyl group on the backbone.[56,57] Hence, it seems that the hydrophobic groups are at the origin of this behavior.

We also verified the long-term stability of the polymer in an aqueous environment by testing whether the photo-modulated shifts of T_{CP} can be observed over several irradiation cycles or after extended storage. Hence, an aqueous solution (1 g L^{-1}) of the polymer p(DMAm-*co*-AzBnAm$_{11.5}$) is stored in the dark at 20 °C for 1 d after preparation, and the T_{CP} is measured before and after UV-light irradiation. Then, the sample is stored for 3 months under the same conditions, and the T_{CP} is measured again before and after irradiation. This procedure is repeated once more after an even more extended storage time of 21 months. Over these prolonged storages, we observe each time moderate but notable increases of the T_{CP} by about 2 °C in the *E*-state, *i.e.*, before irradiation, while the T_{CP} value is virtually

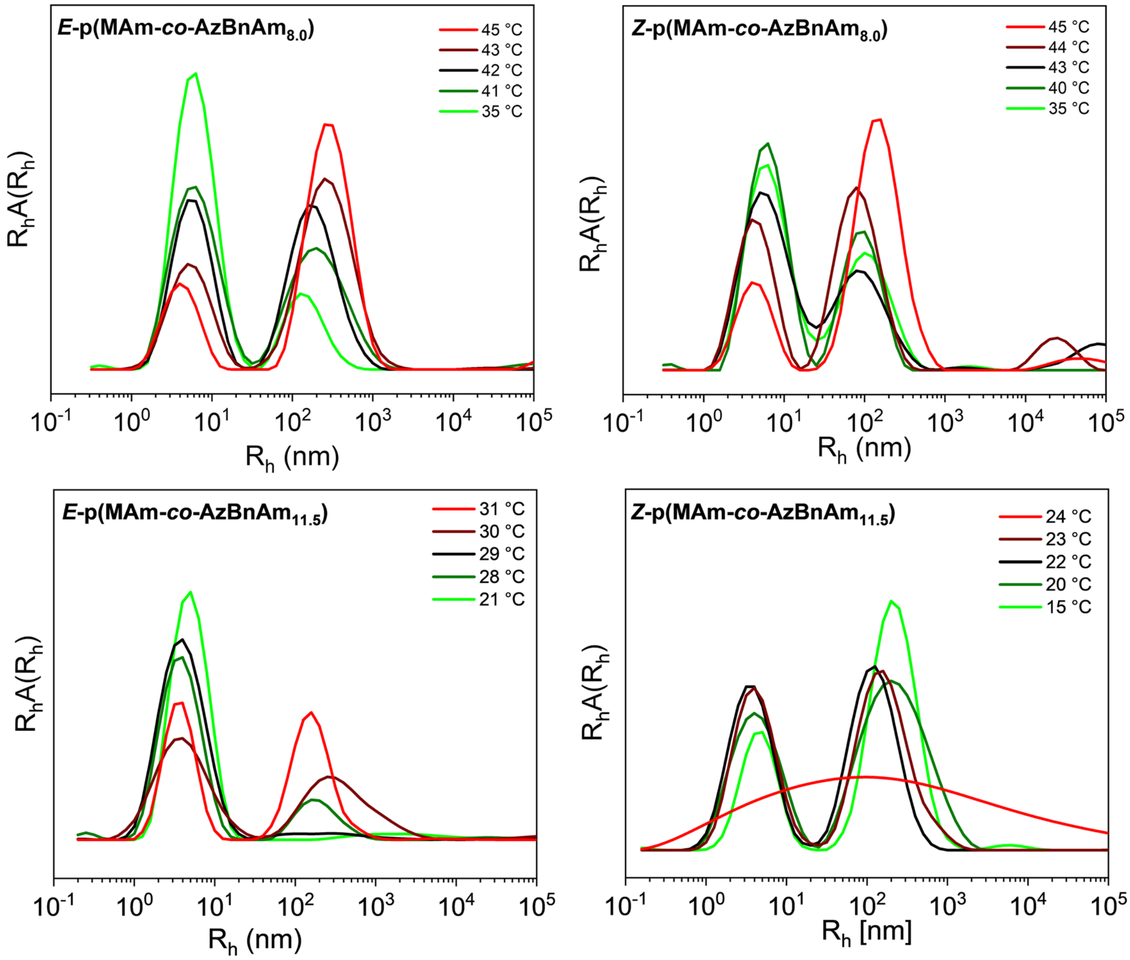


Fig. 8 Selected distribution functions of hydrodynamic radii from temperature-resolved DLS measurements on p(MAm-*co*-AzBnAm$_{8.0}$) in *E* and *Z*-states (top row) and p(MAm-*co*-AzBnAm$_{11.5}$) in the *E*- and the *Z*-state (bottom row) in water (1 g L^{-1}), displaying the particle size distribution at different temperatures.

preserved in the *Z*-state, *i.e.*, after irradiation, possibly increasing marginally after the very long storage time of 21 months. Given the constant behavior of the copolymers after irradiation (with the azobenzene moieties mostly in the *Z*-state), we conclude that under these conditions, neither hydrolytic cleavage of amide bonds occurs, thereby changing the overall hydrophilicity of the polymers, nor do we find any hint to hypothetical other decomposition reactions over time, or to photo bleaching due to

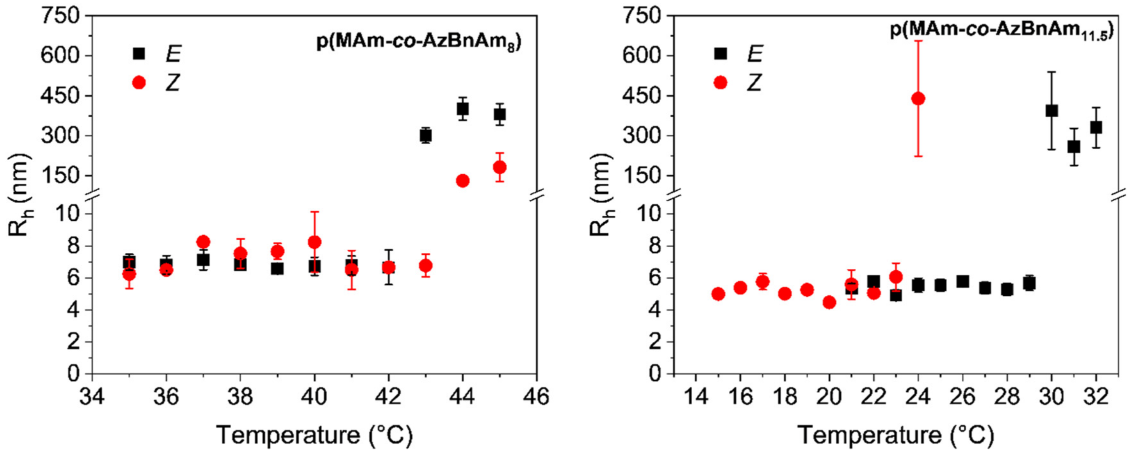


Fig. 9 Hydrodynamic radii R_h from DLS in dependence on the temperature for both the *E*- and *Z*-states of p(MAm-*co*-AzBnAm$_x$) copolymers (left: x = 8.0%, right: x = 11.5%) in water (1 g L^{-1}).

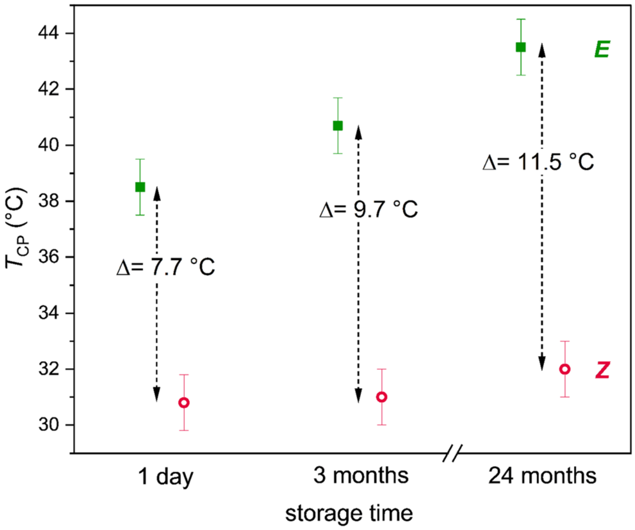


Fig. 10 Repeated photo-switching of p(DMAm-*co*-AzBnAm$_{11.5}$) dissolved in water (1 g L^{-1}). The sample is stored for 1 day in the dark at 20 °C, and T_{CP} is measured before and after irradiation at 365 nm (15 min). Subsequently, the sample is stored under the same conditions for 3 months before the experiment is repeated. Afterwards, the procedure is repeated once after a storage time of 21 more months.

the multiple irradiations. Any such hypothetical degradation process would have changed the values of T_{CP} and/or the shifts of T_{CP} after UV-light irradiation, which is not observed. The respective values of T_{CP} and the resulting values for ΔT are illustrated in Fig. 10.

In contrast to the data showing that T_{CP} after irradiation (red dots) remains virtually stable throughout all measuring protocols, T_{CP} before irradiation (green squares) increases somewhat with the prolongation of the storage time in the dark. As this favors the *Z*-to-*E* relaxation, the finding might indicate that annealing for 1 d is not sufficient for the system to fully relax thermally to the *E*-state, in agreement with the rather long half-life of the *Z*-isomer in the copolymers. Still, after 3 months of storage, virtually the full relaxation to the *E*-state should be achieved considering the outcome of the relaxation experiments as illustrated in Fig. 3. Therefore, the further increase of T_{CP} by another 2 °C after additional 21 months of storage in the dark is difficult to rationalize by a yet incomplete *Z*-to-*E* relaxation. Instead of this putative explanation, the effect might alternatively result from an ongoing slow aggregation of the azobenzene moieties in the *E*-state upon storage, thereby reducing their hydrophobic impact and thus, improving the polymer solubility in water.

Conclusions

Three series of non-ionic water-soluble copolymers with the azobenzene functionalized acrylamide AzBnAm are synthesized and analyzed with respect to their polymerization rate, the spectroscopic properties upon irradiation by near UV-light, and their behavior in aqueous solution. AzBnAm is found to decelerate the copolymerization with all three comonomers, *i.e.*, *N*-methyl acrylamide (MAm), *N*-ethyl acrylamide (EAm), and *N*,*N*-dimethyl acrylamide (DMAm). The retardation effect increases with the amount of azobenzene-functionalized monomer in the reaction feed. Yet, it is not clear if this known effect originates from the azobenzene moiety by itself, or whether trace impurities contained in the azobenzene-functionalized monomer are accountable for it. The azobenzene chromophore of AzBnAm can be photo-isomerized from the *E*-state to a majority *Z*-state (*E* : *Z* ratio 21 : 79) with 365 nm UV-light and shows a half-life for the thermal back relaxation of almost 40 h at 20 °C in DMSO. Also, for the copolymers of AzBnAm in aqueous solution, a rather extended half-life of about 12 h is observed, thus rendering the polymers *a priori* attractive for uses, where largely bi-stable states are aspired.

Regarding the temperature-dependent water solubility of the copolymers, the spectrum covers the full range, from complete water-solubility between 0–85 °C *via* the occurrence of a lower critical solution temperature (LCST) to complete insolubility. The useful window of functionalization by AzBnAm for the occurrence of a cloud point and its modulation is limited to moderate contents of the azobenzene chromophore due to the steep reduction of T_{CP} with the azobenzene content, presumably due to its marked hydrophobicity. Most interestingly, we find that T_{CP} may both increase or decrease after irradiation and concomitant *E*-to-*Z*-isomerization of the dye, depending on the precise chromophore content of the polymers. While copolymers with low amounts of azobenzene show the intuitively expected behavior that T_{CP} increases after irradiation, copolymers with low-to-moderate dye contents feature a reduction of the T_{CP} after irradiation, thus showing a counter-intuitive change of water-solubility. This effect is also reflected in temperature-resolved DLS measurements, which reveal that, at all temperatures and in both the *E*- and the *Z*-state, small clusters are formed by the chains, probably mediated by the hydrophobic azobenzene side groups. These coexist with large aggregates. Although our findings do not allow for an unambiguous explanation of the counter-intuitive change of copolymer solubilities upon photo-isomerization, the large decreases of the T_{CP} that can be achieved after irradiation even of simple azobenzene groups seem highly attractive for implementing effective photo-switching of smart, photo-responsive polymers. A priori, both marked increases or decreases of the polymer phase transition temperature represent useful tools for photo-triggered switching purposes.

Author contributions

The manuscript was written with the contributions of all authors. All authors approved the final version of the manuscript.

Data availability

The data supporting this article are included either in the manuscript text, or in the ESI† file.

Conflicts of interest

There are no conflicts to declare.

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