Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Femtosecond spectroscopy reveals huge differences in the photoisomerisation dynamics between azobenzenes linked to polymers and azobenzenes in solution

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Contents

S1. General

All commercially available compounds were purchased from Merck and Sigma-Aldrich and used without further purification. The purity of Disperse Red 1-methacrylate was checked by NMR spectroscopy. 4,4'-Bis(acetamido)azobenzene and 4,4'-bis(methacryloylamido)azobenzene were synthesised in a reaction known from literature between 4,4'-diaminoazobenzene and acetyl chloride and between 4,4'-diaminoazobenzene and methacryloyl chloride, respectively [S1, S2]. The purity was checked by NMR spectroscopy. Used solvents were dried according to standard procedures. NMR data were acquired with a Bruker AV-600 spectrometer. UV/VIS absorption spectra were taken on a Shimadzu UV-2401 desktop spectrometer. A light emitting diodes (Nichia) with emission maximum at 455 nm (NS4C107E, 400 mW) was used for the photoisomerisation experiments. The light intensity was attenuated to 150 mW. Dynamic light scattering (DLS) and static light scattering (SLS) measurements in water and in toluene were performed with an ALV 5000 E autocorrelator equipped with a red laser ($\lambda = 633$ nm; in some cases a blue laser with $\lambda = 473$ nm was used; due to dominant absorption, DR1 samples in organic media could only be measured reliably with the red laser). For DLS, the time-resolved signal of two single photon counting modules (SPCM-CD 2969; Perkin Elmer) was cross-correlated (sampling time ≈ 2 min) to obtain the intensity autocorrelation function. Hereby, the decay times τ of the field autocorrelation function (as obtained from the intensity autocorrelation function obtained by use of the Siegert relation [S3]) were extracted by the second-order cumulant analysis. The inverse of τ, the decay rate Γ, was plotted against the squared length of the scattering vector q^2. The slope gave the diffusion coefficient D and its value was transformed to the hydrodynamic radius R_h by the Stokes-Einstein equation. For SLS, the count rate at each angle was weighted with the scattering volume and corrected for solvent scattering to obtain the scattering intensity $I(q)$ and plotted against q (I in arbitrary units). A collection of the scattering data is given in Tablea S1 and S2. Form factor analysis provided the respective hard sphere radius R_{hs}. An exemplary form factor of P-BAAB-P (1:50) (Sample 2) is given in Figure S1. It indicates a narrow size distribution both in organic and aqueous dispersion.

S2. Syntheses of the azobenzene functionalised polymer colloids

Side- and main-chain azobenzene functionalised polymer colloids with a poly(butyl methacrylate) (PBMA) backbone and a cross-linking ratio of 1:10 for P-DR1 and 1:10 as well as 1:50 for P-BAAB-P were synthesised by radical co-polymerisation in surfactant-free emulsion polymerisation. All particles were synthesised twice following slightly different variants.

S2.1. First synthesis variant for P-DR1 (1:10) and P-BAAB-P (1:10 and 1:50) (Sample 1)

All particles were synthesised in the same way. The different concentrations of monomer, cross-linker and respective co-monomer are given in Table S1.

Table S1: Ratios of monomer (butyl methacrylate), cross-linker (ethylene glycol dimethacrylate) and co-monomer (Disperse Red 1-methacrylate or 4,4-bis(methacryloylamido)azobenzene) used for the radical copolymerisation in surfactant-free emulsion polymerisation.

	monomer	cross-linker	co-monomer
P-DR1 (1:10)	42 mmol (6 g)	4.2 mmol (0.83 g)	0.42 mmol (0.16 g)
P-BAAB-P (1:50)	42 mmol (6 g)	0.42 mmol (0.083 g)	0.42 mmol (0.13 g)
P-BAAB-P (1:10)	42 mmol (6 g)	3.78 mmol (0.74 g)	0.42 mmol (0.13 g)

Typical synthesis procedure: Butyl methacrylate (BMA), ethylene glycol dimethacrylate (EGDMA) and the respective co-monomer were dissolved in 30 ml acetone in order to solubilise the azobenzene derivative in the mixture. This mixture was added under nitrogen and under stirring to 150 ml of deionised water, which was heated to $\vartheta = 80\,^{\circ}\mathrm{C}$. Not fully dissolved dye was then fully soluble in the monomer droplets. Potassium peroxodisulfate (KPS, 0.10 g) was dissolved in 5 ml of deionised water and then injected to the heated monomer mixture. After 1 h the same amount of radical starter was added to the reaction mixture again to complete the polymerisation. The course of the reaction was followed by DLS measurements. The polymerisation was stopped after about 3 h. Afterwards, formed aggregates were removed by filtration. The filtrate was centrifuged and redispersed in acetone. The filtration/redispergation was repeated a few times in order to remove unreacted monomer until the supernatant was colourless. Then the particles were redispersed in dioxane. Finally this dioxane dispersion was freeze-dried. A small part of the acetone dispersion was diluted then dialysed against water to measure the hydrodynamic radius and the radius of gyration in the collapsed state after further dilution. To measure the hydrodynamic radius in the swollen state a small amount was swollen in toluene. The results of the light scattering measurements are shown in Table S2.

Table S2: Sample 1: Hydrodynamic radii (R_h) and hard sphere radii (R_{hs}, obtained from the first minimum of the form factor) in water (aq) and in toluene (tol). Due to a limited q range the form factor minimum could not be reached for all samples. Errorlimits indicate errors in the fitting procedure.

	R_h (aq) / nm	R_h (tol) / nm	R_{hs} (aq) / nm	R_{hs} (tol) / nm
P-DR1 (1:10)	196 ± 2	240 ± 2	0.18	-
P-BAAB-P (1:50)	80 ± 1	150 ± 2	-	-
P-BAAB-P (1:10)	101 ± 1	170 ± 2	-	0.14

S2.2. Second synthesis variant for P-DR1 (1:10) and P-BAAB-P (1:10 and 1:50) (Sample 2)

All particles were synthesised in the same way. The different concentrations of monomer, cross-linker and respective co-monomer are given in Table S1.

Typical synthesis procedure: Butyl methacrylate (BMA), ethylene glycol dimethacrylate (EGDMA) and the respective co-monomer were dissolved in acetone (30 ml) in order to solubilise the azobenzene in the mixture. This mixture was added to 150 ml of deionised water, which was heated to $\vartheta = 80\,^{\circ}\mathrm{C}$ under stirring and under nitrogen. Not fully dissolved dye was then fully soluble in the monomer droplets. Potassium peroxodisulfate (KPS) as radical starter was dissolved in 5 ml of deionised water and then injected to the heated monomer mixture. During polymerisation, some polymer tends to aggregate, though still a large part of the polymer is dispersed as latex. The polymerisation was stopped after 3 h and the aggregates were removed by filtration. The filtrate was centrifuged and redispersed in acetone. Then, the centrifugation/redispergation was repeated with acetone and dioxane in order to remove unreacted monomer. In the end the supernatant was colourless. For further purification, the dioxane dispersion was freeze-dried and redispersed in toluene in order to dialyse the sample for 3 d against toluene (MWCO 12000) and 2 d against an acetone/isopropanol mixture (1/1 by volume). This mixture was filtered again by use of a syringe filter (0.8 m) and the main part was dialysed against dioxane in order to perform the final freeze-drying. A small part of the acetone dispersion was diluted and then dialysed against water in order to measure the hydrodynamic radius and the radius of gyration in the collapsed state after further dilution. To measure the hydrodynamic radius in the swollen state a small amount was swollen in toluene. The results of the light scattering measurements are shown in Table S3.

Table S3: Sample 2: Hydrodynamic radii (R_h) and hard sphere radii (R_{hs}, obtained from the first minimum of the form factor) in water (aq) and in toluene (tol). Due to a limited q range the form factor minimum could not be reached for all samples. Errors indicate errors in the fitting procedure.

	R_h (aq) / nm	R_h (tol) / nm	R_{hs} (aq) / nm	R_{hs} (tol) / nm
P-DR1 (1:10)	196 ± 2	239 ± 1	0.19	-
P-BAAB-P (1:50)	205 ± 2	335 ± 3	0.20	0.30
P-BAAB-P (1:10)	173 ± 1	223 ± 4	0.17	0.22

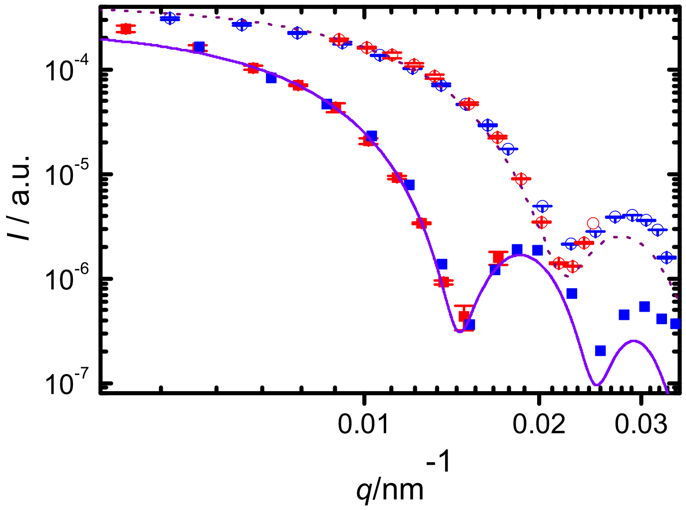

Fig. S1: Exemplary SLS results: form factor of P-BAAB-P (1:50; sample 2) in toluene (solid squares) and water (open circles) measured with red (red symbols) and blue laser (blue symbols). Lines indicate the fit results of a polydisperse hard sphere form factor model (with radius $R_{hs} = 306 \pm 17$ nm and $R_{hs} = 200 \pm 17$ nm, respectively).

S3. Thermal back-isomerisation of BAAB and P-BAAB-P (1:50 and 1:10)

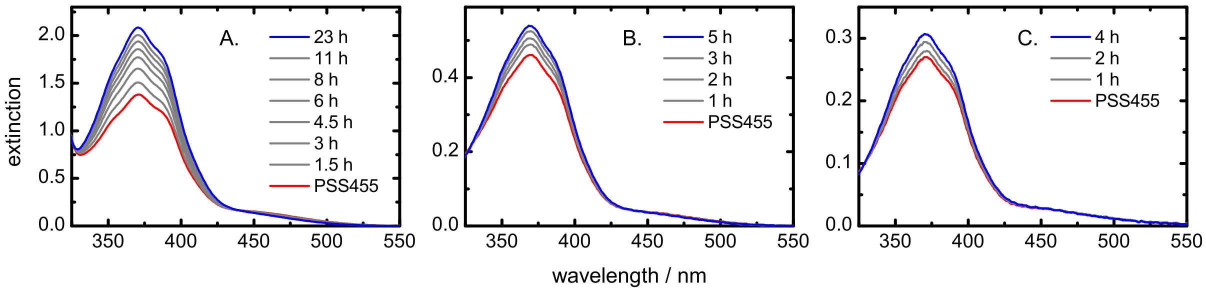

Fig. S2: UV/VIS absorption spectra of a) **BAAB**, b) **P-BAAB-P** (1:50) and c) **P-BAAB-P** (1:10) in 2-fluorotoluene as of time after excitation to the photostationary state PSS455 at $t = 0$ (red). The spectra of the respective E isomer are shown in blue. The thin black lines show the evolution of the spectra in course of the thermal back-isomerisation from the respective PSS after $\Delta t = 1.4$, 3, 4.5, 6, 8, 11 and 23 h for BAAB, $\Delta t = 1$, 2, 3, and 5 h for P-BAAB-P (1:50) and $\Delta t =$ 1, 2, and 4 h for P-BAAB-P (1:10). The switching efficiency in the polymer is only $\approx 40 - 50$ % of the value in solution. The observed effects are related to the strong pulling forces acting on the AB in the main-chain of the polymer.

References

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