Electronic Supporting Information

Counter-intuitive Photo-Modulation of the Aqueous Phase Behavior of Azo Dye-Functionalized Polyacrylamides

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Calculation of Half-life

The decay of the photo-stationary states follows 1st order kinetics. Accordingly, the half-life $t_{½}$ can be calculated from the slope of the plotted absorbance or the normalized ^{1}H NMR signals, respectively as a function of time, using equation (1).

$$t_{½} = \frac{\ln(2)}{slope} \quad (1)$$

For the monomer AzBnAm **3**, the content of the *Z*-state is determined from the normalized ^{1}H NMR spectra. Figure S1 shows the linearized decay as well as the function of the linear regression.

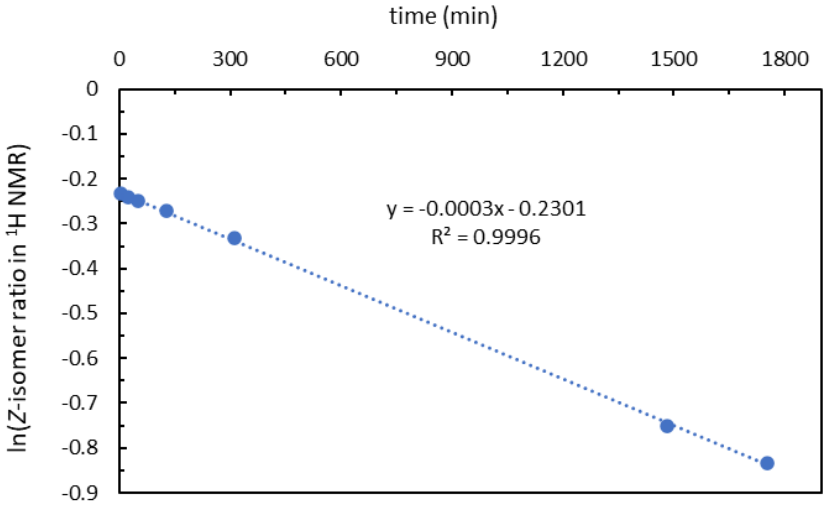

Figure S1: Linearized decay of the *Z*-isomer fraction of monomer AzBnAm **3** in DMSO solution after irradiation at 365 nm for 15 min from the ^{1}H NMR spectra in DMSO-d6 at 20 °C.

Spectra

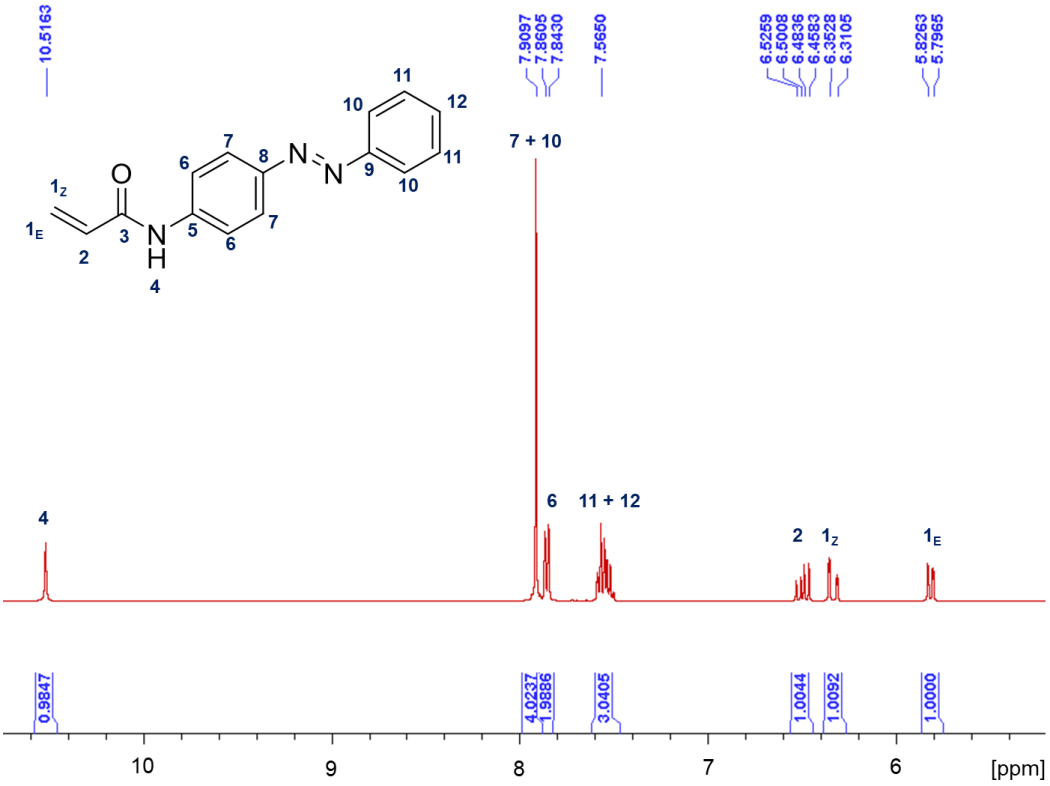

Figure S2: ^{1}H NMR spectrum of monomer AzBnAm **3** in deuterated dimethylsulfoxide DMSO-d6.

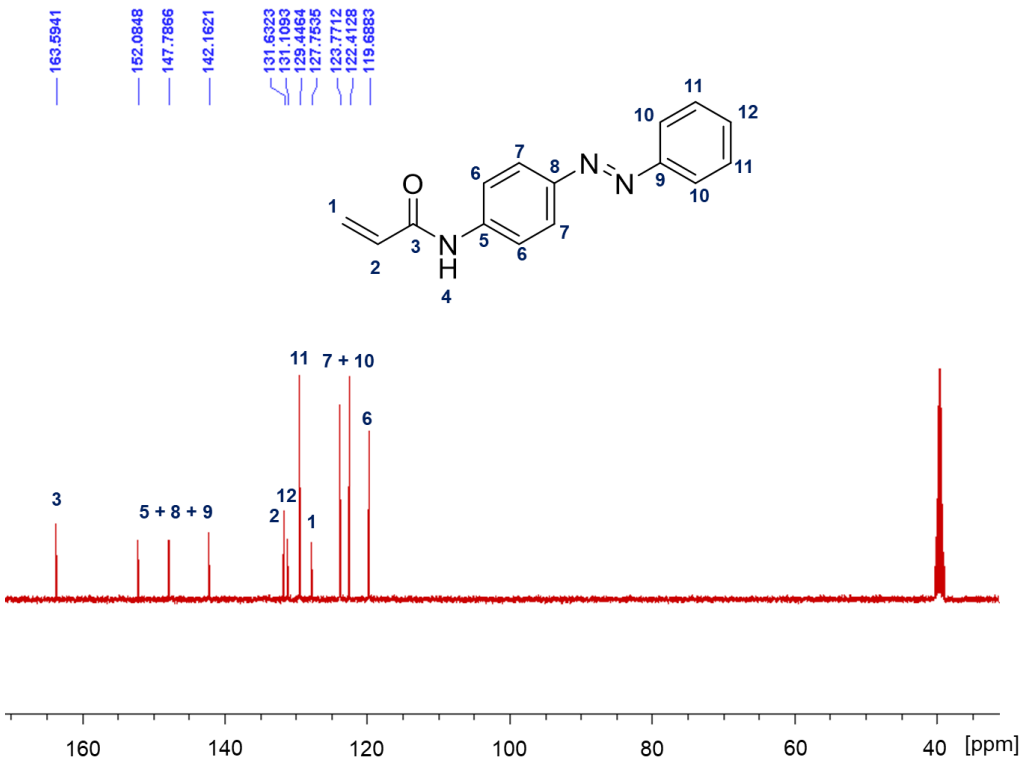

Figure S3: ^{13}C NMR spectrum of monomer AzBnAm **3** in DMSO-d6.

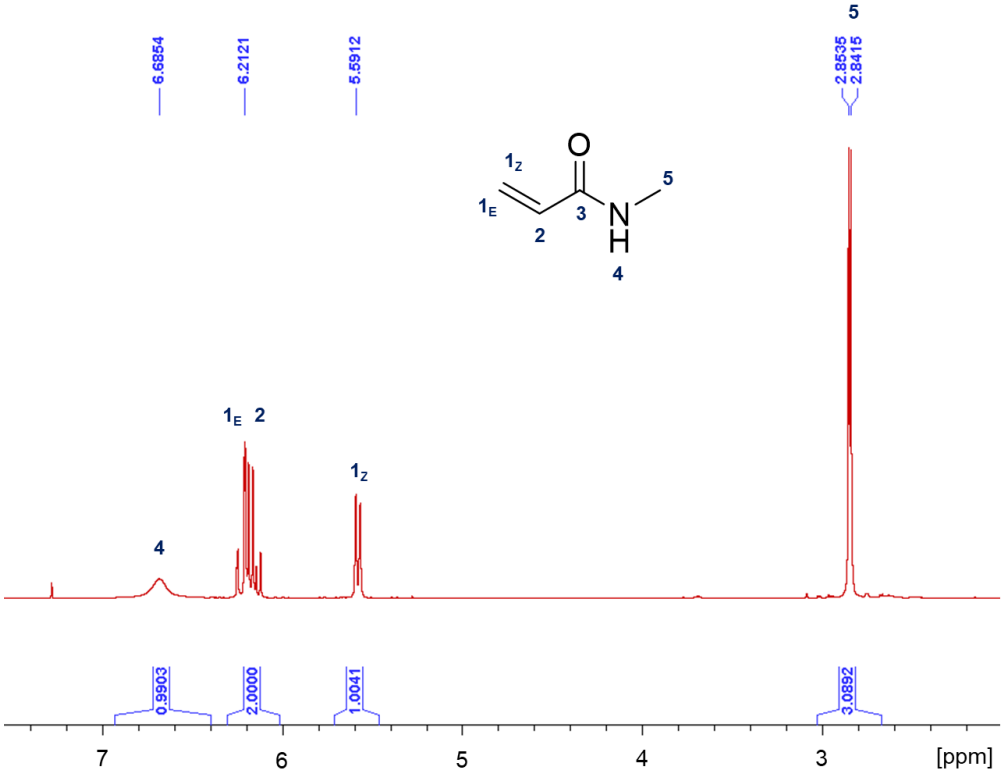

Figure S4: ^{1}H NMR spectrum of monomer MAm 6 in chloroform $CDCl_3$.

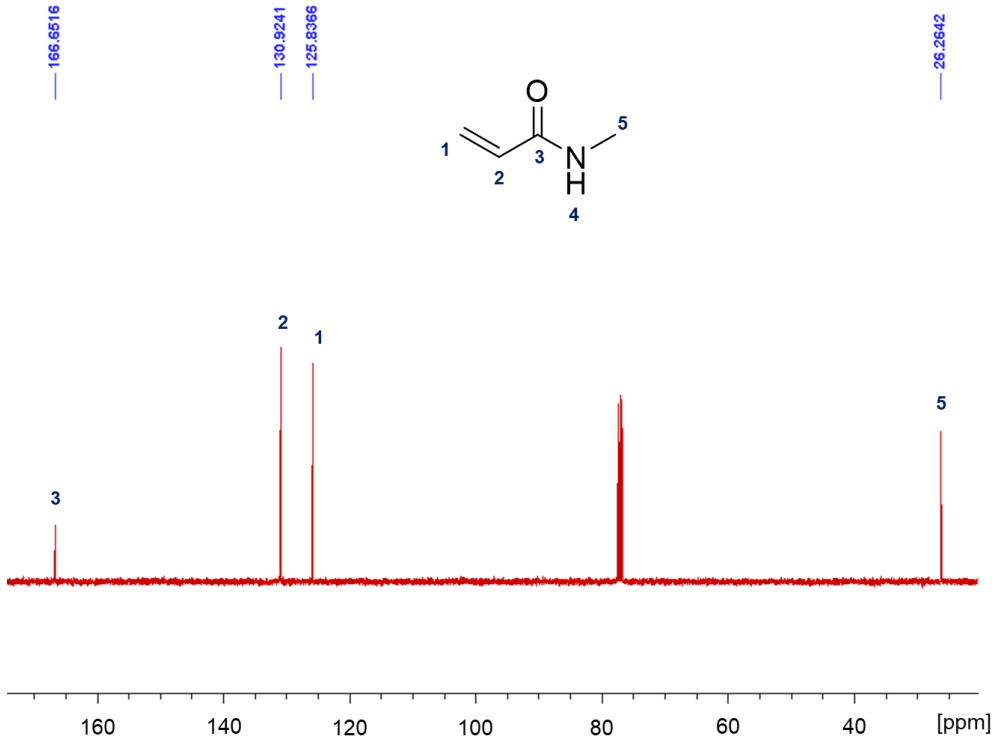

Figure S5: ^{13}C NMR spectrum of monomer MAm **6** in $CDCl_3$.

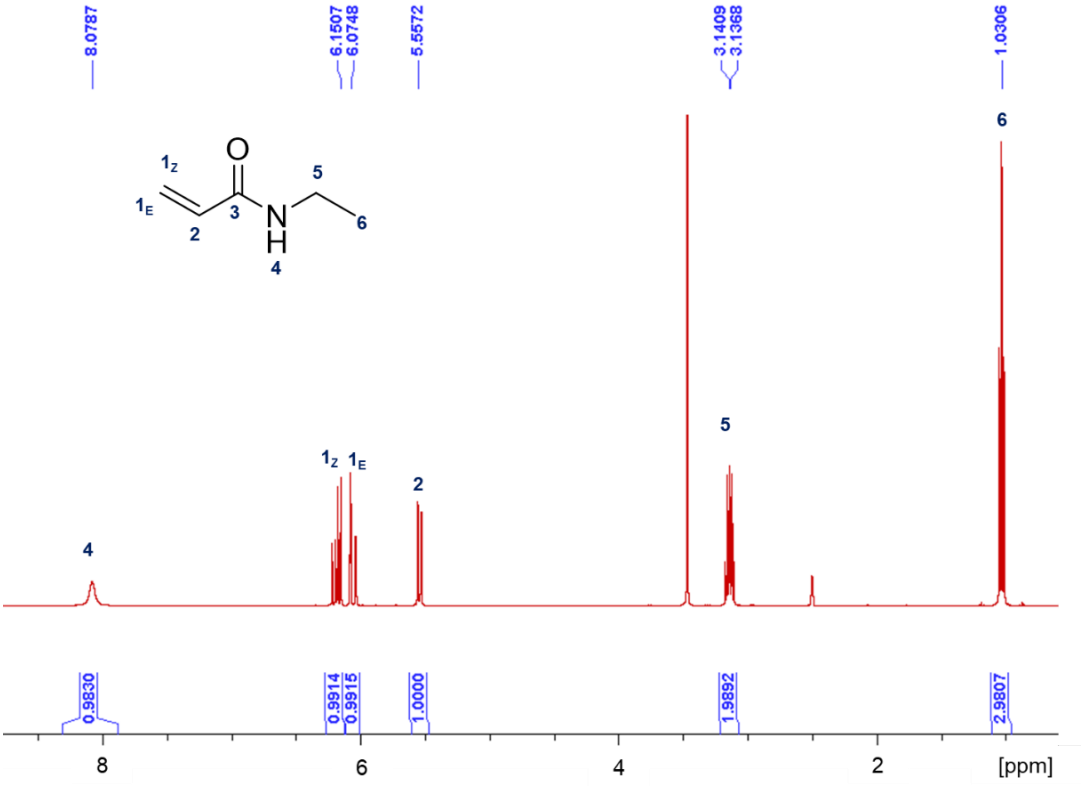

Figure S6: ^{1}H NMR spectrum of monomer EAm **7** in DMSO-d6.

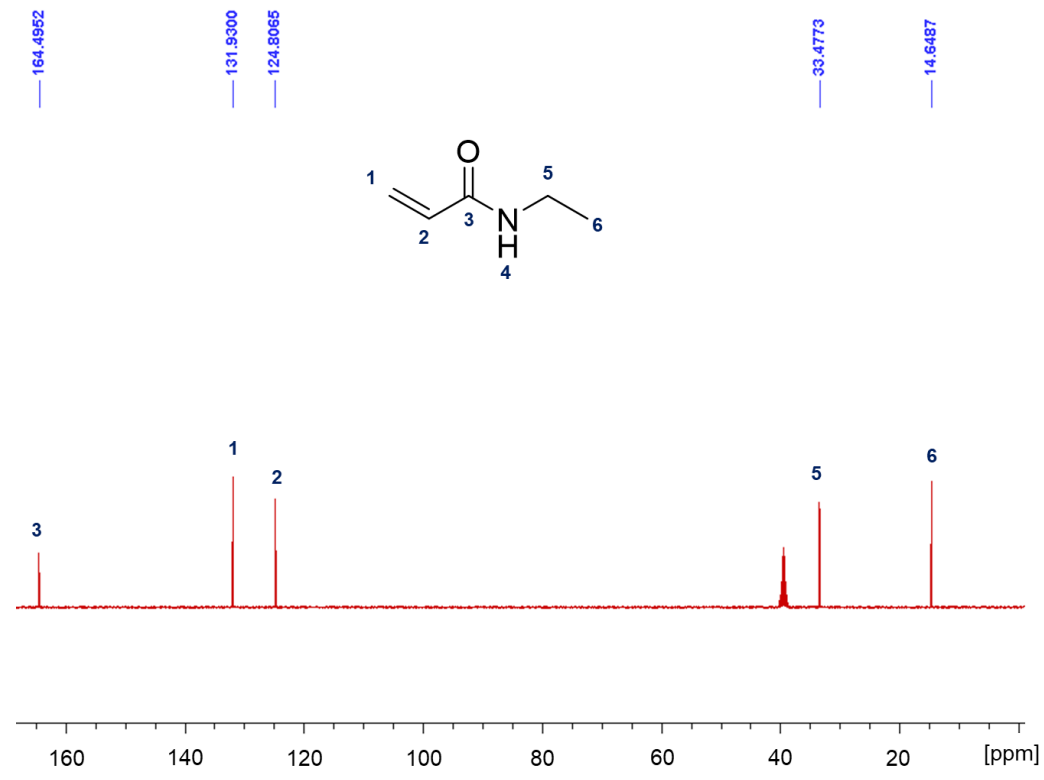

Figure S7: ^{13}C NMR spectrum of monomer NEAm **7** in DMSO-d6.

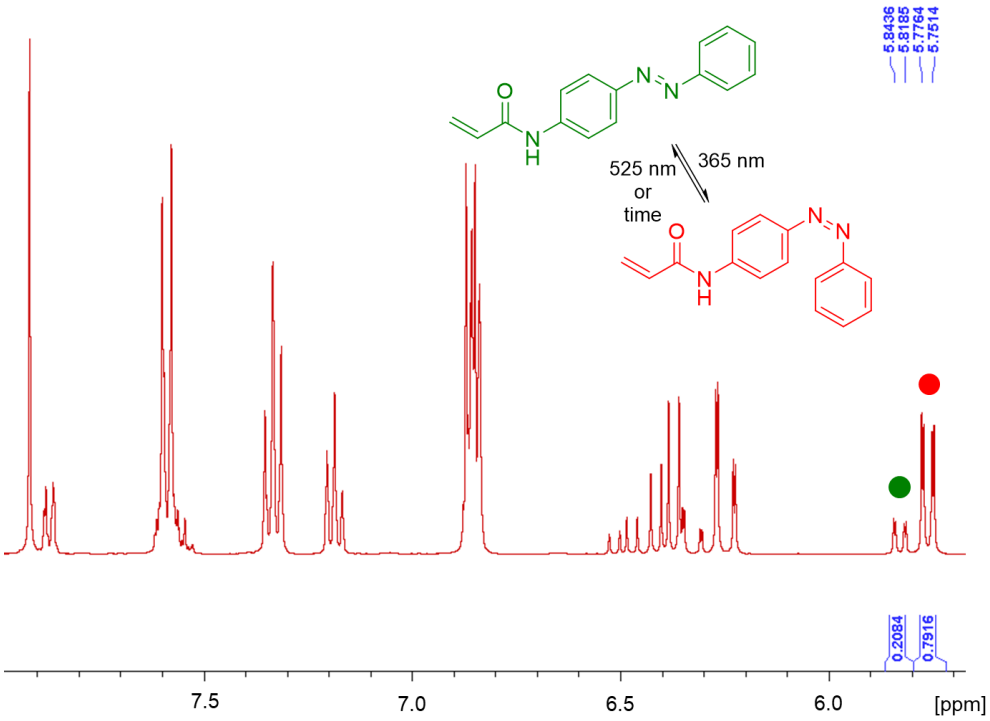

Figure S8: ^{1}H NMR spectrum of monomer AzBnAm **3** in DMSO-d6 after irradiation at 365 nm for 15 min. The integrals of the corresponding *E* and *Z* states are normalized to calculate the ratio of *E*: *Z* (21:79).

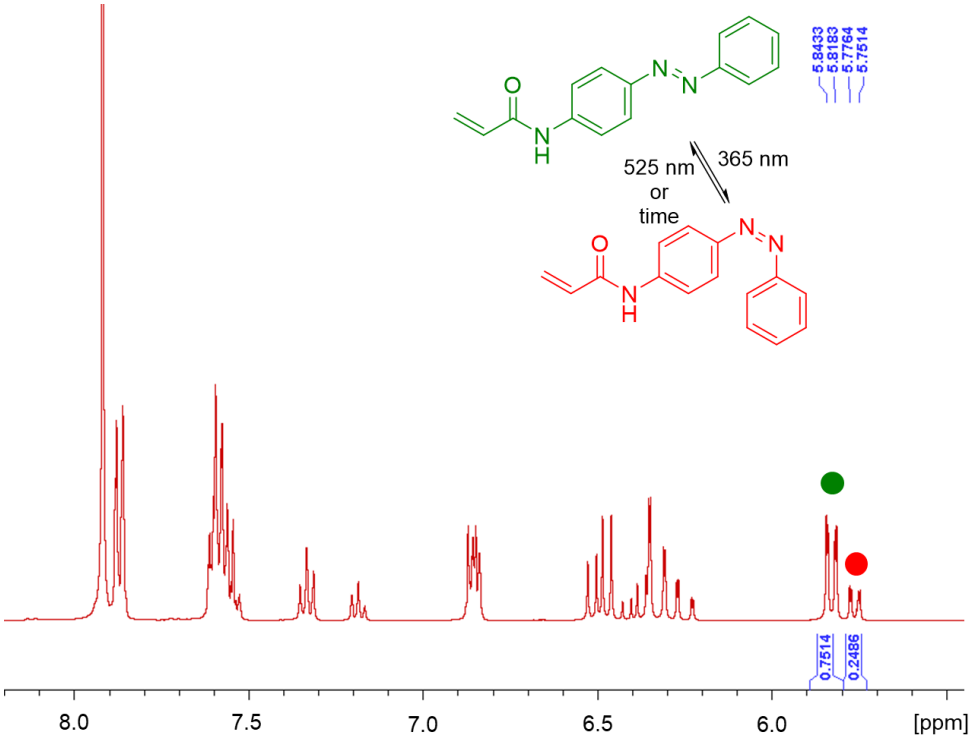

Figure S9: ^{1}H NMR spectrum of monomer AzBnAm **3** in DMSO-d6 after irradiation at 525 nm for 15 min. The integrals of the corresponding *E* and *Z* states are normalized to calculate the ratio of *E*: *Z* (75:25).

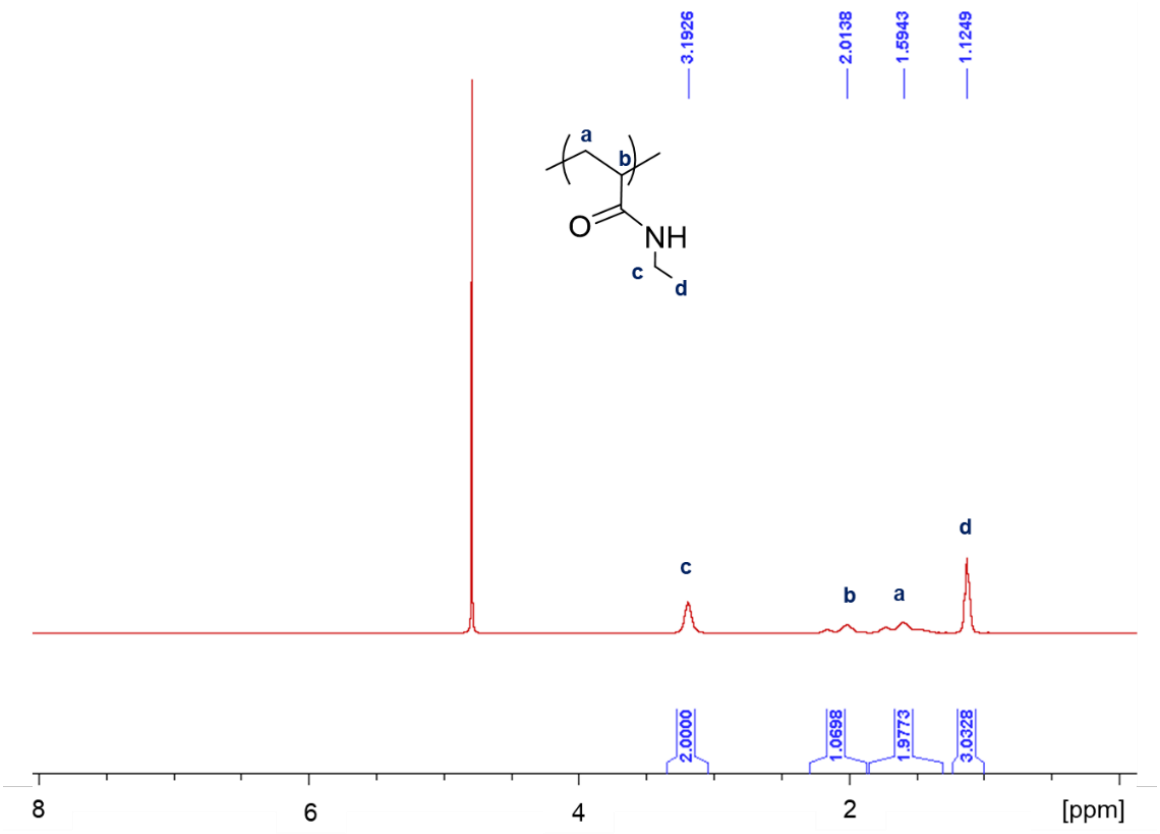

Figure S10: ^{1}H NMR of homopolymer p(EAm) in D_2O.

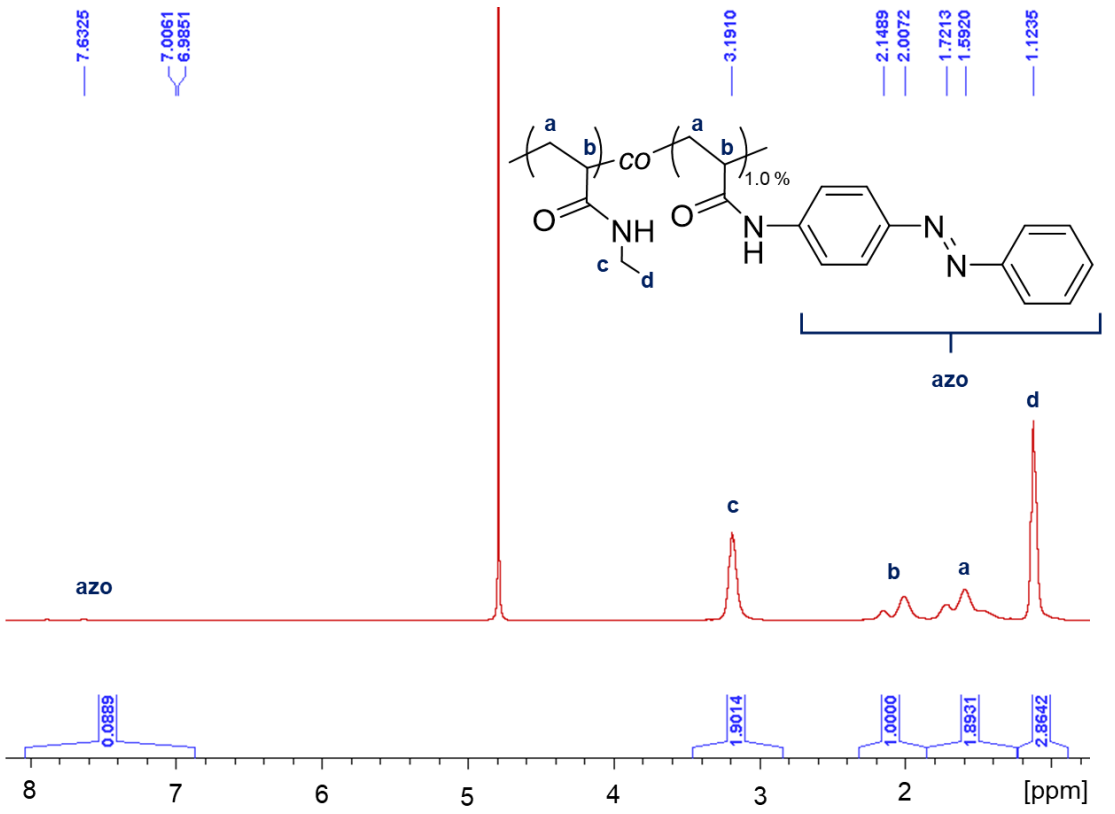

Figure S11: ^{1}H NMR of copolymer p(EAm-*co*-AzBnAm$_{1.0}$) in D_2O.

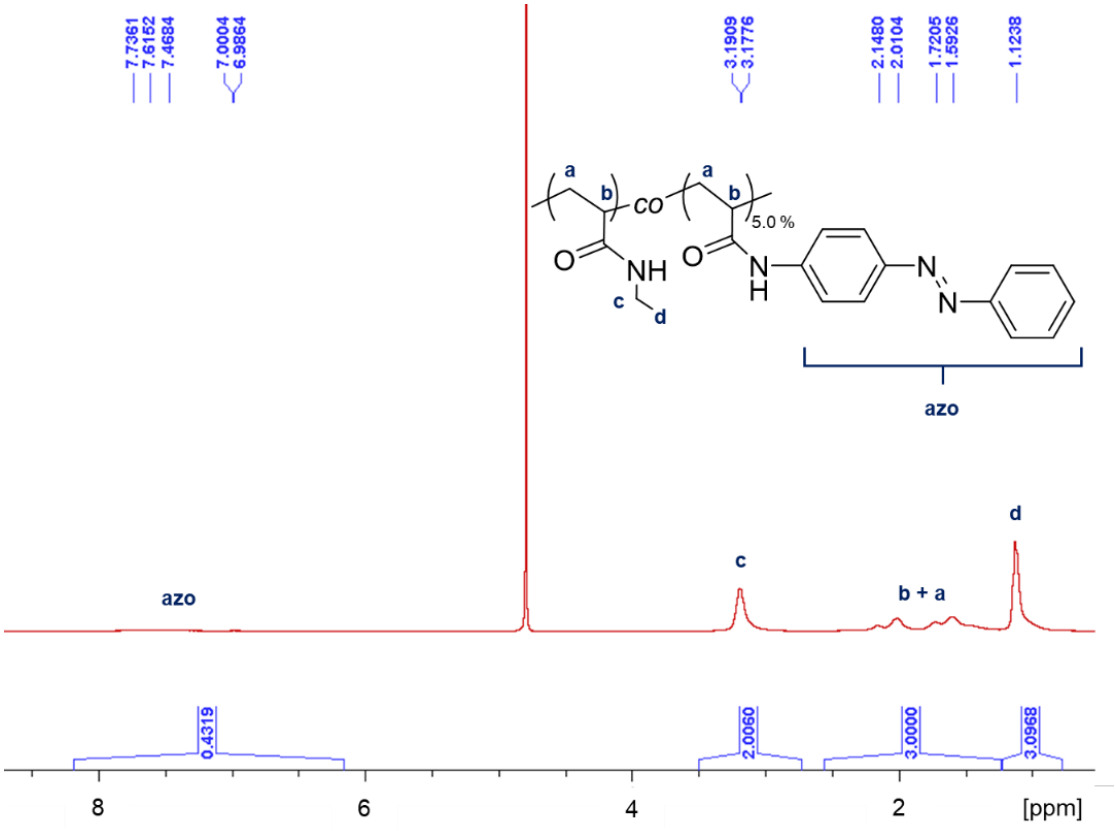

Figure S12: ^{1}H NMR of copolymer p(EAm-*co*-AzBnAm$_{5.0}$) in D_2O.

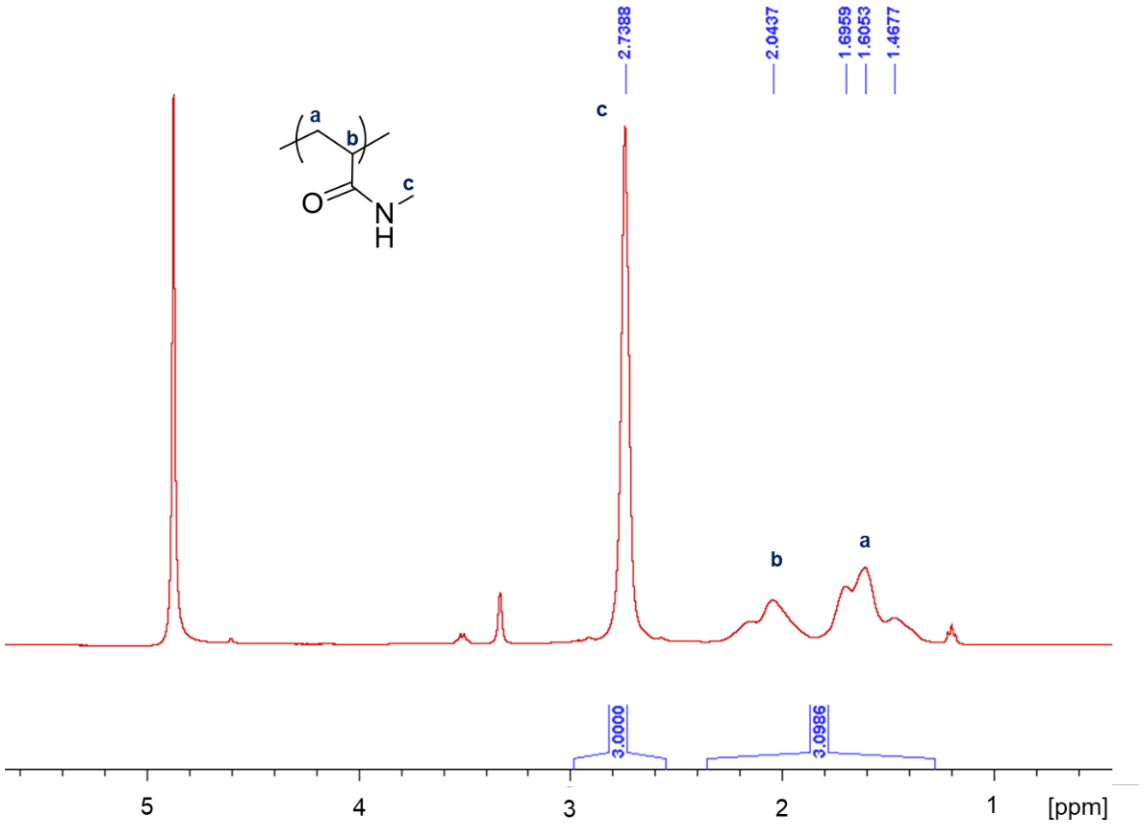

Figure S13: ^{1}H NMR of p(MAm) in methanol d4, CD_3OD.

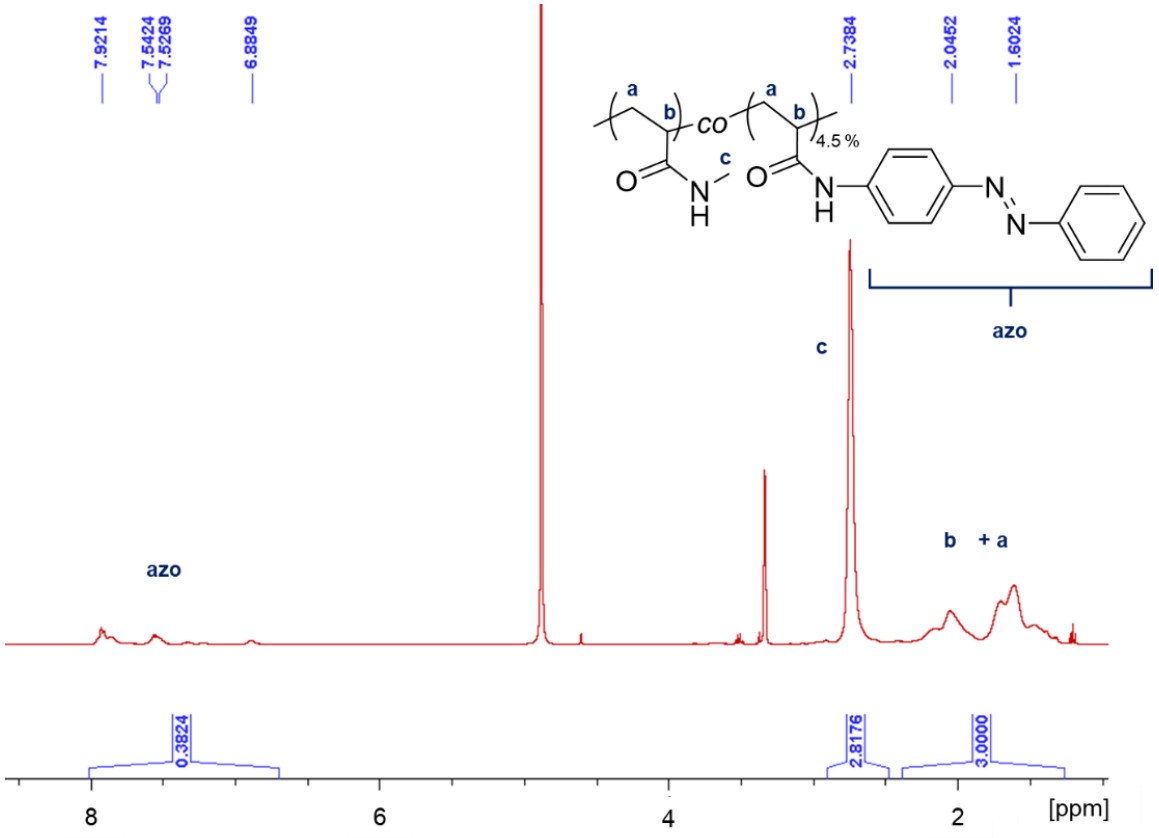

Figure S14: ^{1}H NMR of copolymer p(MAm-*co*-AzBnAm$_{4.5}$) in CD_3OD.

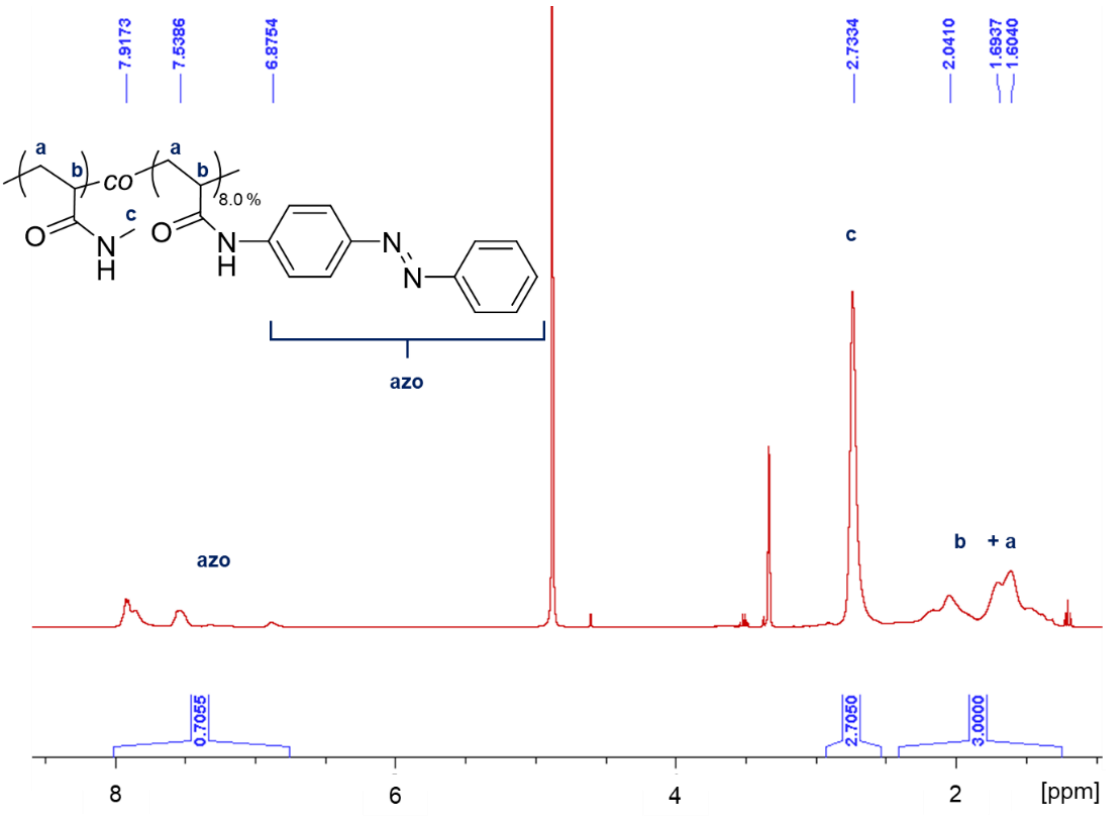

Figure S15: ^{1}H NMR of copolymer p(MAm-*co*-AzBnAm$_{8.0}$) in CD_3OD.

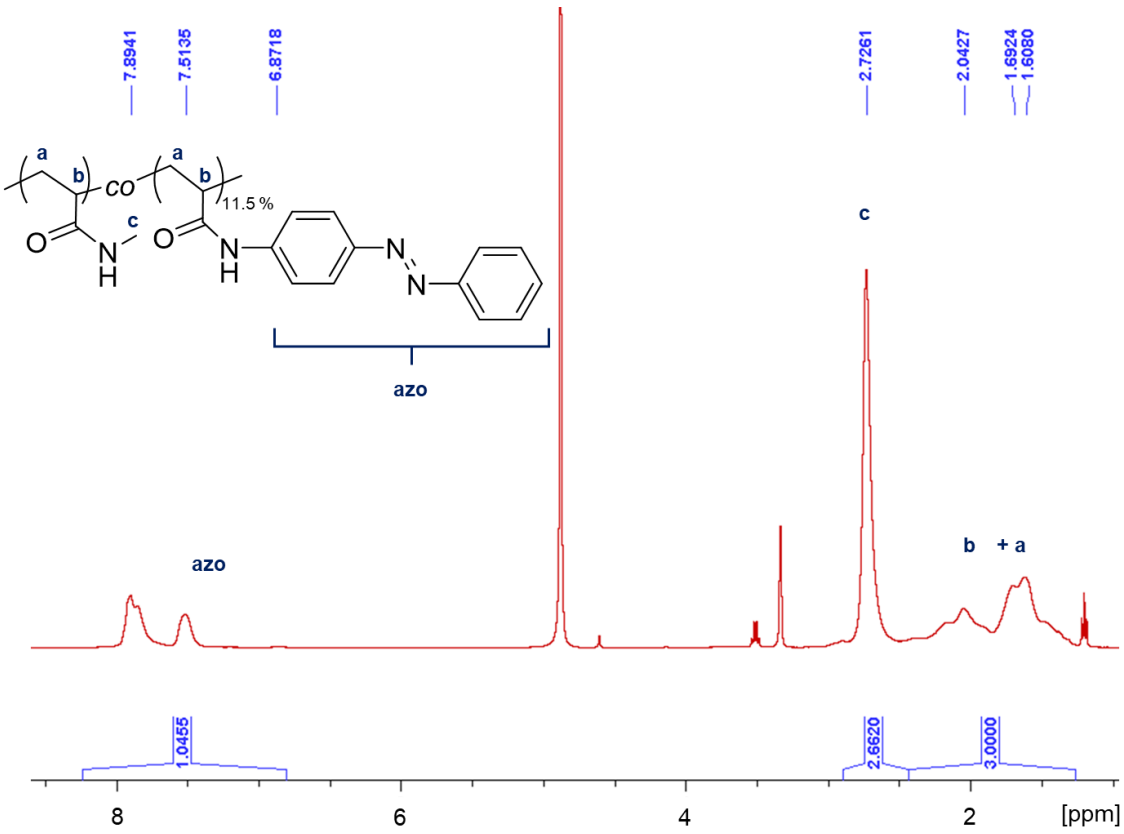

Figure S16: ^{1}H NMR of copolymer p(MAm-*co*-AzBnAm$_{11.5}$) in CD_3OD.

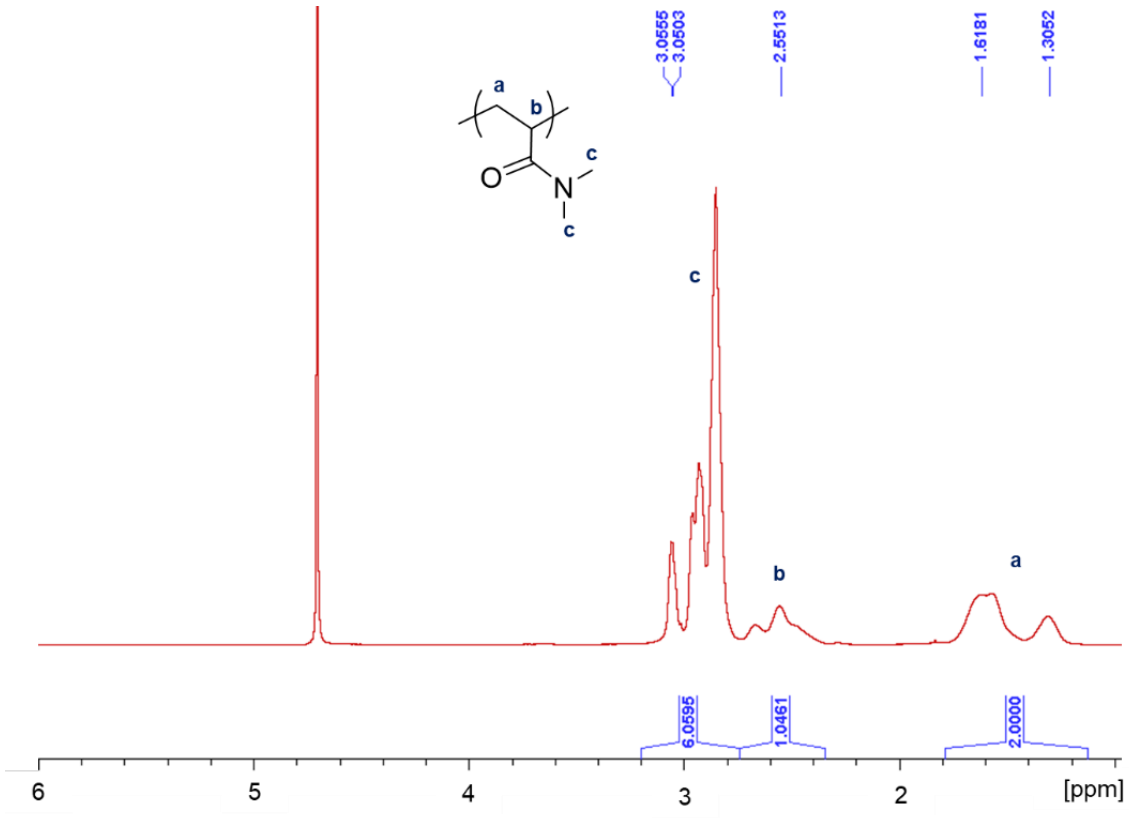

Figure S17: ^{1}H NMR of p(DMAm) in D_2O.

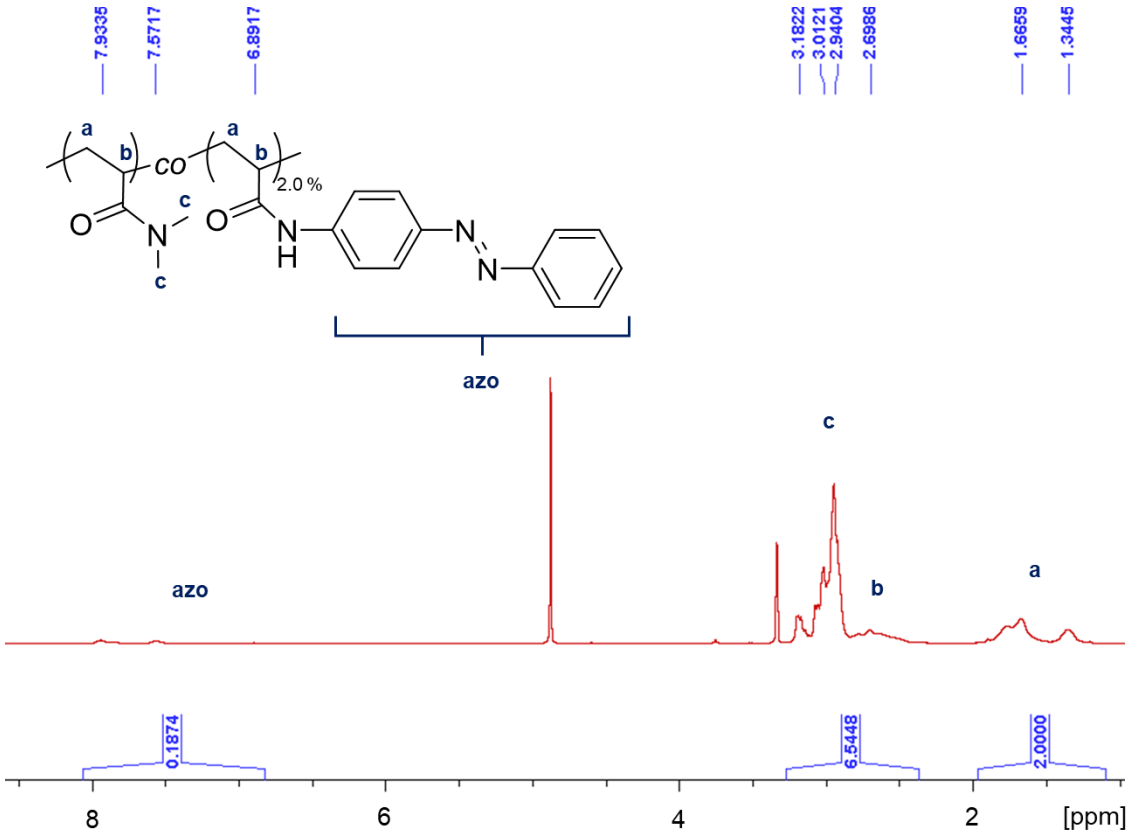

Figure S18: ^{1}H NMR of copolymer p(DMAm-*co*-AzBnAm$_{2.0}$) in CD_3OD.

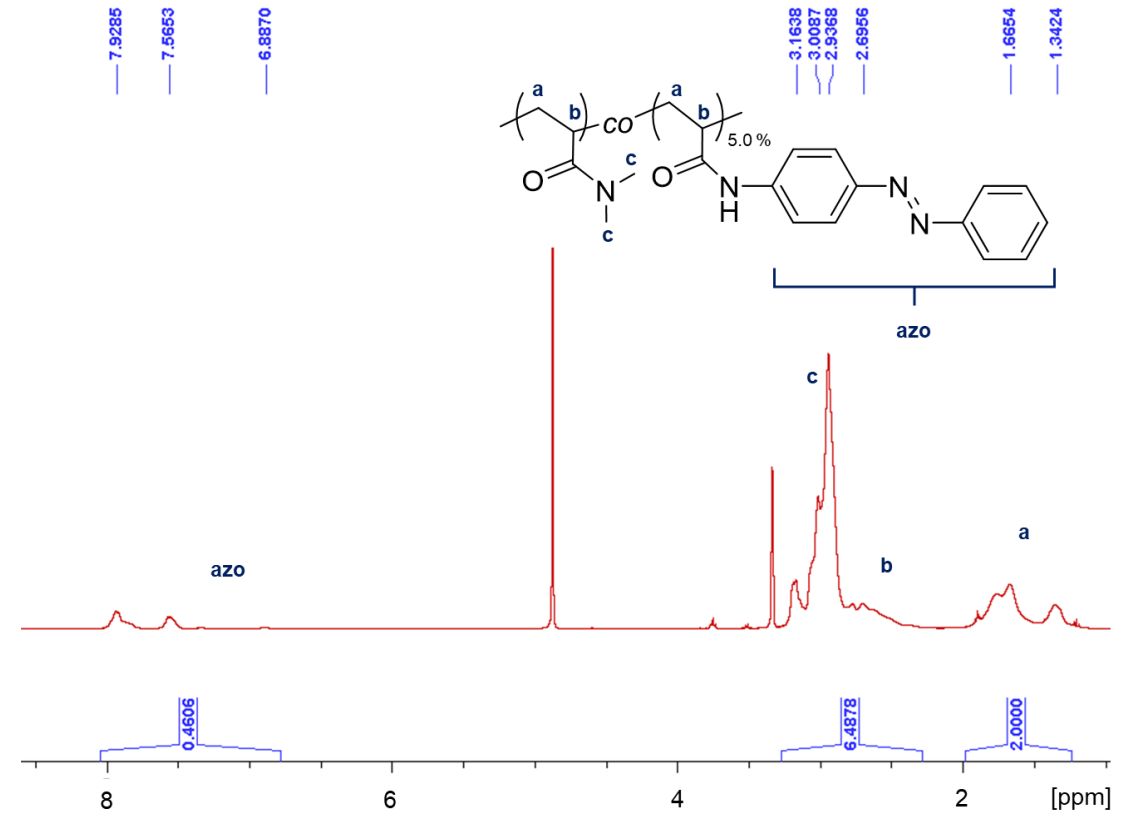

Figure S19: ^{1}H NMR of copolymer p(DMAm-*co*-AzBnAm$_{5.0}$) in CD_3OD.

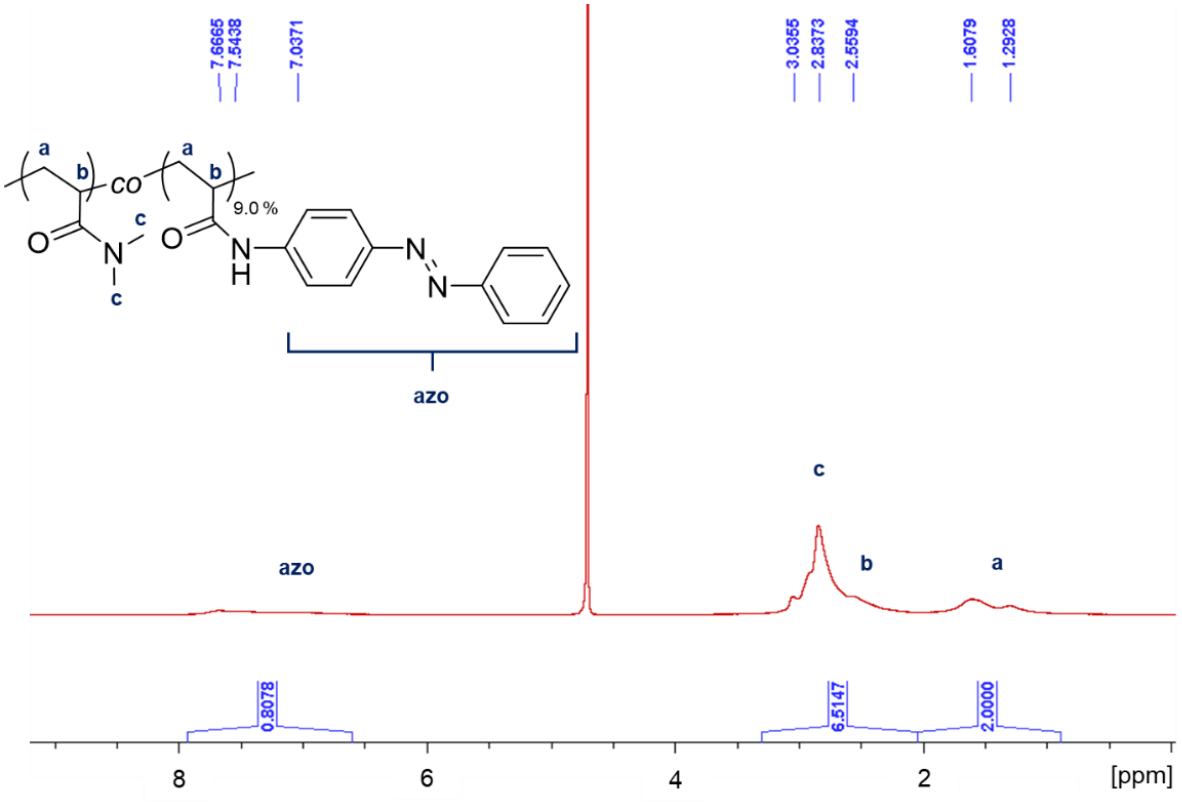

Figure S20: ^{1}H NMR of copolymer p(DMAm-*co*-AzBnAm$_{9.0}$) in CD_3OD.

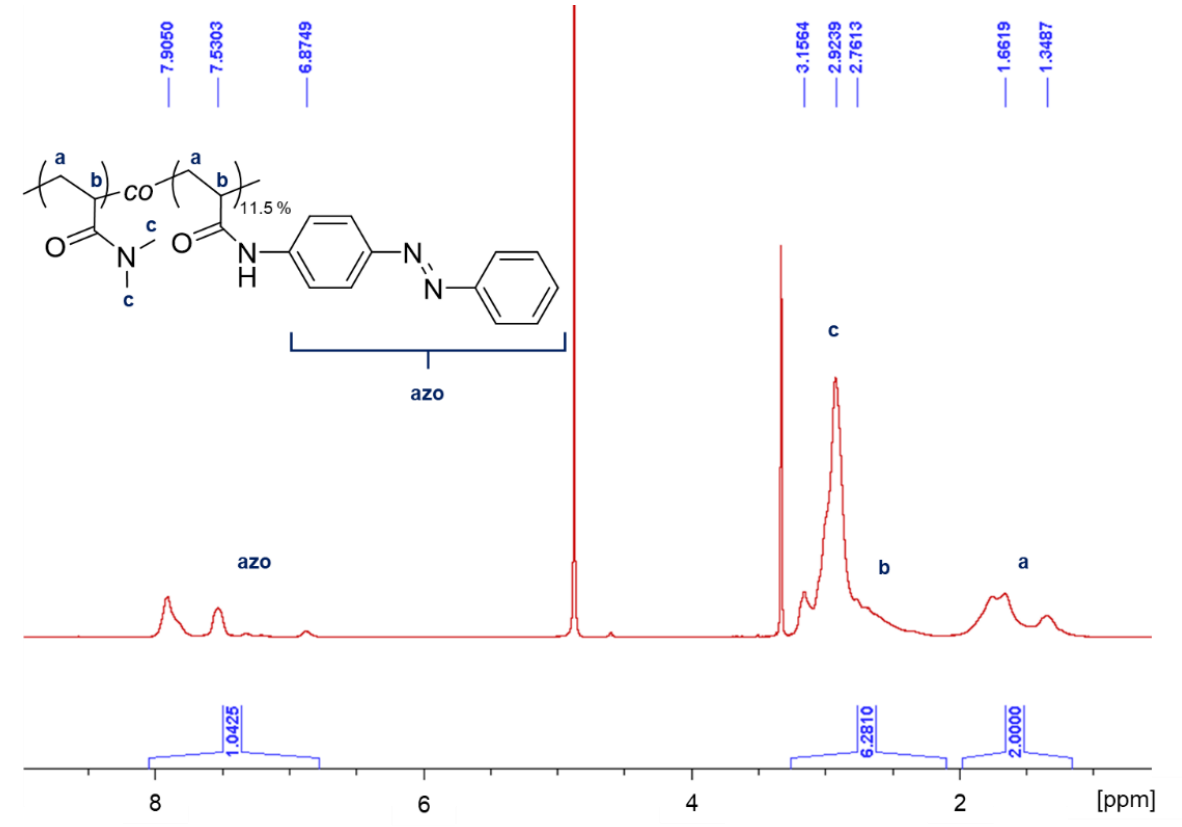

Figure S21: ^{1}H NMR of copolymer p(DMAm-*co*-AzBnAm$_{11.5}$) in CD_3OD.

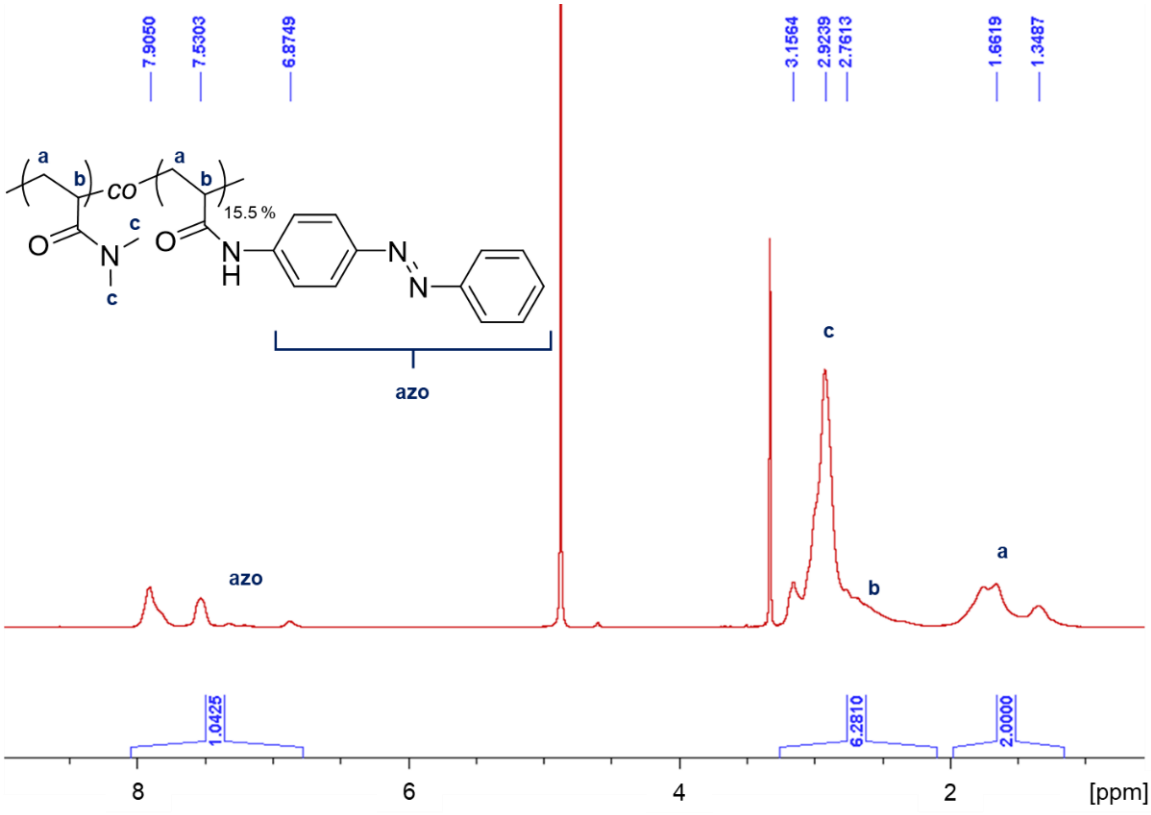

Figure S22: ^{1}H NMR of copolymer p(DMAm-*co*-AzBnAm$_{15.5}$) in CD_3OD.

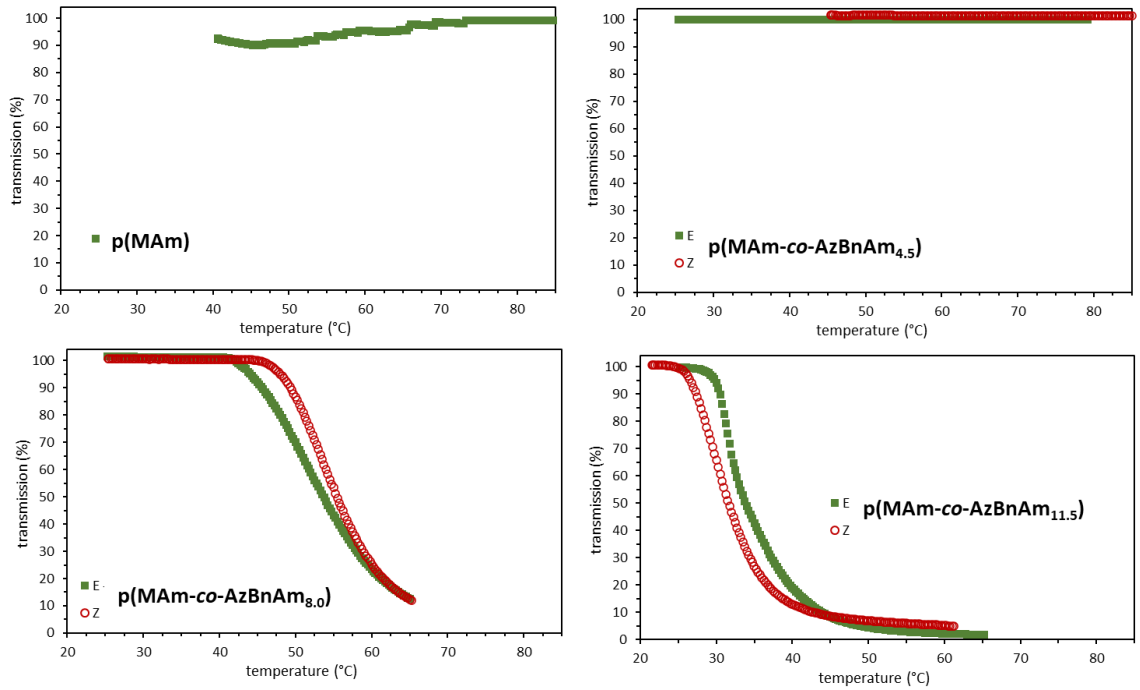

Figure S23: Turbidity studies of the p(MAm-*co*-AzBnAm$_x$) copolymer series in water (c = 1g·L^{-1}) as function of the temperature and of the state of the photo-isomerization, heating rate 0.5 K min^{-1}. Green symbols indicate solutions equilibrated in the dark (all in *E*-state), red symbols indicate solutions in the photo-stationary state after 15 min of irradiation by 365 nm light, containing a majority of the *Z*-isomer.

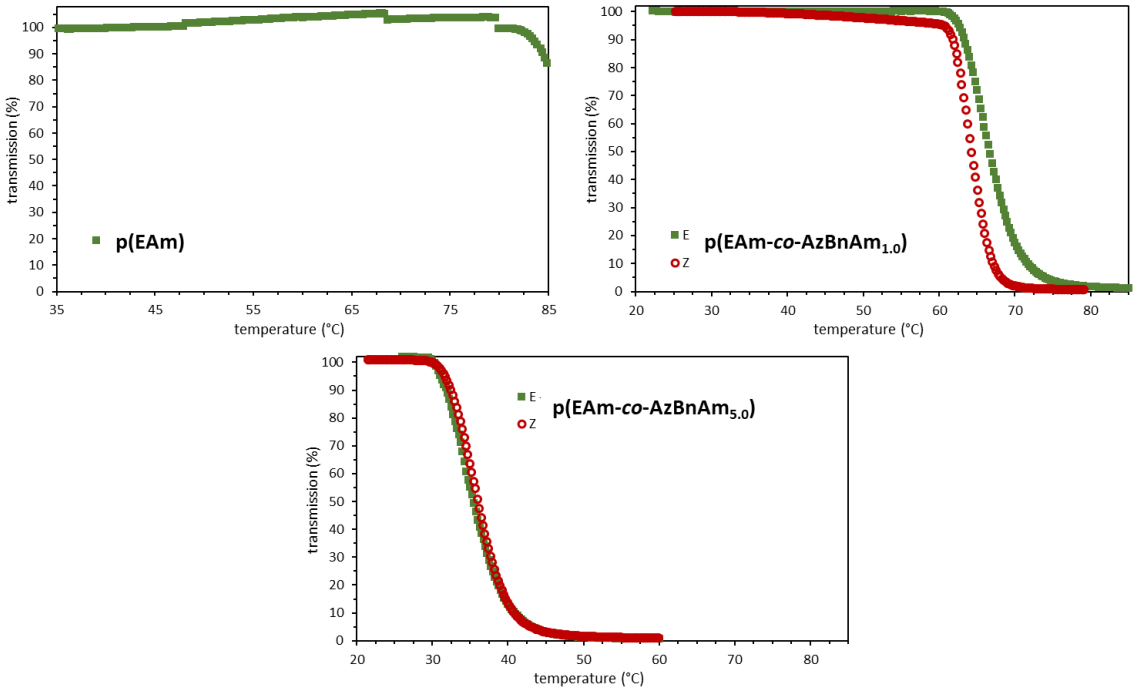

Figure S24: Turbidity studies of the p(EAm-*co*-AzBnAm$_x$) copolymer series in water (c = 1g·L^{-1}) as function of the temperature and of the state of the photo-isomerization, heating rate 0.5 K min^{-1}. Green symbols indicate solutions equilibrated in the dark (all in *E*-state), red symbols indicate solutions in the photo-stationary state after 15 min of irradiation by 365 nm light, containing a majority of the *Z*-isomer.

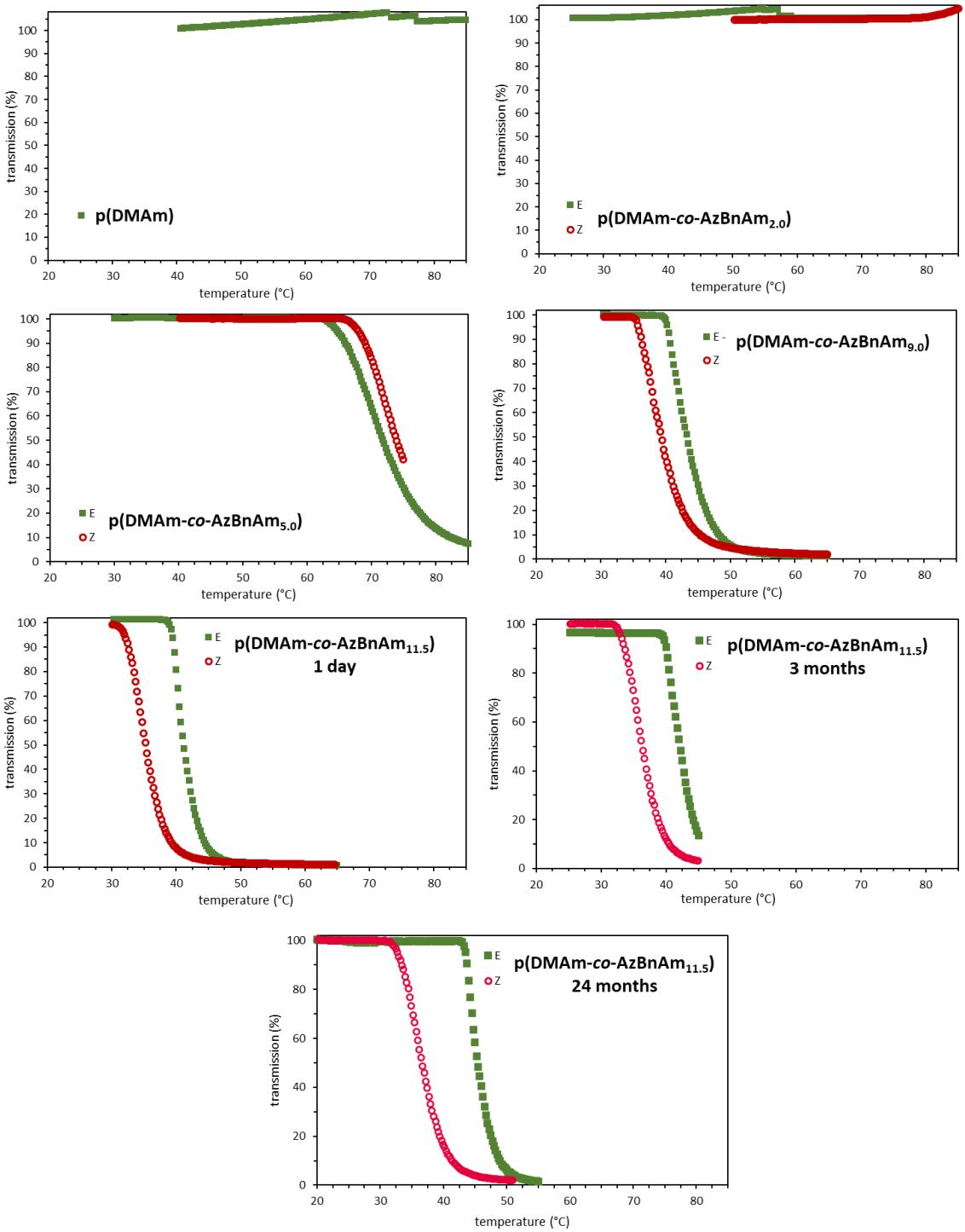

Figure S25: Turbidity studies of the p(DMAm-*co*-AzBnAm) copolymer series in water (c = 1g·L^{-1}) as function of the temperature and of the state of the photo-isomerization, heating rate 0.5 K min^{-1}. Green symbols indicate solutions equilibrated in the dark (all in *E*-state), red symbols indicate solutions in the photo-stationary state after 15 min of irradiation by 365 nm light, containing a majority of the *Z*-isomer.

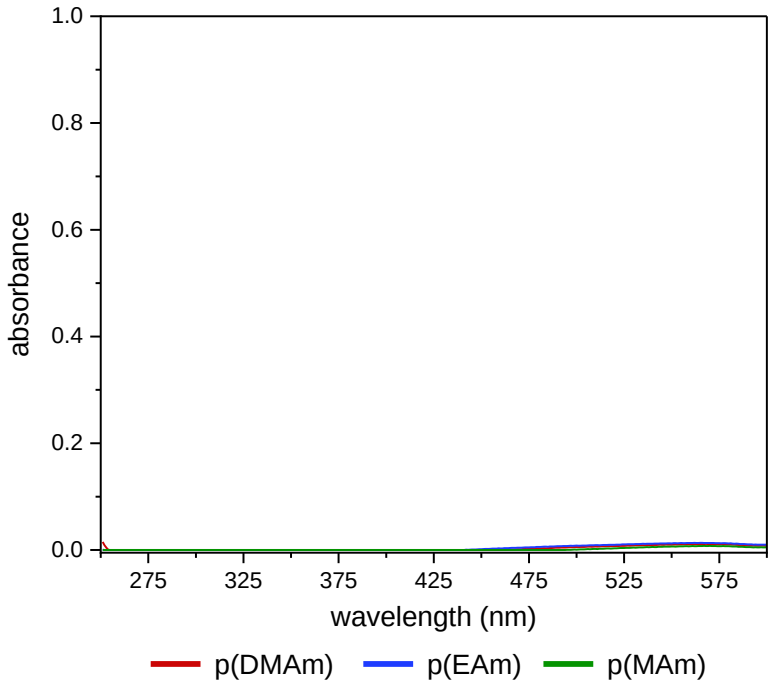

Figure S26: UV-Vis spectra of the of the homopolymers p(DMAm) (red), p(EAm) (blue) and p(MAm) (green) in water (1 g·L^{-1}), showing no absorption in the wavelength range >250 nm in which the azobenzene monomer used (AzBnAm) is absorbing.

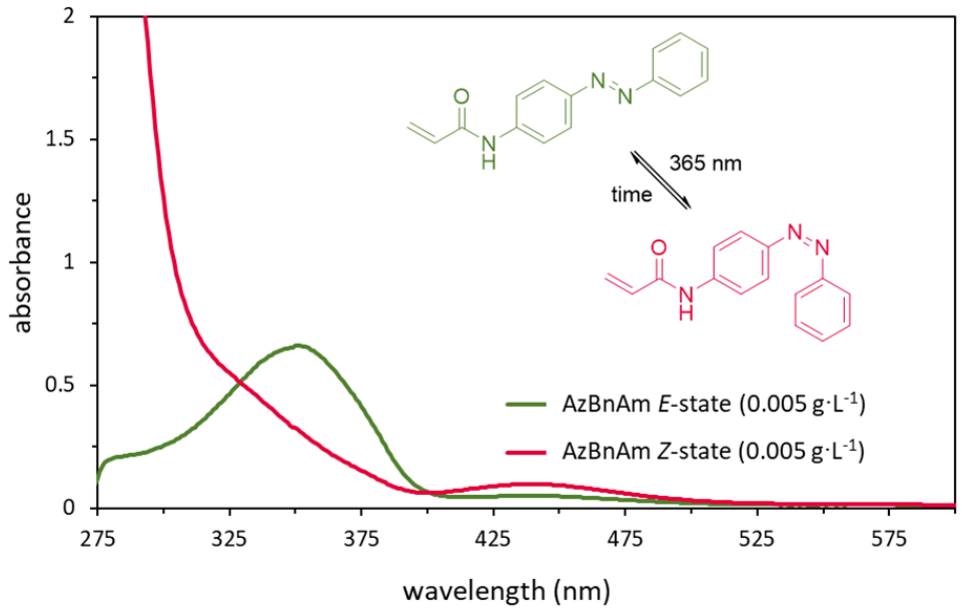

Figure S27: UV-Vis spectra of monomer AzBnAm **3** in methanol (c = 0.005 g·L^{-1}) before (green) and after irradiation (red) at 365 nm for 15 min.

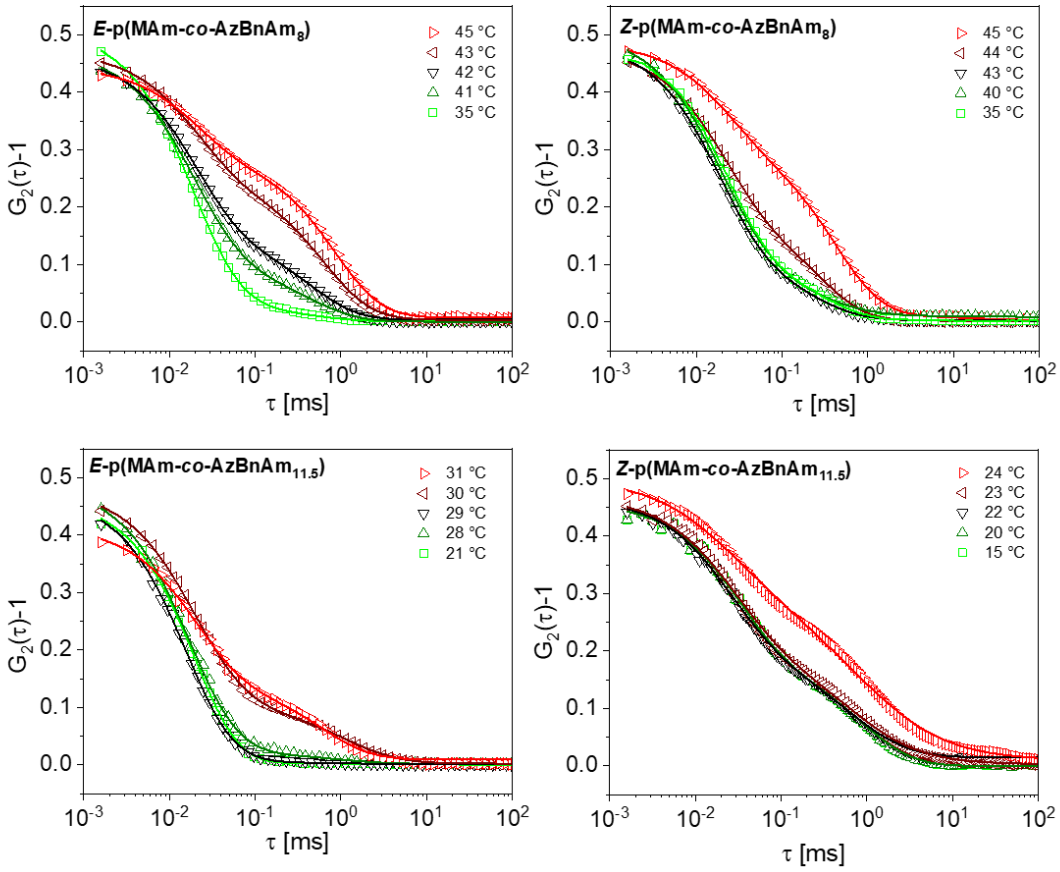

Figure S28: Selected intensity autocorrelation functions $G_2(\tau)$-1 of aqueous solutions of copolymers p(MAm-*co*-AzBnAm$_x$), concentration: 1 g·L^{-1}.
Top left: *E*-p(MAm-*co*-AzBnAm$_8$), top right: *Z*-p(MAm-*co*-AzBnAm$_8$),
bottom left: *E*–p(MAm-*co*-AzBnAm$_{11.5}$), bottom right: *Z*-p(MAm-*co*-AzBnAm$_{11.5}$).