

# Supporting Information

## Boosting the Photo-switchability of Double-responsive Water-soluble Polymers by Incorporating Arylazopyrazole Dyes.

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## General Working Conditions

### Chemicals:

Commercially available reagents and solvents are used as received unless stated otherwise.

Tetrahydrofuran (THF, purity > 98%) for polymerizations is dried over CaH<sub>2</sub> and then distilled under an argon atmosphere.

*N,N*-Dimethylacrylamide (DMAM, TCI, purity > 98.0 %, stabilised with 4-methoxyphenol) is filtered through Aluminium oxide (AlOx, Sigma-Aldrich, activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å) to remove the inhibitor.

Water (electric conductivity < 1 µS/cm) for purification and sample preparation is desalinated *via* reverse osmosis.

Silica (Merk Millipore, Geduran<sup>®</sup> Si 60, 0.063 – 0.200 mm) is used for column filtrations or column chromatography.

### Protective gas:

Argon grade 5.0 is used as inert gas without further treatment.

### Thin layer chromatography (TLC):

Qualitative thin-layer chromatography (TLC) is performed on TLC Silica gel 60 F<sub>254</sub> aluminum sheets with a layer thickness of 0.175-0.225 mm (Merck KGaA, Darmstadt/Germany). Chromatograms are developed by iodine vapor, and under a UV lamp (254 and 365 nm).

### Nuclear magnetic resonance (NMR) spectroscopy:

NMR spectra are recorded on the spectrometer Bruker Avance Neo 400 MHz. The spectra are evaluated with the Topspin software, version 4.07. The chemical shifts  $\delta$  are given in ppm. The residual proton signal of the solvent or, respectively, its C signal is used to calibrate the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>13</sup>C NMR are recorded proton decoupled.

CDCl<sub>3</sub>: (<sup>1</sup>H  $\delta$ CHCl<sub>3</sub> = 7.26 ppm, <sup>13</sup>C  $\delta$ CHCl<sub>3</sub> = 77.16 ppm).

MeOD-D4: (<sup>1</sup>H  $\delta$ MeOD = 3.31 ppm, <sup>13</sup>C  $\delta$ MeOD = 49.00 ppm).

CD<sub>2</sub>Cl<sub>2</sub>: (<sup>1</sup>H δ<sub>CD<sub>2</sub>Cl<sub>2</sub></sub> = 5.32 ppm, <sup>13</sup>C δ(CD<sub>2</sub>Cl<sub>2</sub>) = 53.50 ppm).

The fine structures of the proton signals are indicated by "s" for singlet, "d" for doublet, "t" for triplet, "m" for multiplet, "dd" for double doublet, *etc.*

#### **Fourier transform infrared (IR) spectroscopy:**

A spectrometer of the model Nexus 47 (Thermo Nicolet) is used. Samples are measured with a smart endurance diamond ATR unit. The respective characteristic bands for a given compound are listed and assigned to functional groups.

#### **Ultraviolet-Visible Light (UV-Vis) Spectroscopy and Turbidimetry:**

UV-Vis und Turbidimetry measurements are made on a dual beam spectrometer model Carry 500 (Agilent). Samples (concentration = 1 gL<sup>-1</sup> in water) for turbidimetry are prepared at least 1 day before the measurement, and are stored at room temperature in the dark. Samples are heated at a rate of 0.5 K min<sup>-1</sup> and the transmission at 600 nm is collected every 0.25 K. The cloud point (T<sub>CP</sub>) is defined as the onset of the decay of the transmission.

#### **Mass spectrometry (MS):**

ESI mass spectra were recorded using an maXis mass spectrometer (Quadrupole- Time of Flight) from Bruker equipped with an ESI source in positive ion modus.

#### **Elemental analyses (EA):**

Elemental analyses are performed by a FlashEA 1112 CHNS/O automatic elemental analyser (Thermo Scientific).

#### **Irradiation set-up**

All irradiations were carried out with a Alonefire SV47 12 W 365 nm UV flashlight (Shenzhen Shiwang Technology Co. Ltd., Shenzhen/China). The samples are irradiated with an irradiance of 200 mW·cm<sup>-2</sup> as determined by an optical power meter PM100D with a sensor S170C (Thorlabs, Newton/USA).

#### **Size exclusion cosmography (SEC):**

SEC is conducted with a home-assembled equipment equipped with a isocratic pump (Thermo Fischer Scientific, Dreieich/Germany) and a refractive index detector (Shimadzu RID-6A, Shimadzu Corporation, Kyoto/Japan), a GRAM-precolumn (10µm 8x50) and a main column GRAM-linear (7µm 8x300mm) 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.

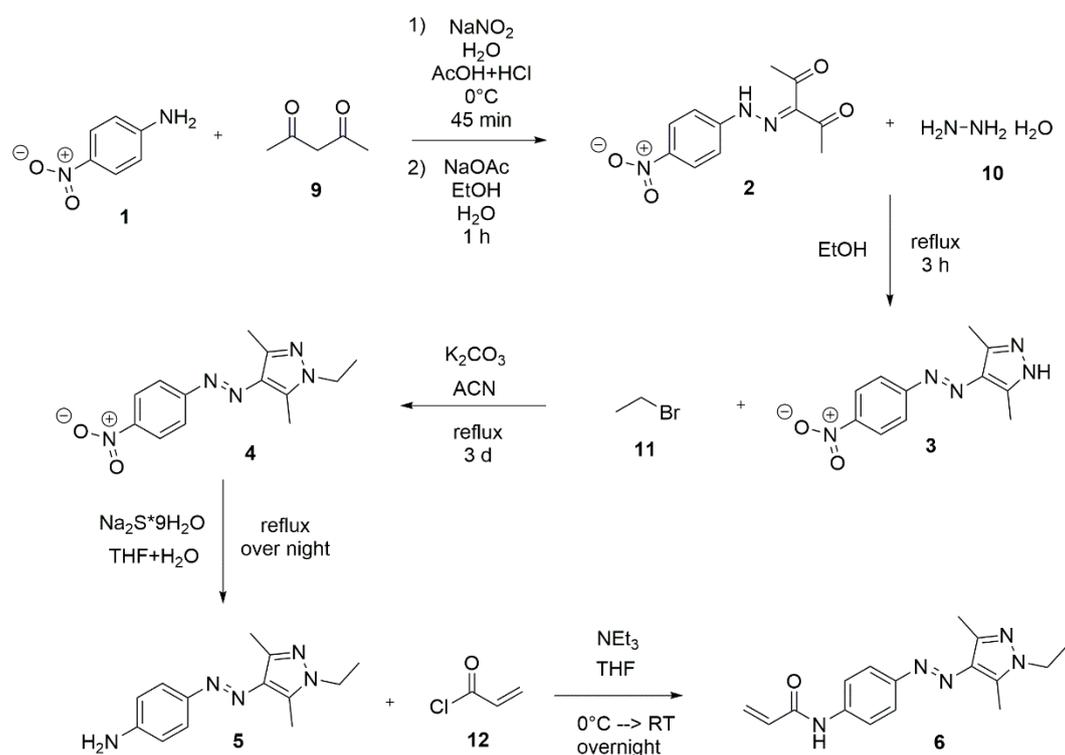
#### **Differential scanning calorimetry (DSC):**

DSC is performed on a DSC 214 Polyma (Netzsch, Selb/Germany) with alumina crucibles. Samples are heated from 0 °C to 180 °C with a heating rate of 10 K·min<sup>-1</sup> under a nitrogen

atmosphere. The DSC data is processed with the Netzsch Proteus software, version 8.0.3. The onset of the endothermic melting peak is defined as the melting point.

## Synthesis

The synthesis of the AAP-bearing monomer is shown in Scheme S1, and follows the route established by Ravoo and coworkers<sup>1</sup> until compound **3**. The syntheses of compounds **4** and **5** adapt also their procedures, but use a different alkylation agent in reaction 3. The amidation of **5** to synthesize compound **6** uses a standard procedure.



Scheme S1: Synthesis route for AAP-bearing monomer **6**.

## Monomer Synthesis

### Synthesis of 3-(2-(4-nitrophenyl)hydrazinylidene)pentane-2,4-dione (compound **2**)

1.80 g (26.1 mmol; 1.20 Eq.) of NaNO<sub>2</sub> are dissolved in 2.5 mL of water. The solution is dropped into a cooled solution of 3.00 g (21.7 mmol; 1.00 Eq.) of *p*-nitroaniline **1** in 33 mL of acetic acid (AcOH, Merk Millipore, purity > 99 %) and 5.0 mL of 12 M HCl. The solution is stirred for 45 min and added as a whole into a suspension of 2.83 g (28.23 mmol; 1.30 Eq.) of penta-2,4-dione **9** and 5.35 g (65.16 mmol; 3.00 Eq.) of sodium acetate in 22.0 mL of EtOH and 13.0 mL (0.6 mL·mmol<sup>-1</sup>) of water. The mixture is stirred for 1 h. Then, the yellow precipitate formed is filtered off, and washed with water and a 1:1 (v:v) water:EtOH mixture (20.0 mL each). After drying overnight in vacuum, the product **2** is received as a yellow solid (yield 4.71 g, 87 %)

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K): δ =14.46 (s, 1H, 7-H), 8.33 (m, 2 H, 2-H), 7.57 (m, 2 H 3-H), 2.63, 2.54 (s, 6 H, 8-H) ppm (Figure S4).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K):  $\delta$  = 198.55, 196.71 (6-C), 146.86 (4-C), 144.43 (1-C), 135.07 (5-C), 125.64 (2-C), 115.82 (3-C) 31.53, 26.43 (8-C) ppm (Figure S5).

#### **(E)-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole (compound 3)**

1.40 g (5.62 mmol; 1.00 Eq.) of the hydrazone-pentadione **2** are suspended in 5 mL of EtOH and 0.28 g (5.62 mmol; 1.00 Eq.) of hydrazine hydrate (64% w/w) **10** was dropped to the suspension. Heating the reaction mixture to reflux dissolves the hydrazone-pentadione **2**. After heating the reaction mixture to reflux for 3 h, it is cooled to RT, dried over  $\text{MgSO}_4$ , concentrated under reduced pressure and the residue finally dried in the vacuum oven for 3 d at  $40^\circ\text{C}$ , to yield the orange solid **3** (yield 1.34 g, 97 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 8.34 (m, 2 H, 2-H), 7.92 (m, 2 H 3-H), 2.65 (s, 6 H, 7-H) ppm (Figure S6).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 156.94 (4-C), 147.73 (1-C), 142.82 (6-C), 135.44 (5-C), 124.70 (2-C), 122.34 (3-C) 12.33 (7-C) ppm (Figure S7).

#### **(E)-1-ethyl-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole (compound 4)**

2.70 g (11.0 mmol; 1.00 Eq.) of aryl azopyrazole **3**, 1.44 g (13.2 mmol; 1.20 Eq.) of bromoethane **11**, and 7.61 g (55.1 mmol; 5 Eq.) of  $\text{K}_2\text{CO}_3$  are suspended in 300 mL of acetonitrile (ACN, purity > 99.9 %) and heated to reflux for 3 d. The solids are filtered off and the solvent of the filtrate is removed under reduced pressure. The crude solid product is dissolved in 200 mL of DCM and water each. The organic phase is separated, washed with 100 mL portions of water and brine, dried over  $\text{MgSO}_4$ , and then filtered through a short column filled with 10 g of silica. After drying overnight in the vacuum oven at  $40^\circ\text{C}$ , the product **4** is received as an orange solid (yield 2.73 g, 91%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 8.33 (m, 2 H, 2-H), 7.88 (m, 2 H 3-H), 4.14 (q, 2 H, 8-H), 2.63, 2.52 (s, 6 H, 7-H), 1.47 (t, 3 H, 9-H) ppm (Figure S8).

$^3J_{10-11} = 7.2$  Hz

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 157.21 (4-C), 147.45 (1-C), 142.90, 135.89 (6-C), 139.92 (5-C), 124.65 (2-C), 122.22 (3-C), 44.15 (8-C), 15.08, 14.19 (7-C), 9.83 (9-C) ppm (Figure S9).

#### **(E)-4-((1-ethyl-3,5-dimethyl-1H-pyrazol-4-yl)diazenyl)aniline (compound 5)**

2.70 g (9.88 mmol; 1.00 Eq.) Ethyl aryl azopyrazole of **4** are dissolved in 100 mL of THF and 40 mL of water. 2.57 g (10.7 mmol; 3.00 Eq.) of  $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$  are added. The mixture is heated to reflux and stirred overnight. The solvent is removed under reduced pressure, the remaining solid dissolved in 150 mL of DCM, and washed with 50 mL water, and twice with 100 mL of brine. Afterwards the organic phase is dried over  $\text{MgSO}_4$ , and the solvent is removed under reduced pressure. Finally the crude product is purified *via* silica column chromatography with petrol ether : ethyl acetate (2:3 v/v) as eluent. The product **5** is obtained as an orange solid (yield 1.63 g, 68%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  = 7.69 (m, 2 H, 2-H), 6.73 (m, 2 H 3-H), 4.08 (q, 2 H, 8-H), 3.93 (s, 2 H, 10-H) 2.57, 2.51 (s, 6 H, 7-H), 1.43 (t, 3 H, 9-H) ppm (Figure S10).

$^3J_{10-11} = 7.2$  Hz

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta = 148.03$  (4-C), 146.53 (1-C), 142.03, 134.85 (6-C), 136.53 (5-C), 123.49 (2-C), 114.77 (3-C), 43.85 (8-C), 15.27, 13.87 (7-C), 9.74 (9-C) ppm (Figure S11).

TLC (PE:EE 1:1):  $R_f = 0.36$

(E)-N-(4-((1-ethyl-3,5-dimethyl-1H-pyrazol-4-yl)diazenyl)phenyl)acrylamide (AAPEAm) (compound **6**)

1.63 g (6.70 mmol; 1.00 Eq.) of aniline aryl azopyrazole **5** and 0.81 g (8.04 mmol; 1.10 Eq.) of triethylamine ( $\text{NEt}_3$ , purity > 99.5 %) are dissolved in 70 mL of THF. After cooling the mixture with an ice bath, a solution of 0.67 g (7.37 mmol; 1.10 Eq.) of freshly distilled acryloyl chloride **12** (Merk Millipore, purity > 96%, stabilised with phenothiazine) in 8.0 mL of THF are added dropwise over 30 min. The mixture is stirred vigorously overnight at RT. The precipitate of  $\text{NEt}_3 \cdot \text{HCl}$  is filtered off, and the solvent is removed under reduced pressure. The solid residue is dissolved in 60 mL of DCM and washed twice with 20.0 mL of water as well as 20.0 mL of brine. The organic phase is dried over  $\text{MgSO}_4$ , the solvent removed under reduced pressure, and the residue dried overnight in the vacuum oven at 40°C. The product is obtained as an orange solid (yield 1.96 g, 99%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta = 8.47$  (s, 1H, 10-H), 7.77 (s, 4 H, 2+3-H), 6.45 (m, 2 H  $13_z+12$ -H), 5.77 (dd, 1 H,  $13_E$ -H), 4.10 (q, 2 H, 8-H), 2.57, 2.50 (s, 6 H, 7-H), 1.43 (t, 3 H, 9-H) ppm (Figures S12 and S14).

$^3J_{10-11} = 7.2$  Hz

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta = 150.18$  (11-C), 142.35 (4-C), 139.08 (1-C), 137.81, 131.19 (6-C), 137.81 (5-C), 128.00 (13-C), 122.60 (2+3-C), 120.14 (12-C), 43.93 (8-C), 15.21, 13.92 (7-C), 9.76 (9-C) ppm (Figures S13 and S15).

TLC (PE:EE 1:1):  $R_f = 0.20$

$T_{\text{melt}}$  (by DSC): 153 °C

ATR-FTIR spectrum (powder):

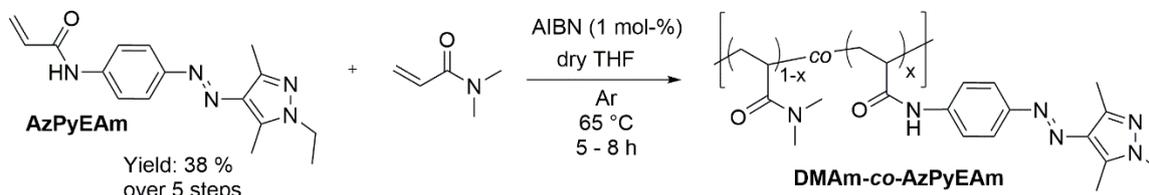
wavenumber ( $\text{cm}^{-1}$ )	assignment	group
3282	$\nu(\text{N-H})$	amine
2978	$\nu(\text{C-H})$	alkane
1663	$\nu(\text{C=O})$	amide
1413	$\nu(-\text{C}=\text{C})$	aromatic ring resonance

ESI-MS (m/z) for  $\text{C}_{16}\text{H}_{19}\text{N}_5\text{O}$  calculated 297.36; found 298.077  $[\text{M} + \text{H}]^+$ .

EA:	Calculated	Found
	C: 64.63 %	C: 64.44
	H: 6.44 %	H: 6.66
	N: 23.55 %	N: 22.67

## Polymerization

A set of several p(DMAm-co-AAPEAm) copolymers was produced *via* free radical polymerization (Scheme S2). Following the scheme, a general polymerization procedure is described.



Scheme S2: Free radical copolymerization of DMAm and AAPEAm in dry THF with AIBN as a thermal initiator.

In a typical procedure 500-700 mg of DMAm (100 mol %), AAPEAm (2, 5, 8, 9, 10 or 14 mol % relative to DMAm), and AIBN (1 mol % relative to the sum of both monomers) are placed in a dry Schlenk tube, and dissolved in dry THF to prepare a 2 mol·L<sup>-1</sup> solution. The tube is sealed with a septum, and the mixture is purged with a gentle argon stream for 15 min to remove the oxygen. The solution is then immersed into a preheated 65 °C hot oil bath and stirred for 5 – 8 h. Conversion is monitored by <sup>1</sup>H NMR, observing the decay of the acrylic proton signal at around 5.8 ppm. The polymerization is stopped by removing the septum and exposing the mixture to air, and cooling the vessel rapidly to RT. The cooled mixture is diluted with 4 ml of THF, precipitated into diethyl ether, and the precipitated polymer is collected *via* filtration. The process is repeated until no monomer signal is visible in the <sup>1</sup>H NMR spectrum. At last, the polymer is dried under vacuum in the drying oven at 40°C.

## Calculation of Half-life time

The decay of the photo-stationary states follows 1st order kinetics. Accordingly, the half-life time  $\tau_{1/2}$  can be calculated from the slope of the plotted absorbance or the normalized <sup>1</sup>H NMR signals, respectively as a function of time, using equation (1).

$$\tau_{1/2} = \frac{\ln(2)}{\text{slope}} \quad (1)$$

For the aqueous polymer solution, the absorbance of the n→π\* absorption band of the *cis* state (442 nm for 20 °C measurement and 443 nm for the 40 °C measurement) is recorded. For monomer AAPEAm **6**, the content of the *cis*-state is determined from the normalized <sup>1</sup>H NMR spectra. Figures S1-S3 show the linearised decay as well as the function of the linear regression.

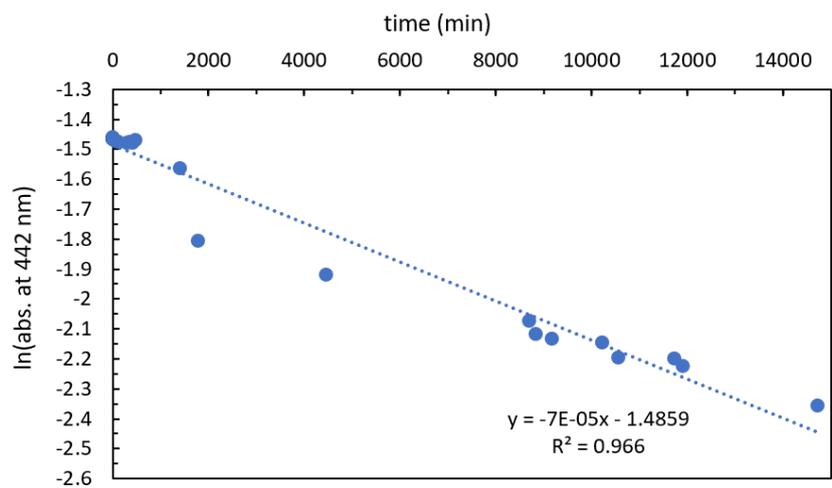


Figure S1: Linearised decay of the absorption at 442 nm for copolymer DMAM-coAAPEAm<sub>9.5</sub> in water at 20 °C.

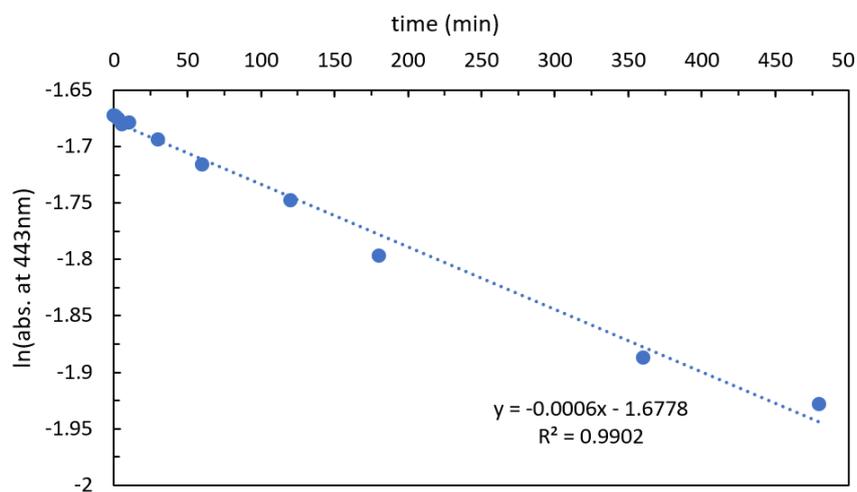


Figure S2: Linearised decay of the absorption at 443 nm for copolymer DMAM-coAAPEAm<sub>9.5</sub> in water at 40 °C.

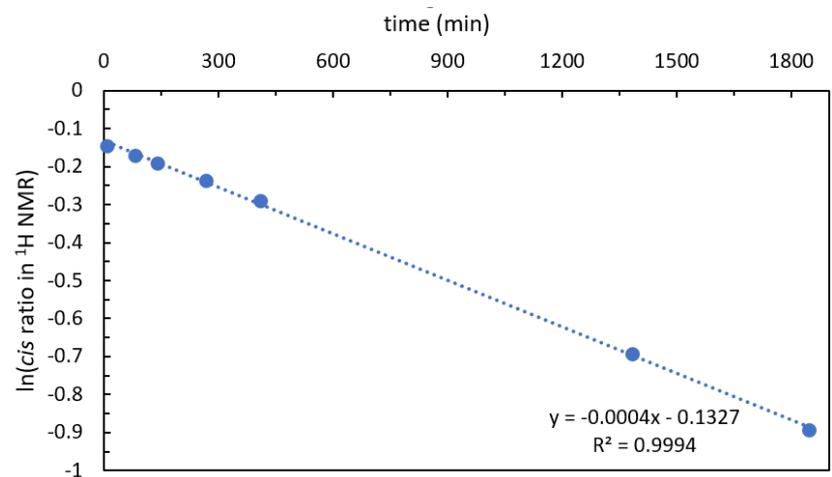


Figure S3: Linearised decay of the absorption at 442 nm for monomer AAPEAm 6 in MeoD-D<sub>4</sub> at 20 °C.

# Spectra

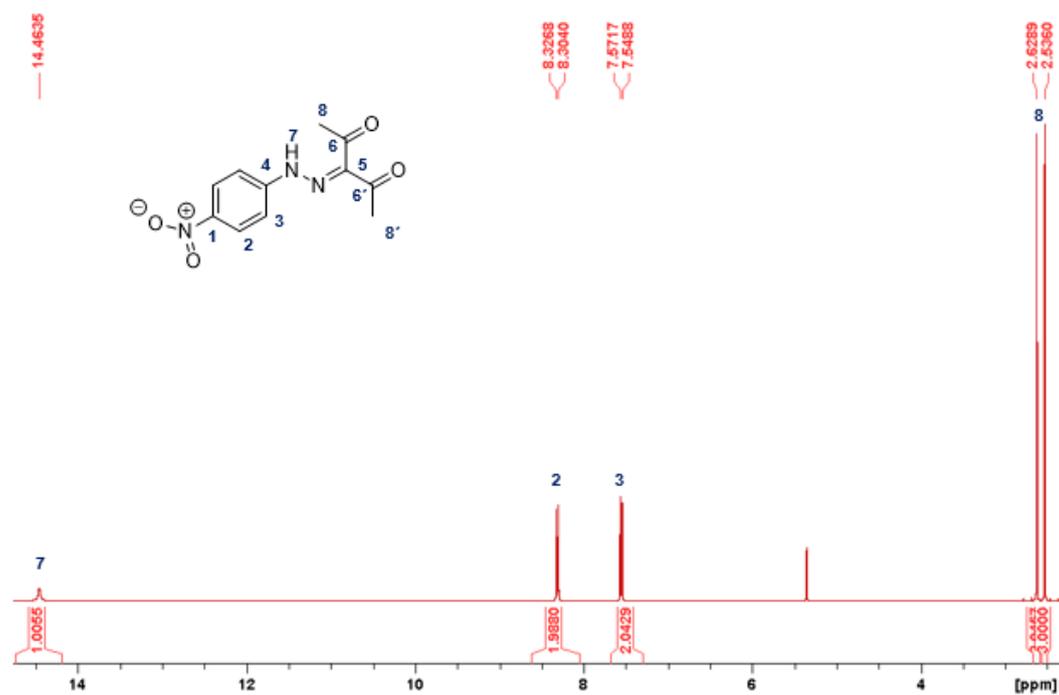


Figure S4: <sup>1</sup>H NMR spectrum of compound 2 in CDCl<sub>2</sub>.

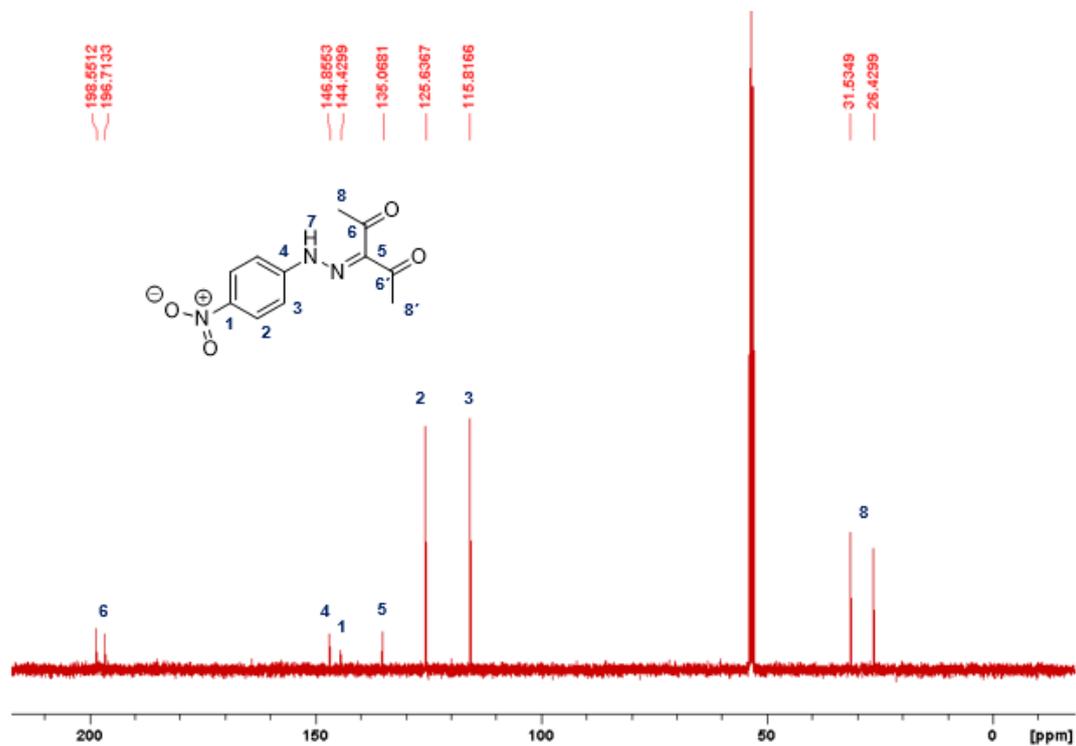


Figure S5: <sup>13</sup>C NMR spectrum of compound 2 in CDCl<sub>2</sub>.

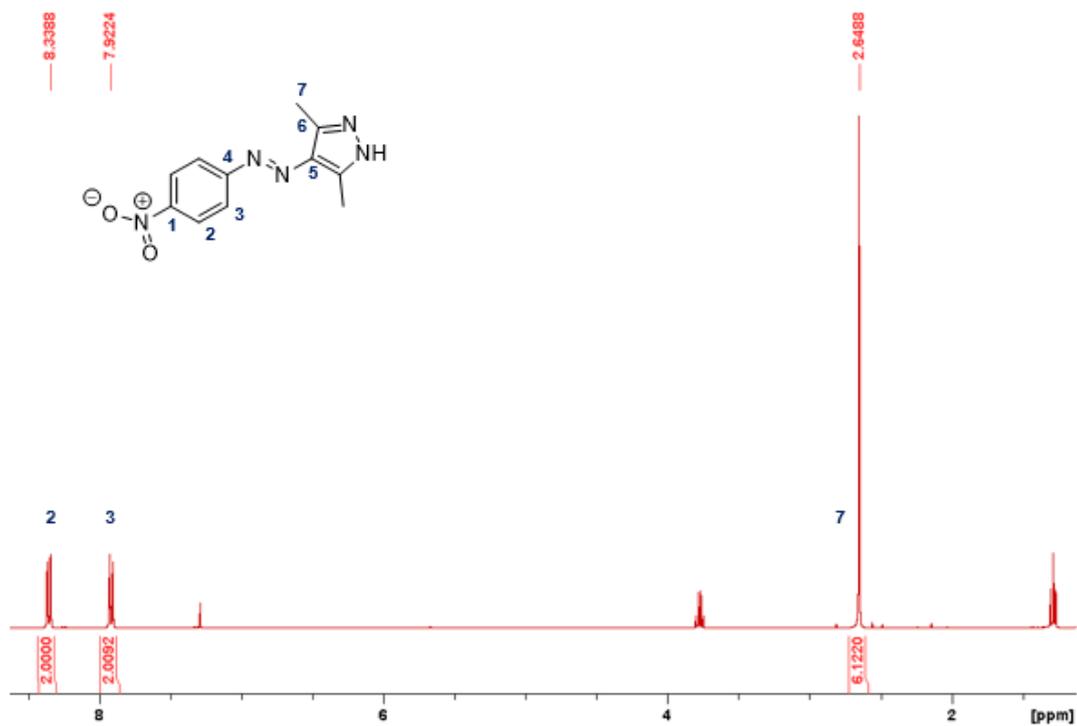


Figure S6: <sup>1</sup>H NMR spectrum of compound **3** in CDCl<sub>3</sub>.

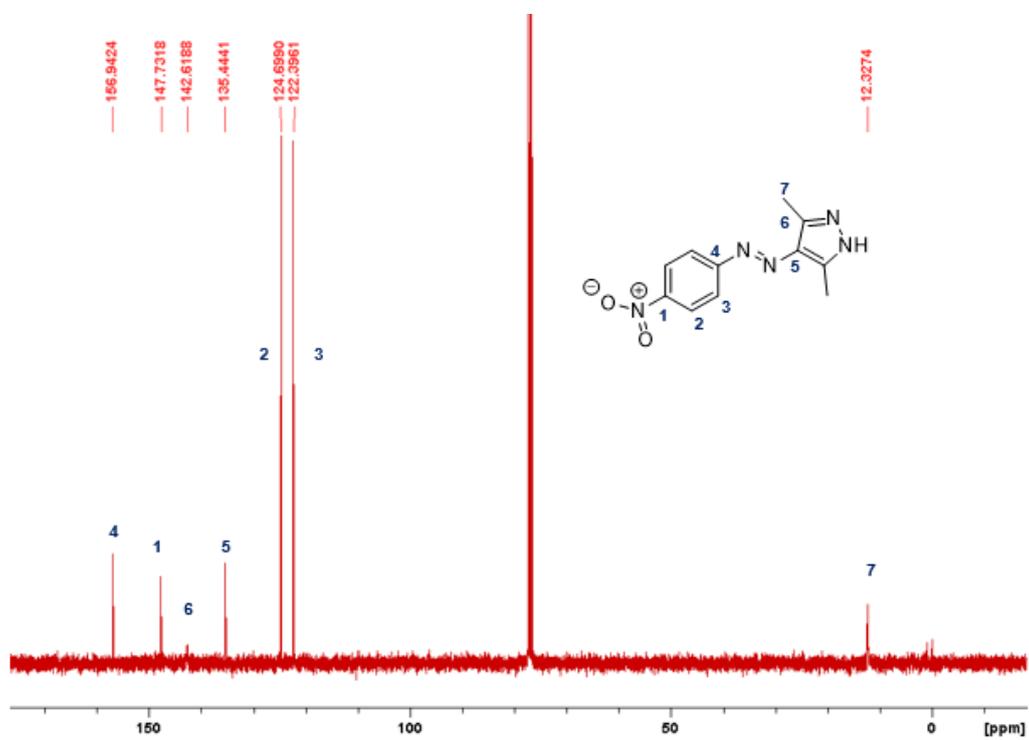


Figure S7: <sup>13</sup>C NMR spectrum of compound **3** in CDCl<sub>3</sub>.

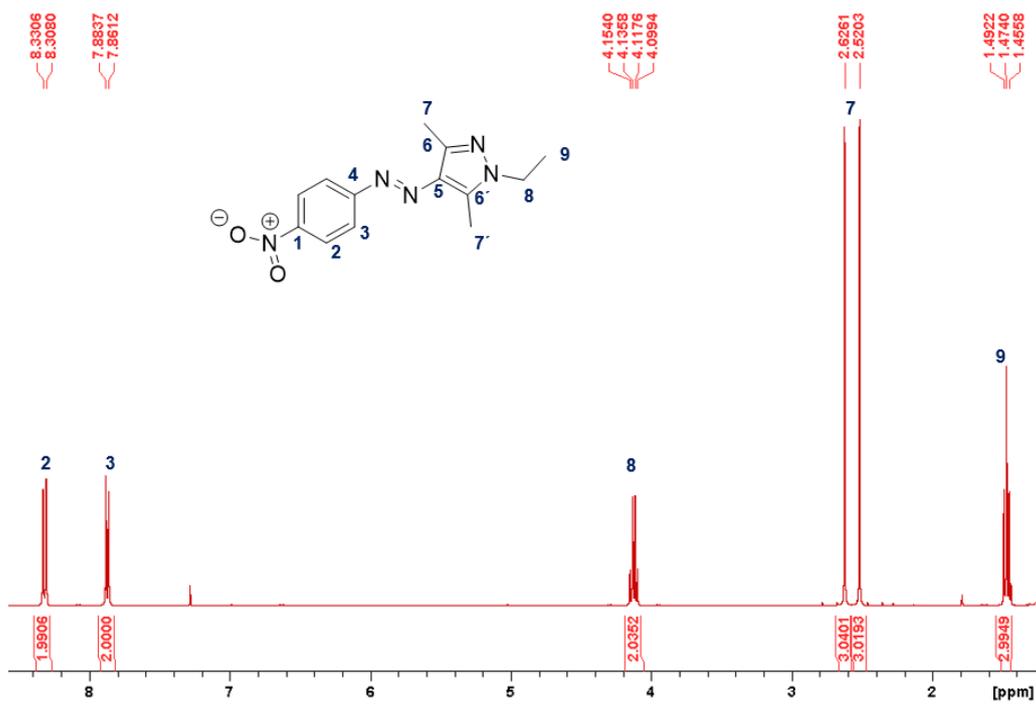


Figure S8: <sup>1</sup>H NMR spectrum of compound 4 in CDCl<sub>3</sub>.

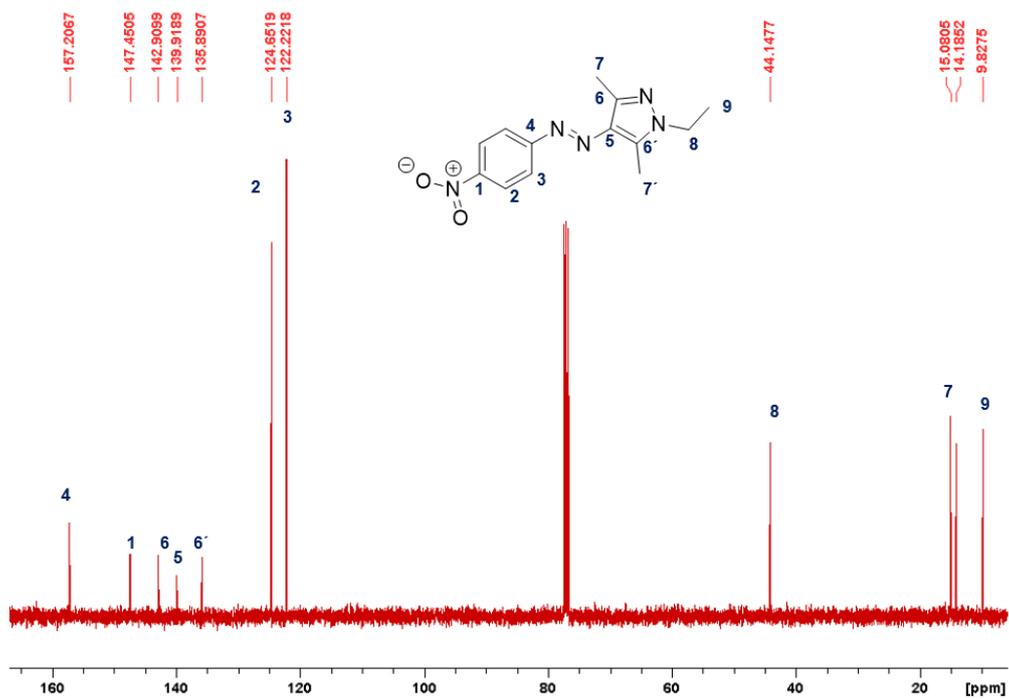


Figure S9: <sup>13</sup>C NMR spectrum of compound 4 in CDCl<sub>3</sub>.

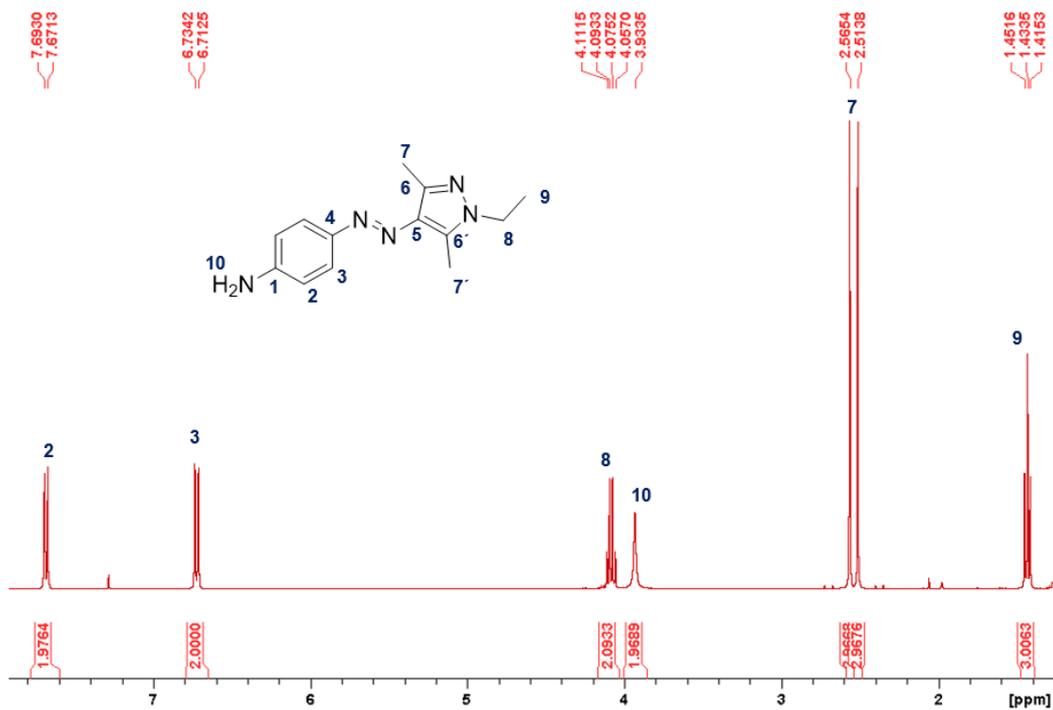


Figure S10: <sup>1</sup>H NMR spectrum of compound 5 in CDCl<sub>3</sub>.

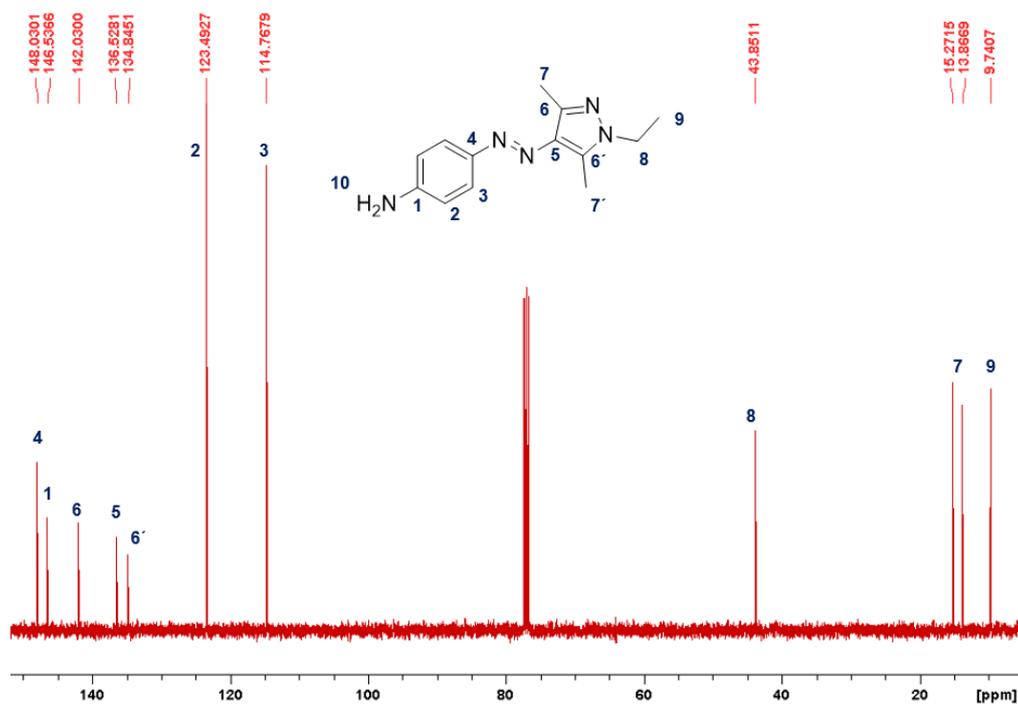


Figure S11: <sup>13</sup>C NMR spectrum of compound 5 in CDCl<sub>3</sub>.

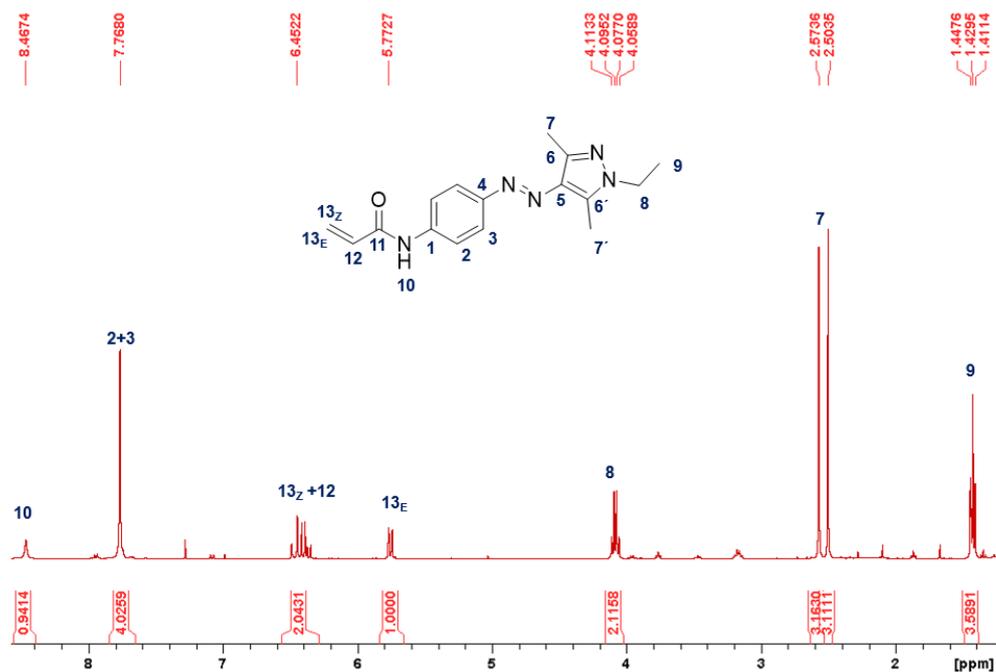


Figure S12: <sup>1</sup>H NMR spectrum of monomer AAPEAm 6 in CDCl<sub>3</sub>. Note that due to short exposure to daylight during sample handling prior to measurement, the compound contains a small amount (< 2 mol %) of Z (*cis*) isomer.

Mol%)

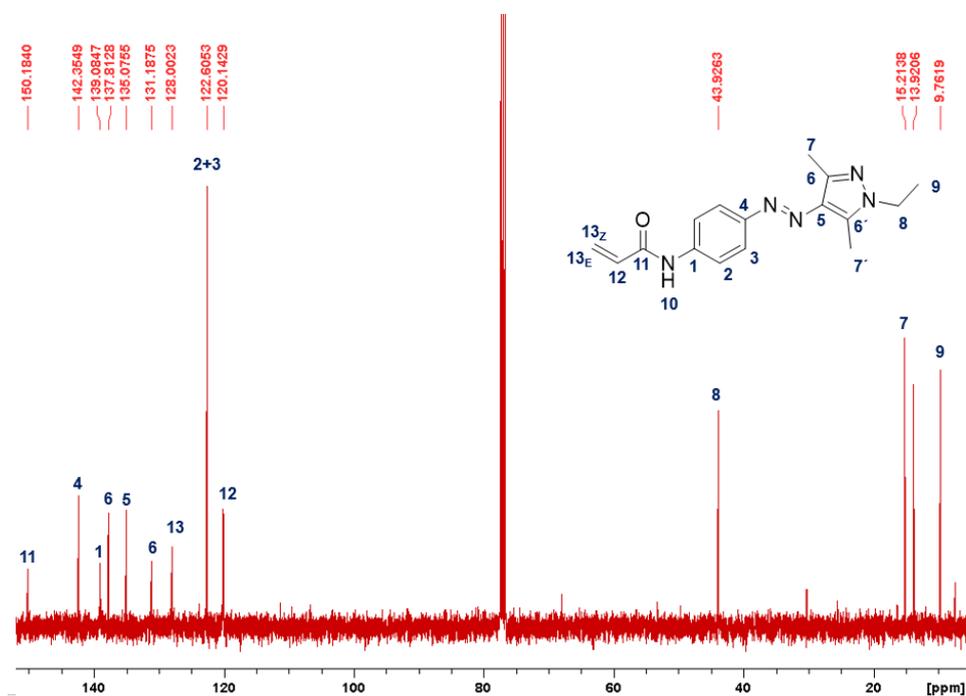


Figure S13: <sup>13</sup>C NMR spectrum of monomer AAPEAm 6 in CDCl<sub>3</sub>.

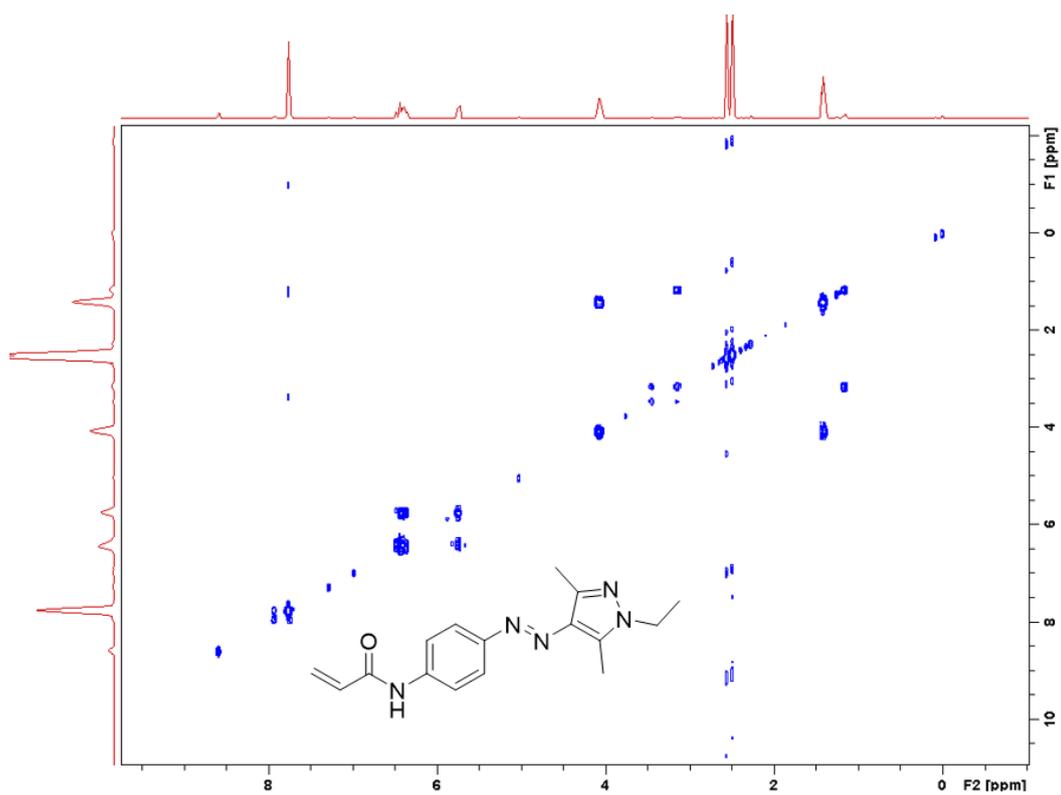


Figure S14: COSY spectrum of monomer AAPEAm **6** in CDCl<sub>3</sub>.

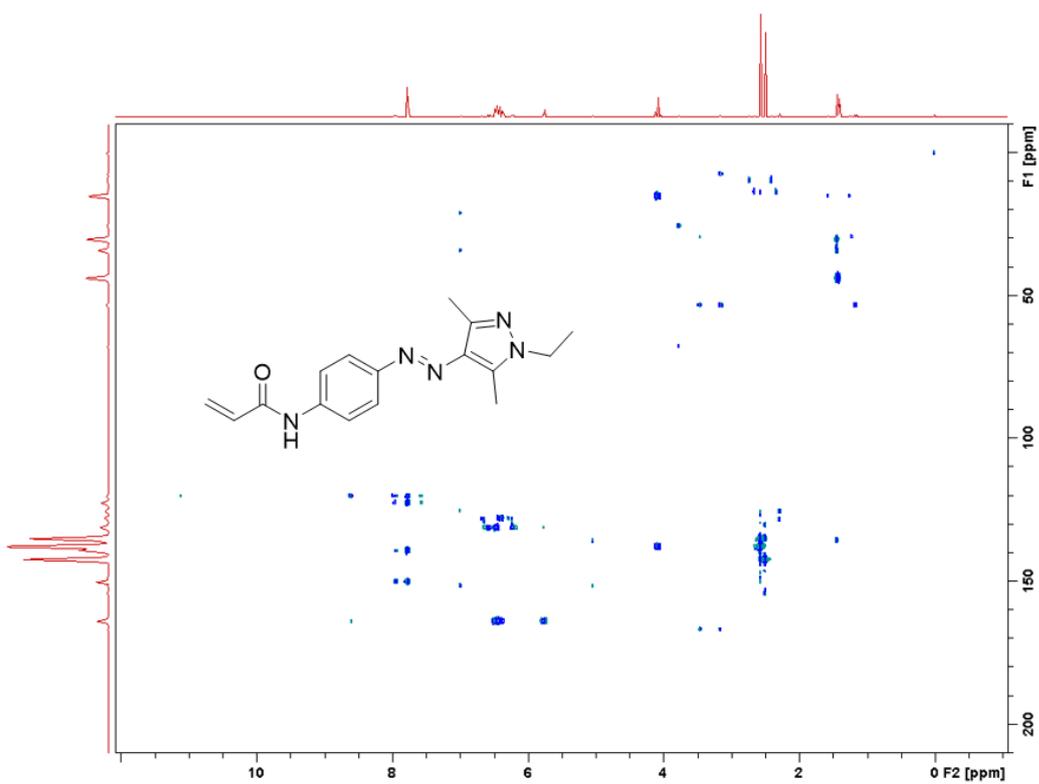


Figure S15: HMBC spectrum of monomer AAPEAm **6** in CDCl<sub>3</sub>.

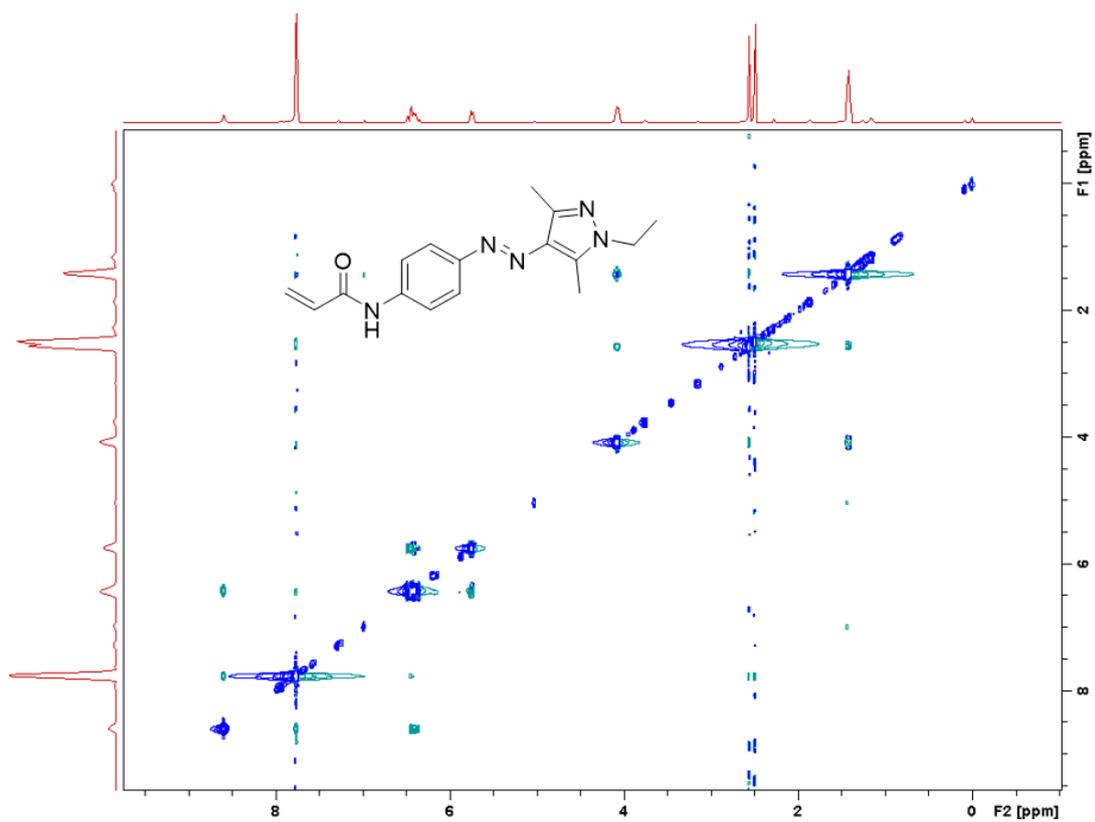


Figure S16: NOESY spectrum of monomer AAPEAm 6 in  $\text{CDCl}_3$ .

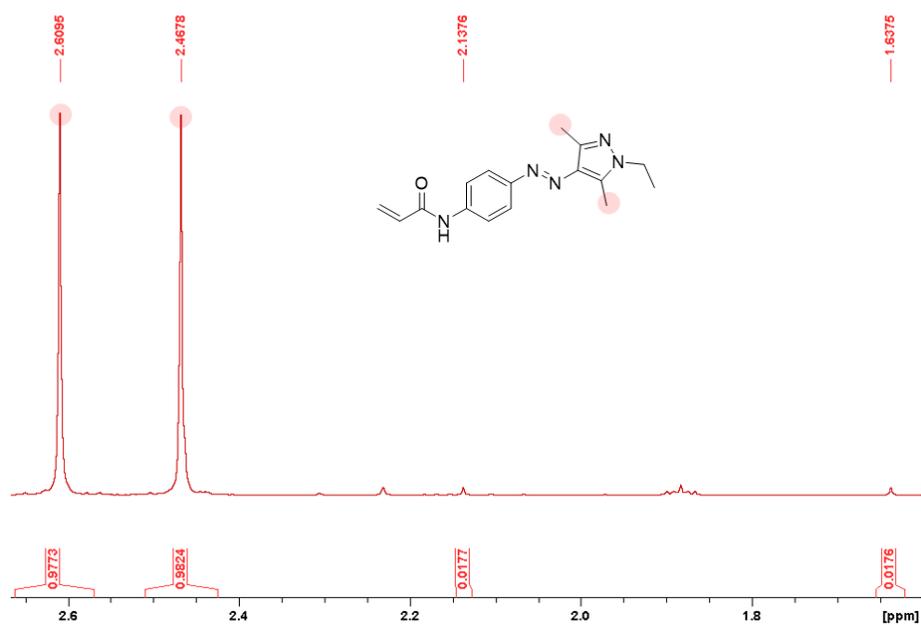


Figure S17:  $^1\text{H}$  NMR spectrum of monomer AAPEAm 6 in  $\text{MeOD-D}_4$  before irradiation. The integrals of the corresponding *trans* and *cis* states are normalized to calculate the ratio of *trans* : *cis* (98:2).

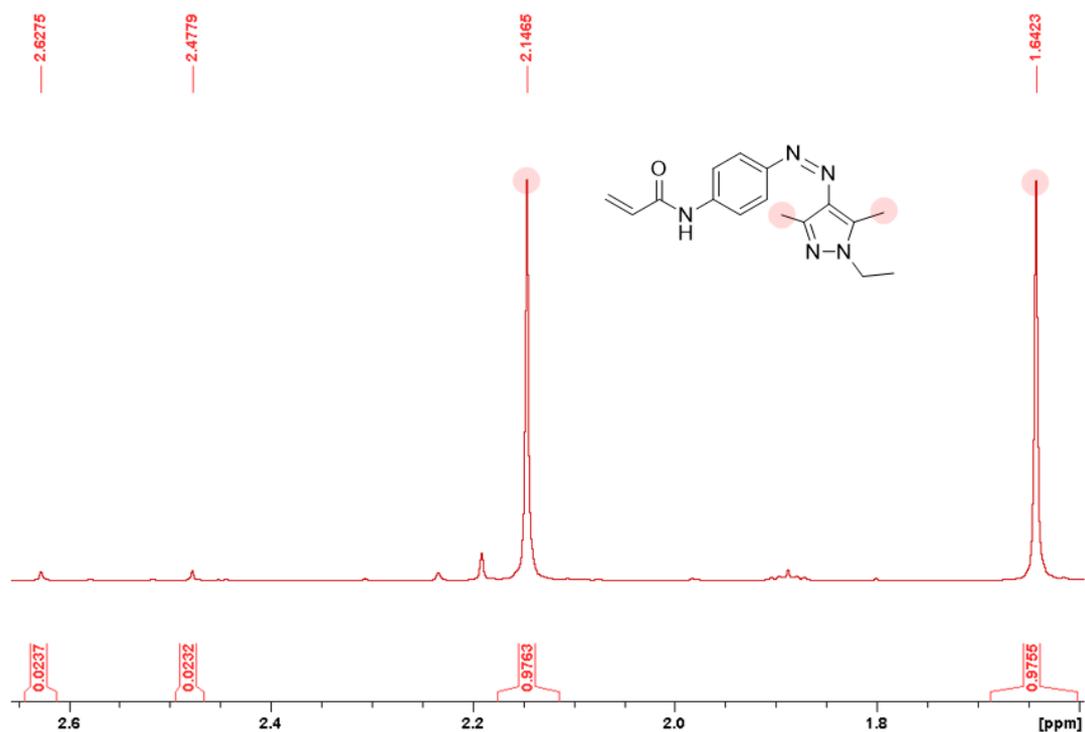


Figure S18:  $^1\text{H}$  NMR spectrum of monomer AAPEAm **6** in MeOD-D<sub>4</sub> after irradiation at 365 nm. The integrals of the corresponding *trans* and *cis* states are normalized to calculate the ratio of *trans* : *cis* (2:98).

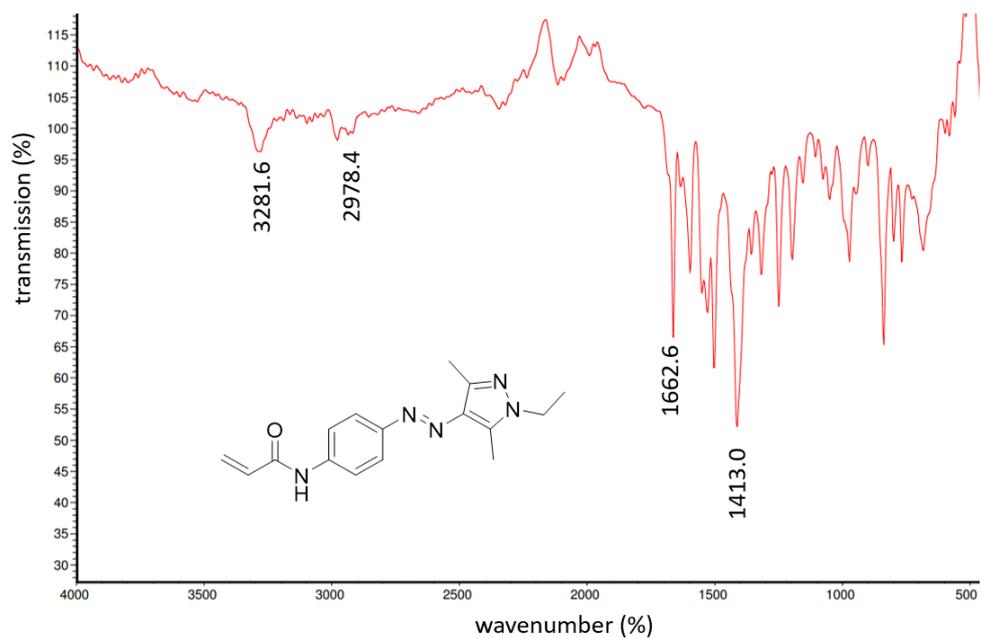


Figure S19: ATR-FTIR spectra of monomer AAPEAm **6**.

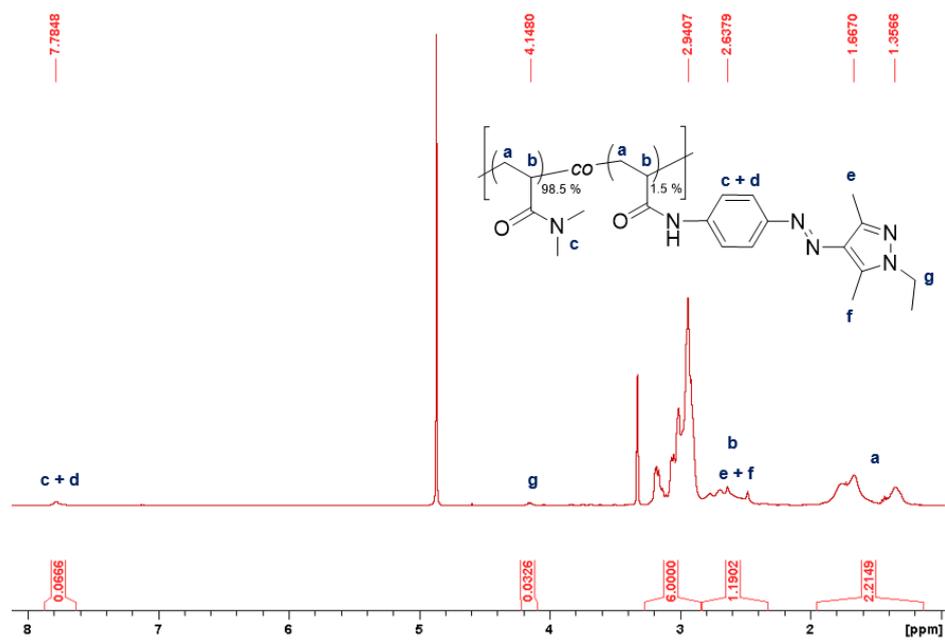


Figure S20:  $^1\text{H}$  NMR of copolymer p(DMAm-co-AAPEAm<sub>1.5</sub>) in MeOD-D<sub>4</sub>.

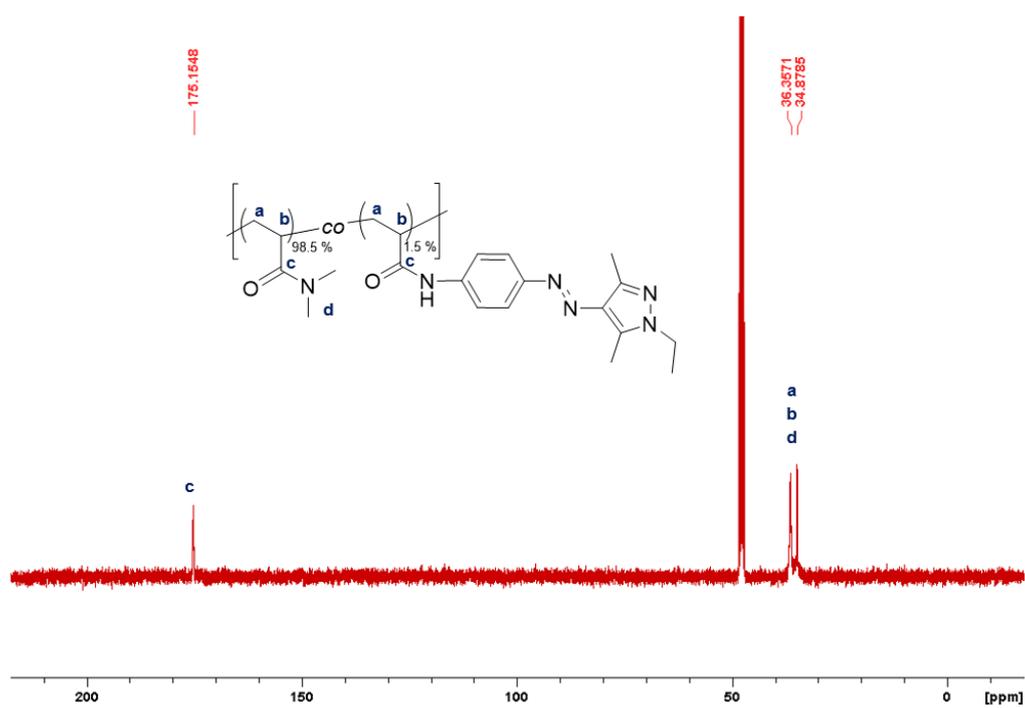


Figure S21:  $^{13}\text{C}$  NMR of copolymer p(DMAm-co-AAPEAm<sub>1.5</sub>) in MeOD-D<sub>4</sub>.

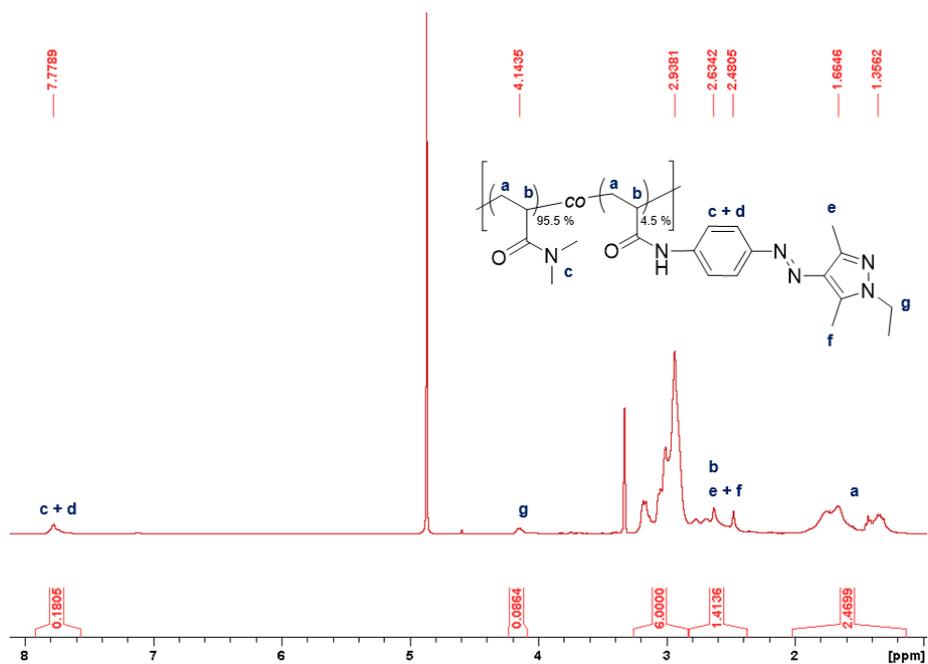


Figure S22:  $^1\text{H}$  NMR of copolymer  $p(\text{DMAm-co-AAPEAm}_{4.5})$  in  $\text{MeOD-D}_4$ .

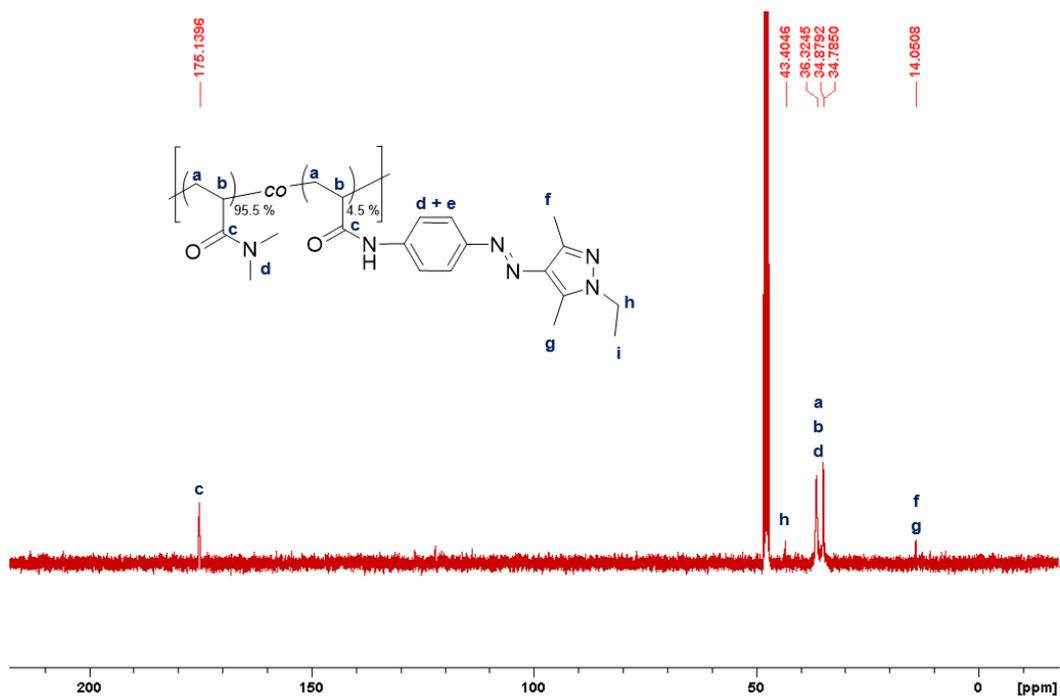


Figure S23:  $^{13}\text{C}$  NMR of copolymer  $p(\text{DMAm-co-AAPEAm}_{4.5})$  in  $\text{MeOD-D}_4$ .

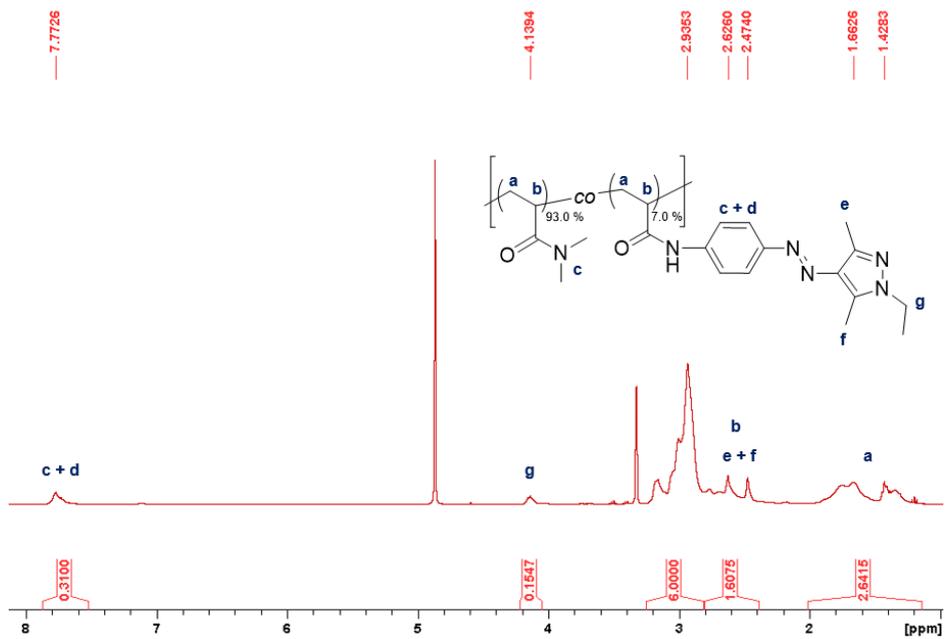


Figure S24: <sup>1</sup>H NMR of copolymer p(DMAm-co-AAPEAm<sub>7</sub>) in MeOD-D<sub>4</sub>.

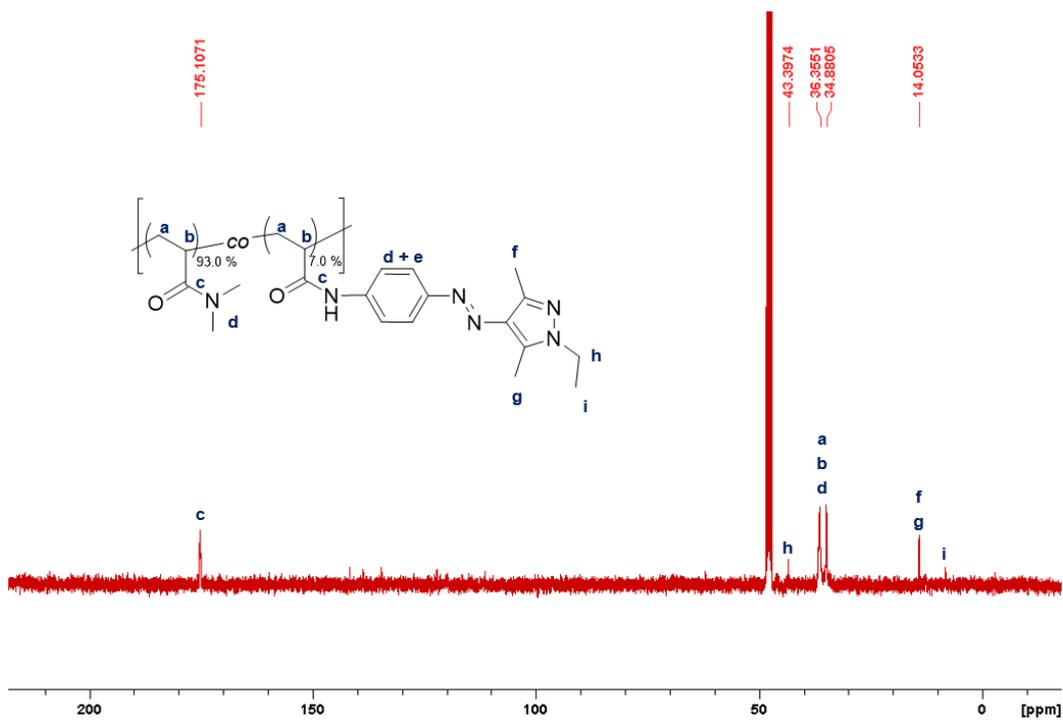


Figure S25: <sup>13</sup>C NMR of copolymer p(DMAm-co-AAPEAm<sub>7</sub>) in MeOD-D<sub>4</sub>.

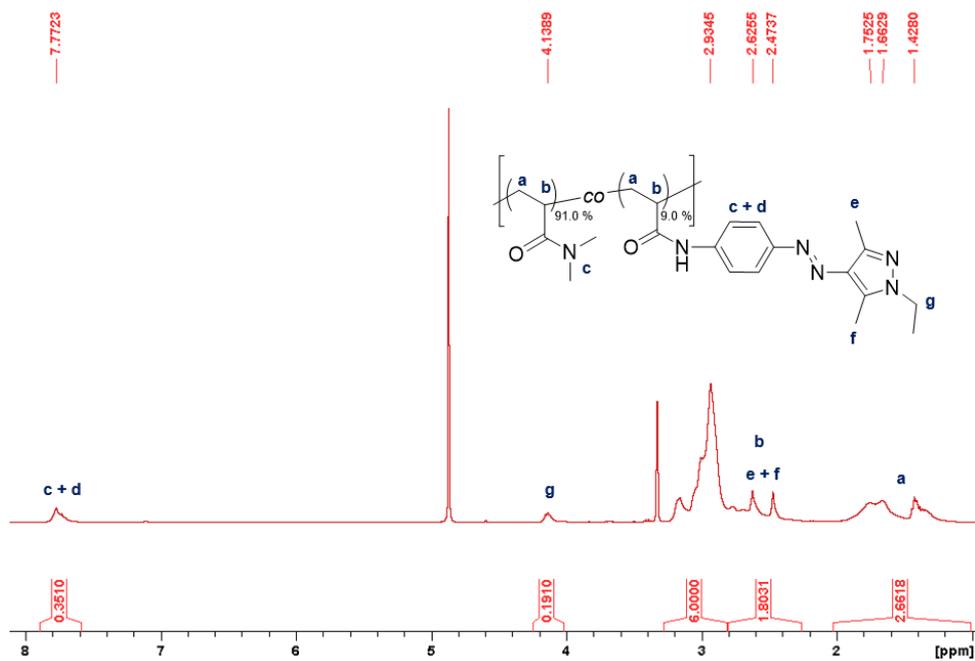


Figure S26: <sup>1</sup>H NMR of copolymer p(DMAm-co-AAPEAm<sub>8</sub>) in MeOD-D<sub>4</sub>.

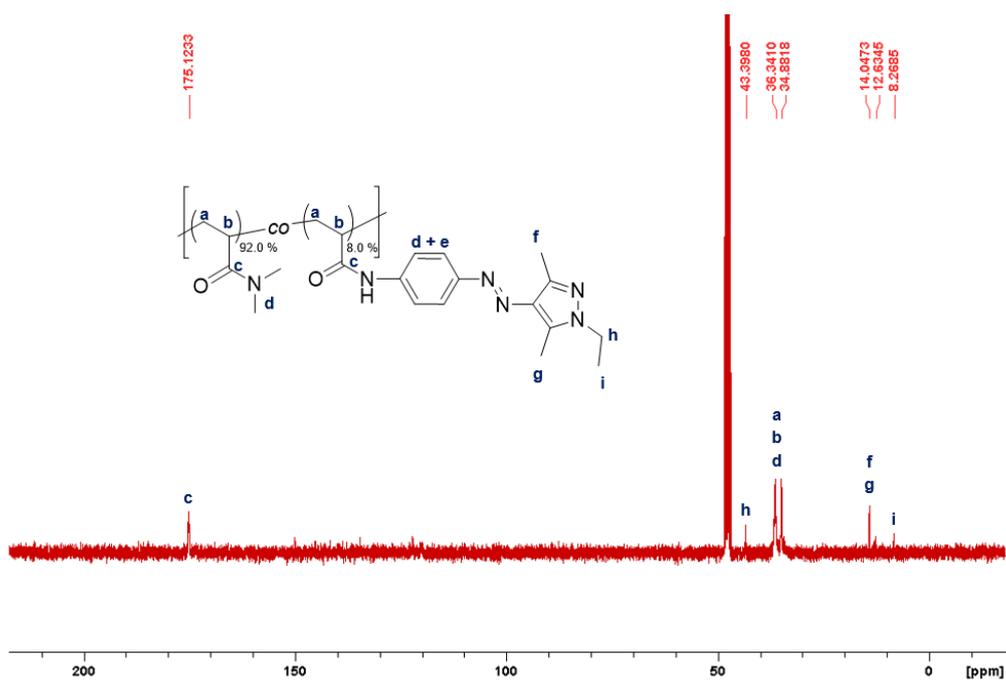


Figure S27: <sup>13</sup>C NMR of copolymer p(DMAm-co-AAPEAm<sub>8</sub>) in MeOD-D<sub>4</sub>.

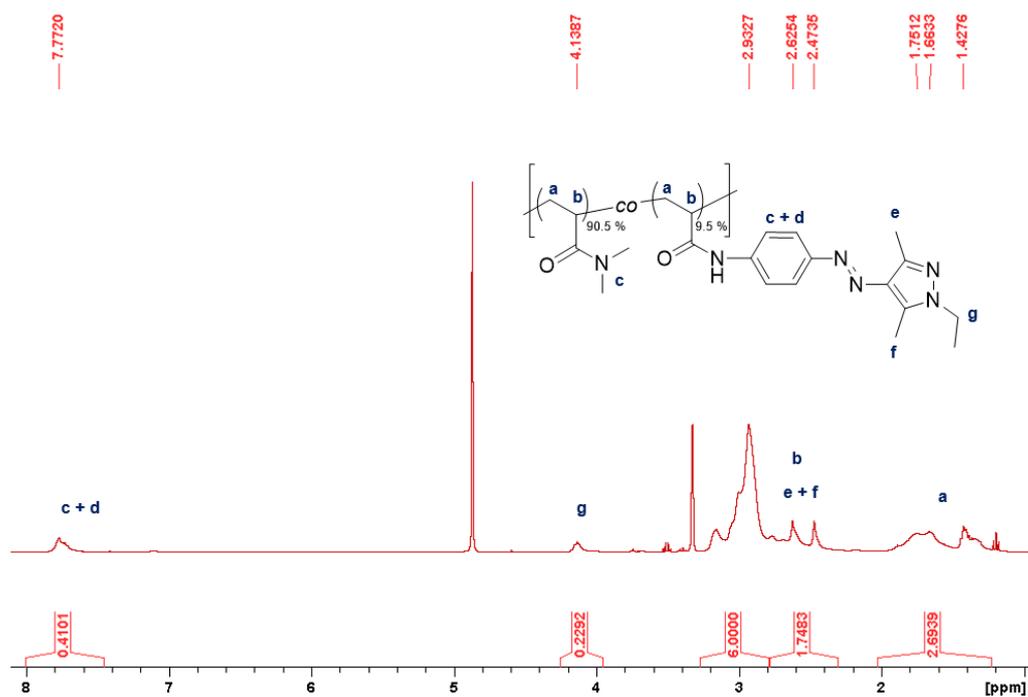


Figure S28: <sup>1</sup>H NMR of copolymer p(DMAm-co-AAPEAm<sub>9.5</sub>) in MeOD-D<sub>4</sub>.

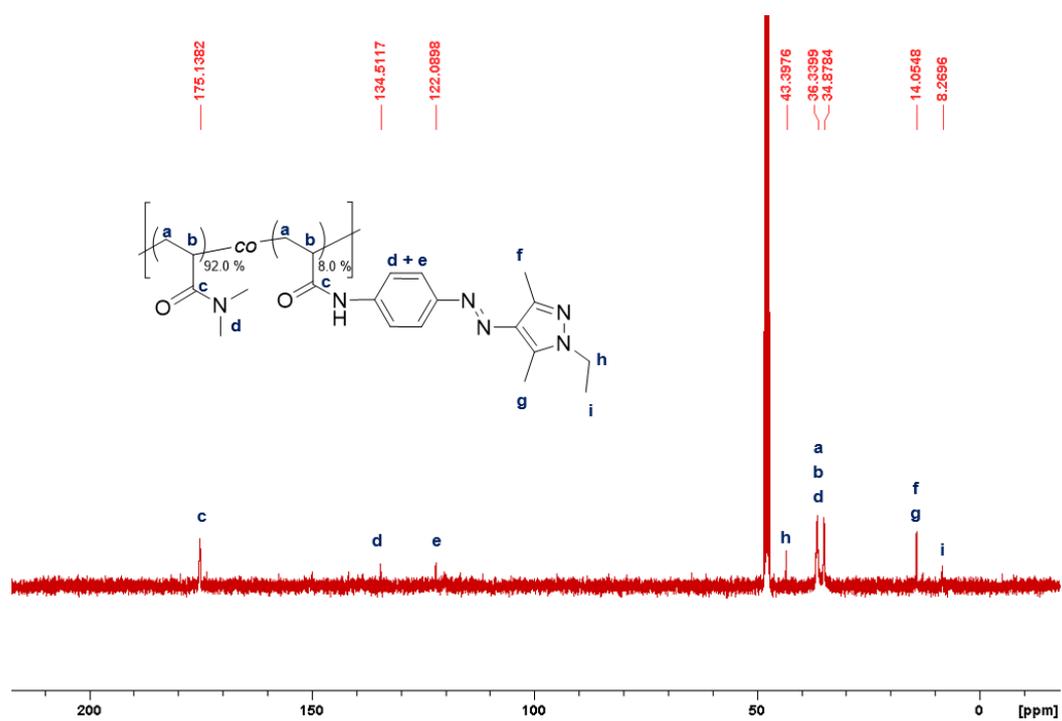


Figure S29: <sup>13</sup>C NMR of copolymer p(DMAm-co-AAPEAm<sub>9.5</sub>) in MeOD-D<sub>4</sub>.

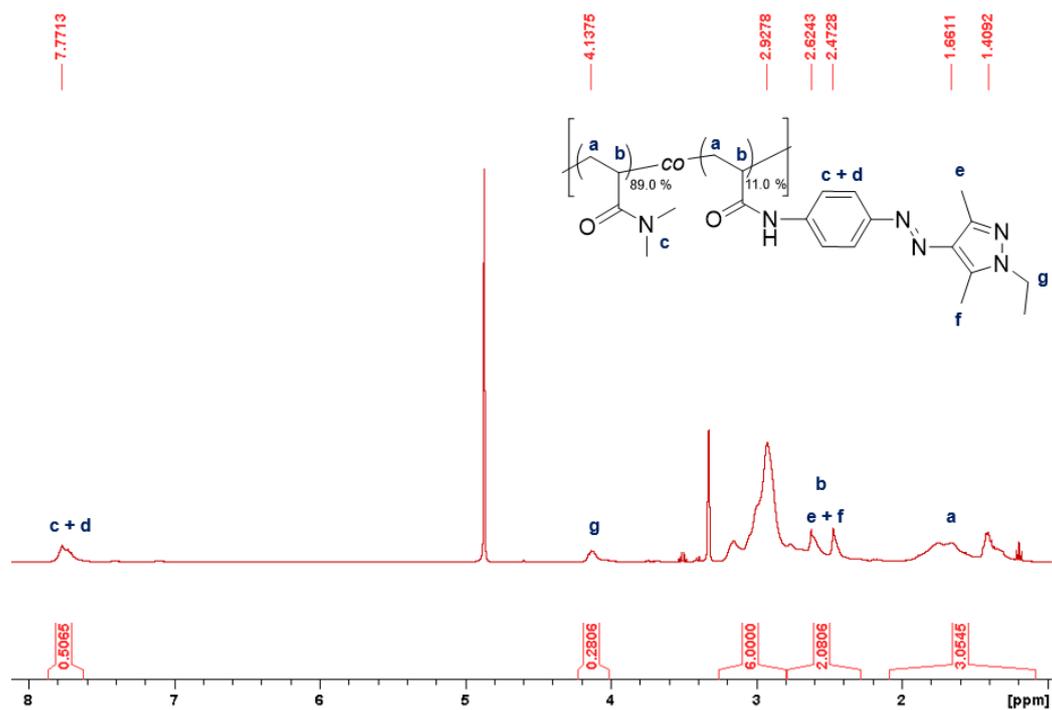


Figure S30: <sup>1</sup>H NMR of copolymer p(DMAm-co-AAPEAm<sub>11</sub>) in MeOD-D<sub>4</sub>.

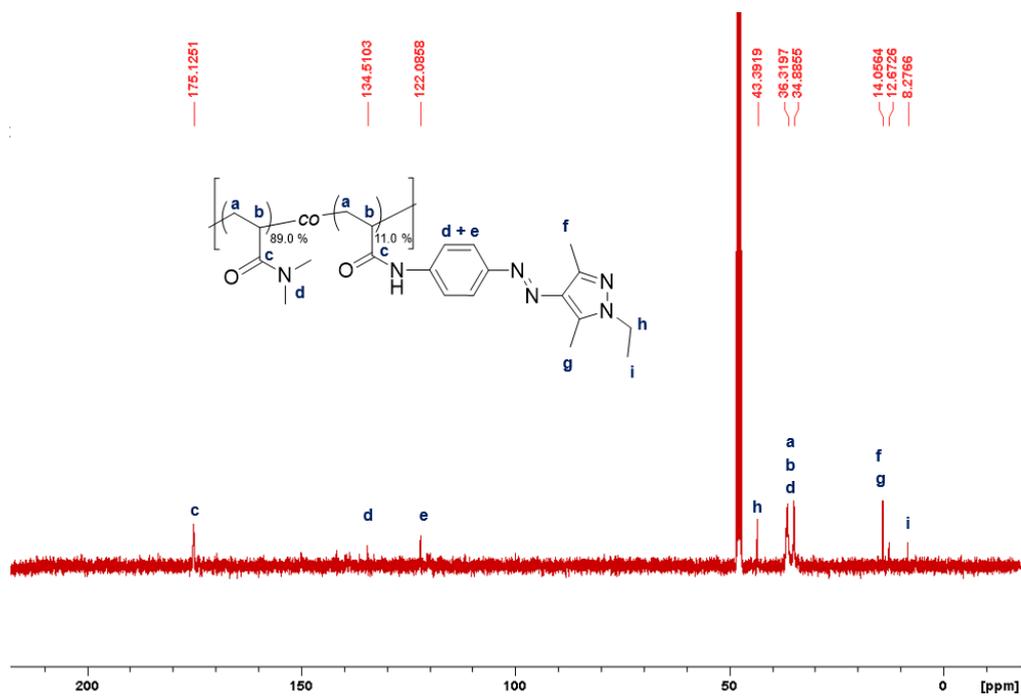


Figure S31: <sup>13</sup>C NMR of copolymer p(DMAm-co-AAPEAm<sub>11</sub>) in MeOD-D<sub>4</sub>.

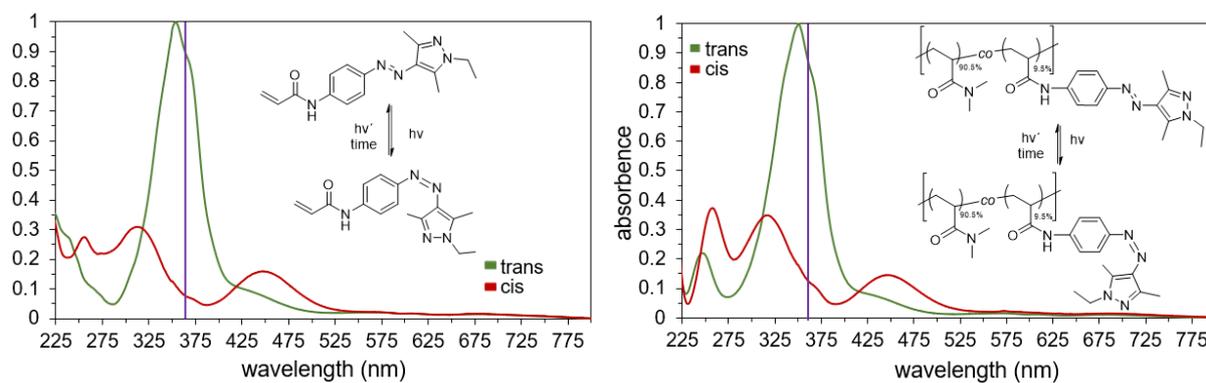


Figure S32: UV-vis absorption spectra in methanol at room temperature. Before irradiation (green) and after irradiation (red). Left monomer AAPEAm 6 ( $c = 0.005 \text{ g}\cdot\text{L}^{-1}$ ), right copolymer p(DMAm-co-AAPEAm<sub>9.5</sub>) ( $c = 0.033 \text{ g}\cdot\text{L}^{-1}$ ). The purple line indicates the irradiation wavelength.

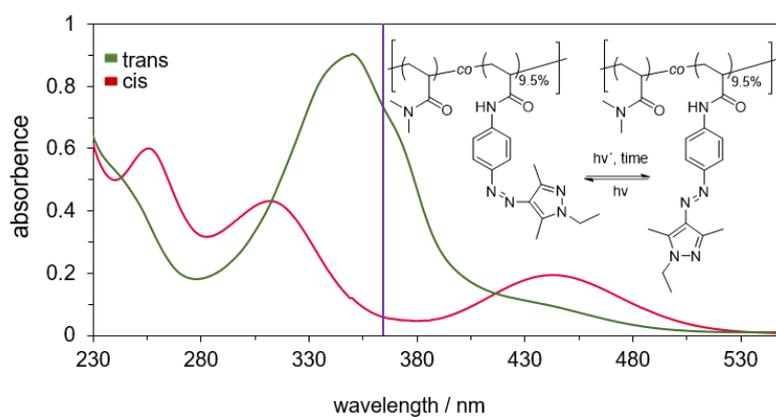


Figure S33: UV-vis absorption spectra of copolymer p(DMAm-co-AAPEAm<sub>9.5</sub>) ( $c = 0.033 \text{ g}\cdot\text{L}^{-1}$ ) in water at room temperature. Before irradiation (green) and after irradiation (red). The purple line indicates the irradiation wavelength.

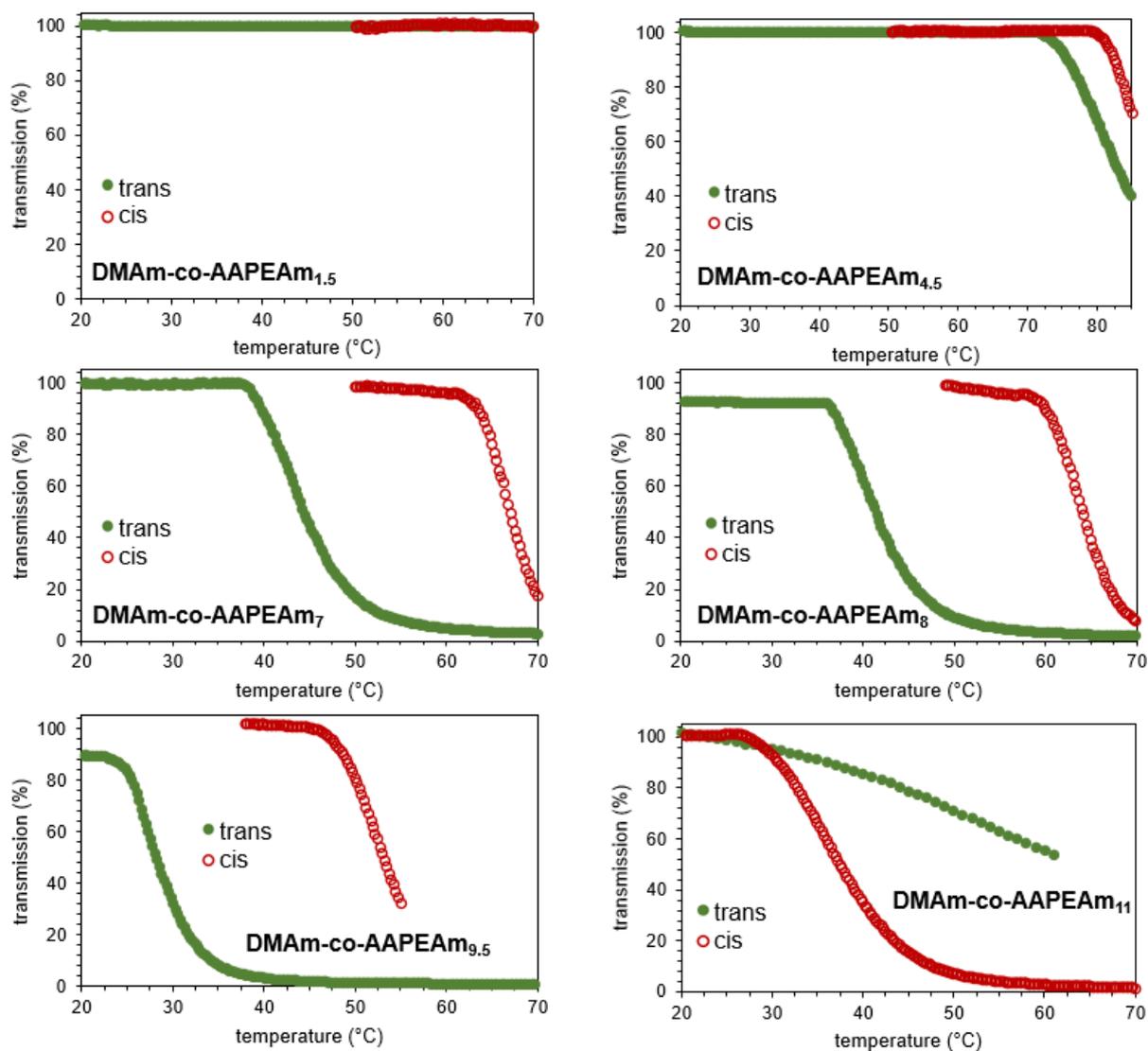


Figure S34: Turbidity of the AAPEAm-functionalised copolymers in water ( $c = 1\text{g}\cdot\text{L}^{-1}$ ) as a function of the temperature and of the state of the photo-isomerization. Heating cycles, heating rate  $0.5\text{K}\cdot\text{min}^{-1}$ . Green symbols indicate solutions equilibrated in the dark (all trans-state), red symbols solutions solutions in the photo-stationary state after 15 min of irradiation by 365 nm light.

## References

1. C.-W. Chu, L. Stricker, T. M. Kirse, M. Hayduk and B. J. Ravoo, *Chemistry*, 2019, **25**, 6131–6140.