Electronic Supplementary Material (ESI) for Soft Matter.

Light-Responsive Azo-Containing Organogels

Electronic Supplementary Information

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1. Experimental Part

Materials. 2,2'-Azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] was kindly provided by Wako Pure Chemical Industries, Ltd. (catalogue number VA-086) and was dried overnight in vacuo at room temperature prior to use. All other reagents and compounds were commercially obtained from Sigma-Aldrich and used without further purification. Anhydrous dimethyl sulfoxide (DMSO) was used.

Chemical Analytics. A Bruker Avance III HD NMR spectrometer was utilized to record ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra. Chemical shifts (δ) are reported as parts per million (ppm) in reference to the residual solvent signal, relative to tetramethylsilane. Elemental analyses (EA) were carried out on a CE Instruments EA 1110 involving flash combustion and GC separation. Fourier transformation infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 65 spectrometer equipped with an attenuated total reflection (ATR) setup. Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu UV-2401PC spectrophotometer.

Mechanical Testing. The analysis of the mechanical properties of the organogels and adhesive lap joints were performed at ambient conditions using a Zwick/Roell Z010 tensile tester mounted with a 200 N load cell. For compressive stress-strain measurements of the organogels cylindrical specimen (14 x 10 mm) were prepared with custom made poly(tetrafluoroethylene) (PTFE) moulds and the measurements were performed with a pre-load of 1 kPa and a strain rate of 10 mm/min. The Young’s modulus was established from the slope of the stress-strain trace between 1 and 10% of strain. Adhesive lap joint shear tests were performed at a strain rate of 0.5 mm/min.

Dynamic Light Scattering. Light-scattering measurements were performed with a 3D LS Spectrometer (LS Instruments AG, Switzerland) equipped with linearly polarized and collimated laser beam operating at 660 nm. The measurements were performed at scattering angles of 30° at a temperature of 25 °C.

UV Irradiation. High power irradiation was performed using a Hönle Bluepoint 4 Ecocure lamp equipped with a 320-390 nm filter for UV light or a 390-500 nm filter for visible light, respectively. The power density of the lamp was set to 600 mW/cm^2 and the distance between the optical fibre and the sample was adjusted to 15 mm when using the 320–390 nm filter or 30 mm when using the 390–500 nm filter. Low power UV irradiation (365 nm) with a power density of 1 mW/cm^2 was carried out with a UVP 3UV™-38 lamp. The specimen temperature before and during irradiation experiments was measured with an Optris PI 160 infrared camera.

Preparation of Organogels. Stock solutions of poly(vinyl alcohol) (PVOH) of different molecular weights in DMSO were prepared by dissolving commercial PVOH (>98% hydrolyzed, M_w = 13–23, 31–50, or 85–124 kDa) in anhydrous DMSO under mechanical agitation at 80 °C over the course of 1 hour. The concentration of the PVOH stock solutions was of 15 wt% calculated on the basis of the molecular weight of the repeating unit of the polymer ($C_2H_4O \sim 44$ g/mol). The desired amount of cross-linker **azo-CX** was added to a glass vial and dissolved in anhydrous DMSO (1 mL) under magnetic agitation at ambient conditions (maximum concentration of 65 mg/mL). The **azo-CX** solution was added to a second glass vial containing the desired amount of the stock solution of PVOH and the mixture was homogenized by manual agitation with a glass rod over the course of 30 s. To prepare gels of a particular shape, the mixture was rapidly transferred to an appropriate container (e.g., PTFE molds). As previously reported for similar organogels,[1] the gelation was observed within minutes but the reaction was allowed to complete overnight in a desiccator. Organogels without responsive cross-links were prepared following the same procedure and using hexamethylene diisocycanate as the cross-linking agent. An overview of the compositions of all organogels is provided in Table S3. The cross-link density was calculated assuming a reaction efficiency of 100% and based on the molecular weight of the repeating unit of the polymer. Cross-link density is expressed in mol%, and may also be described as the frequency of cross-links (f_{CX}) or the molecular weight between cross-links (M_c).

Photography. Photographs were taken with a Nikon D7100 digital camera equipped with a AF-S DX Zoom-NIKKOR 18-135mm lens (f/3.5-5.6G IF-ED).

Preparation of Adhesive Lap Joints. Organogels were prepared according to the above described general procedure. The solution containing the cross-linker was added to the PVOH stock solution and the mixture was homogenized by manual agitation with a glass rod over the course of 30 s. A pipet was used to deposit two drops of the mixture onto the previously marked overlap area (26 x 15 mm) of one side of a microscopy glass slide (76 x 26 mm). A second glass slide was aligned so that the marked segment was covered and light pressure was applied for 5 s onto the lap joint. The joined glass slides were stored overnight in a desiccator to allow the cross-linking reaction of the organogel to complete.

Synthesis of the azo-containing cross-linker (azo-CX). In a dried 100 mL Schlenk round-bottomed flask, 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (2.500 g, 8.670 mmol, 1 eq) was dispersed in hexamethylene diisocycanate (45 mL, 280.130 mmol, 32 eq) at room temperature under an inert nitrogen gas atmosphere. The mixture was stirred and dibutyltin dilaurate (10 drops) was added and the reaction was allowed to proceed overnight at room temperature. The solution was separated into five aliquots, each aliquot was poured into cold pentane (0 °C, 250 mL), and the precipitates of all fractions were collected, combined, and dried overnight in vacuo to yield **azo-CX** as a faintly yellow powder (5.256 g, 8.413 mmol, 97%). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ = 7.61 (t, 2H, NH), 7.08 (t, 2H, NH), 3.99 (t, 4H, CH_2-O), 3.35 (q, 4H, CH_2-NH, obstructed), 3.33 (t, 4H, CH_2-NCO), 2.94 (q, 4H, CH_2-NH), 1.53 (quint, 4H, CH_2), 1.38 (quint, 4H, CH_2), 1.27 (quint, 8H, CH_2, obstructed), 1.27 (s, 12H, CH_3). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ = 172.93, 156.15, 121.49, 74.21, 61.78, 42.46, 30.45, 29.20, 25.64, 25.53, 25.31, 22.77. FT-IR (ATR, cm^{-1}): 3408, 3328, 2935, 2860, 2263, 1724, 1520, 1461, 1372, 1246, 1192, 1148, 1033, 854, 779, 646. Anal. Calcd. for $C_{28}H_{48}N_8O_8$: C, 53.83; H, 7.74; N, 17.94; found: C, 54.34; H, 8.00; N, 17.99.

2. Supplementary Figs. S1–S7

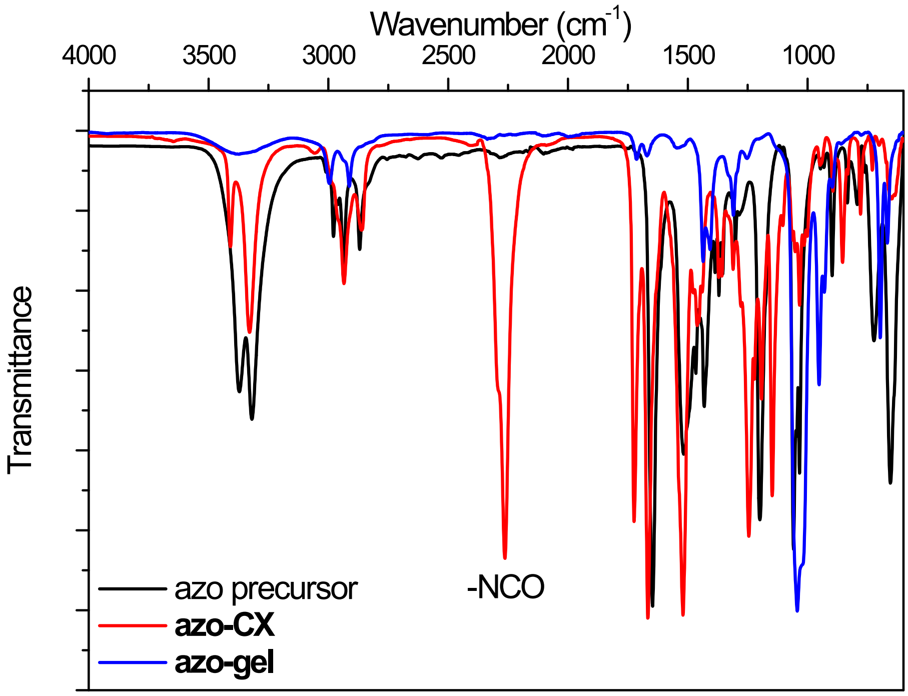


Fig. S1. Fourier-transform infrared (FT-IR) spectra of the starting material 2,2'-azobis[2-methyl*N*-(2-hydroxy-ethyl)propionamide] (black line), the diisocyanate-functionalized cross-linking agent **azo-CX** (red line) and an organogel (**azo-gel**) were obtained upon reaction of **azo-CX** with poly(vinyl alcohol) (blue line; representative example for material made with PVOH of a M_w of 31-50 kDa and a cross-link density of 10 mol%). The comparison that a strong signal corresponding to the isocyanate moieties is only present in **azo-CX,** confirming the successful formation and complete consumption of the isocyanate moieties upon curing the gel.

Fig. S2. Optical properties of the organogels made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%. Comparison of the visual appearance of the azo-free reference organogel (**ref-gel,** left) and the azo-containing organogel (**azo-gel**, right) in cuvettes.

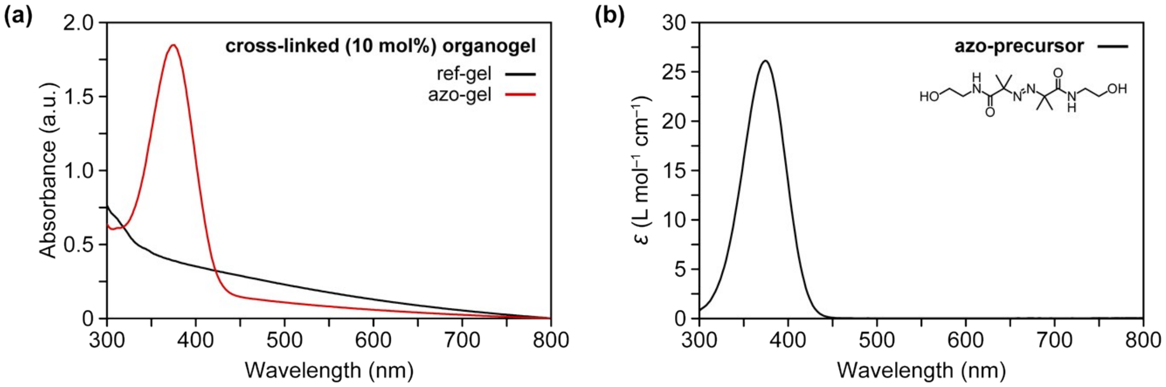


Fig. S3. (a) Optical properties of the organogels made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%. UV-Vis absorption spectra of the **ref-gel** (black line) and **azo-gel** (red line), respectively, contained in quartz cuvettes having a path length of 1 cm. (b) The solution UV-Vis spectrum of the parent azo-precursor 2,2'-azobis-[2-methyl-*N*(2hydroxyethyl)propionamide] (c(DMSO) = 0.1 mol/L) provides an indication of the molar absorptivity of the azo-motif ($\varepsilon_{374} = 26.12\ \mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$).

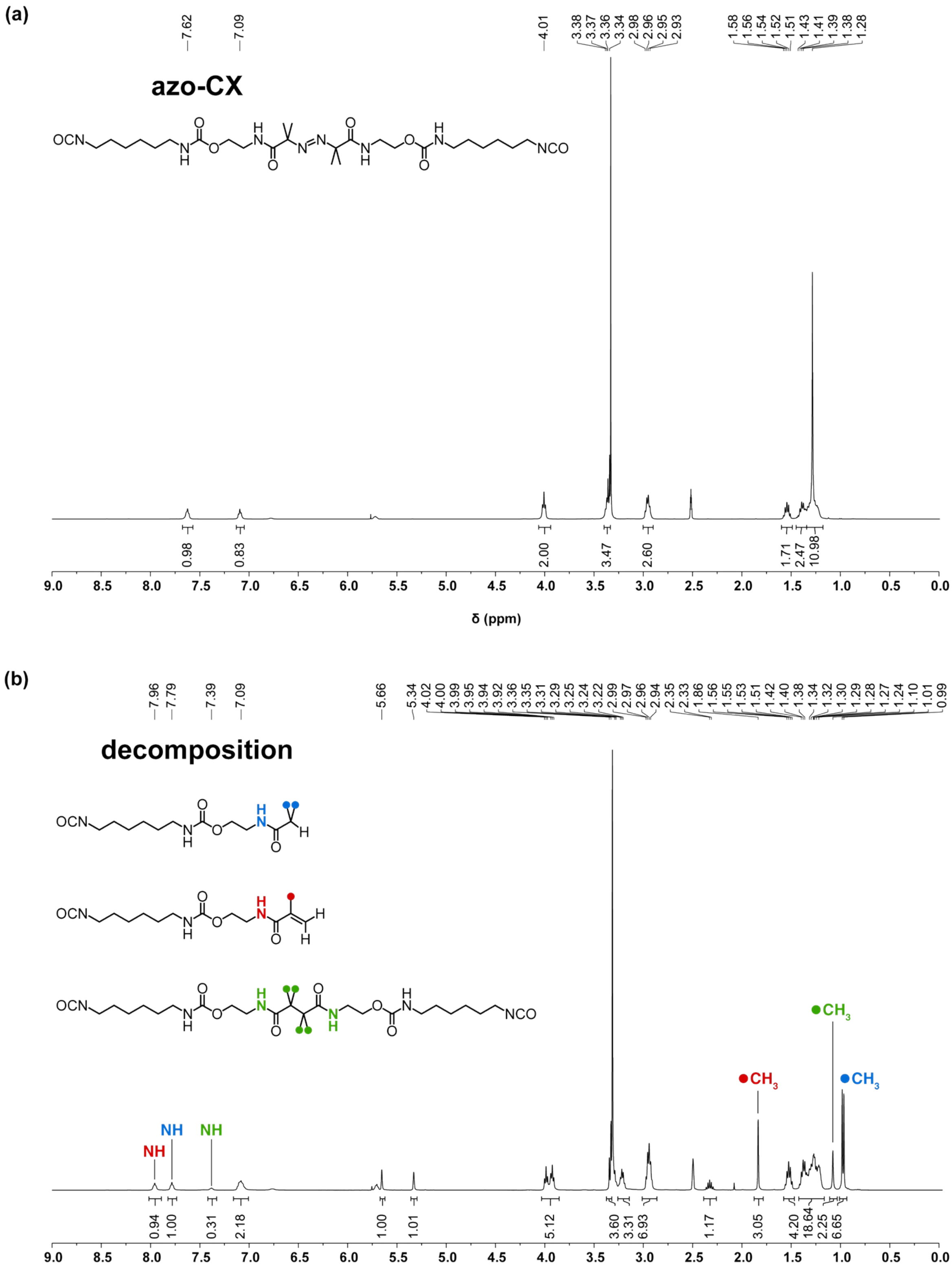


Fig. S4. Comparison of the ^{1}H NMR spectra (400 MHz, DMSO-d_6) of (a) the light-responsive cross-linker **azo-CX** and (b) the spectrum obtained after complete decomposition of the cross-linker by UV irradiation (120s, 320–390 nm, 600 mW/cm^2). In accordance with literature reports,[2] three main decomposition products are observed, i.e., the two products of the disproportionation reaction and the product of recombination. The integration of the signals of the amide (NH) and the methyl (CH$_3$) protons in the spectrum suggests that most radicals disproportionate (> 90%) and a low fraction of recombination occurs (< 10%).

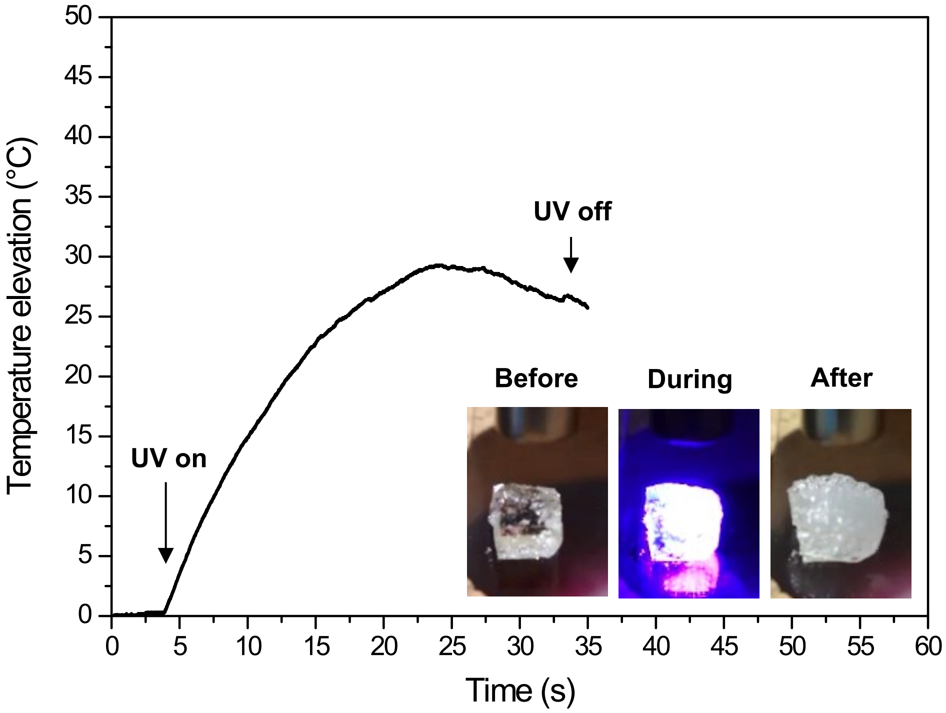


Fig. S5. Temperature vs. time curve of an azo-cross-linked gel (**azo-gel**, made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%) upon irradiation with UV light (320-390 nm, 600 mW/cm^2). The temperature was monitored with an IR camera. The inserted photographs show the sample before, during, and after the irradiation.

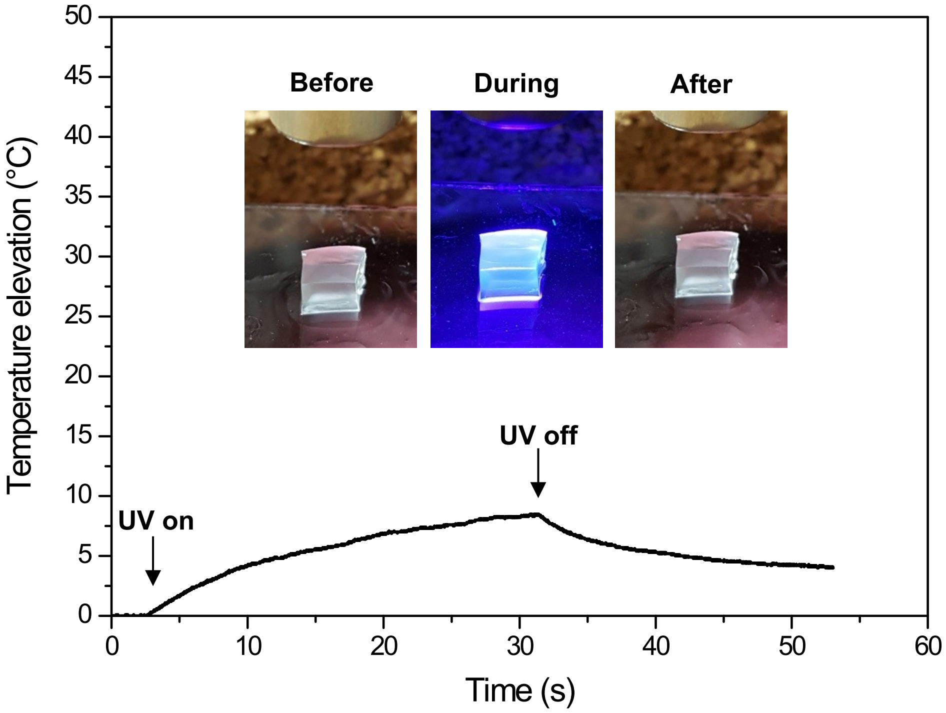


Fig. S6. Temperature vs. time curve of a reference azo-free organogel (**ref-gel**, made with PVOH of a M_w of 31-50 kDa and HMDI as cross-linker and having a cross-link density of 10 mol%) upon irradiation with UV light (320-390 nm, 600 mW/cm^2). The temperature was monitored with an IR camera. The inserted photographs show the sample before, during, and after the irradiation.

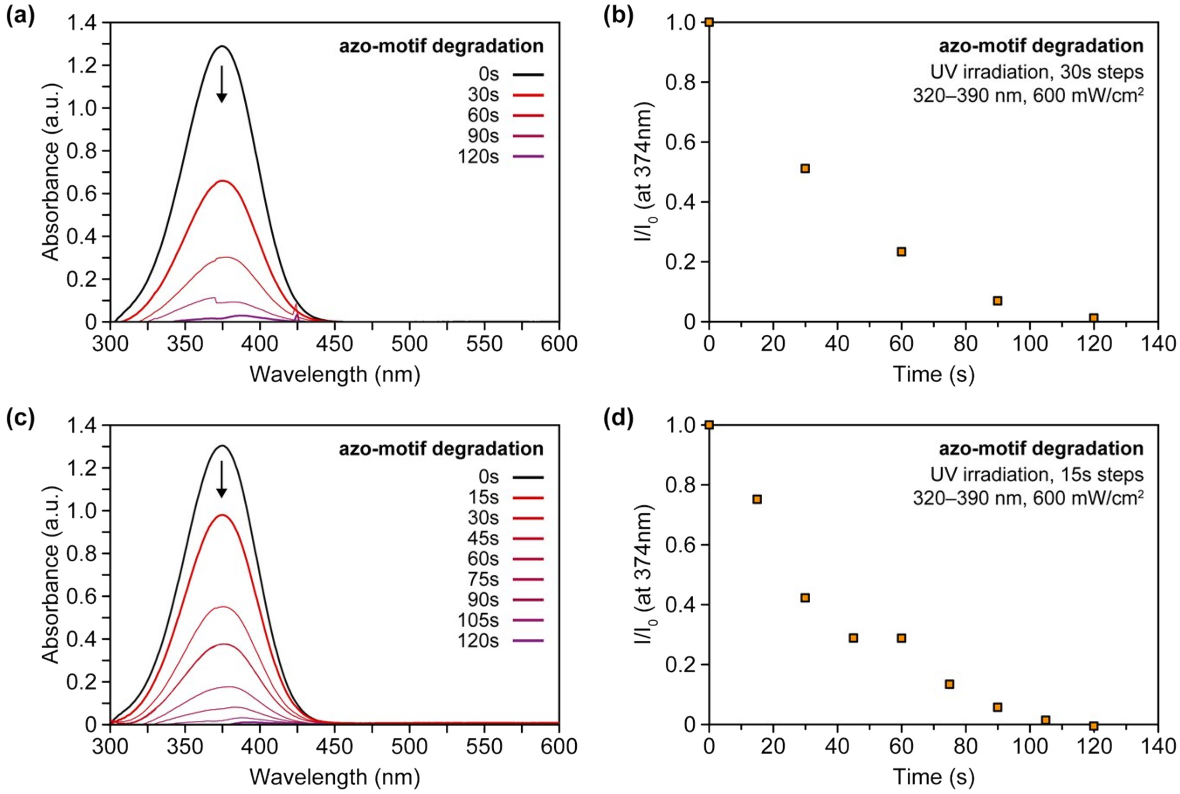


Fig. S7. The irradiation-induced degradation of the azo-motif was investigated by UV-Vis spectroscopy with the parent 2,2'-azobis[2-methyl-*N*(2hydroxyethyl)propionamide] (c = 0.1 mol/L, glass cuvettes, path length of 5 mm) as a model compound. (a) UV-Vis absorption spectra of 2,2'-azobis[2-methyl-*N*(2hydroxyethyl)propionamide] before (black line) and after (red to purple lines) UV irradiation (320–390 nm, 600 mW/cm^2) in steps of 30 s, and (b) the corresponding relative absorption intensity vs. irradiation time for UV irradiation in steps of 30 s. (c) UV-Vis absorption spectra of 2,2'-azobis[2-methyl-*N*(2hydroxyethyl)propionamide] before (black line) and after (red to purple lines) UV irradiation (320–390 nm, 600 mW/cm^2) in steps of 15 s, and (d) the corresponding relative absorption intensity vs. irradiation time for UV irradiation in steps of 15 s.

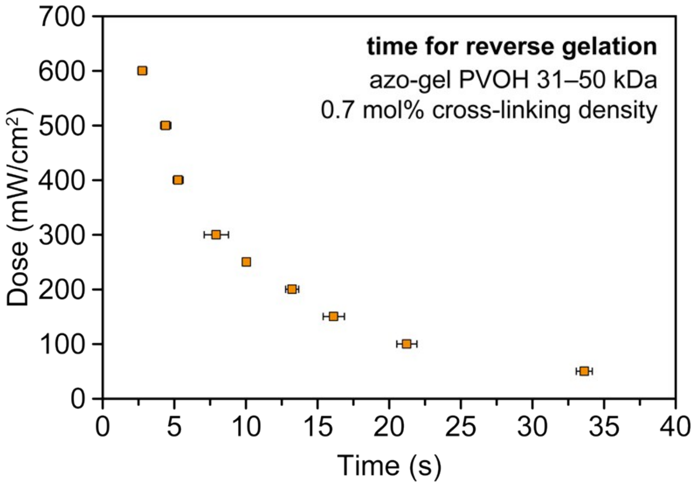


Fig. S8. Dose vs. time for reverse gelation curve for an azo-cross-linked gel (**azo-gel**, with PVOH of a M_w of 31–50 kDa and a cross-linking density of 0.7 mol%) under irradiation with UV light (320–390 nm). The average reverse gelation time over three measurements is indicated by the symbols with standard deviation.

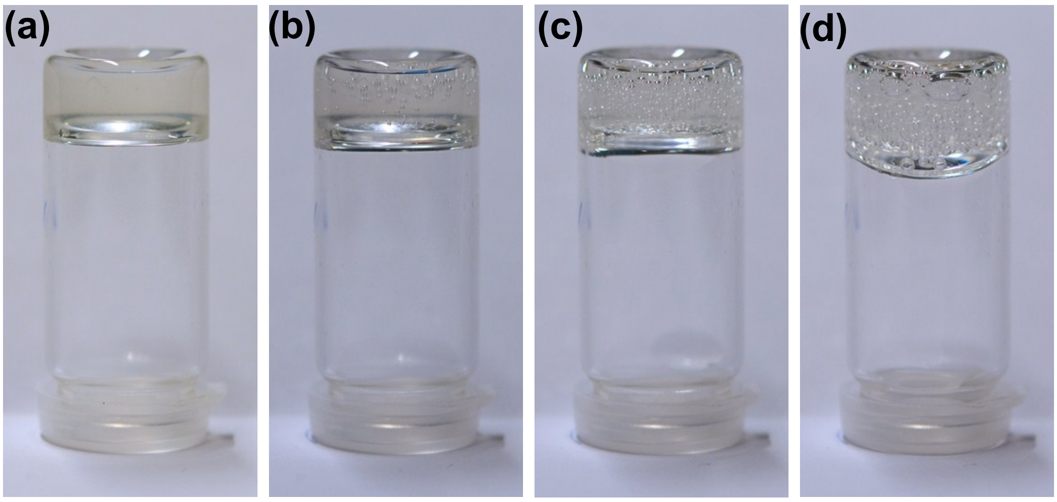


Fig. S9. Photographs showing azo-cross-linked organogels (**azo-gels**, made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%) (a) before, and after (b) 30 s, (c) 60 s, and (d) 90 s of visible light irradiation (390-500 nm, 600 mW/cm^2).

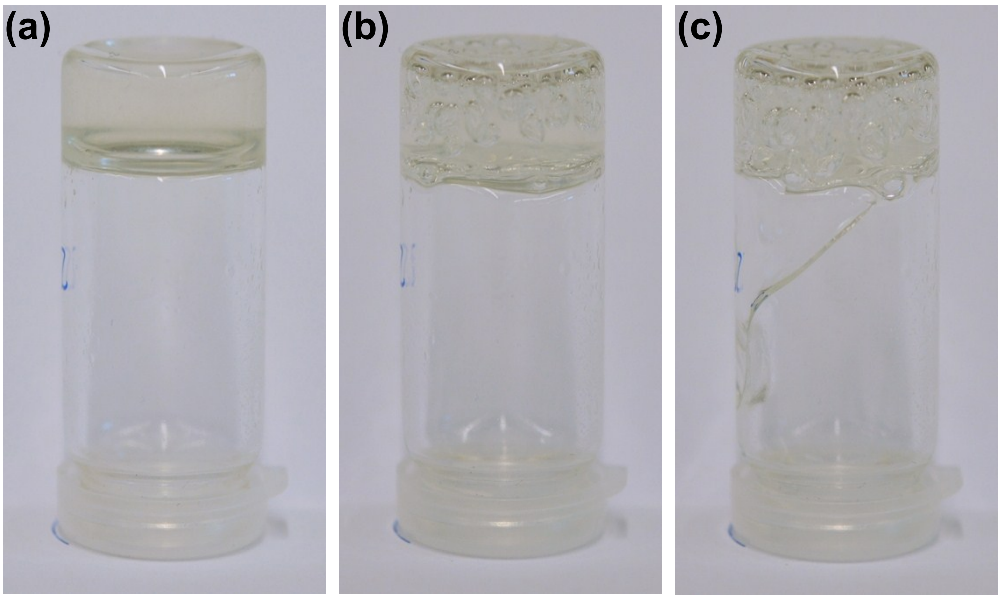


Fig. S10. Photographs showing azo-cross-linked organogels (**azo-gels**, made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%) (a) before, and after (b) 1 and (c) 2 hours of low-power UV light irradiation (365 nm, 1 mW/cm^2).

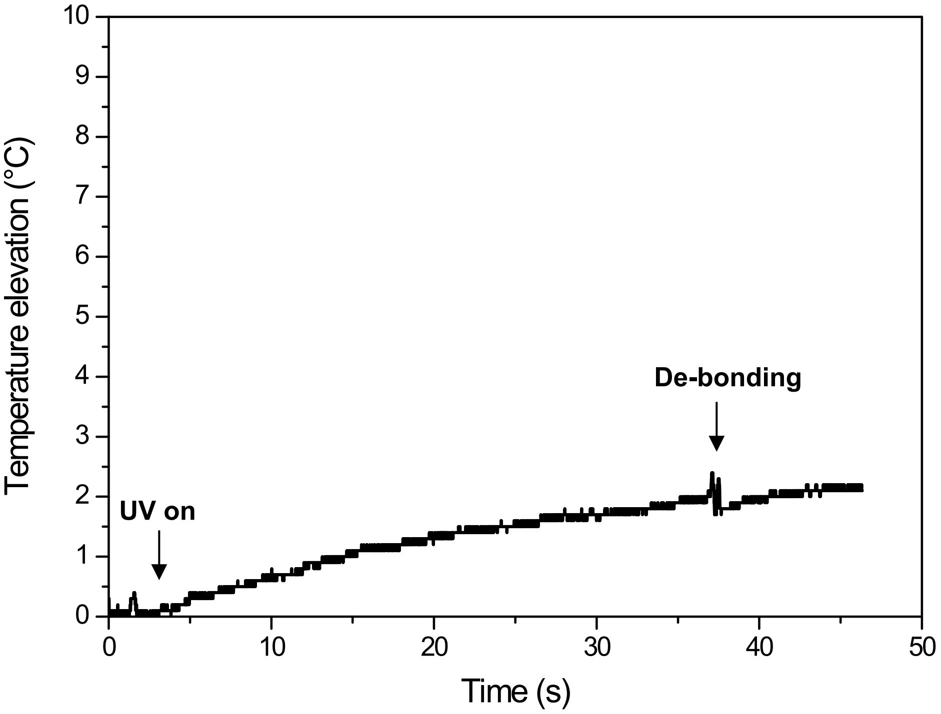


Fig. S11. Temperature vs. time curve of a lap-joint prepared with an azo-cross-linked gel (**azo-gel**, made with PVOH of a M_w of 31-50 kDa and having a cross-link density of 10 mol%) upon irradiation with UV light (320-390 nm, 600 mW/cm^2). The temperature was monitored with an IR camera.

3. Supplementary Tables S1–S3

Table S1. Overview of the composition of organogels made with PVOH of M_w of 31-50 kDa with different cross-link densities. The indicated quantities yield approximately 1.5 g of the respective organogels. The cross-link density is expressed in mol%, as the frequency of cross-links (f_{CX}), or the molecular weight between cross-links (M_c). These samples were used for all experiments involving direct UV irradiation. For larger sample quantities, the employed amounts were scaled up proportionately.

Cross-link density			**Solution 1**			**Solution 2**	
mol%[a]	f_{CX}[b]	M_c[c]	**azo-CX**		**DMSO**	**PVOH**[d]	
		g/mol	mg	mmol	mL	mg	mmol[e]
9.80	5	176[f]	63.8	0.1021	1	306.1	1.0423
4.95	10	396	32.0	0.0512	1	303.8	1.0345
2.54	20	836	16.2	0.0259	1	299.6	1.0202
1.07	50	2156	6.8	0.0109	1	298.6	1.0168
0.82	60	2596	5.3	0.0085	1	302.5	1.0301
0.69	70	3036	4.5	0.0072	1	305.3	1.0396
0.62	80	3476	4.0	0.0064	1	301.3	1.0260
0.54	90	3916	3.5	0.0056	1	301.4	1.0263
0.51	100	4356	3.2	0.0051	1	297.5	1.0131

*[a] Calculated based on the number of PVOH repeating units. [b] Value indicating a cross-link every xth alcohol functionality. [c] Molecular weight between cross-links. [d] Stock solutions (15 wt% in DMSO) of PVOH with M_w=31–50 kDa (as indicated by Sigma-Aldrich). [e] Number of PVOH repeat units. [f] Reference organogels without the responsive cross-links (**ref-gel**) were prepared using hexamethylene diisocyanate (16.7 mg, 0.0993 mmol) instead of **azo-CX**.*

Table S2. Overview of the mechanical properties of organogels made with the responsive, azo-based cross-linker (**azo-CX**). The values for the Young's modulus (E), stress at break (σ), and strain at break (ε) were derived from compressive stress-strain measurements on organogels with cross-link densities of 10, 5, as well as 2.5 mol%. The provided values constitute the average over three experiments. Note: The reference gels that were cross-linked with HDMI (**ref-gel**) constitute a point of comparison for the light-responsive behavior, but not for the mechanical properties due to the different lengths of the cross-linkers (**azo-CX** with 34-atoms in the main chain; HMDI with 10-atoms in the main chain).

PVOH type (M_w)[a] kDa	**Cross-link density[b]** mol%	**Young's modulus (E)** kPa	**Stress at break (σ)** kPa	**Strain at break (ε)** %
13–23	10	9.5 ± 0.4	40.0 ± 15.9	57 ± 4
	5	n/a[c]	n/a[c]	n/a[c]
	2.5	n/a[c]	n/a[c]	n/a[c]
31–50	10	27.7 ± 2.1	31.6 ± 4.1	48 ± 2
	5	15.4 ± 0.5	34.5 ± 4.5	59 ± 2
	2.5	10.7 ± 0.6	14.0 ± 3.0	46 ± 2
85–124	10	38.1 ± 2.2	49.2 ± 12.9	51 ± 1
	5	12.4 ± 0.1	70.9 ± 9.9	69 ± 2
	2.5	9.2 ± 0.4	172.4 ± 49.8	73 ± 1

[a] Weight-average molecular weight (M_w), as indicated by Sigma-Aldrich. [b] Calculated based on the ratio of cross-linking agent to the number of PVOH repeat units. [c] Not measurable because the mechanical properties were too weak.

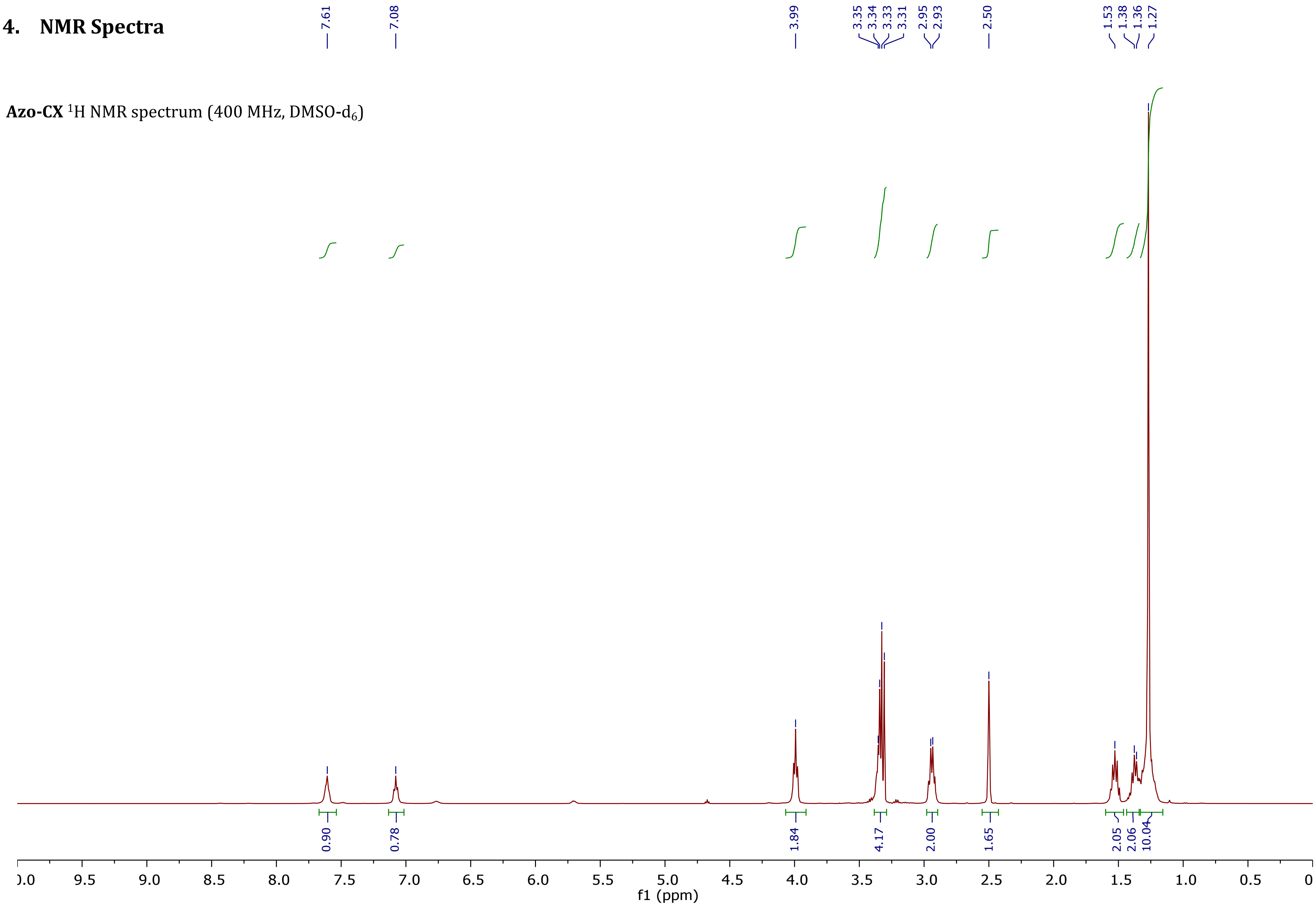
Table S3. Overview of the mechanical properties of lap joints affixed with the responsive organogels (**azo-gels**) with a cross-link density of 10 mol% and different PVOH molecular weight distributions (M_w). The provided values for shear strength (τ) and shear force (F) constitute the average over three experiments.

PVOH type (M_w)[a] kDa	**Cross-link density[b]** mol%	**Shear strength (τ)** kPa	**Shear force (F)** N
13-23	10	16.3 ± 2.4	6.1 ± 0.9
31-50	10	26.3 ± 2.9	9.9 ± 1.1
85-124	10	5.3 ± 3.4	2.0 ± 1.3

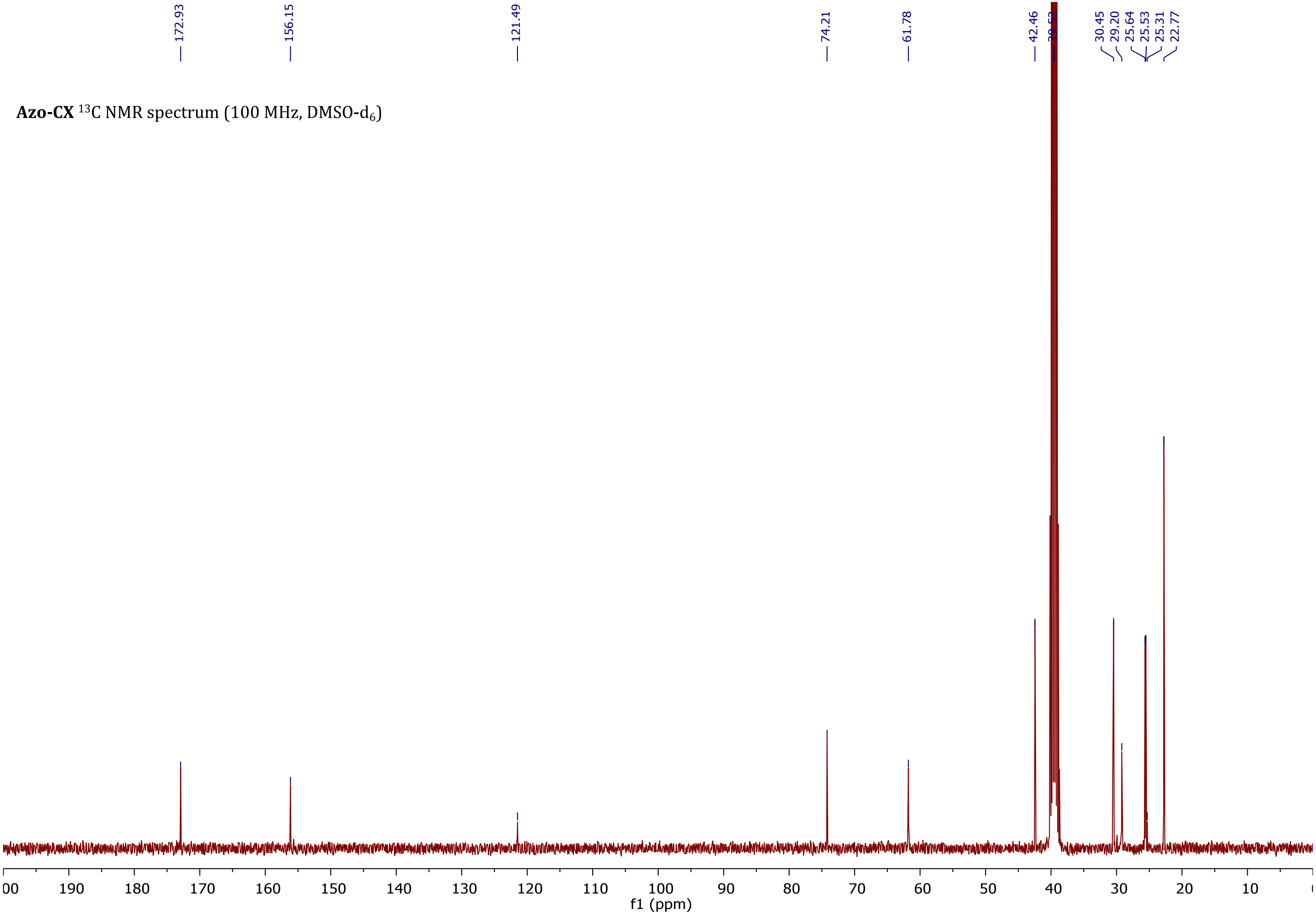
[a] *Mass-average molecular weight (M_w), as indicated by Sigma-Aldrich.* [b] *Calculated based on the ratio of cross-linker to the number of PVOH repeat units.*

4. NMR Spectra

Azo-CX ^{1}H NMR spectrum (400 MHz, DMSO-d_6)



Azo-CX ^{13}C NMR spectrum (100 MHz, DMSO-d_6)



5. References

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