

## Electronic Supplementary Information

# Modeling Ultrasound-Induced Molecular Weight Decrease of Polymers with Multiple Scissile Azo-Mechanophores

Mathieu A. Ayer,<sup>a</sup> Ester Verde-Sesto,<sup>a,b</sup> Cheyenne H. Liu,<sup>c</sup> Christoph Weder,<sup>a</sup> Marco Lattuada<sup>\*a,d</sup> and Yoan C. Simon<sup>\*a,c</sup>

---

<sup>a</sup> Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland.

<sup>b</sup> Centro de Física de Materiales (CSIC, UPV/EHU) and Materials Physics Center MPC, Paseo Manuel de Lardizabal 5, E-20018 San Sebastián, Spain

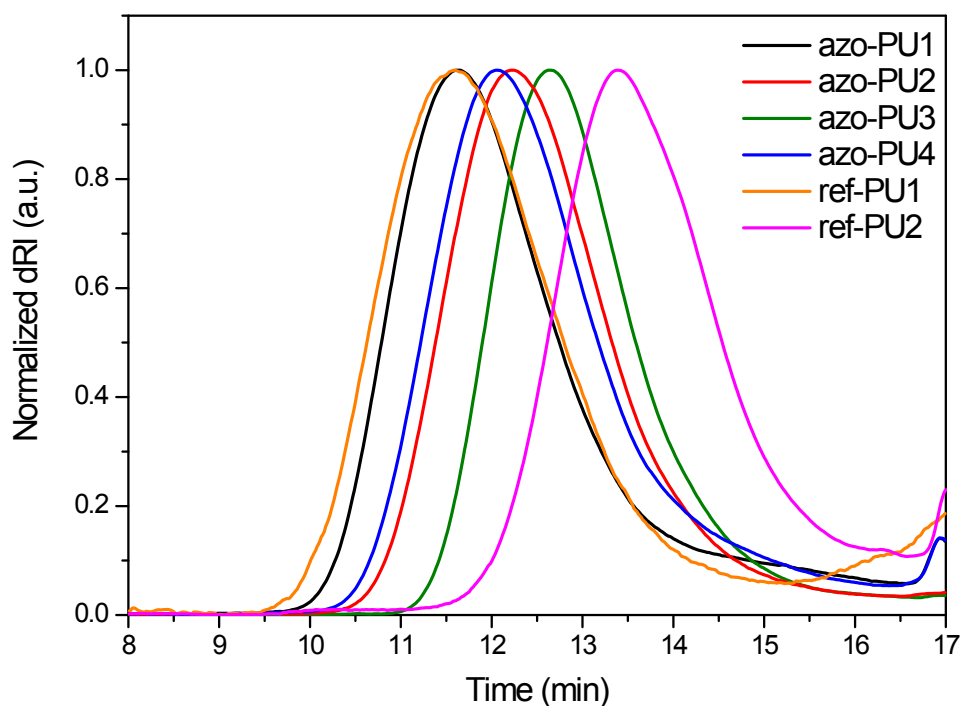
<sup>c</sup> School of Polymer Science and Engineering, The University of Southern Mississippi, 118 College Dr., Hattiesburg MS 39406, USA. Email: yoan.simon@usm.edu

<sup>d</sup> Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700-Fribourg, Switzerland. Email: marco.lattuada@unifr.ch

### Table of content

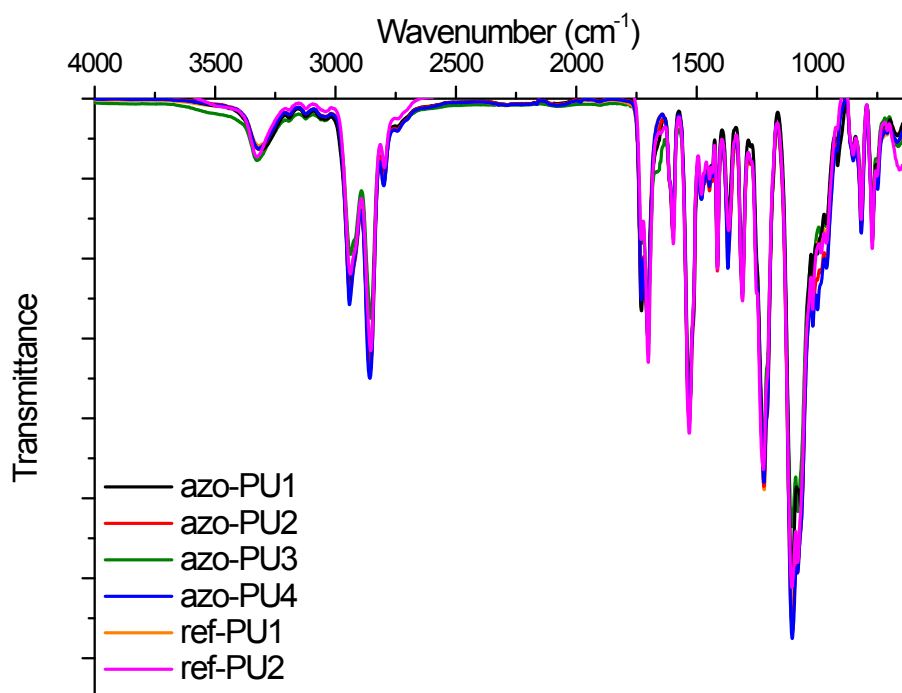
Fig. S1. Size exclusion chromatography (SEC) traces	2
Fig. S2. Fourier transformation infrared (FT-IR) spectra	3
Fig. S3-S8. <sup>1</sup> H NMR spectra in THF-d <sub>8</sub>	4
Fig. S9-S13. Study of ultrasonic degradation by size exclusion chromatography (SEC)	10
Explanation of the fitting procedure	15
Calculation of the polymer molecular weight after UV scission	15
Fig. S14-S17. Simulated size exclusion chromatography (SEC) traces	17
Fig. S18-S21. Effective scission constants as a function of time	22

## Size exclusion chromatography (SEC) traces



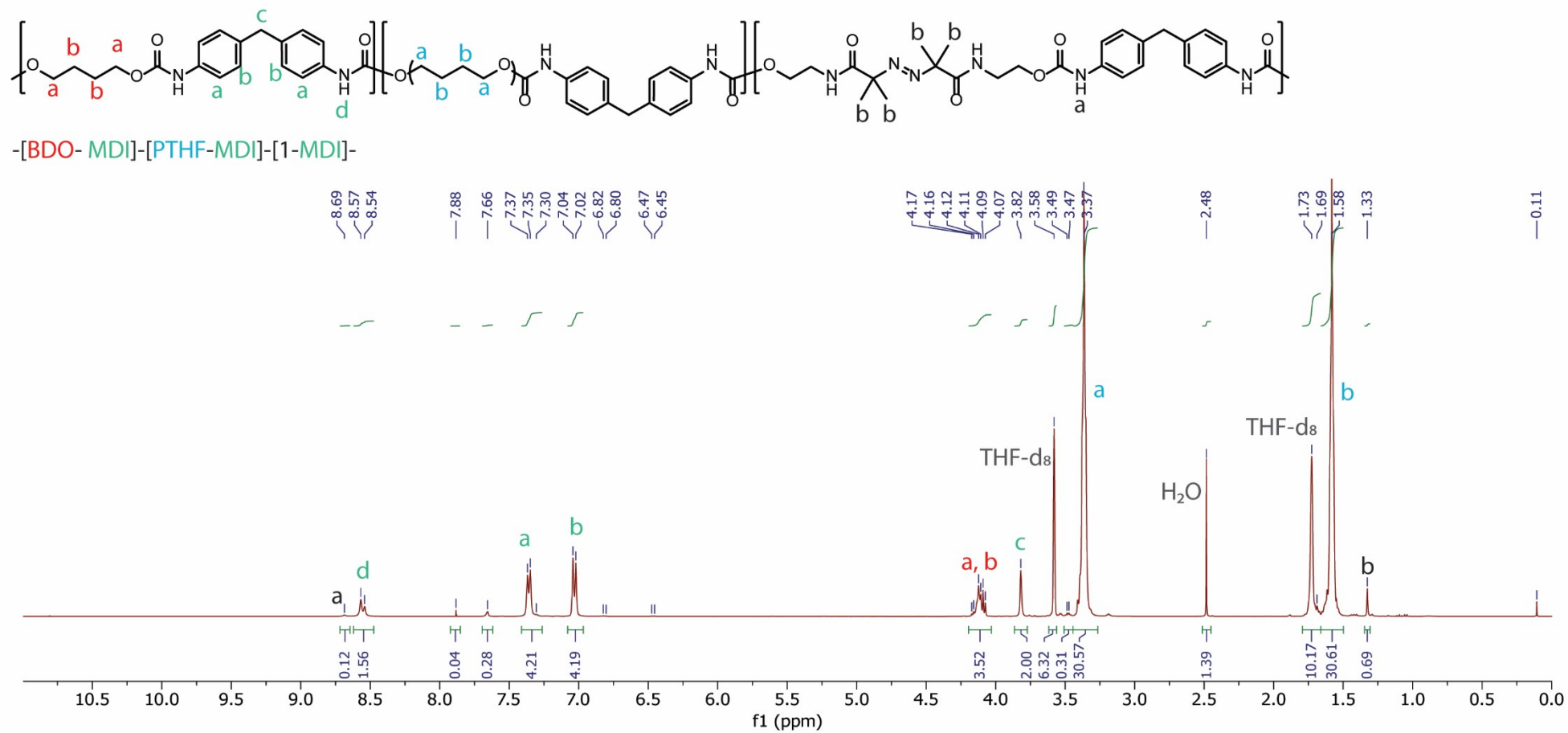
**Fig. S1.** Size exclusion chromatography (SEC) traces of the azo-containing polyurethanes **azo-PU1** ( $M_n=119,000$  g/mol, black line), **azo-PU2** ( $M_n=70,900$  g/mol, red line), **azo-PU3** ( $M_n=51,300$  g/mol, green line), and **azo-PU4** ( $M_n=77,200$  g/mol, blue line), and of the azo-free reference polymers **ref-PU1** ( $M_n=119,400$  g/mol, orange line), and **ref-PU2** ( $M_n=24,000$  g/mol, magenta line). The number-average molecular weight ( $M_n$ ) values were determined by comparison with poly(styrene) standards.

## Fourier transformation infrared (FT-IR) spectra



**Fig. S2.** FT-IR spectra of the azo-containing polyurethanes **azo-PU1** (black line), **azo-PU2** (red line), **azo-PU3** (green line), **azo-PU4** (blue line), and the azo-free polymers **ref-PU1** (orange line), and **ref-PU2** (magenta line).

Fig. S3. 400 MHz  $^1\text{H}$  NMR spectrum of azo-PU1 in THF- $d_8$



**Fig. S4.** 400 MHz  $^1\text{H}$  NMR spectrum of **azo-PU2** in  $\text{THF-d}_8$

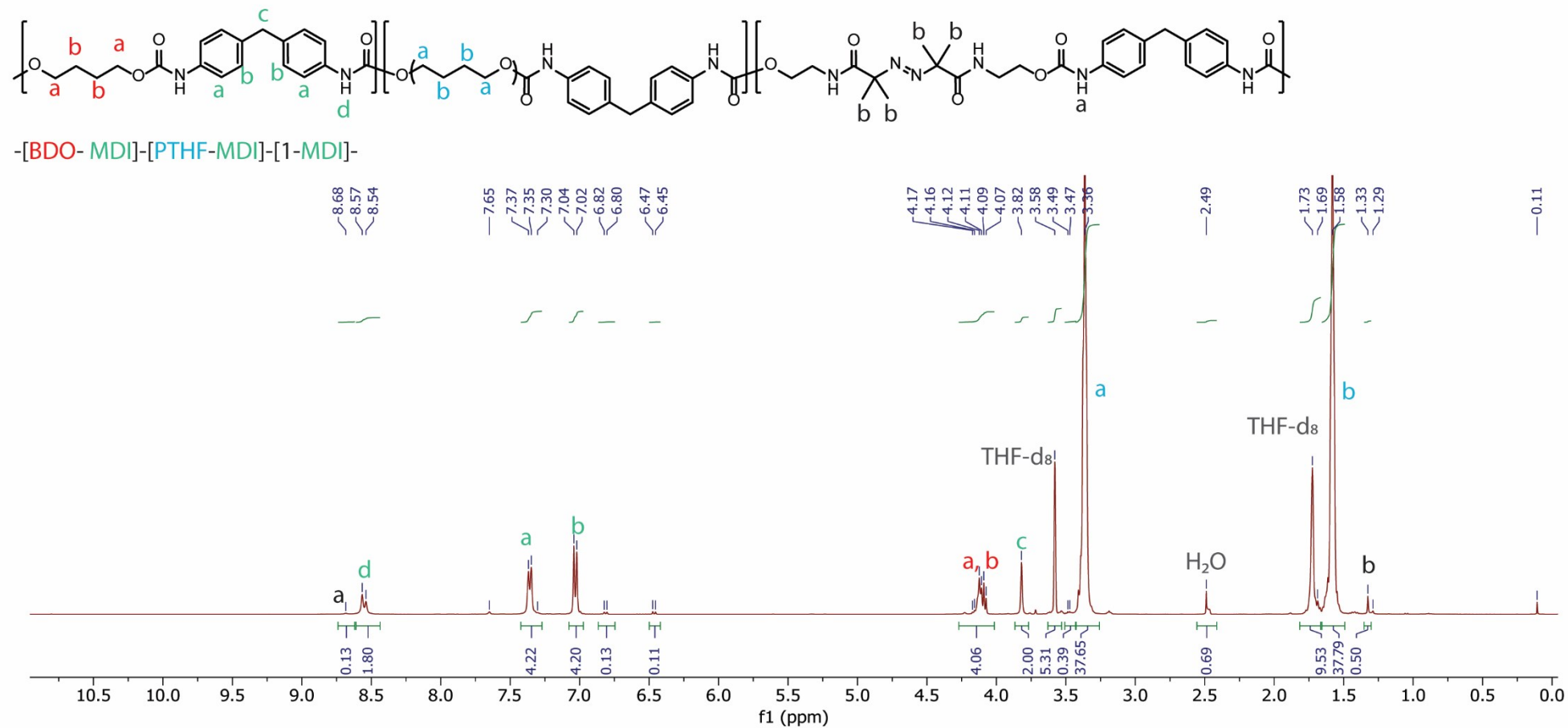


Fig. S5. 400 MHz  $^1\text{H}$  NMR spectrum of **azo-PU3** in  $\text{THF-d}_8$

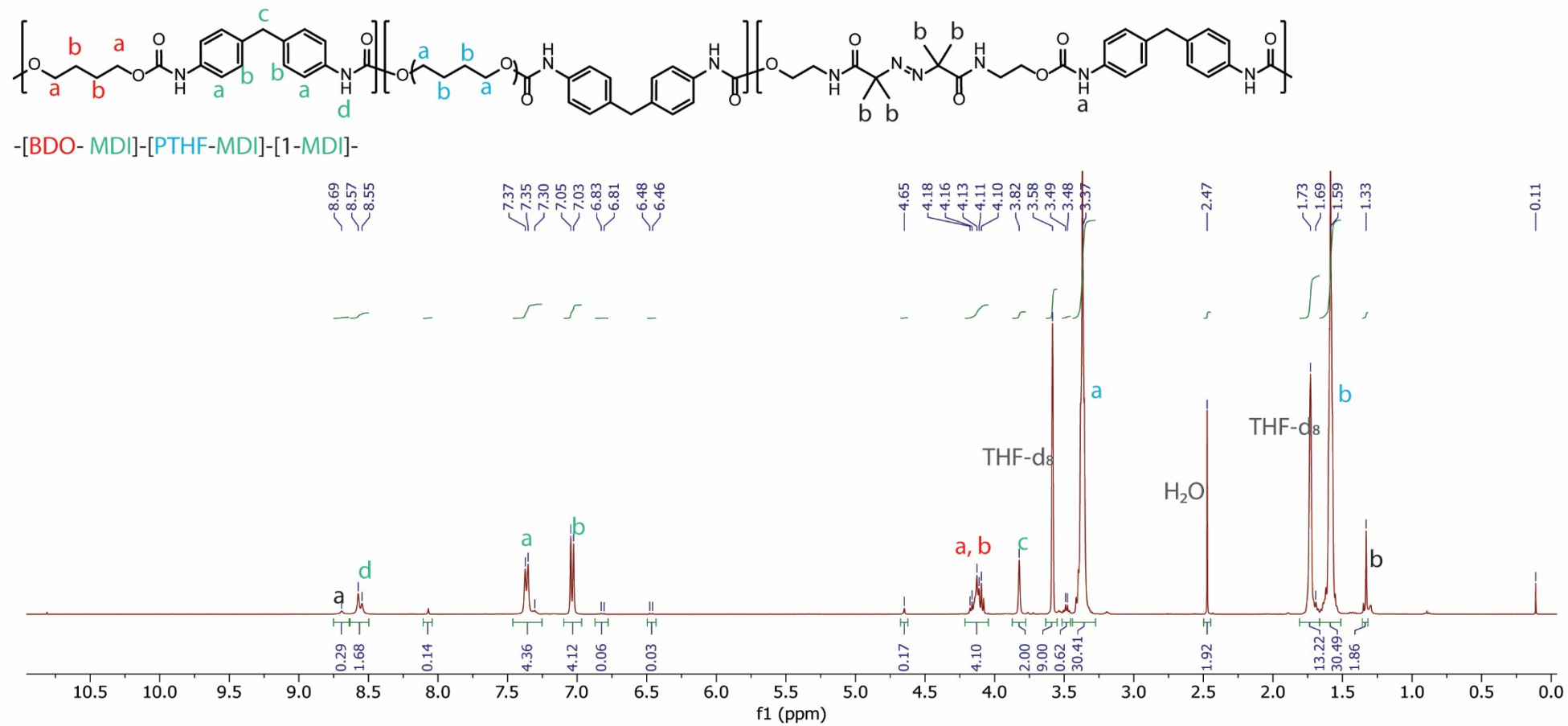


Fig. S6. 400 MHz  $^1\text{H}$  NMR spectrum of **azo-PU4** in  $\text{THF-d}_8$

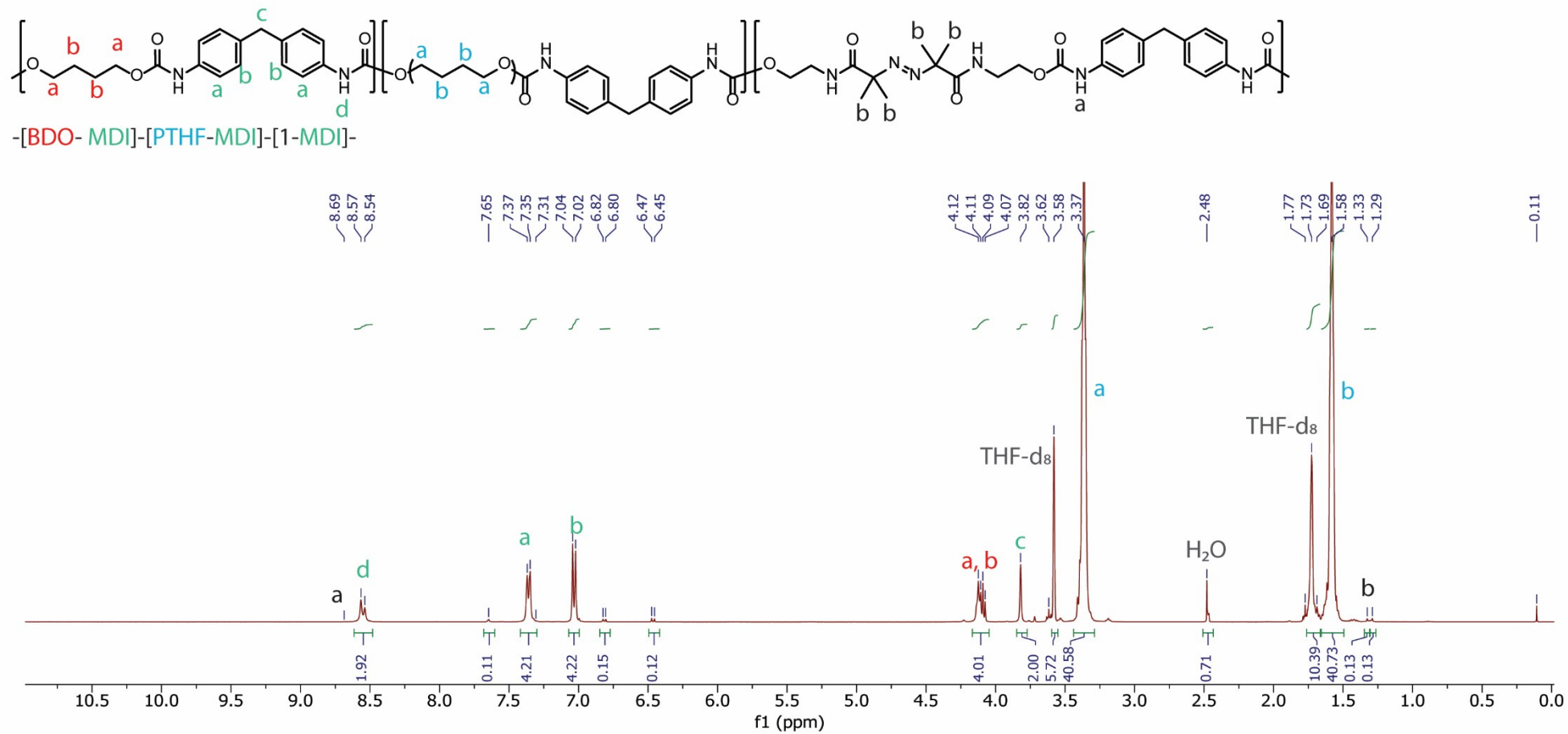


Fig. S7. 400 MHz  $^1\text{H}$  NMR spectrum of **ref-PU1** in  $\text{THF-d}_8$

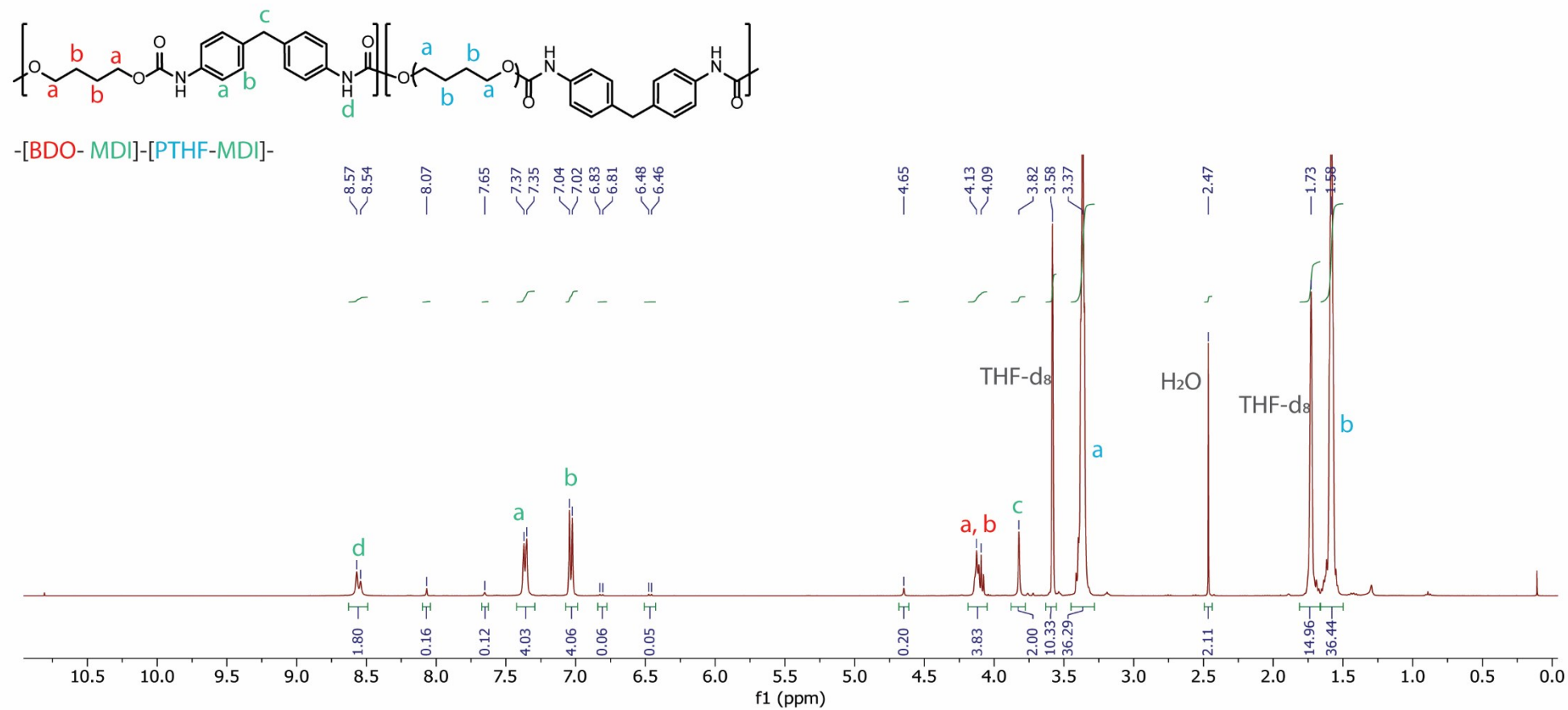
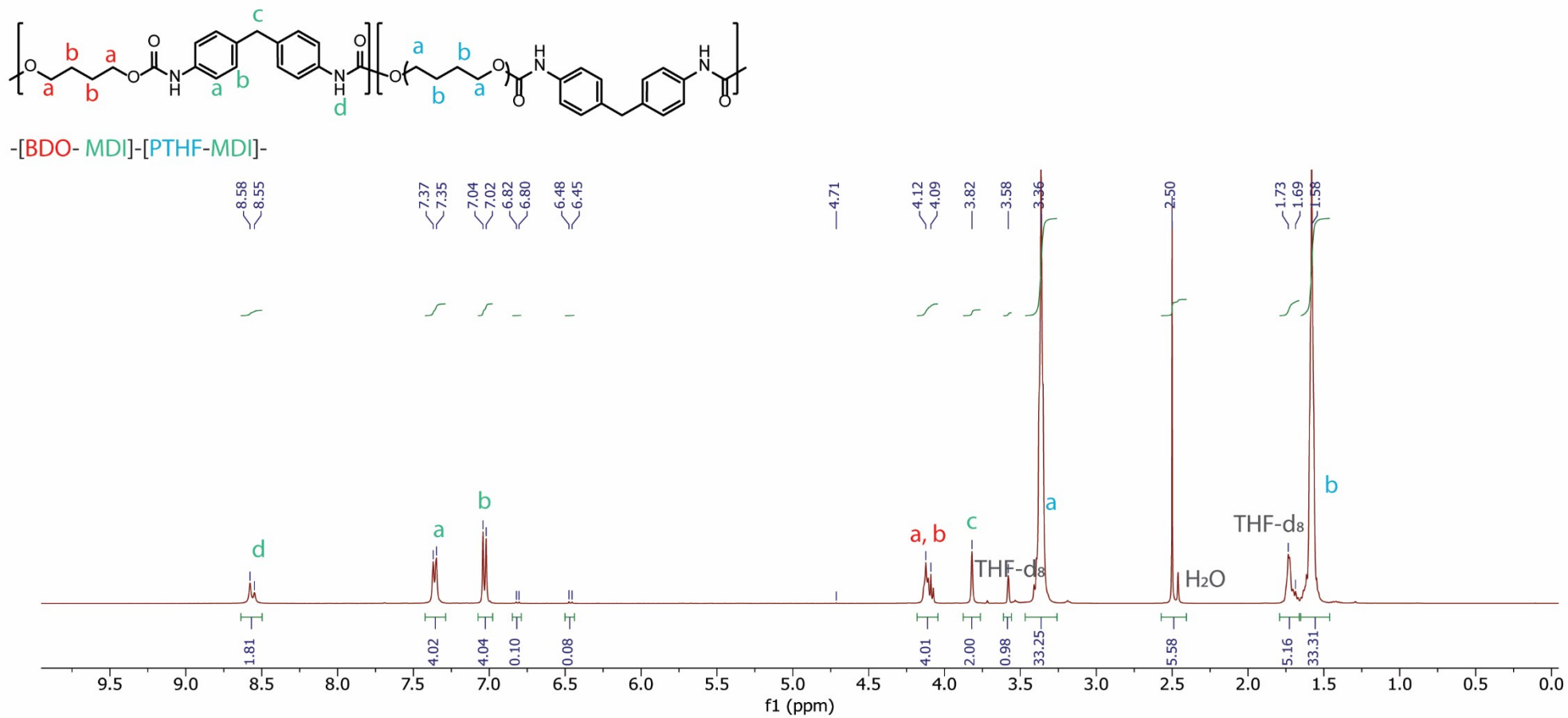
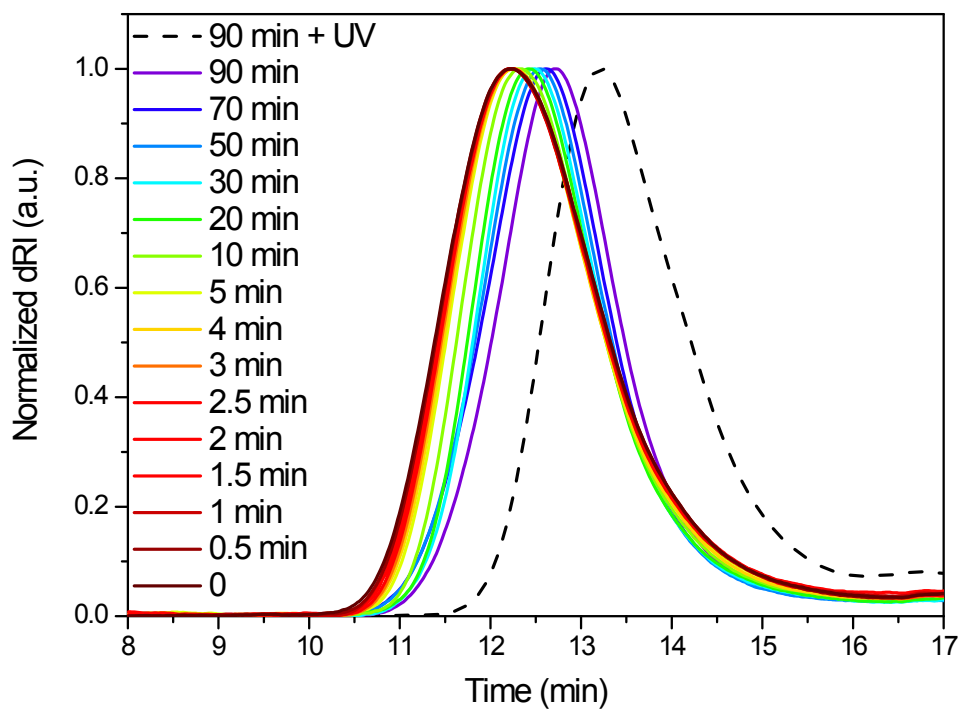




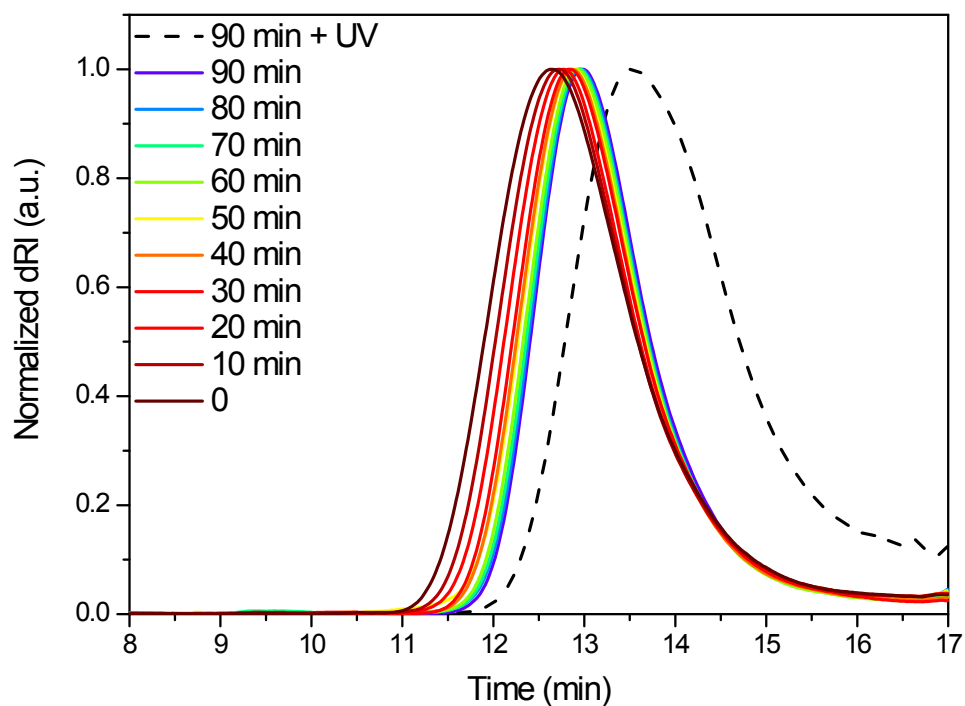
Fig. S8. 400 MHz  $^1\text{H}$  NMR spectrum of ref-PU2 in THF- $d_8$



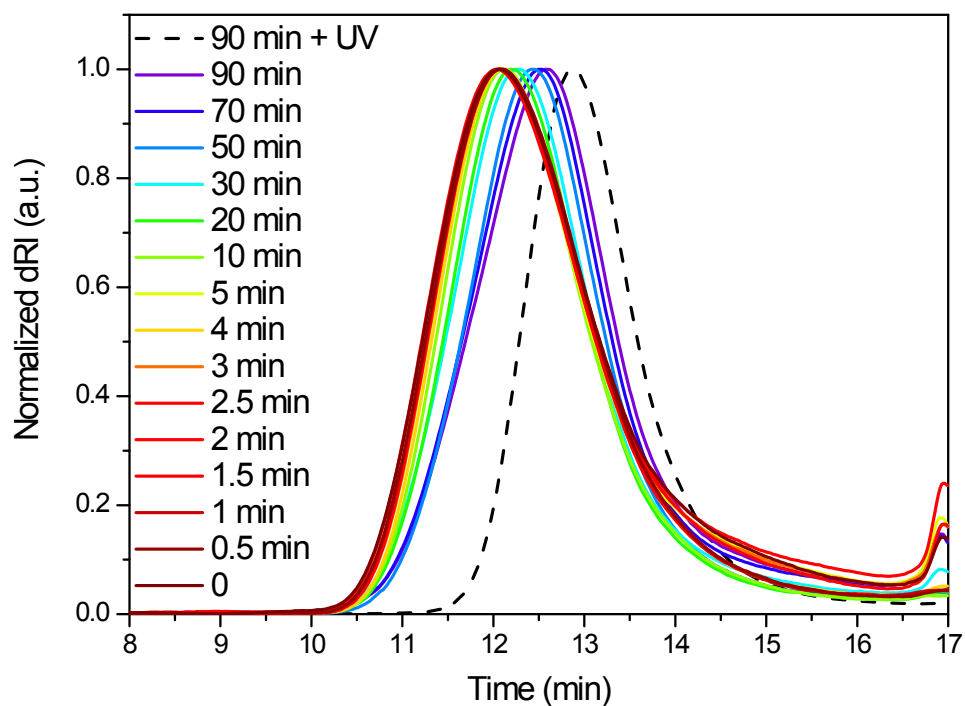
## Study of ultrasonic degradation by size exclusion chromatography (SEC)



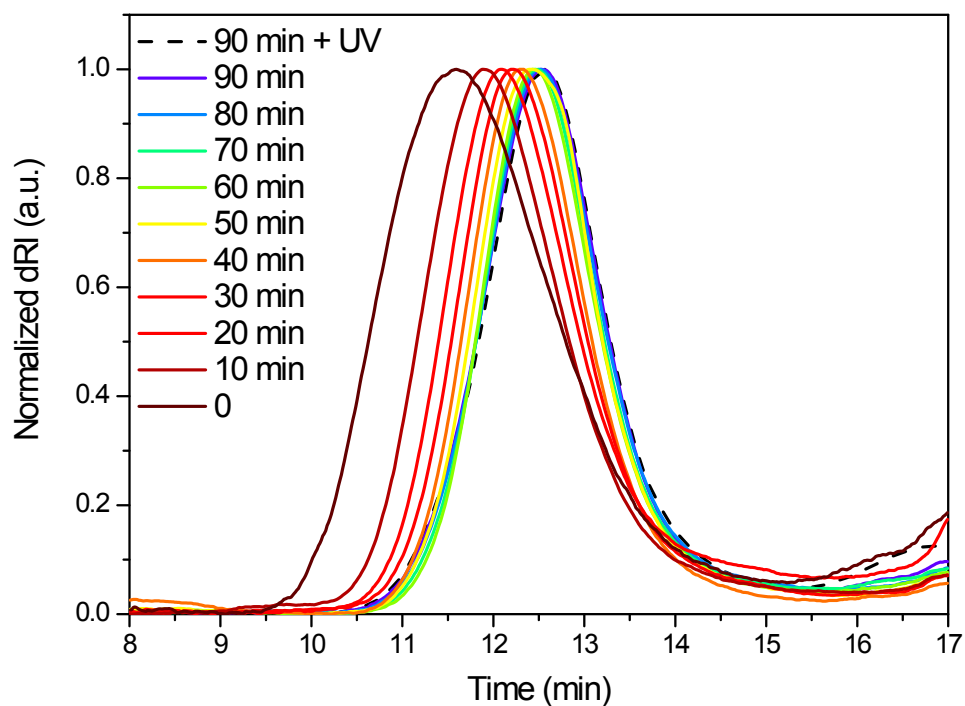
**Fig. S9.** Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the azo-containing polyurethane **azo-PU2** (0.75 mg/mL in THF, 10.4 mW/cm<sup>2</sup>, 0 °C) followed by a further degradation provoked by exposure to UV light (600 mW/cm<sup>2</sup>, 30 s).



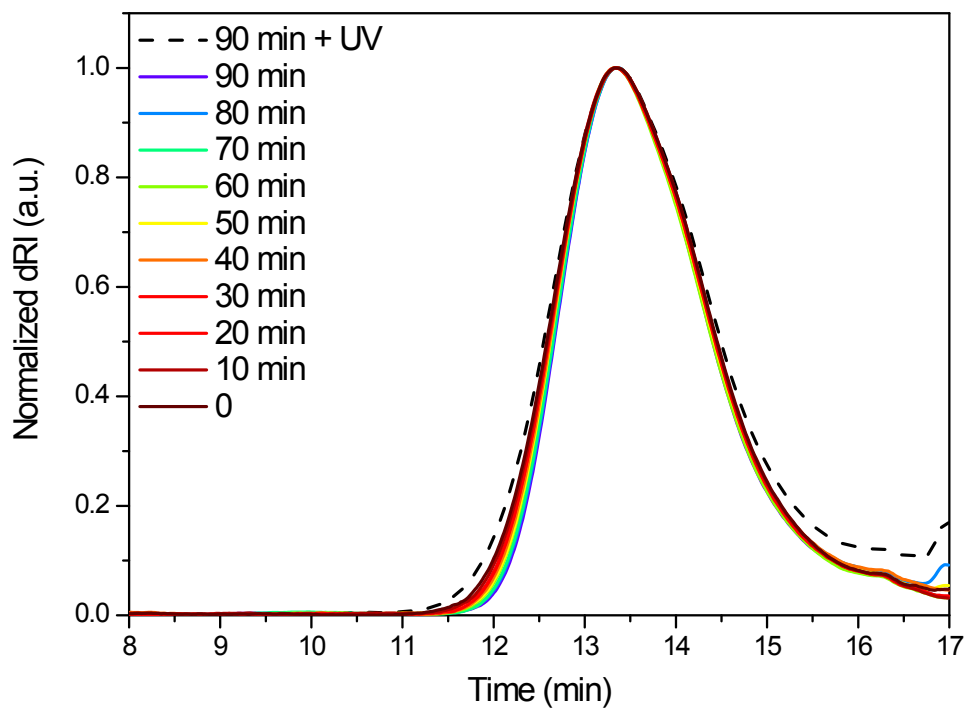
**Fig. S10.** Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the azo-containing polyurethane **azo-PU3** (0.75 mg/mL in THF, 10.4 mW/cm<sup>2</sup>, 0 °C) followed by a further degradation provoked by exposure to UV light (600 mW/cm<sup>2</sup>, 30 s).



**Fig. S11.** Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the azo-containing polyurethane **azo-PU4** (0.75 mg/mL in THF, 10.4 mW/cm<sup>2</sup>, 0 °C) followed by a further degradation provoked by exposure to UV light (600 mW/cm<sup>2</sup>, 30 s).



**Fig. S12.** Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the azo-containing polyurethane **ref-PU1** (0.75 mg/mL in THF, 10.4 mW/cm<sup>2</sup>, 0 °C) followed by a further degradation provoked by exposure to UV light (600 mW/cm<sup>2</sup>, 30 s).



**Fig. S13.** Representative size exclusion chromatography (SEC) traces acquired to monitor the ultrasound-induced degradation of the azo-containing polyurethane **ref-PU2** (0.75 mg/mL in THF, 10.4 mW/cm<sup>2</sup>, 0 °C) followed by a further degradation provoked by exposure to UV light (600 mW/cm<sup>2</sup>, 30 s).

## Explanation of the fitting procedure

The fitting procedure works as follows: the two parameters,  $\kappa_S$  and  $\kappa_F$  in Equation (4), are used to fit the average molecular weight decay as a function of time, as well as the GPC curves. The two parameters have been determined as follows.  $\kappa_S$  has been determined by fitting the data of the azo-PU polymer, which does not contain any azo moieties. The same value has been used in all the simulations of the azo-containing polymers, and the  $\kappa_F$  value has been adjusted in order to well fit all the data. It has been found that one value of the parameter is sufficient to well simulate all the experimental data.

## Calculation of the polymer molecular weight after UV scission

The calculation of the molecular weight distribution of the polymer subject to UV irradiation after sonication process has been calculated by assuming scission of all azo moieties that survived the sonication process. A second assumption, necessary for the calculation, is that the azo moieties are randomly distributed in the polymer chains. Starting from the calculated molecular weight distribution of the polymer chains at the end of the sonication process, what is required is the fragment distribution of each chain resulting from the scission of all azo units present in it. The assumption of random distribution of azo-moieties is used now.

Given one chain containing  $x$  monomer units,  $n$  of which cleavable, the fraction of fragment chains with  $m$  monomer units is given by the following expression:

$$f_m(x, n) = B \frac{\binom{x-m+n-1}{n-1}}{\binom{x+n}{n}} \quad \backslash^*$$

MERGEFORMAT (1.1)

$B$  is a normalization constant, which is determined by the mass conservation, stating that the sum of the mass of all fragments has to be equal to the mass of the original chain:

$$\sum_m m \cdot f_m(x, n) = x \quad \backslash^*$$

MERGEFORMAT (1.2)

In order to show the function dependence of the fragment distribution, we here report its dependence of both the chain length  $x$  and the number of azo-moieties, for  $n$  up to 3:

$$f_m(x, n=1) = B \frac{1}{x+1}$$

$$f_m(x, n=2) = B \frac{2(x-m+1)}{(x+2)(x+1)} \quad \backslash^*$$

$$f_m(x, n=3) = B \frac{3(x-m+2)(x-m+1)}{(x+3)(x+2)(x+1)}$$

MERGEFORMAT (1.3)

It is possible to observe that the fragment distribution is uniform when only one azo groups is present, linear with  $m$  when two azo groups are present, and quadratic in  $m$  when 3 azo units are present. In general, the fragment distribution scales as  $m^{n-1}$ .

Therefore, the final molecular weight distribution is obtained by adding all fragments with a given mass generated by scission of all chains present in the system:

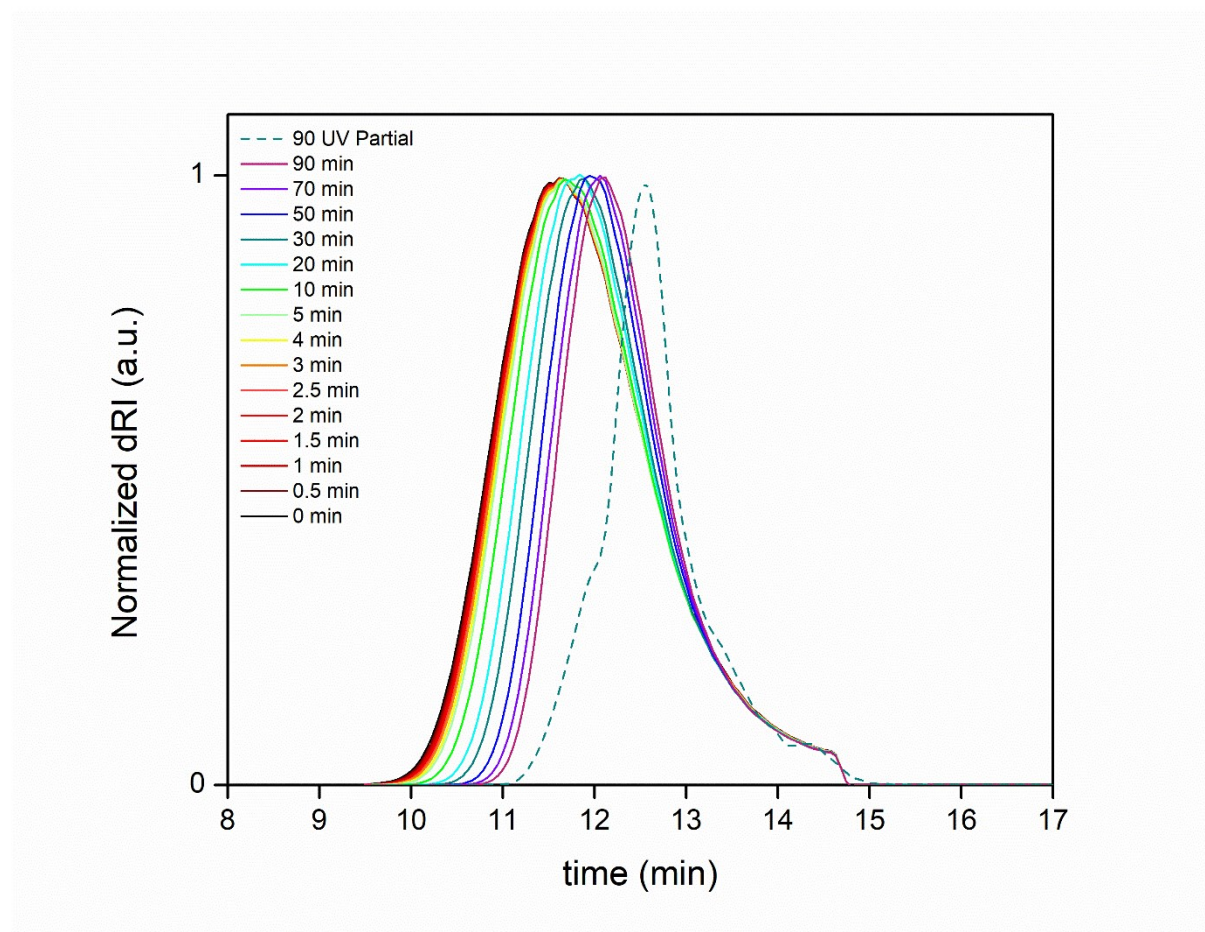
$$N_{n,UV} = \sum_x f_n(x, n) N_{x,AS} \quad \backslash^*$$

MERGEFORMAT (1.4)

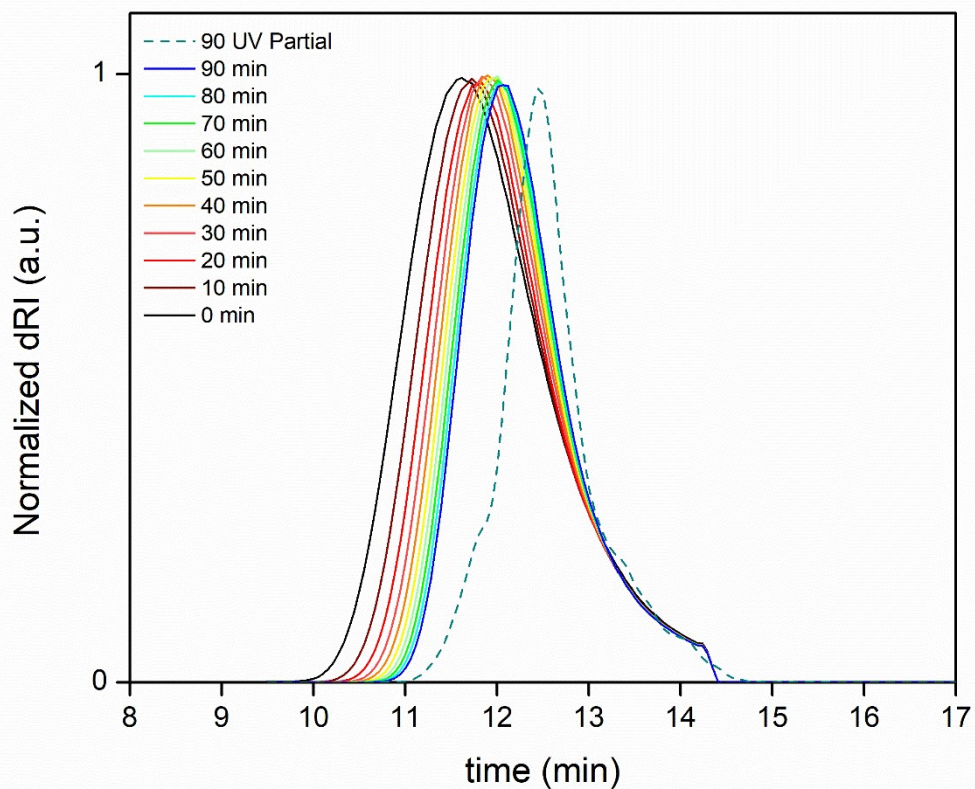
In equation \\* MERGEFORMAT (1.4),  $N_{n,UV}$  is the number concentration of chains with  $n$  monomer units after UV irradiation, while  $N_{x,AS}$  is the number concentration of chains with  $x$  monomer units at the end of the sonication process, before exposure to UV irradiation.



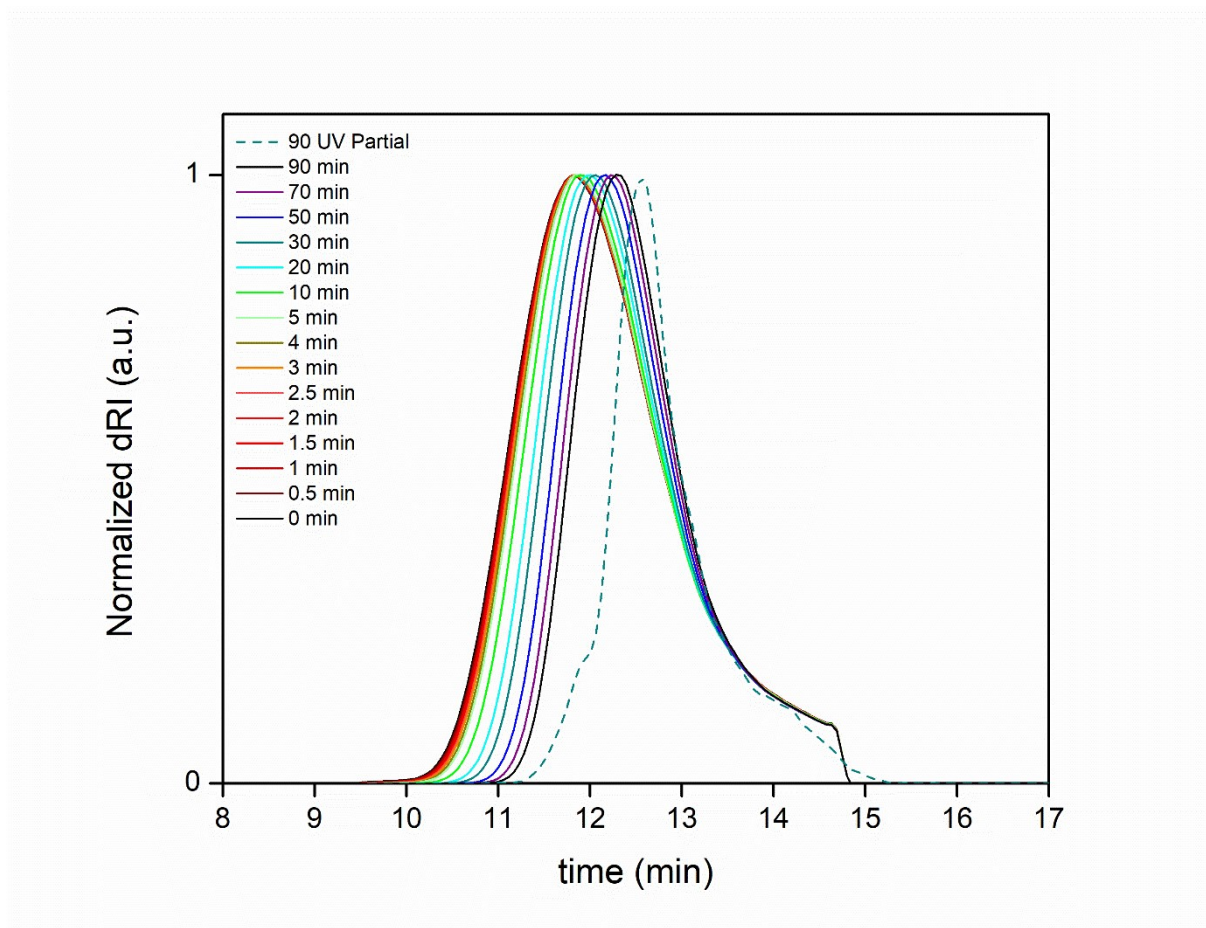
### Simulated size exclusion chromatography (SEC) traces



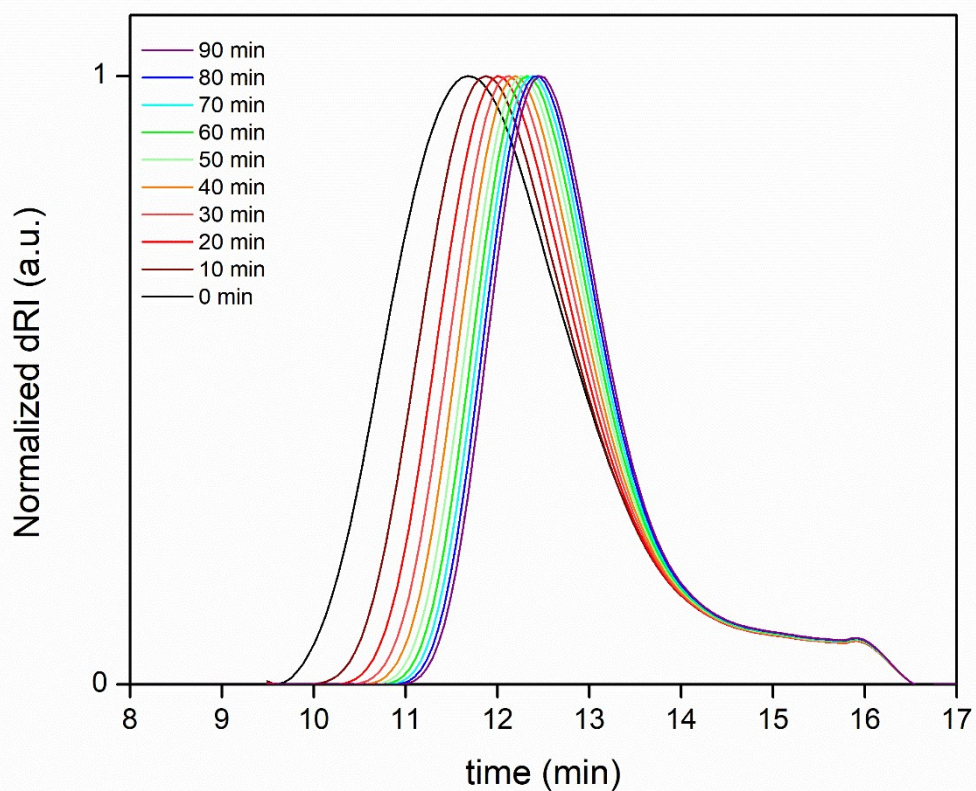
**Fig. S14.** Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation and the UV-light-triggered decomposition of the azo-containing polyurethane **azo-PU2**.



**Fig. S15.** Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation and the UV-light-triggered decomposition of the azo-containing polyurethane **azo-PU3**.

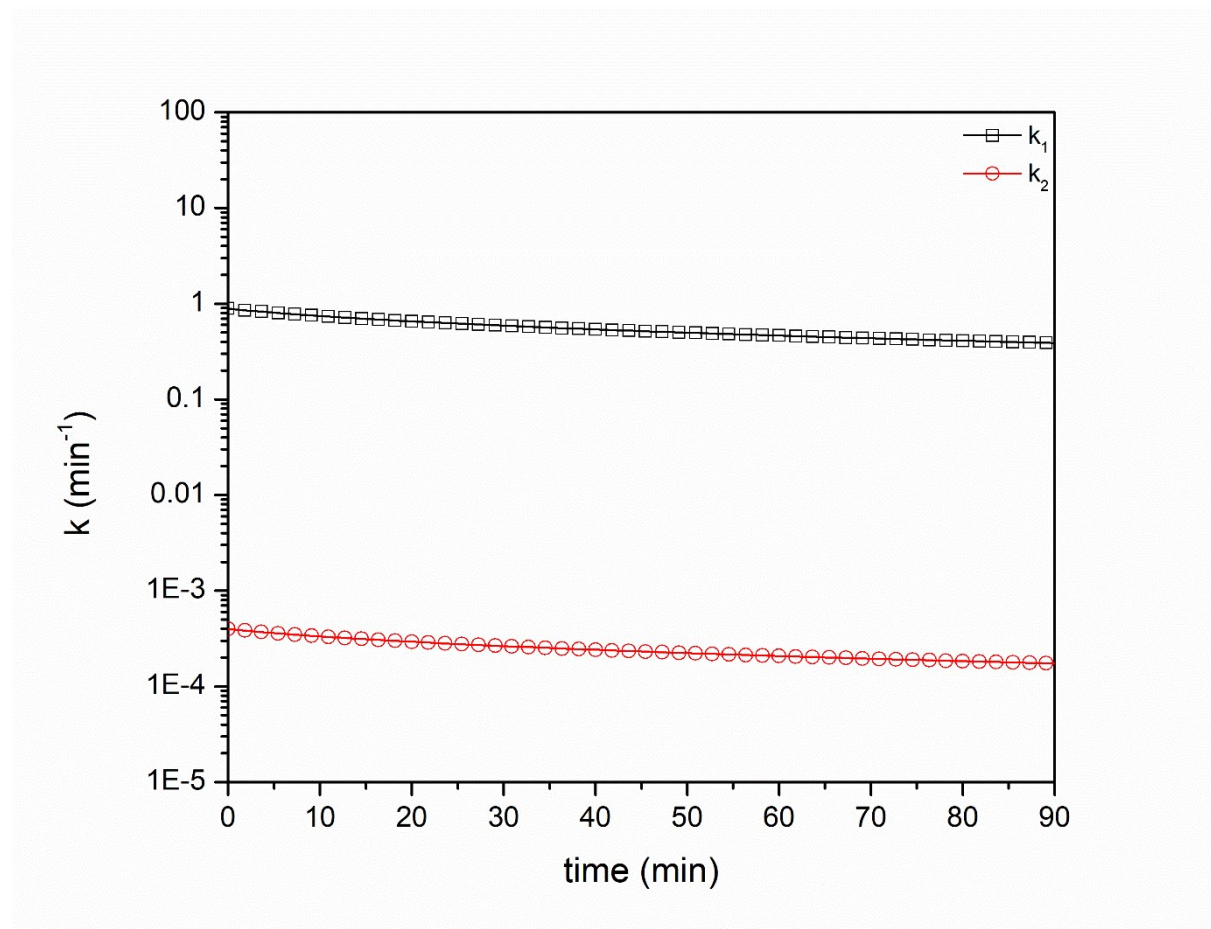


**Fig. S16.** Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation and the UV-light-triggered decomposition of the azo-containing polyurethane **azo-PU4**.

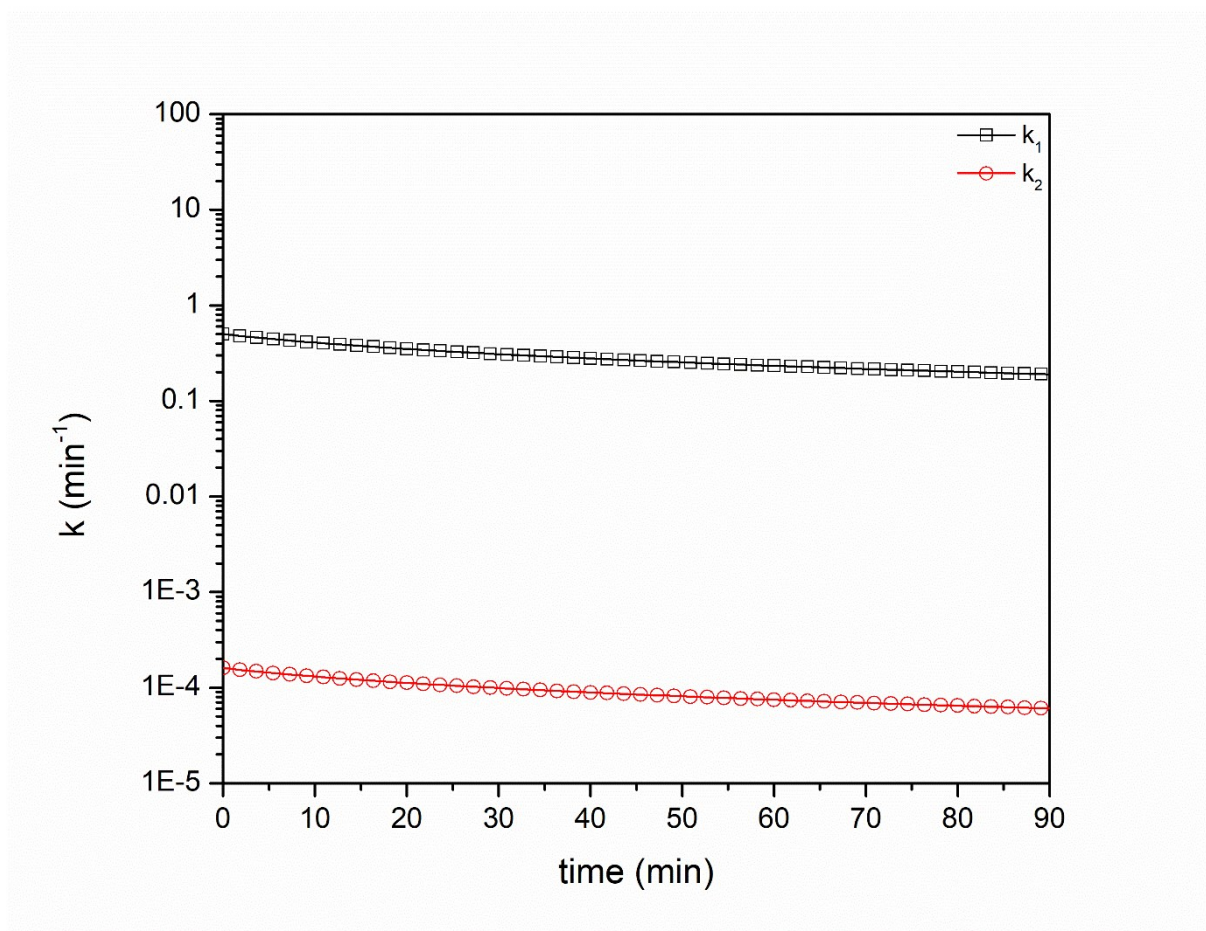


**Fig. S17.** Simulated size exclusion chromatography (SEC) traces modelling the ultrasound-induced degradation and the UV-light-triggered decomposition of the azo-free reference polyurethane **ref-PU1**.

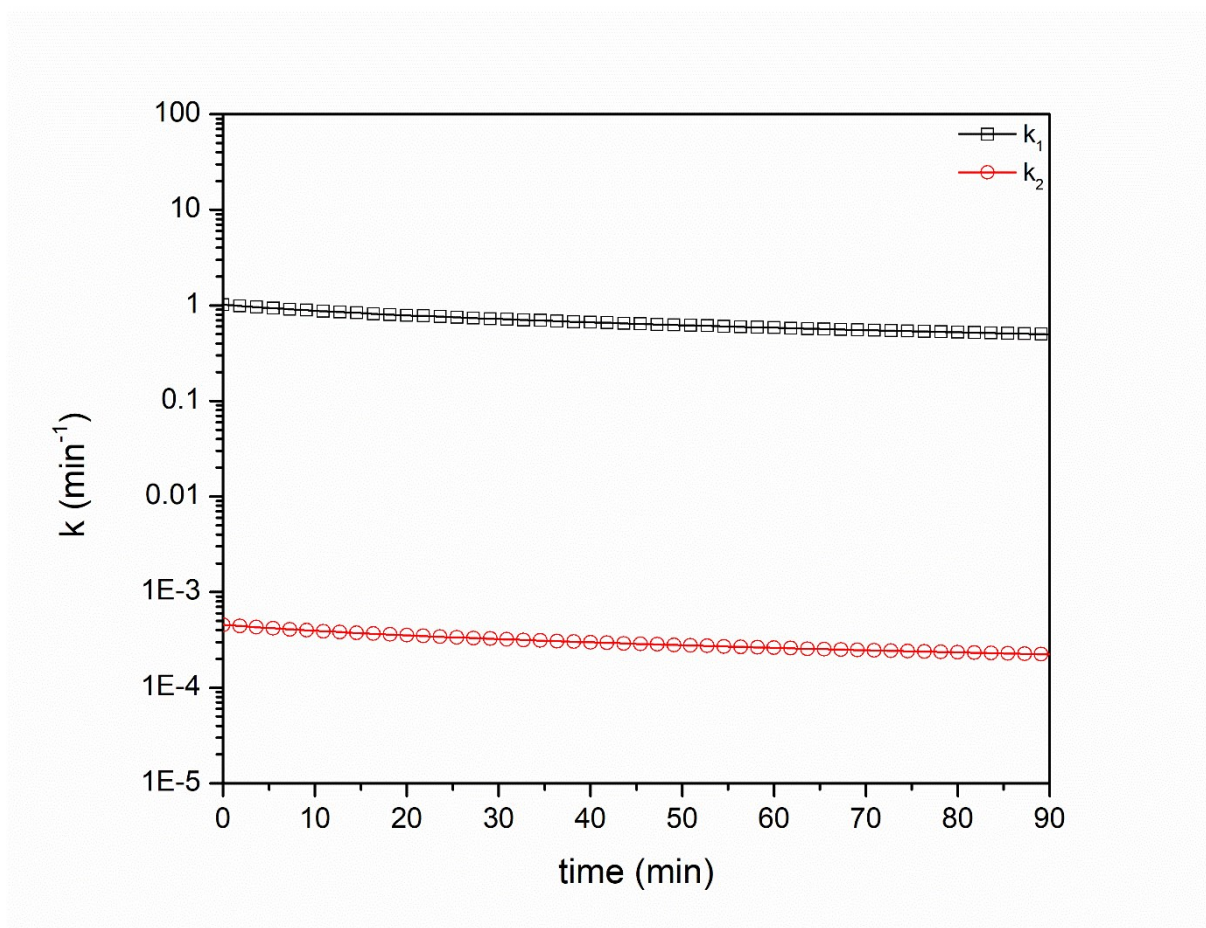
### Effective scission constants as a function of time



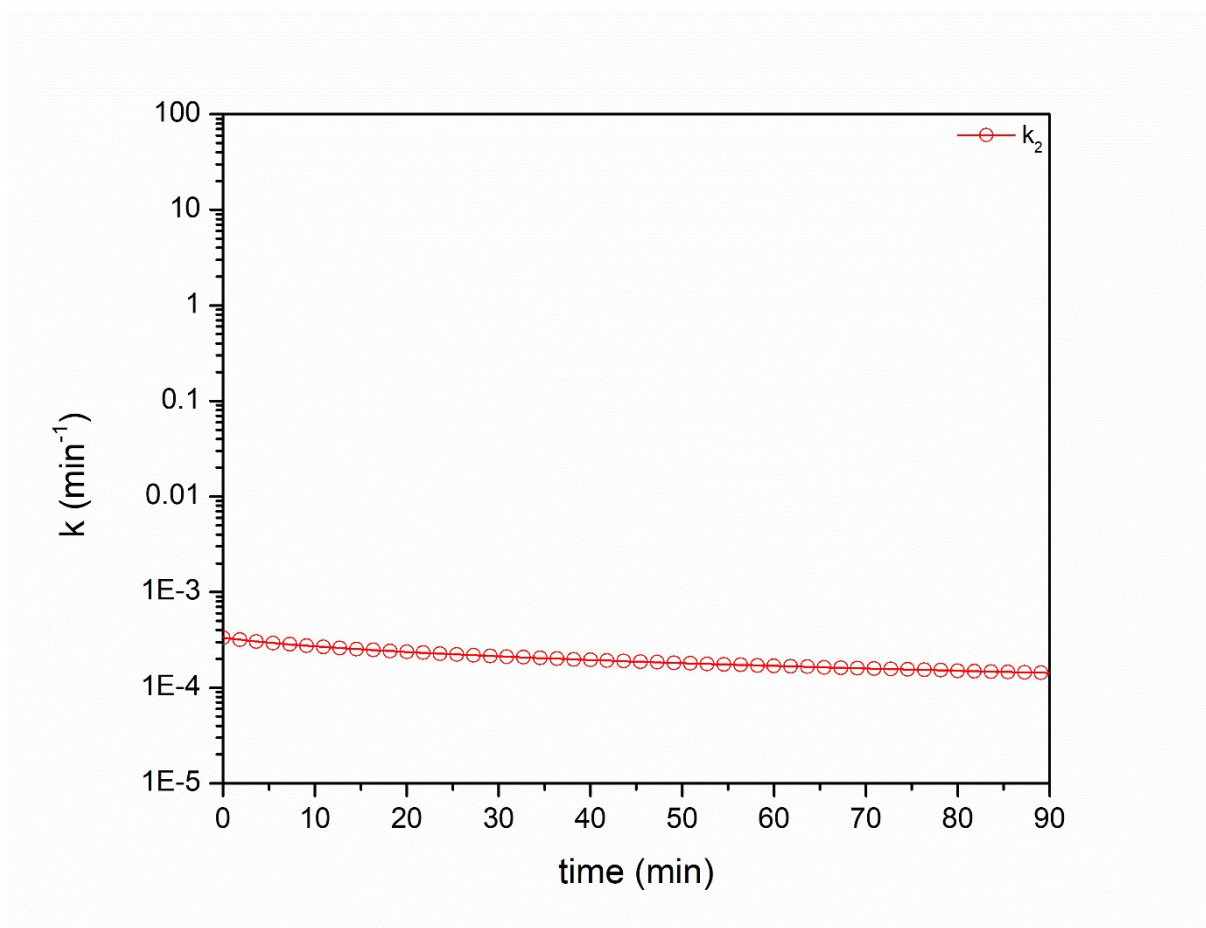
**Fig. S18.** Effective scission rate constants for the azo-containing polyurethane **azo-PU2** polymer as a function of time.



**Fig. S19.** Effective scission rate constants for the azo-containing polyurethane **azo-PU3** polymer as a function of time.

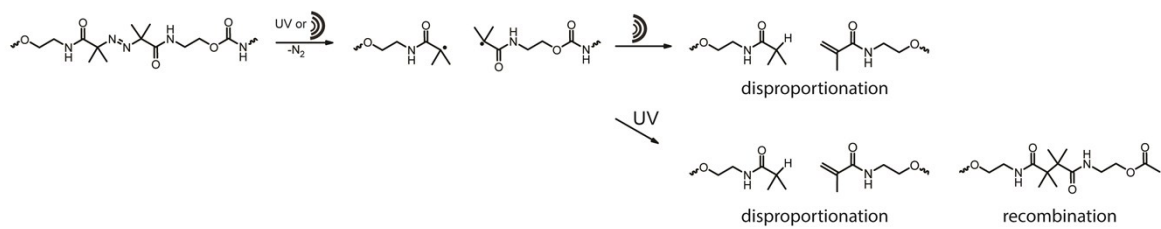


**Fig. S20.** Effective scission rate constants for the azo-containing polyurethane **azo-PU4** polymer as a function of time.



**Fig. S21.** Effective scission rate constant for the azo-free reference polyurethane **ref-PU1** polymer as a function of time.





**Fig. S22.** Degradation pathways from sonication (top), or UV irradiation (bottom). In accordance with previous work, the primary degradation products from sonication are expected to be primarily disproportionation and H-abstraction products whereas UV irradiation results in both disproportionation and recombination products.