*Supporting Information for:*

# Blue Light Driven Free-Radical Polymerization using Arylazo sulfones as Initiators

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# 1. Experimental Section

**General Experimental.** *t*-Butyl acrylate was purified by distillation before use, and all other monomers were purified by a short pad using alumina to remove stabilizers. All other commercially available reagents were used as received. All experiments were conducted in a photoreactor equipped with a 40 W Kessil lamp, shown in Figure S1. $^1$H and $^{13}$C NMR spectra were recorded from solutions in $CDCl_3$ on 200, 300 or 400 MHz instruments and calibrated with the solvent residual proton signal. GC-MS was carried out using a ThermoScientific spectrometer. The UV-Vis spectra were recorded by means of a JASCO V-550 spectrophotometer. The molecular weights of all polymers were determined by a Waters GPC chromatography system equipped with a Refractve Index detector, a set of two universal columns (Styragel 4E and 5E) in series. The mobile phase (1 mL/min, 40˚C) was THF, stabilized with 250 ppm BHT (2,6-di-*tert*-butyl-4-methylphenol). Samples were prefiltered using 0.4 μm PTFE filters and then directly injected. Molecular weight distribution data ($M_w$, $M_n$ and $Đ$) have been obtained through elaboration with the software Breeze, using 12 low polydispersity polystyrene standards for the calibration curve (Fluka kit). The quantum yield of decomposition of the photoinitiators were performed on a solution of 2.5 mL of the corresponding AZS in MeCN (see Table S5). The solution was deaerated for 5 minutes with argon before the irradiation. A LED@456 nm with a 40 W Kessil lamp for 25 min was used as the light source.

**General Procedure for the Synthesis of Arylazo Sulfones 1-6.** Arylazo sulfones **1-5**[S1] and **6**[S2] have been previously prepared and fully characterized[S1-S4] by our research groups by the following procedure. Diazonium salts were prepared from the corresponding aniline[S5] and purified by dissolving in acetone and precipitation by adding cold diethyl ether before use.

To a cooled (0 °C) suspension of the chosen diazonium salt (1 equiv., 0.3 M) in $CH_2Cl_2$ was added sodium methanesulfinate (1.2 equiv.) in one portion. The temperature was allowed to rise to room temperature, and the mixture stirred overnight. The solvent was then removed by filtration and the obtained solution was evaporated. The crude residue was finally dissolved in $CH_2Cl_2$ and precipitated by adding cold *n*-hexane, to afford the pure arylazo sulfone.

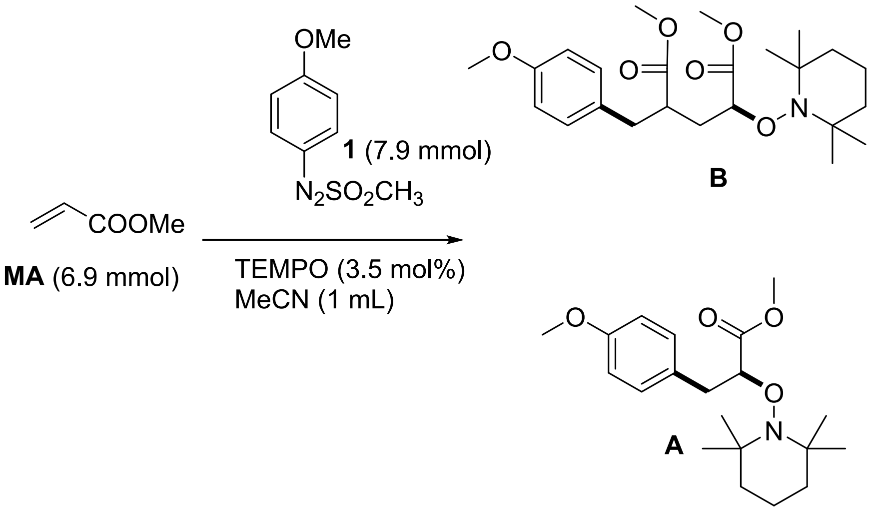
**General procedure for the bulk polymerization process.** *Polymerization of tBA. t*BA (1 mL, 6.9 mmol) and the chosen AZS (1.7 mg, 7.2-8.6×$10^{-3}$ mmol, 1/500 w/w %) were added in sequence in a 4 mL vial. The reaction vessel was closed with a stopper and the solution was deaerated for 10 min with argon to remove oxygen, and then irradiated with blue LED@456 nm with a 40 W Kessil lamp for 4 h. The reaction mixture was dissolved in THF (10 mL) and precipitated in MeOH/$H_2O$ (3/1 v/v) mixture (300 mL). After filtration, residual solvent was removed under vacuum for 1 h to give pure product as a white solid (78-87% yield, see Table 1).

**General procedure for the polymerization in solution.** *t*BA (1 mL, 6.9 mmol), AZS (1.7 mg, 7.2-8.6×$10^{-3}$ mmol, 1/500 w/w %) and the chosen solvent (1-10 mL) were added in sequence in a reaction vessel. Reaction vessel was closed with a stopper and the solution was deaerated for 10 min with argon to remove oxygen, and then irradiated with blue LED@456 nm with a 40 W Kessil lamp for 4 h. The obtained polymeric material was dissolved in THF (10 mL) and precipitated in MeOH/$H_2O$ (3/1 v/v) mixture (300 mL). After filtration, residual solvent was removed under vacuum for 1 h to give pure product as white solid (22-100% yield, see Table S1).

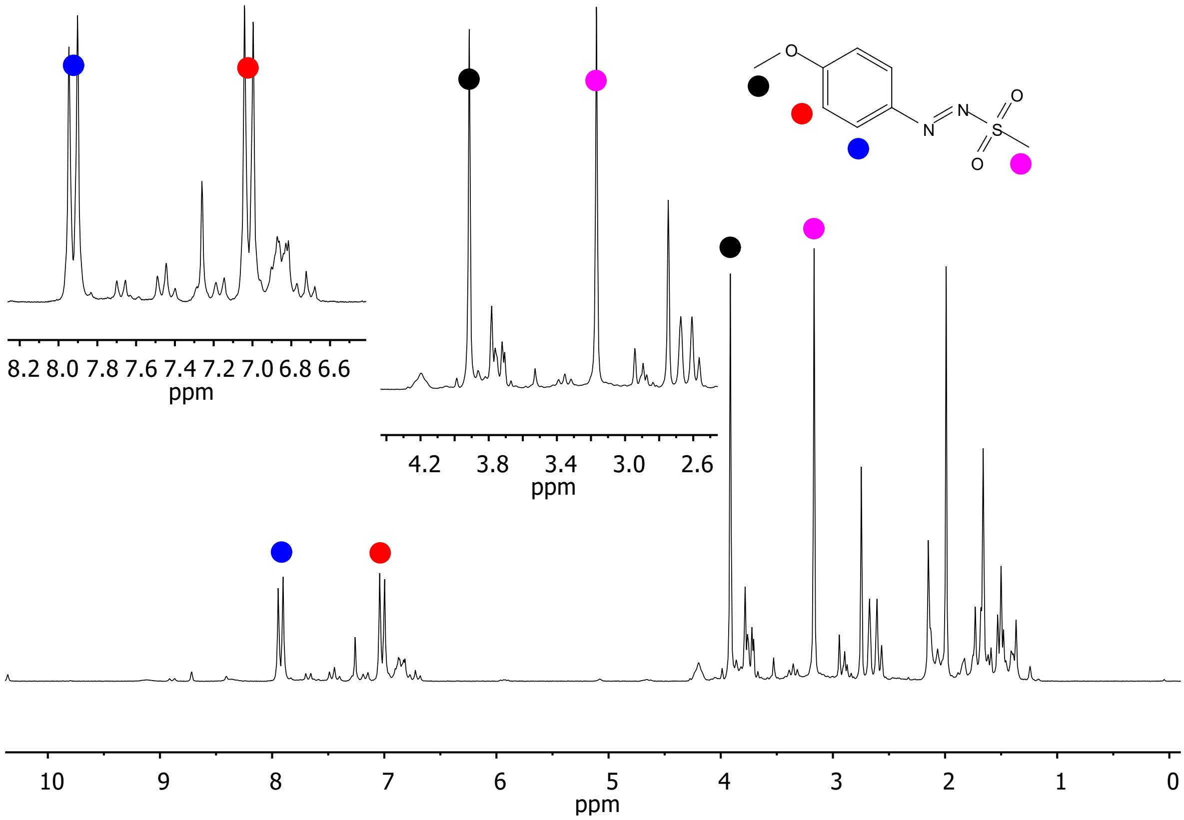
**General procedure for the kinetic experiments.** *t*BA (1 mL, 6.9 mmol) and AZS **5** (1.7 mg, 7.2×$10^{-3}$ mmol, 1/500 w/w %) were added in sequence in several 4 mL vials (otherwise identical in composition). The reaction vessels were closed with a stopper and the solution was deareated for 10 min with argon to remove oxygen, and then irradiated with blue LED@456 nm with a 40 W Kessil lamp for different amount of times (5, 10, 15, 20, 25 and 30 min). The obtained polymeric material was dissolved in THF (10 mL) and precipitated in MeOH/$H_2O$ (3/1 v/v) mixture (300 mL). After filtration, residual solvent was removed under vacuum for 1 h to give pure product as a white solid.

## 2. Trapping Experiment with TEMPO

The trapping experiment with TEMPO was performed following a literature procedure.[S6] The protocol was adapted using methyl acrylate (MA) as monomer and AZS **1** as initiator. The experiment consisted in the slow and continuous addition of a solution of TEMPO (0.24 mmol) to a solution of MMA (6.9 mmol) and **1** (7.9 mmol) in acetonitrile (1 mL) irradiated with LED@456 nm.

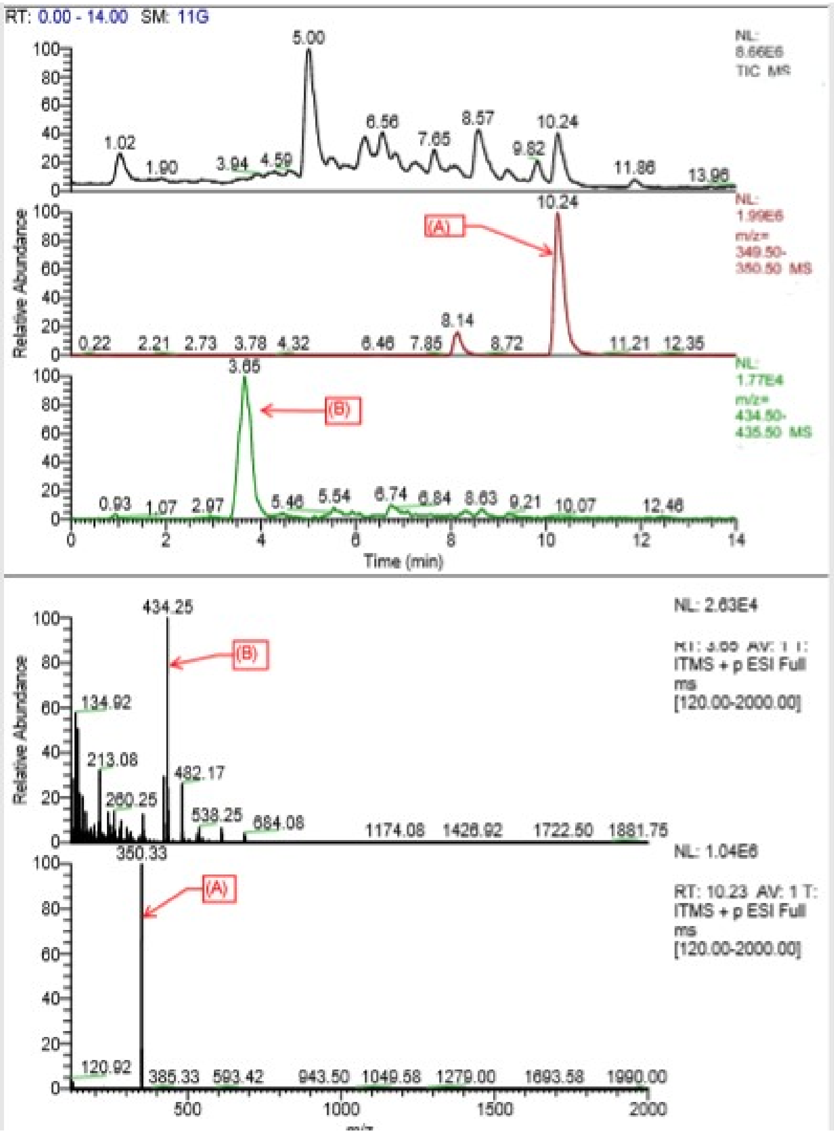


The reaction mixture was then analyzed by $^1$H NMR and GC-MS. The $^1$H NMR spectrum of the crude reaction mixture after the addition of TEMPO is shown below. The unreacted arylazo sulfone **1** (indicated by colored markers) is easily detectable in the spectrum as well as several doublets with marked roof effects (see enlargement of the 8-6.5 ppm range) typical of *para-* substituted anisole derivatives, while in the aliphatic region a group of singlets attributed to methoxy groups are detectable (enlargement of the 4.2-2.5 ppm range, by comparison the -$OCH_3$ signal of anisole is at 3.74 ppm). The spectrum is therefore consistent with species containing a substituted anisole fragment in position 4 formed by the reaction of anisyl radical with one or more MA units.



$^1$H NMR ($CDCl_3$, 293 K) of the crude reaction mixture

The GC-MS chromatogram of the crude reaction mixture is shown below. The reported mass spectra are related to the retention times of 3.65 and 10.24 min, respectively. With the isolation of ionic current of selected ions, we identified species attributed to the entrapment of specific radicals with TEMPO (compounds **A** and **B**).



*Top:* TIC chromatogram of the crude reaction mixture (black, see reaction above), and chromatogram of selected ions with *m/z* 349 (red) and *m/z* 434 (green). *Below:* Mass spectra of isolated ions.

## 3. Additional Figures

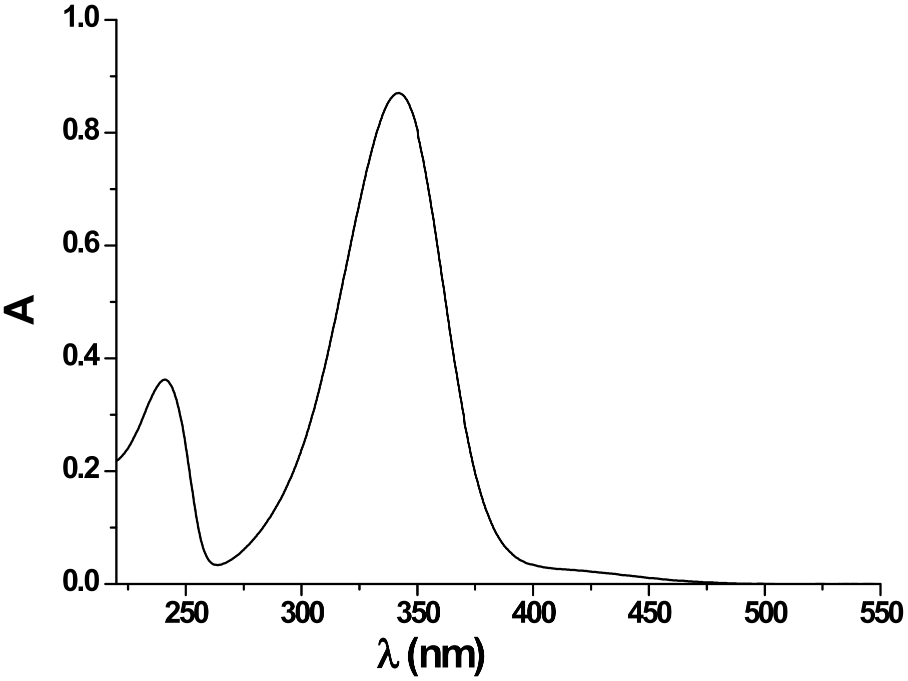


**Figure S1**. UV-Vis absorption spectrum of compound **1** in MeCN ($5\times10^{-5}$ M)

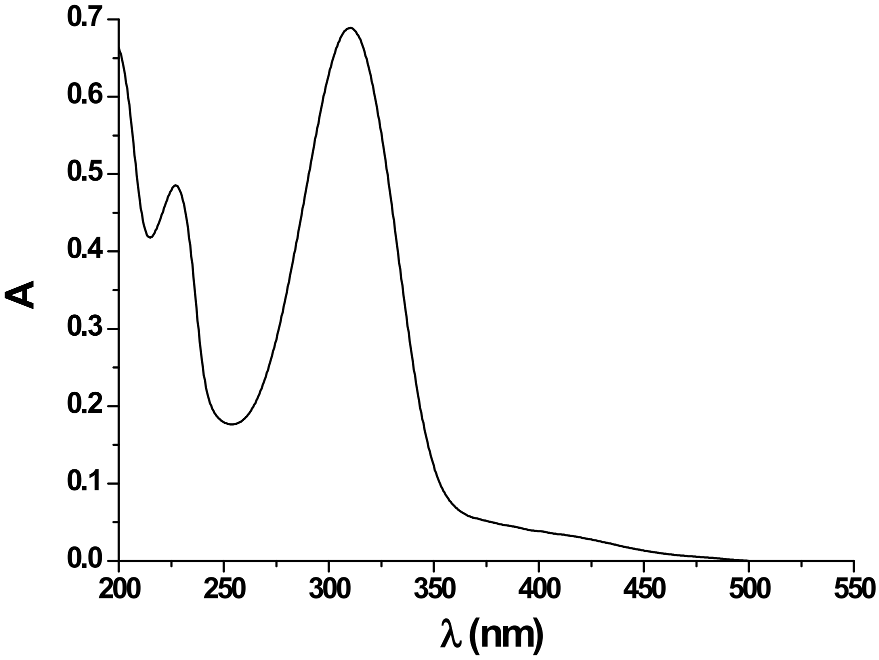


**Figure S2**. UV-Vis absorption spectrum of compound **2** in MeCN ($5\times10^{-5}$ M)

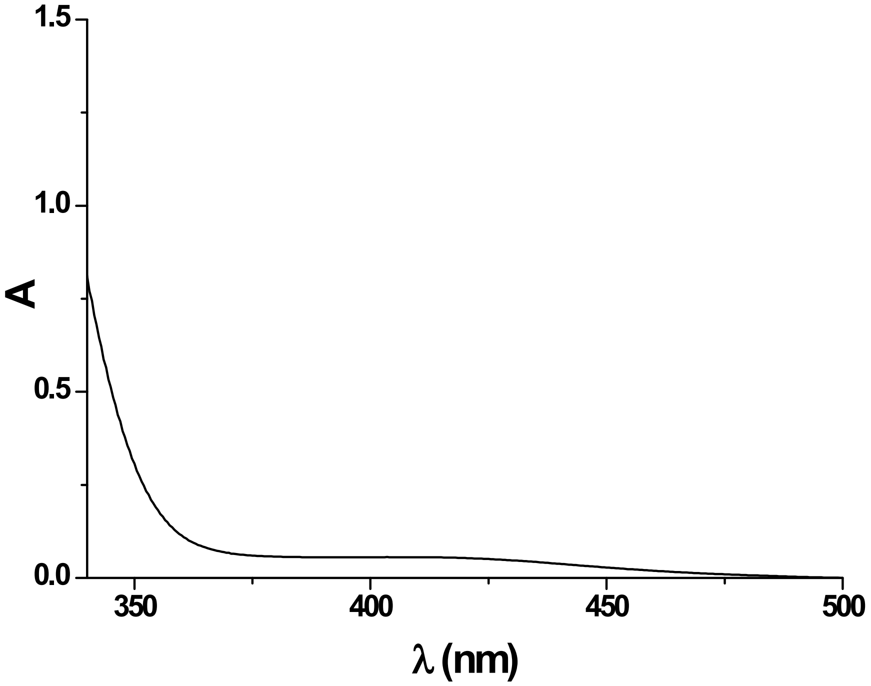


**Figure S3.** UV-Vis absorption spectrum of compound **2** in MeCN (2×10$^{-4}$ M)

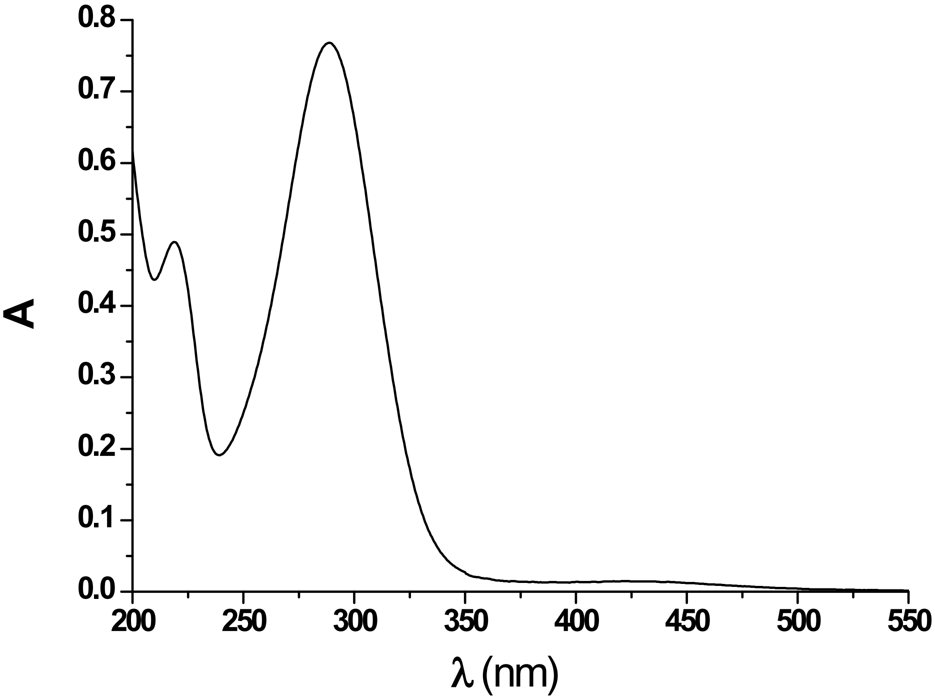


**Figure S4**. UV-Vis absorption spectrum of compound **3** in MeCN (5×10$^{-5}$ M)

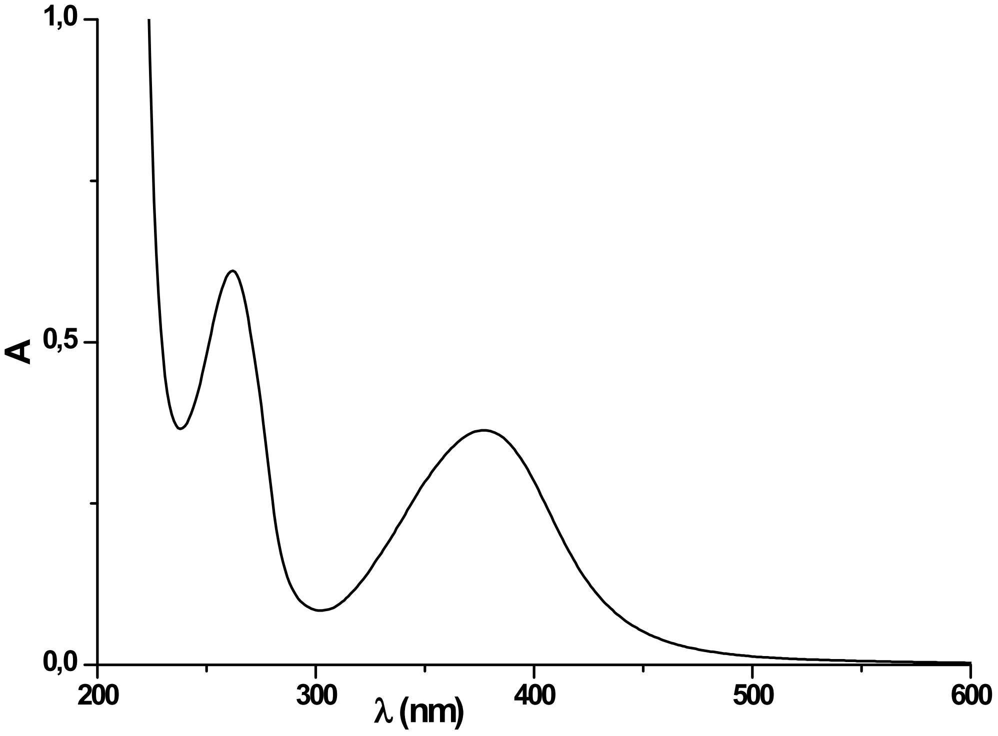


**Figure S5.** UV-Vis absorption spectrum of compound **4** in MeCN ($5\times10^{-5}$ M)

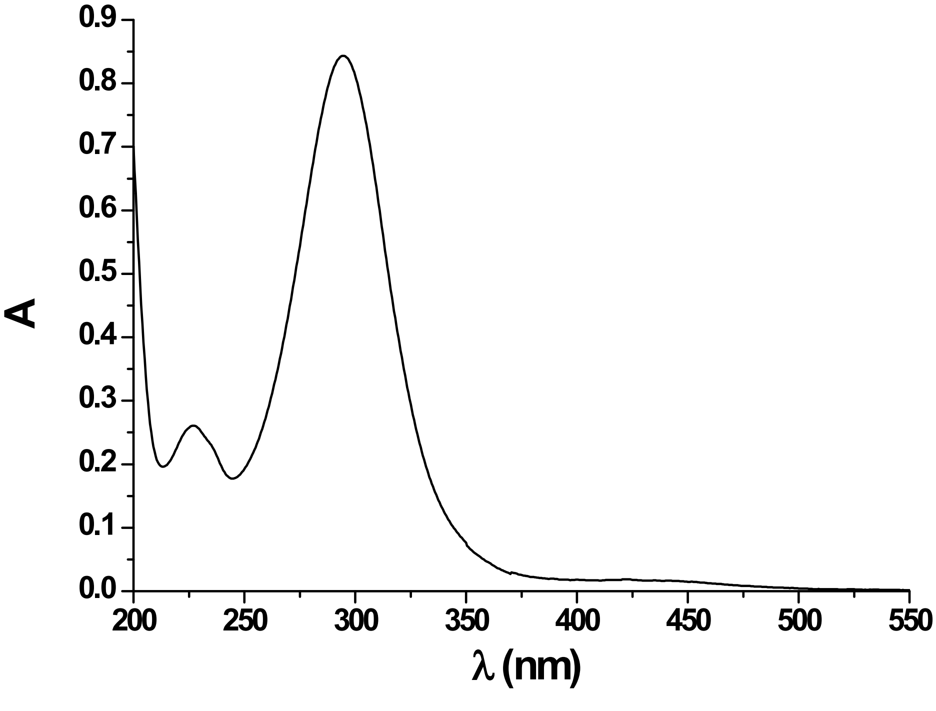


**Figure S6.** UV-Vis absorption spectrum of compound **5** in MeCN ($5\times10^{-5}$ M)

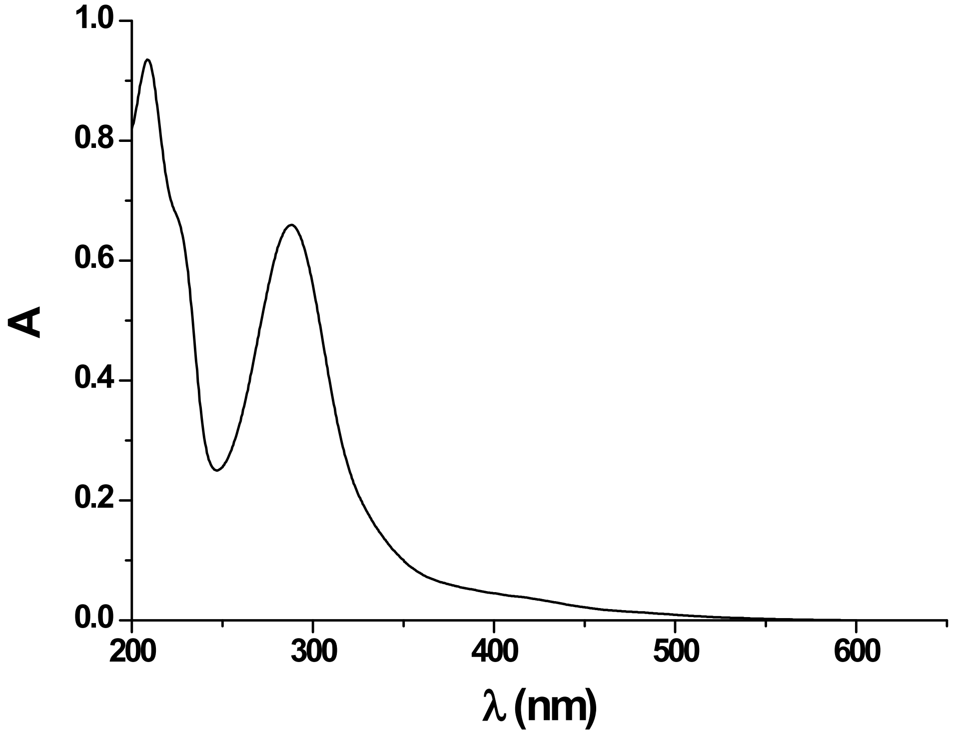


**Figure S7.** UV-Vis absorption spectrum of compound **6** in MeCN ($5\times10^{-5}$ M)

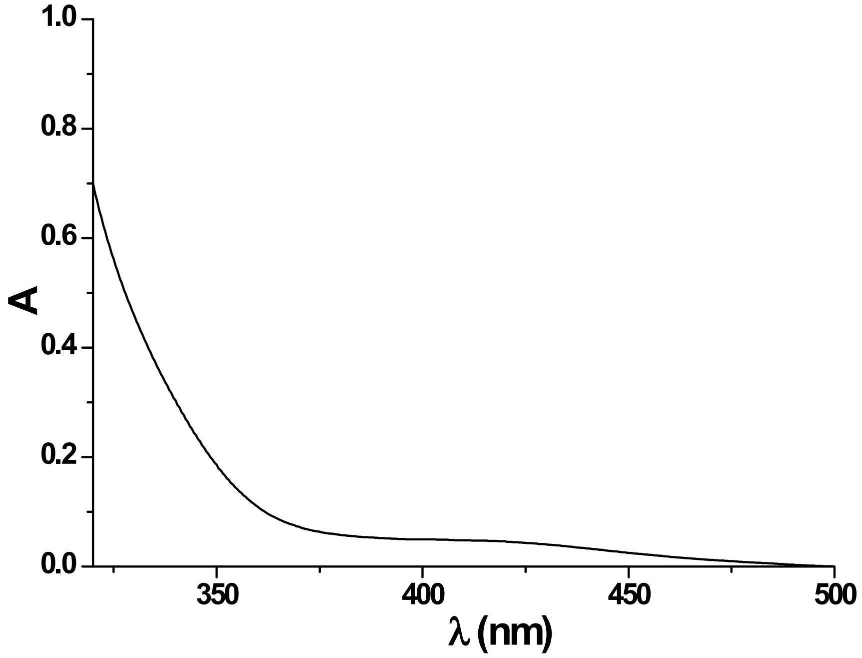


**Figure S8.** UV-Vis absorption spectrum of compound **6** in MeCN ($2\times10^{-4}$ M)

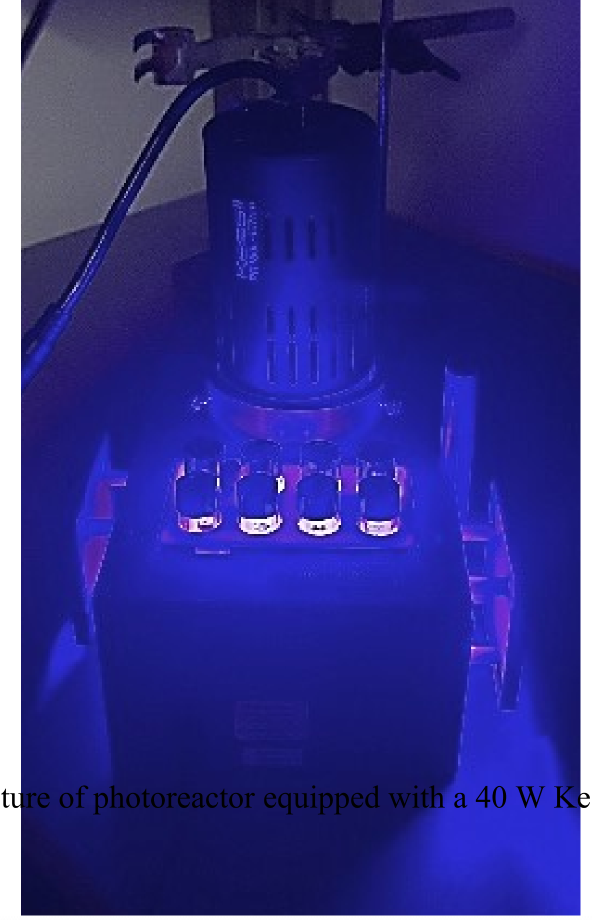


**Figure S9.** Picture of photoreactor equipped with a 40 W Kessil lamp.

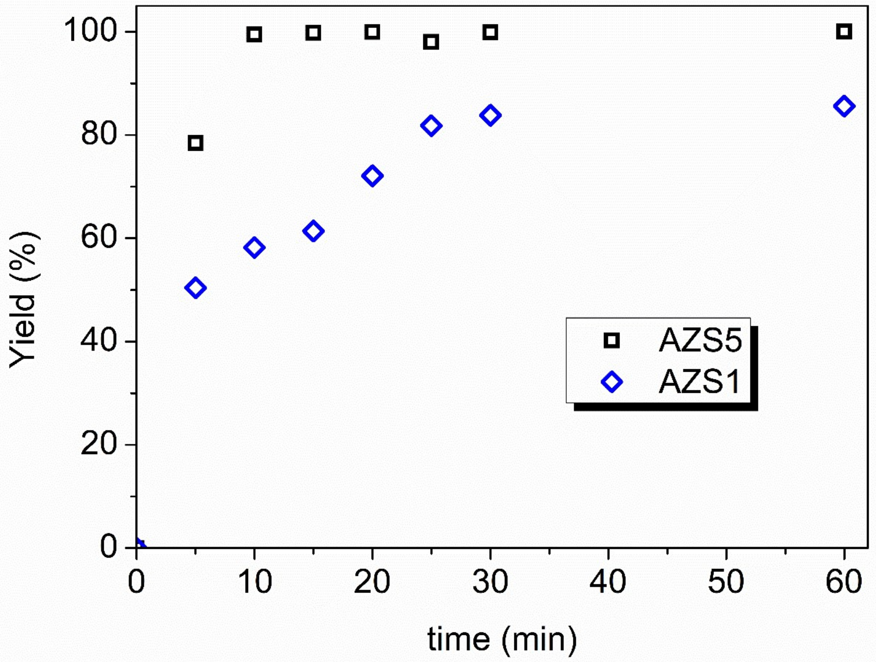


**Figure S10.** Yield of PTBA obtained with variable irradiation times on a 1/500 initiator (**1** or **5**)/monomer ratio (w/w %). Purification by precipitation in MeOH/$H_2O$ (3/1 v/v).

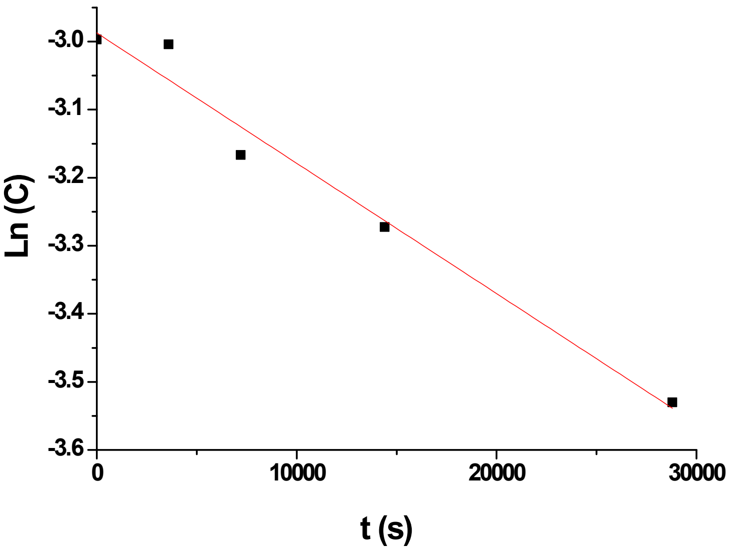


**Figure S11.** Kinetic data for the degradation of **1** in MeCN ($k_{app} = 1.9\times10^{-5}$ $s^{-1}$)

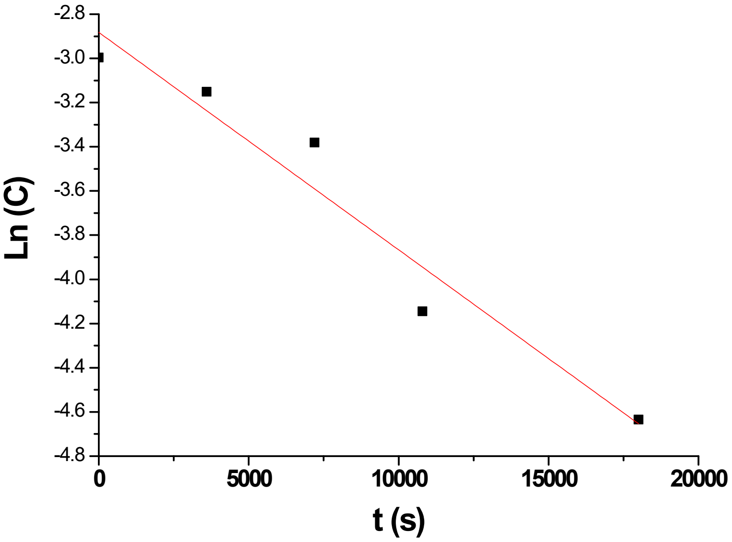


**Figure S12.** Kinetic data for the degradation of **5** in MeCN ($k_{app} = 9.8\times10^{-5}$ $s^{-1}$)

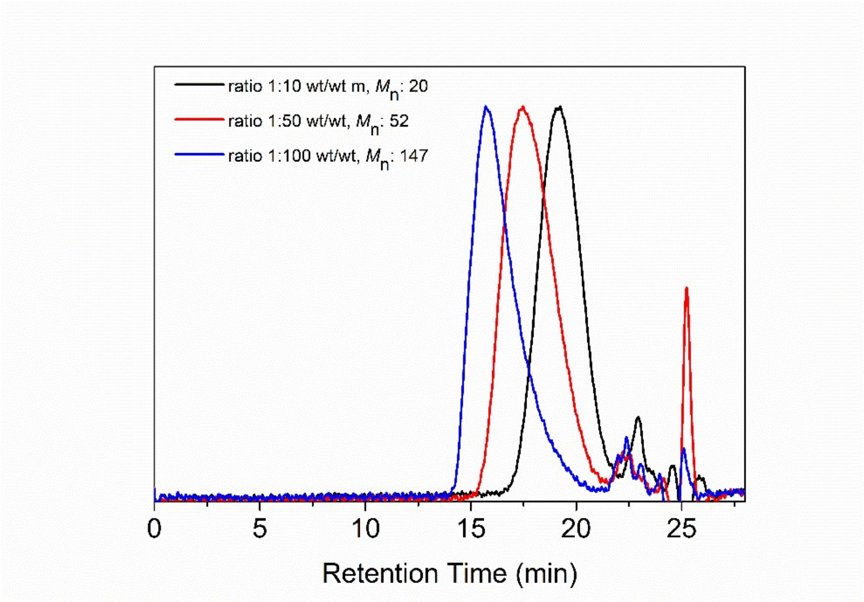


**Figure S13.** GPC traces of experiments at different **5**/*t*BA ratio (entries 1, 3 and 4 in Table S4). $M_n$ values were reported in kDa.

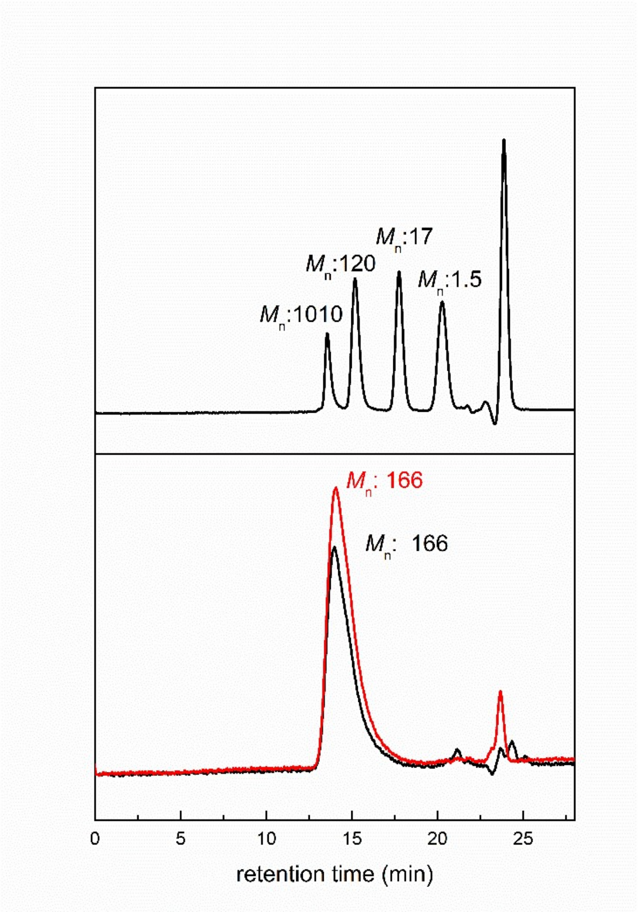


**Figure S14.** Top: GPC traces of calibration standards (red standards in Fluka kit®). Bottom: GPC traces of PTBA polymers obtained by photopolymerizatation in DCM (black line, entry 16 of Table S1) and MeOH (red line, entry 19 of Table S1). $M_n$ values were reported in kDa.

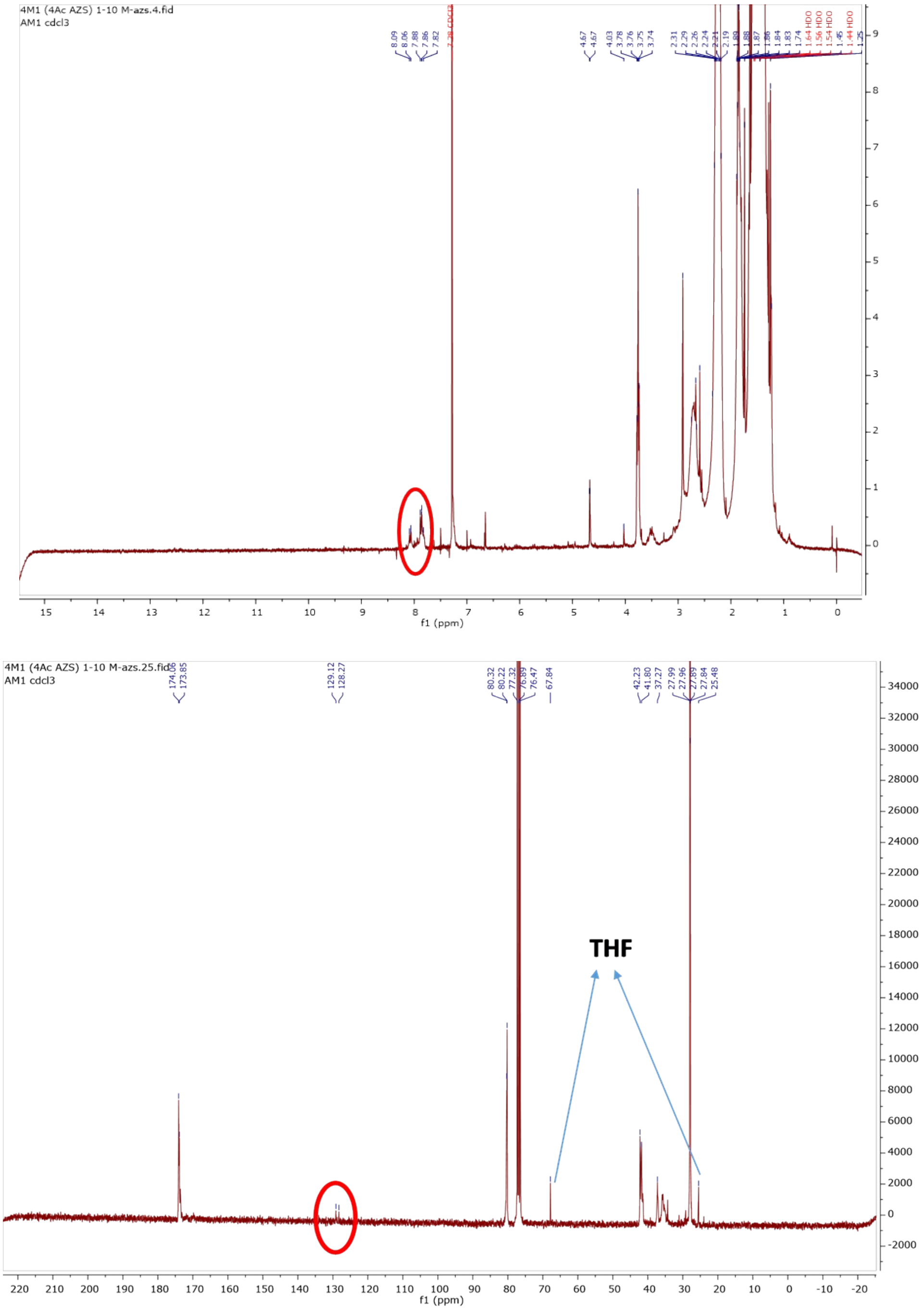


**Figure S15.** $^1$H NMR (top) and $^{13}$C NMR (bottom) spectra of PTBA obtained with a **5**/*t*BA ratio of 1/10 after precipitation and removal of residual monomer. The aromatic signals in the 7.5-8.5 ppm range are attributed to the acetophenone fragment attached to the polymer chains as a result of AZS **5** fragmentation and initiation.

## 4. Additional Tables

**Table S1**. UV/Vis absorption data (in MeCN) for AZSs **1-6**.

| **Compound** | **$\lambda_{abs}$, nm ($\varepsilon$, mol L$^{-1}$ cm$^{-1}$)$^a$** |
|---|---|
| **1**[S3] | 425 (230); 342 (17405) |
| **2** | 415, (280); 310 (13400) |
| **3**[S3] | 377 (7200); 262 (12200) |
| **4**[S3] | 435 (155); 288.5 (15360) |
| **5**[S3] | 424 (215); 294 (16870) |
| **6** | 416 (230); 287 (13200) |

**Table S2.** Detailed data for the experiments summarized in Figure 4 in the main text (reaction time = 240 min).

| **Entry** | **5/*t*BA Ratio (w/w %)** | **Solv.** | **V (mL)** | **Yield (%)** | ***$M_w$* *(kDa)*** | ***$M_n$* *(kDa)*** | ***Đ*** |
|---|---|---|---|---|---|---|---|
| 1 | 1/800 | ACN | 1 | 86 | 366 | 159 | 2.31 |
| 2 | 1/600 | ACN | 1 | 86 | 295 | 126 | 2.33 |
| 3 | 1/500 | ACN | 1 | 80 | 334 | 150 | 2.23 |
| 4 | 1/400 | ACN | 1 | 99 | 305 | 153 | 1.99 |
| 5 | 1/200 | ACN | 1 | 98 | 246 | 115 | 2.14 |
| 6 | 1/50 | ACN | 1 | 87 | 112 | 57 | 1.97 |
| 7 | 1/30 | ACN | 1 | 65 | 64 | 35 | 1.79 |
| 8 | 1/10 | ACN | 1 | 29 | 30 | 18 | 1.61 |
| 9 | 1/500 | ACN | 1 | 99 | 315 | 131 | 2.41 |
| 10 | 1/500 | ACN | 2 | 100 | 283 | 128 | 2.21 |
| 11 | 1/500 | ACN | 3 | 88 | 199 | 94 | 2.10 |
| 12 | 1/500 | ACN | 10 | 54 | 79 | 57 | 1.40 |
| 13 | 1/500 | THF | 1 | 71 | 59 | 34 | 1.55 |
| 14 | 1/500 | ACN | 1 | 80 | 315 | 131 | 2.41 |
| 15 | 1/500 | $CHCl_3$ | 1 | 83 | 429 | 167 | 2.57 |
| 16 | 1/500 | DCM | 1 | 82 | 398 | 166 | 2.39 |
| 17 | 1/500 | acetone | 1 | 84 | 593 | 217 | 2.44 |
| 18 | 1/500 | DMF | 1 | 84 | 458 | 170 | 2.59 |
| 19 | 1/500 | MeOH | 1 | 79 | 379 | 165 | 2.28 |
| 20 | 1/500 | Toluene | 1 | 85 | 362 | 154 | 2.34 |

**Table S3.** Further experiments at varying AZS **1**/*t*BA ratios.

| **Entry** | **AZS** | **AZS/*t*BA Ratio (w/w %)** | **[AZS]/[*t*BA] ratio (molar)** | **Solv.** | **V (mL)** | **Yield[a] (%)** | **$M_w$ *(KDa)*** | **$M_n$ *(KDa)*** | ***Đ*** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 1:400 | 0.01/6.9 | - | - | 81 | 513 | 224 | 2.29 |
| 2 | **1** | 1:200 | 0.02/6.9 | - | - | 77 | 452 | 119 | 3.79 |
| 3 | **1** | 1:100 | 0.04/6.9 | - | - | 91 | 335 | 150 | 2.23 |
| 4 | **1** | 1:50 | 0.1/6.9 | - | - | 90 | 214 | 81 | 2.63 |
| 5[b] | **1** | 1:50 | 0.05/3.45 | ACN | 2 | 69 | 132 | 63 | 2.10 |
| 6[c] | **1** | 1:11.32 | 0.1/1 | ACN | 3.44 | 25 | 44 | 24 | 1.81 |
| 7[c] | **1** | 1:5.66 | 0.2/1 | ACN | 3.44 | 20 | 28 | 17 | 1.69 |
| 8 | **1** | 1:500 | 0.008/6.9 | ACN | 1 | 70 | 583 | 201 | 2.89 |
| 9 | **1** | 1:500 | 0.008/6.9 | ACN | 1 | 74 | 609 | 211 | 2.88 |
| 10 | **1** | 1:500 | 0.008/6.9 | ACN | 1 | 78 | 551 | 185 | 3.00 |
| 11 | **1** | 1:200 | 0.02/6.9 | ACN | 1 | 71 | 366 | 146 | 2.49 |
| 12 | **1** | 1:200 | 0.02/6.9 | ACN | 1 | 70 | 331 | 134 | 2.46 |

[a] All solutions were irradiated for 240 min. Yield determined after precipitation in MeOH/$H_2O$ (3/1 v/v). [b] [M]= 3.45 mol·L$^{-1}$. [c] [M]= 1 mol·L$^{-1}$.

**Table S4.** Further experiments at varying AZS **5**/*t*BA ratios in ACN.

| **Entry** | **AZS** | **AZS/*t*BA Ratio (w/w %)** | **[AZS]/[*t*BA] ratio (molar)** | **Solv.** | **V (mL)** | **time (min)** | **$m_{PTBA}$ (g)** | **Yield[a] (%)** | **$M_w$ *(KDa)*** | **$M_n$ *(KDa)*** | ***Đ*** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1[b] | **5** | 1:10 | 0.2/3.45 | ACN | 2 | 240 | 0.44 | 50 | 31 | 20 | 1.54 |
| 2[b] | **5** | 1:20 | 0.1/3.45 | ACN | 2 | 240 | 0.77 | 87 | 198 | 68 | 2.92 |
| 3[b] | **5** | 1:50 | 0.04/3.45 | ACN | 2 | 240 | 0.67 | 76 | 122 | 52 | 2.34 |
| 4[b] | **5** | 1:100 | 0.02/3.45 | ACN | 2 | 240 | 0.39 | 44 | 396 | 147 | 2.69 |
| 5[c] | **5** | 1:11.32 | 0.1/1 | ACN | 3.44 | 240 | 0.18 | 20 | 46 | 28 | 1.67 |
| 6[c] | **5** | 1:5.66 | 0.2/1 | ACN | 3.44 | 240 | 0.06 | 7 | 30 | 21 | 1.41 |

[a] All solutions were irradiated for 240 min. Yield determined after precipitation in MeOH/$H_2O$ (3/1 v/v). [b] [M]= 3.45 mol·L$^{-1}$. [c] [M]= 1 mol·L$^{-1}$.

**Table S5**. Quantum Yield data (in MeCN) for AZSs **1** and **5**.

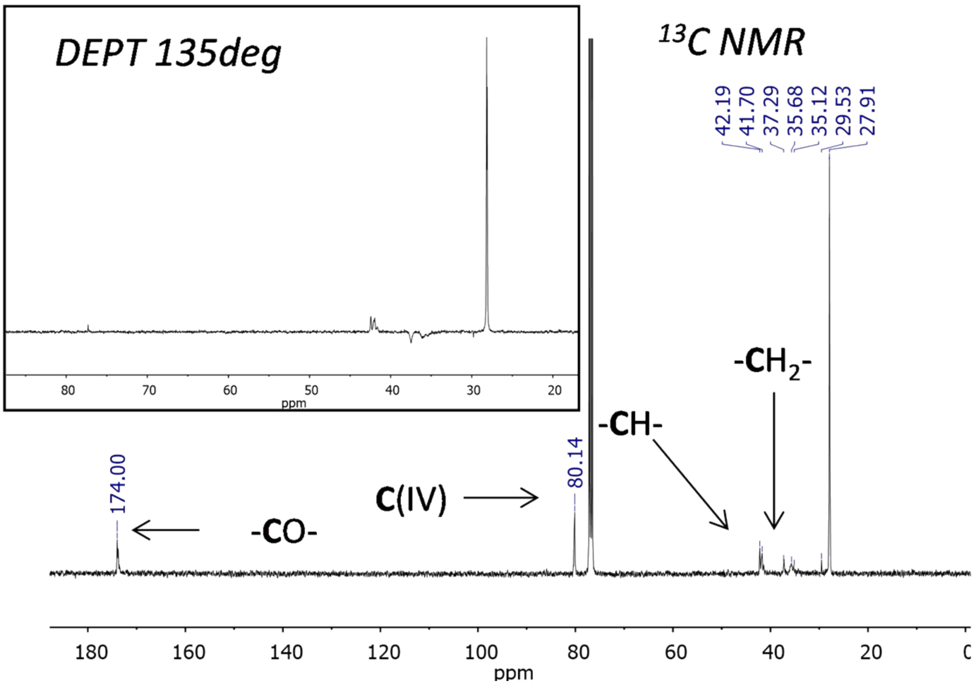
| Compound | Concentration (mol/L) | Φ (%) |
|---|---|---|
| **1** | $4.9\times10^{-3}$ | 1 |
| **5** | $5.1\times10^{-3}$ | 1.7 |

**Table S6**. Further experiments at varying photoinitiators/*t*BA ratios

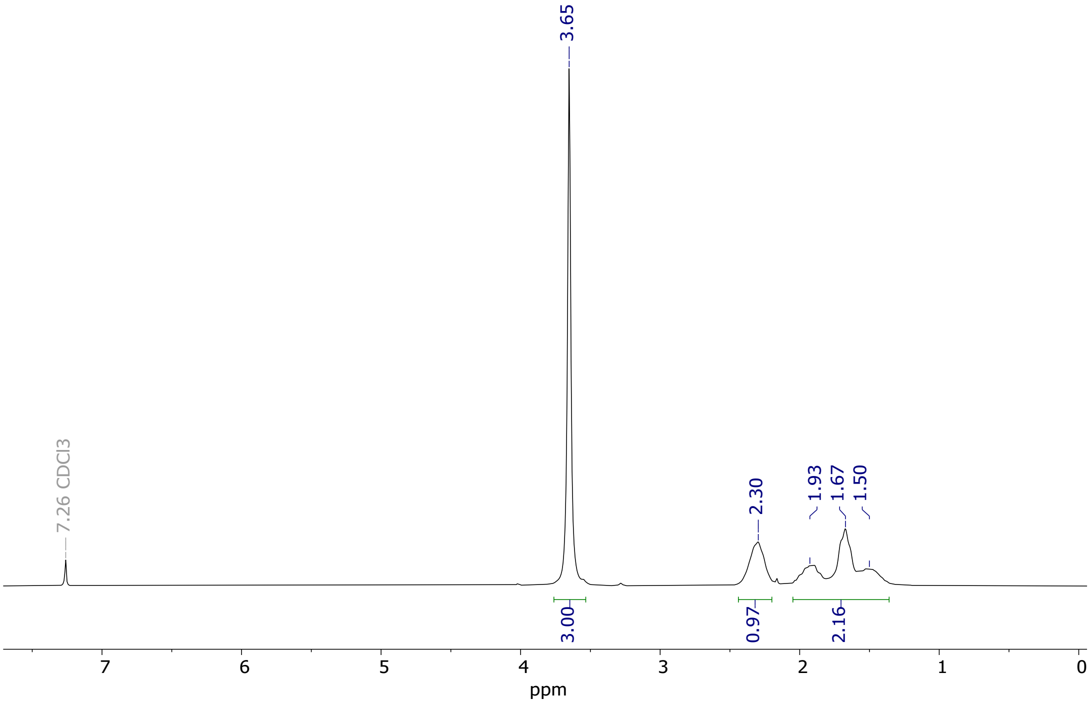
| Entry | Photoinitiators | AZS/*t*BA Ratio (w/w %) | Solv. | V (mL) | Yield[a] (%) | $M_w$ *(KDa)* | $M_n$ *(KDa)* | *Đ* |
|---|---|---|---|---|---|---|---|---|
| 1 | **AZS 1** | 1:500 | ACN | 1 | 78 | 554 | 183 | 3.00 |
| 2 | **AZS 5** | 1:500 | ACN | 1 | 77 | 335 | 150 | 2.23 |
| 3 | **IRGACURE 184**[b] | 1:500 | ACN | 1 | 73 | 268 | 85 | 3.13 |
| 4 | **IRGACURE 184**[b] | 1:500 | DCM | 1 | 74 | 245 | 83 | 2.98 |

[a] All solutions were irradiated for 240 min. Yield determined after precipitation in MeOH/$H_2O$ (3/1 v/v). [b] Experiments performed at 390 nm.

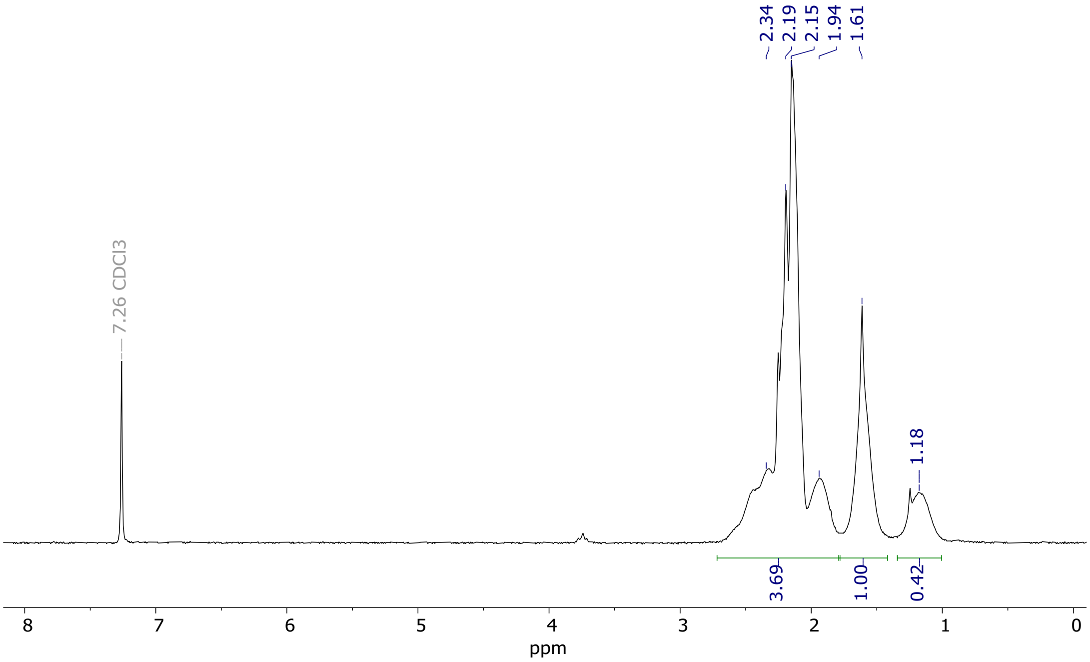
## 5. Copies of NMR Spectra of Polymers



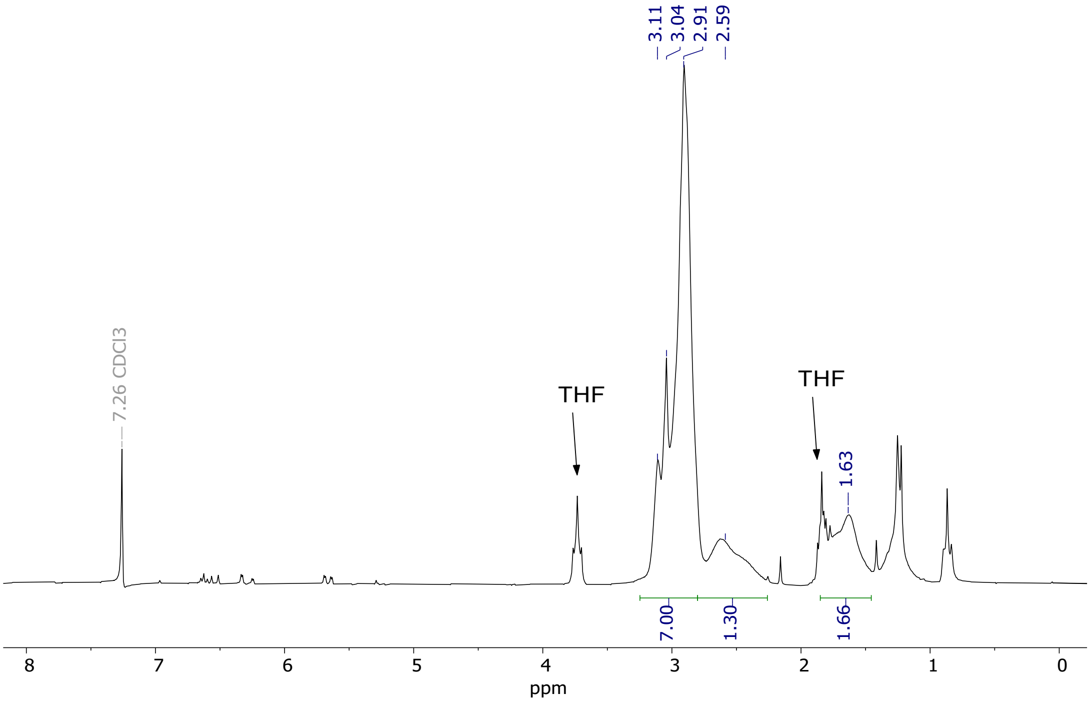
$^{13}$C NMR spectrum (CDCl$_3$, 75 MHz, 293 K) of poly(*t*-butyl acrylate).



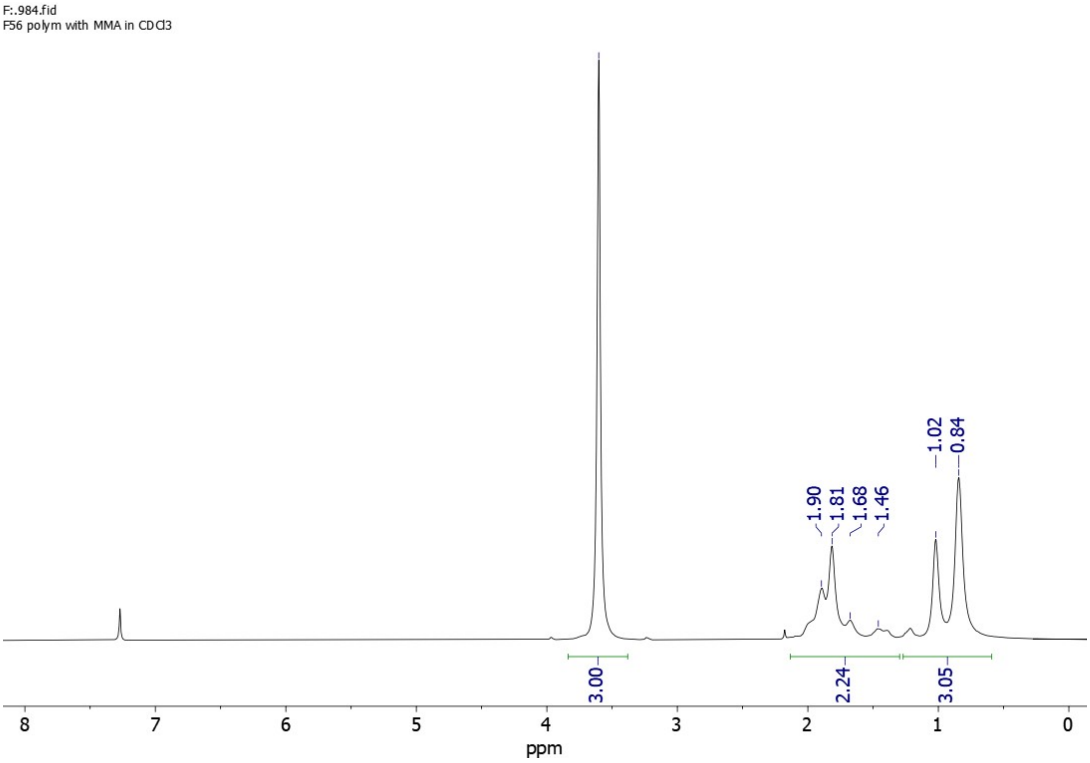
$^1$H NMR spectrum (CDCl$_3$, 200 MHz, 293 K) of poly(methyl acrylate).



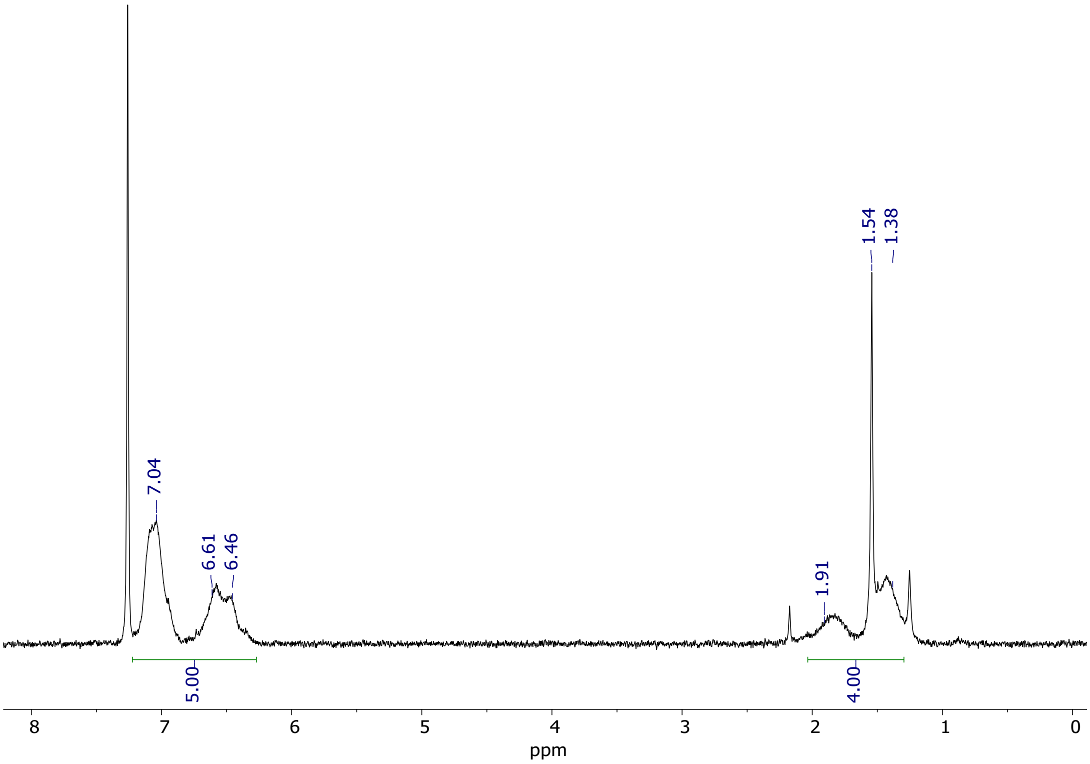
$^{1}$H NMR spectrum ($CDCl_3$, 200 MHz, 293 K) of poly(vinyl ketone).



$^{1}$H NMR spectrum ($CDCl_3$, 200 MHz, 293 K) of poly(dimethylacrylamide).



$^1H$ NMR spectrum ($CDCl_3$, 200 MHz, 293 K) of poly(methyl methacrylate).



$^1H$ NMR spectrum ($CDCl_3$, 200 MHz, 293 K) of polystyrene.

## 6. Additional References

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(S5) Y. Li, W. Xie and X. Jiang, *Chem. - Eur. J.* 2015, **21**, 16059−16065.

(S6) W. K. Busfield, I. D. Jenkins and P. Van Le, *Polym. Bull.* 1997, **38**, 149–155.