Electronic Supplementary Information

for

Stress-induced colouration and crosslinking of polymeric materials by mechanochemical formation of triphenylimidazolyl radicals

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Contents

1. Materials and methods

1.1. Analytical instrumentation

NMR spectra were recorded on a 400 MHz (100 MHz for ^{13}C) Varian Mercury VX spectrometer or on a 400 MHz (100 MHz for ^{13}C) Bruker Avance III HD spectrometer at room temperature using residual protonated solvent signals[1] as internal standards (^{1}H: $\delta(CDCl_3)$ = 7.26 ppm, $\delta((CD_3)_2SO)$ = 2.50 ppm, $\delta(C_6D_6)$ = 7.16 ppm, $\delta((CD_3)_2CO)$ = 2.05 ppm; ^{13}C: $\delta(CDCl_3)$ = 77.16 ppm, $\delta((CD_3)_2SO)$ = 39.52 ppm, $\delta(C_6D_6)$ = 128.06 ppm, $\delta((CD_3)_2CO)$ = 29.84 ppm.

Purity and exact mass of the synthesized compounds was determined using a LCQ Fleet (Thermo Finnigan) ion-trap mass spectrometer equipped with a Surveyor autosampler and Surveyor PDA detector (Thermo Finnigan). Solvents were pumped with a flow of 0.2 $mLmin^{-1}$ using a high-pressure gradient system using two LC-10AD pumps (Shimadzu). Before mass analysis, the crude was ran over a reverse phase C18 column (GraceSmart 2 x 50 mm, Grace) using a 2-90% acetonitrile linear gradient in water with 0.1 % formic acid (FA).

Gel permeation chromatography (GPC) employing THF or $CHCl_3$ as solvent were carried out on a Shimadzu Prominence-i LC-2030C 3D system equipped with a RID-20A refractive index detector. Molecular weights were calculated relative to narrow-disperse PS standards. GPC with DMF as solvent was performed on a Varian PL-GPC 50, using a KD-804 column. Molecular weights were calculated relative to narrow-disperse PEO standards. TLC was performed on Merck Silica Gel 60 F254 TLC plates with a fluorescent indicator employing a 254 nm UV-lamp for visualization. UV/vis absorption spectroscopy was performed on a PerkinElmer Lambda 900 spectrometer at room temperature. FTIR spectra were recorded at room temperature on a Perkin Elmer Spectrum One

spectrometer equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory. Sonochemical irradiation experiments were carried out with a Sonics VCX 500 W ultrasonic processor purchased from Sonics & Materials Inc.

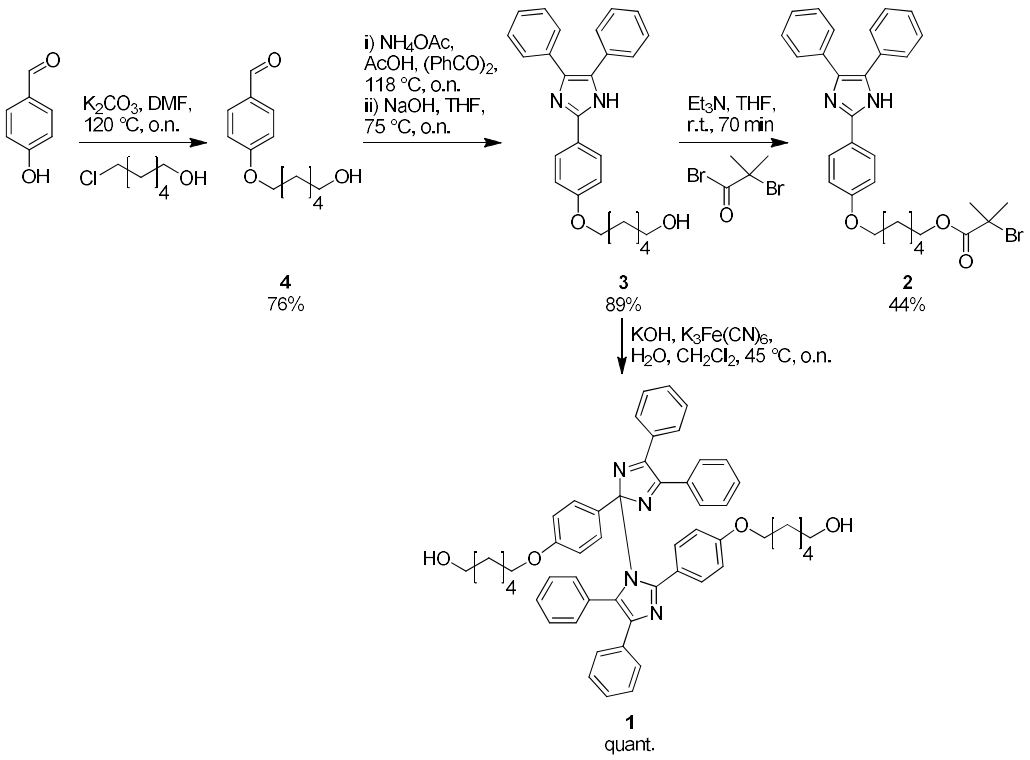
1.2. Chemicals and solvents

Solvents and commercial starting materials were used as supplied. Monomers were purified prior to polymerization by passing over a short column of inhibitor remover or Al_2O_3. The solvents were dried before use, if necessary, employing an MBraun MB-SPS-800 solvent purification system. Silica gel for chromatography (0.040–0.063 mm, 60 Å) was used for column chromatography.

2. Synthetic procedures and characterization data

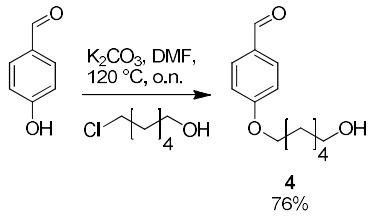
2.1. Small molecule target compounds

Small molecule target compounds were synthesized according to Scheme S1.



Scheme S1. Synthesis pathway towards small molecule target compounds.

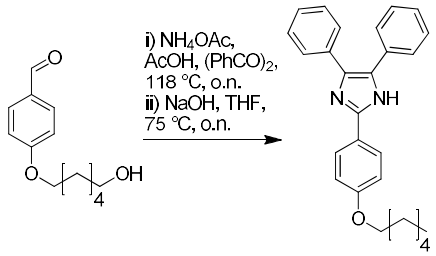
2.1.1. 4-((6-hydroxyhexyl)oxy)benzaldehyde 4



4
76%

Synthesis of 4-((6-hydroxyhexyl)oxy)benzaldehyde **4** was obtained from adapting literature procedure.[2] 4-hydroxybenzaldehyde (3.00 g, 24.57 mmol), K_2CO_3 (10.19 g 73.7 mmol) and 6-chloro-hexanol (4.36 g, 31.9 mmol) were added to DMF (50 mL) and the mixture was allowed to stir at 120 °C overnight under Ar atmosphere. After cooling to r.t., the mixture was filtered to remove potassium carbonate, solvent was removed *in vacuo*, and the crude mixture was purified by column chromatography (silica, heptane : EtOAc = 1 : 1) yielding 4-((6-hydroxyhexyl)oxy)benzaldehyde **4** (76% yield) as a light yellow oil. **^{1}H-NMR (400 MHz, ($CDCl_3$)**: δ(ppm)= 9.85 (s, 1H, $CH_{aldehyde}$), 7.80 (d, J = 8.8 Hz, 2H, CH_{ar}), 6.96 (d, J = 8.8 Hz, 2H, CH_{ar}), 4.02 (t, J = 6.6 Hz, 2H, CH_2), 3.64 (t, J = 6.4 Hz, 2H, CH_2), 1.81 (quin, J = 6.4 Hz, 2H, CH_2), 1.67-1.76 (br, 1H, OH), 1.59 (quin, J= 6.8 Hz, 2H, CH_2), 1.39-1.52 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ(ppm)= 190.9, 164.2, 132.0, 129.7, 114.7, 68.2, 62.7, 32., 29.0, 25.78, 25.49. **HPLC-MS(ESI$^+$)**: *m*/*z* = 223.17 (calcd. 223.13 for $C_{13}H_{19}O_3^+$)

2.1.2. 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol 3

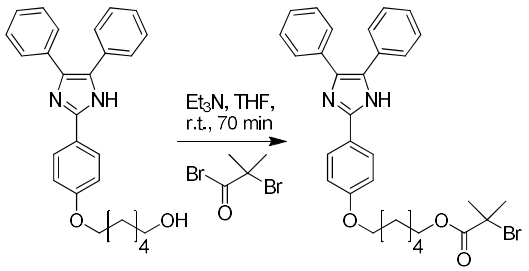


4 **3**
89%

Synthesis of 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol **3** was obtained from adapting literature procedure.[2] A mixture of 4-((6-hydroxyhexyl)oxy)benzaldehyde **4** (1.68 g, 7.54 mmol), benzil (1.59 g, 7.54 mmol), and NH_4OAc (4.92 g, 63.8 mmol) in AcOH (60 mL) was refluxed for 16 h under Ar atmosphere. After cooling to r.t., the solvent was removed under reduced pressure and the

crude mixture was redissolved in ethyl acetate and washed with a saturated aqueous K_2CO_3 solution and water. After removal of the solvent, the reaction mixture was redissolved in a mixture containing THF (10 mL) and a 3 M aqueous NaOH solution (25 mL) and allowed to stir at 75 °C overnight. Subsequently the THF was removed, the precipitate collected and eventually recrystallized in MeCN yielding 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol **3** (89% yield) as white needles. **^{1}H-NMR (400 MHz, $(CD_3)_2SO$):** δ(ppm)= 12.46 (br, 1H, NH), 7.94 (d, J = 8.8 Hz, 2H, CH_{ar}), 7.49 (d, J = 8.4 Hz, 4H, CH_{ar}), 7.25 (t, J = 7.6 Hz, 4H, CH_{ar}), 7.13 (t, J = 7.2 Hz, 2H, CH_{ar}), 6.90 (d, J = 8.8 Hz, 2H, CH_{ar}), 3.96 (d, J = 6.2 Hz 2H, CH_2), 3.38 (d, J = 6.2 Hz 2H, CH_2), 1.70 (quin, J= 6.4 Hz, 2H, CH_2), 1.29-1.46 (m, 6H, CH_2). **^{13}C-NMR (400 MHz, $(CD_3)_2SO$):** δ(ppm)= 159.3, 146.2, 128.80, 128.14 (br), 127.41 (br), 127.15, 123.5, 115.0, 68.0, 61.1, 33.0, 29.2, 25.9, 25.8. Due to signal-broadening, not all carbons could be assigned. **HPLC-MS(ESI$^+$)**: *m/z* = 413.33 (calcd. 413.53 for $C_{27}H_{29}N_2O_2^+$).

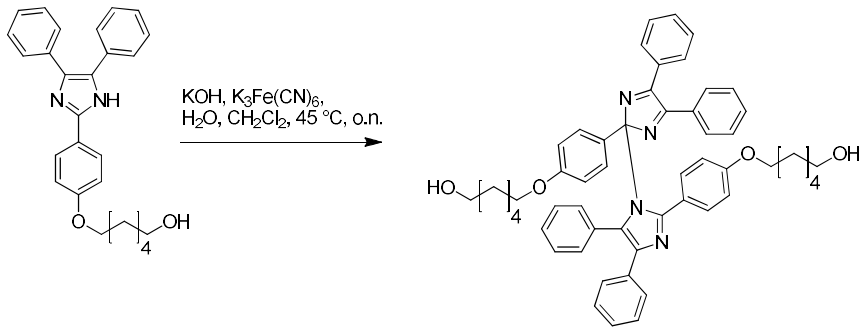
2.1.3. 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexyl 2-bromo-2-methylpropanoate 2



First, a THF solution (40 mL) containing 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol **3** (1.00 g, 2.42 mmol) and Et_3N (0.68 mL, 4.85 mmol) was cooled down to 0°C. Subsequently, α -bromoisobutyryl bromide (0.27 mL, 2.18 mmol) was added dropwise and the reaction mixture was allowed to warm to r.t. and stirred over 70 min. The crude mixture was washed with an aqueous K_2CO_3 solution, dried over $MgSO_4$, the solvent was removed *in vacuo* and purified by column chromatography (silica, heptane : EtOAc = 1 : 1) yielding 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexyl 2-bromo-2-methylpropanoate **2** (44% yield) as a white solid. **^{1}H-NMR (400 MHz, $(CD_3)_2CO$)**: δ(ppm)= 9.28 (br, 1H), 7.82 (d, J = 8.8 Hz, 2H), 7.23-7.63 (m, 10H), 6.95 (d, J = 8.4 Hz,

2H), 4.19 (t, J = 6.6 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 1.93 (s, 6H), 1.83 (quin, J = 6.4 Hz, 2H), 1.74 (quin, J = 6.4 Hz, 2H), 1.45-1.58 (m, 4H). **^{13}C-NMR (400 MHz, ($CDCl_3$):** δ(ppm)= 171.8, 159.5, 146.4, 132.9 (br), 128.4, 127.9, 127.2, 126.9, 122.7, 114.6, 67.8, 66.0, 56.0, 30.8, 29.1, 28.3, 25.66, 25.58. Due to signal-broadening, not all carbons could be assigned. **HPLC-MS(ESI$^+$)**: *m*/*z* = 563.17 (calcd. 563.17 for $C_{31}H_{34}BrN_2O_3^+$).

2.1.4. 6,6'-(((4,4',5,5'-tetraphenyl-2'H-[1,2'-biimidazole]-2,2'-diyl)bis(4,1-phenylene))bis(oxy))bis(hexan-1-ol) 1

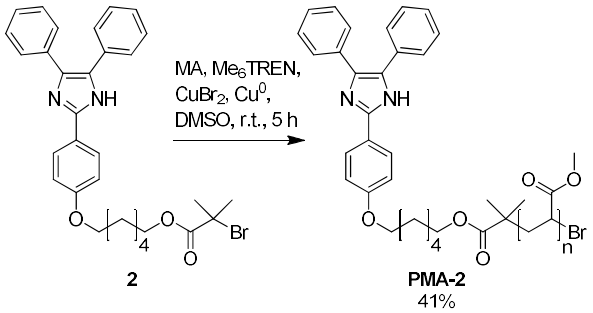


Synthesis of 6,6'-(((4,4',5,5'-tetraphenyl-2'H-[1,2'-biimidazole]-2,2'-diyl)bis(4,1-phenylene))bis(oxy))bis(hexan-1-ol) **1** was obtained from adapting literature procedure.[2] To a vigorously stirred solution of 6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexan-1-ol **2** (1.00 g, 2.42 mmol) in CH_2Cl_2 (80 mL), a solution of $K_3Fe(CN)_6$ (3.56 g, 10.81 mmol) and potassium hydroxide (12.99 g, 232.00 mmol) in water (80 mL) was added dropwise over the period of 1.5 h in the absence of light and under Ar atmosphere. The mixture was then refluxed at 45 °C over night under these conditions. After cooling to room temperature the organic layer was collected, washed with water, dried over anhyd. $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was recrystallized in diethyl ether/heptane, yielding 6,6'-(((4,4',5,5'-tetraphenyl-2'H-[1,2'-biimidazole]-2,2'-diyl)bis(4,1-phenylene))bis(oxy))bis(hexan-1-ol) (**3**) (quantitative yield) as green crystals. **^{1}H-NMR (400 MHz, (CD_3)$_2$SO):** δ(ppm)= 8.30 (d, J = 8.8 Hz, 1H, CH_{ar}), 7.73 (d, J = 8.8 Hz, 1H, CH_{ar}), 7.50 (t, J = 8.2 Hz, 2H, CH_{ar}), 7.31-7.38 (m, 6H, CH_{ar}), 7.15-7.23 (m, 12H, CH_{ar}), 6.98 (d, J = 8.8 Hz, 2H, CH_{ar}), 6.78 (d, J = 8.8 Hz, 2H, CH_{ar}), 6.48 (d, J= 8.8 Hz, 2H, CH_{ar}), 4.32-4.39 (m, 4H, CH_2), 3.89

(t, J = 6.4 Hz, 2H, CH_2), 3.79 (t, J = 6.4 Hz, 2H, CH_2), 1.66-1.71 (m, 2H, CH_2), 1.57-1.64 (m, 4H, CH_2), 1.28-1.49 (m, 10H, CH_2). **^{13}C-NMR (400 MHz, $(CD_3)_2SO$):** δ(ppm)= 191.2, 173.5, 166.3, 162.8, 158.98, 158.97, 149.2, 148.6, 138.4, 137.2, 134.92, 134.80, 133.9, 133.11, 132.93, 131.88, 131.76, 131.65, 131.56, 131.25, 130.48, 130.36, 130.15, 129.90, 129.3, 128.63, 128.37, 128.32, 128.25, 127.6, 127.1, 126.9, 126.75, 126.73, 126.56, 123.25, 115.4, 114.0, 113.8, 113.6, 112.3, 110.0, 99.6, 68.4, 67.92, 67.84, 67.78, 61.13, 61.08, 32.98, 32.96, 32.93, 31.7, 29.2, 29.0, 28.8, 25.93, 25.89, 25.80, 25.77, 25.76, 25.72, 25.68, 22.6, 14.4. Due to the thermal equilibrium of HABI with its radicals, some additional peaks were observed. **HPLC-MS(ESI$^+$)**: *m*/*z* = 823.33 (calcd. 823.41 for $C_{54}H_{55}N_4O_4^+$).

2.2. Reactions towards PMA-2, PMA-1 and PU-1

2.2.1. SET-LRP towards PMA-2



6-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)hexyl 2-bromo-2-methylpropanoate **2** (22.7 mg, 0.04 mmol), Me_6TREN (1.7 µl, 6,5 µmol), methyl acrylate (3.4 mL, 37.6 mmol), and $CuBr_2$ (0.45 mg, 2.0 µmol) were dissolved in DMSO (3.4 mL) in a Schlenk tube and degassed by 3 consecutive freeze-pump-thaw cycles. During that time, copper wire (0.5 cm) was activated in conc. HCl, subsequently washed with water and dried. This was then added to the solution and the polymerization was allowed to run at r.t. for 5 h. Then, the viscous solution was diluted with THF, passed through a plug of basic Al_2O_3, and after concentration *in vacuo* added dropwise to stirred, ice-cold MeOH. After repeating the precipitation process 2 times and 2 times from CH_2Cl_2, the polymer was dried *in vacuo* and received

as a ductile white solid (41% yield). M_n **(GPC):** 97 kD, M_n (**^{1}H-NMR):** 75 kD. $Đ$ **(GPC):** 1.06. (compare Figure S1)

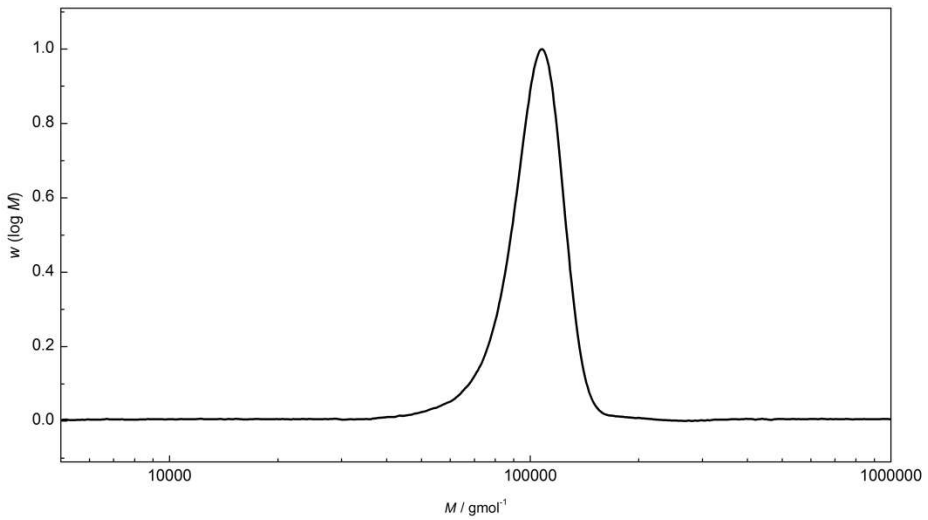


Figure S1. Differential molecular weight distribution of GPC RI chromatogram of **PMA-2**.

2.2.2. Oxidative coupling to PMA-1

To a degassed solution of **PMA-2** (200 mg, 2.1 µmol) in C_6H_6 (4 mL) were added PbO_2 (493 mg, 2.06 mmol) and Na_2SO_4 (146 mg, 1.03 mmol) and the slurry was vigorously stirred for 19 h at r.t. Afterwards, the solution was filtered over celite and directly employed in sonication experiments without any further work-up (compare Figure S2).

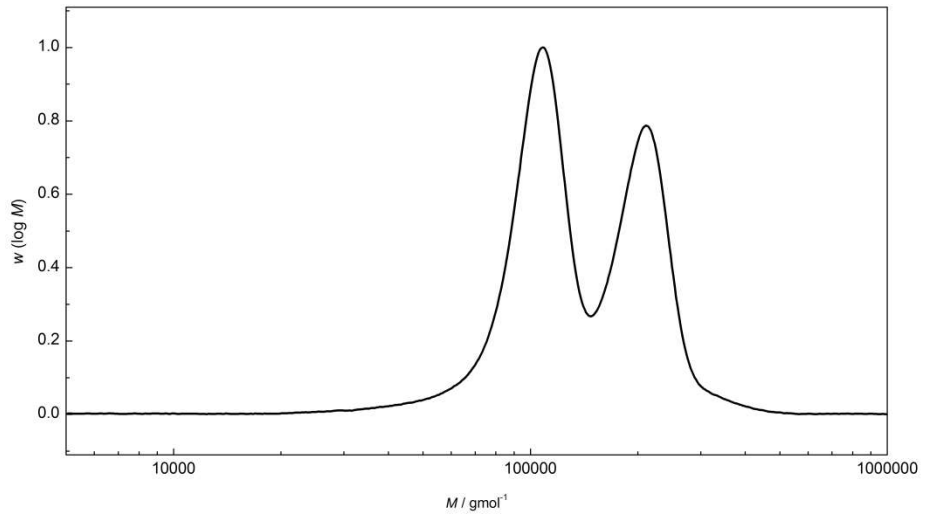
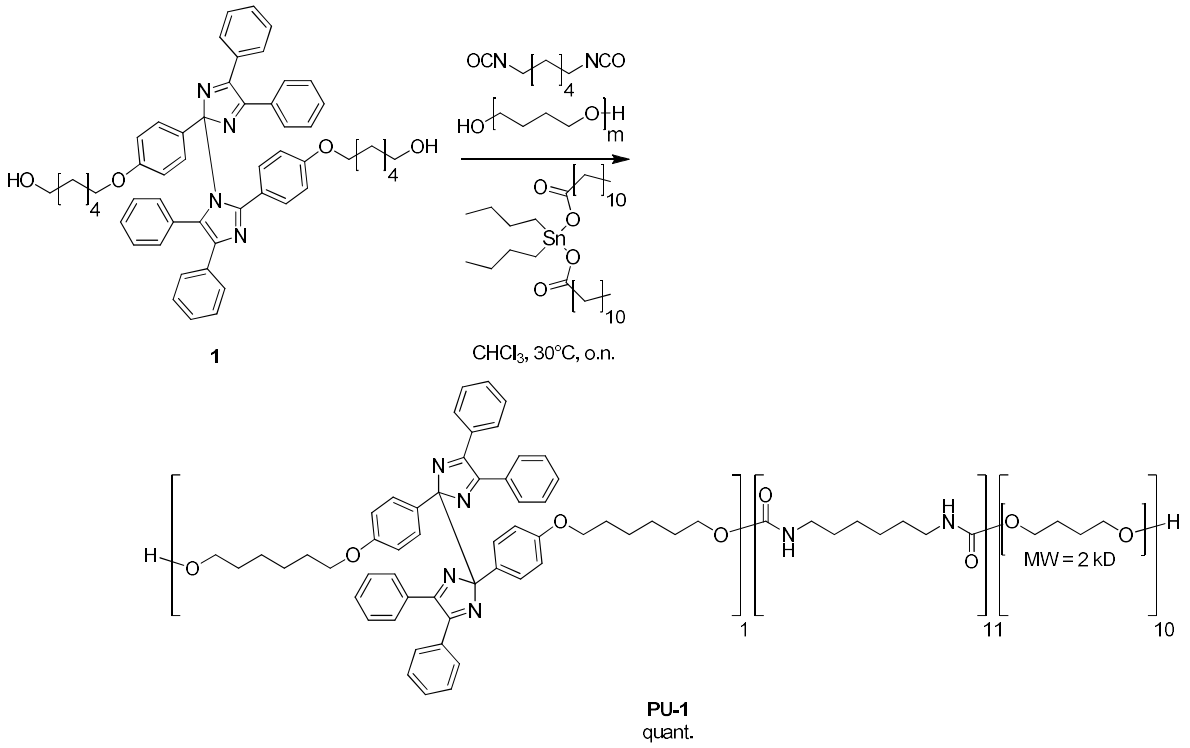


Figure S2. Differential molecular weight distribution of GPC RI chromatogram of **PMA-2**.

2.2.3. Polycondensation towards PU-1



Synthesis of **PU-1** was carried out by adapting a literature procedure.[3] A mixture of **1** (63.3 mg, 0.077 mmol) and a drop of dibutyltin dilaurate were dissolved in freshly distilled $CHCl_3$ (2.5 mL) and were added dropwise to a solution of hexamethylene diisocyanate (143 mg, 0.85 mmol) in freshly destilled $CHCl_3$ (0.5 ml). The solution was allowed to stir for 1h at 30 °C and subsequently poly(tetrahydrofuran) (1.54 g, 0,77 mmol) dissolved in freshly destilled $CHCl_3$ (2 mL) was added to the mixture and stirred at 30 °C overnight. The resulting viscous solution was precipitated in *n*-hexane and washed 3× with *n*-hexane and dried overnight in the vacuum over at 50 °C. The resulting blue gel was stored overnight in the dark to let the radicals recombine to obtain a yellow gel. $\boldsymbol{M_n}$ **(GPC):** 23 kDa, $\boldsymbol{Đ}$ **(GPC):** 2.40 (compare Figure S3).

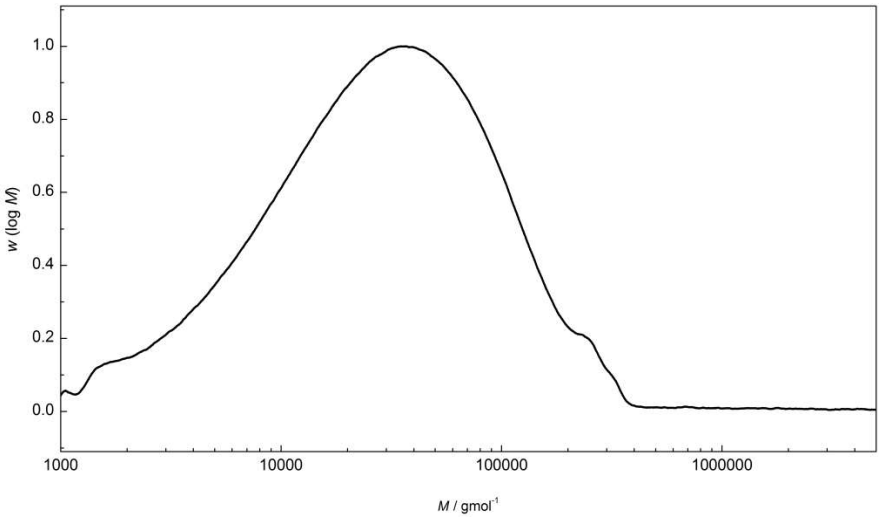


Figure S3. Differential molecular weight distribution of GPC RI chromatogram of **PU-1**.

3. Mechanical scission experiments

3.1. Sonication experiments

A 13 mm probe was used at a frequency of 20 kHz, at 30% of the maximum amplitude of 125 µm. Samples were withdrawn at the beginning, during, and at the end of each experiment and analyzed by GPC. The polymer was dissolved in benzene, placed in a cooled Suslick cell (2 °C), and a constant flow of CH_4 was applied to the setup. Then, the mixture was exposed to constant sonication for a given time and samples for GPC were taken during the process. Removal of the solvent *in vacuo* yielded the cleaved polymer which was used for further ^{1}H-NMR spectroscopy studies.

3.2. Compression experiments

Samples of **PU-1** as well as reference polyurethane with solution blended HABI were compressed with a pellet press exerting a weight equivalent of 15 t on the sample for 10-20 s (Figure S4). The recombination of the TPI radicals of PU-1 occurred on the timescale of seconds complicating further optical analysis. Reference polyurethane containing not covalently attached HABI was prepared by blending unsubstituted HABI (compare Scheme 1a in the manuscript for structural formula) and polyurethane prepared from HDI and polyTHF in toluene and subsequently evaporating the solvent in vacuo. Note the background activation for solution blended unsubstituted HABI in the reference

polyurethane. We attribute this behavior to the higher translational mobility of the small molecules in the material as compared to HABI incorporated into the polymer backbone.

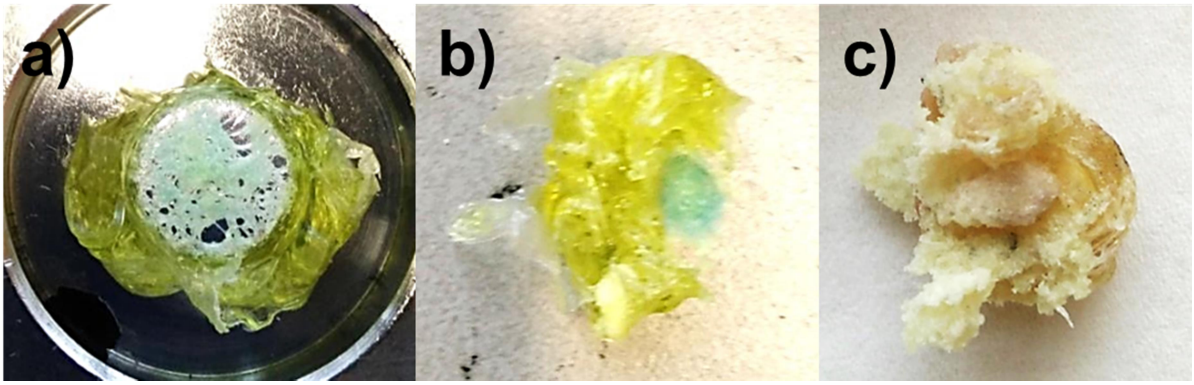


Figure S4. Compression of **PU-1** as well as reference polyurethane with solution blended HABI. a) **PU-1** after compression in the pellet press and b) outside the pellet press on white background. c) Compression of solution blended reference polyurethane.

3.3. Freezing experiments

For mechanical activation by freezing, samples of **PU-1** as well as of reference polyurethane containing not covalently attached HABI were immersed in liquid N_2 for several seconds whereupon a green coloration (superposition of blue TPI radicals and yellow material) can be observed only for **PU-1**.

For freezing induced polymerization reactions, chunks of **PU-1** were swollen either in a 50/50 mol% mixture of ethylene glycol dimethacrylate (1.7 mL, 9 mmol) and methyl 3-mercaptopropionate (1 mL, 9 mmol), only in ethylene glycol dimethacrylate, or in a 50/50 mol% mixture of methyl acrylate (0.8 mL, 9 mmol) and methyl 3-mercaptopropionate (1 mL, 9 mmol) overnight to ensure uniform swelling. The reagents have been degassed by three consecutive free pump-thaw cycles before immersion of the polyurethane. Subsequently, the Schlenk tubes were immersed in liquid N_2 for several minutes and then thawed to room temperature.

For the EGDMA experiment, when methyl 3-mercaptopropionate was present, the decoloration of the TPI radicals proceeded much quicker (Figure S5a). After 3 freezing and thawing cycles both chunks were stirred in copious DMF for multiple days. While the chunk of the reference **PU-1** swollen only in ethylene glycol dimethacrylate completely dissolved, a white residue was obtained for **PU-1** swollen

in a 50/50 mol% mixture of ethylene glycol dimethacrylate and 3-mercaptopropionate (Figure S5b). The residue was then dried *in vacuo*.

For the MA experiment, after 3 freezing and thawing cycles 1 drop of the residual mixture of MA and MMP was transferred to an NMR tube or GPC vial and analyzed by ^{1}H-NMR spectroscopy and GPC indicating oligomerization of the methyl acrylate (Figure S6). No vacuum or heating was applied to avoid evaporation of the volatile methyl acrylate.

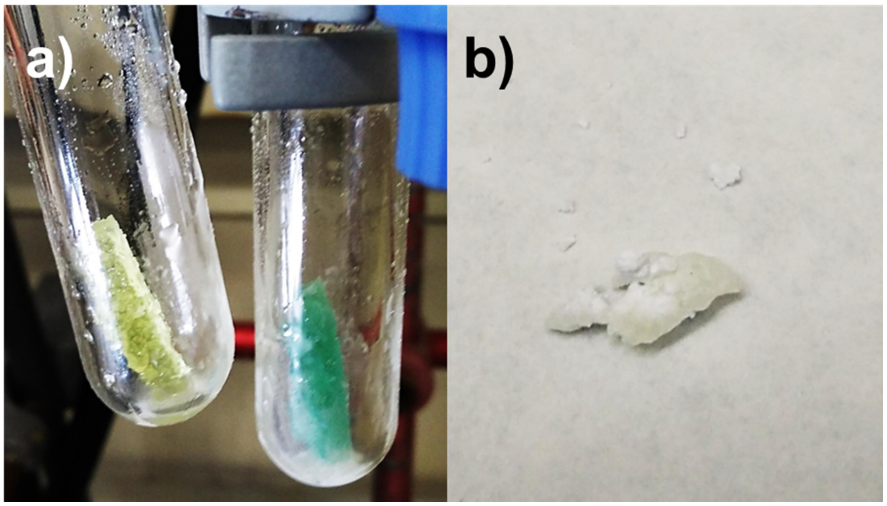


Figure S5. a) Freezing of **PU-1** swollen in either a 50/50 mol% mixture of ethylene glycol dimethacrylate and 3-mercaptopropionate (left) as well as only in ethylene glycol dimethacrylate (right). b) Solid residue obtained after freezing induced radical polymerization.

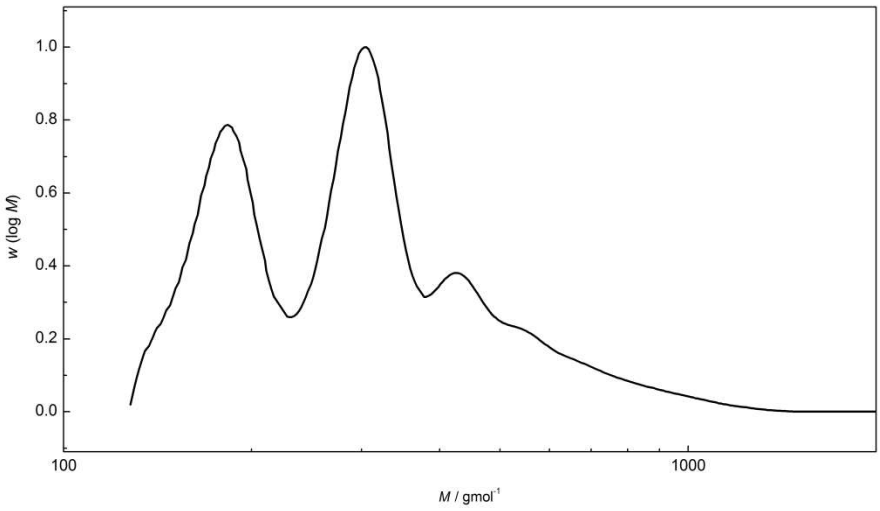


Figure S6. Differential molecular weight distribution of GPC RI chromatogram of MA and MMP mixture oligomerized by mechanochemical TPI radical generation.

4. References

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2 S. S. Sathe, D. Ahn and T. F. Scott, *Ind. Eng. Chem. Res.*, 2015, **54**, 4203–4212.

3 Y. Chen and R. P. Sijbesma, *Macromolecules*, 2014, **47**, 3797–3805.