

Supporting Information

Recycling and Self-healing of Dynamic Covalent Polymer Networks with Precisely Tuneable Crosslinking Degree

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1. Method

The polymer networks were synthesized via solvothermal method in the oven Memmert UF30plus and dried in supercritical CO₂ using Leica Systems CPD300.

Solvents, reagents and chemicals were purchased from MERCK MILLIPORE, EURISOTOP, SIGMA-ALDRICH, ABCR, ALFA AESAR and FISHER SCIENTIFIC. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Absolute toluene was obtained by refluxing over sodium, followed by distillation and was kept under Argon. Reactions with air- and/or water sensitive reagents were done under Argon using standard SCHLENK technique. The synthesis of isoindoline derivatives²⁻⁷ are based on literature procedures. Toluene and methanol for the synthesis of the polymer were degassed three times via freeze-pump-thaw prior to use.

NMR spectra were recorded on a BRUKER *Avance* 400 (¹H: 400 MHz, ¹³C: 100 MHz) of solutions in CDCl₃, CD₂Cl₂ and DMSO-*d*₆. Chemical shifts (δ) are expressed in parts per million (ppm) and are referenced to CHCl₃ (¹H: 7.26 ppm, ¹³C: 77.0 ppm) respectively CH₂Cl₂ (¹H: 5.32 ppm, ¹³C: 53.8 ppm) or DMSO-*d*₆ (¹H: 2.50 ppm, ¹³C: 39.4 ppm) as internal standard. All coupling constants (*J*) are absolute values and *J* values are expressed in Hertz (Hz). The description of signals includes: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, hept = heptett, m = multiplatt, kb = complex area and AA'BB' for a more complex system (no first order). The spectra were analysed according to first order. The signal structure in ¹³C-NMR was analysed by DEPT (Distortionless Enhancement by Polarization Transfer) and is described as follows: + = primary or tertiary C-atom (positive signal), - = secondary C-atom (negative signal) and C_{quart.} = quarternary C-atom (no signal).

Attenuated total reflection fourier transform infrared spectroscopy (ATR-FT-IR) was recorded on a Bruker model Tensor-27 at ambient temperature. The absorption band is given in wave numbers $\tilde{\nu}$ in cm⁻¹. The forms and intensities of the bands were characterized as follows: vs = very strong 0 – 9% T, s = strong 10 – 39% T, m = medium 40 – 69% T, w = weak 70 – 89% T, vw = very weak, 90 – 100% T.

Analytical thin layer chromatography (TLC) was carried out on MERCK silica gel coated aluminium plates (silica gel 60, F₂₅₄), detected under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. EI (Electron Ionization) and FAB (Fast Atom Bombardment) mass spectra were obtained using a FINNIGAN *MAT* 95 mass spectrometer. The indication of the molecular fragments was carried out as the ratio of mass to charge *m/z*; the intensity of the signals was expressed in percent relative to the intensity of the base signal (100%). ESI (Electrospray Ionization) mass spectra was obtained using X500R QTOF mass spectrometer. The sample was measured in TOFMS positive mode. The indication of the molecular weight was carried out as mass to charge *m/z*.

The EA measurements were performed on an ELEMENTAR VARIO *MICRO* device using a SARTORIUS *M2P* precision balance. The following abbreviations were used: calcd. = calculated data, found = measured data. The values of carbon (C), hydrogen (H) and nitrogen (N) are stated in mass percent. Melting points were measured on an *OptiMelt (Automated Melting Point System; Digital Image Processing Technology)* from STANFORD RESEARCH SYSTEMS. Ultrasonications were done on a BANDELIN *Sonorex Digitec*.

Electron paramagnetic resonance (EPR) spectroscopy was performed on a Bruker EMXNano spectrometer. If not otherwise noted, all sample are measured in toluene at 23 °C. The following parameters were used for the measurement: Centre field: 3434 G; sweep width: 100 G; sweep time: 180 s; sample g-factor: 2.00; receiver gain: 40 dB; modulation amplitude: 0.452 G; number of scans: 1; microwave attenuation: 60 dB; number of points: 2212; modulation frequency: 100 kHz, modulation phase: 0; conversion time: 81.38 ms; time constant: 1.28 ms; points/modulation amplitude: 10.

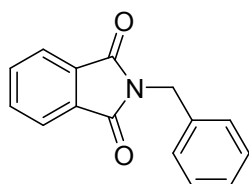
Fluorescence measurement was performed on a Perkin Elmer EnSpire 2300 Multimode Reader. The excitation wavelength is 320 nm and the emission wavelength is from 340 nm – 1000 nm. Gas sorption measurements are performed on a Quantachrome Autosorb-1 with Argon at 87 K. Sample tubes of known weight were loaded with approximately 30 mg of sample under an argon atmosphere. Samples were degassed at 25 °C for 120 h and measured by submerging the sample in a liquid argon bath.

Thermogravimetric analysis was made on a NETZSCH STA 449 C in the temperature range 35 °C to 1000 °C with a heating rate of 5 K/min and was carried out under an argon atmosphere.

RAMAN measurements were carried out on a HORIBA LabRam Evolution HR with an excitation wavelength of 633 nm.

2. Experimental

2.1 Synthetic Procedures of the multi-fold building blocks

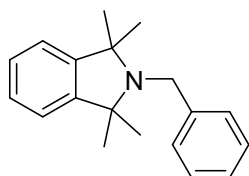


N-Benzylphthalimide:¹ 75.0 g phthalic anhydride (506 mmol, 1.00 equiv.) and 65.0 mL benzylamine (63.9 g, 592 mmol, 1.17 equiv.) in 300 mL glacial acetic acid were refluxed for 4 h. After cooling to room temperature 700 mL water were added. The precipitate was filtered off and washed with water. The crude product was recrystallized from ethanol. 106 g of a colorless solid (446 mmol) were obtained. Yield: 88%. – mp: 115–117 °C. – ¹H NMR (400 MHz, CDCl₃):

δ (ppm) = 4.85 (s, 2 H, CH₂), 7.23–7.36 (m, 3 H, C_{Ar}H), 7.41–7.46 (m, 2 H, C_{Ar}H), 7.70 (AA'BB', ³J_{HH} = 5.5 Hz, ⁴J_{HH} = 3.1 Hz, 2 H, C_{Ar}H), 7.84 (AA'BB', ³J_{HH} = 5.5 Hz, ⁴J_{HH} = 3.1 Hz, 2 H, C_{Ar}H). – ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 41.7 (–, CH₂), 123.5 (+, C_{Ar}H), 127.9 (+, C_{Ar}H), 128.7 (+, C_{Ar}H), 128.8 (+, C_{Ar}H), 132.2 (C_{quart.}, C_{Ar}), 134.1 (+, C_{Ar}H), 136.5 (C_{quart.}, C_{Ar}), 168.2 (C_{quart.}, CO). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3458 (vw), 3057 (vw), 2946 (vw), 1763 (w), 1705 (m), 1491 (w), 1465 (w), 1431 (w), 1389 (m), 1330 (w), 1296 (w), 1204 (w), 1184 (w), 1156 (w), 1101 (w), 1086 (w), 1061 (w), 935 (w), 824 (vw), 792 (w), 762 (w), 713 (m), 694 (m), 623 (w), 589 (w), 521 (w), 404 (vw). – MS (EI, 70 eV, 60 °C), *m/z* (%): 237/238/239 (100/16/1.7) [M⁺], 209 (12) [M⁺ – CO], 104/105 (6.7/1.9) [C₇H₄O⁺]. – HR-MS (C₁₅H₁₁NO₂): calcd. 237.0784, found 237.0784.

The experimental data are consistent with the literature.¹

2-Benzyl-1,1,3,3-tetramethylisoindoline:^{2,3} Under an Argon atmosphere, 800 mL of a 3 M MeMgI-solution (2.40 mol, 6.70 equiv. MeMgI) in diethyl ether and 50 mL of abs. toluene were placed in a 2 L three-necked flask with reflux condenser, thermometer and attached cooling trap. The diethyl ether was distilled off the solution at vacuum and 30 °C until the mixture was slightly cloudy. A solution of 85.0 g *N*-benzylphthalimide (0.358 mol, 1.00 equiv.) in 600 mL abs. toluene

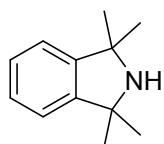


were added slowly. Afterwards, solvent was removed by distillation until the reaction mixture refluxed at 110 °C and it was refluxed for additional 19 h. Then toluene was removed by distillation, cooled to room temperature and 1 L of *n*-hexane was added. The mixture was refluxed for another 16 h and again cooled to room temperature. The mixture was filtered over Celite® and the filter cake was washed three times with *n*-hexane. Air was bubbled through the filtrate overnight and then passed over a column of basic alumina using *n*-pentane as eluent until the eluent was amine-free. The solvent was removed under reduced pressure and the crude product recrystallized from ethanol. A slightly beige solid was obtained (20.6 g, 77.7 mol). Yield: 22%. – mp: 62–63 °C. – ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.32 (s, 12 H, 4 × CH₃), 4.00 (s, 2 H, CH₂), 7.12–7.17 (m, 2 H, C_{Ar}H), 7.20–7.27 (m, 3 H, C_{Ar}H), 7.27–7.33 (m, 2 H, C_{Ar}H), 7.45–7.50 (m, 2 H, C_{Ar}H). – ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 28.6 (+, CH₃), 46.4 (–,

CH₂), 65.3 (C_{quart.}, C(CH₃)₂), 121.5 (+, C_{Ar}H), 126.5 (+, C_{Ar}H), 126.9 (+, C_{Ar}H), 128.0 (+, C_{Ar}H), 128.5 (+, C_{Ar}H), 143.6 (C_{quart.}, C_{Ar}), 148.0 (C_{quart.}, C_{Ar}). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3020 (vw), 2958 (w), 2922 (w), 1602 (vw), 1487 (w), 1446 (w), 1371 (w), 1356 (w), 1321 (w), 1300 (w), 1266 (w), 1212 (w), 1195 (w), 1161 (w), 1104 (w), 1073 (w), 1026 (w), 945 (w), 905 (w), 874 (w), 791 (vw), 743 (m), 701 (m), 624 (w), 572 (w), 551 (w), 526 (w), 480 (vw), 440 (vw). – MS (EI, 70 eV, 50 °C), *m/z* (%): 265/266 (3.9/0.87) [M⁺], 250/251 (100/19) [M⁺ – CH₃], 144/145 (4.0/1.5) [M⁺ – Bn – 2 × CH₃], 91/92 (56/3.7) [Bn⁺]. – HR-MS (C₁₉H₂₃N): calcd. 265.1825, found 265.1825.

The experimental data are consistent with the literature.^{2,3}

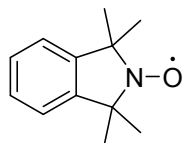
1,1,3,3-Tetramethylisoindoline: A suspension of 9.28 g 2-benzyl-1,1,3,3-tetramethylisoindoline (35.0 mmol, 1.00 equiv.) and 1.12 g Pd/C (10%, 1.05 mmol (Pd), 3 mol%) in 120 mL glacial acetic acid was stirred for 24 h under a hydrogen atmosphere at ambient pressure at room temperature. Afterwards, the reaction mixture was filtered over Celite® and the filter cake was washed with conc. acetic acid, water and a small amount of diethyl ether.



The filtrate was extracted with diethyl ether three times and the organic phase was discarded. Afterwards the aqueous phase was made alkaline (pH = 10) using NaOH and again extracted with diethyl ether three times. The combined organic phases were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the obtained colorless solid (4.36 g, 24.9 mmol) was used without further purification. Yield: 71%. – ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 1.42 (s, 12 H, 4 × CH₃), 1.81 (bs, 1 H, NH), 7.10–7.15 (m, 2 H, C_{Ar}H), 7.20–7.26 (m, 2 H, C_{Ar}H). – ¹³C NMR (101 MHz, CD₂Cl₂): δ (ppm) = 32.5 (+, CH₃), 63.1 (C_{quart.}, C(CH₃)₂), 121.9 (+, C_{Ar}H), 127.5 (+, C_{Ar}H), 149.6 (C_{quart.}, C_{Ar}). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2959 (m), 2920 (w), 1481 (w), 1448 (w), 1372 (w), 1360 (w), 1317 (w), 1237 (vw), 1166 (w), 1107 (w), 1022 (w), 991 (w), 883 (vw), 723 (m), 671 (w), 524 (w), 414 (vw). – MS (EI, 70 eV, 70 °C), *m/z* (%): 175 (1.7) [M⁺], 174 (12) [M⁺ – H], 160/161 (100/13) [M⁺ – CH₃], 159 (9.0) [M⁺ – CH₃ – H], 145/146 (34/5.1) [M⁺ – 2 × CH₃], 144 (29) [M⁺ – 2 × CH₃ – H]. – HR-MS (C₁₂H₁₇N): calcd. 175.1356, found. 175.1354.

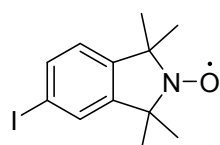
The experimental data are consistent with the literature.^{2,3}

1,1,3,3-Tetramethylisoindoline-2-yloxy radical: To a solution of 4.35 g 1,1,3,3-tetramethylisoindoline (24.9 mmol, 1.00 equiv.) in 150 mL dichloromethane were added 9.12 g *m*CPBA (70%, 37.4 mmol, 1.00 equiv.). After stirring at room temperature for 8 h the reaction mixture was washed three times with 10% NaOH solution as well as brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the obtained yellow solid (4.61 g, 24.2 mmol) was used without further purification. Yield: 97%. – mp: 123–125 °C. – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2973 (w), 2926 (vw), 1483 (w), 1450 (w), 1373 (vw), 1355 (w), 1317 (vw), 1279 (w), 1165 (w), 1120 (w), 1022 (vw), 760 (m), 678 (vw), 614 (vw), 550 (w), 466 (vw). – MS (EI, 70 eV, 50 °C), *m/z* (%): 190/191 (67/9.8) [M⁺], 175/176 (54/16) [M⁺ – CH₃], 160/161 (58/9.5) [M⁺ – 2 × CH₃], 158 (20), 145/146 (100/12) [M⁺ – 3 × CH₃], 129 (10), 117 (16). HR-MS (C₁₂H₁₆NO·): calcd. 190.1226, found 190.1225.



The experimental data are consistent with the literature.²⁻⁴

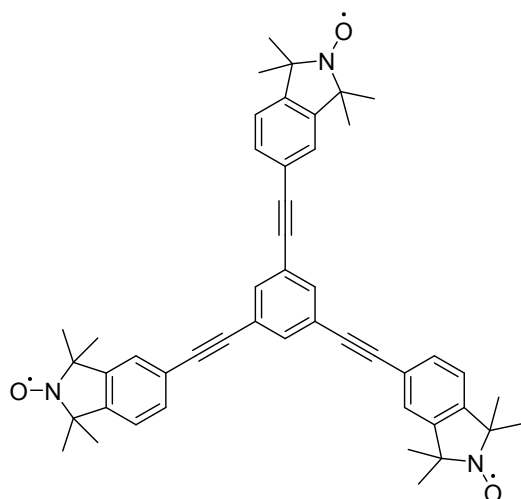
5-Iodo-1,1,3,3-tetramethylisoindoline-2-yloxy radical: At 0 °C, 2.21 g KI (13.3 mmol, 0.550 equiv.) were added in small portions to a solution of 1.00 g periodic acid in 80 mL conc. sulfuric acid. After the addition was completed the mixture was stirred for further



15 min. Then, 4.61 g 1,1,3,3-tetramethylisoindolin-2-yloxy radical (24.2 mmol, 1.00 equiv.) were added at 0 °C. The reaction mixture was warmed up slowly to room temperature while stirring for further 3 h. Afterwards the mixture was poured on 200 mL ice and was made alkaline (pH = 10) using NaOH pellets and 7 M NaOH-solution. The aqueous phase was extracted with dichloromethane three times and the combined organic phases were washed with sodium thiosulfate solution, water and brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, 7 × 20 cm, CH/CH₂Cl₂ = 1:5). 3.05 g of a yellow solid (9.65 mmol) were obtained as clean product as well as 0.725 g of starting material and a mixed fraction of both starting material and a small amount of product (3%). Yield (clean fraction): 40%. – mp: 135–138 °C. – R_f (CH/CH₂Cl₂ = 1:5) = 0.36. – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3040 (vw), 2969 (w), 2924 (vw), 1598 (vw), 1447 (vw), 1429 (vw), 1398 (vw), 1372 (vw), 1356 (vw), 1306 (w), 1277 (w), 1164 (w), 1120 (w), 1076 (w), 910 (vw), 887 (vw), 830 (w), 820 (w), 790 (vw), 771 (vw), 625 (vw), 548 (w), 494 (w), 382 (vw). – MS (EI, 70 eV, 60 °C), m/z (%): 316/317 (100/18) [M⁺], 301/302 (30/22) [M⁺ – CH₃], 286/287 (46/7.3) [M⁺ – 2 × CH₃], 271 (37/4.3) [M⁺ – 3 × CH₃], 144 (29) [M⁺ – 3 × CH₃ – I], 143 (11) [M⁺ – 2 × CH₃ – I – O], 129 (20), 128 (17). – HR-MS (C₁₂H₁₅INO): calcd. 316.0193, found 316.0193.

The experimental data are consistent with the literature.⁵

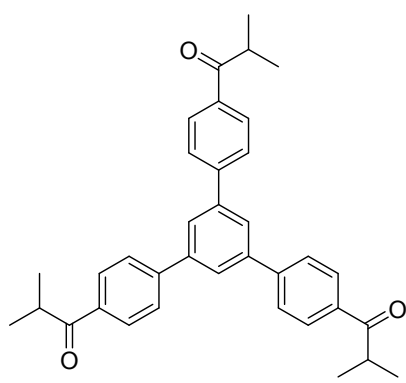
1,3,5-Tris(5'-ethynyl-1',1',3',3'-tetramethylisoindolin-2'-yloxy)benzene 2: Under an argon atmosphere,



300 mg 1,3,5-triethynylbenzene (2.00 mmol, 1.00 equiv.), 2.84 g 5-iodo-1,1,3,3-tetramethylisoindoline-2-yloxy radical (8.98 mmol, 4.50 equiv.), 103 mg Cu(I)I (0.540 mmol, 27.0 mol%) and 100 mg [Pd(PPh₃)₂]Cl₂ (0.142 mmol, 7.00 mol%) were placed in a three-necked flask and 40 mL of abs. THF and 40 mL of degassed NEt₃ were added. The reaction mixture was stirred at 55 °C for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was dissolved in 50 mL of dichloromethane and 50 mL of water. The phases were separated and the organic layer was washed with diluted HCl solution, water and brine as well as dried over Na₂SO₄. The solvent was removed

under reduced pressure and the residue was purified via column chromatography (SiO₂, 6 × 20 cm, CH₂Cl₂ → CH₂Cl₂/EA 50:1 → 40:1 → 30:1 → 10:1). The solvent was again removed under reduced pressure and the residue was recrystallized from ethanol. 1.01 g (1.41 mmol) of a yellow, crystalline product were obtained. – Yield: 71%.

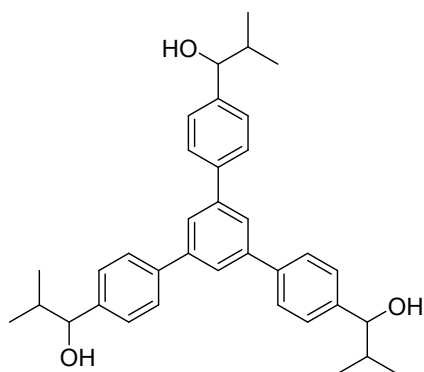
mp: 152 – 153 °C. – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2972 (w), 2927 (vw), 2207 (vw), 1735 (vw), 1578 (w), 1488 (w), 1431 (w), 1372 (vw), 1358 (w), 1311 (w), 1281 (vw), 1243 (vw), 1162 (w), 1119 (w), 1044 (vw), 979 (w), 875 (w), 827 (w), 699 (vw), 678 (w), 624 (vw), 594 (w), 573 (vw), 548 (w), 465 (w), 434 (vw). – MS (FAB, 3-NBA), m/z (%): 714/715/716/717 [M⁺], 699/700/701/702 [M⁺ – CH₃], 683/684/685/686 [M⁺ – 2 × CH₃], 668/669/670/671 [M⁺ – 3 × CH₃], 652/653/654/655 [M⁺ – 4 × CH₃]. – HR-MS (C₄₈H₄₈N₃O₃): calcd. 714.3690, found 714.3690. – EA (C₄₈H₄₈N₃O₃, 714.9): calcd. C 80.64, H 6.77, N 5.88; found. C 77.39, H 6.53, N 5.61.



1,3,5-Tris(4'-isobutyronylphenyl)benzene: Under an argon atmosphere, 13.1 g AlCl₃ (97.9 mmol, 15.0 equiv.) and 2.00 g

1,3,5-triphenylbenzene (6.53 mmol, 1.00 equiv.) in 60 mL of dichloromethane were placed in a 250 mL Schlenk-flask. At 0 °C, 10.5 mL isobutyryl chloride (10.7 g, 100 mmol, 15.3 equiv.) were added slowly. The reaction mixture was allowed to warm up to room temperature and was stirred for 16 h. Afterwards, the mixture was poured carefully on ice and conc. HCl was added to dissolve all solids. After stirring for 30 min, the phases were separated and the organic layer was washed with water, 7 M KOH solution, water and brine as well as dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was recrystallized from acetone. 2.43 g (4.70 mmol) of a slightly yellow solid were obtained. – Yield: 72%.

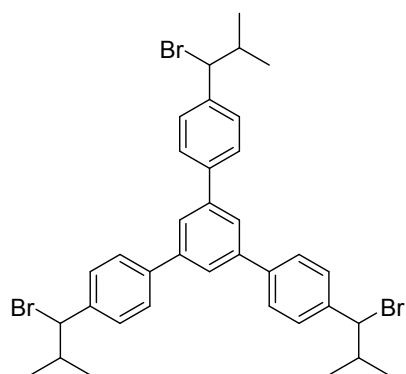
mp: 197 – 198 °C. – R_f (CH/CH₂Cl₂ = 1:4) = 0.22. – ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.26 (d, ³J = 6.8 Hz, 18 H, CH₃), 3.61 (hept, ³J = 6.8 Hz, 3 H, CH(CH₃)₂), 7.79 (AA'BB', ³J = 8.5 Hz, 6 H, C_mH), 7.87 (s, 3 H, C_{aromat.}H), 8.09 (AA'BB', ³J = 8.5 Hz, 6 H, C_oH). – ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 19.3 (+, CH₃), 35.6 (+, CH), 126.2 (+, C_{aromat.}H), 127.7 (+, C_mH), 129.2 (+, C_oH), 135.5 (C_{quart.}, C_{aromat.}), 141.7 (C_{quart.}, C_p), 144.9 (C_{quart.}, C₁), 204.1 (C_{quart.}, CO). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2965 (vw), 2929 (vw), 1673 (w), 1596 (w), 1561 (vw), 1465 (vw), 1381 (w), 1348 (vw), 1282 (vw), 1220 (w), 1159 (w), 977 (w), 842 (w), 827 (w), 759 (w), 720 (vw), 692 (w), 607 (vw), 573 (vw), 517 (vw), 490 (vw). – MS (EI, 70 eV, 220 °C), m/z (%): 516 (18) [M⁺], 473 (100) [M⁺ – CH(CH₃)₂], 402 (21) [M⁺ – CO – 2 × CH(CH₃)₂]. – HR-MS (C₃₆H₃₆O₃): calcd. 516.2659, found. 516.2659.



1,3,5-Tris(4'-(2''-methylpropan-1''-ol)phenyl)benzene: Under an argon atmosphere, 73.5 mg LiAlH₄ (1.94 mmol, 2.00 equiv.) and 0.500 g 1,3,5-tris(4'-isobutyronylphenyl)benzene (0.968 mmol, 1.00 equiv.) were placed in a 50 mL Schlenk flask and 20 mL abs. THF were added. After stirring for 16 h, 10 mL of water and 2 M HCl were added until all solids were dissolved. The phases were separated and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure. The residue was suspended in a few milliliters of a CH/EA mixture and ultrasonicated for 2 min. The remaining

solid was filtered off, washed with cyclohexane and dried. The solvent of the filtrate was removed under reduced pressure and the procedure was repeated several times. The combined solids were dried and 0.391 g (0.748 mmol) of a colorless solid were obtained. – Yield: 77%.

mp: 169 – 170 °C. – ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 0.80 (d, ³J = 6.7 Hz, 9 H, CH₃), 0.90 (d, ³J = 6.7 Hz, 9 H, CH₃), 1.78–1.92 (kb, 3 H, CH(CH₃)₂), 4.32 (dd, ³J = 6.0, 4.4 Hz, 3 H, CHOH), 5.16 (d, ³J = 4.4 Hz, 3 H, OH), 7.41 (AA'BB', ³J = 8.2 Hz, 6 H, C_mH), 7.80 (AA'BB', ³J = 8.2 Hz, 6 H, C_oH), 7.86 (s, 3 H, C_{aromat.}H). – ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 18.0 (+, CH₃), 19.1 (+, CH₃), 35.0 (+, CH(CH₃)₂), 77.2 (+, CHOH), 123.8 (+, C_{aromat.}H), 126.4 (+, C_mH), 127.1 (+, C_oH), 138.4 (C_{quart.}, C_{aromat.}), 141.5 (C_{quart.}, C_p), 144.6 (C_{quart.}, C₁). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3249 (w), 2958 (vw), 2925 (vw), 1744 (vw), 1595 (vw), 1512 (vw), 1467 (vw), 1384 (w), 1226 (w), 1205 (vw), 1101 (vw), 1018 (w), 934 (vw), 863 (vw), 825 (w), 792 (w), 704 (w), 646 (vw), 611 (vw), 580 (w), 504 (w), 398 (vw). – MS (EI, 70 eV, 220 °C), m/z (%): 522 (10) [M⁺], 479 (100) [M⁺ – CH(CH₃)₂], 181 (6.9) [M⁺ – CH(CH₃)₂ – 2 × PhCH(OH)CH(CH₃)₂]. – HR-MS (C₃₆H₄₂O₃): calcd. 522.3128, found 522.3127.

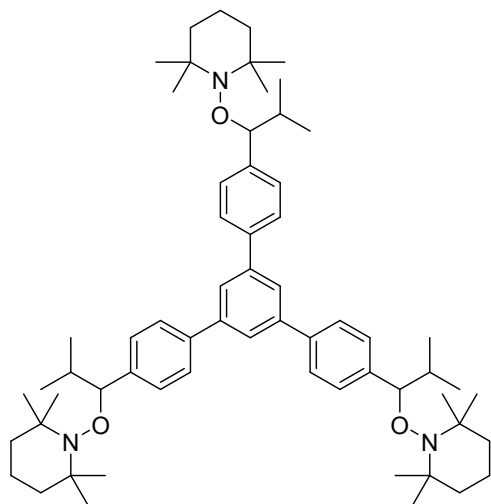


1,3,5-Tris(4'-(1''-bromo-2''-methylpropyl)phenyl)benzene: 875 mg 1,3,5-tris(4'-(2''-methylpropan-1''-ol)phenyl)benzene (1.67 mmol, 1.00 equiv.) were suspended in 40 mL dichloromethane. At 0 °C, 1.80 mL of HBr in acetic acid (33 wt%, 843 mg HBr, 10.4 mmol

HBr, 6.23 equiv.) were added and the reaction mixture was stirred at room temperature for 3 h. Afterwards, 50 mL of water were added and the phases were separated. The organic layer was washed with a saturated NaHCO₃-solution, water and brine as well as dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was recrystallized from acetone. 1.01 g (1.42 mmol) of a colorless, crystalline solid were obtained. – Yield: 85%.

mp: 197 – 198 °C. – ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.92 (d, ³J = 6.6 Hz, 9 H, CH₃), 1.24 (d, ³J = 6.6 Hz, 9 H, CH₃), 2.39 (kb, ³J = 8.5, 6.6 Hz 3 H, CH(CH₃)₂), 4.79 (d, ³J = 8.5 Hz, 3 H, CHBr), 7.48 (AA'BB', ³J = 8.3 Hz, 6 H, C_mH), 7.65 (AA'BB', ³J = 8.3 Hz, 6 H, C_oH), 7.77 (s, 3 H, C_{aromat}H). – ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 20.7 (+, CH₃), 21.8 (+, CH₃), 36.7 (+, CH(CH₃)₂), 64.1 (+, CHBr), 125.3 (+, C_{aromat}H), 127.5 (+, C_mH), 128.5 (+, C_oH), 140.8 (C_{quart.}, C_{aromat.}), 141.2 (C_{quart.}, C_p), 141.9 (C_{quart.}, C₁). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2957 (w), 2866 (vw), 1594 (vw), 1509 (w), 1464 (vw), 1384 (w), 1365 (vw), 1305 (vw), 1242 (vw), 1210 (w), 1170 (w), 1120 (vw), 1018 (vw), 942 (vw), 888 (vw), 821 (w), 786 (w), 770 (w), 744 (w), 707 (w), 668 (w), 633 (w), 612 (w), 574 (w), 533 (vw), 507 (vw), 403 (vw). – MS (FAB, 3-NBA), *m/z* (%): 709/711/713/715 [M⁺ + H], 629/631/633 [M⁺ – Br]. – HR-MS (C₃₆H₃₉⁷⁹Br₃ + H): calcd. 709.0675, found. 709.0674; (C₃₆H₃₉⁷⁹Br₂⁸¹Br): calcd. 711.0654, found. 711.0654.

1,3,5-Tris(4'-(2''-methyl-1''-((2''',2''',6''',6'''-tetramethylpiperidin-1'''-yl)oxy)propyl)phenyl)benzene 1:



Under an argon atmosphere, 0.100 g 1,3,5-tris(4'-(1''-brom-2''-methylpropyl)phenyl)benzene (0.141 mmol, 1.00 equiv.), 0.265 g TEMPO (1.69 mmol, 12.0 equiv.), 50.4 mg copper powder (0.793 mmol, 6.01 equiv.), 8.4 mg Cu(OTf)₂ (23.2 μmol, 9.15 mol%) und 15.4 mg 4,4'-di-*tert*-butyl-2,2'-dipyridyl (57.4 μmol, 23.0 mol%) were suspended in 4.0 mL abs. acetonitrile and stirred at 75 °C for 16 h. After, the reaction mixture was filtrated over silica gel and the filter residue was washed with dichloromethane. The solvent was removed under reduced pressure. TEMPO was removed from the crude product via sublimation (70 °C) and the residue was recrystallized from an acetone/dichloromethane mixture. 80.2 mg (85.3 μmol) of a colorless solid were obtained. – Yield: 60%.

mp: 192 – 194 °C. – ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.70 (bs, 9 H, C^TH₃), 0.84 (kb, 18 H, CH₃), 1.04 (bs, 9 H, C^TH₃), 1.13 – 1.60 (kb, 36 H, C^TH₃, C^TH₂), 2.50 – 2.36 (kb, 3 H, CH(CH₃)₂), 4.60 (d, ³J = 5.2 Hz, 3 H, CHO), 7.31 (AA'BB', ³J = 7.9 Hz, 6 H, C_mH), 7.64 (AA'BB', ³J = 7.9 Hz, 6 H, C_oH), 7.81 (s, 3 H, C_{aromat}H). – ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 16.3 (+, CH₃), 17.3 (–, C^TH₂), 20.3 (+, CH₃), 31.3 (+, CH(CH₃)₂), 40.8 (–, C^TH₂), 60.0 (C_{quart.}, C^T(CH₃)₂), 91.2 (+, CHO), 124.8 (+, C_{aromat}H), 126.1 (+, C_mH), 129.3 (+, C_oH), 139.5 (C_{quart.}, C_{aromat.}), 139.7 (C_{quart.}, C_p), 142.2 (C_{quart.}, C₁). – IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2928 (w), 1599 (vw), 1509 (vw), 1468 (w), 1374 (w), 1359 (w), 1310 (vw), 1242 (vw), 1182 (vw), 1132 (w), 1011 (w), 989 (w), 954 (w), 914 (vw), 879 (vw), 842 (w), 817 (w), 707 (w), 618 (vw), 587 (vw), 550 (vw), 454 (vw), 430 (vw). – MS (FAB, 3-NBA), *m/z* (%): 940 [M⁺ + H], 799 [M⁺ – C₉H₁₈N], 783 [M⁺ – TEMPO], 643 [M⁺ – TEMPO – C₉H₁₈N], 627 [M⁺ – 2 × TEMPO], 486 [M⁺ – 2 × TEMPO – C₉H₁₈N], 471 [M⁺ – 3 × TEMPO], 157 [TEMPO⁺], 140 [C₉H₁₈N⁺]. – HR-MS (C₆₃H₉₃N₃O₃ + H): calcd. 940.7290, found 940.7288.

2.2 Synthetic and investigation procedures of the polymer networks

Synthesis of polymer network 3: The polymer network was prepared by multiple nitroxide exchange reaction of the three-fold nitroxide radical **2** (1.00 equiv., 0.063 mmol) and the three-fold alkoxyamine species **1** (1.00 equiv., 0.063 mmol) in 0.9 mL of a toluene/methanol-mixture (9/1). The toluene/methanol bi-solvent system proved as the most effective among the solvents evaluated. The solvent mixture was freeze-dried before use and added to the starting materials under oxygen free conditions in a glovebox. The vial was sealed with a cap and placed in an oven for 24 h at 100 °C. The crude network was washed five times with toluene to remove the released TEMPO byproduct. After washing, the network was dried with a critical point dryer using supercritical CO₂ to give 71.1 mg (0.06 mmol) of a slightly yellow product. – Yield: 95%

IR: $\nu_{\max}/\text{cm}^{-1}$ 2971 (asym. aliphatic-CH₃), 2929, 2871 (sym. aliphatic-CH₃), 2361, 2339, 1685, 1578 (CONH), 1360 (NO), 1262, 1162 (C-C), 1119 (1,4 aryl-CH), 1004 (1,3 aryl-CH), 977 (1,3,5 aryl-CH), 877, 824 (1,3,5 aryl-CH); Raman: $\nu_{\max}/\text{cm}^{-1}$ 3061 (aryl-CH), 2934 (aliphatic-CH), 2210 (alkyne), 1613, 1578 (CONH), 1348 (NO), 1169 (aryl-CH), 1062 (aryl-CH), 993 (aryl-CH); S_{BET} (Ar, 87 K): 90 m²/g; EA: (C₈₄H₈₇N₃O₃, 1186.64): calcd.: C 85.02, H 7.39, N 3.54; found: C 83.27, H 7.38, N 3.64; TGA: T(5% weight lost): 292°C.

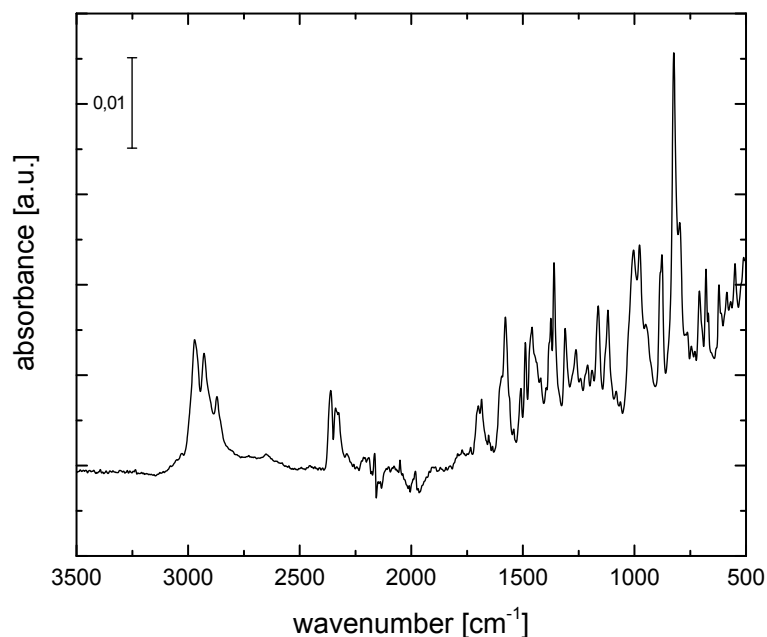


Figure S 1: IR spectra of the polymer network.

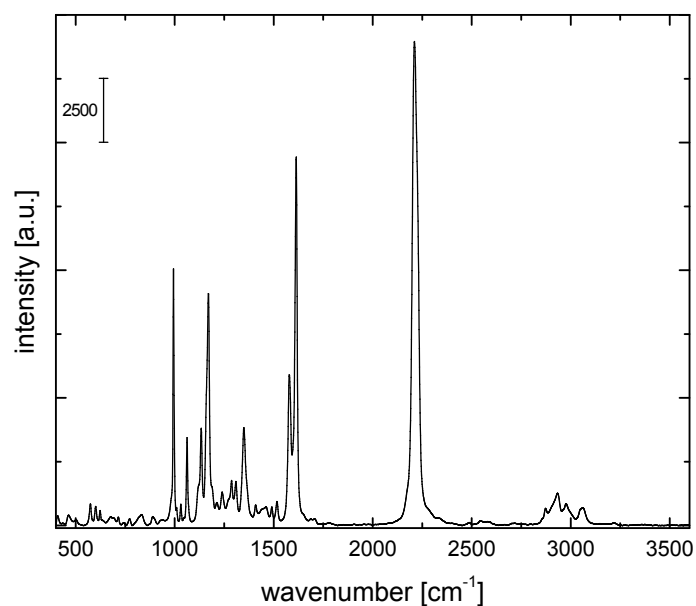


Figure S 2: Raman spectra of the polymer network.

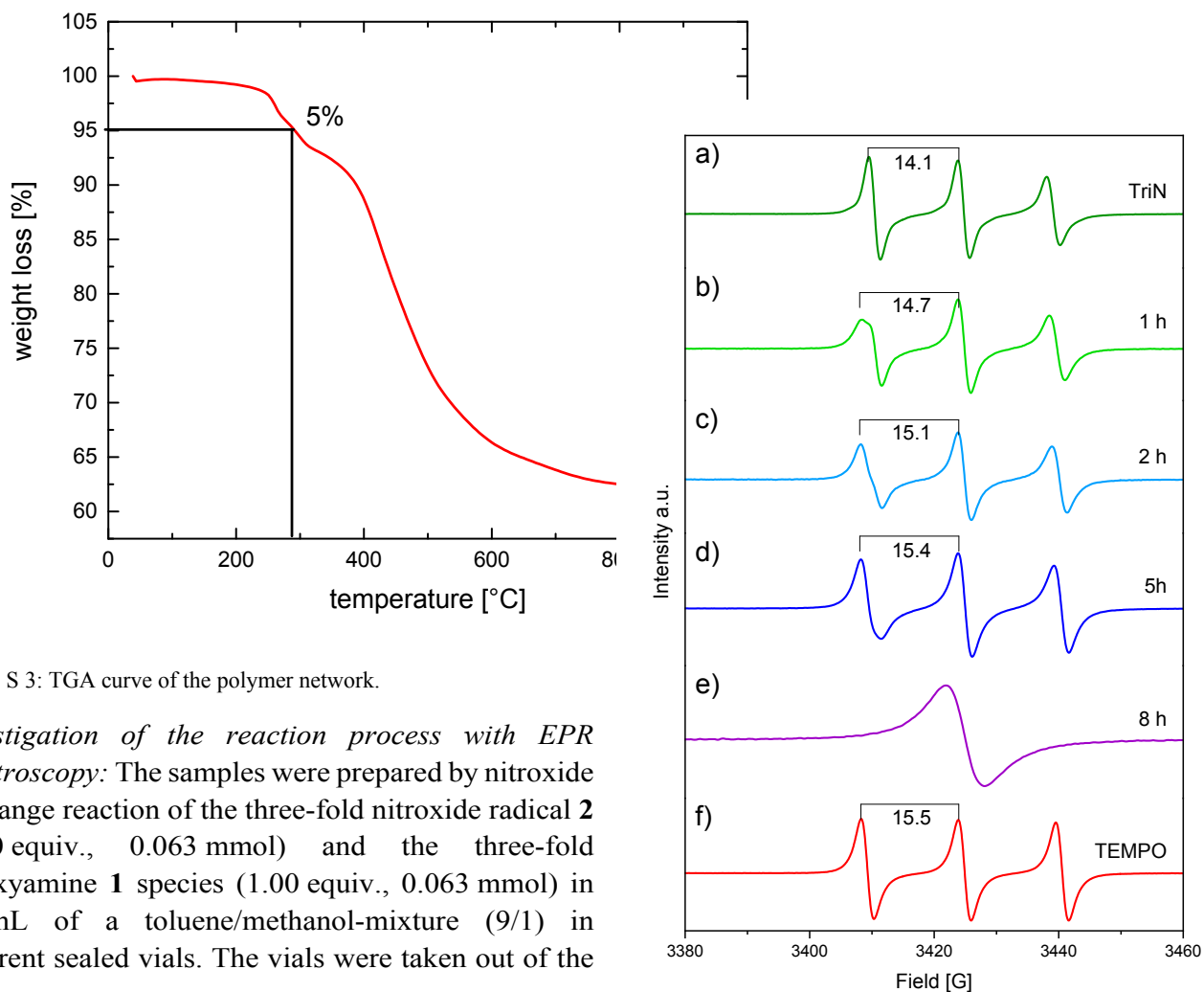


Figure S 3: TGA curve of the polymer network.

Investigation of the reaction process with EPR spectroscopy: The samples were prepared by nitroxide exchange reaction of the three-fold nitroxide radical **2** (1.00 equiv., 0.063 mmol) and the three-fold alkoxyamine **1** species (1.00 equiv., 0.063 mmol) in 0.9 mL of a toluene/methanol-mixture (9/1) in different sealed vials. The vials were taken out of the

Figure 1: Investigation of the reaction process *via* EPR spectroscopy; a) reference spectrum of the trinitroxide (TriNO) **1**; EPR spectra of the reaction mixture after b) 1 h, c) 2 h and d) 5 h; e) solid EPR spectrum of the network product; f) reference spectrum of the by-product TEMPO.

oven after 1 h, 2 h and 5 h. 0.01 mL of the sample were abstracted and diluted with 1.0 mL DEF (diethylformamide) to proceed for EPR measurements.

Investigation of the reaction process via fluorescence spectroscopy: The samples were prepared by nitroxide exchange reaction of the three-fold nitroxide radical **2** (1.00 equiv., 0.063 mmol) and the three-fold alkoxyamine **1** species (1.00 equiv., 0.063 mmol) in 0.9 mL of a toluene/methanol-mixture (9/1) in a sealed vial. 100 μ L aliquot were taken out of the vial after 1 h, 2 h, 5 h respectively. The polymer network was observed after 8 h. A piece (10 mg) of the network was cut and washed five times. After that, the fluorescence was investigated at 320 nm excitation wavelength.

Swelling experiments:

First, the polymer network was washed with toluene constantly, until TEMPO in the washing solution is not measurable anymore in EPR. Afterwards, the polymer network was dried with the critical point dryer using supercritical CO₂. The swelling behaviour was successively investigated with toluene, at pristine, annealed and softened state at 25 °C. For this purpose, the dried polymer network was placed in pure solvent at room temperature. After 15 min, 30 min, 1 h, 2 h, 6 h, 12 h, 24 h, 36 h, and 48 h, the solvent was removed, and the weight of the network was measured to determine the swelling degree (Q). After that, the polymer network was annealed at 100°C for 24 h and dried again with the critical point dryer. The swelling degree (Q) was investigated using the same conditions as before. Afterwards, the polymer network was decrosslinked with 5 equiv. TEMPO (0.026 mmol) at 100 °C for 24 h and dried again with the critical point dryer. The swelling degree (Q) was investigated using the same conditions as before.

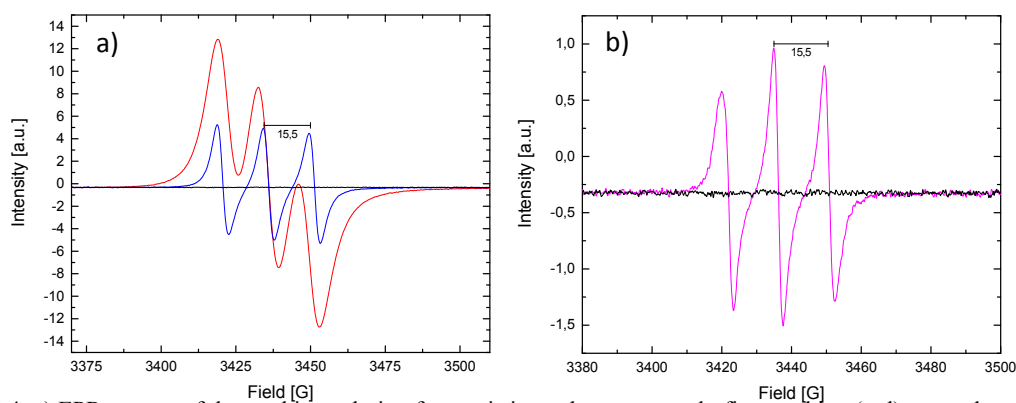


Figure S 4: a) EPR spectra of the washing solution from pristine polymer network: first washing (red), second washing (blue) and fifth washing (black). b) EPR spectra of the solution before annealing (black) and solution after annealing at 100°C (magenta).

Disassembly (decrosslinking) experiment:

For the disassembly experiment, 0.492 g of TEMPO (18 equiv., 3.15 mmol) in 2 mL toluene was added to the polymer network in a vial and sealed under inert condition. The solvent was freeze-dried before use. The vial was heated for 24 h at 100 °C. The gel-sol transition was checked after 3 h, 6 h and 24 h. For further investigation with mass spectrometry, the excess amount of TEMPO was removed via sublimation and the reaction mixture was investigated with FAB-MS. Three-fold nitroxide radical **2** as well as three-fold alkoxyamine **1** and their fragmentations were detected. m/z (%): 784 [TriAA – TEMPO+H⁺], 716 [TriNO + 2 × H⁺], 702 [TriNO – CH₃ + 2 × H⁺], 686 [TriNO – 2 × CH₃], 670 [TriNO – 3 × CH₃ + H⁺], 654 [TriNO – 4 × CH₃], 471 [TriAA – 3 × TEMPO], 156 [TEMPO], 140 [C₉H₁₈N⁺].

Since the mass at 471 can also be a fragment of TriNO, this mass was investigated again with HR-MS. In the HR-MS, $m/z = 471.3052$ was found which confirmed the presence of fragment from TriAA. After investigation with ESI-TOFMS, the mass of TriNO was detected as m/z (%): 715,3595 [TriNO + H⁺].

Control experiment:

The as synthesized polymer network was placed in a Schlenk flask with 5 mL toluene. The reaction mixture was refluxed for 72 h at 120°C under ambient air. The polymer network was completely dissolved after 72 h.

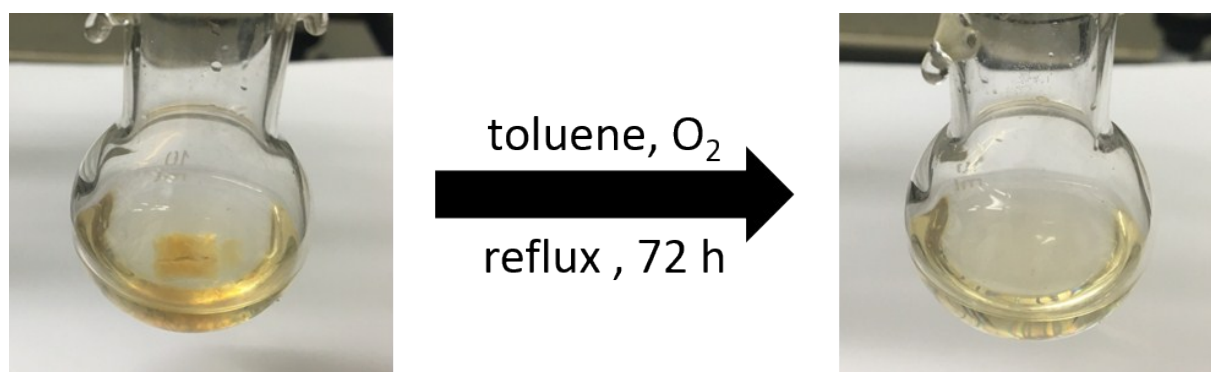


Figure S 5: Irreversible destruction of the polymer gel by refluxing under ambient air.

Self-healing experiment:

The as synthesized polymer network was cut in two pieces with a scalpel and placed in a vial with 2 mL toluene under oxygen free condition. The vial was then filled with 3 mm glass beads to fix the position of the polymer network. The self-healing property was observed after 24 h. The experiment was repeated for additional two cycles. The self-healing property was observed during all cycles.

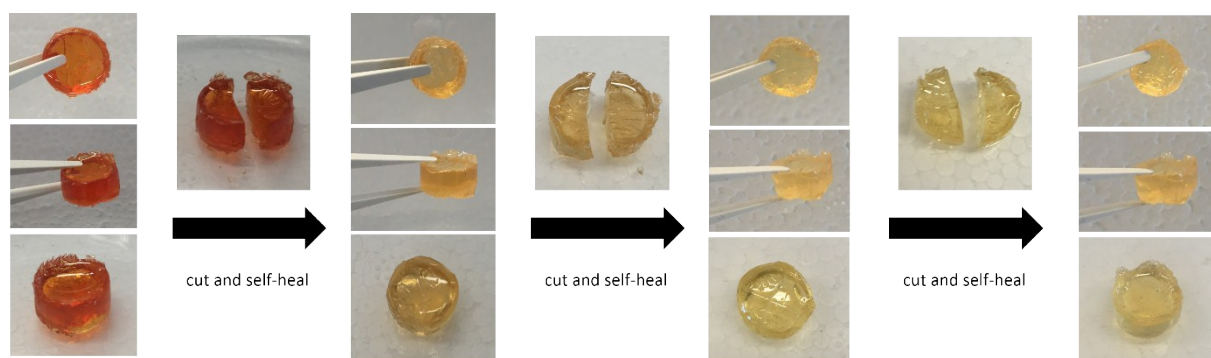


Figure S 6: Three Self-healing cycles of the polymer network.

Calculation of TEMPO and TriNO nitroxide concentration in the reaction mixtures

The concentration of TEMPO and TriNO nitroxide of the reaction mixture were analysed using SpinFit and Spin Count features of program Xenon from Bruker BioSpin.

The spectra of pure TEMPO and TriNO were recorded and saved as the reference nitroxides. The spectra of 1 h, 2 h and 5 h were fitted with the reference nitroxides using the feature SpinFit. The concentrations were obtained using the Spin Count feature by entering the sample height and tube diameter (Table S1).

Table S1: Calculated concentration of TEMPO and TriNO at 1 h, 2 h and 5 h.

	TriNO	1 h	2 h	5 h	TEMPO
c(TEMPO) [mol/L]	0	6,97E-04	9,25E-04	2,86E-03	4,68E-03
c(TriNO)[mol/L]	1,00E-02	1,18E-03	6,15E-04	9,00E-04	0

With the concentration of both nitroxide species, the ratio of TEMPO and TriNO were calculated in Table S2.

Table S2: Ratio of TEMPO and TriNO at 1 h, 2 h and 5 h.

	TriNO	1 h	2 h	5 h	TEMPO
TEMPO [%]	0	37.1	60.0	76.0	100
TriNO [%]	100	62.9	40.0	24.0	0

Calculation of swelling degree Q and crosslinking degree CLD

The swelling degree Q was calculated as follows:

$$Q = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

Where W_{wet} is the weight of the wet polymer and W_{dry} is the weight of the dry polymer.

The crosslinking degree CLD was calculated as follows:

$$N_s(0\%CL) = \frac{m_p}{M_s} \cdot N_A \cdot 3 \quad (2)$$

$$CLD = 100 - ((N_s(0\%CL) - N_s(x\%CL)) \cdot 100) \quad (3)$$

$N_s(0\%CL)$ is the spin count of the starting material with 0% crosslinking and can be calculated from the employed total mass of the measured polymer m_p , the total molecular weight of employed starting materials M_s and the Avogadro's number N_A . Since the three-fold-nitroxide has three spins, it needs to be multiplied by 3. (equation (2)) $N_s(x\%CL)$ is given through the spin count of the EPR measurement of the measured polymer.⁶ The crosslinking degree CLD is given in percent and can be calculated using the equation (3).

Table S3: Calculation of CLD for the polymer network.

	m_p [mg]	M_s [g/mol]	$N_s(0\%CL)$	$N_s(x\%CL)$	CLD[%]
TriNO+TriA A	10.2	1655.39	1.11E+19	-	0
pristine	2.0	1655.39	2.18E+18	1.05E+17	95.20±0.04
annealed	3.1	1655.39	3.38E+18	3.57E+16	99.2±0.04
decrosslinked	5.0	1655.39	5.46E+18	1.82E+17	96.7±0.02

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