Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Dynamic Covalent Polymer Networks via Combined Nitroxide Exchange Reaction and Nitroxide Mediated Polymerization

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Methods

The EPR spectra were recorded on a BRUKER *EMXNano* spectrometer at room temperature (298 K). The solid samples were washed with argon, and the soluble compounds were dissolved in toluene and deoxygenated by bubbling argon for several minutes then sealed before EPR measurements. Typical parameter settings utilized for the EPR measurements were modulation frequency: 100 kHz; modulation amplitude: 0.452 G; modulation phase: 0; number of scans: 1; microwave attenuation: 60 dB; centre field: 3434 G; sweep width: 100 G; sweep time: 180 s; sample g-factor: 2.00; receiver gain: 40 dB; number of points: 2212; conversion time: 81.38 ms; time constant: 1.28 ms; points/modulation amplitude: 10.

The apparent number average molecular weight (M_n), mass average molecular weight (M_w) and dispersity ($Đ = M_w/M_n$) were measured via the *EcoSEC* SEC system equipped with TOSOH *EcoSEC* pump, PSS *SECcurity* refractive index detector, TOSOH *EcoGPC* UV detector, and four PLgel 5µ Mixed-C columns with the different pore size (pre-column, 10^2 Å, 10^3 Å, 10^5 Å). All the samples were prepared with a concentration of 2 g/L in THF and filled in 2 ml vials. The measurements were carried out with 50 µL injection volume per sample at 35 °C in THF with a flow rate of 1 mL/min. The molecular weight calibration of the SEC system was based on 16 narrow molecular weight linear polystyrene standards ranging from 266 to $2.52 \cdot 10^6$ g/mol. The calculation of the molecular weight proceeded by utilizing the Mark-Houwink-Sakurada (MHS) parameters for polystyrene in THF at 30 °C, i.e., $K = 13.63 \cdot 10^{-3}$ mL/g, $\alpha = 0.714$. All measurements and the evaluation of data were carried out with the software PSS WinGPC Unity.

The goal of inverse size-exclusion chromatography (ISEC) is to determine the pore-size distribution (PSD) of a column packing material by monitoring the residence times of solutes of varying molecular diameter. [1] The size exclusive chromatography in the inverse mode was performed on an *HP 1260* AGILENT HPLC instrument in collaboration with Birgit Huber at the Institute of Biological Interfaces (IBG) of KIT and Christoph Pfeifer at the Institute of Technical Chemistry and Polymer Chemistry (ITCP) of KIT. The ISEC system is similar to the SEC system, equipped with a pump, RI, and UV detector. Only the column is self-packed instead of the commercial column. The sample material was packed in the middle of the chromatographic column with a max. bed length of 200 mm and an inner diameter of 10 mm. After connecting the column to the instrument, the sample material was conditioned with the mobile phase THF at a flow rate of 0.1 mL/min for about 30 min to remove air bubbles in interstices of the material. Polystyrene standards (**Table S1**) were supplied by Polymer Standards Service GmbH, Mainz, Germany, and prepared with a concentration of 2 mg/ml in THF and filled in 2 ml vials. All experiments were carried out with 20 µL injection volume at

35 °C in THF with a flow rate of 0.2 mL/min and were repeated three times to ensure sufficient accuracy for the experimental size-exclusion data. The following table shows the specific data of the utilized polystyrene standards.

Table S1: Different molecular weights and polydispersities of polystyrenes from Polymer Standards Service GmbH, Mainz, Germany.

M_p [g/mol]	M_w [g/mol]	M_n [g/mol]	*Đ*
162	162	162	1.00
370	370	370	1.00
578	607	533	1.14
1620	1560	1500	1.06
2090	2090	1990	1.05
3420	3470	3280	1.06
4290	4330	4160	1.06
6540	6670	6320	1.05
18100	17900	17300	1.03
32500	31700	30480	1.04
67500	65000	64000	1.02
128000	121000	115000	1.05
246000	226000	214000	1.06

M_p is the molecular weight at the peak maximum, M_w and M_n are the mass average and number average molecular weight. *Đ* is the polydispersity index. Data supplied by producer.

The elution volume of the PS standards is plotted against their molecular weight. A curve with a single distinct exclusion limit is obtained, which is characteristic of a monomodal mesh size distributions in the stationary phase material.

In order to determine the pore/mesh size of the sample materials, the pore/mesh size distribution curve was generated by analyzing the data via the software PSS Porocheck version 2.5. Both, the slip pore and the cylindrical pore model, were used in the analysis of the data.

The results of both models are listed in **Table S2**. Since both modes give comparable results we used only the analysis based on the slit pores model for the discussion in the manuscript.

Table S2: Mesh size radius of **[2+4]**-STEM networks in different pore model.

STEM networks	**Slit-like mesh size radius P_{ms} [nm]**	**Cylindrical mesh size radius P_{ms} [nm]**
[2+4]P	7.6 ± 1.7	6.9 ± 0.3
[2+4]O	4.2 ± 1.1	3.6 ± 0.0
[2+4]E	9.8 ± 2.3	8.1 ± 0.6

The DSC measurements were performed on a Mettler *Toledo* DSC instrument, in a sealed 40 µL aluminum crucibles under nitrogen atmosphere. Approximately 8 mg of sample materials were analyzed by using a heat/cool/heat cycle with a heating or cooling rate of 5 K/min. In this cyclic thermal measurement, the sample materials were heated from –50 °C to 200 °C, then cooled to 0 °C and reheated to 200 °C. All measured data were analyzed with the software STAR^e SW 9.30 and plotted in a diagram. The glass transition temperature T_g was given as the turning point of the curve.

NMR spectra were recorded on a BRUKER *Avance* 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) on solutions in $CDCl_3$. Chemical shifts δ were expressed in parts per million (ppm), related to tetramethylsilane (TMS), which were referenced to $CHCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm) as the internal standard. All coupling constants (J) are absolute values and J values are expressed in Hertz (Hz). The spectra were analyzed according to first order. All ^{1}H-NMR data were reported as follows: chemical shift δ, multiplicity (m = multiplet, bs = broad singlet), multiplets (m) were given over the range (ppm). The signal structure in ^{13}C-NMR was analyzed 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_q = quaternary C-atom (no signal).

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was conducted on a BRUKER model *Tensor-27* or *Alpha T* at ambient temperature with the software OPUS. The position of the absorption band was given in wavenumbers ν in cm^{-1}. The shapes and intensities of the bands were characterized as follows: vs = very strong 0-10% T, s = strong 11-40% T, m = medium 41-70% T, w = weak 71-90% T, vw = very weak, 91-100% T.

EI (Electron Ionization) 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%). For high resolution mass spectrometry (HR-MS) the following abbreviations were used: calcd. = calculated mass, found = mass found in the analysis.

Materials/Chemicals

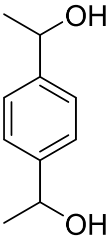
If not mentioned otherwise, all chemicals were purchased from commercial sources and used without further purification. All solvents and styrene were degassed with at least three freeze-pump-thaw cycles before using, and all reactions were carried out under argon/nitrogen atmosphere using Schlenk technique if not stated otherwise. Absolute toluene was obtained by refluxing over sodium, followed by distillation and was kept under Argon. Analytical thin layer chromatography (TLC) was carried out on MERCK silica gel coated aluminium plates (silica gel 60, F_{254}), detected under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. Styrene was filtered over Celite® to remove stabilizers, stored under argon atmosphere with –15°C and degasses with freeze-pump-thaw prior to use. The **Tetra-NO** and the **Di-AA** building blocks were synthesized and provided by Yannick Matt and Dr. Isabelle Wessely at the Institute of Organic Chemistry (IOC) of KIT. Polystyrene standards used in inverse SEC were purchased from Polymer Standards and used as received.

The **Tetra-NO** was synthesized according to a literature procedure, the analytics are consistent with the literature.

I. Wessely, V. Mugnaini, A. Bihlmeier, G. Jeschke, S. Bräse, M. Tsotsalas, *Rsc Adv.* **2016**, *57*, 55715–55719. *Radical exchange reaction of multi-spin isoindoline nitroxides followed by EPR spectroscopy.*

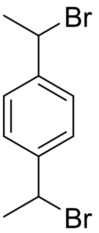
Synthetic Procedures

1,4-Bis(1'-hydroxyethyl)benzene: 3.00 g 1,4-Diacetylbenzene (18.5 mmol, 1.00 equiv.) were dissolved in 150 mL dry THF and cooled to 0 °C before 1.05 g $\mathrm{LiAlH_4}$ (27.8 mmol, 1.50 equiv.) were added in portions. The reaction mixture was slowly warmed to room temperature and then stirred for 1.5 h at this temperature. Afterwards, the mixture was hydrolyzed with ice water, acidified with conc. HCl (~ 16 mL) and the phases were separated. The aqueous phase was extracted with ethyl acetate three times and the combined organic phases were washed with water and brine. After drying over sodium sulfate, the solvent was removed under reduced pressure. 2.92 g (17.6 mmol) of a colorless, crystalline solid was obtained and used without further purification. Yield: 95%. – mp: 85 – 86 °C. – ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 1.47 (d, ^3J = 6.5 Hz, 6 H, $\mathrm{C}H_3$), 2.35 (s, 2 H, $\mathrm{O}H$), 4.86 (q, ^3J = 6.5 Hz, 2 H, $\mathrm{C}H\mathrm{OH}$), 7.32 (s, 4 H, $\mathrm{C_{Ar}}H$). – ^{13}C-NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 25.2 (+, $C\mathrm{H_3}$), 70.2 (+, $C\mathrm{HOH}$), 125.7 (+, $C_{\mathrm{Ar}}\mathrm{H}$), 145.1 ($\mathrm{C_{quart.}}$, C_{Ar}). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3282 (w), 2967 (w), 2923 (vw), 1510 (vw), 1410 (w), 1364 (w), 1289 (w), 1207 (w), 1118 (vw), 1064 (w), 1002 (w), 893 (w), 827 (w), 642 (w), 568 (w), 465 (w), 385 (vw). – MS (EI, 70 eV, 50 °C), *m/z* (%): 166 (32) [$\mathrm{M^+}$], 151 (100) [$\mathrm{M^+ - CH_3}$], 121 (14) [$\mathrm{M^+ - C_2H_5O}$], 106 (12) [$\mathrm{M^+ - C_2H_5O - CH_3}$], 105 (4) [$\mathrm{M^+ - C_2H_5O - H - CH_3}$]. – HR-MS ($\mathrm{C_{10}H_{14}O_2}$): calcd. 166.0988, found 166.0990.

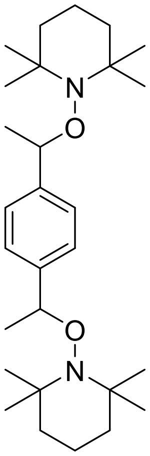


The experimental data are consistent with the literature.
J. S. Wallace, B. W. Baldwin, C. Morrow, *J. Org. Chem.* **1992**, *57*, 5231–5239. *Separation of remote diol and triol stereoisomers by enzyme-catalyzed esterification in organic media or hydrolysis in aqueous media*.

1,4-Bis(1'-bromoethyl)benzene: 3.58 g 1,4-Bis(1'-hydroxyethyl)benzene (21.5 mmol, 1.00 equiv.) were dissolved in 150 mL dichloromethane at 0 °C before 10.0 mL HBr in acetic acid (33 wt%, 4.69 g HBr, 57.9 mmol, 2.69 equiv.) were added. After the reaction was stirred for 3.5 h at this temperature, 70 mL water were added, the phases were separated and the organic phase was washed with a saturated $\mathrm{NaHCO_3}$-solution, water and brine before being dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was recrystallized from hexane to obtain 5.22 g (17.9 mmol) of a colorless, crystalline solid. Yield: 83%. – mp: 106 – 107 °C. – ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 2.04 (d, ^3J = 6.9 Hz, 6 H, $\mathrm{C}H_3$), 5.20 (q, ^3J = 6.9 Hz, 2 H, $\mathrm{C}H\mathrm{Br}$), 7.41 (s, 4 H, $\mathrm{C_{Ar}}H$). – ^{13}C-NMR (100 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 26.9 (+, $C\mathrm{H_3}$), 48.9 (+, $C\mathrm{HBr}$), 127.3 (+, $C_{\mathrm{Ar}}\mathrm{H}$), 143.4 ($\mathrm{C_{quart.}}$, C_{Ar}). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2962 (vw), 1512 (vw), 1438 (w), 1424 (vw), 1372 (vw), 1329 (vw), 1297 (vw), 1212 (w), 1175 (w), 1121 (vw), 1076 (vw), 1042 (w), 1017 (w), 961 (w), 833 (w), 713 (w), 648 (w), 596 (m), 535 (w), 413 (vw), 387 (vw). – MS (EI, 70 eV, 40 °C), *m/z* (%): 290/292/294 (1.8/3.3/1.6) [$\mathrm{M^+}$], 211/213 (77/83) [$\mathrm{M^+ - Br}$], 132 (100) [$\mathrm{M^+ - 2 \times Br}$], 117 (37) [$\mathrm{M^+ - 2 \times Br - CH_3}$], 115 (12). – HR-MS ($\mathrm{C_{10}H_{12}{}^{79}Br_2}$): calcd. 289.9300, found 289.9302.

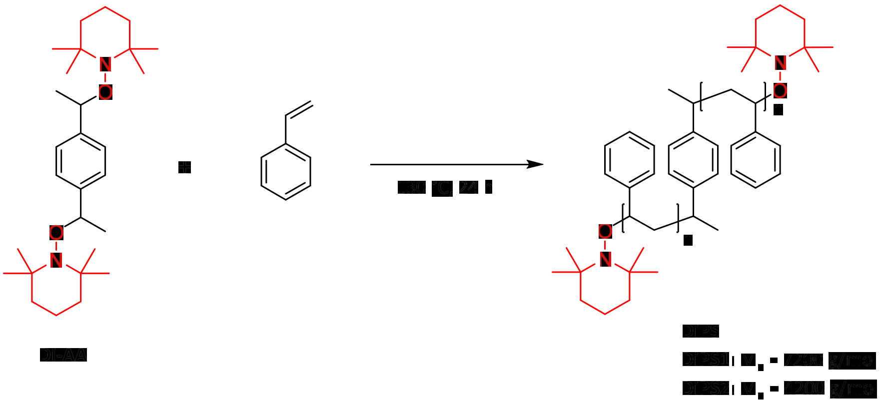


The experimental data are consistent with the literature.
C. Zhang, J. Ling, Q. Wang, *Macromolecules* **2011**, *44*, 8739–8743. *Radical Addition-Coupling Polymerization (RACP) toward periodic copolymers*.



1,4-Bis(1'-((2'',2'',6'',6''-tetramethylpiperidin-1''-yl)oxy)ethyl)benzene: Under an argon atmosphere, 0.300 g 1,4-Bis(1'-bromoethyl)benzene (1.03 mmol, 1.00 equiv.), 0.485 g TEMPO (3.08 mmol, 3.00 equiv.), 196 mg copper powder (3.08 mmol, 3.00 equiv.), 18.6 mg $Cu(OTf)_2$ (51.5 µmol, 5.00 mol%) and 27.6 mg 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (103 µmol, 10.0 mol%) were suspended in 6.0 mL abs. toluene. The reaction mixture was stirred for 3 d at 80 °C, before being cooled to room temperature and filtered over silica using dichloromethane. The solvent was removed under reduced pressure and the crude product recrystallized from acetonitrile to obtain 0.249 g (0.542 mmol) of a colorless, crystalline solid. Yield: 53%. – mp: 150 °C. – ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.59 (bs, 6 H, $\mathrm{C^T}H_3$), 1.01 (bs, 6 H, $\mathrm{C^T}H_3$), 1.16 (bs, 6 H, $\mathrm{C^T}H_3$), 1.20–1.60 (m, 18 H, $\mathrm{C^T}H_3$, $\mathrm{C^T}H_2$), 1.47 (d, ^3J = 6.7 Hz, 6 H, $\mathrm{CHC}H_3$), 4.74 (q, ^3J = 6.7 Hz, 2 H, $\mathrm{C}H\mathrm{CH_3}$), 7.24 (s, 4 H, $\mathrm{C_{Ar}}H$). – ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 17.4 (–, $C^{\mathrm{T}}\mathrm{H_2}$), 20.5 (+, $C^{\mathrm{T}}\mathrm{H_3}$), 23.5 (+, $C\mathrm{H_3}$), 34.5 (+, $C^{\mathrm{T}}\mathrm{H_3}$), 40.5 (–, $C^{\mathrm{T}}\mathrm{H_2}$), 59.6 ($\mathrm{C_{quart.}}$, $C^{\mathrm{T}}\mathrm{(CH_3)_2}$), 59.9 ($\mathrm{C_{quart.}}$, $C^{\mathrm{T}}\mathrm{(CH_3)_2}$), 83.2 (+, $C\mathrm{HCH_3}$), 126.5 (+, $C_{\mathrm{Ar}}\mathrm{H}$), 144.4 ($\mathrm{C_{quart.}}$, C_{Ar}). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2999 (vw), 2969 (w), 2927 (w), 1463 (vw), 1443 (w), 1359 (w), 1258 (vw), 1240 (vw), 1208 (w), 1182 (vw), 1130 (w), 1089 (vw), 1057 (w), 1018 (vw), 984 (w), 953 (w), 932 (w), 880 (w), 835 (w), 789 (vw), 747 (vw), 692 (w), 605 (vw), 572 (w), 505 (vw), 430 (vw), 393 (vw). – MS (EI, 70 eV, 120 °C), *m/z* (%): 288 (4.9) [M^+ – TEMPO], 156 (100) [$TEMPO^+$], 132 (4.9) [M^+ – 2 × TEMPO]. – HR-MS ($C_{19}H_{30}NO$, M^+ – TEMPO): calcd. 288.2322, found 288.2320.

Experimental description of NMP followed by NER approach (i)



Scheme S1: nitroxide mediated polymerization of styrene with **Di-AA**.

Synthesis of di-polystyrene **DiPS1** with n=50: Under argon atmosphere, styrene (3.30 mL, 3.00 g, 28.8 mmol, 100 equiv.) and **Di-AA** (0.128 g, 0.288 mmol, 1.00 equiv.) were added to a Schlenk tube. The reaction mixture was heated and stirred for 24 h at 130 °C. During the reaction, several samples were taken at different time points, using an Argon flushed pipette. These samples were analyzed by NMR and SEC to monitor the reaction progress. The crude product was dissolved in THF (7 mL) and precipitated into cold MeOH (70 mL). The precipitate was filtered off and washed several times with MeOH. After drying of the

product under vacuum the desired **DiPS1** was obtained as a white powder (1.87 g, 0.265 mmol, 60% yield). $M_{n,theo} = M_{n,styrene} \bullet 100$ (equiv.) + $M_{n,Di\text{-}AA}$ =10845 g/mol, SEC results: $M_{n,SEC}$ = 7200 g/mol, $M_{w,SEC}$ = 7800 g/mol, PDI = 1.09. – ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.19 – 1.44 (m, CH_3), 1.66 – 1.95 (m, CH_2), 6.39 – 6.69 (m, aryl-CH), 6.97 – 7.35 (m, aryl-CH). – IR (ATR):
$\tilde{\nu}$ (cm^{-1}) = 3081 (vw), 3061 (vw), 3025 (m), 2925 (s), 2847 (m), 2362 (w), 2337 (w), 1601 (m), 1584 (w), 1496 (s), 1454 (s), 1374 (vw), 1183 (vw), 1158 (vw), 1069 (m), 1029 (m), 982 (vw), 966 (vw), 909 (m), 842 (w), 756 (s), 696 (vs), 622 (vw), 539 (s).
The polymerization reaction was followed by ^{1}H-NMR and SEC (**Figure S1**). To monitor the reaction process, samples were taken after a certain reaction time. Through the ^{1}H NMR spectra, the conversion of styrene to polystyrene could be calculated by comparing the integration of two vinyl protons of the remaining styrene at 5.70 ppm and 5.18 ppm with the integration of the range 6.75–7.15 ppm containing five aromatic protons of the formed polymer., the molecular weight and the dispersity were determined by SEC (**Table S3**).

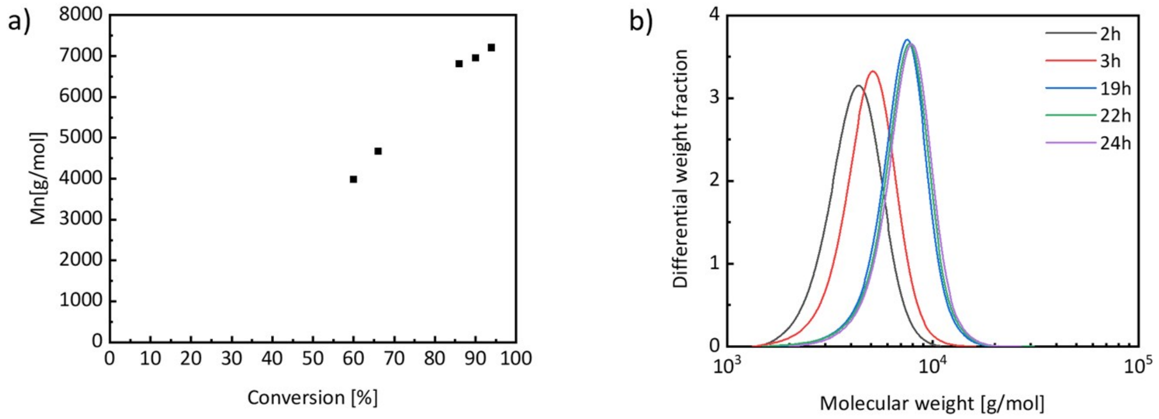


Figure S1: a) Molecular weight as a function of the conversion for **DiPS1**. b) SEC traces for the nitroxide mediated polymerization of styrene related to **Table S3**.

After 24 hours, the reaction of **DiPS1** is 94% converted with a molecular weight of 7200 g/mol and dispersity of 1.09. These indicate a very controlled polymerization. However, the final molecular weight only reached 70% of the theoretical molecular weight.

Table S3: Conversion, molecular weight, and dispersity of **DiPS1** with 100 equiv. styrene at different reaction times.

Time [h]	**Conversion [%]**	***M*$_n$ [g/mol]**	***Đ***
2	60	3900	1.09
3	66	4600	1.10
19	86	6800	1.09
22	90	6900	1.09
24	94	7200	1.09

Synthesis of STEM network **[2+4]P**: A mixture of **DiPS1** (0.20 g, 0.028 mmol, 2.00 equiv.) and **Tetra-NO** (0.019 g, 0.014 mmol, 1.00 equiv.) was dissolved in DCM (1 mL) and added to a Schlenk tube. Subsequently, the DCM was distilled off using a rotary evaporator. The remaining DCM was then removed in vacuum. After removing of DCM, the reaction mixture was degassed under vacuum and purged with argon. Afterwards, this mixture was heated and stirred for 72 h at 130 °C. The crude product was washed with THF (10 mL) to remove the unreacted starting material and by-product TEMPO. After centrifugation and intensive washing with THF (5 × 10 mL), the resulting insoluble STEM network was dried under vacuum to afford as a rufous solid (0.120 g, 56%). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3083 (vw), 3059 (w), 3027 (m), 2920 (s), 2850 (m), 2365 (s), 2338 (s), 1603 (w), 1580 (vw), 1497 (s), 1452 (s), 1370 (vw), 1310 (m), 1184 (vw), 1157 (vw), 1021 (s), 908 (m), 828 (m), 755 (s), 695 (vs), 539 (s).

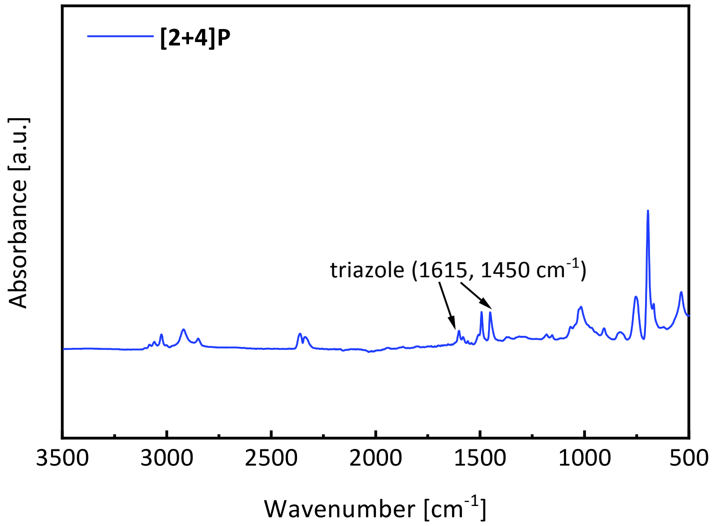


Figure S2: IR spectrum of **[2+4]P**~~.~~

Experimental description of one-pot approach (ii)

Synthesis of STEM network **[2+4]O**: **Di-AA** (0.021g, 0.048 mmol, 2.00 equiv.) and **Tetra-NO** (0.032 g, 0.024 mmol, 1.00 equiv.) were suspended under an inert atmosphere (Ar) in freeze-dried styrene (0.55 mL, 0.50 g, 4.80 mmol, 100 equiv.) and the mixture was heated for 72 h at 130 °C. The crude product was washed with in THF (15 mL) to remove the unreacted starting materials and by-product TEMPO. After centrifugation and intensive washing with THF (5 × 10 mL), the resulting insoluble STEM network was dried under vacuum and obtained as a dark yellow solid (0.199 g, 0.0088 mmol, 37%). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3083 (vw), 3060 (w), 3026 (m), 2925 (s), 2854 (m), 2366 (s), 2338 (s), 1777 (s), 1727 (w), 1601 (m), 1514 (w), 1493 (s), 1452 (s), 1362 (m), 1312 (vw), 1232 (w), 1163 (m), 1121 (w), 1067 (m), 1032 (m), 995 (m), 927 (vw), 908 (w), 828 (m), 755 (s), 697 (vs), 542 (s).

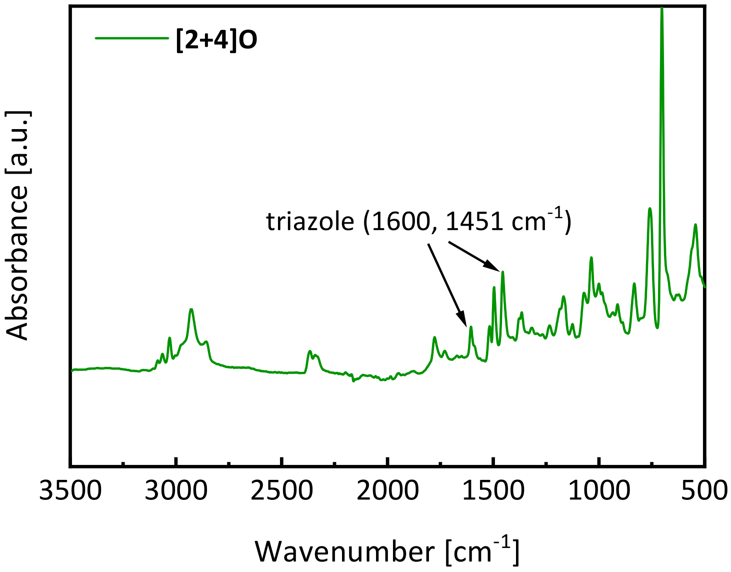


Figure S3. IR spectrum of the **[2+4]O** network.

The washing solution from the crude product was stored and additionally investigated with NMR after precipitation in MeOH. Since the precipitate contains just a slight amount of **Tetra-NO** and TEMPO by-product, the NMR spectrum (**Figure S4**) displays only the signal of polystyrene.

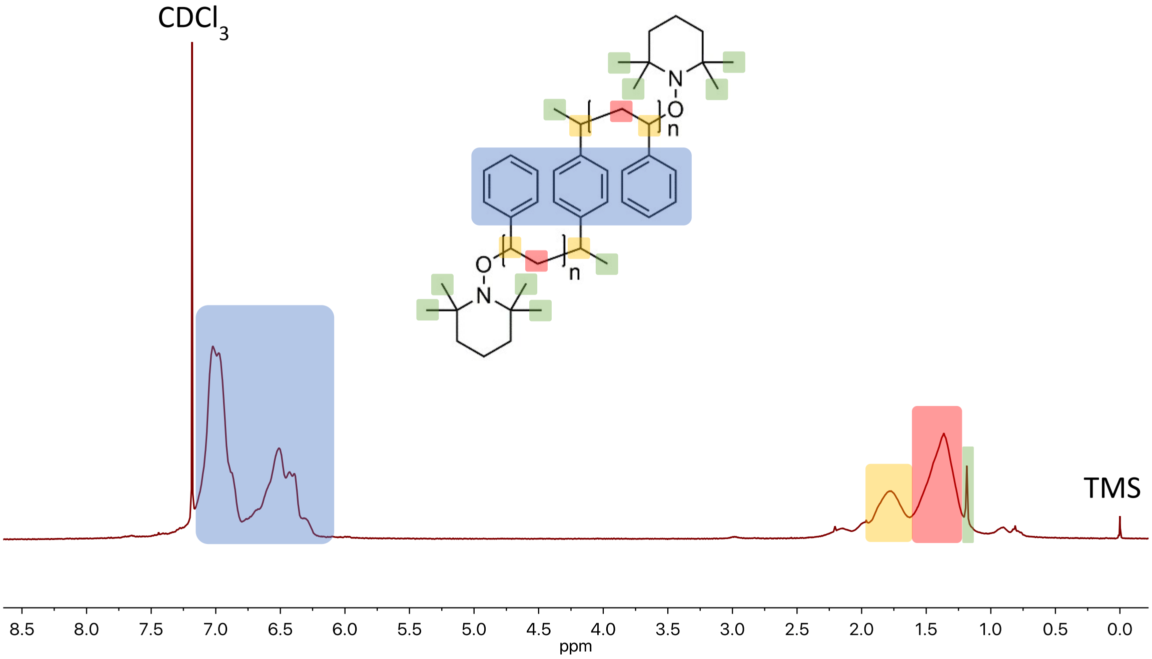
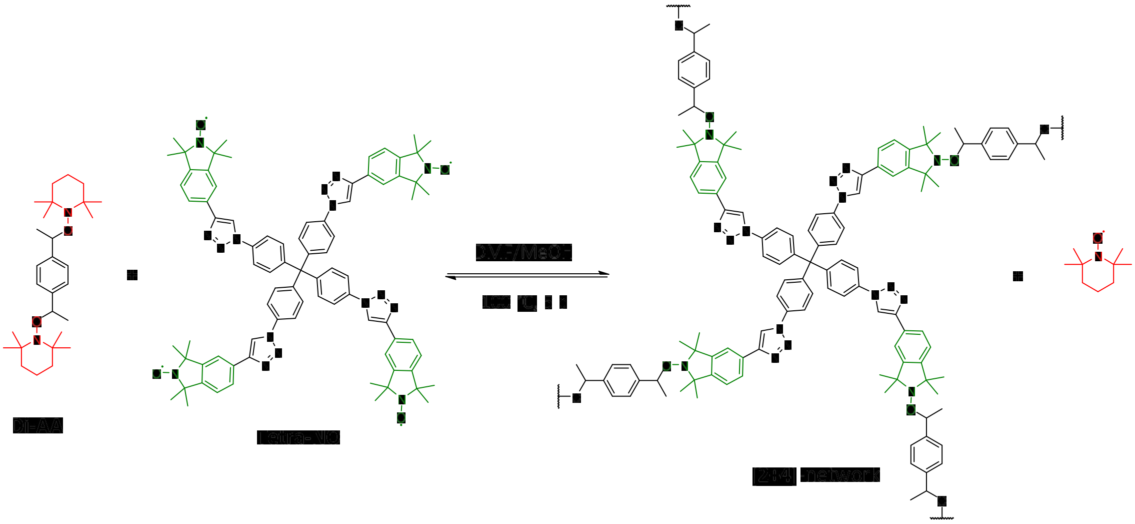


Figure S4. ^{1}H NMR spectrum of the THF washing solution after precipitation in MeOH.

Experimental description of NER followed by NMP approach (iii)



Scheme S2: Synthesis of **[2+4]** network with **Di-AA** and **Tetra-NO**.

Synthesis of the **[2+4]** network: A mixture of **Di-AA** (0.042 g, 0.095 mmol, 2.00 equiv.) and **Tetra-NO** (0.063g, 0.047 mmol, 1.00 equiv.) in a vial was degassed under vacuum and purged with Argon. Subsequently, in an oxygen-free glovebox, the mixture was dissolved in 1 mL solution of DMF/methanol mixture (9/1). The vial was sealed and placed in an oven for 5 days at 100 °C. Afterwards, the resulting network was washed with toluene (5 × 3 mL) to remove the in situ released TEMPO by-product. After washing and drying under vacuum the **[2+4]** network was obtained as a beige solid (0.0535 g, 0.046 mmol, 98% yield). $M_{n,[2+4]} = M_{n,\text{Di-AA}} \bullet 2 + M_{n,\text{Tetra-NO}} - 4 \bullet M_{n,\text{TEMPO}}$ = 1161 g/mol. – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2975 (vs), 2929 (s), 2867 (m), 2363 (s), 2337 (s), 1664 (m), 1606 (s), 1514 (vs), 1485 (s), 1443 (s), 1407 (m), 1378 (s), 1316 (m), 1293 (m), 1263 (m), 1228 (s), 1184 (w), 1165 (m), 1121(m), 1067 (s), 1036(vs), 999 (s), 981 (w), 886 (s), 829(vs), 789 (s), 746, 731, 715, 697 (m), 669 (w), 637 (m), 616 (m), 549 (vs), 512, 500 (m).

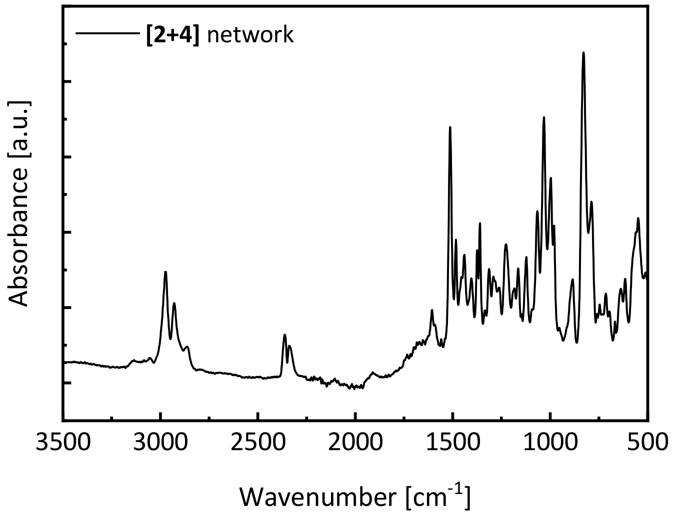


Figure S5. IR spectra of the **[2+4]** network.

Synthesis of STEM network **[2+4]E**: The native **[2+4]** network (0.0114 g, 0.0095 mmol, 1.00 equiv.) was suspended under an inert atmosphere (Ar) in freeze-dried styrene (0.22 mL, 0.20

g, 1.9 mmol, 200 equiv.) and mesitylene (0.10 mL). The reaction mixture was heated for 72 h at 130 °C. Afterwards, the crude product was dissolved in THF (10 mL) to remove the unreacted starting materials. After centrifugation and intensive washing with THF (5 × 10 mL), the resulting insoluble STEM network was dried under vacuum and obtained as a yellow solid (0.108 g, 0.0049 mmol, 52%). – IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3085 (vw), 3060 (w), 3023 (m), 2922 (s), 2852 (m), 2366 (s), 2339 (s), 1727 (vw), 1713 (vw), 1602 (m), 1496 (s), 1452 (s), 1371 (w), 1316 (vw), 1235 (vw), 1184 (w), 1159 (w), 1119 (vw), 1064 (m), 1027 (s), 964 (m), 928 (m), 909 (m), 833 (m), 754 (s), 697 (vs), 669 (w), 620 (vw), 539 (s).

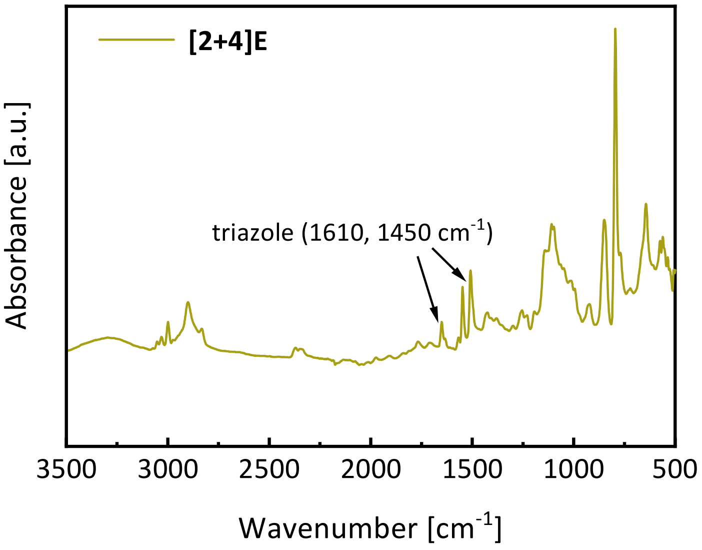


Figure S6. IR spectrum of the **[2+4]E** network.

The soluble parts from the synthesis of this network were investigated with EPR spectroscopy. Since the native **[2+4]** network was annealed before the polymerization, the washing solution from **[2+4]E** network should be EPR silence (**Figure S7a).** The soluble part was precipitated in MeOH to recover potentially formed polystyrene. Those polystyrene were polymerized in an uncontrolled way according to the SEC result (**Figure S7b**).

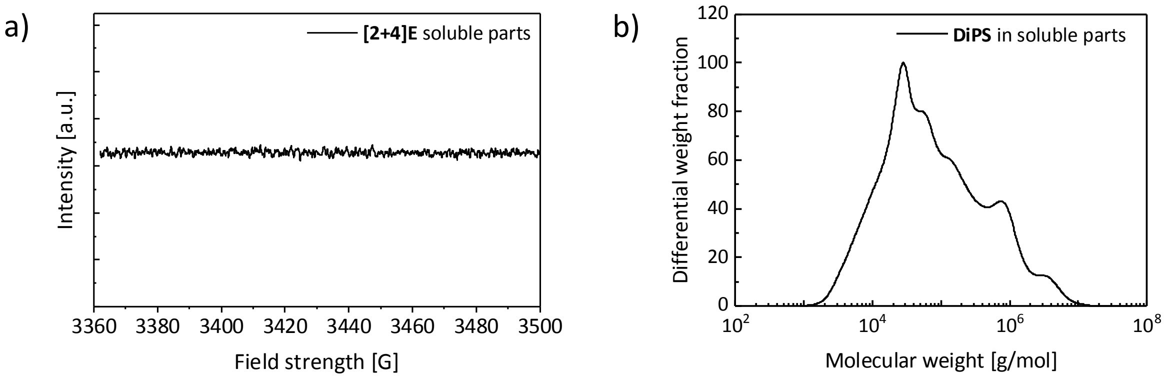


Figure S7. a) EPR spectrum of the washing solution from the crude product. b) SEC results of the soluble parts.

Dissolution of STEM networks for SEC evaluation of strand length

For STEM networks dissolution, a mixture of 10 mg STEM and 0.25 g TEMPO was degassed under vacuum and purged with Argon. Subsequently, in an oxygen-free glove box 0.5 mL DMF was added to the mixture. The mixture was sealed and placed in an oven at 100 °C until total dissolution of STEM, usually three days. Afterwards, the resulting polystyrene was precipitated into cold MeOH and collected after centrifugation. After washing and drying in vacuum, the polystyrene of the different samples were analyzed by SEC.

Swelling experiment

The swelling experiments of **[2+4]**-STEMs from different approaches and the **[2+4]** network were performed in THF. The dried samples were weighed on an analytical balance and was moved into a glass vial, which would be filled with THF at room temperature. The weight of the swollen gel was measured after 5 days. The swelling degree (Q) can be calculated using **equation S1**. Accordingly, the swelling degree was calculated and displayed in **Figure S8**.

$$Q = \frac{W_w - W_d}{W_d} \cdot 100$$ **equation S1**

Where W_w and W_d represent the weight of wet and dried networks.

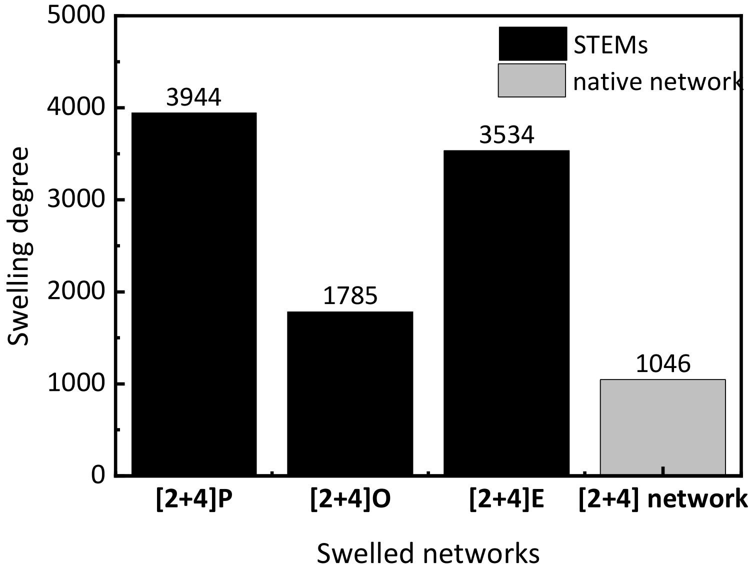


Figure S8. Swelling degree of **[2+4]**-STEMs and **[2+4]** network in THF.

Crosslinking efficiency

Using EPR spectroscopy (**Figure S9**), we were able to determine the defect density in native **[2+4]** network and STEM networks, since only unreacted moieties of the **Tetra-NO** crosslinker are EPR active, while the reacted moieties form alkoxyamines, which are EPR silent.

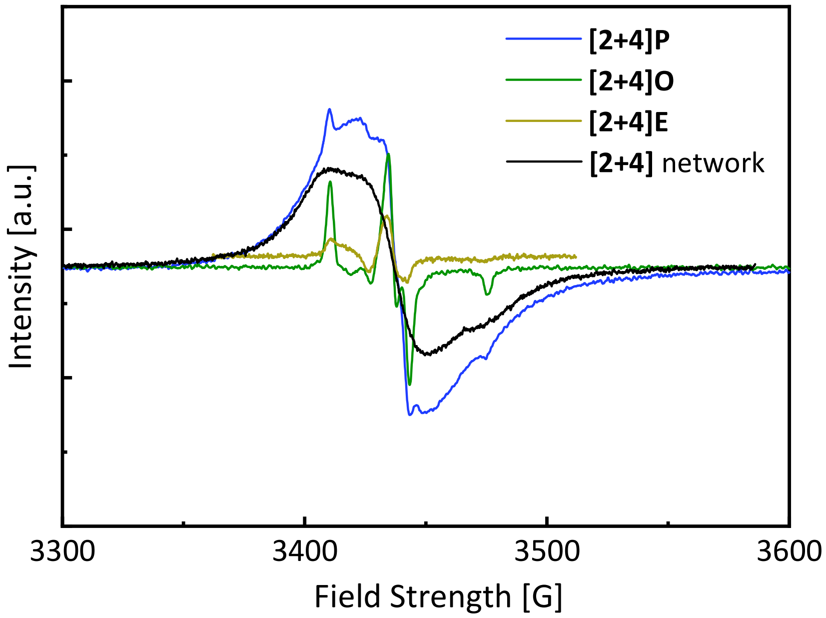


Figure S9. EPR spectra of **[2+4]** network and three different **[2+4]**-STEM networks.

Therefore, determining the spin count in EPR provides a direct measure of the number of defect sites in the networks. From the number of defect sites, the crosslinking efficiency (CLE) can be calculated using **equation S2** and **equation S3**.

$$S_{0\%CL} = \frac{m_{STEM}}{M_s} \cdot N_A \cdot x \qquad \textbf{equation S2}$$

$$CLE = 100 - 100 \cdot (S_{STEM} / S_{0\%CL}) \qquad \textbf{equation S3}$$

The spin count of a 1:2 mixture of the starting materials with 0% crosslinking is given as $S_{0\%CL}$, which can be calculated out of the applied mass m_{STEM} of the measured STEM. M_s is the molecular weight of the employed starting materials and N_A is the Avogadro`s constant. The x refers to the number of spins per crosslinker, in our case, $x = 4$. S_{STEM} represents the EPR spin count of the investigated STEM network. **Table S4** summarizes the obtained values for $S_{0\%CL}$, S_{STEM}, and CLE of the STEM networks.

Table S4: The summary of the substantial variables for the calculation of the CLE of STEMs.

STEM networks	**m_{STEM} [mg]**	**M_s [g/mol]**[a]	**$S_{0\%CL}$**	**S_{STEM}**	**CLE [%]**
[2+4]P	10.4	15742	$1.6 \cdot 10^{18}$	$8.8 \cdot 10^{16}$	94.5
[2+4]O	6.4	9942	$1.6 \cdot 10^{18}$	$5.3 \cdot 10^{15}$	99.7
[2+4]E	9.3	15742	$1.4 \cdot 10^{18}$	$4.2 \cdot 10^{15}$	99.7

[a] Calculated from the molecular weight of building blocks: $M_s = 2 \cdot M_{DiPS} + M_{Tetra\text{-}NO}$, M_{DiPS} is the apparent number average molecular weight of **DiPS**.

Additional extension of STEM networks

Extension of STEM network [2+4]P to [2+4]PE:

[2+4]P (0.0112 g) was suspended under an inert atmosphere (Ar) in freeze-dried styrene (1.10 mL, 1.00 g, 9.60 mmol) and mesitylene (1.00 mL). The reaction mixture was heated for 48 h at 130 °C. The reaction mixture was token and suspended in THF (10 mL) to remove the unreacted starting materials and byproducts. After centrifugation and intensive washing with THF (5 × 10 mL), the resulting insoluble products was dried under vacuum and obtained as yellow solid (0.107 g).

Extension of STEM network [2+4]O to [2+4]OE:

[2+4]O (0.0116 g) was suspended under an inert atmosphere (Ar) in freeze-dried styrene (1.10 mL, 1.00 g, 9.60 mmol) and mesitylene (1.00 mL). The reaction mixture was heated for 48 h at 130 °C. The reaction mixture was token and suspended in THF (10 mL) to remove the unreacted starting materials and byproducts. After centrifugation and intensive washing with THF (5 × 10 mL), the resulting insoluble products was dried under vacuum and obtained as yellow solid (0.103 g).

Dissolution of extended STEM networks for SEC evaluation of strand length

A mixture of 10 mg STEM and 0.25 g TEMPO was degassed under vacuum and purged with Argon. Subsequently, in an oxygen-free glove box 0.5 mL DMF was added to the mixture. The mixture was sealed and placed in an oven at 100 °C until total dissolution of STEM, usually three days. Afterwards, the resulting polystyrene was precipitated into cold MeOH and collected after centrifugation. After washing and drying in vacuum, the polystyrene of the different samples were analyzed by SEC.

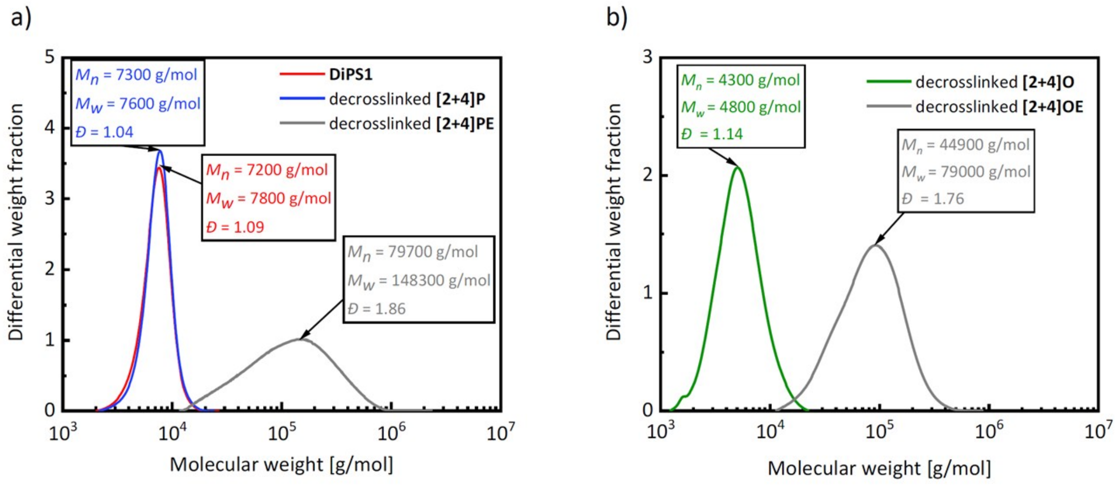


Figure S10. a) SEC results of polystyrenes DiPS1, decrosslinked [2+4]P network and decrosslinked [2+4]PE network after additional extension; b) SEC results of decrosslinked [2+4]O network and decrosslinked [2+4]OE network after additional extension.

Table S5

Network	m[2+4] (g)	n(alkoxyamine) mol[a]	Styrene equivalents (N(styr))[b]	M_n (th) [g/mol][c]	M_n *(exp)* [g/mol][d]	Styrene conversion (%)[e]
[2+4]PE	0.0112	$2.85*10^{-6}$	6747	708933	79700	10.2
[2+4]OE	0.0116	$4.67*10^{-6}$	4115	432235	44900	8.7

$^{a}\ n(alkoxyamine) = \dfrac{m[2+4]}{0.5 * Mn(PS) + 0.25 * Mn(TetraNO)}$

$^{b}\ N(Styr) = \dfrac{n(styr)}{n(alkoxyamine)}{*2}$

$^{c}\ Mn\,(th) = Mn([2+4]) + N(Styr) * M(Styr)$

^{d} Determined by SEC after decrosslinking

$^{e}\ conversion\,(Styr) = \dfrac{Mn\,(exp) - Mn\,[2+4]}{Mn(th)} *100$

Table S6

Network	m[2+4] (g)	m[2+4]E (g)	n_i*(Styr) incorporated*[a]	Styrene conversion (%)[b]	Styrene equivalents (N(styr))[c]	M_n *(cal)* [g/mol][d]	M_n *(exp)* [g/mol][e]
[2+4]PE	0.0112	0.107	0.000921	9.6	647	74534	79700
[2+4]OE	0.0116	0.103	0.000879	9.2	377	46376	44900

$^{a}\ n_i(styr) = \dfrac{m[2+4]E - m[2+4]}{M(Styr)}$

$^{b}\ conversion\,(Styr) = \dfrac{n_i(Styr)}{n_0(Styr)} * 100$

$^{c}\ N(Styr) = \dfrac{n_i(styr)}{n(alkoxyamine)}{*2}$

^{d} M_n(calc) = M_n[2+4]+N(Styr)*M(Styr)

^{e} Determined by SEC after decrosslinking

The in situ polymerization of styrene in the network **[2+4]P** and **[2+4]O** was investigated to show the “livingness” of our system. The native networks were put in the presence of an excess of styrene. For more details, see Table S5. After decrosslinking in the presence of TEMPO, the molecular weights of the strands were determined by SEC. The increase from 7200 g/mol to 79 700 g/mol for **[2+4]P** and from 4300 g/mol to 44900 g/mol for **[2+4]O** showed the success of this post-modification. In both cases, this increase corresponds to a conversion of styrene of around 10%, which could be enhanced by using a longer reaction time. A styrene conversion of around 10% was also determined gravimetrically (Table S6). The molecular weights calculated from these data were in good agreements with the experimental data measured by SEC after decrosslinking, i.e. 74 534 g/mol against 79 700 g/mol for **[2+4]P** and 46 376 g/mol against 44 900 g/mol for **[2+4]O.**

[1] M. Goto, B. J. McCoy, *Chemical Engineering Science* **2000**, *55*, 723-732.