

Supplementary Information

Visible-Light-Induced ATRP under High-Pressure: Synthesis of Ultra-High-Molecular-Weight Polymers

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Supplementary Information

Table of contents

| | |
|--|----------|
| Materials | 3 |
| Instruments | 3 |
| Nuclear magnetic resonance spectroscopy (NMR)..... | 3 |
| Size exclusion chromatography Low-Angle Laser Light Scattering (SEC-LALLS) | 3 |
| Procedures | 3 |
| General procedures for EY/Cu-catalyzed ATRP of OEOMA ₅₀₀ | 3 |
| General procedures for EY/Cu-catalyzed ATRP of HEA..... | 5 |
| Polymerizations | 6 |
| Chain-extension polymerization | 6 |
| Figure S1. High-pressure setup | 7 |
| Figure S2. ¹ H (a) and ¹³ C (b) NMR spectra of the synthesized P(OEOMA ₅₀₀) <i>via</i> HP&LI ATRP..... | 8 |
| Figure S3. The semilogarithmic kinetic plots as a function of time for OEOMA ₅₀₀ HP&LI ATRP at different pressure values. | 9 |
| Figure S4. Conversion <i>vs</i> polymerization time plots for OEOMA ₅₀₀ HP&LI ATRP at different pressure values..... | 10 |
| Figure S5. Pressure dependence of K _{ATRP} for HP&LI ATRP of OEOMA ₅₀₀ | 11 |
| Figure S6. SEC-LALLS traces of the P(OEOMA ₅₀₀) synthesized <i>via</i> HP&LI ATRP. | 12 |
| Figure S7. SEC-LALLS traces of P(OEOMA ₅₀₀) (a) and P(OEOMA ₅₀₀)- <i>bl</i> -P(OEOMA ₅₀₀) (b) obtained <i>via</i> HP&LI ATRP | 13 |
| Figure S8. ¹ H NMR spectra of the chain-extension polymerization mixture of OEOMA ₅₀₀ -P(OEOMA ₅₀₀). | 14 |
| Table S1. Results of OEOMA ₅₀₀ HP&LI ATRP at different conditions. | 15 |
| Table S2. Results of HEA HP&LI ATRP at different conditions..... | 15 |
| Figure S9. ¹ H NMR spectra of the synthesized PHEA <i>via</i> HP&LI ATRP. | 16 |
| Figure S10. SEC-LALLS traces of the PHEA obtained <i>via</i> HP&LI ATRP with TPMA (a) and Me ₆ TREN (b) as a catalyst. | 17 |

Supplementary Information

Materials

All chemicals were purchased from Sigma-Aldrich. Tris(2-pyridylmethyl)amine (TPMA, 98%), tris[2-(dimethylamino)ethyl]amine (**Me₆TREN**), Eosin Y (**EYH₂**, 99%), copper (II) bromide (**CuBr₂**, 99%), ethyl α -bromoisobutyrate (**EBiB**, 98%) and Dulbecco's Phosphate Buffered Saline (**PBS**, pH=7.1 - 7.5) were purchased from *Sigma-Aldrich*. Poly(ethylene glycol) methyl ether methacrylate (average $M_n = 500$, **PEOMA₅₀₀**) and 2-hydroxyethyl acrylate (**HEA**) were purchased from *Sigma-Aldrich* and passed through a basic alumina column to remove the inhibitor prior to use. Dimethyl sulfoxide (**DMSO**, $\geq 99.7\%$) were purchased from *Chempur*. Water was purified using automatic distillation apparatus (DE 5, *Polna*) prior to use.

Instruments

Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance (¹H and ¹³C NMR) spectra were collected using a Bruker Ascend 500 MHz spectrometer in D₂O as a solvent. Standard experimental conditions and the standard Bruker program were used.

Size exclusion chromatography Low-Angle Laser Light Scattering (SEC-LALLS)

Molecular weights and dispersities were determined by size exclusion chromatography (SEC) with Viscotek GPC Max VE 2001 and a Viscotek TDA 305 triple detection system (refractometer, viscosimeter and low angle laser light scattering) was used for data collection and OmniSec 5.12 for processing. Two T6000M general mixed columns were used for separation. The measurements were carried out in DMF/LiBr (0.01M) as an eluent at 303 K with a flow rate of 0.7 mL/min. The apparatus was used in a triple detection mode, and the absolute molar mass (M_n and M_w) and the dispersity (\mathcal{D}) were determined by triple detection (estimated $dn/dc=0.05$ for P[OEOMA]₅₀₀; $dn/dc=0.079$ for PHEA). Due to obtaining polymers with WHMW and UHMW before performing SEC-LALLS measurements, approximately 1 mg of polymer was dissolved in 1 mL of DMF+LiBr solution. We did double check of the MW using GPC-LALLS, analyzing the sample dissolved in DMF after several days and a month. This allowed us to obtain reliable data.

Procedures

General procedures for EY/Cu-catalyzed ATRP of OEOMA₅₀₀

[OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 200/1/0.005/0.2/0.6; 10% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (16.75 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO) and EYH₂ (9.7 mg in 10 mL DMSO)

Supplementary Information

were prepared. The ATRP cocktail was then prepared as follows. In a 4 mL dark-glass vial, 600 mg of OEOMA₅₀₀ was weighed. Subsequently, CuBr₂ stock (160 μ L), TPMA stock (80 μ L), EBiB stock (100 μ L), EYH₂ stock (20 μ L), DMSO (40 μ L) and PBS solution (400 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were OEOMA₅₀₀ (300 mM), EBiB (1.5 mM), EYH₂ (7.5 μ M), CuBr₂ (0.3 mM), TPMA (0.9 mM), DMSO (10% v/v).

[OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 1000/1/0.0025/1/1.5; 30% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO) and EYH₂ (9.7 mg in 10 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. In a 4 mL dark-glass vial, 600 mg of OEOMA₅₀₀ was weighed. Subsequently, CuBr₂ stock (100 μ L), TPMA stock (40 μ L), EBiB stock (20 μ L), EYH₂ stock (2 μ L), DMSO (1.040 mL) and PBS solution (80 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were OEOMA₅₀₀ (300 mM), EBiB (0.3 mM), EYH₂ (0.75 μ M), CuBr₂ (0.3 mM), TPMA (0.45 mM), DMSO (30% v/v).

[OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 10000/1/0.0025/1/1.5; 30% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO) and EYH₂ (0.97 mg in 10 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. In a 4 mL dark-glass vial, 600 mg of OEOMA₅₀₀ was weighed. Subsequently, CuBr₂ stock (10 μ L), TPMA stock (4 μ L), EBiB stock (2 μ L), EYH₂ stock (2 μ L), DMSO (1.182 mL) and PBS solution (8 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were OEOMA₅₀₀ (300 mM), EBiB (0.03 mM), EYH₂ (0.075 μ M), CuBr₂ (0.03 mM), TPMA (0.045 mM), DMSO (30% v/v).

[OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 30000/1/0.0025/1/1.5; 30% DMSO

Prior to polymerization, stock solutions of EBiB (0.88 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (1.31 mg in 1.0 mL DMSO) and EYH₂ (9.7 μ g in 1 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. In a 4 mL dark-glass vial, 600 mg of OEOMA₅₀₀ was weighed. Subsequently, CuBr₂ stock (3.33 μ L), TPMA stock (13.33 μ L), EBiB stock (6.67 μ L), EYH₂ stock (6.67 μ L), DMSO (1.184 mL) and PBS solution (8 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were OEOMA₅₀₀ (300 mM), EBiB (0.01 mM), EYH₂ (0.025 μ M), CuBr₂ (0.01 mM), TPMA (0.015 mM), DMSO (30% v/v).

Supplementary Information

General procedures for EY/Cu-catalyzed ATRP of HEA

[HEA]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[Cat]₀: 200/1/0.005/0.2/0.6; 30% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO), Me₆TREN (12.06 μ L in 1.0 mL DMSO) and EYH₂ (9.7 mg in 10 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. 137.8 μ L of HEA was placed in a 4 mL dark-glass vial. Subsequently, CuBr₂ stock (100 μ L), TPMA/Me₆TREN stock (80 μ L), EBiB stock (100 μ L), EYH₂ stock (20 μ L), DMSO (900 μ L) and PBS solution (400 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were HEA (300 mM), EBiB (1.5 mM), EYH₂ (7.5 μ M), CuBr₂ (0.3 mM), TPMA/Me₆TREN (0.9 mM), DMSO (30% v/v).

[HEA]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[Cat]₀: 1000/1/0.0025/1/1.5; 30% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO), Me₆TREN (12.06 μ L in 1.0 mL DMSO) and EYH₂ (9.7 mg in 10 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. 137.8 μ L of HEA was placed in a 4 mL dark-glass vial. Subsequently, CuBr₂ stock (100 μ L), TPMA/Me₆TREN stock (40 μ L), EBiB stock (20 μ L), EYH₂ stock (2 μ L), DMSO (1.040 mL) and PBS solution (80 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were HEA (300 mM), EBiB (0.3 mM), EYH₂ (0.75 μ M), CuBr₂ (0.3 mM), TPMA/Me₆TREN (0.45 mM), DMSO (30% v/v).

[HEA]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 10000/1/0.0025/1/1.5; 30% DMSO

Prior to polymerization, stock solutions of EBiB (8.8 μ L in 1.0 mL DMSO), CuBr₂ (26.88 mg in 10.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO), Me₆TREN (12.06 μ L in 1.0 mL DMSO) and EYH₂ (0.97 mg in 10 mL DMSO) were prepared. The ATRP cocktail was then prepared as follows. 137.8 μ L of HEA was placed in a 4 mL dark-glass vial. Subsequently, CuBr₂ stock (10 μ L), TPMA/Me₆TREN stock (4 μ L), EBiB stock (2 μ L), EYH₂ stock (2 μ L), DMSO (1.182 mL) and PBS solution (8 μ L) were added. Finally, the vial was filled with distilled water and the reaction mixture was stirred on a vortex. The final concentrations were HEA (300 mM), EBiB (0.03 mM), EYH₂ (0.075 μ M), CuBr₂ (0.03 mM), TPMA/Me₆TREN (0.045 mM), DMSO (30% v/v).

Supplementary Information

Polymerizations

The ATRP cocktail was transferred to a quartz ampoule equipped with a magnetic stirrer and sealed with two Teflon caps (**Figure S1b**). The sealed ampoule was installed in the optical pressure chamber with a sapphire window (U103, *Unipress*) allowing compression in the range of 0.1 MPa – 250 MPa (**Figure S1a**). Then, the ampoule was compressed using a pressure generator (17-4 PH/AISI 316Ti, *Sitec*) to the determined pressure conditions (**Figure S1c**). The polymerization mixture was stirred at 750 rpm under green LED light ($\lambda = 530$ nm, $9.46 \mu\text{W}/\text{mm}^2$). All experiments were carried out at 298.15 K with a constant 5 cm distance between the light source (M530L4, *ThorLabs*) and HP chamber's sapphire window (**Figure S1d**). Samples were taken and analyzed by ^1H NMR and SEC techniques.

Chain-extension polymerization

To confirm chain-end fidelity, a chain extension experiment was performed. The macroinitiator P(OEOMA₅₀₀) was synthesized with [OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀ molar ratios of 1000/1/0.0025/1/1.5 (conv. = 7 %, $M_{n\text{SEC-LALLS}} = 33\,700$, $\text{Đ} = 1.119$, sample S6). Produced sample (MI) was used to prepare an ATRP “cocktail” with OEOMA₅₀₀ monomer of [OEOMA₅₀₀]₀/[MI]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀ molar ratios of 10000/1/0.0025/1/1.5. The sample was taken from the reaction mixture after 6 h of green light irradiation which allowed for complete monomer conversion (**Figure S8**). SEC analysis demonstrated a clear shift towards higher MW without any shoulder or tailing at lower MW (**Figure 7b**) and the resulting copolymer had absolute $M_{n\text{SEC-LALLS}}=1\,234\,300$ g/mol and $\text{Đ}=1.290$.

Supplementary Information

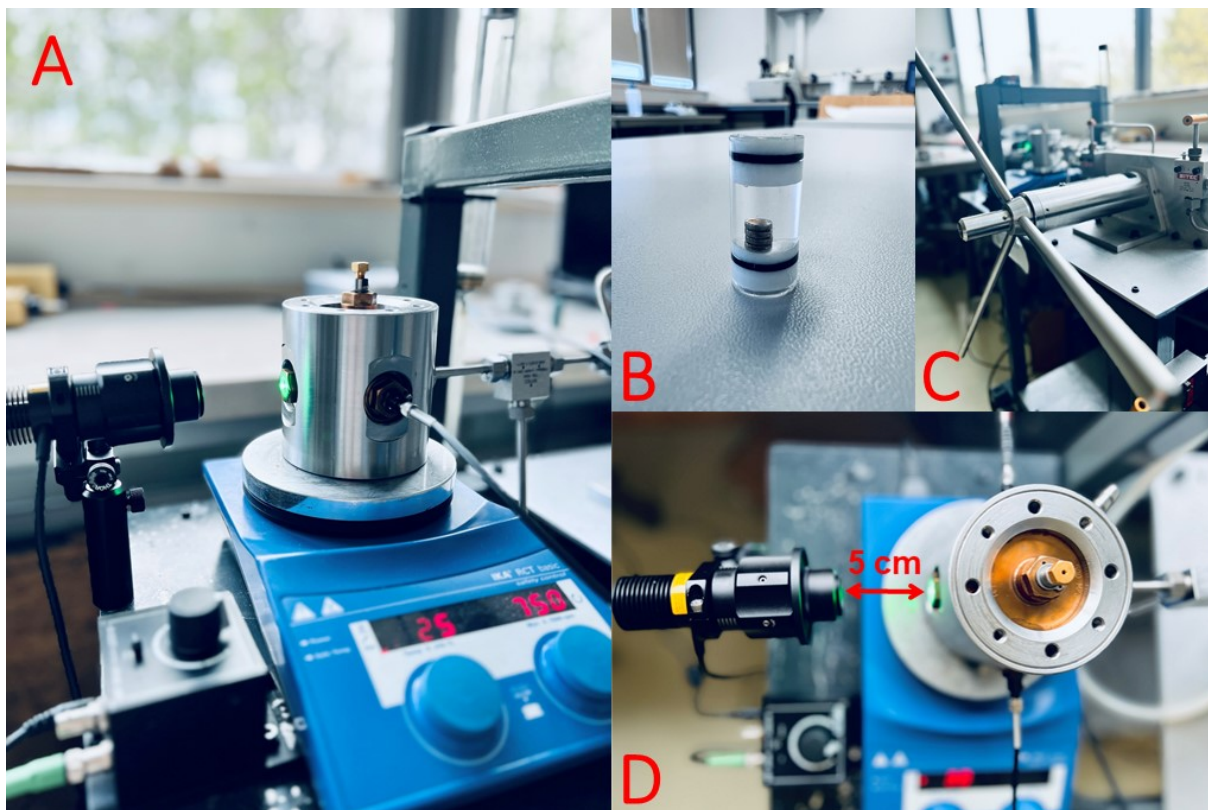


Figure S1. High-pressure setup: (a) optical pressure chamber and light source, (b) quartz ampule with a stirrer, (c) pressure generator, (d) optical pressure chamber with sapphire windows.

Supplementary Information

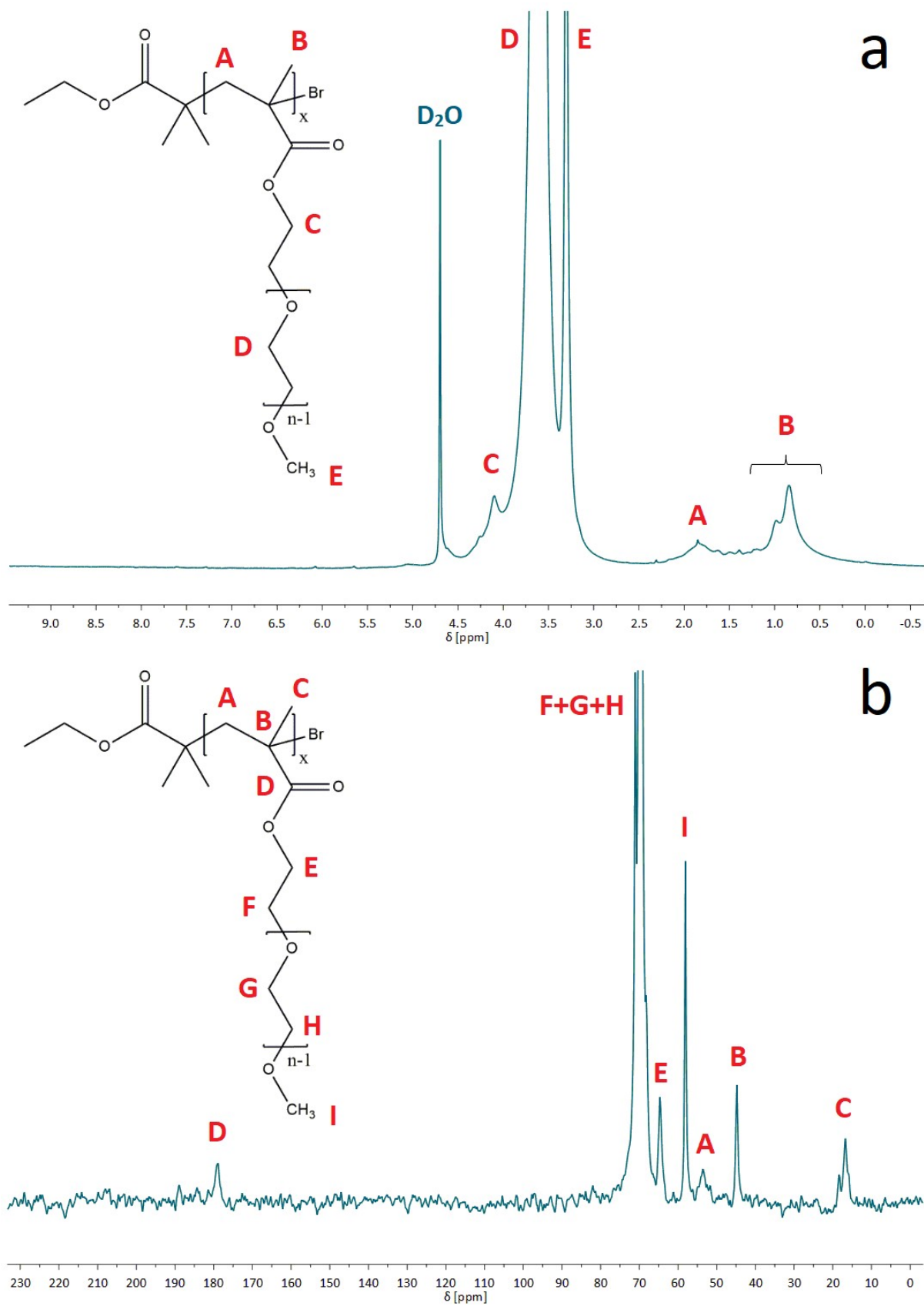


Figure S2. ^1H (a) and ^{13}C (b) NMR spectra of the synthesized P(OEOMA₅₀₀) via HP&LI ATRP.

Supplementary Information

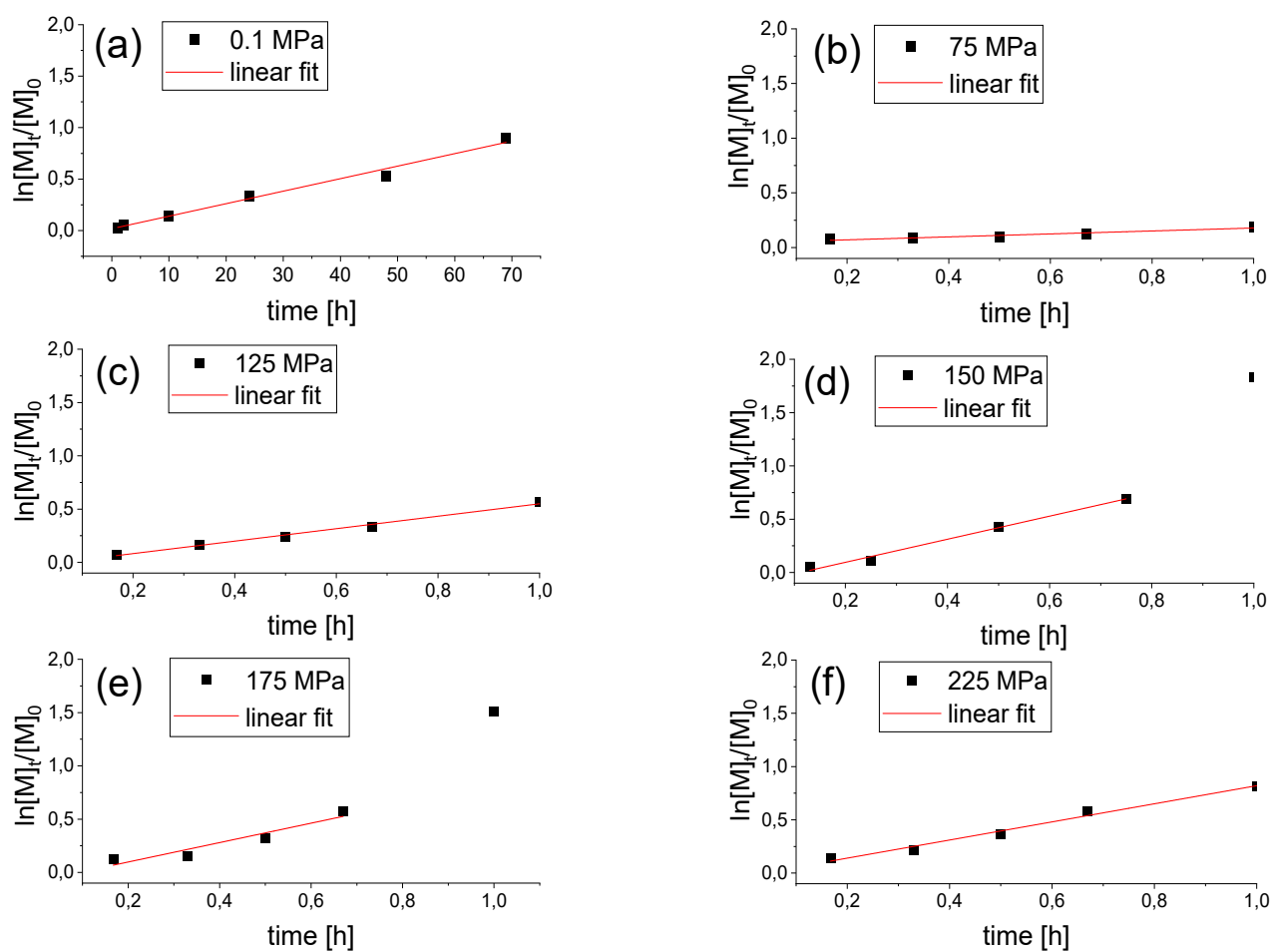


Figure S3. The semilogarithmic kinetic plots as a function of time for OEOMA₅₀₀ HP&LI ATRP at different pressure values.

Supplementary Information

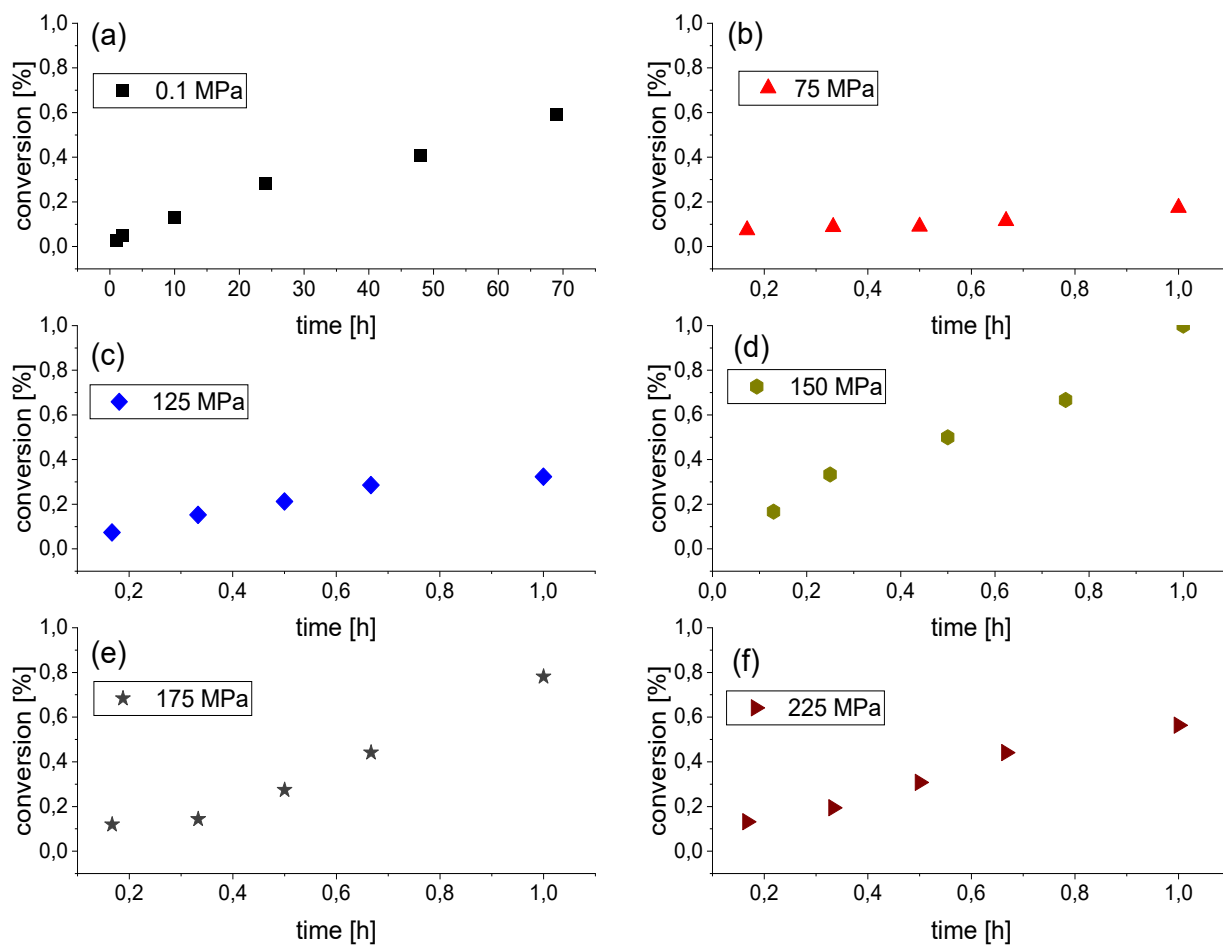


Figure S4. Conversion vs polymerization time plots for OEOMA₅₀₀ HP&LI ATRP at different pressure values.

Supplementary Information

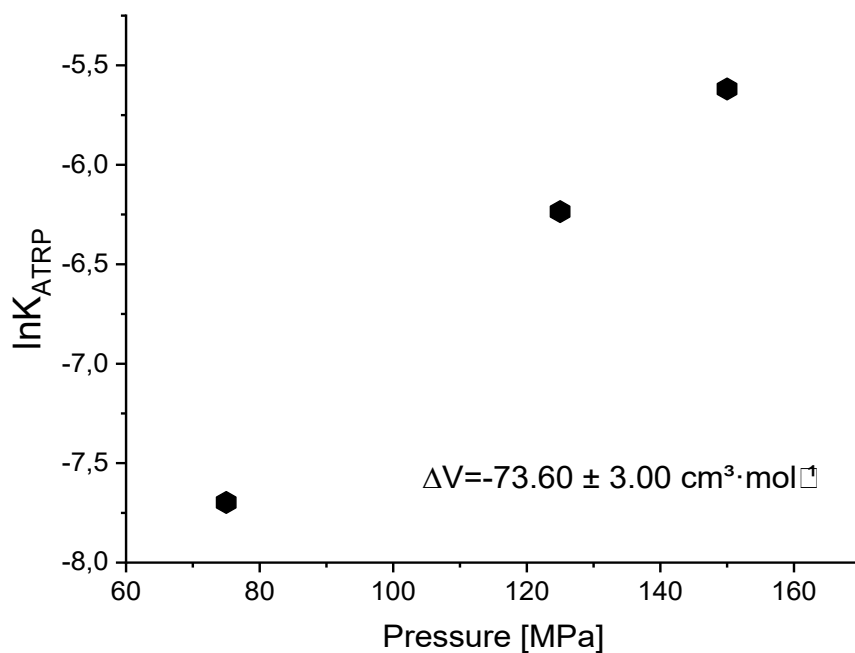


Figure S5. Pressure dependence of K_{ATRP} for HP&LI ATRP of OEOMA₅₀₀. Reaction conditions: $[\text{OEOMA}_{500}]_0/[\text{EBiB}]_0/[\text{EYH}_2]_0/[\text{CuBr}_2]_0/[\text{TPMA}]_0 = 1000/1/0.0025/1/3$. $[\text{OEOMA}_{500}] = 300 \text{ mM}$, in PBS with DMSO (30% v/v) without deoxygenation of the reaction mixture, under green LEDs irradiation (530 nm, 370 mW/cm²) at 0.1–150 MPa.

Supplementary Information

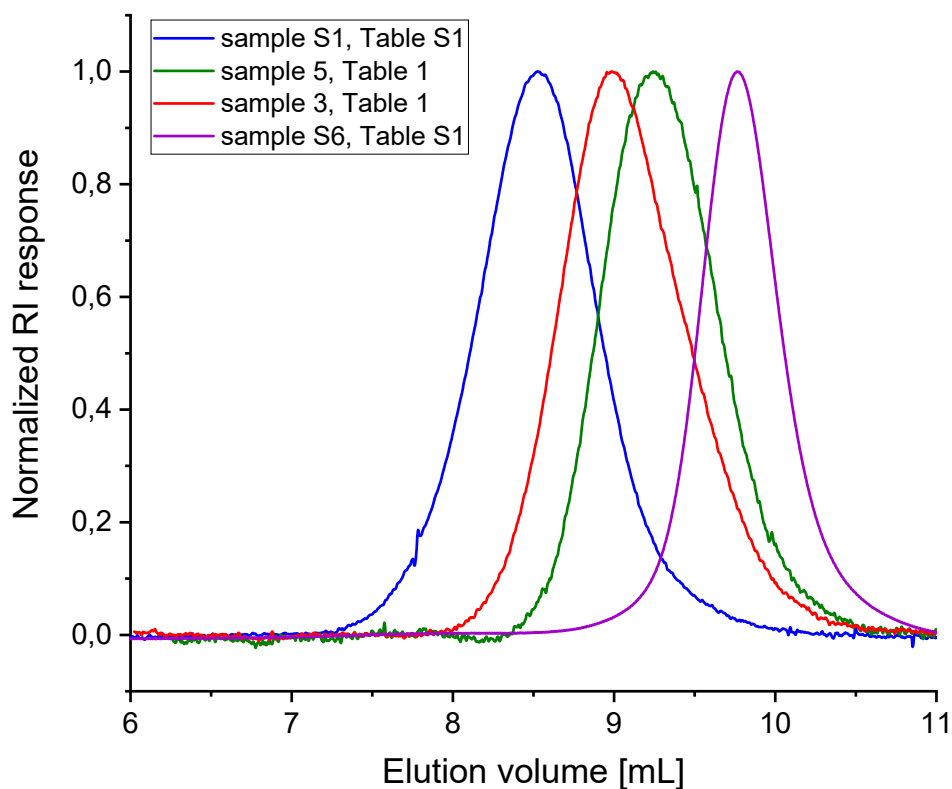


Figure S6. SEC-LALLS traces of the P(OEOMA₅₀₀) synthesized *via* HP&LI ATRP. Reaction conditions: [OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀ = 200/1/0.01/0.2/0.6 10% v/v DMSO (sample S1), 1000/1/0.0025/1/3 30% v/v DMSO (sample 5), 1000/1/0.0025/1/3 10% v/v DMSO (sample 3), 1000/1/0.0025/1/1.5 30% v/v DMSO; [OEOMA₅₀₀] = 300 mM in PBS without deoxygenation of the reaction mixture, under green LEDs irradiation (530 nm, 370 mW/cm²) at 0.1-125 MPa.

Supplementary Information

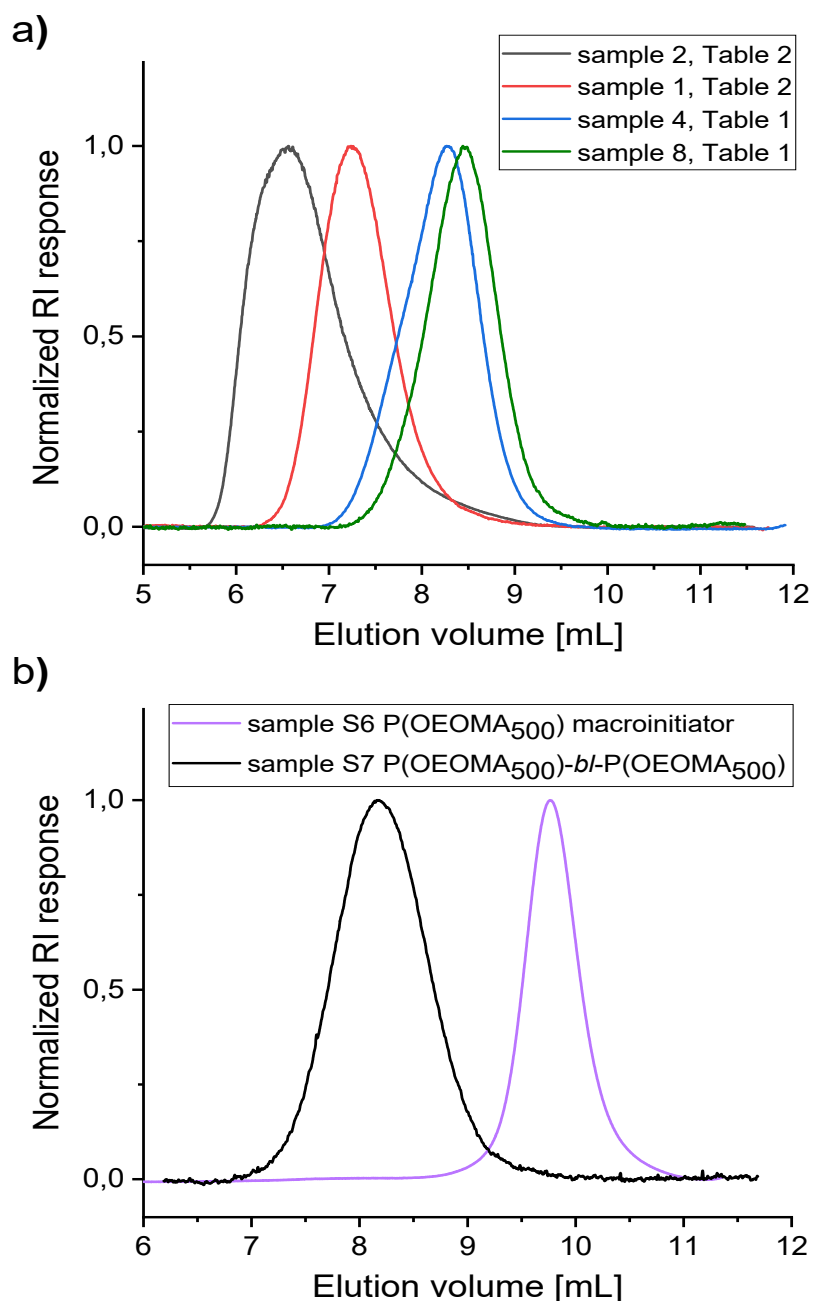


Figure S7. SEC-LALLS traces of P(OEOMA₅₀₀) (a) and P(OEOMA₅₀₀)-bl-P(OEOMA₅₀₀) (b) obtained *via* HP&LI ATRP with molar ratios of: [OEOMA₅₀₀]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀ = 1000/1/0.0025/1/3 (sample 4), 1000/1/ 0.0025/1/1.5 (sample 8), 10000/1/0.0025/ 1/1.5 (sample 1), 30000/1/0.0025/1/1.5 (sample 2). Sample S6 ($M_n=33700$, $\bar{D}=1.119$) was used as MI instead of EBiB in chain extension reaction with molar ratios of: [OEOMA₅₀₀]₀/[MI]₀/[EYH₂]₀/[CuBr₂]₀/[TPMA]₀: 10000/1 /0.0025/1/1.5. [OEOMA₅₀₀] = 300 mM, in PBS with DMSO (30% v/v) without deoxygenation of the reaction mixture, under green LEDs irradiation (530 nm, 370 mW/cm²) at 0.1-225 MPa.

Supplementary Information

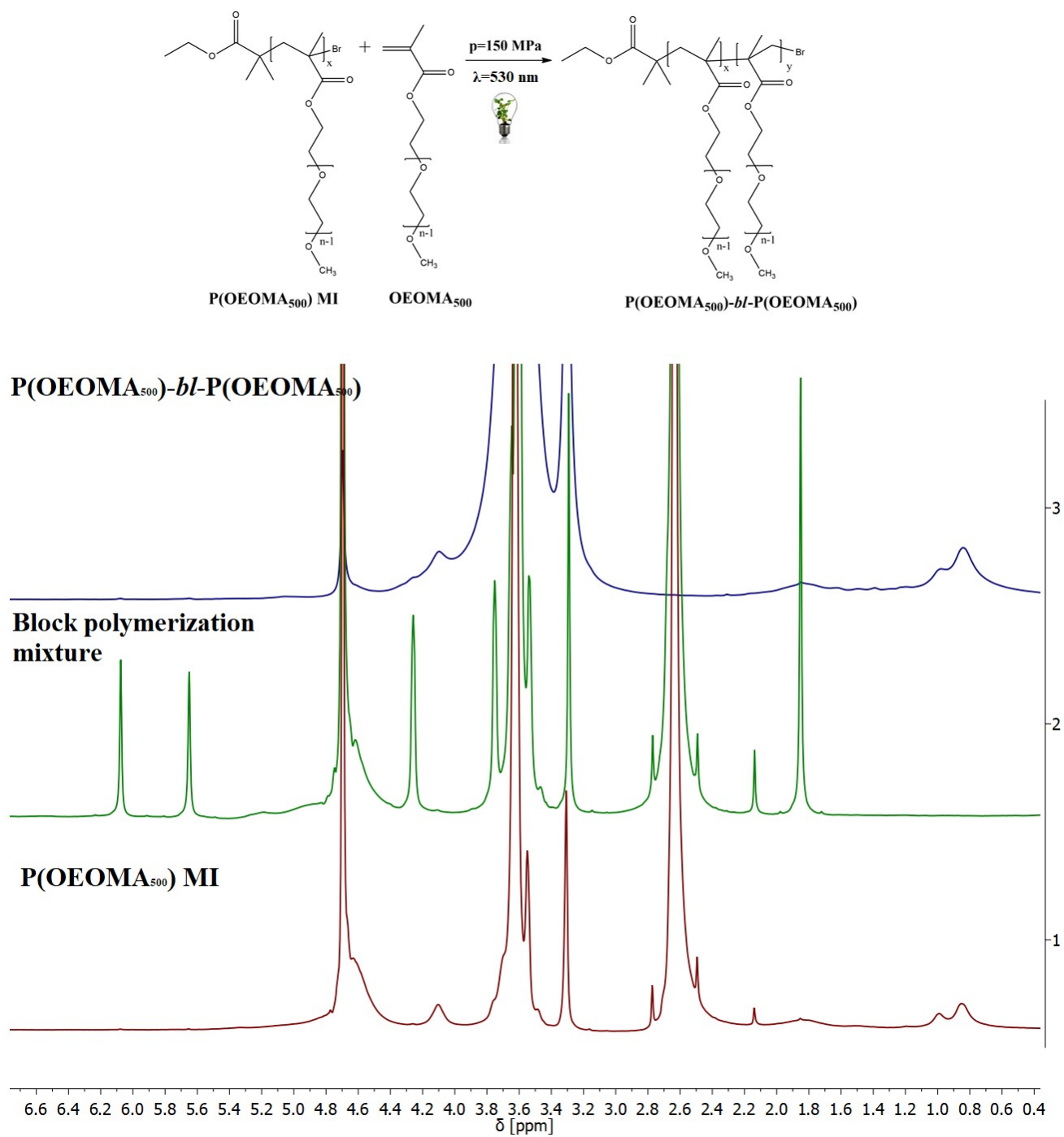


Figure S8. ¹H NMR spectra of the chain-extension polymerization mixture of OEOMA₅₀₀-P(OEOMA₅₀₀).

Supplementary Information

Table S1. Results of OEOMA₅₀₀ HP&LI ATRP at different conditions.

| No | [OEOMA ₅₀₀] ₀ /[EBiB] ₀ /[EYH ₂] ₀ /[CuBr ₂] ₀ /[TPMA] ₀ | DMSO v/v [%] | Time [h] | p [MPa] | Conv. ^a [%] | DP ^a | M _{nth} ^a | M _{nSEC-LALLS} ^b | Đ ^b |
|-----|---|--------------|----------|---------|------------------------|-----------------|-------------------------------|--------------------------------------|----------------|
| S1 | 200/1/0.01/0.2/0.6 | 10 | 0.5 | 125 | >99 | 200 | 100 000 | 121 970 | 1.473 |
| S2 | 200/1/0.005/0.2/0.6 | 10 | 0.5 | 250 | >99 | 200 | 100 000 | 101 100 | 1.512 |
| S3 | 1000/1/0.005/1/3 | 10 | 1 | 0.1 | 63 | 630 | 315 000 | 65 554 | 1.544 |
| S4 | 1000/1/0.0025/1/3 | 10 | 2 | 0.1 | 42 | 420 | 210 000 | 27 000 | 1.222 |
| S5 | 1000/1/0.0025/1/3 | 10 | 2 | 125 | 79 | 790 | 395 000 | 59 100 | 1.405 |
| S6 | 1000/1/0.0025/1/1.5 | 30 | 0.16 | 75 | 7 | 70 | 35 000 | 33 700 | 1.119 |
| S7* | 10000/1/0.0025/1/1.5 | 30 | 6 | 150 | >99 | 9900 +70 | 4 985 000 | 1 234 300 | 1.290 |

^adetermined with ¹H NMR spectroscopy; ^bdetermined by SEC with low angle light scattering detector triple detection (SEC-LALLS) assuming 100% mass recovery (DMF+LiBr); sample S6 was used instead of EBiB as the macroinitiator for HP&LI chain extension experiment with OEOMA₅₀₀ macromonomer (dn/dc=0.031)

Table S2. Results of HEA HP&LI ATRP at different conditions.

| No | [HEA] ₀ /[EBiB] ₀ /[EYH ₂] ₀ /[CuBr ₂] ₀ /[Cat] ₀ | Catalyst | DMSO v/v [%] | Time [h] | p [MPa] | Conv. ^a [%] | DP ^a | M _{nth} ^a | M _{nSEC-LALLS} ^b | Đ ^b |
|-----|--|----------------------|--------------|----------|---------|------------------------|-----------------|-------------------------------|--------------------------------------|----------------|
| S1 | 200/1/0.005/0.2/0.6 | TPMA | 30 | 1 | 225 | 81 | 162 | 18 811 | 24 850 | 1.295 |
| S2 | 200/1/0.005/0.2/0.6 | Me ₆ TREN | 30 | 1 | 225 | >99 | 200 | 23 224 | 35 680 | 1.644 |
| S3 | 200/1/0.01/0.2/0.3 | Me ₆ TREN | 10 | 0.5 | 225 | 51 | 102 | 11 844 | 12 560 | 1.591 |
| S4 | 1000/1/0.0025/1/1.5 | TPMA | 30 | 1 | 0.1 | 10 | 100 | 11 612 | 10 300 | 1.329 |
| S5 | 1000/1/0.0025/1/1.5 | TPMA | 30 | 1 | 225 | 51 | 510 | 59 221 | 68 950 | 1.288 |
| S6 | 1000/1/0.0025/1/1.5 | Me ₆ TREN | 30 | 1 | 0.1 | 49 | 490 | 56 899 | 97 200 | 1.336 |
| S7 | 1000/1/0.0025/1/1.5 | Me ₆ TREN | 30 | 1 | 225 | 94 | 940 | 109 153 | 149 900 | 1.380 |
| S8 | 1000/1/0.0025/1/1.5 | TPMA | 100 | 1 | 225 | - | - | - | - | - |
| S9 | 10000/1/0.0025/1/1.5 | TPMA | 30 | 70 | 225 | 41 | 4100 | 476 092 | 566 670 | 1.647 |
| S10 | 10000/1/0.0025/1/1.5 | Me ₆ TREN | 30 | 70 | 225 | 31 | 3100 | 359 972 | 1 134 000 | 1.699 |

^adetermined with ¹H NMR spectroscopy; ^bdetermined by SEC with low angle light scattering detector triple detection (SEC-LALLS) assuming 100% mass recovery (DMF+LiBr).

Supplementary Information

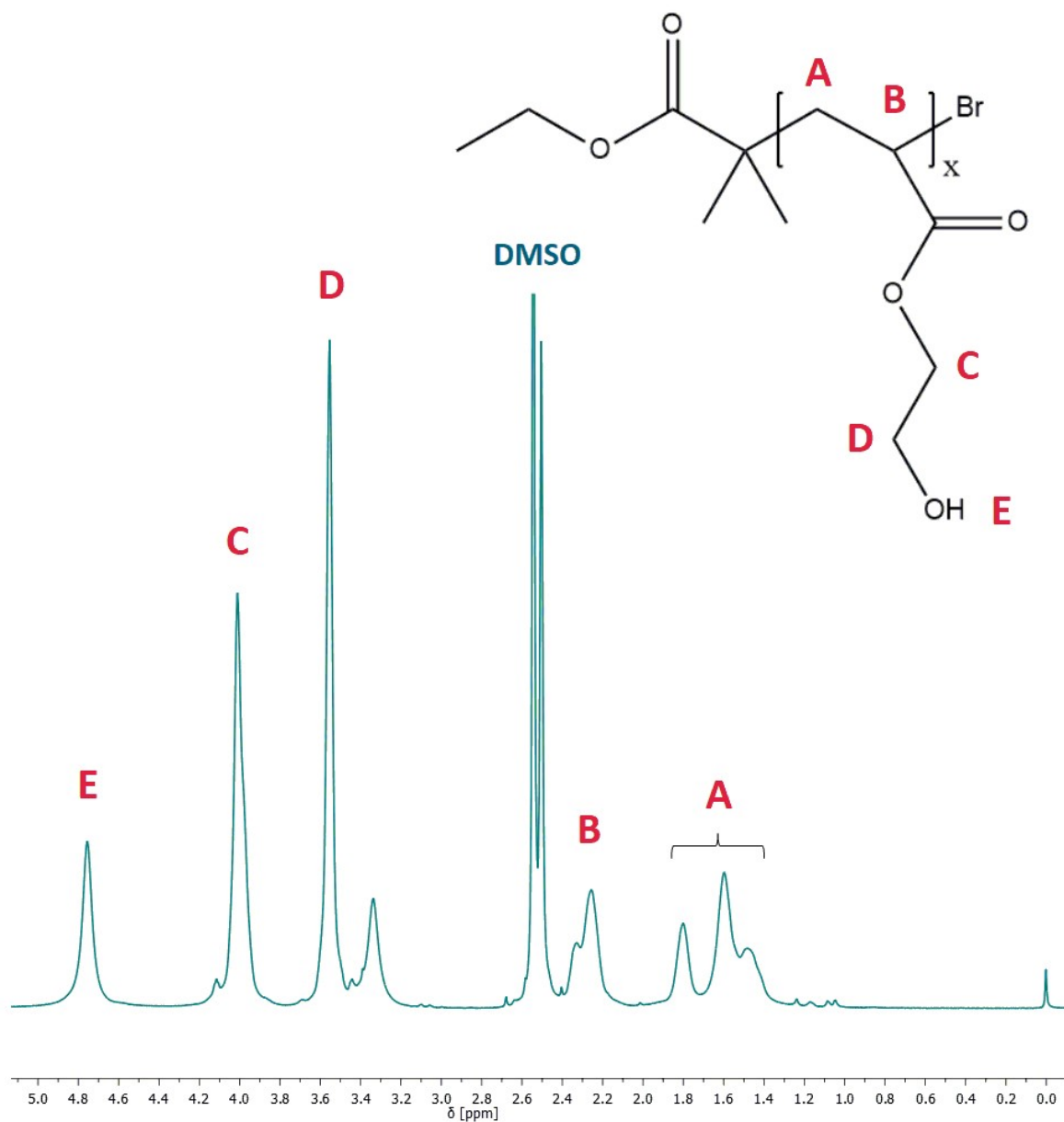


Figure S9. ¹H NMR spectra of the synthesized PHEA *via* HP&LI ATRP.

Supplementary Information

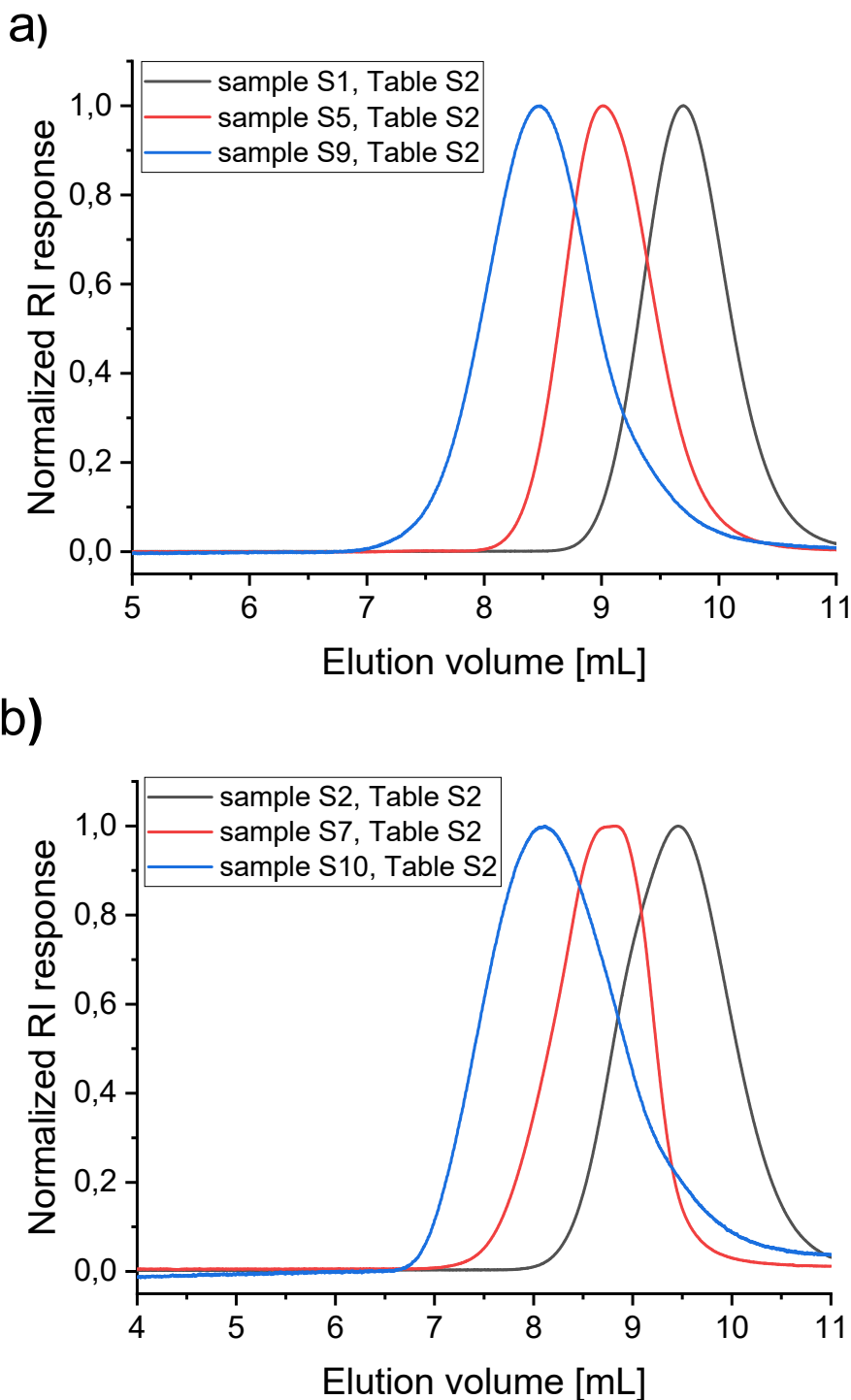


Figure S10. SEC-LALLS traces of the PHEA obtained *via* HP&LI ATRP with TPMA (a) and Me₆TREN (b) as a catalyst. Reaction conditions: [HEA]₀/[EBiB]₀/[EYH₂]₀/[CuBr₂]₀/[Cat]₀ = 200/1/0.01/0.2/0.6 (sample S1&S2), 1000/1/0.0025/1/3 (sample S5&S7), 10000/1/0.0025/1/3 10% v/v DMSO (sample S9&S10); 30% v/v DMSO; [HEA] = 300 mM in PBS without deoxygenation of the reaction mixture, under green LEDs irradiation (530 nm, 370 mW/cm²) at 225 MPa.