# Supporting Information

# (Meth)Acrylic Monomers with Heteroatom-Containing Ester Side Chains: A Systematic PLP-SEC and Polymerization Study

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The Supporting Information section is divided into two main chapters containing: (*i*) a detailed description of the PLP-SEC method and the Experimental Section and (*ii*) supporting analytical data.

# The Pulsed Laser Polymerization – Size Exclusion Chromatography (PLP– SEC) Method<sup>1</sup>

In PLP experiments, solutions of the respective monomer with a photoinitiator (and a solvent) are exposed to repetitive laser pulses. The laser pulses generate repetitively high radical concentrations which lead to a fast termination of the main part of the radical population. However, some of the radicals survive the short period directly after a laser pulse and can propagate until the next laser pulse is emitted, when the radical concentration is again significantly increased. Most polymer molecules, which are generated via PLP, have propagated for one dark time period (i.e., the time span between two subsequent laser pulses) and have therefore a characteristic molar mass,  $M_1$ , which depends on the monomer specific propagation rate coefficient. In parallel, some of the macroradicals arising from the first laser pulse survive the subsequent laser pulse(s) and propagate therefore for two (or three, ..., *i*) dark times. Consequently, their molar masses ( $M_2, M_3, ..., M_i$ ) should be the exact double (triple, ..., *i*-times) of the molar mass of the macroradicals, which were terminated after one dark time. Thus, the ratio ( $M_1 \cdot i$ )/ $M_i$  is one of the several consistency criteria that have to be fulfilled in a PLP experiment to obtain a reliable valid propagation rate coefficient.<sup>2</sup>

The PLP experiment results in a characteristic shape of the SEC chromatograms, i.e., of the molar mass distributions of the polymer sample. Typical PLP structures with at least two inflection points (identified by the maxima in the first derivative) are exemplarily shown in the Supporting Information section for each of the currently studied polymers (refer to Figure S1 and Figure S2). From these maxima in the first derivative, the propagation rate coefficient can be deduced according to Equation 1

$$L_{\rm i} = \frac{M_{\rm i}}{MW_{\rm M}} = i \cdot k_{\rm p} \cdot c_{\rm M} \cdot t_0 \tag{1}$$

where  $L_i$  is the degree of polymerization,  $M_i$  is the molar mass of the inflection point number *i*,  $MW_M$  is the molecular weight of the monomer, *i* is the number of the inflection point,  $c_M$  is the monomer concentration, and  $t_0$  is the time between two subsequent laser pulses.

For the calculation of the propagation rate coefficients, the absolute molar mass values at the inflection points are required. In the current study, the absolute molar masses for both polymers are accessed via on-line SEC-MALLS (multiangle laser light scattering). We did not have the possibility to additionally analyze the samples with a triple detector SEC setup, for instance consisting of a refractive index detector and a light-scattering detector coupled with a viscosimeter detector. Consequently, no Mark-Houwink-Kuhn-Sakurada (MHKS) parameters could be determined for the currently investigated monomers, which would have allowed for a universal calibration of the SEC systems. Therefore, we chose the more elaborate (and precise) method of analyzing each single PLP sample via a MALLS detector connected to a SEC determining its absolute molar mass distribution. In order to obtain a high signal-to-noise ratio in the light-scattering detector, several pulse repetition rates were employed for each temperature in order to fine-tune the temperature-specific optimum PLP conditions. The accuracy of the SEC calibration via the MALLS detector is mainly dependent on the high-molar-mass fraction within the polymer sample. High-molar-mass fractions originate during the PLP experiment from two aspects: (i) a low pulse repetition rate and (ii) the ever-present uncontrolled free-radical polymerization background. To a limited extent, non-PLP-based polymerization can occur during sample preparation and the sample work-up until an additional inhibitor (e.g., methyl hydroquinone (MeHQ)) is added. Such a background polymerization is often undesired, as it reduces the monomer concentration without generating polymer with a chain length that was regulated by the repetitive laser pulses. A (significantly) reduced monomer concentration

violates the necessary assumption in Equation 1 that the actual monomer concentration,  $c_M$ , is equal to the initial one.

Here, however, the background polymerization is – to a certain extent – helpful to ensure an accurate SEC calibration. The inflection points of the SEC distribution, which determine the value of the propagation rate coefficient, are usually in the range between 10 000 and 60 000 g·mol<sup>-1</sup>, whereas the high-molar-mass fraction of the polymer sample – responsible for a valid SEC-MALLS evaluation that can be extrapolated into the low molar mass region – is commonly well above 100 000 g·mol<sup>-1</sup>. It has to be noted that the accuracy of the light-scattering detector is significantly decreased for molecules smaller than approx. 30 000 g·mol<sup>-1</sup>.

In order to fulfill all consistency criteria of the PLP-SEC method, the PLP conditions have therefore to be tuned in such a way to strike a balance between a valid SEC-MALLS analysis, not too low molar masses of the inflections points, the occurrence of higher inflection points, and a limitation of the overall polymerization to low conversion. The detailed PLP sample conditions are collated in Table S1 and in Table S2 in the Supporting Information section.

## **Experimental Section**

#### Materials

2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), 4-methyl hydroquinone (MeHO, Aldrich, 99 %). hydroquinone (HO, Fluka. >99 %). 2-(dodecylthiocarbonothioylthio)propionic acid (DoPAT, Sigma-Aldrich, 97 %), 2-cyanopropan-2yl benzodithioate (CPDB, Sigma-Aldrich, 97 %,), tetrahydrofuran (THF, HPLC grade, not stabilized), and N,N-dimethylacetamide (DMAc, Sigma Aldrich,  $\geq$  99.9%) were used as received. Hydroxypropylcarbamate acrylate (HPCA, isomeric mixture, < 20 ppm MeHQ) and ureidoethyl methacrylate (UMA, < 40 ppm MeHQ) were used as received from BASF. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Acros, 98 %) was re-crystallized in ethanol prior to use. Styrene (Acros, 99%), methyl acrylate (VWR, 99%) and *n*-butyl acrylate (Acros, > 99%) was passed over basic alumina to remove the stabilizer.

Cumyl phenyldithioacetate (CPDA),<sup>3</sup> *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1 or DEPN),<sup>4</sup> and 2-methyl-2-[*N-tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionic acid (MAMA-SG1 or MAMA-DEPN)<sup>5</sup> were synthesized according to previously published procedures.

#### **Pulsed Laser Polymerization Experiments**

Pulsed laser polymerizations were carried out using two pulsed-laser setups as are available at the participating institutes. The employed experimental PLP setup at the KIT (Karlsruhe) has been described previously:<sup>6,7</sup> Since the polymers of both currently investigated monomers, UMA and HPCA, are not soluble in THF, DMAc was chosen as solvent for polymerization and analysis. Monomer solutions (1 M in DMAc) containing varying initiator concentrations (2,2dimethoxyacetophenone, DMPA, 1-15 mmol $\cdot$ L<sup>-1</sup>) were transferred into sample vials (containing about 0.5 mL of reaction solution each) and sealed with rubber septa. Oxygen was removed by purging the samples with nitrogen for approx. 2 min. The sample vial was subsequently placed into a stainless steel sample holder that was brought to temperature by a thermostat (VWR 1196D). The samples were allowed to equilibrate at the preset temperature for several minutes and were subsequently initiated by laser pulsing at varying repetition rates of up to 500 Hz. The temperature was measured directly at the sample and in none of the numerous PLP samples we observed a relevant temperature increase throughout or after the polymerization process. Since high repetition laser pulsing might induce a temperature increase, the measurement of the temperature in the sample was carried out in a previous study<sup>6</sup> and an average increase of less than 1 °C was observed. Laser initiation was achieved by a Coherent Xantos XS-500 (which is a compact version of the ExciStar XS-500) operating at the XeF line of 351 nm. The laser beam, which was adjusted to an energy of close to 2 mJ·pulse<sup>-1</sup> hitting the sample, was redirected to illuminate the vial from the bottom.

The experimental PLP setup at the Polymer Institute (SAS, Bratislava) consisted of a Coherent ExciStar XS-500 laser also operating at the XeF line of 351 nm and providing laser pulse repetitions rates of up to 500 Hz, too. The general sample preparation procedure was the same as applied at the KIT. The laser beam, which was adjusted to an energy of close to 2 mJ·pulse<sup>-1</sup>, was directed to hit the sample solution (approx. 1 mL in QS 110 cuvette of 10 mm path length, Hellma-Worldwide) horizontally. Temperature equilibration was achieved using a thermostat (Julabo ED) and monitored for several samples during the PLP experiment. Again, no significant temperature increase was observed under the applied PLP conditions.

After polymerization, MeHQ dissolved in DMAc was added and the samples were filtered and analyzed directly via SEC, since the monomers do not evaporate (as they are solids at ambient temperature). Possible influence of the conversion on the resulting propagation rate coefficient values was assessed by variation of the pulse repetition number (between 300 and 1500 pulse repetitions) and found to be negligible in the applied range of pulse repetitions. Every individual PLP distribution was assessed for consistency in terms of the appearance of at least  $L_2$  and the resulting ratio of  $k_{p,1}/k_{p,2}$ . Only samples that showed a ratio of  $k_{p,1}/k_{p,2}$  within 0.95 and 1.2 were admitted to the final Arrhenius data set; the majority of the  $k_{p,1}/k_{p,2}$  ratios are between 1.03 and 1.12. The individual  $k_{p,1}/k_{p,2}$  ratios for each sample are collated in Table S1 and in Table S2 in the Supporting Information section.

#### Size Exclusion Chromatography (SEC) – Determination of Absolute Molar Masses

Absolute SEC analysis of the molar mass distributions was performed at the Polymer Institute of the Slovak Academy of Sciences (SAS) in Bratislava with the eluent N,N-dimethylacetamide (DMAc) containing 0.1 wt% LiBr on a Polymer Standards Service (PSS) column setup (Mainz, Germany) consisting of an  $8 \times 50$  mm PSS GRAM 10 µm guard column and three  $8 \times 300$  mm PSS GRAM 10 µm columns with pore sizes of 100, 1000, and 3000 Å placed in a column heater set to 45 °C. The flow rate of 0.8 mL·min<sup>-1</sup> was controlled by using toluene as the flow rate marker in a Waters SEC system (degasser, autosampler 717 with loop volume 100 µL, 515 pump, column heater). A direct calibration of the SEC columns was not possible due to the nonavailability of narrowly distributed polymer calibration standards. Therefore the use of MALLS-RI detection was required. A MALLS absolute detector PSS SLD7000 (PSS, Mainz, Germany) in conjunction with a Waters 2410 DRI detector provided absolute molar masses.<sup>8</sup> The values of the refractive index increment, dn/dc, were determined on a DnDc2010 (PSS, Mainz, Germany) differential refractometer to be 0.084 and 0.068 mL $\cdot$ g<sup>-1</sup> for polyUMA and polyHPCA, respectively. These numbers were measured at 620 nm and are assumed to be the same as for 633 nm, which is the wavelength employed by the MALLS detector. A narrow PS calibration standard of 67 500 g·mol<sup>-1</sup> molecular mass (PSS, Mainz, Germany) was used as the isotropic scatterer. Effective calibration was achieved using polystyrene (PS) standards, each of narrow molecular mass distribution, for the range from 376 to 2 300 000 g·mol<sup>-1</sup> (PSS, Mainz, Germany). PSS WinGPC7.2.1 was used for data acquisition and evaluation. The MALLS detector signal was sufficient to allow a precise molar mass distribution analysis for all samples currently incorporated into the Arrhenius plots.

#### Size Exclusion Chromatography (SEC)

SEC measurements of the polymer samples obtained in the RDRP experiments were performed at the Karlsruhe Institute of Technology (KIT) on a PL-SEC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column ( $50 \times 7.5$  mm) followed by three PLgel 5 µm Mixed C column ( $300 \times 7.5$  mm) and a differential refractive index (RI) detector using *N*,*N*-dimethylacetamide (DMAc) containing 0.3 wt% LiBr as the eluent at 50 °C with a flow rate of 1 mL·min<sup>-1</sup>. The SEC system is calibrated using linear polystyrene standards ranging from 160 to  $6 \cdot 10^6$  g·mol<sup>-1</sup> and linear poly(methyl methacrylate) standards ranging from 700 to  $2 \cdot 10^6$  g·mol<sup>-1</sup>. SEC calculations are carried out applying an effective calibration by using the Mark-Houwink-Kuhn-Sakurada (MHKS) parameters for polystyrene (*K* =  $14.1 \cdot 10^{-3}$  cm<sup>3</sup>·g<sup>-1</sup> and  $\alpha = 0.7$ ).<sup>12</sup> No absolute molar mass information was available for the RDRP samples, since the MHKS parameters of polyUMA and polyHPCA are not available. In contrast to the PLP samples, the RDRP samples do not contain high molar mass polymer chains, which would allow for a valid extrapolation to the low molar mass range via MALLS detector analysis.

#### NMR Spectroscopy

NMR measurements at the KIT were conducted on a Bruker AM250 spectrometer at 250 MHz and a Bruker AM400 spectrometer at 400 MHz for hydrogen nuclei for conversion determination and for structure verification. At the Institute of Chemistry of the Faculty of Natural Sciences, Comenius University in Bratislava, the in-situ NMR measurements were conducted on a Varian VNMRS 600 MHz. Samples were dissolved in DMSO-d<sub>6</sub> using residual solvent peaks for shift correction.

Furthermore, conversion vs. time evolutions were recorded for the free-radical polymerization of both monomers employing AIBN as the initiator. Thus, in-situ NMR measurements of monomer solutions ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ;  $1 \text{ mol} \cdot \text{L}^{-1}$ ;  $2 \text{ mol} \cdot \text{L}^{-1}$ ) in DMSO-d<sub>6</sub> containing 12 mmol $\cdot \text{L}^{-1}$ AIBN were carried out with a heatable sample head at 70 °C and spectra were recorded every 20 and 40 seconds, respectively. The necessary shimming and lock to the NMR tube was performed with an identical NMR tube containing the pure monomer in the NMR solvent without initiator. After the preparation of the NMR experiment the NMR tubes were exchanged so that the first spectrum of the polymerization could already be recorded after 20 or 40 s, instead of after several minutes, which are necessary for the shimming and lock. Monitoring the continuous decay of the resonances associated with the vinylic protons (i.e., at  $\delta$ = 5.95 ppm for HPCA and at  $\delta$ = 5.65 ppm for UMA); normalized in each spectrum to resonances associated with protons of the ester side chain (i.e., the tertiary proton in HPCA at  $\delta$ = 4.85 ppm and the CH<sub>2</sub> group in the side chain in UMA at  $\delta$ = 3.95 ppm) provided the conversion vs. time evolutions.

#### **Standard Procedures Applied in RDRP Techniques**

As we will present below, the  $M_n$  data of batch polymerizations determined via SEC-RI were correlated with the conversion values obtained via <sup>1</sup>H-NMR experiments at elevated temperatures. Therefore, a stock solution containing solvent, monomer, controlling agent, and initiator was filtered and portioned in a number of SEC sample vials, after removal of the oxygen by standard freeze-pump-thaw techniques (up to 4 cycles). The SEC vials were subsequently placed into a metal heating block (60 °C for RAFT polymerization experiments for both monomers, as well as 90 and 110 °C for NMP of UMA and HPCA, respectively) with magnetic stirring during polymerization. After pre-set time intervals the polymerization in the SEC vial was stopped by addition of solvent containing inhibitor (methyl hydroquinone, MeHQ) and the mixture was subsequently analyzed via SEC-RI, without further purification. A similar polymerization solution containing deuterated solvent with the same concentrations of initiator, controlling agent and monomer was prepared and degassed directly in the NMR tube for the RAFT polymerization of HPCA. The conversion values were determined via integration of the resonances associated with the vinylic protons in the repetitive measured NMR spectra (every 100 s) at the same temperature as the above described batch polymerizations, i.e., 60 °C.

## **Supporting Analytical Data**

For the PLP-SEC experiments exemplary SEC chromatograms are shown for each monomer at 4 temperatures as well as tables with the exact PLP samples conditions. Furthermore, the temperature-dependent density curves for each monomer and the differential scanning calorimetry (DSC) curves are provided and the results are summarized in Table 1 in the main article. Concomitantly, the <sup>1</sup>H-NMR spectrum of pure HPCA, employed to determine the isomeric composition, is depicted. The conversion vs. time evolutions of the free-radical polymerization obtained via in-situ <sup>1</sup>H-NMR at elevated temperatures are shown jointly with

their kinetic analysis, yielding the apparent polymerization rate coefficients summarized in Table 4 in the main article. The same analysis is included for the RAFT polymerization of HPCA together with the SEC traces of a corresponding RAFT polymerization. The combination of these data results in the linear evolution of  $M_n$  vs. conversion depicted in Figure 5. Furthermore, the conversion vs. time,  $M_n$  vs. conversion, and corresponding linear first-order kinetic plots of the RAFT and NMP experiments employing UMA as the monomer are provided. Finally, the SEC traces of the NMP chain extension experiment and the SEC traces of the NMP experiments targeting different molar masses are included.



**Figure S1.** Exemplary molar mass distributions (red dashed lines) and their first derivative (solid black lines) for PLP experiments of UMA in 1 M solution in *N*,*N*-dimethylacetamide. The sample-specific conditions are displayed in the diagrams and also collated in Table S1 for 1 M solution in *N*,*N*-dimethylacetamide. The typical PLP structure is observed for all samples.



**Figure S2.** Exemplary molar mass distributions (red dashed lines) and their first derivative (solid black lines) for PLP experiments of HPCA in 1 M solution in *N*,*N*-dimethylacetamide. The sample-specific conditions are displayed in the diagrams and also collated in Table S2 for 1 M solution in *N*,*N*-dimethylacetamide. The typical PLP structure is observed for all samples.

|        | f  | п    | θ     | $T^{-1}$                 | $\ln(k_{p1})$ | $k_{\rm p1}/k_{\rm p2}$ | $M_1$               | $M_2$               | $\mathcal{C}_{\mathrm{M}}$ | $k_{\rm p1}$              | $k_{\rm p2}$              |
|--------|----|------|-------|--------------------------|---------------|-------------------------|---------------------|---------------------|----------------------------|---------------------------|---------------------------|
| sample | Hz | _    | °C    | $10^{-3} \text{ K}^{-1}$ | —             | _                       | g∙mol <sup>-1</sup> | g·mol <sup>−1</sup> | $mol \cdot L^{-1}$         | $mol \cdot L^{-1} s^{-1}$ | $mol \cdot L^{-1} s^{-1}$ |
| AH1022 | 2  | 800  | -10.7 | 3.810                    | 5.2308        | 1.087                   | 19409               | 35727               | 1.048                      | 187                       | 172                       |
| AH1021 | 1  | 1200 | -10.4 | 3.810                    | 5.0145        | 1.019                   | 31261               | 61376               | 1.047                      | 151                       | 148                       |
| AH1021 | 1  | 1200 | -10.4 | 3.810                    | 5.1619        | 1.042                   | 36224               | 69502               | 1.047                      | 174                       | 167                       |
| AH1023 | 2  | 1200 | -10.0 | 3.800                    | 5.1162        | 1.089                   | 17298               | 31769               | 1.047                      | 167                       | 153                       |
| AH1024 | 1  | 800  | 1.1   | 3.650                    | 5.4135        | 1.026                   | 46132               | 89950               | 1.037                      | 224                       | 219                       |
| AH1025 | 1  | 1200 | 1.5   | 3.640                    | 5.3677        | 1.007                   | 44055               | 87498               | 1.037                      | 214                       | 213                       |
| AH1026 | 2  | 800  | 1.5   | 3.640                    | 5.5589        | 1.050                   | 26669               | 50816               | 1.037                      | 260                       | 247                       |
| AH1027 | 2  | 1200 | 1.5   | 3.640                    | 5.4415        | 1.007                   | 23714               | 47098               | 1.037                      | 231                       | 229                       |
| AH976  | 2  | 300  | 9.4   | 3.540                    | 5.9654        | 1.016                   | 40087               | 78886               | 1.038                      | 390                       | 383                       |
| AH977  | 4  | 300  | 9.4   | 3.540                    | 6.1404        | 1.089                   | 23878               | 43853               | 1.038                      | 464                       | 426                       |
| AH903  | 2  | 1200 | 12.1  | 3.510                    | 6.0875        | 1.052                   | 44771               | 85114               | 1.026                      | 440                       | 419                       |
| AH904  | 4  | 800  | 12.1  | 3.510                    | 6.1014        | 1.040                   | 22699               | 43652               | 1.026                      | 446                       | 429                       |
| AH905  | 4  | 1200 | 12.1  | 3.510                    | 6.1659        | 1.062                   | 24210               | 45604               | 1.026                      | 476                       | 449                       |
| AH898  | 2  | 800  | 12.2  | 3.500                    | 6.0070        | 1.030                   | 41305               | 80168               | 1.026                      | 406                       | 394                       |
| AH978  | 3  | 300  | 28.6  | 3.310                    | 6.6708        | 0.991                   | 53211               | 107399              | 1.021                      | 789                       | 796                       |
| AH979  | 6  | 300  | 28.7  | 3.310                    | 6.8459        | 0.975                   | 31696               | 65013               | 1.021                      | 940                       | 964                       |
| AH907  | 3  | 1200 | 29.6  | 3.300                    | 6.5681        | 1.062                   | 47534               | 89536               | 1.010                      | 712                       | 671                       |
| AH910  | 3  | 800  | 29.8  | 3.300                    | 6.5989        | 1.047                   | 49091               | 93756               | 1.012                      | 734                       | 701                       |
| AH908  | 6  | 800  | 29.8  | 3.300                    | 6.6036        | 1.030                   | 24660               | 47863               | 1.012                      | 738                       | 716                       |
| AH909  | 6  | 1200 | 29.8  | 3.300                    | 6.6611        | 1.052                   | 26122               | 49659               | 1.012                      | 781                       | 743                       |
| AH918  | 4  | 800  | 47.0  | 3.120                    | 7.0692        | 1.019                   | 57016               | 111944              | 0.979                      | 1175                      | 1154                      |
| AH919  | 4  | 1200 | 47.1  | 3.120                    | 7.0509        | 1.009                   | 55976               | 110917              | 0.979                      | 1154                      | 1143                      |
| AH920  | 8  | 800  | 47.2  | 3.120                    | 7.1293        | 1.005                   | 30269               | 60256               | 0.979                      | 1248                      | 1242                      |
| AH921  | 8  | 1200 | 47.3  | 3.120                    | 6.9890        | 0.991                   | 26303               | 53088               | 0.979                      | 1085                      | 1095                      |
| AH922  | 5  | 800  | 68.3  | 2.930                    | 7.6546        | 1.138                   | 80353               | 141254              | 0.960                      | 2110                      | 1855                      |
| AH923  | 5  | 1200 | 69.3  | 2.920                    | 7.4967        | 0.995                   | 68549               | 137721              | 0.960                      | 1802                      | 1810                      |
| AH924  | 10 | 800  | 69.3  | 2.920                    | 7.7477        | 1.069                   | 44055               | 82414               | 0.960                      | 2316                      | 2167                      |
| AH925  | 10 | 1200 | 69.3  | 2.920                    | 7.6050        | 1.016                   | 38194               | 75162               | 0.960                      | 2008                      | 1976                      |
| AH926  | 7  | 800  | 89.5  | 2.760                    | 7.8287        | 1.019                   | 66988               | 131522              | 0.942                      | 2512                      | 2466                      |
| AH927  | 7  | 1200 | 91.7  | 2.740                    | 7.9205        | 1.064                   | 73282               | 137721              | 0.940                      | 2753                      | 2587                      |
| AH928  | 15 | 800  | 91.9  | 2.740                    | 8.0013        | 1.047                   | 37068               | 70795               | 0.940                      | 2985                      | 2850                      |
| AH929  | 15 | 1200 | 92.0  | 2.740                    | 8.0382        | 1.109                   | 38459               | 69343               | 0.940                      | 3097                      | 2792                      |

**Table S1.**Detailed PLP sample conditions, absolute molar masses of the first two inflectionpoints, and the resulting propagation rate coefficients of UMA polymerized in 1 M solution inDMAc.

| 1.     | f   | n    | θ     | $T^{-1}$                 | $\ln(k_{p1})$ | $k_{\rm p1}/k_{\rm p2}$ | $M_1$              | $M_2$              | с <sub>М</sub>     | $k_{\rm pl}$              | $k_{\rm p2}$              |
|--------|-----|------|-------|--------------------------|---------------|-------------------------|--------------------|--------------------|--------------------|---------------------------|---------------------------|
| sample | Hz  | _    | °C    | $10^{-3} \text{ K}^{-1}$ | _             | _                       | $g \cdot mol^{-1}$ | $g \cdot mol^{-1}$ | $mol \cdot L^{-1}$ | $mol \cdot L^{-1} s^{-1}$ | $mol \cdot L^{-1} s^{-1}$ |
| AH992  | 50  | 750  | -14.5 | 3.866                    | 8.5863        | 1.062                   | 19634              | 36983              | 1.058              | 5358                      | 5046                      |
| AH993  | 50  | 1500 | -13.8 | 3.856                    | 8.2945        | 1.094                   | 14655              | 26792              | 1.057              | 4002                      | 3658                      |
| AH994  | 75  | 750  | -11.8 | 3.826                    | 8.5843        | 1.026                   | 13032              | 25410              | 1.056              | 5347                      | 5213                      |
| AH997  | 50  | 1500 | -8.0  | 3.771                    | 8.7027        | 1.077                   | 21928              | 40738              | 1.052              | 6019                      | 5591                      |
| AH997  | 50  | 1500 | -8.0  | 3.771                    | 8.5231        | 1.005                   | 18323              | 36475              | 1.052              | 5030                      | 5006                      |
| AH1000 | 100 | 750  | -7.5  | 3.764                    | 8.8373        | 1.079                   | 12331              | 22856              | 1.034              | 6886                      | 6382                      |
| AH1006 | 100 | 750  | -0.3  | 3.665                    | 8.8393        | 1.035                   | 12274              | 23714              | 1.027              | 6900                      | 6665                      |
| AH1004 | 75  | 750  | 0.1   | 3.660                    | 8.7961        | 1.038                   | 15668              | 30200              | 1.027              | 6608                      | 6369                      |
| AH1002 | 50  | 750  | 0.3   | 3.657                    | 8.9618        | 1.130                   | 27733              | 49091              | 1.027              | 7800                      | 6903                      |
| AH934  | 100 | 750  | 11.5  | 3.513                    | 9.1653        | 1.072                   | 17140              | 31989              | 1.035              | 9559                      | 8921                      |
| AH932  | 200 | 750  | 12.0  | 3.507                    | 8.9563        | 0.989                   | 6950               | 14060              | 1.035              | 7756                      | 7846                      |
| AH932  | 200 | 750  | 12.0  | 3.507                    | 9.3362        | 1.069                   | 10162              | 19011              | 1.035              | 11341                     | 10608                     |
| AH982  | 250 | 750  | 28.8  | 3.312                    | 9.7425        | 1.114                   | 11858              | 21281              | 1.005              | 17025                     | 15278                     |
| AH983  | 250 | 1500 | 28.8  | 3.312                    | 9.6112        | 1.099                   | 10399              | 18923              | 1.005              | 14931                     | 13585                     |
| AH980  | 150 | 750  | 29.0  | 3.310                    | 9.3308        | 1.117                   | 13092              | 23442              | 1.005              | 11281                     | 10100                     |
| AH1010 | 400 | 750  | 49.7  | 3.097                    | 9.9526        | 1.057                   | 8933               | 16904              | 0.982              | 21006                     | 19875                     |
| AH1013 | 500 | 500  | 49.9  | 3.095                    | 9.8121        | 1.021                   | 6209               | 12162              | 0.982              | 18253                     | 17878                     |
| AH1011 | 400 | 1000 | 50.0  | 3.095                    | 9.7594        | 0.984                   | 7362               | 14962              | 0.982              | 17317                     | 17597                     |

**Table S2.**Detailed PLP sample conditions, absolute molar masses of the first two inflectionpoints, and the resulting propagation rate coefficients of HPCA polymerized in 1 M solution inDMAc.



**Figure S3.** Temperature-dependent densities for the 1 M solutions of the HPCA (**upper part**) and UMA (**lower part**) in *N*,*N*-dimethylacetamide. Methyl hydroquinone (MeHQ) was added in replacement of 2,2-dimethoxy-2-phenylacetophenone (DMPA) to prevent the solutions from polymerization inside the density measurement device. The temperature-dependent densities are summarized in Table 1 according to  $\rho(T[^{\circ}C]) = \rho_0 - b \cdot T[^{\circ}C]$ .



**Figure S4.** Differential scanning calorimetry of polyUMA (upper part) and polyHPCA (lower part). The glass transition temperatures are indicated in Table 1.



**Figure S5.** <sup>1</sup>H-NMR of HPCA. The integral of the vinylic proton ( $\delta = 5.94$  ppm) is set to unity. The ratio of the integrals corresponding to the signals labeled B and C is B : C = 2 : 1. B and C are a doublet of doublets associated with the CH<sub>2</sub> group (marked with a red dot) in alpha position of the ester and carbamate functionalities, respectively. Consequently, the upper structure labeled with B is the dominant isomer in HPCA.



**Figure S6.** Conversion vs. time evolutions for the FRP of UMA (top left) and HPCA (top right) in DMSO-d<sub>6</sub> solution recorded via in-situ NMR and the corresponding linear first order analysis according to Equation 3 for UMA (bottom left) and HPCA (bottom right). The polymerizations were executed at 70 °C in DMSO-d<sub>6</sub> employing AIBN as initiator (12 mmol·L<sup>-1</sup>). The black squares and grey straight lines correspond to a monomer concentration of 0.2 mol·L<sup>-1</sup>, the red dots and dashed brown lines correspond to a monomer concentration of 1 mol·L<sup>-1</sup>, and the green triangles and dark green dotted lines correspond to a monomer concentration of 1 mol·L<sup>-1</sup>, and the green triangles are linear fits of the early polymerization times (e.g., up to 150 s in the case of 2 mol·L<sup>-1</sup> HPCA or up to 1800 s in the case of 1 mol·L<sup>-1</sup> UMA); the corresponding slope m is stated in the graphs legend and is equal to the apparent polymerization rate coefficient  $k^{app}$ . The apparent polymerization rate coefficient values are summarized in Table 4 jointly with the corresponding radical concentrations and the thereof deduced estimates of the termination rate coefficients.



**Figure S7.** Conversion vs. time evolution determined by <sup>1</sup>H-NMR spectroscopy (**top left**) and the corresponding linear first-order plot according to Equation 3 (**top right**) for the RAFT polymerizations of UMA (26 eq. and 172 eq., respectively) in DMSO (2:1 w/w) at 60 °C. The polymerization mixture contains AIBN (0.2 eq.) and the RAFT agent CPDB (1 eq.). The initial inhibition period, when no polymerization is taking place, can readily be recognized in the conversion vs. time evolution followed by NMR. The kinetic analysis yields apparent polymerization rate coefficients of  $k^{app} = 6.33 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (26 eq. UMA) and

 $k^{\text{app}} = 4.17 \cdot 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (172 eq. UMA) corresponding to a radical concentration of  $[\text{R}^*] = 3.96 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$  (26 eq. UMA) and  $[\text{R}^*] = 2.60 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$  (172 eq. UMA) resulting in average overall termination rate coefficients of  $\overline{k_t} = 1.28 \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (26 eq. UMA) and  $\overline{k_t} = 4.35 \cdot 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (172 eq. UMA). An exemplary critical comparison of the  $\overline{k_t}$  obtained from RAFT polymerizations with the ones obtained from FRP is given in the main article. Additionally, the  $M_n$  vs. conversion evolutions (**bottom**) are depicted in combination with the corresponding dispersity values. The linear fits of  $M_n$  vs. conversion evolution feature almost exactly the same slopes as their corresponding theoretical evolutions. The lines connecting the dispersity values are solely for guiding the eye; they are no fits.



**Figure S8.** Conversion vs. time evolution determined by <sup>1</sup>H-NMR spectroscopy (**top left**) and the corresponding linear first-order analysis according to Equation 3 (**top right**) for the NMP experiments with UMA (25 eq. and 172 eq., respectively) in DMSO (2:1 w/w) at 90 °C employing styrene (2 eq. and 15 eq., respectively) as a controlling comonomer. The polymerization mixture contains MAMA-SG1 (1 eq.) and SG1 (0.09 eq.). The kinetic analysis yields apparent polymerization rate coefficients of  $k^{app} = 4.75 \cdot 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (25 eq. UMA) and  $k^{app} = 2.32 \cdot 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  (172 eq. UMA) corresponding to a radical concentration of

 $[R^{\bullet}] = 2.08 \cdot 10^{-8} \text{ mol} \cdot L^{-1}$  (25 eq. UMA) and  $[R^{\bullet}] = 1.02 \cdot 10^{-8} \text{ mol} \cdot L^{-1}$  (172 eq. UMA). Additionally, the  $M_n$  vs. conversion evolutions (**bottom**) are depicted in combination with the corresponding dispersity values. The linear fits of the  $M_n$  vs. conversion evolution feature slightly decreased slopes as their corresponding theoretical evolutions. The lines connecting the dispersity values are solely for guiding the eye; they are no fits.



**Figure S9.** SEC-RI traces (**top**) and conversion vs. time evolution recorded via <sup>1</sup>H-NMR spectroscopy (**bottom right**) for the RAFT polymerizations of HPCA (100 eq.) in DMSO (2:1 w/w) at 60 °C. The polymerization mixture contains AIBN (0.1 eq.) and the RAFT agent CPDA (1 eq.). The initial inhibition period, when no polymerization takes place, can readily be identified in the conversion vs. time evolution recorded via NMR. Additionally, the linear first-order plot according to Equation 3 is depicted (**bottom left**) resulting in an apparent polymerization rate coefficient  $k^{app} = 3.29 \cdot 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  corresponding to a radical concentration of  $[\text{R}^*] = 1.44 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$  and average overall  $\overline{k_t} = 1.82 \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ . The critical comparison of the  $\overline{k_t}$  obtained from RAFT polymerization with the ones obtained from FRP is given in the main article.



**Figure S10.** SEC traces acquired for the NMP of HPCA (203 eq.) targeting a  $M_n$  of 35 000 g·mol<sup>-1</sup> employing MAMA-SG1 (1 eq.) and a slight excess of the SG1 (0.085 eq.) at 110 °C in DMAc solution (2:1 w/w). Despite the fact that all dispersities feature values above D = 1.5, a clear and uniform shift of the polymer signal is observable. The high dispersities may associated with the evaluation of the SEC traces employing polystyrene MHKS in lack of MHKS parameters of HPCA. The traces are normalized to their polymer peak (around 22 min retention time) in order to emphasize the decreasing monomer content (around 28 min retention time).



**Figure S11.** SEC traces acquired during the NMP of HPCA (406 eq.) targeting a  $M_n$  of 70 000 g·mol<sup>-1</sup> employing MAMA-SG1 (1 eq.) and a slight excess of SG1 (0.085 eq.) at 110 °C in DMAc solution (2:1 w/w). Despite the fact that all dispersities feature values above D = 1.5, a clear and uniform shift of the polymer signal can be observed. The high dispersities may be associated with the evaluation of the SEC traces employing polystyrene MHKS in lack of MHKS parameters of HPCA. The traces are normalized to their polymer peak (around 22 min retention time) in order to emphasize the decreasing monomer content (around 28 min retention time).



**Figure S12.** SEC traces acquired for the NMP of HPCA (23 eq.) and styrene (10 eq.) targeting a  $M_n$  of 5 000 g·mol<sup>-1</sup> employing MAMA-SG1 (1 eq.) and a slight excess of SG1 (0.085 eq.) at 110 °C in DMAc solution (2:1 w/w). The dispersities of the polymer are stated in the legend together with the related polymerization time and are in the range of D = 1.3. The traces are normalized to their maximum peak which is at the beginning the monomer and solvent signal around 28 min retention time and towards the end of the polymerization the polymer signal around 24.5 min retention time.



**Figure S13.** SEC traces acquired for the NMP of HPCA (157 eq.) and styrene (29 eq.) targeting a  $M_n$  of 35 000 g·mol<sup>-1</sup> employing MAMA-SG1 (1 eq.) and a slight excess of SG1 (0.085 eq.) at 110 °C in DMAc solution (2:1 w/w). Despite the fact that all dispersities feature values above D = 1.5, a clear and uniform shift of the polymer signal can be observed. The high dispersities may be associated with the evaluation of the SEC traces employing polystyrene MHKS in lack of MHKS parameters of HPCA. The traces are normalized to their polymer peak (around 22 min retention time) in order to emphasize the decreasing monomer content (around 28 min retention time).



**Figure S14.** SEC traces acquired for the NMP of HPCA (366 eq.) and styrene (67 eq.) targeting a  $M_n$  of 70 000 g·mol<sup>-1</sup> employing MAMA-SG1 (1 eq.) and a slight excess of SG1 (0.085 eq.) at 110 °C in DMAc solution (2:1 w/w). Despite the fact that all dispersities feature values above D = 1.5, a clear and uniform shift of the polymer signal is evident. The high dispersities may be associated with the evaluation of the SEC traces employing polystyrene MHKS in lack of MHKS parameters of HPCA. The traces are normalized to their polymer peak (around 22 min retention time) in order to emphasize the decreasing monomer content (around 28 min retention time).



**Figure S15.** SEC traces obtained in the NMP chain extension experiment of HPCA with *n*-butyl acrylate (BA). HPCA (50 eq.,  $M_n^{\text{theo}} = 9\,900\,\text{g}\cdot\text{mol}^{-1}$ ) was polymerized with MAMA-SG1 (1 eq.) and a slight excess of SG1 at 110 °C in DMAc solution (2:1 w/w). After 45 min reaction time a HPCA polymer featuring a  $M_n = 4\,000\,\text{g}\cdot\text{mol}^{-1}$  and a dispersity of D = 1.2 was obtained. BA was added directly as additional monomer in order to produce a copolymer via NMP featuring a  $M_n = 16\,300\,\text{g}\cdot\text{mol}^{-1}$  and a dispersity of D = 1.4 after 4 h reaction time, which is exceeding the initial  $M_n^{\text{theo}}$  at full conversion of 9 900 g·mol<sup>-1</sup>.

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