Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for "Impact of side reactions on molar mass distribution, unsaturation level and branching density in solution free radical polymerization of *n*-butyl acrylate under well-defined lab-scale reactor conditions"

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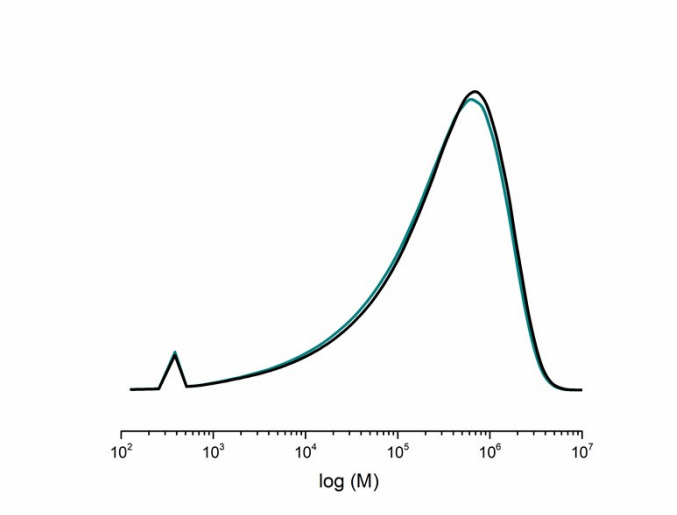

Figure S1. Sensitivity of log-MMD to the macromonomer addition reaction at 99% monomer conversion (entry 2 in Table 2, otherwise Parameter Table 1). All side reaction except macromonomer addition (chain transfer to monomer, backbiting, beta-scission, chain transfer to polymer) - dark cyan, all side reactions including macromonomer addition – black.

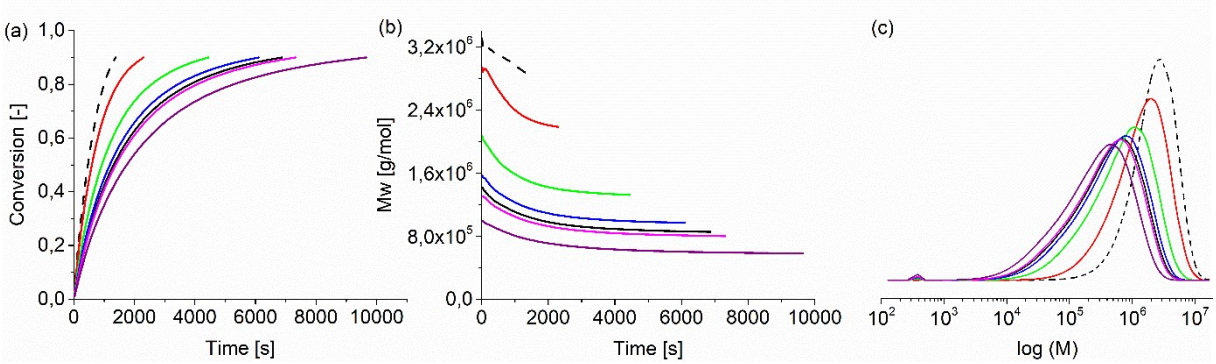

Figure S2. Influence of backbiting reaction rate coefficient on (a) monomer conversion as a function of time, (b) mass average molar mass M_m as a function of time and (c) log-MMD of *n*BuA FRP (entry 3 in Table 2) with variation of k_{BB}; black dashed line: 10 s^{-1} , red line: 10^2 s^{-1}, green line: 4×10^2 s^{-1}, blue line: 7×10^2 s^{-1}, black full line: reference value 8.5×10^2 s^{-1}, magenta line: 9.5×10^2 s^{-1}, purple line: 1.5×10^3 s^{-1}. Extra for Figure 2 in the main text.

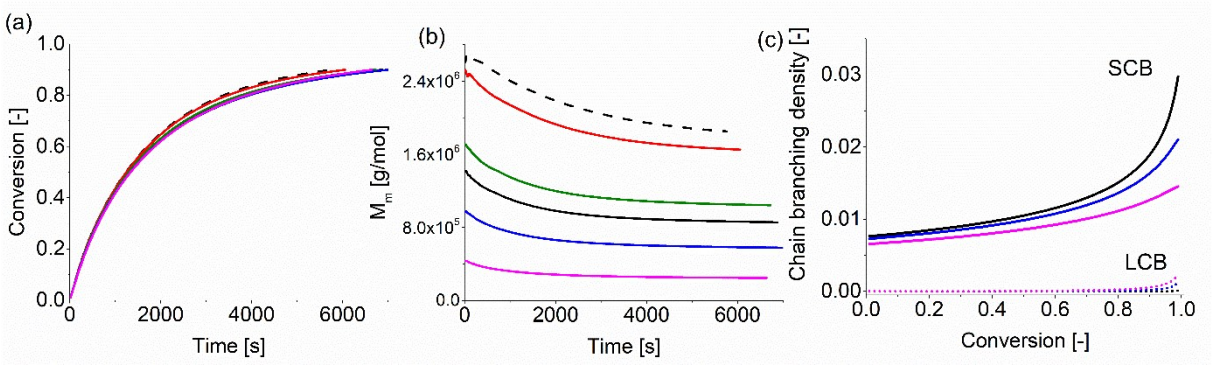

Figure S3. Influence of β-scission reaction rate coefficient on (a) monomer conversion as a function of time, (b) mass average molar mass M_m as a function of time and (c) SCBD and LCBD as a function of time (entry 4 in Table 2) with variation of the $k_{\beta\text{-sc}}$; black long dashed line: 1.5 10^{-2} s^{-1}, red line: 1.5 10^{-1} s^{-1}, green line: 1.0 s^{-1}, black full line: 1.48 s^{-1}, blue line: 3 s^{-1}, purple line: 10 s^{-1}. Extra for Figure 3 in the main text.

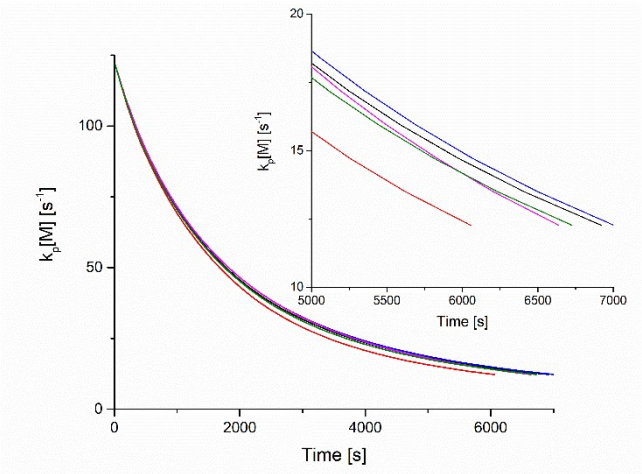

Figure S4. Evolution of $k_{p,mcr}$[M] *vs.* time for various values of k_{β_sc}; red line: 1.5 10^{-1} s^{-1}, green: 1 s^{-1}, black full line: 1.48 s^{-1}, blue line: 3 s^{-1}, purple line: 10 s^{-1}. Extra for Figure 3 in the main text.

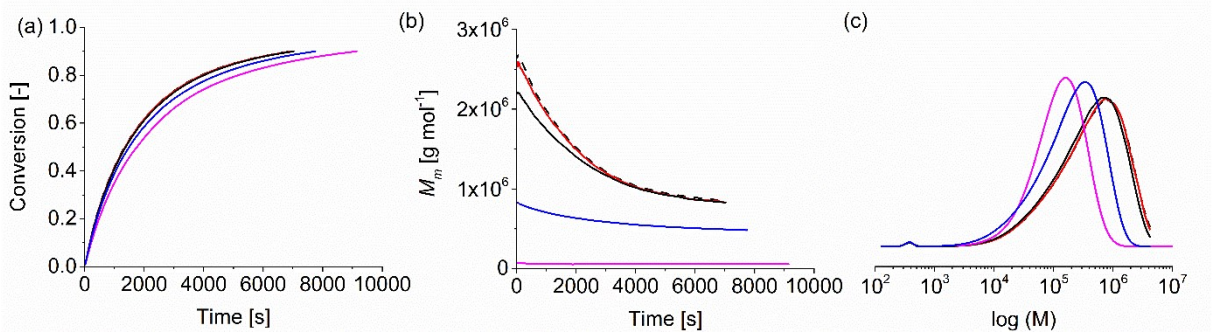

Figure S5. Influence of chain transfer to solvent coefficient C_{trS} on the (a) monomer conversion as a function of time, (b) mass average molar mass M_m as a function of time and (c) log-MMD of *n*BuA FRP (entry 6 in Table 2) with variation of the C_{trS}; dashed black line: 2 × 10^{-7}, red line: 2 × 10^{-6}, black full line: 2 × 10^{-5}, blue line: 2 × 10^{-4}, magenta line: 2 × 10^{-3}.

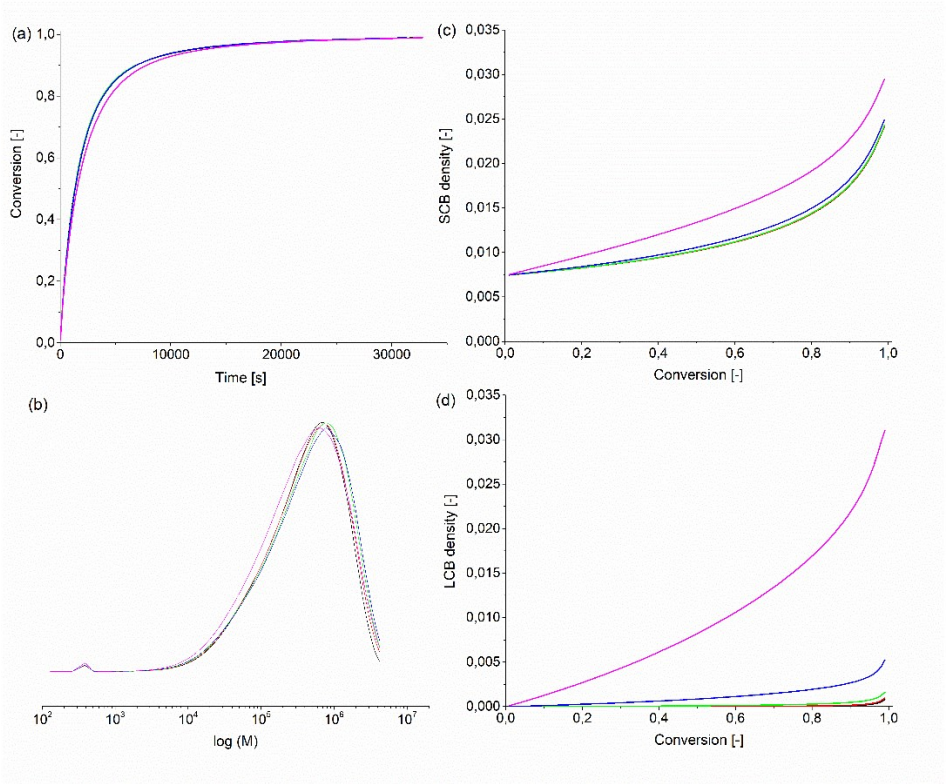

Figure S6. Influence of chain transfer to polymer reaction rate coefficient k_{trP} on the (a) monomer conversion as a function of time, (b) log-MMD at 0.9 monomer conversion, (c) short chain branching density *vs.* monomer conversion and (d) long chain branching density *vs.* monomer conversion of *n*BuA polymerization (entry 7 in Table 2) with variation of the k_{trP}; black line: k_{trP} = 0, red line: k_{trP} = 1 L mol^{-1} s^{-1}, green line: k_{trP} = 10 L mol^{-1} s^{-1}, blue line: k_{trP} = 100 L mol^{-1} s^{-1}, magenta line: k_{trP} = 10^3 L mol^{-1} s^{-1}. Only with very unrealistic values an effect is encountered (not defined per monomer unit at 333 K).

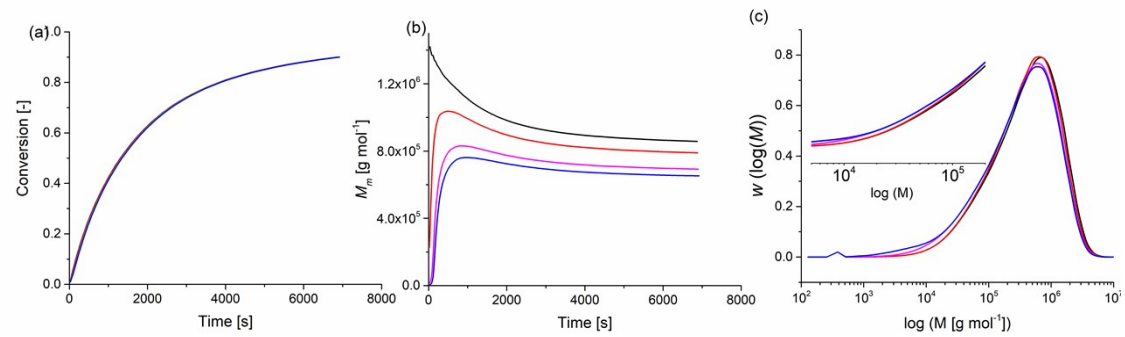

Figure S7. Influence of chain transfer agent concentration characterized by C_{CTA} = 10 on (a) monomer conversion as a function of time, (b) mass average molar mass M_m as a function of time and (c) log-molar mass distribution (MMD) at 0.9 of monomer conversion for isothermal solution free radical polymerization (FRP) of *n*-butyl acrylate (*n*BuA). The concentrations of [CTA]$_0$ are; black: 0 representing the reference case, red: 5× 10^{-5} mol L^{-1}, magenta: 1× 10^{-3} mol L^{-1}, blue: 3× 10^{-3} mol L^{-1} (entry 12 in Table 2).

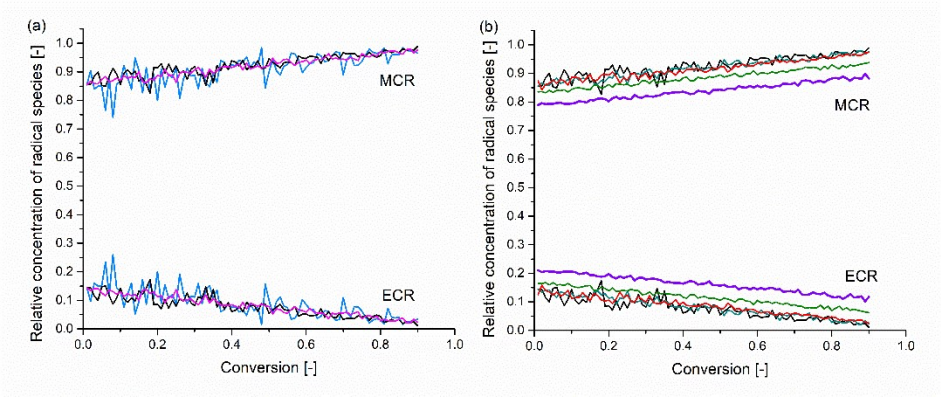

Figure S8. Relative concentrations of MCRs and ECRs *vs.* monomer conversion at different temperatures; blue: 313 K, magenta: 323 K , black: 333 K, dark cyan: 353 K , red: 363 K, olive green: 393, purple 413 K. Extra information for Figures 11 and 12 in the main text.

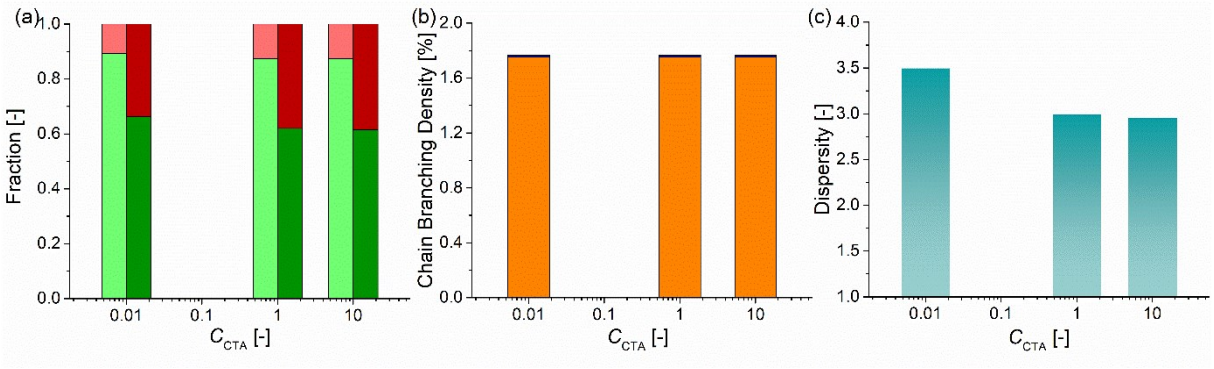

Figure S9. (a) Number fraction (light-green and light-red colors) and mass fraction (dark-green and dark-red colors) of macromonomer (green) and 'dead' polymer (red) *vs.* chain transfer to CTA coefficient C_{CTA} for free radical polymerization (FRP) of *n*-butyl acrylate (*n*BuA) and otherwise reference conditions from Table 2 (entry 1); kinetic parameters from Table 1 (solvent S1). The structures of polymer species contributing to the macromonomers and 'dead' polymers population are shown in Scheme 1 in green and red boxes respectively. (b) Long (blue) and short (orange) chain branching density *vs.* chain transfer to CTA coefficient C_{CTA}. The structures of polymer species contributing to the SCBD and LCBD are shown in Scheme 1 in orange and blue. (c) Dispersity at 0.9 of monomer conversion *vs.* chain transfer to CTA coefficient C_{CTA}.

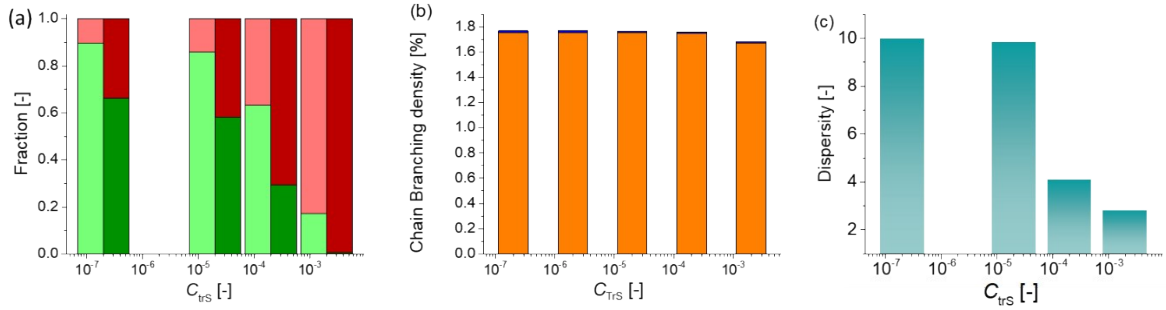

Figure S10. (a) Number fraction (light-green and light-red colors) and mass fraction (dark-green and dark-red colors) of macromonomer (green) and 'dead' polymer (red) *vs.* chain transfer to solvent coefficient C_{trS} for free radical polymerization (FRP) of n-butyl acrylate (*n*BuA) and otherwise reference conditions from Table 2 (entry 1); kinetic parameters from Table 1 (solvent

S1). The structures of polymer species contributing to the macromonomers and 'dead' polymers population are shown in Scheme 1 in green and red boxes respectively. (b) Long (blue) and short (orange) chain branching density *vs.* chain transfer to solvent coefficient C_{trS}. The structures of polymer species contributing to the SCBD and LCBD are shown in Scheme 1 in orange and blue. (c) Dispersity at 0.9 of monomer conversion *vs.* chain transfer to solvent coefficient C_{trS}.

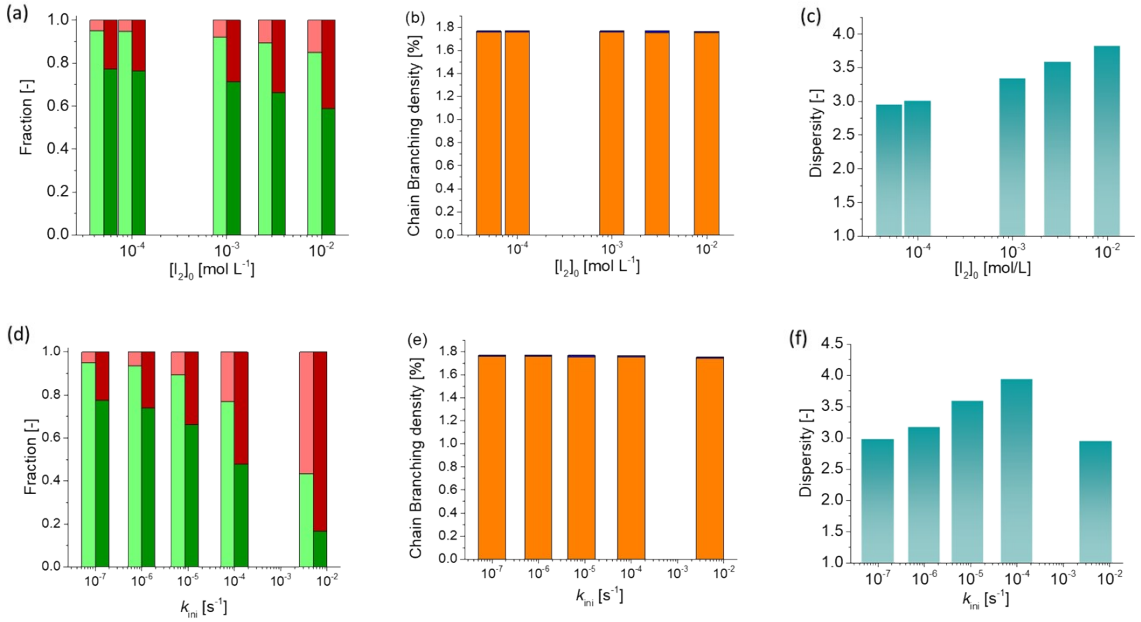

Figure S11. (a, d) Number fraction (light-green and light-red colors) and mass fraction (dark-green and dark-red colors) of macromonomer (green) and 'dead' polymer (red) *vs.* initial initiator concentration (a) and initiation rate coefficient (d) for free radical polymerization (FRP) of n-butyl acrylate (*n*BuA) and otherwise reference conditions from Table 2 (entry 1); kinetic parameters from Table 1 (solvent S1). The structures of polymer species contributing to the macromonomers and 'dead' polymers population are shown in Scheme 1 in green and red boxes respectively. (b, e) Long (blue) and short (orange) chain branching density *vs.* initial initiator concentration (b) and initiation rate coefficient (e). The structures of polymer species contributing to the SCBD and LCBD are shown in Scheme 1 in orange and blue. (c, f) Dispersity at 0.9 of monomer conversion *vs.* initial initiator concentration (c) and initiation rate coefficient (f).

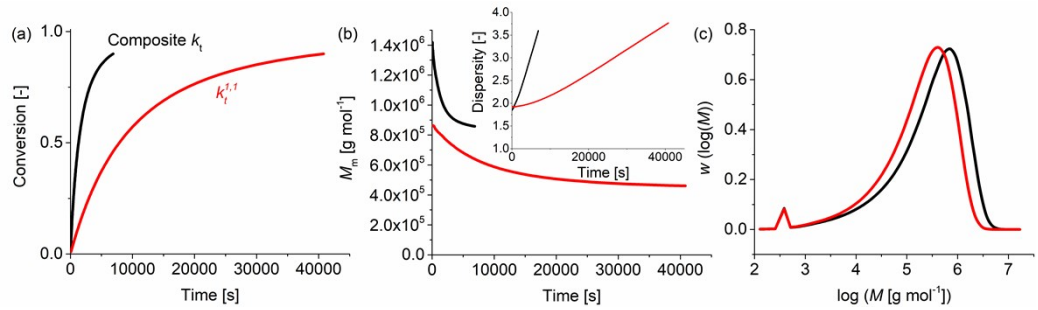

Figure S12. Relevance of chain length and monomer conversion dependent apparent termination rate coefficients by comparison with model outcome in which a constant value (evaluated at unimer length is used); subplots for reference conditions in the main text; a) monomer conversion as a function of time, (b) mass average molar mass M_m as a function of time and (c) log-MMD at 0.9 monomer conversion; inset of subplot (b) shows the dispersity $Đ$ as a function of time.

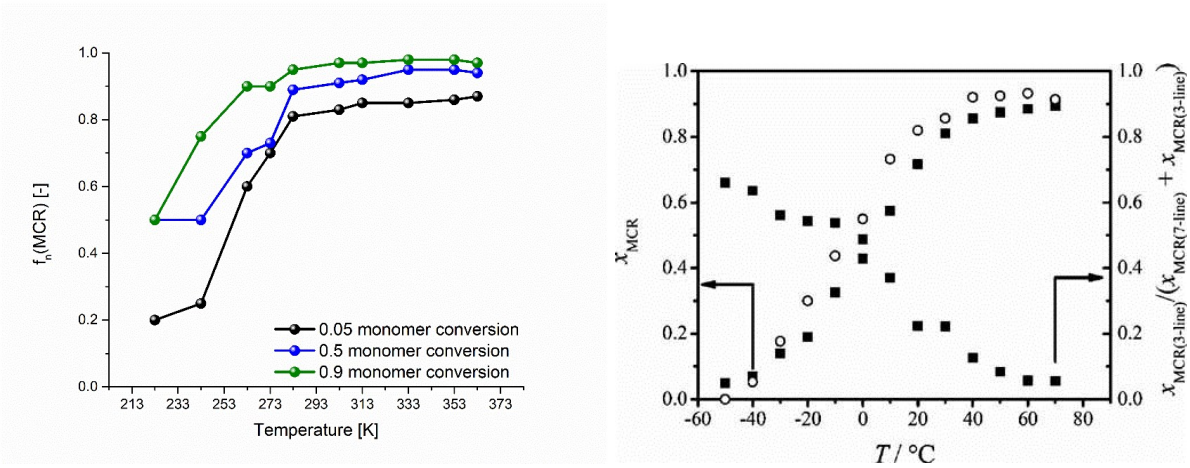

Figure S13: Comparison of MCR fractions with literature data. Left: number fraction of MCRs *vs.* temperature for various monomer conversion; black: 0.05 monomer conversion, blue: 0.5 monomer conversion, green: 0.9 monomer conversion. Right: fraction of MCRs observed experimentally by Barth *et. al.* [J. Barth, M. Buback, P. Hesse, T. Sergeeva, Macromol. Rapid Commun. 2009, 30, 1969-1974], reproduced with the permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2009