Supporting Information

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Controlled One-Pot Synthesis of Polystyrene-block-Polycaprolactone Copolymers by Simultaneous RAFT and ROP

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S1. Results

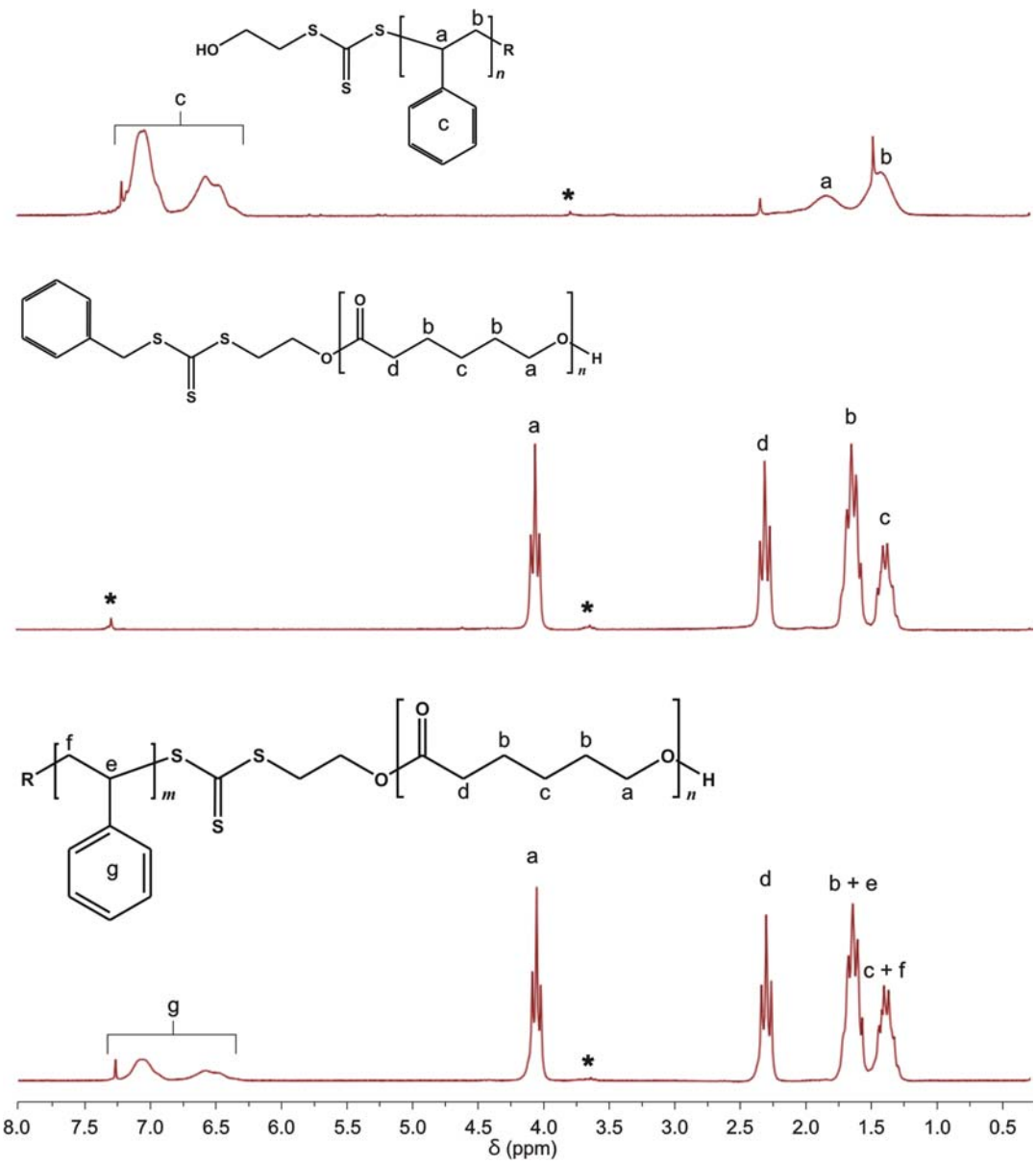

Figure S1. Assigned ^{1}H NMR spectra in $CDCl_3$ for PCL, PS and PS-*b*-PCL polymers synthesized using **(1)** in the dual roles of CTA for RAFT of styrene and coinitiator for ROP of ε-CL mediated by DPP. Selected shifts associated with **(1)** are indicated by a symbol (*).

GPC analysis with selective detection of trithiocarbonate function by UV at 433 nm

(chain extension experiment)

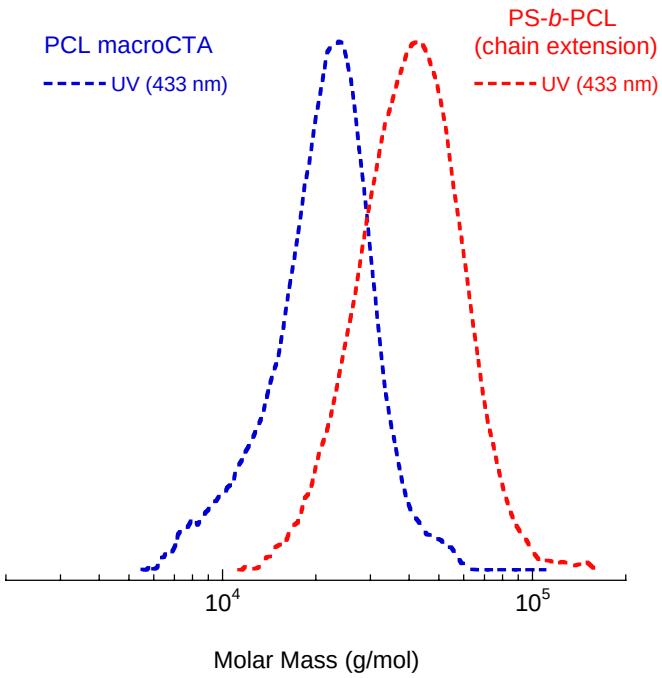

Figure S2. GPC chromatograms recorded with UV-vis detector set at the λ_{max} of **(1)** (433 nm) for a PCL macroCTA prepared using DPP as the catalyst for the ROP process (Table 1, entry 1), and corresponding chain extension by RAFT polymerization of styrene (Table 1, entry 2).

Analysis of chain-end functionalization with triothiocarbonate groups by UV-vis

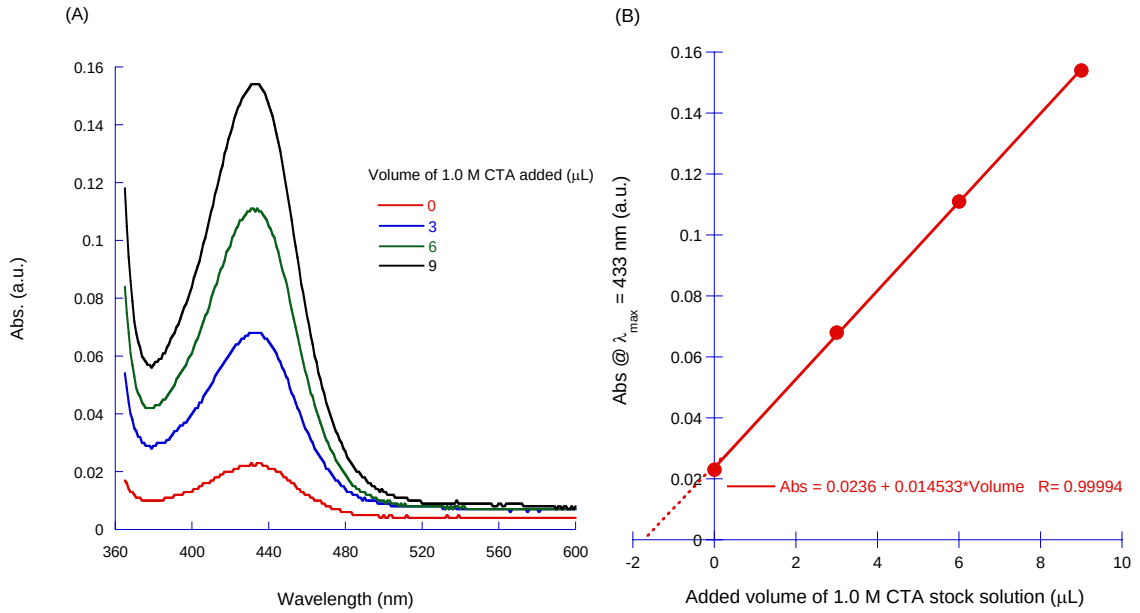

Figure S3. (a) UV-vis spectra recorded in THF showing the typical absorption band of **(1)** centered at 433 nm for a 15.0 mg/3.0 mL PCL macroCTA sample (entry 1, Table1, main document) and subsequent addition of indicated volumes of 1.0 M CTA stock solution; (b) corresponding standard addition plot used to determine the amount of CTA present in the polymer sample. The amount of CTA found corresponds to 105% chain-end functionalization for the PCL macroCTA sample (entry 1, Table 1, main document).

Conversion and M_n(theo) calculation

Theoretical molar masses (M_n(theo)) and degree of polymerization (DP(theo)), were calculated from the conversion of styrene determined by ^{1}H NMR analysis of a reaction aliquot containing anisole as the internal reference, assuming quantitative efficiency of **(1)** (Figure S2, spectrum **a** and **b**), and from ^{1}H NMR integral ratio corresponding to PS A(7.3-6.3) and PCL A(4.2 - 3.9) protons (Figure S2, spectrum **c**). The NMR integral area between 3.77 and 3.68 ppm A(3.77 - 3.68) , assigned to -OCH_3 anisole protons, is initially set to 3.0 at t = 0, where t is the reaction time (Figure S2, spectrum **a**).

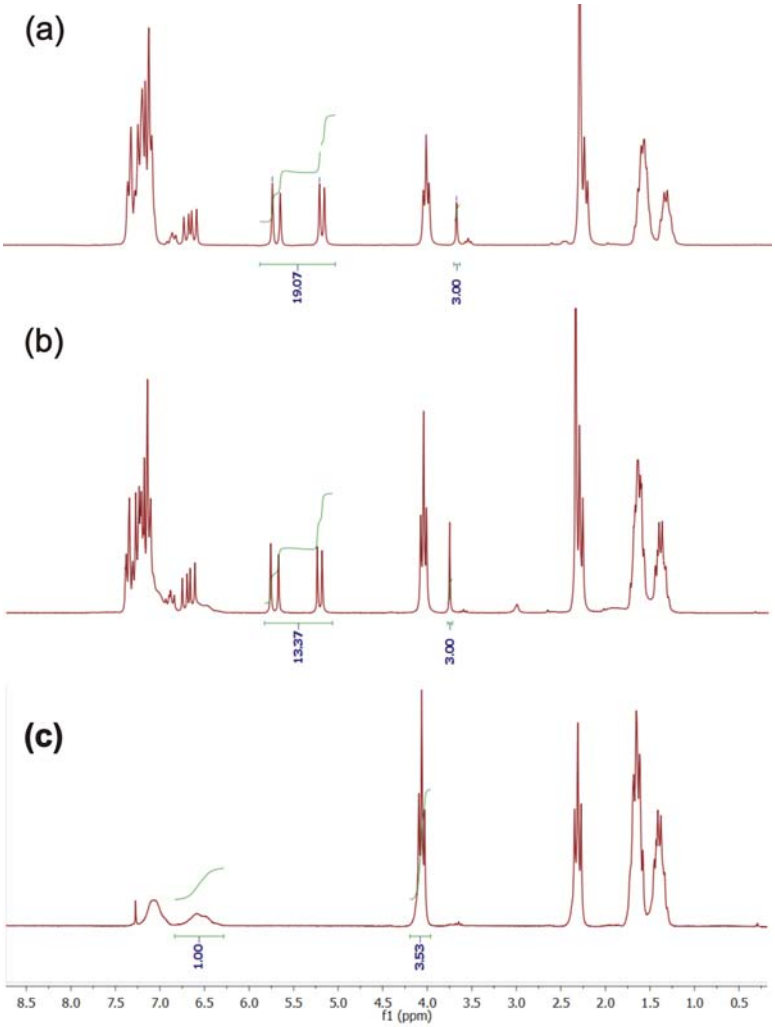

Figure S4. ^{1}H NMR spectra in $CDCl_3$ for a one-pot reaction mixture before (A) and after (B) the polymerization, and for the pure (precipitated) PS-*b*-PCL copolymer product (C).

Hydrolysis of PS-*b*-PCL block copolymer yielding PS homopolymer as product

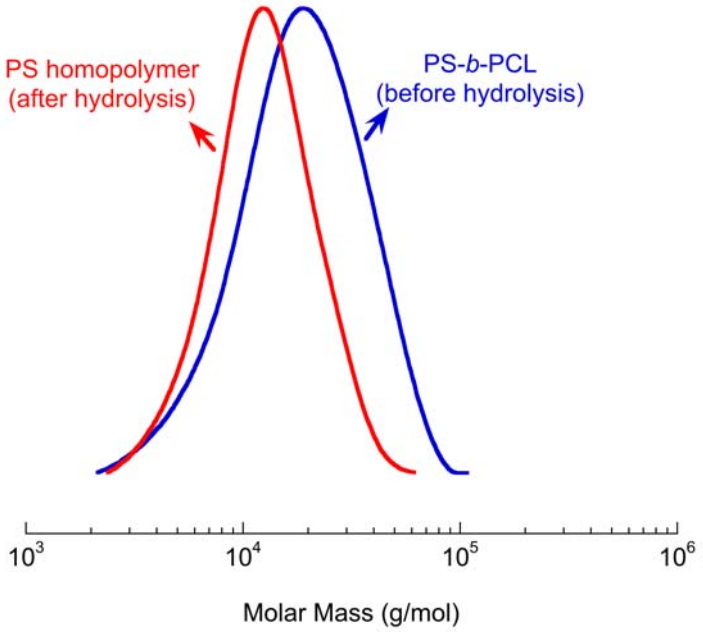

Figure S5. GPC traces of a PS-*b*-PCL copolymer synthesized in a one-pot polymerization procedure and corresponding hydrolyzed product obtained after 24 h of reaction at 85 °C in 30% wt. HCl.

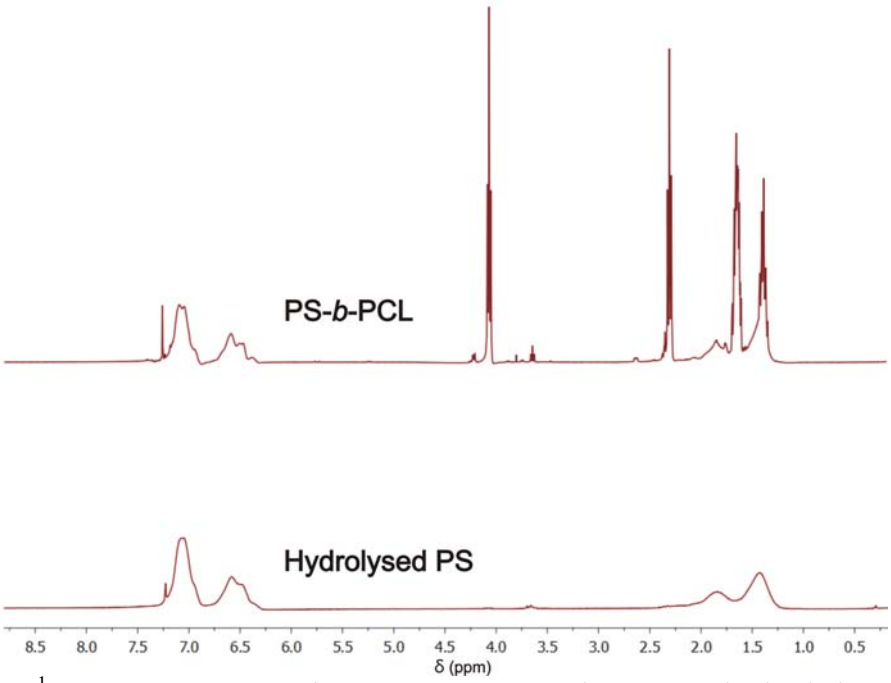

Figure S6. ^{1}H NMR spectra of a PS-*b*-PCL copolymer synthesized in a one-pot polymerization procedure and corresponding hydrolyzed product obtained after 24 h of reaction at 85 °C in 30% wt. HCl.

Chain extension experiment using a $Sn(Oct)_2$-made PCL macroCTA for the RAFT polymerization of styrene

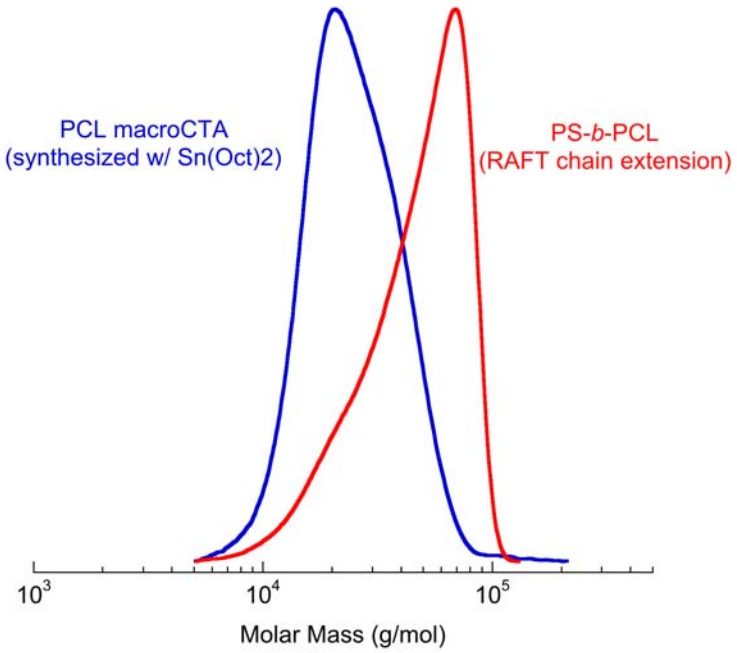

Figure S7. GPC chromatograms of a PCL macroCTA prepared using $Sn(oct)_2$ as catalyst for ROP process (Table 1, entry 10), and corresponding chain extension by RAFT polymerization of styrene (Table 1, entry 11).

GPC analysis with selective detection of trithiocarbonate function by UV at 433 nm

(one-pot reaction with $Sn(Oct)_2$ catalyst)

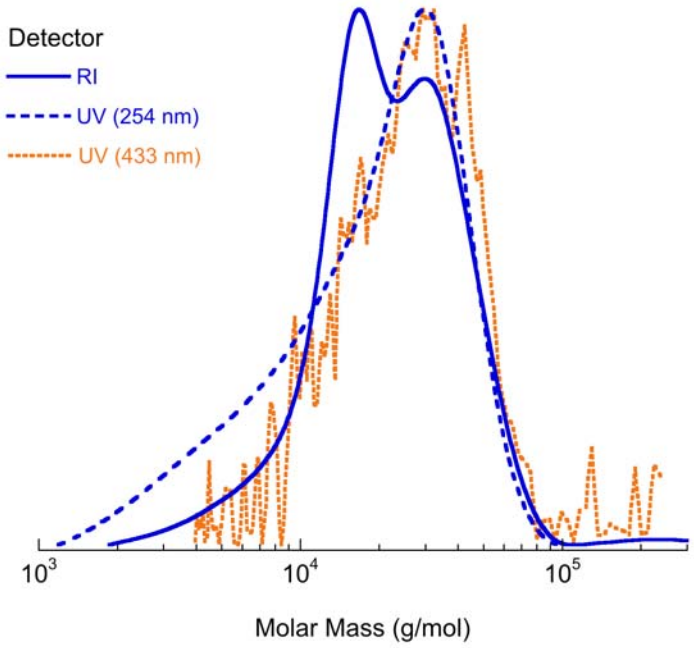

Figure S8. GPC chromatograms recorded with three detection settings (as indicated) in THF for 5.0 mg/mL of polymer sample resulting from a one-pot polymerization experiment involving simultaneous RAFT and ROP processes in the presence of $Sn(Oct)_2$ catalyst (Table 1, entry 12, main document).

Chain extension experiment using PS-*b*-PCL macroCTA made in a one-pot simultaneous RAFT and ROP in presence of Sn(Oct)2

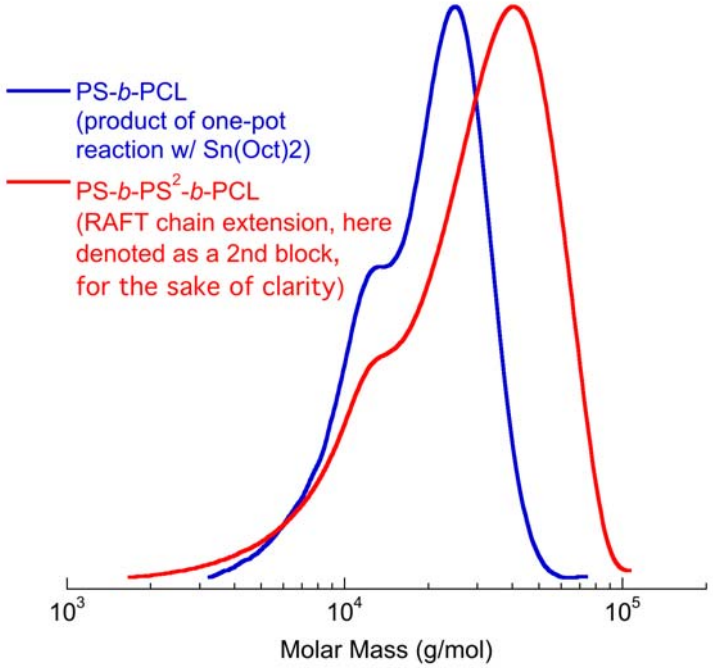

Figure S9. GPC chromatograms of a PS-*b*-PCL copolymer prepared using $Sn(oct)_2$ as the catalyst for ROP process (experimental conditions: [CTA]:[I]:[$Sn(Oct)_2$]:[St]:[CL] = 1:0.25:0.5:150:150, $[St]_0 = [CL]_0 = 2.88$ M, T = 120 ˚C) and used for further chain extension by RAFT polymerization of styrene (experimental conditions: [PS-*b*-PCL macroCTA]:[I]:[$Sn(Oct)_2$]:[St]:[CL] = 1:0.25:–:200:–, $[St]_0 = 2.88$ M, T = 120 °C).

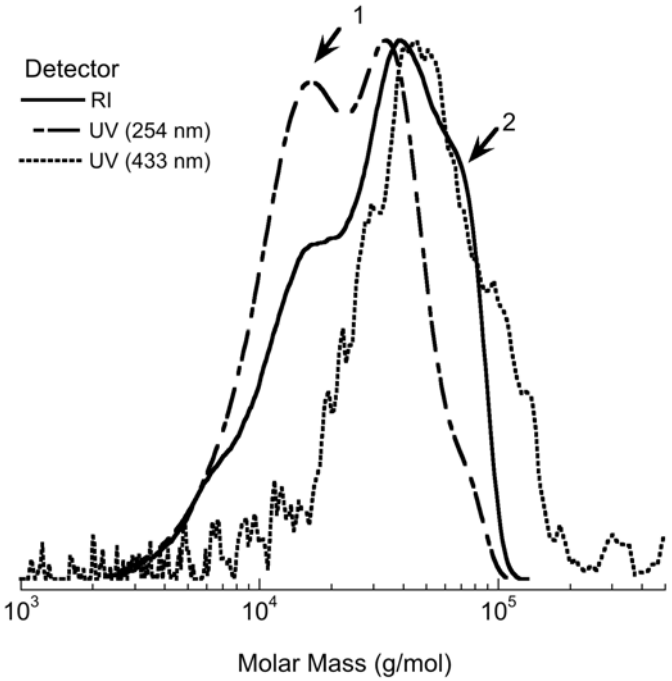

Figure S10. GPC chromatograms in THF at 5.0 mg/mL of the polymer obtained in a one-pot/two-step polymerization experiment involving RAFT first (step 1, 7 h), and then simultaneous RAFT (thermally initiated) and ROP processes in the presence of $Sn(Oct)_2$ catalyst (step 2, + 5 h, conv.(St) = 73%, conv.(CL) = 77%). Experimental conditions: $[CTA]:[I]:[Sn(Oct)_2]:[St]:[CL] = 1:0.25:0.5:200:200$, $[St]_0 = [CL]_0 = 2.88$ M, T = 120 ˚C.