Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile Synthesis of Graft Copolymers of Controlled Architecture. Copolymerization of Fluorinated and Non-Fluorinated Poly(dimethylsiloxane) Macromonomers with Trialkylsilyl Methacrylates using RAFT Polymerization

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Figure 1. ^{1}H NMR spectrum of PDMSMAsymm Macro RAFT agent in $CDCl_3$

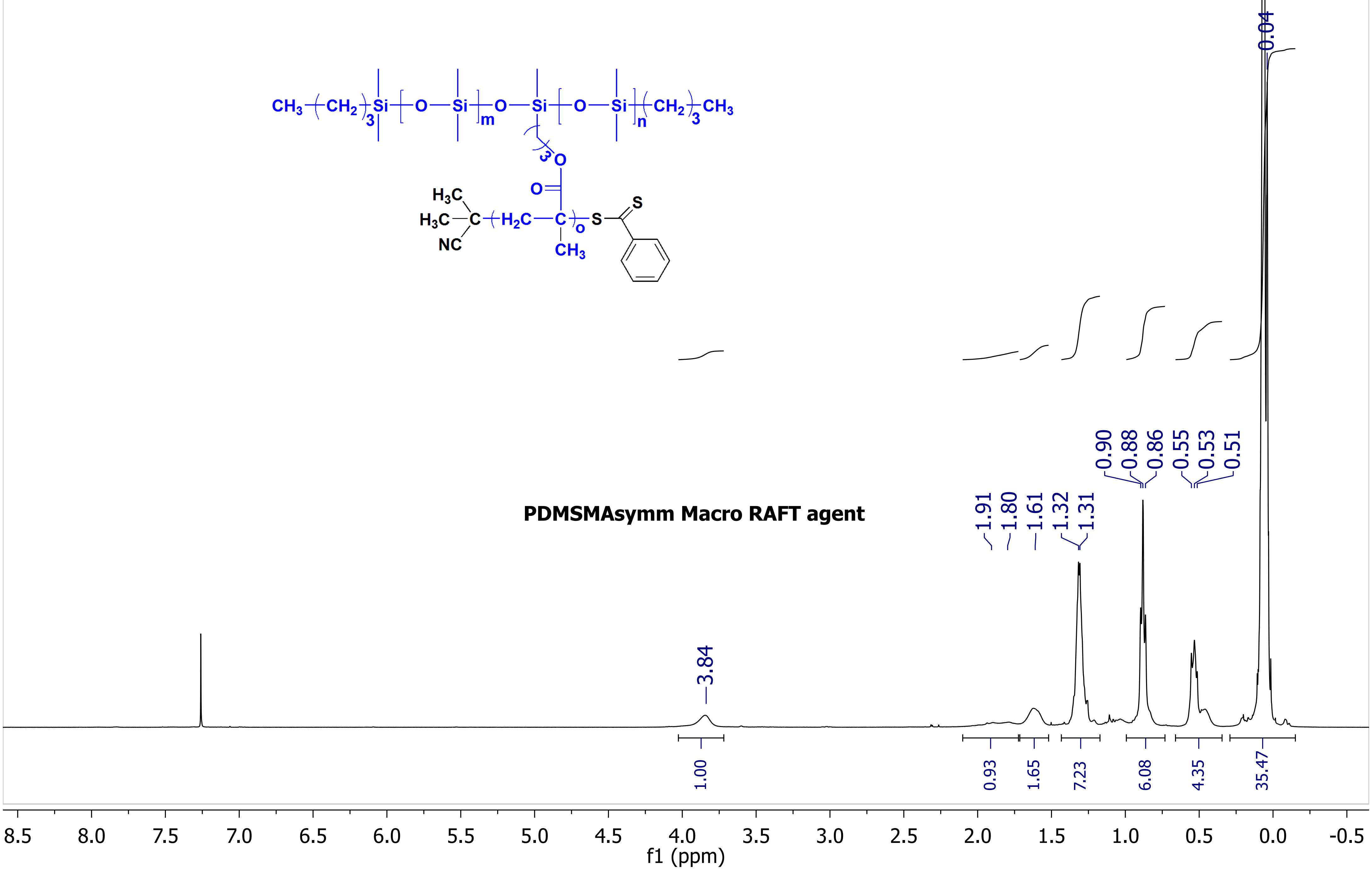

Figure 2. ^{1}H NMR spectrum of PDMSMAfluor symm Macro RAFT agent in $CDCl_3$

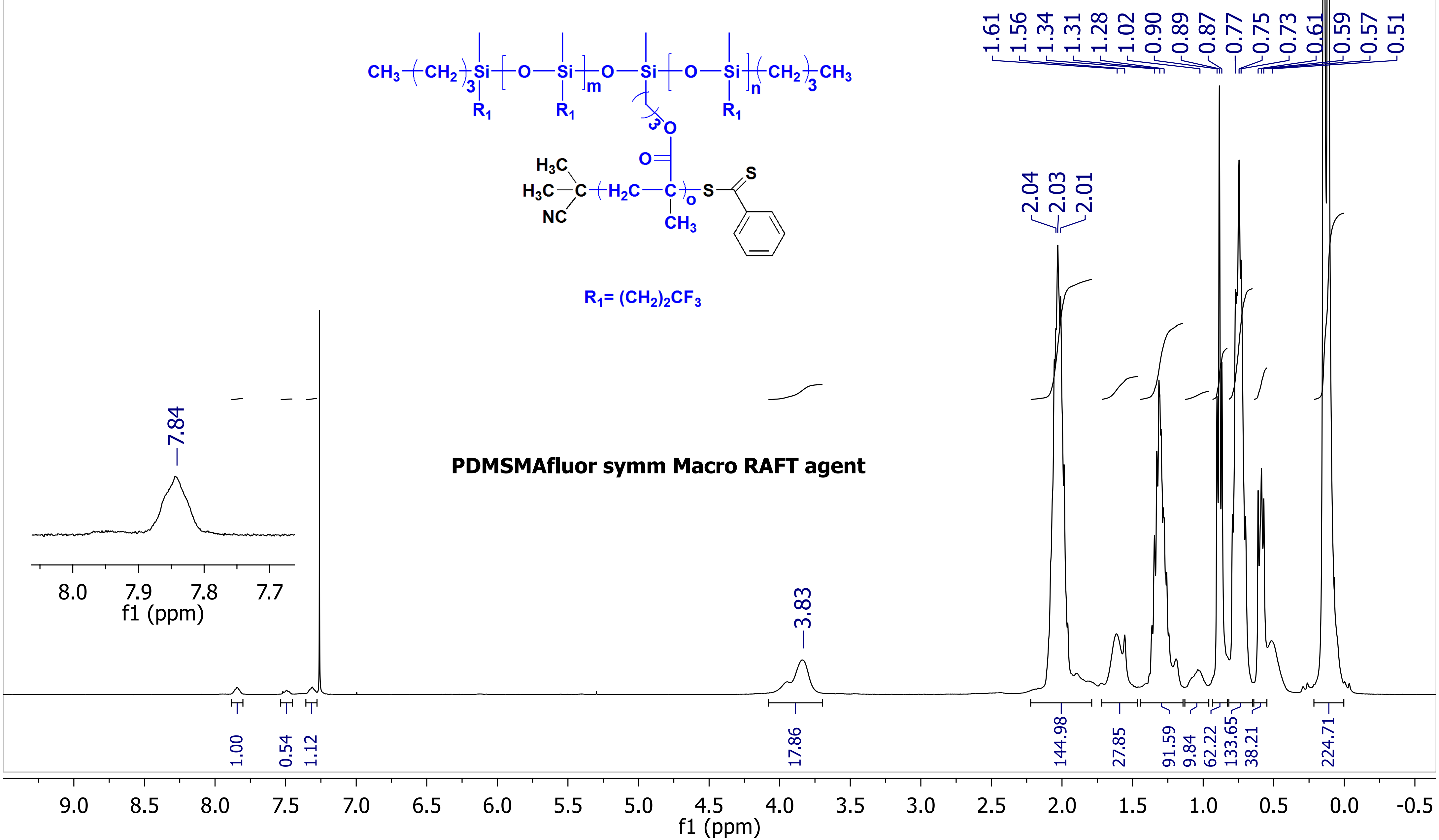

Figure 3. ^{1}H NMR spectrum of p(PDMSMAsymm)-b-p(TBDMSMA) in $CDCl_3$

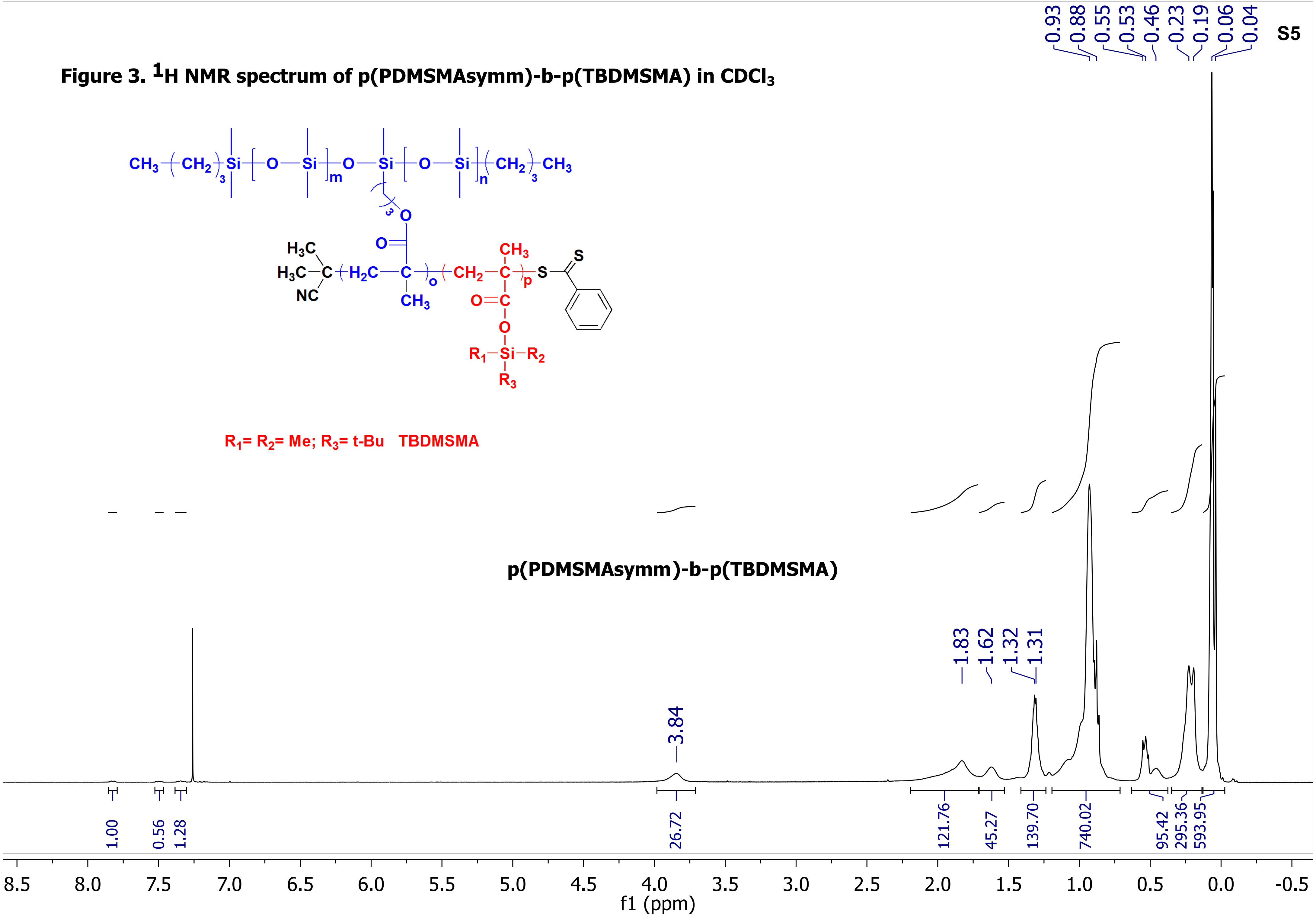

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Figure 4. ^{1}H NMR spectrum of p(PDMSMAfluor symm)-b-p(TBDMSMA) in $CDCl_3$

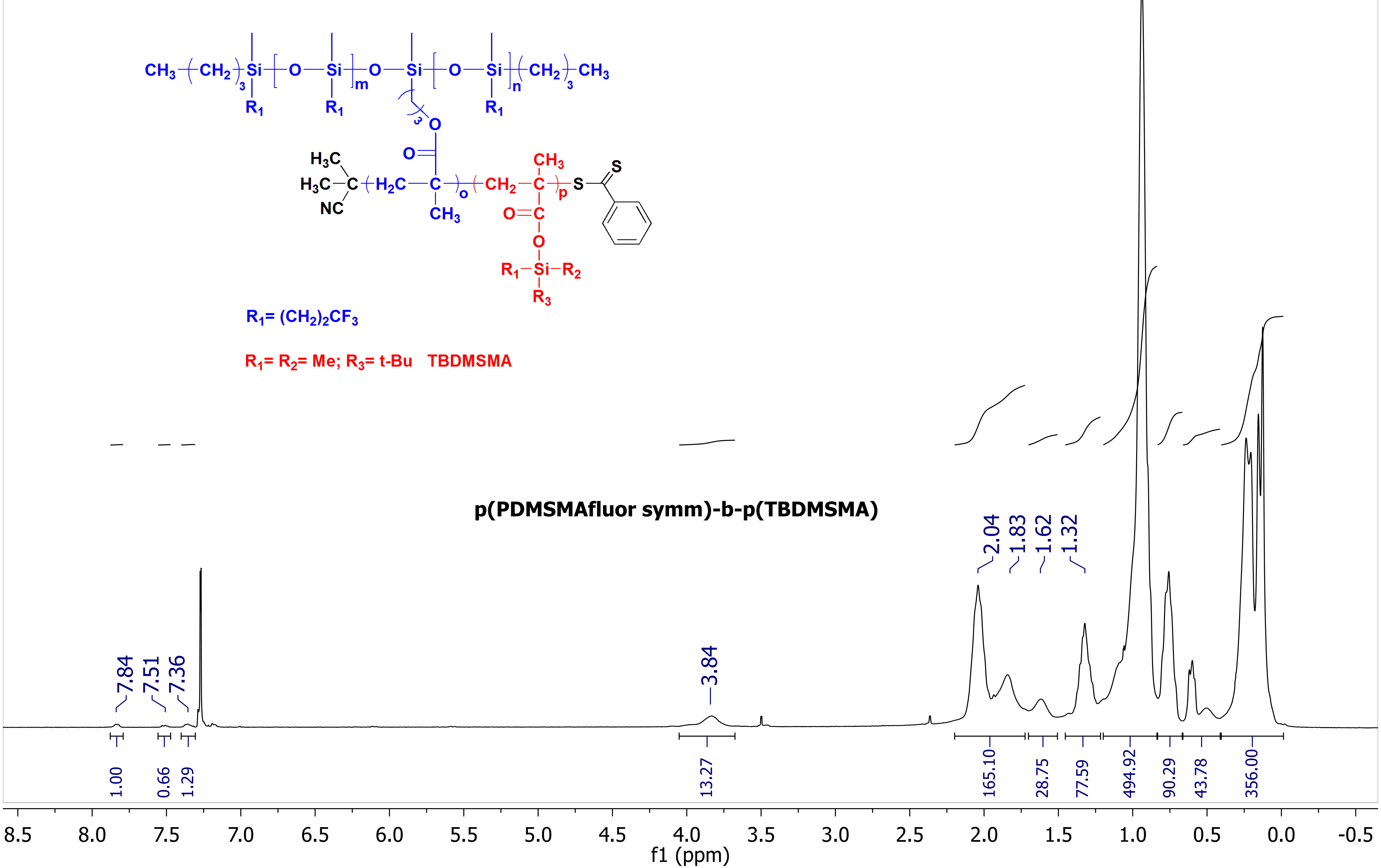


Figure 5. ^{1}H NMR spectrum of p(PDMSMAsymm)-b-p(TIPSMA) in $CDCl_3$

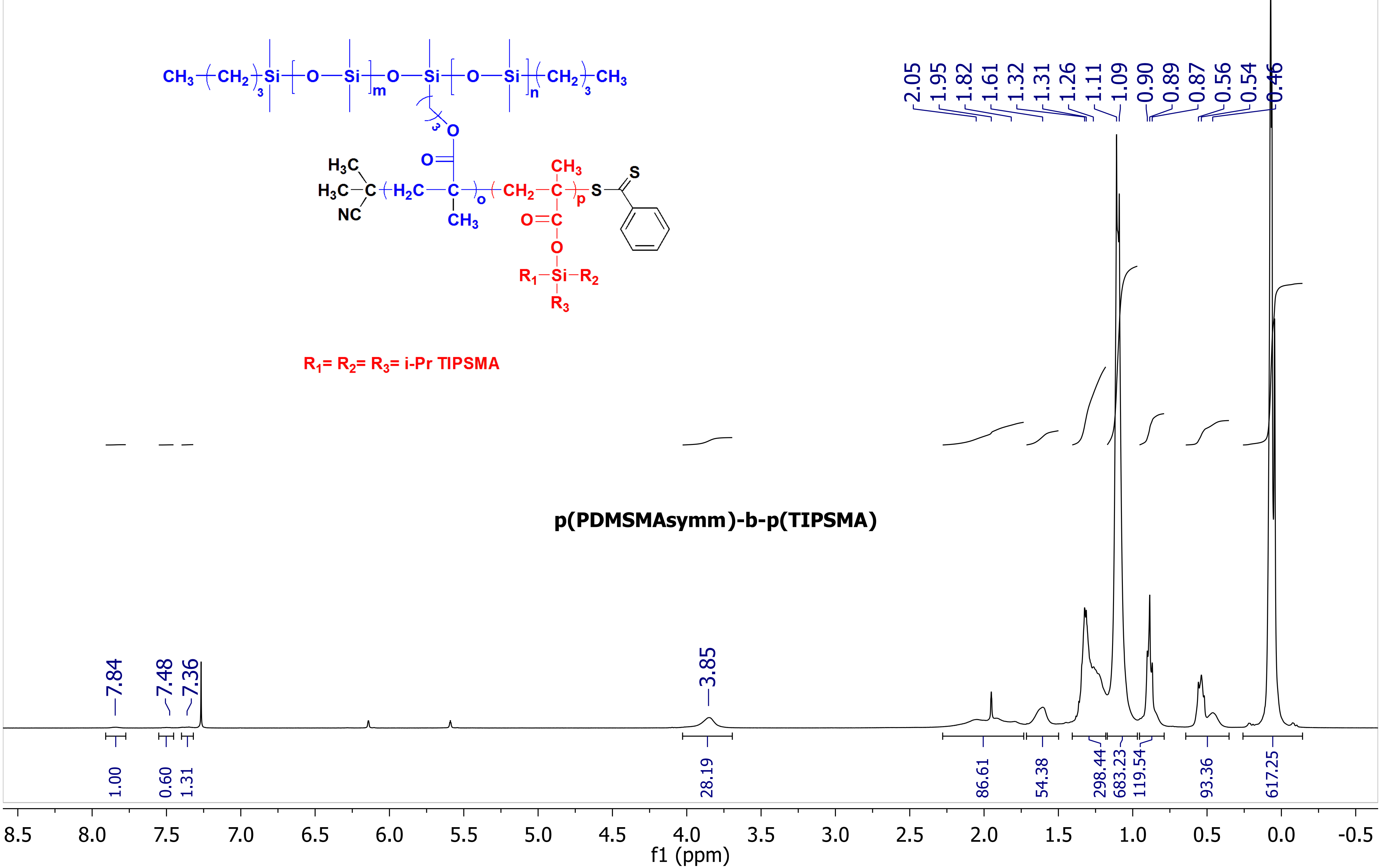
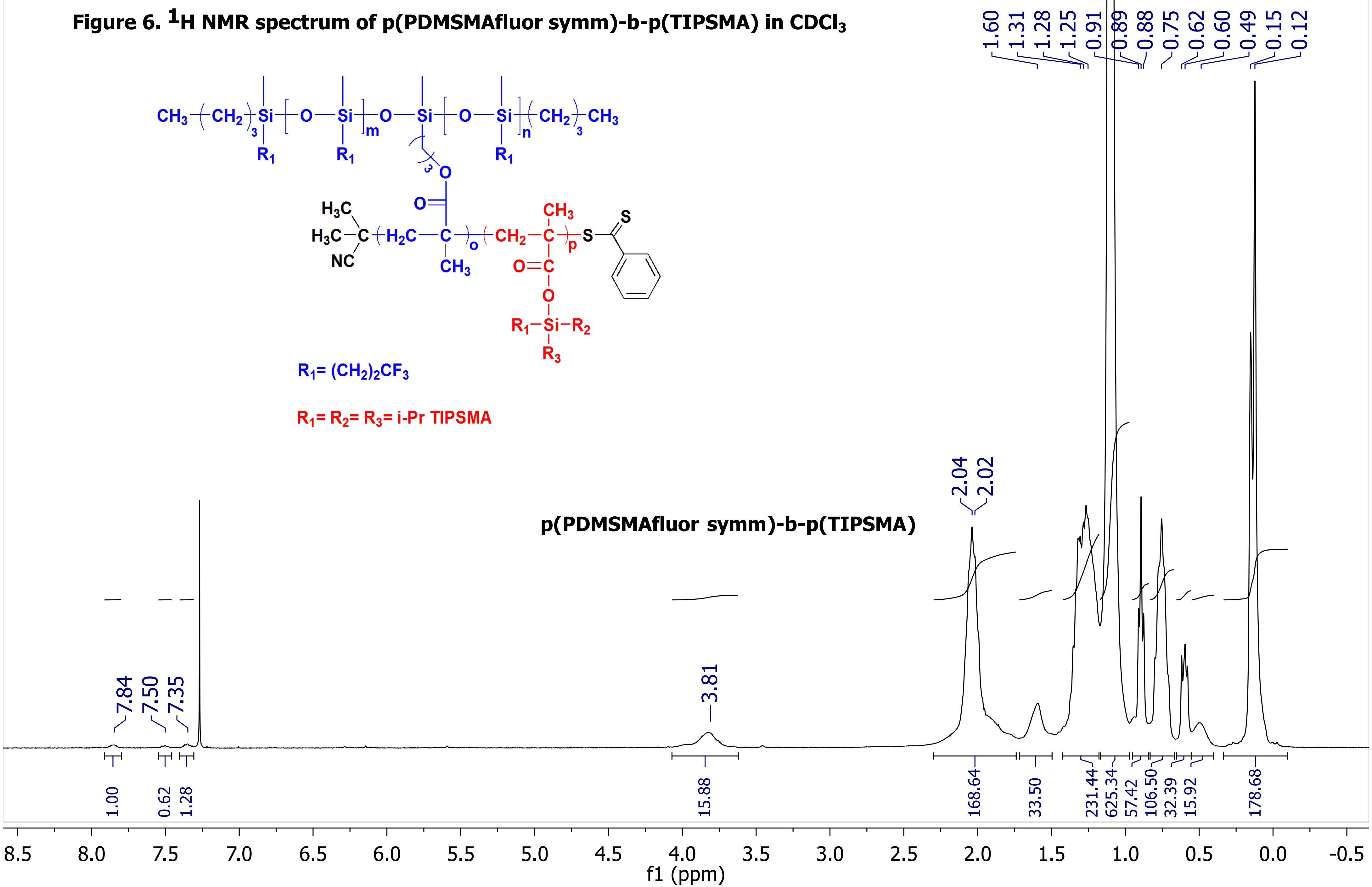


Figure 6. ^{1}H NMR spectrum of p(PDMSMAfluor symm)-b-p(TIPSMA) in $CDCl_3$



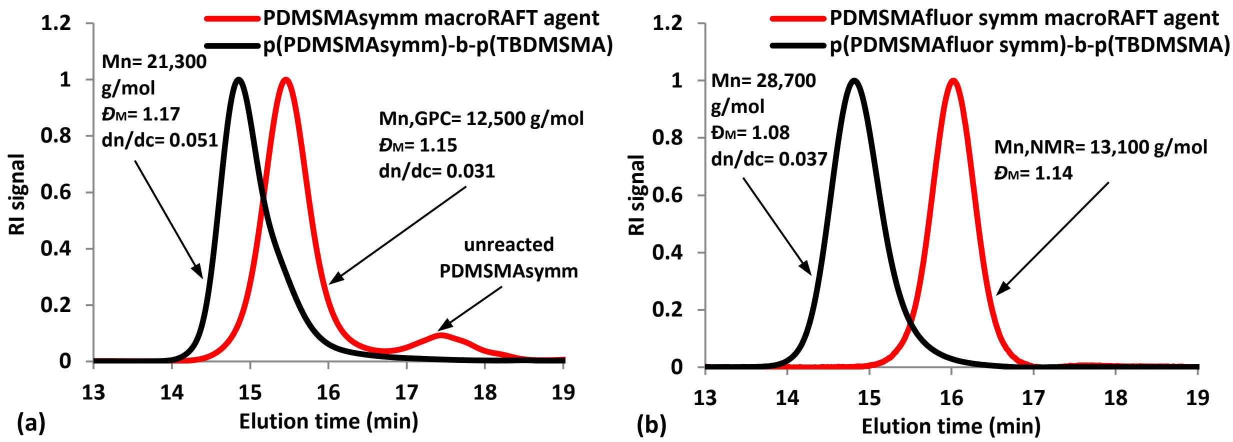


Figure S7. (a) TD-SEC traces of PDMSsymm macro RAFT agent (M_n= 12 500 g/mol and $Đ_M$= 1.15) and p(PDMSMAsymm)-b-p(TBDMSMA) block copolymer (M_n= 21 300 g/mol and $Đ_M$= 1.17) obtained by *in situ* chain extension of macro RAFT agent with TBDMSMA monomer at 70°C in toluene. For the determination of $M_{n,TD\text{-}SEC}$ crude PDMSsymm macro RAFT agent was used. **(b)** TD-SEC traces of PDMSfluor symm macro RAFT agent ($M_{n,NMR}$= 13 100 g/mol and $Đ_M$= 1.14) and p(PDMSMAfluor symm)-b-p(TBDMSMA) block copolymer (M_n= 28 700 g/mol and $Đ_M$= 1.08) obtained by *in situ* chain extension with TBDMSMA at 70° C in toluene. For the determination of $M_{n,NMR}$ precipitated PDMSfluor symm macro RAFT agent was used.

Determination of global kinetic constants of trialkylsilyl methacrylates and PDMS macromononomers

The global kinetic constants (k_g) of polymerization of trialkylsilyl methacrylates and PDMSMA macromonomers were determined using an overall kinetics law of the following form (Equation 1)[1]:

$$V_p = -\frac{d[M]}{dt} = k_p \times [M] \times [P_n] \quad (1)$$

where k_p is the propagation rate constant, $[M]$ is the monomer molar concentrations, and $[P_n]$ is the radical concentration in the reaction media. In the quasi-stationary state, characterized by a constant concentration of radical species in the reaction medium, the amount of the initiated radicals is equal to the amount of the terminated radicals as shown in Equation 2:

$$2 \times f \times k_d \times [A] = 2 \times k_t \times [P_n] \times [P_n] \quad (2)$$

where k_d is the rate constant of decomposition of the initiator (initiation rate constant), *f* is the efficiency of the initiator, [*A*] and [A_0] are the initial and instantaneous concentrations of the initiator, and k_t is the termination rate constant. Therefore, it follows:

$$[P_n] = \sqrt[2]{(f \times k_d \times [A]/k_t} \;=\; \sqrt[2]{(f \times k_d \times [A_0] \times e^{-k_d t}/k_t} \quad (3)$$

By substituting Equation (3) in Equation (1), it follows:

$$V_p = -\frac{d[M]}{dt} = k_p \times \, [M] \times \sqrt[2]{f \times k_d \times [A_0] \times e^{-k_d t}/k_t} \quad (4)$$

If the initiator concentration is considered constant, the integration of the Equation (4) gives:

$$ln\,\frac{[M_0]}{[M]} = k_p \times \sqrt[2]{f \times k_d \times [A_0]/k_t} \quad (5)$$

The values of global rate constants of RAFT polymerization ($k_g = k_p \times \sqrt[2]{f \times k_d/k_t}$) were therefore calculated from the slope of the each straight line in Figure S8.

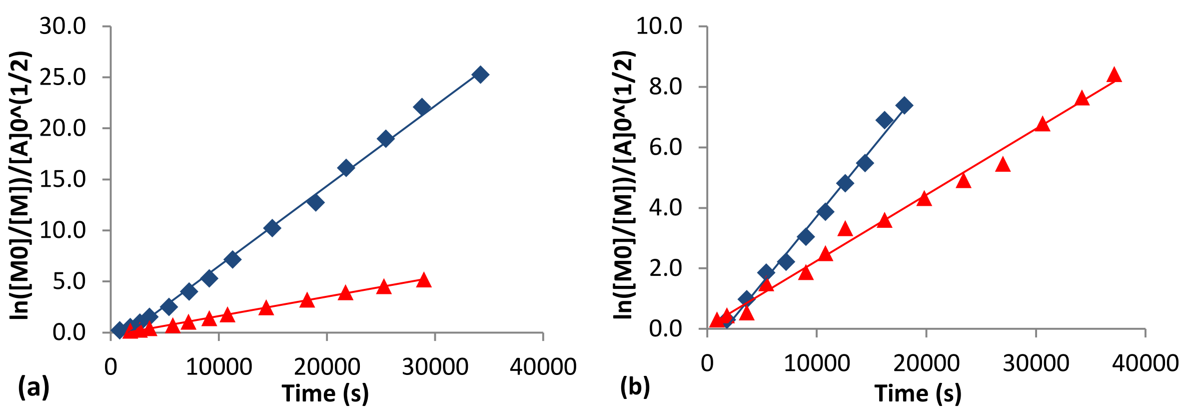


Figure S8. (a) Plots of ln([M_0]/[M])/$[A]_0^{1/2}$ versus polymerization time for TBDMSMA (♦) and TIPSMA (▲) polymerization in toluene at 70°C ([CPDB]/[AIBN]= 5/1): k_g(TBDMSMA)= 8.0 x 10^{-4} L $mol^{-1/2}$ s^{-1} (R^2= 0.997); k_g(TIPSMA)= 2.0 x 10^{-4} L $mol^{-1/2}$ s^{-1} (R^2= 0.999). **(b)** Plots of ln([M_0]/[M])/$[A]_0^{1/2}$ versus polymerization time for symmetrical PDMSMA (♦) , and fluorinated symmetrical PDMSMA (▲) polymerization in toluene at 70°C ([CPDB]/[AIBN]= 2/1): k_g(PDMSMA symm)= 4.0 x 10-4 L mol-1/2 s-1 (R2= 0.991); k_g(PDMSMA fluor symm)= 2.0 x 10-4 L mol-1/2 s-1 (R2= 0.991) .

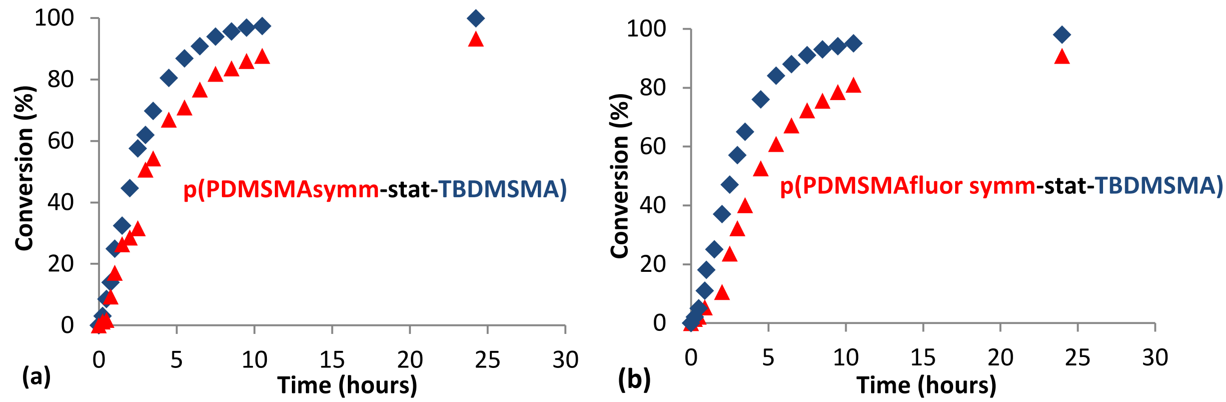


Figure S9. (a) Plot of monomer conversion versus time for RAFT copolymerization of TBDMSMA (♦) and symmetrical PDMSMA macromonomer ($PDMSMA_{symm}$, ▲), in the presence of CPDB at 70°C in toluene. **(b)** Plot of monomer conversion *versus* time for RAFT copolymerization of TBDMSMA (♦) and symmetrical fluorinated PDMSMA macromonomer ($PDMSMA_{fluor\ symm}$, ▲), in the presence of CPDB at 70°C in toluene.

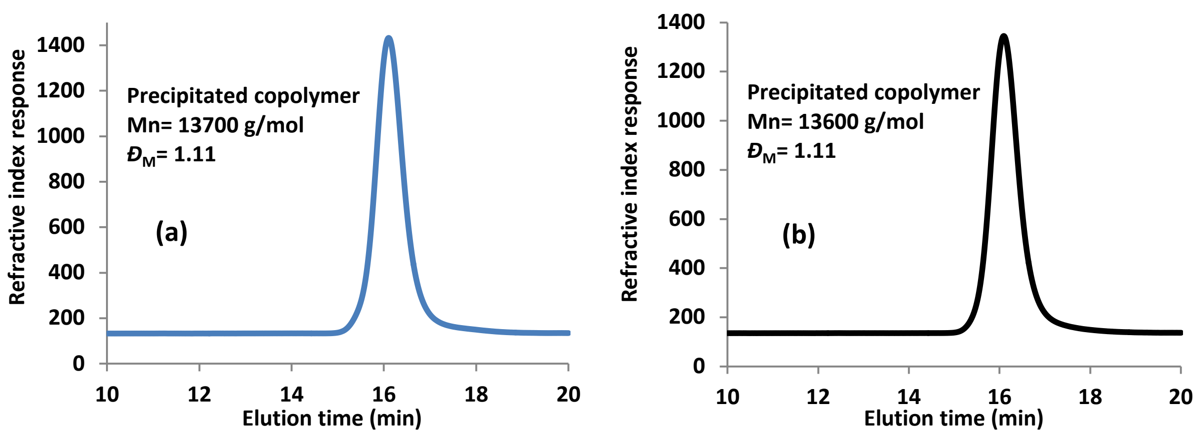


Figure S10. TD-SEC traces of statistical copolymers obtained by CPDB-mediated RAFT copolymerization of TBDMSMA and either PDMSsymm or PDMSMAfluor symm macromonomers at 70°C in toluene. (a) p(PDMSMAsymm-stat-TBDMSMA) (Mn= 13 700 g/mol and ĐM= 1.11). (b) p(PDMSMAfluor symm-stat-TBDMSMA) (Mn= 13 600 g/mol and ĐM= 1.11).

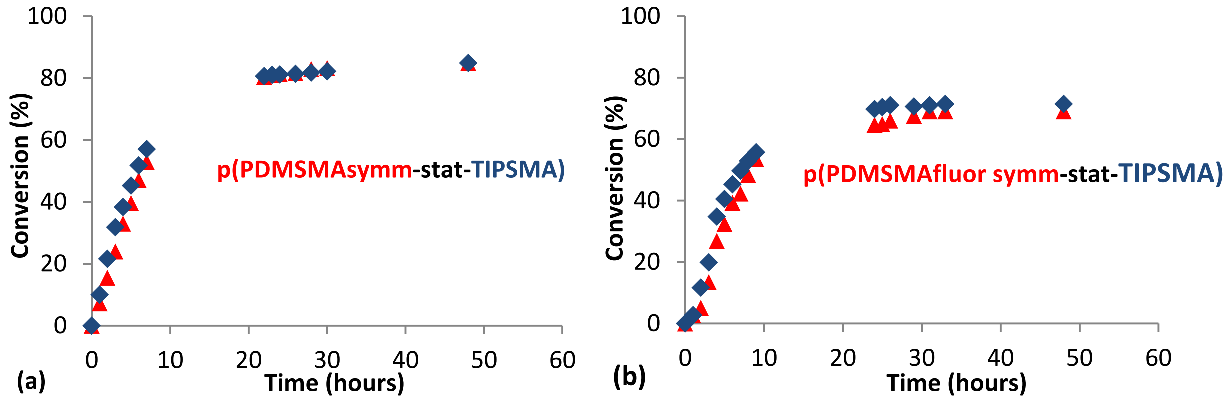


Figure S11. (a) Plot of monomer conversion *versus* time for RAFT copolymerization of TIPSMA (♦) and symmetrical PDMSMA macromonomer (▲) ($PDMSMA_{symm}$), in the presence of CPDB at 70°C in toluene. **(b)** Plot of monomer conversion *versus* time for RAFT copolymerization of TIPSMA (♦) and symmetrical fluorinated PDMSMA macromonomer ($PDMSMA_{fluor\ symm}$, (▲)), in the presence of CPDB at 70°C in toluene.

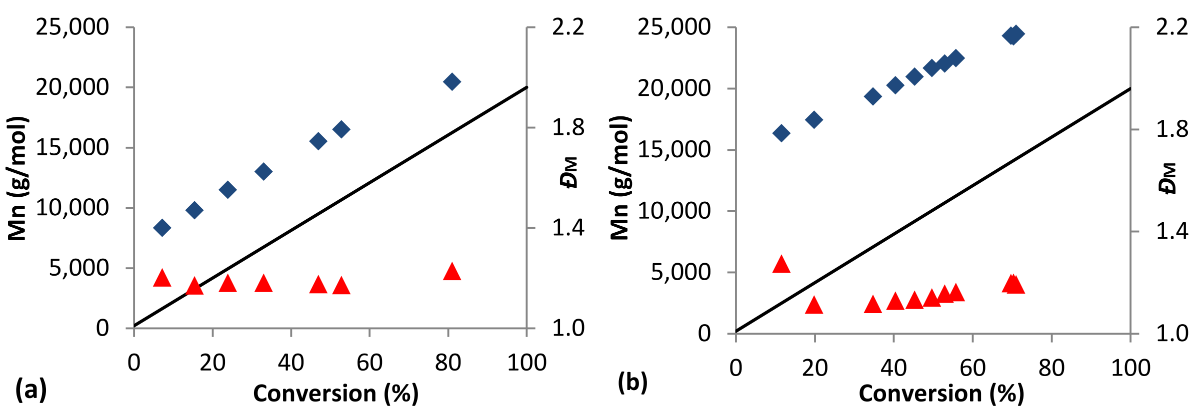


Figure S12. Evolution of the number-average molar mass M_n (♦) and dispersity $Đ_M$ (▲) with monomer conversion in the statistical copolymerization of TIPSMA and either $PDMSMA_{symm}$ **(a)** or $PDMSMA_{fluor\ symm}$ **(b)** at 70°C mediated by CPDB.

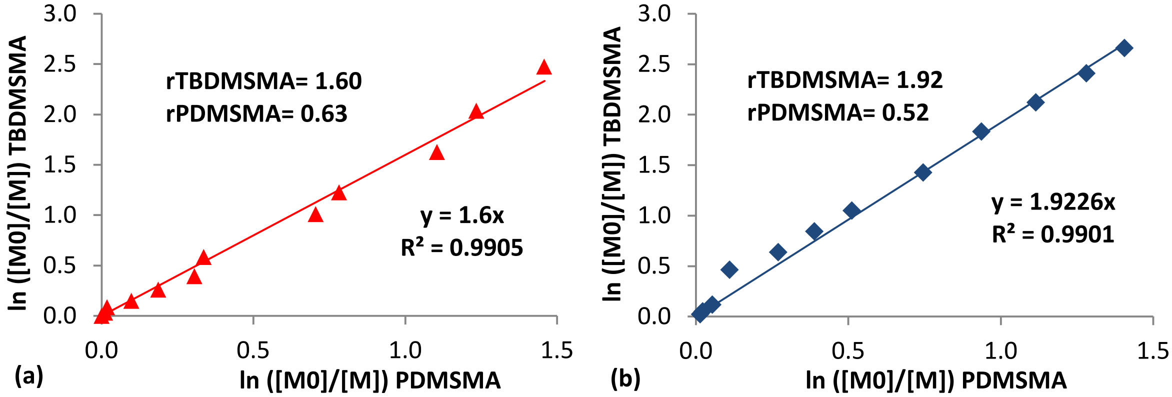


Figure S13. Jaacks plot for the RAFT polymerization of TBDMSMA and $PDMSMA_{symm}$ **(a)**, and $PDMSMA_{fluor\ symm}$ **(b)** in toluene at 70°C.

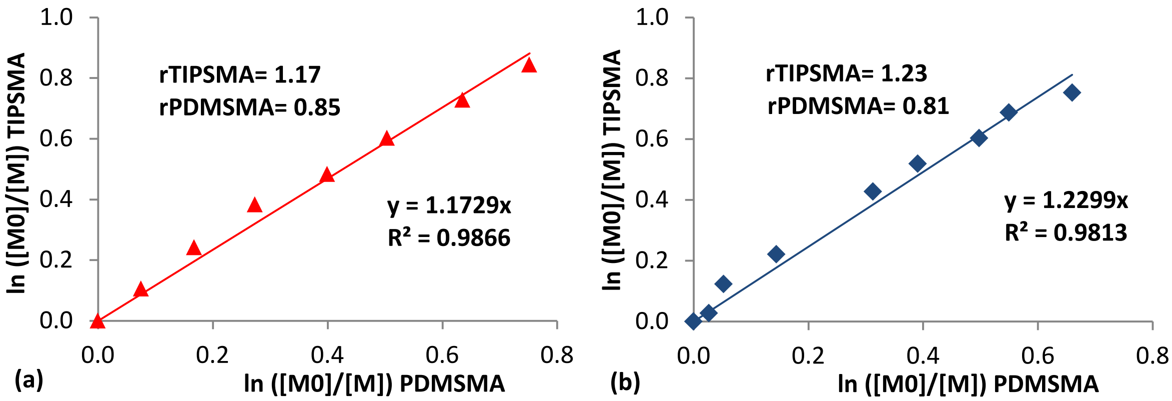


Figure S14. Jaacks plot for the RAFT polymerization of TIPSMA and $PDMSMA_{symm}$ **(a)**, and $PDMSMA_{fluor\ symm}$ **(b)** in toluene at 70°C.

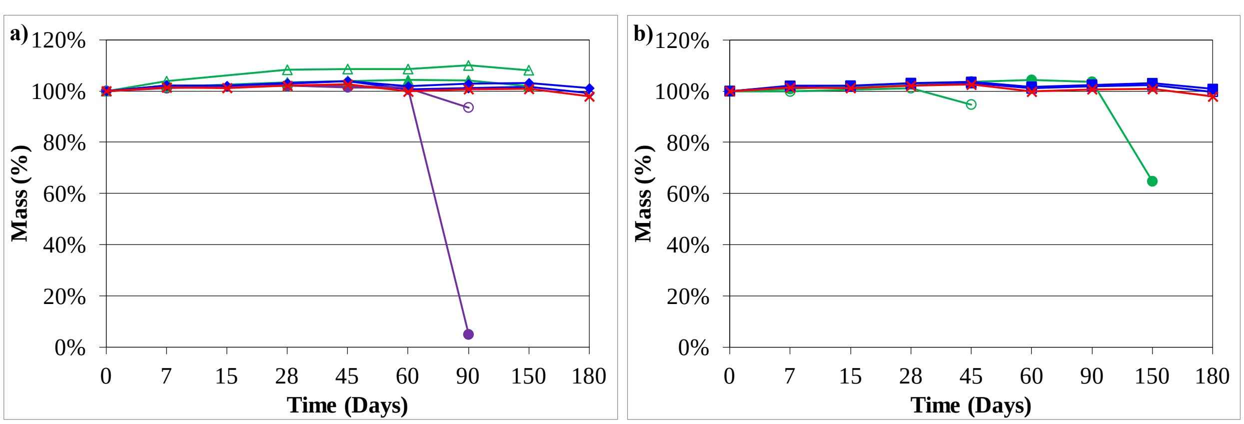


Figure S15. Evolution of the mass with immersion time in artificial seawater. **(a)** Coatings composed of statistical graft copolymers (◊) p(PDMSMAsymm-stat-TIPSMA) 50/50, (♦) p(PDMSMAfluor symm-stat-TIPSMA) 50/50, (o) p(PDMSMAsymm-stat-TBDMSMA) 20/80, (•) p(PDMSMAfluor symm-stat-TBDMSMA) 20/80, (Δ) p(PDMSMAsymm-stat-TBDMSMA) 50/50, (▲) p(PDMSMAfluor symm-stat-TBDMSMA) 50/50 **(b)** coatings composed of diblock graft copolymers (□) p(PDMSMAsymm)-b-pTIPSMA 50/50, (■) p(PDMSMAfluor symm)-b-pTIPSMA 50/50, (o) p(PDMSMAsymm)-b-pTBDMSMA 50/50, (•) p(PDMSMAfluor symm)-b-pTBDMSMA 50/50. The film-forming hydrolyzable homopolymer pTIPSMA (×) is used as reference.

References

1) Matyjaszewski, K.; Davis, T. P. Handbook of Radical Polymerization; John Wiley & Sons Inc., 2002.