

Accessory Publication

Synthesis of Core–Shell Nanoparticles with Polystyrene Core and PEO Corona from Core-Crosslinked Micelles by the RAFT Process

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Experiment Part

Materials

All reagents were purchased from Sigma-Aldrich with the highest purity and were used as supplied unless otherwise specified. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) ($M_n = 300 \text{ g mol}^{-1}$) and styrene (STY) were deinhibited by passing them through a column of basic alumina. 2,2-Azobisisobutyronitrile (AIBN) (Fluka, 98%) was purified by recrystallization from methanol before use.

RAFT polymerization of POEGMA

4-Cyanopentanoic acid dithiobenzoate (CPADB) was prepared according to a procedure described elsewhere.⁴⁵ OEGMA (2.58 g, $8.60 \times 10^{-3} \text{ mol}$), CPADB RAFT agent ($2.40 \times 10^{-2} \text{ g}$, $8.60 \times 10^{-5} \text{ mol}$) and AIBN ($2.80 \times 10^{-3} \text{ g}$, $1.70 \times 10^{-5} \text{ mol}$) were dissolved in 20 mL of toluene. The reaction mixture was divided equally into 6 vials to study the kinetics of the polymerization. Each vial was then sealed with rubber septum, placed in an ice bath and purged with nitrogen for 30 minutes. The reaction mixtures were then immersed in a pre-heated oil bath to 70°C and samples were taken over a period of 17 h. The polymerization was terminated by quenching the samples in an ice bath for 5 minutes. By comparing the intensity of vinyl proton peaks (6.1 and 5.6 ppm) to that of aliphatic proton peaks (1.1–1.3 ppm), the conversion of monomer during the course of polymerization was determined. After 17 h, a conversion of 85% was obtained. The molecular weight of the polymer after 17 h reaction time was measured to be 25,800 g mol^{-1} (PDI = 1.18).

The polymer was purified three times by precipitation in excess petroleum spirits (boiling range of 40–60°C) followed by centrifugation (7000 rpm for 15 min), under reduced

pressure at room temperature. The samples were stored in a freezer for further chain extension.

POEGMAmacroRAFT with theoretical number-average molecular weight $M_n(\text{theo})$ of $11,800 \text{ g mol}^{-1}$ and number-average molecular weight determined by size exclusion chromatography (SEC) $M_n(\text{SEC})$ (DMAc as mobile solvent and PSTY standards) of $12,200 \text{ g mol}^{-1}$, PDI=1.19 was used for further extension with STY.

Synthesis of POEGMA-*block*-P(STY)

POEGMAmacroRAFT with 40 repeating units ($M_n(\text{theo})=11,800 \text{ g mol}^{-1}$, $M_n(\text{SEC})=12,200 \text{ g mol}^{-1}$) was used for chain extension with styrene. The number of repeating units of POEGMA was calculated from the monomer conversion obtained from ^1H NMR. The POEGMA macroRAFT agent ($6.45 \times 10^{-1} \text{ g}$, $5.28 \times 10^{-5} \text{ mol}$) was completely dissolved in 6 mL (5.45 g , $5.25 \times 10^{-2} \text{ mol}$) of STY. The resulting stock reaction mixture was divided into 6 vials for the block copolymerization kinetic study and then purged with nitrogen for one hour in an ice bath to avoid the evaporation of styrene. The polymerizations were carried out in a preheated oil bath to 100°C . The vials were removed from the oil bath at preset time intervals over a period of 24h. The polymerizations were terminated by placing the samples in an ice bath for 5 min. The copolymer was purified under reduced pressure to remove unreacted styrene and kept at 2°C for further core crosslinking experiments.

POEGMA₄₀-*b*-PS₉₉ with theoretical number-average molecular weight $M_n(\text{theo})$ of $22,100 \text{ g mol}^{-1}$ and number-average molecular weight determined by size exclusion chromatography (SEC) $M_n(\text{SEC})$ (DMAc as mobile solvent and PSTY standards) of $20,500 \text{ g mol}^{-1}$, PDI=1.22 was used for further crosslinking with divinylbenzene (DVB) and control chain extension reaction with STY.

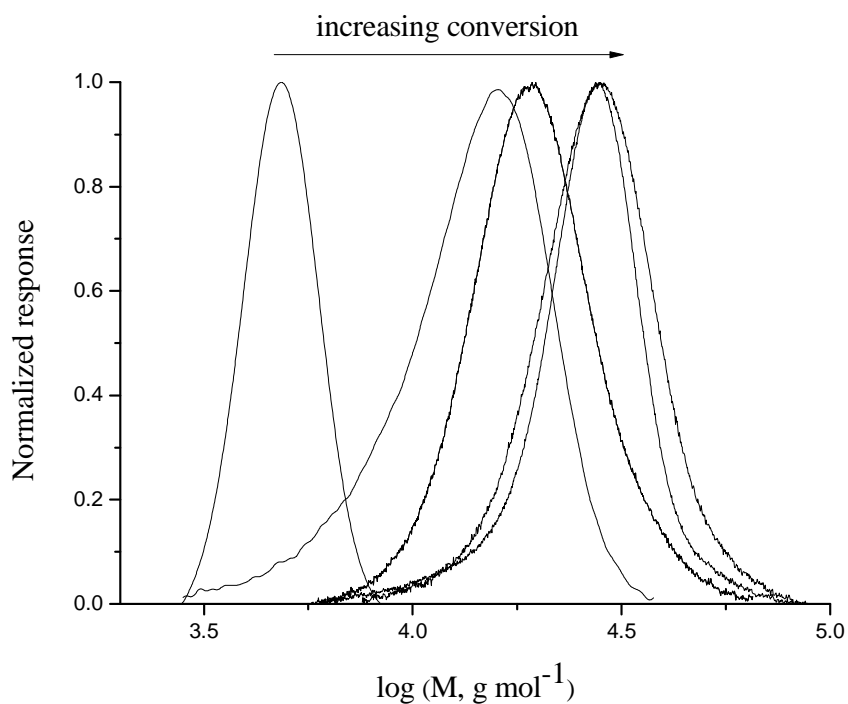
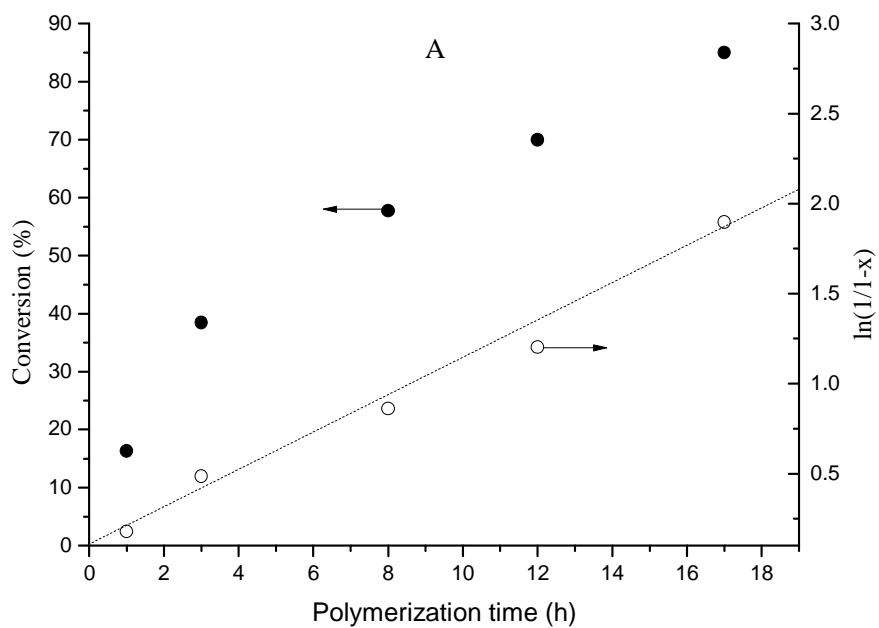
ESI. Table S1 Summary of results of the homopolymerization of POEGMA in toluene at 70 °C in the presence of CPADB. [OEGMA] = $3.83 \times 10^{-1} \text{ mol L}^{-1}$, [CPADB] = $3.83 \times 10^{-3} \text{ mol L}^{-1}$, [AIBN] = $7.66 \times 10^{-4} \text{ mol L}^{-1}$

Time/	Conversion/% ^a	M_n (theo)/ g mol^{-1} ^b	M_n (SEC)/ g mol^{-1} ^c	PDI
1	16.32	5,170	4,700	1.03
3	38.45	11,800	12,200	1.19
8	57.76	17,600	17,700	1.12
12	69.98	21,300	23,800	1.14
17	85.00	25,800	24,400	1.16

^a The monomer conversion was calculated from the ¹H NMR of the reaction mixture by comparing the intensity of vinyl proton peaks (at *ca.* 6.1 and 5.6 ppm) to that of aliphatic proton peaks (at *ca.* 1.2 ppm)

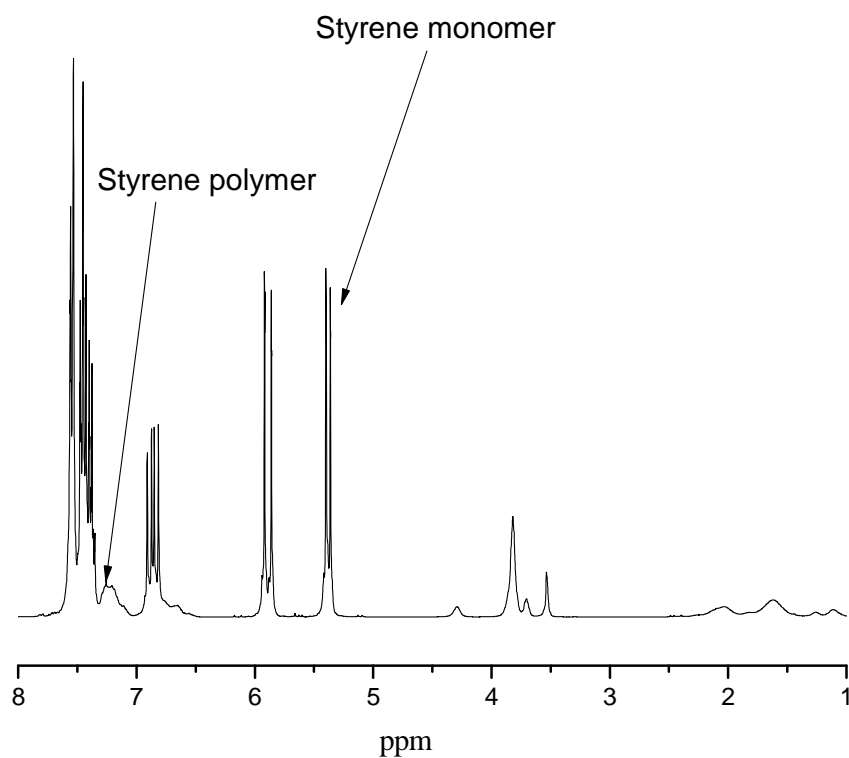
^b Theoretical molecular weight was calculated from linear relationship between molecular weight and conversion according to $M_n = ([M]_0/[RAFT]_0) * x * M_{wmonomer} + M_{wRAFT}$, where $[M]_0$, $[RAFT]_0$, x , $M_{wmonomer}$, and M_{wRAFT} are monomer and RAFT agent concentration, monomer conversion, molecular weight of monomer and RAFT agent, respectively.

^c The experimental M_n and PDI was measured by SEC using dimethyl acetamide (DMAc) (0.05% w/v BHT and 0.03% w/v LiBr) as eluent and polystyrene standards with the molecular weight ranging from 168 to 10^6 g mol^{-1})



ESI. Figure S1. RAFT polymerization of POEGMA using CPADB as RAFT agent in toluene at 70 °C ([M]:[RAFT]:[AIBN] = 100:1:0.2). (A) Monomer conversion at different time interval and pseudo-first-order kinetic plot for the homopolymerization; (B) SEC profiles of acetal-POEGMA at 16.32, 38.45, 57.76, 69.98, 85.00 % monomer conversions.

^1H NMR spectroscopy was employed to monitor the degree of polymerization of STY by dividing the integral of polystyrene with the sum of polystyrene and styrene integrals as illustrated in ESI. Figure S2.



ESI. Figure S2. ^1H NMR graph of reaction mixture in the synthesis of POEGMA-b-PS in bulk at 100°C

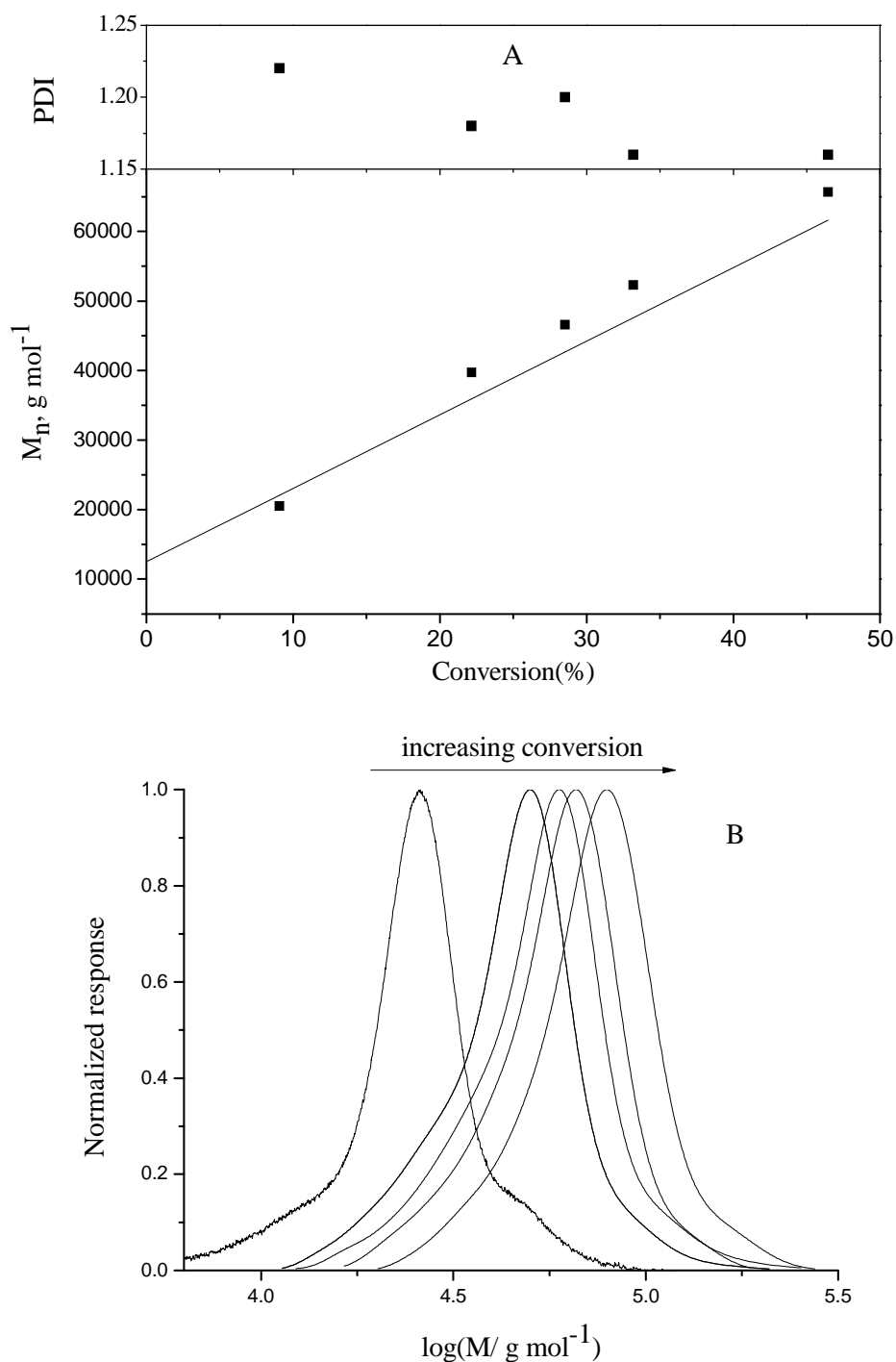
ESI. Table S2. Summarized results of the chain extension of POEGMAmacroRAFT with styrene in bulk at 100°C. [POEGMAmacroRAFT] = 8.59×10^{-3} mol L⁻¹, [STY] = 8.74 mol L⁻¹.

Time/ h	Conversion/ % ^a	M _n (theo)/ g mol ⁻¹ ^b	M _n (SEC)/ g mol ⁻¹ ^c	PDI
1	9.08	22,100	20500	1.22
2	22.17	35,960	39,700	1.18
3	28.53	42,680	46,600	1.2
5	33.18	47,600	52,300	1.16
7	46.45	61,600	65,700	1.16

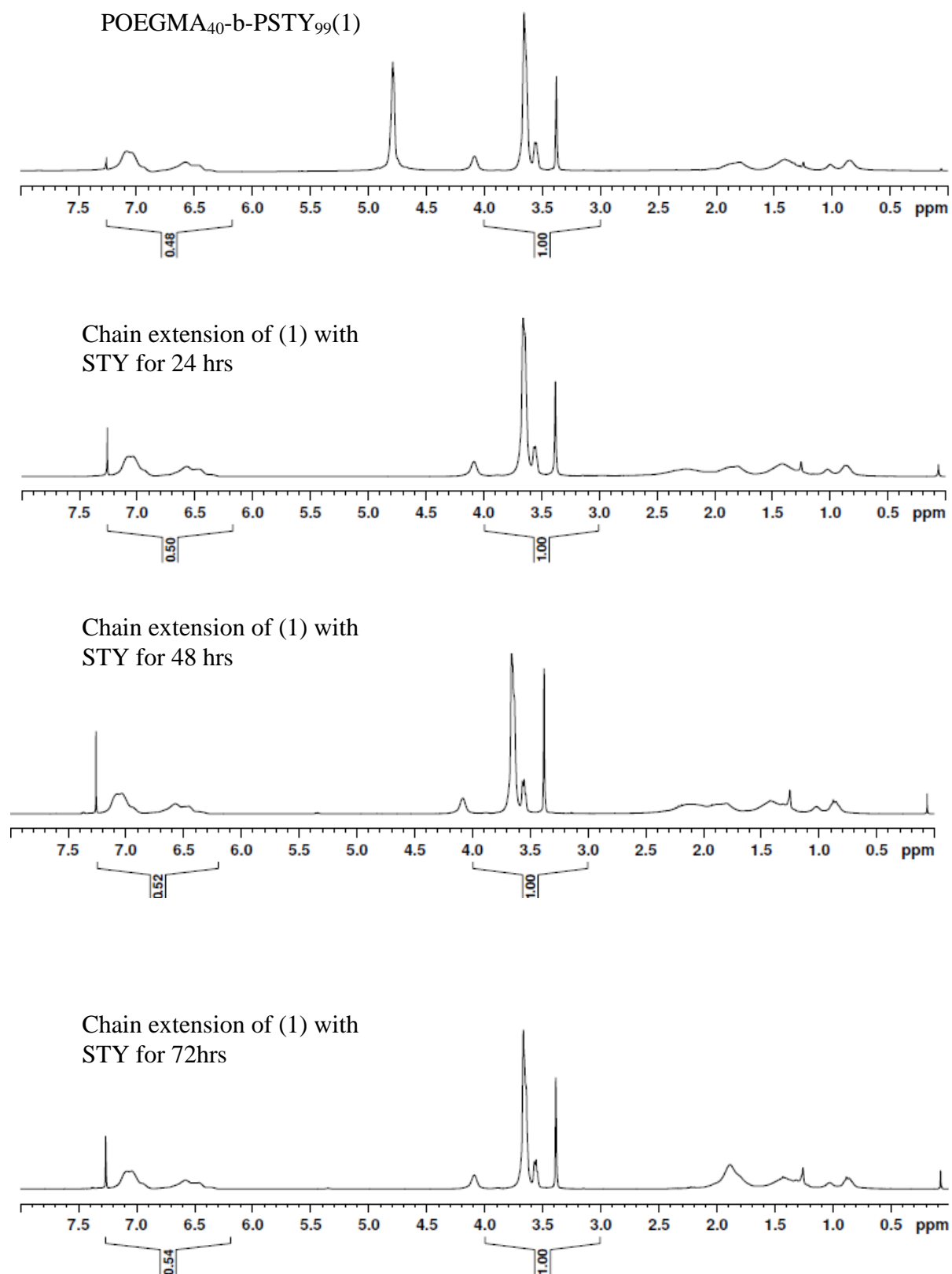
^a The monomer conversion was calculated from the ¹H NMR of the reaction mixture by dividing the integral of polystyrene with the sum of polystyrene and styrene integrals

^b Theoretical molecular weight was calculated from linear relationship between molecular weight and conversion according to $M_n = ([M]_o/[RAFT]_o) * x * M_{wmonomer} + M_{nmacroRAFT}$, where $[M]_o$, $[RAFT]_o$, x , $M_{wmonomer}$, and $M_{nmacroRAFT}$ are monomer and RAFT agent concentration, monomer conversion, molecular weight of styrene and macroRAFT agent, respectively.

^c The experimental M_n and PDI was measured by SEC using dimethyl acetamide (DMAc) (0.05% w/v BHT and 0.03% w/v LiBr) as eluent and polystyrene standards with the molecular weight ranging from 168 to 10⁶ g mol⁻¹)



ESI. Figure S3. Chain extension of POEGMA₄₀MacroRAFT with STY at 100°C in bulk (A) Evolution of the molecular weights and polydispersities with monomer conversion. The straight lines represent the theoretical values calculated from $M_n = ([M]/[RAFT])^x \cdot M_{\text{monomer}} + M_{\text{macro-RAFT}}$ (x: conversion). $[\text{macro-RAFT}] = 8.59 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{Styrene}] = 8.74 \text{ mol L}^{-1}$. (B) SEC profiles POEGMA-block-PS at different conversions of 9, 22, 28, 33, and 46%..



ESI. Figure S4. ¹H-NMR of the purified product obtained after the polymerization of styrene in a micellar system based on POEGMA₄₀-*b*-PS₉₉ in CDCl₃ (300 MHz).