Supporting Information

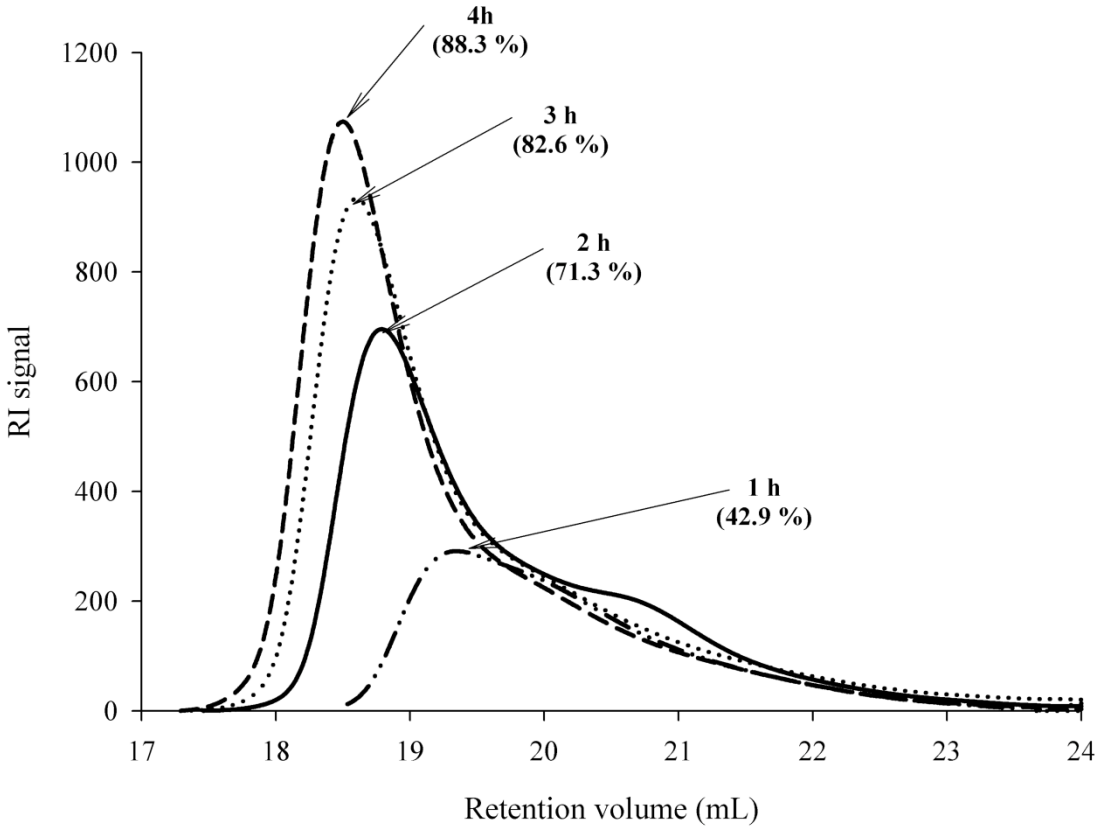

Figure S1 – GPC traces of PDMAEMA samples taken at different reaction times. Conditions: $[DMAEMA]_0/[IPA]$ = 1/1.25 (v/v); $[DMAEMA]_0/[EBiB]_0/[CuBr]_0/[PMDETA]$ = 50/1/1/1 (molar); T=60ºC.

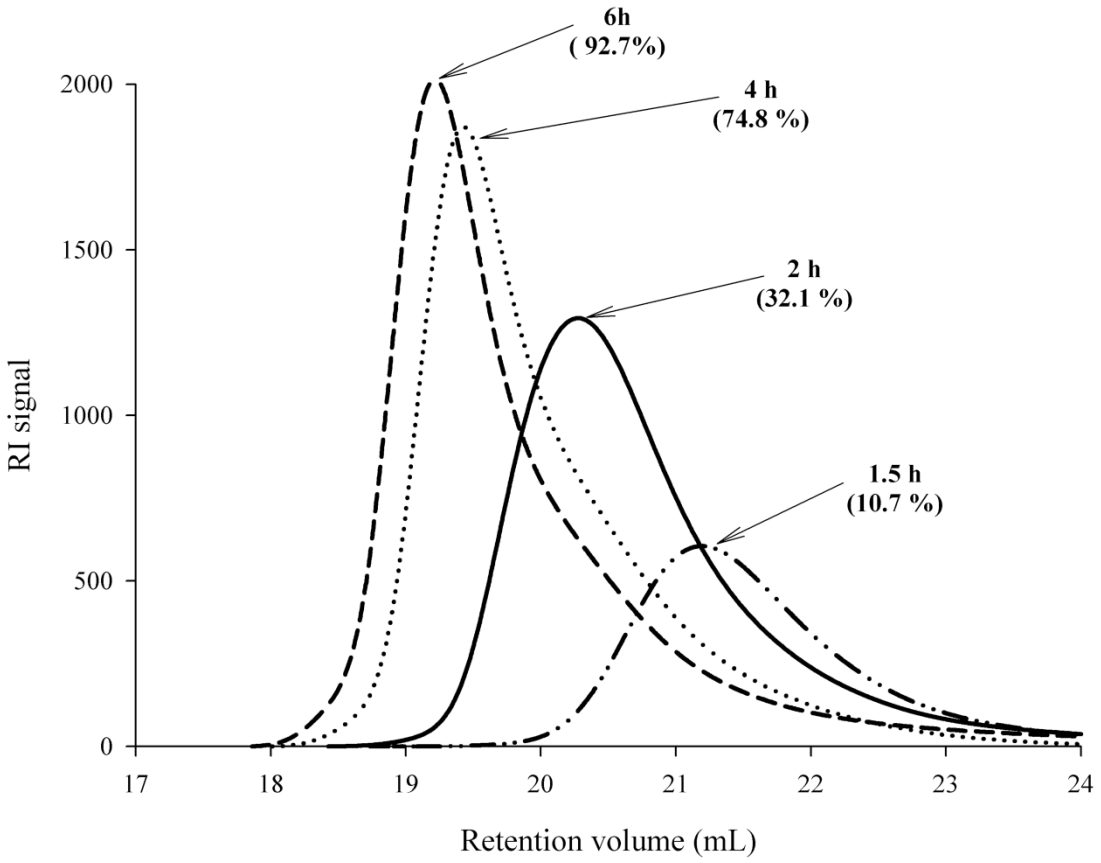

Figure S2 - GPC traces of PDMAEMA samples taken at different reaction times. Conditions: $[DMAEMA]_0/[IPA]/[H_2O]$ = 1/0.9/0.1 (v/v); $[DMAEMA]_0/[EBiB]_0/[Fe(0)]_0/[CuBr_2]_0/[PMDETA]$ = 45/1/1/0.1/1 (molar); T=25ºC.

Synthesis of cholesteryl-2-bromoisobutyrate (CHO-Br)

Cholesteryl-2-bromoisobutyrate was synthesized through an adaption of the synthesis of Br-PEG-Br in the literature [1]. 4-Dimethylaminopyridine (4.5 g, 37.5 mmol), dry dichloromethane (50 mL) and triethylamine (3.5 mL, 25 mmol) were placed into a 500 ml flask. A solution with 2-bromoisobutyryl bromide (7.7 mL, 62.5 mmol) and dry dichloromethane (50 mL) was added dropwise. When the addition was finished, a solution of cholesterol (CHO) (4.8 g, 12.4 mmol) and dry dichloromethane (250 mL) were added dropwise over a period of 30 min, in a dry ice bath. The resulting solution was further refluxed under nitrogen. After 24 h, there was a yellow dispersion, which was further washed with sodium chloride saturated aqueous solution. Magnesium sulphate was then added, and the final solution was filtered and concentrated. The cholesteryl-2-bromoisobutyrate (CHO-Br) product was recovered by precipitation in ethanol, leading to a white precipitated that was collected and dried in vacuum. The crude product was purified by recrystallization in ethyl acetate/ethanol (95/5, v/v). The FTIR-ATR and ^{1}H NMR spectra are shown, respectively in Figures S1 and S2. **^{1}H NMR** (600 MHz, $CDCl_3$): δ=0.68 (s, 3 H, cholesteryl CH_3), 0.86 (d, 6 H, cholesteryl CH_3), 0.912 (d, 3 H, cholesteryl CH_3), 1.046 (s, 3 H, cholesteryl CH_3), 0.95 – 2.00 (m, 28 H, cholesteryl C*H* and CH_2), 1.92 (s, 6 H, $(CH_3)_2$-C-Br), 2.37 (d, 1 H, CH=C-CH_2), 4.66 (m, 1H, C*H*-O-COC$(CH_3)_2$Br), 5.39 (s, 1 H, CH=C). **FTIR-**

ATR (cm^{-1}): 3016-2782 (C-H stretching), 1723 (ester, C=O stretch), 1463-1370 (C=C aromatic), 1280-1100 (ester, C-O stretch).

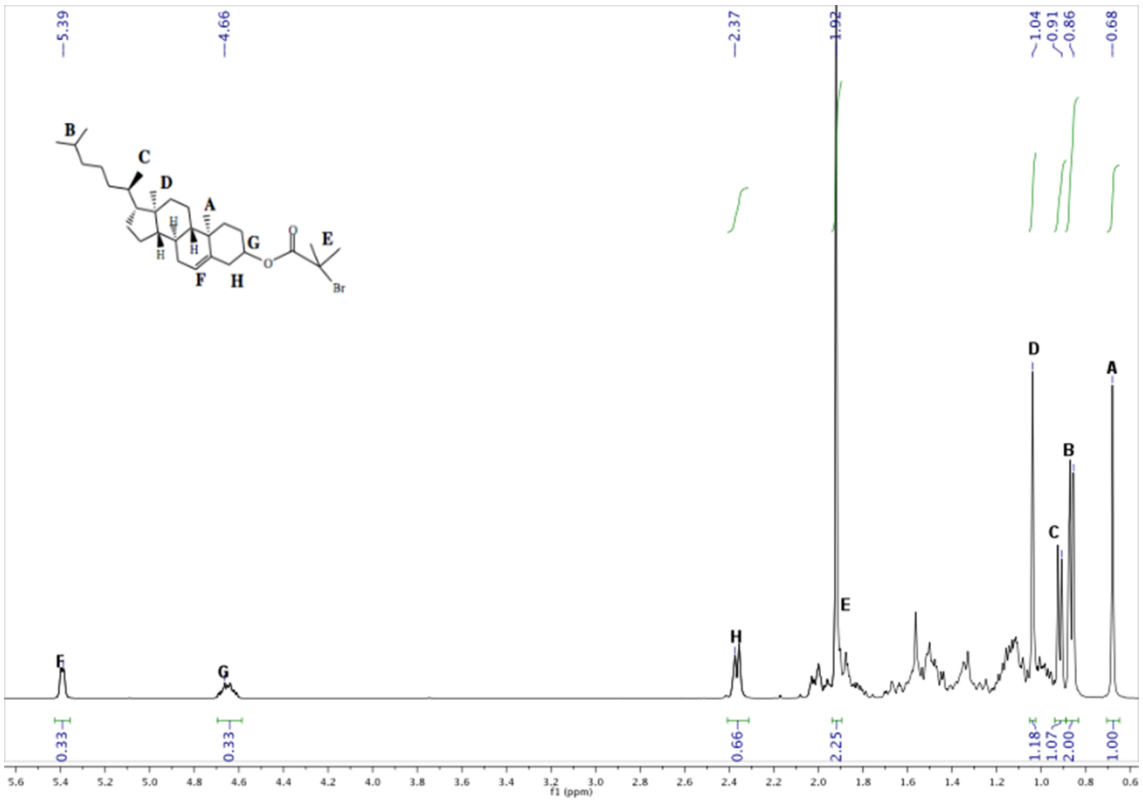

Figure S3 – ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) and structural assignment of CHO-Br.

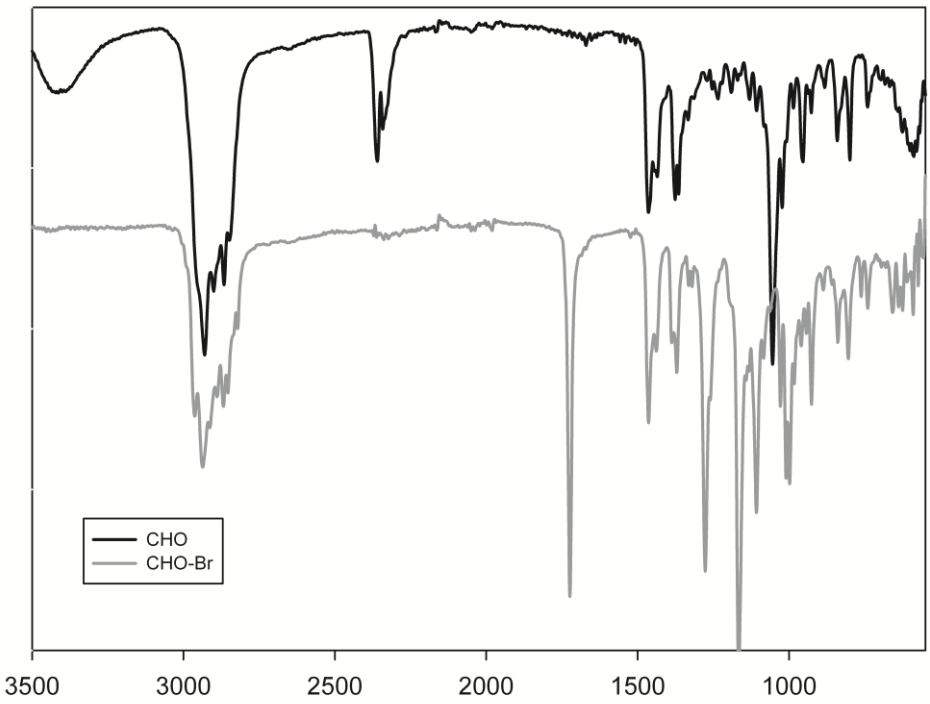

Figure S4 – FTIR-ATR spectrum of cholesterol (black line) and cholesterol initiator (grey line).

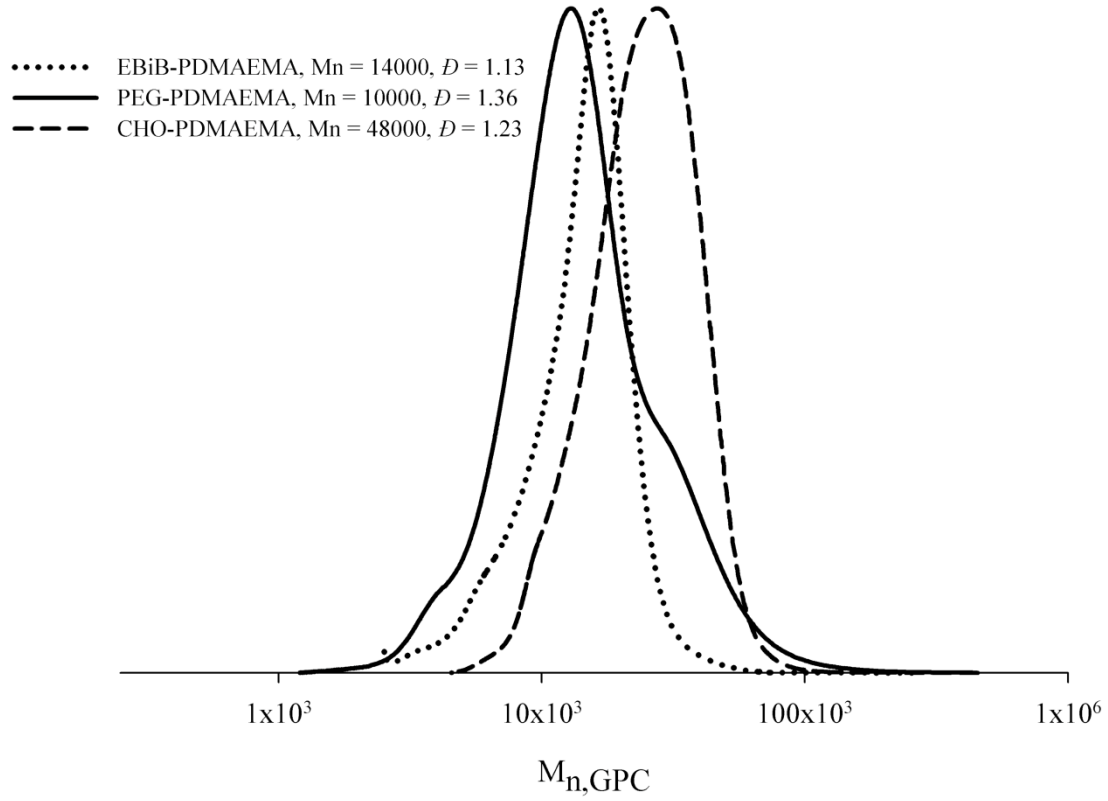

Figure S5 – GPC traces of PDMAEMA using mPEG-Br, CHO-Br or EBiB as ATRP initiators. Conditions: $[DMAEMA]_0/[IPA]/[H_2O]$ = 1/0.9/0.1 (v/v); $[DMAEMA]_0/[initiator]_0/[Fe(0)]_0/[CuBr_2]_0/[PMDETA]$ = 90/1/1/0.1/1 (molar).

References

1. K. Jankova, X. Y. Chen, J. Kops and W. Batsberg, *Macromolecules*, 1998, **31**, 538-541.