The Influence of Thiocarbonylthio Compounds on the $B(C_6F_5)_3$ Catalyzed Cationic Polymerization of Styrene

Aurélie Destephen, Estíbaliz González de San Román, Nicholas Ballard
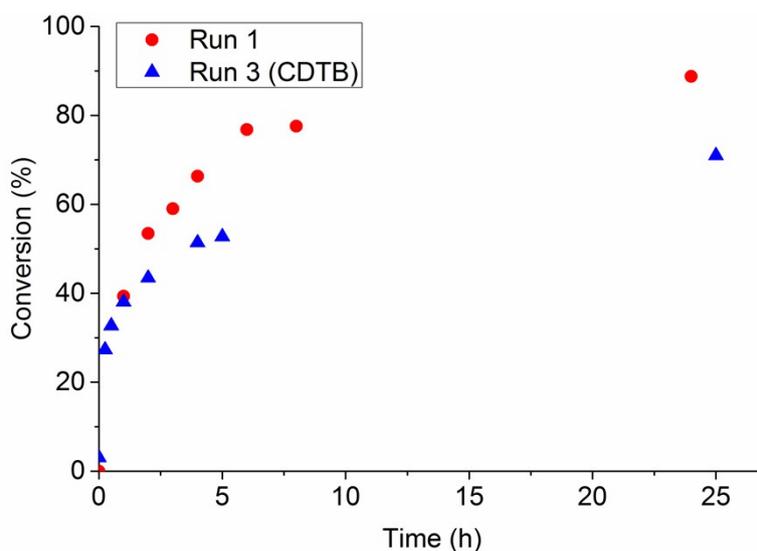
Supporting information

Figure S1: Evolution of the conversion with time for the polymerization of styrene performed without initiator and without any thiocarbonylthio compound (Run 1, red spheres) or using CDTB (Run 3, blue triangles).

Table S1: Final molecular weight and dispersity for reactions conducted in the absence of initiator without the addition of CDTB (Run 1) and with addition of CDTB (Run 3).

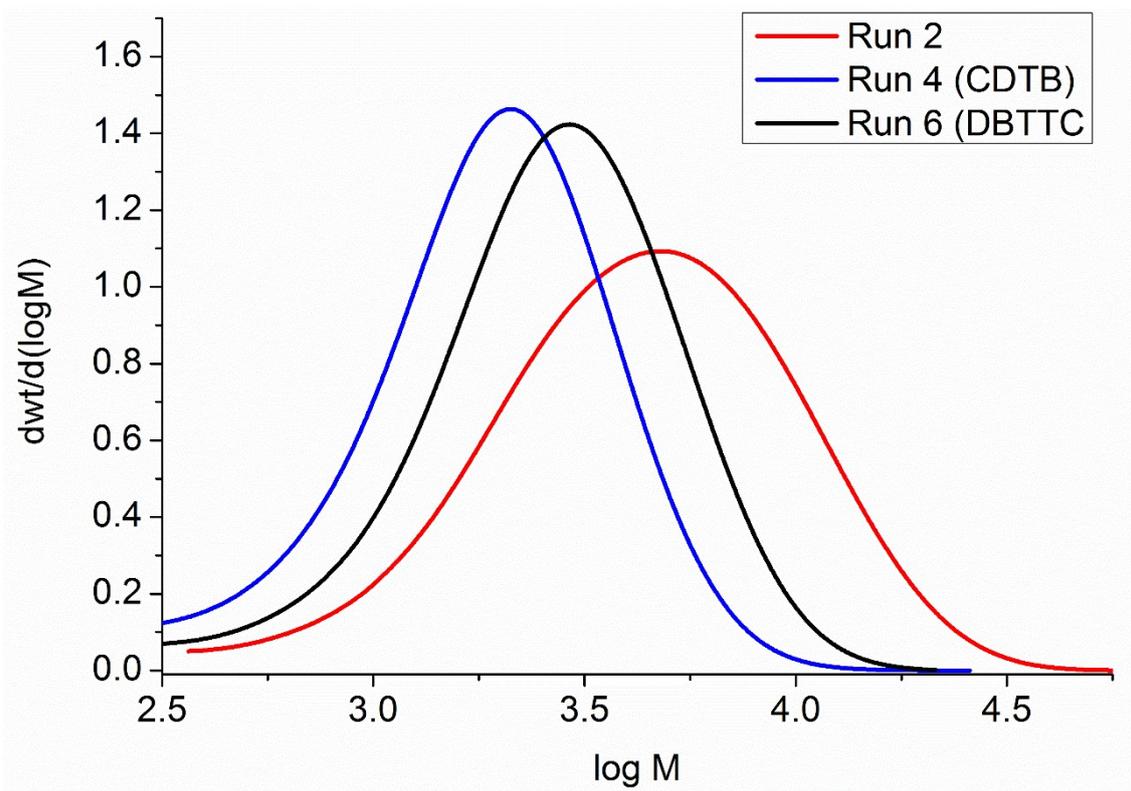| Run	Time (h)	Conversion (%)	M_n (g/mol)	Đ
1	24	89	3,100	3.3
3	25	71	940	1.9

Figure S2: Final molecular weight distributions of precipitated polymers from the cationic polymerization of styrene without any added thiocarbonylthio compound (Run 2, red), and in the presence of CDTB (Run 4, blue) or DBTTC (Run 6, black).
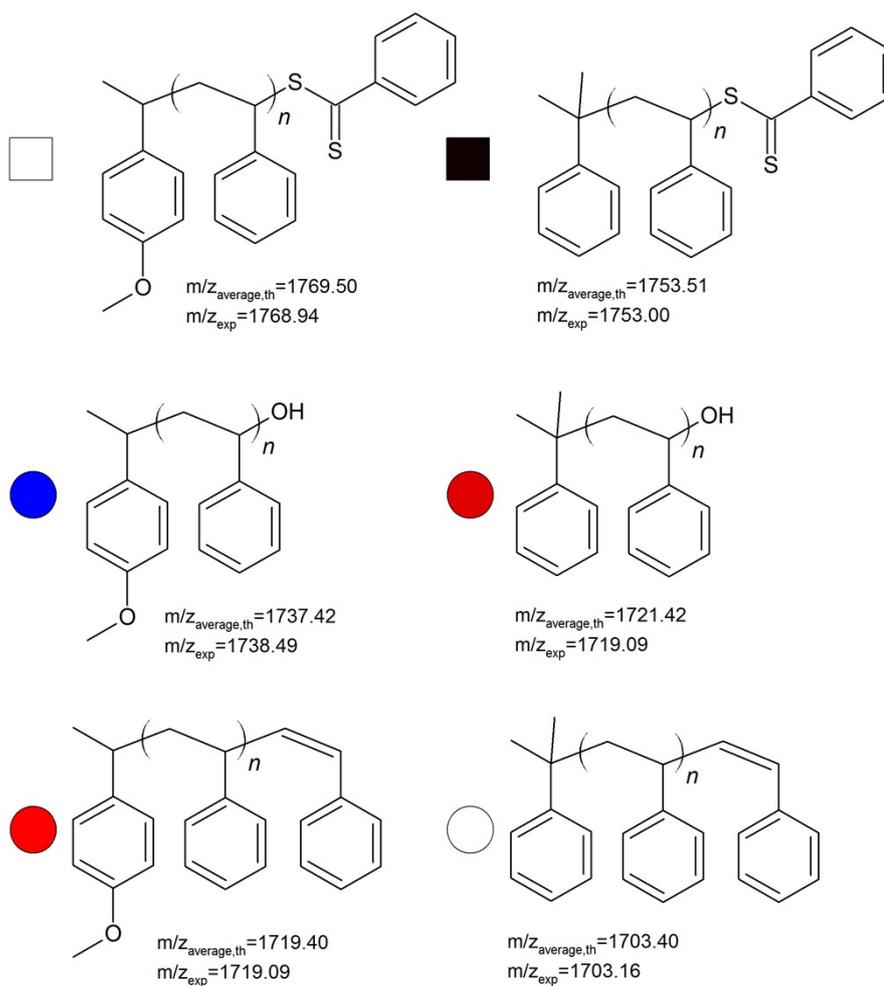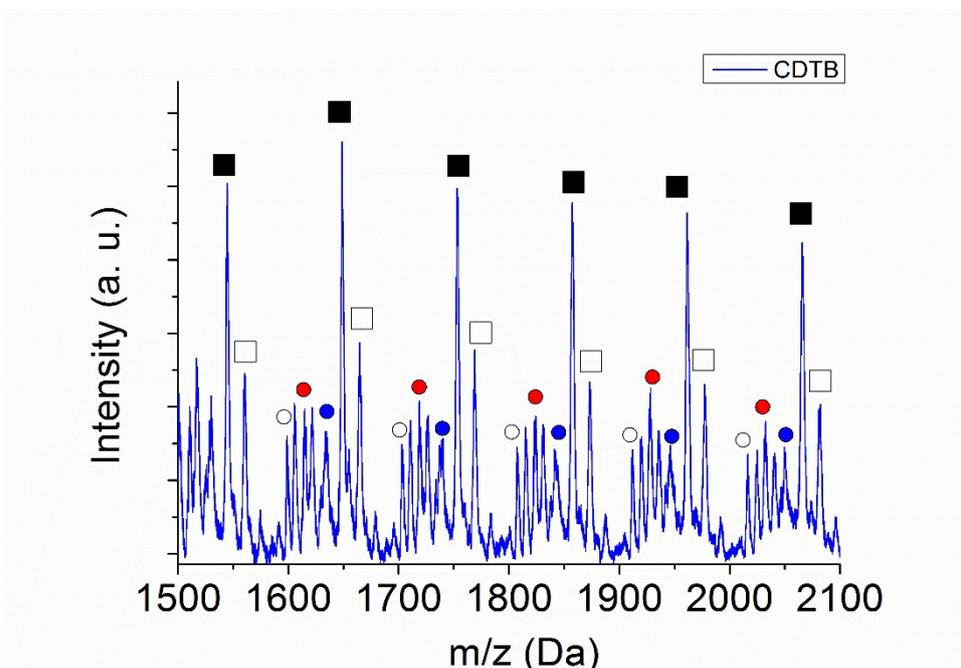
Figure S3: MALDI-ToF spectra of the polystyrenes obtained using NaTFA as cationization agent using CDTB (middle, blue) and the structures corresponding to the different peaks. All masses correspond to the [M+Na]$^+$ species.
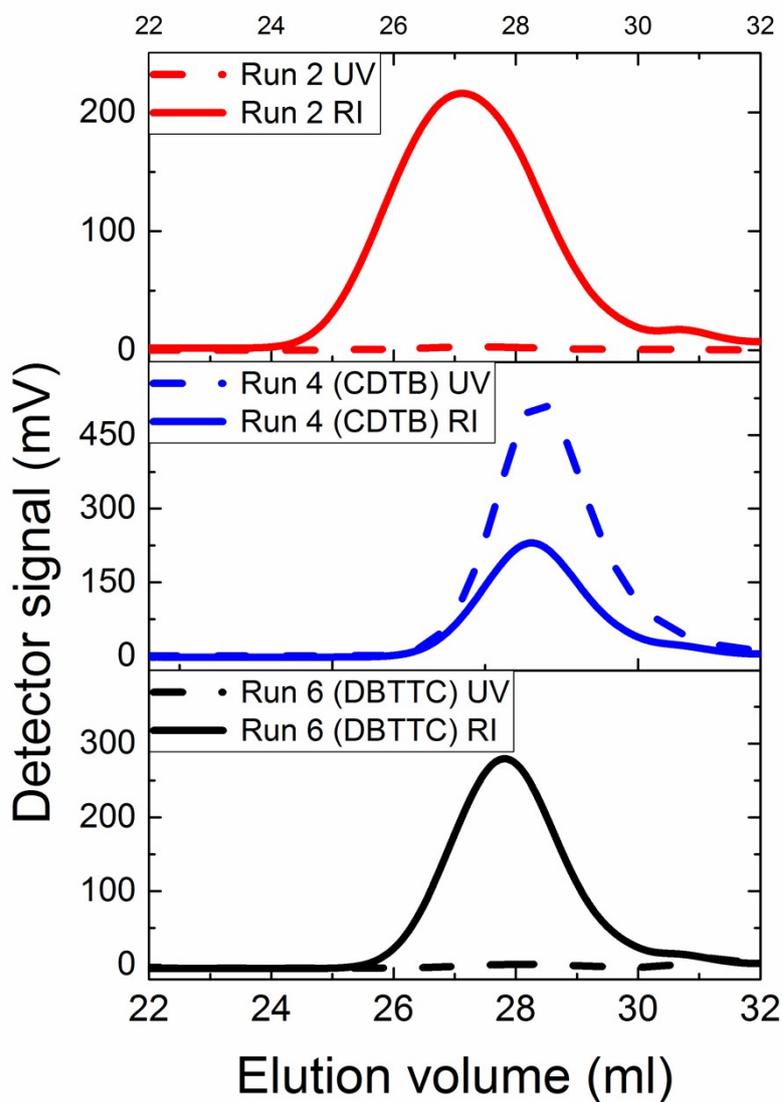
Figure S4: SEC traces using refractive index (full line) and UV detector (λ=310 nm, dashed line) without any thiocarbonylthio compound (red), using CDTB (blue) and DBTTC (black).
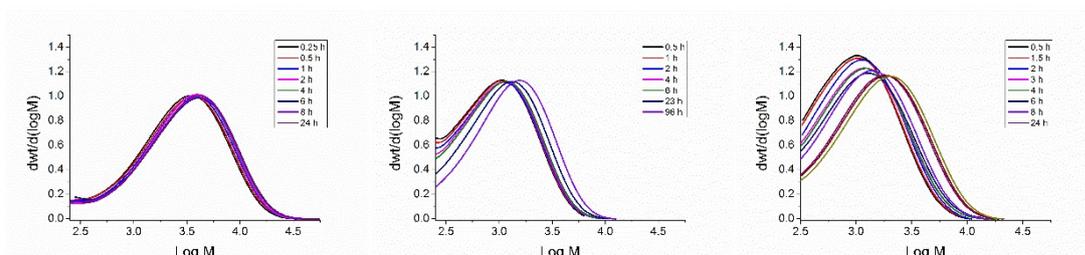

Figure S5: Evolution of molecular weight distributions with time for reactions without any thiocarbonylthio compound (Run 2, left), using CDTB (Run 4, middle) and DBTTC (Run 6, right).
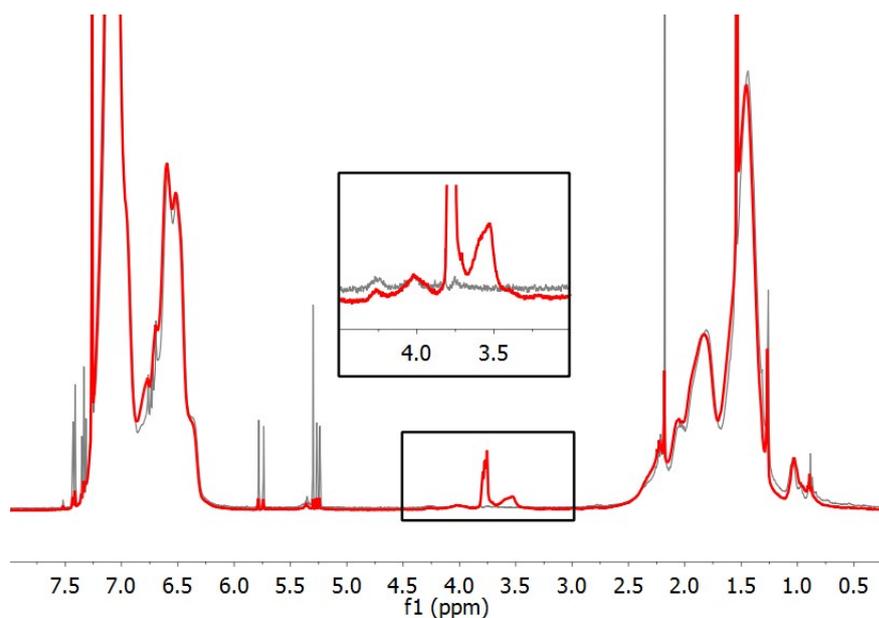
Figure S6: ^{1}H NMR spectra of polymers synthesized in the absence of any thiocarbonylthio compound with (Run 2, red) and without initiator (Run 1, grey). The insert shows an enlargement of the region 3-4.5 ppm where the peaks arising from O-CH$_3$ groups of the initiator moiety appear. Note that at 1 ppm the protons arising from both initiator and proton initiated chains can be observed.
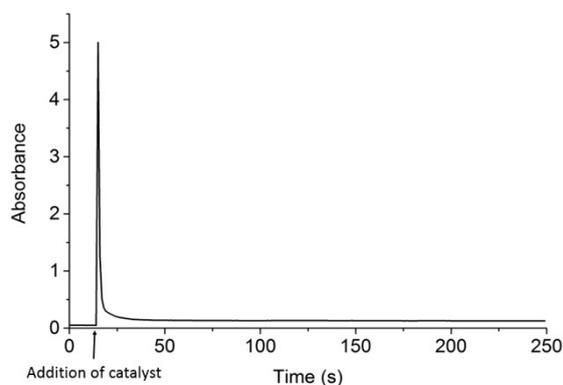

Figure S7: Evolution of the absorbance at 340 nm with time following the addition of B(C$_6$F$_5$)$_3$ using [St] = 0.65 M, [I] = 0.02 M, [B(C$_6$F$_5$)$_3$] = 0.02 M.
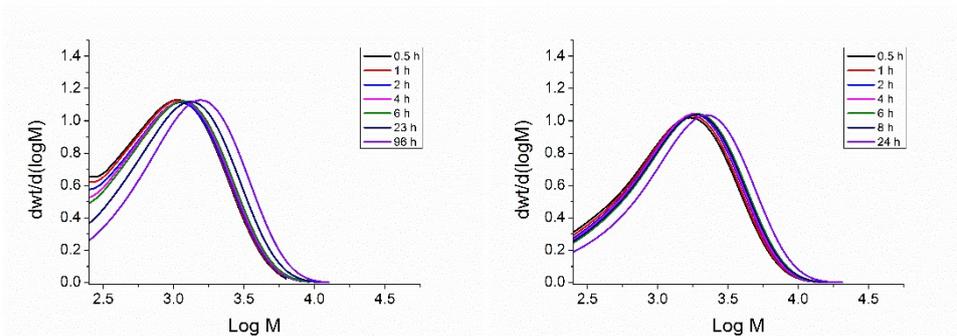
Figure S8: Evolution of molecular weight distributions with time for reactions using (left) CDTB (0.03 M, Run 4) and (right) CDTB (0.01 M, Run 5)
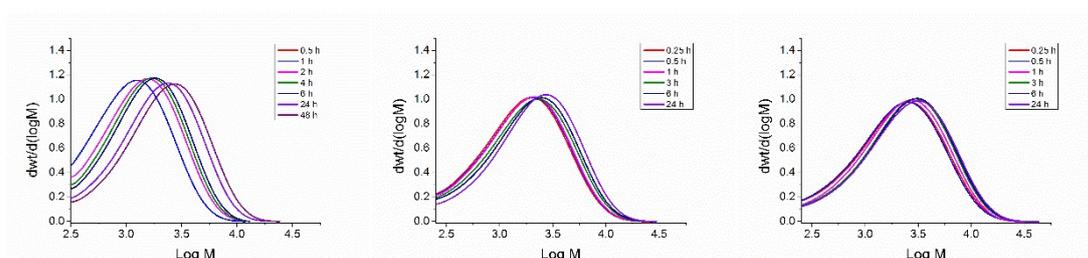

Figure S9: Evolution of molecular weight distributions with time for reactions using (left) DBTTC (0.03 M, Run 7), (middle) DBTTC (0.02 M ,Run 8) and (right) DBTTC (0.01 M, Run 9).
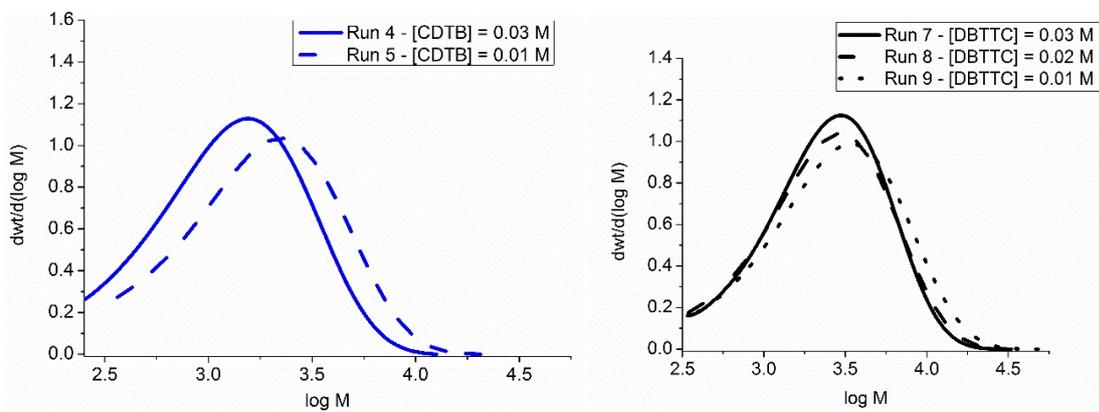

Figure S10: Final molecular weight distributions synthesized using (left) CDTB (0.03 M ,Run 4, full line) and CDTB (0.01 M, Run 5, dashed line) and (right) DBTTC (0.03 M, Run 7, full line), DBTTC (0.02 M, Run 8, dashed line) and DBTTC (0.01 M, Run 9, dotted line).
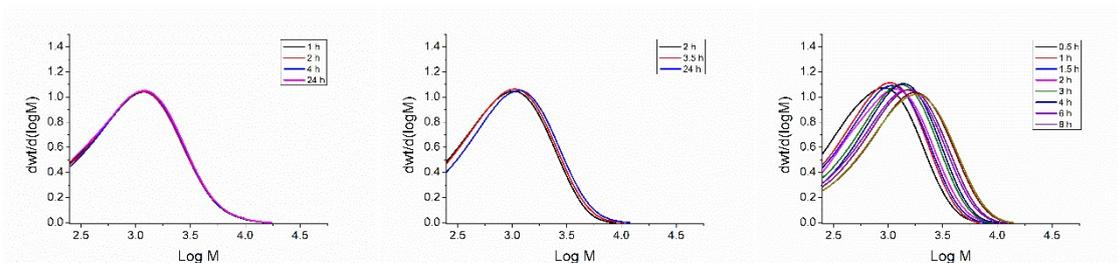
Figure S11: Evolution of molecular weight distributions with time for reactions using (left) CPBDT (Run 10), (middle) BPCDT (Run 11) and (right) BDTB (Run 12).
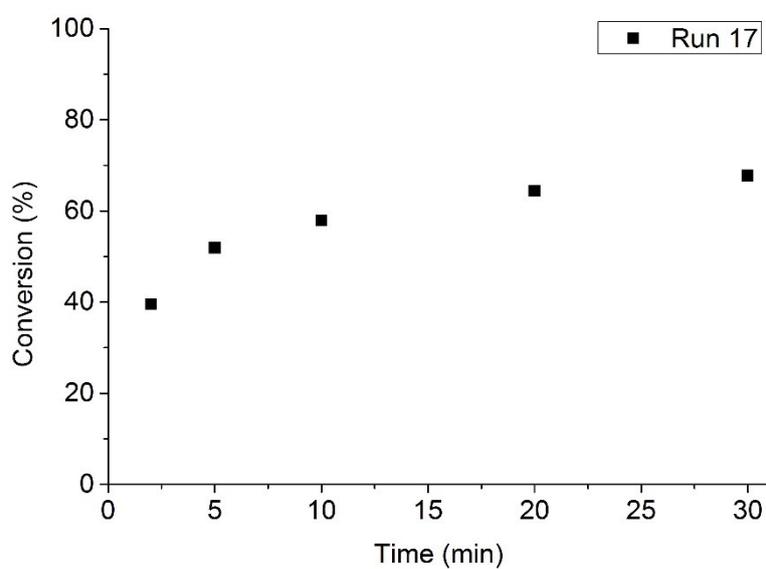

Figure S12: Evolution of the conversion with time for the polymerization of pMOS performed in the presence of benzyl 1H-pyrrole-1-carbodithioate (Run 17).
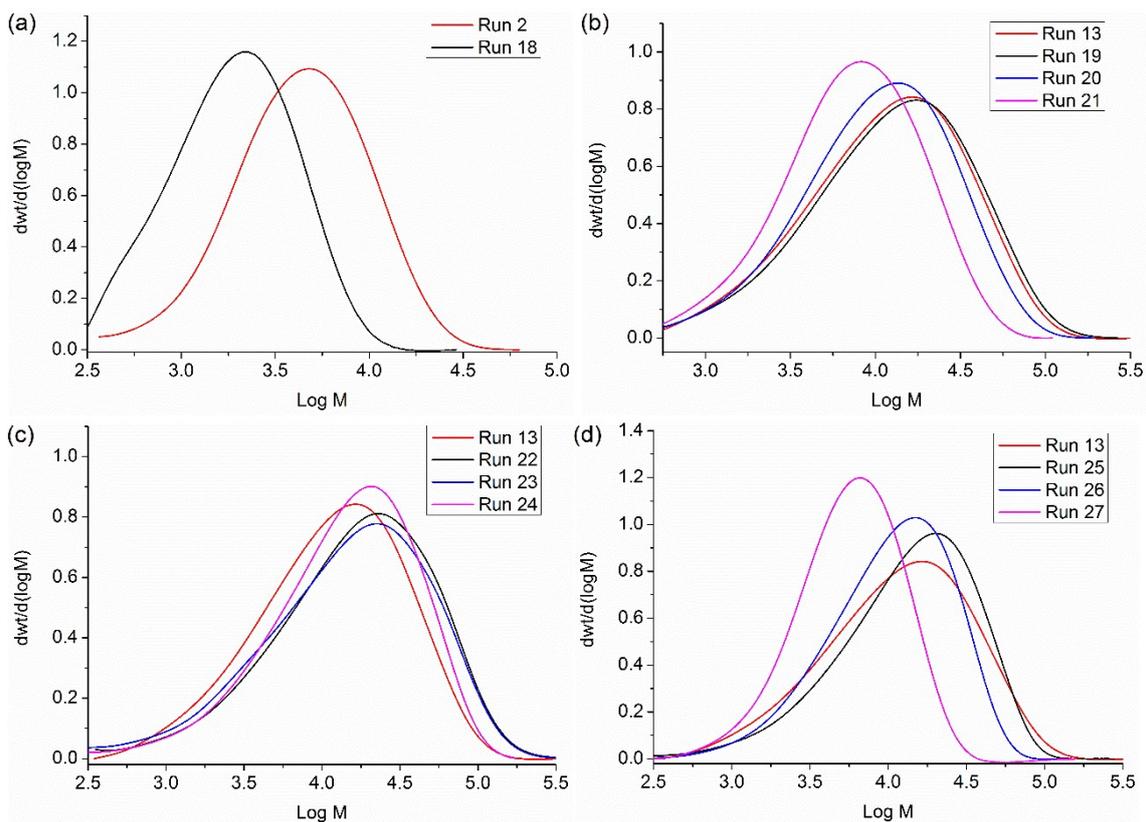
Figure S13: GPC traces of the final polymers obtained for the polymerization of (a) styrene using phenyl disulfide and (b to d) pMOS using (b) phenyl disulfide, (c) diphenyl sulfide and (d) dibenzyl sulfide [Sulfide] = 0 M (red), 0.03 M (black), 0.1 M (blue) and 0.5 M (pink).