Supporting Information

Catechol/boronic acid chemistry for the creation of block copolymers with a multi-stimuli responsive junction

Fanny Coumes[1], Aurélie Malfait[1], Marc Bria[2], Joël Lyskawa[1], Patrice Woisel*[1] and David Fournier*[1]

[1] Université Lille 1, Unité des Matériaux Et Transformations (UMET, UMR CNRS 8207), Ingénierie des Systèmes Polymères (ISP) team, 59655 Villeneuve d'Ascq Cedex, France

[2] Centre Commun de mesure RMN, Université Lille 1, Villeneuve d'Ascq Cedex, France

*Corresponding author: david.fournier@univ-lille1.fr

Characterization of Boro-CTA:

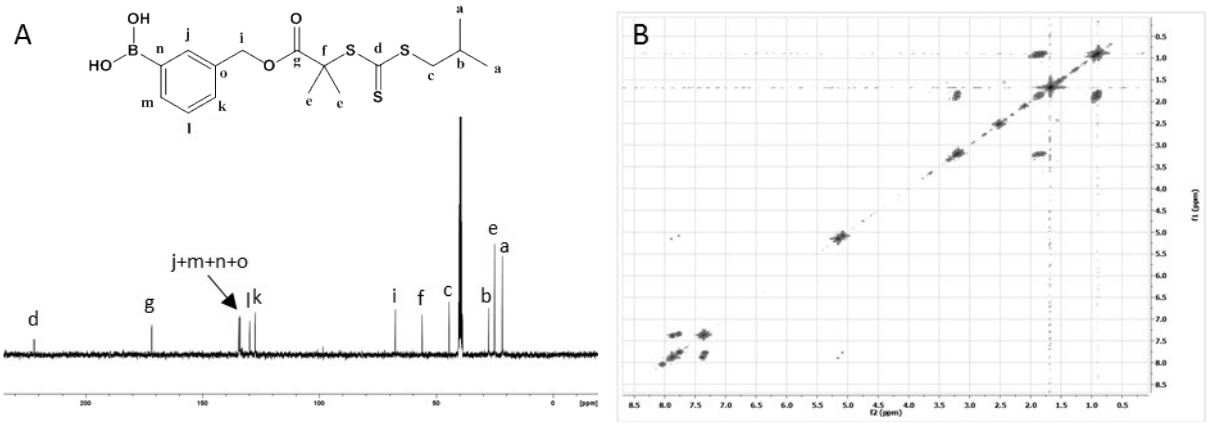

Figure S1. (A) ^{13}C NMR of Boro-CTA (B) COSY NMR of Boro-CTA.

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm/TMS): 0.93 (d, 6H, CH-(CH_3)$_2$), 1.68 (s, 6H, C(CH_3)$_2$), 1.86 (m, 1H, CH_2-C*H*-(CH_3)$_2$), 3.18 (t, 2H, S-CH_2-CH), 5.08 (s, 2H, CH_2-Aryl), 7.35 (d, 2H, Aryl-H_j H_l), 7.75 (s, 1H, Aryl-H_k), 7.87 (s, 1H, Aryl-H_m)

^{13}C NMR (75 MHz, DMSO-d_6): 21.6 (C_a), 24.9 (C_e), 27.4 (C_b), 44.4 (C_c), 56.0 (C_f), 67.4 (C_i), 127.4 (C_k), 129.7 (C_l), 133.9 (C_j), 134 (C_m), 134.4 (C_o), 131.7 (C_n), 171.7 (C_g), 220.3 (C_d).

Characterization of ND-CTA :

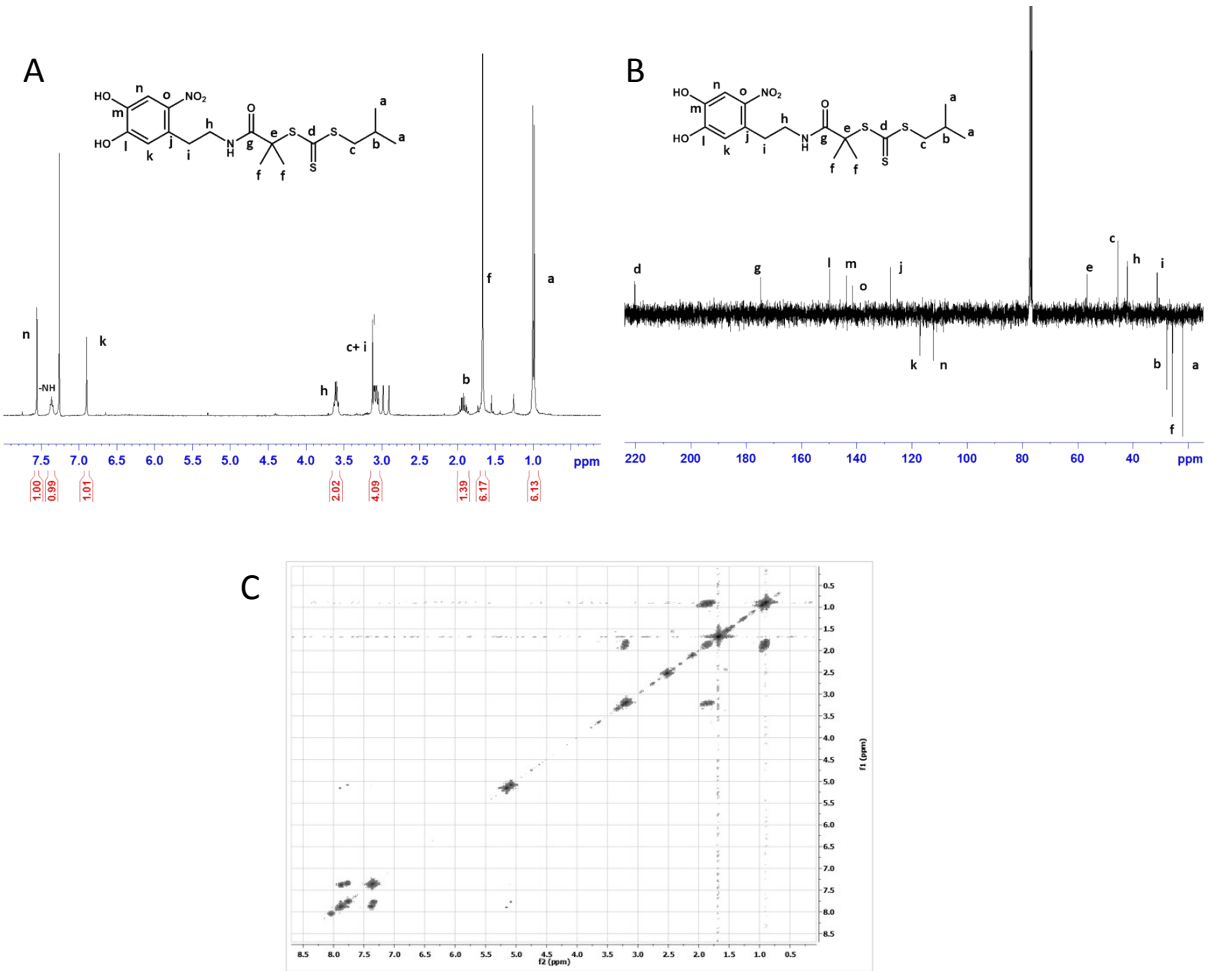

Figure S2. (A) ^{1}H NMR, (B) ^{13}C NMR and (C) COSY NMR of ND-CTA .

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm/TMS):

0.99 (d, 6H, $CH(CH_3)_2$), 1.66 (s, 6H, $C(CH_3)_2$-CO), 1.92 (sept, 1H, CH_2-$CH(CH_3)_2$), 3.06 (t, 2H, CH_2-CH_2-Aryl), 3.10 (d, 2H, S-CH_2-CH), 3.60 (q, 2H, NH-CH_2-CH_2), 6.89 (s, 1H, Aryl-H_k), 7.38 (t, 1H, CH_2-NH-CO), 7.55 (s, 1H, Aryl-H_n).

^{13}C NMR (75 MHz, $CDCl_3$):

22.1 (C_a), 25.7 (C_f), 27.8 (C_b), 31.3 (C_i), 42.1 (C_h), 45.5 (C_c), 56.7 (C_e), 112.2 (C_n), 117.1 (C_k), 127.8 (C_j), 141, (C_o), 143.6 (C_m), 149.7 (C_l), 174.7 (C_g), 220.3 (C_d).

HRMS (ESI): m/z calcd. for $C_{17}H_{24}N_2O_5S_3Na$ $[M+Na]^+$ 455.074, Found 455.073.

Typical procedure for the polymerization of monomer using functionalized ND-CTA or Boro-CTA

Tableau S1. Method of purification of polymers and time of polymerization

Monomer	Abbreviation	Time of polymerization	Purification
Dimethylacrylamide	DMAc	1h	Precipitation in Et_2O
N-isopropylacrylamide	NIPAM	1h30	Precipitation in Et_2O
Styrene	Sty	48h	Precipitation in MeOH
n-butyl acrylate	*n*BuA	1h	Precipitation in MeOH/H_2O (50/50)
Tert-butyl acrylate	*t*BuA	1h	Precipitation in MeOH/H_2O (50/50)
Methyl Acrylate	MA	40min	Precipitation in MeOH/H_2O (50/50)
Di(ethylene glycol) methyl ether acrylate	DEGA	2h	Dialysis in acetone
Poly(ethylene glycol) methyl ether acrylate (M_n=480 g.mol^{-1})	PEGA	2h	Dialysis in acetone

From Figure 2A could be extracted the apparent rate constants (s^{-1}) of the RAFT polymerizations involving **Boro-CTA** with DMAc ($8x10^{-4}$), NIPAM ($3x10^{-4}$), MA ($5x10^{-4}$), PEGA ($4x10^{-4}$), DEGA ($6x10^{-4}$), *n*BuA ($11x10^{-4}$) and *t*BuA ($6x10^{-4}$).

From Figure 3A could be extracted the apparent rate constants (s^{-1}) of the RAFT polymerizations involving **ND-CTA** with DMAc ($8x10^{-4}$), NIPAM ($3x10^{-4}$), MA ($26x10^{-4}$), PEGA ($3x10^{-4}$), DEGA ($4x10^{-4}$), *n*BuA ($4x10^{-4}$) and *t*BuA ($8x10^{-4}$).

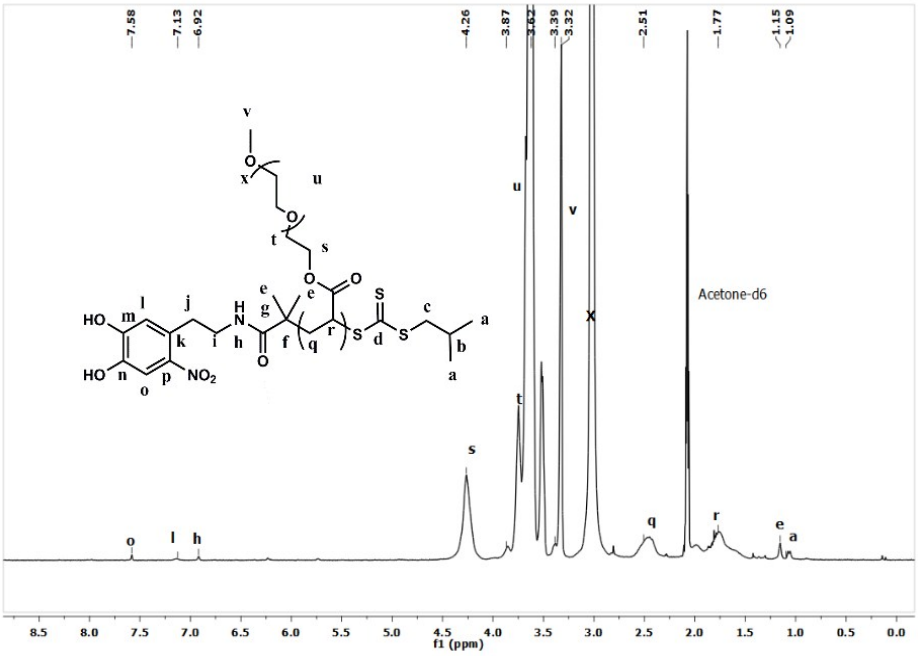

Figure S3. ^{1}H NMR spectrum of typical ND-PPEGA ($M_{n,NMR}$ = 12000 g.mol^{-1}, $Đ$=1.2)

^{1}H NMR (300 MHz, Acetone-d_6), δ (ppm/TMS): 7.58 (H_o); 7.12 (H_l); 6.92 (H_h); 4.26 (H_s); 3.87 (H_t); 3.62 (H_u); 3.32 (H_v); 2.51 (H_q); 1.77 (H_r); 1.15 (H_e); 1.09 (H_a)

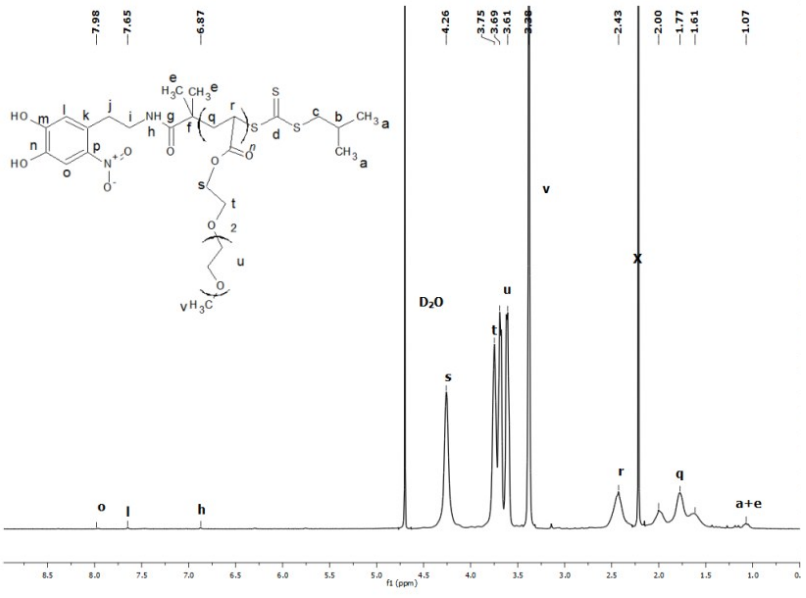

Figure S4. ^{1}H NMR spectrum of typical ND-PDEGA ($M_{n,NMR}$ = 17000 g.mol^{-1}, $Đ$=1.2)

^{1}H NMR (300 MHz, D_2O), δ (ppm/TMS): 7.98 (H_o); 7.65 (H_l); 6.87 (H_h); 4.26 (H_s); 3.75 (H_t); 3.69+3.61 (H_u); 3.38 (H_v); 2.43 (H_r); 1.77 (H_q); 1.07 (H_{a+e})

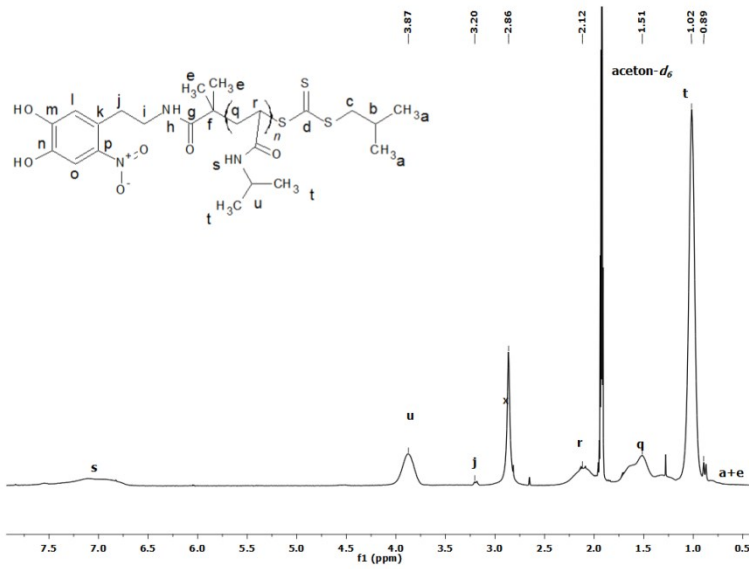

Figure S5. ^{1}H NMR spectrum of typical ND-PNIPAM ($M_{n,NMR}$ = 4400 g.mol^{-1}, $Đ$=1.2)

^{1}H NMR (300 MHz, aceton-d_6), δ (ppm/TMS): 7.0 (H_s+Ar*H*); 3.87 (H_u); 3.2 (H_j); 2.12 (H_r); 1.51 (H_q); 1.02 (H_t); 0.89 (H_{a+e})

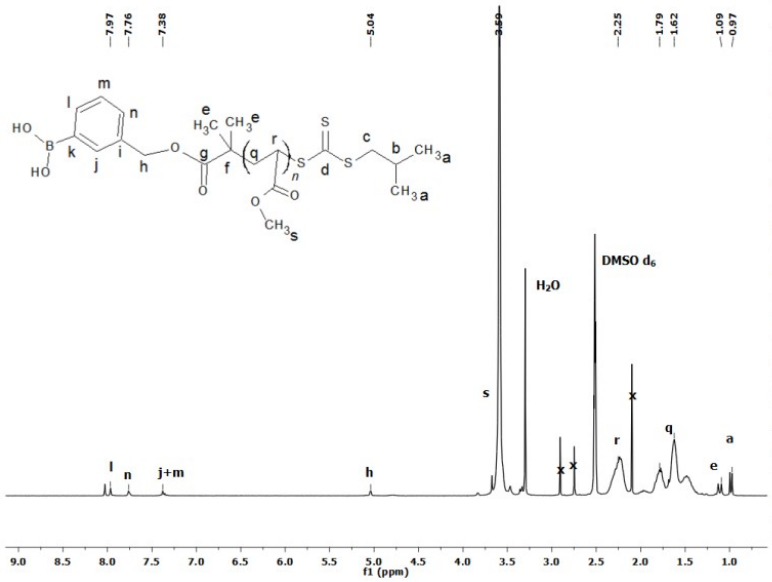

Figure S6. ^{1}H NMR spectrum of typical Boro-PMA ($M_{n,NMR}$ = 4600 g.mol^{-1}, $Đ$=1.1)

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm/TMS): 7.97 (H_l); 7.76 (H_n); 7.38 (H_{j+m}); 5.04 (H_h); 3.75 (H_s); 2.25 (H_r); 1.62 (H_q); 1.09 (H_e); 0.97 (H_a)

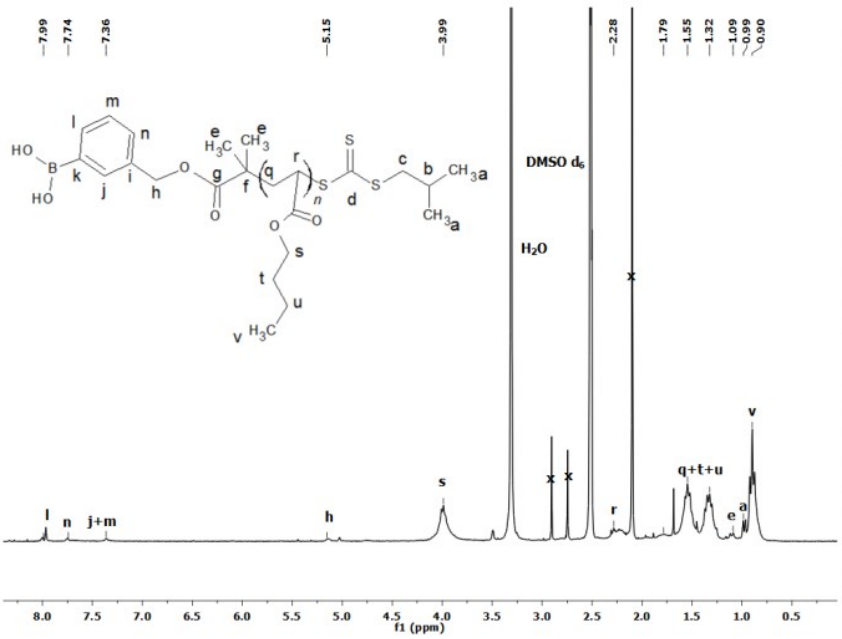

Figure S7. ^{1}H NMR spectrum of typical Boro-PnBuA ($M_{n,NMR}$ = 3700 g.mol^{-1}, $Đ$=1.1)

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm/TMS): 7.99 (H_l); 7.74 (H_n); 7.36 (H_{j+m}); 5.15 (H_h); 3.99 (H_s); 2.28 (H_r); 1.55+1.32 (H_{q+t+u}); 1.09 (H_e); 0.99 (H_a); 0.90 (H_v)

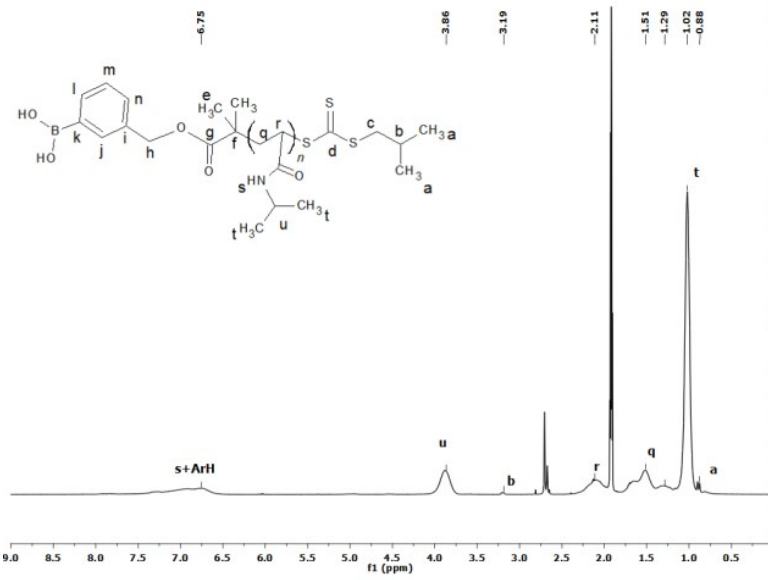

Figure S8. ^{1}H NMR spectrum of typical Boro-PNIPAM ($M_{n,NMR}$ = 4500 g.mol^{-1}, $Đ$=1.2)

^{1}H NMR (300 MHz, aceton-d_6), δ (ppm/TMS): 6.75 (H_s+Ar*H*); 3.86 (H_u); 2.11 (H_r); 1.29 (H_q); 1.02 (H_t); 0.88 (H_a)