Supporting Information

Synthesis of PMMA-based block copolymers by consecutive irreversible and reversible addition-fragmentation chain transfer polymerizations

Cédric Bergerbit, Barbara Farias-Mancilla, Lucie Seiler, Vincent Monteil, Simon Harrisson, Franck D'Agosto,* Mathias Destarac*

Contents

| 1. | Experimental details for the Mayo plot experiments | 2 |
|-----|--|----|
| 2. | ¹ H NMR spectrum of XD | .2 |
| 3. | ¹ H NMR spectrum of TD | .3 |
| 4. | Mayo plot for MMA polymerization in the presence of XD | 4 |
| 5. | Influence of AIBN and XD concentrations on the polymerization of MMA | 4 |
| 6. | ¹ H NMR analysis of PMMA-X1 (crude, precipitated once and precipitated twice) | 6 |
| 7. | Experimental details for the synthesis of PMMA- <i>b</i> -PVAc copolymer with PMMA-X1 | 6 |
| 8. | RI and UV traces of PMMA-b-PVAc and starting macroCTA PMMA-X1 obtained by SEC | 7 |
| 9. | Mayo plot for MMA polymerization in the presence of TD | 7 |
| 10. | ¹ H NMR spectrum of PMMA-T2 | .8 |
| 11. | SEC traces obtained for the block copolymerization of PMMA-T2 with VAc at 60°C | 8 |
| 12. | Evolution of VAc conversion upon block copolymerization with PMMA-T2 and PMMA-T3 | 8 |

1. Experimental details for the Mayo plot experiments

| Table S1. Experimental details for the Mayo plot experiments. Polymerization performed at 80°C, $[AIBN]_0/[MMA]_0 = 0$ a) MMA conversion determined by ¹ H NMR, b) Determined by SEC-RI in THF, PMMA calibration | | | | | | | | |
|--|--|-----|------------|---|-------|--|--|--|
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| Entry | СТА | [CTA]:[MMA] | [MMA] ₀ (mol L ⁻¹) | Time (min) | Conv ^a (%) | <i>M</i> _w ^₅ (g mol ⁻¹) |
|-------|-----|-------------|--|---------------|--------------------------|--|
| 1 | XD | 0 | 9.38 | 15 | 9.09 | 74 000 |
| 2 | XD | 0.001 | 9.38 | 15 | 6.54 | 52 500 |
| 3 | XD | 0.002 | 9.38 | 15 | 6.54 | 28 800 |
| 4 | XD | 0.005 | 9.38 | 15 | 5.66 | 15 000 |
| 5 | XD | 0.010 | 9.38 | 15 | 7.40 | 9 700 |
| 6 | XD | 0.020 | 9.38 | 15 | 1.96 | 7 200 |
| 7 | TD | 0 | 3.26 | 25 | 10.71 | 9 890 |
| 8 | TD | 0.001 | 3.26 | 25 | 5.66 | 8 200 |
| 9 | TD | 0.002 | 3.26 | 25 | 9.91 | 7 170 |
| 10 | TD | 0.005 | 3.26 | 25 | 2.91 | 4 570 |
| 11 | TD | 0.010 | 3.26 | 25 | 3.85 | 2 400 |
| 12 | TD | 0.020 | 3.26 | 25 | 1.96 | 1 380 |

2. ¹H NMR spectrum of XD



Figure S1. ¹H NMR spectrum of XD in CDCl₃.

3. ¹H NMR spectrum of TD



Figure S2. ¹H NMR spectrum of TD. [†]NMR solvent CDCl₃.

4. Mayo plot for MMA polymerization in the presence of XD



Figure S3. Mayo plot for the determination of the chain transfer constant to XD in MMA polymerization at 80°C. $2/DP_w$ vs [XD]/[MMA] (2) with the corresponding fit line (—).



5. Influence of AIBN and XD concentrations on the polymerization of MMA

Figure S4. Evolution of MMA (S4a) and XD (S4b) conversion as a function of time for different initial AIBN concentrations. $[MMA]_0 = 4.1 \text{mol } L^{-1}$. Solvent = toluene.

6. ¹H NMR analysis of PMMA-X1 (crude, precipitated once and precipitated twice)



Figure S5. a) Comparison of ¹H NMR spectra of PMMA-X1 ($M_n = 4 \ 100 \ \text{g} \ \text{mol}^{-1}$) at different stages: crude product, precipitated once and precipitated twice, with their respective integration values of terminal –S-(C=S)-OCH₂CH₃ (**B**, 4.55-4.77 ppm) and PMMA (**A**, 3.50-3.65 ppm) regions. The corresponding PMMA and MMA assignments are also shown. b) Zoom in the characteristic zone of the xanthate chain end. Analysis performed in CDCl₃.

7. Experimental details for the synthesis of PMMA-b-PVAc copolymer with PMMA-X1

Table S2. Experimental details and macromolecular characteristics of PMMA-*b*-PVAc. *M*_{n,theo} = 25 000 g mol⁻¹.

| Copolymer | [PMMA-X1] (mol L ⁻¹) | [VAc] (mol L-1) | [AIBN] (mol L ⁻¹) | Time (h) | т (°С) | Conv ^a (%) | M _{n ,SEC} ^b (g mol ⁻¹) | M _{w,SEC} ^b (g mol⁻¹) | Ðb |
|----------------------|-------------------------------------|--------------------|----------------------------------|-------------|-----------|--------------------------|--|--|------|
| PMMA- b -PVAc | 0.029 | 8.50 | 0.088 | 6 | 60 | 98 | 24 800 | 44 900 | 1.80 |
| | | | | | | | | | |

a) Determined by 1H NMR; b) Determined by SEC-RI in THF

8. RI and UV traces of PMMA-*b*-PVAc and starting PMMA-X1 macro-CTA obtained by SEC in THF



Figure S6. SEC RI(—) and UV (---) traces for PMMA-b-PVAc and PMMA-X1.

9. Mayo plot for MMA polymerization in the presence of TD



Figure S7. Mayo plot for MMA polymerization mediated by TD at 80°C, 2/DP_w vs [TD]/[MMA] (2) with the corresponding linear fit line (—).

10. ¹H NMR spectrum of PMMA-T2



Figure S8. ¹H NMR spectrum of PMMA-T2 (M_n = 5 600 g mol⁻¹). Analysis performed in CDCl₃.

11. SEC-RI traces obtained for the block copolymerization of PMMA-T2 with VAc at 60°C



Figure S9. SEC-RI traces for the chain extension of PMMA-T2 with VAc at 60°C. THF eluent.

12. Evolution of VAc conversion upon block copolymerization with PMMA-T2 and PMMA-T3



Figure S10. Evolution of VAc conversion with polymerization time, macro-CTA (2.84x10⁻⁵ mol L⁻¹), AIBN (0.95x10⁻⁵ mol L⁻¹), VAc (8x10⁻³ mol L⁻¹). -- \blacksquare --: PMMA-T2, T = 60°C; -- \blacksquare --: PMMA-T3, T = 70°C.