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

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1. Experimental details for the Mayo plot experiments

Table S1. Experimental details for the Mayo plot experiments. Polymerization performed at 80°C, [AIBN]/[MMA]₀ = 0.001. a) MMA conversion determined by ¹H NMR, b) Determined by SEC-RI in THF, PMMA calibration

<table>
<thead>
<tr>
<th>Entry</th>
<th>CTA</th>
<th>[CTA]₀/[MMA]₀</th>
<th>[MMA]₀ (mol L⁻¹)</th>
<th>Time (min)</th>
<th>Conv (mol %)</th>
<th>Mₘ (g mol⁻¹)</th>
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<tr>
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2. ¹H NMR spectrum of XD

Figure S1. ¹H NMR spectrum of XD in CDCl₃.
3. $^1$H NMR spectrum of TD

Figure S2. $^1$H NMR spectrum of TD. $^1$H NMR solvent CDCl$_3$.

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] (●) with the corresponding fit line (—).
Figure S4. Evolution of MMA (S4a) and XD (S4b) conversion as a function of time for different initial AIBN concentrations. 
$[\text{MMA}]_0= 4.1\text{mol L}^{-1}$. Solvent = toluene.
6. $^1$H NMR analysis of PMMA-X1 (crude, precipitated once and precipitated twice)

Figure S5. a) Comparison of $^1$H NMR spectra of PMMA-X1 ($M_n = 4\ 100\ g\ mol^{-1}$) at different stages: crude product, precipitated once and precipitated twice, with their respective integration values of terminal −S-(C=S)-OC$H_2$CH$_3$ (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 CDCl$_3$.

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$^{-1}$.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>[PMMA-X1] (mol L$^{-1}$)</th>
<th>[VAc] (mol L$^{-1}$)</th>
<th>[AIBN] (mol L$^{-1}$)</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>Conv $^a$ (%)</th>
<th>$M_n$SEC $^b$ (g mol$^{-1}$)</th>
<th>$M_w$SEC $^b$ (g mol$^{-1}$)</th>
<th>$\bar{D}$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-$b$-PVAc</td>
<td>0.029</td>
<td>8.50</td>
<td>0.088</td>
<td>6</td>
<td>60</td>
<td>98</td>
<td>24 800</td>
<td>44 900</td>
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$^a$ Determined by $^1$H 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

![SEC traces for PMMA-b-PVAc and PMMA-X1](image)

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

![Mayo plot for MMA polymerization mediated by TD](image)

Figure S7. Mayo plot for MMA polymerization mediated by TD at 80°C, 2/DPₜ vs [TD]/[MMA] (●) with the corresponding linear fit line (—).
10. $^1$H NMR spectrum of PMMA-T2

Figure S8. $^1$H NMR spectrum of PMMA-T2 ($M_n = 5600 \text{ g mol}^{-1}$). Analysis performed in CDCl$_3$.

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

![Graph showing VAc conversion over time with polymerization time, macro-CTA (2.84x10^{-5} mol L^{-1}), AIBN (0.95x10^{-5} mol L^{-1}), VAc (8x10^{-3} mol L^{-1}).]

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}). - - - - - - PMMA-T2, T = 60°C, - - - - - - PMMA-T3, T = 70°C.