

Synthesis of poly(methyl methacrylate)-*b*-polyethylene (PMMA-*b*-PE) block copolymers via conventional emulsion polymerization

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Supporting information

1. Reaction of the aqueous phase of PMMA₁₆ latex with APS

In order to confirm that the shorter chains of the PMMA₁₆ seed latex were in the aqueous phase and could react with the initiator (APS), this aqueous phase was extracted by centrifugation. The analysis of the latter by ¹H NMR in D₂O confirmed that short oligomers were indeed located in the continuous phase of this latex (Figure S1a). APS and NaHCO₃ were then added to this aqueous phase under the same conditions than for the seeded emulsion polymerization of ethylene with PMMA₁₆ (i.e., run 1, Table 2). The solution was stirred during 2 h at 80 °C and the final product was analyzed by ¹H NMR. All the vinyl functions disappeared indicating that they were consumed by reaction with APS in the medium (Figure S1b).

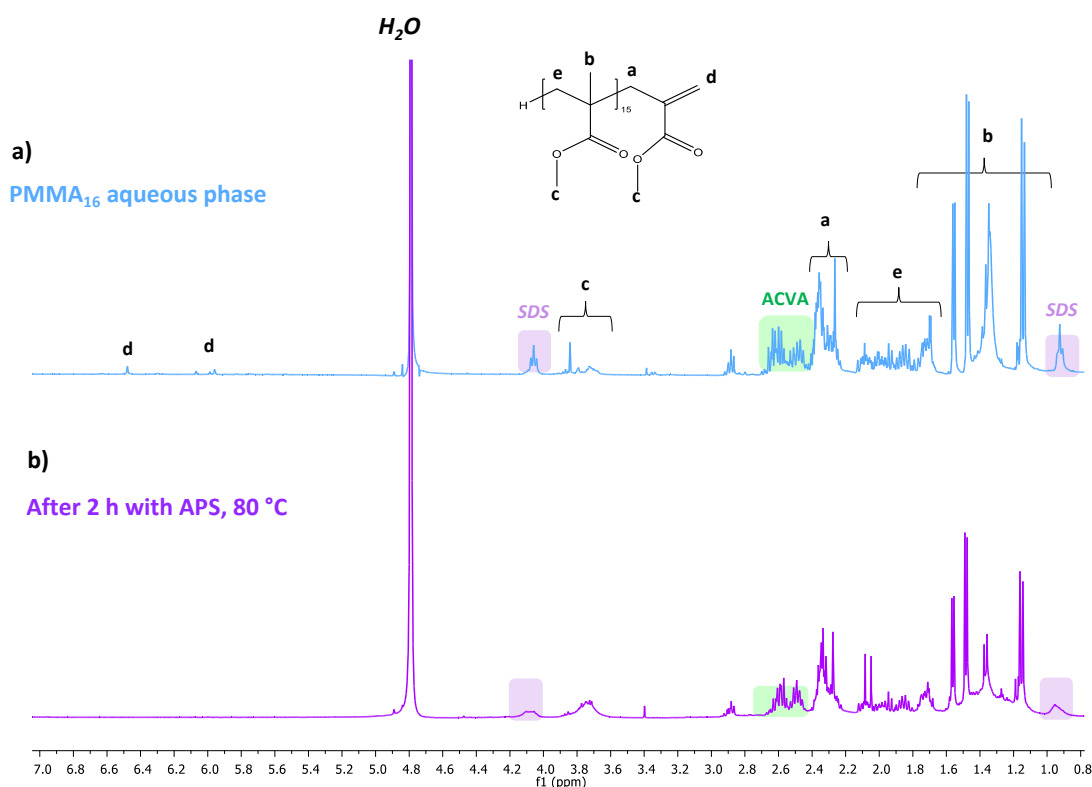
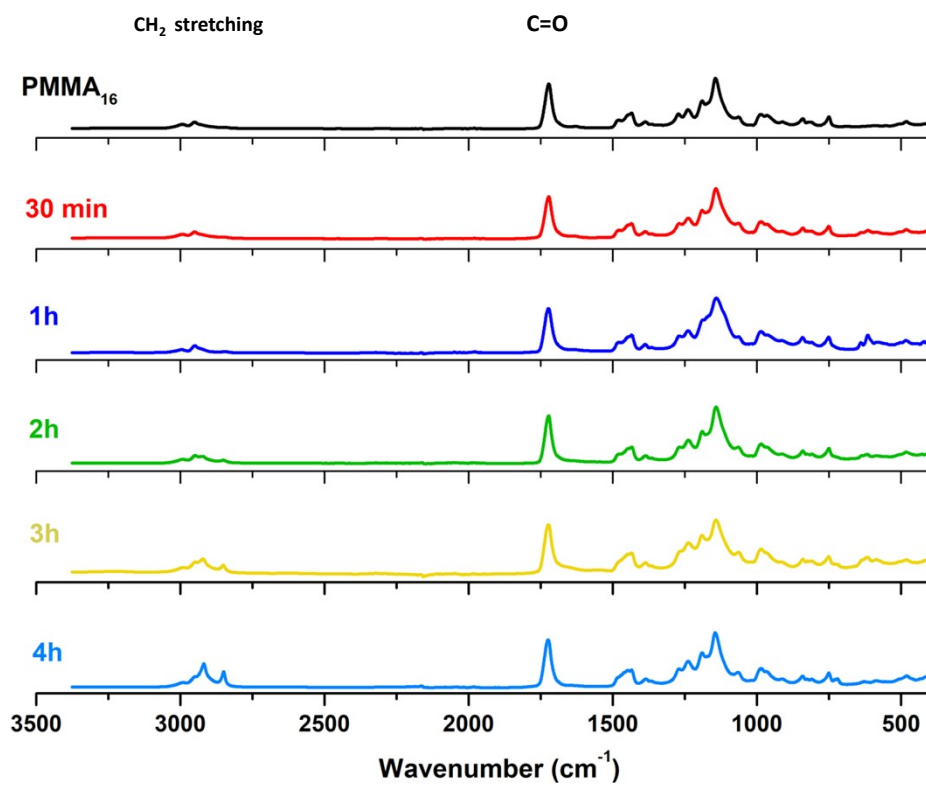


Figure S1. ¹H NMR spectra (400 MHz, D₂O at 25 °C) of a) the aqueous phase of PMMA₁₆ and b) the product of reaction after 2 h at 80 °C.

2. Study of the formation of PE homopolymer by FT-IR analysis

a)



b)

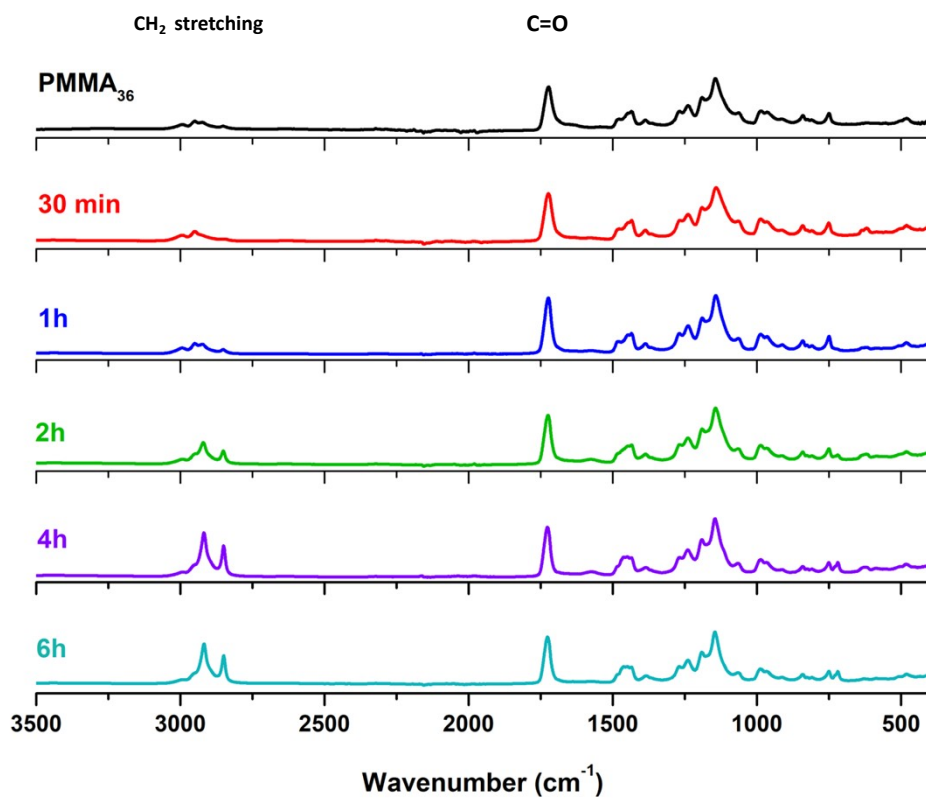


Figure S2. FT-IR spectra of copolymers obtained with a) PMMA₁₆ and b) PMMA₃₆ (respectively runs 3 and 4 in Table 2).

Thermal analysis by DSC (heating curves)

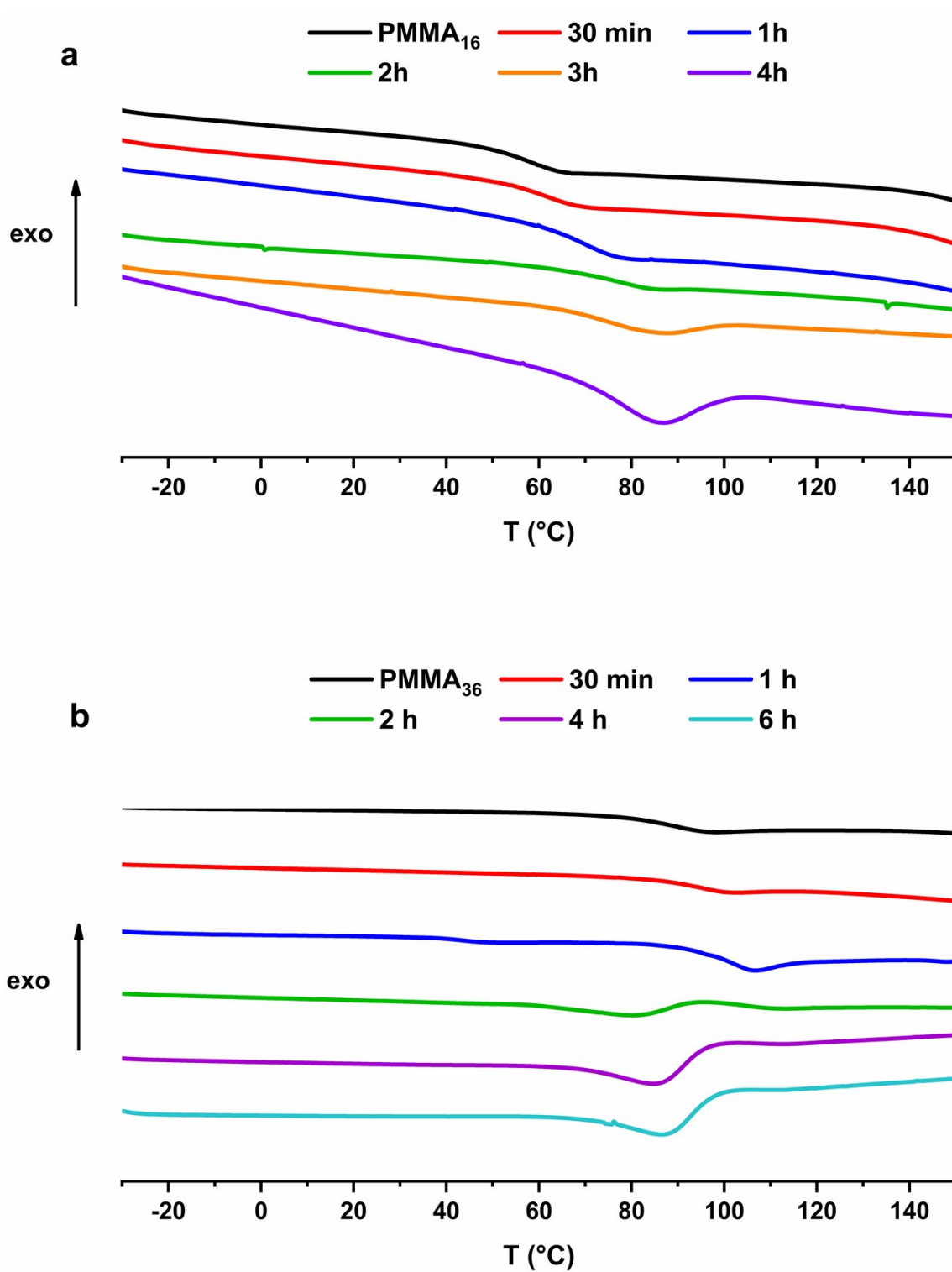


Figure S3. DSC analyses (heating) of the samples presented Table 2 for the polymerization with a) PMMA₁₆ and b) PMMA₃₆.

3. Synthesis of polyethylene by radical emulsion polymerization in water

In order to compare the thermal behavior of these PMMA₁₆-*b*-PE to a physical blend of PMMA₁₆ and PE, a PE homopolymer was synthesized by radical emulsion polymerization in water. The synthesis was adapted from previous work realized by our group with APS and SDS¹ to be in similar conditions than the seeded system used in this work with PMMA_x latexes.

APS (41.1 mg, 0.18 mmol), SDS (150 mg, 0.52 mmol) and NaHCO₃ (50.4 mg, 0.60 mmol) were dissolved in water (50 mL) and this solution was introduced after deoxygenating into the preheated and inert autoclave at 80 °C. Ethylene gas was then introduced into the reactor until the desired pressure (100 bar) was reached. The reaction medium was stirred at 250 rpm during 4 h. The autoclave was cooled with iced water. When the temperature inside the autoclave dropped below 35 °C, the remaining pressure was carefully released. The latex was dried before being mixed with PMMA₁₆ dried latex.

The DLS analysis revealed that the latex was composed of two particles populations, a majority of small particles (around 40 nm) and some big particles (around 600 nm). The dried extract was analyzed by HT-SEC and presented in Figure S4.

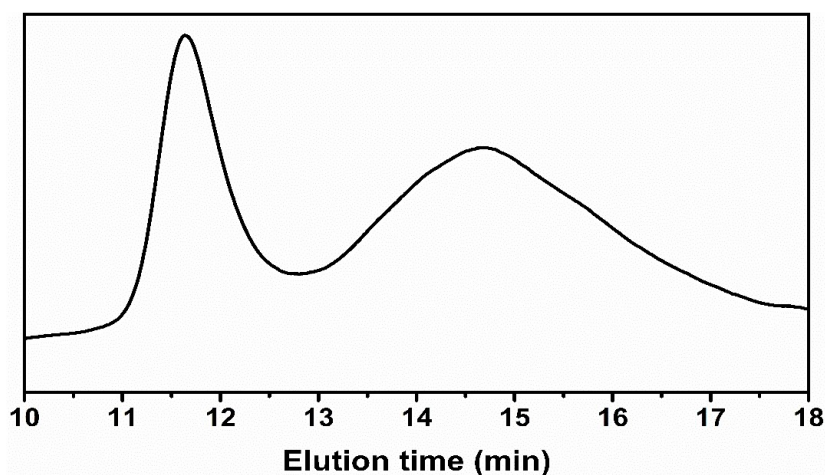


Figure S4. HT-SEC chromatogram of the dry extract from the PE homopolymer synthesized by radical emulsion polymerization.

4. Synthesis of PMMA by free radical emulsion polymerization in water

Table S1. Aqueous free radical emulsion polymerization of MMA^[a]

Run	<i>t</i> (h)	$\tau_{s,f}^{[b]}$ (%)	$X_{MMA}^{[b]}$ (%)	$Z_{ave}^{[c]}$ (nm)	PDI ^[c]	$M_{n, SEC}^{[d]}$ (g mol ⁻¹)	$\mathcal{D}^{[d]}$	$T_g^{[e]}$ (°C)
PMMA-FRP	0	10.2	96	42	0.07	138 000	5.5	106

[a] KPS (4 mM), NaHCO₃ (8 mM), SDS (14 mM), MMA (10 wt%) and water (100 mL) at 70 °C. [b] Determined by gravimetric analysis. [c] Determined by DLS, in intensity. [d] Determined by SEC-THF. [e] Determined by DSC.

References

1. F. Baffie, G. Patias, A. Shegiwal, F. Brunel, V. Monteil, L. Verrieux, L. Perrin, D. M. Haddleton and F. D'Agosto, *Angew. Chem. Int. Ed.*, 2021, **60**, 25356–25364.