Electronic supplementary information

Synthetic methodology effect on the microstructure and thermal properties of poly (*n*-Butyl Acrylate - *co* - Methyl MethAcrylate) synthesized by nitroxide mediated polymerization

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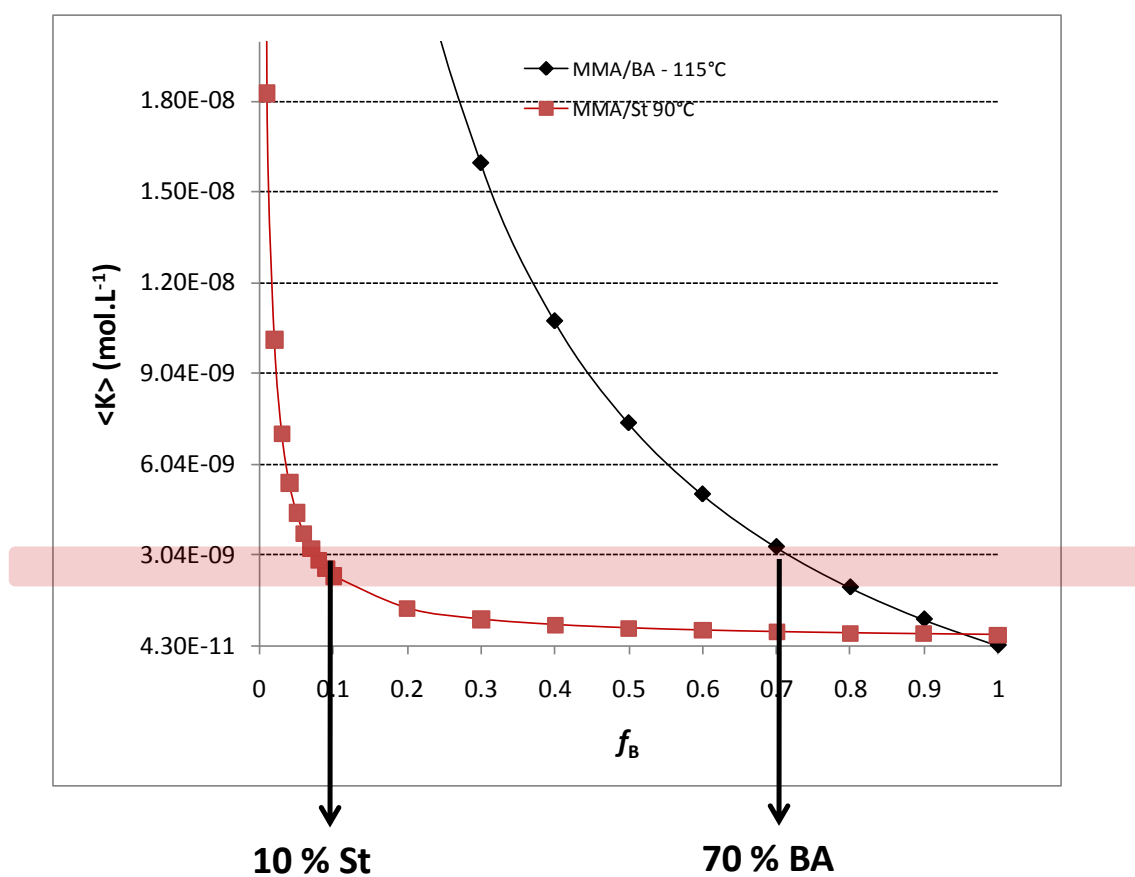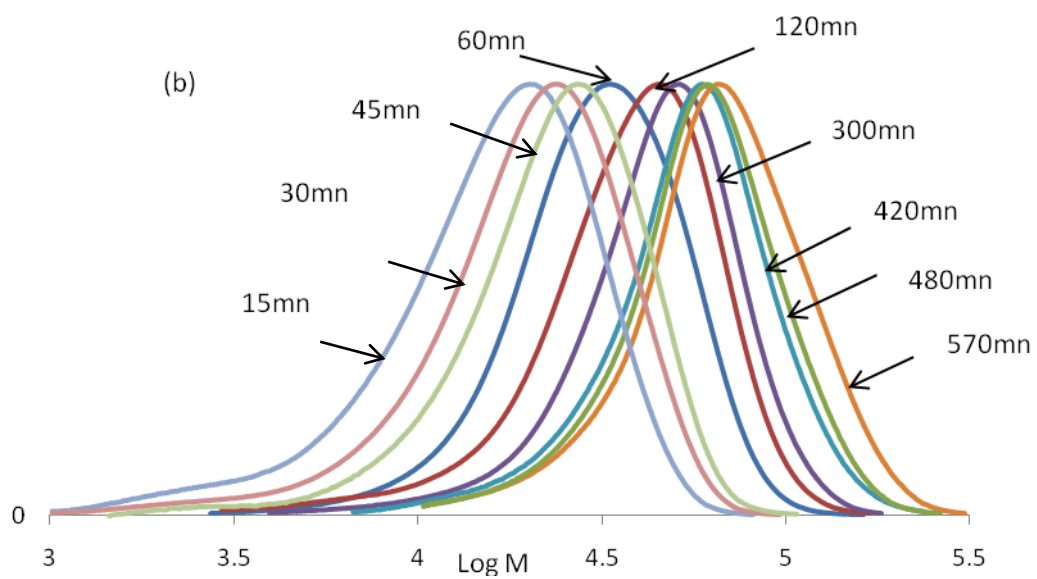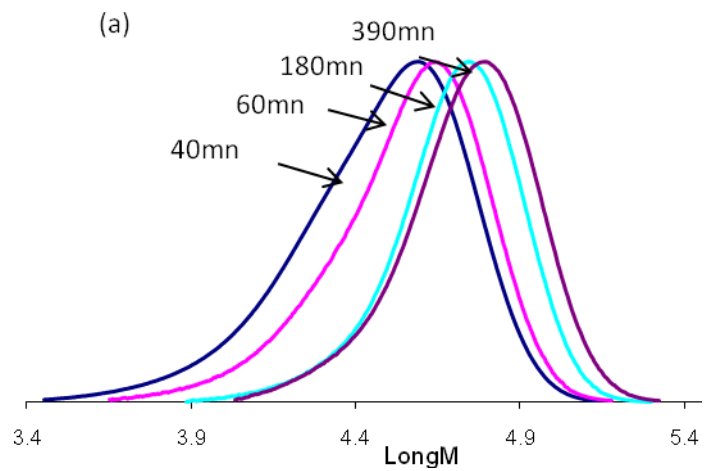
Figure SI-1. Theoretical average activation-deactivation equilibrium constant <K> for the copolymerization of methyl methacrylate (MMA) with either styrene (St, red plots) at 90°C or with n-butyl acrylate (BA, black plots) at 115°C as a function of the molar fraction of the comonomer in the monomer mixture. <K> was calculated from the following equation (reference

[1]):

$$\langle K \rangle = \dfrac{\dfrac{r_A f_A}{k_{p,A}} + \dfrac{r_B f_B}{k_{p,B}}}{\dfrac{r_A f_A}{k_{p,A} K_A} + \dfrac{r_B f_B}{k_{p,B} K_B}}$$

With A corresponding to MMA and B to either styrene or n-butyl acrylate. The numerical values used to calculate <K> are reported in reference 1 for MMA/St copolymerization and in the notes of the present article.

(a)

390mn
180mn
60mn
40mn

3.4   3.9   4.4   4.9   5.4

LongM

(b)

120mn
60mn
45mn
30mn
15mn

300mn
420mn
480mn
570mn

0

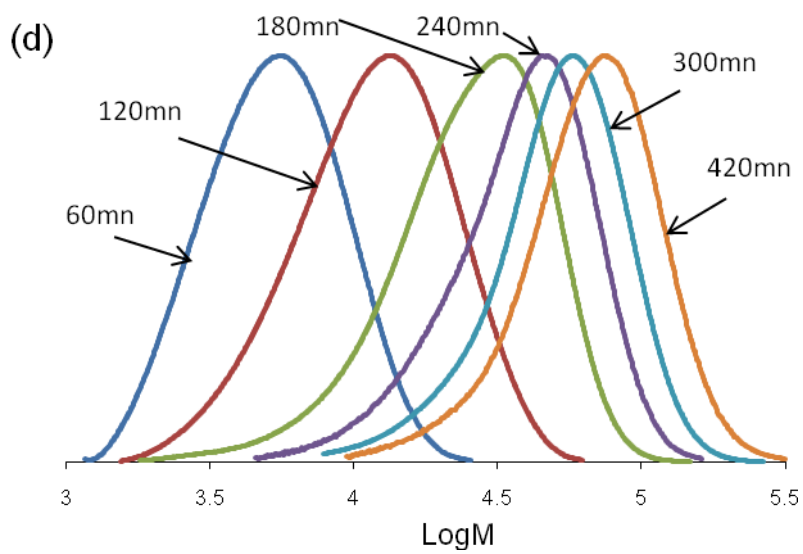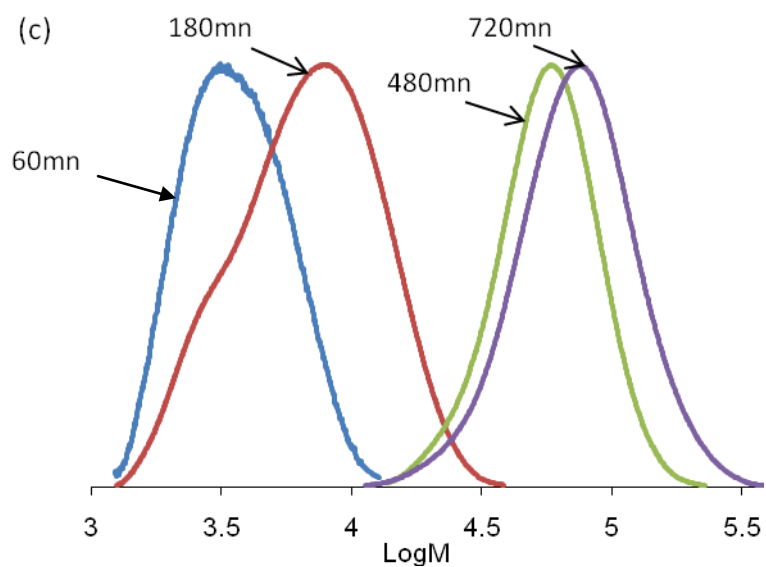3   3.5   4   Log M   4.5   5   5.5

Figure SI-2. SEC traces of the copolymers versus time (a) G-Batch, (b) Batch75/25, (c) Semibatch-2.2 and (d) Semibatch-4.3
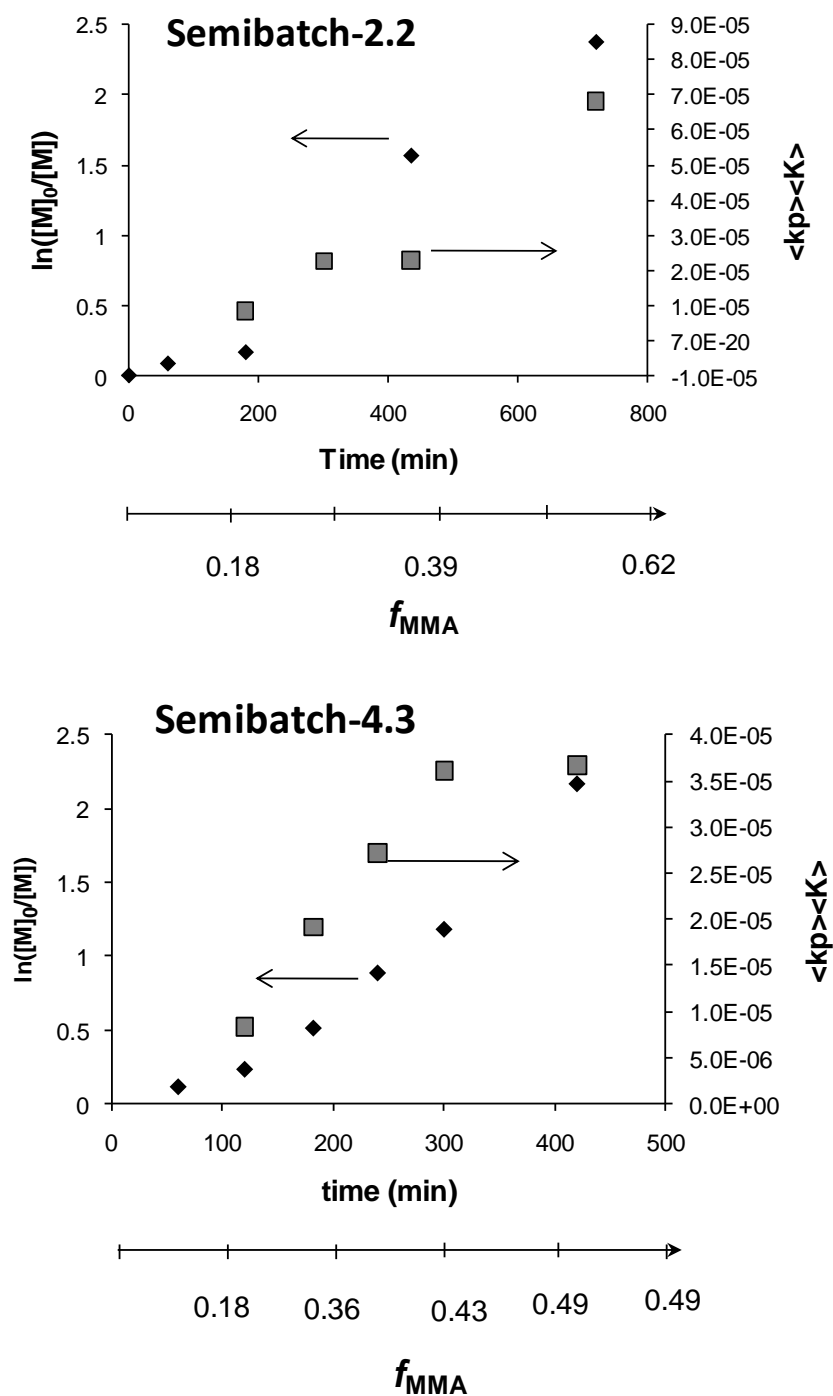
Figure SI-3 Evolution of $\ln[M]_0/[M]$ versus time (black diamond symbols) and corresponding variation of the values of the theoretical product of the average activation-deactivation equilibrium constant with the average propagation rate constant $\langle k_p \rangle \langle K \rangle$ (grey square symbols) as a function of time. For each sample, the corresponding molar fraction of methyl methacrylate in the comonomer mixture is plotted in a second x axis. Semi-batch copolymerizations of n-butyl acrylate and methyl methacrylate at 115°C (Semibatch-2.2 and Semibatch-4.3).

The $\ln[M_0]/[M]$ versus time was calculated by consideration of the overall number of moles of BA and MMA at each time of the polymerization. So in the calculation of M0, we consider at each time, the sum of the initial BA amount (0.192 mol) and the overall amount of

MMA introduced during the reaction and which continuously changes. For a MMA addition rate of 4.3 ml / h, this quantity is 4.3 ml after 60min, 8.6 ml after 120min and so on ...
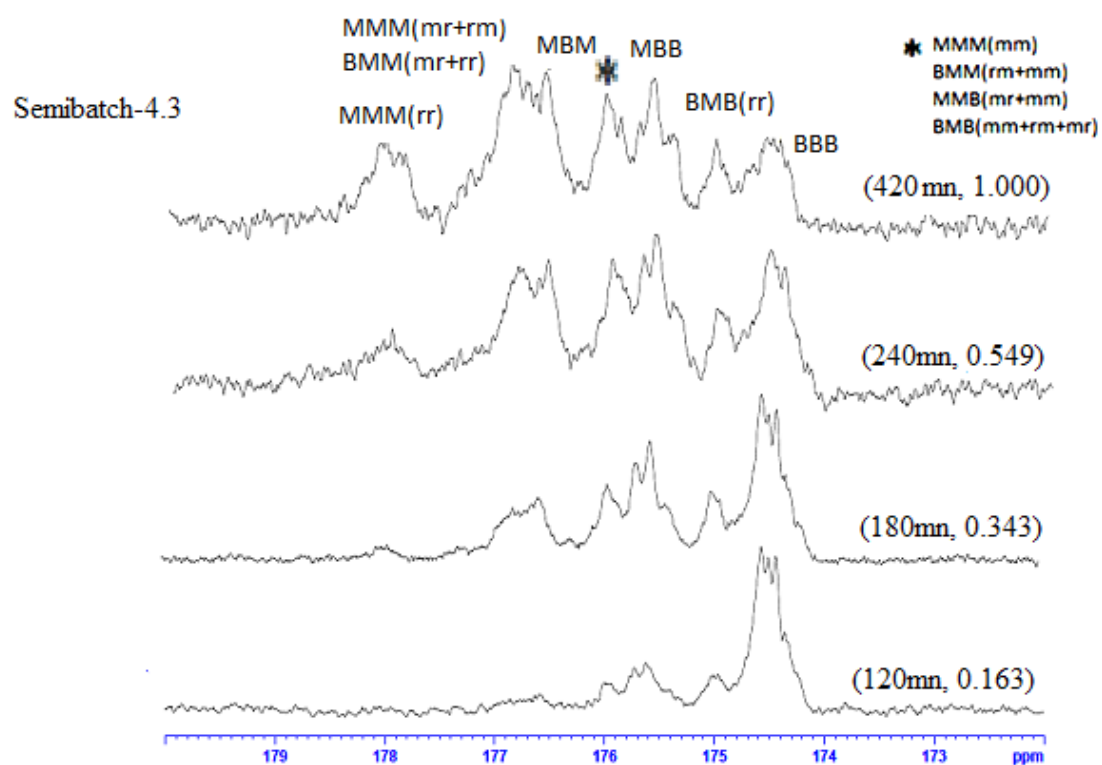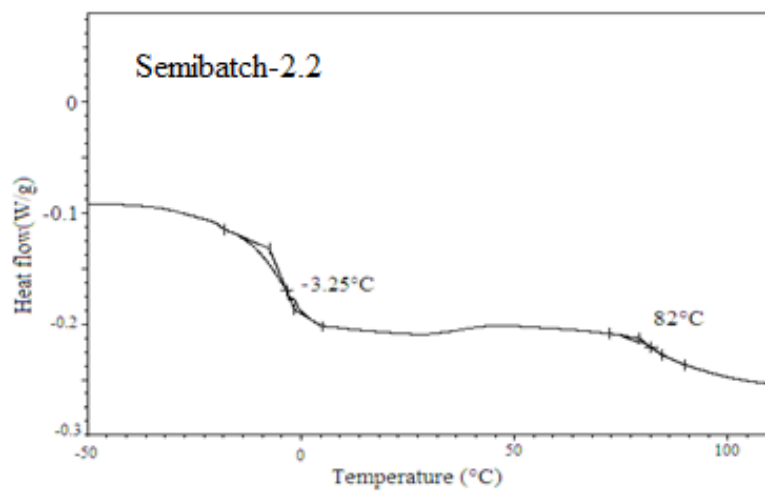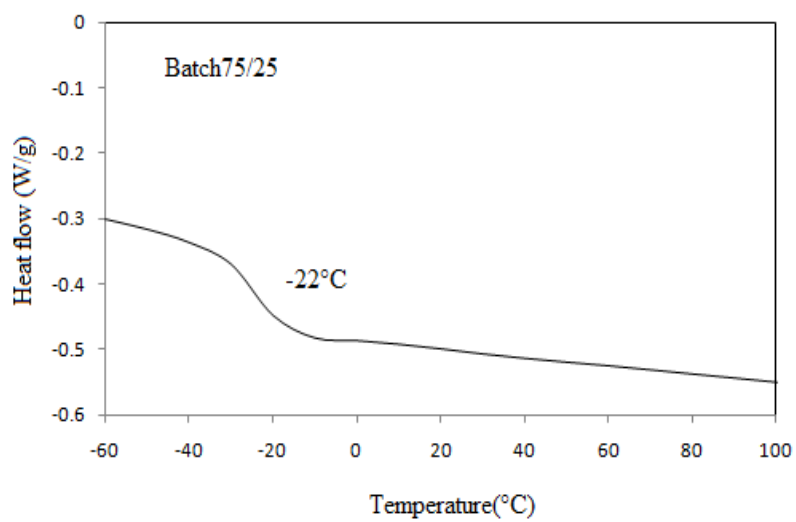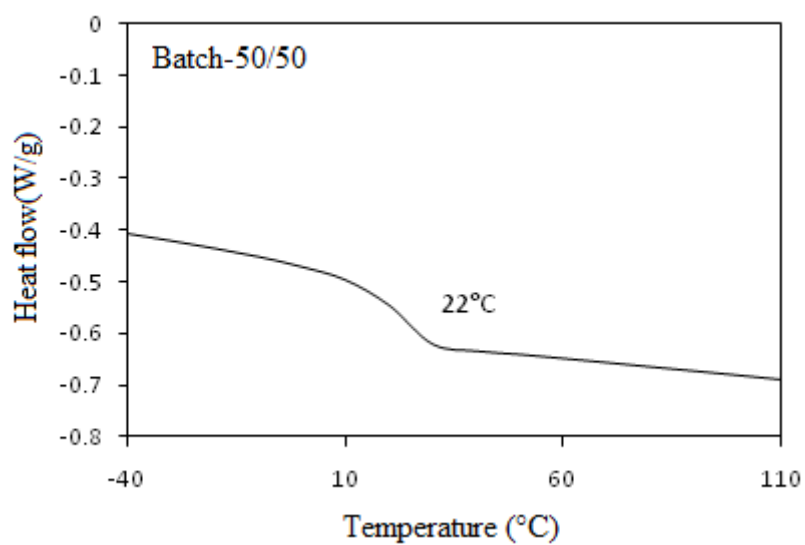
Figure SI-4. ^{13}C NMR spectra showing the carbonyl region of Semibatch-4.3 copolymers as function of time and apparent normalized chain length

Batch-50/50, showing DSC heat flow trace with transition at 22°C.

Batch75/25, showing DSC heat flow trace with transition at -22°C.

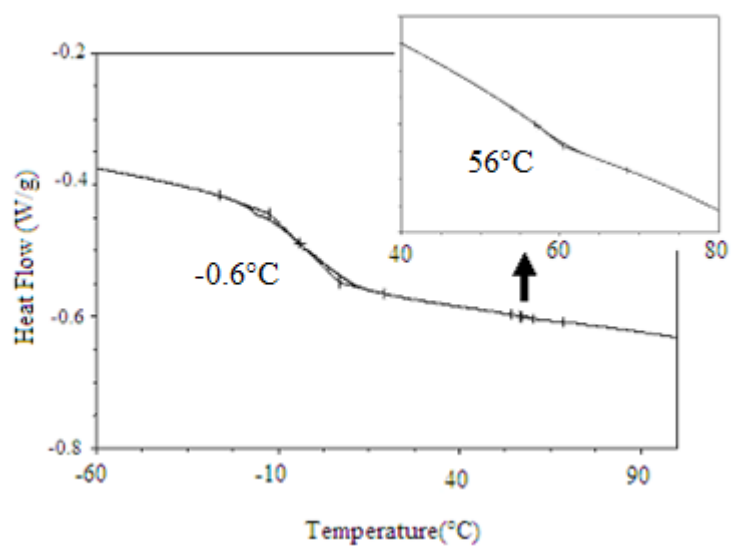Semibatch-2.2, showing DSC heat flow trace with transitions at -3.25°C and 82°C.

Figure SI-5. DSC heating curves for Batch50/50, batch75/25, Semibatch-2.2 and Smibatch-4.3

[1]   B. Charleux, J. Nicolas, O. Guerret, *Macromolecules* 2005, **38**, 5485.