Supplementary information

"Synthesis and characterization of diblock and statistical copolymers based on hydrolyzable siloxy silylester methacrylate monomers"

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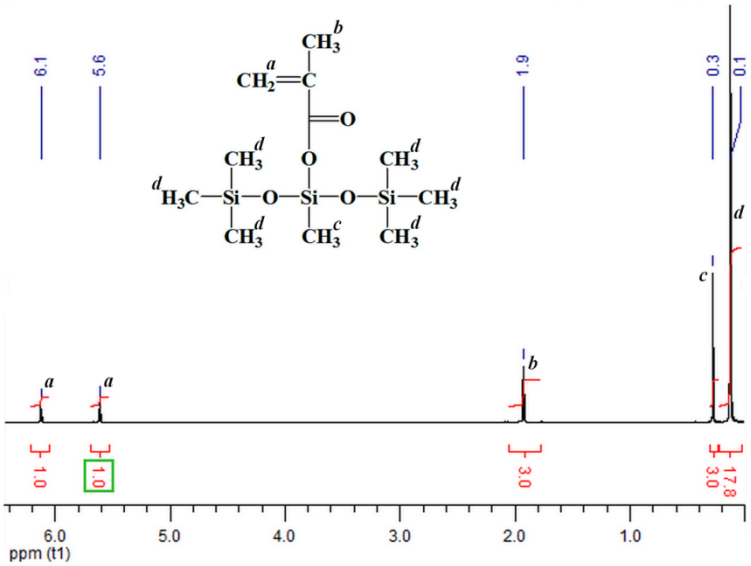

Figure S1 : ^{1}H-NMR spectrum of MATM2 monomer ($CDCl_3$).

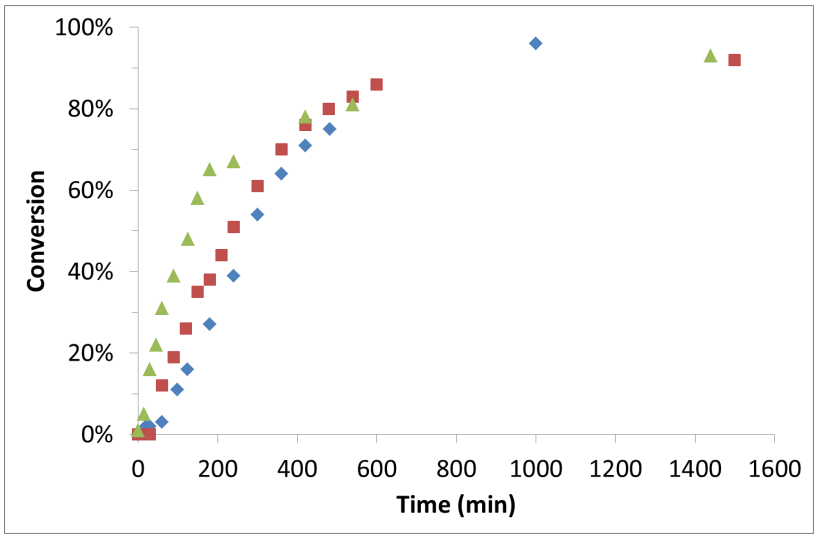

Figure S2 : Evolution of the conversion versus time, for the RAFT homopolymerization of MATM2, using ◆ CPDB and ■ CTA-0610 as chain transfer agent, and ▲ without CTA. Conditions: xylene, 70°C, [MATM2] = 1.5 mol.L^{-1}, [CTA]/[AIBN] = 5.

Determination of the reactivity ratios

The reactivity ratios were determined by the last squares method using the Solver function of Excel Microsoft software, by determining the values of r_{MATM2} and r_{MMA} which minimize the sum of the squares of the difference between experimental values of F_{MATM2} and the values calculated with the Mayo-Lewis equation S1.

$$F_{MATM2} = \frac{r_{MATM2} \times f_{MATM2}^2 + f_{MATM2} \times f_{MMA}}{r_{MATM2} \times f_{MATM2}^2 + r_{MMA} \times f_{MMA}^2 + 2 \times f_{MATM2} \times f_{MMA}}$$

Table 1 : Experimental values of f_{MATM2} and F_{MATM2}.

	f_{MATM2}	F_{MATM2}
1	0.10	0.13
2	0.27	0.37
3	0.42	0.52
4	0.59	0.65
5	0.75	0.81
6	0.91	0.93

Estimation of d*n*/d*c* values:

Estimated values of dn/dc were calculated using Eq. S2, in the following cases:

- For p(MATM2-*stat*-MMA) statistical copolymers s30 and s50 which cannot be purified by precipitation
- For pMATM2-*block*-pMMA diblock copolymer b20 during the formation of the second block.

$$\left(\frac{dn}{dc}\right)_{copolymer} = \left(\frac{dn}{dc}\right)_{MATM2} \omega_{MATM2} + \left(\frac{dn}{dc}\right)_{MMA} \omega_{MMA} \qquad \text{(Eq. S2)}$$

where $(dn/dc)_{MATM2}$ and $(dn/dc)_{MMA}$ are the refractive index increment of the homopolymer pMATM2 and pMMA respectively, and ω_i the weight fraction of monomer unit i in the copolymer.

This estimation was confirmed with the experimental values of d*n*/d*c* determined for the purified diblock and statistical copolymers of MATM2 and MMA (Figure S3).

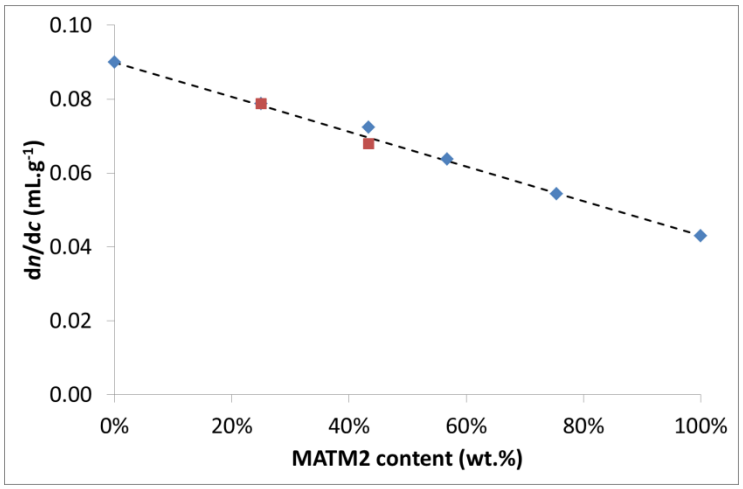

Figure S3 : Evolution of the values of the refractive index increments (d*n*/d*c*) versus MATM2 content, ◆ experimental values for pMATM2-*block*-pMMA, ■ experimental values for p(MATM2-*stat*-MMA), - - - theoretical values calculated with Eq. S2.

The molar masses determined by TD-SEC using these calculated d*n*/d*c* values were considered closer to reality than those determined by conventional pMMA calibration, since the calculated d*n*/d*c* values take into account the proportion of MATM2 and MMA in the copolymer.