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Electronic supplementary information to

Controlling block copolymer one-dimensional self-assembly in polymeric matrices

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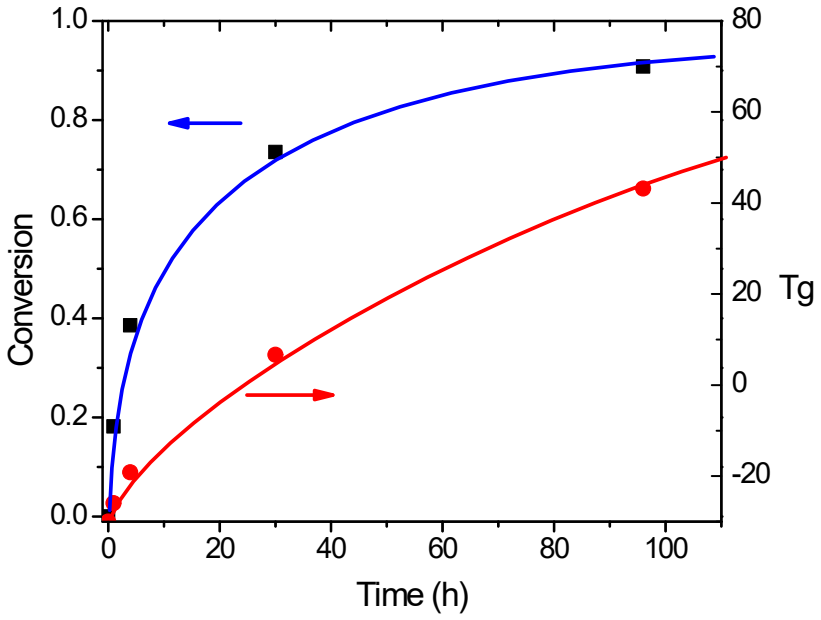

Figure S-1: Conversion of vinyl groups and evolution of Tg of the matrix as a function of irradiation time at RT. The lines are drawn to guide the eye.

Styrene monomer was photocured in bulk at room temperature. A two-component system consisting in CQ (2 wt%) and EDMAB (2 wt%) was employed as photoinitiator of the radical polymerization. CQ has a maximum of absorption in λ=460nm, which allow the use of visible light to photocure the samples. The role of EDMAB is to catalyze the reaction. The reaction mechanism is briefly explained here: CQ is first excited to its singlet by visible light irradiation but rapidly undergoes intersystem crossing to its triplet. The excited triplet state is reduced by EDMAB to generate ketyl and α-amino free radicals. While the free ketyl radicals only dimerize, the amino free radicals initiate the polymerization of St. Figure S-1 shows the conversion of styrene as a function of irradiation time, measured by size exclusion chromatography. As can be appreciated, 96 hours of irradiation were necessary to achieve a conversion close to 0.9.

The evolution of the glass transition temperature of the reacting system as a function of conversion (x) was calculated using equation 1 *(Journal of Polymer Science Part B: Polymer Physics, 1990, 28, 85–95)* Where Tg_0 is the glass transition temperature of the initial reactive mixture, Tg_∞ is the glass transition temperature of the matrix polymerized to full conversion, and $\lambda = \Delta cp_\infty/\Delta cp_0$, is the ratio of changes in the specific heat through the glass transition for the fully polymerized matrix and the initial sample.

$$(Tg - Tg_0)/(Tg_\infty - Tg_0) = \lambda x/[1 - (1 - \lambda)x] \quad (1)$$

Figure S-1 shows the obtained conversion-time curve (squares) and the evolution of the Tg of the matrix with the conversion degree (dots) as predicted by equation 1, where λ=0.158, Tg_0=−30 °C and Tg_∞=90 °C.

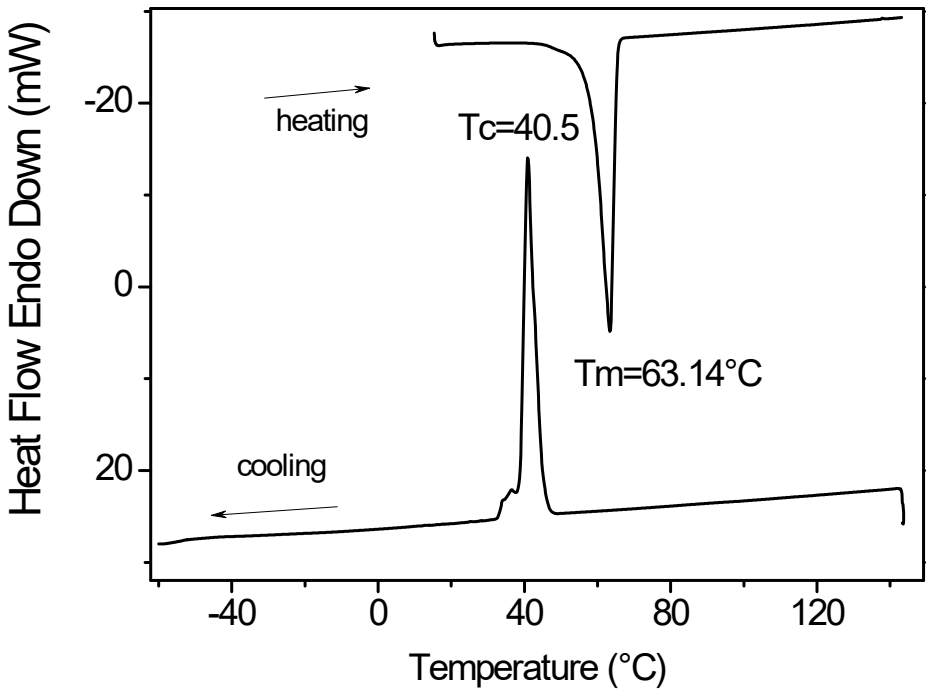

Figure **S-2**: DSC cooling and heating scan at 10°C/min of PEO homopolymer (Mn= 13,000Da).

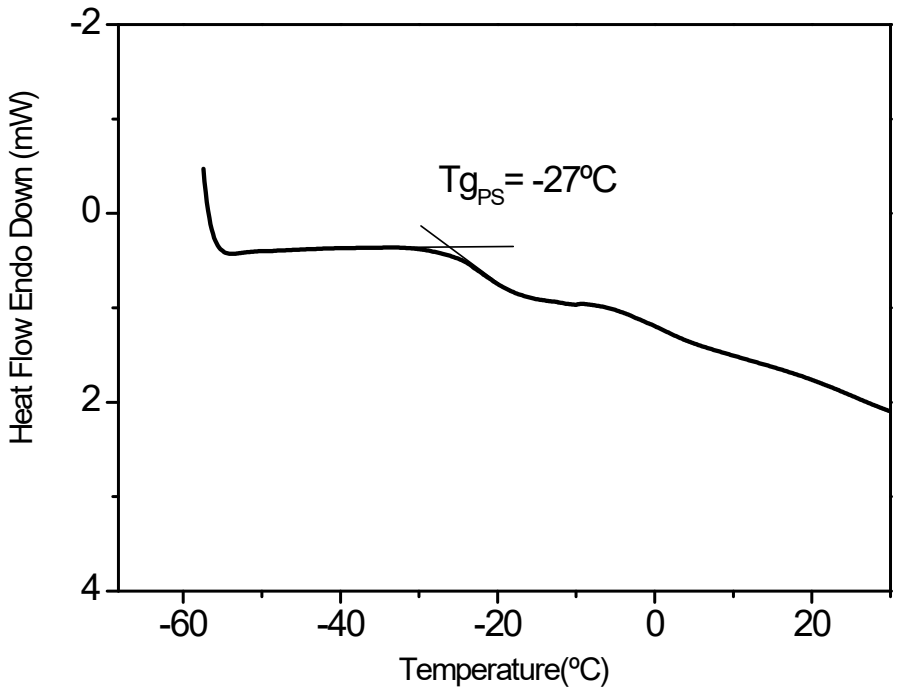

Figure **S-3**: Glass transition temperature of the matrix at the moment that PEO-block microphase separates, $T_{g,matrix}$= -27°C.