Kinetic differences in the intercalation of linear and cyclic penta(ethylene oxide)s into graphite oxide leading to separation by topology

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S1. SUPPLEMENTAL GRAPHS

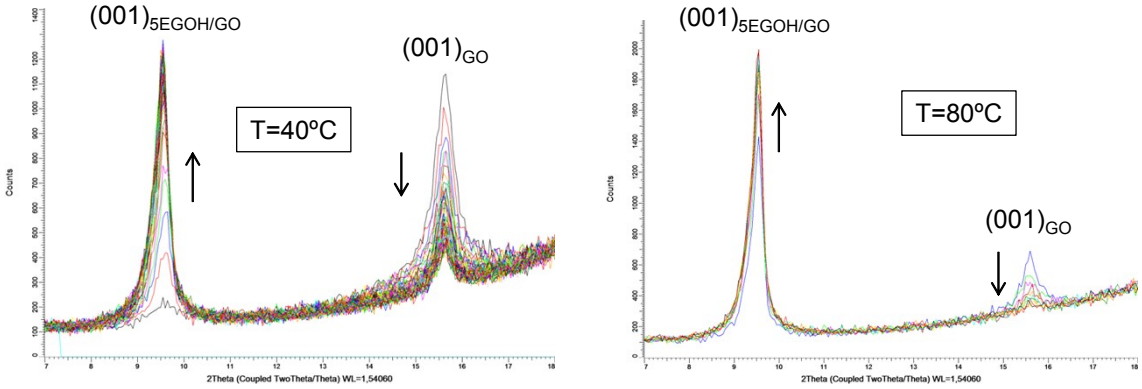

Fig. S1. *In situ* XRD data of GO and an excess of $5EG_{OH}$ showing monolayer intercalation as a function of time at 40 °C and 80°C. The diffractograms were recorded every 3.7 min.

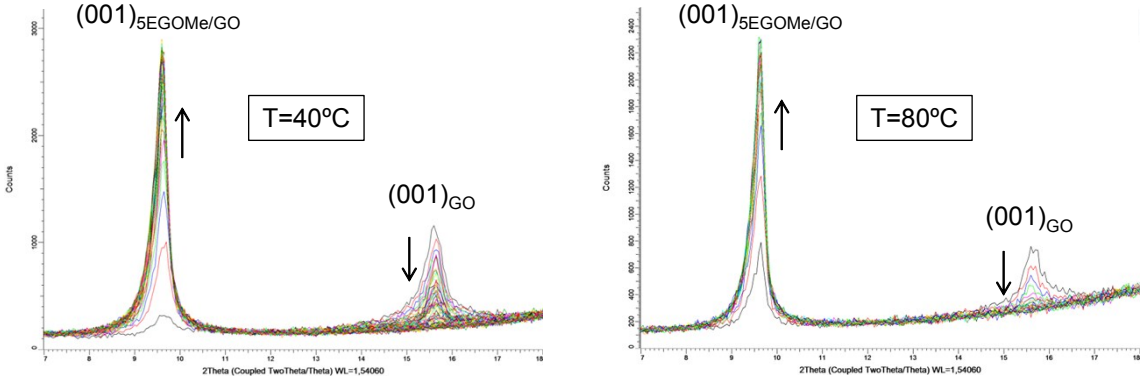

Fig. S2. *In situ* XRD data of GO and an excess of $5EG_{OMe}$ showing monolayer intercalation as a function of time at 40 °C and 80°C. The diffractograms were recorded every 3.7 min.

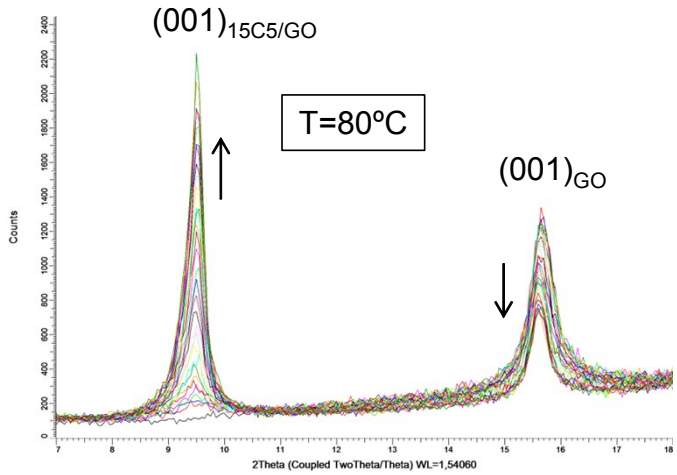

Fig. S3. *In situ* XRD data of GO and an excess of 15C5 showing monolayer intercalation as a function of time at 80 °C. The diffractograms were recorded every 30 min.

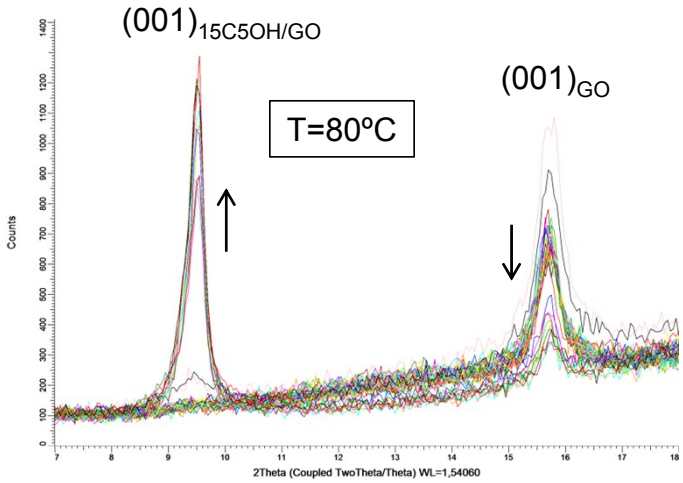

Fig. S4. XRD data of GO and an excess of $15C5_{OH}$ showing monolayer intercalation as a function of time. Total time = 19 days. Intercalation was carried out in an oven at 80 °C.

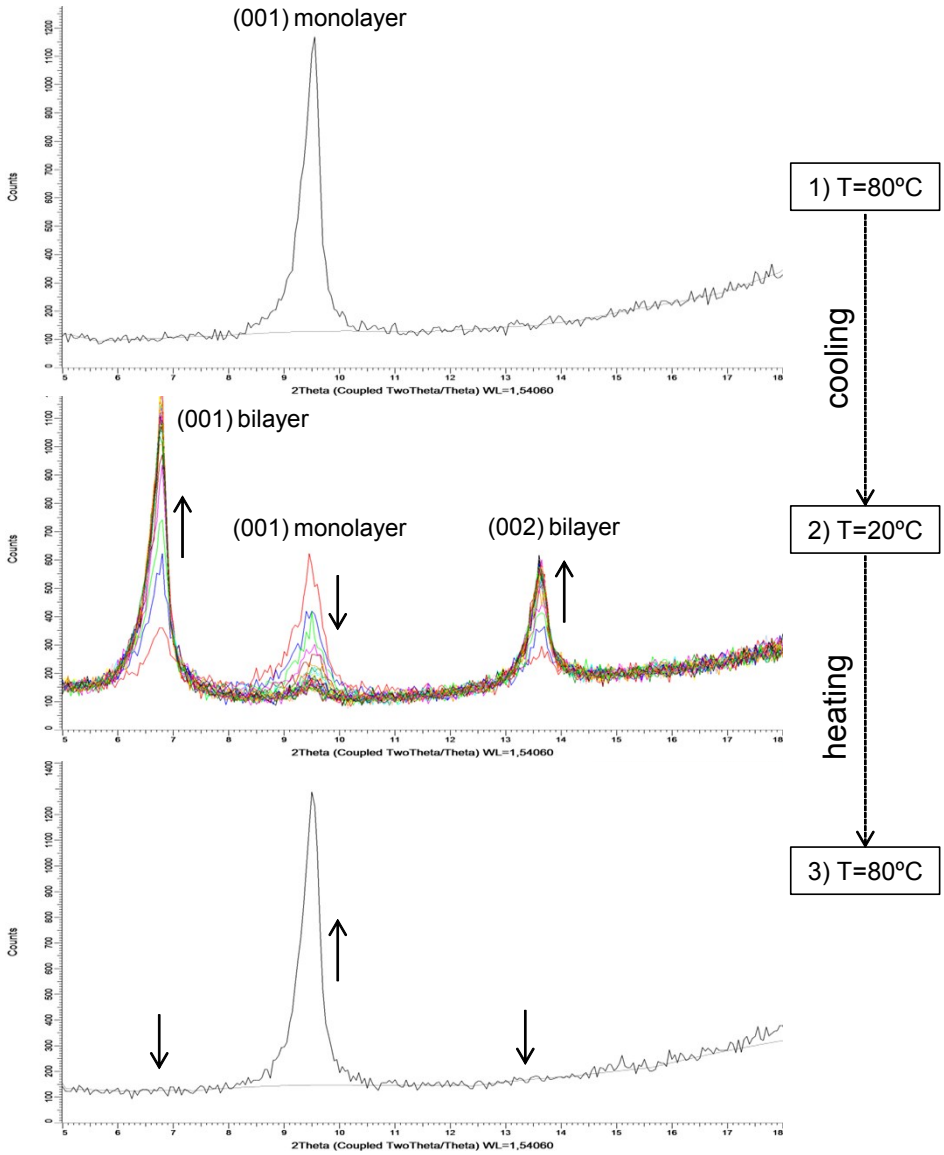

Fig. S5. XRD data showing the monolayer/bilayer reversibility for $5EG_{OH}$ intercalated in GO by cooling and heating. Upon fast cooling to 20 ºC, the formation of the bilayer and the total disappearance of the monolayer occur in about 1.5 h. Upon fast heating to 80 ºC, the formation of the monolayer and the total disappearance of the bilayer are practically instantaneous.

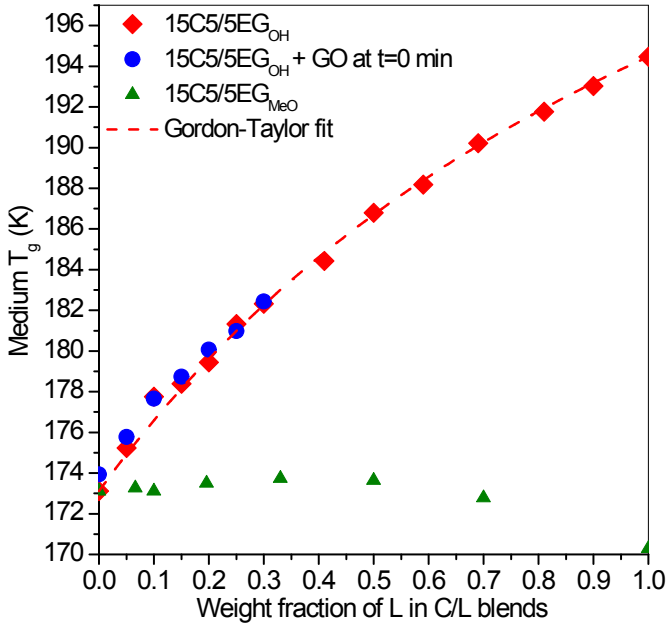

Fig. S6. Variation of T_g with the weight fraction of linear chains (L) in blends of cyclic/linear chains (C/L). Dashed line shows the Gordon-Taylor fit using the Eq. S2.

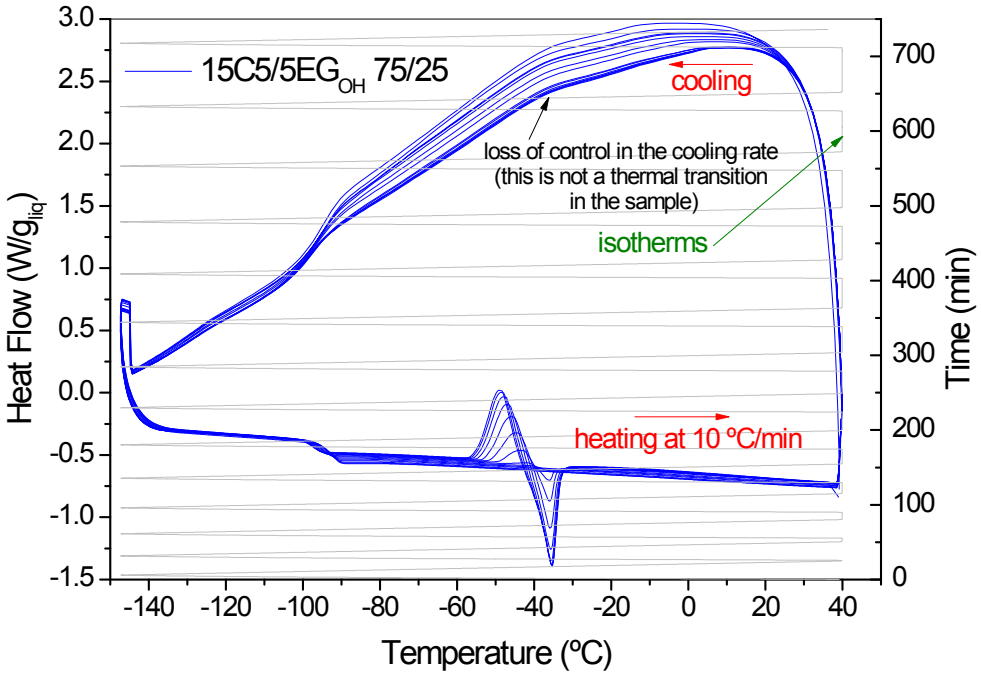

Fig. S7. (Left axis) Whole DSC thermogram for the *in situ* intercalation of a blend (75/25 wt% 15C5/5EG$_{OH}$) in GO by using a GO/5EG$_{OH}$ ratio of 80/20 wt% at heating rates of 10 ºC/min and nominal cooling rates of 50 ºC/min (since the equipment cannot follow this cooling rate in the whole temperature range, a change in the heat flow at about -30 ºC is observed). (Right axis) Time-temperature lines following the cooling, heating and isothermal runs.

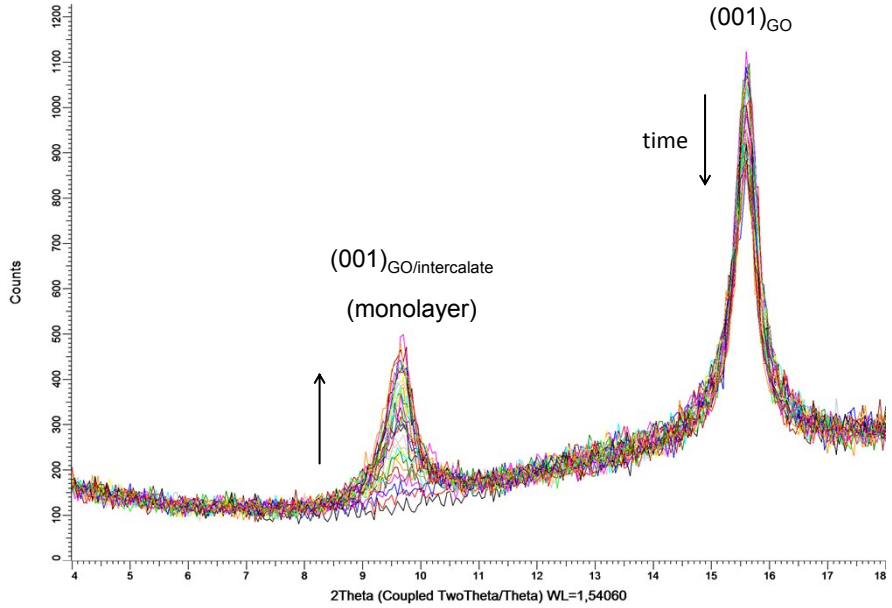

Fig. S8. XRD data of a mixture of GO and 90:10 wt% 15C5:5EG$_{OH}$ showing monolayer intercalation as a function of time at 40°C. Total intercalation time = 140 min.

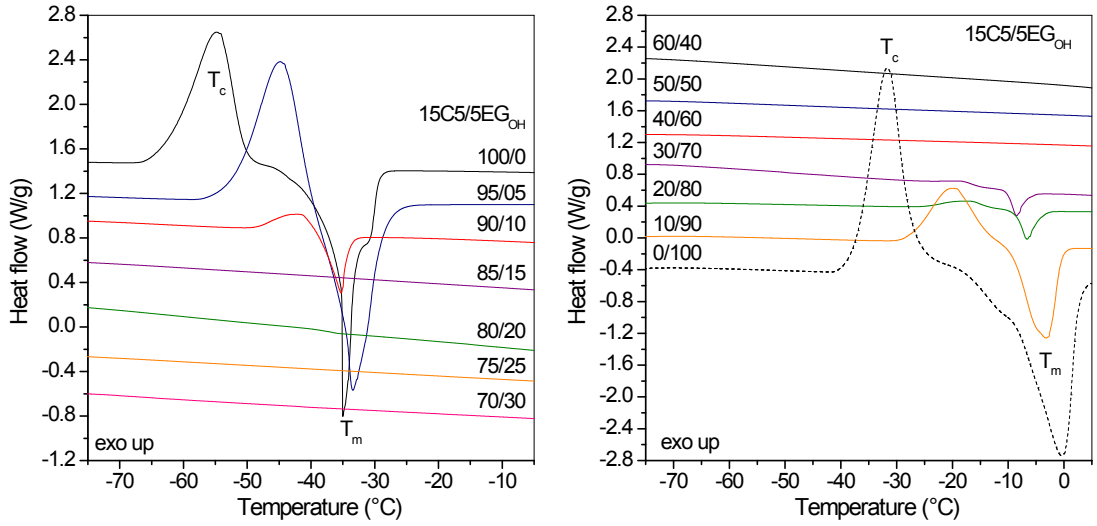

Fig. S9. Cold crystallization and melting of 15C5/5EG$_{OH}$ blends of different composition (wt%).

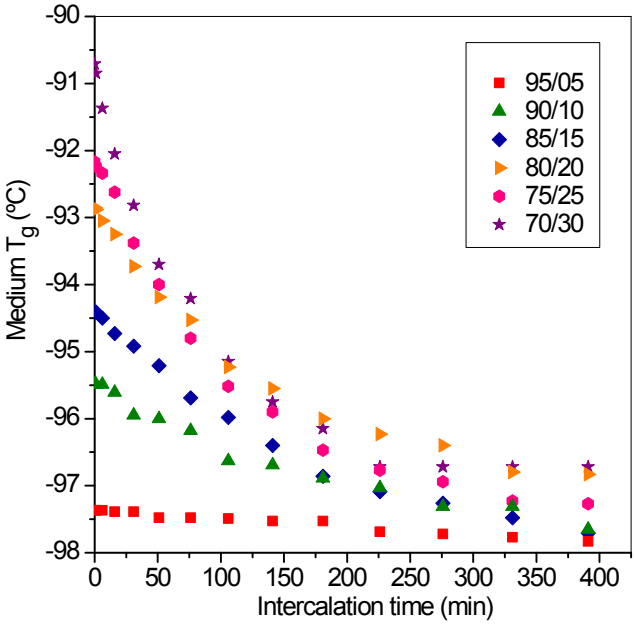

Fig. S10. Variation of T_g as a function of intercalation time in DSC experiments for *in situ* intercalation of blends of 15C5 and $5EG_{OH}$ at 40 °C (composition indicated in 15C5/$5EG_{OH}$ wt%).

S2. EVALUATION OF DATA

S2.1 Extent of reaction

The extent of intercalation at any time (t) is defined as follows: [1]

$$\alpha(t) = I_{001}(t)/I_{001}(t_\infty) \qquad \text{Eq S1}$$

where $I_{001}(t)$ represents the integrated intensity of the 001 reflection at time t, and $I_{001}(t_\infty)$ is the integrated intensity when the intercalation is complete. $I_{001}(t_\infty)$ was determined from the y intercept obtained by linearly fitting the $I_{001}(t)$ of intercalate *vs* the $I_{001}(t)$ of GO.

S2.2 Composition of non-intercalated liquid

In blends of 15C5 and $5EG_{OH}$, the large T_g variation allowed us to establish a method to quantify the composition of non-intercalated liquid in GO (red diamonds of Figure S6). This method could not be established for the 15C5/$5EG_{OMe}$ blends due to the insignificant variation of T_g at low amounts of the linear component (green triangles of Figure S6). The higher T_g observed for $5EG_{OH}$ respect to that for 15C5 can be attributed to hydrogen-bond interactions in the hydroxyl-terminated linear compound. This effect is not present in the methoxyl-terminated linear compound, $5EG_{OMe}$, resulting in a T_g slightly lower than that of 15C5, in agreement with theoretical and experimental expectations.[2, 3]

To calculate the composition of non-intercalated liquid in GO, we used the concentration dependence of T_g of Figure S6 as a calibration curve. The variation of the T_g data for 15C5/5EG$_{OH}$ showed a composition dependence that is well-described by the Gordon−Taylor equation.[4]

$$T_g = \frac{f_1 T_{g,1} + K_{GT}(1 - f_1) T_{g,2}}{f_1 + K_{GT}(1 - f_1)} \qquad \text{Eq S2}$$

T_g is the glass transition temperature of the blend at the $f_1$composition, $f_1$is the fraction of 5EG$_{OH}$ in the blend, $f_1 = 1 - f_2$, f_2 is the fraction of 15C5 in the blend, $T_{g,1} = 194.46\ K$, $T_{g,2} = 173.11\ K$ and $K_{GT} = 0.576$, as obtained from the fitting (R^2 =0.999). The parameter K_{GT} shows unequal contributions of both components to the blend; observed as different heat capacity steps (ΔC_p) at the glass transition: ΔC_p (15C5)= 0.86 J/gK and ΔC_p (5EG$_{OH}$) = 1.50 J/gK.

The composition of f_1 in the non-intercalated liquid was determined by isolating f_1 from Eq S2:

$$f_1 = \frac{K_{GT}(T_{g,2} - T_g)}{K_{GT}(T_{g,2} - T_g) + (T_g - T_{g,1})} \qquad \text{Eq S3}$$

In this case, T_g is the glass transition of non-intercalated liquid during intercalation.

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(3) Tezuka, Y., *Topological Polymer Chemistry. Progress of Cyclic Polymers in Syntheses, Properties and Functions*. Word Scientific Publishing Co. Pte. Ltd.: 2013.

(4) Gordon, M.; Taylor, J. S. Ideal copolymers and the second-order transitions of synthetic rubbers. i. non-crystalline copolymers. *J. Appl. Chem.* **1952,** *2*, 493-500