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 5EGOH 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 5EGOME 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\textsubscript{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 5EGOH 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% 15C5:5EGOH showing monolayer intercalation as a function of time at 40°C. Total intercalation time = 140 min.

Fig. S9. Cold crystallization and melting of 15C5/5EGOH blends of different composition (wt%).
S2. EVALUATION OF DATA

S2.1 Extent of reaction

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

\[
\alpha(t) = \frac{I_{001}(t)}{I_{001}(t_\infty)}
\]

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 \( \text{vs} \) the \( I_{001}(t) \) of GO.

S2.2 Composition of non-intercalated liquid

In blends of 15C5 and 5EGOH, 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 15C5/5EGOMe 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 5EGOH 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, 5EGOMe, 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.\textsuperscript{4}

$$T_g = \frac{f_1 T_{g1} + K_{GT} (1 - f_1) T_{g2}}{f_1 + K_{GT} (1 - f_1)}$$

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, $T_{g1} = 194.46 \, \text{K}$, $T_{g2} = 173.11 \, \text{K}$ 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 ($\Delta C_p$) at the glass transition: $\Delta C_p (15C5) = 0.86 \, \text{J/gK}$ and $\Delta C_p (5EG_{OH}) = 1.50 \, \text{J/gK}$.

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

$$f_1 = \frac{K_{GT} (T_{g2} - T_g)}{K_{GT} (T_{g2} - T_g) + (T_g - T_{g1})}$$

Eq S3

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

REFERENCES


