Supporting information

Facile and low environmental impact approach to prepare thermally conductive nanocomposites based on polylactide and graphite nanoplatelets

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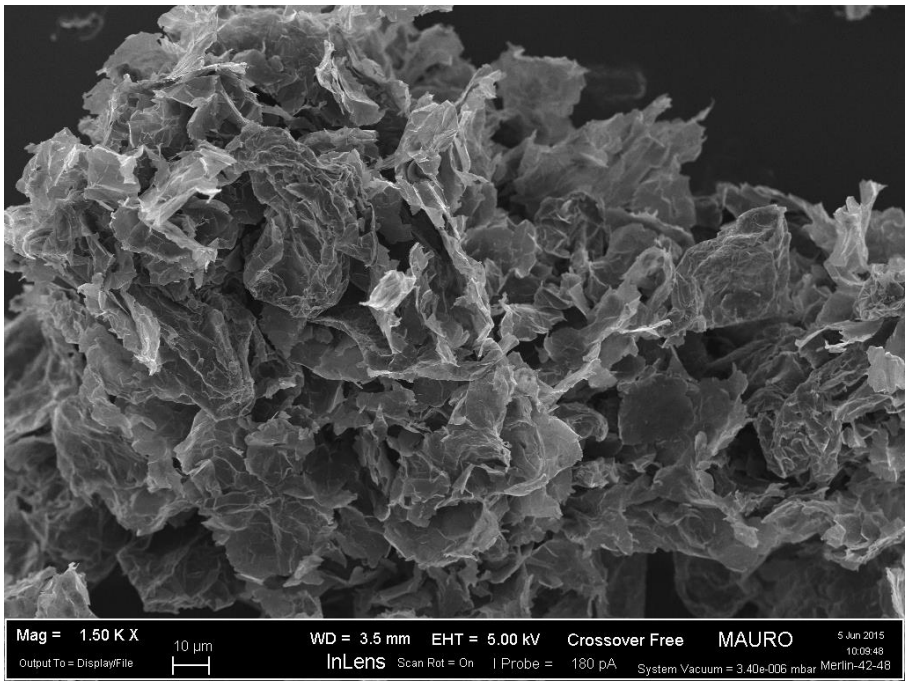

Figure S1. FE-SEM of graphite nanoplatelets G2Nan grade from Nanesa (I).

Pyr-D synthesis. In detail, about 10 g of D-la (previously recrystallized and dried) were charged under argon flow into the reactor (*i.e.*, a 50-mL two-neck round-bottom flask equipped with a magnetic stirrer) containing a predetermined amount of accurately weighed and in-situ dried Pyr-OH. The feeding ratio of the D-la monomer to the initiator was adjusted to obtain different molecular masses. After the introduction of D-la the flask was evacuated for 15 min and purged with argon, and the exhausting/refilling process repeated thrice in order to fully dry the reaction environment. The reaction vessel was then immersed into a thermostatically controlled oil bath set at 120 °C, under vigorous stirring: as soon as the mixture was completely molten and homogenized, about 0.15 mL of a freshly prepared solution of $Sn(Oct)_2$ in toluene ([D-la]/[$Sn(Oct)_2$] = 10^3) were added under argon through a micro-pipette, and the reaction allowed to proceed for 24 hours under inert atmosphere.

The crude product was then cooled down, dissolved in toluene and poured into an excess of cold methanol: after filtering and drying in vacuum at 40 °C to constant weight, the as-purified oligomer was obtained as a fine, yellowish powder.

Scanning Probe Microscopy methods. The VITA-HE-NANOTA-200 contact mode Si probes were adopted which feature a resonant frequency of about 55-80 kHz, a spring constant of 0.5-3 N/m and a tip radius < 30 nm. Moreover, in these probes there is a resistive heater integrated at the end of the cantilever, which can be repeatedly and reliably heated up to 350 °C. Thus, after having recorded standard contact-mode topography images, the probe can be placed in correspondence of the regions of interest (domains, features, phases etc.), for performing localized NanoTA. In a NanoTA measurement, the chosen location is heated by the probe and temperature-dependent properties, such as softening and melting, are investigated by recording the cantilever deflection vs temperature curves. The probes are calibrated by using three standards with known melting points,

i.e. PCL (Tm=55°C), PE (Tm=116°C) and PET (Tm=235°C): when these samples are heated, the deflection increases due to the thermal expansion until it suddenly drops at the input power that corresponds to that specific melting temperature. The softening temperatures were calculated by fitting linearly the closest interval before and after the sudden variation of the deflection slope.

FMM measurements were carried out using FESPA-V2 probes that feature a nominal resonant frequency of 75 kHz and a spring constant of 2.8 N/m. In FMM, the probe oscillates in contact with the sample and the mechanical properties of the material under study can be investigated and compared by detecting both force amplitude and phase. The oscillation frequency was optimized in order to maximize the contrast in the amplitude and phase signals. The topography and lateral signals were also simultaneously recorded.

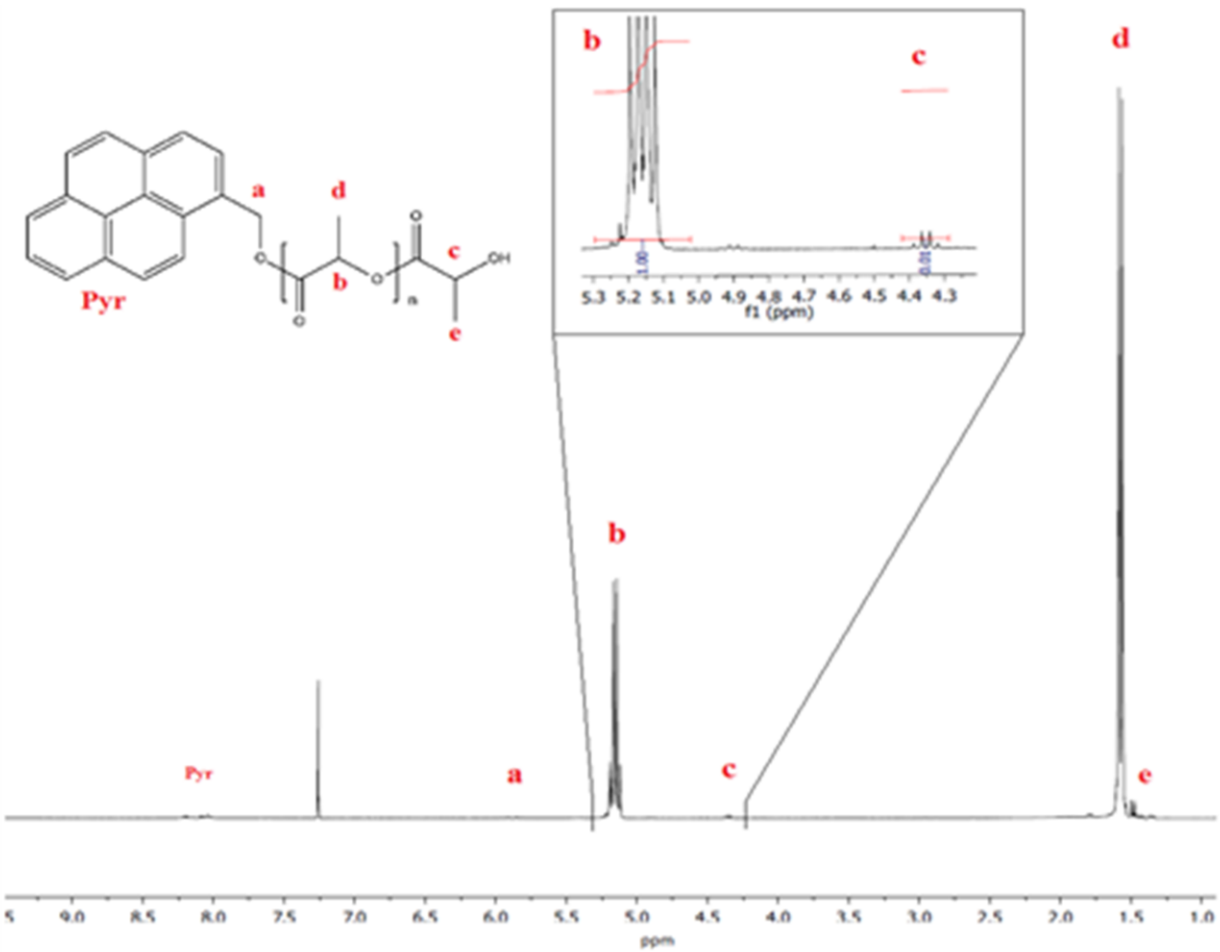

Figure S2. ^{1}H-NMR of Pyr-D_8000.

Sample	DP_{NMR}[a]	M_{nNMR}[b] [g/mol]
Pyr-D_2500	17	2500
Pyr-D_8000	54	7800

[a]Average degree of polymerization of D-la evaluated from ^{1}H-NMR spectroscopy [by comparing the peak integral of the methine protons in the chain (at δ 5.16 ppm) with that of the methine protons at the chain end (at δ 4.35 ppm), according to the equation: $DP_{NMR} = 1/2 \cdot (I_{5.16} + I_{4.35})/I_{4.35}$]. [b] Numeric average molecular weight of Pyr-D calculated as: $Mn_{NMR} = DP_{NMR} \cdot 144.13 + MPyr\text{-}OH$, where 144.13 is the molecular mass of D-la.

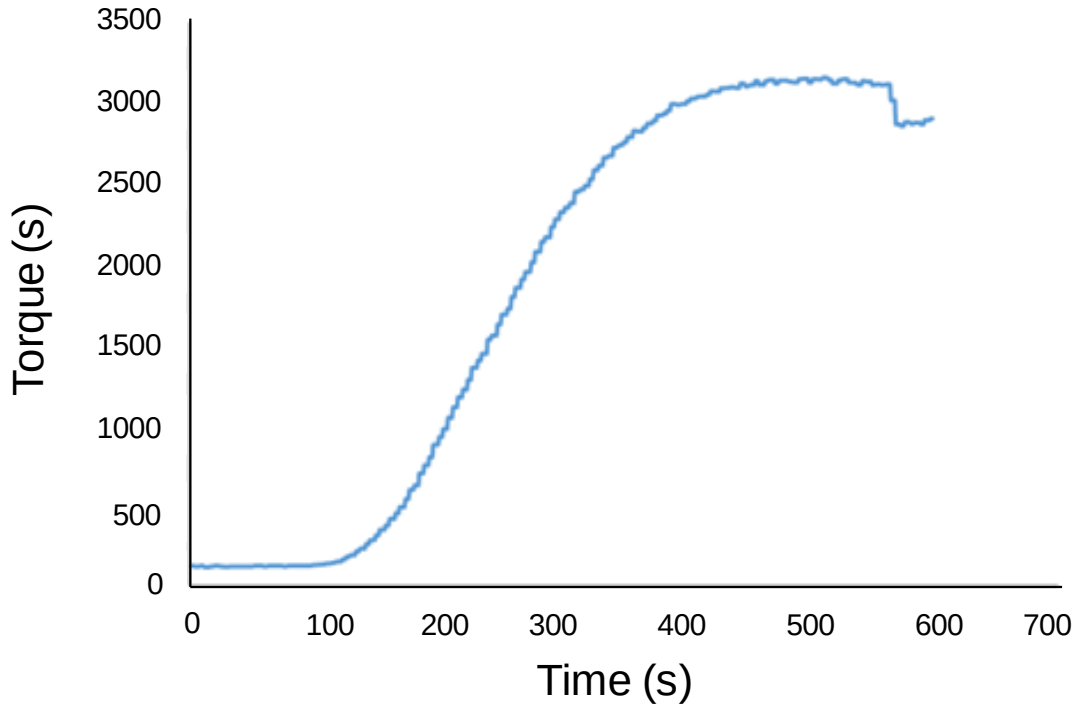

Figure S3 . Torque as a function of time for the sample PLLA_DOD_R.

Table S1. Characteristics of the prepared samples

Sample code	Reator type	M_n [g·mol^{-1}]	M_w [g·mol^{-1}]	MWD
PLLA_DOD_B	batch	50600	77200	1.5
PLLA_DOD_R	REX	30800	44050	1.3

Table S2. Crystallinity of the prepared samples

Sample code	Xm [%]	Xm_s [%]	$X_{m,total}$ [%]
PLLA_DOD_R	61	-	61
PLLA_DOD_R_G	62	-	62
PLLA_Pyr_2500_R	51	2	53
PLLA_Pyr_2500_R_G	49	7	56
PLLA_Pyr_8000_R	43	11	54
PLLA_Pyr_8000_R_G	50	8	58

The subscript m_s indicates the value measured for the stereocomplexed fractio

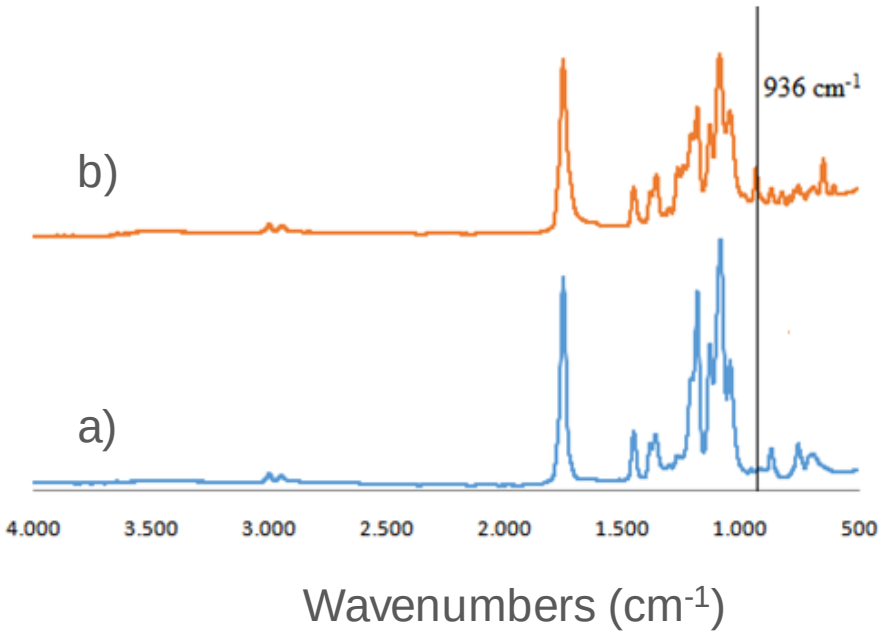

Figure S4. FTIR spectra of: a) PLLA_DOD_R and b) PLLA_DOD_B.

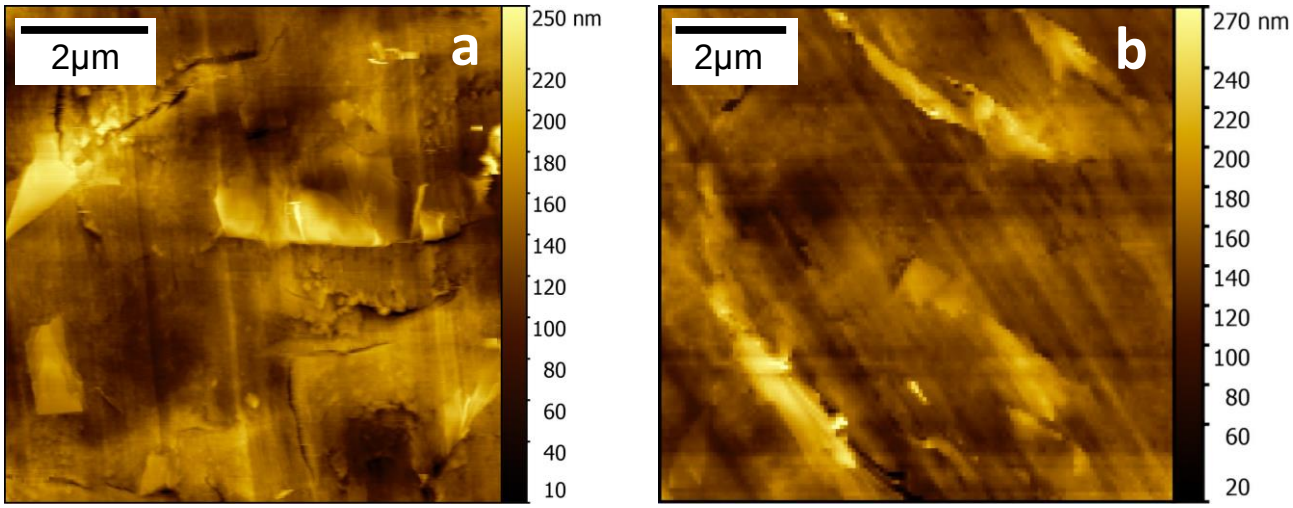

Figure S5. Representative topography images for dispersed GNP flakes within the polymer: a) PLLA_DOD_R_G and b) PLLA_Pyr_8000_R_G. in both cases, GNP flakes arising above the polymer surface, as a consequence of ultracryotomy, are clearly visible

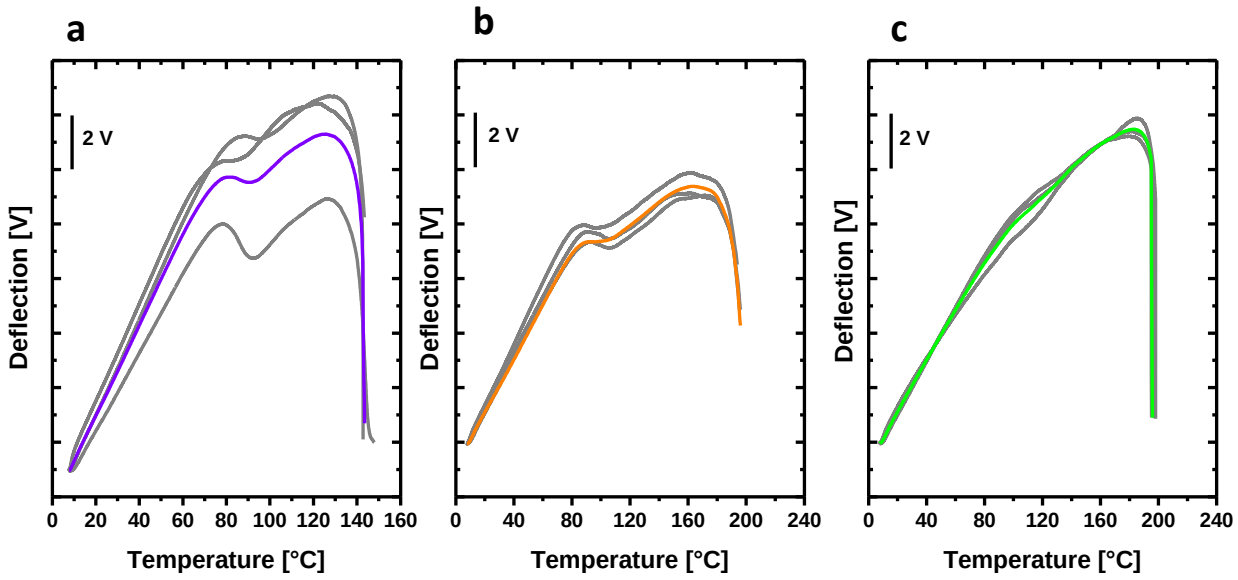

Figure S6. Nano-TA deflection vs temperature plots for PLLA (a), a mixture of PDLA and PLLA (1:2 ratio) forming 50% stereocomplex (b) and a mixture of PDLA and PLLA (1:1 ratio) forming 100% stereocomplex.

Typical NanoTA plots for PLA (Figure 5S) show increasing vertical deflection caused by thermal expansion of the sample until the temperature at which cold crystallization of PLA occurs above 80°C, leading to a reduction of vertical deflection of the cantilever. Once cold crystallization is completed, at temperature above 100°C, vertical deflection increases again as a consequence of further thermal expansion, until melting of the crystalline phase, corresponding to the penetration of the probe and related drop in the deflection curve, observed at 141±1°C. These two features in the deflection vs temperature curve result in a typical M-shaped plot, in agreement with a previous report. In the presence of PLA stereocomplexation, the shape of the plot is modified proportionally

to the amount of stereocomplexation. In a mixture of PDLA and PLLA (1:2 ratio) forming 50% stereocomplex, the local minima in the deflection related to cold crystallization is significantly reduced while the temperature for the probe penetration is increased to 190±2°C. For fully stereo-complexed 1:1 PDLA and PLLA mixture, only traces of the low temperature feature assigned to cold crystallizazion are observed, while the average penetration temperature is observed at 192±4°C.