SUPPLEMENTARY INFORMATION

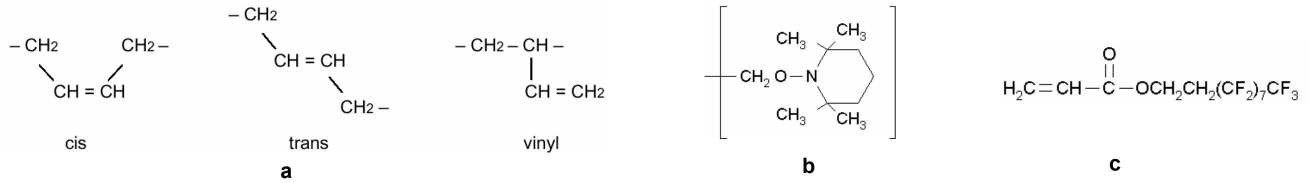

Figure S1 **Chemical formula.** (a) the cis, trans and vinyl monomeric units in the precursor polybutadiene polymer from left to right; (b) the TEMPO-nitroxide capping agent and (c) the AC8 monomer.

DSC & SAXS characterizations of the composites.

Apart from the transmission electron microscopy (TEM) and differential calorimetric (DSC) experiments presented in the methods of the main body of the article, the structures formed in the reacted films were also characterized using small- and wide-angle X-ray scattering (WAXS and SAXS, respectively). Two different set-ups were used with the same rotating anode generator (RU-200, Rigaku Co. Ltd.) using Cu KR radiation. Small-angle X-ray diffraction patterns were recorded on a linear position sensitive detector (LPS 50 INEL) and wide-angle X-ray diffraction patterns on a curve position sensitive detector (CPS 120 INEL).

The strength of the phase separation between LCP and PBd, as expected, is remarkable: from TEM, the LCP/PBd interface seems very sharp, a feature that can be easily verified using DSC and SAXS. Indeed, DSC traces (see Supplementary Figure 2) usually present a glass transition at –92°C associated with PBd, while a fusion peak at +78°C, associated with the smectic B-to-isotropic transition characteristic of LCP, is observed. In the same way, the intensity scattered at small wave-vector *q* in a SAXS experiment (see Supplementary Figure 3) shows the q^{-4}-dependence of the so-called Porod regime associated with the existence of a sharp LCP/PBd interface in the composites. Both results, not displayed here for obvious redundance with TEM, are completely consistent with our conclusions: neither the glass transition temperature of the PBd matrix, nor the fusion temperature of the LCP domains are affected by the grafting and the microphase separation, as they have the values they would as separate homopolymers. However, one may question the impact of phase separation on the crystallinity of the LCP inclusions. In the literature,[3,4,5] the structural organization of a LC homopolymer (hLCP) is described as a smectic B liquid crystal of period 33.3 Å exactly twice the size of one extended monomer, and a lattice parameter of 5.7 Å corresponding to the distance between two adjacent fluorinated pendant groups. WAXS patterns obtained on the composites show correlation peaks whose positions relative to $q^*=0.191$ Å^{-1} verify 1:2:3, are characteristic of a smectic order. The measured period $d=2\pi/q^*=32.8$ Å is close to the value 33.3 Å in hLCP. The Bragg peak at 2.54 Å^{-1} corresponds to the hexagonal lattice parameter of 5.7 Å, in agreement with literature. All peaks are superimposed on two amorphous halos known in the melt state of hLCP. In hLCP, only approximately 30% of the material crystallizes as a smectic B, the rest of hLCP remaining amorphous. It appears to be the same in our composites: decomposing crystalline and amorphous peaks in the WAXS spectra, we computed a degree of crystallinity T_C of LCP domains of approximately 30% for all grafted specimens. Therefore, the microphase separation of LCP domains inside a crosslinked PBd matrix, has little impact on the fraction of crystallinity in the LCP domains.

Reactivity of a composite to an external stimulus : Response to a temperature jump.

We investigate how fast a given composite (f_{LCP}=0.581) reacts to a temperature jump. Dynamic deformation were carried out as a function of temperature, at a 1Hz-frequency and 1%-deformation as usual. As an example, Supplementary Figure 4 shows the storage G' and loss G" moduli of composite f_{LCP}=0.581, as well as the chamber temperature T plotted as a function of time, during a sudden temperature jump inside the rheometric chamber: (a) a decrease from 90 to 30°C; (b) an increase from 40 to 90°C. Upon a temperature decrease, G' and G" increase, while they decrease upon a temperature increase. Supplementary Figure 5 shows the corresponding derivatives of the storage modulus G' (taken as an example) and of the chamber temperature T with respect to time t. Whether upon an increase or upon a decrease of the chamber temperature, the evolution of G' and G" seems to follow immediately that of the temperature. The derivatives show even more clearly that the rate of change in temperature $\partial T/\partial t$ exactly corresponds the rate of change in storage modulus $\partial G'/\partial t$. One is in fact simply limited by the rate of temperature increase or decrease of the ARES apparatus itself, obviously much larger than the "reaction time" of the composite material, that is, the delay which one would expect between *the stimulus* (temperature change) and *the response* (the modulus change). Although this delay is difficult to assess experimentally, this simple experiment suggests that it is on the order of a second or less, upon an increase or a decrease of temperature.

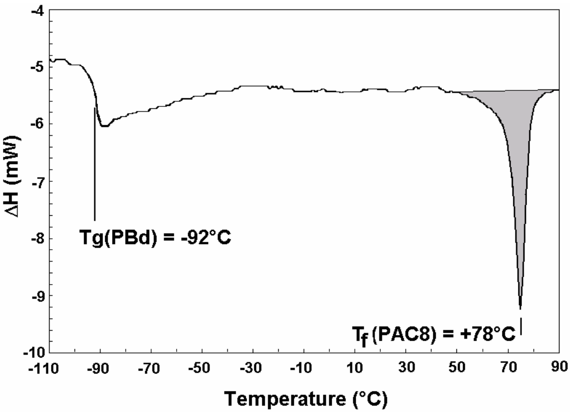

Figure S2 **Typical differential scanning calorimetric signature of a composite.** The DSC carried out on a PAC8-grafted poly(butadiene), showing the glass transition temperature of PBd at –92°C, and the fusion peak of PAC8 at +78°C.

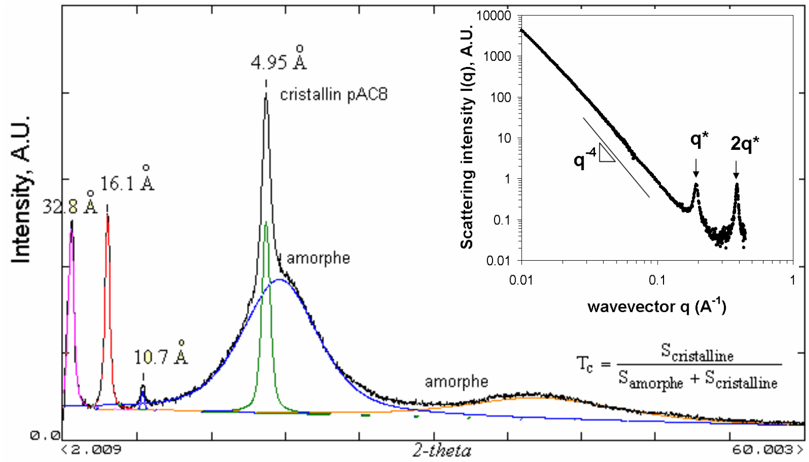

Figure S3 **Typical WAXS & SAXS signatures of a composite.** WAXS intensity I(q) in arbitrary units, as a function of scattering angle 2θ, from a PAC8-grafted poly(butadiene). The formula indicates how the degree of crystallinity has been calculated, taking into account the several cristalline peaks, and the two amorphous peaks known in the melt of a LC homopolymer. Inset : SAXS scattered intensity I(q) in arbitrary units, as a function of wavevector q, for the same specimen. The two first structure peaks are observed. The line is a q^{-4}-dependance characteristic of a Porod's regime.

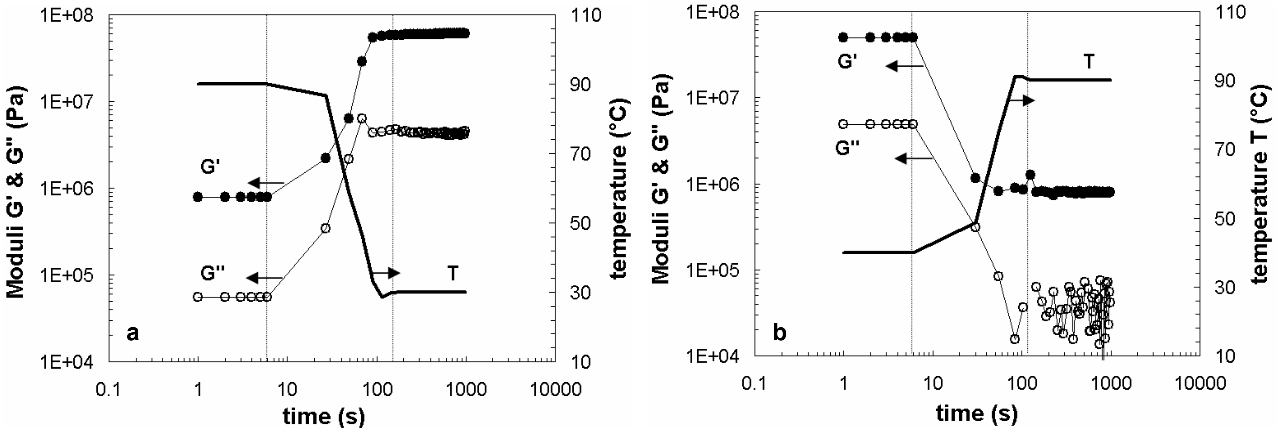

Figure S4 **Mechanical response of a composite to a sudden temperature change.** Storage G' (●) and loss G" (○) moduli of composite f_{LCP}=0.581, as well as the temperature are plotted as a function of time, during a sudden temperature jump inside the rheometric chamber: (a) a decrease from 90 to 30°C; (b) an increase from 40 to 90°C. In both figures, the vertical dotted line define the time range required for the temperature to go from the starting to the ending consign.

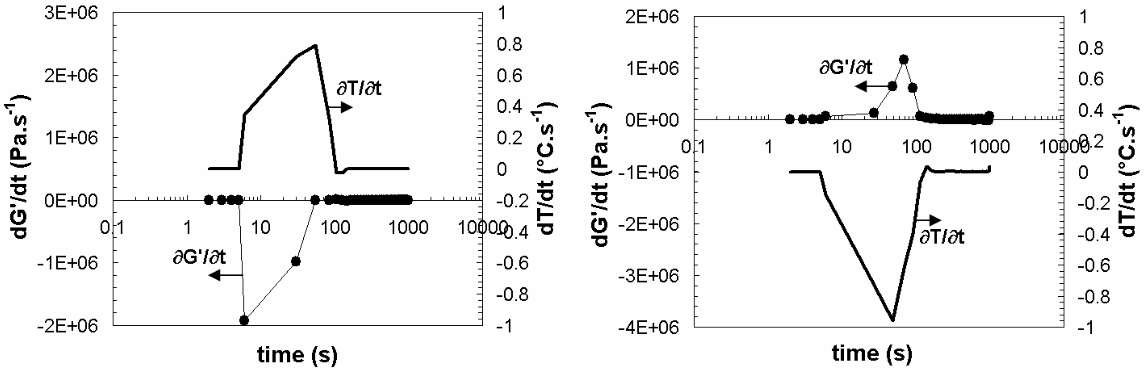

Figure S5 **Mechanical response of a composite to a sudden temperature change.** Derivative of the storage G’ (●) and loss G” (○) moduli of composite f_{LCP}=0.581, as well as the derivative of temperature with respect to time, plotted as a function of time: (a) a decrease from 90 to 30°C; (b) an increase from 40 to 90°C.

References

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