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Stereodynamic control of star-epoxy/anhydride crosslinking actuated by liquid-crystalline phase transitions

Jean-Mathieu Pin*[a], Alice Mija [a], Nicolas Sbirrazzuoli*[a]

[a]Université Côte d'Azur, CNRS, Laboratoire de Physique de la Matière Condensée LPMC – UMR 7336, Parc Valrose, 06100 Nice, France. E-mail: jeanmathieu.pin@gmail.com, Nicolas.SBIRRAZZUOLI@unice.fr

Contents:

I. Materials and general methods

Methods and sample preparation:

The tri-component formulation has been prepared by finely grounding the monomer (TriaEP), the crosslinker (SA) and the initiator (2MI) together followed by a re-crystallization from acetone. The mixture has been dried under vacuum at 50°C for 3H. Then the resulting powder has been immediately used for DSC, rheology, optical microscopy and FT-IR as uncured mix. The polymer has been cured for 1h at 160°C and 1h at 180°C for X-ray and FT-IR experiments.

II. FT-IR apparatus description and polymer characterization

An infrared Perkin Elmer Spectrum BX II spectrophotometer was used in Attenuated Total Reflectance (ATR) mode, with a diamond crystal. The spectrum of air was recorded as background. A total of 120 scans with a resolution of $1cm^{-1}$ have been done for both background and samples.

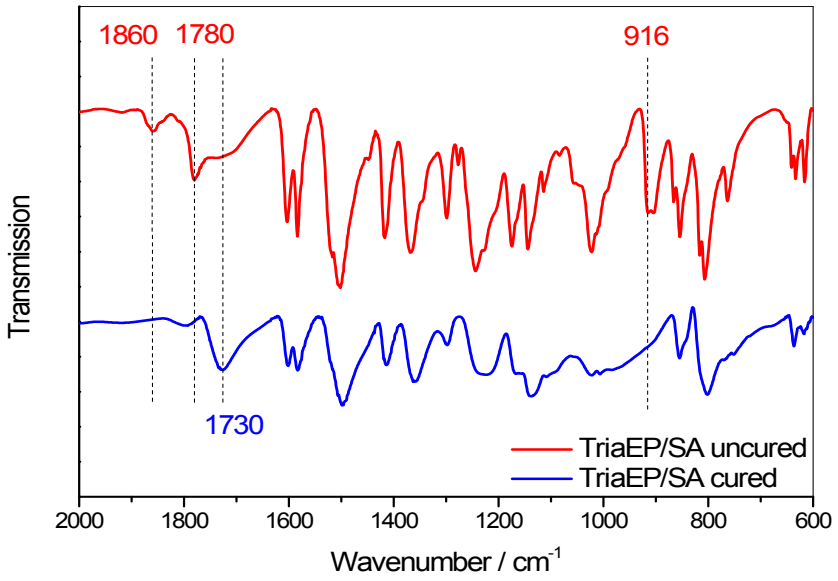

Figure S1. FT-IR on TriaEP/SA uncured mix and TriaEP/SA cured polymer 1h at 160°C and 1h at 180°C

III. Thermokinetic theoretical statement

$A \underset{\leftarrow}{\rightarrow} B \qquad v_1, K_1, \Delta_r G_1^0$

$B \rightarrow C \qquad v_2, k_2, E_2$

$A \rightarrow C \qquad v_{app}, k_{app}, E_{app}$

$$K_1 = \frac{C_B}{C_A} \Leftrightarrow C_B = K_1 C_A$$

$$v_2 = k_2 C_B = k_2 K_1 C_A = \frac{dC_C}{dt}$$

$$v_{app} = k_{app} C_A = \frac{dC_C}{dt}$$

$$k_{app} C_A = k_2 K_1 C_A$$

$$K_1 = \exp\left(-\frac{\Delta_r G^0}{RT}\right) = \exp\left(-\frac{\Delta_r H^0 - T\Delta_r S^0}{RT}\right)$$

$$k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right)$$

$$k_{app} = k_2 K_1 = A_2 \exp\left(-\frac{E_2}{RT}\right)\exp\left(-\frac{\Delta_r G^0}{RT}\right)$$

$$k_{app} = A_{app} \exp\left(-\frac{E_{app}}{RT}\right)$$

$$A_{app} \exp\left(-\frac{E_{app}}{RT}\right) = A_2 \exp\left(-\frac{E_2}{RT} - \frac{\Delta_r G^0}{RT}\right)$$

$$E_{app} = E_2 + \Delta_r G^0$$

This shows that if the absolute value of $\Delta_r G°$ is higher than that of E_2 and its value negative, then E_{app} will be negative.