

# **Supporting Information**

## **Catalyst Control of Nanoscale Characteristic Length of the Glass Transition in Organic Strong Glass-Formers**

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## EXPERIMENTAL SECTION

**Materials.** All the chemical products are commercially available and were used as received without further purification. Diglycidyl ether of bisphenol A (DGEBA, DER 332, M.W.=340.14 g/mol), adipic acid (AA, 99.5%), dodecanedioic acid (DA, 99.0%), 1,5,7-triazabicyclo [4,4,0] dec-5-ene (TBD, 98.0%), triphenylphosphine (PPh<sub>3</sub>, 99.0%), were purchased from Sigma-Aldrich. Chlorobenzene and methanol were obtained from Alfa Aesar.

**Preparation of epoxy-based CANs.** The epoxy-based CANs using different crosslinker and catalyst were prepared following the procedures given in the literatures.<sup>1-2</sup> The weight ratio of DGEBA:crosslinker was adjusted to maintain the stoichiometric ratios between epoxy groups and carboxyl groups. The mixture of DGEBA and crosslinker was heated to 160 °C with stirring. Then, the catalyst was added in the mixture. The precursors were stirred until homogeneous and then, the viscous solution was rapidly poured into a preheated PTFE molds and cured in an oven at 160 °C for 6 hours and then at 180 °C for 2 hours.

**Characterizations.** Differential scanning calorimetry (DSC) experiments were performed on a TA DSC25 equipped with a RCS90 refrigerated cooling system. Samples were heated from room temperature to 150 °C under a nitrogen atmosphere and maintained at this temperature for 3 min to erase thermal history. The samples were then cooled to -30 °C and re-heated to 150 °C. The heating and cooling rates were 10 °C/min. Glass transition temperatures ( $T_g$ ) were recorded during the second heating ramp.

Temperature modulated DSC (TMDSC) were performed on a TA DSC25. Calibration in temperature and energy was carried out using standard values of indium and zinc. The specific heat capacity was measured using sapphire as a reference. The TMDSC experiments were performed with an oscillation amplitude of  $\pm 1^\circ\text{C}$  and a modulation period of 60 s at a heating rate of  $2^\circ\text{C}/\text{min}$ . The sample weights were about 10 mg and all experiments were carried out under  $\text{N}_2$  atmosphere.

Dynamic mechanical analyses (DMA) were performed on a TA Q850 in the sheet tension geometry under multi-frequency-strain mode, with a rectangular tension sheet dimension of 14 mm x 6 mm x 1.5 mm. The heating ramp was applied at a rate of  $3^\circ\text{C}/\text{min}$  from  $-30$  to  $150^\circ\text{C}$  with a frequency of 1 Hz and a strain of 0.1%. The strain sweep tests confirm that the selected strain is in the linear viscosity region.

Stress relaxation analysis (SRA) experiments were performed on a TA Q850 in a strain control with sample dimension of 15 mm x 6 mm x 1.5 mm. The strain sweep tests of all produced samples were carried out at different temperatures to determine the linear viscoelastic region. To ensure a good contact of the sample with the geometries, a preload force of 0.001 N was applied. The samples were first equilibrated at specified temperature for 5 min and then were subjected to a 1% strain. The stress was monitored over time while maintaining the constant strain of 1%. The stress relaxation time  $\tau$  was determined until the stress was relaxed to at least  $1/e$  of its initial value.

Dilatometry experiments were performed using a dynamic mechanical analyzer (TA Q850) in controlled force tension mode by applying stress of 50 kPa and heated from -

20 °C to 250 °C at a heating rate of 2.5 °C/min. The sample dimension was 30 mm × 6mm × 1.3 mm.

Tensile tests were performed on an Instron 3345 tensile machine according to the ISO 527-1 standard at room temperature. The strain rate was 2 mm/min with a sample dimension of 25 mm × 4 mm × 1.5 mm. Each result represents an average of at least 5 specimens.

The crosslinking density, or the average molecular weight between cross-links ( $M_c$ ) was calculated by the following equation using storage modulus of rubbery plateau.<sup>3</sup>

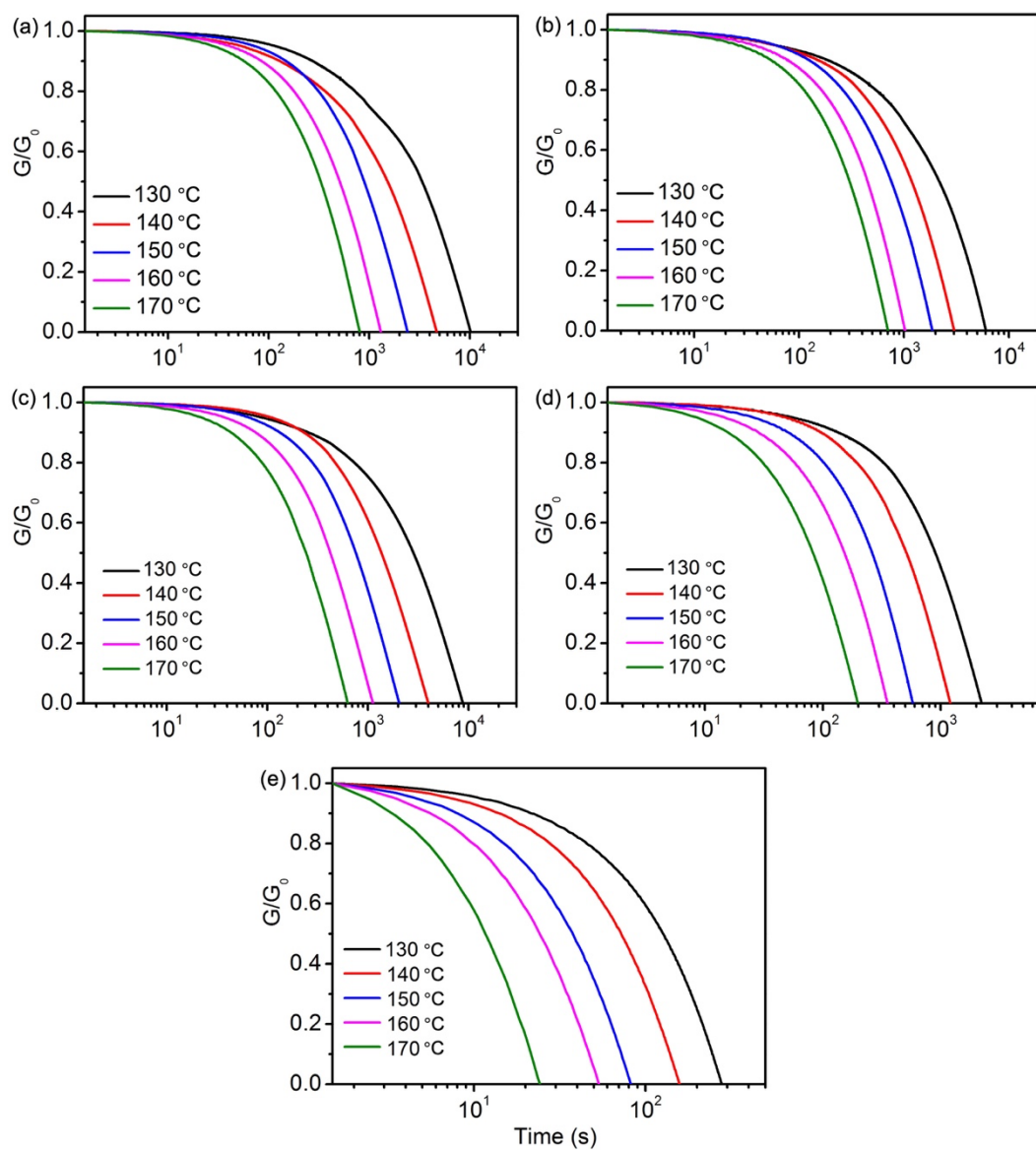
$$M_c = 2(1 + \nu)\rho RT / E'$$

$\nu$  : Poisson's ratio (for epoxy resin=0.33),

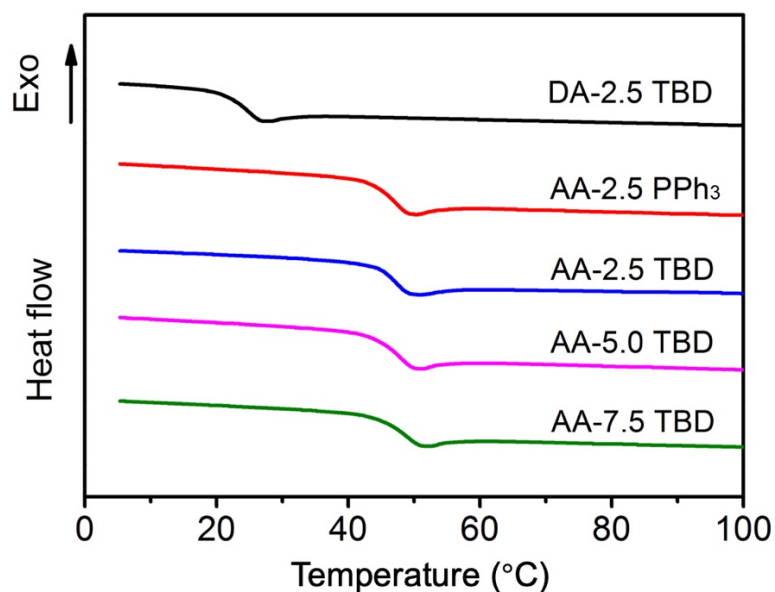
$\rho$  : density (epoxy resin: 1.56 g/cm<sup>3</sup>),

$R$  : universal gas constant,

$E'$  : storage modulus of rubbery plateau.



**Figure S1.** Normalized stress relaxation curves of epoxy-based CANs. (a) DA-2.5 TBD, (b) AA-2.5 PPh<sub>3</sub>, (c) AA-2.5 TBD, (d) AA-5.0 TBD, and (e) AA-7.5 TBD.



**Figure S2.** DSC curves of the epoxy-based CANs.

## References

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- (2) Zhao, B.; Yuan, Q.; Yang, H.; Russell, T. P.; Wang, D. Interfacial Reaction Induced Disruption and Dissolution of Dynamic Polymer Networks. *Macromol. Rapid Commun.* **2021**, *42*, 2100023.
- (3) Gutierrez-Lemini, D. Engineering Viscoelasticity, Springer: Boston, 2014.