

Electronic Supplementary Information

Durable liquid-crystalline vitrimer actuators

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1. Synthesis of the vitrimer-based LCE

1.1. Materials

Triazobicyclodecene (TBD, Sigma-aldrich) and sebacic acid (Aladdin) were used directly without further purification. 4,4'-dihydroxy-a-methylstilbene (DHMS) and diglycidyl ether of 4,4'-dihydroxy-a-methylstilbene (DGE-DHMS) were synthesized according to *Mol. Cryst. Liq. Cryst.* **1995**, 266, 9.

From the ^1H NMR spectra (Fig. S1 and Fig. S2), the specific signals of the two compounds could be clearly identified, suggesting the successful preparation of the desired monomers.

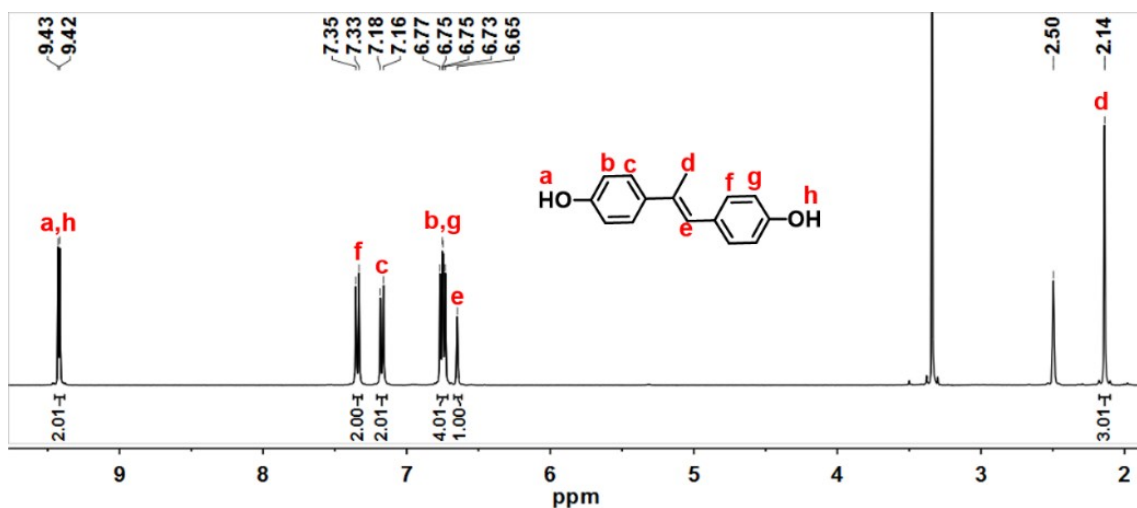


Fig. S1 The ^1H NMR spectrum of 4,4'-dihydroxy-a-methylstilbene (DHMS).

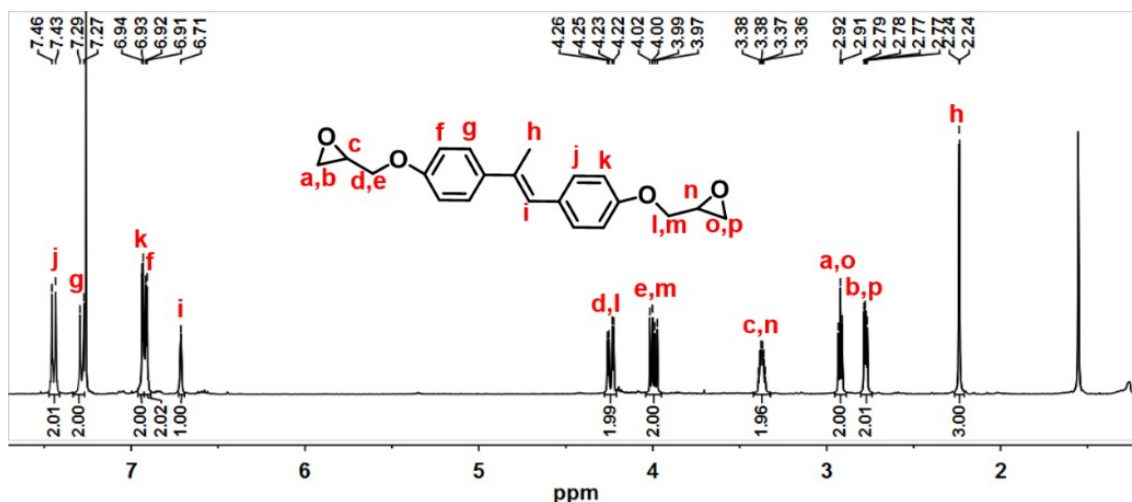


Fig. S2 The ¹H NMR spectrum of diglycidyl ether of 4,4'-dihydroxy- α -methylstibene (DGE-DHMS).

1.2. Preparation of the vitrimer-based LCEs

Stoichiometric amount of DGE-DHMS and sebacic acid were added into a Teflon mold. Then the mixture was heated to 160°C to be melted with manually stirring for 5 minutes. TBD (0.25 mol% to -COOH groups) was introduced and stirred manually until the system was too viscous to flow. Then the mixture was transferred into a mold and cured at 180°C for 6 h under a pressure of 5 MPa. The vitrimer-based LCEs with other catalyst contents were prepared by the similar process.

2. Characterizations of the vitrimer-based LCEs

The thermal transition temperatures of the sample with a catalyst content of 0.25 mol% was measured on a differential scanning calorimetry (DSC, TA Q2000) instrument. The measure procedure consists of two scanning cycles, where both the heating and cooling rate were 10°C min⁻¹ and the first scanning was in order to eliminate the thermal history of the sample. As is shown in Fig. S3, the glass transition temperature T_g and isotropic transition temperature T_i are about 29°C and 63°C upon heating, respectively.

The thermal stability of the sample with a catalyst content of 0.25 mol% was measured on a thermo gravimetric analyzer (TGA, *TA Q50*) under air and nitrogen atmosphere. (Fig. S4)

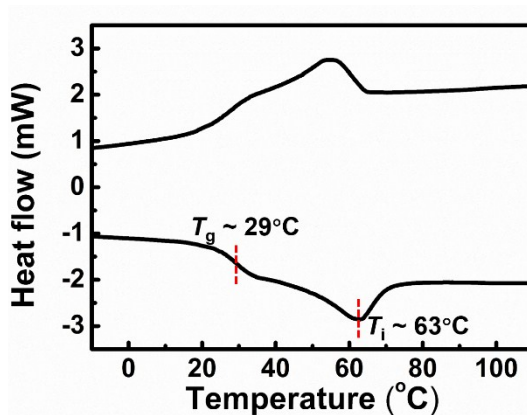


Fig. S3 DCS curve of the sample with a catalyst content of 0.25 mol%.

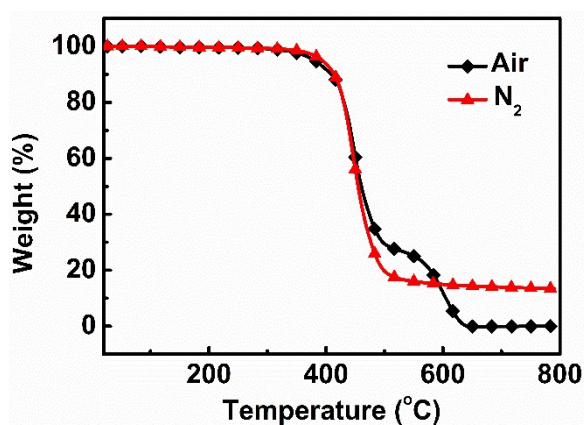


Fig. S4 TGA curves of the sample with a catalyst content of 0.25 mol%. Onset of decomposition (1% weight loss) under air and nitrogen atmosphere are 309°C and 325°C, respectively.

3. Stress relaxation experiments

Stress relaxation experiments were performed on a *TA-ARG2* rheometer using an 8 mm parallel-plate geometry in a constant strain ($\gamma = 1\%$) at varying temperatures. The sample was equilibrated at the target test temperature for 2 min. To ensure a good contact, a constant normal force of 10 N was applied. The stress relaxation was monitored over time until the stress relaxation modulus had relaxed to less than 37% (1/e) of its initial value. The stress relaxation experiments were performed at least three times for each sample.

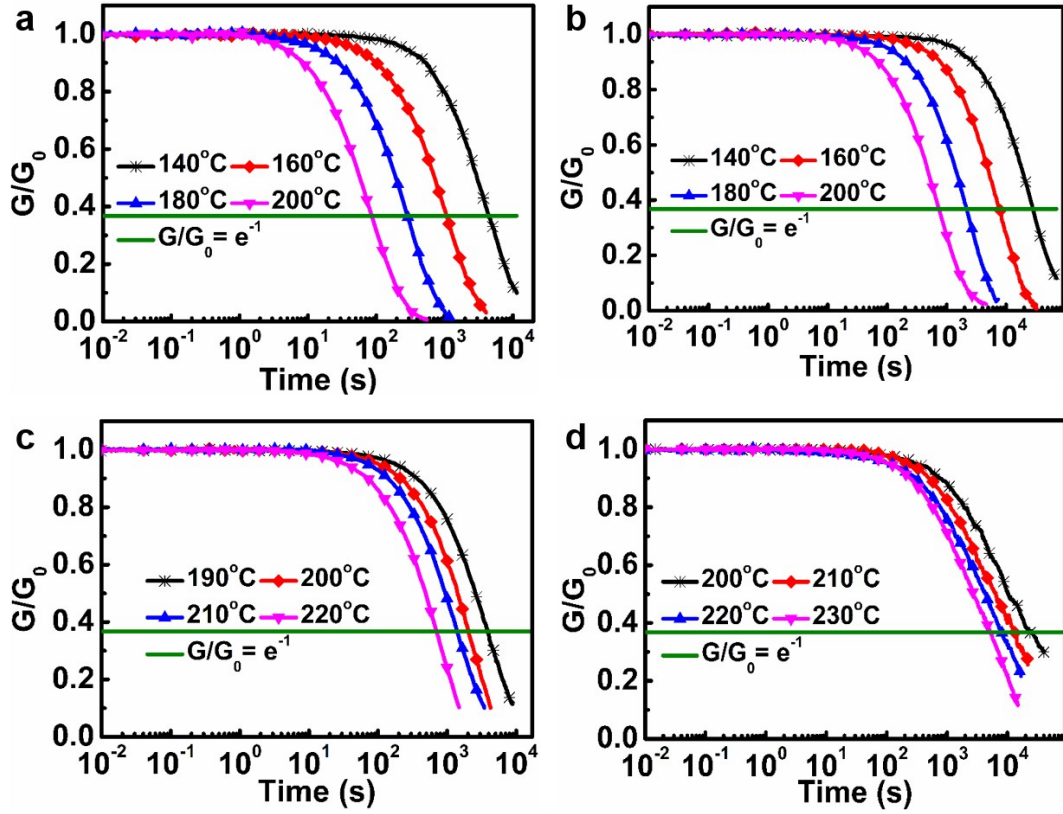


Fig. S5 Stress relaxation curves of the vitrimer-based LCEs with catalyst contents of 5% (a), 2.5% (b), 1% (c) and 0.25% (d) at varying temperatures.

4. Topology freezing transition temperature (T_v) determination

The characteristic relaxation time (τ^*) was defined as the time required for the stress relaxation modulus to reach 37% ($1/e$) of its initial value. $\ln \tau^*$ at vary temperatures were then plotted versus $1000/T$ and fit to the Arrhenius relationship in equation S1:

$$\ln \tau^*(T) = \tau_0 e^{E_a/RT} \quad (\text{S1})$$

Where τ_0 is the characteristic relaxation time at infinite T , E_a is the activation energy of the transesterification reaction (kJ mol^{-1}), R is the universal gas constant and T is the target test temperature.

T_v is defined as the point at which the viscosity reaches $10^{12} \text{ Pa s}^{-1}$ (the liquid to solid transition viscosity). Using the Maxwell relation (equation S2), the shear modulus G was estimated from the

tensile modulus (E') as measured by dynamic thermomechanical analysis (DMA, *TA Q800*) with the relation (equation S3). E' of the samples with different catalyst contents were calculated as the average modulus at temperature varying from 120°C to 220°C from the modulus-temperature curves (Fig. S6). The average plateau modulus of the samples with 5 mol%, 2.5 mol%, 1 mol% and 0.25 mol% catalyst contents are 1.22 MPa, 1.48 MPa, 1.50 MPa and 2.22 MPa, respectively. It reveals that the tensile modulus increases slightly with the catalyst contents decreasing. Swelling experiments of the four samples were carried out in tetrahydrofuran at room temperature for 24 h. The volumes of the samples with 5 mol%, 2.5 mol%, 1 mol% and 0.25 mol% catalyst contents increase by 255.0%, 246.8%, 235.2% and 226.2% (three films were tested for each sample), respectively. The swelling results reveal that the crosslinking density also increases slightly with the catalyst content decreasing, which is in accordance with the tendency of the average plateau modulus. The Poisson's ratio ν is chosen as the value 0.5, which is usually used for rubbers.

$$\eta = G\tau^* \quad (\text{S2})$$

$$G = E' / (2(1 + \nu)) \quad (\text{S3})$$

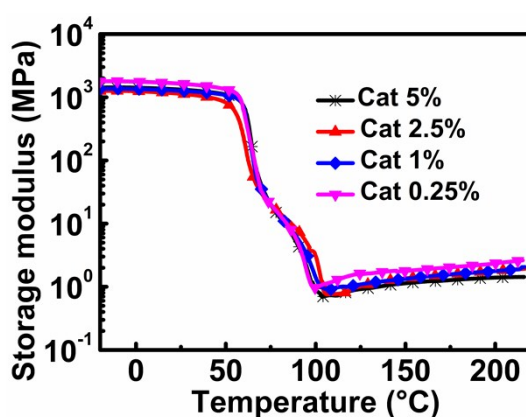


Fig. S6 Modulus-temperature curves of the vitrimer-based LCE with different contents of catalyst.

5. X-ray Analysis

X-ray diffraction analysis were conducted on a Bruker D8 Discover diffractometer to determine the orientational and translational order of the material. Fig. S7 shows the X-ray diffraction images of the unaligned and aligned LCE films, where the arrow indicates the alignment direction. We can find the difference between the two images of X-ray diffraction. The X-ray image of the unaligned film shows two rings, suggesting no orientational bias in either wide-angle (nematic) or small-angle (smectic) scattering. On the contrary, the X-ray image of the aligned film shows arcs, indicating that liquid crystal units have been well-oriented. Fig. S8 shows the Azimuthal intensity scan of the X-ray diffraction pattern from a monodomain LCE. We calculated the order parameter based on the Hermans-Stein orientation distribution function:

$$f = \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \quad (\text{S4})$$

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (\text{S5})$$

Where I is the intensity and ϕ is the azimuthal angle as shown in Fig. S8. The calculated order parameter is about 0.70.

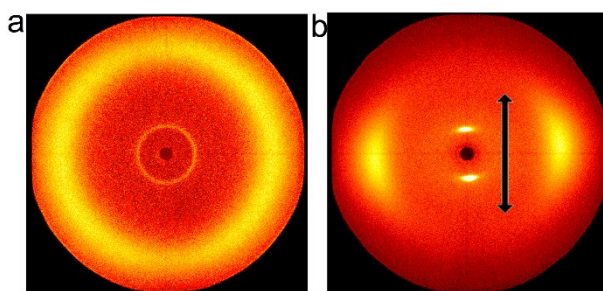


Fig. S7 X-ray diffraction images from an unaligned LCE film (a) and from a monodomain LCE film (b).

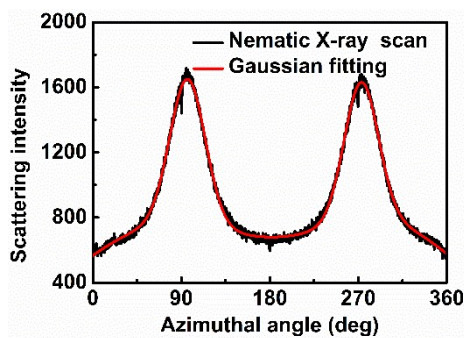


Fig. S8 Intensity scan of X-ray diffraction pattern from the aligned LCE film.

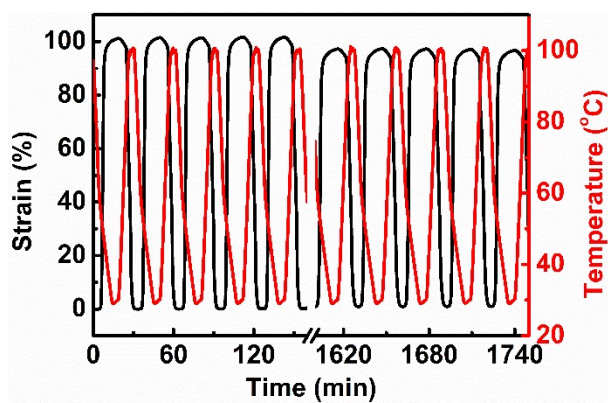


Fig. S9 Repeated actuation stability investigations of the monodomain LCE with 1 mol% catalyst (the curves before break is the first 5 cycles and after break is the curves after 50 cycles).