Electronic Supplementary Information

Enhancing intrinsic thermal conductivities of epoxy resins by introducing biphenyl mesogen-containing liquid crystalline co-curing agents

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Main materials

Bisphenol A epoxy resin (E-51, chemically pure) was purchased from Laizhou Baichen Insulation Materials Co., Ltd. (Shandong, China). 4,4'-diaminodiphenylmethane (DDM, 97%) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). 4,4'-dihydroxybiphenyl (BP, 97%) and 1,6'-dibromohexane (97%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Potassium hydroxide (KOH, analytical grade) and absolute ethanol (EtOH, analytical grade) were purchased from Guangdong Guanghua Technology Co., Ltd. (Guangdong, China). Hydrochloric acid (HCl, analytical grade, 1 mol/L) was purchased from Chengdu Kelong Chemical Co., Ltd. (Sichuan, China).

Characterizations

The molecular structures of the samples were characterized by ^{1}H and ^{13}C nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR, Bruker Avance 400 MHz, Bruker, Germany) using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent with tetramethylsilane (TMS) as the internal standard. High-resolution mass spectroscopy (HRMS) was obtained by electron spray ionization on a quadrupole-orbitrap mass spectrometer (QExactive, ThermoFisher Scientific). Briefly, the mobile phase consisted of (A) Milli-Q water and (B) HPLC-grade methanol. The HPLC-MS was operated with electrospray ionization in positive/negative polarity mode. Fourier transform infrared (FT-IR, Bruker Tensor II, Bruker, Germany) spectroscopy was used to characterize the functional groups of the samples. The test method was attenuated total reflectance (ATR), and the test range was 400~4000 cm^{-1}. The microphase structures of the samples were characterized by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) using a Xeuss system equipped with Genix

source of Cu Ka (Xenocs, France) and a Mar345 detector, where the distances between the sample and the detector were 180.9 mm (WAXD) and 2340.0 mm (SAXS), respectively. The exposure times (transmission mode) for WAXD and SAXS were 1800 s and 3600 s, respectively. Data reduction from 2D pattern to 1D curve was performed using Fit2D. The crystallinity of LCERs was determined by calculating the ratio of the integration of the diffraction peaks to the whole peak of the LCERs in the WAXD curves using Origin software. Thermal gravimetric analyses (TGA, STA449F3, Germany) was used to characterize the thermal properties of the samples. The test temperature range was 30-800°C with the heating rate of 10°C/min under argon atmosphere. Differential scanning calorimetry (DSC, DSC1, Mettler-Toledo, Switzerland) was used to characterize the curing process and liquid crystalline behavior of the samples. The heating rate was 10°C/min under nitrogen atmosphere. The liquid crystalline behavior of the samples was observed and characterized by a hot-stage polarized light microscopy (POM, WMP-6880, Shanghai Wumo Optical Instrument, China) with the heating rate of 10°C/min. A thermal constant analyzer (TPS2200, Hot Disk, Sweden) was used to measure the thermal conductivity of the samples using the modular method according to the standard ISO 22007-2: 2008 with the sample size of 20 mm×20 mm×2 mm. Nanoindenter (Agilent G200) was used to test the indentation depth, elastic modulus, and hardness of the samples. The thickness of the sample was 3~8 mm and the width was 5~30 mm. The upper and lower surfaces of the sample were polished before test.
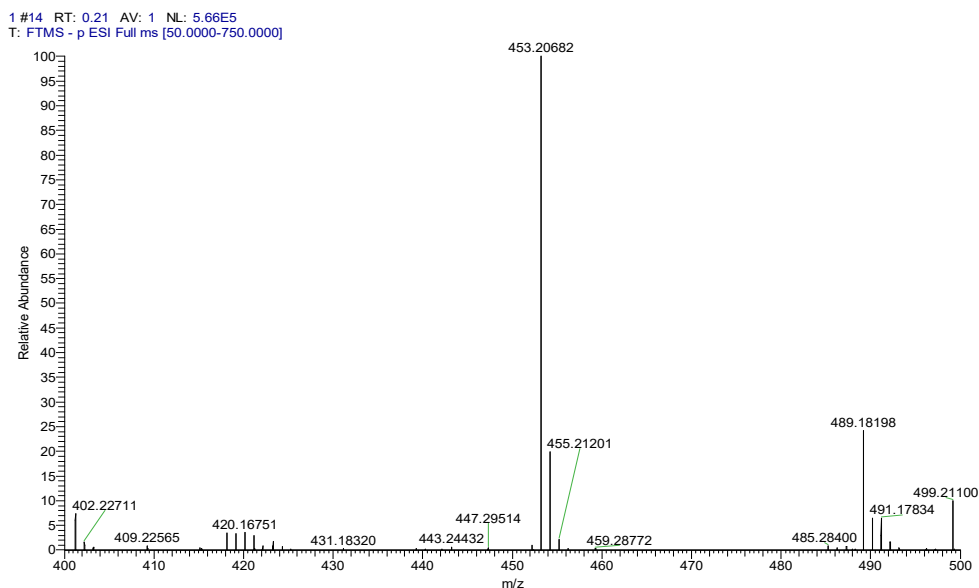
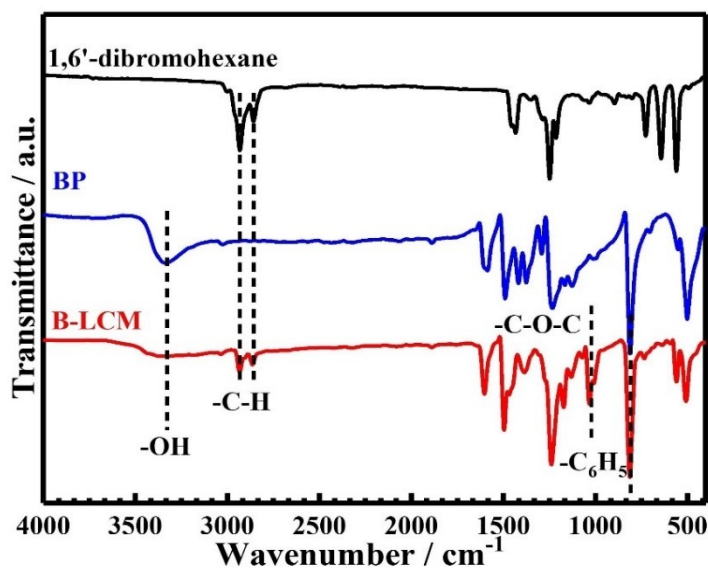**Figure S1** High-resolution mass spectroscopy of BLCM

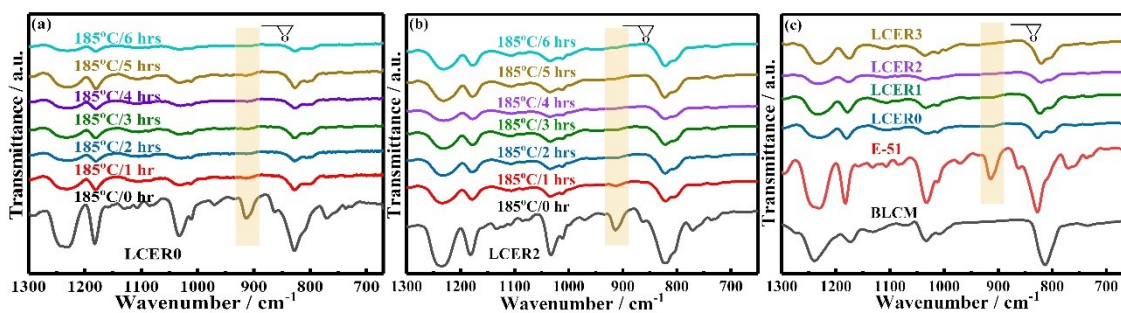**Figure S2** FT-IR spectra of BLCM, BP, and 1,6'-dibromohexane

Figure S3 Zoomed-in FT-IR spectra of the fingerprint region for LCER0 (a) and LCER2 (b) at

different time during the curing process; Zoomed-in FT-IR spectra of the fingerprint region for
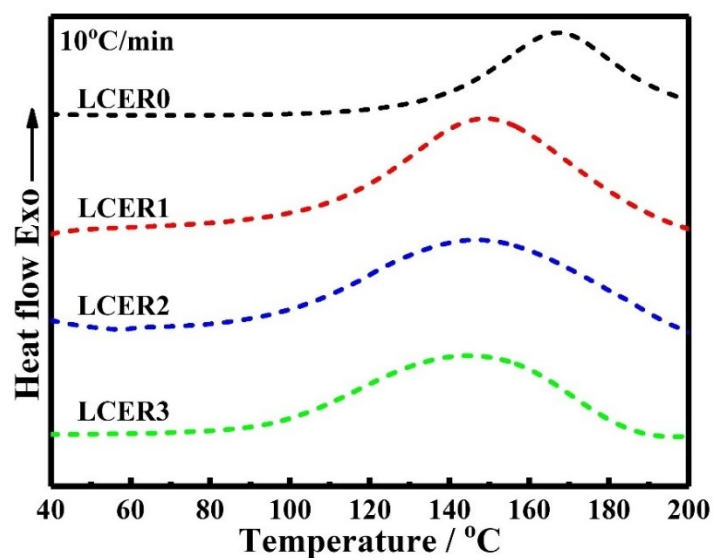
cured LCER, E-51, and BLCM (c)

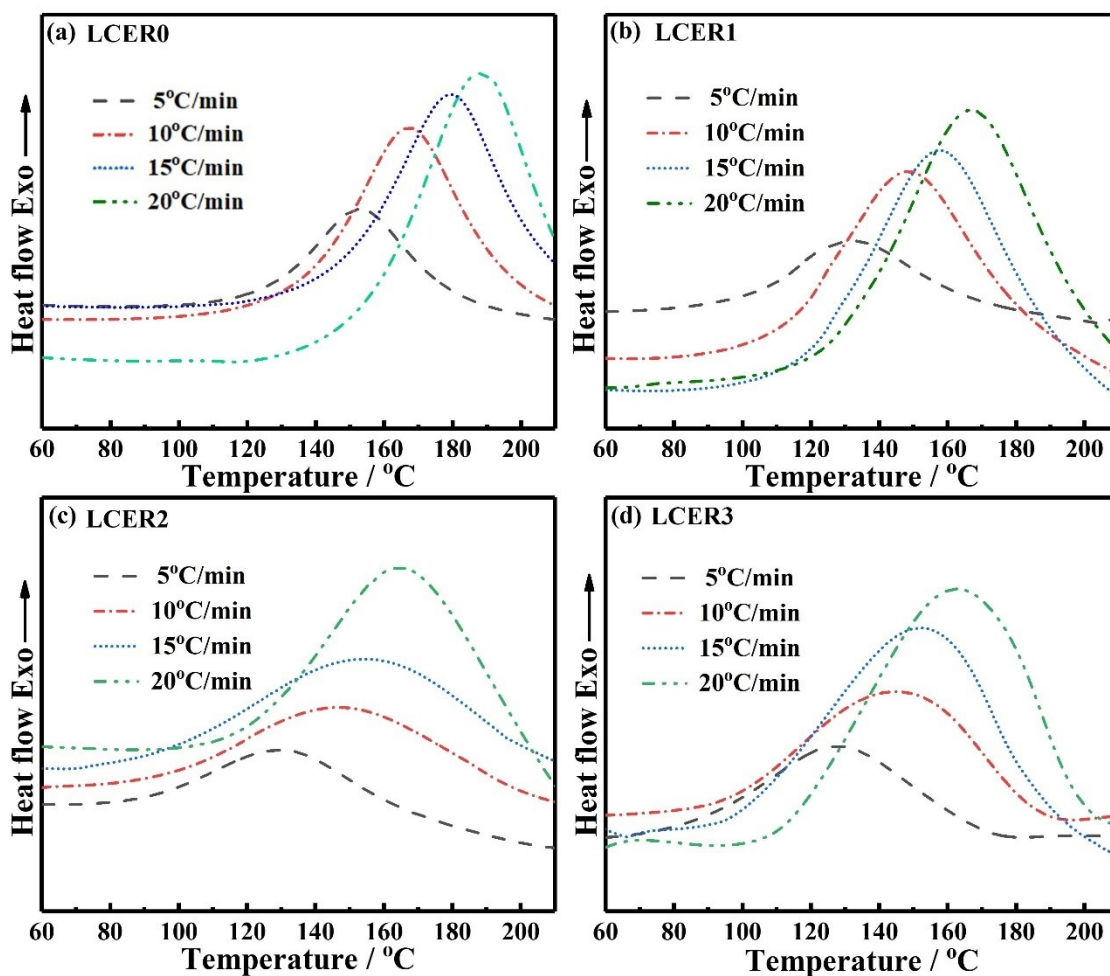**Figure S4** DSC curves of the curing processes for LCERs

Figure S5 DSC curves of LCERs at different heating rates

Table S1 Peak temperatures of LCERs at different heating rates

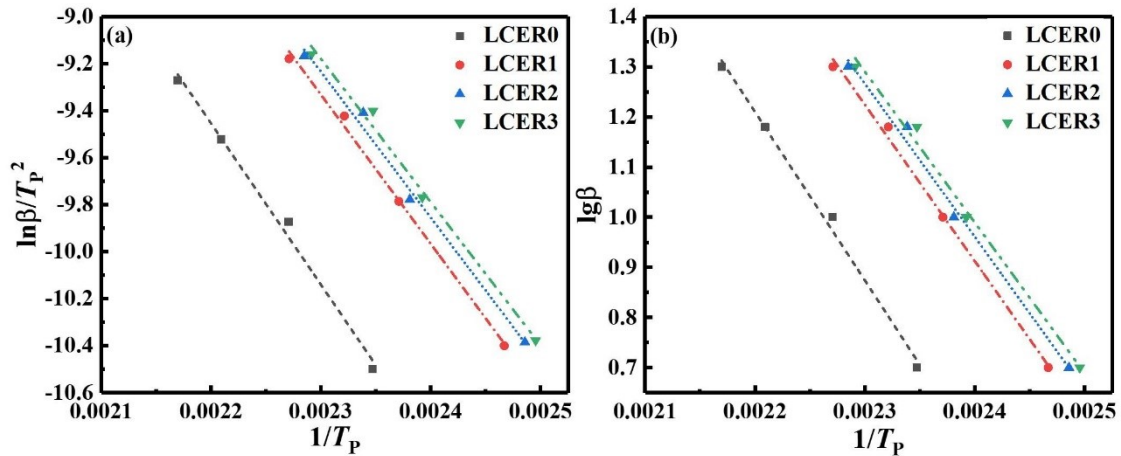| Samples	Peak temperature/°C			
	5°C/min	10°C/min	15°C/min	20°C/min
LCER0	152.9	167.3	179.5	187.8
LCER1	132.2	148.6	157.6	167.2
LCER2	129.1	146.8	154.5	164.5
LCER3	127.6	144.8	152.9	163.3

Figure S6 Kinetic curves of LCERs obtained by Kissinger (a) and Ozawa (b) methods

$$In\frac{\beta}{T_p^2} = In\frac{AR}{E} - \frac{E}{RT_p} \tag{S1}$$

$$lg\beta = lg\frac{AE}{RG(a)} - 2.315 - 0.4567\frac{E}{RT_p} \tag{S2}$$

where β is the heating rate (K·min^{-1}); T_p is the peak temperature (K); A is the frequency factor (min^{-1}); R is the ideal gas constant (8.314 J·mol^{-1}·K^{-1}); E is the apparent activation energy (kJ·mol^{-1}); $G(a)$ is a function related to the conversion rate.

Table S2 Apparent activation energy of LCERs calculated by Kissinger and Ozawa methods

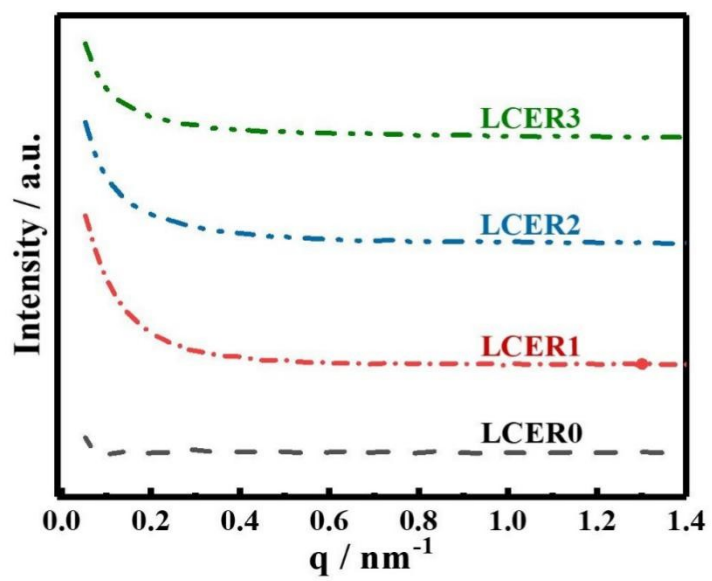| Samples	Apparent activation energy/kJ·mol^{-1}		frequency factor/min^{-1}
	Kissinger	Ozawa	A
LCER0	57.5	61.5	1.9×10^3
LCER1	51.8	55.8	1.2×10^3
LCER2	50.4	54.4	0.9×10^3
LCER3	49.4	53.4	0.7×10^3

Figure S7 SAXS curves of LCERs