Supporting Information
for
Interpenetrating Liquid Crystal Polyurethane/Polyacrylate Elastomer with Ultrastrong Mechanical Property

Hai-Feng Lu, Meng Wang, Xu-Man Chen, Bao-Ping Lin, Hong Yang*

School of Chemistry and Chemical Engineering, Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, State Key Laboratory of Bioelectronics, Institute of Advanced Materials, Southeast University, Nanjing 211189, China

E-mail: yangh@seu.edu.cn.
General considerations.

4-Dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) were purchased from Energy Chemical Corp. Hydroquinone, 4-hydroxybenzoic acid, 6-chlorohexan-1-ol, 2,2-dimethoxy-2-phenylacetophenone (DMPA), hexane-1,6-diyl diacrylate (HADA) and N,N-dimethylaniline were purchased from Aladdin Inc. Dibutyltin dillaurate (DBTL), poly(ethylene glycol) (PEG-400) and acryloyl chloride were purchased from TCI Inc. N,N-Dimethylformamide (DMF) was distilled from CaH₂ under nitrogen.

All ^1^H NMR spectra were recorded on a Bruker HW600 MHz spectrometer (AVANCE AV-600) or a Bruker HW300 MHz spectrometer (AVANCE AV-300), using CDCl₃ or DMSO-d₆ as the solvent and δ 7.26 (CDCl₃) or δ 2.50 (DMSO) as the interior reference. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q2000 instrument (New Castle, DE) under nitrogen purge with a heating/cooling rate of 5 °C/min. Both one-dimensional (1D) WAXS and two-dimensional (2D) WAXD experiments were performed on Anton Paar SAXS point 2.0 with a TCStage 300 temperature controller. The specimen (in a TCS sample holder) was placed in the sample chamber, which was evacuated to a pressure below 3 mbar in order to minimize the atmospheric scattering of the X-ray beam. All XRD Data were collected at a sample-to-detector distance (SDD) of 79 mm using an incident X-ray beam (50.047 keV, 0.999 mA, 1.542 Å wavelength). For each specimen, six frames of 900-s exposures were collected and averaged. Two-dimensional data was transformed to one-dimensional curves by using SAXS analysis software (Anton Paar).
Polarized optical microscopy (POM) observations of all the liquid crystalline textures of the samples were performed on an Olympus BX53P microscope equipped with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software. The light intensities of the UV lamp illuminating at different distances were accurately measured by using an optic power meter (LP-3B, Physcience Opto-Electronics, China). A high-intensity ultraviolet lamp (LP-40, Shanghai Luyang Instrument Co. Ltd., emission spectral range: 365±5 nm) was used to irradiate on the samples.

All mechanical property studies of the polymeric samples were performed on a dynamic mechanical analyzer (DMA Q800, TA Instrument) using tension clamp. All the experiments were performed in triplicate. The examined specimens were prepared with a dimension of ca. 22.51 mm long × 5.42 mm wide × 0.48 mm thick. In the isoforce experiments, the samples were heated and cooled between 40 and 140 °C under a preload force of 0.001 N at a rate of 3.00 °C/min. In the isostrain experiments, the generated contractile force by the IPN-LCE samples was measured along with the temperature variation when the IPN-LCE film was elongated by a constant 0.01% strain in tension. In the quasi-static stress-strain experiments, the strain rate was set as 0.1 N/min. The samples were uniaxially stretched along the mesogenic director orientation in the temperature range from 30 to 140 °C.

The atomic force microscopy (AFM) was performed on Dimension ICON (Bruker-AFM, America). The SEM images were recorded on an Inspect F50 S3 field emission scanning electron microscope (FEI-SEM, America). Fourier transform infrared
spectroscopy (FT-IR) spectra were recorded on a Nicolet 5700 Fourier Infrared Spectrometer (Thermo Electron Scientific Instruments Corporation, America).

Synthesis of 4-((6-hydroxyhexyl)oxy)phenyl-4-((6-hydroxyhexyl)oxy)benzoate (Y1901).

![Figure S1. The synthetic route of LC monomer Y1901](image)

**4-Hydroxyphenyl-4-hydroxybenzoate.** Hydroquinone (8.80 g, 79.92 mmol) and 4-hydroxybenzoic acid (1.38 g, 9.99 mmol) were added into a three-neck round-bottom flask under nitrogen. The mixture was stirred at 260 °C for 2 h. After cooling to room temperature, 500 mL water was added into the above mixture. The yellow crude product was obtained by filtration. After recrystallization from ethanol/water (1:1 v/v), 4-hydroxyphenyl-4-hydroxybenzoate (1.37 g, yield: 59.57%) was obtained.

**4-((6-Hydroxyhexyl)oxy)phenyl-4-((6-hydroxyhexyl)oxy)benzoate (Y1901).** 4-Hydroxyphenyl-4-hydroxybenzoate (1.00 g, 4.34 mmol), acetone (50 mL), potassium iodide (14.00 mg, 0.08 mmol) and potassium carbonate (4.75 g, 34.37 mmol) were added into a three-neck round-bottom flask under nitrogen. Subsequently, 6-chloroheaxan-1-ol (1.36 g 9.95 mmol) was added dropwise into the three-neck round-bottom flask over 20 min. The above mixture was stirred at 68 °C for 30 h and the
solvent was removed under vacuum. After purification by column chromatography (ethyl acetate/petroleum ether, 1/3), compound Y1901 (1.00 g, yield: 53.52%) was obtained as a white powder. $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$: 8.04 (d, $J = 8.4$ Hz, 2H), 7.11 (m, 4H), 6.96 (d, $J = 8.6$ Hz, 2H), 4.34 (t, $J = 5.2$ Hz, 2H), 4.02 (m, 4H), 3.40 (m, 4H), 1.73 (m, 4H), 1.41 (m, 12H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$: 164.44, 163.08, 156.29, 143.95, 131.85, 122.63, 120.95, 114.93, 114.59, 114.35, 67.95, 67.82, 60.64, 32.47, 32.44, 28.73, 28.54, 25.41, 25.31, 25.27, 25.23. ESI-MSI m/z: [M + Na]$^+$, calculated 430.2, found 453.2.

Figure S2. $^1$H NMR spectrum of Y1901
Figure S3. $^{13}$C NMR spectrum of Y1901.

Figure S4. ESI-MS spectra spectrum of LC monomer Y1901.
Synthesis of 2-methyl-1,4-phenylene-bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (RM82).\(^1\)

**Figure S5.** The synthetic route of LC monomer RM82.

4-((6-Hydroxyhexyl)oxy)benzoic acid. 4-Hydroxybenzoic acid (11.00 g, 79.64 mmol), KOH (11.20 g, 199.61 mmol), potassium iodide (265.6 mg, 1.60 mmol), EtOH (56 mL) and distilled water (28 mL) were added into a three-neck round-bottom flask under nitrogen. To the flask, 6-chlorohexan-1-ol (10.90 g, 79.78 mmol) was added dropwise over 20 minutes. The above mixture was stirred at 90 °C for 16 h. After cooling to room temperature, the mixture was poured into a dilute aqueous hydrochloric acid solution and then extracted with methylene chloride. The organic layer was washed three times with water, dried over Na\(_2\)SO\(_4\). The organic solvent was removed under reduced pressure and the residue was purified by recrystallization from ethanol to afford 4-((6-hydroxyhexyl)oxy)benzoic acid as a white crystal (13.20 g, yield 69.57%).

4-((6-(Buta-1,3-dien-2-yloxy)hexyl)oxy)benzoic acid. To an ice-cooled solution of 4-((6-hydroxyhexyl)oxy)benzoic acid (13.00 g, 54.56 mmol), N,N-dimethylaniline (7.90 g, 65.19 mmol) and anhydrous 1,4-dioxane (60 mL), acryloyl chloride (5.05 g, 55.79 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 0.5 h, then warmed to 55 °C and stirred for another 3 h. The solution was cooled to room temperature and poured into ice water. A white precipitate was
collected by filtration. After washed by water twice, the product was purified by recrystallization from isopropanol to afford 4-((6-(buta-1,3-dien-2-yloxy)hexyl)oxy) benzoic acid as a white crystal (12.00 g, 75.23%).

2-Methyl-1,4-phenylene-bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (RM82). A solution of 4-((6-(buta-1,3-dien-2-yloxy)hexyl)oxy) benzoic acid (12.00 g, 41.05 mmol), 2-methylbenzene-1,4-diol (2.48 g, 19.98 mmol) and dimethylaminopyridine (463.42 mg, 3.73 mmol) in anhydrous dichloromethane (80 mL) was stirred at room temperature. Then dicyclohexylcarbodiimide (12.36 g, 59.90 mmol) and anhydrous dichloromethane (40 mL) were added into the flask dropwise. The reaction mixture was stirred at room temperature for 48 h. After that, the reaction mixture was filtered and washed three times by sodium bicarbonate aqueous solution (conc. = 5 wt%), twice with distilled water, three times with a saturated sodium chloride solution and dried over sodium sulfate. The crude solid was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:3) as eluent to give RM82 as a white solid (9.51 g, 70.76%). $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.09 (t, $J = 9.1$ Hz, 4H), 7.26 (d, $J = 8.7$ Hz, 2H), 7.20 – 7.14 (m, 1H), 7.11 (m, 4H), 6.32 (m, 2H), 6.17 (m, 2H), 5.92 (m, 2H), 4.11 (m, 8H), 2.17 (s, 3H), 1.75 (m, 4H), 1.65 (m, 4H), 1.43 (m, 8H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 165.47, 164.19, 163.85, 163.25, 163.19, 148.05, 146.70, 131.98, 131.95, 131.35, 131.18, 128.40, 124.06, 123.05, 120.74, 120.54, 120.29, 114.73, 114.66, 67.91, 63.98, 40.41, 40.13, 39.85, 39.57, 39.29, 39.01, 38.74, 28.34, 28.01, 25.09, 25.05, 15.72.
Figure S6. $^1$H NMR spectrum of RM82.

Figure S7. $^{13}$C NMR spectrum of RM82.
The preparation procedure of pure LCPU film.

A mixture of Y1901 (431 mg, 1.00 mmol), PEG400 (268 mg, 0.67 mmol), MDI (445 mg, 1.78 mmol), TMP (8 mg, 0.06 mmol) and DBTL (21 mg, 0.03 mmol) dissolved in dry DMF (35 mL) was added into a Schlenk flask. The above solution was stirred at 78 °C under nitrogen for 4.5h. After that, most of the organic solvent (ca. 90 vol %) was then removed by vacuum to provide a viscous solution. Subsequently, the resulting mixture was poured into a PTFE mold (3 cm long × 3 cm wide × 3 cm deep) and heated in a vacuum oven at 70 °C for 5.5 h. After cooling to room temperature, the LCPU film was carefully removed from the PTEF mold and cut into a stripe. The stripe film was slowly uniaxial-stretched to ca. 200% of the original length and kept in an oven at ca. 100 °C for 48 h, to provide the desired pure LCPU film.

The preparation procedure of pure LCPA thermoset.

A mixture of RM82 (673 mg, 1.00 mmol), HADA (23 mg, 0.10 mmol) and DMPA (3.00 mg, 0.01 mmol) were dissolved in 1.50 mL CH\textsubscript{2}Cl\textsubscript{2}. Ultrasonication process was carried out for about 3 mins to ensure a homogeneous dispersion of the above mixture. The organic solvent was then removed in vacuum to prepare a homogeneous LC mixture. The resulting solid mixture was heated to 120 °C and quickly poured into a PTFE mold (30 mm long × 5 mm wide × 0.5 mm deep). After irradiated under UV light (365 nm, 7.2 mW.cm\textsuperscript{-2}) at 100 °C for 20 min, the desired pure LCPA thermoset was obtained as a yellow strip.
The preparation procedure of IPN-LCE film.

A mixture of Y1901 (431 mg, 1.00 mmol), PEG400 (268 mg, 0.67 mmol), MDI (440 mg, 1.76 mmol), TMP (8 mg, 0.06 mmol), DBTL (19 mg, 0.03 mmol), RM82 (673 mg, 1.00 mmol), HADA (23 mg, 0.10 mmol), DMPA (3.00 mg, 0.01 mmol) dissolved in dry DMF (40 mL) was added into a Schlenk flask. The above solution was stirred at 78 °C for 4.5 h. Subsequently, most of the organic solvent (ca. 90 vol %) was then removed by vacuum to provide a viscous solution, which was immediately extruded through a syringe (needle hole: 1.51 mm diameter) into a polytetrafluoroethylene (PTFE) rectangular mold (3 cm long × 3 cm wide × 3 cm deep) and meanwhile illuminated under UV light (365 nm, 6.9 mW.cm⁻²), for a short time period of ca. 20 s. The mold was heated in a vacuum oven at 70 °C for 5.5 h. After cooling to room temperature, the resulting pre-crosslinked IPN-LCE film was carefully removed from the PTFE mold, and sliced into a strip (25.48 mm long × 6.91 mm wide × 0.68 mm thick) which was further longitudinally stretched to ca. 200% of its original length. The stretched strip was fixed on a hollow PTFE frame and kept at 100 °C for 48 h, meanwhile irradiated under UV light (365 nm, 7.2 mW.cm⁻²) from both sides of the film, to give the desired IPN-LCE sample.
FT-IR experiments

FT-IR experiments were applied to analyze the full conversion of the functional groups of IPN-LCE sample as shown in Figure S8. The FT-IR spectra of Y1901, PEG400 and TMP showed the characteristic -OH absorption peak at ca. 3445 cm\(^{-1}\).\(^2\)

The characteristic acrylic -C=C- peak of RM82 and HADA was found at around 1408 cm\(^{-1}\).\(^3\)

The characteristic -N=C=O absorption peak of MDI was found at approximately 2260 cm\(^{-1}\).\(^4\)

All the characteristic absorption peaks of -OH, acrylic -C=C- and -N=C=O groups were also appeared in the FT-IR spectrum of the unreacted monomer mixture.

After the polymerization reaction, the absences of -OH absorption (~3445 cm\(^{-1}\)), -N=C=O absorption (~2260 cm\(^{-1}\)) and acrylic -C=C- absorption (~1408 cm\(^{-1}\)), as well as the appearance of the characteristic -NH- (formed by the reaction between isocyanate

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**Figure S8.** FT-IR spectra of Y1901, PEG400, TMP, MDI, RM82, HADA, the unreacted monomer mixture and the prepared IPN-LCE sample.
groups (-N=C=O) and the hydroxyl groups (-OH)) absorption peak (~3298 cm$^{-1}$), indicated a complete conversion of the functional groups in the prepared IPN-LCE sample.

**Swelling experiment.**

According to the previously reported method, swelling experiment was executed to investigate the formation of two networks. The original dimensions and weight of IPN-LCE sample were 15.02 mm long $\times$ 5.54 mm wide $\times$ 0.42 mm thick and 36.87 mg respectively. After swollen in methylene chloride solvent for 18 h, the dimensions of the IPN-LCE sample changed to 17.85 mm long $\times$ 6.67 mm wide $\times$ 0.61 mm thick, and its weight became 36.21 mg. The volume in the state of swelling was 2.08 times the original volume, the weight loss was ca. 1.79%, after swelling and drying in the oven under vacuum at 50 °C for 10 h.

![Figure S9. Swelling experiment of IPN-LCE sample.](image)
Figure S10. DSC curves of (A) LC monomer RM82, (B) LC monomer Y1901, (C) LCPA, (D) LCPU and (E) IPN-LCE.
Figure S11. POM images of IPN-LCE film with the molecular director either (A) 45° tilt or (B) parallel to the polarizer.

Polarized optical microscope (POM) was used to examine the alignment effect of IPN-LCE. The highest transmittance of IPN-LCE was found when the stretching direction was 45° tilt to the polarizer. The transmittance minimized when the stretching direction was parallel to the polarizer or analyzer.

Figure S12. POM images of IPN-LCE sample at (A) 60 °C and (B) 140 °C, pure LCPU sample at (C) 60 °C and (D) 140 °C.
Figure S13. 1D-WAXS patterns of IPN-LCE sample on (A) heating and (B) cooling. 2D-WAXD patterns of IPN-LCE samples at (C) 30 °C, (D) 100 °C and (E) 140 °C.

Figure S14. 1D-WAXS patterns of LCPU sample on (A) heating and (B) cooling. 2D-WAXD patterns of LCPU samples at (C) 30 °C, (D) 90 °C and (E) 140 °C.
The order parameters of the IPN-LCE were calculated as ca. 0.73, 0.65 and 0.18 at 30 °C, 90 °C and 140 °C respectively according to the previously reported method, which indicated a high-quality uniaxial orientation of the mesogenic directors inside the IPN-LCE network. Meanwhile, the order parameters of the pure LCPU were calculated as ca. 0.77, 0.68 and 0 at 30 °C, 90 °C and 140 °C respectively.
Figure S16. Schematic illustration of the preparation protocol of LCE samples used for the SEM and AFM experiments.

Figure S17. SEM images, AFM images and the height profiles of (A-C) LCPU, (D-F) LCPA, (G-I) IPN-LCE samples.
**Figure S18.** Stress-strain diagrams of LCPA sample measured at varied temperatures.

**Figure S19.** Stress-strain diagrams of LCPU sample measured at varied temperatures.
**Figure S20.** Stress-strain diagrams of IPN-LCE sample measured at varied temperatures.

**Figure S21.** Isostrain (0.01%) measurements of three IPN-LCE film samples.

Three IPN-LCE film samples were used to perform isostrain (0.01%) measurements. As shown in Figure S21, the maximum actuation stress values of the three IPN-LCE samples were almost the same (2.53MPa).
Figure S22. Isostrain (0.01%) measurements of (A) LCPU film and (C) LCPA film. The strain (in isoforce mode) and the corresponding temperature diagrams of (B) LCPU film and (D) LCPA film plotted against time.

Figure S23. The set-up of temperature-controlled heating coil equipment.
Work capacity calculation:

The work capacity was calculated by using eq 1-3. W was the amount of work during the actuating process, V was the active volume in the actuating process. In the actuating process, an average force (F) equaled to the gravity (G) of the load (ca. 605 g). Thus the average force was 5.95 N according to eq 2. The amount of work could be calculated using eq 3, where \( \Delta L \) was the moved displacement. A displacement (\( \Delta L \)) of 6.2 mm which was the change from 15.2 mm at 40 °C to 9 mm at 140 °C, was measured during the actuating process. Thus, \( 36.89 \times 10^{-3} \) J of work was expended during the process according to eq 3. The active dimension of IPN-LCE film before actuating was 10.8 mm length, 5.5 mm of width, and 0.49 mm of thickness. So the active IPN-LCE film volume (V) was calculated as \( 29.1 \times 10^{-9} \) m\(^3\). Consequently, the work capacity was calculated as 1267.7 KJ/m\(^3\) according to eq 1.

\[
\text{Work density } = \frac{W}{V} \quad (1)
\]

\[
F = G = m \times g \quad (2)
\]

\[
W = F \times \Delta L \quad (3)
\]
Table S1. A summary of breaking strengths and elastic moduli (above $T_{\text{iso}}$) of the previously reported works and this work.

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