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Supporting Information

Allyl Sulfide Based Visible Light-Induced Dynamically Reshaped Liquid Crystalline Elastomer/SWCNT Nanocomposites Capable of Multimode NIR Photomechanical Actuations

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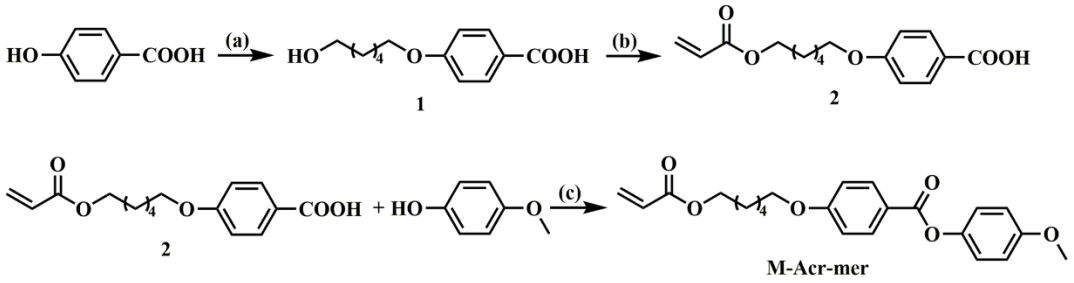
S1.1 Synthesis and characterization of the phenyl benzoate acrylate monomer M-Acr-mer



Scheme S1. Synthetic routes for the mesogenic monomer phenyl benzoate acrylate M-Acr-mer. Reaction conditions: (a) $Br(CH_2)_6OH$, KOH, $EtOH/H_2O$ (v/v, 1/2), reflux, 36 h; (b) Acryloyl chloride, N,N-dimethylaniline, THF, r.t., 48 h; (c) DMAP, DCC, DCM, r.t., 48 h.

Synthesis and characterization of the intermediate compound **1**

The synthesis of compound **1** was according to a modified literature procedure.[1] To a 250 mL round bottom flask equipped with a reflux condenser and a stirring bar was added *p*-hydroxybenzoic acid (3.45 g, 25.0 mmol), 6-bromo-1-hexanol (4.53 g, 25.0 mmol) and potassium hydroxide (3.93 g, 70.0 mmol), and 150 mL mixed solvent ($EtOH/H_2O$, v/v, 1/2). The reaction mixture was refluxed for 36 h. After cooling to room temperature, the pH value of the mixture solution was adjusted within the range of 3-4 by the addition of hydrochloric acid (2.5 mol/L). The thus formed precipitate was filtrated and recrystallized from ethanol to afford the intermediate **1** as a white solid (3.87 g, 18.4 mmol, 73.6% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.58 (s, 1H), 7.88 (d, 2 H), 7.01 (d, 2 H), 4.45-4.25 (s, 1 H) 4.03 (t, 2 H), 3.38 (t, 2 H), 5.37 (d, 1 H), 4.65 (d, 2 H), 4.13 (t, 2 H), 3.72 (t, 2 H), 1.78-1.68 (m, 4 H), 1.49-1.30 (m, 4 H).

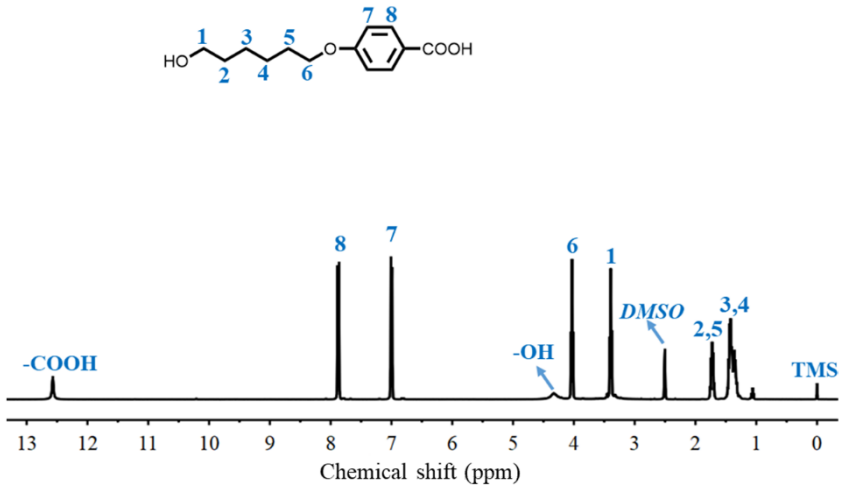


Fig. S1. ^{1}H NMR spectrum of the intermediate compound **1** in DMSO-d_6 at room temperature.

Synthesis and characterization of the intermediate compound **2**

The synthesis of the compound **2** was according to a modified literature procedure.[2] To a 250 mL round bottom flask equipped with an addition funnel and a stirring bar was added the as-prepared compound **1** (1.90 g, 8.0 mmol), *N,N*-dimethylaniline (1.9 mL, 50.0 mmol), and THF (50 mL). With the flask cooled in an ice bath, a solution of acryloyl chloride (1.2 mL, 24.6 mmol) in THF (20 mL) was added dropwise over 30 min. The reaction mixture was warmed up to room temperature and allowed to stir for another 48 h. Then the reaction mixture was poured into cold water and acidified by the addition of HCl (aq, 2.5 mol/L) until its pH value in the range of 3-4. The precipitate was filtrated and then purified by column chromatography through a silica gel column with the eluent mixture solvent of petroleum and dichloromethane (v/v, 1/1) to afford the compound **2** as a white solid (1.68 g, 5.8 mmol, 72.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, 2 H), 6.92 (d, 2 H), 6.43 (d, 1 H), 6.14 (m, 1 H), 5.81 (d, 1 H), 4.20 (t, 2 H), 4.01 (t, 2 H), 1.85-1.68 (m, 4 H), 1.47 (m, 4H).

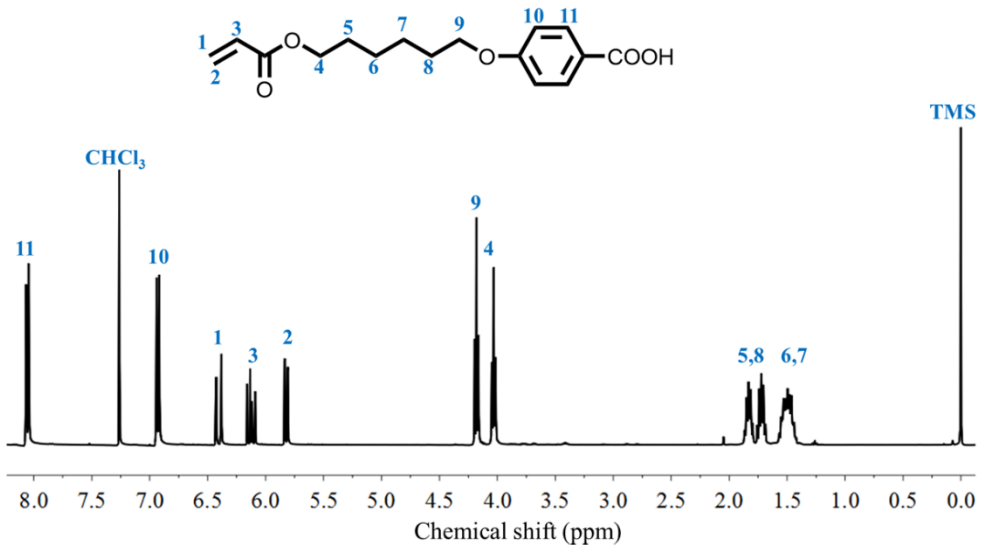


Fig. S2. ^{1}H NMR spectrum of the compound **2** in $CDCl_3$ at room temperature.

Synthesis and characterization of the phenyl benzoate acrylate monomer **M-Acr-mer**

The synthesis of the phenyl benzoate acrylate monomer was according to a modified literature procedure.[1, 3] To a 250 mL round bottom flask equipped with an addition funnel and a stirring bar was added the as-prepared compound **2** (1.46 g, 5.0 mmol), *p*-hydroxyanisole (0.81 g, 6.5 mmol), 4-dimethylaminopyridine (DMAP) (0.18 g, 1.5 mmol), and anhydrous dichloromethane (50 mL). With the flask cooled in an ice bath, a solution of *N*,*N*-dicyclohexylcarbodiimide (DCC) (1.34 g, 6.5 mmol) in anhydrous dichloromethane (20 mL) was added dropwise over 30 min. The reaction mixture was warmed up to room temperature and allowed to stir for another 48 h. The precipitated solid was removed by sucking filtration and the organic filtrate was washed with water (3 × 100 mL). The collected organic layer was dried with anhydrous magnesium sulfate, and then concentrated via rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with the eluent of petroleum and ethyl acetate (v/v, 5/1) to afford the monomer **M-Acr-mer** as a white solid (1.21 g, 3.0 mmol, 60.7% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, 2 H), 7.13 (d, 2 H), 6.95 (d, 4 H), 6.43 (d, 1 H), 6.12 (m, 1 H), 5.83 (d, 1 H), 4.18 (t, 2 H), 4.04 (t, 2 H), 3.83 (s, 3 H), 1.85-1.68 (m, 4 H), 1.50 (m, 4 H).

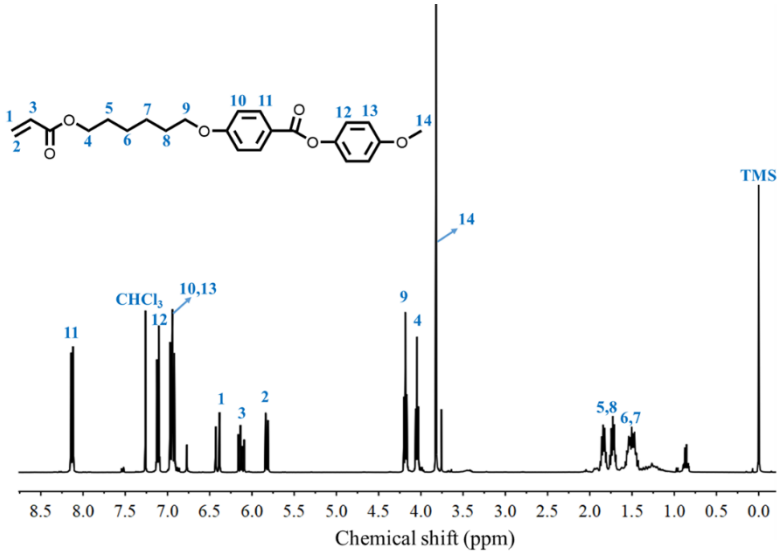
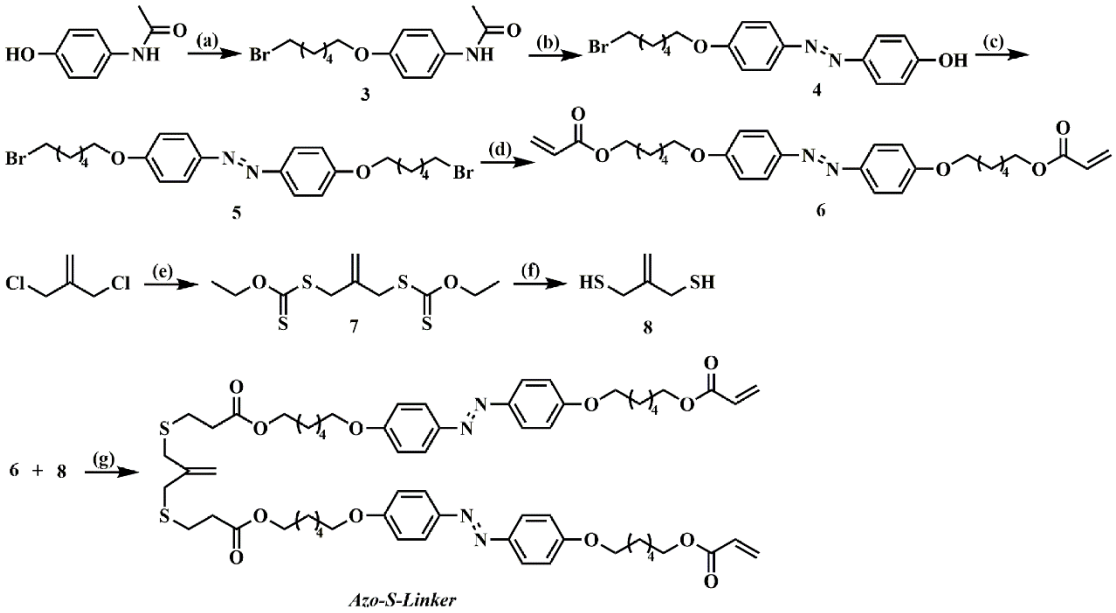


Fig. S3. ^{1}H NMR spectrum of the monomer **M-Acr-mer** in $CDCl_3$ at room temperature.

S1.2 Synthesis and characterization of azobenzene-containing allyl sulfide-based diacrylate dynamic crosslinker Azo-S-Linker



Scheme S2. Synthetic routes for the azobenzene-containing allyl sulfide-based diacrylate dynamic crosslinker Azo-S-Linker. Reaction conditions: (a) $Br(CH_2)_6Br$, K_2CO_3, KI, acetone, reflux, 24 h; (b) (i) 37% HCl, ethanol, reflux, 24 h; (ii) 1 M HCl, $NaNO_2$, H_2O, 0 °C, 1h, (iii) Phenol, NaOH, H_2O, 0 °C, 2 h; (c) $Br(CH_2)_6Br$, K_2CO_3, KI, acetone, reflux, 24 h; (d) Acrylic acid, NaOH, hydroquinone, DMF, 120 °C; (e) Potassium ethyl xanthogenate, ethanol; (f) Ethylene diamine/H_2O; (g) Et_3N, THF, 0 °C.

Synthesis and characterization of the intermediate compound **3**

The synthesis of the compound **3** was according to a modified literature procedure.[3] To

a 250 mL round bottom flask equipped with a reflux condenser and a stirring bar was added 4-acetamidophenol (16.00 g, 106.0 mmol), 1,6-dibromohexane (77.58 g, 318.0 mmol), potassium carbonate (K_2CO_3, 14.65 g, 106.0 mmol), catalytic amount of potassium iodide (KI, 0.17 g, 1 mmol), and anhydrous acetone (200 mL). The reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into deionized water (1000 mL). The precipitate was filtrated and washed with deionized water to afford the intermediate compound **3** as a white solid (27.59 g, 87.9 mmol, 82.9% yield).

Synthesis and characterization of the intermediate compound **4**

The synthesis of the compound **4** was according to a modified literature procedure.[3] To a 200 mL round bottom flask equipped with a reflux condenser and a stirring bar was added the as-prepared compound **3** (25.00 g, 79.6 mmol), 37% concentrated hydrochloric acid (70 mL), and ethanol (250 mL). The reaction mixture was refluxed for 24 h with a vigorous stirring. After cooling down to room temperature, the dark red reaction mixture was poured into ice water (200 mL) with a vigorous stirring (1200 rpm), and turned into light yellow gradually. The mixture solution was neutralized and further slightly alkalinized to pH 7-8 with the addition of NaOH (aq, 2.0 mol/L). Afterwards, the above solution was extracted with dichloromethane (3 × 100 mL). The combined organic later was washed with deionized water (2 × 100 mL), dried with sodium sulfate and then concentrated via rotary evaporation to obtain a brown solid, which was directly used for the next reaction without further purification.

In a three-neck round bottom flask (500 mL) equipped with a stirring bar, the above produced brown solid was dispersed in a 1.0 M HCl aqueous solution (200 mL). With the system cooled down in an ice bath, a solution of $NaNO_2$ (4.24 g, 61.5 mmol) in water (20 mL) at 0 ^oC was added dropwise into the flask. After a vigorous stirring for 1 h, a solution of phenol (5.79 g, 61.5 mmol), and NaOH (4.00 g, 100.00 mmol) in water (50 mL) at 0 ^oC was added dropwise into the above reaction solution. The mixture solution was neutralized and further slightly alkalinized to pH 8-9 through the addition

of NaOH (aq, 2.0 mol/L) at 0 °C. The reaction mixture was warmed up to room temperature and allowed to stir for another 2 h. The pH value of the mixture solution was adjusted to 4 with the addition of HCl (aq, 2.8 mol/L). The yellow precipitate was filtered and washed with deionized water (3 × 100 mL), after dried at 50 °C under reduced pressure in a vacuum oven the crude product was obtained. The crude product was purified by flash chromatography on a silica gel column with dichloromethane as the elution solvent to afford the compound **4** as a yellow solid (18.05 g, 47.8 mmol, 60.1% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.08 (s, 1 H), 7.87 (d, 4 H), 7.08 (d, 4 H), 4.13 (t, 2H), 3.72 (t, 2 H), 1.75 (m, 4 H), 1.64-1.28 (m, 4 H).

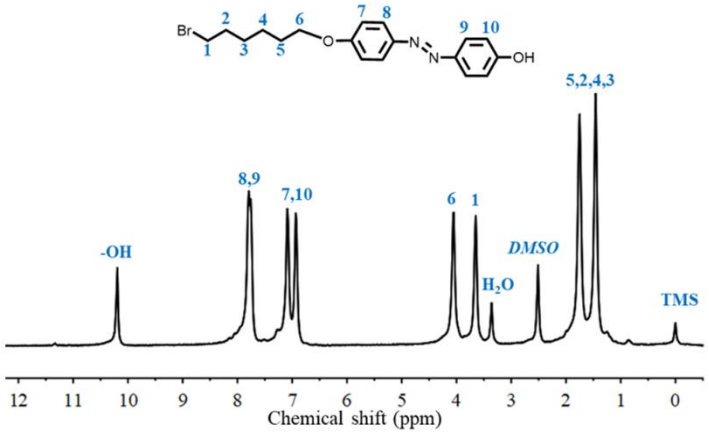


Fig. S4. ^{1}H NMR spectrum of the compound **4** in DMSO-d_6 at room temperature.

Synthesis and characterization of the intermediate compound **5**

The synthesis of the compound **5** was according to a modified literature procedure.[4] To a 250 mL round bottom flask equipped with a reflux condenser and a stirring bar was added the as-prepared compound **4** (9.43 g, 25.0 mmol), 1,6-dibromohexane (18.30 g, 75.0 mmol), potassium carbonate (K_2CO_3, 10.36 g, 75.0 mmol), catalytic amount of KI (0.17 g, 1 mmol), and anhydrous acetone (200 mL). The reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into deionized water (500 mL). The precipitate was filtrated and purified through flash chromatography on a silica gel column with the eluent of petroleum and dichloromethane (v/v, 1/1) to afford the compound **5** (6.13 g, 11.35 mmol, 45.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, 4 H), 6.98 (d, 4 H), 4.23 (t, 4 H), 3.62 (t,

4 H), 1.88-1.69 (m, 8 H), 1.38-1.64 (m, 8 H).

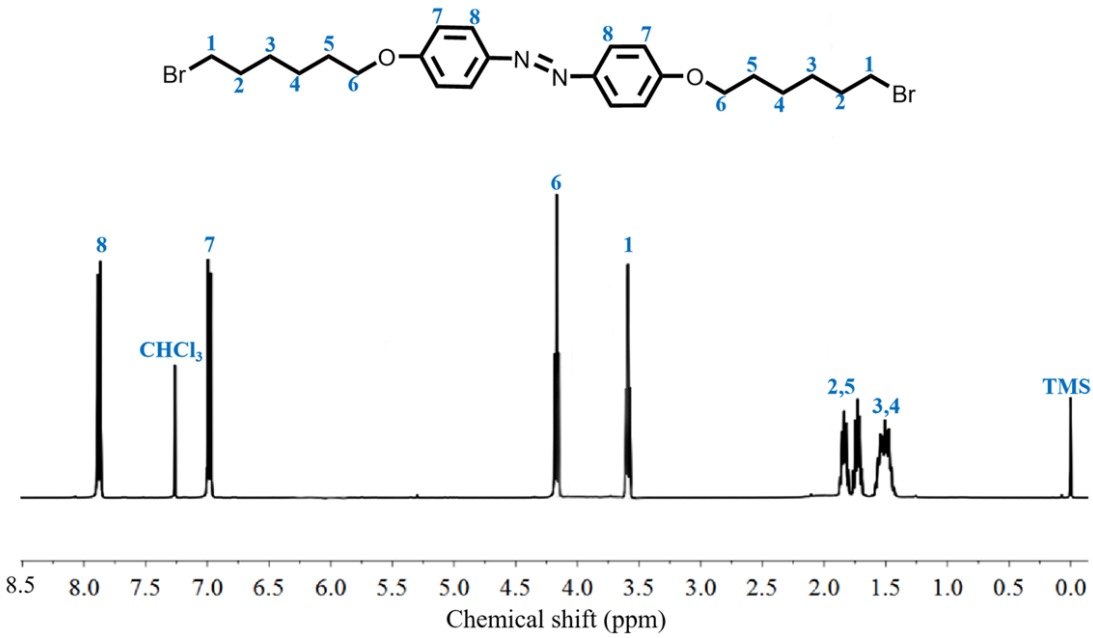


Fig. S5. ^{1}H NMR spectrum of the compound **5** in $CDCl_3$ at room temperature.

Synthesis and characterization of the precursor compound azobenzene-containing diacrylate **6**

The synthesis of the precursor compound **6** was according to a modified literature procedure.[5] To a 250 mL round bottom flask equipped with a reflux condenser and a stirring bar was added the as-prepared intermediate **5** (4.32 g, 8.0 mmol), NaOH (1.20 g, 30.0 mmol), acrylic acid (1.38 g, 19.2 mmol), a small amount of polymerization inhibitor hydroquinone (0.11 g, 1 mmol), and DMF (50 mL). The reaction mixture was vigorously stirred at 120 ºC for 24 h. After cooling to room temperature, the reaction mixture was poured into deionized water (200 mL), and extracted with chloroform (200 mL). The organic phase was washed with deionized water (3 × 100 mL). The collected organic layer was dried with magnesium sulfate and concentrated via rotary evaporation, after purified through flash chromatography on a silica gel column with dichloromethane as the elution solvent to afford the diacrylate precursor compound **6** (3.42 g, 6.54 mmol, 82.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07 (d, 4 H), 6.89 (d, 4 H), 6.33 (m, 2 H), 6.17 (d, 2 H), 5.87 (d, 2 H), 4.25 (t, 4 H), 4.03 (t, 4 H), 1.88-1.68 (m, 8 H), 1.28-1.64 (m, 8 H).

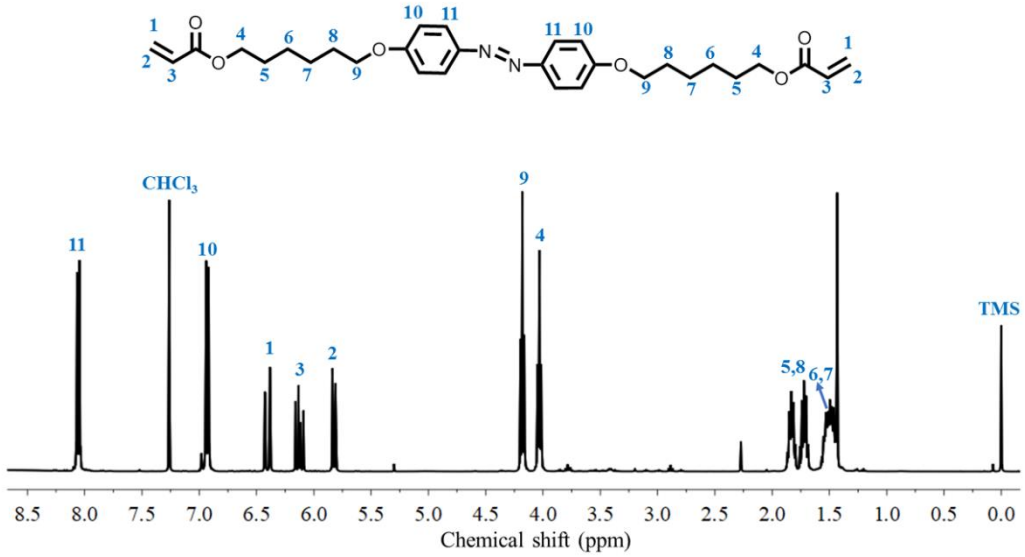


Fig. S6. ^{1}H NMR spectrum of the diacrylate **6** in $CDCl_3$ at room temperature.

Synthesis and characterization of the intermediate compound **7**

The synthesis of the compound **7** was according to a modified literature procedure.[6, 7] To a 250 mL three-neck round bottom flask equipped with an addition funnel and a stirring bar, 3-chloro-2-chloromethyl-1-propene (5.00 g, 40.0 mmol), potassium ethyl xanthogenate (14.11 g, 88.0 mmol), and ethanol (150 mL) were added, the mixture solution was reacted with vigorously stirring overnight under nitrogen at room temperature. Then the reaction mixture was concentrated via rotary evaporation, and the obtained crude product was redissolved in ethyl ether (200 mL) and washed with deionized water (3 × 150 mL), after dried with magnesium sulfate, concentrated via rotary evaporation and dried to afford the compound **7** (7.49 g, 25.2 mmol, 63.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.27 (s, 2 H), 4.65 (m 4 H), 3.83 (s, 4 H), 1.47 (t, 6 H).

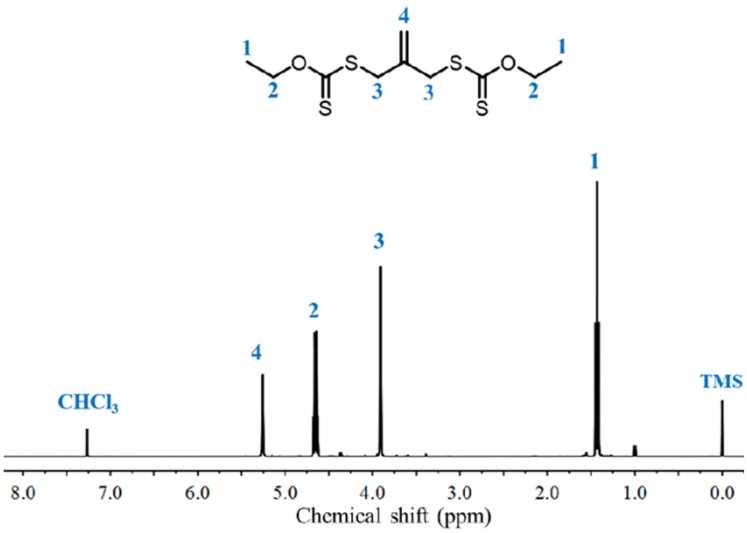


Fig. S7. ^{1}H NMR spectrum of the compound **7** in $CDCl_3$ at room temperature.

Synthesis and characterization of the precursor compound allyl dithiol **8**

The synthesis of the precursor compound **8** was according to a modified literature procedure.[6, 7] To a 250 mL three-neck round bottom flask equipped with an addition funnel and a stirring bar was added ethylene diamine (1.12 mL, 16.8 mmol), and deionized water (10 mL). Then the as-prepared compound **7** (5.00 g, 16.8 mmol) was added dropwise over 30 min with stirring at room temperature. After stirring at room temperature for another 4 h, the reaction mixture was poured into sulfuric acid (1.3 mol/L, 200 mL), and extracted with diethyl ether (150 mL). The collected organic layer was washed with deionized water (3 × 150 mL), and dried with sodium sulfate, after concentrated via rotary evaporation to obtain the crude product, further through reduced pressure distillation (80 °C, 1 mm Hg) to afford the precursor compound allyl dithiol **8** (1.92 g, 16.0 mmol, 95.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.02 (s, 2 H), 3.38 (m, 4 H), 1.51 (t, 2 H).

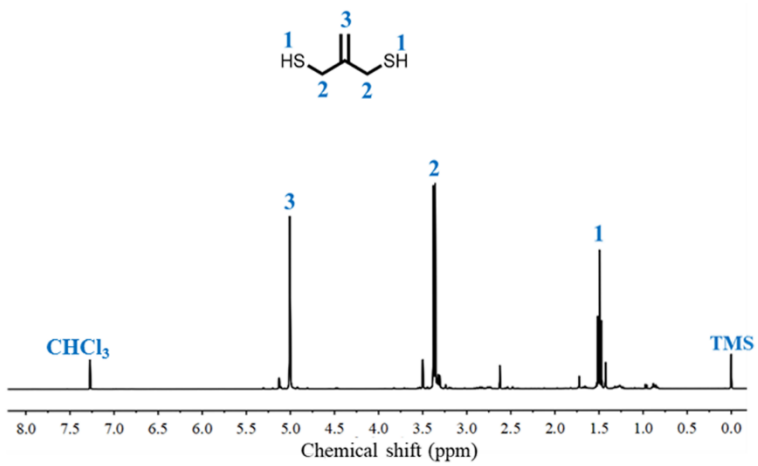


Fig. S8. ^{1}H NMR spectrum of the allyl dithiol **8** in $CDCl_3$ at room temperature.

S2. Supplementary figures

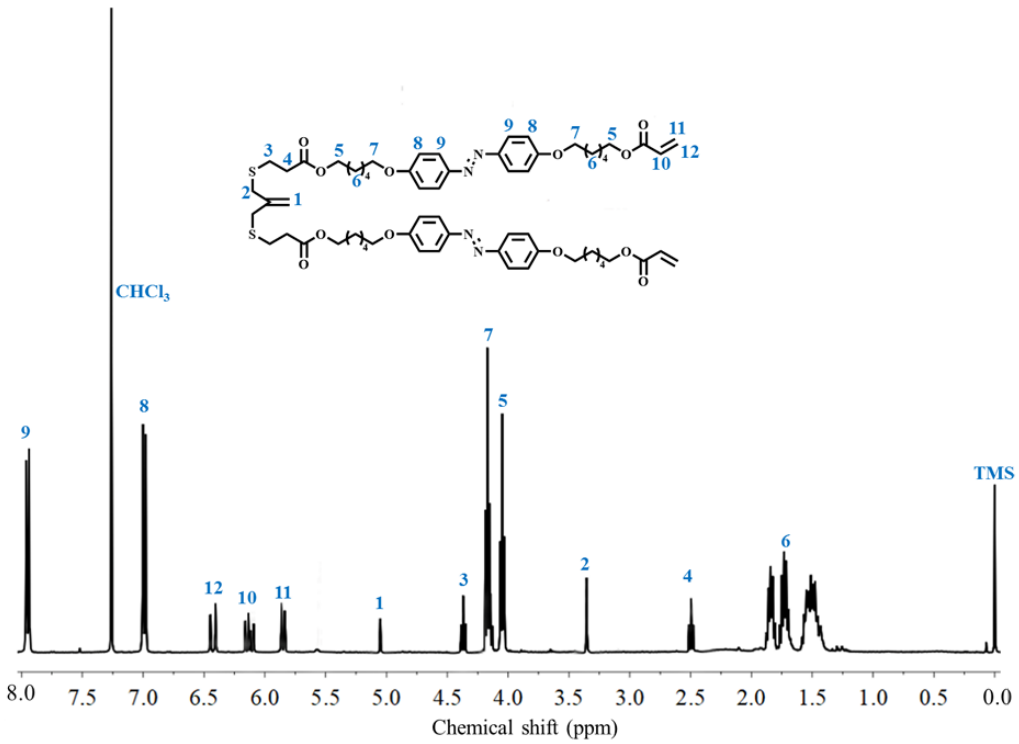


Fig. S9 ^{1}H NMR spectrum of azobenzene-containing allyl sulfide-based diacrylate dynamic crosslinker **Azo-S-Linker** in $CDCl_3$ at room temperature.

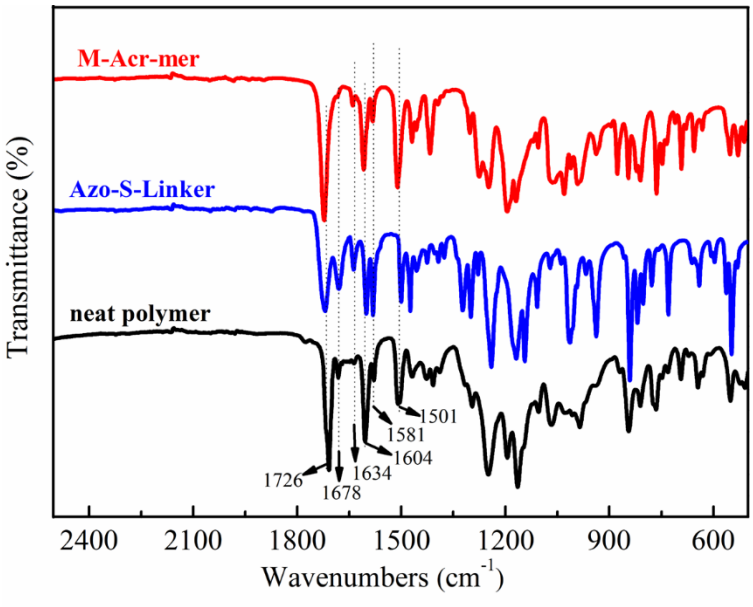


Fig. S10 FTIR spectra comparison of the monomer M-Acr-mer, the crosslinker Azo-S-Linker and the neat LCE polymer.

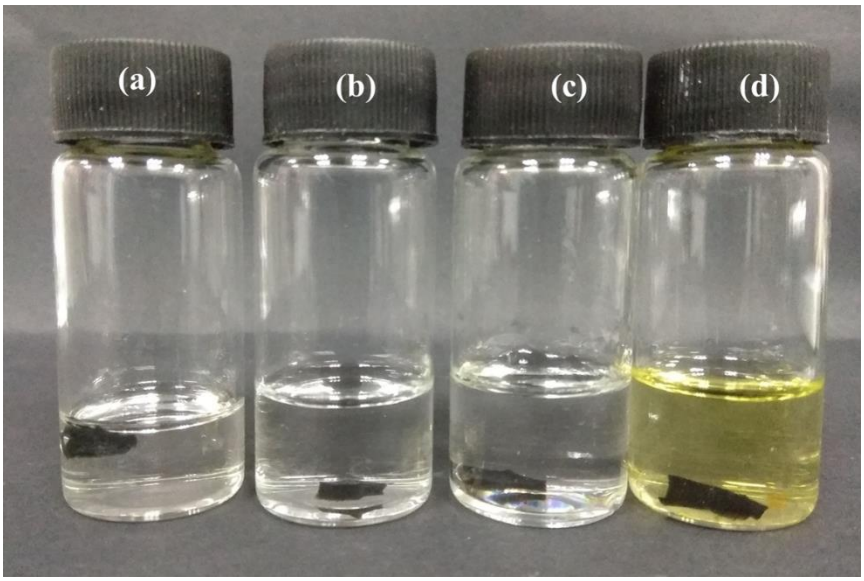


Fig. S11 Swelling experiments of polydomain SWCNT/LCE composite films in various organic solvents: (a) DCM, (b) THF, (c) toluene, and (d) DMF.

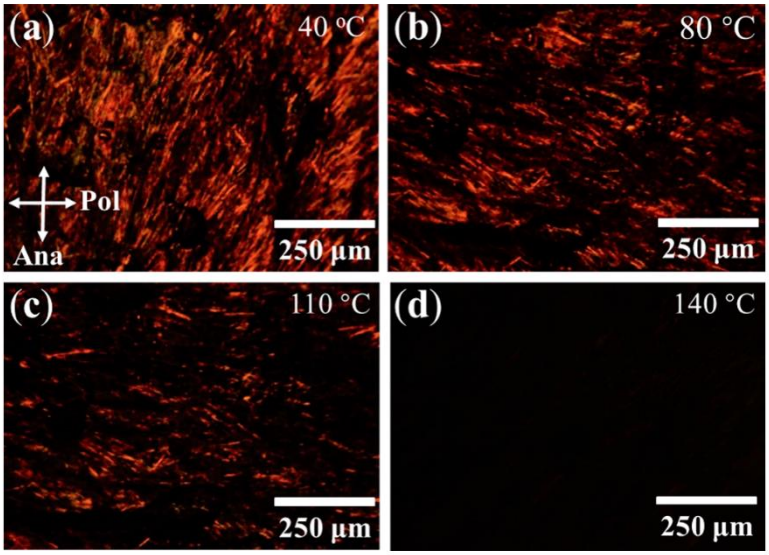


Fig. S12 POM images of a polydomain SWCNT/LCE composite film at different temperature of (a) 40 ºC, (b) 80 ºC, (c) 110 ºC, (d) 140 ºC. Pol: polarizer, Ana: analyzer, Scale bar: 250 µm.

S3. Supplementary references

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