Electronic Supplementary Information

Preparation, Photo-induced Deformation Behavior and Application of Hydrogen-bonded Crosslinked Liquid Crystalline Elastomers Based on α-Cyanostilbene

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The nuclear magnetic data for monomers are listed as follows.

M0CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.67 (d, *J* = 8.7 Hz, 2H, Ar-***H***), 7.43 (s, 1H, -C=C-***H***), 7.20 (d, *J* = 8.7 Hz, 2H, Ar-***H***), 6.96 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 6.37 (s, 1H, -C=C-***H***), 5.79 (s, 1H, -C=C-***H***), 4.01 (t, *J* = 6.5 Hz, 2H, -OC***H***$_2$-), 2.07 (s, 3H, -C=C-C***H***$_3$), 1.87 – 1.70 (m, 2H, -C***H***$_2$-), 1.45 (dd, *J* = 15.1, 7.1 Hz, 2H, -C***H***$_2$-), 1.29 (d, *J* = 21.9 Hz, 16H, -C***H***$_2$-), 0.88 (t, *J* = 6.8 Hz, 3H, -C***H***$_2$-). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.30, 162.36, 151.68, 142.60, 133.90, 132.45, 129.19, 127.81, 126.65, 125.38, 121.39, 121.16, 114.61, 108.47, 69.66, 31.73, 29.10, 28.80, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{31}H_{39}NO_3$, 473.57; found, 473.29.

M2CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H, Ar-***H***), 7.59 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.35 (s, 1H, -C=C-***H***), 6.96 (dd, *J* = 8.4, 7.1 Hz, 4H, Ar-***H***), 6.16 (s, 1H, -C=C-***H***), 5.61 (s, 1H, -C=C-***H***), 4.52 (t, 2H, -OC***H***$_2$-), 4.27 (t, 2H, -OC***H***$_2$-), 4.01 (t, *J* = 6.5 Hz, 2H, -OC***H***$_2$-), 1.96 (s, 3H, -C=C-C***H***$_3$), 1.87 – 1.70 (m, 2H, -C***H***$_2$-), 1.54 – 1.40 (m, 2H, -C***H***$_2$-), 1.41 – 1.06 (m, 16H, -C***H***$_2$-), 0.88 (t, *J* = 6.8 Hz, 3H, -C***H***$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.15, 162.36, 158.57, 142.60, 137.72, 132.45,

128.37, 127.81, 125.31, 124.72, 121.16, 116.15, 114.61, 108.47, 69.66, 67.38, 62.34, 31.73, 29.10, 28.80, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{33}H_{43}NO_4$, 517.70; found, 517.38.

M4CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.56 (d, *J* = 8.9 Hz, 2H, Ar-***H***), 7.34 (s, 1H, -C=C-***H***), 6.94 (dd, *J* = 8.8, 7.5 Hz, 4H, Ar-***H***), 6.11 (s, 1H, -C=C-***H***), 5.56 (s, 1H, -C=C-***H***), 4.23 (t, *J* = 5.9 Hz, 2H, -OC***H***$_2$-), 4.01 (dd, *J* = 13.4, 6.6 Hz, 4H, -OC***H***$_2$-), 1.95 (s, 3H, -C=C-C***H***$_3$), 1.84 – 1.67 (m, 4H, -C***H***$_2$-), 1.45 (dd, *J* = 14.9, 7.2 Hz, 2H, -C***H***$_2$-), 1.29 (d, *J* = 21.9 Hz, 16H, -C***H***$_2$-), 0.87 (t, *J* = 6.8 Hz, 3H, -C***H***$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.15, 162.36, 158.57, 142.60, 137.72, 132.45, 128.37, 127.81, 125.31, 124.72, 121.16, 116.15, 114.61, 108.47, 69.66, 66.85, 31.73, 29.10, 28.80, 27.43, 26.93, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{35}H_{47}NO_4$, 545.57; found, 545.35.

M6CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.56 (d, *J* = 8.9 Hz, 2H, Ar-***H***), 7.34 (s, 1H, -C=C-***H***), 6.94 (dd, *J* = 8.8, 7.5 Hz, 4H, Ar-***H***), 6.11 (s, 1H, -C=C-***H***), 5.56 (s, 1H, -C=C-***H***), 4.23 (t, *J* = 5.9 Hz, 2H, -OC***H***$_2$-), 4.01 (dd, *J* = 13.4, 6.6 Hz, 4H, -OC***H***$_2$-), 1.95 (s, 3H, -C=C-C***H***$_3$), 1.84 – 1.67 (m, 2H, -C***H***$_2$-), 1.45 (dd, *J* = 14.9, 7.2 Hz, 6H, -C***H***$_2$-), 1.29 (d, *J* = 21.9 Hz, 16H, -C***H***$_2$-), 0.87 (t, *J* = 6.8 Hz, 3H, -C***H***$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.15, 162.36, 158.57, 142.60, 137.72, 132.45, 128.37, 127.81, 125.31, 124.72, 121.16, 116.15, 114.61, 108.47, 69.66, 66.85, 31.73, 29.32, 29.10, 28.80, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{37}H_{51}NO_4$, 573.18; found, 573.38.

M8CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.57 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.35 (s, 1H, -C=C-***H***), 6.94 (dd, *J* = 8.7, 6.9 Hz, 4H, Ar-***H***), 6.10 (s, 1H, -C=C-***H***), 5.55 (s, 1H, -C=C-***H***), 4.15 (t, *J* = 6.7 Hz, 2H, -OC***H***$_2$-), 4.00 (dd, *J* = 14.4, 6.7 Hz, 4H, -OC***H***$_2$-), 1.95 (s, 3H, -C=C-C***H***$_3$), 1.86 – 1.74 (m, 4H, -C***H***$_2$-), 1.68 (dd, *J* = 13.6, 6.8 Hz, 2H, -C***H***$_2$-), 1.52 – 1.42 (m, 4H, -C***H***$_2$-), 1.38 (s, 6H, -C***H***$_2$-), 1.29 (d, *J* = 22.5 Hz, 16H, -C***H***$_2$-), 0.88 (t, *J* = 6.8 Hz, 3H, -C***H***$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.15, 162.36, 158.57, 142.60, 137.72, 132.45, 128.37, 127.81,

125.31, 124.72, 121.16, 116.15, 114.61, 108.47, 69.66, 66.85, 31.73, 29.32, 29.10, 28.80, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{39}H_{55}NO_4$, 601.86; found, 601.41.

M10CS12 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.57 (d, *J* = 8.8 Hz, 2H, Ar-***H***), 7.35 (s, 1H, -C=C-***H***), 6.94 (dd, *J* = 8.7, 6.4 Hz, 4H, Ar-***H***), 6.10 (s, 1H, -C=C-***H***), 5.55 (s, 1H, -C=C-***H***), 4.14 (t, *J* = 6.7 Hz, 2H, -OC***H***$_2$-), 4.00 (dd, *J* = 14.9, 6.6 Hz, 4H, -OC***H***$_2$-), 1.95 (s, 3H, -C=C-C***H***$_3$), 1.79 (dd, *J* = 12.6, 6.4 Hz, 4H, -C***H***$_2$-), 1.72 – 1.61 (m, 2H, -C***H***$_2$-), 1.54 – 1.41 (m, 4H, -C***H***$_2$-), 1.30 (d, *J* = 23.0 Hz, 26H, -C***H***$_2$-), 0.88 (t, *J* = 6.8 Hz, 3H, -C***H***$_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.15, 162.36, 158.57, 142.60, 137.72, 132.45, 128.37, 127.81, 125.31, 124.72, 121.16, 116.15, 114.61, 108.47, 69.66, 66.85, 31.73, 29.32, 29.10, 28.80, 26.58, 23.16, 19.10, 14.00. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{41}H_{59}NO_4$, 629.91; found, 629.44.

ME6UPy ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.14 (s, 1H, -N***H***-), 11.87 (s, 1H, -N***H***-), 10.15 (s, 1H, -N***H***-), 6.13 (s, 1H, -C=C-***H***), 5.85 (s, 1H, -C=C-***H***), 5.59 (s, 1H, -C=C-***H***), 5.01 (s, 1H, -N***H***-), 4.32 (s, 4H, -OC***H***$_2$-), 3.34 – 3.01 (m, 4H, , NH-C***H***$_2$-), 2.24 (s, 3H, -C=C-C***H***$_3$), 1.95 (s, 3H, -C=C-C***H***$_3$), 1.77 – 1.26 (m, 99, -C***H***$_2$-). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.16, 162.50, 158.13, 156.84, 156.45, 148.06, 137.72, 124.72, 111.57, 62.67, 60.77, 41.16, 40.10, 29.58, 27.49, 19.70, 19.10. Mass Spectrometry (MS) (m/z) [M] Calcd for $C_{19}H_{29}N_5O_6$, 423.46; found, 423.21.

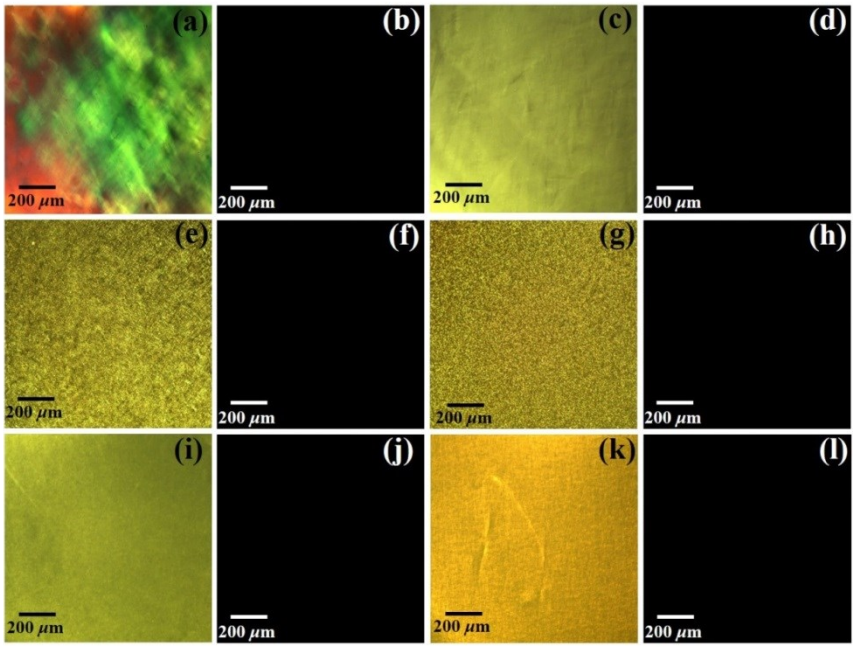

Fig. S1 POM photographs of LCE-0CS at 122℃ (a) and 125℃ (b), LCE-2CS at 102℃ (c) and 105℃ (d), LCE-4CS at 95℃ (e) and 98℃ (f), LCE-6CS at 82℃ (g) and 85℃ (h), LCE-8CS at 67℃ (i) and 70℃ (j), LCE-10CS at 71℃ (k) and 74℃ (l).

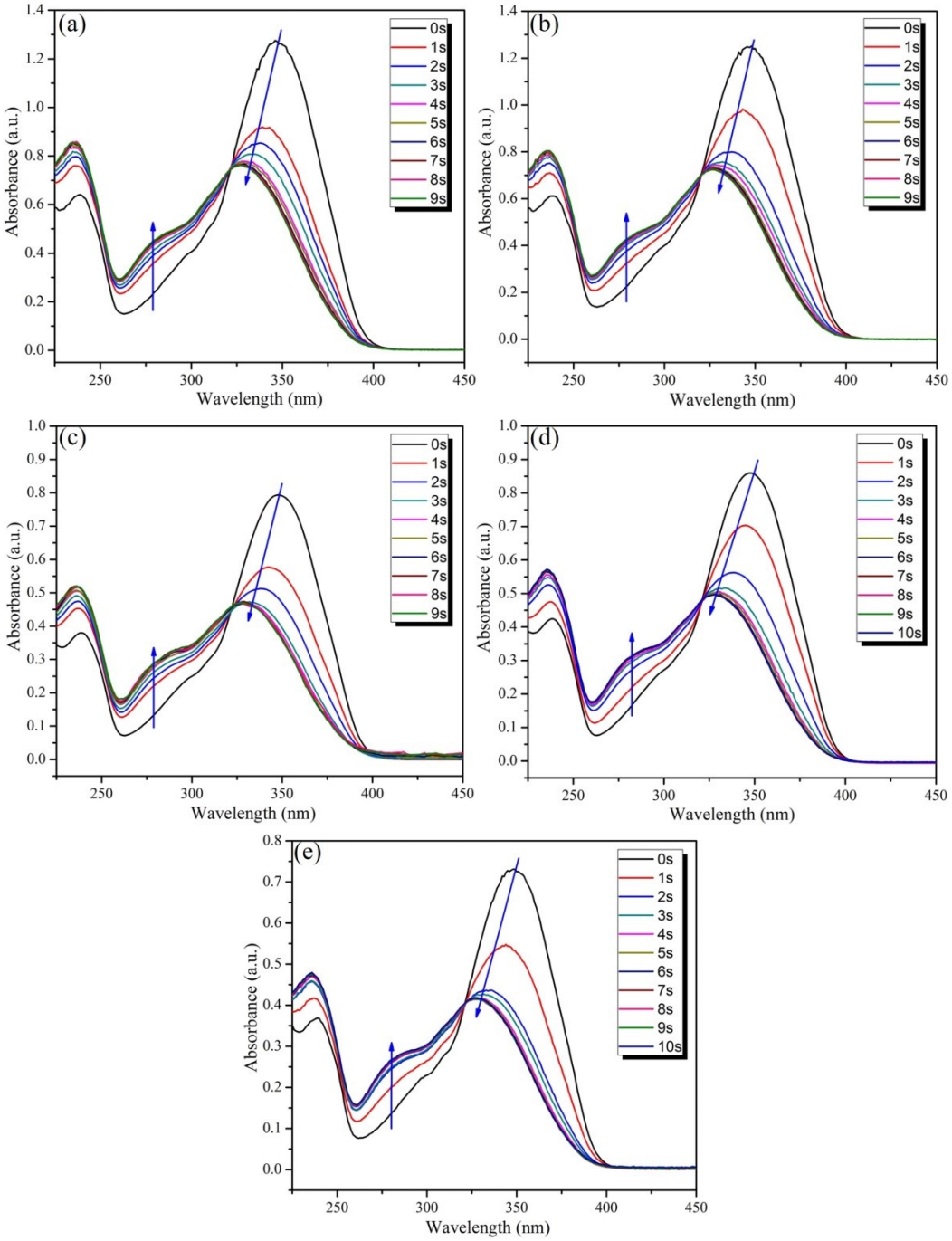

Fig. S2 UV-vis spectral changes in dependence of time for LCE-mCS dilute THF solution upon exposure to 365 nm UV light. (a) LCE-0CS, (b) LCE-2CS, (c) LCE-4CS, (d) LCE-6CS, (e) LCE-10CS.

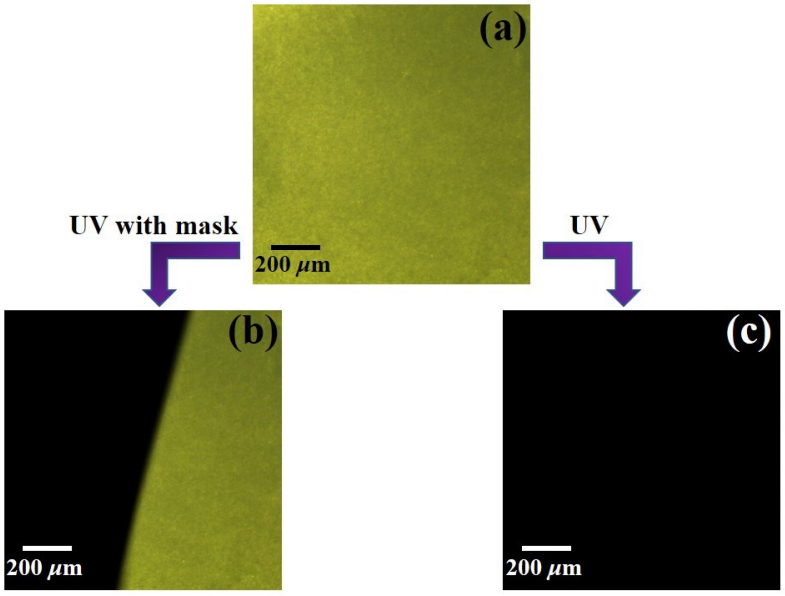

Fig. S3 POM images of LCE-8CS film taken at 25℃ (a) and then irradiated with 365 nm UV light (120 mW cm^{-2}) for 30 min with (b) or without a mask (c).