Supporting Information for

**Photo-Responsive Polysiloxane-Based Azobenzene Liquid Crystalline
Polymers Prepared by Thiol–Ene Click Chemistry**

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4-(4-Butoxy-phenylazo)-benzene-1,3-diol (3): ^1H NMR (500 MHz, CDCl_3) δ 7.77 (m, 3H), 6.99(d, J = 6.8 Hz, 2H), 6.54(m, 2H), 4.03 (t, J = 6.8 Hz, 2H), 1.81 (m, 2H), 1.51 (m, 2H), 1.01 (t, 3H, J = 6.5 Hz).

Figure S1. ^1H NMR spectrum of Compound 3.

4-Butoxy-benzoic acid 4-(4-butoxy-phenylazo)-3-hydroxy-phenyl ester (5): ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.9$ Hz, 2H), 7.93 (d, $J = 8.9$ Hz, 2H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.02-6.89 (m, 6H) , 4.07 (t, $J = 6.5$ Hz, 4H) , 1.86 (m, 4H) , 1.59 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H)

Figure S2. ^1H NMR spectrum of Compound 5.

4-Butoxy-benzoic acid 4-(4-butoxy-phenylazo)-3-hex-5-enyloxy-phenyl ester

(A44V6): ^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.9$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 1H), 6.99 (dd, $J = 8.9$, 2.1 Hz, 5H), 6.87 (dd, $J = 8.8$, 2.2 Hz, 1H), 5.84 (m, , 1H), 5.14 – 4.84 (m, 2H), 4.18 (t, $J = 6.4$ Hz, 2H), 4.06 (t, $J = 6.5$ Hz, 4H), 2.17 (m, 2H), 2.01 – 1.88 (m, 2H), 1.88 – 1.73 (m, 4H), 1.73 – 1.60 (m, 4H), 1.53 (m, 4H), 1.00 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 163.7, 138.6, 132.3, 124.8, 117.6, 114.7, 114.4, 114.1, 108.3, 69.8, 68.1, 33.4, 31.2, 28.6, 25.4, 19.2, 13.8.

Figure S3. ^1H NMR spectrum of A44V6.

Figure S4. ^{13}C NMR spectrum of A44V6.

PMMS-A44V6: ^1H NMR (500 MHz, CDCl_3) δ 8.17 (s, 2H), 7.95 (s, 2H), 7.80 (s, 1H), 7.01 (s, 5H), 6.90 (s, 1H), 4.19 (s, 2H), 4.08 (s, 4H), 2.71 (s, 4H), 2.54 (s, 2H), 1.94 – 1.30 (m, 20H), 1.03 (s, 6H), 0.66 (s, 2H), 0.12 (s, 4H).

Figure S5. ^1H NMR spectrum of polymer **PMMS-A44V6**.