Supporting Information for

First Thiol-yne Click Chemistry approach for Liquid Crystalline Elastomer preparation

D. Martella,\textsuperscript{a,b,c} C. Parmeggiani,*\textsuperscript{a,d} D. S. Wiersma,\textsuperscript{a} M. Piñol\textsuperscript{b} and L. Oriol\textsuperscript{b}

\textsuperscript{a}European Laboratory for Non-Linear Spectroscopy (LENS), University of Florence, Via Nello Carrara 1, 50019 Sesto Fiorentino, Italy. E-mail: camilla.parmeggiani@lens.unifi.it
\textsuperscript{b}Dipartimento di Chimica “Ugo Schiff”, University of Florence, via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy.
\textsuperscript{c}Instituto de Ciencia de Materiales de Aragón (ICMA), Departamento de Química Orgánica, Facultad de Ciencias, CSIC-Universidad de Zaragoza, C./Pedro Cerbuna 12, 50009 Zaragoza, Spain.E-mail: loriol@unizar.es
\textsuperscript{d}Istituto Nazionale di Ottica (CNR-INO), U.O.S. Sesto Fiorentino, Via Nello Carrara 1, 50019 Sesto Fiorentino, Italy.
Summary

Figure S1. $^1$H-NMR spectrum (400 MHz, CDCl$_3$) of compound M1. S3

Figure S2. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of compound M1. S3

Figure S3. $^1$H-NMR spectrum (400 MHz, CDCl$_3$) of compound M2. S4

Figure S4. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of compound M2. S4

Figure S5. DSC traces on heating and on cooling of M1, 7 and M2. S5

Figure S6. FTIR spectra of the monomers. S6

Figure S7. FTIR spectra of the LCE films. S7

Figure S8. POM images and XDR trace for E-CL$_1$$^{20}$ film. S7

Figure S9. DSC traces corresponding on heating and on cooling of LCE films. S8

Figure S10. POM images of E-CL$_1$$^{20}$ film at different temperatures. S9

Figure S11. TGA traces of LCE films. S9

Figure S12. Stress-strain curves for E-CL$_1$$^{20}$ film. S10
Figure S1. $^1$H-NMR spectrum (400 MHz, CDCl$_3$) of compound M1.

Figure S2. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of compound M1.
Figure S3. $^1$H-NMR spectrum (400 MHz, CDCl$_3$) of compound M2.

Figure S4. $^{13}$C-NMR spectrum (100 MHz, CDCl$_3$) of compound M2.
Figure S5. DSC traces (10 °C/min) corresponding to the second cycle of heating and cooling of M1, 7 and M2.
Figure S6. FTIR spectra of the monomers.
Figure S7. FTIR spectra of the LCE films.

Figure S8. POM images and XDR trace for E-CL\textsubscript{20} film. a) POM image of the film (20); b) same image rotates of 45° in respect of the analyzer. c) XRD pattern, the arrow indicates the alignment direction.
Figure S9. DSC traces (10 °C/min) corresponding to the second cycle of heating and cooling of LCE films.
Figure S10. POM images of E-CL_{10} film at different temperatures. Images registered at 90 °C, 120 °C and 160 °C (up to down) while rotating the sample 0, 45 and 90° in relation to the preferential alignment direction (left to right).

Figure S11. TGA traces of the LCE films.
Figure S12. Stress-strain curves for E-CL20 at room temperature.