Supporting Information

Synthesis of body temperature-triggerable dynamic liquid crystal elastomers using Diels-Alder crosslinkers

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1. Experimental section

1.1. Materials

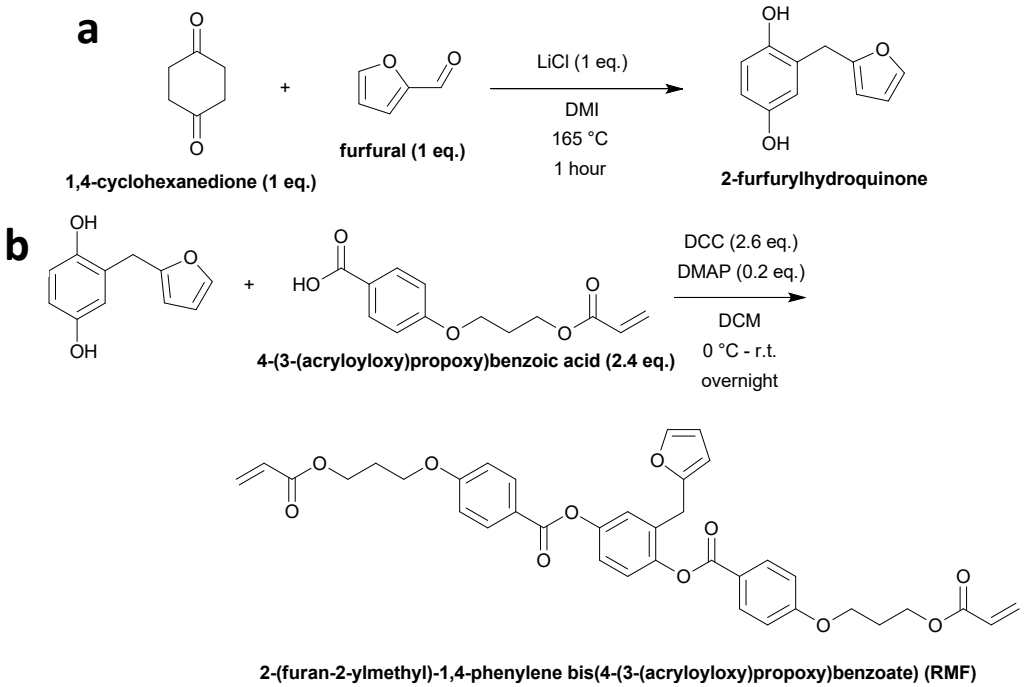
All commercially available chemicals were used without further purification.

For the synthesis of the comonomers, the Diels-Alder (DA) adducts and liquid crystal elastomers (LCEs), 1,1'-(methylenedi-1,4-phenylene)bismaleimide (BM, 95%), 4-methoxyphenol (MEHQ, Reagent Plus®, 99%), anhydrous lithium chloride (LiCl), furfural (99%), 1,3-dimethyl-2-imidazolidinone (DMI), N,N'-Dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP), dichloromethane (DCM, ≥99,5%), acryloyl chloride (≥97%, contains ~400 ppm phenothiazine as stabilizer), triethylamine (TEA, ≥99%), tetrahydrofuran (THF, ≥99,5%), dipropylamine (DPA, 99%) and 2,2'-(ethylenedioxy) diethanethiol (EDDET, 95%) were purchased from Sigma-Aldrich. 1,4-bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]−2-methylbenzene (RM257, 98%) from Daken Chemicals. 2,5-furandimethanol (98%) from AA Blocks Inc. 4-(3-(acryloyloxy)propoxy)benzoic acid (97%) from AmBeed. Aluminum oxide (activated, neutral, Brockmann Grade 11) from Alfa Aesar. 1,4-cyclohexanedione, sodium hydroxide (NaOH, pellets, certified ACS) and sand (20-30 mesh) from Fisher Scientific.

1.2. Characterizations

^{1}H and ^{13}C NMR spectra of the synthesized comonomers, RMF and BAMF, and their respective Diels-Alder adducts with the BM were recorded on a Bruker Advance-III 300 MHz spectrometer. For the kinetic study of the Diels-Alder reaction between the comonomers and the BM, the ^{1}H NMR spectra were recorded on a Bruker 400 MHz apparatus. Chemical shifts were reported in parts per million (ppm). Deuterated dimethylsulfoxide (DMSO-d_6 : δ = 2.500 ppm (^{1}H NMR) and δ = 39.520 ppm (^{13}C NMR)) was used as a reference for the chemical shifts and tetramethylsilane (TMS) as an internal standard. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the DADCB LCEs were recorded on a Cary 630 FTIR spectrometer. The mechanical properties measurements of the LCE strips were performed with an Instrom5965 universal testing system at room temperature. Thermal phase transitions of the RMF comonomer and LCEs with different contents of comonomers were measured using a TA Q200 differential scanning calorimeter with a temperature range of -50 to 170 °C at a rate of 10 °C/min. The experiments were under a nitrogen atmosphere (flow rate of 50 mL/min) with a quantity of 5 to 10 mg of sample. 2D-Wide-angle X-ray scattering (2D-WAXS) measurements were performed on a Bruker AXS Nanostar system equipped with a Microfocus Copper Anode at 45 kV/0.65 mA, MONTAL OPTICS, and a VANTEC 2000 2D-detector at a distance of 55 mm from the samples and calibrated with a Silver Behenate standard. High-resolution mass spectra (HRMS) were obtained using a Shimadzu LC-QqTOF Nexera coupled to a Bruker maXis mass spectrometer, allowing for electrospray ionization (ESI). Polarized optical microscopy (POM) observations were carried out on a LEICA DMRP equipped with a LEICADC300 camera.

1.3. Synthesis of the comonomers, DA adducts and LCEs



Scheme S1. Synthetic route of the RMF comonomer. (A) Aldol-condensation followed by isomerization of the α, β – unsaturated ketone. (B) Alcohol and carboxylic acid coupling using DCC.

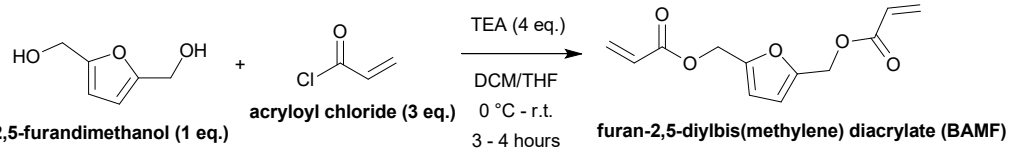
Synthesis of 2-furfurylhydroquinone

As shown in Scheme S1a, 1,4-cyclohexanedione (1.00 g, 8.92 mmol), furfural (0.8571 g, 8.92 mmol), anhydrous LiCl (0.3782 g, 8.92 mmol) and DMI (10 mL) were mixed in a 50 mL flask and stirred for 10 minutes at room temperature. The mixture was then heated to 165 ℃ for 1 hour. The reaction completion was followed by TLC. Afterwards, it was cooled to room temperature, mixed with water (60 mL) and extracted with ethyl acetate (2 x 30 mL). The combined organic layers were washed with water (2 x 20 mL), dried with anhydrous $MgSO_4$ and filtered. The organic solvent was evaporated in vacuo and brown liquid was recovered as the crude product. The compound was purified by flash chromatography (90:10 hexane:ethyl acetate) to obtain a lightly yellow oil (1.43 g, 84.4%).

Synthesis of 2-(furan-2-ylmethyl)-1,4-phenylene bis(4-(3-(acryloyloxy)propoxy)benzoate) (RMF)

In a 100 mL flask, 2-furfurylhydroquinone (1.05 g, 5.54 mmol), 4-(3-(acryloyloxy)propoxy)benzoic acid (3.33 g, 13.85 mmol), DCC (2.97 g, 14.40 mmol), DMAP (135.4 mg, 1.11 mmol) and DCM (0.2 M, 27.7 mL) were mixed at 0 ℃. The resulting mixture was then slowly heated to room temperature and left overnight. The reaction completion was determined by TLC, then the precipited urea was filtered off. Afterwards, the mixture was washed with a saturated solution of sodium bicarbonate ($NaHCO_3$), water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. A brown

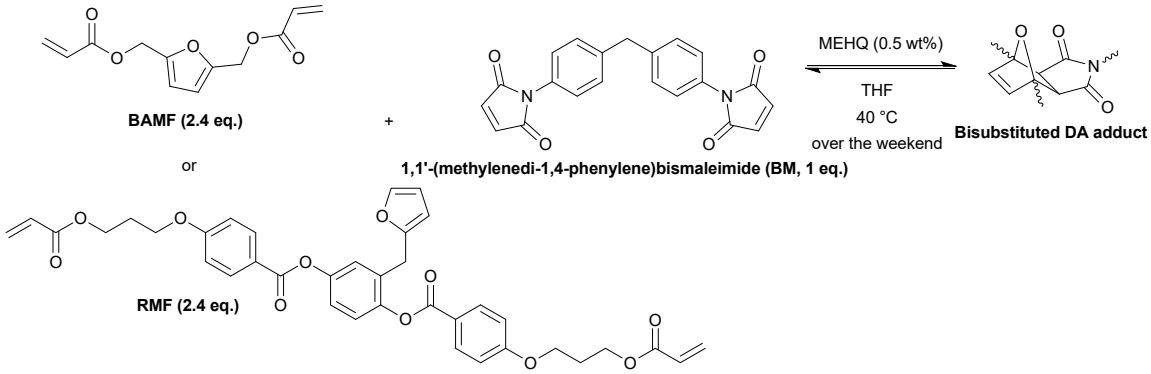
solid is obtained and purified by flash chromatography (95:5 hexane:ethyl acetate). The resulting yellow solid is further purified by recrystallization using an ethyl acetate/hexane solvent mixture. The final product is a white solid (1.58 g, 43.6%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.08 (dd, *J* = 8.8, 4.2 Hz, 4H), 7.47 (d, *J* = 1.0 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.29-7.19 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 4H), 6.44-6.28 (m, 3H), 6.19 (dd, *J* = 17.3, 10.2 Hz, 2H), 6.02 (d, *J* = 3.0 Hz, 1H), 5.95 (dd, *J* = 10.2, 1.7 Hz, 2H), 4.29 (t, *J* = 6.3 Hz, 4H), 4.20 (t, *J* = 5.8 Hz, 4H), 3.95 (s, 2H), 2.13 (p, J = 6.2 Hz, 4H) (see **Figure S1**). ^{13}C NMR (76 MHz, DMSO-d_6) δ 165.95, 164.64, 164.28, 163.45, 152.67, 148.54, 146.67, 142.45, 132.53, 132.19, 132.08, 128.74, 124.36, 124.10, 121.82, 121.33, 121.26, 115.20, 110.93, 107.03, 65.34, 61.54, 28.91, 28.38 (see **Figure S2**). **HRMS (ESI)** m/z : calcd. for $[M+Na]^+$: 677.1993, found 677.1992 (see **Figure S11**).



Scheme S2. Synthetic route for the BAMF comonomer.[1]

Synthesis of furan-2,5-diylbis(methylene) diacrylate (BAMF)

In a three-necked flask, 2,5-furandimethanol (2.50 g, 19.51 mmol) was dissolved in DCM (70 mL) and a few drops of THF. The solution was then cooled to 0 °C in an ice bath and put under an inert atmosphere (N_2). TEA (7.90 g, 78.04 mmol) was added dropwise to the solution and the mixture was stirred for 10 minutes. Meanwhile, acryloyl chloride (5.30 g, 58.53 mmol) is diluted in DCM (30 mL). Afterwards, the acryloyl chloride solution is slowly added dropwise to the first mixture (~15 minutes). When the addition is complete, the mixture is slowly heated to room temperature and left to react overnight while stirring. The formed solution has a deep red colour and the reaction completion is determined by TLC. Hexane is then added to the solution and the mixture is stirred for 10 minutes at room temperature. A precipitate forms and is filtered off. Next, the solution is concentrated under reduced pressure. The brown crude product obtained is dissolved in ethyl acetate, washed with brine (2 x 50 mL), dried with anhydrous $MgSO_4$, filtered and the resulting organic layer is, again, concentrated under reduced pressure. A reddish oil is obtained, it is dissolved in a ethyl acetate/hexane mixture (10:1 ethyl acetate:hexane). A brown precipitate forms and the solution is filtered through a plug of aluminum oxide twice. Each plug is washed with a solution of ethyl acetate/hexane (1:4 ethyl acetate:hexane) after their respective filtration. A clear solution is harvested and concentrated under reduced pressure. The final product is a yellowish oil (3.1221 g, 67.7%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.55 (s, 2H), 6.36 (dd, *J* = 17.2, 1.6 Hz, 2H), 6.20 (dd, *J* = 17.2, 10.2 Hz, 2H), 5.96 (dd, *J* = 10.2, 1.6 Hz, 2H), 5.14 (s, 4H) (see **Figure S3**). ^{13}C NMR (76 MHz, DMSO-d_6) δ 165.00, 149.94, 132.16, 127.82, 111.94, 57.68 (see **Figure S4**). **HRMS (ESI)** m/z : calcd. for $[M+Na]^+$: 259.0577, found 259.0588 (see **Figure S12**).



Scheme S3. Diels-Alder adduct synthetic route for both comonomers.[2]

Synthesis of the Diels-Alder adducts (example for the BAMF comonomer)

BAMF (1.26 g, 5.33 mmol), BM (0.796 g, 2.22 mmol) and MEHQ (6.3 mg, 0.5 wt%) are mixed in a 20 mL vial and dissolved in THF (6.87 mL, 1.1 M of BAMF and BM). The mixture is heated to 40 °C and stirred over the weekend (~70 hours). The reaction completion is determined by TLC and ^{1}H NMR. The mixture is concentrated under reduced pressure and a yellow solid is obtained. The crude product is purified by flash chromatography (70:30 hexane:ethyl acetate with gradual changes to 30:70 hexane:ethyl acetate towards the end of the purification). The final product is a white solid with a yellowish taint (1.77 g, 95%). **RMF adduct :** ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.09 (d, *J* = 8.2 Hz, 8H), 7.51-7.47 (m, 2H), 7.42-6.85 (m, 20H), 6.51-6.48 (m, 4H), 6.35 (d, *J* = 17.3 Hz, 4H), 6.27-6.08 (m, 4H), 5.96-5.90 (m, 4H), 5.15 (s, 2H), 4.29 (m, 8H), 4.24-4.08 (m, 8H), 3.99 (s, 2H), 3.62-3.37 (m, 4H), 3.11 (dd, *J* = 44.8, 6.4 Hz, 4H), 2.12 (m, 8H) (see **Figure S5**). ^{13}C NMR (76 MHz, DMSO-d_6) δ 175.33, 174.22, 169.89, 165.46, 164.12, 163.98, 162.95, 147.71, 146.71, 140.89, 138.01, 137.10, 134.59, 132.03, 131.53, 130.59, 130.06, 129.00, 128.23, 128.20, 126.80, 124.98, 123.56, 121.32, 120.86, 114.69, 90.66, 80.47, 64.85, 61.05, 50.50, 49.64, 29.36, 27.90 (see **Figure S6**). **BAMF adduct :** ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.54-6.98 (m, 8H), 6.64-6.59 (m, 4H), 6.51-6.10 (m, 8H), 6.00 (d, *J* = 10.4 Hz, 4H), 5.04 – 4.39 (m, 8H), 4.02 (s, 2H), 3.79 (s, 4H) (see **Figure S7**). ^{13}C NMR (76 MHz, DMSO-d_6) δ 173.46, 165.08, 141.43, 135.75, 132.47, 132.16, 129.15, 127.71, 126.85, 89.51, 89.04, 61.77, 48.10 (see **Figure S8**). **HRMS (ESI, RMF adduct)** m/z : calcd. for $[M+2Na]^{2+}$: 856.2470, found 856.2457 (see **Figure S13**). **HRMS (ESI, BAMF adduct)** m/z : calcd. for $[M+Na]^{+}$: 853.2215, found 853.2208 (see **Figure S14**).

Synthesis of monodomain liquid crystal elastomer (example for R25DA)[3]

In a 20 mL vial, RM257 (151.4 mg, 0.257 mmol), MEHQ (1 mg, 0.5 wt% to bulk) and RMF+BM adduct (71.5 mg, 0.0429 mmol) are first dissolved in THF (200 µL) using an ultrasonic bath. The molar fraction of acrylate functions belonging to the RM257 is 0.75, the other fraction (0.25) originates from the Diels-Alder adduct. Once the compounds are fully dissolved, EDDET (62.5 mg, 0.34288 mmol) is added to the mixture with the quantity of thiol functions corresponding exactly to the total amount of acrylate functions. The solution is then mixed with a vortex mixer. Finally, a volume of a 1:50 DPA:THF solution (28.78 µL, 0.5 mol% of DPA in reference to the molar quantity of thiol functions) is added to the mixture. After quickly mixing the solution with a vortex mixer, it is poured inside a Teflon mold corresponding to the desired LCE

shape. The precursor mixture is left under a hood at room temperature for 24 h. The thiol-acrylate Michael addition polymerization is followed using ATR-FTIR (**Fig S15**). The polymerized sample is then removed from the mold and further dried under vacuum at 45 °C for 24 h using a vacuum oven to remove the residual THF. The resulting polydomain LCE is slightly opaque at room temperature and easily deformable.

In the case where the selected LCE shape is a thin flat strip and the desired reversible deformation is a material able to go from an elongated state (nematic phase) to a contracted state (isotropic phase), and vice versa, the procedure is as follows. It is put inside an oven at 120 °C for a short period of time (1 minute and 30 seconds). This leads to breaking a fraction of the DA crosslinks with the retro-Diels-Alder reaction. Then, the LCE is quickly cooled to room temperature (under the T_{NI}) and mechanically stretched to approximately 100% strain for mesogen alignment. Finally, the material is kept under strain for 24 h which results in the reformation of the broken DA crosslinks and a monodomain LCE.

Procedure for the kinetic study of the Diels-Alder reaction between the comonomers and the BM[2]

An equal number of furan, using the RMF (555.5 mg, 0.8485 mmol) or BAMF (200.4 mg, 0.8485 mmol) comonomers, and bismaleimide groups, using BM (152.0 mg, 0.4242 mmol), are dissolved in DMSO-d_6 (636.4 µL, 2M) with a small quantity of MEHQ (5.55 mg, 0.5 wt% to bulk) inside a vial. The mixture is then quickly transferred to an NMR tube and it is put inside a Bruker 400 MHz apparatus at 40 °C. Multiple ^{1}H NMR spectra are then taken after different times (5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, 32 h, 48 h, 66 h) to follow the reaction. The resulting data for each comonomer is shown in **Figures S9 and S10**. After attributing the peaks to each proton in the chemical structure of the Diels-Alder adduct and the reactants, the peaks that correspond to the protons in position 3 and 4 of the furan in the comonomer structure are selected for the furan conversion determination. The initial value of the total integration of the peak/s for the protons is taken at 5 minutes. This value corresponds to a 0% conversion of the furan group following the DA reaction. With this value, the furan conversion can be determined at the different analysis times during the kinetic study, by using the following equation:

$$Furan\ conversion\ (\%) = \left(\frac{I_0 - I_t}{I_0}\right) \times 100\%$$

Where I_0 is the initial total integration value of the peaks and I_t is the total integration value of the peaks at time t. The results can then be plotted in a furan conversion vs time graph (**Fig 1B**) for the two comonomers.

2. NMR spectra

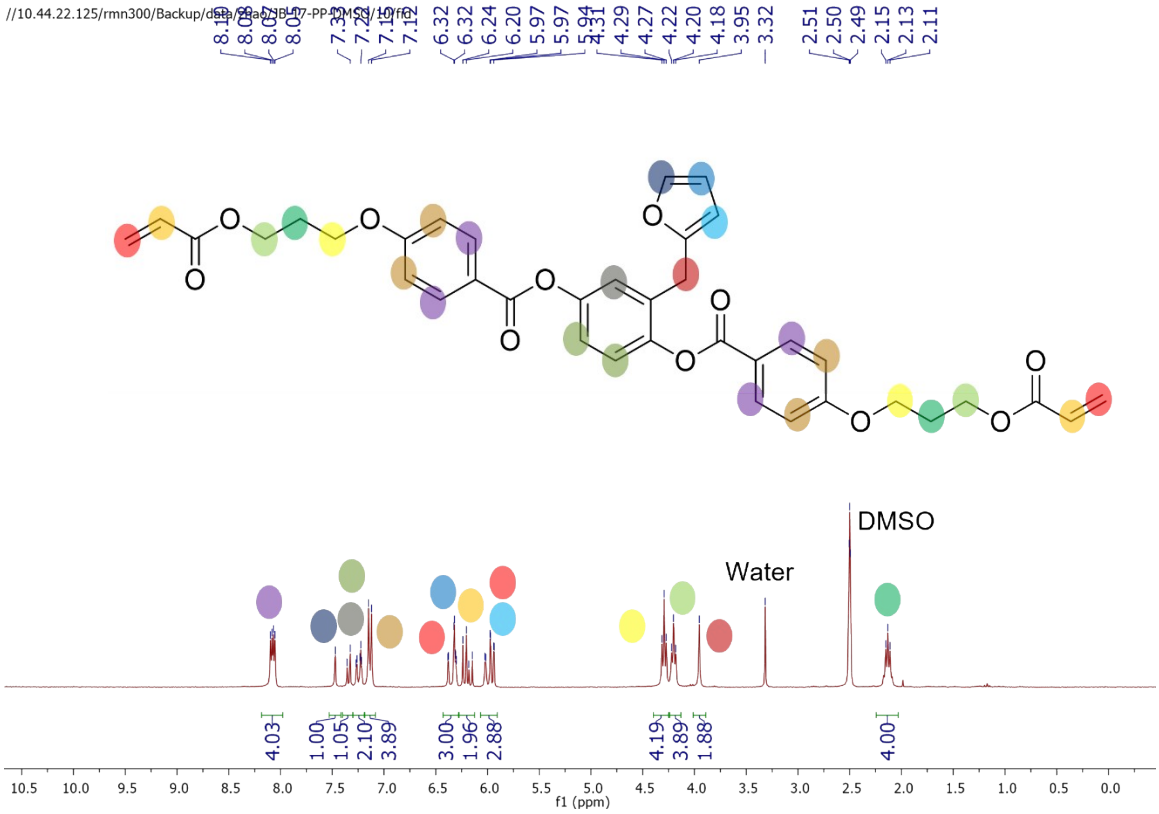


Figure S1. ^{1}H NMR spectrum of the RMF comonomer.

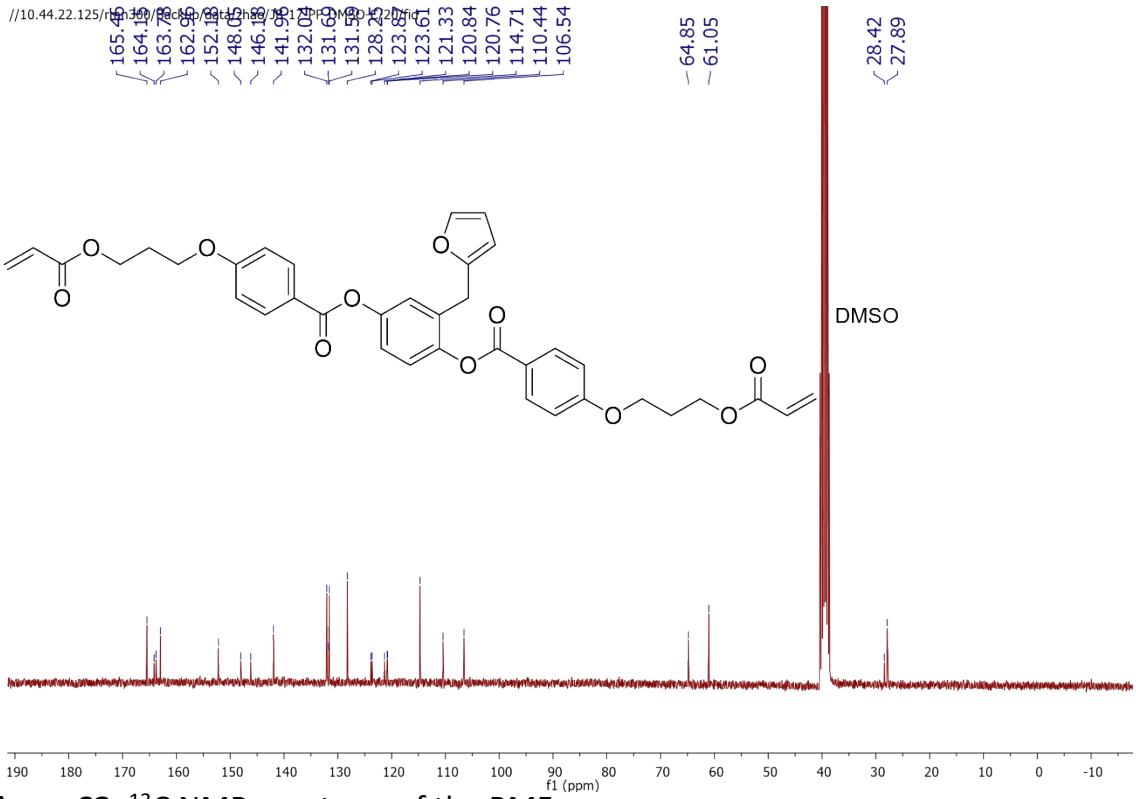


Figure S2. ^{13}C NMR spectrum of the RMF comonomer.

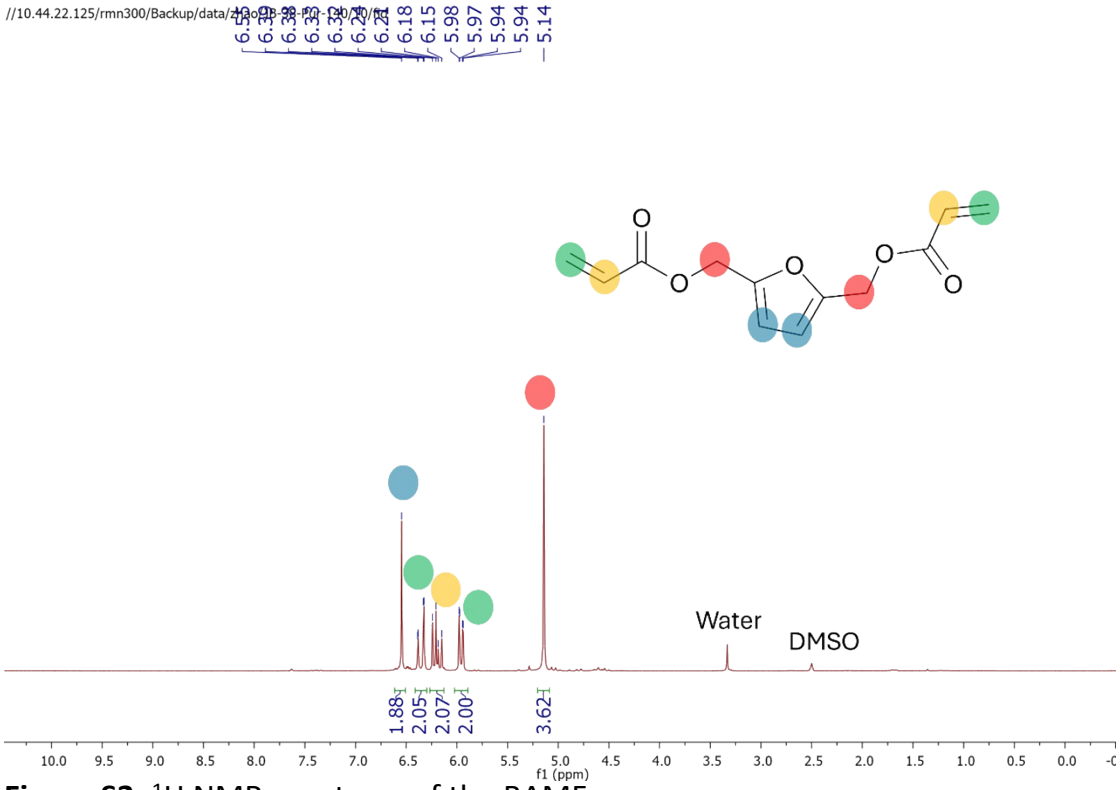


Figure S3. ^{1}H NMR spectrum of the BAMF comonomer.

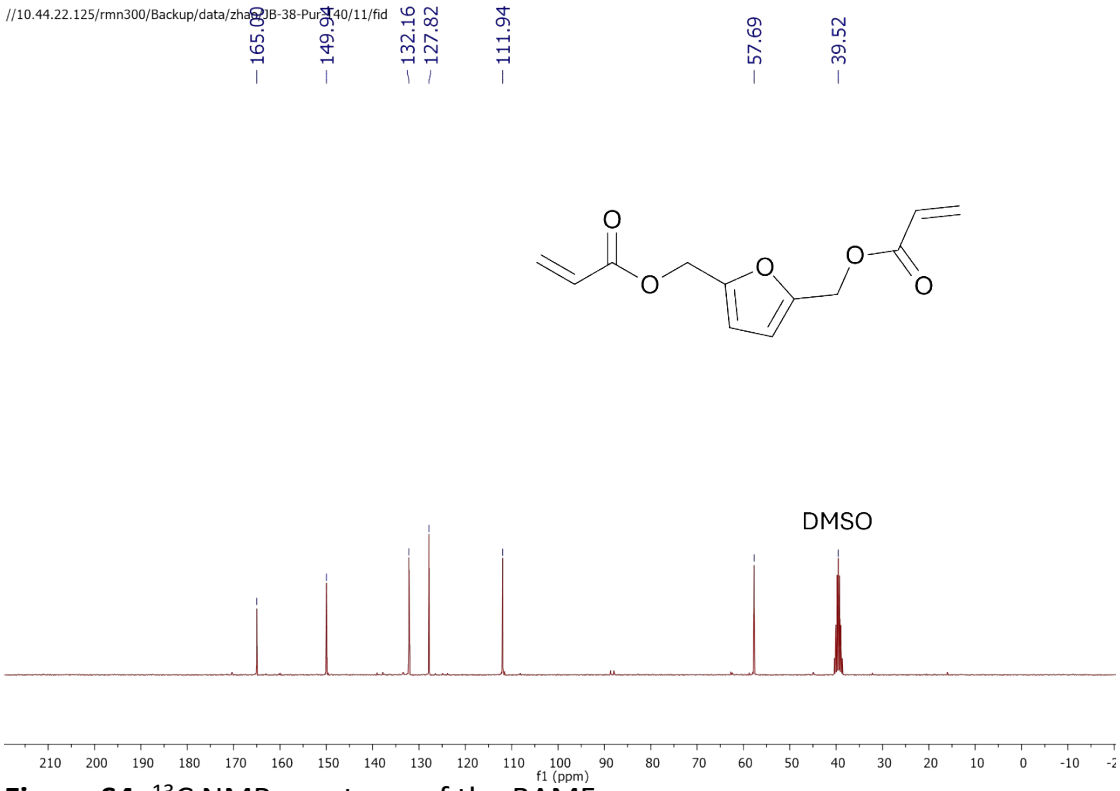


Figure S4. ^{13}C NMR spectrum of the BAMF comonomer.

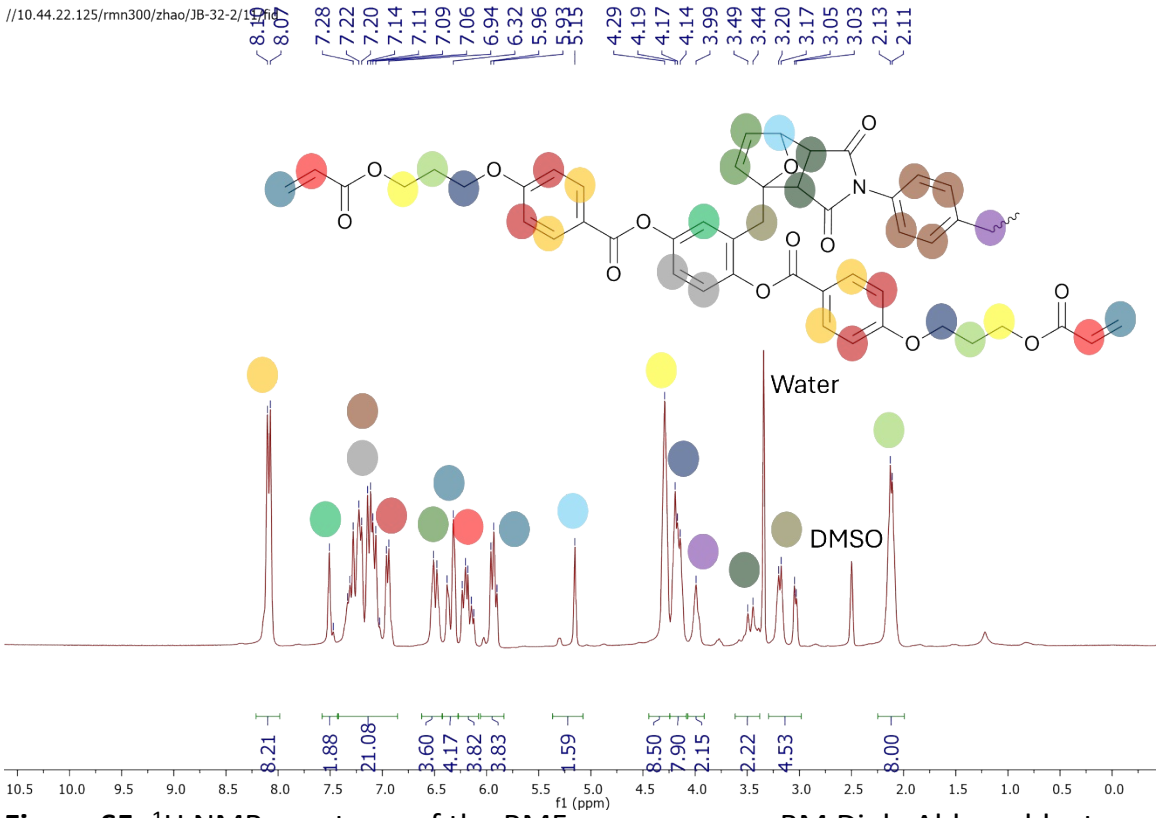


Figure S5. ^{1}H NMR spectrum of the RMF comonomer + BM Diels-Alder adduct.

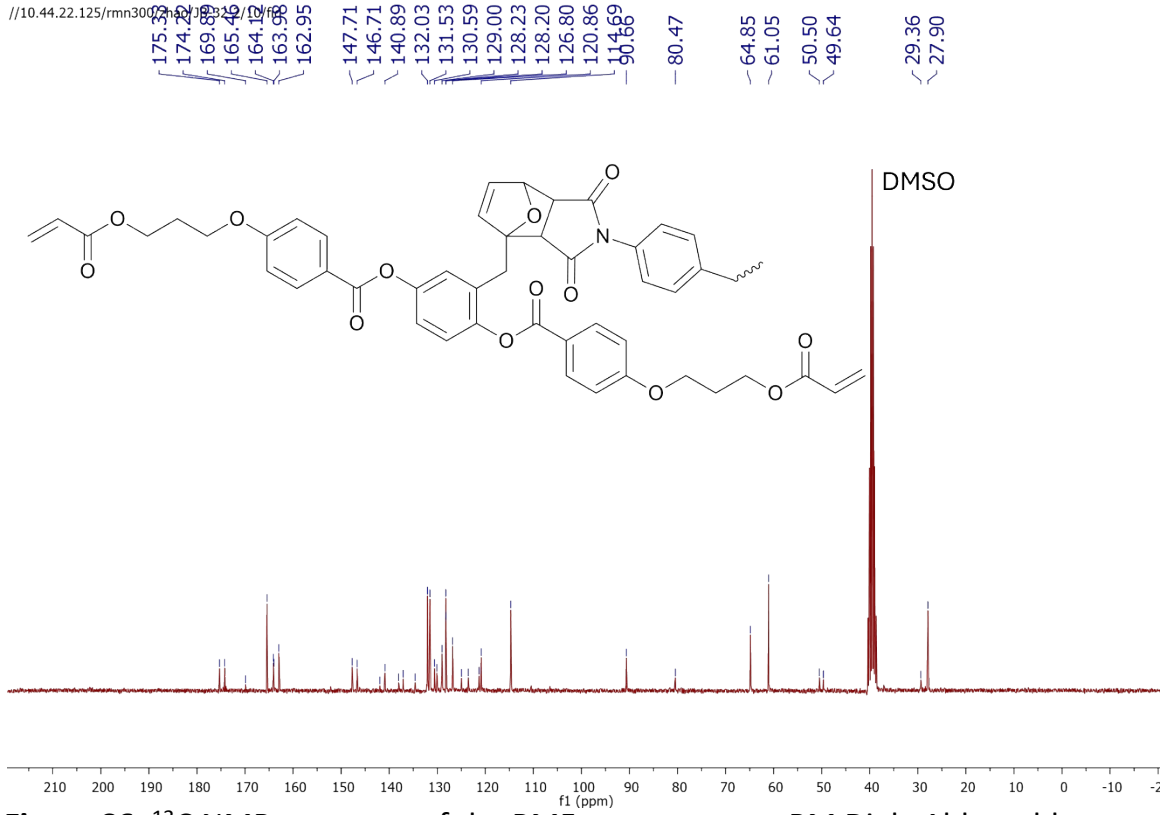


Figure S6. ^{13}C NMR spectrum of the RMF comonomer + BM Diels-Alder adduct.

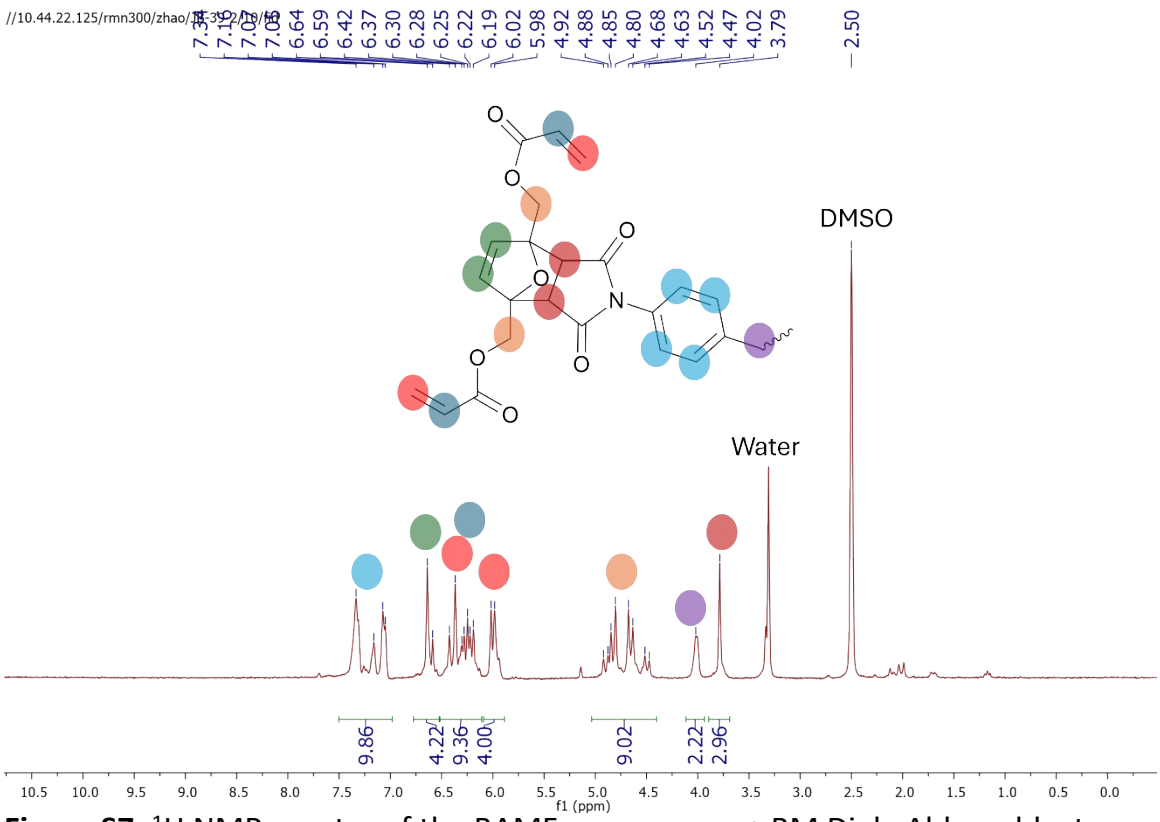


Figure S7. ^{1}H NMR spectra of the BAMF comonomer + BM Diels-Alder adduct.

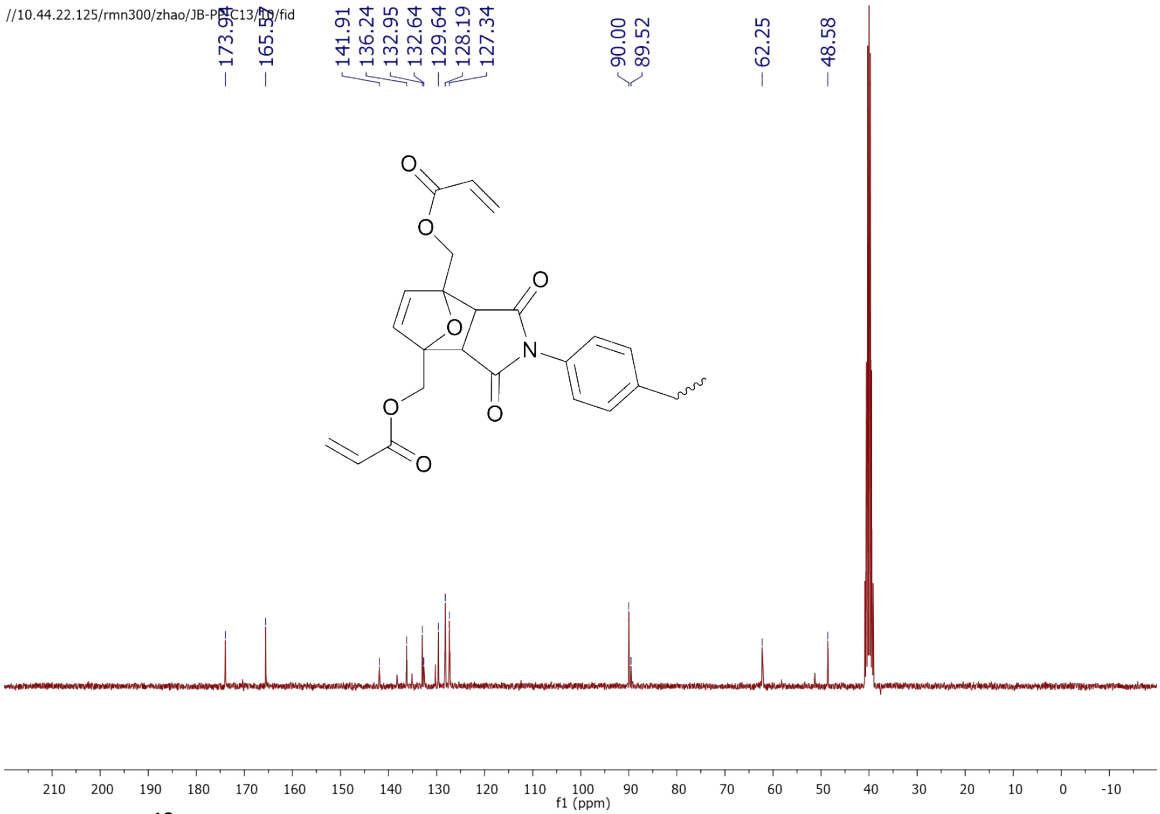


Figure S8. ^{13}C NMR spectra of the BAMF comonomer + BM Diels-Alder adduct.

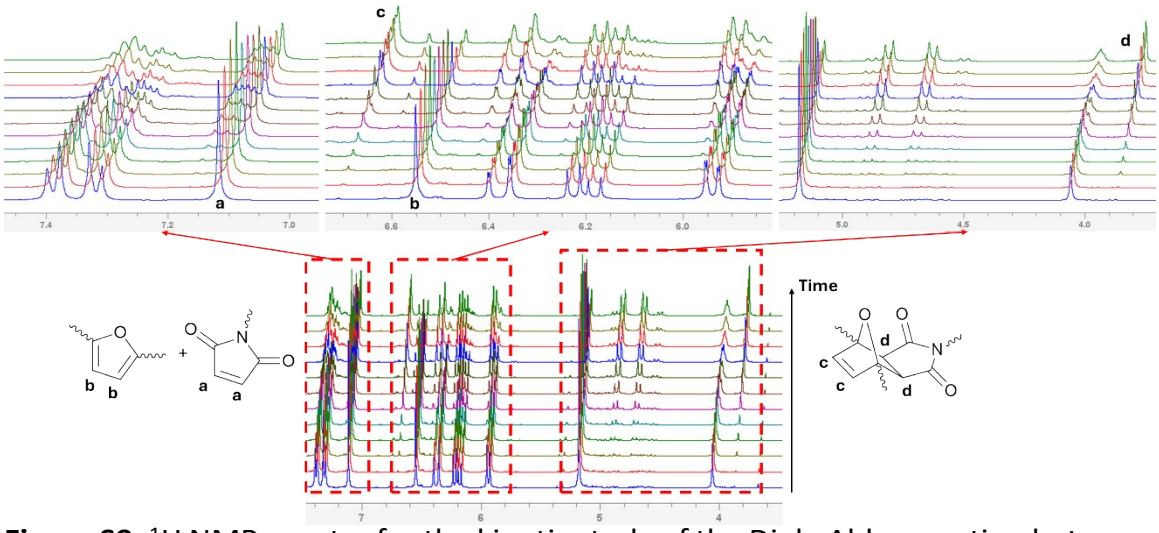


Figure S9. ^{1}H NMR spectra for the kinetic study of the Diels-Alder reaction between the BAMF comonomer and the BM. The integration of the peak for protons **b** was used for the determination of the furan conversion (%) in function of time in Fig 1B.

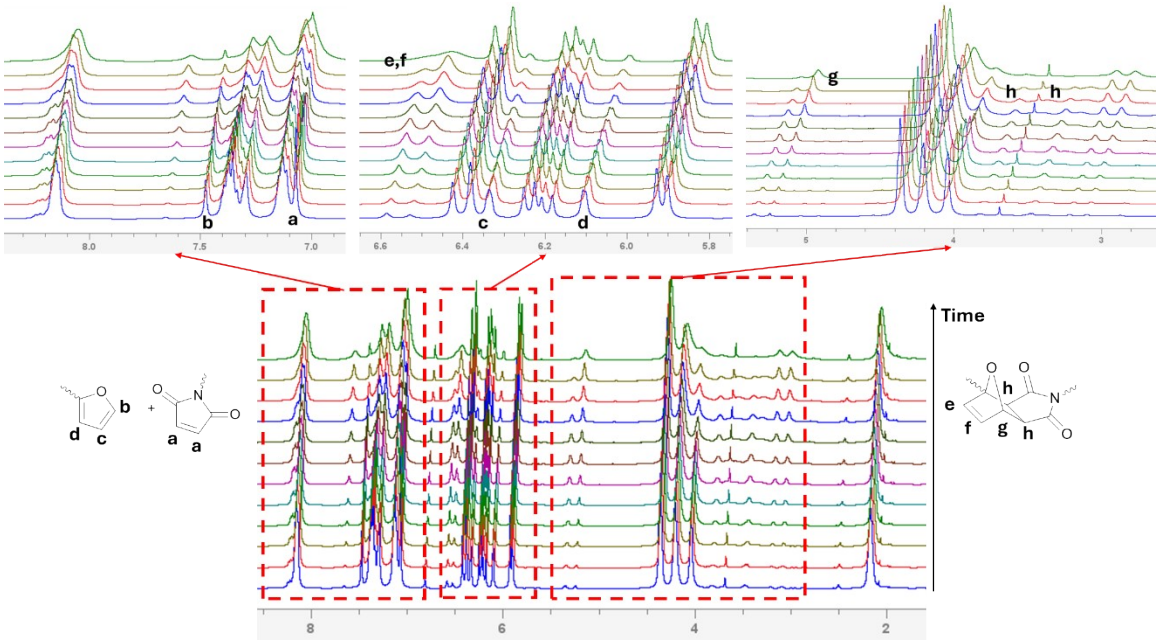


Figure S10. ^{1}H NMR spectra for the kinetic study of the Diels-Alder reaction between the RMF comonomer and the BM. The total integration of the peaks for protons **c** and **d** was used for the determination of the furan conversion (%) in function of time in Fig 1B.

3. High-resolution mass spectra (HRMS)

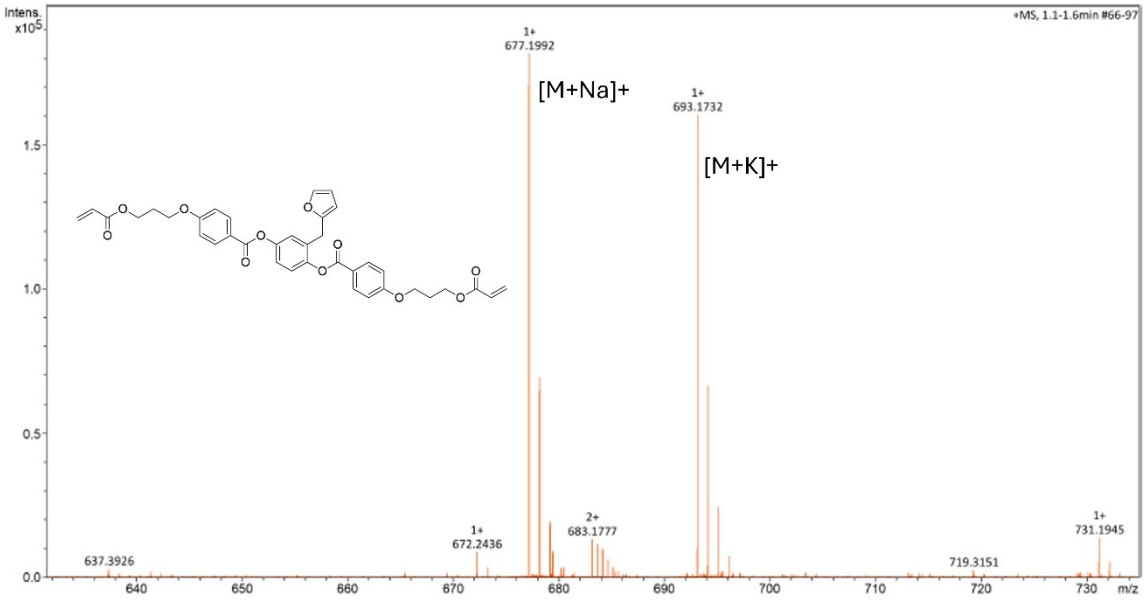


Figure S11. HRMS of the RMF comonomer.

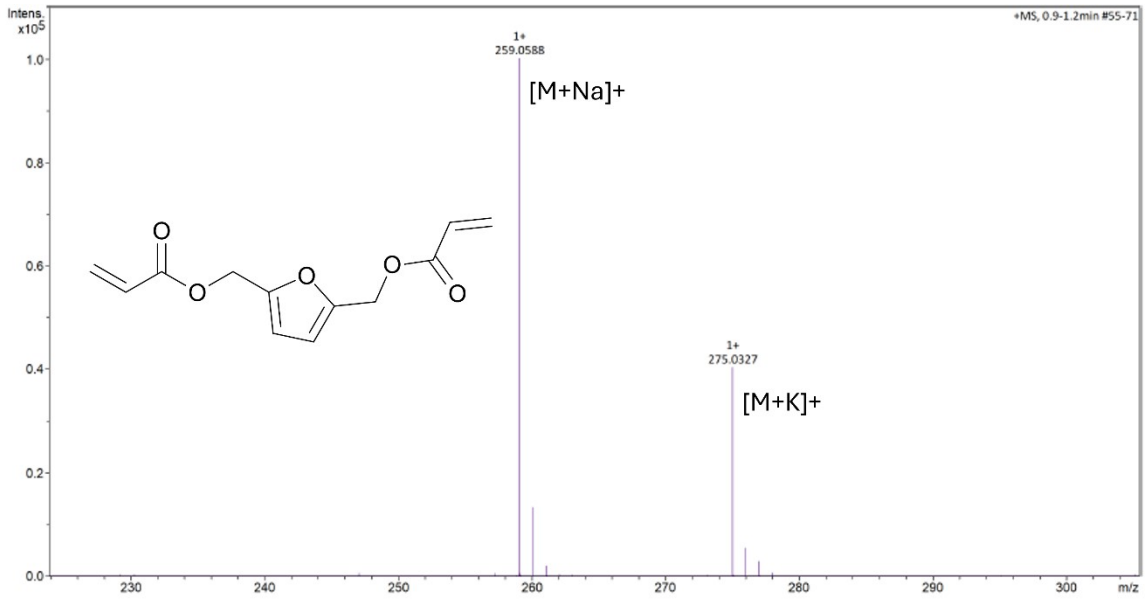


Figure S12. HRMS of the BAMF comonomer.

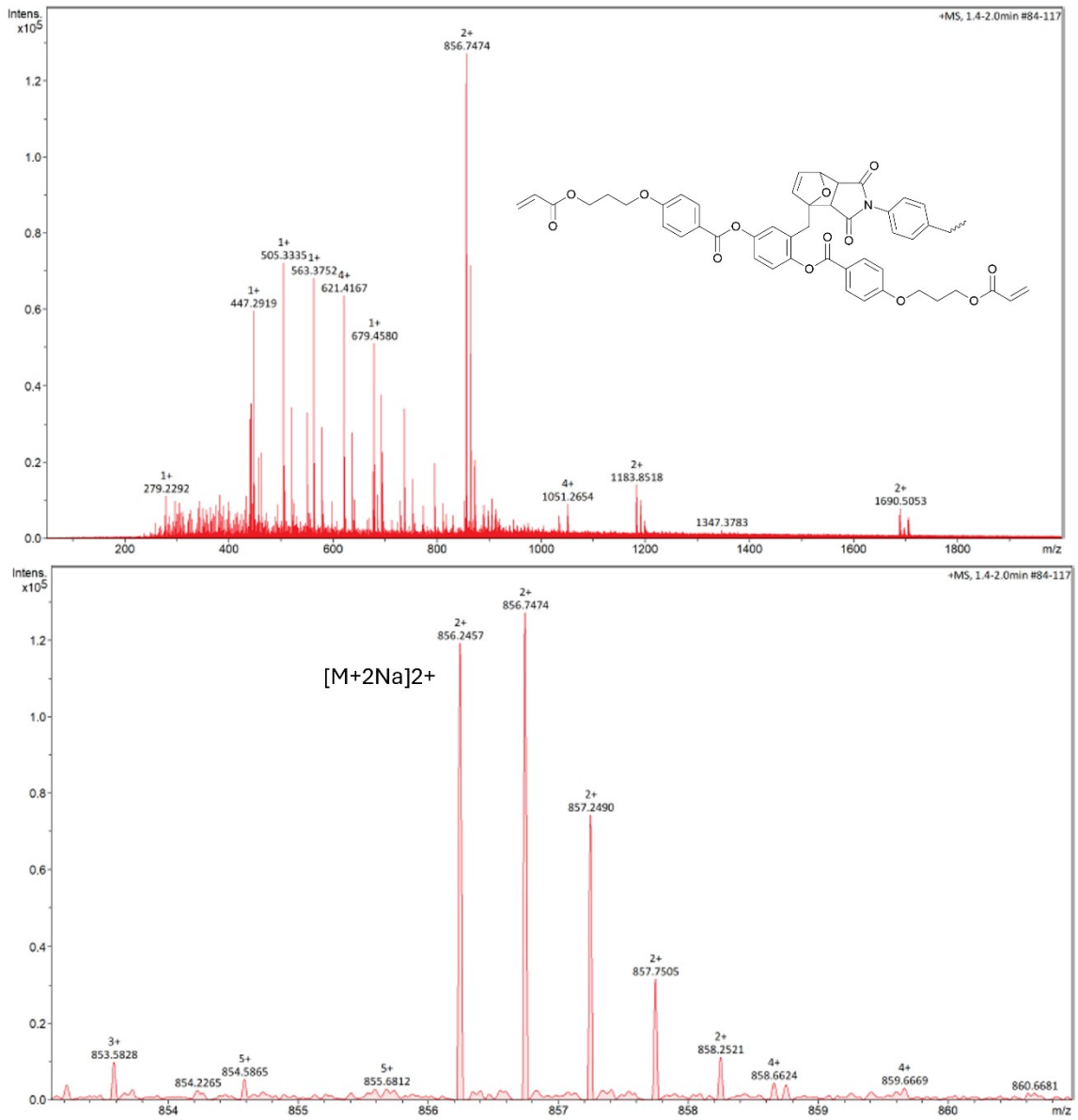


Figure S13. HRMS of the RMF comonomer + BM Diels-Alder adduct.

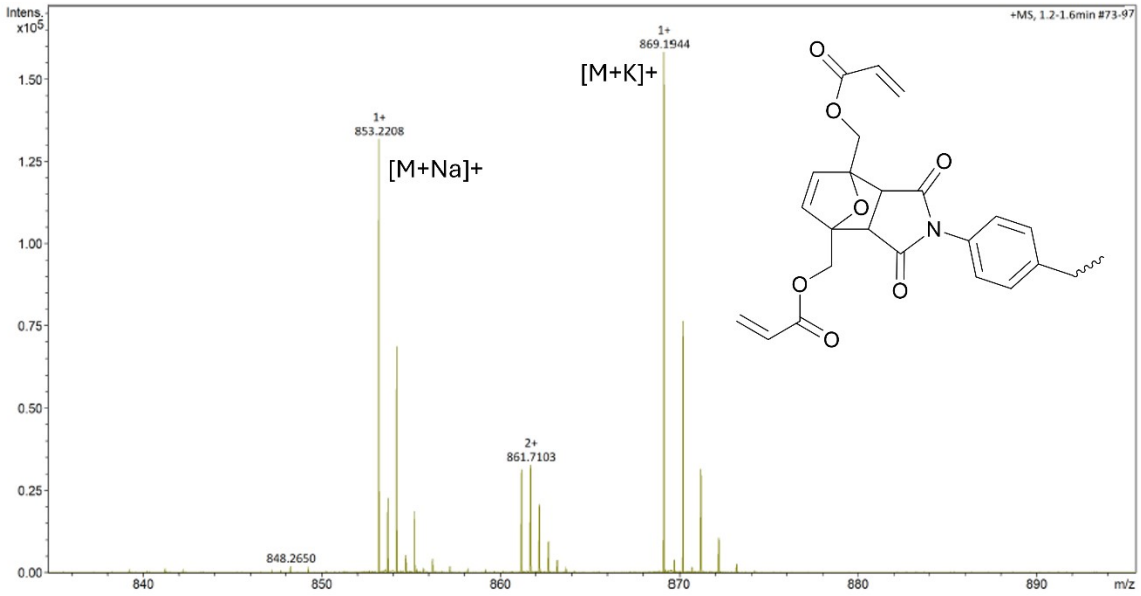


Figure S14. HRMS of the BAMF comonomer + BM Diels-Alder adduct.

4. Thermal phase transitions

Table S1. Thermal phase transition values for LCE with DADCBs determined by DSC.

Sample code	T_g (°C)[a]	T_{NI} (°C)[a]	ΔH_{NI} (J/g)[a]	ΔH_{r-DA} (J/g)[b]
R15DA	-6.9	38.0	-0.32	-1.99
R20DA	-1.4	36.6	-0.36	-7.54
R25DA	1.9	34.4	-0.08	-8.28
R28DA	-0.9	N.A.	N.A.	-8.72
B10DA	-8.4	37.2	-0.30	-5.43
B12DA	-10.0	33.1	-0.08	-6.07
B15DA	-11.5	30.5	-0.05	-2.90
B18DA	-11.2	14.9	-0.33	-8.28

[a]Values measured on third DSC heating scan from -50 °C to 170 °C.
[b]Measured on first DSC heating scan from -50 °C to 170 °C.

5. ATR-FTIR spectra

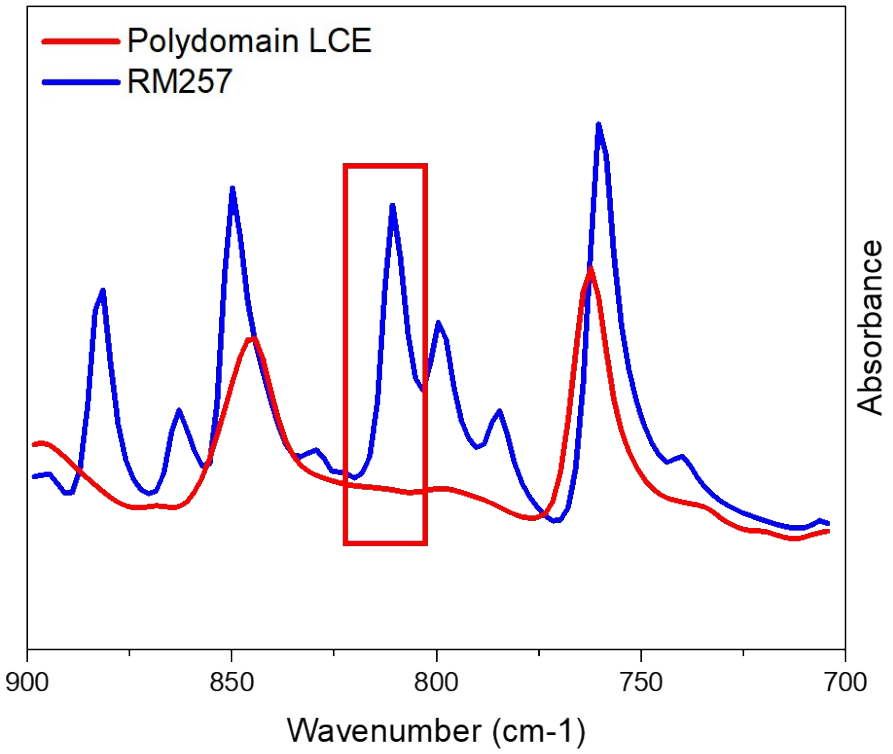


Figure S15. ATR-FTIR absorbance spectra comparison of the starting product (RM257) and polydomain LCE post-polymerization.[3]

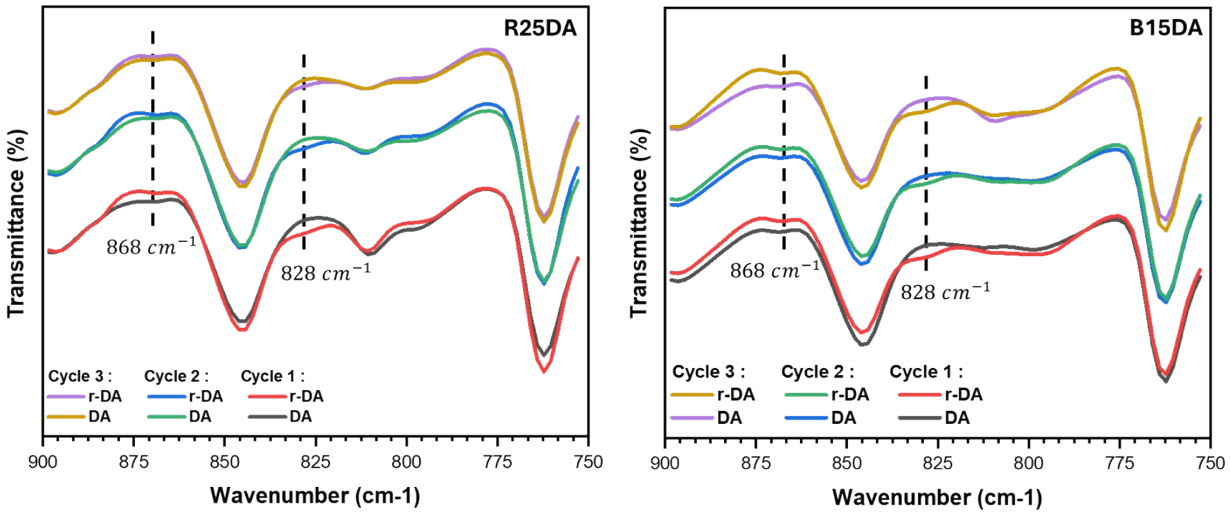


Figure S16. Changes in ATR-FTIR transmittance spectra of R25DA and B15DA during cycles of heating to 120 °C for 20 min and cooling to room temperature for 24 h to allow the retro-DA and DA reactions, respectively, to occur.[2]

In each cycle, after heating the sample to 120 °C for 20 minutes one spectrum was taken immediately after cooling to room temperature (for the after retro-DA reaction state) and another one taken 24 h later (after DA reaction). After the retro-DA reaction, the band at $868\ cm^{-1}$, ascribed to the furan-maleimide cycloadduct, decreases its intensity, while the band at $821\ cm^{-1}$ from free maleimide increases its intensity. The opposite changes were observed after the DA reaction.

6. POM images of R25DA and B15DA

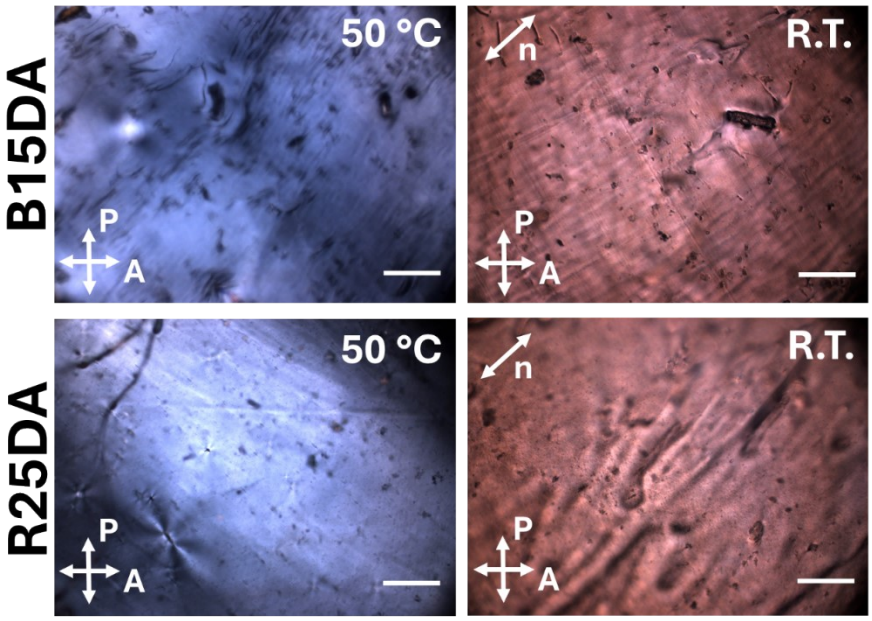


Figure S17. POM images of LCE actuator samples over and under their respective T_{NI}, the mesogen alignment direction being set at 45 ° to crossed polarizers. Scale bar = 200 μm.

7. Heating by photothermal effect

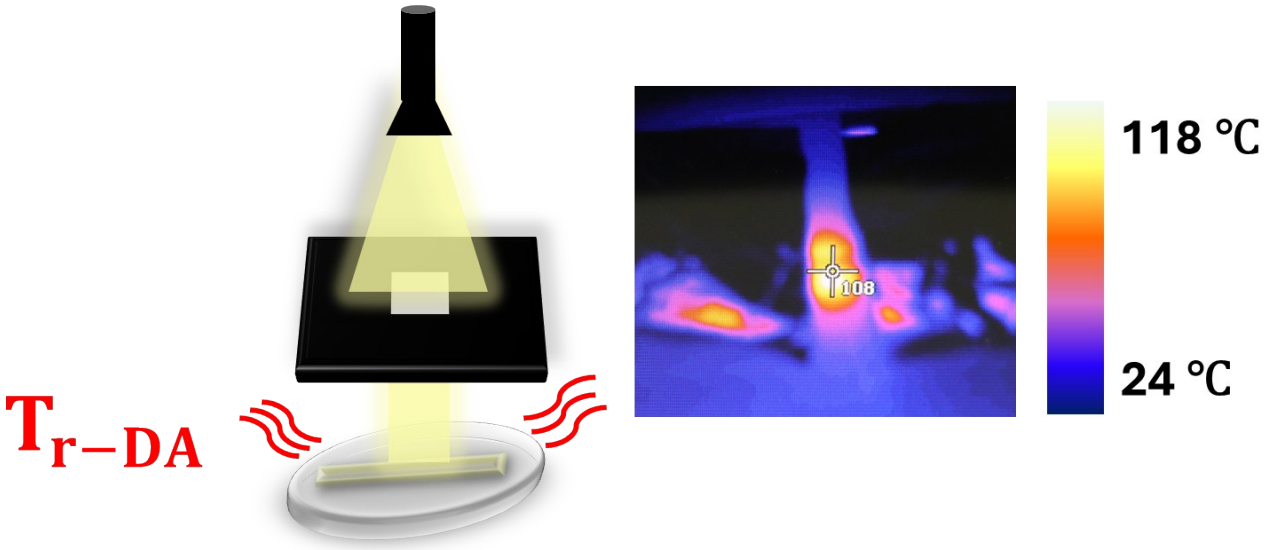


Figure S18. Schematic of the setup used to heat the LCE sample using a powerful flashlight (left) and picture taken by an IR camera showing the temperature (~ T_{r-DA}) of the exposed area of the LCE (right).

8. Recyclability test

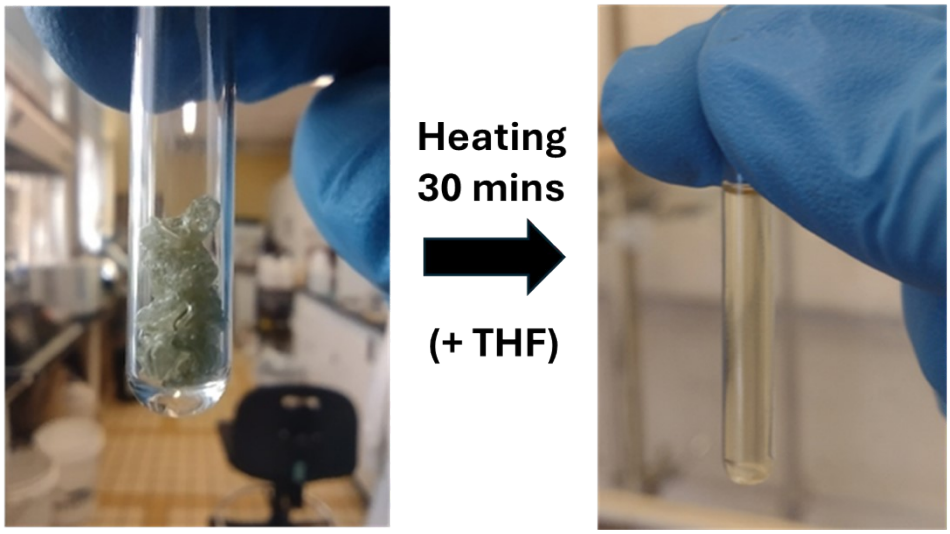


Figure S19. Recyclability test of the R25DA by dissolving the post-heating LCE pieces in THF.

By breaking the DA crosslinks inside a R25DA sample using a heating treatment (120 °C for 30 minutes), the elastomeric network becomes linear polymer chains, which can easily be dissolved in solvents. The solution can later be reused and poured inside a mold to form another LCE after the solvent's evaporation. It is also possible to avoid using a solvent and simply deform the post-heated sample in the desired shape and leave the material at room temperature for the reformation of the LCE network. This allows the same material to have multiple permanent shapes, giving it the ability to be recyclable.

9. Non-mesogen confirmation of RMF comonomer

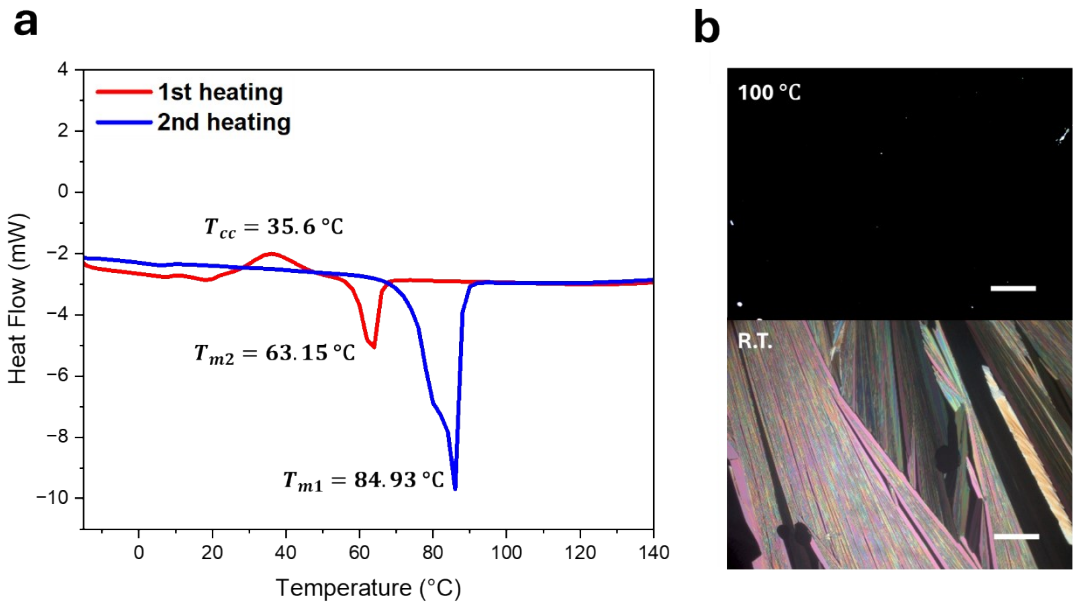


Figure S20. (A) DSC heating scans of the RMF comonomer, the heating rate is 10 °C/min. (B) POM images of the RMF comonomer over (100 °C) and under (room temperature) its melting temperature. Scale bar = 200 μm.

By using the DSC analysis, it is possible to confirm that only the melting/crystallization phase transitions are present during the heating cycles, which is characteristic of a non-mesogenic molecule. The same can be said for the POM images in **Figure S20B**, where there is no clear liquid crystalline texture, only the isotropic (at 100 °C) and crystalline (at low temperatures) phases are visible during the heating/cooling cycles. These tests thus confirmed that the RMF comonomer is a non-mesogenic diluent in the LCEs.

10. Movies

Movie S1. Actuation of a flat R25DA strip upon heating to body temperature (contraction) and cooling to room temperature on water surface (elongation).

Movie S2. 3D bulk actuation of R25DA from cube to “pie” shape while cooling to room temperature.

Movie S3. 3D bulk actuation of R25DA from sphere to ellipsoid while cooling to room temperature.

Movie S4. Actuation of helicoidal shape B15DA strip upon cooling to room temperature in water (twisting).

11. References

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2 T. T. Truong, H. T. Nguyen, M. N. Phan and L. T. Nguyen, *J. Polym. Sci. Part A: Polym. Chem.*, 2018, **56**, 1806–1814.

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