

## Electronic Supporting Information

### **Mechanochromic elastomers with different thermo- and mechano-responsive radical-type mechanophores**

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## 1. General Information

### Materials

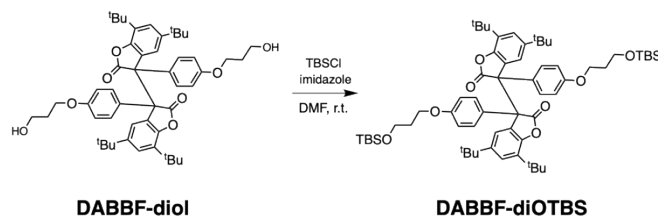
All reagents and solvents were purchased from Sigma-Aldrich, FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry and Kanto Chemical, and used as received, unless otherwise noted. Hexyl methacrylate (HMA) was purified by basic alumina column (Merck KGaA) to remove the stabilizer prior to use. DFSN-dimethacrylate was synthesized according to previously published methods<sup>1</sup>.

### Instruments

<sup>1</sup>H NMR spectroscopic measurements were carried out using 500 MHz Bruker spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* (CDCl<sub>3</sub>). Electrospray ionization mass spectrometry (ESI-TOF-MS) measurements were carried out on Bruker micrOTOF II. IR spectra were recorded on a JASCO FT/IR-4100 Fourier transform infrared spectrometer as thin films with KBr. Size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000 and 2500), a differential refractive index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ( $M_n = 4430\text{--}3242000$ ;  $M_w/M_n = 1.03\text{--}1.08$ ) were used to calibrate the SEC system. DSC measurements were carried out using a SHIMADZU DSC-60A Plus with a heating rate 10 °C/min. Uniaxial tensile tests were performed using a SHIMADZU AUTOGRAPH AGS-X with constant temperature bath TCE-N300. Stress relaxation measurements were carried out using Hitachi High-Tech Science TMA7100 under N<sub>2</sub> flow.

## 2. Synthetic Procedure

### Synthesis of DABBF-diOTBS



In a round-bottomed flask, a solution of DABBF-diol (2.00 g, 2.53 mmol), imidazole (0.52 g, 7.58 mmol) and *N,N*-dimethylformamide (DMF, 70 mL) was prepared under  $N_2$  atmosphere. A solution of *tert*-butyldimethylsilyl chloride (TBSCl, 1.15 g, 7.58 mmol) in dichloromethane (20 mL) was added dropwise to this mixture at 0 °C. The reaction mixture was stirred at room temperature for 2 h and then poured into water. The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with brine, dried over anhydrous  $MgSO_4$ , and the solvent was removed. The crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/9, v/v). The solvent was removed and dried under vacuum to give DABBF-diOTBS as a white solid (2.12 g, 83%).

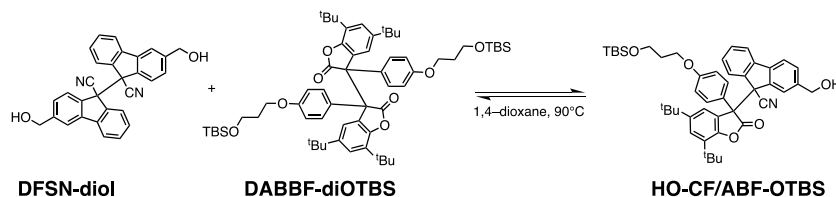
$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$ /ppm 7.28 (br, 6H, aromatic), 6.81 (d,  $J = 7.5$  Hz, 6H, aromatic), 4.08 (m, 4H,  $OCH_2CH_2CH_2$ ), 3.80 (t,  $J = 5.9$  Hz, 4H,  $OCH_2CH_2CH_2$ ), 1.99 (quin, 4H,  $J = 5.9$  Hz,  $OCH_2CH_2CH_2$ ), 1.46–0.99 (br, 18H,  $C(CH_3)_3$ ), 0.89 (s, 9H,  $Si(CH_3)_3$ ), 0.05 (s, 6H,  $Si(CH_3)_2$ ).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$ /ppm 159.17, 149.18, 133.46, 132.26, 123.87, 113.14, 64.50, 59.46, 34.72, 34.38, 32.34, 31.57, 29.71, 25.96, 18.33, -5.10

FT-IR (KBr,  $cm^{-1}$ ): 3574, 2958, 2739, 2555, 1799, 1608, 1576, 1510, 1473, 1412, 1394, 1364, 1295, 1257, 1187, 1086, 1019, 970, 927, 885, 835, 776, 720, 663, 637, 623, 569, 540, 496, 432, 412.

ESI-MS ( $m/z$ ):  $[M+Na]^+$  calcd. for  $C_{46}H_{47}NO_6Na$ , 1041.6066; Found, 1041.6050.

### Synthesis of HO-CF/ABF-OTBS



In a round-bottomed flask, a solution of DFSN-diol (0.90 g, 2.04 mmol), **DABBF-**

**diOTBS** (2.08 g, 2.04 mmol), and 1,4-dioxane (300 mL) was prepared. The mixture was bubbled with nitrogen for 1 h. The reaction mixture was stirred at 90 °C for 3 h. The crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/4, v/v). The solvent was removed and dried in vacuo to give **HO-CF/ABF-OTBS** as a white solid (1.76 g, 59%).

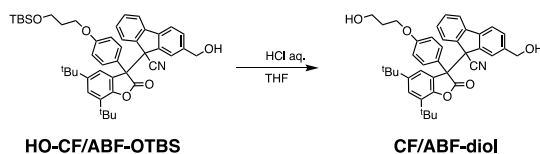
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ/ppm 7.94 (br, 2H, aromatic), 7.63 (d, *J* = 7.8 Hz, 1H, aromatic), 7.50 (t, *J* = 6.7 Hz, 2H, aromatic), 7.40 (d, *J* = 7.7 Hz, 2H, aromatic), 7.29 (d, *J* = 7.9 Hz, 1H, aromatic), 7.19 (quint, *J* = 7.9 Hz, 1H, aromatic), 7.00 (q, *J* = 3.6 Hz, 3H, aromatic), 6.45 (br, 1H, aromatic), 4.58 (m, 2H, CCH<sub>2</sub>OH), 4.14 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.84 (dt, *J* = 2.0 and 6.0 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.03 (quin, 2H, *J* = 6.0 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.63 (t, *J* = 5.9 Hz, 1H, OH), 1.18 (br, 9H, CH<sub>3</sub>), 1.03 (br, 9H, CH<sub>3</sub>), 0.90 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), 0.07 (d, *J* = 1.7 Hz, 6H, Si(CH<sub>3</sub>)<sub>2</sub>).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ/ppm 159.69, 148.23, 145.63, 141.59, 141.37, 141.20, 140.75, 140.11, 139.39, 139.26, 132.93, 132.78, 130.72, 130.20, 129.70, 128.73, 128.36, 128.13, 127.57, 124.59, 123.58, 120.69, 120.54, 120.38, 119.98, 119.83, 118.69, 114.49, 64.81, 59.48, 57.21, 55.05, 34.43, 32.29, 29.33, 18.36, -5.33.

FT-IR (KBr, cm<sup>-1</sup>): 3525, 2956, 2858, 1796, 1607, 1576, 1511, 1470, 1413, 1394, 1364, 1296, 1257, 1187, 1168, 1123, 1090, 1024, 885, 835, 777, 752, 727, 664, 640, 620, 559, 539, 504, 461, 434, 405.

ESI-MS (*m/z*): [M+Na]<sup>+</sup> calcd. for C<sub>46</sub>H<sub>47</sub>NO<sub>6</sub>Na, 1041.2741; Found, 752.3724.

### Synthesis of CF/ABF-diol



In a round-bottomed flask, a solution of **HO-CF/ABF-OTBS** (0.70 g, 0.96 mmol), 1N HCl (2.9 mL) and tetrahydrofuran (70 mL) was prepared. The reaction mixture was stirred at r.t. for 1 h. The reaction mixture was quenched with water and extracted with ethyl acetate, and the organic layer was washed with brine, dried over anhydrous MgSO<sub>4</sub>, and the solvent was removed. The crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/4, v/v). The solvent was removed and dried in vacuo to give **CF/ABF-diol** as a white solid (0.39 g, 67%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ/ppm 7.95 (br, 2H, aromatic), 7.63 (d, *J* = 7.5 Hz, 1H, aromatic), 7.50 (t, *J* = 6.9 Hz, 2H, aromatic), 7.41 (d, *J* = 6.9 Hz, 2H, aromatic), 7.29 (d, *J* = 7.5 Hz, 1H, aromatic), 7.19 (t, *J* = 6.9 Hz, 1H, aromatic), 7.00 (d, *J* = 9.0 Hz, 3H,

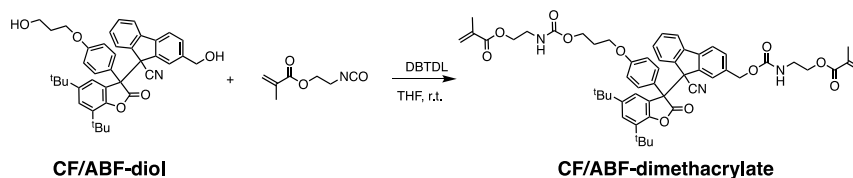
aromatic), 6.45 (br, 1H, aromatic), 4.61 (t,  $J = 6.0$  Hz, 2H,  $CCH_2OH$ ), 4.21 (dt,  $J = 1.5$  Hz and 5.5 Hz, 2H,  $OCH_2CH_2CH_2$ ), 3.91 (q,  $J = 5.5$  Hz, 2H,  $OCH_2CH_2CH_2$ ), 2.10 (quin, 2H,  $J = 5.8$  Hz,  $OCH_2CH_2CH_2$ ), 1.76 (br, 1H,  $CH_2CH_2OH$ ), 1.69 (t, 1.17,  $J = 5.9$  Hz, 1H,  $CH_2OH$ ), 1.18 (br, 9H,  $CH_3$ ), 1.04 (br, 9H,  $CH_3$ ).

$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta/ppm$  159.42, 148.17, 141.57, 139.99, 139.17, 132.83, 130.75, 130.25, 128.40, 127.62, 126.20, 124.93, 123.58, 120.69, 120.37, 119.97, 118.73, 114.63, 65.63, 64.75, 60.16, 57.19, 54.89, 34.45, 34.13, 31.96, 31.14, 29.25.

FT-IR (KBr,  $cm^{-1}$ ): 3376, 3068, 2957, 2871, 2239, 1794, 1607, 1577, 1512, 1477, 1414, 1394, 1364, 1297, 1273, 1257, 1188, 1170, 1124, 1091, 1056, 988, 884, 826, 777, 753, 726, 664, 640, 623, 562, 539, 434, 415.

ESI-MS ( $m/z$ ):  $[M+Na]^+$  calcd. for  $C_{46}H_{47}NO_6Na$ , 638.2876; Found, 638.2867.

### Synthesis of CF/ABF-dimethacrylate



**CF/ABF-diol** (1.06 g, 1.72 mmol) was added to a sample tube. After  $N_2$  purge, tetrahydrofuran (THF) (10 mL), 2-isocyanatoethyl methacrylate (0.82 mL, 6.02 mmol) and di-*n*-butyltin dilaurate (DBTDL) (1 drop) was added to the mixture, then stirring for 3 h at room temperature. The crude product was quenched with water and extracted with ethyl acetate, and the organic layer was washed with brine, dried over anhydrous  $MgSO_4$ , and the solvent was removed. The crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/1, v/v). The solvent was removed and dried in vacuo to give **CF/ABF-dimethacrylate** as a white solid (1.33 g, 85%).

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta/ppm$  7.95 (br, 2H, aromatic), 7.63 (t,  $J = 7.5$  Hz, 1H, aromatic), 7.51 (d,  $J = 7.8$  Hz, 2H, aromatic), 7.40 (d,  $J = 6.9$  Hz, 2H, aromatic), 7.22 (t,  $J = 7.4$  Hz, 1H, aromatic), 7.16 (t,  $J = 7.6$  Hz, 1H, aromatic), 7.00 (t,  $J = 6.5$  Hz, 3H, aromatic), 6.45–6.36 (br, 1H, aromatic), 6.12 (d,  $J = 8.8$  Hz, 2H,  $CH_2=C$ ), 5.59 (m, 2H,  $CH_2=C$ ), 5.17 (m, 1H, NH), 5.04 (m, 2H,  $CCH_2OH$ ), 4.30 (t,  $J = 6.5$  Hz, 2H,  $OCH_2CH_2CH_2$ ), 4.24 (quin, 4H,  $J = 5.2$  Hz,  $COOCH_2CH_2$ ), 4.12 (m, 2H,  $OCH_2CH_2CH_2$ ), 3.52 (m, 4H,  $COOCH_2CH_2$ ), 2.16 (quin, 2H,  $J = 4.4$  Hz,  $OCH_2CH_2CH_2$ ), 1.94 (d,  $J = 5.8$  Hz, 6H,  $C=C(CH_3)COO$ ), 1.17 (d,  $J = 4.6$  Hz, 9H,  $CH_3$ ), 1.03 (br, 9H,  $CH_3$ ).

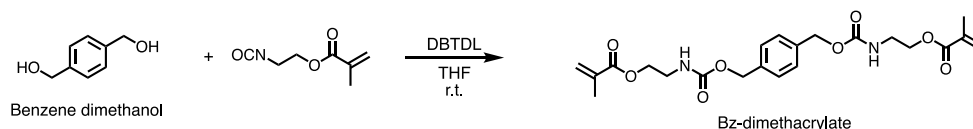
$^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta/ppm$  167.30, 159.40, 156.45, 156.13, 148.16, 141.67, 141.36, 139.96, 139.30, 135.93, 132.93, 130.78, 130.28, 129.78, 126.13, 123.59, 120.67, 120.48, 120.32, 118.59, 114.53, 66.26, 64.71, 63.70, 61.73, 57.16, 55.00, 40.22, 34.40,

34.10, 31.11, 29.30, 28.96, 18.32.

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3359, 2958, 2239, 1795, 1720, 1637, 1607, 1512, 1468, 1412, 1365, 1320, 1298, 1254, 1167, 1090, 1052, 941, 886, 825, 777, 755, 726, 638, 540, 474, 462, 447, 436, 422, 413.

ESI-MS ( $m/z$ ):  $[M+Na]^+$  calcd. for  $\text{C}_{46}\text{H}_{47}\text{NO}_6\text{Na}$ , 948.4028; Found, 948.4020.

### Synthesis of Bz-dimethacrylate

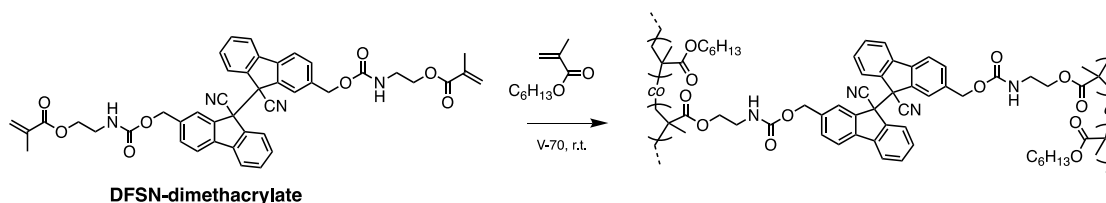


1,4-Benzendimethanol (0.700 g, 2.92 mmol) was added to a sample tube. After  $\text{N}_2$  purge, tetrahydrofuran (THF) (10 mL), 2-isocyanatoethyl methacrylate (1.24 mL, 8.78 mmol), di-*n*-butyltin dilaurate (DBTDL) (1 drop) was added to the mixture, then stirring for 6 h at room temperature. The crude product was purified by precipitation in hexane. The obtained solid was further purified by silica gel column chromatography eluting with ethylacetate / *n*-hexane (1/1, v/v). The solvent was removed and dried under vacuum to give Bz-dimethacrylate as a white solid (0.647 g, 76%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ /ppm 7.44 (br, 4H, aromatic), 6.12 (d,  $J = 8.8$  Hz, 2H,  $\text{CH}_2=\text{C}$ ), 5.59 (m, 2H,  $\text{CH}_2=\text{C}$ ), 5.17 (br, 1H, NH), 5.10 (s, 4H,  $\text{CH}_2\text{OCO}$ ), 4.24 (quin, 4H,  $J = 5.2$  Hz,  $\text{COOCH}_2\text{CH}_2$ ), 3.52 (m, 4H,  $\text{COOCH}_2\text{CH}_2$ ), 1.94 (d,  $J = 5.8$  Hz, 6H,  $\text{C}=\text{C}(\text{CH}_3)\text{COO}$ ).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$ / ppm 167.27, 156.27, 136.43, 135.94, 128.34, 126.05, 66.47, 63.66, 40.25, 18.28.

FAB-MS ( $m/z$ ):  $[M+H]^+$  calcd. for  $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_8$ , 449.1924; Found, 449.1924.

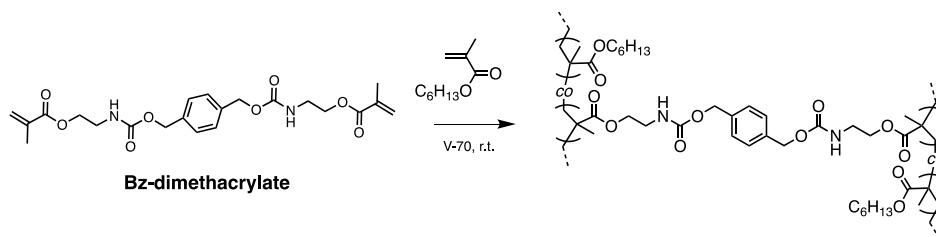
### Synthesis of $\text{CP}_{\text{DFSN}}$



A solution of HMA (2.21 g, 13.0 mmol), **DFSN-dimethacrylate** (98.0 mg, 0.130 mmol), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 40.0 mg, 0.13 mmol) and dry *N,N*-dimethylacetamide (DMAc, 2.33 g, ca. 50wt%) was degassed by freeze pump thaw cycle three times. After 15 minutes stirring at  $25\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ , the solution was transferred via syringe into a petri dish inside of a  $\text{N}_2$ -filled separable flask, which was left for 48 hours. The reaction was quenched by exposure to air, and the obtained polymer film was

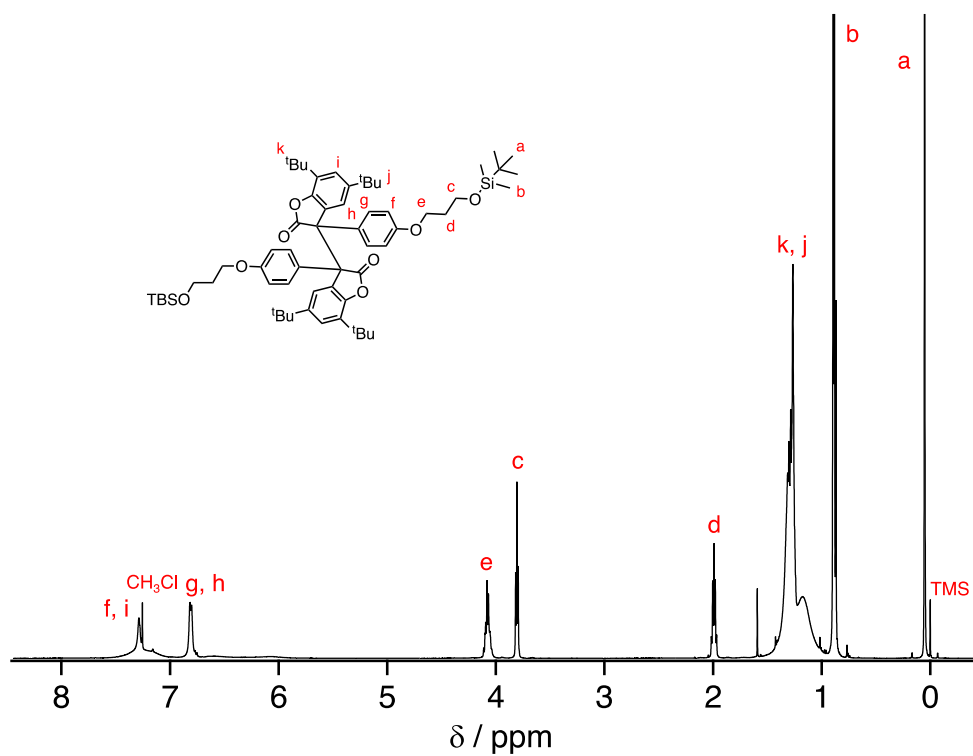
washed with the mixture of chloroform/methanol (gradient from 1/1 to 1/3) for several times. The washed film was dried at room temperature for 12 h and then in vacuo at elevated temperatures (gradually from 25 °C to 40 °C) to afford a colorless film of **CP<sub>DFSN</sub>** (2.07 g, 89% yield).

### Synthesis of **CP<sub>Bz</sub>**

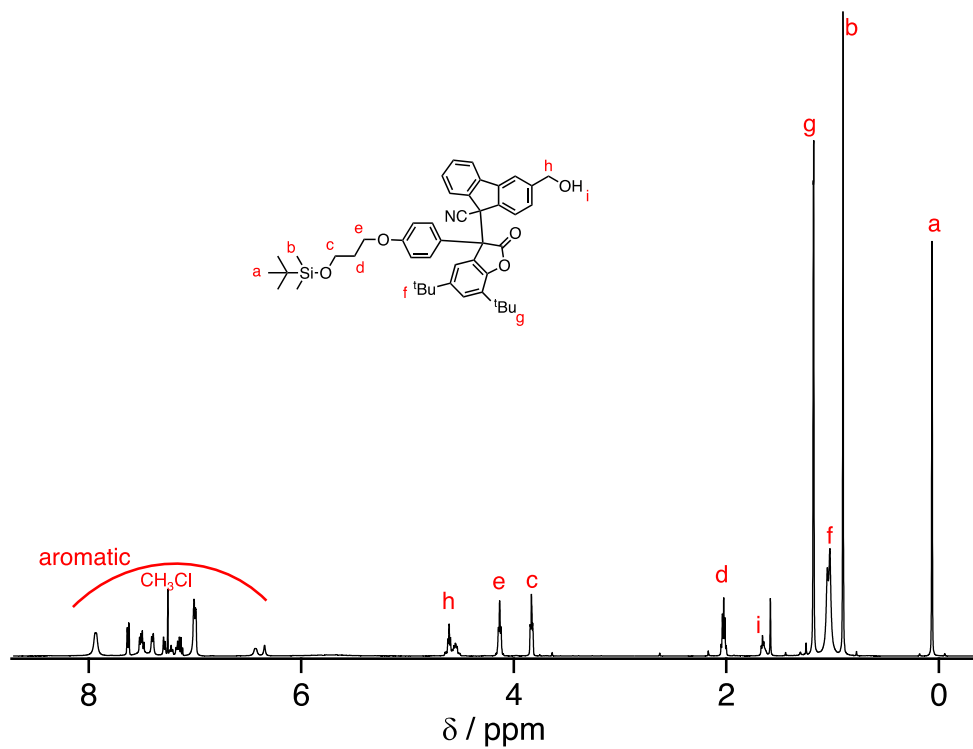


A solution of HMA (2.21 g, 13.0 mmol), Bz-dimethacrylate (58.0 mg, 0.130 mmol), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 40.0 mg, 0.13 mmol) and dry *N,N*-dimethylacetoamide (DMAc, 2.33 g, ca. 50wt%) was degassed by freeze pump thaw cycle three times. After 15 minutes stirring at 25 °C ± 5 °C, the solution was transferred via syringe into a petri dish inside of a N<sub>2</sub>-filled separable flask, which was left for 48 hours. The reaction was quenched by exposure to air, and the obtained polymer film was washed with the mixture of chloroform/methanol (gradient from 1/1 to 1/3) for several times. The washed film was dried at room temperature for 12 h and then in vacuo at elevated temperatures (gradually from 25 °C to 40 °C) to afford a colourless film of **CP<sub>Bz</sub>** (2.01 g, 88% yield).

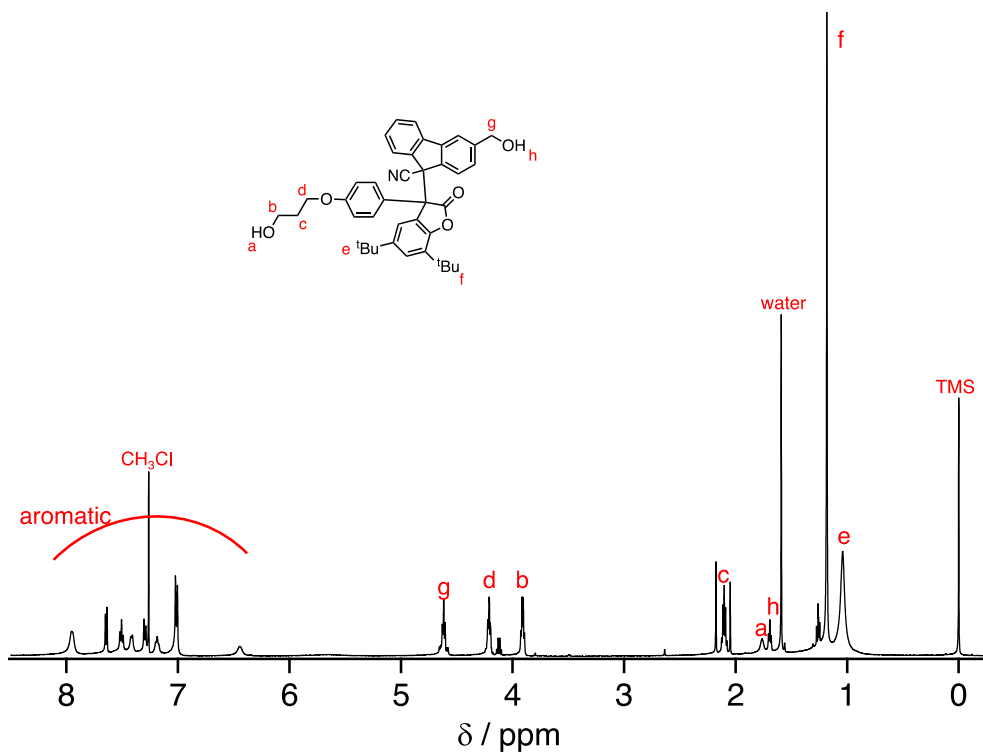




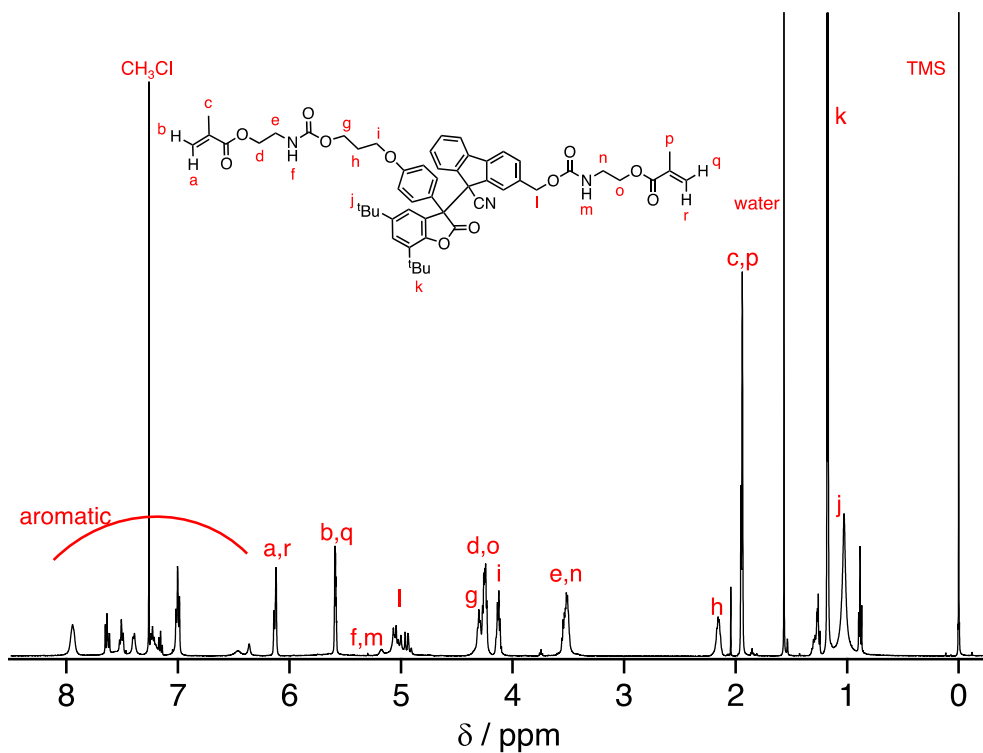
**Figure S1.** <sup>1</sup>H NMR spectrum of **DABBF-diOTBS** (500 MHz, CDCl<sub>3</sub>).



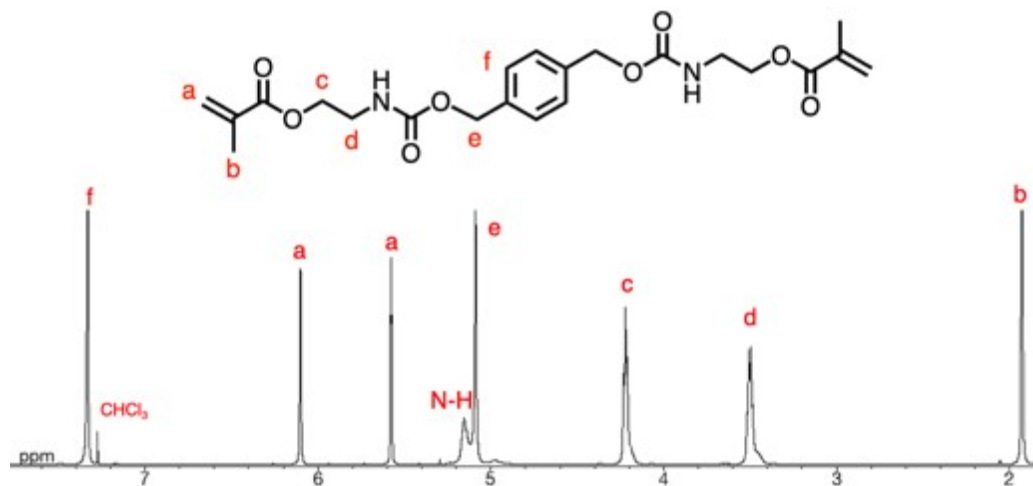
**Figure S2.** <sup>1</sup>H NMR spectrum of **HO-CF/ABF-OTBS** (500 MHz, CDCl<sub>3</sub>).



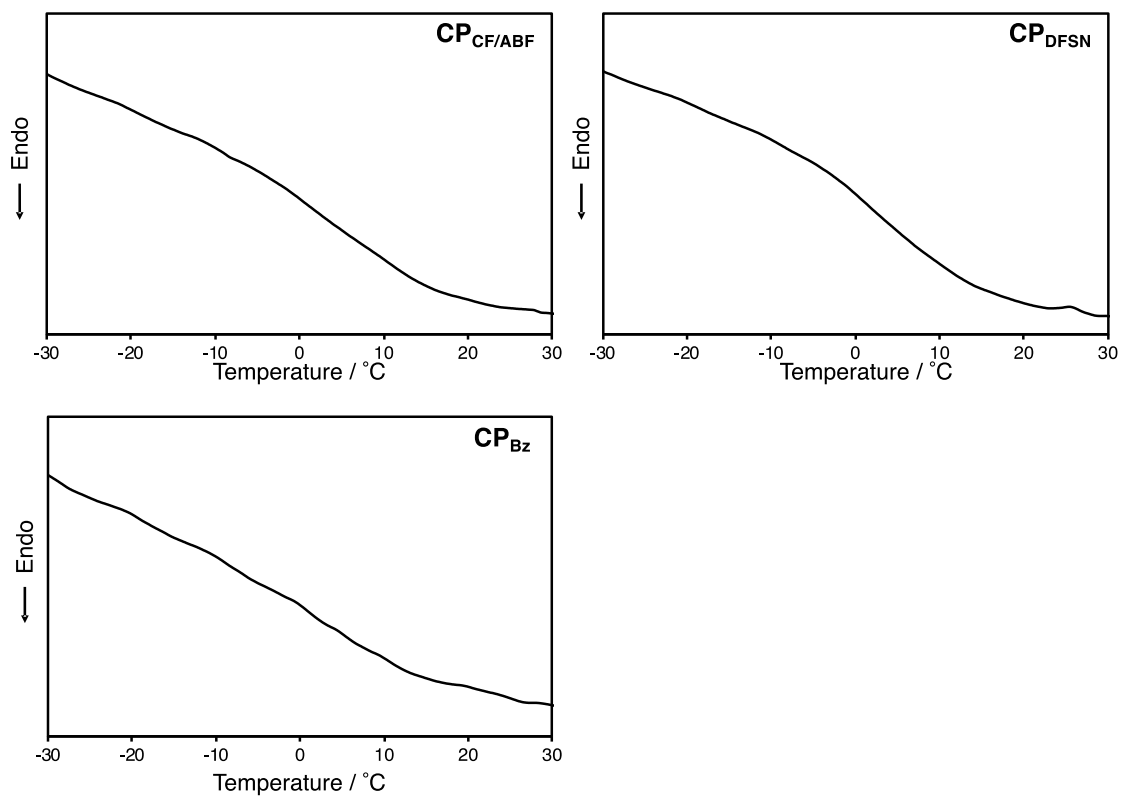
**Figure S3.** <sup>1</sup>H NMR spectrum of CF/ABF-diol (500 MHz, CDCl<sub>3</sub>).



**Figure S4.** <sup>1</sup>H NMR spectrum of CF/ABF-dimethacrylate (500 MHz, CDCl<sub>3</sub>).



**Figure S5.** <sup>1</sup>H NMR spectrum of **Bz-dimethacrylate** (500 MHz, CDCl<sub>3</sub>).



**Figure S6.** DSC curves of CP<sub>x</sub> (10 °C/min).

## Swelling Tests

In a screw-capped vial in the dark, a piece of **CP<sub>CF/ABF</sub>**, **CP<sub>DFSN</sub>**, and **CP<sub>Bz</sub>** films (approx. 3 mm × 3 mm × 0.7 mm) was immersed in anisole at room temperature for 24 h. The ratio of weight increase was calculated by the weights of swollen gel and the original pieces (1). The weight of the gels was measured at out of the solution after removing excess solution from the surface.

$$\text{Swelling degree} = \frac{W_{gel} - W_{dry}}{W_{dry}} \quad (1)$$

**Table S1.** Properties of **CP<sub>x</sub>**.

Cross-linked polymer	Yield (%)	$T_g^a$ (°C)	Swelling degree <sup>b</sup>
<b>CP<sub>CF/ABF</sub></b>	92	-3.6	10.0±0.16
<b>CP<sub>DFSN</sub></b>	89	-3.6	10.7±0.22
<b>CP<sub>Bz</sub></b>	88	-3.9	10.3±0.23

<sup>a</sup> Determined by DSC Measurement (heating rate, 10 °C/min for those polymers)

<sup>b</sup> Estimated by eq 1

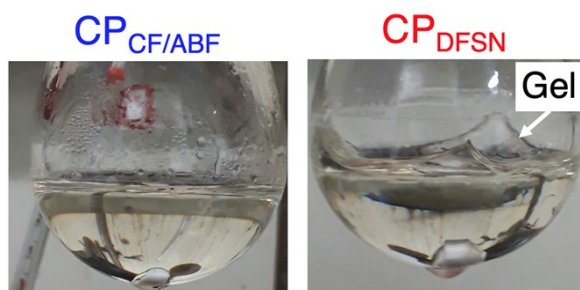
### 3. De-cross-linking reaction

#### De-cross-linking reaction of $CP_{CF/ABF}$

$CP_{CF/ABF}$  (0.200 g, *ca.* 0.0121 mmol of CF/ABF) was immersed in a 4.8 mL anisole solution of DFSN (0.106 g, 0.241 mmol) and degassed by freeze-pump-thaw cycling three times. The solution was stirred at 100 °C in  $N_2$  atmosphere for 1 h. The resulting solution was concentrated, and the obtained polymer ( $M_n$ : 85000 g/mol  $M_w/M_n = 2.69$ ) was purified by reprecipitation into methanol for 2 times. The precipitates were collected by filtration and dried under reduced pressure (0.150 mg).

#### De-cross-linking reaction of $CP_{DFSN}$

$CP_{DFSN}$  (0.202 g, *ca.* 0.0121 mmol of CF/ABF) was immersed in a 4.8 mL anisole solution of DFSN (0.106 g, 0.241 mmol) and degassed by freeze-pump-thaw cycling three times. The solution was stirred at 100 °C in  $N_2$  atmosphere for 24 h. The resulting solution was concentrated, and the obtained polymer ( $M_n$ : 81000 g/mol  $M_w/M_n = 3.48$ ) was purified by reprecipitation into methanol for 2 times. The precipitates were collected by filtration and dried under reduced pressure (0.183 mg).



**Figure S7.** Photographs of  $CP_{DFSN}$  and  $CP_{CF/ABF}$  after 1 h of de-cross-linking reactions.

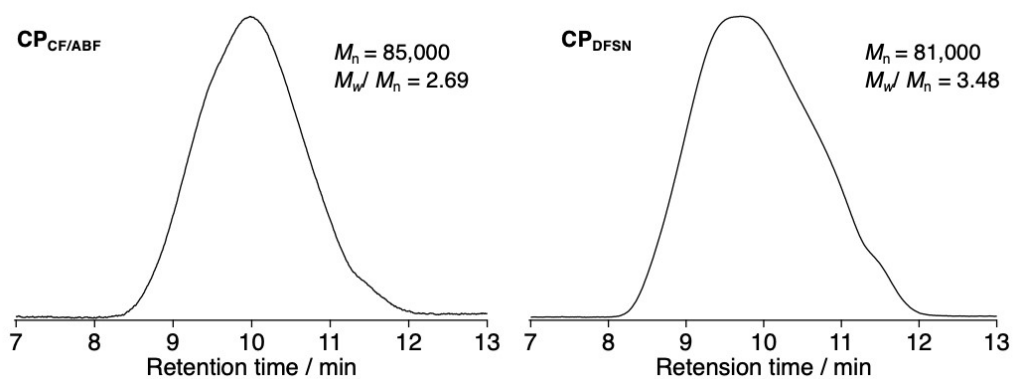


Figure S8. GPC profiles of de-cross-linked  $\text{CP}_{\text{CF/ABF}}$  and  $\text{CP}_{\text{DfSN}}$  (THF, PS standard).

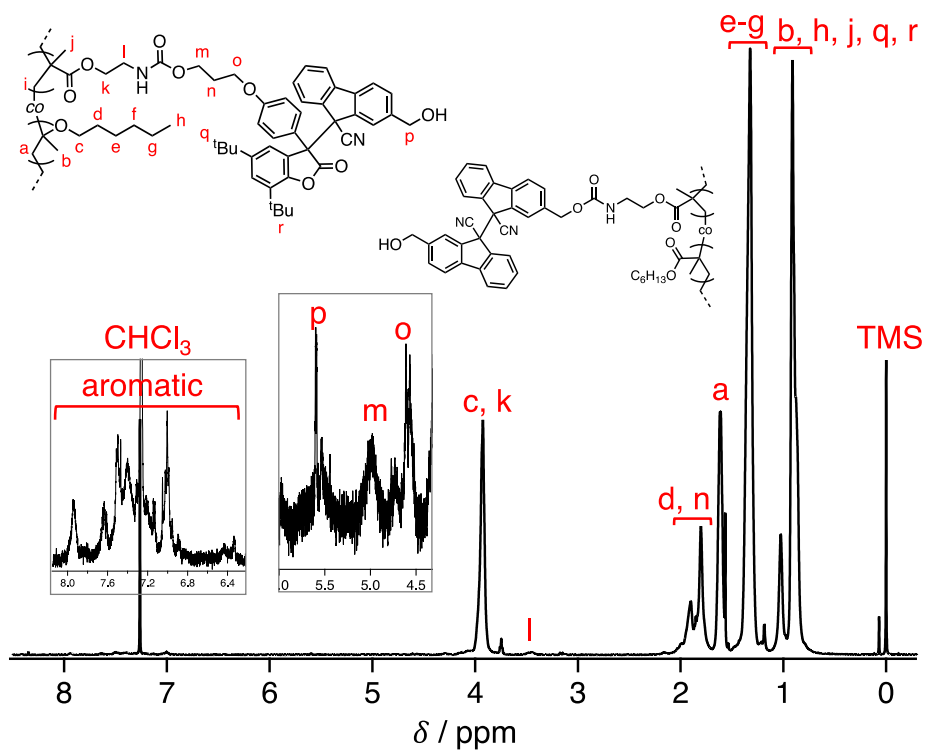
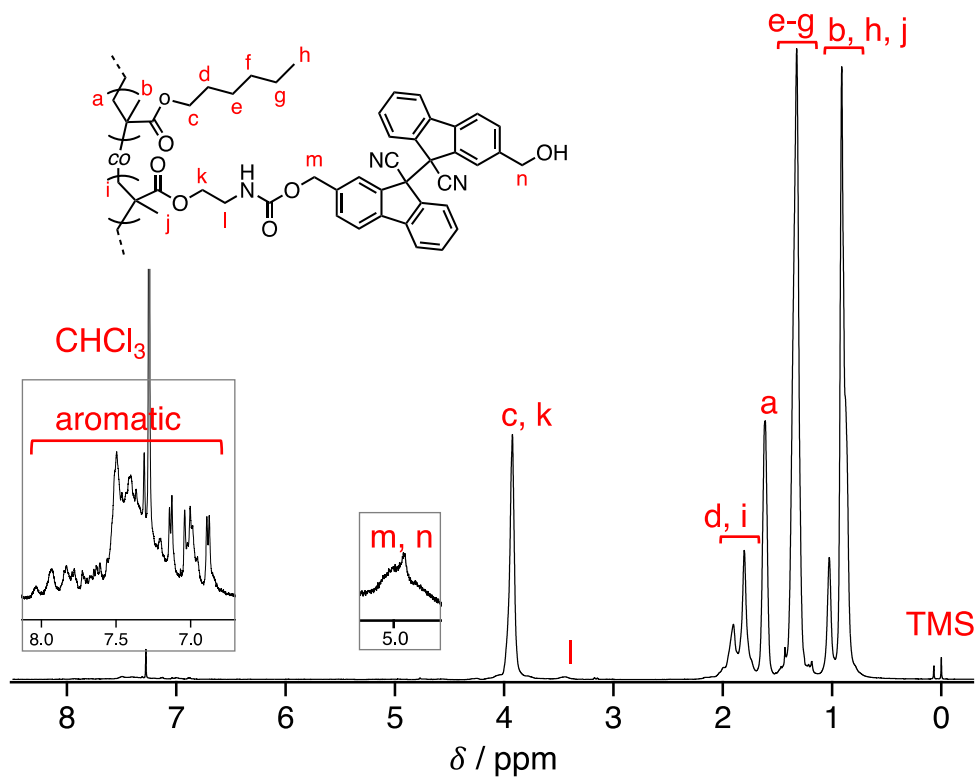
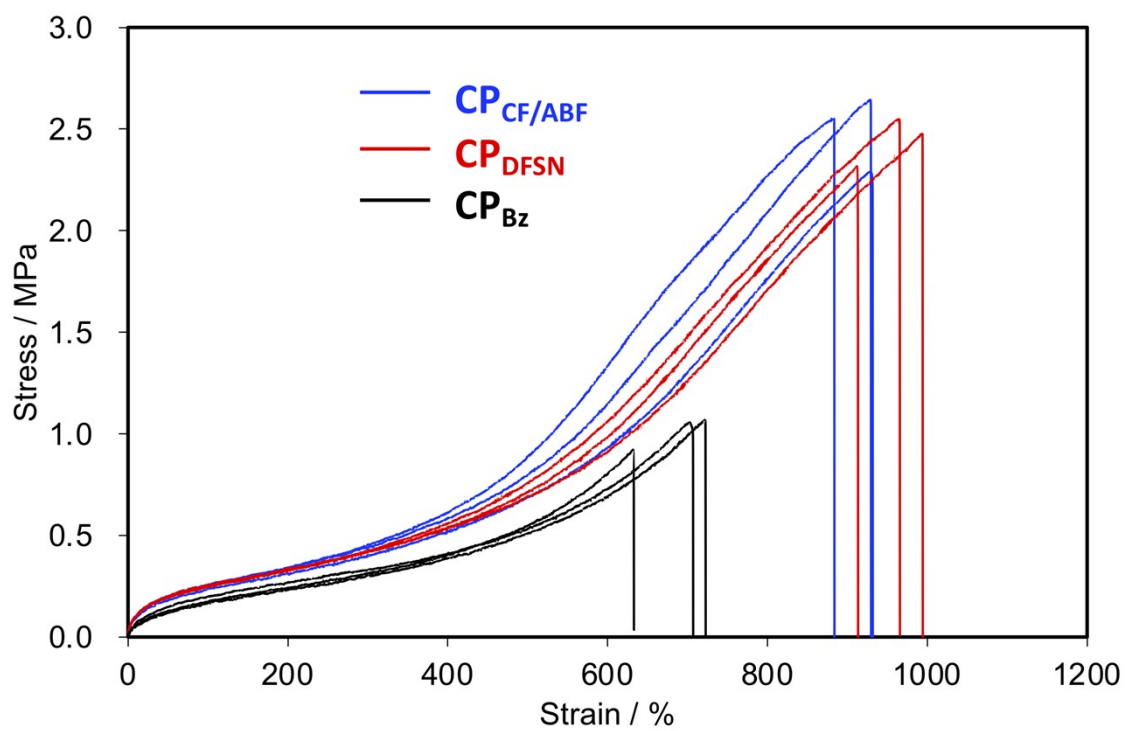


Figure S9.  $^1\text{H}$  NMR spectrum of de-cross-linked  $\text{CP}_{\text{CF/ABF}}$  (500 MHz,  $\text{CDCl}_3$ ).



**Figure S10.**  $^1\text{H}$  NMR spectrum of de-cross-linked  $\text{CP}_{\text{DFSN}}$  (500 MHz,  $\text{CDCl}_3$ ).

#### 4. Tensile tests



**Figure S11.** Stress–strain curves of **CP<sub>CF/ABF</sub>** (blue), **CP<sub>DFSN</sub>** (red) and **CP<sub>Bz</sub>** (black) films (three samples each, 100 mm/min, 30 °C).

## 5. Reference

- 1 H. Sakai, D. Aoki, K. Seshimo, K. Mayumi, S. Nishitsuji, T. Kurose, H. Ito and H. Otsuka, *ACS Macro Lett.*, 2020, **9**, 1108–1113.