Supporting Information

Additive Manufacturing of Poly(dicyclopentadiene) and Carbon-Fiber Composites via Heating at a Patterned Photothermal Interface

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Synthesis of poly(tetracyclododecene)-imide-norbornene (pTD-NB)

General Information

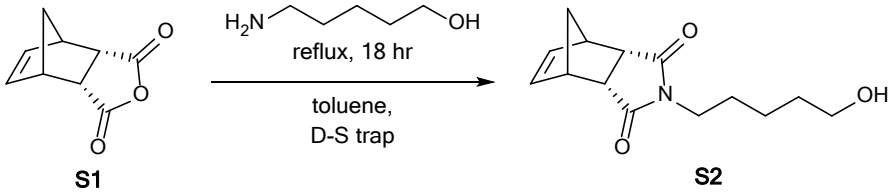
Materials and General Considerations. Dichloromethane, 1,2-dichloroethane, and 1, 2-dichlorobenzene (*o*-DCB) used for MF-ROMP were dried over 3Å molecular sieves for at least 24 h before use. Tetracyclododecene was provided by Promerus as a 95:5 mixture of the endo-endo:endo-exo isomer and used without further purification. 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate was synthesized following a literature procedure.[1] Metal-Free ROMP (MF-ROMP) was conducted with a Norman Lamps blue LED lamp (part #: LED-MR16-4W-BLU). Automated flash chromatography was performed using a Biotage Selekt with Biotage Sfär Silica-D – Duo 60 µm prepacked columns using the elution gradient suggested by the software for the reported TLC conditions. All other reagents and solvents were acquired from commercial sources and used without purification unless otherwise noted.

Characterizations. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 or 500 MHz spectrometers. ^{1}H NMR shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using protio-solvent (residual) as internal standard ($CDCl_3$, δH = 7.26 ppm). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad. ^{13}C NMR chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using protio-solvent (residual) as internal standard (CDCl3, δC = 77 ppm). Gel permeation chromatography (GPC) was performed using the following setup: an Agilent Technologies 1260 Infinity II pump with two inline Agilent PLgel (part #: PL1113-6300) columns, Wyatt Technology mini-DAWN light scattering, and Agilent

1260 Infinity II RI detectors, using HPLC grade toluene as the mobile phase, at a flow rate of 1 mL min^{-1}. The absolute weight-average molecular weight of polymeric substrates was determined by MALS using their respective dn/dc values. Values of each polymer's dn/dc were determined using Wyatt's ASTRA software assuming 100% mass recovery from the GPC columns.

Initiator Synthesis

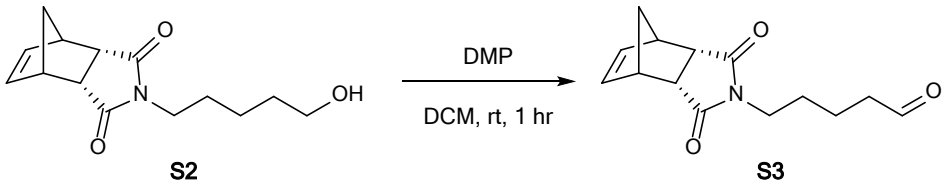
S2



S2 was prepared according to a previously reported procedure[2].

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (s, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 3.41 – 3.36 (m, 2H), 3.34 (t, *J* = 7.3 Hz, 2H), 3.24 (d, *J* = 1.8 Hz, 2H), 1.73 (d, *J* = 8.8 Hz, 1H), 1.61 – 1.51 (m, 3H), 1.47 (p, *J* = 7.4 Hz, 2H), 1.32 (tt, *J* = 9.7, 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.81, 134.45, 62.63, 52.25, 45.76, 44.92, 38.21, 32.13, 27.53, 23.00. **MS-ESI** (m/z) $[M+H]^+$ calculated for $C_{14}H_{19}NO_3$ = 250.1438; found 250.1434 (1.6 ppm).

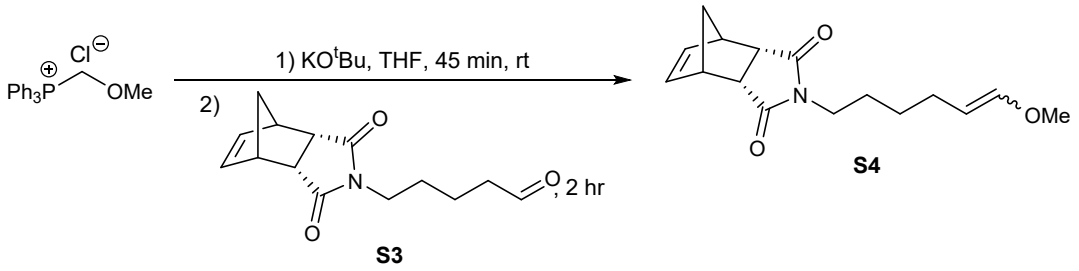
S3



To a flame-dried stirred flask of DMP (12.09g, 28.5 mmol, 1.2 equiv.) in DCM (150 mL) was added **S2** (5.92 g, 28.5 mmol, 1.0 equiv.) in 100 mL DCM. Reaction was stirred for 45 minutes. Reaction was diluted with diethyl ether (100 mL), and 1.3M NaOH (200 mL) was added. Reaction was stirred for 30 minutes. Organic layer was isolated and washed with NaOH, H_2O, and brine. Reaction mixture was concentrated under reduced pressure. The crude product was used without further purification.

76% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 6.10 (s, 2H), 3.41 – 3.37 (m, 2H), 3.34 (t, *J* = 7.0 Hz, 2H), 3.24 (d, *J* = 1.4 Hz, 2H), 2.44 (td, *J* = 7.2, 1.4 Hz, 2H), 1.76 – 1.70 (m, 1H), 1.61 – 1.43 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.78, 177.73, 134.50, 134.49, 52.30, 45.78, 44.93, 43.17, 37.82, 27.15, 19.21. **MS-ESI** (m/z) $[M+H]^+$ calculated for $C_{14}H_{17}NO_3$ = 248.1281; found 248.1277 (1.6 ppm).

S4



A solution of potassium tert-butoxide (3.62 g, 32.3 mmol, 1.50 equiv.) in 15 mL of dry THF was slowly added to a solution of (methoxymethyl)triphenylphosphonium chloride (11.1 g, 32.3 mmol, 1.50 equiv.) in 40 mL of dry THF. After stirring the red solution at room temperature for 45 min, a solution of **S3** (5.32 g, 21.5 mmol, 1.00 equiv.) in 10 mL of dry THF was slowly added and allowed to stir at room temperature for an additional 2 h. The solvent was removed under vacuum and the yellow oil was diluted with a 1:1 mixture of hexanes and Et_2O. The organic layer was washed with water (3 x 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting oil was purified by flash chromatography to yield a clear yellow oil. TLC on silica in 1 : 1 EtOAc : hexanes, product R_f=0.33. The product was visualized as a yellow spot on a pink background after staining with $KMnO_4$. 34% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26 (d, *J* = 12.5 Hz, 0.65 H, *trans*), 6.09 (t, *J* = 1.9 Hz, 2H), 5.86 (dt, *J* = 6.2, 1.5 Hz, 0.35 H, *cis*), 4.67 (dt, *J* = 12.7, 7.3 Hz, 0.65 H, *trans*), 4.28 (td, *J* = 7.4, 6.2 Hz, 0.35 H, *cis*), 3.56 (s, 1.05 H, *cis*), 3.49 (s, 1.95 H, *trans*), 3.38 (dp, *J* = 3.6, 1.8 Hz, 2H), 3.32 (td, *J* = 7.3, 1.5 Hz, 2H), 3.23 (ddd, *J* = 4.3, 3.0, 1.5 Hz, 2H), 2.03 (qd, *J* = 7.4, 1.4 Hz, 0.70 H, *cis*), 1.90 (qd, *J* = 7.3, 1.2 Hz, 1.30 H, *trans*), 1.72 (ddt, *J* = 8.8, 3.4, 1.7 Hz, 1H), 1.55 – 1.49 (m, 1H), 1.44 (dddd, *J* = 10.5, 8.8, 6.7, 5.0 Hz, 2H), 1.34 – 1.21 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.75, 147.37, 146.45, 134.44, 106.12, 102.38, 59.46, 55.92, 52.24, 45.75, 44.92, 38.24, 27.97, 27.17, 23.33. **MS-ESI** (m/z) $[M+H]^+$ calculated for $C_{16}H_{21}NO_3$ = 276.1594; found 276.1590 (1.4 ppm).

Macromonomer Synthesis

Synthesis of MMs by MF-ROMP

S4 (1 equiv.) and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (0.5 equiv.) were weighed into a 2-dram vial with PTFE-lined screw cap and containing a magnetic stir bar. Then TD monomer (12.5-100 equiv., 2.5 mmol) was added gravimetrically. 2.5 mL each of dry DCM and dry *o*-DCB were added to the vial for a resulting monomer concentration of 0.5 M, followed by 1 to 2 drops of 1,2-dichloroethane (DCE). An aliquot was taken, diluted with $CDCl_3$, and analyzed by ^{1}H NMR spectroscopy to determine the initial DCE to initiator ratio. The solution was irradiated with blue LED light for 1 hour with stirring. After 1 hour the light was turned off and an aliquot of the solution was taken, diluted with $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy to determine the final DCE to initiator ratio, as well as monomer conversion. A

second aliquot was taken, diluted with THF or toluene, and analyzed by GPC. The remaining crude polymer solution was precipitated in rapidly stirred cold (-78 °C) MeOH, resulting in the formation of solids. The solids were isolated by vacuum filtration, then redissolved in THF and precipitated again to remove any residual monomer. The resulting solids were dried overnight under high vacuum.

S2

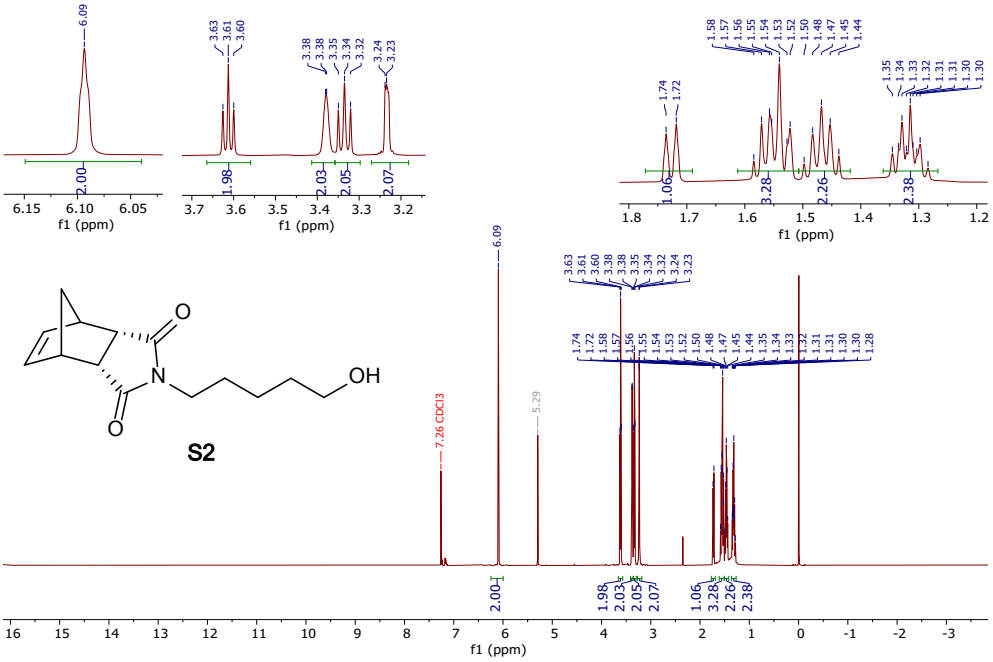


Fig. S1 500 MHz ^{1}H NMR spectrum of **S2** in $CDCl_3$.

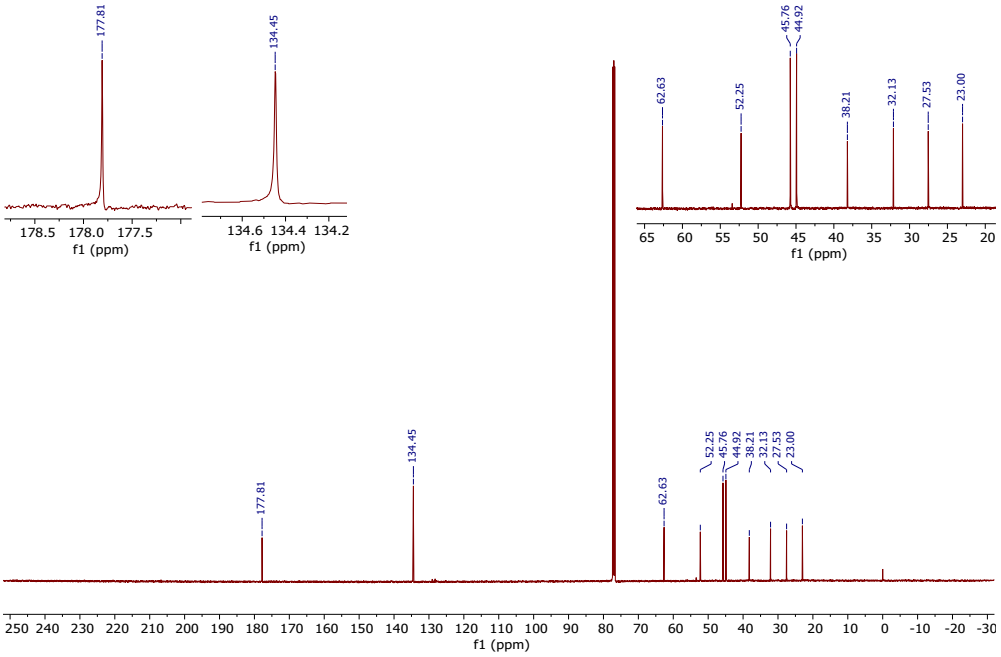


Fig. S2 126 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **S2** in $CDCl_3$.

S3

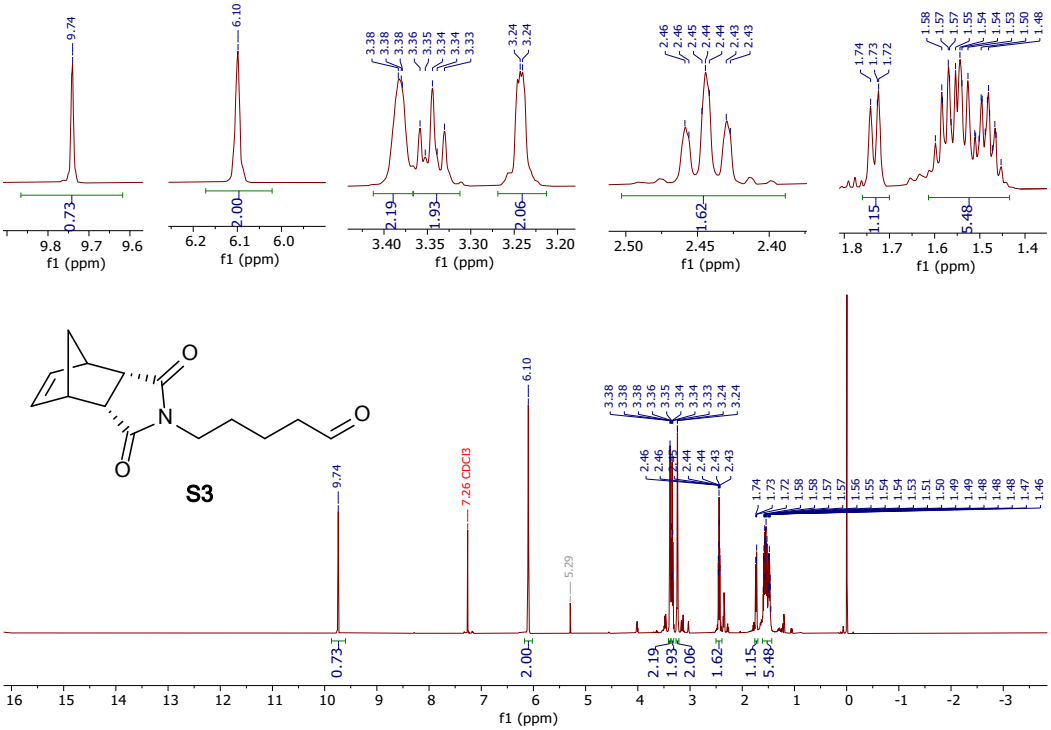


Fig. S3 500 MHz ^{1}H NMR spectrum of **S3** in $CDCl_3$.

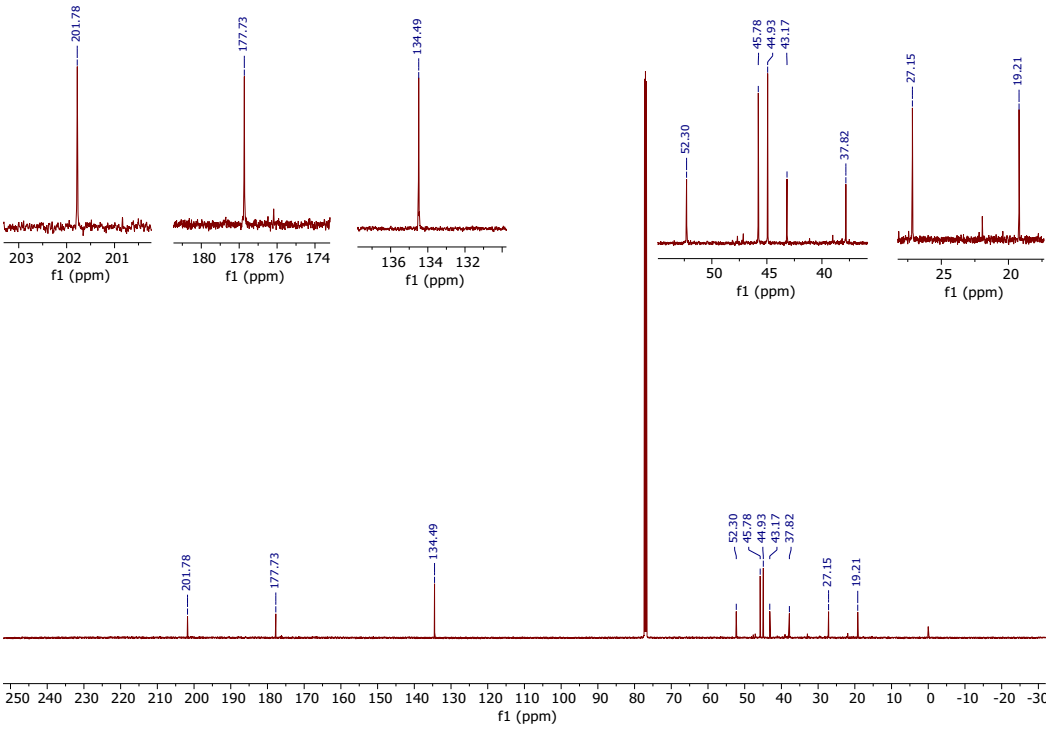


Fig. S4 126 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **S3** in $CDCl_3$.

S4

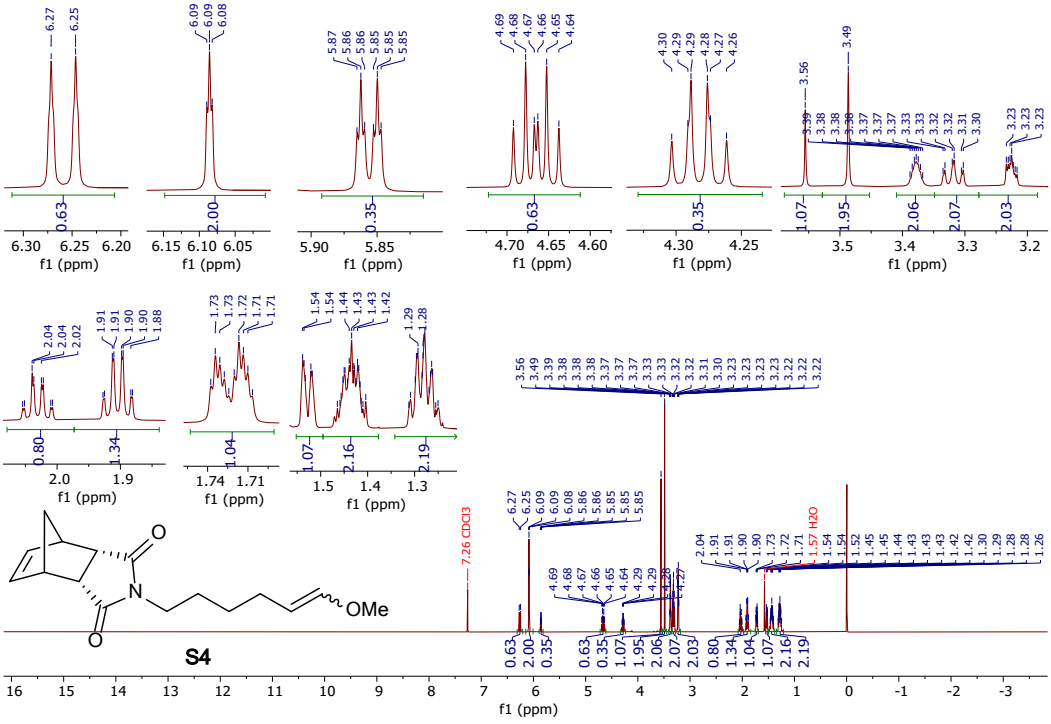


Fig. S5 500 MHz ^{1}H NMR spectrum of **S4** in $CDCl_3$.

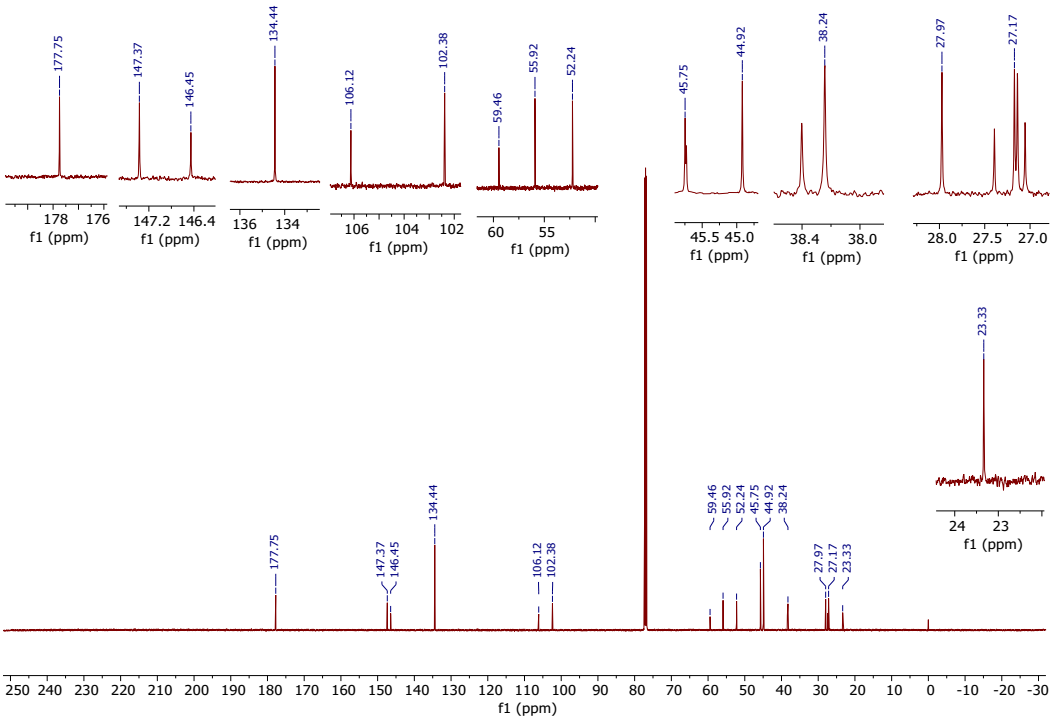


Fig. S6 126 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **S4** in $CDCl_3$.

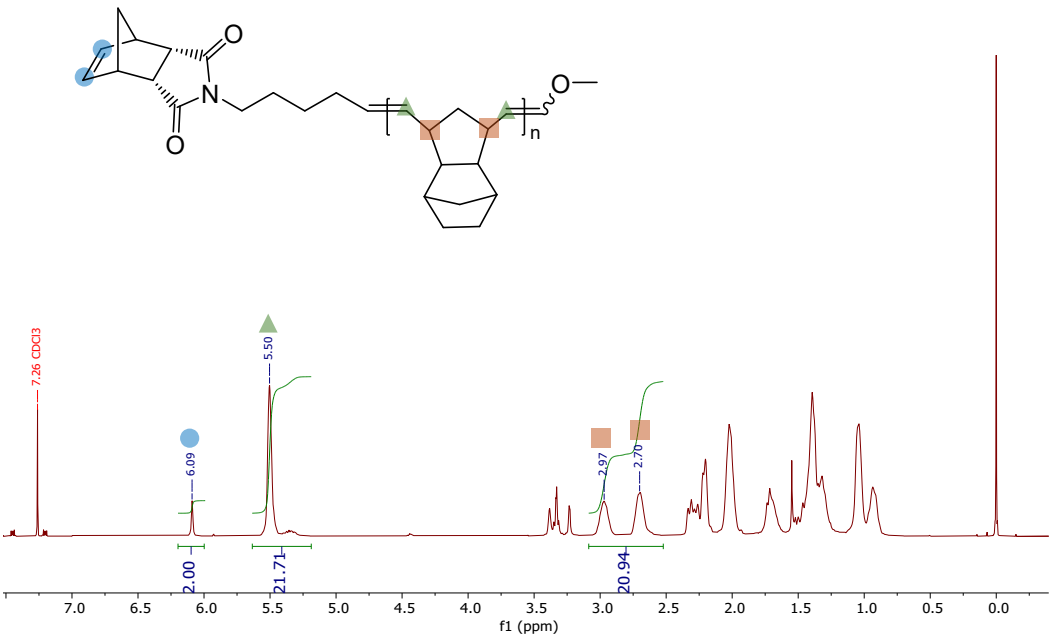
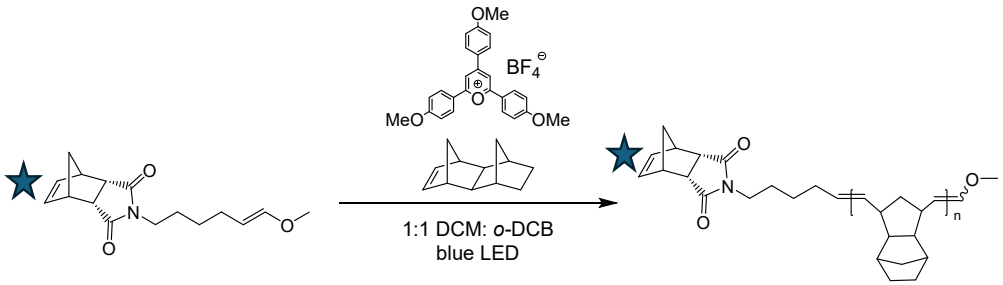


Fig. S7 500 MHz ^{1}H NMR spectrum of **$TD_{2.5k}$-NBI-*endo*** in $CDCl_3$.



[TD] : [I] : [PC]	t (min)	conv.	M_n (kDa)	Đ	*f*
50 : 1 : 0.05	60	76%	13.1	1.32	46%

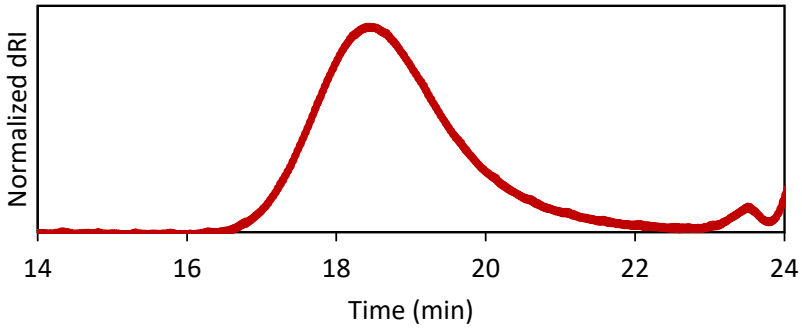


Fig. S8 Crude GPC (toluene) dRI trace of MF-ROMP of **S4** after 60 minutes of irradiation.

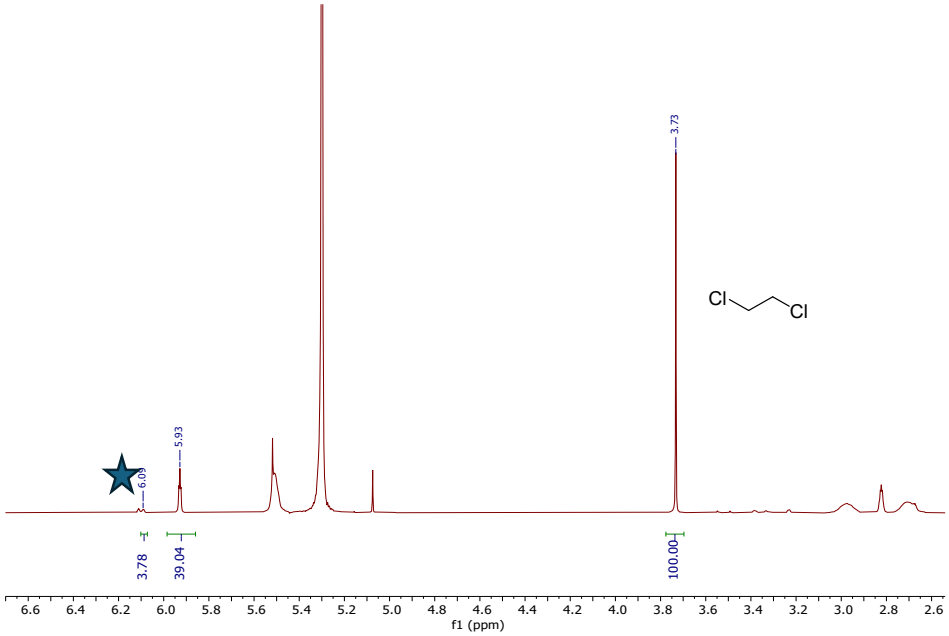


Fig. S9 400 MHz ^{1}H NMR of MF-ROMP with *endo*-norbornene imide enol ether initiator before (top) and after (bottom) 60 minutes of irradiation. Integration of norbornene-imide alkene at 6.09 ppm (indicated by star) relative to the integration of a DCE internal standard at 3.73 ppm does not change over the course of the reaction.

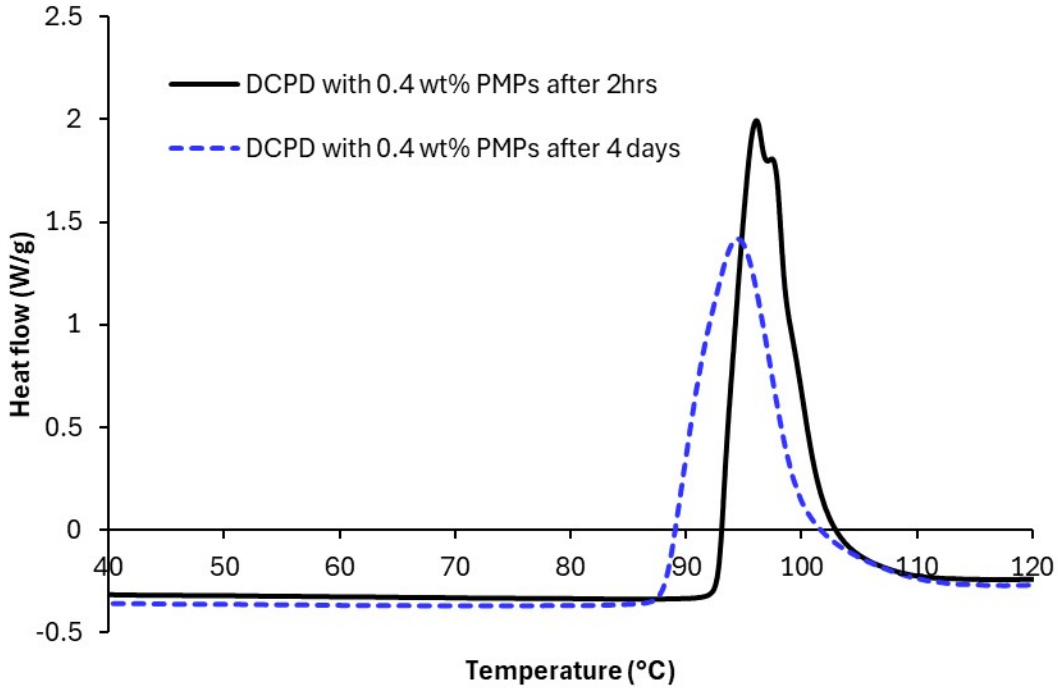


Fig. S10 DSC thermograms of DCPD with 0.4 wt% PSU-PMPs after stirring for 2 hrs (solid black line) and DCPD with 0.4 wt% PSU-PMPs after stirring for 4 days (blue dashed line).

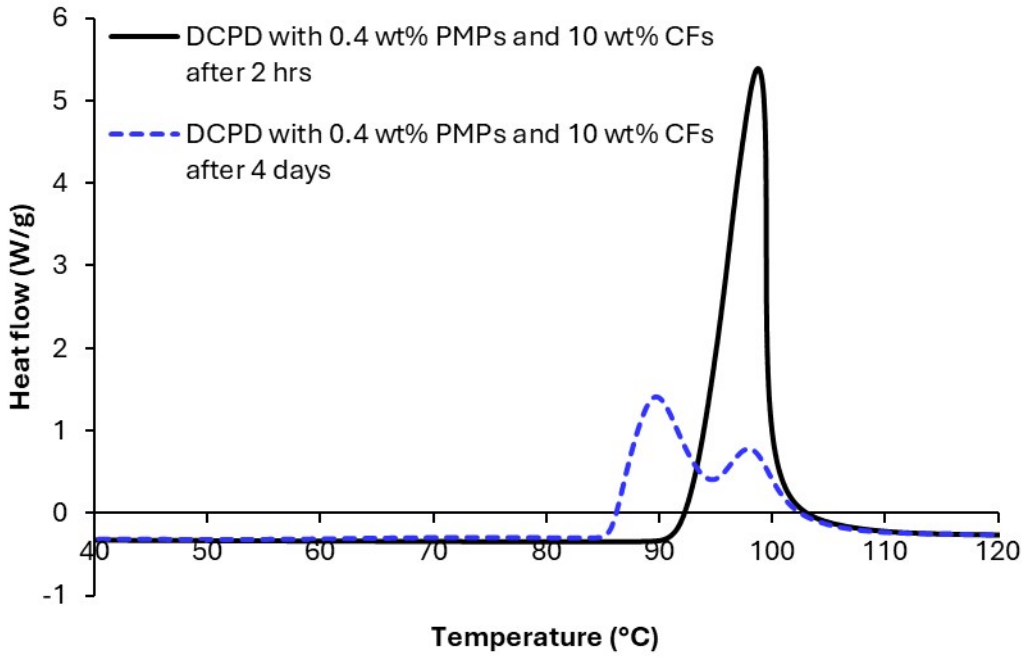


Fig. S11 DSC thermograms of DCPD with 0.4 wt% PSU-PMPs and 10 wt% CFs after stirring for 2 hrs (solid black line) and DCPD with 0.4 wt% PSU-PMPs and 10 wt% CFs after stirring for 4 days (blue dashed line).

Table S1 DSC results of DCPD or DCPD with 10% CFs after stirring 2 hrs or 4 days.

	Onset (˚C)	Peak (˚C)	Enthalpy (J/g)
DCPD after 2 hrs	93	96	76
DCPD after 4 days	87	95	90
DCPD + 10%CF after 2 hrs	98	91	136
DCPD _ 10%CF after 4 days	85	90, 97	99

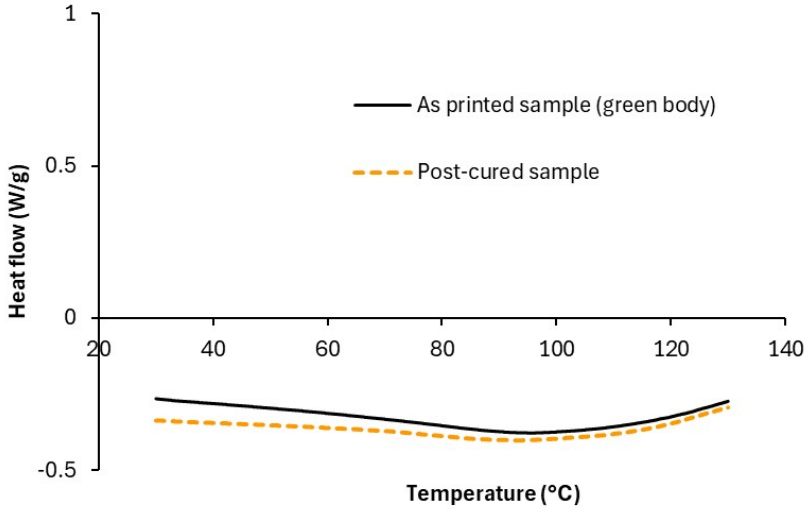


Fig. S12 DSC thermograms of a printed dogbone (solid black) and a dogbone after post-curing at 150 C for 3 hrs (orange dashed line).

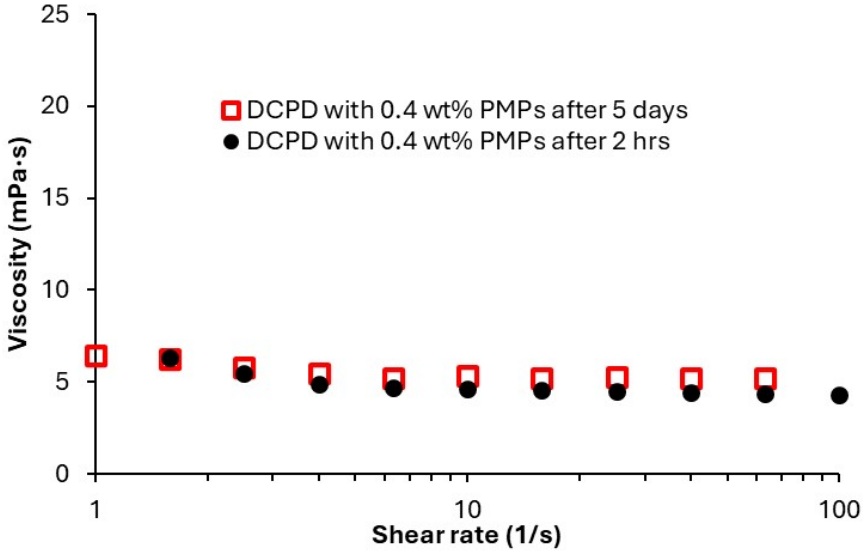


Fig S13. Apparent viscosity of DCPD with 0.4 wt% PMPs after stirring for 2 hrs or 5 day.

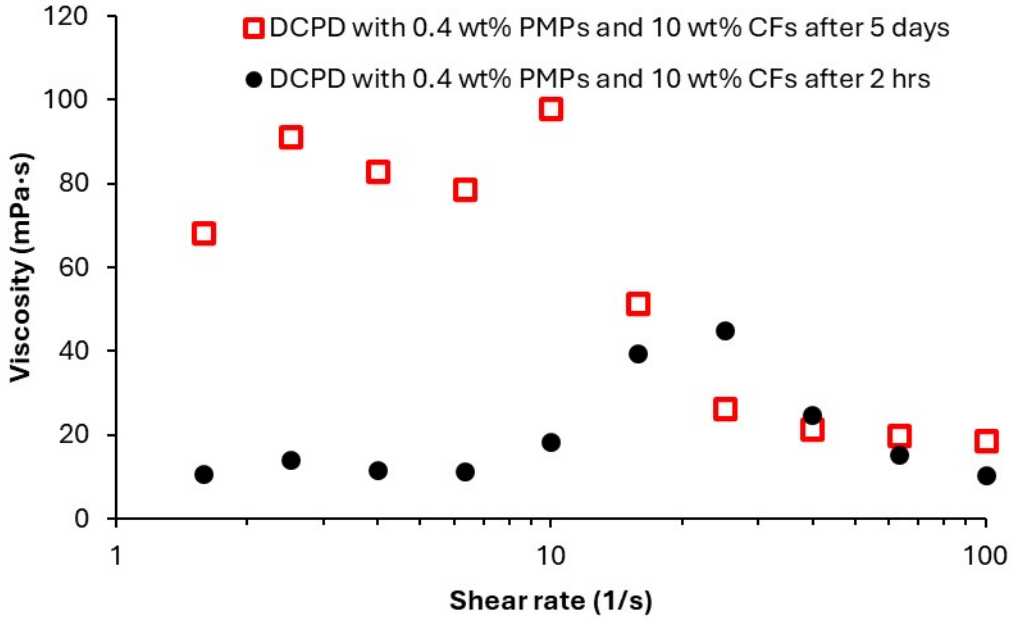


Fig S14. Apparent viscosity of DCPD with 0.4 wt% PMPs and 10 wt% CFs after stirring for 2 hrs or 5 day.

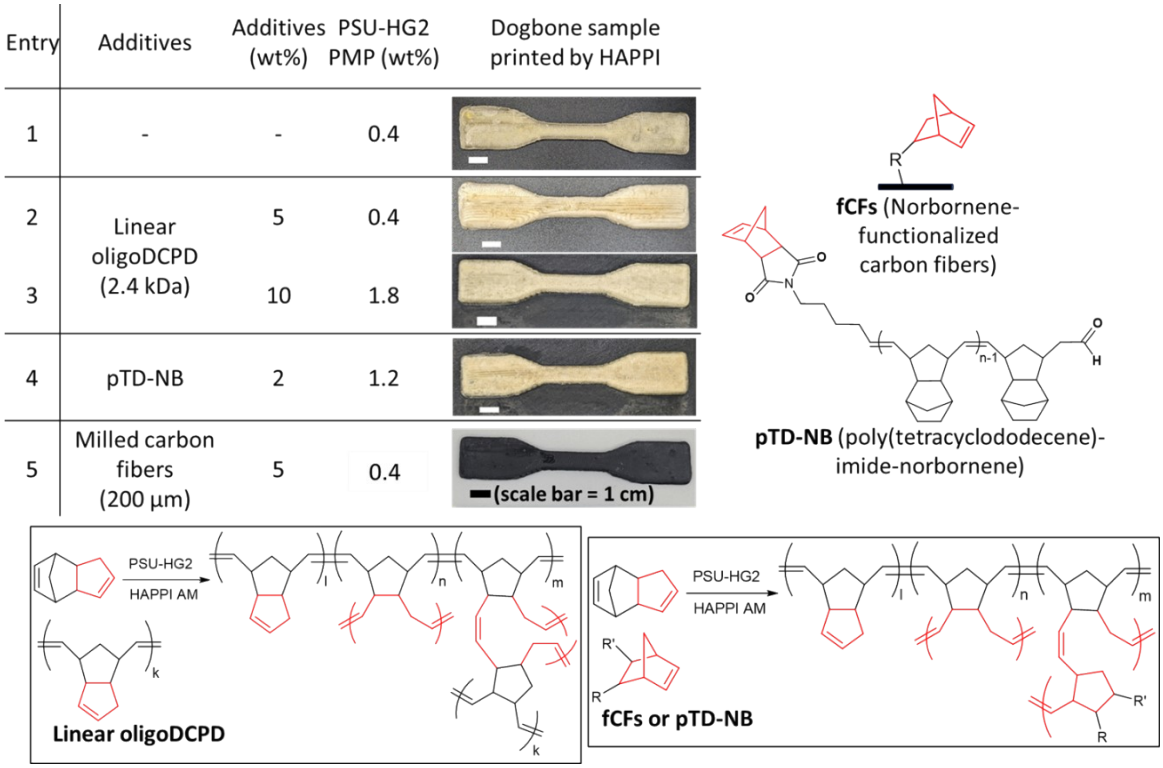


Fig. S15 Dogbone samples of pDCPD or pDCPD with various additives, linear oligoDCPD, pTD-NB or milled CF produced by HAPPI AM and reaction scheme for metathesis reaction of

DCPD with the additives. Note: Dogbone samples were width of 7.5 mm, thickness of 3 mm, and length of 3 to 4 mm.

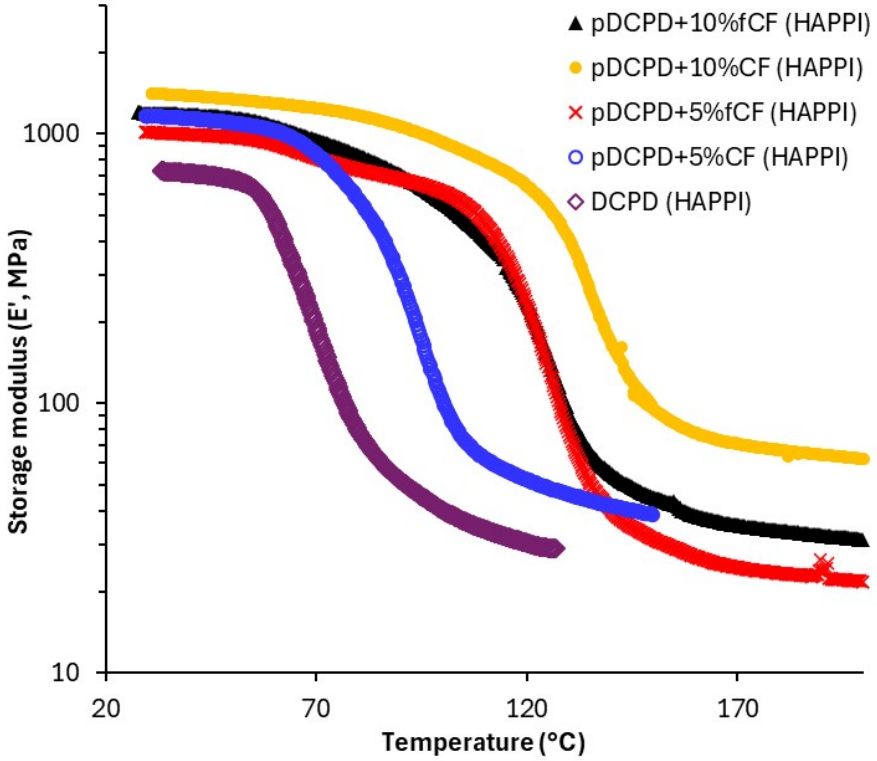


Fig. S16 Storage modulus (E', MPa) of pDCPD, pDCPD-5%CF, pDCPD-5%fCF, pDCPD-10%CF, and pDCPD-10%fCF rectangles prepared by HAPPI AM.

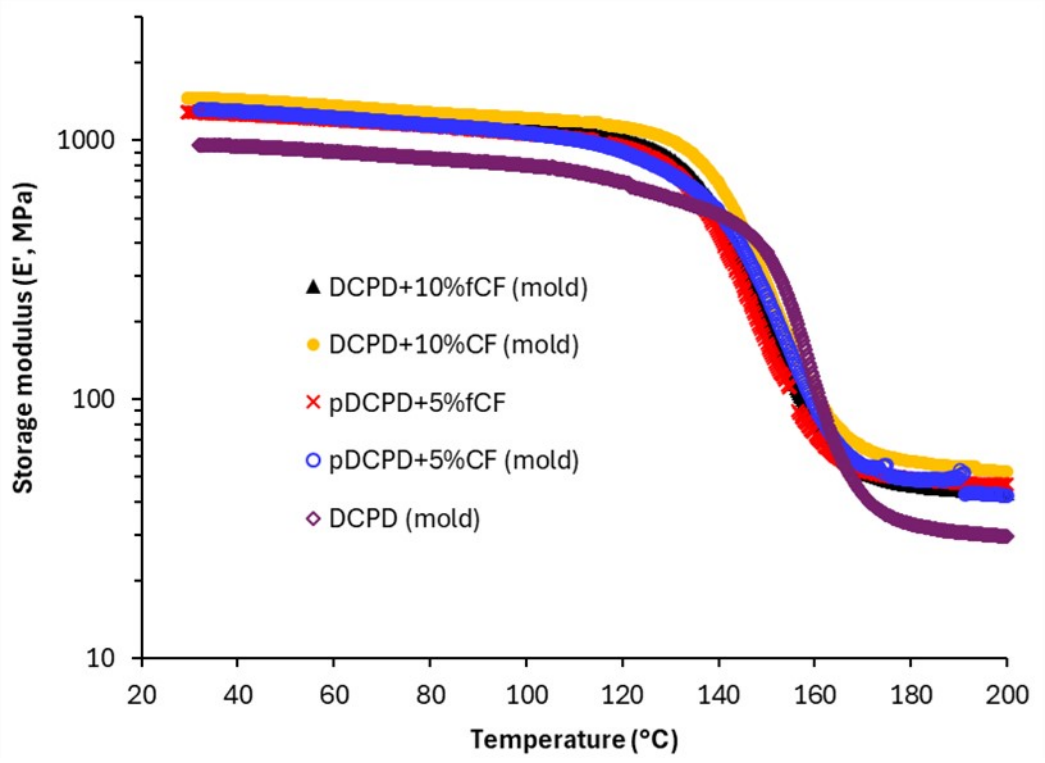


Fig. S17 Storage modulus (E', MPa) of pDCPD, pDCPD-5%CF, pDCPD-5%fCF, pDCPD-10%CF, and pDCPD-10%fCF rectangles prepared by molding.

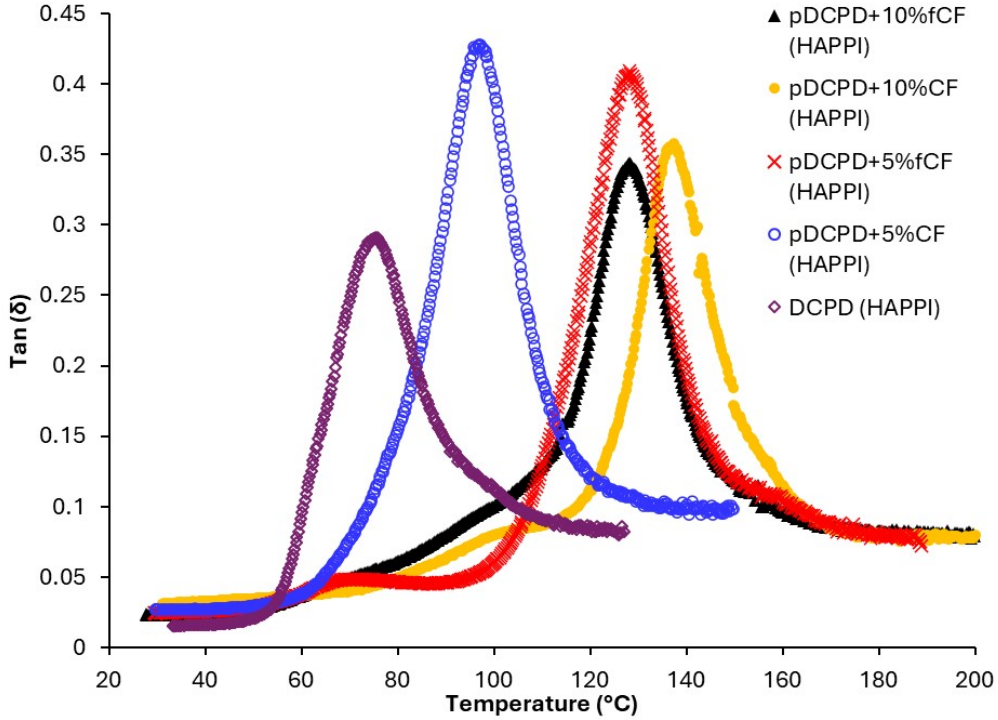


Fig. S18 Tan (δ) of pDCPD, pDCPD-5%CF, pDCPD-5%fCF, pDCPD-10%CF, and pDCPD-10%fCF rectangles prepared by HAPPI AM.

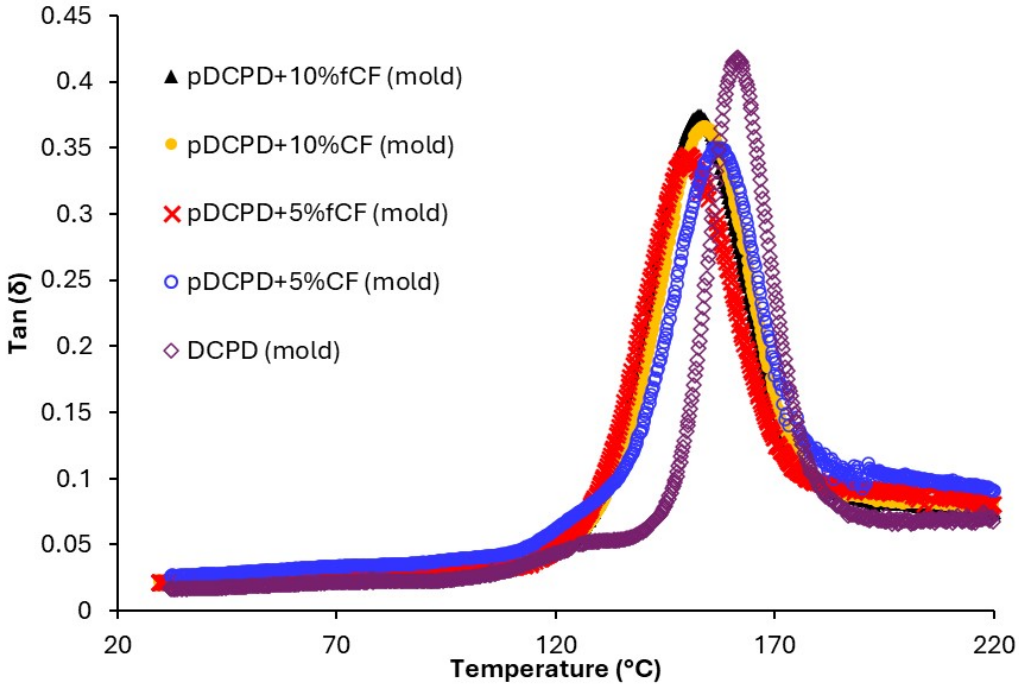
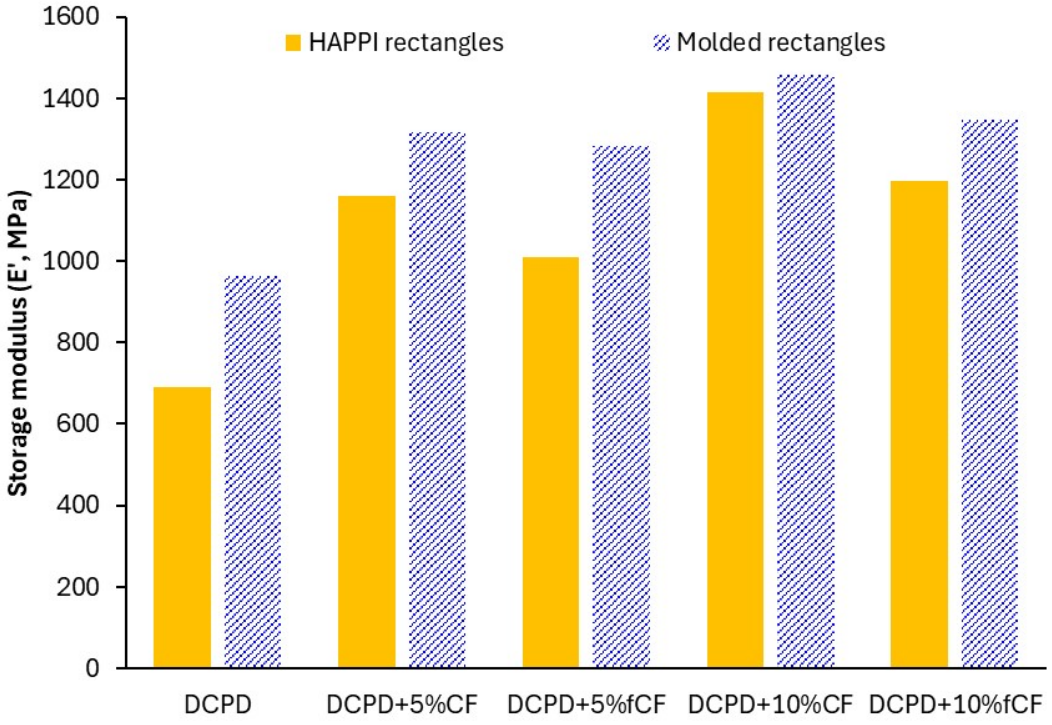


Fig. S19 Tan (δ) of pDCPD, pDCPD-5%CF, pDCPD-5%fCF, pDCPD-10%CF, and pDCPD-10%fCF rectangles prepared by HAPPI AM.

Table S2 Comparison between samples of pDCPD, pDCPD+5% CF, pDCPD+5%fCF, pDCPD+10%CF, and pDCPD+10% fCF prepared by HAPPI versus molding from DMA results shown in Figs. S16 through S19.

Formulation	Storage modulus (E', MPa) at 33 °C		T_g from tan(δ) peak (°C)	
	HAPPI	Molded	HAPPI	Molded
DCPD	690	962	89	161
pDCPD+5%CF	1160	1316	97	157
pDCPD+5%fCF	1009	1281	128	150
pDCPD+10%CF	1414	1458	137	154
pDCPD+10%fCF	1198	1346	128	153



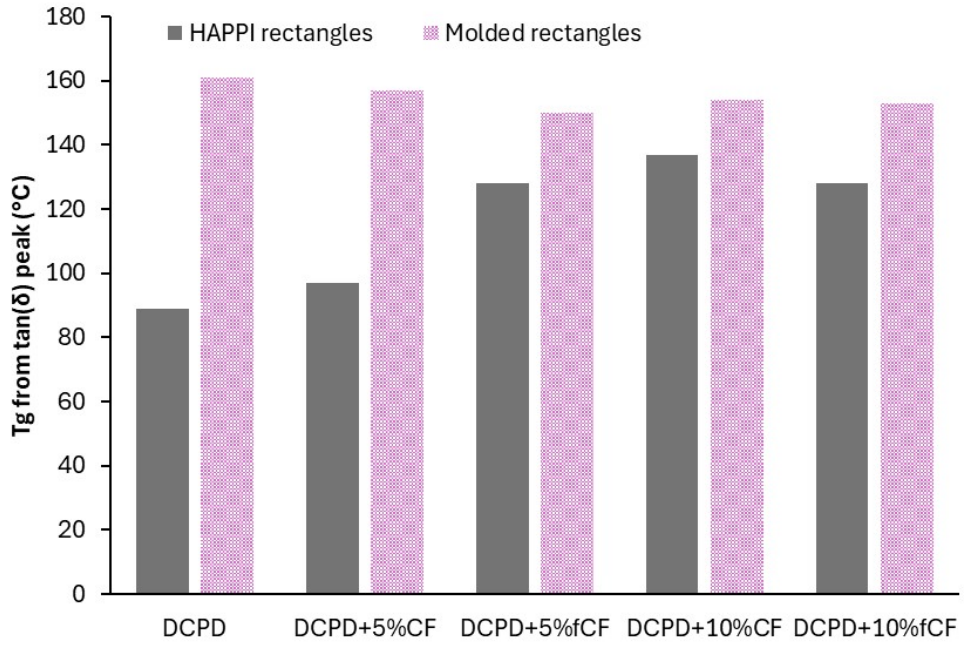


Fig. S20 Comparison of storage modulus (E') at 33 °C and T_g from tan (δ) peak samples prepared by HAPPI AM to those by molding shown in Table S2.

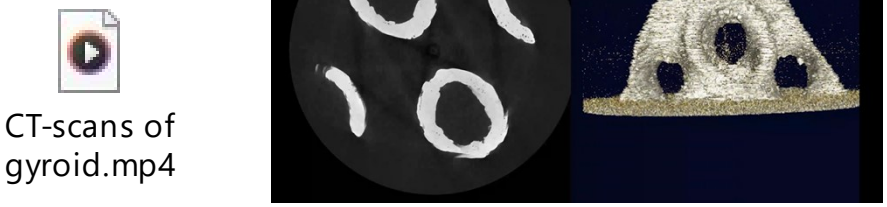


Fig. S21 Video showing CT-scans of gyroid (presented in Fig. 3) and a still image of it.

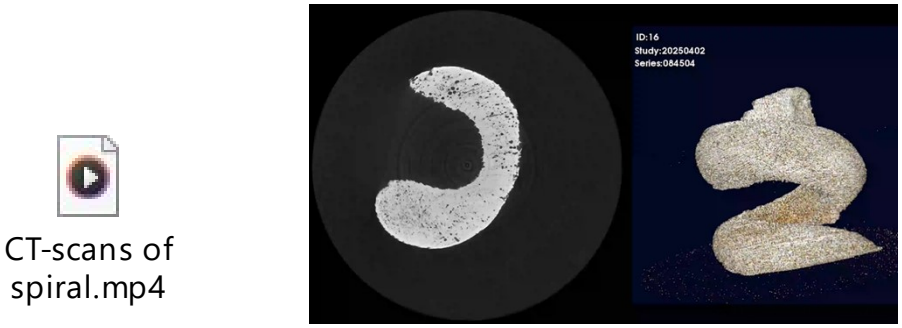


Fig. S22 Video showing CT-scans of spiral (presented in Fig. 3) and a still image of it.

References

1 K. A. Ogawa, A. E. Goetz and A. J. Boydston, *J. Am. Chem. Soc.*, 2015, **137**, 1400–1403.