Supplementary Information for

Expanding Monomer Scope and Enabling Post-Modification in Photocontrolled Radical Ring-Opening Polymerization of Vinylcyclopropanes by An Iodine Transfer Strategy

Dong-Yang Zhang,[†,§] Dong Han,[‡,§] Yue Li,[†] Dian-Feng Chen*[,†]

[†]Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China. [‡]Department of Oral and Maxillofacial Surgery, Hefei First People's Hospital, Hefei, Anhui 230001, China.

[§]These authors contributed equally to this work

*Correspondence to: cdf@ustc.edu.cn

Table of Contents

1. Materials and Methods

1.1 Materials

All Chemicals were purchased from TCI, J&K, Energy Chemical, and Adamas-beta, and were used as received without further purification.

Deuterated chloroform was purchased from Cambridge Isotope Laboratories.

All anhydrous solvents were purchased from J&K and were used as received.

1.2 Methods

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker 400 Hz (100 Hz for ^{13}C) spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent ($CHCl_3$) signal.

Analysis of polymer molecular weight and dispersity was performed using an Agilent HPLC 1260 system (with one guard column and three PLgel 5 μm MIXED-C gel permeation columns) coupled with a Wyatt Technology TrEX differential refractometer and a Wyatt Technology mini DAWN TREOS light scatter detector or a Waters e2695 system (with one guard column and two Styragel columns) coupled with Waters 2414 refractive index detector (calibrated with PS standards). The analysis was performed at 35 °C using THF as the eluent at a flow rate of 1.0 mL/minute.

Glass transition temperatures (T_g) and melting point (T_m) of the polymers were measured by differential scanning calorimetry (DSC) on a TA Q20 DSC at a rate of 10 °C/min. Decomposition temperatures (Td) at 5% of weight loss and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a TA Q50 TGA by heating the polymer samples from 25°C to 700 °C at the rate of 10 °C/min.

Analysis of low molecular weight polymer was performed on a Autoflex matrix-assisted laser desorption/ionization time-of-flight spectrometer (Bruker Daltonics). trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix and CF_3CO_2Na was used as the cationic reagent.

White-light LED beaker: a 25 cm white LEDs strip (Yifaguang, item no. 5050, 14.4 W/meter) was wrapped around the inside of a 400 mL beaker, and powered by a 12VDC power Supply (Yifaguang, item no. 12V8A96W). The wattage of this setup is ~3.6W.

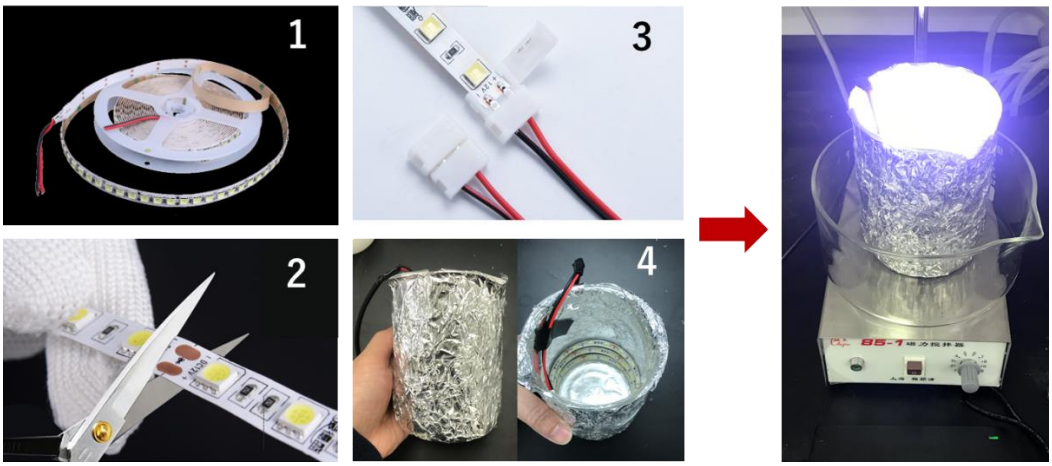
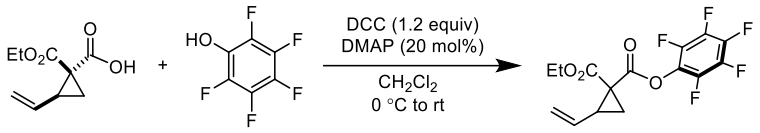


Fig. S1 Lighting beaker setup.

2. Synthesis of VCP Monomers

EtVCP, BuVCP, BnVCP, and EtVCP-CN were synthesized according to the literature.[1]



To a solution of EtVCP-CO_2H (2.03 g, 1.1 equiv),[2] pentafluorophenol (1.84 g, 1.0 equiv), and DMAP (244 mg, 0.2 equiv) in 50 mL of anhydrous DCM (0.2 M) at 0 °C, DCC (2.48 g, 1.2 equiv) was added in portions. The reaction was then vigorously stirred at room temperature for 12 h. The white precipitate was filtered off and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash chromatography using hexane/EtOAc (10:1) as the eluent to give the EtVCP-PFP (dr >20:1) as a white solid (2.93 g, 84% yield). R_f = 0.35 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.55 (ddd, *J* = 17.0, 10.1, 8.2 Hz, 1H), 5.40 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.24 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.37 – 4.11 (m, 2H), 2.87 – 2.65 (m, 1H), 1.99 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.80 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 141.2 (dm, *J* = 250 Hz), 139.6 (dm, *J* = 250 Hz), 137.9 (dm, *J* = 250 Hz), 131.7, 124.8 (m), 120.0, 62.1, 35.1, 32.6, 21.7, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -152.5 (m), -157.6 (t, *J* = 21.6 Hz), -162.2 (m).

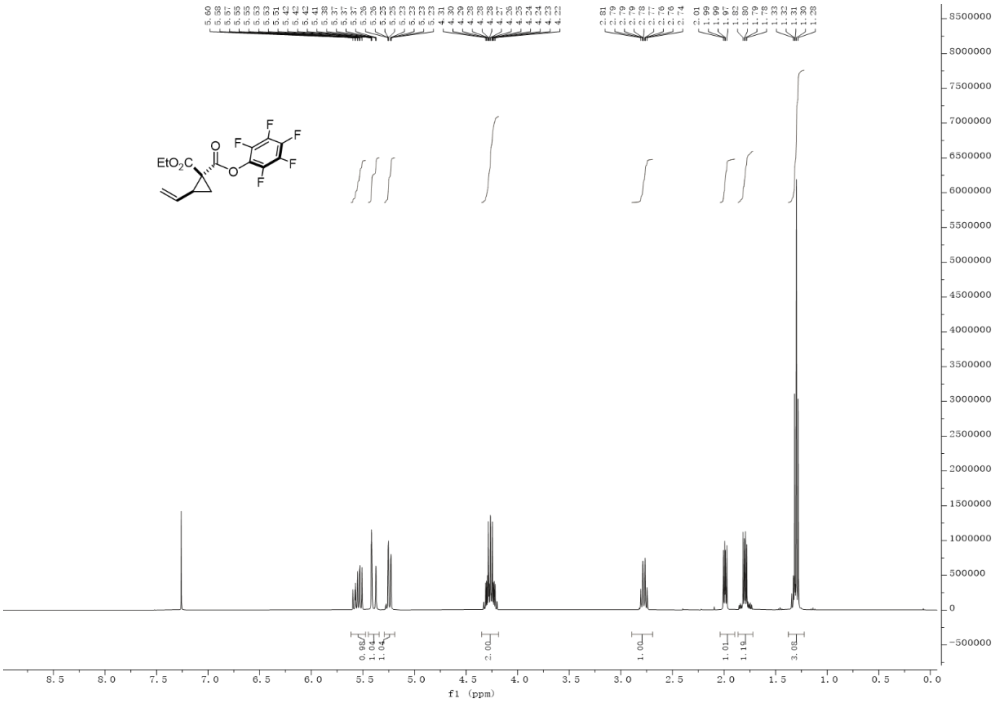


Fig. S2 ^{1}H NMR spectrum of EtVCP-PFP in $CDCl_3$

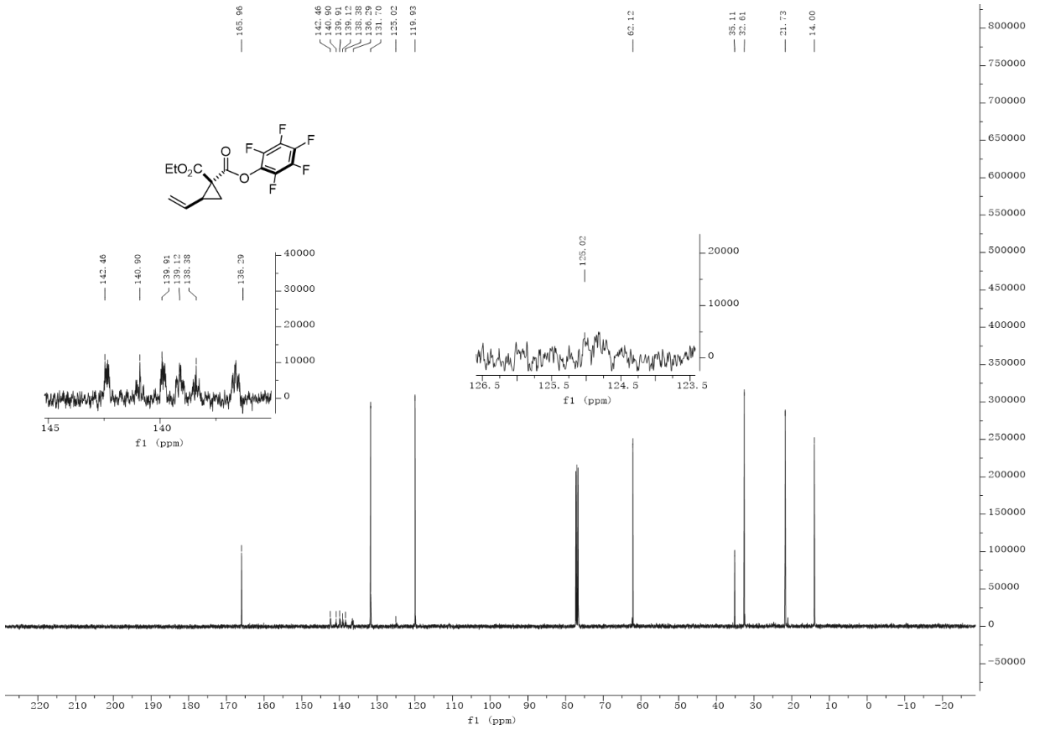


Fig. S3 ^{13}C NMR spectrum of EtVCP-PFP in $CDCl_3$

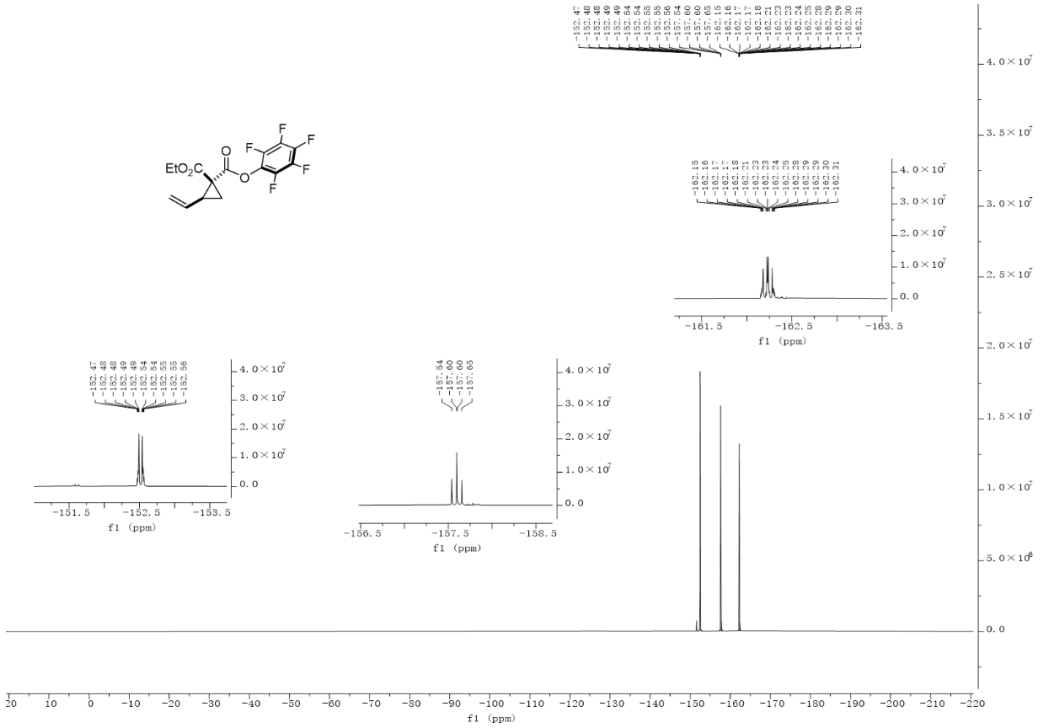


Fig. S4 ^{19}F NMR spectrum of EtVCP-PFP in $CDCl_3$

3. Visible-Light-Driven ITP of VCP Monomers

3.1 General Polymerization Procedure

An oven-dried 5 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, VCP monomer (1.0 mmol), anhydrous PhCl or EtOAc, and the alkyl iodide stock solution (0.10 M) were sequentially added. The vial was then tightly capped and placed under white LED irradiation while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 °C. For the progress analysis, an aliquot of the reaction mixture was taken via syringe and immediately quenched by injecting into a 1.5 mL vial containing ~0.6 mL of $CDCl_3$ with 250 ppm butylated hydroxytoluene (BHT). This aliquot was analyzed via ^1H NMR for monomer conversion, then dried under vacuum for direct GPC analysis to obtain the M_n and $Đ$. For further purification, the reaction mixture was slowly added into 20.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL × 2) and dried overnight under vacuum at 50 °C to a constant weight.

3.2 Optimization for the Polymerization of EtVCP

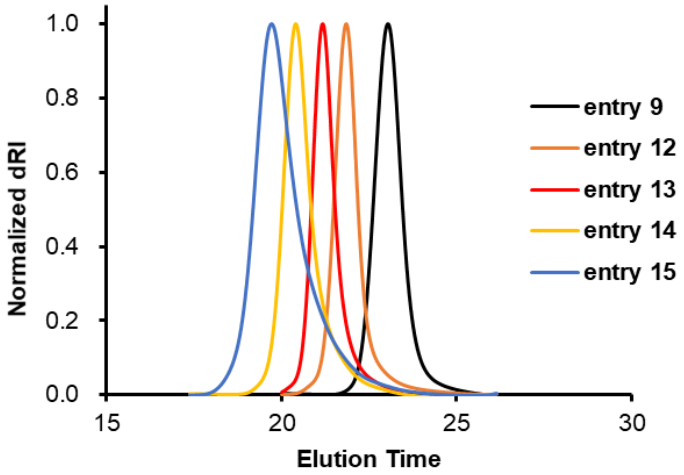


Fig. S5 Overlay of GPC traces for P(EtVCP) in Table 1

3.3 Kinetic Study

Table S1. Results of progress analysis for polymerization of EtVCP[a]

Entry	Time	Conv. (%)	M_n(kDa)	$Đ(M_w/M_n)$	S_L(%)
1	1	0	-	-	-
2	2	1	-	-	-
3	4	9	2.4	1.16	97
4	6	21	4.6	1.16	98
5	8	38	8.4	1.11	98
6	10	50	11.5	1.07	98
8	14	65	14.8	1.06	98
9	18	75	16.9	1.06	98

[a]The polymerization of [EtVCP]/[**4**] (100/1) was performed in 0.2 mL of anhydrous PhCl, with 3.6 W white LED irradiation at ~30 °C.

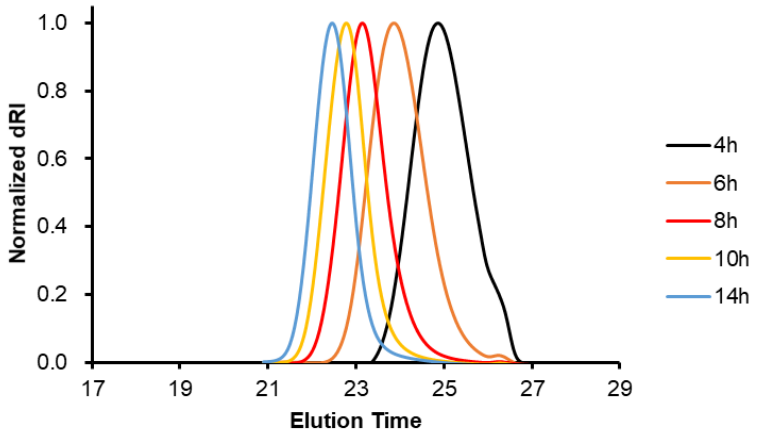


Fig. S6 Overlay of GPC traces for P(EtVCP) in Table S1

3.4 Pusled-Irradiation Experiment

Table S2. Results of Pusled-Irradiation Experiment of EtVCP at ~30 °C[a]

Entry	Time	Conv. (%)	M_n(kDa)	$Đ(M_w/M_n)$	S_L(%)
1	0	0	-	-	-
2	8	35	7.6	1.09	98
3	16	35	7.6	1.09	98
4	24	66	14.6	1.04	98
5	40	66	14.6	1.04	98
9	45	86	19.1	1.06	98

[a]The polymerization of [EtVCP]/[**4**] (100/1) was performed in 0.2 mL of anhydrous PhCl, with 3.6 W white LED irradiation at ~30 °C.

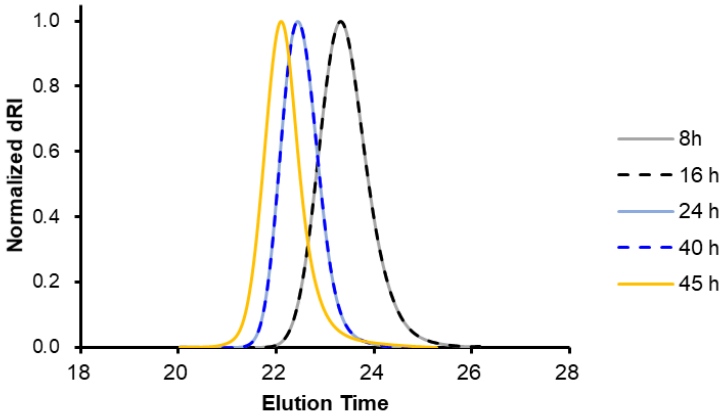


Fig. S7 Overlay of GPC traces for P(EtVCP) in Table S2

3.5 Chain-Extension Experiment

Synthesis of P(EtVCP) macroinitiator. An oven-dried 5 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, EtVCP (3.0 mmol) and 0.60 mL of the stock solution of **4** in PhCl (0.10 M) were added. The vial was then tightly capped and placed in the beaker wrapped with white LED strips while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 °C. After 20 h, the reaction mixture was slowly added into 50.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL ×2) and dried overnight under vacuum at 50 °C to a constant weight. 510 mg, M_n = 9.5 kDa, $Đ$ = 1.07, S_L = 98%.

Chain-Extension Experiment. An oven-dried 5 mL charged with a magnetic stir bar and P(EtVCP) macroinitiator (95 mg, 0.010 mmol) was transferred into a N_2-filled glovebox. To this vial, VCP monomer (0.50 mmol) and 0.20 mL of anhydrous solvent were quickly added. The vial was then tightly capped and irradiated in the beaker equipped with white LED strips while stirring in the glove box. A cooling fan was used to keep the temperature at ~30 °C. After 16 h, an aliquot was taken for ^{1}H NMR analysis. The aliquot was then dried under vacuum for direct GPC analysis.

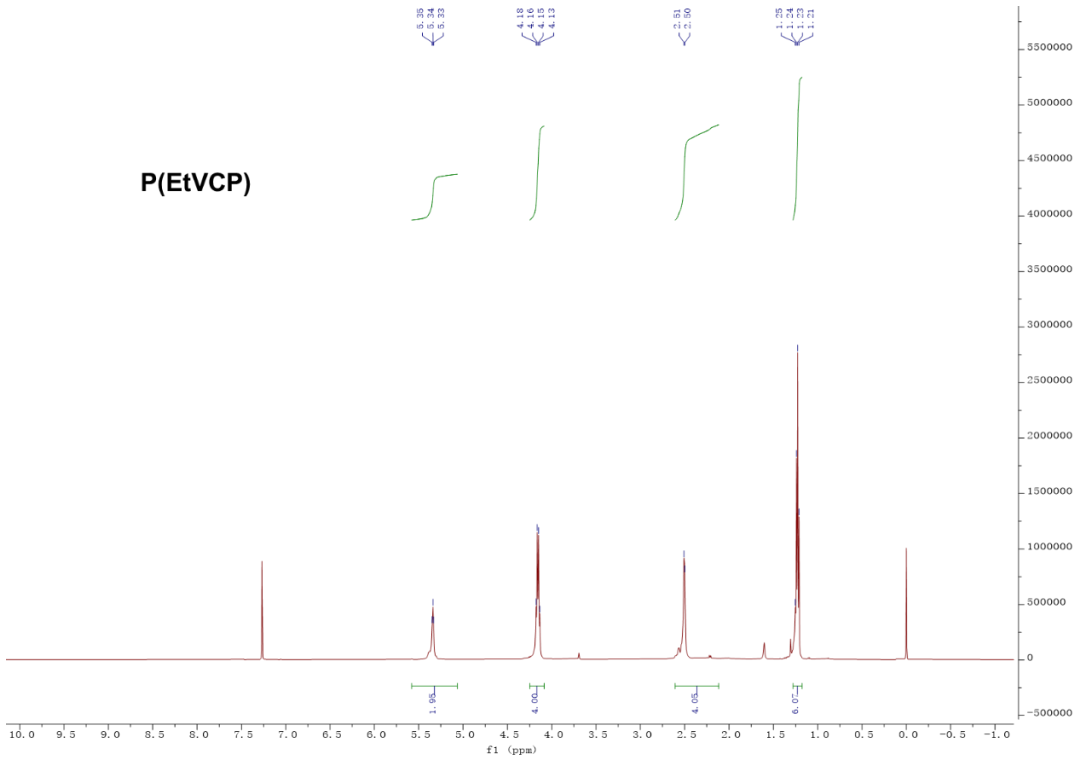


Fig. S8 ^{1}H NMR spectrum of Chain-Extended P(EtVCP) in $CDCl_3$ (M_n = 20.6 kDa, $Đ$ = 1.12, S_L = 98%)

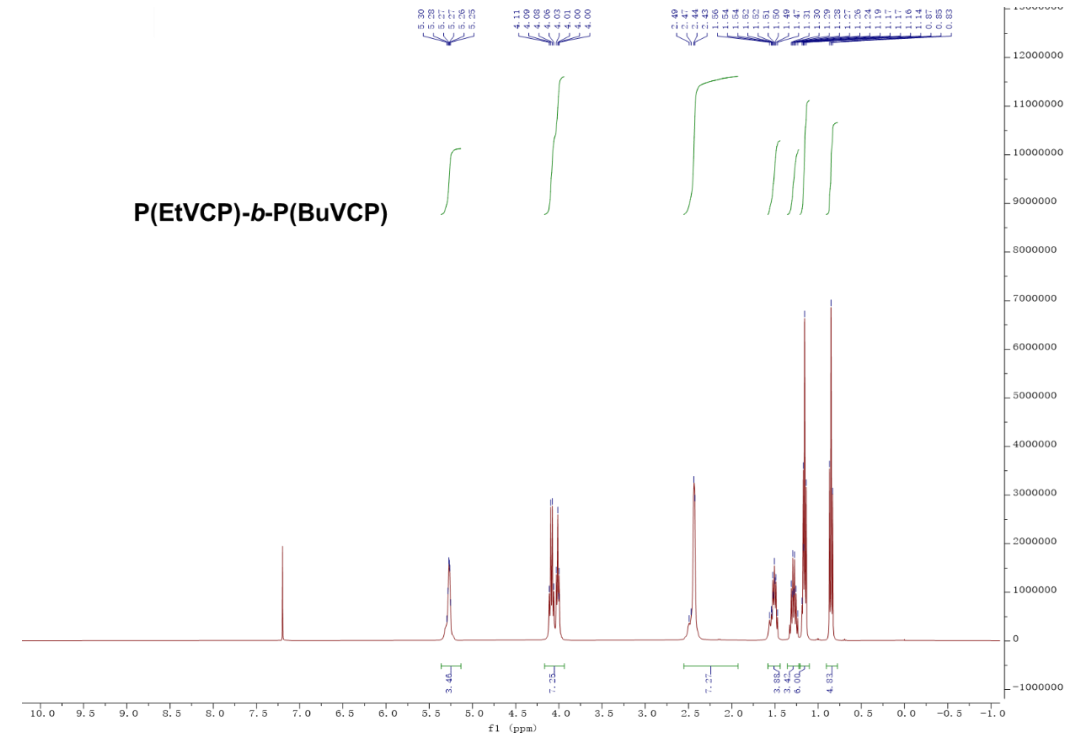


Fig. S9 ^{1}H NMR spectrum of P(EtVCP)-*b*-P(BuVCP) in $CDCl_3$ (M_n = 20.0 kDa, $Đ$ = 1.10, S_L = 96%)

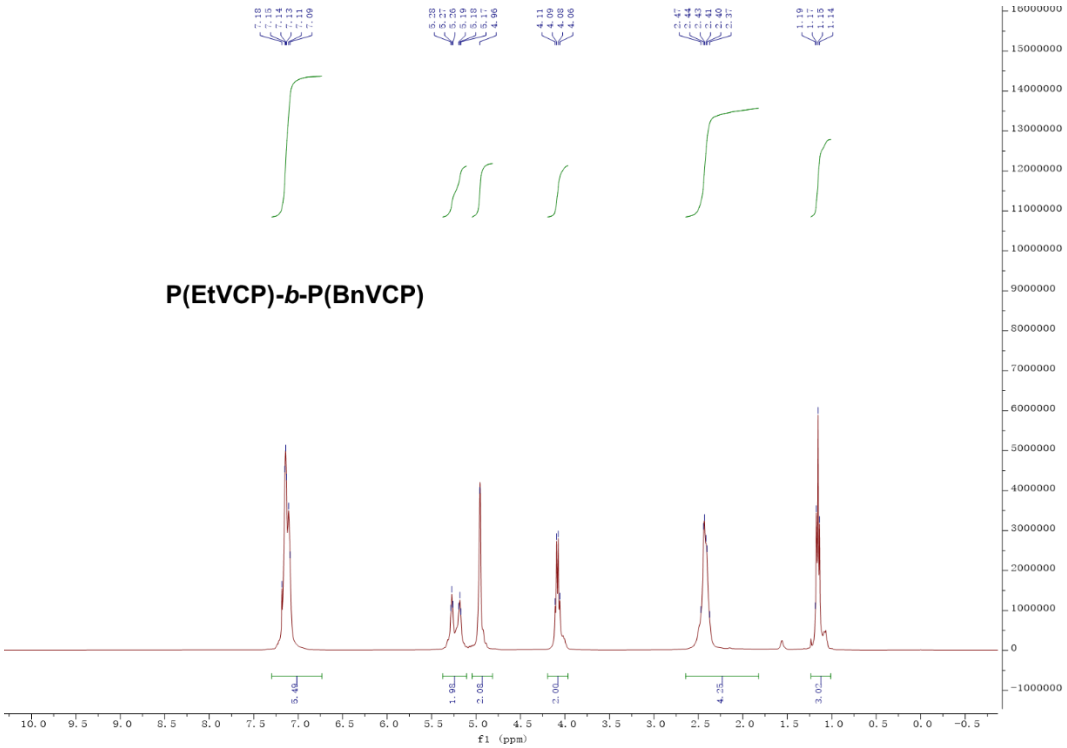


Fig. S10 ^{1}H NMR spectrum of P(EtVCP)-*b*-P(BnVCP) in $CDCl_3$ (M_n = 26.9 kDa, $Đ$ = 1.13, S_L = 97%)

3.6 ^{1}H NMR Spectra of P(BuVCP), P(BnVCP), P(PhVCP), and P(EtVCP-CN)

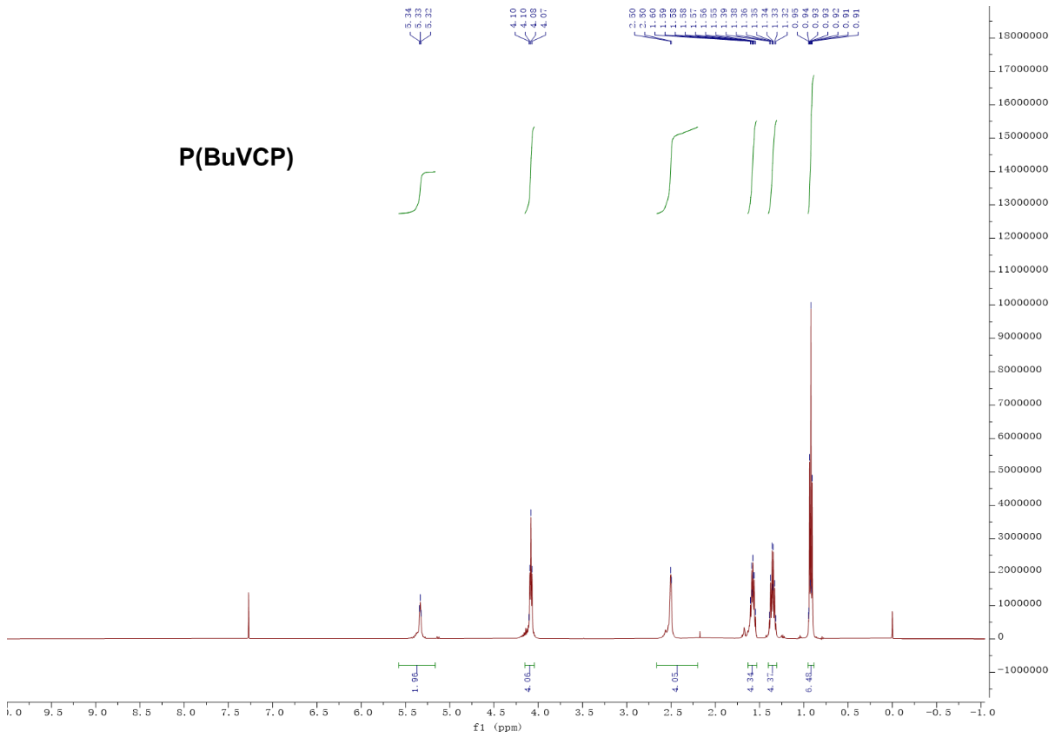


Fig. S11 ^{1}H NMR spectrum of P(BuVCP) in $CDCl_3$ (M_n = 28.0 kDa, $Đ$ = 1.09, S_L = 98%)

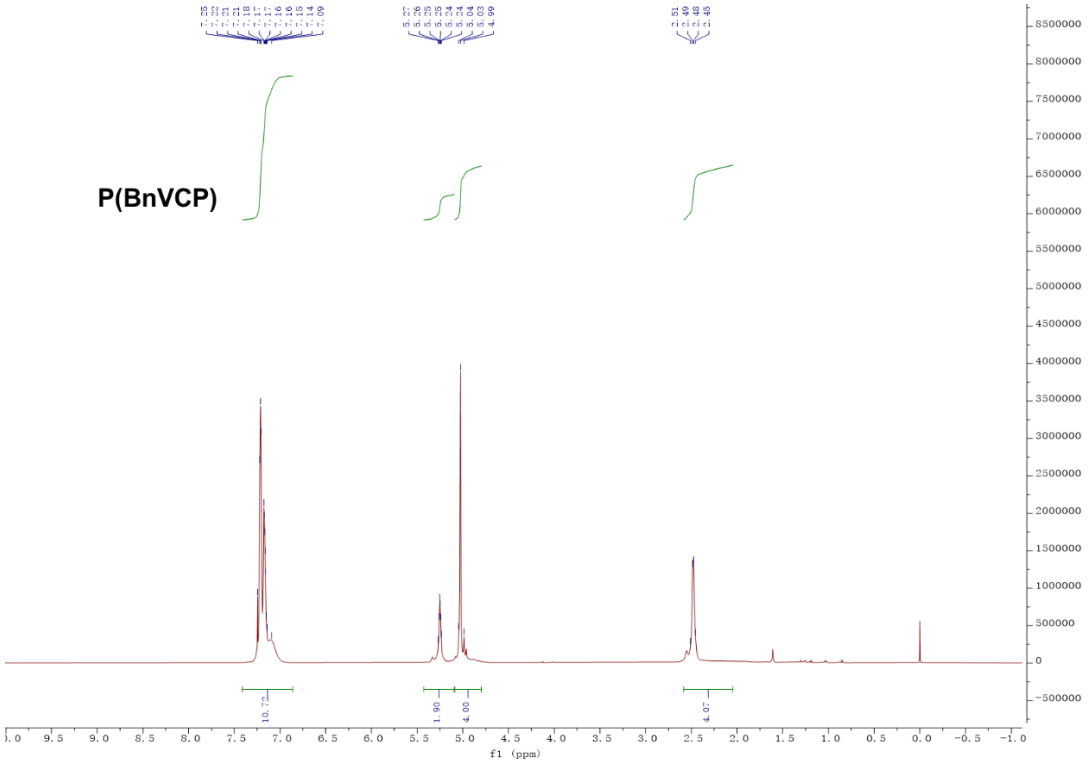


Fig. S12 ^{1}H NMR spectrum of P(BnVCP) in $CDCl_3$ (M_n = 28.5 kDa, $Đ$ = 1.12, S_L = 95%)

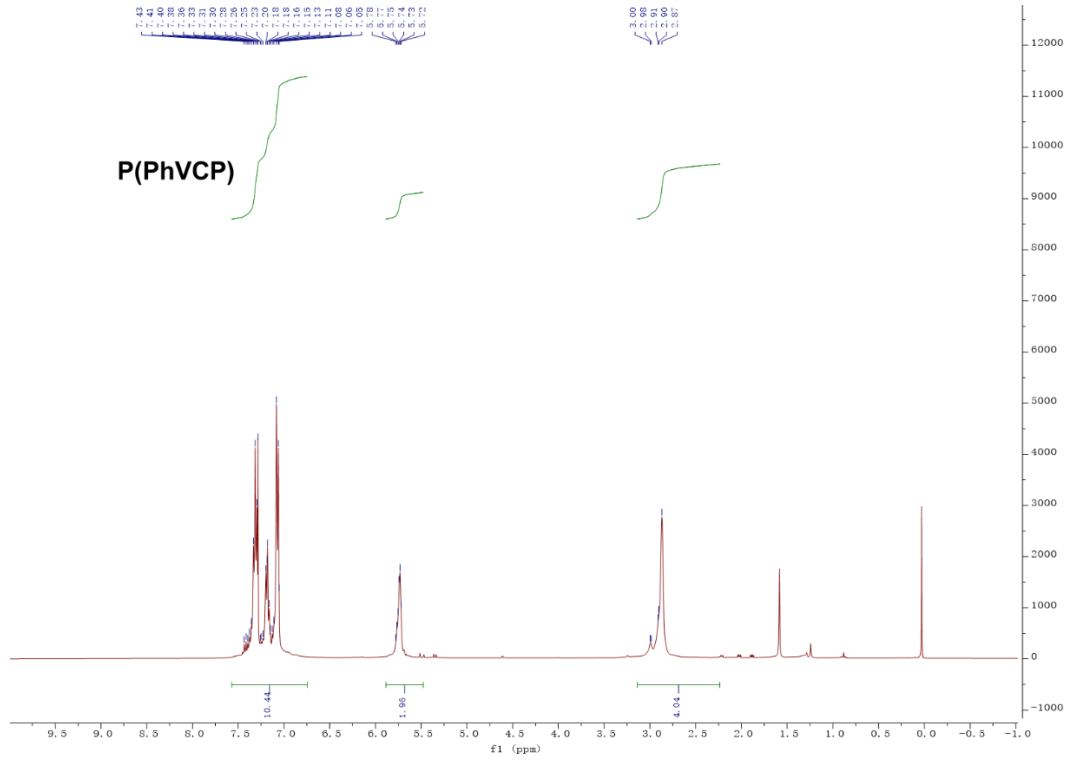


Fig. S13 ^{1}H NMR spectrum of P(PhVCP) in $CDCl_3$ (M_n = 28.5 kDa, $Đ$ = 1.09, S_L = 98%)

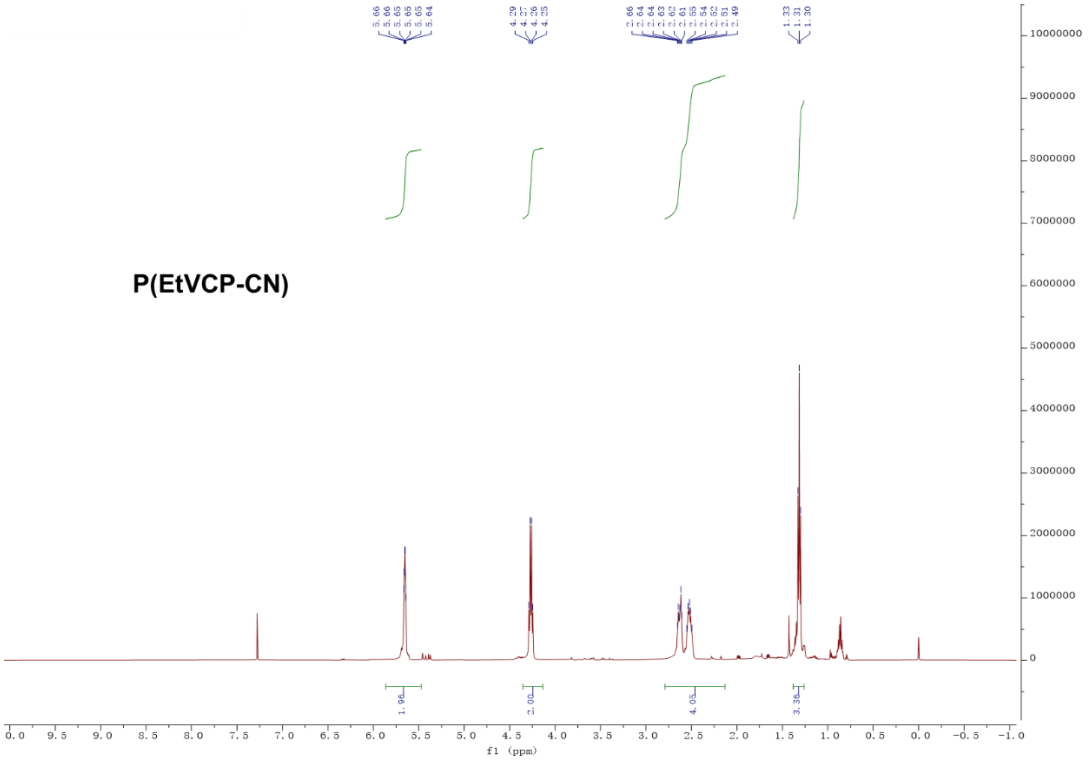


Fig. S14 ^{1}H NMR spectrum of P(EtVCP-CN) in $CDCl_3$ (M_n = 28.0 kDa, $Đ$ = 1.09, S_L = 98%)

3.7 GPC Traces of P(BuVCP), P(BnVCP), P(PhVCP), and P(EtVCP-CN)

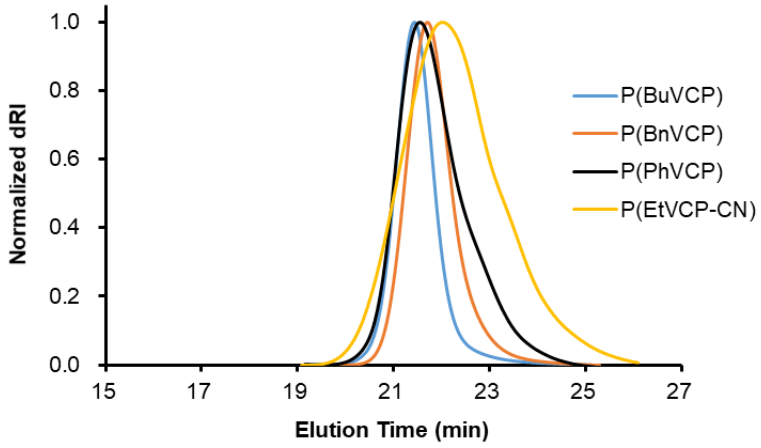


Fig. S15 Overlay of GPC traces for P(EtVCP) P(BnVCP), P(PhVCP), and P(EtVCP-CN) in Table 1

4. Visible-Light-Driven ITP of Fluorinated VCP Monomers

4.1 General Polymerization Procedure

An oven-dried 5 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, EtVCP-PFP (1.0 mmol), anhydrous solvent, and the stock solution of **4** (0.10 M) were sequentially added. The vial was then tightly capped and placed under white LED irradiation while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 °C. An aliquot was taken and analyzed via ^{1}H NMR for monomer conversion, then dried under vacuum for direct GPC analysis to obtain the M_n and $Đ$. For further purification, the reaction mixture was slowly added into 20.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL ×2) and dried overnight under vacuum at 50 °C to a constant weight. ^{1}H NMR (400 MHz, CDCl3) δ 5.55 – 5.32 (br, 1.96H), 4.33 – 4.01 (br, 2H), 2.83 – 2.05 (br, 4.05H), 1.26 – 0.98 (br, 3H). ^{19}F NMR (376 MHz, CDCl3) δ -152.3 (br, 2F), -157.5 (m, 1F), -162.2 (m, 2F).

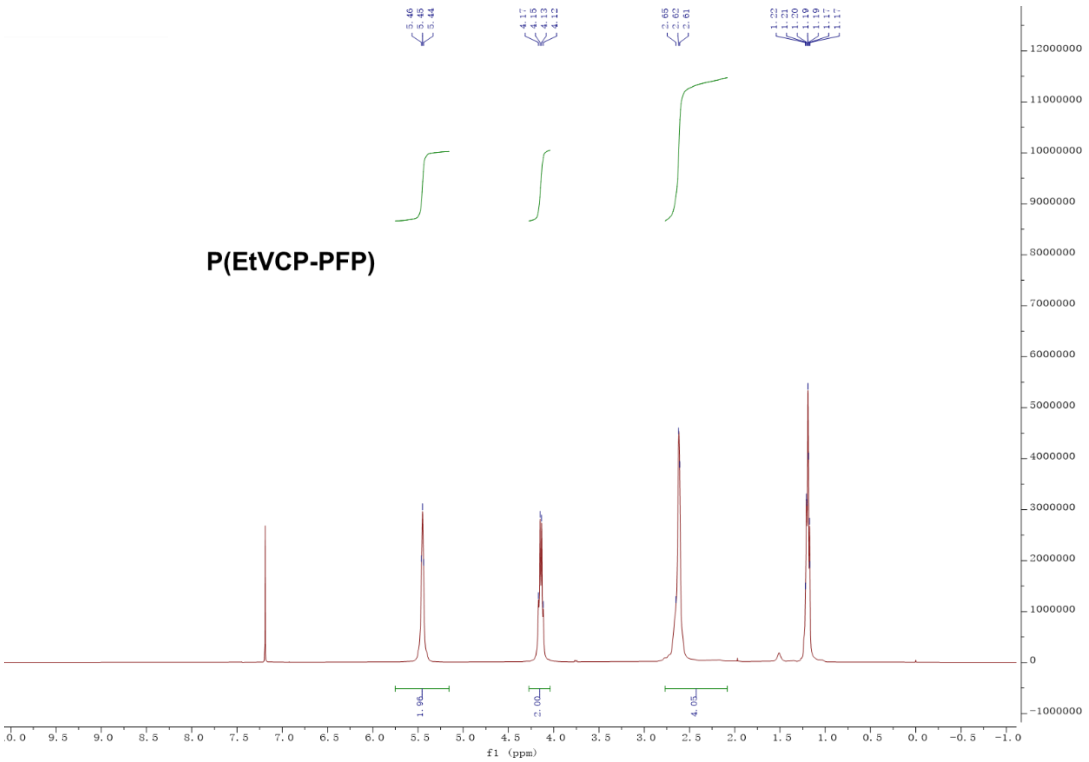


Fig. S16 ^{1}H NMR spectrum of P(EtVCP-PFP) in $CDCl_3$ (Table 2, entry 1, M_n = 17.3 kDa, $Đ$ = 1.17, S_L = 98%)

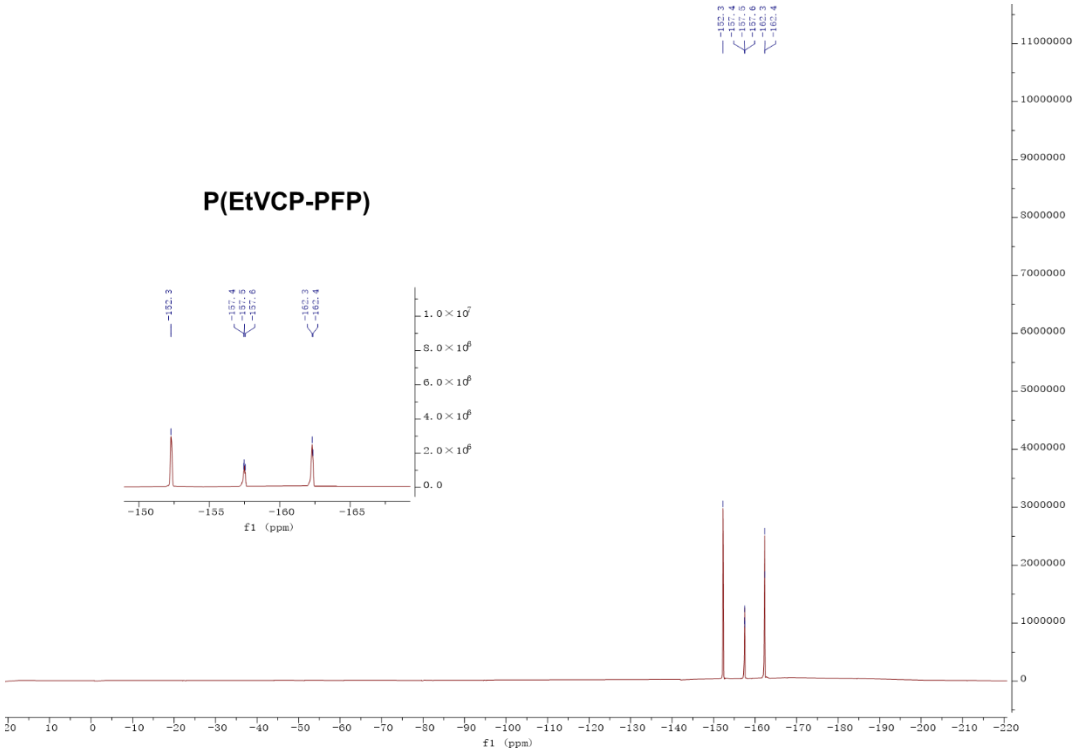
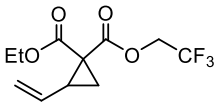


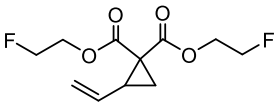
Fig. S17 ^{19}H NMR spectrum of P(EtVCP-PFP) in $CDCl_3$ (Table 2, entry 2, M_n = 17.3 kDa, $Đ$ = 1.17, S_L = 98%)

4.2 Optimization

Table S3. Polymerization of VCP Monomers Bearing a Fluoroalkyl Group[a]



EtVCP-CF_3

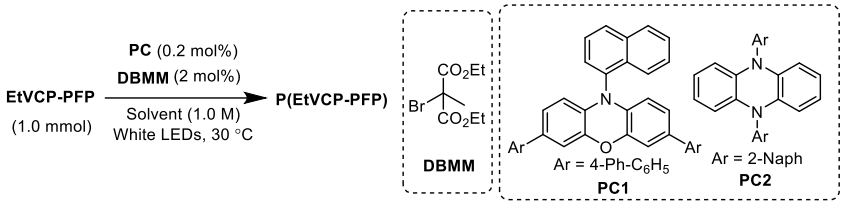


FEtVCP

Entry	Monomer	Solvent	Conv. (%)	M_n(kDa)	$Đ(M_w/M_n)$	S_L(%)
1	EtVCP-CF_3	EtOAc	15	-	-	-
2	EtVCP-CF_3	PhCl	12	-	-	-
3	EtVCP-CF_3	$PhCF_3$	20	-	-	-
4	FEtVCP	EtOAc	0	-	-	-
5	FEtVCP	PhCl	0	-	-	-
6	FEtVCP	$PhCF_3$	0	-	-	-

[a]The polymerization of [M]/[**4**] = 50/1 was performed in 0.2 mL of anhydrous solvent, with 3.6 W white LED irradiation at ~30 °C.

Table S4. Photoredox rROP of EtVCP-PFP[a]



Entry	PC	Solvent	Conv. (%)	M_n(kDa)	$Đ(M_w/M_n)$	S_L(%)
1	$Ir(ppy)_3$	EtOAc	0	-	-	-
2	**PC1**	EtOAc	0	-	-	-
3	**PC2**	EtOAc	0	-	-	-
4	**PC2**	DMAc	0	-	-	-
5	**PC2**	PhCl	0	-	-	-
9	**PC2**	$PhCF_3$	0	-	-	-

[a]The polymerization of [EtVCP-PFP]/[DBMM]/[PC] = 500/10/1 was performed in 1.0 mL of anhydrous solvent with 3.6 W white LED irradiation at ~30 °C for 16 h.

Table S5. Solvent and Concentration Effect on Polymerization of EtVCP-PFP[a]

Entry	Solvent	Volume (mL)	Conv. (%)	M_n(kDa)	$Đ(M_w/M_n)$	S_L(%)
1	EtOAc	0.2	65	17.3	1.53	98
2	PhCl	0.2	84	18.0	1.44	98
3	anisole	0.2	78	17.8	1.37	98
4	$PhCF_3$	0.2	85	13.2	1.39	98
5	$PhCF_3$	0.4	90	17.3	1.17	98
6	$PhCF_3$	0.6	88	16.5	1.28	98

[a]The polymerization of [EtVCP-PFP]/[**4**] = 50/1 was performed in anhydrous solvent with 3.2 W white LED irradiation at ~30 °C for 16 h.

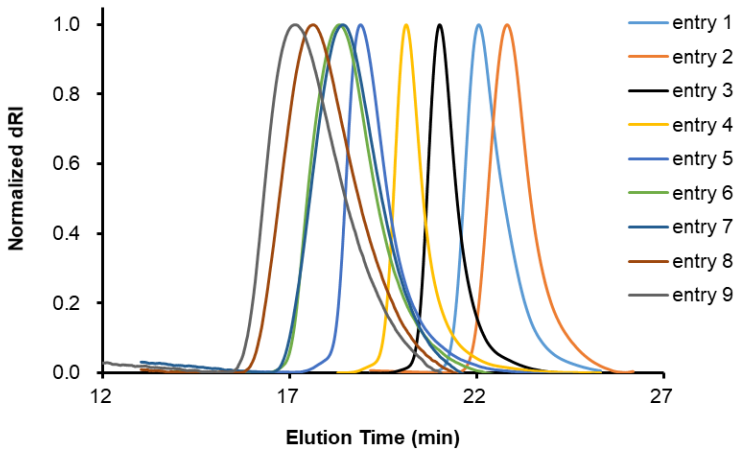


Fig. S18 Overlay of GPC traces for P(EtVCP-PFP) in Table 2

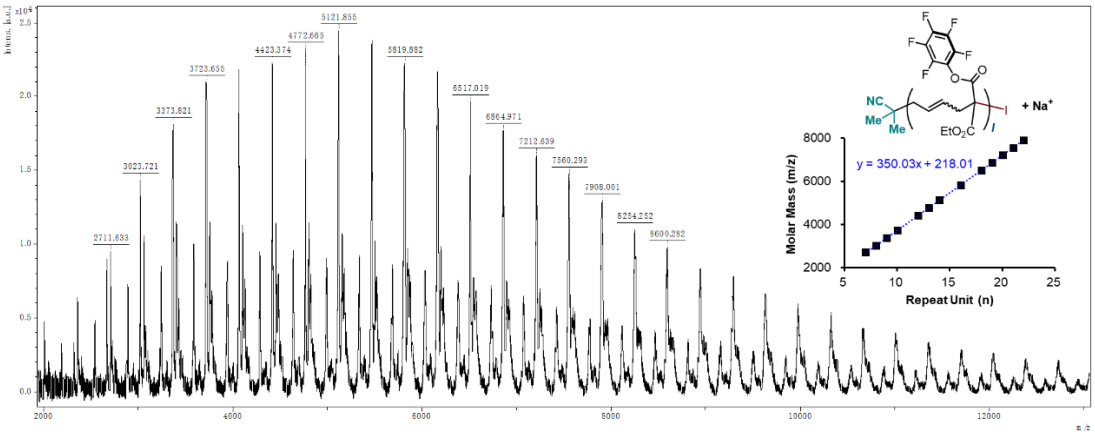


Fig. S19 MALDI-TOF Analysis of P(EtVCP-PFP)

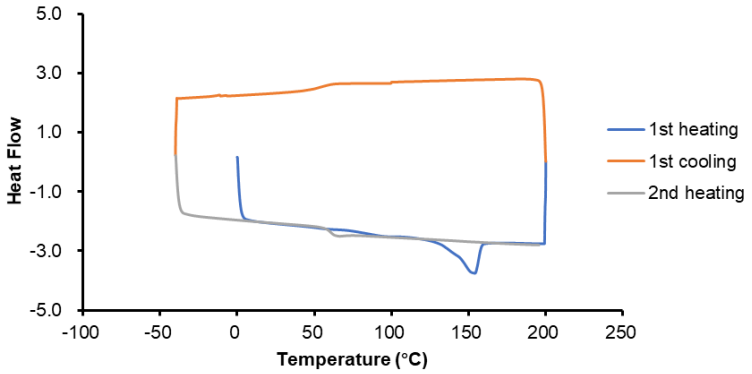


Fig. S20 DSC curves of P(EtVCP-PFP) (17.3 kDa, $Đ$ = 1.17, S_L = 98%). T_g = 61 °C, (2nd heating scan), T_m = 151 °C (1st heating scan).

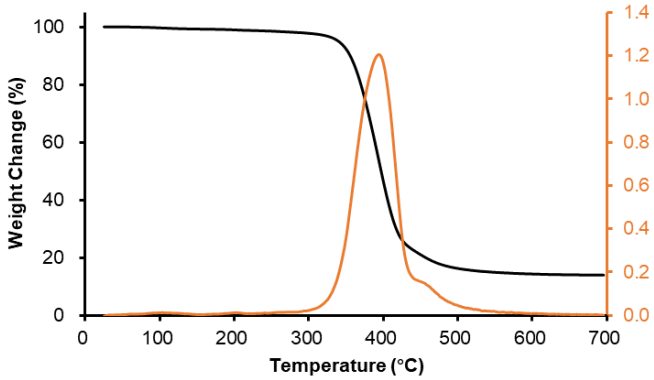


Fig. S21 TGA and DTG curves of P(EtVCP-PFP) (17.3 kDa, $Đ$ = 1.17, S_L = 98%). $T_d^{5\%}$ = 340 °C, T_{max} = 394 °C.

4.3 Chain-Extension Experiment to Synthesize P(EtVCP-PFP)-*b*-P(EtVCP)

An oven-dried 5 mL charged with a magnetic stir bar and P(EtVCP-PFP) macroinitiator (15.2 kDa, $Đ$ = 1.22, S_L = 98%; 152 mg, 0.010 mmol) was transferred into a N_2-filled glovebox. To this vial, EtVCP (106 mg, 0.50 mmol) and 0.20 mL of anhydrous PhCl were quickly added. The vial was then tightly capped and irradiated in the beaker equipped with white LED strips while stirring in the glove box. A cooling fan was used to keep the temperature at ~30 °C. After 16 h, an aliquot was taken for ^{1}H NMR analysis and GPC analysis.

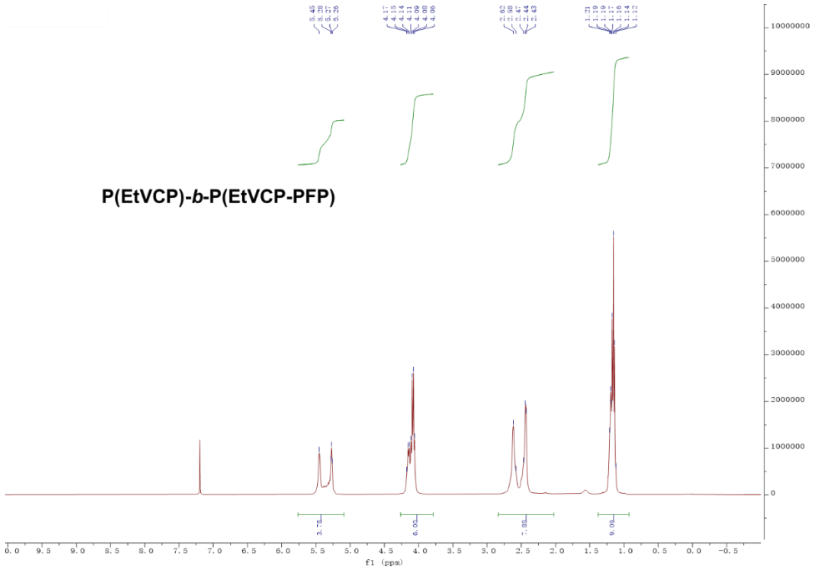


Fig. S22 ^{1}H NMR spectrum of P(EtVCP-PFP)-*b*-P(EtVCP) in $CDCl_3$ (28.1 kDa, $Đ$ = 1.19, S_L = 97%)

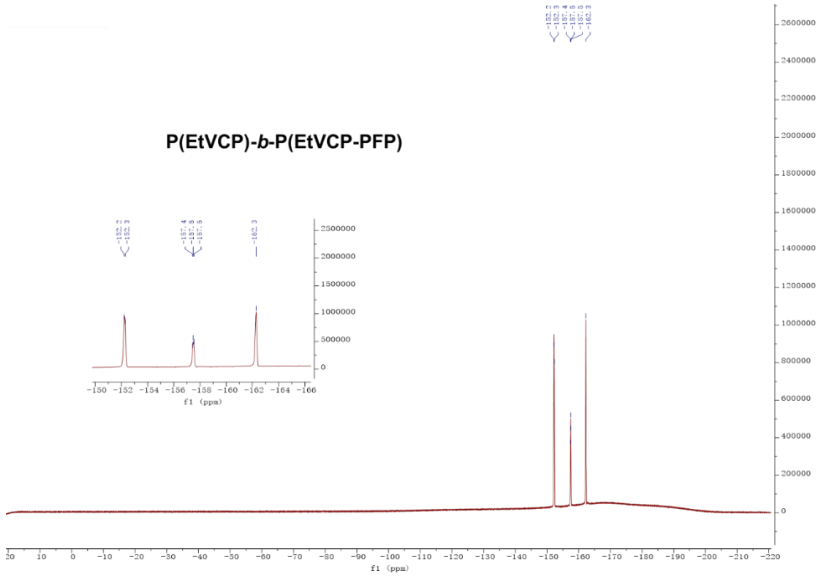


Fig. S23 ^{19}H NMR spectrum of P(EtVCP-PFP)-*b*-P(EtVCP) in $CDCl_3$ (28.1 kDa, $Đ$ =

1.19, S_L = 97%)

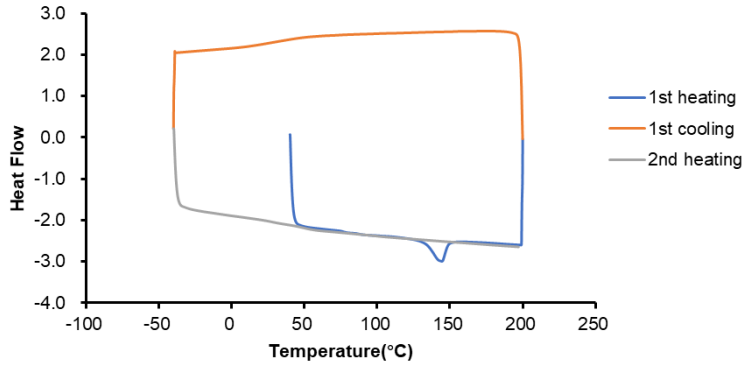


Fig. S24 DSC curves of P(EtVCP-PFP)-*b*-P(EtVCP) (28.1 kDa, $Đ$ = 1.19, S_L = 97%). T_{g1} = 28 °C, T_{g2} = 52 °C (2nd heating scan), T_m = 145 °C (1st heating scan).

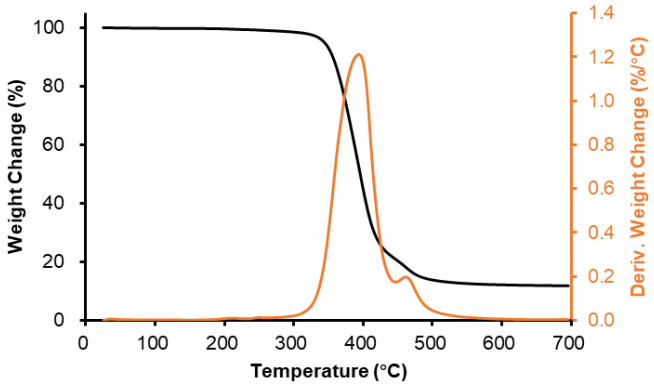


Fig. S25 TGA and DTG curves of P(EtVCP-PFP)-*b*-P(EtVCP) (28.1 kDa, $Đ$ = 1.19, S_L = 97%). $T_d^{5\%}$ = 340 °C, T_{max} = 393 °C.

5. Post-Modifications of P(EtVCP-PFP)

5.1 Large-Scale Synthesis of P(EtVCP-PFP)

An oven-dried 20 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, EtVCP-PFP (5.0 mmol), 1.0 mL of anhydrous $PhCF_3$, and 1.0 mL of the stock solution of **4** in $PhCF_3$ (0.10 M) were sequentially added. The vial was then tightly capped and placed in the beaker wrapped by white LED strips while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 ˚C. After 24 h, the reaction mixture was slowly added into 50.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL ×2) and dried overnight under vacuum at 50 °C to a constant weight. M_n = 14.6 kDa, $Đ$ = 1.34, S_L = 98%.

5.2 General Procedures for Post-Modification

To an oven-dried 5 mL vial charged with a small magnetic stir bar, P(EtVCP-PFP) (100 mg), 0.6 mL of anhydrous THF, amine or alcohol (0.286 mmol, 1.0 equiv), and Et_3N or DBU (0.286 mmol, 1.0 equiv) were added sequentially. The mixture was stirred at room temperature for 12 h. An aliquot was taken for ^{1}H NMR analysis to determine the conversion. For purification, the reaction mixture was added into 20 mL of aq. HCl (0.5 M) while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with H_2O (5 mL) and dried overnight under vacuum at 50 ˚C to a constant weight. GPC analysis was then performed to obtain the M_n and $Đ$.

5.3 Probe of the Chain-End

*Model reaction of **1** with propylamine.* To an oven-dried 8 mL vial charged with a small magnetic stir bar, alkyl iodide **1** (90 mg, 0.3 mmol, 1.0 equiv), 0.6 mL of anhydrous THF, propylamine (24.7 uL, 0.3 mmol, 1.0 equiv) and Et_3N (41.7 uL, 0.3 mmol, 1.0 equiv) were added sequentially. The mixture was stirred at room temperature for 12 h. An aliquot was taken for direct ^{1}H NMR analysis.

*Reaction of **1** with trifluoroethanol*. To an oven-dried 8 mL vial charged with a small magnetic stir bar, alkyl iodide **1** (90 mg, 0.3 mmol, 1.0 equiv), 0.6 mL of anhydrous THF, trifluoroethanol (22 uL, 0.3 mmol, 1.0 equiv) and DBU (41.2 uL, 0.3 mmol, 1.0 equiv) were added sequentially. The mixture was stirred at room temperature for 12 h.

An aliquot was taken for direct ^{1}H NMR analysis.

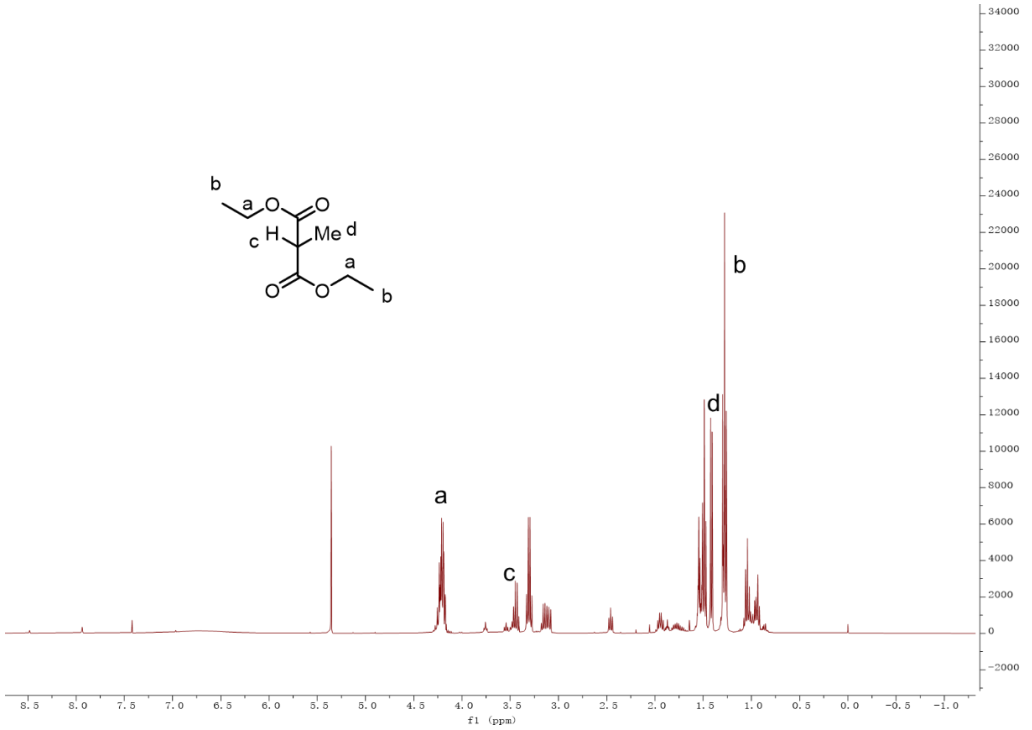


Fig. S26 Crude ^{1}H NMR spectrum of reaction of **1** with propylamine ($CDCl_3$).

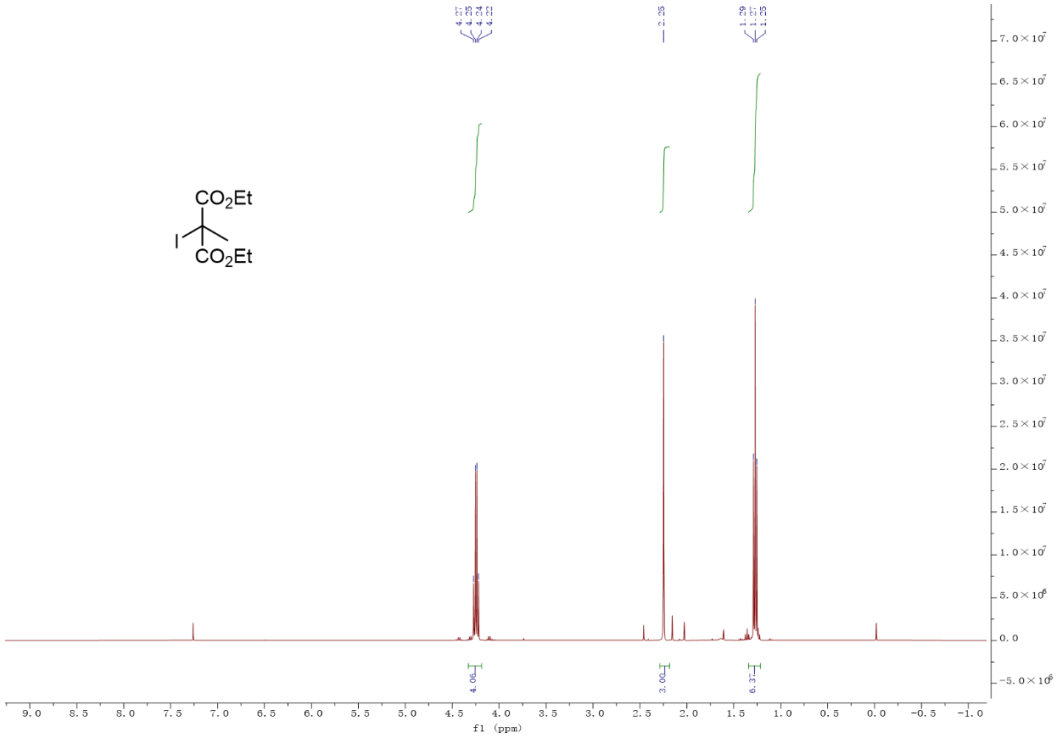


Fig. S27 ^{1}H NMR of alkyl iodide **1** in $CDCl_3$.

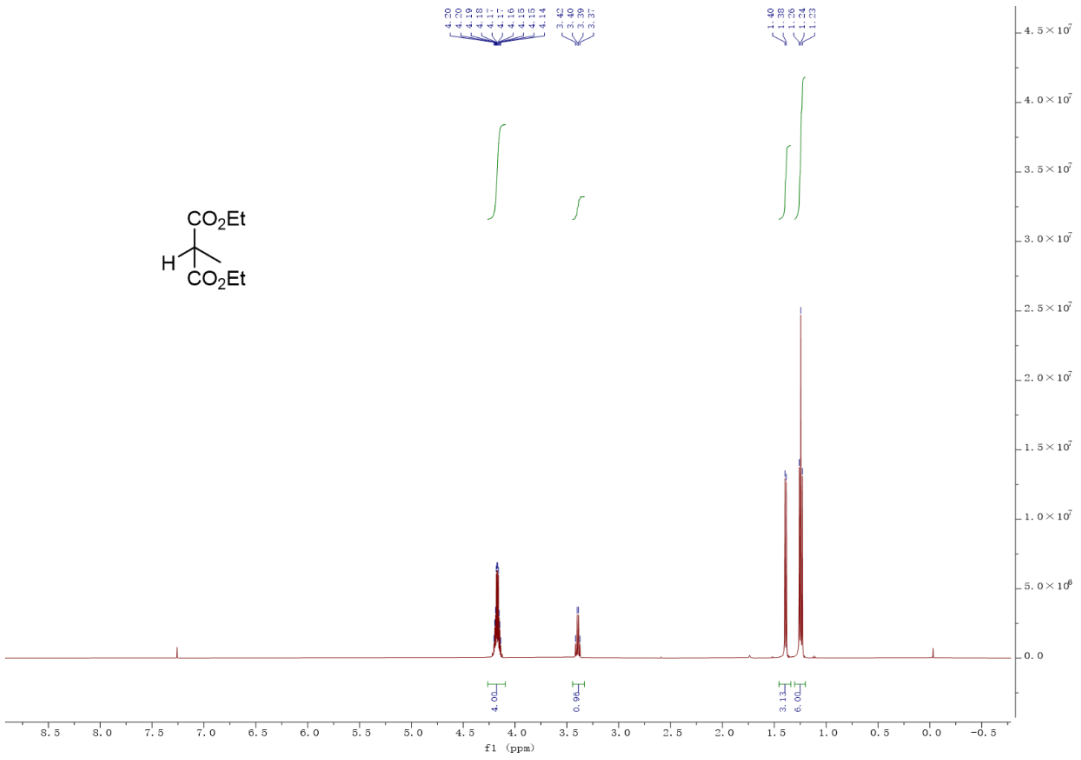


Fig. S28 ^{1}H NMR of diethyl-2-methylmalonate in $CDCl_3$.

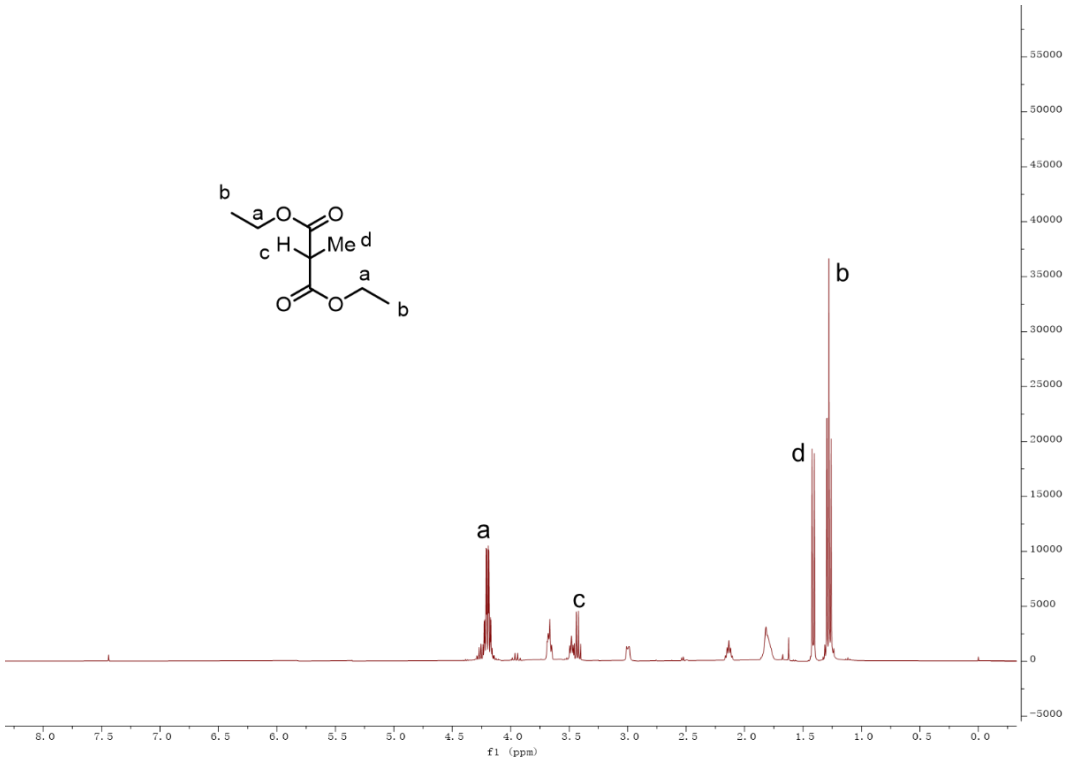


Fig. S29 Crude ^{1}H NMR spectrum of reaction of **1** with trifluoroethanol ($CDCl_3$)

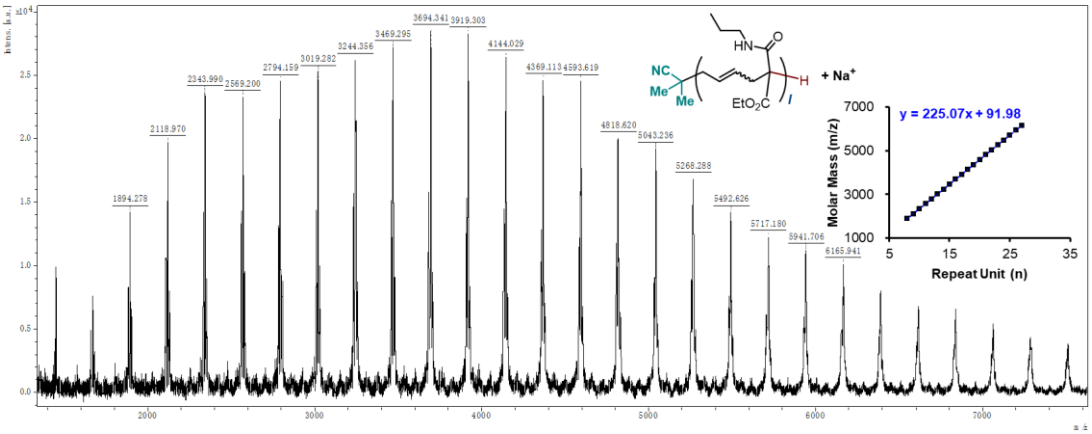


Fig. S30 MALDI-TOF Analysis of **P1**

5.4 NMR Spectra of Modified P(VCPs)

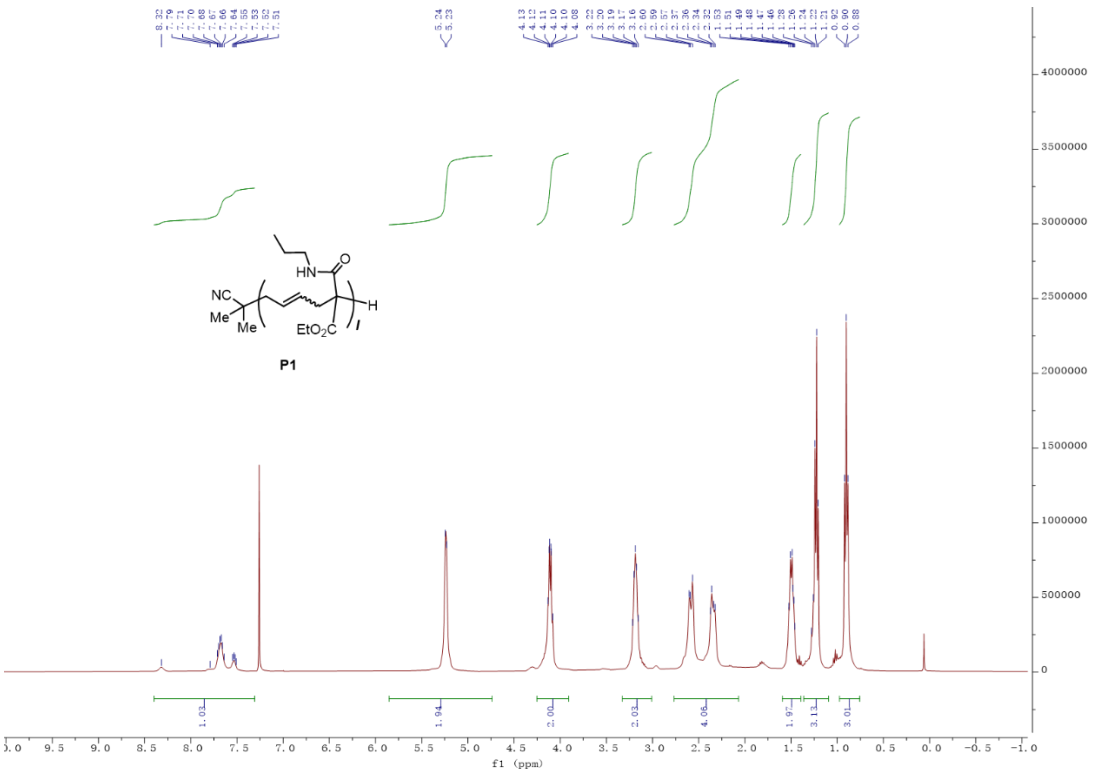


Fig. S31 ^{1}H NMR spectrum of **P1** in $CDCl_3$

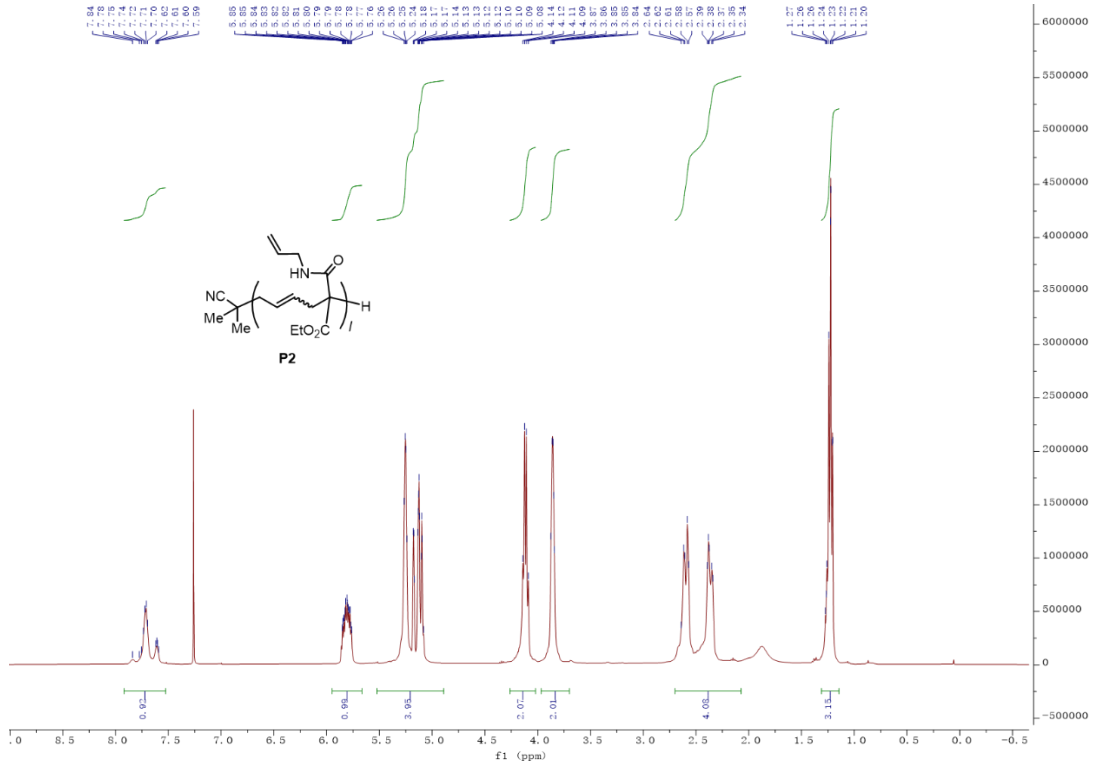


Fig. S32 ^{1}H NMR spectrum of **P2** in $CDCl_3$

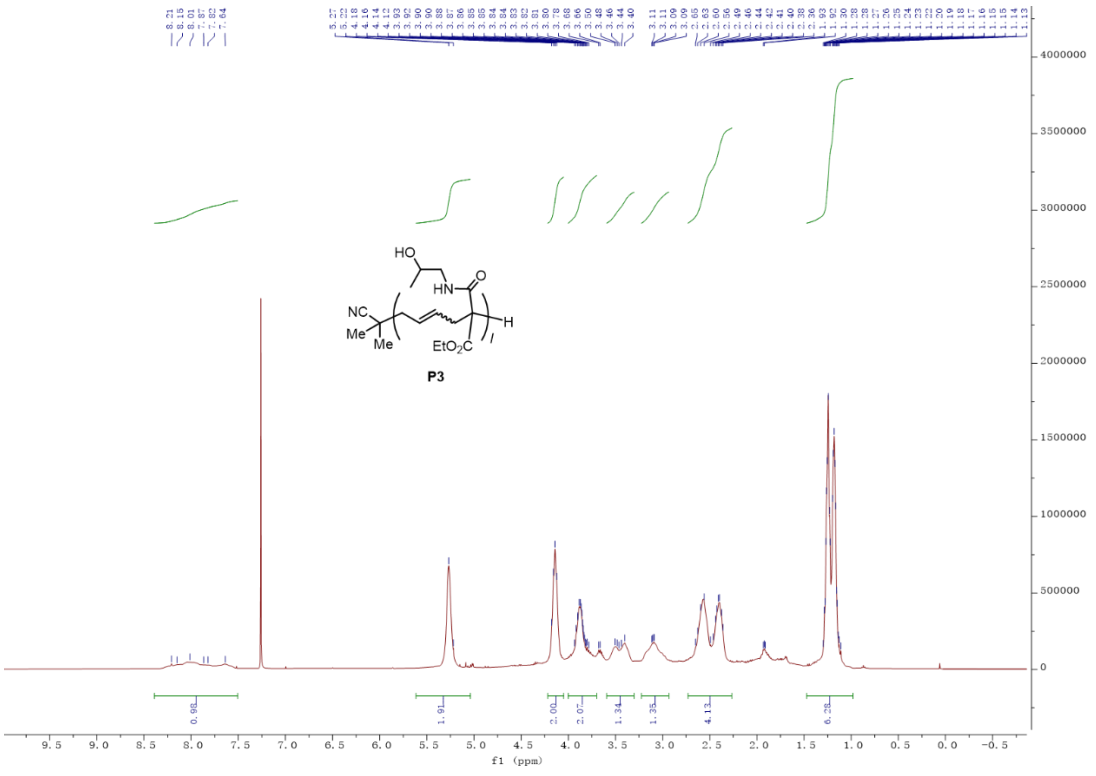


Fig. S33 ^{1}H NMR spectrum of **P3** in $CDCl_3$

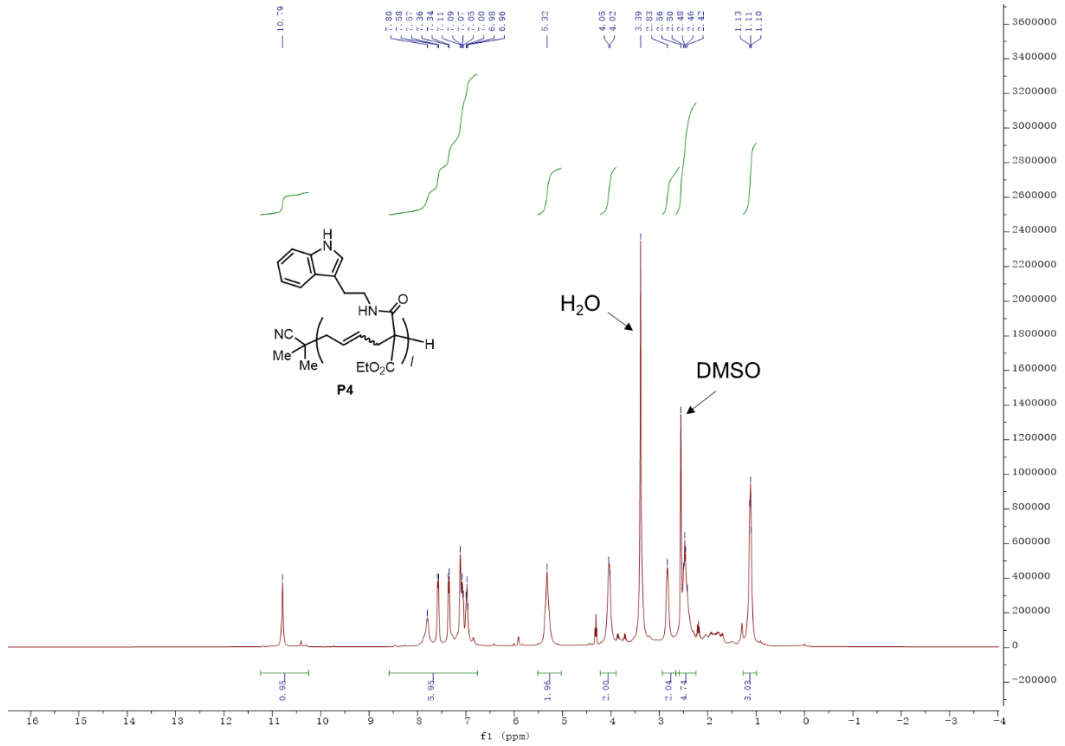


Fig. S34 ^{1}H NMR spectrum of **P4** in DMSO-d_6

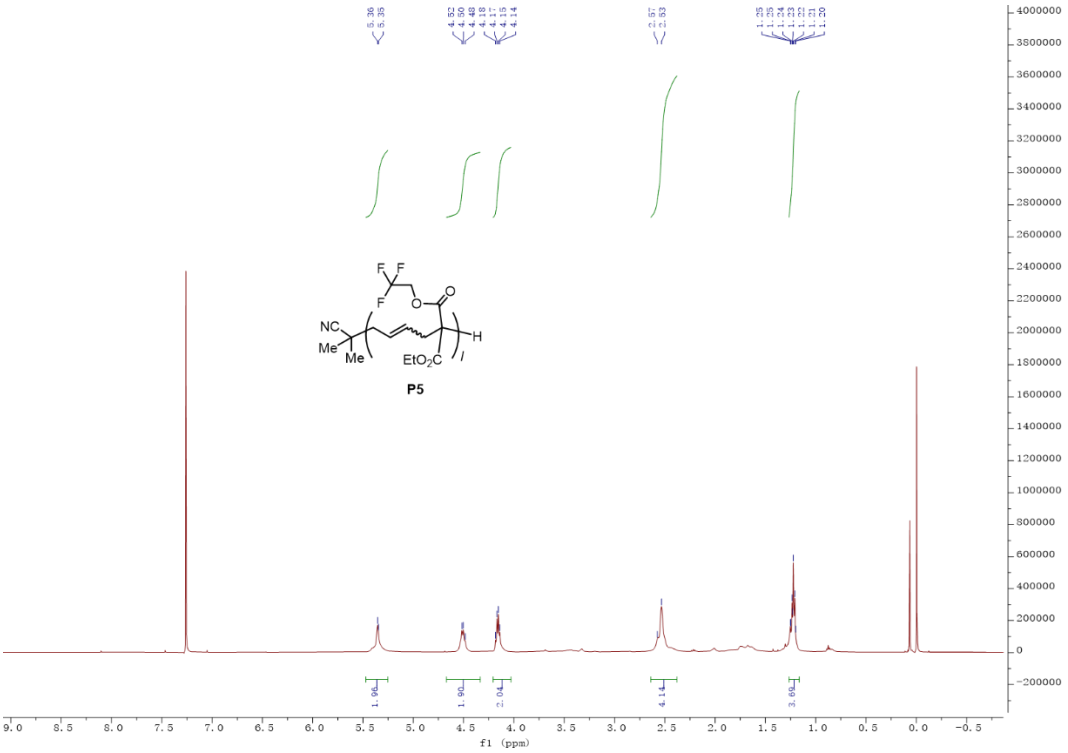


Fig. S35 ^{1}H NMR spectrum of **P5** in $CDCl_3$

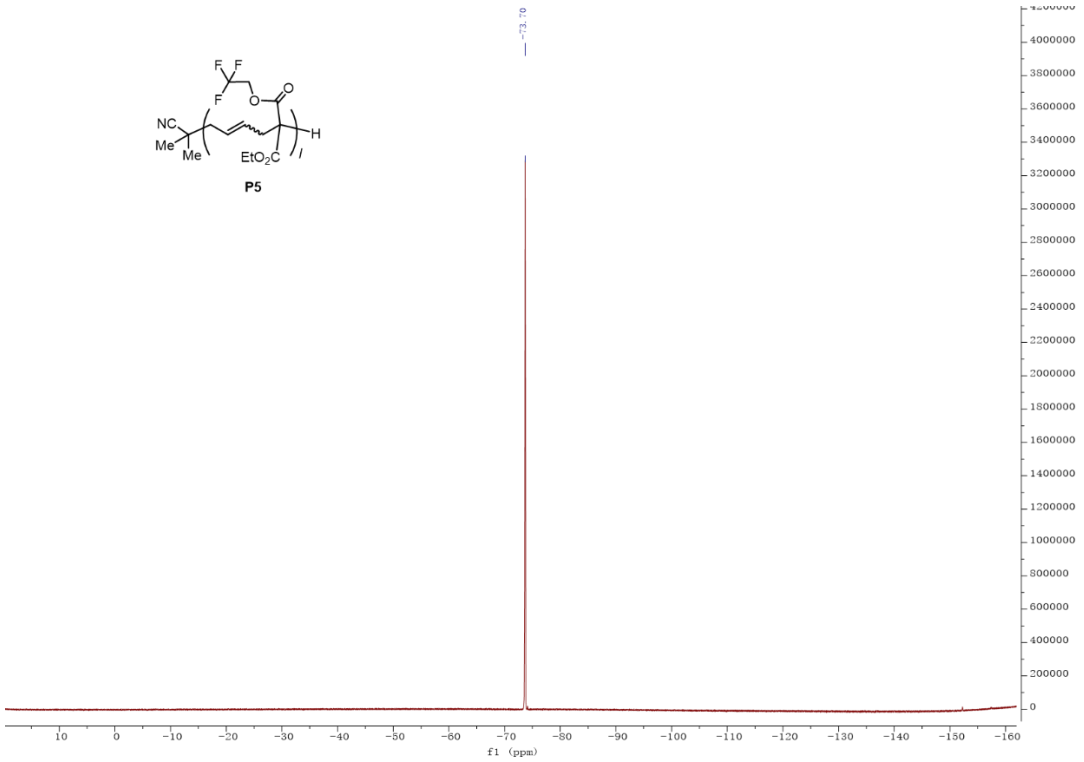


Fig. S36 ^{19}F NMR spectrum of **P5** in $CDCl_3$

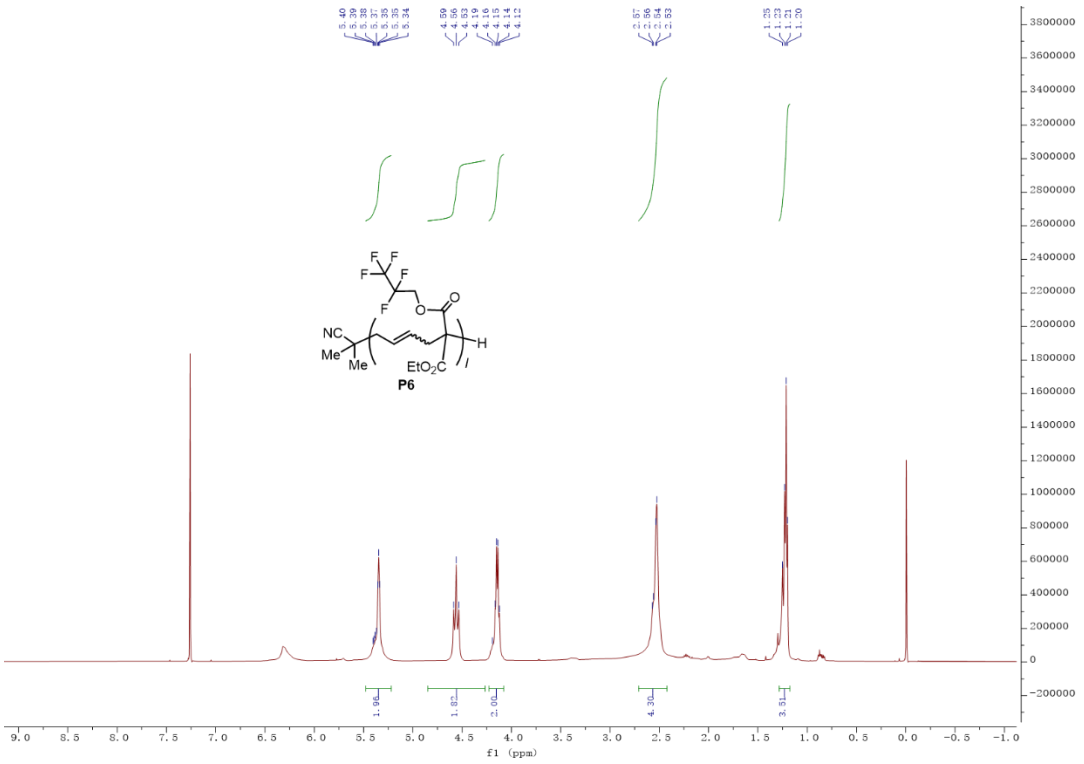


Fig. S37 ^{1}H NMR spectrum of **P6** in $CDCl_3$

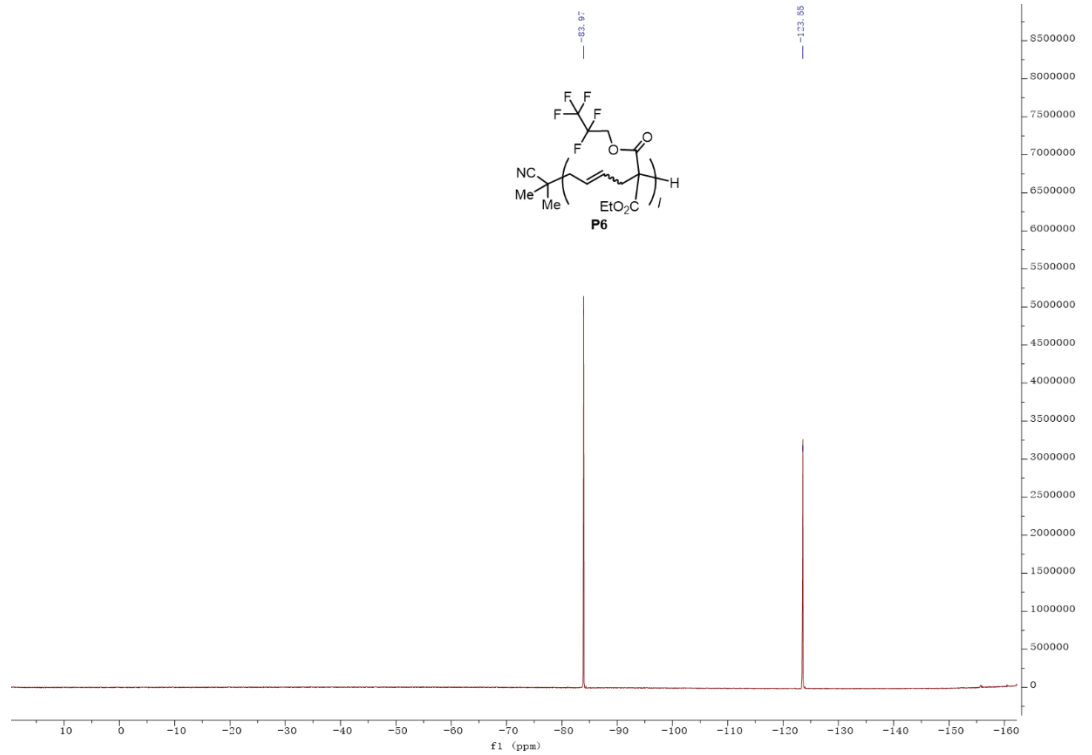


Fig. S38 ^{19}F NMR spectrum of **P6** in $CDCl_3$

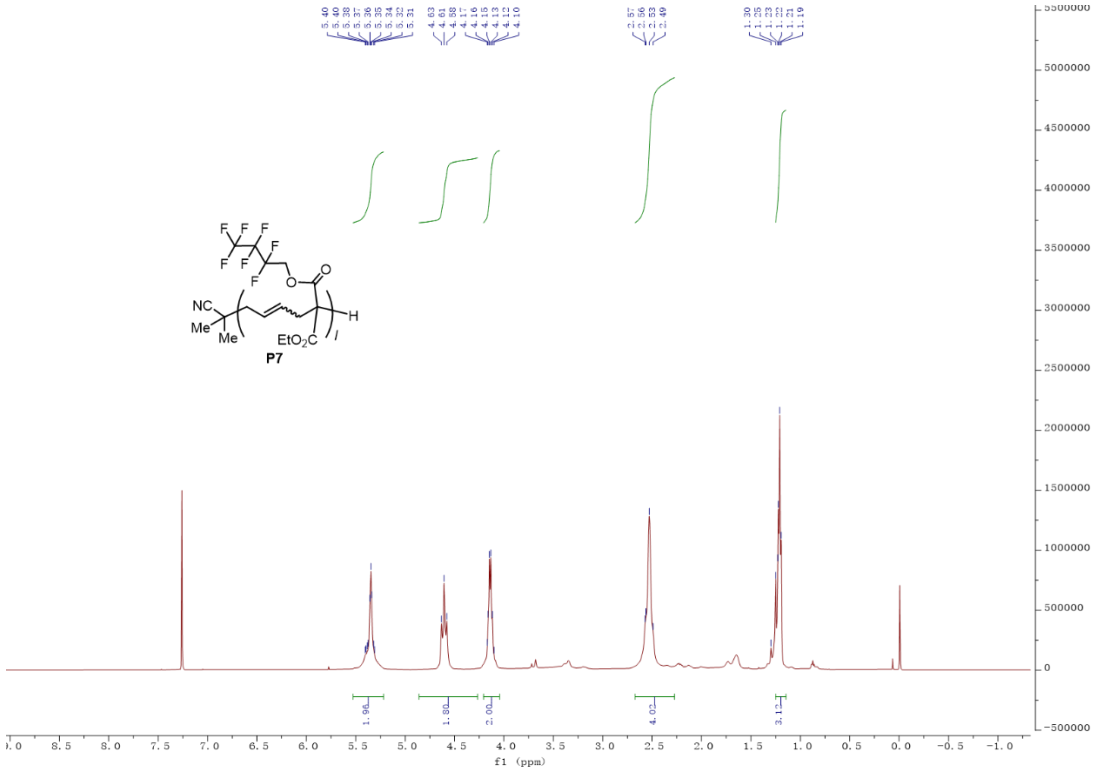


Fig. S39 ^{1}H NMR spectrum of **P7** in $CDCl_3$

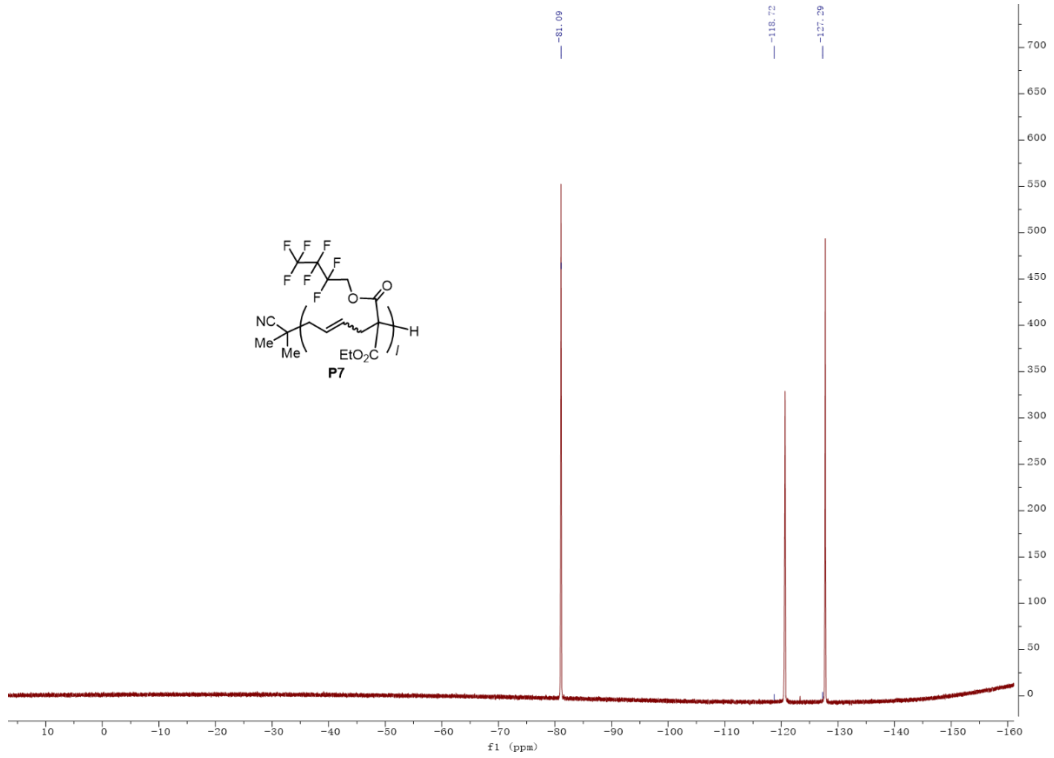


Fig. S40 ^{19}F NMR spectrum of **P7** in $CDCl_3$

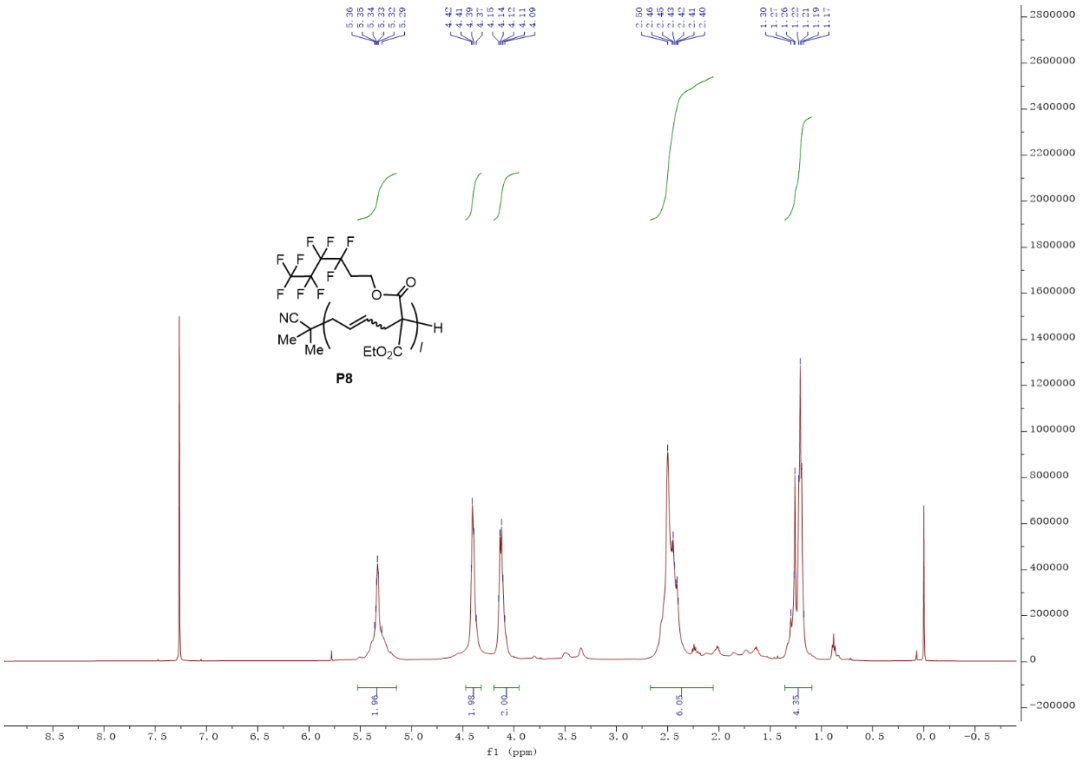


Fig. S41 ^{1}H NMR spectrum of **P8** in $CDCl_3$

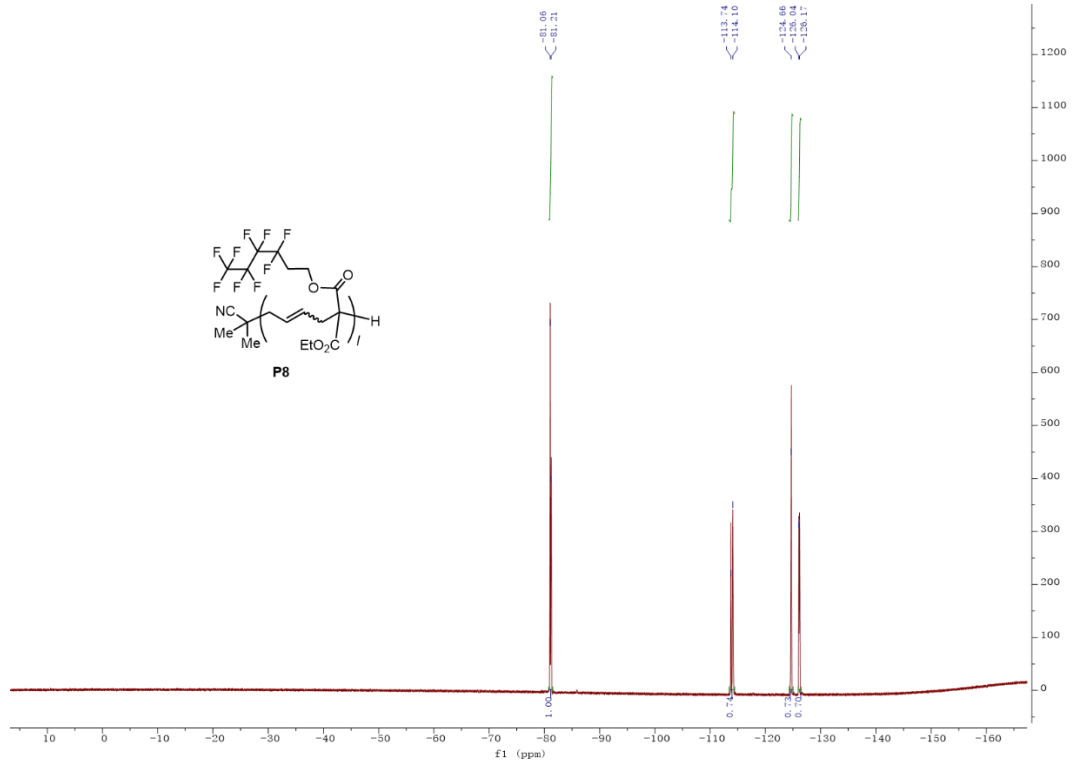


Fig. S42 ^{19}F NMR spectrum of **P8** in $CDCl_3$

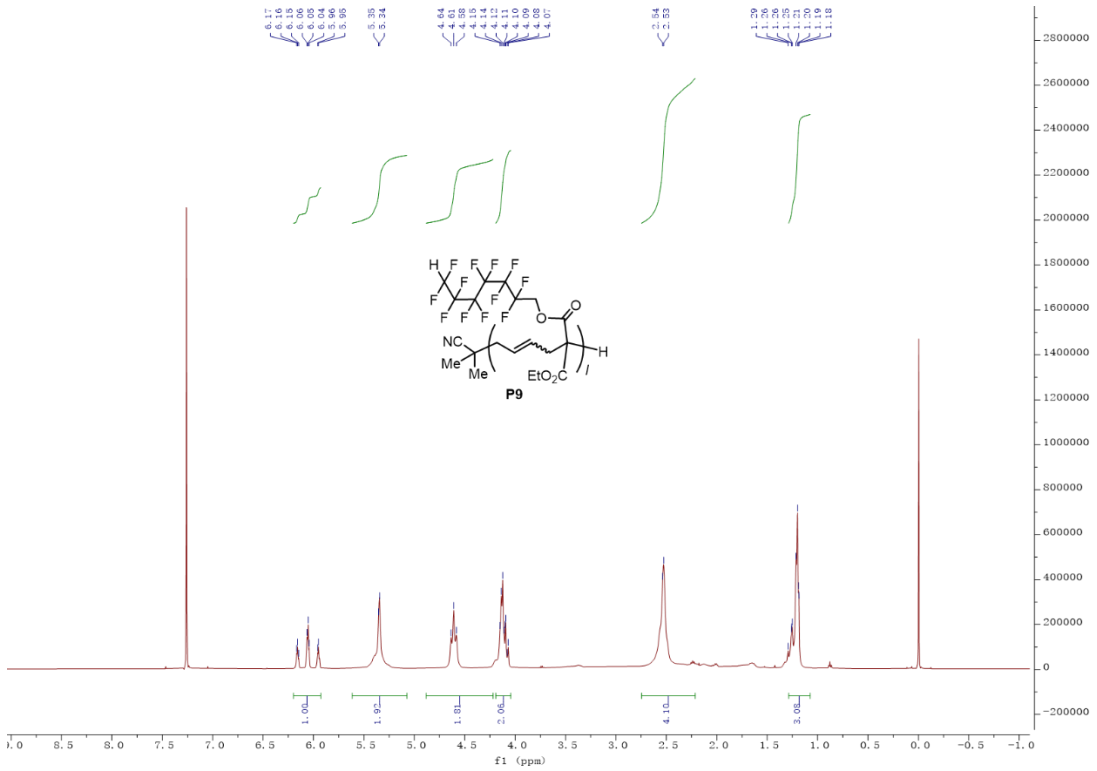


Fig. S43 ^{1}H NMR spectrum of **P9** in $CDCl_3$

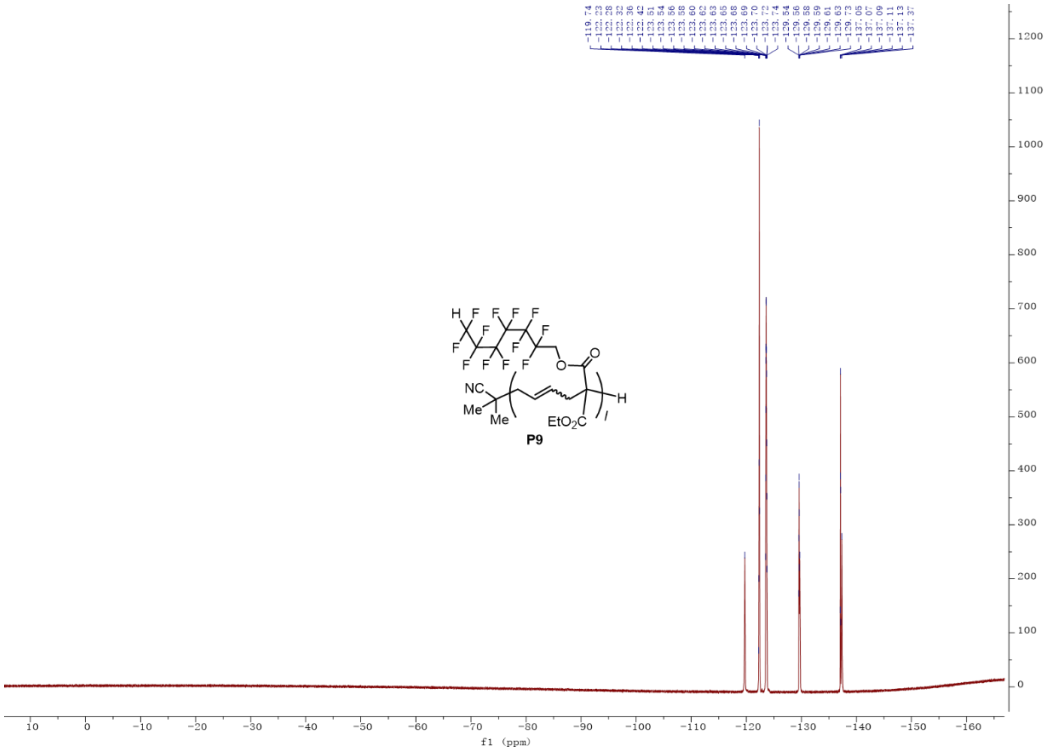


Fig. S44 ^{19}F NMR spectrum of **P9** in $CDCl_3$

5.5 GPC Traces of Modified P(VCPs)

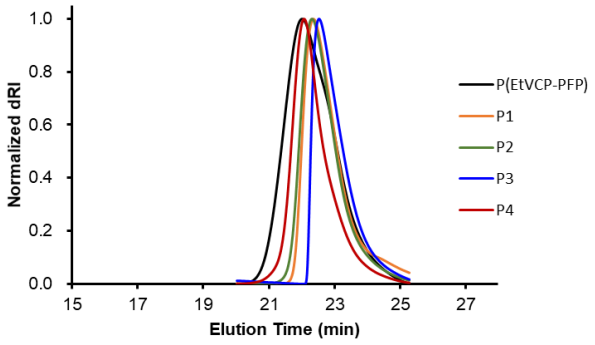


Fig. S45 Overlay of GPC traces of P(EtVCP-PFP) and **P1**–**P4** in Figure 3c

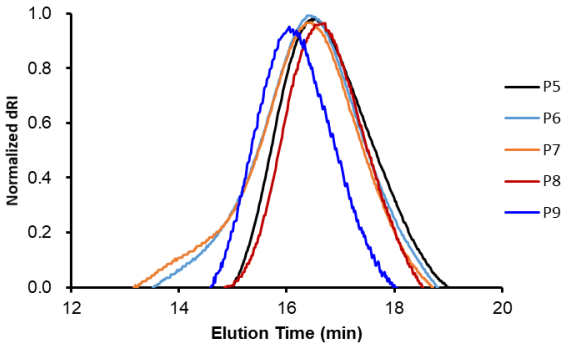


Fig. S46 Overlay of GPC traces of **P5**–**P9** in Figure 3d

5.6 DSC and TGA Curves of Modified P(VCPs)

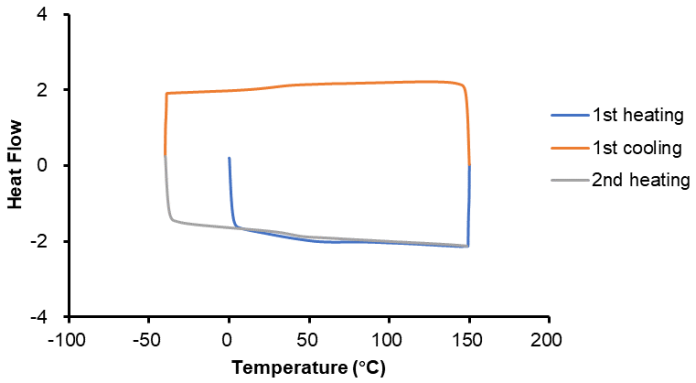


Fig. S47 DSC curves of **P1** (13.0 kDa, $Đ$ = 1.16, S_L = 97%). T_g = 42 °C (2nd heating scan).

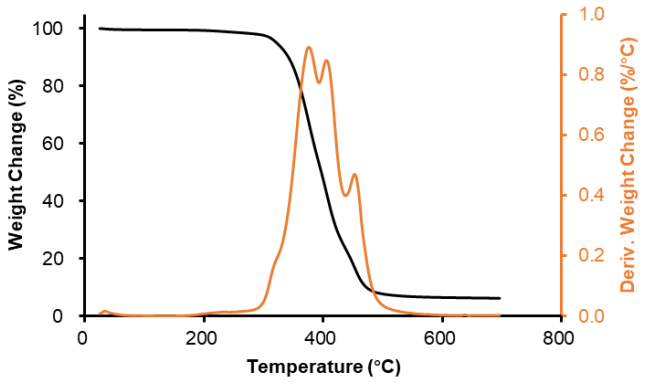


Fig. S48 TGA and DTG curves of **P1** (13.0 kDa, $Đ$ = 1.16, S_L = 97%). $T_d^{5\%}$ = 322 °C, T_{max1} = 376 °C, T_{max1} = 405 °C.

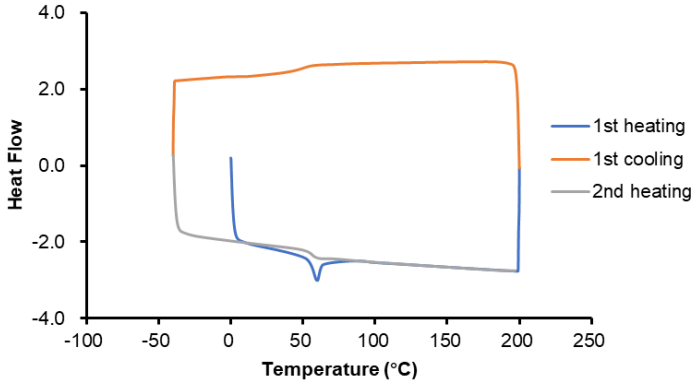


Fig. S49 DSC curves of **P2** (13.1 kDa, $Đ$ = 1.13, S_L = 99%). T_g = 56 °C (2nd heating scan).

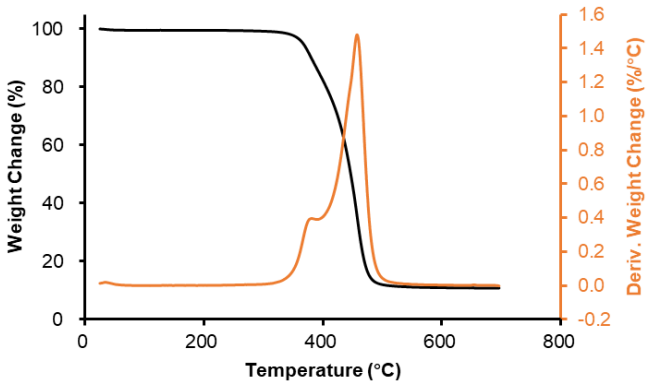


Fig. S50 TGA and DTG curves of **P2** (13.1 kDa, $Đ$ = 1.13, S_L = 99%). $T_d^{5\%}$ = 366 °C, T_{max1} = 376 °C, T_{max1} = 456 °C.

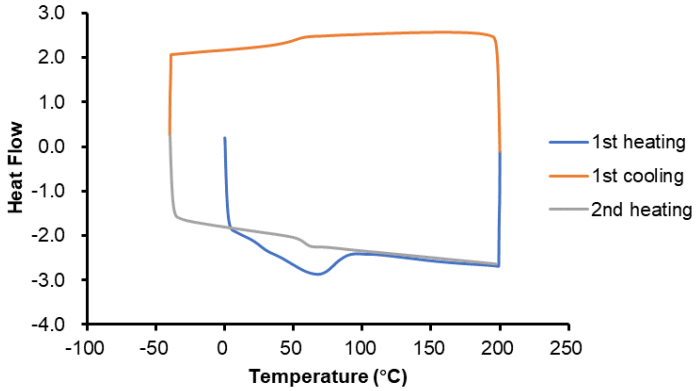


Fig. S51 DSC curves of **P3** (12.6 kDa, $Đ$ = 1.15, S_L = 96%). T_g = 58 °C (2nd heating scan).

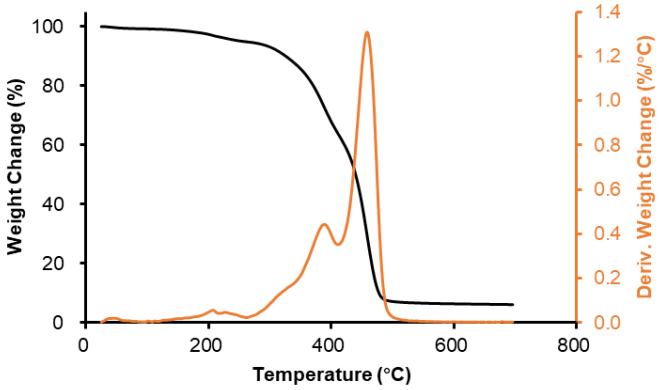


Fig. S52 TGA and DTG curves of **P3** (12.6 kDa, $Đ$ = 1.15, S_L = 96%). $T_d^{5\%}$ = 257 °C, T_{max} = 458 °C.

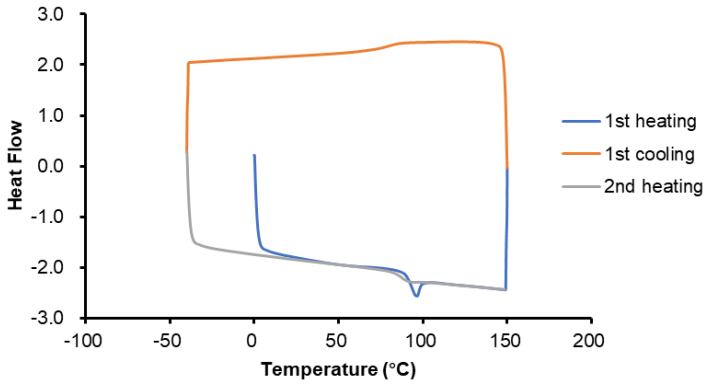


Fig. S53 DSC curves of **P4** (16.8 kDa, $Đ$ = 1.15, S_L = 98%). T_g = 87 °C (2nd heating scan).

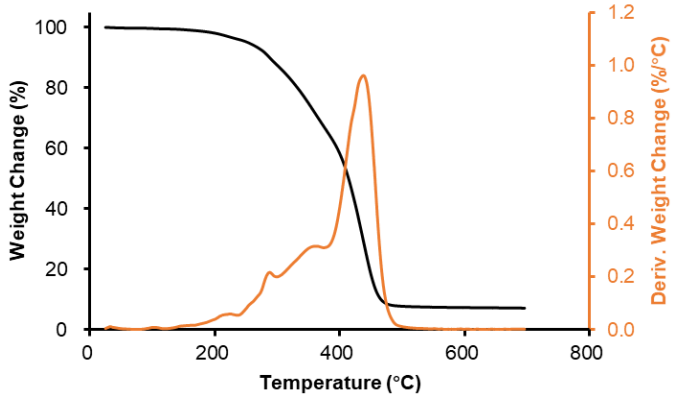


Fig. S54 TGA and DTG curves of **P4** (16.8 kDa, $Đ$ = 1.15, S_L = 98%). $T_d^{5\%}$ = 253 °C, T_{max} = 438 °C.

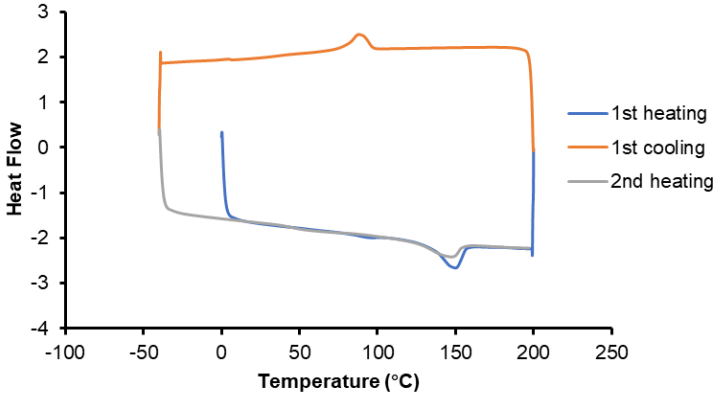


Fig. S55 DSC curves of **P5** (13.1 kDa, $Đ$ = 1.30, S_L = 98%). T_g = 48 °C (2nd heating scan), T_c = 88 °C (1st cooling scan), T_m = 147 °C (2nd heating scan).

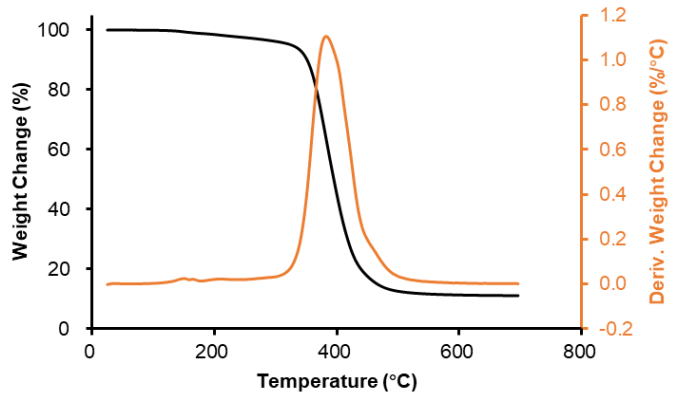


Fig. S56 TGA and DTG curves of **P5** (13.1 kDa, $Đ$ = 1.30, S_L = 98%). $T_d^{5\%}$ = 325 °C, T_{max} = 380 °C.

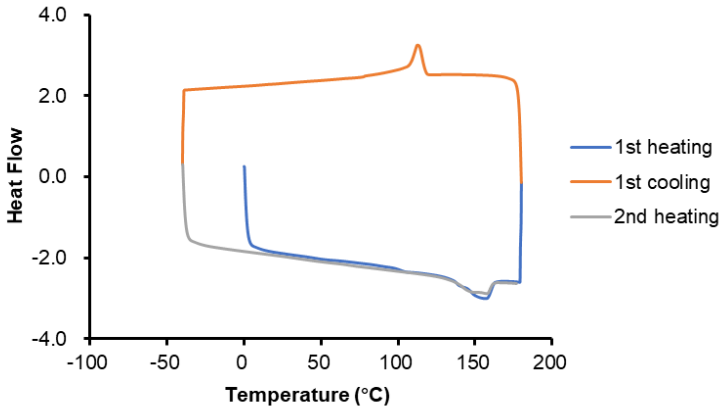


Fig.S57 DSC curves of **P6** (13.4 kDa, $Đ$ = 1.45, S_L = 97%). T_g = 46 °C (1st heating scan), T_c = 112 °C (1st cooling scan), T_m = 157 °C (2nd heating scan).

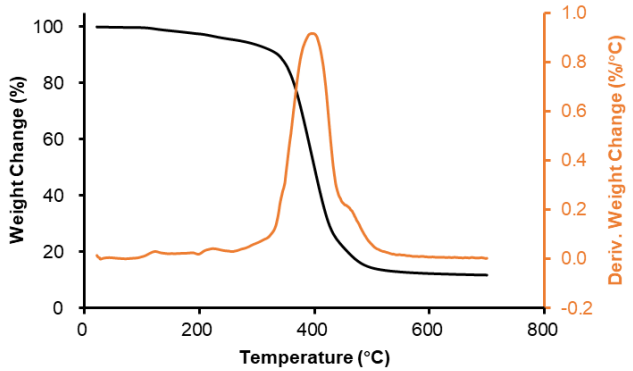


Fig. S58 TGA and DTG curves of **P6** (13.4 kDa, $Đ$ = 1.45, S_L = 97%). $T_d^{5\%}$ = 271 °C, T_{max} = 398 °C.

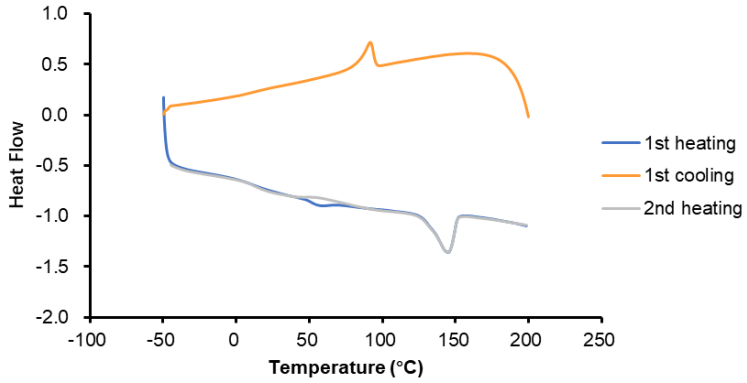


Fig. S59 DSC curves of **P7** (13.5 kDa, $Đ$ = 1.37, S_L = 97%). T_g = 21 °C (2nd heating scan), T_c = 92 °C (1st cooling scan), T_m = 144 °C (2nd heating scan).

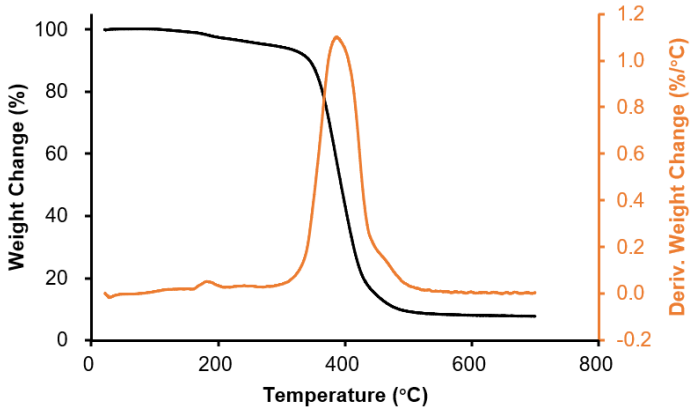


Fig. S60 TGA and DTG curves of **P7** (13.5 kDa, $Đ$ = 1.37, S_L = 97%). $T_d^{5\%}$ = 281 °C, T_{max} = 387 °C

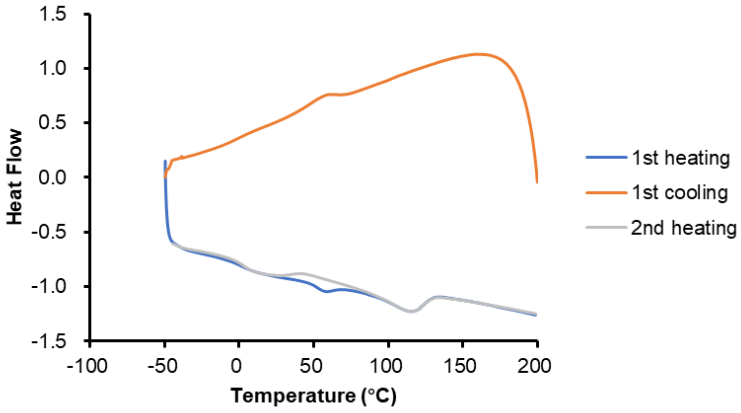


Fig. S61 DSC curves of **P8** (12.1 kDa, $Đ$ = 1.24, S_L = 97%). T_g = 6 °C (2nd heating scan), T_c = 62 °C (1st cooling scan), T_m = 116 °C (2nd heating scan)

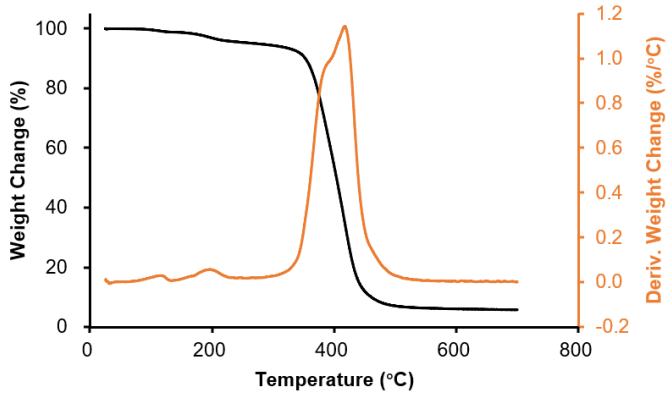


Fig. S62 TGA and DTG curves of **P8** (12.1 kDa, $Đ$ = 1.24, S_L = 97%). $T_d^{5\%}$ = 268 °C, T_{max} = 415 °C

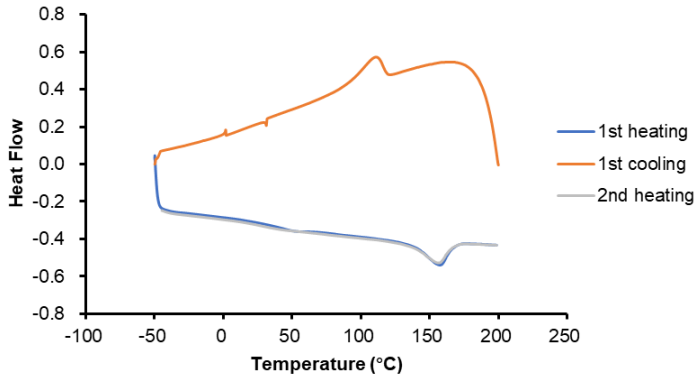


Fig. S63 DSC curves of **P9** (17.9 kDa, $Đ$ = 1.21, S_L = 97%). T_g = 47 °C (2nd heating scan), T_c = 111 °C (1st cooling scan), T_m = 158 °C (2nd heating scan)

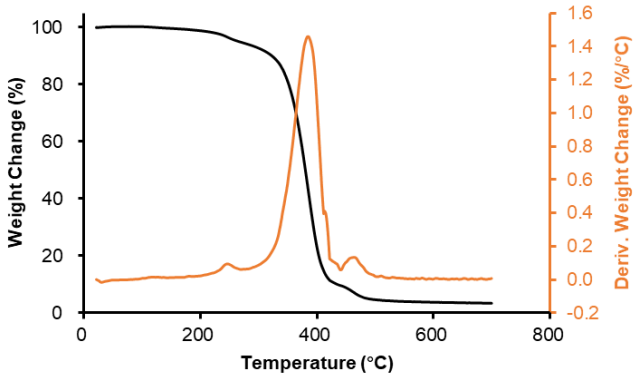


Fig. S64 TGA and DTG curves of **P9** (17.9 kDa, $Đ$ = 1.21, S_L = 97%). $T_d^{5\%}$ = 266 °C, T_{max} = 385 °C

6. Reference

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[2] M. R. Emmett and M. A. Kerr, *Org. Lett.* **2011**, *13*, 4180–4183.