Supporting Information For

Heat-Resistant Poly(methyl methacrylate) by Modification with Perfluorocyclobutyl Methacrylamide Monomers

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EXPERIMENTAL DETAILS

Materials

Dimethylsulfoxide (DMSO, Alfa Aesar, 99%) was dried over CaH_2 and distilled under reduced pressure prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol. Triethylamine (TEA, Alfa Aesar, 99%) was dried over KOH and distilled over CaH_2 under N_2 prior to use. Granular zinc was activated by washing in 0.1 N HCl followed by drying at 140°C *in vacuo* for 10 h. Tetrahydrofuran (THF) were dried over CaH_2 for several days and distilled from sodium and benzophenone under N_2 prior to use. Acetonitrile was dried over CaH_2 and distilled under N_2 prior to use. Methyl methacrylate (MMA, Aldrich, 99%) was purified by passing through a column of neutral alumina. 1,2-Dibromotetrafluoroethane (Macklin, 98%), caesium carbonate(Aldrich, 99%), 4-methoxylphenol (Aldrich, 99%), 4-bromophenol (Aldrich, 99%), tetrakis(triphenylphosphine)-palladium(0) (Aldrich, 99%), potassium carbonate (Aldrich, 99%), methacryloyl chloride (Alfa Aesar, 97%), ethylene dimethacrylate (EGDMA, Adamas, 98%) and 4-aminophenylboronic acid pinacol ester (Aldrich, 97%) were used as received unless otherwise specified.

Instrumentation

^{1}H, ^{13}C and ^{19}F NMR spectra of intermediates were recorded on a JEOL resonance ECZ 400S spectrometer (400 MHz) in $CDCl_3$. Tetramethylsilane (TMS) and $CDCl_3$ were used as internal standards for ^{1}H and ^{13}C NMR, respectively; CF_3CO_2H was used as external standard for ^{19}F NMR. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer and PerkinElmer Spectrum Two with a 4 cm^{-1} resolution. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were obtained on a conventional gel permeation chromatography (GPC) system equipped with a Waters 515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000) and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurement was carried out at 35°C using tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Differential scanning calorimetry (DSC) was performed on a TA Q200 DSC instrument in N_2 with a heating rate of 10°C/min. Thermogravimetry analysis (TGA) was conducted on a TA Discovery TGA 55 thermal analysis system in N_2 with a heating rate of 10°C/min.

Synthesis of methacrylamide monomer containing PFCB (PFCBMA)

Firstly, the cross-dimer, 1-bromo-4-(1,2,2,3,3,4-hexafluoro-4-(4-methoxyphenoxy)-cyclobutoxy)benzene, was prepared by the cross-coupling reaction from 1-bromo -4-((1,2,2-trifluorovinyl)oxy)benzene and 1-methoxy-4-((1,2,2-trifluorovinyl) oxy)-benzene, which were obtained from 4-methoxylphenol, 4-bromophenol and 1,2-dibromotetrafluoroethane according to previous reports.[1,2]

The aminobiphenyl intermediate containing PFCB (PFCBNH_2) was prepared by

Suzuki coupling reaction from 1-bromo-4-(1,2,2,3,3,4-hexafluoro-4-(4-methoxyphenoxy)cyclobutoxy)benzene and 4-aminophenylboronic acid pinacol ester. Into a 500 mL round-bottom flask were added the cross-dimer (20.2506 g, 44.3 mmol), 4-aminophenylboronic acid pinacol ester (12.0354 g, 54.9 mmol), K_2CO_3 (24.5244 g, 177.4 mmol), ethanol (50 mL) and toluene (150 mL). After degassing the resulting mixture via N_2 bubbling for 30 minutes, tetrakis(triphenylphosphine)palladium(0) (2.0460 g, 1.77 mmol) was charged. The reaction mixture was then heated to 85^{o}C for 8 hours under N_2. The solvents were removed by rotary evaporation, and the residue was subjected to column chromatography (eluent: *n*-hexane/ethyl acetate, v:v = 1:1) to afford $PFCBNH_2$ as a grey solid (10.3417 g, 49.7 % yield). ^{1}H NMR (DMSO-d_6): δ (ppm): 3.78 (s, 3H) ,5 .27 (s, 2H) , 6.62 (dd, 2H) ,6.98 (m, 2H) ,7.20 (dd, 2H) , 7.33 (dd, 2H) , 7.59 (m, 2H). ^{19}F NMR (DMSO-d_6): δ (ppm): -128.55~-132.17.

The methacrylamide monomer containing PFCB was prepared by amidation reaction between $PFCBNH_2$ and methacryloyl chloride. Into a 500 mL round-bottom flask were added methacryloyl chloride (2.2 mL, 5.1 mmol), TEA (6.20 mL, 10.0 mmol) and THF (175 mL). After the mixture was cooled in an ice-water bath, a solution of $PFCBNH_2$ (10.3300 g, 5.0 mmol) in THF (60 mL) was added dropwise via syringe. The resulting mixture was warmed to room temperature and allowed to stir for another 12 hours followed by adding water to quench the reaction. THF was removed by rotary evaporation and the residue was extracted by 150 mL of CH_2Cl_2. The organic phase was washed with 5% aqueous K_2CO_3 (150 mL×2) as well as brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After CH_2Cl_2 was evaporated, the crude product was purified by column chromatography (eluent: *n*-hexane/ethyl acetate, v:v = 5:1) to afford PFCBMA as a white powder (1.7475 g, 65% yield). ^{1}H NMR ($CDCl_3$): δ (ppm): 2.08 (s, 3H), 3.78 (d, 3H), 5.49 and 5.81 (2H), 6.82 (m, 2H),7.10 (m, 2H), 7.20 (m, 2H), 7.53 (m, 4H), 7.56 (s, 1H), 7.63 (d, 2H). ^{13}C NMR ($CDCl_3$): 18.8, 55.6, 114.6, 118.5, 119.9, 120.1, 120.5, 127.5, 128.1, 136.0, 137.3, 140.9, 146.2, 152.0, 157.0, 166.7. ^{19}F NMR ($CDCl_3$-d_6): δ (ppm): -128.3~-131.6. ESI-MS: ($[M+H]^+$ calcd as $C_{27}H_{22}NO_8F_6$ = 538.14) m/z (%): 538.14 (100).

Synthesis of dimethacrylamide monomer containing PFCB (MAPFCBMA)

Firstly, the bis(4-biphenylamine) compound containing PFCB ($PFCB(NH_2)_2$) was prepared by Suzuki coupling reaction from 1-bromo-4-(1,2,2,3,3,4-hexafluoro-4-(4-methoxyphenoxy)cyclobutoxy)benzene and 4-aminophenylboronic acid pinacol ester according to a previous report.[3]

The dimethacrylamide monomer containing PFCB was prepared by amidation reaction between $PFCB(NH_2)_2$ and methacryloyl chloride. Into a 500 mL round-bottom flask were added methacryloyl chloride (5.54 mL, 57.2 mmol), TEA (13.0 mL, 93.8 mmol) and THF (170 mL). After the mixture was cooled in an ice-water bath, a solution of $NH_2PFCBNH_2$ (12.4923 g, 23.5 mmol) in THF (60 mL) was added dropwise via syringe. The resulting mixture was warmed to room temperature and allowed to stir for another 12 hours followed by adding water to quench the reaction. THF was removed by rotary evaporation and the residue was extracted by 150 mL of CH_2Cl_2. The organic phase was washed with 5% aqueous K_2CO_3 (150 mL×2) as well as brine (150 mL×2), dried over anhydrous $MgSO_4$ and filtered. After CH_2Cl_2 was evaporated, the crude product was purified by column chromatography (eluent: *n*-hexane/ethyl acetate, v:v = 1:1) to afford MAPFCBMA as a white powder (8.1062 g, 52% yield). ^{1}H NMR (DMSO-d_6): δ (ppm): 9.87 (2H), 7.79 (4H), 7.75 (4H), 7.63 (4H), 7.29 (4H), 5.82 (2H), 5.53 (2H), 1.96 (6H). ^{13}C NMR (DMSO-d_6): 18.8, 118.5, 120.1, 120.5, 126.8, 128.1, 133.6, 137.4, 138.8, 140.4, 151.0, 167.0. ^{19}F NMR (DMSO-d_6): δ (ppm): -127.7 to -131.2.

Copolymerization of PFCBMA and MMA

PPFCBMA-*co*-PMMA copolymers were prepared by copolymerization of PFCBMA and MMA with various feed ratios ([PFCBMA]:[MMA] = 1:5, 1:10 and 1:15). Take PPFCBMA-*co*-PMMA-1 as an example, the procedure is as below.

AIBN (78.7 mg, 0.480 mmol) was firstly added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing. Next, PFCBMA (4.0120 g, 7.46 mmol), MMA (4.1 mL, 38.6 mmol) and DMF (17 mL) were introduced via a gastight syringe. The solution was degassed by five freeze-pump-thaw cycles followed by immersing the flask into an oil bath preset at 60°C to start the polymerization. The polymerization was terminated by putting the flask into liquid nitrogen after 15 hours. After repeated purification by dissolving in DMF and precipitating in methanol three times, 5.1487 g (65%) of white powder, PPFCBMA-*co*-

PMMA-1, was obtained after drying *in vacuo*. GPC: M_n = 57,600 g/mol, M_w/M_n = 1.72. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.48, 7.40, 7.16, 7.07, 6.78, 3.72, 3.57, 3.47, 1.64-2.22, 0.71-1.50. ^{13}C NMR ($CDCl_3$): δ (ppm): 177.9, 177.2, 157.1, 151.8, 146.0, 137.6, 136.3, 128.1, 127.6, 120.9, 120.6, 118.9, 114.6, 54.5, 51.9, 44.7, 18.8, 16.6. ^{19}F NMR ($CDCl_3$): δ (ppm): -128.2 ~ -132.0. FT-IR (KBr): ν (cm^{-1}): 3612, 3395, 2995, 2950, 2841, 1732, 1507, 1448, 1317, 1296, 1247, 1195, 1149, 962, 827, 750.

Copolymerization of MAPFCBMA and MMA

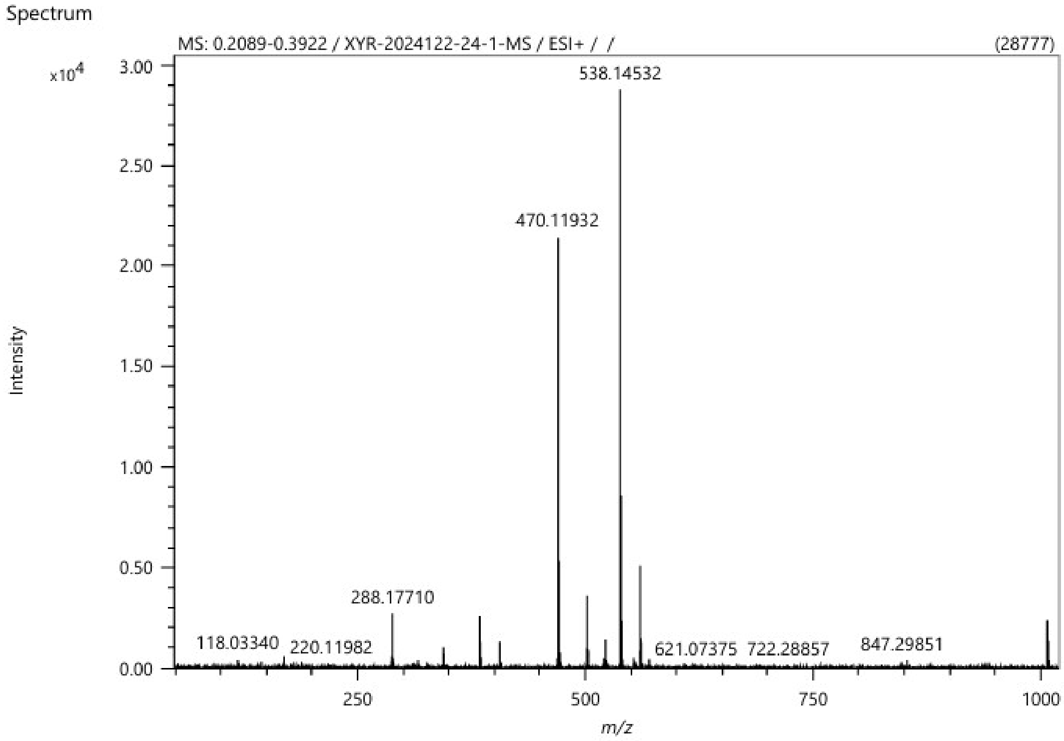
Cross-PFCB-PMMA copolymers were prepared by copolymerization of MAPFCBMA and MMA with various feed ratios ([MAPFCBMA]:[MMA] = 1:5, 1:10 and 1:15). Take Cross-PFCBMA-1 as an example, the procedure is as below.

Into a dried Schlenk tube were added MAPFCBMA (1.8670 g, 2.8 mmol), MMA (1.50 mL, 14.0 mmol), AIBN (27.6 mg, 0.168 mmol) and DMF (4 mL). The mixture was degassed by three cycles of freezing-pumping-thawing. The Schlenk tube was kept in a preheated oil bath at 70°C for 24 hours. After cooling to room temperature, the mixture was crushed and washed with methanol several times. 2.8435 g of white powder (87%) was obtained after drying *in vacuo*. FT-IR (KBr): ν (cm^{-1}): 2992, 2952, 2922, 2851, 1725, 1495, 1432, 1386, 1264, 1193, 1145, 960, 820, 749.

Copolymerization of ethylene dimethacrylate and MMA

Into a dried Schlenk tube were added EGDMA (0.568 g, 2.8 mmol), MMA (3.0 mL, 28.0 mmol), AIBN (50.6 mg, 0.308 mmol) and DMF (3.3 mL). The mixture was degassed by three cycles of freezing-pumping-thawing. The Schlenk tube was kept in a preheated oil bath at 70°C for 24 hours. After cooling to room temperature, the mixture was crushed and washed with methanol several times, affording 3.4456 g of white powder (100 %) after drying *in vacuo*.

SUPPORTING FIGURES



Elemental Composition

Parameters

Tolerance:	±5.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-1.5 - 200.0

Elements Set 1:

Symbol	C	H	N	O	Na	Si	Cl	S
Min	0	0	0	0	0	0	0	0
Max	200	200	3	8	0	0	0	0

Symbol	F	Br	D	P
Min	6	0	0	0
Max	6	0	0	0

Results

Mass	Intensity	Intensity [%]	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
538.14532	28777.29	100.00	C27 H22 N O4 F6	538.14475	0.56	1.05	14.5
			C30 H20 N2 O F6	538.14743	-2.12	-3.93	19.0

Figure S1. ESI-MS of PFCBMA monomer.

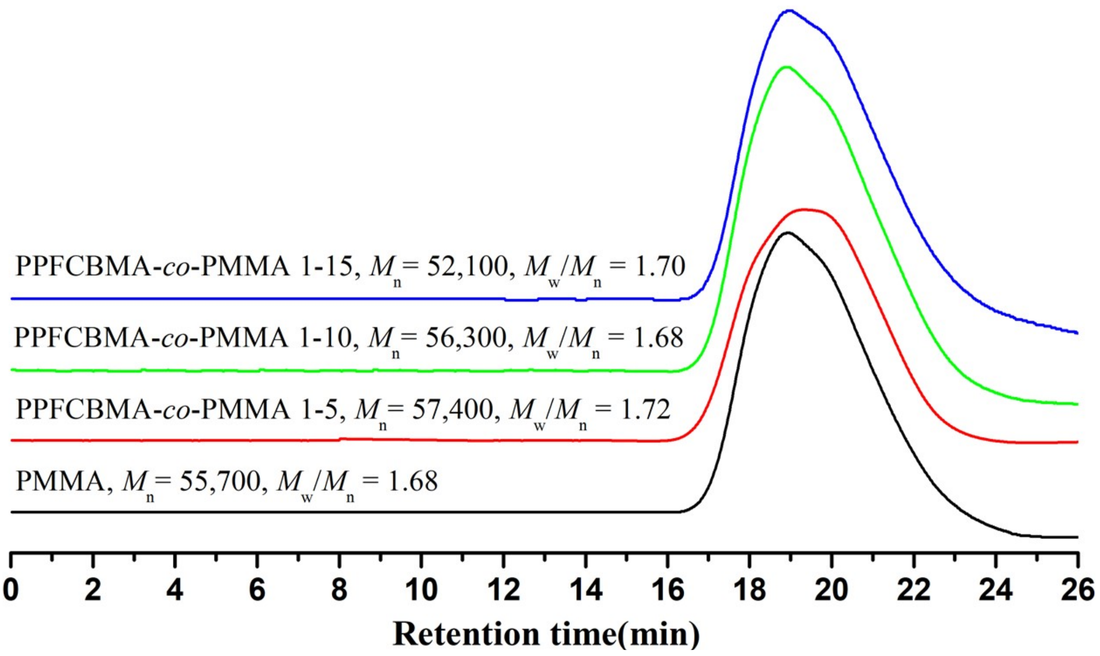


Figure S2. GPC curves of PPFCBMA-*co*-PMMA.

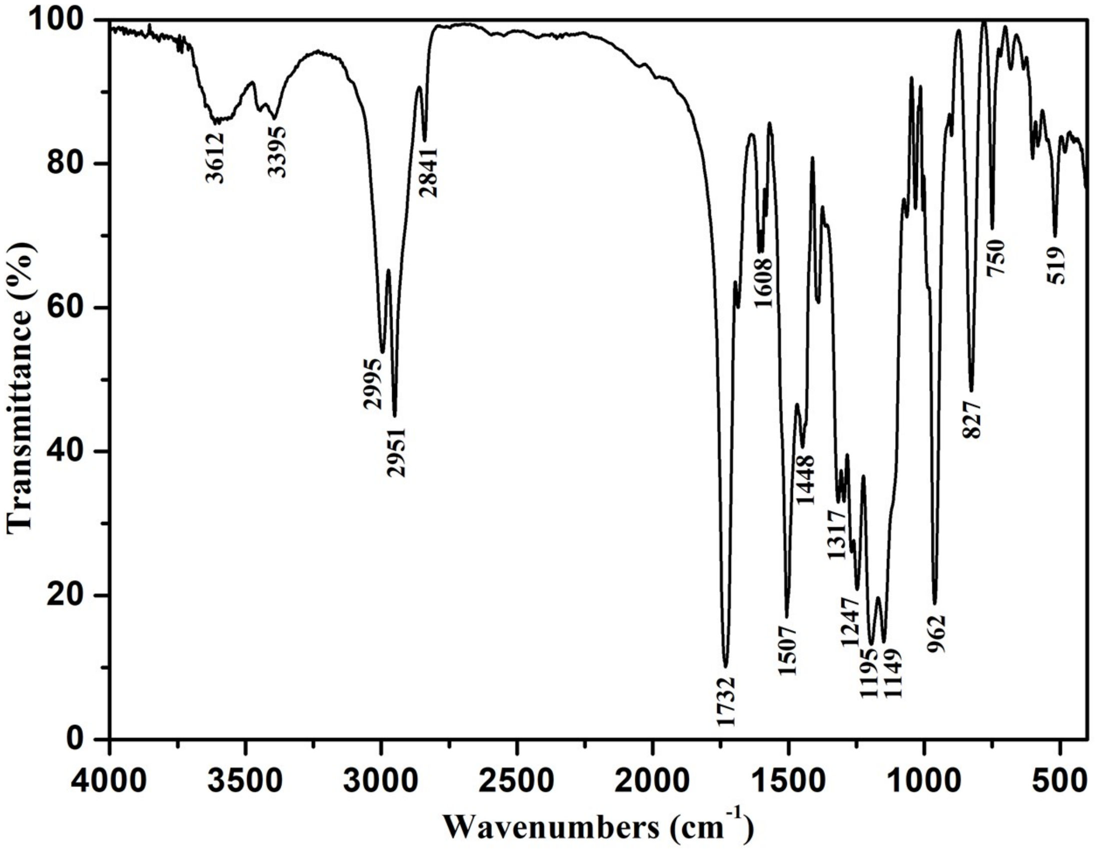


Figure S3. FT-IR spectrum of PPFCBMA-*co*-PMMA.

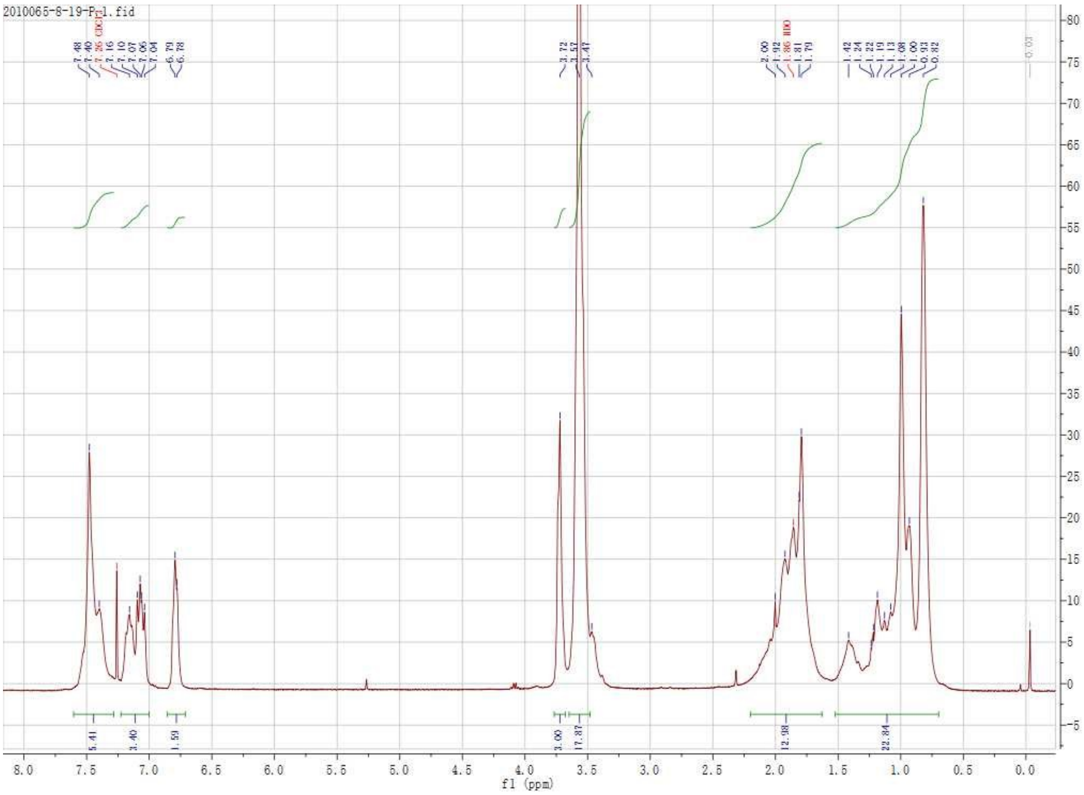


Figure S4. ^{1}H NMR spectrum of PPFCBMA-*co*-PMMA 1-5 in CDCl$_3$.

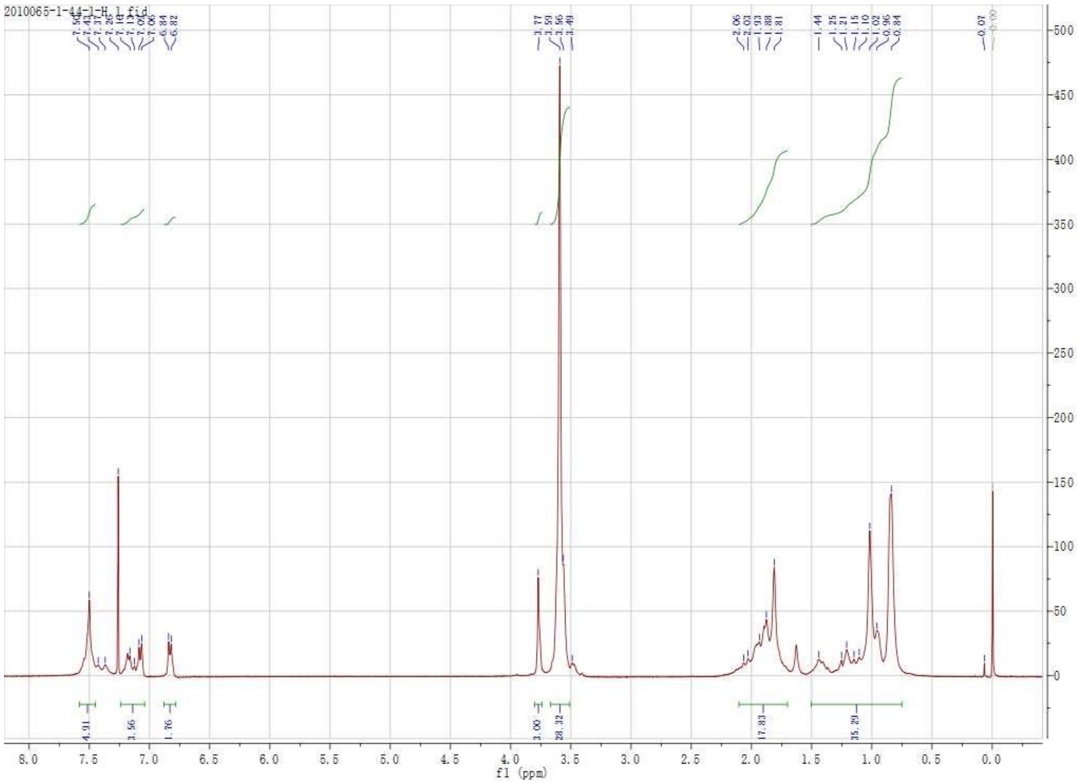


Figure S5. ^{1}H NMR spectrum of PPFCBMA-*co*-PMMA 1-10 in CDCl$_3$.

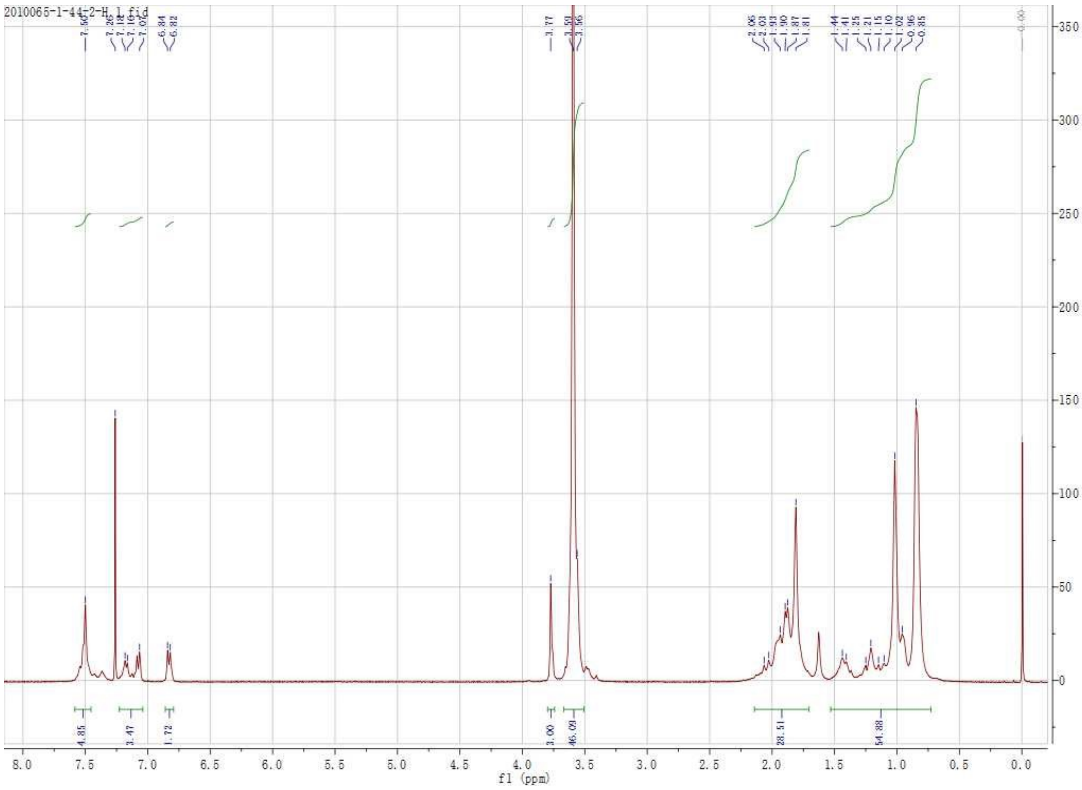


Figure S6. ^{1}H NMR spectrum of PPFCBMA-*co*-PMMA 1-15 in CDCl$_3$.

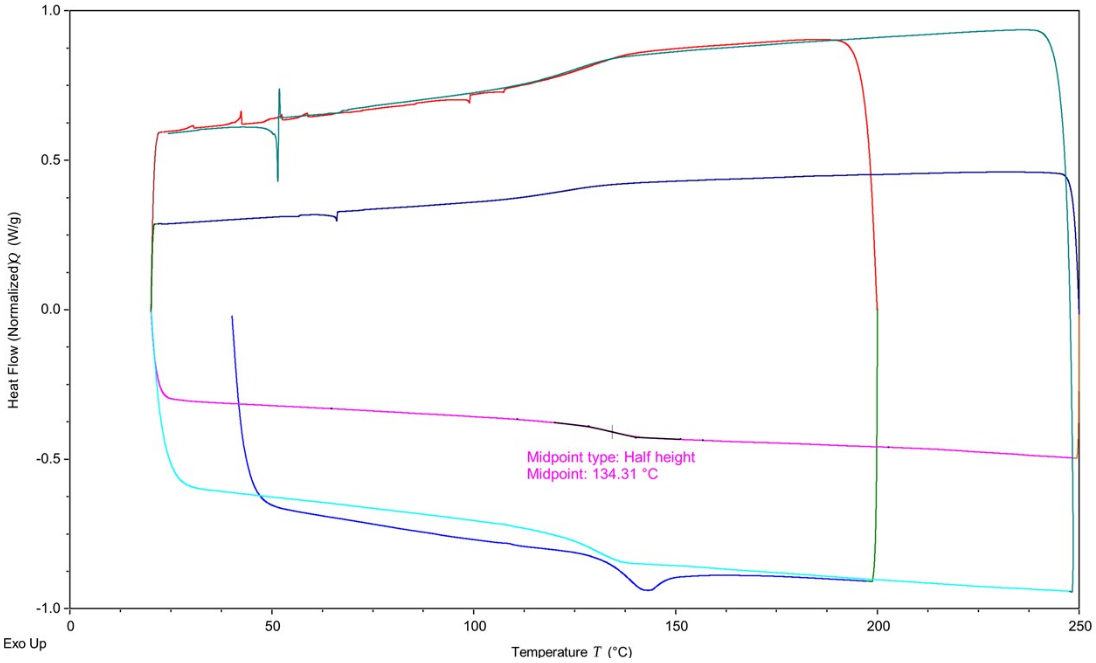


Figure S7. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of PPFCBMA-*co*-PMMA 1-5.

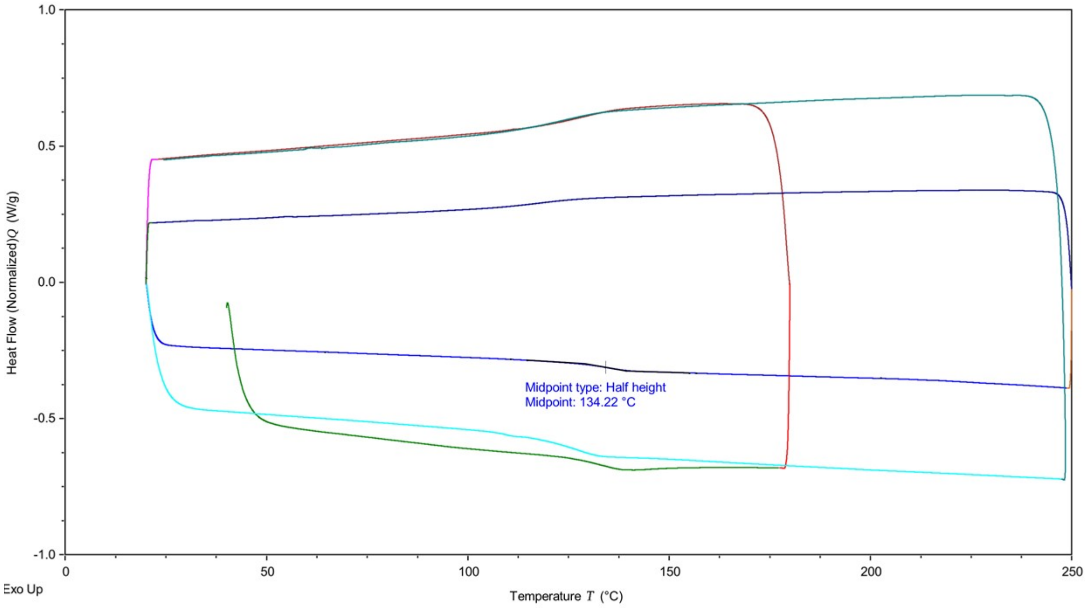


Figure S8. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of PPFCBMA-*co*-PMMA 1-10.

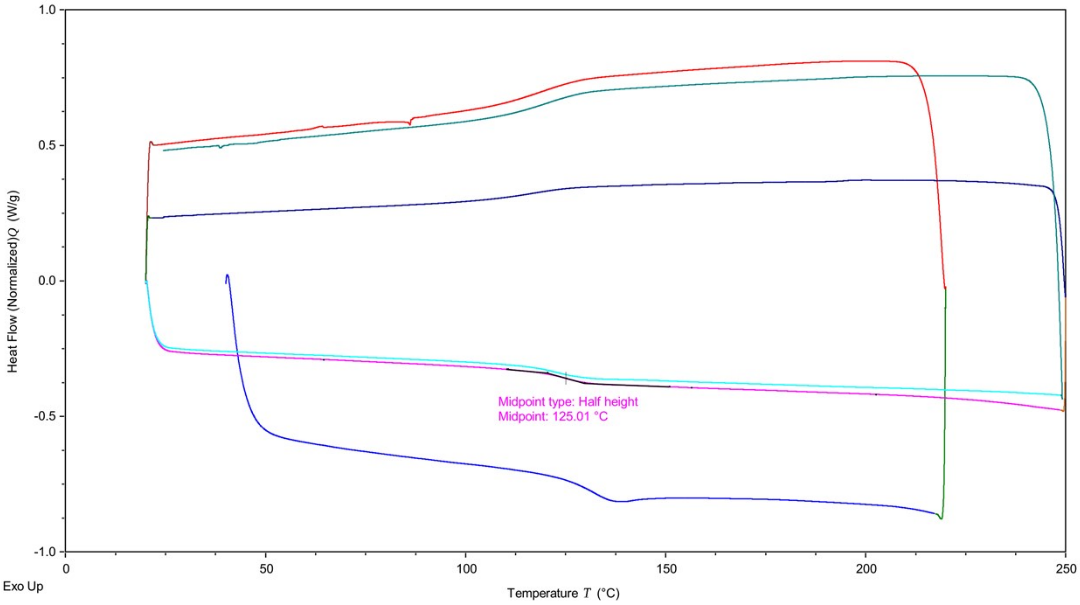


Figure S9. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of PPFCBMA-*co*-PMMA 1-15.

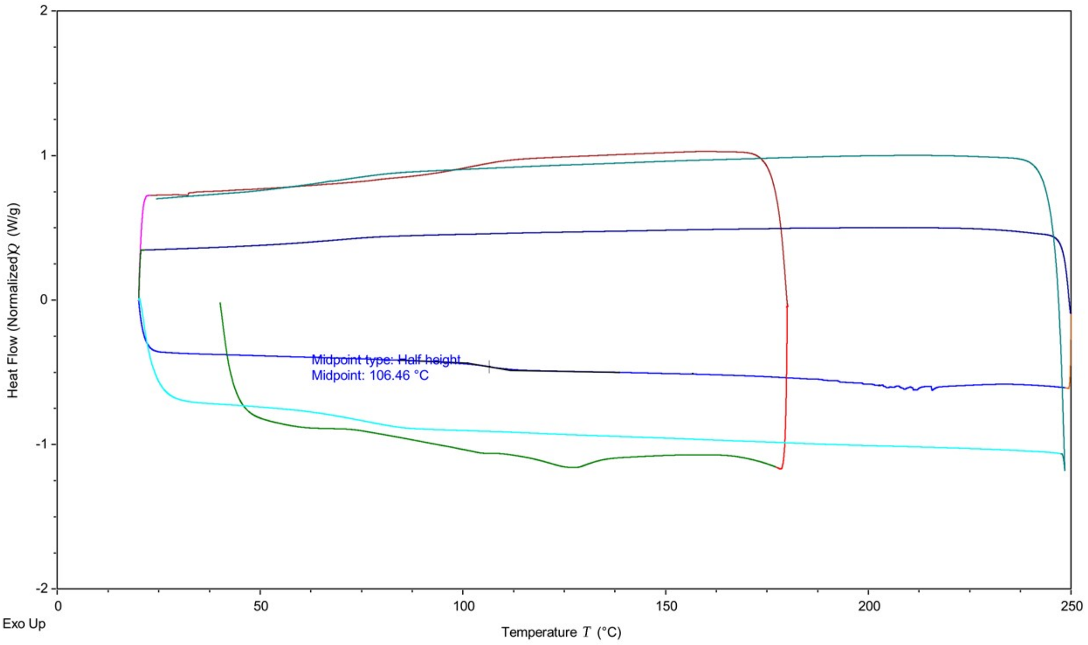


Figure S10. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of PMMA.

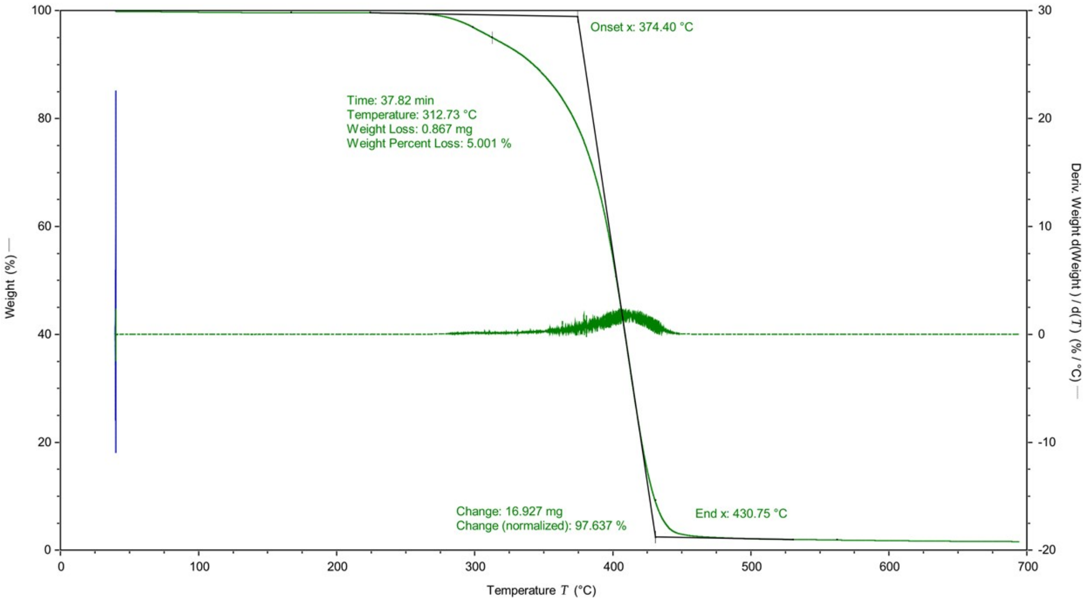


Figure S11. TGA curves (in N_2) of PPFCBMA-*co*-PMMA 1-5 with a heating rate of 10^{o}C/min.

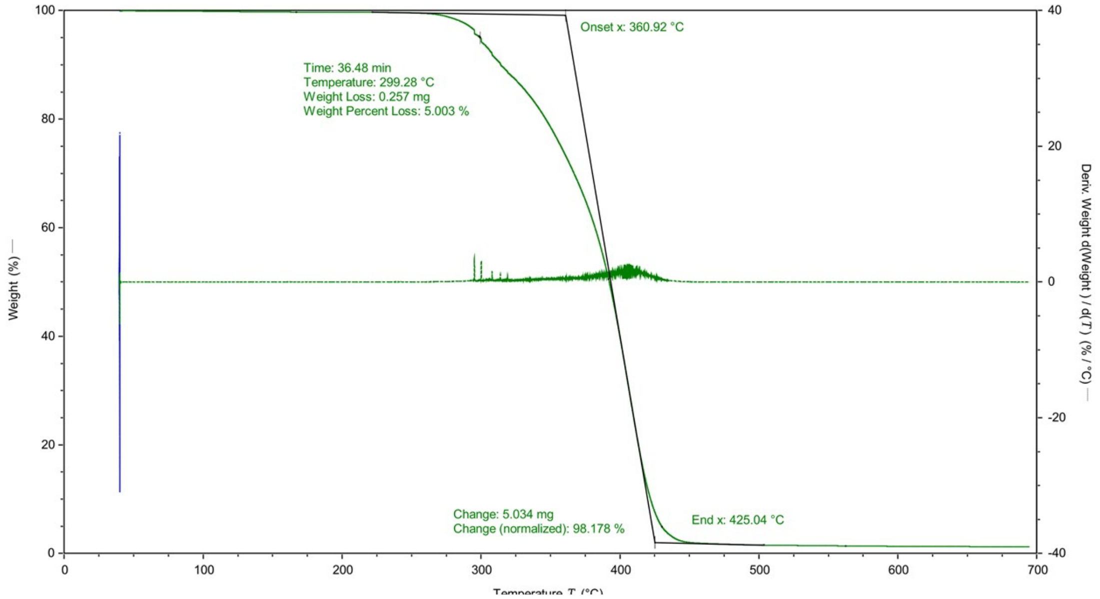


Figure S12. TGA curves (in N_2) of PPFCBMA-*co*-PMMA 1-10 with a heating rate of 10^{o}C/min.

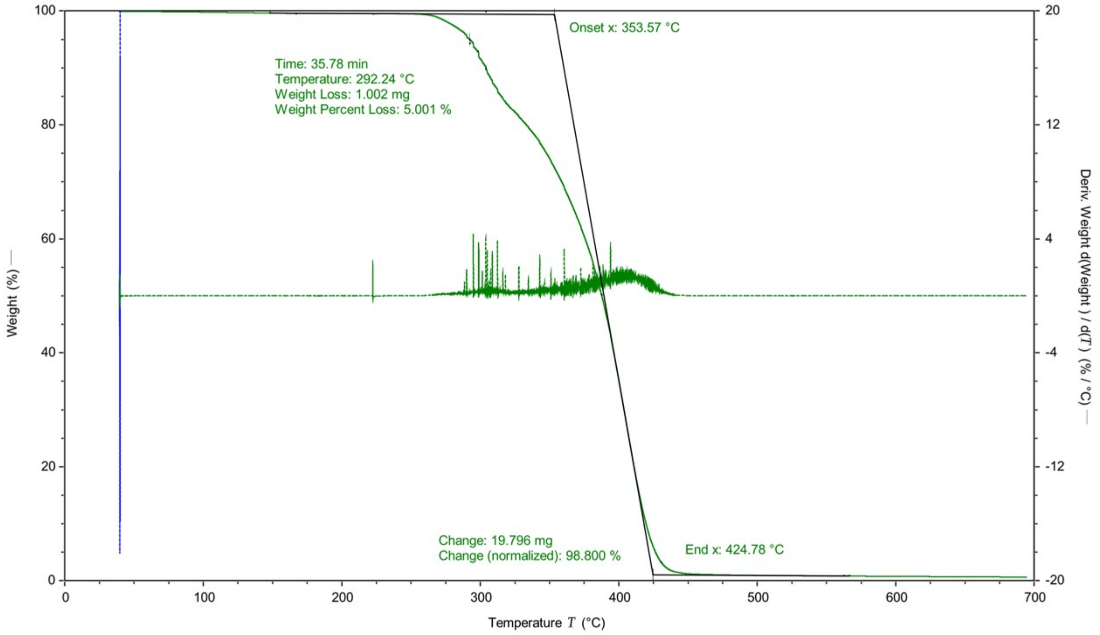


Figure S13. TGA curves (in N_2) of PPFCBMA-*co*-PMMA 1-15 with a heating rate of 10^{o}C/min.

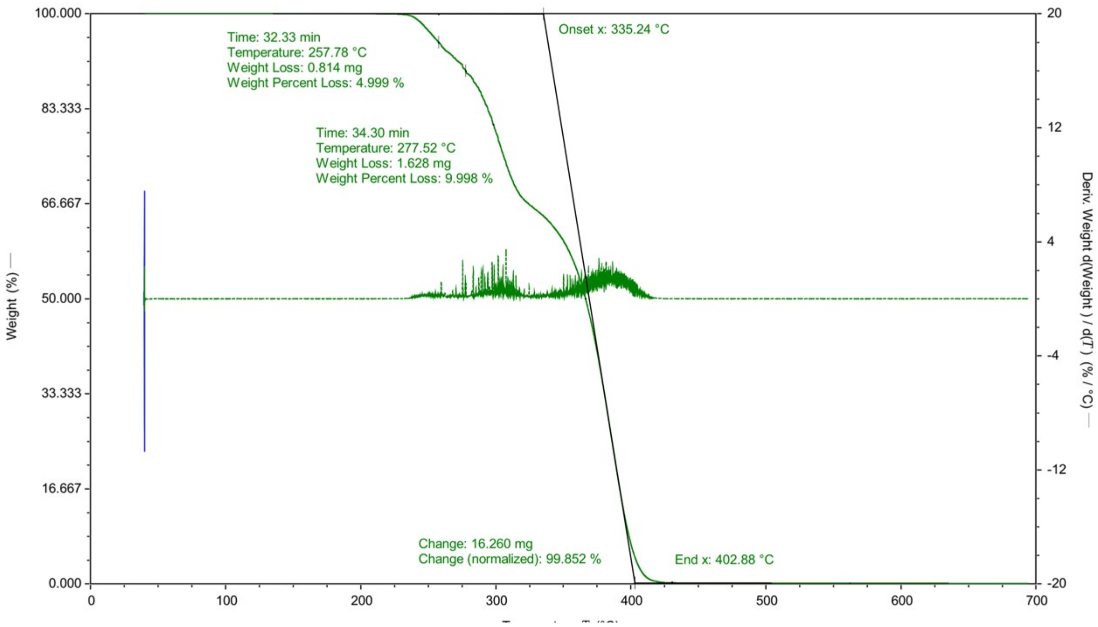


Figure S14. TGA curves (in N_2) of PMMA with a heating rate of 10°C/min.

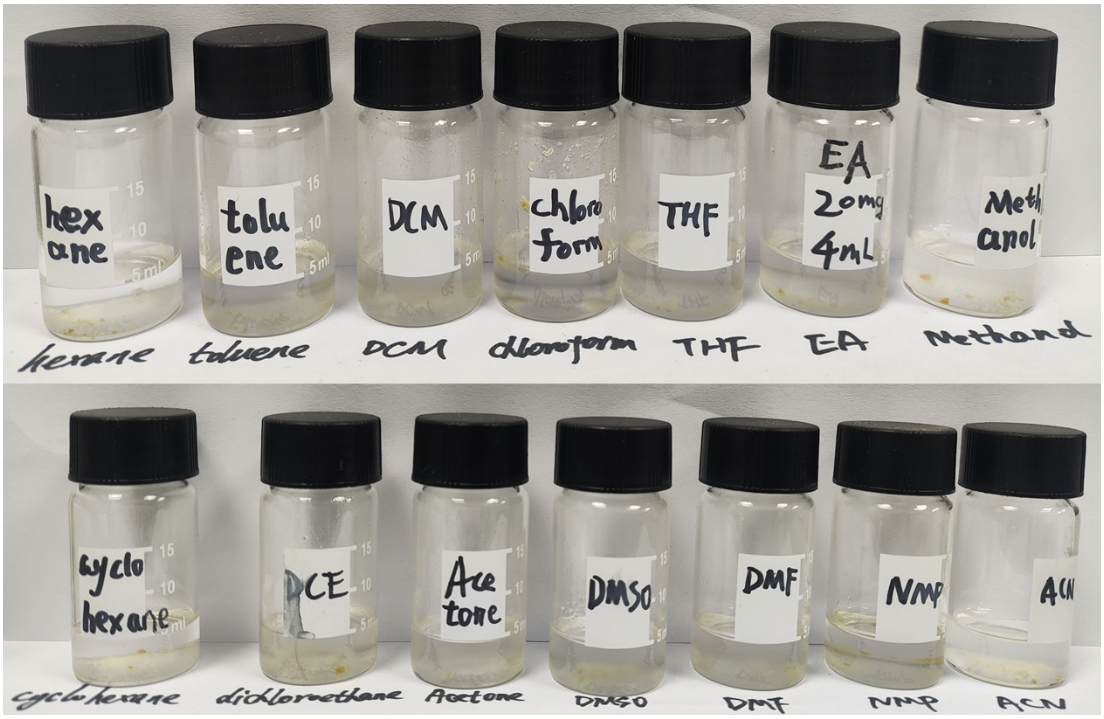


Figure S15. Photograph of solubility test of Cross-PFCB-PMMA copolymers.

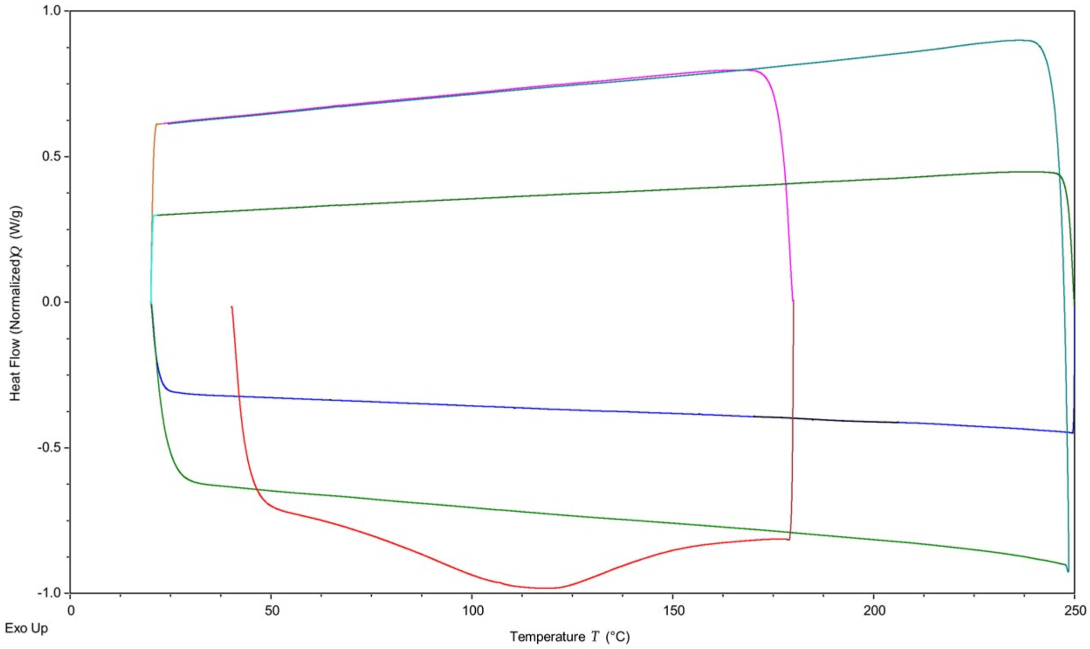


Figure S16. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of Cross-PFCB-PMMA 1-5.

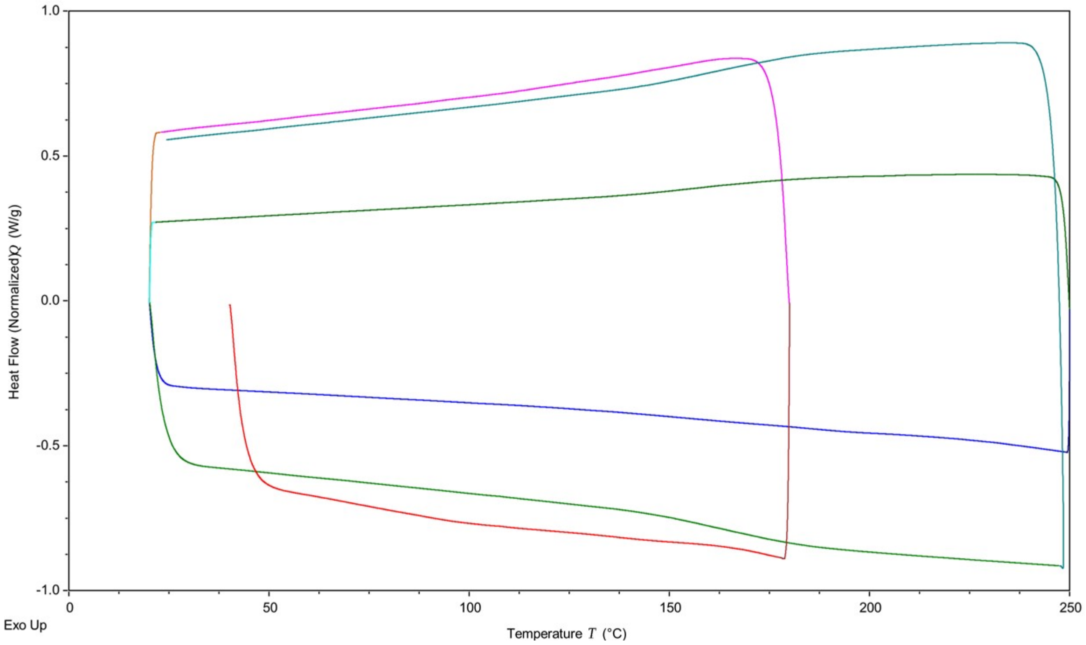


Figure S17. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of Cross-PFCB-PMMA 1-10.

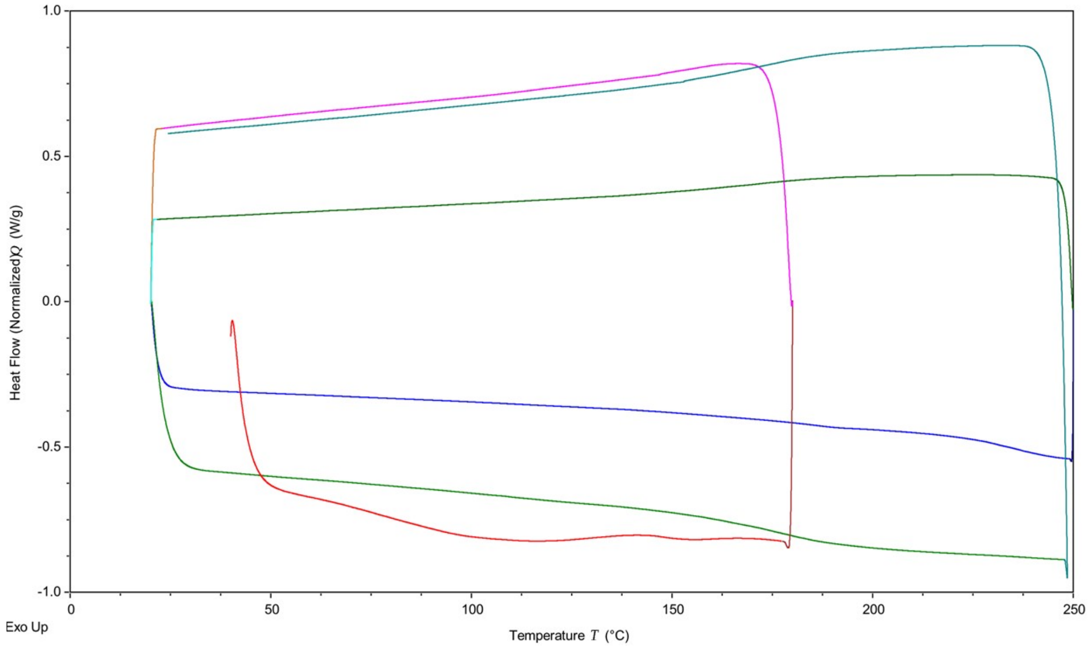


Figure S18. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of Cross-PFCB-PMMA 1-15.

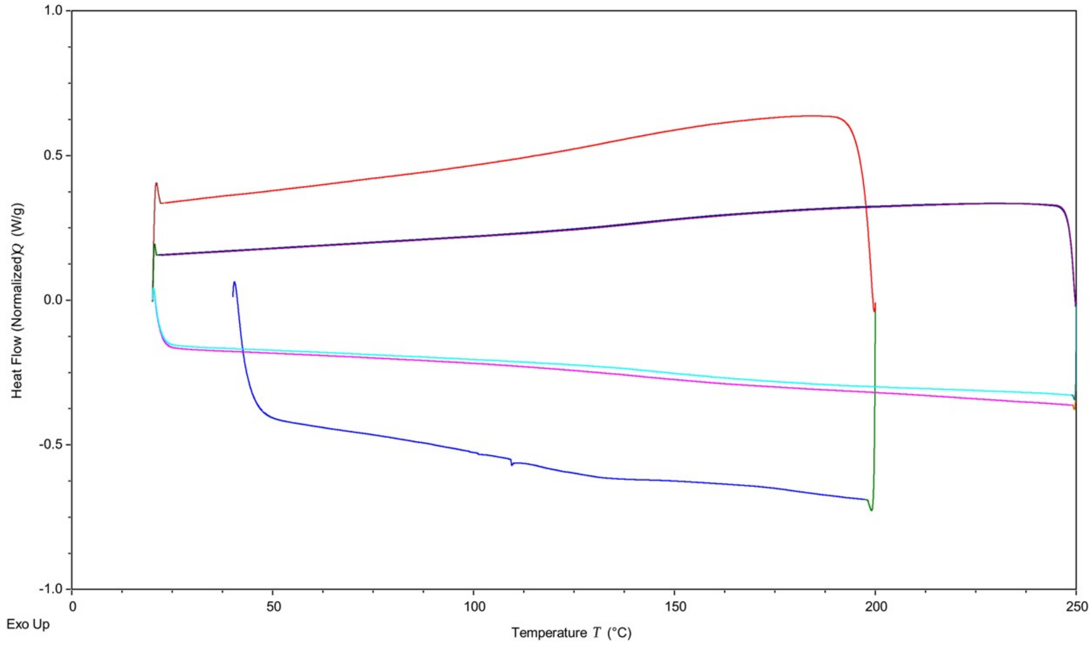


Figure S19. DSC cycles (heating-cooling-heating-cooling-heating-cooling) of Cross-PMMA.

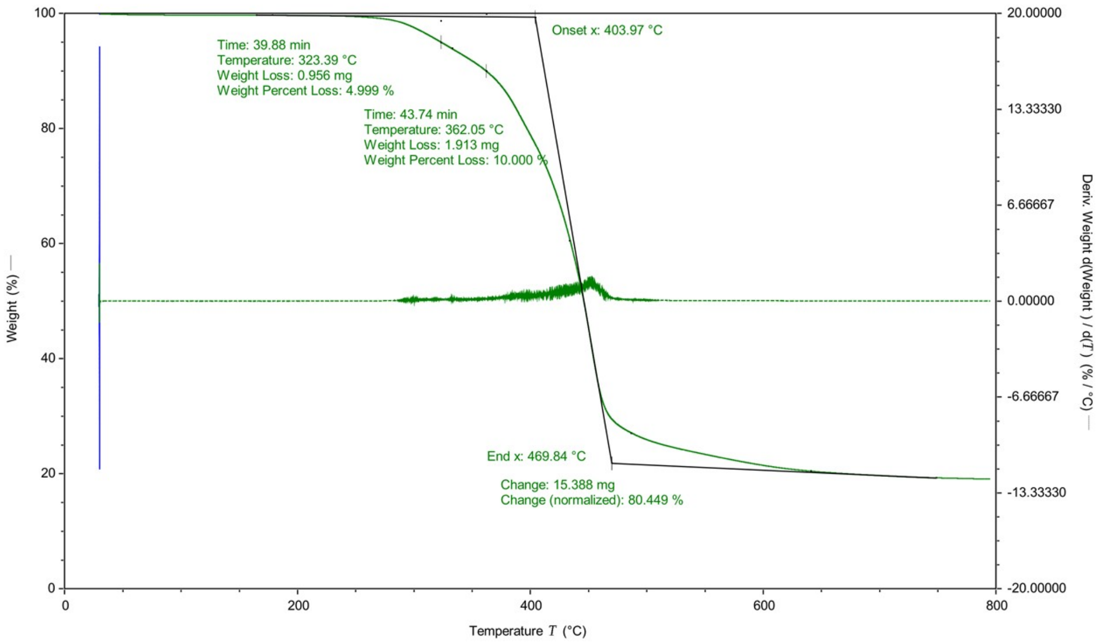


Figure S20. TGA curves (in N_2) of Cross-PFCB-PMMA 1-5 with a heating rate of 10°C/min.

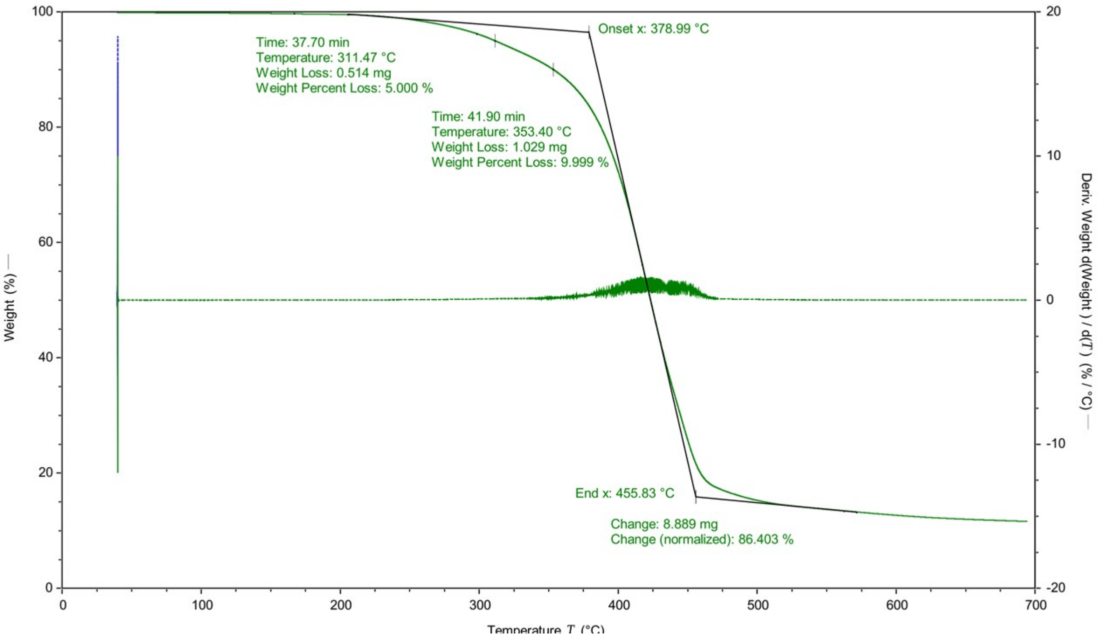


Figure S21. TGA curves (in N_2) of Cross-PFCB-PMMA 1-10 with a heating rate of 10°C/min.

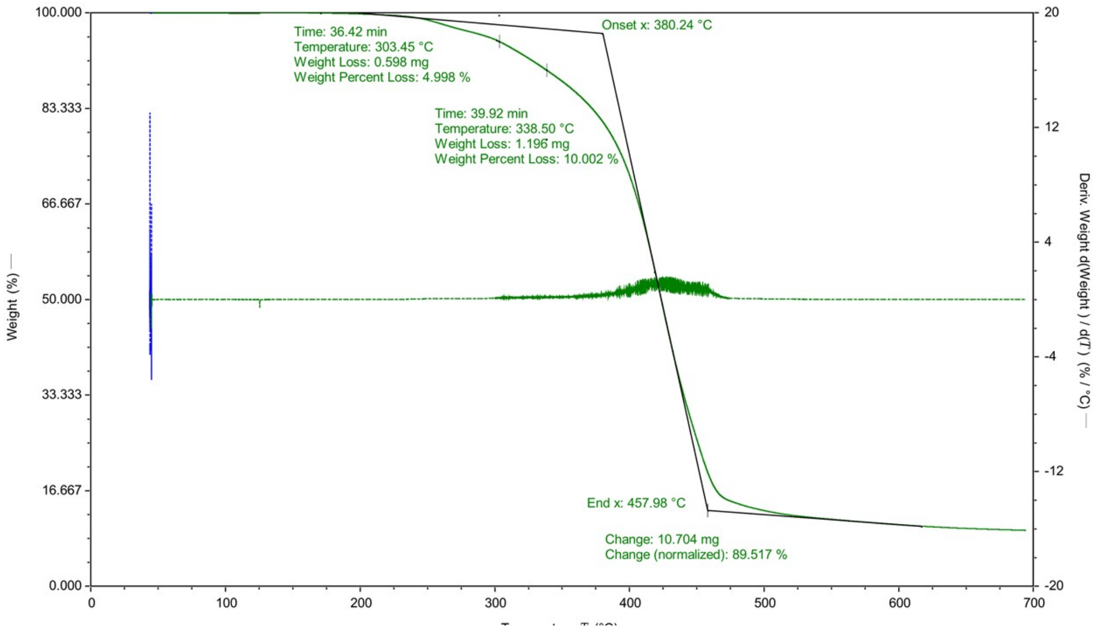


Figure S22. TGA curves (in N_2) of Cross-PFCB-PMMA 1-15 with a heating rate of 10°C/min.

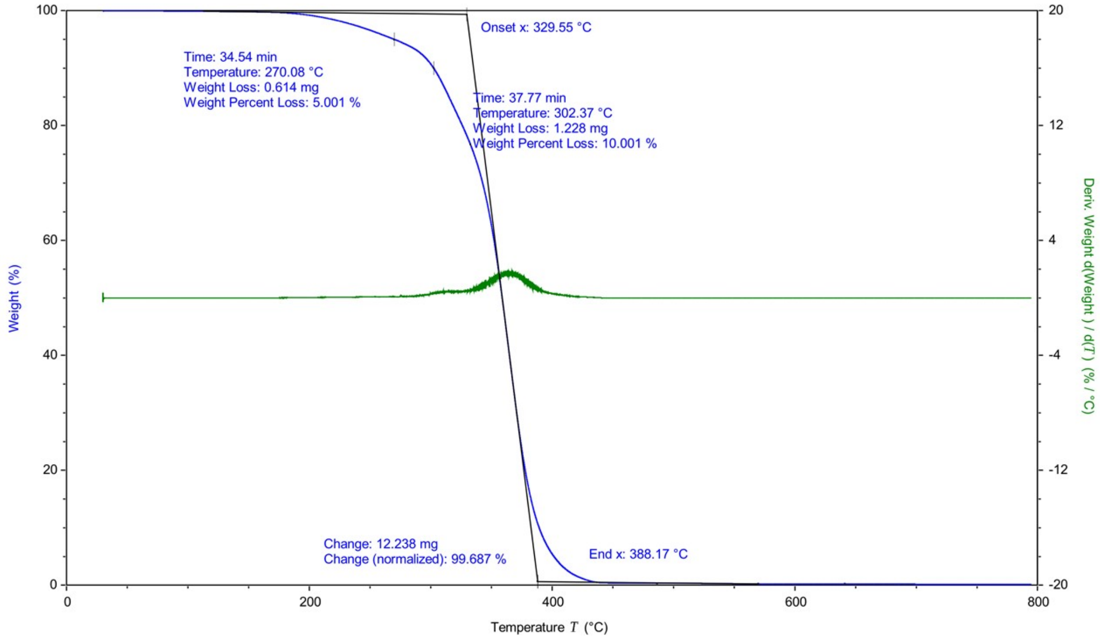


Figure S23. TGA curves (in N_2) of Cross-PMMA with a heating rate of 10°C/min.

References

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[2] M. T. Zhou, G. X. Gu, S. Zhang, G. L. Lu, J. Xu, X. Y. Huang, *Eur. Polym. J.* **2019**, *120*, 109250.

[3] M. C. Jia, Y. J. Li, C. Q. He, X. Y. Huang, *ACS Appl. Mater. Interfaces*, **2016**, *8*, 26352-26358.