Electronic Supplementary Material (ESI) for Polymer Chemistry.

Preparation of fluorinated polyesters by reversible addition–fragmentation chain transfer step-growth polymerization

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Step-growth polymerization theoretical calculation formula

According to Flory's theory on step-growth polymerization,[1] for step-growth polymerization under balanced stoichiometry, the theoretical number-average molecular weight ($M_{n,th}$) can be calculated by Eq. S1, where M_0 is the average molecular weight of monomers, and p is the extent of reaction. For step-growth polymerization under non-stoichiometric conditions, the $M_{n,th}$ can be calculated by eqn (S2), where M_0 is the average molecular weight of monomers, p is the extent of reaction, and r is the stoichiometric ratio of functional groups.

$$M_{n,th} = M_0 \frac{1}{1-p} \quad (S1)$$

$$M_{n,th} = M_0 \frac{1+r}{1+r-2rp} \quad (S2)$$

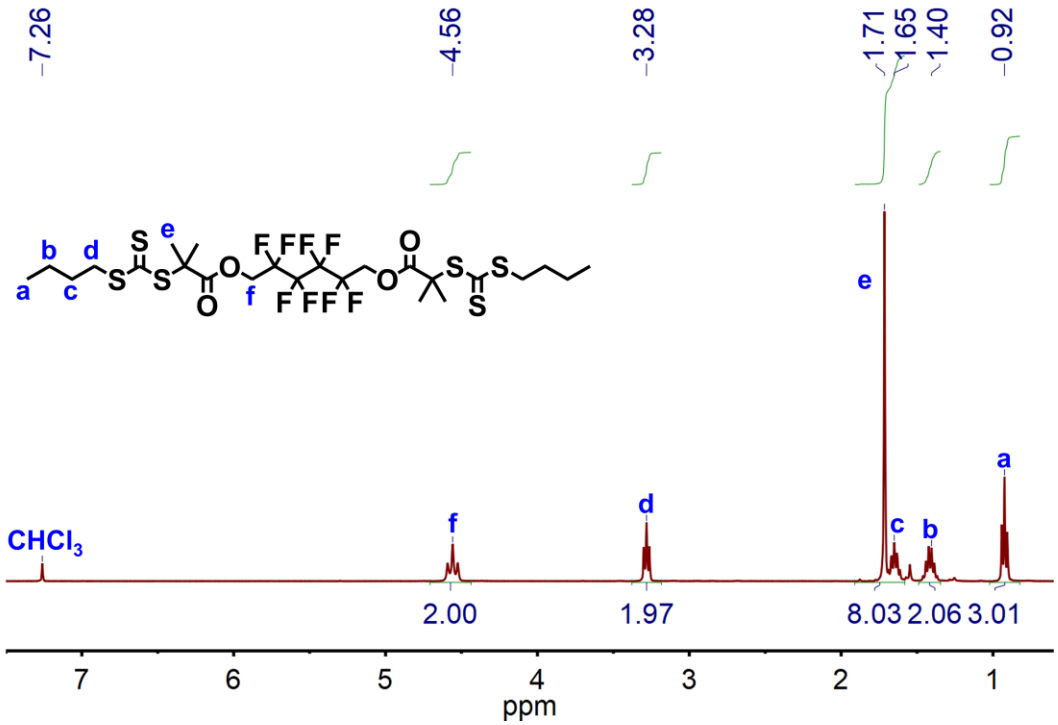

Fig. S1 ^{1}H NMR spectrum of $BDMAT_{8F}$ in $CDCl_3$.

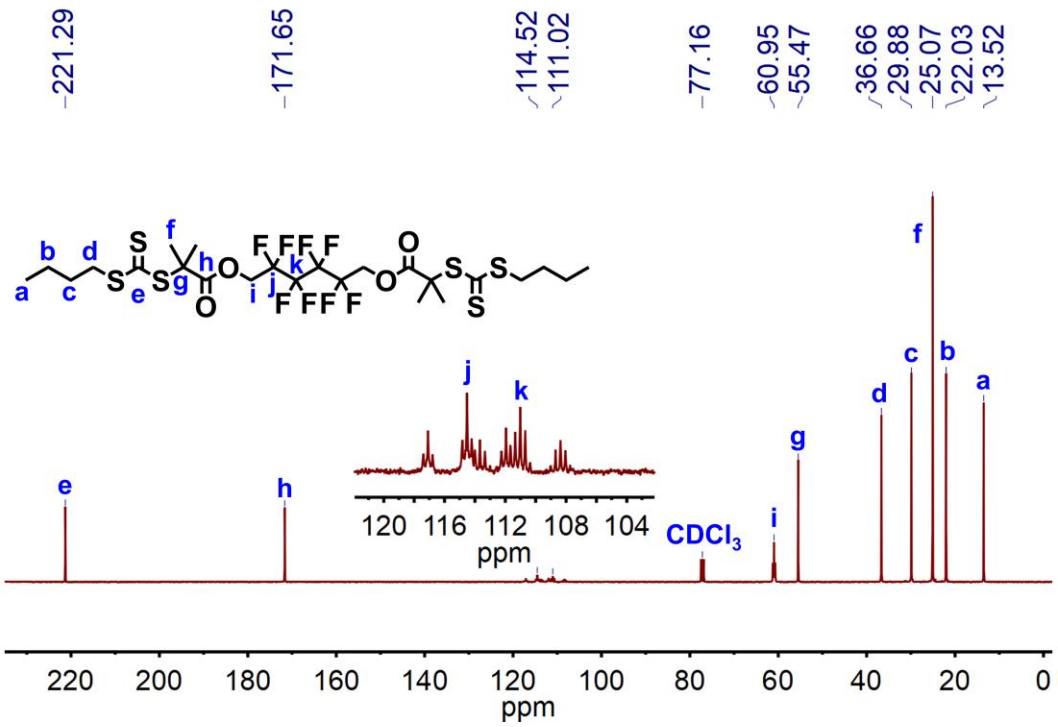

Fig. S2 ^{13}C NMR spectrum of $BDMAT_{8F}$ in $CDCl_3$.

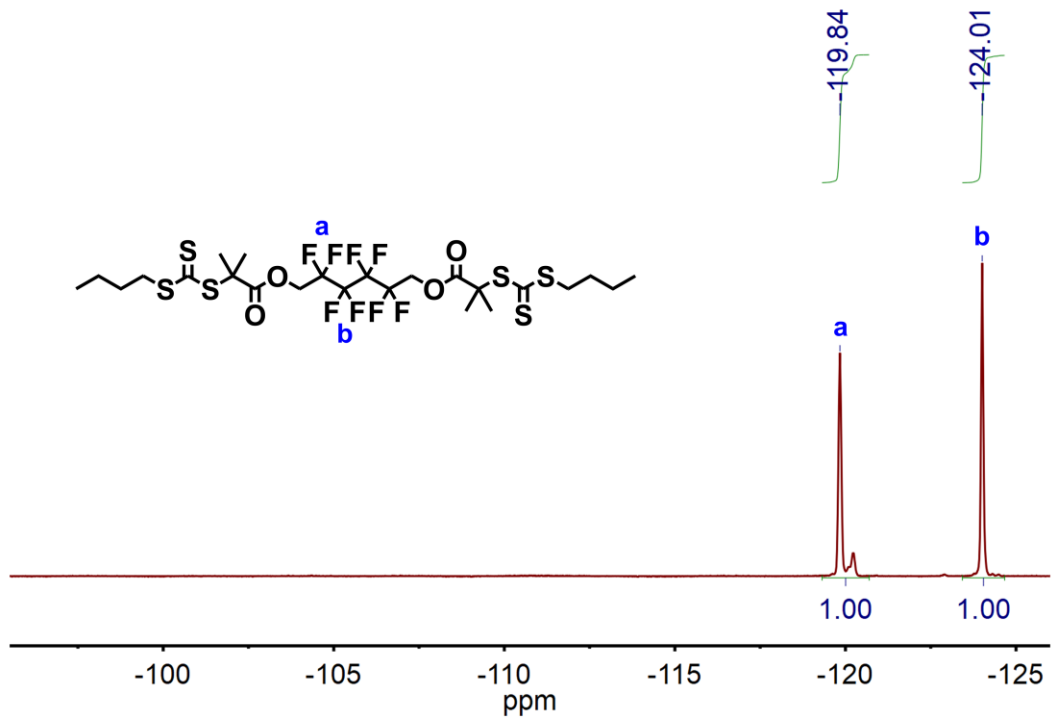

Fig. S3 ^{19}F NMR spectrum of $BDMAT_{8F}$ in $CDCl_3$.

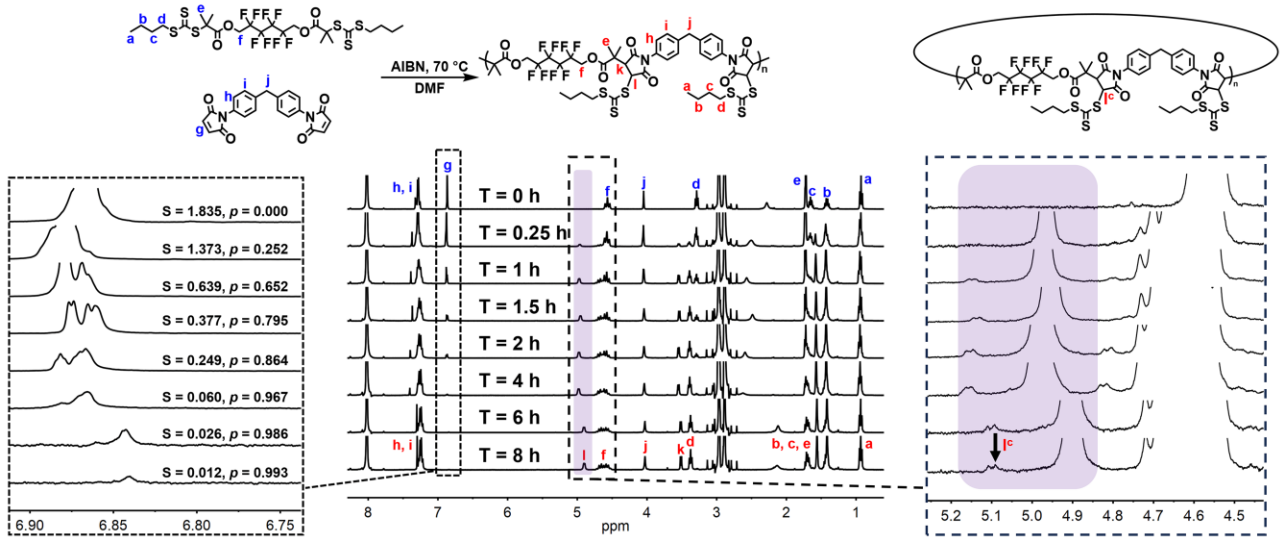

Fig. S4 ^{1}H NMR of the RAFT step-growth polymerization of $BDMAT_{8F}$ and M_{2A} in DMF. Z-group of $BDMAT_{8F}$ (peak a, C*H*$_3$) was used as an internal reference. The *p* was calculated according to the change of the vinyl protons of the maleimide groups (peak g).

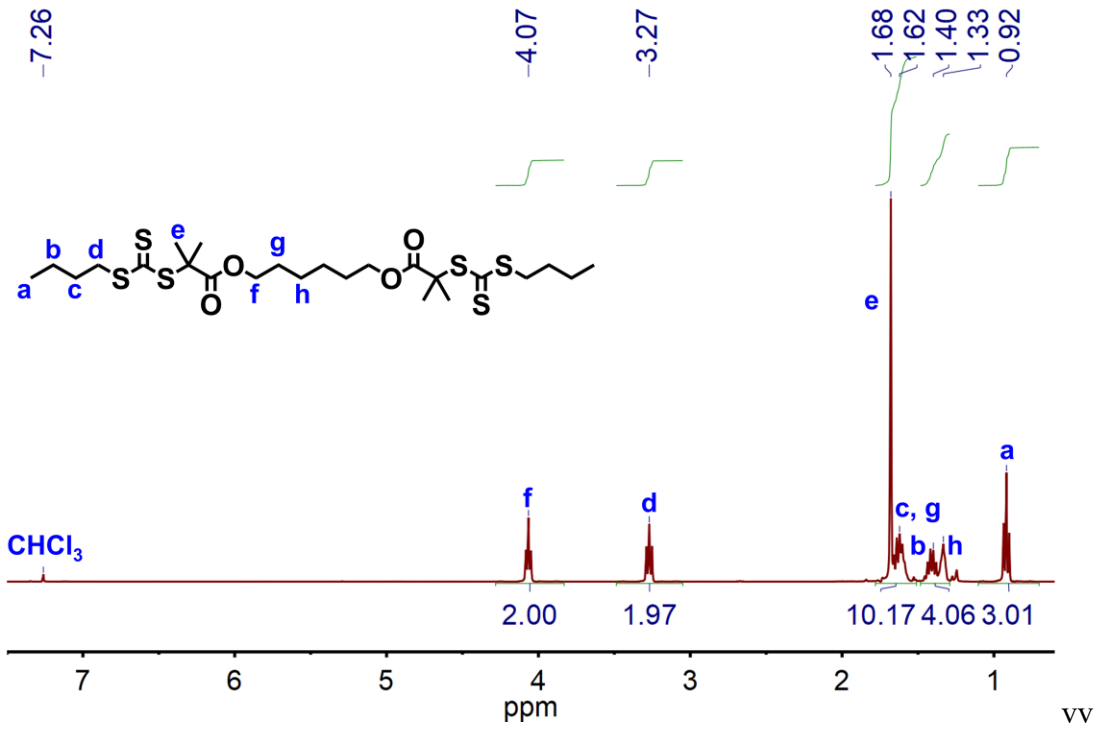

Fig. S5 ^{1}H NMR spectrum of $BDMAT_{2A}$ in $CDCl_3$.

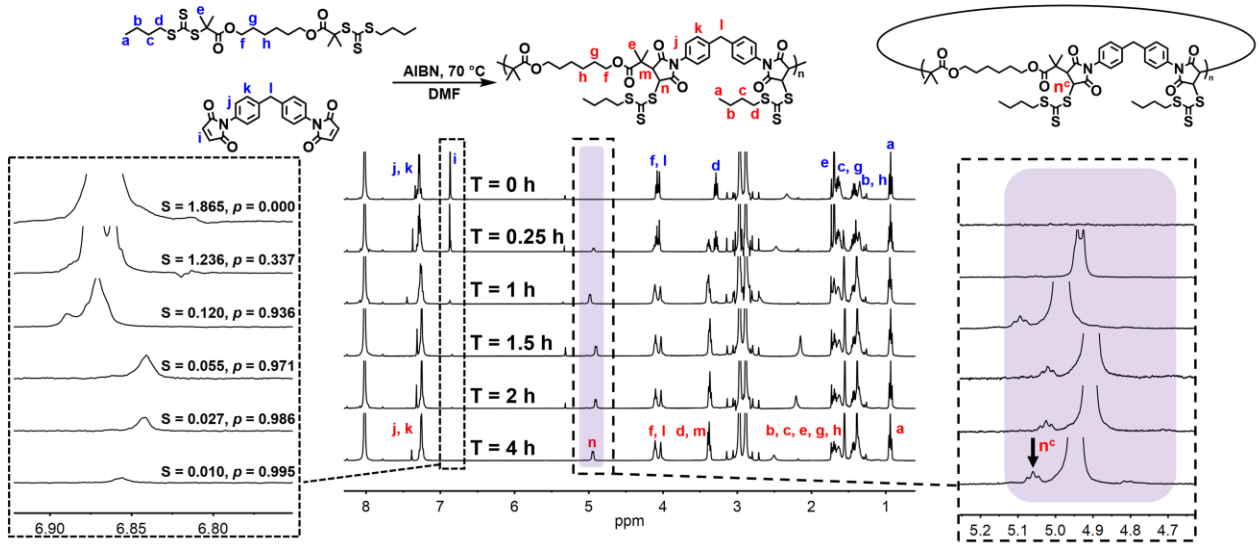

Fig. S6 ^{1}H NMR of the RAFT step-growth polymerization of $BDMAT_{2A}$ and M_{2A} in DMF. Z-group of $BDMAT_{2A}$ (peak a, CH_3) was used as an internal reference. The *p* was calculated according to the change of the vinyl protons of the maleimide groups (peak i).

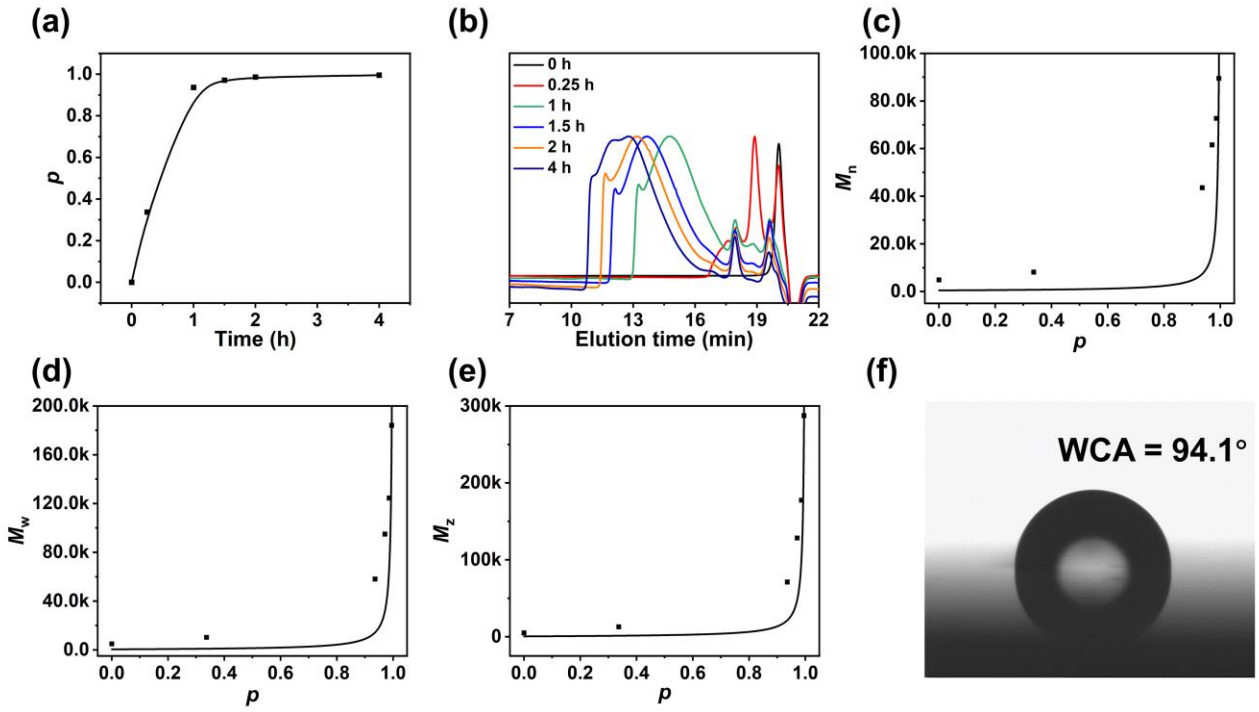

Fig. S7 Preparation of P(BDMAT$_{2A}$-*alt*-M$_{2A}$) *via* RAFT step-growth polymerization in DMF at 70 °C. [M$_{2A}$]$_0$/[BDMAT$_{2A}$]$_0$/[AIBN]$_0$ = 0.500/0.500/0.0500. (a) The evolution of the extent of reaction *p* against time. (b) SEC elution curves of obtained F-free polyesters. The evolution of (c) M_n, (d) M_w and (e) M_z of P(BDMAT$_{2A}$-*alt*-M$_{2A}$) against the extent of reaction (*p*), plotted together with the theoretical curve predicted by Flory's equation. (f) The water contact angle of P(BDMAT$_{2A}$-*alt*-M$_{2A}$).

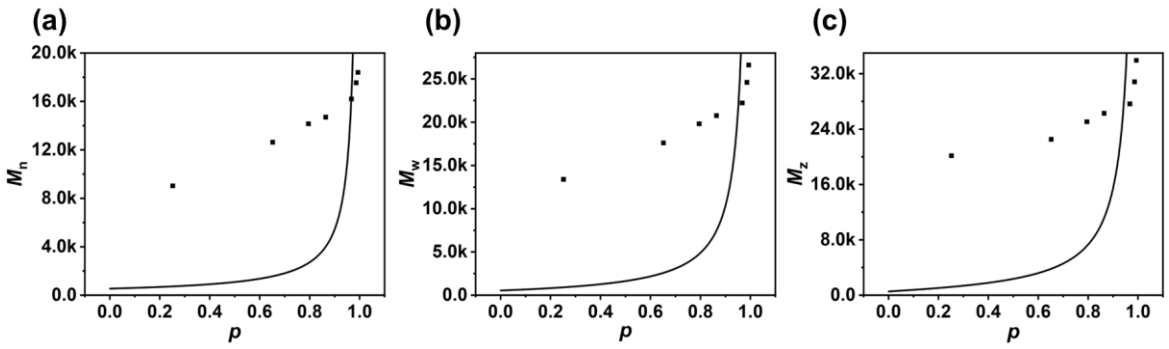

Fig. S8 The evolution of (a) M_n, (b) M_w and (c) M_z of P(BDMAT$_{8F}$-*alt*-M$_{2A}$) against the extent of reaction (p), plotted together with theoretical curve predicted by Flory's equation.

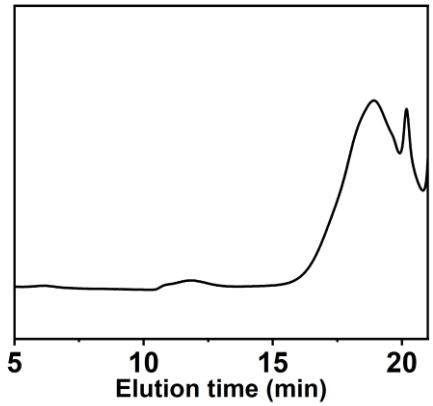

Fig. S9 SEC curve of the P(BDMAT$_{8F}$-*alt*-M$_{2A}$) copolymer that was synthesized using TCE as the reaction solvent. [BDMAT$_{8F}$]$_0$/[M$_{2A}$]$_0$/[AIBN]$_0$ = 0.500/0.500/0.0500. p = 0.983 after 10 h of polymerization. $M_{n,\,SEC}$ = 10.8 kDa, $Đ$ = 1.12.

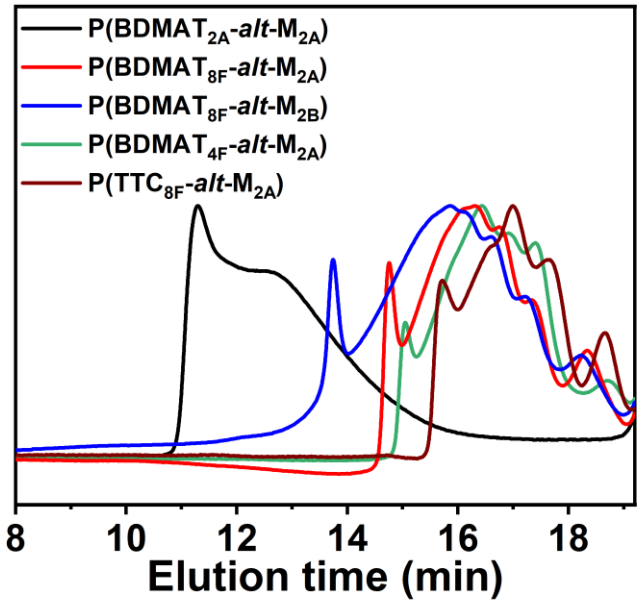

Fig. S10 SEC curves of synthesized fluorinated polyesters and F-free polyester.

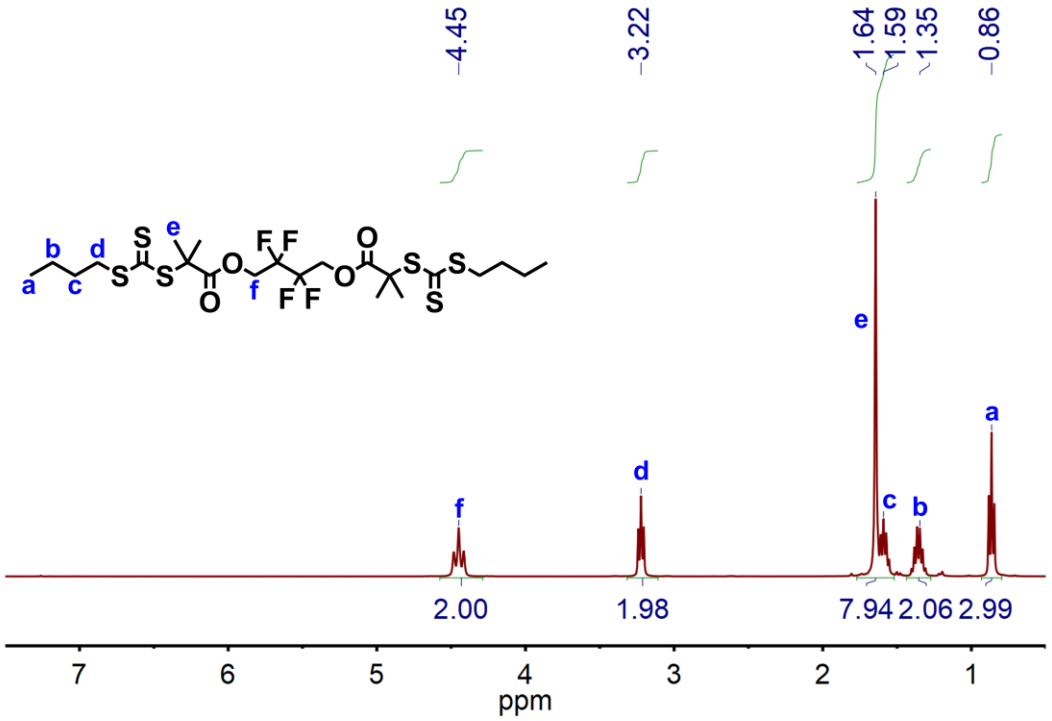

Fig. S11 ^{1}H NMR spectrum of $BDMAT_{4F}$ in $CDCl_3$.

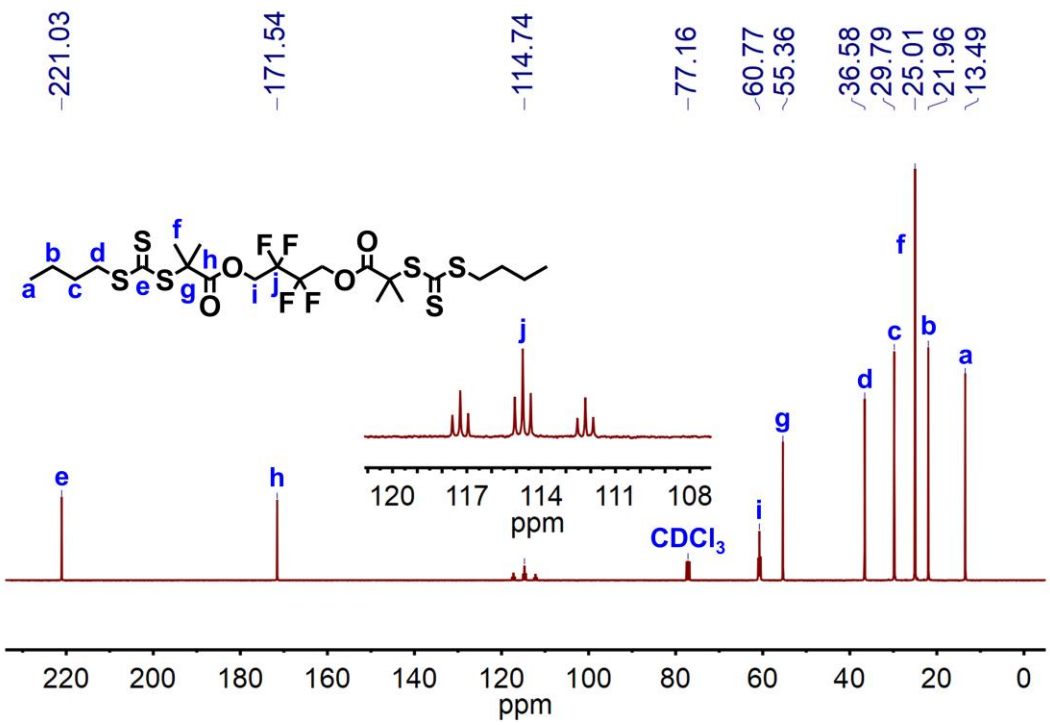

Fig. S12 ^{13}C NMR spectrum of $BDMAT_{4F}$ in $CDCl_3$.

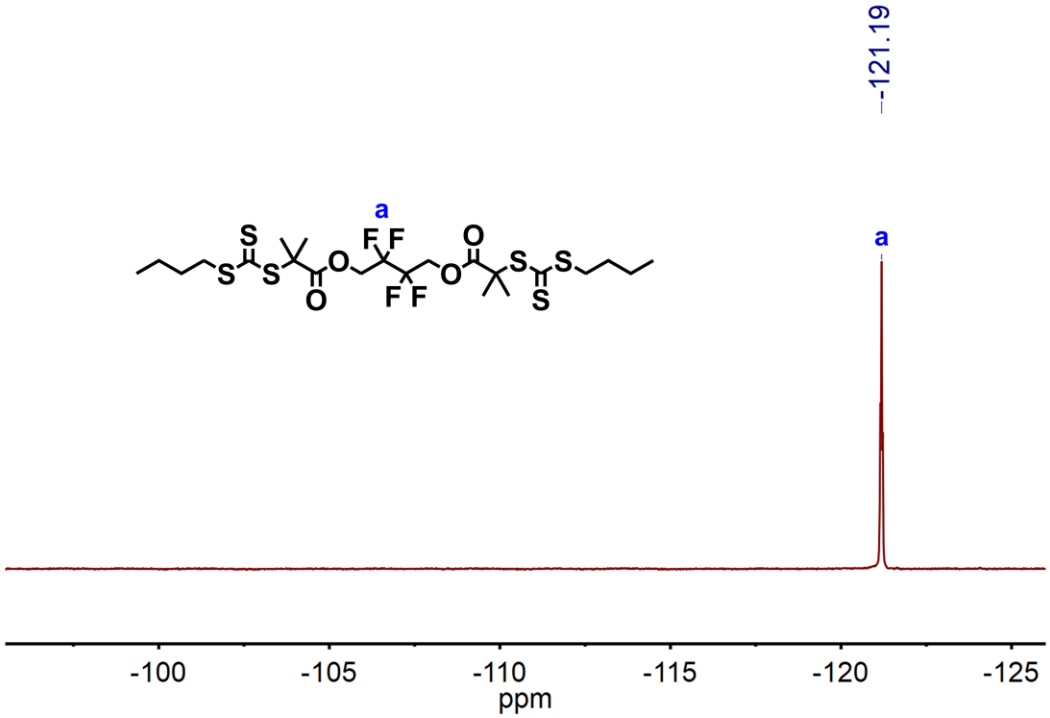

Fig. S13 ^{19}F NMR spectrum of $BDMAT_{4F}$ in $CDCl_3$.

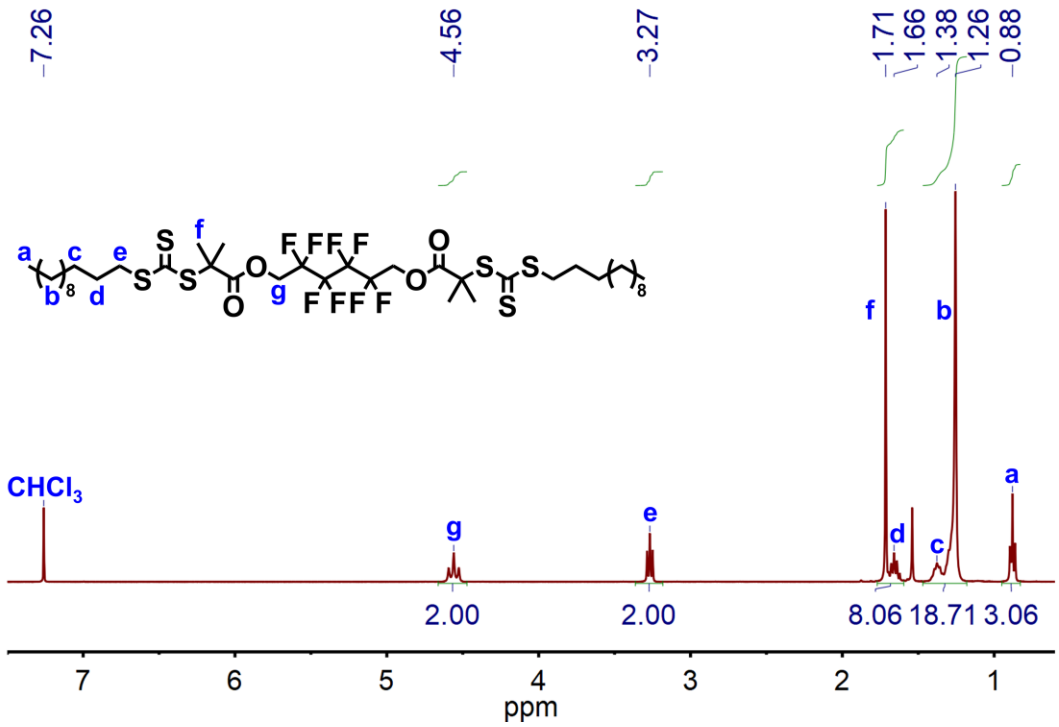

Fig. S14 ^{1}H NMR spectrum of TTC_{8F} in $CDCl_3$.

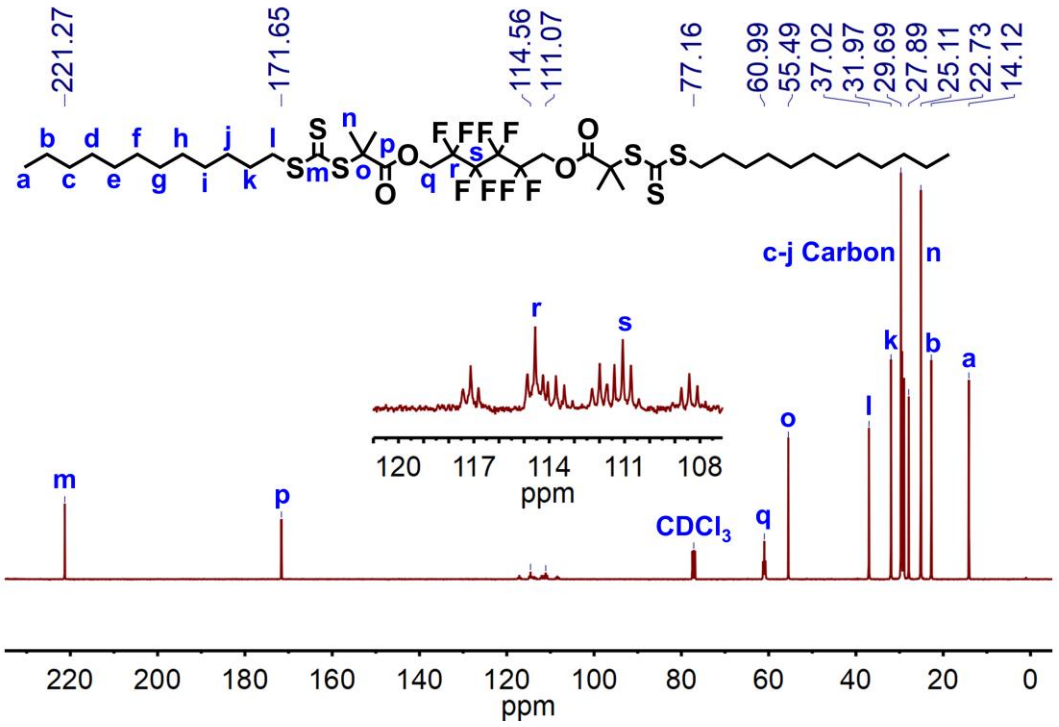

Fig. S15 ^{13}C NMR spectrum of TTC_{8F} in $CDCl_3$.

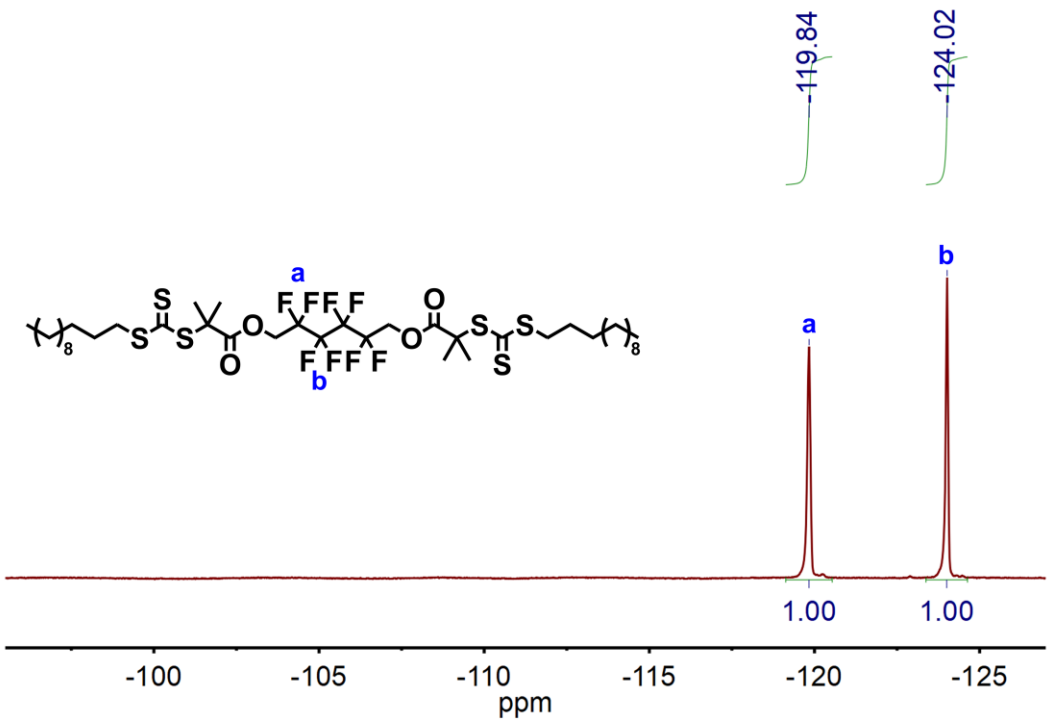

Fig. S16 ^{19}F NMR spectrum of TTC_{8F} in $CDCl_3$.

Table S1. Kinetic study of the RAFT step-growth polymerization of $BDMAT_{8F}$ and M_{2A} under balanced stoichiometry.

Time / h	Solvent	p[a]	$M_{n,th}$ / kDa[b]	$M_{n,SEC}$ / kDa[c]	$Đ$[d]	f_c / %[f]
0	DMF	0	0.545	5.26	1.01	-
0.25	DMF	0.252	0.729	9.03	1.48	5.85
1.00	DMF	0.652	1.57	12.6	1.28	11.3
1.50	DMF	0.795	2.66	14.2	1.40	12.4
2.00	DMF	0.864	4.01	14.7	1.41	11.0
4.00	DMF	0.967	16.5	16.2	1.37	11.3
6.00	DMF	0.986	38.9	17.5	1.40	10.4
8.00	DMF	0.993	77.9	18.4	1.45	10.9

[a] Calculated according to ^{1}H NMR.

[b] Calculated according to eqn (S1).

[c] Determined by SEC.

[d] $Đ = M_w/M_n$.

[e] Fraction of cyclic polyesters calculated according to the integral area of the SEC curves.

Table S2. Kinetic study of the RAFT step-growth polymerization of $BDMAT_{2A}$ and M_{2A} in DMF under balanced stoichiometry.

Time / h	Solvent	p[a]	$M_{n,\,th}$ / kDa[b]	$M_{n,\,SEC}$ / kDa[c]	$Đ$[d]	f_c / %[f]
0	DMF	0	0.473	4.85	1.01	-
0.25	DMF	0.337	0.713	8.13	1.26	14.5
1.00	DMF	0.936	7.39	43.6	1.33	7.14
1.50	DMF	0.971	16.3	61.5	1.54	5.20
2.00	DMF	0.986	33.8	72.7	1.71	3.92
4.00	DMF	0.995	94.6	89.5	2.06	2.29

[a] Calculated according to ^{1}H NMR.

[b] Calculated according to eqn (S1).

[c] Determined by SEC.

[d] $Đ = M_w/M_n$.

[e] Fraction of cyclic polyesters calculated according to the integral area of the SEC curves.

Table S3. The syntheses and molecular characterization of P($BDMAT_{8F}$-*alt*-M_{2A}) under imbalanced stoichiometry and different concentrations.

Entry	$[BDMAT_{8F}]_0/[M_{2A}]_0$	Time / h	*r*	*p*[a]	$M_{n,th}$ / kDa[b]	$M_{n,SEC}$ / kDa[c]	*Đ*[d]
1	0.250 M/0.250 M	4	1.00	0.547	1.20	9.41	1.05
2	0.500 M/0.500 M	4	1.00	0.967	16.5	16.2	1.37
3	1.00 M/1.00 M	4	1.00	0.973	20.2	12.4	1.29
4	0.525 M/0.475 M	4	0.905	0.971	6.90	13.1	1.37
5	0.550 M/0.450 M	4	0.818	0.989	4.95	12.7	1.27

[a] Calculated according to ^{1}H NMR.

[b] Calculated according to eqn (S1) or eqn (S2).

[c] Determined by SEC.

[d] $Đ = M_w/M_n$.

Table S4 Molecular characteristics and thermal properties of the fluorinated polyesters after purification.

Entry	$M_{n,\,SEC}$[a] (kDa)	$Đ$[b]	Mass loss of first stage (%)	Theoretical mass ratio of trithiocarbonate (%)	$T_{1,\,max}$ (°C)	$T_{2,\,max}$ (°C)	T_g (°C)	T_m (°C)
P(BDMAT$_{8F}$-*alt*-M$_{2A}$)	16.3	1.60	30.8	30.4	256	445	72.9	-
P(BDMAT$_{8F}$-*alt*-M$_{2B}$)	21.0	1.74	23.8	25.4	258	442	97.3	-
P(BDMAT$_{4F}$-*alt*-M$_{2A}$)	13.0	1.66	36.0	33.4	267	460	-	84.7
P(TTC$_{8F}$-*alt*-M$_{2A}$)	15.0	1.37	41.0	42.3	263	458	45.6	-
P(BDMAT$_{2A}$-*alt*-M$_{2A}$)	141	1.49	34.2	35.0	260	424	80.2	-

[a] Determined by SEC.

[b] $Đ = M_w/M_n$.

References

1. P. J. Flory, *J. Am. Chem. Soc.*, 1936, **58**, 1877-1885.