Supporting Information for

Synthesis of amphiphilic copolymers based on acrylic acid, fluoroalkyl acrylates and *n*-butyl acrylate in organic, aqueous-organic and aqueous media via RAFT polymerization

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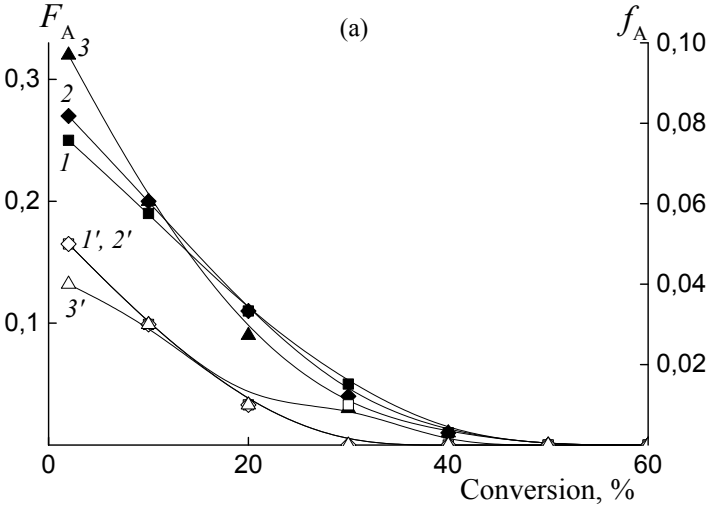
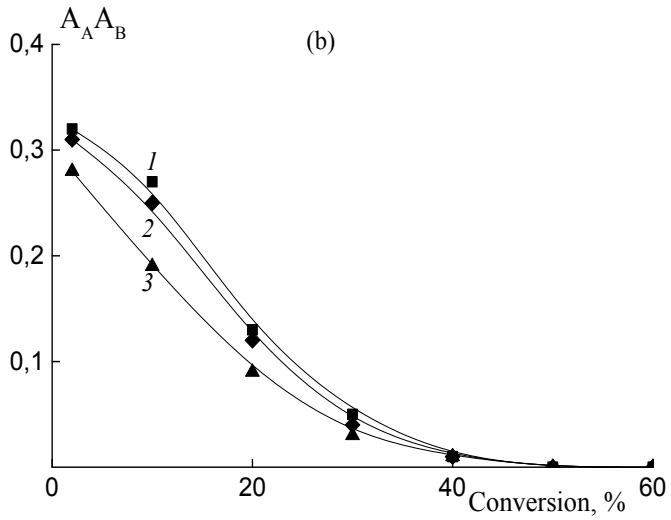
Fig. S1. The instantaneous values of monomer (1′–3′) and copolymer (1–3) composition (a); dyad composition A_AA_A (b) and A_AA_B (c) calculated according to the terminal unit model using r_A = 0.9, r_B =0.1 (1), r_A = 3.0, r_B =0.1 (2), and r_A = 10.0, r_B =0.1 (3) for monomer mixture containing 5 mol. % of monomer A.





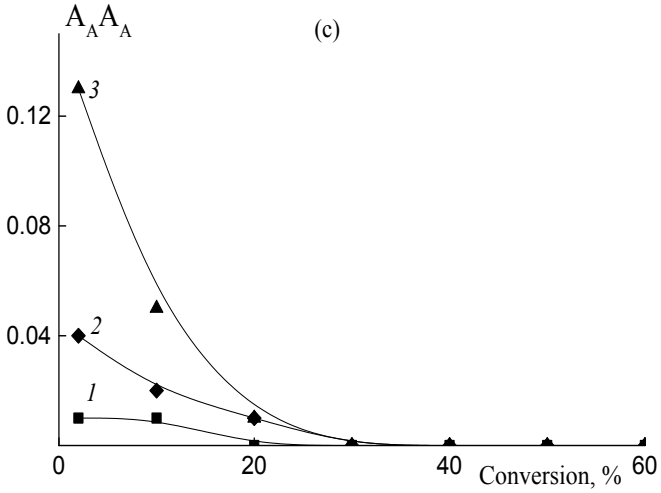
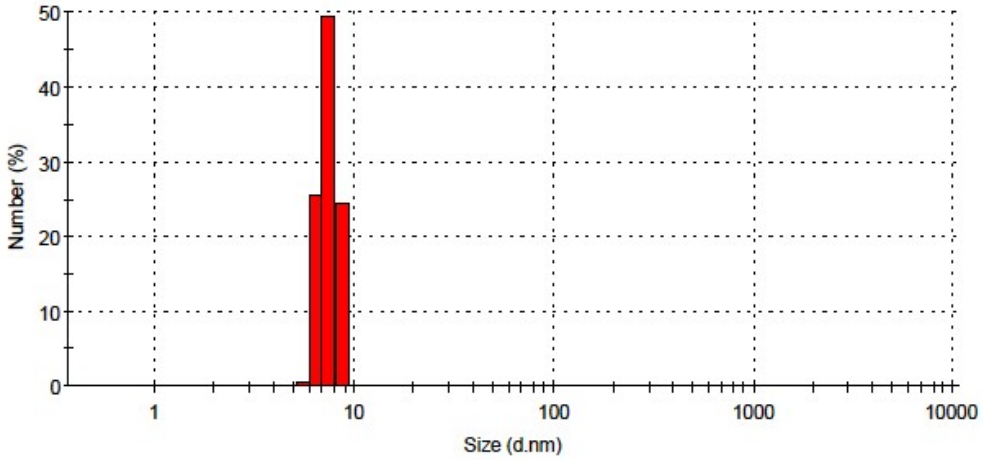


Fig. S2. The particle size distribution for 3 wt. % solution of Cop-O2 in DMF (a) and in the mixture DMF/acrylic acid/OFPA (b); DMF/monomers = 70/30 v/v, acrylic acid/OFPA = 90/10 mole %.

(a)



(b)

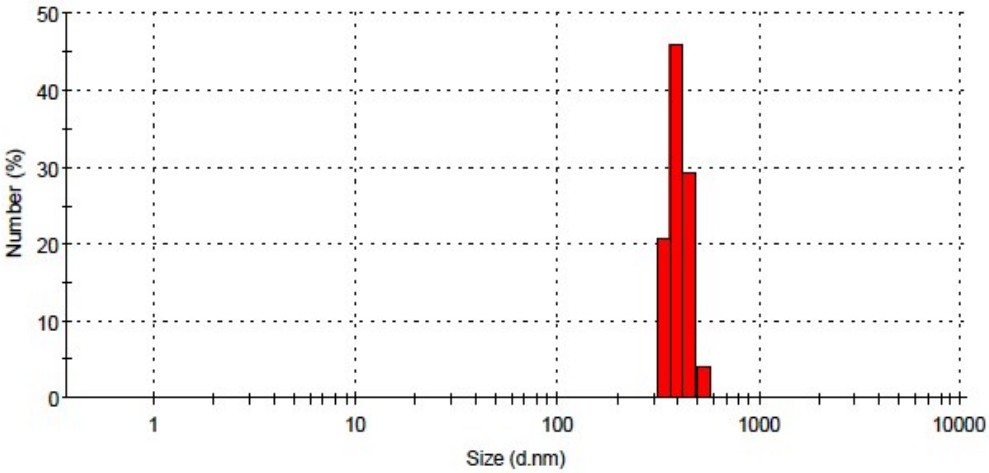


Fig. S3. ^{1}H NMR (a) and ^{19}F NMR (b) spectra of the copolymer obtained at 76 % monomer conversion in copolymerization of acrylic acid and 2,2,3,4,4,4-hexafluorobutyl acrylate in DMF in the presence of BTC and subjected to methylation; acrylic acid/HFBA = 90/10 mole %.

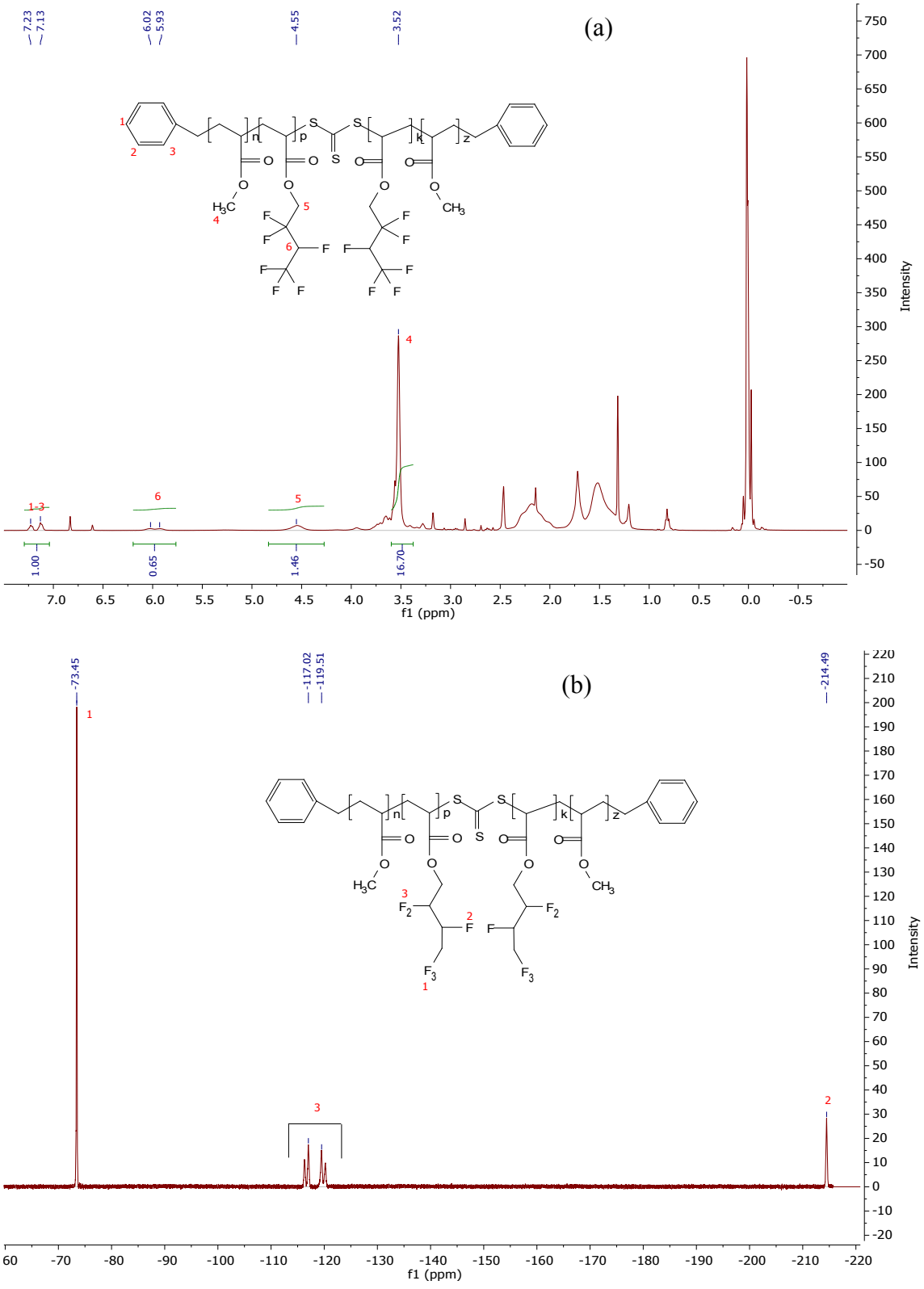


Fig. S4. The SEC curves normalized by the unit area for triblock copolymers synthesized in DMF (70 wt.%) in the presence of Pol-A; [Pol-A] = 3.0×10^{-3} mole/L, [AIBN] = 5.0×10^{-4} mole/L, 75°C; molar ratio of butyl acrylate to HFBA 90 : 10 (a) and 85 :15 (b).

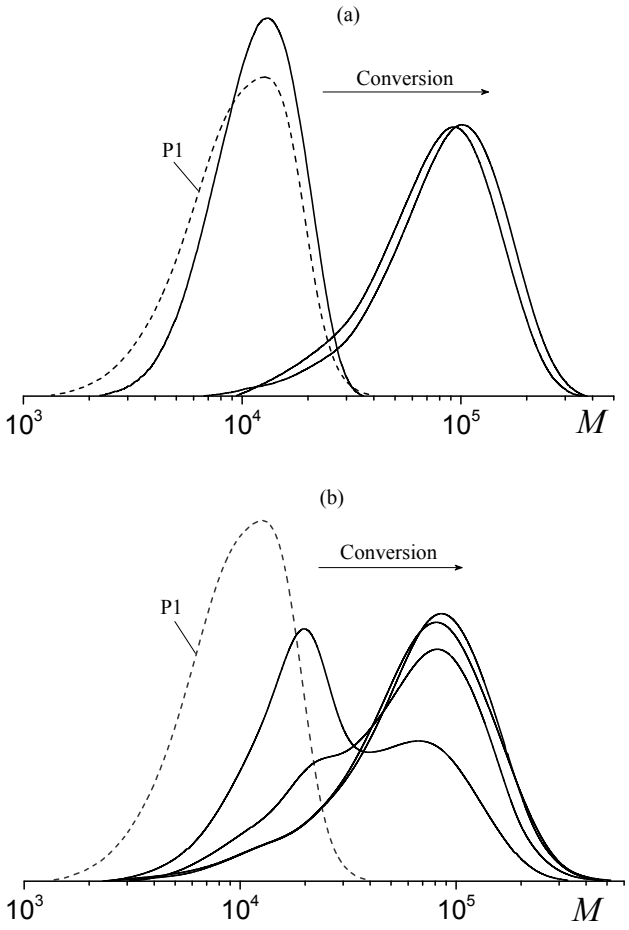
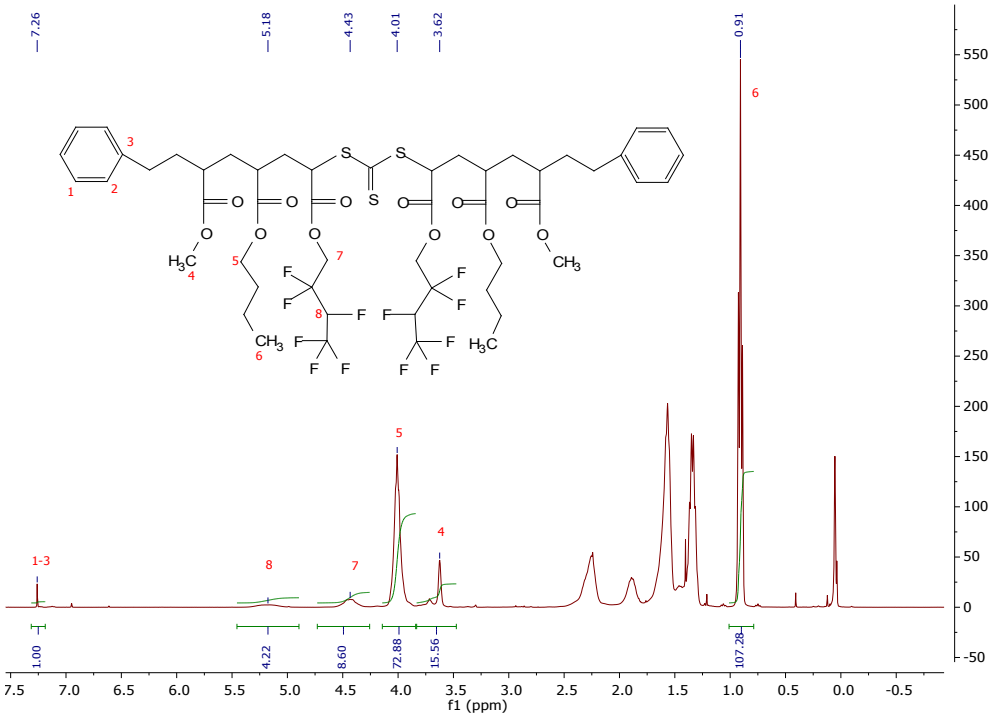


Fig. S5. ^{1}H NMR (a) and ^{19}F NMR (b) spectra of the triblock copolymer obtained at 99 % monomer conversion in copolymerization of butyl acrylate and 2,2,3,4,4,4-hexafluorobutyl acrylate in the presence of Pol-A in DMF and subjected to methylation; [Pol-A] = 3.0×10^{-3} mole/L, [AIBN] = 5.0×10^{-4} mole/L, DMF/monomers = 70/30 v/v, [butyl acrylate]/[HFBA] = 90/10 mole %.

(a)



(b)

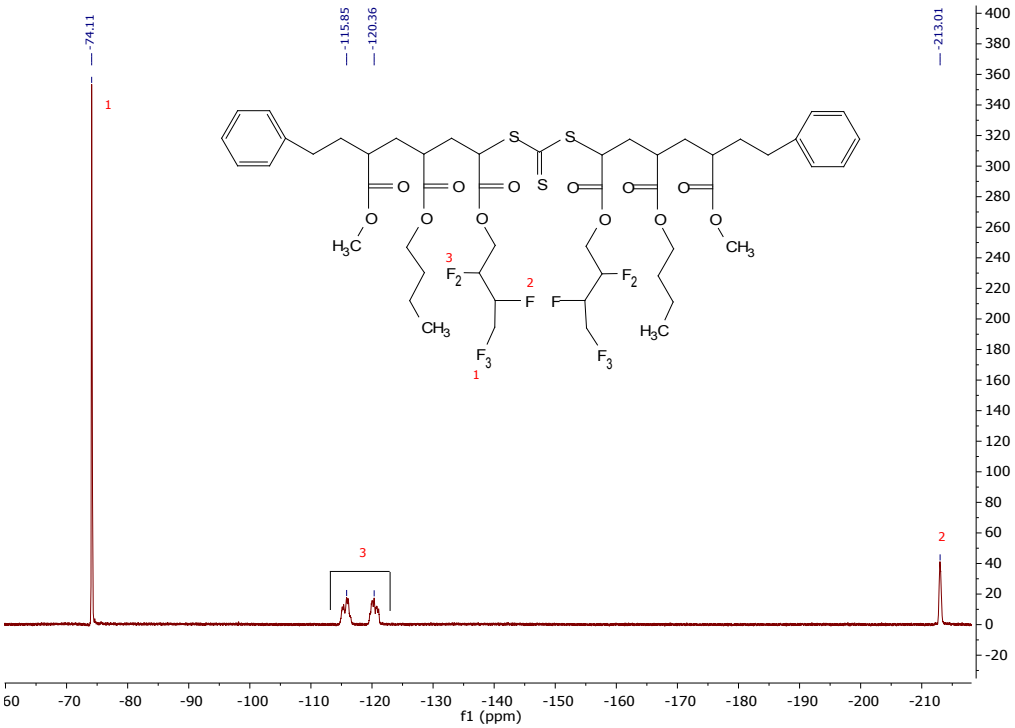
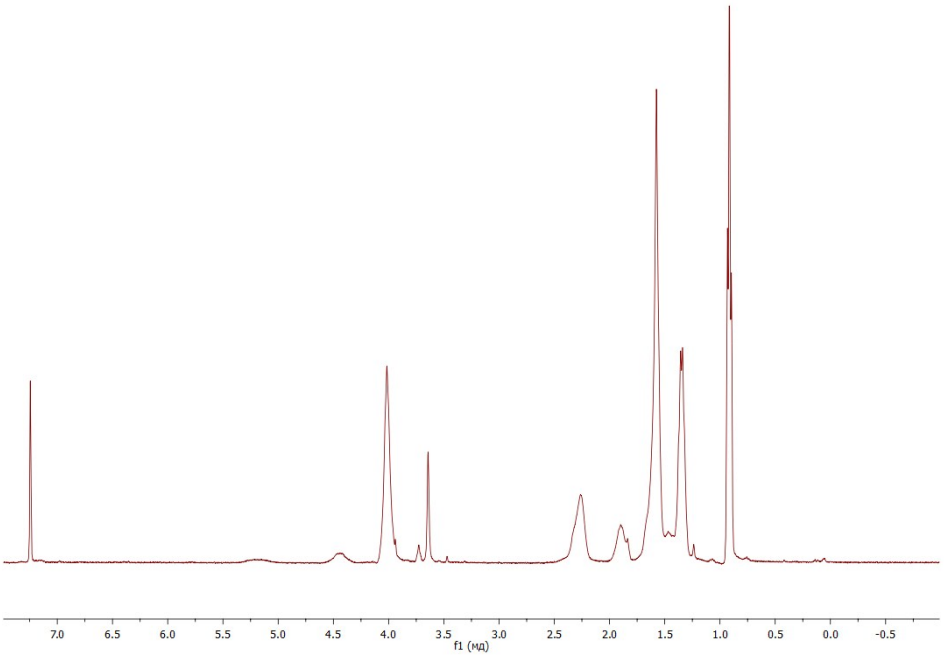


Fig. S6. ^{1}H NMR (a) and ^{19}F NMR (b) spectra of the triblock copolymer obtained at 99 % monomer conversion in emulsion copolymerization of butyl acrylate and 2,2,3,4,4,4-hexafluorobutyl acrylate in the presence of Pol-A and subjected to methylation; [Pol-A] = 7.7×10^{-4} mole/L, [PSK] = 2.6×10^{-4} mole/L, monomers : water = 1 : 6 v/v, [butyl acrylate]/[HFBA] = 90/10 mole %.

(a)



(b)

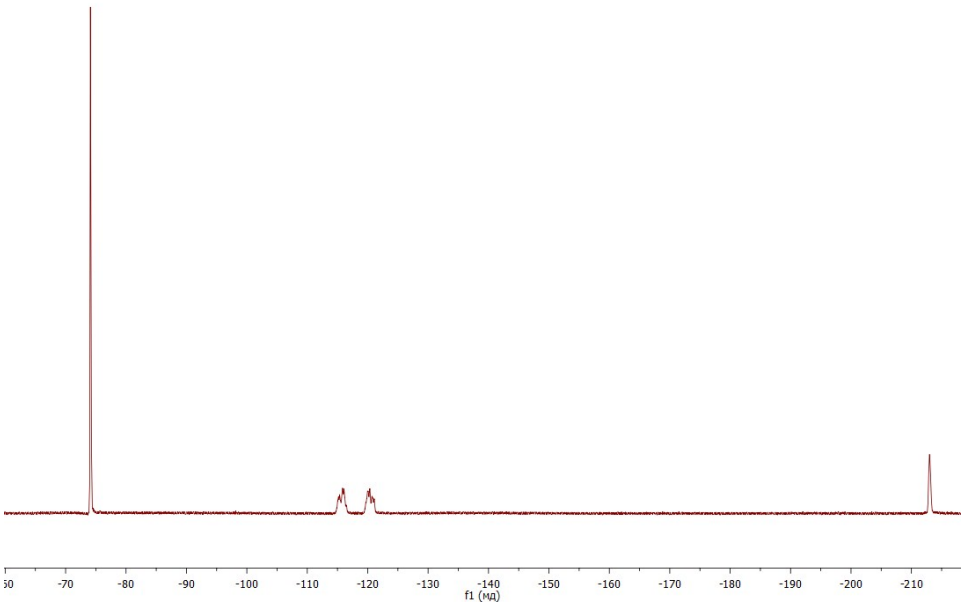
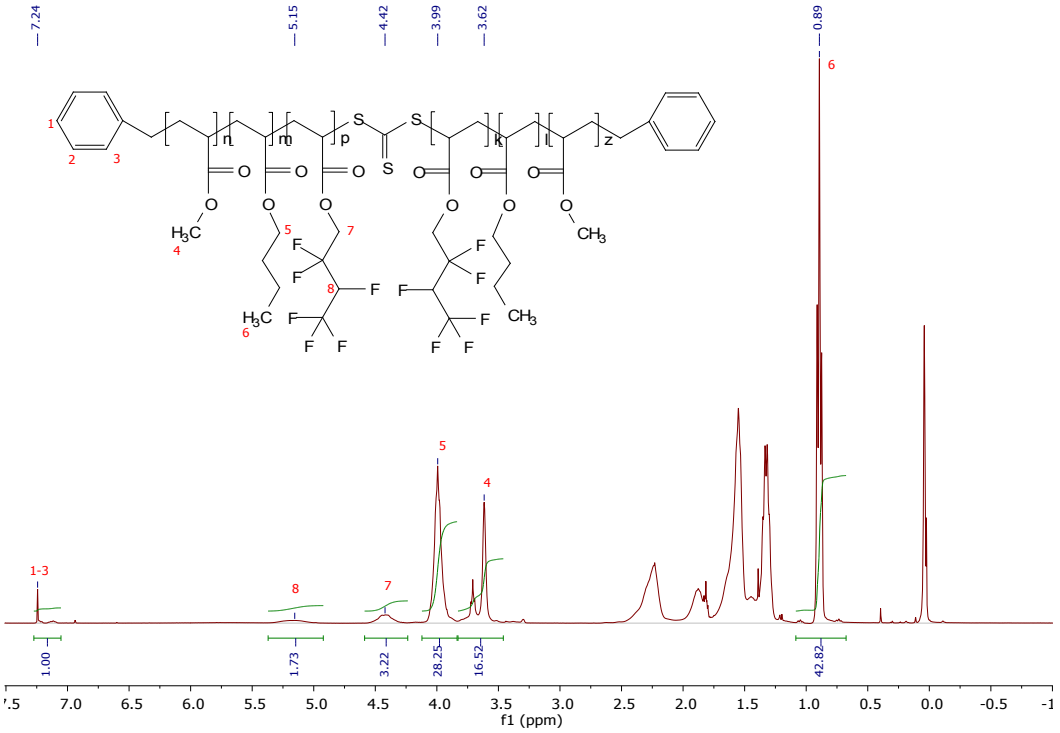


Fig. S7. ^{1}H NMR (a) and ^{19}F NMR (b) spectra of the triblock copolymer obtained at 91 % monomer conversion in dispersion copolymerization of butyl acrylate and 2,2,3,4,4,4-hexafluorobutyl acrylate in the presence of Pol-A in methanol/water (80/20 v/v) mixture and subjected to methylation; media/monomers = 7/1 v/v, [butyl acrylate]/[HFBA] = 90/10 mole %; [Pol-A] = 2.2×10^{-3} mole/L, [AIBN] = 1.1×10^{-3} mole/L.

(a)



(b)

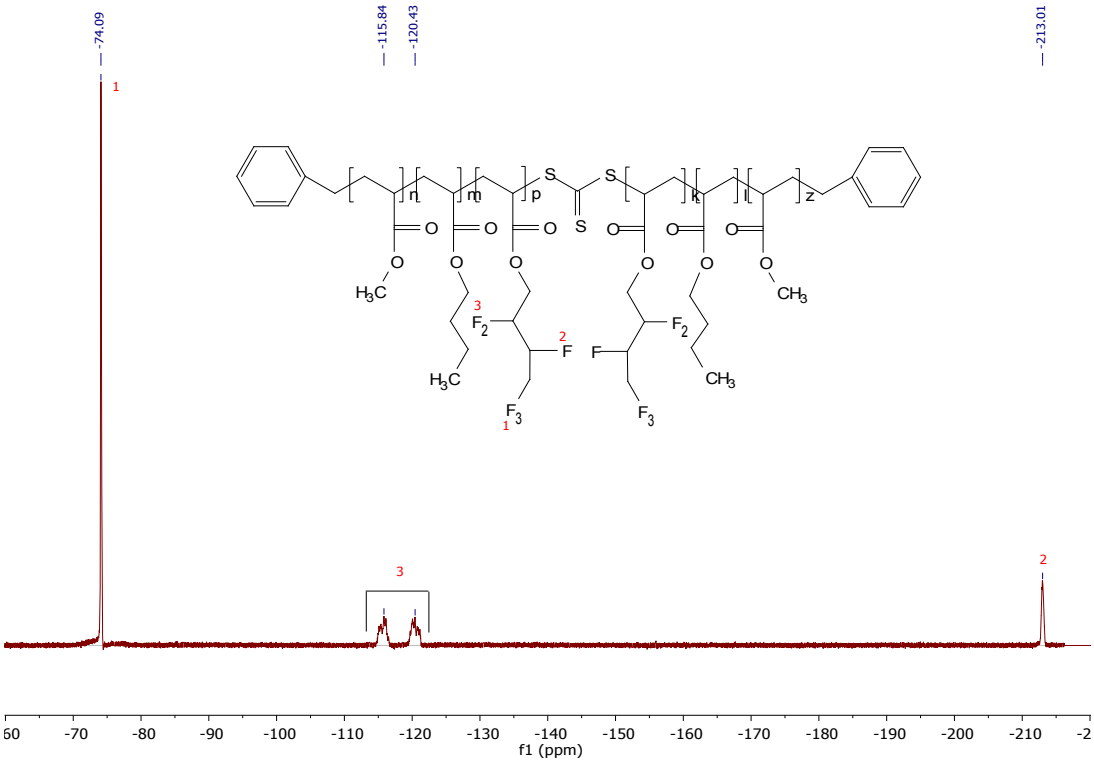


Table S1. Molecular weight characteristics of the copolymers of acrylic acid and 2,2,3,4,4,4-hexafluorobutyl acrylate (95 : 5 mole %), acrylic acid and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (90 : 10 mole %) synthesized in DMF in the presence of trithiocarbonates.

RAFT agent	Monomer	Conversion, %	M_n, kDa	M_n^{theor}, kDa	M_w/M_n
BTC	HFBA	18.3	2.1	1.7	1.23
5×10^{-2}		41.2	3.2	3.4	1.33
mole/L		72.7	4.4	5.7	1.36
		96.6	4.9	7.5	1.38
Cop-H5	HFBA	0	5.8	4.0	1.40
3×10^{-3}		5.3	16.5	8.7	1.55
mole/L		12.4	27.5	12.7	1.58
		42.2	45.7	29.2	1.59
		77.2	50.5	48.5	1.71
BTC	OFPA	0.3	9.6	1.0	1.43
6×10^{-3}		12.4	11.1	9.7	1.40
mole/L		51.6	25.2	39.4	1.42
		77.5	29.9	59.0	1.40
		86.7	32.1	66.0	1.40
		93.9	33.8	71.4	1.47
Cop-O2	OFPA	0	4.8	4.3	1.20
6×10^{-3}		0.6	32.0	5.0	1.22
mole/L		71.7	61.1	29.0	1.58
		91.3	68.7	35.5	1.59

Note: In the case of Cop-H5 and Cop-O2, the molecular weight characteristics of the "grown" copolymers (mode 2) are given.

Table S2. Molecular weight characteristics of the "grown" copolymers (mode 2) of butyl acrylate and 2,2,3,4,4,4-hexafluorobutyl acrylate synthesized in DMF in the presence of trithiocarbonates.

RAFT agent	HFBA, mole %	Conversion, %	M_n, kDa	M_w/M_n
BTC	10	15.3	10.6	1.52
		36.0	19.6	1.48
		64.6	33.1	1.56
		96.9	46.9	1.43
Pol-A	20	4.1	11.9	1.27
		43.7	47.3	1.48
		63.5	56.4	1.32
		94.1	58.1	1.36
Cop-H5	20	10.9	56.5	1.35
		48.4	56.8	1.45
		65.8	60.3	1.44
		93.2	60.4	1.45

Table S3. Molecular weight characteristics of the "grown" copolymers of butyl acrylate and 2,2,3,4,4,4-hexafluorobutyl acrylate, butyl acrylate and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (mode 2) synthesized by emulsifier-free emulsion polymerization in the presence of trithiocarbonates.

RAFT agent	Monomer, mole %	Conversion, %	M_n, kDa	M_w/M_n
Pol-A	HFBA, 10	3.2	780.0	1.44
		19.9	950.0	1.60
		44.4	1030.0	1.58
Cop-H5	HFBA, 10	7.4	1190.0	1.34
		19.9	1340.0	1.37
		47.9	1300.0	1.44
Cop-O2	OFPA, 20	1.1	7.3	1.12
		19.6	40.5	1.13
		57.1	61.7	1.32
		85.4	77.4	1.47
		93.8	93.0	1.72
Cop-O10	OFPA, 20	32.6	28.3	1.20
		64.9	42.9	1.67
		84.5	50.6	1.91