Supplemental Information for:
Block copolymers containing stable radical and fluorinated blocks with long-range ordered morphologies prepared by anionic polymerization

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Table S1 Molecular weight, dispersities and yield of PTFEMA homopolymers using various [Na+]:[DB18C6] ratios. All reactions had a molecular weight target of 50,000 g/mol.

| Entry	[I]:[Na$^+$]:[DB18C6]	NMR[a] M_n (g mol^{-1})	SEC[b] Đ	Yield
1	1:5:0	4,500	2.33	12.1%
2	1:0:10	25,500	1.86	43.8%
3	1:1:1	2,900	1.43	3.6%
4	1:5:5	10,200	1.64	85.7%

[a] Determined by ^{1}H NMR (500 MHz, THF d-8). [b] Determined by SEC (THF, PS Standards).
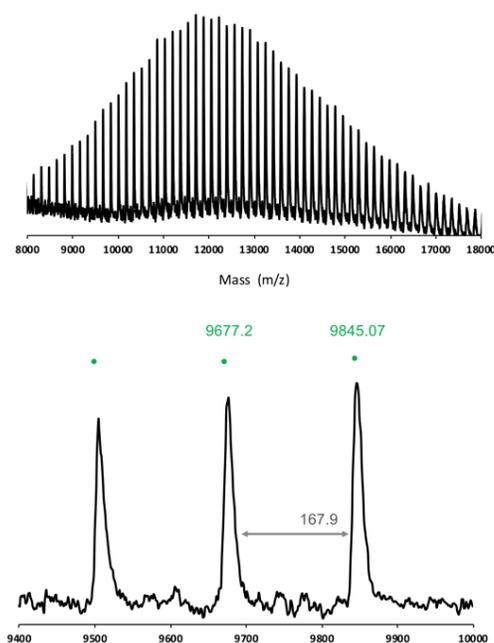
Figure S1. MALDI-TOF-MS spectrum of PTFEMA synthesized using a Na$^+$/DB18C6 counterion complex
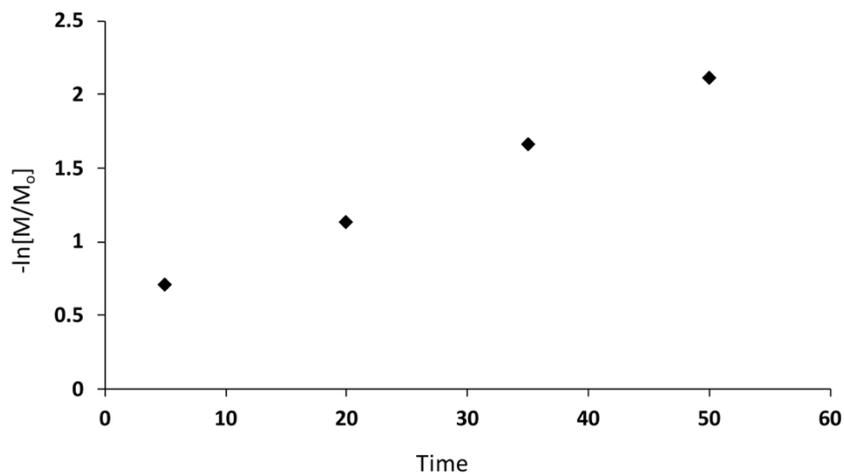
Figure S2. Kinetics plot of a PTMA homopolymerization with target molecular weight of 8,000 g/mol. Aliquots of samples were taken at 15 minute intervals for 50 minutes.
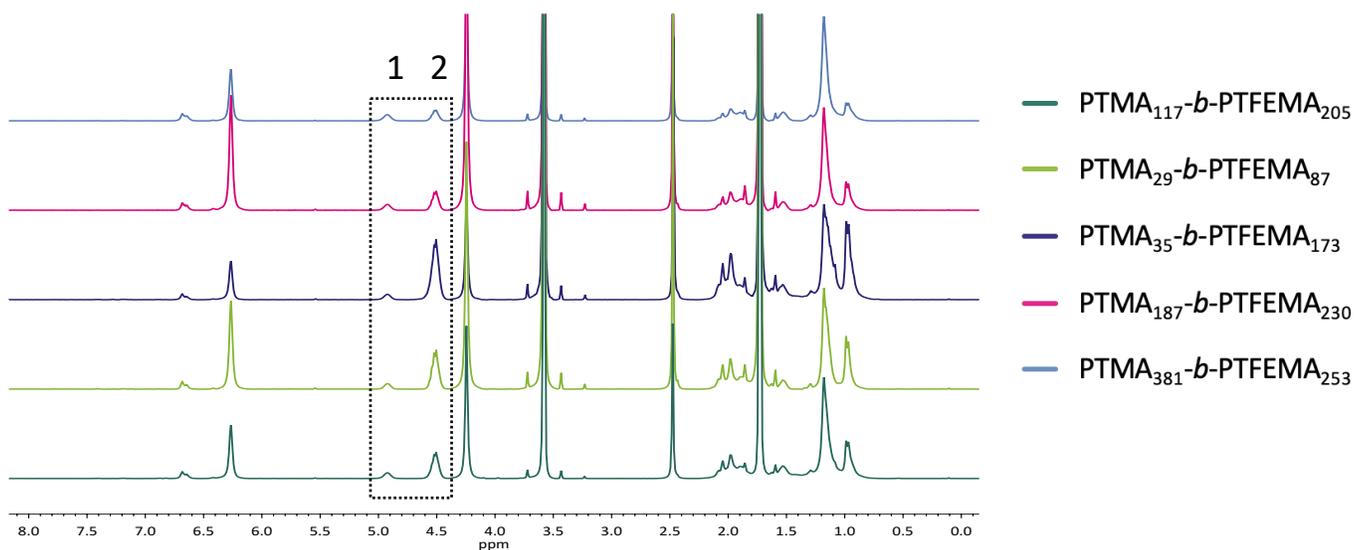

Figure S3. ^{1}H NMR spectrum (THF, d-8) of all PTMA-b-PTFEMA block copolymers reduced with pentafluorophenylhydrazine. The PTMA and PTFEMA peaks used to quantify block ratios are labeled (1 and 2, respectively).
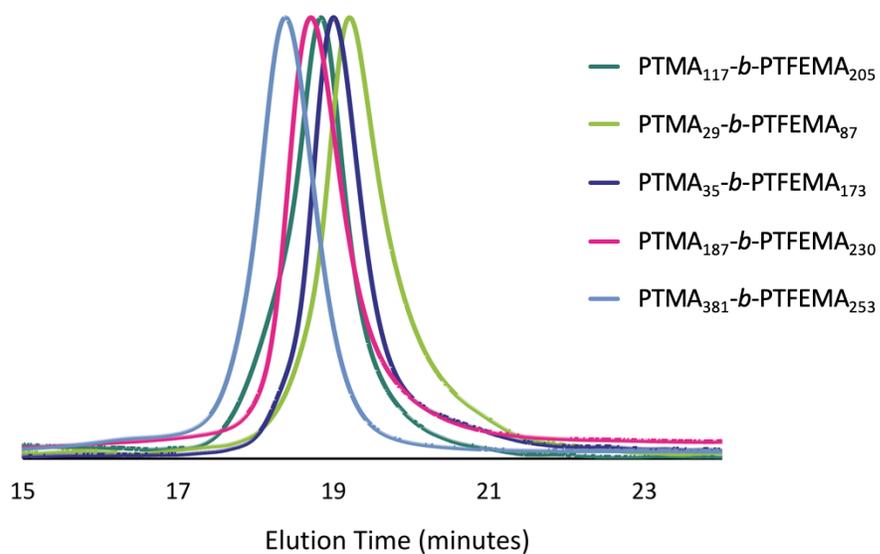
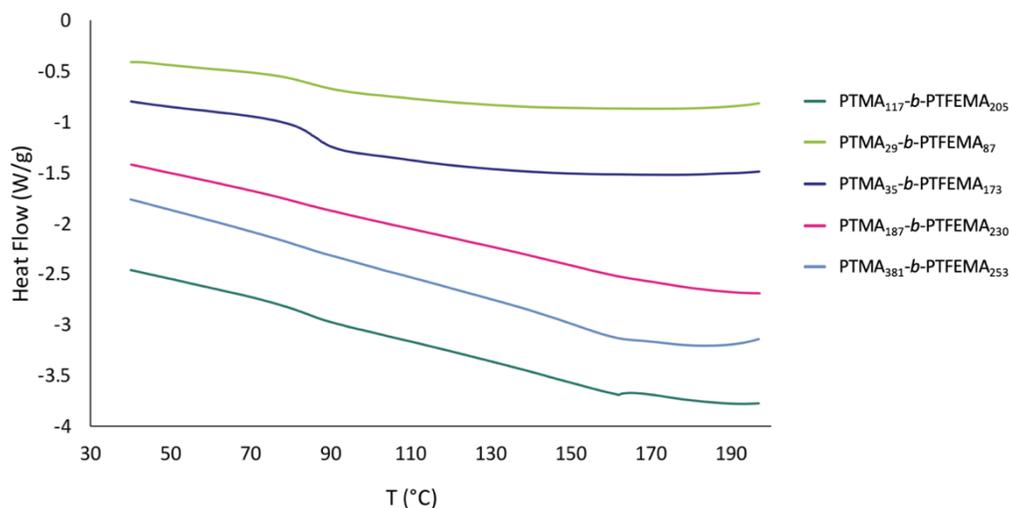**Figure S4**. GPC traces of all PTMA-b-PTFEMA block copolymers with THF as eluent.
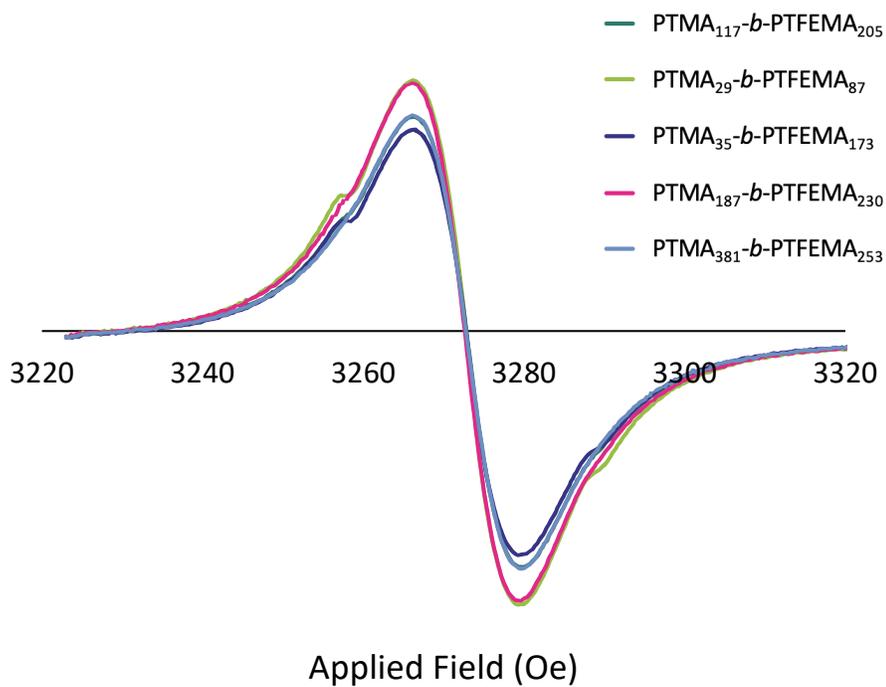
**Figure S5.** EPR spectra of all PTMA-b-PTFEMA polymers dissolved in THF at a 1mM radical concentration.
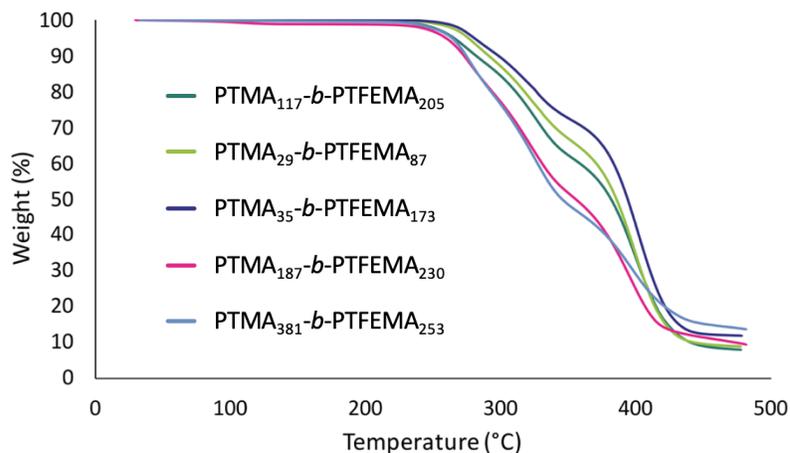
Figure S6. TGA analysis of all PTMA-b-PTFEMA block copolymers.

TGA traces were collected on a TA Instruments TGA Q500 using a 10°C/min rate, heating up to 445°C. Traces were evaluated with TA Instruments Universal Analysis 2000.


Figure S7. DSC analysis of all PTMA-b-PTFEMA block copolymers.

DSC traces were collected on a TA Instruments DSC Q2000 using a 10°C/min rate, heating up to 200°C. Traces were evaluated with TA Instruments Universal Analysis 2000.
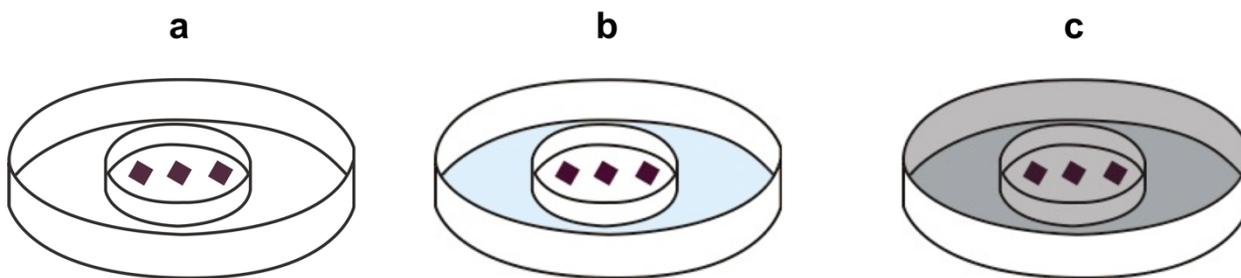
Figure S8. Schematic of glass chamber used to vapor-anneal block copolymer thin films

To anneal, spin-coated polymer samples on 1x1cm Si wafer pieces were placed in a glass chamber (composed of petri dishes of various sizes) which held both thin film samples and annealing solvent together, but without contact. To the larger petri dish, 10-15 mL of chloroform were added (Fig. S8b) to create a pool of annealing solvent around a smaller petri dish containing the thin film polymer samples. Once the annealing solvent was added, the glass chamber was enclosed with a lid (Fig. S8c) and annealed for 6 hours.
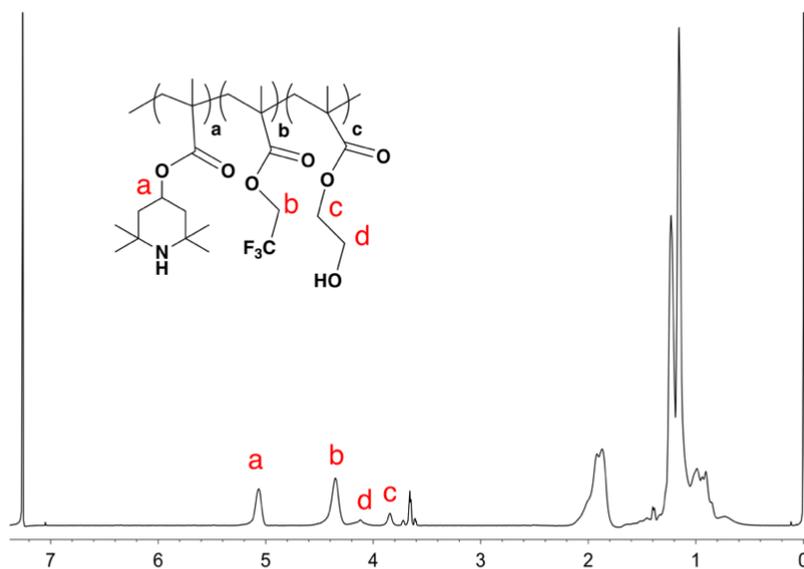
Figure S9. ^{1}H NMR (500 MHz in CDCl$_3$) spectra of the precursor polymer of PTMA-ran-PTFEMA-ran-PHEMA (RTP-1) before oxidation.
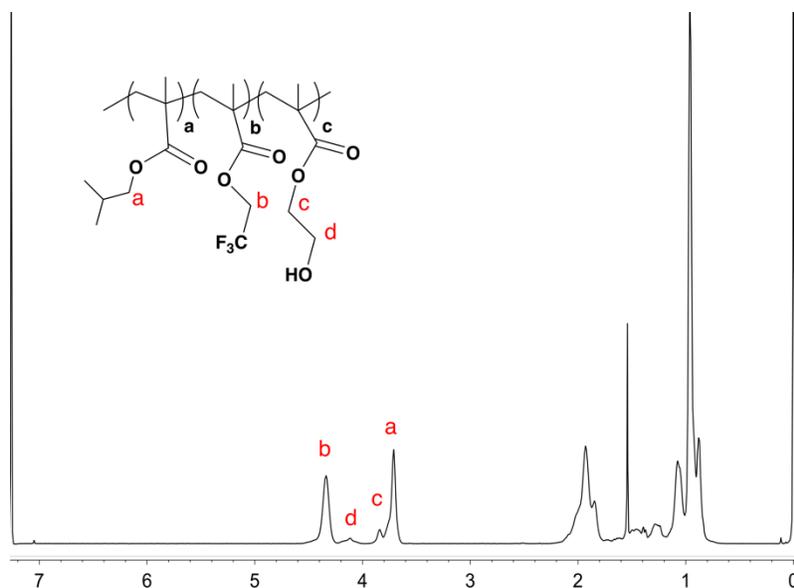
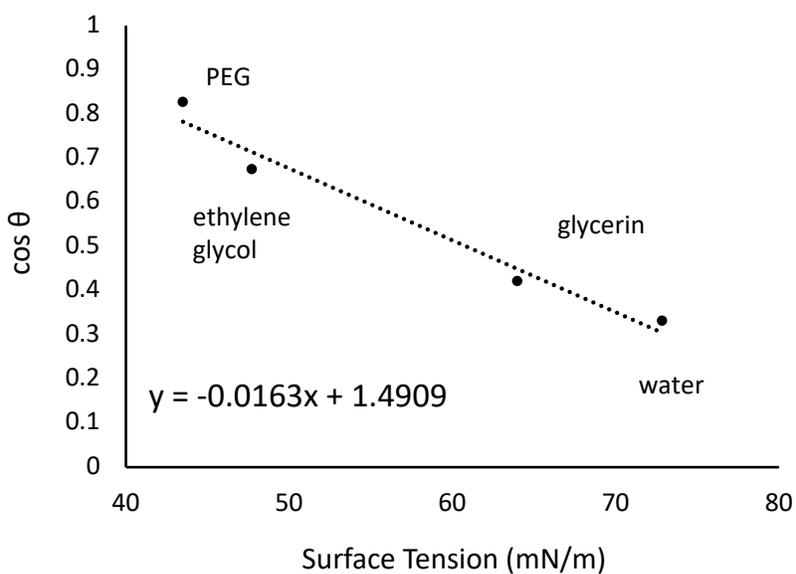**Figure S10**. ¹H NMR spectra (500 MHz in CDCl₃) of the precursor polymer of PTMA-ran-PTFEMA-ran-PHEMA (RTP-1) before oxidation.

Table S2 *Random terpolymer (neutral underlayer) characteristics.*

Sample	$f_{TMA/iBMA}{}^a$	$f_{TFEMA}{}^a$	$f_{HEMA}{}^a$	$M_n{}^b$	$Đ^b$
RTP-1	0.52 (TMA)	0.42	0.06	6,200	1.40
RTP-2	0.47 (iBMA)	0.47	0.06	7,400	1.64

ᵃ Determined by ¹H NMR (500 MHz, CDCl₃). ᵇ Determined by SEC (THF, PS Standards).

Figure S11. Zisman plot used to estimate the surface energy PTMA.