SUPPORTING INFORMATION

pH-Sensitive Amphiphilic Block-Copolymers for Transport and Controlled Release of Oxygen

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1. Nomenclature and Abbreviations

 Abbreviation	Description
 AFM	Atomic Force Microscopy
AiBN	2,2'-azobis(2-methylpropionitrile)
CPCPA	4-cyano-4-(phenylcarbonothioylthio) pentanoic acid
CTA	chain transfer agent
DLS	dynamic light scattering
DMAEM	2-(dimethylamino)ethyl methacrylate
DO	dissolved oxygen
HFBA	2,2,3,3,4,4,4-heptafluorobutyl acrylate
M _n	number-average molecular weight
M _w	weight-average molecular weight
PFDA	1H,1H,2H,2H-perfluorodecyl acrylate
PDI	polydispersity index
RAFT	reversible addition-fragmentation transfer
RID	refractive index detector
SEC	size exclusion chromatography
TDFOA	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate
TEM	transmission electron microscopy
THF	tetrahydrofuran
TFT	a,a,a-trifluorotoluene

Table S1. Nomenclature and Abbreviations

2. Materials and Methods

Materials:

Commercial reagents were purchased from Sigma Aldrich or VWR and, unless indicated otherwise, used without further purification. Monomers including 1H, 1H, 2H, 2H-perfluorodecyl acrylate, 2, 2, 3, 3, 4, 4, 4-heptafluorobutyl acrylate, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8-tridecafluorooctyl acrylate distilled under reduced pressure (25 mbar) before use. 2-(dimethylamino)ethyl methacrylate was passed through basic Al₂O₃ before use. 2, 2'-Azobis(2-methylpropionitrile) was recrystallized from methanol and stored at -20°C. α , α , α -trifluorotoluene and 1, 4-dioxane were distilled before use over calcium hydride.

Nuclear Magnetic Resonance:

¹H, ¹³C, ¹⁹F NMR analyses were performed on a Bruker AVQ 400 MHz instrument at 298 K. Chemical shifts are reported as δ (ppm) values, and coupling constants (*J*) in Hz. TMS or residual solvent signals such as CDCl₃ (δ : 7.26) were used as reference peaks.

Size Exclusion Chromatography:

The molecular weight and PDI of polymers were determined by SEC using an Agilent 1290 liquid chromatography system fitted with refractive index (RID) and UV-Vis detectors, using two identical PLgel columns (5 µm, MIXED-C) in connected series with THF as the mobile phase (1 mL/min). The column and flow path were temperature controlled at 25 °C. Data analysis was performed using GPC-Addon for ChemStation software provided by Agilent.

Dissolved Oxygen Measurements:

Dissolved oxygen concentration was measured using a Mettler Toledo SG6 SevenGO Pro instrument with an Inlab 605 electrochemical dissolved oxygen probe.

Dynamic Light Scattering:

The DLS measurements were performed using a Malvern Zetasizer Nano ZS instrument equipped with a 632.8 nm He-Ne laser. The measurement angle was 173°. For each analysis, micellar dispersions were prepared via dispersion in DI water and filtered through a 0.45 μ m nylon filter to exclude macroscopic dust particles. The cells were temperature-controlled at 4 ± 0.1, 25 ± 0.1 and 37 ± 0.1 °C.

Transmission Electron Microscopy:

Imaging was performed on a Titan G2 80–300 kV transmission electron microscope (FEI Inc.) equipped with a 4 k×4 k CCD camera (US4000, Gatan, Inc.). Cryo-TEM: Imaging was performed in low dose mode on a Titan Krios operating at 300 kV. Images were recorded in zero loss-imaging modes using an energy filter (GIF Tridiem, Gatan, Inc) with a slit width of 20 eV. On a typical exposure, the samples received a dose of ~150 e-/Å².

Atomic Force Microscopy:

15 mg/mL dispersions of polymers in water were spin-coated on top of silicon wafer substrates (3500 revolutions per minute). Prior to deposition, substrates were treated with "piranha" solution. AFM measurements were conducted on an Agilent 5500 SPM in acoustic AC mode. For this technique, careful selection of the probing conditions helped in elucidating the micelle formation contrast (tapping frequency f₀ 300 kHz and force contrast k:2-5 N/m, Bruker AFM Probes).

3. Synthesis of the Block-Copolymers

Three linear polymers were synthesized from three fluorous monomers via RAFT polymerization. A second DMAEM block was then added to each polymer and 3 aliquots were extracted over a period of time resulting in nine different amphiphilic block copolymers (Table 1 in the main text). A general procedure for each polymerization step is given below.

Preparation of the Fluorous Blocks



Using a general procedure, polymerization of the HFBA was carried out in a Schlenk tube equipped with a magnetic stirring bar. HFBA (2.5 g, 9.8 mmol), CPCPA (0.018 g, 0.066 mmol), AiBN (0.001 g, 0.0066 mmol) and 1,4-dioxane (5 mL) were added to the Schlenk tube and argon was bubbled through the system for 20 min to purge oxygen from the tube. The reaction mixture was cooled in a liquid nitrogen bath and then subjected to five freeze-pump-thaw cycles before initiating the polymerization in a 73 °C oil bath. The reaction was run for 5 h under positive argon pressure and quenched via cooling to room temperature and exposure to air. The solution was concentrated by rotary evaporation, and the polymer was dissolved in THF and precipitated from hexane and dried under high vacuum for 24 h. The resultant polymer was dissolved in THF and re-precipitated from chilled hexane twice, filtered, and dried once under high vacuum for 24 h to give a white solid polymer. The polymerizations of TDFOA and PFDA monomers were performed similarly. Specific details are provided in Table S2.

¹H NMR of poly(HFBA) (CDCl₃) δ (ppm): 7.49 and 7.07 (endgroup), 4.58 (2H, -OCH₂(CF₂)₂CF₃), 2.98-2.90 (4H, -CH₂ of RAFT), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1-1.1 (3H, -CH and -CH₂ backbone of PHFBA).

¹⁹F NMR poly(HFBA) (CDCl₃) δ (ppm): -81.3 (m, 3F, -CF₃) and -121 to -128 (m, 4F, (CF₂)₂).

¹H NMR of poly(TDFOA) (CDCl₃) δ (ppm): 7.49 and 7.06 (endgroup), 4.36 (2H, -OCH₂CH₂(CF₂)₅CF₃), 2.98-2.90 (4H, -CH₂ of RAFT), 2.5 (2H, -OCH₂CH₂(CF₂)₅CF₃), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1- 1.1 (3H, -CH and -CH₂ backbone of PTDFOA).

¹⁹F NMR poly(TDFOA) (CDCl₃) δ (ppm): -81.1 (m, 3F, -CF₃), -114 (m, 2F, CF₂CH₂) and -122 to -126 (m, 8F, (CF₂)₄)

¹H NMR of poly(PFDA) (CDCl₃) δ (ppm): 7.49 and 7.05 (endgroup), 4.36 (2H, -OCH₂CH₂(CF₂)₇CF₃), 2.98-2.90 (4H, -CH₂ of RAFT), 2.4 (2H, -OCH₂CH₂(CF₂)₇CF₃), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1- 1.1 (3H, -CH and -CH₂ backbone of PPFDA).

¹⁹F NMR poly(PFDA) (CDCl₃) δ (ppm): -80.7 (m, 3F, -CF₃), -113.6 (m, 2F, CF₂CH₂) and -121 to -126 (m, 12F, (CF₂)₆).

Table S2. Experimental conditions and results of the controlled radical homopolymerization of PFDA, HFBA, and TDFOA initiated by AiBN and controlled by CPCPA for the preparation for the perfluorinated macroinitiators.

	ernaenn		i illo proparation	01 01 7 10		by rabit and	Intiatoa
t Yield NMR Mn SEC Mw SEC Mr	t	Т	[M]:[CTA]:[I]	CTA	Initiator	Monomer	Entry
(hrs) (%) (g/mol) ^a (g/mol) ^b (g/mol) ^b	(hrs)	(°C)	(Mol %)				
5 44 5900 7800 6200	5	73	150:1:0.1	CPCPA	AiBN	HFBA	1
5 38 4200 4400 4800	5	73	180:1:0.1	CPCPA	AiBN	TDFOA	2
5 31 3200 3700 3400	5	73	180:1:0.1	CPCPA	AiBN	PFDA	3
5 44 5900 7800 6200 5 38 4200 4400 4800 5 31 3200 3700 3400	5 5 5	73 73 73	150:1:0.1 180:1:0.1 180:1:0.1	CPCPA CPCPA CPCPA	AiBN AiBN AiBN	HFBA TDFOA PFDA	1 2 3

^aDetermined from ¹H NMR spectroscopy using the following formula: $M_n = M_{CTA} + M_{monomer} x$ (DP_n of monomer) [Where, $M_{CTA} = 279.38$; $M_{monomer} = 518.17$, 418.15 and 254.10 for PFDA, TDFOA and HFBA, respectively; ^b Determined by SEC calibrated with linear polystyrene standards.

Preparation of the Block-Copolymers



 $R = CH_2(CF_2)_7CF_3$ (PFDA), $CH_2(CF_2)_5CF_3$ (TDFOA), C_3F_7 (HFBA)

The poly(HFBA) macroinitiator (0.45 g, 0.008 mmol) bearing a RAFT end-group was introduced into a 50 mL Schlenk tube along with AiBN (0.01 mg, 0.0008 mmol), DMAEM (6.2 g, 39 mmol) 3 mL of 1,4-dioxane and 2 mL of TFT. The reaction was subjected to five freeze-pump-thaw cycles to remove oxygen. The polymerization reaction was carried out at 73°C under positive argon pressure for 2 hours, and was quenched via cooling to room temperature and exposure to air. The solvent was removed via rotary evaporation. The copolymer was dissolved in THF, precipitated from chilled hexane, filtered and then dried under high vacuum. The resultant polymer was dissolved in THF and re-precipitated chilled hexane twice more, filtered and dried under high vacuum for 24 h to yield a white product. Similar reactions were run for 4 hours and 6 hours resulting in three different block copolymers from the poly(HFBA) macroinitiator. The reaction times (2, 4 and 6 hours) were determined during preliminary optimization experiments monitored by SEC analysis.

Copolymerization reactions were run similarly for poly(TDFOA) and polymer(PFDA) macroinitiators to yield a total of nine different block-copolymers.

¹H NMR of poly(HFBA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): 7.53 and 7.02 (endgroup), 4.54 (2H, -OC*H*₂(CF₂)₂CF₃), 4.06 (2H, -OC*H*₂CH₂N(CH₃)₂), 2.96-2.87 (4H, -CH₂ of RAFT), 2.57 (2H, -OCH₂CH₂N(CH₃)₂), 2.28 (6H, -OCH₂CH₂N(CH₃)₂), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH₂ and -CH₃ backbone of PHFBA and PDMAEM). ¹⁹F NMR poly(HFBA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): -82 (m, 3F, -CF₃) and -121 to -128 (m, 4F, (CF₂)₂).

¹H NMR of poly(TDFOA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): 7.55 and 7.01 (endgroup), 4.31 (2H, -OCH₂(CF₂)₅CF₃), 4.07 (2H, -OCH₂CH₂N(CH₃)₂), 2.96-2.88 (4H, -CH₂ of RAFT), 2.5 (2H, -OCH₂CH₂(CF₂)₅CF₃), 2.57 (2H, -OCH₂CH₂N(CH₃)₂), 2.29 (6H, -OCH₂CH₂N(CH₃)₂), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH₂ and -CH₃ backbone of PTDFOA and PDMAEM). ¹⁹F NMR poly(TDFOA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): -82.5 (m, 3F, -CF₃), -114.6 (m, 2F, CF₂CH₂) and -121 to -127 (m, 8F, (CF₂)₄).

¹H NMR of poly(PFDA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): 7.51 and 7.00 (endgroup), 4.28 (2H, -OCH₂(CF₂)₇CF₃), 4.07 (2H, -OCH₂CH₂N(CH₃)₂), 2.96-2.87 (4H, -CH₂ of RAFT), 2.5 (2H, -OCH₂CH₂(CF₂)₇CF₃), 2.57 (2H, -OCH₂CH₂N(CH₃)₂), 2.28 (6H, -OCH₂CH₂N(CH₃)₂), 2.2 (3H, -CH₃ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH₂ and -CH₃ backbone of PPFDA and PDMAEM). ¹⁹F NMR poly(PFDA)-*b*-poly(DMAEM) (CDCl₃) δ (ppm): -82 (m, 3F, -CF₃), -114.7 (m, 2F, CF₂CH₂) and -123 to -127 (m, 12F, (CF₂)₆).

Kinetics

A series of copolymerization reactions were run between DMAEM and one of the fluorinated macroinitiators (PHFBA, PTDFOA and PPFDA) in the presence of CPCPA. Aliquots were collected at different time intervals, and M_n was determined for each aliquot using NMR and PDI data was determined using SEC analysis. The M_n increased linearly with time in all cases (Figures S1-S3), indicating a constant number of propagating centers. Furthermore, throughout the copolymerization reactions, SEC traces of the copolymers shifted towards higher molar masses as time increased (SEC images in Section 7). These data demonstrate that CPCPA is a suitable controlling agent for the block copolymerization of fluorinated acrylates with DMAEM.



Figure S1. M_n of the block copolymers from the 2-, 4- and 6-hour copolymerization reactions of PHFBA₂₅ with DMAEM.



Figure S2. Mn of the block copolymers from the 2-, 4- and 6-hour copolymerization reactions of PTDFOA₁₀ with DMAEM.



4. Dissolved Oxygen Measurements

General Procedure

Dissolved oxygen (DO) measurements were performed through a previously established method.¹ Data were recorded in triplicate for each dispersion and for DI water at pH 2, 5 and 7 and at 4, 20 and 37 °C.

In a 40 mL vial, each dispersion was stirred at 300 rpm for 10 minutes at 25 °C. After this time, the vials were continually flushed with a flow of O_2 for 1 minute, then capped and vigorously shaken. The caps were removed and DO values were recorded at t = 5min (oxygen atmosphere) and at t = 60 min (air saturation) (Figures S5-S10). Measurements were collected using a Mettler Toledo SG6 SevenGo Pro with an Inlab 605 dissolved oxygen probe (Figure S4). Data was collected every 5 minutes for experiments run at pH 2 (Figure S11).

We found that the lower critical solution temperature of the DMEAM block²⁻³ caused the block copolymers to precipitate at 37 °C, pH 7. Although decreasing the temperature resulted in the copolymer re-dispersing in water we could not collect DO data for these conditions.



Figure S4. The experimental set up used to obtain oxygen solubility measurements.



Figure S5. Oxygen concentrations at O₂ atmosphere and air saturation of block copolymers containing the PHFBA₂₅ fluorous block. Each plot compares PHFBA₂₅-b-PDMAEM₉₇, PHFBA₂₅-b-PDMAEM₁₃₉, PHFBA₂₅-b-PDMAEM₁₈₀ and water collected under the same pH and temperature conditions.

PHFBA25-b-PDMAEMx



Figure S6. Oxygen concentrations at O₂ atmosphere and air saturation of block copolymers containing the PPFDA₆ fluorous block. Each plot compares PPFDA₆-b-PDMAEM₁₁₄, PPFDA₆-b-PDMAEM₁₂₆, PPFDA₆-b-PDMAEM₁₃₈ and water collected under the same pH and temperature conditions.

PTDFOA10-b-PDMAEMx



Figure S7. Oxygen concentrations at O₂ atmosphere and air saturation of block copolymers containing the PTDFOA₁₀ fluorous block. Each plot compares the DO measurements of PTDFOA₁₀-b-PDMAEM₆₄, PTDFOA₁₀-b-PDMAEM₈₈, PTDFOA₁₀-b-PDMAEM₁₃₀ and water collected under the same pH and temperature conditions.



Block copolymers with a 15 wt % of the fluorinated block

 O_2 atm. Air sat. O_2 atm. Air sat. O_2 atm. Air sat. O_2 atm. Sat. O_2 atmosphere and air saturation of block copolymers with a 15 % w/w fluorinated block plotted. Each plot compares polymers made up of different monomers and the DO data collected under the same pH and temperature conditions.

Block copolymers with a 23 wt % of the fluorinated block



Figure S9. Oxygen concentrations at O₂ atmosphere and air saturation of block copolymers with a 23 % w/w fluorinated block plotted. Each plot compares polymers made up of different monomers and the DO data collected under the same pH and temperature conditions.

Block copolymers with a 29 wt % of the fluorinated block



Figure S10. Oxygen concentrations at O₂ atmosphere and air saturation of block copolymers with a 29 % w/w fluorinated block plotted. Each plot compares polymers made up of different monomers and the DO data collected under the same pH and temperature conditions.



Figure S11. Oxygen concentrations collected every 5 minutes for each block copolymer at pH 2; each set is plotted against DO data collected in water at the same pH and temperature.

5. Cryo-TEM Analysis

Representative Images



Figure S12. Cryo-TEM image of the PHFBA₂₅-b-PDMAEM₉₇ block copolymer at pH 2.



Figure S13. Cryo-TEM images of the PHFBA₂₅-*b*-PDMAEM₁₃₉ block copolymer at pH 2 showing A) the "broken glass" structures frozen in solution, B) an dark fluorinated core surrounded by the DMAEM corona and C) a partially dried aggregate.











Figure S16. Cryo-TEM image of the PTDFOA₁₀-*b*-PDMAEM₈₈ block copolymer at pH 2.



Figure S17. Cryo-TEM image of the PTDFOA₁₀-*b*-PDMAEM₁₃₀ block copolymer at pH 2 showing A) the "broken glass" structures, A,B) large aggregates and B) small random aggregates.



Figure S18. Cryo-TEM image of the PPFDA₆-*b*-PDMAEM₁₁₄ block copolymer at pH 2 showing A, C) core-shell structures that formed above the ice B) random aggregates and "broken glass" structures



Figure S19. Cryo -TEM image of the PPFDA₆-*b*-PDMAEM₁₂₆ block copolymer at pH 2 showing random aggregates and the "broken glass" structures.



Figure S20. Cryo-TEM image of the PPFDA₆-*b*-PDMAEM₁₃₈ block copolymer at pH 2 showing some A) broken glass structures and A, B) large cores with a faint corona.

Summary of Observations

Samples of the PPFDA₆-*b*-PDMAEM₁₁₄, PPFDA₆-*b*-PDMAEM₁₂₆, PTDFOA₁₀-*b*-PDMAEM₆₄ and PHFBA₂₅-*b*-PDMAEM₁₃₉ emulsions dried quickly during sample preparation allowing us to obtain images of aggregates in the ice, on top the ice and even some images of aggregates existing between these two phases. A particle is known be out of the ice when there is a white outline around the aggregate indicating that the structure is out of phase with the ice that is being focused on by the beam. Collecting these images allowed us to see the DMEAM blocks more easily (as they appeared as a solid grey shell rather than an indistinct "hairy" corona). The images of dried aggregates that were obtained include Figure S69C (PHFBA₂₅-*b*-PDMAEM₁₃₉) Figure S74A and C (PPFDA₆-*b*-PDMAEM₁₁₄) and Figure S75A (PPFDA₆-*b*-PDMAEM₁₂₆). Figure S71A shows a PTDFOA₁₀-*b*-PDMAEM₆₄ micelle that is only partially inside the ice.

6. AFM Analysis

General Procedure

By adjusting the strength of the tapping mode-AFM, phase contrast of the spin coated films were used to directly visualize and evaluate the block-copolymer micelles. According the topography images, the HFBA blocks appear to phase segregate with inner cores forming with specific size distributions. In all samples, the shape of the micelles remained spherical after repeated scanning of several latitudes under the same measurement conditions. The individual and round shape of the micelles could clearly be seen from the phase images irrespective of film roughness.



Figure S21. A,C) Height and B,D) Phase AFM images of the PHFBA₂₅-*b*-PDMAEM₉₇ block copolymer spin coated onto the film from A,B) 15 mg/mL and C,D) 3 mg/mL dispersions.



Figure S22. A) Height and B) Phase AFM images of the PTDFOA₁₀-*b*-PDMAEM₆₄ block copolymer spin coated onto the film from a 15 mg/mL dispersion.



7. SEC Data

Each perfluorinated macroinitiator and block copolymer was dissolved in THF for SEC analysis.

It should be noted that due to the nature of the polymers (detailed in the main text). M_w and PDI values determined by SEC analysis were used as an indicator or aggregation rather than of actual molecular weight.



Figure S24. SEC traces (RID) of the PPFDA6 macroinitiator and the corresponding block copolymers in THF.



Figure S26. SEC traces (RID) of the PHFBA₂₅ macroinitiator and the corresponding block copolymers in THF.

8. DLS Data

Determining Solubility Range

Preliminary observations of the copolymers in dispersions showed that solubility decreased as pH increased. As such, the highest possible concentration at pH 7 was determined and then used throughout the rest of the experiments. To determine the maximum concentration that could be used for analysis, an oversaturated dispersion was prepared by stirring 70 mg of PHFBA₂₅*b*-PDMAEM₉₇ in 5 mL of DI water at pH 7. The mixture was stirred overnight at room temperature, centrifuged (7500 rpm for 15 min) in a tarred vial, and then decanted into a volumetric flask. The centrifuge vial was dried under vacuum and the remaining solid copolymer (24 mg) was used to determine that the concentration of the dispersion was 0.92 wt%. As such all DO and DLS experiments were performed at ~0.92 wt %.

A 0.92 wt %. concentration allowed us to disperse the copolymer at all temperatures and pH levels except for at 37 $^{\circ}$ C, pH 7. We found that under these conditions, the lower critical solution temperature of the DMEAM block²⁻³ caused the block copolymers to precipitate out. Decreasing the temperature resulted in the copolymer re-dispersing in water.

General Procedure

DLS analysis was used to determine the effects of temperature and pH on the aggregate size distribution of each copolymer. 5 ml of 0.92 wt % dispersions were prepared at pH 2, 5 and 7. The pH 7 dispersions were prepared in DI water, stirred overnight and used for analysis the next day. pH 2 dispersions were prepared in the presence of H₂SO₄; the pH was verified before analysis via a pH meter. Once analysis of the pH 2 dispersions was complete, each sample was dialyzed against DI water (10,000 g/mol cut-off Slide-A-Lyzer 10K Dialysis Cassettes) overnight yielding pH 5 copolymer dispersions, which were once again verified using a pH meter. For each dispersion prepared, measurements were collected at 4, 25 and 37 °C.













В

D









Ε











PPFDA6-b-PDMAEM138

В

D









Ε



















Figure S36. DLS measurements of block copolymers containing the PHFBA₂₅ fluorous block. Each plot compares the DLS measurements of PHFBA₂₅-b-PDMAEM₉₇ (purple), PHFBA₂₅-b-PDMAEM₁₃₉ (green) and PHFBA₂₅-b-PDMAEM₁₈₀ (orange) collected under the same pH and temperature conditions.



Figure S37. DLS measurements of block copolymers containing the PPFDA₆ fluorous block. Each plot compares the DLS measurements of PPFDA₆-b-PDMAEM₁₁₄ (purple), PPFDA₆-b-PDMAEM₁₂₆ (green) and PPFDA₆-b-PDMAEM₁₃₈ (orange) collected under the same pH and temperature conditions.

PTDFOA10-b-PDMAEMx



Figure S38. DLS measurements of block copolymers containing the PTDFOA₁₀ fluorous block. Each plot compares the DLS measurements of PTDFOA₁₀-b-PDMAEM₆₄ (purple), PTDFOA₁₀-b-PDMAEM₈₈ (green) and PTDFOA₁₀-b-PDMAEM₁₃₀ (orange) collected under the same pH and temperature conditions.

Summary of Observations

Generally, at least two populations or a wide size distribution was observed for each experiment, implying different sized micelles within the same block copolymer dispersion. The size and polydispersity of each block copolymer increased with pH. This is due to the deprotonation of the PDMAEM block. PDMAEM is known to deprotonate and crash out under neutral conditions at ~40 °C.³⁻⁴ Deprotonation that occurs at pH increases will have a similar effect, resulting in larger, less stable aggregates and more turbid dispersions. This variation in size may also explain the trend observed with PHFBA₂₅-*b*-PDMAEM_x block copolymer dispersions where oxygen solubility decreased with increasing pH.

Although PTDFOA₁₀-*b*-PDMAEM_x dispersions did display slightly higher concentrations of oxygen that PPFDA₆-*b*-PDMAEM_x dispersions, both of these systems were comparable to water under many of the temperature and pH conditions. DLS analyses of these block copolymers (Figures S64-S66, ESI) suggest that the aggregates that formed were not as stable as those forming in PHFBA₂₅-*b*-PDMAEM_x dispersions and therefore cannot dissolve oxygen as well. This decreased stability led to the negligible effects of fluorine content within the PTDFOA₁₀-*b*-PDMAEM_x and PPFDA₆-*b*-PDMAEM_x dispersions.

Entry	Polymer	pH 7			рН 5			pH 2		
		Temp (°C)	Z-Avg. (d. nm)	PDI	Temp (°C)	Z-Avg. (d. nm)	PDI	Tem p (°C)	Z-Avg. (d. nm)	PDI
1	PHFBA ₂₅ - <i>b</i> -PDMAEM ₉₇	4	232	0.237	4	564	0.267	4	396	0.274
2	PHFBA25- <i>b</i> -PDMAEM97	20	198	0.226	20	589	0.205	20	407	0.256
3	PHFBA ₂₅ - <i>b</i> -PDMAEM ₉₇	37	817	0.028	37	567	0.210	37	427	0.263
4	PHFBA25-b-PDMAEM139	4	123	0.499	4	573	0.173	4	385	0.265
5	PHFBA ₂₅ -b-PDMAEM ₁₃₉	20	187	0.719	20	573	0.194	20	402	0.270
6	PHFBA ₂₅ -b-PDMAEM ₁₃₉	37	4635	0.217	37	578	0.208	37	429	0.252
7	PHFBA25-b-PDMAEM180	4	194	0.322	4	725	0.275	4	418	0.303
8	PHFBA ₂₅ -b-PDMAEM ₁₈₀	20	154	0.314	20	720	0.237	20	430	0.316
9	PHFBA25-b-PDMAEM180	37	3417	0.375	37	714	0.258	37	458	0.311
10	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₆₄	4	74	0.636	4	626	0.298	4	405	0.641
11	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₆₄	20	60	0.575	20	624	0.325	20	485	0.484
12	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₆₄	37	7911	0.027	37	599	0.312	37	728	0.769
13	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₈₈	4	61	0.638	4	808	0.299	4	319	0.704
14	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₈₈	20	51	0.531	20	790	0.264	20	342	0.612
15	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₈₈	37	2974	0.569	37	847	0.319	37	382	0.581
16	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₁₃₀	4	55	0.999	4	741	0.257	4	311	0.648
17	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₁₃₀	20	54	0.610	20	750	0.243	20	331	0.666
18	PTDFOA ₁₀ - <i>b</i> -PDMAEM ₁₃₀	37	1559	0.224	37	768	0.283	37	352	0.581
19	PPFDA ₆ - <i>b</i> -PDMAEM ₁₁₄	4	70	0.650	4	402	0.245	4	155	0.632
20	PPFDA ₆ - <i>b</i> -PDMAEM ₁₁₄	20	59	0.634	20	425	0.260	20	169	0.570
21	PPFDA ₆ - <i>b</i> -PDMAEM ₁₁₄	37	252	0.086	37	442	0.240	37	185	0.614
22	PPFDA ₆ - <i>b</i> -PDMAEM ₁₂₆	4	58	0.725	4	661	0.244	4	363	0.538
23	PPFDA ₆ - <i>b</i> -PDMAEM ₁₂₆	20	51	0.614	20	650	0.258	20	415	0.488
24	PPFDA6- <i>b</i> -PDMAEM126	37	218	0.136	37	689	0.295	37	499	0.516
25	PPFDA6- <i>b</i> -PDMAEM138	4	82	0.783	4	562	0.229	4	172	0.681
26	PPFDA ₆ - <i>b</i> -PDMAEM ₁₃₈	20	71	0.670	20	548	0.246	20	202	0.621
27	PPFDA ₆ - <i>b</i> -PDMAEM ₁₃₈	37	166	0.146	37	788	0.478	37	239	0.606

Table S3 7-average a	nd PDI as	determined by	/ DLS at differ	ent temnerature	s and nH levels
Table 33 Z-average a	iu i Di as		V DLO al unici	eni iemperature	5 anu pri ieveis.

Measurements at Low Concentrations

The general DLS experiments (above) were performed to explore the effects of different pH and temperatures on the selfassembly of the block copolymers in water. Data were collected using 0.92 wt % copolymer dispersions (~10 mg/mL) because oxygen solubility experiments were run using these concentrations.

However, 10 mg/mL is a relatively high concentration for DLS analysis and at least two populations sizes were generally recorded for each block copolymer. As such, similar experiments were run using 3 mg/mL dispersions (at pH 2, 20 °C) to determine if the multiple-populations were a consequence of the relatively high dispersion concentrations. Although the population sizes were shown to decrease slightly with concentration, the number of populations present did not display a clear dependence on the concentration.





Table S4. DLS data showing the size, Z-average and PDI values for the 3 and 10 mg/mL block copolymer dispersions at pH 2, 20 °C.

	3 mg/mL Disp	ersions		10 mg/mL Dispersions			
Polymer	d. nm (percent)	PDI	Z-Avg. (nm)	d. nm (percent)	PDI	Z-Avg. (nm)	
PHFBA ₂₅ -b-PDMAEM ₉₇	400 (90 %), 91 (10 %)	0.320	268	519 (95 %), 76 (5 %)	0.256	407	
PHFBA ₂₅ - <i>b</i> -PDMAEM ₁₃₉	365 (95 %), 33 (5 %)	0.282	285	530 (94 %), 105 (6 %)	0.270	402	
PHFBA25-b-PDMAEM180	360 (94 %), 46 (6 %)	0.457	261	622 (91 %), 146 (9 %)	0.316	430	
PTDFOA10-b-PDMAEM64	245 (88 %), 35 (12 %)	0.554	142	412 (84 %), 76 (11 %), 14 (5 %)	0.484	485	
PTDFOA ₁₀ - <i>b</i> -PDMAEM ₈₈	390 (63 %), 137 (26 %), 25 (11 %)	0.642	148	401 (60 %), 173 (34%), 16 (6%)	0.612	342	
PTDFOA10-b-PDMAEM130	399 (77 %), 66 (15 %), 18 (8 %)	0.577	183	696 (82 %), 165 (12 %), 20 (6 %)	0.666	331	
PPFDA ₆ -b-PDMAEM ₁₁₄	236 (88 %), 20 (12 %)	0.557	124	290 (91 %), 17 (9 %)	0.570	169	
PPFDA ₆ -b-PDMAEM ₁₂₆	217 (75 %), 1000, (18 %), 19 (7 %)	0.525	176	774 (70 %), 224 (30 %)	0.488	415	
PPFDA ₆ - <i>b</i> -PDMAEM ₁₃₈	242 (73 %), 42 (14 %), 17 (13 %)	0.588	95	317 (70 %), 173 (18 %), 13 (7 %)	0.621	202	

Aggregation of Block-Copolymers in THF

DLS analysis of block copolymers from each macroinitiator in THF were run at 20 $^{\circ}$ C and 40 $^{\circ}$ C to show that aggregates form for these block copolymers even when organic solvents are used. This explains the unusual behavior observed in SEC analysis (discussion in main text). The macroinitiators do not aggregate in THF: their volume histograms have a single peak centered at ~5 nm (or below), which is more consistent with unimers rather than larger aggregates.



Figure S40. DLS histogram of PHFBA₂₅-*b*-PDMAEM₉₇ in THF showing the intensity (solid line) and volume (dotted line) in 20 °C (purple) and 40 °C (orange) dispersions.



Figure S41. DLS histogram of PTDFOA₁₀-*b*-PDMAEM₆₄ in THF showing the intensity (solid line) and volume (dotted line) in 20 °C (purple) and 40 °C (orange) dispersions.



10. NMR Characterization

¹H NMR Spectra



Figure S43. ¹H NMR spectrum of the PHFBA₂₅ homopolymer in CDCI₃.





















ppm -80 -85 -90 -95 -100 -105 -110 -115 Figure S58. ¹⁹F NMR spectrum of the PHFBA₂₅-*b*-PDMAEM₉₇ block copolymer in CDCl₃.







Figure S62. ¹⁹F NMR spectrum of the PTDFOA₁₀-*b*-PDMAEM₈₈ block copolymer in CDCl₃.





¹³C NMR spectra













11. References

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