SUPPORTING INFORMATION

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

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## 1. Nomenclature and Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AiBN</td>
<td>2,2’-azobis(2-methylpropionitrile)</td>
</tr>
<tr>
<td>CPCPA</td>
<td>4-cyano-4-(phenylcarbonothioylthio) pentanoic acid</td>
</tr>
<tr>
<td>CTA</td>
<td>chain transfer agent</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>DMAEM</td>
<td>2-(dimethylamino)ethyl methacrylate</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>HFBA</td>
<td>2,2,3,3,4,4,4-heptafluorobutyl acrylate</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number-average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight-average molecular weight</td>
</tr>
<tr>
<td>PFDA</td>
<td>1H,1H,2H,2H-perfluorodecyl acrylate</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>RAFT</td>
<td>reversible addition-fragmentation transfer</td>
</tr>
<tr>
<td>RID</td>
<td>refractive index detector</td>
</tr>
<tr>
<td>SEC</td>
<td>size exclusion chromatography</td>
</tr>
<tr>
<td>TDFOA</td>
<td>3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TFT</td>
<td>$\alpha,\alpha,\alpha$-trifluorotoluene</td>
</tr>
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</table>
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 μm 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 kx4 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

![Chemical structure 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 chilled hexane. The solid was filtered 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.

\[\begin{align*}
\text{Synthesis of the Block-Copolymers} \\
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\end{align*}\]
<table>
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<tr>
<th>Entry</th>
<th>Monomer</th>
<th>Initiator</th>
<th>CTA</th>
<th>[M]_i:[CTA]:[I]</th>
<th>T (°C)</th>
<th>t (hrs)</th>
<th>Yield (%)</th>
<th>NMR M&lt;sub&gt;n&lt;/sub&gt; (g/mol)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>SEC M&lt;sub&gt;w&lt;/sub&gt; (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SEC M&lt;sub&gt;n&lt;/sub&gt; (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1</td>
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<td>AiBN</td>
<td>CPCPA</td>
<td>150:1:0.1 (Mol %)</td>
<td>73</td>
<td>5</td>
<td>44</td>
<td>5900</td>
<td>7800</td>
<td>6200</td>
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<tr>
<td>2</td>
<td>TDFOA</td>
<td>AiBN</td>
<td>CPCPA</td>
<td>180:1:0.1 (Mol %)</td>
<td>73</td>
<td>5</td>
<td>38</td>
<td>4200</td>
<td>4400</td>
<td>4800</td>
<td>1.09</td>
</tr>
<tr>
<td>3</td>
<td>PFDA</td>
<td>AiBN</td>
<td>CPCPA</td>
<td>180:1:0.1 (Mol %)</td>
<td>73</td>
<td>5</td>
<td>31</td>
<td>3200</td>
<td>3700</td>
<td>3400</td>
<td>1.09</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined from <sup>1</sup>H NMR spectroscopy using the following formula: \( M_n = M_{CTA} + M_{monomer} \times (DP_n \text{ of monomer}) \) [Where, \( M_{CTA} = 279.38 \); \( M_{monomer} = 518.17, 418.15 \) and 254.10 for PFDA, TDFOA and HFBA, respectively; <sup>b</sup>Determined by SEC calibrated with linear polystyrene standards.}
Preparation of the Block-Copolymers

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.

$^1$H NMR of poly(HFBA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): 7.53 and 7.02 (endgroup), 4.54 (2H, -OCH$_2$(CF$_2$)$_2$CF$_3$), 4.06 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.96-2.87 (4H, -CH$_2$ of RAFT), 2.57 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.28 (6H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.2 (3H, -CH$_3$ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH$_2$ and -CH$_3$ backbone of PHFBA and PDMAEM).

$^{19}$F NMR poly(HFBA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): -82 (m, 3F, -CF$_3$) and -121 to -128 (m, 4F, (CF$_2$)$_2$).

$^1$H NMR of poly(TDFOA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): 7.55 and 7.01 (endgroup), 4.31 (2H, -OCH$_2$(CF$_2$)$_2$CF$_3$), 4.07 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.96-2.88 (4H, -CH$_2$ of RAFT), 2.5 (2H, -OCH$_2$CH$_2$(CF$_2$)$_2$CF$_3$), 2.57 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.29 (6H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.2 (3H, -CH$_3$ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH$_2$ and -CH$_3$ backbone of PTDFOA and PDMAEM).

$^{19}$F NMR poly(TDFOA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): -82.5 (m, 3F, -CF$_3$), -114.6 (m, 2F, CF$_2$CH$_2$) and -121 to -127 (m, 8F, (CF$_2$)$_4$).

$^1$H NMR of poly(PFDA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): 7.51 and 7.00 (endgroup), 4.28 (2H, -OCH$_2$(CF$_2$)$_2$CF$_3$), 4.07 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.96-2.87 (4H, -CH$_2$ of RAFT), 2.5 (2H, -OCH$_2$CH$_2$(CF$_2$)$_2$CF$_3$), 2.57 (2H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.28 (6H, -OCH$_2$CH$_2$N(CH$_3$)$_2$), 2.2 (3H, -CH$_3$ of RAFT), 2.47 and 2.1- 1.1 (8H, -CH, -CH$_2$ and -CH$_3$ backbone of PPFDA and PDMAEM).

$^{19}$F NMR poly(PFDA)-b-poly(DMAEM) (CDCl$_3$) $\delta$ (ppm): -82 (m, 3F, -CF$_3$), -114.7 (m, 2F, CF$_2$CH$_2$) and -123 to -127 (m, 12F, (CF$_2$)$_6$).
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.](image)

![Figure S2. $M_n$ of the block copolymers from the 2-, 4- and 6-hour copolymerization reactions of PTDFOA10 with DMAEM.](image)
Figure S3. $M_n$ of the block copolymers from the 2-, 4- and 6-hour copolymerization reactions of PPFDAs with DMAEM.
4. Dissolved Oxygen Measurements

General Procedure

Dissolved oxygen (DO) measurements were performed through a previously established method. 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 O2 for 1 minute, then capped and vigorously shaken. The caps were removed and DO values were recorded at $t = 5\text{min (oxygen atmosphere)}$ and at $t = 60\text{ min (air saturation)}$ (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 block 2-3 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.](image)
Figure S5. Oxygen concentrations at O\textsubscript{2} atmosphere and air saturation of block copolymers containing the PHFBA\textsubscript{25} fluorous block. Each plot compares PHFBA\textsubscript{25}-b-PDMAEM\textsubscript{97}, PHFBA\textsubscript{25}-b-PDMAEM\textsubscript{139}, PHFBA\textsubscript{25}-b-PDMAEM\textsubscript{180} and water collected under the same pH and temperature conditions.
**Figure S6.** Oxygen concentrations at O$_2$ atmosphere and air saturation of block copolymers containing the PPFDA$_6$ fluorous block. Each plot compares PPFDA$_6$-$b$-PDMAEM$_{114}$, PPFDA$_6$-$b$-PDMAEM$_{126}$, PPFDA$_6$-$b$-PDMAEM$_{138}$ and water collected under the same pH and temperature conditions.
Figure S7. Oxygen concentrations at O2 atmosphere and air saturation of block copolymers containing the PTDOFA10 fluorous block. Each plot compares the DO measurements of PTDOFA10-b-PDMAEM64, PTDOFA10-b-PDMAEM88, PTDOFA10-b-PDMAEM130 and water collected under the same pH and temperature conditions.
**Figure S8.** Oxygen concentrations at O₂ 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.
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.
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 PHFBA_{25}\text{-}b\text{-}PDMAEM_{97} block copolymer at pH 2.

Figure S13. Cryo-TEM images of the PHFBA_{25}\text{-}b\text{-}PDMAEM_{139} 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 S14. Cryo-TEM image of the PHFBA_{25}\text{-}b\text{-}PDMAEM_{180} block copolymer at pH 2.
Figure S15. Cryo-TEM images of the PTDOA\textsubscript{10}-b-PDMAEM\textsubscript{64} block copolymer at pH 2 showing A) a partially dried aggregate and B) an image with dried micelle on top of the ice and a core-shell structure in the ice.

Figure S16. Cryo-TEM image of the PTDOA\textsubscript{10}-b-PDMAEM\textsubscript{88} block copolymer at pH 2.

Figure S17. Cryo-TEM image of the PTDOA\textsubscript{10}-b-PDMAEM\textsubscript{130} 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 PPFDA\textsubscript{6}-b-PDMAEM\textsubscript{114} block copolymer at pH 2 showing A, C) core-shell structures that formed above the ice B) random aggregates and “broken glass” structures.
Summary of Observations

Samples of the PPFDAb-PDMAEM114, PPFDAb-PDMAEM126, PTDOFAb-PDMAEM64 and PHFBA25-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-PDMAEM139) Figure S74A and C (PPFDAb-PDMAEM114) and Figure S75A (PPFDAb-PDMAEM126). Figure S71A shows a PTDOFAb-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.
Figure S23. A) Height and B) Phase AFM images of the PPFDA$_6$-b-PDMAEM$_{114}$ 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 PPFDA$_6$ macroinitiator and the corresponding block copolymers in THF.

Figure S25. SEC traces (RID) of the PTDOA$_{10}$ macroinitiator and the corresponding block copolymers in THF.

Figure S26. SEC traces (RID) of the PHFBA$_{25}$ 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 PHFBA$_{25}$-b-PDMAEM$_{97}$ 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 °C, pH 7. We found that under these conditions, the lower critical solution temperature of the DMEAM block 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 H$_2$SO$_4$; 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.
Figure S27. DLS measurements of PHFBA_{25-b-PDMAEM_{97}} dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S28. DLS measurements of PHFBA\textsubscript{25-}b-PDMAEM\textsubscript{139} dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S29. DLS measurements of PHFB\textsubscript{25-b-PDMAEM\textsubscript{180}} dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S30. DLS measurements of PPFDA₆-b-PDMAEM₁₁₄ dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S31. DLS measurements of PPFDA_{6-b}-PDMAEM_{126} dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S32. DLS measurements of PPFDAn-b-PDMAEM138 dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S33. DLS measurements of PTDFOA10-b-PDMAEM64 dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S34. DLS measurements of PTDOA10-\textit{b}-PDMAEM88 dispersions under different conditions over time A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
Figure S35. DLS measurements of PTDOA\textsubscript{10-}b-PDMAEM\textsubscript{130} dispersions under different conditions over time; A, C and E) compares polymer dispersions at constant pH and B, D and F) compares polymer dispersions at constant temperature.
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 PPFDA\(_6\) fluorous block. Each plot compares the DLS measurements of PPFDA\(_6\)-b-PDMAEM\(_{114}\) (purple), PPFDA\(_6\)-b-PDMAEM\(_{126}\) (green) and PPFDA\(_6\)-b-PDMAEM\(_{138}\) (orange) collected under the same pH and temperature conditions.
Figure S38. DLS measurements of block copolymers containing the PTDOA10 fluorous block. Each plot compares the DLS measurements of PTDOA10-b-PDMAEM_{64} (purple), PTDOA10-b-PDMAEM_{88} (green) and PTDOA10-b-PDMAEM_{130} (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 \(~40\,^\circ C\) \cite{a4}. 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 PHFBA_{25-b-PDMAEM}x block copolymer dispersions where oxygen solubility decreased with increasing pH.

Although PTDOFA_{10-b-PDMAEM}x dispersions did display slightly higher concentrations of oxygen that PPFDA_{6-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 PHFBA_{25-b-PDMAEM}x dispersions and therefore cannot dissolve oxygen as well. This decreased stability led to the negligible effects of fluorine content within the PTDOFA_{10-b-PDMAEM}x and PPFDA_{6-b-PDMAEM}x dispersions.

Table S3 Z-average and PDI as determined by DLS at different temperatures and pH levels.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>pH 7</th>
<th>pH 5</th>
<th>pH 2</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Temp (°C)</td>
<td>Z-Avg. (d. nm)</td>
<td>PDI</td>
</tr>
<tr>
<td>1</td>
<td>PHFBA_{25-b-PDMAEM}97</td>
<td>4</td>
<td>232</td>
<td>0.237</td>
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<tr>
<td>2</td>
<td>PHFBA_{25-b-PDMAEM}97</td>
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<td>198</td>
<td>0.226</td>
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<td>817</td>
<td>0.028</td>
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<td>4</td>
<td>PHFBA_{25-b-PDMAEM}139</td>
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<td>0.499</td>
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<tr>
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<td>0.634</td>
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<td>0.725</td>
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<td>0.614</td>
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<tr>
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<td>218</td>
<td>0.136</td>
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<tr>
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<td>PPFDA_{6-b-PDMAEM}38</td>
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<td>82</td>
<td>0.783</td>
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<td>PPFDA_{6-b-PDMAEM}38</td>
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<td>166</td>
<td>0.146</td>
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</tbody>
</table>
Measurements at Low Concentrations

The general DLS experiments (above) were performed to explore the effects of different pH and temperatures on the self-assembly 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.

Figure S39. Intensity (lined) and volume (dashed) DLS histograms collected for each block copolymer at pH 2, 20 °C using 2 mg/mL (black) and 10 mg/mL (green) dispersions.
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.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>3 mg/mL Dispersions</th>
<th>10 mg/mL Dispersions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d. nm (percent)</td>
<td>PDI</td>
<td>Z-Avg. (nm)</td>
<td>d. nm (percent)</td>
</tr>
<tr>
<td>PHFBA25-b-PDMAEM97</td>
<td>400 (90 %), 91 (10 %)</td>
<td>0.320</td>
<td>268</td>
<td>519 (95 %), 76 (5 %)</td>
</tr>
<tr>
<td>PHFBA25-b-PDMAEM139</td>
<td>365 (95 %), 33 (5 %)</td>
<td>0.282</td>
<td>285</td>
<td>530 (94 %), 105 (6 %)</td>
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<tr>
<td>PHFBA25-b-PDMAEM180</td>
<td>360 (94 %), 46 (6 %)</td>
<td>0.457</td>
<td>261</td>
<td>622 (91 %), 146 (9 %)</td>
</tr>
<tr>
<td>PTDOA10-b-PDMAEM64</td>
<td>245 (88 %), 35 (12 %)</td>
<td>0.554</td>
<td>142</td>
<td>412 (84 %), 76 (11 %), 14 (5 %)</td>
</tr>
<tr>
<td>PTDOA10-b-PDMAEM88</td>
<td>390 (63 %), 137 (26 %), 25 (11 %)</td>
<td>0.642</td>
<td>148</td>
<td>401 (60 %), 173 (34 %), 16 (6 %)</td>
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<tr>
<td>PTDOA10-b-PDMAEM130</td>
<td>399 (77 %), 66 (15 %), 18 (8 %)</td>
<td>0.577</td>
<td>183</td>
<td>696 (82 %), 165 (12 %), 20 (6 %)</td>
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<td>PPFDA11-b-PDMAEM114</td>
<td>236 (88 %), 20 (12 %)</td>
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<td>124</td>
<td>290 (91 %), 17 (9 %)</td>
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<tr>
<td>PPFDA11-b-PDMAEM126</td>
<td>217 (75 %), 1000, (18 %), 19 (7 %)</td>
<td>0.525</td>
<td>176</td>
<td>774 (70 %), 224 (30 %)</td>
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<tr>
<td>PPFDA11-b-PDMAEM138</td>
<td>242 (73 %), 42 (14 %), 17 (13 %)</td>
<td>0.588</td>
<td>95</td>
<td>317 (70 %), 173 (18 %), 13 (7 %)</td>
</tr>
</tbody>
</table>
Aggregation of Block-Copolymers in THF

DLS analysis of block copolymers from each macroinitiator in THF were run at 20 °C and 40 °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 PHFBA$_{25}$-b-PDMAEM$_{97}$ 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 PTDFOA$_{10}$-b-PDMAEM$_{64}$ in THF showing the intensity (solid line) and volume (dotted line) in 20 °C (purple) and 40 °C (orange) dispersions.
Figure S42. DLS histogram of PPFDA₆-b-PDMAEM₁₁₄ in THF showing the intensity (solid line) and volume (dotted line) in 20 °C (purple) and 40 °C (orange) dispersions.
10. NMR Characterization

$^1$H NMR Spectra

Figure S43. $^1$H NMR spectrum of the PHFBA$_{25}$ homopolymer in CDCl$_3$.

Figure S44. $^1$H NMR spectrum of the PTDFOA$_{10}$ homopolymer in CDCl$_3$. 
Figure S45. $^1$H NMR spectrum of the PPFDA$_6$ homopolymer in CDCl$_3$.

Figure S46. $^1$H NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{97}$ block copolymer in CDCl$_3$. 
Figure S47. $^1$H NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{139}$ block copolymer in CDCl$_3$.

Figure S48. $^1$H NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{180}$ block copolymer in CDCl$_3$. 
Figure S49. $^1$H NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{64}$ block copolymer in CDCl$_3$.

Figure S50. $^1$H NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{88}$ block copolymer in CDCl$_3$. 
Figure S51. $^1$H NMR spectrum of the PTDOA$_{10}$-b-PDMAEM$_{130}$ block copolymer in CDCl$_3$.

Figure S52. $^1$H NMR spectrum of the PPFDA$_{6}$-b-PDMAEM$_{114}$ block copolymer in CDCl$_3$. 
Figure S53. $^1$H NMR spectrum of the PPFD$_{66}$-b-PDMAEM$_{126}$ block copolymer in CDCl$_3$.

Figure S54. $^1$H NMR spectrum of the PPFD$_{66}$-b-PDMAEM$_{136}$ block copolymer in CDCl$_3$. 
**19F NMR spectra**

Figure S55. 19F NMR spectrum of the PHFBA25 homopolymer in CDCl3

Figure S56. 19F NMR spectrum of the PTDOA10 homopolymer in CDCl3
Figure S57. $^{19}$F NMR spectrum of the PPFDA$_6$ homopolymer in CDCl$_3$.

Figure S58. $^{19}$F NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{97}$ block copolymer in CDCl$_3$. 
Figure S59. $^{19}$F NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{139}$ block copolymer in CDCl$_3$.

Figure S60. $^{19}$F NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{180}$ block copolymer in CDCl$_3$. 
Figure S61. $^{19}$F NMR spectrum of the PTFOA$_{10}$-b-PDMAEM$_{64}$ block copolymer in CDCl$_3$.

Figure S62. $^{19}$F NMR spectrum of the PTFOA$_{10}$-b-PDMAEM$_{88}$ block copolymer in CDCl$_3$.
Figure S63. $^{19}$F NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{130}$ block copolymer in CDCl$_3$.

Figure S64. $^{19}$F NMR spectrum of the PPFDA$_b$-b-PDMAEM$_{114}$ block copolymer in CDCl$_3$. 
Figure S65. $^{19}$F NMR spectrum of the PPFD$_a$-$b$-PDMAEM$_{126}$ block copolymer in CDCl$_3$.

Figure S66. $^{19}$F NMR spectrum of the PPFD$_a$-$b$-PDMAEM$_{138}$ block copolymer in CDCl$_3$. 
Figure S67. $^{13}$C NMR spectrum of the PHFBA$_{25}$ homopolymer in CDCl$_3$.

Figure S68. $^{13}$C NMR spectrum of the PTDOA$_{10}$ homopolymer in CDCl$_3$. 
Figure S69. $^{13}$C NMR spectrum of the PHFBA_{25}-b-PDMAEM_{97} block copolymer in CDCl$_3$.

Figure S70. $^{13}$C NMR spectrum of the PHFBA_{25}-b-PDMAEM$_{139}$ block copolymer in CDCl$_3$. 
**Figure S71.** $^{13}$C NMR spectrum of the PHFBA$_{25}$-b-PDMAEM$_{180}$ block copolymer in CDCl$_3$.

**Figure S72.** $^{13}$C NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{64}$ block copolymer in CDCl$_3$. 
Figure S73. $^{13}$C NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{88}$ block copolymer in CDCl$_3$.

Figure S74. $^{13}$C NMR spectrum of the PTDFOA$_{10}$-b-PDMAEM$_{130}$ block copolymer in CDCl$_3$. 
Figure S75. $^{13}$C NMR spectrum of the PPFDA$_6$-b-PDMAEM$_{114}$ block copolymer in CDCl$_3$.

Figure S76. $^{13}$C NMR spectrum of the PPFDA$_6$-b-PDMAEM$_{126}$ block copolymer in CDCl$_3$. 
Figure S77. $^{13}$C NMR spectrum of the PPFDA$_6$-b-PDMAEM$_{138}$ block copolymer in CDCl$_3$. 
11. References