Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

For

pH-Switchable Polymer Nanostructures for Controlled Release

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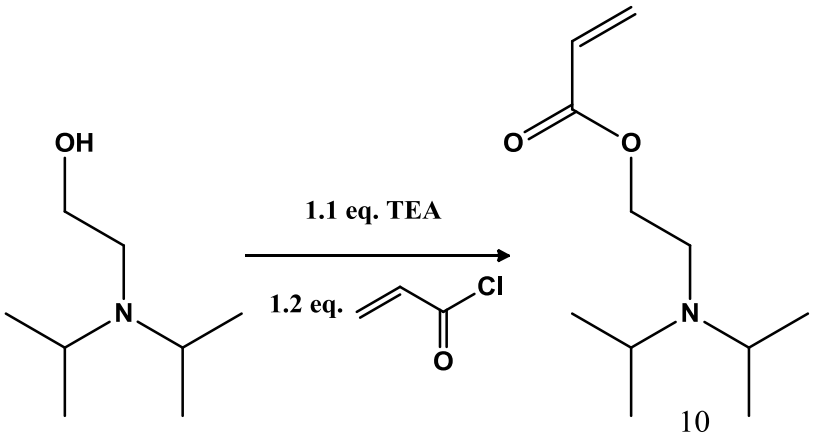
Attempted Polymerizations of *N, N*-diisopropylamino ethylene acrylate

Synthesis of the monomer



Scheme S1. The synthesis of *N, N*-diisopropylamino ethylene acrylate **10**.

2-(*N, N*-diisopropyl)amino ethanol (1.21 mL, 6.89 mmol) and triethylamine (1.06 mL, 7.57 mmol) were dissolved in chloroform (10 mL) and cooled to 0°C. Acryloyl chloride (0.671 mL, 8.26 mmol) in 5 mL chloroform was added dropwize over 1 hour, and the reaction mixture allowed to warm to room temperature before stirring overnight. The solvent was removed in *vacuo*, the reaction mixture redissolved in CH_2Cl_2 (40 mL) and washed with 1M NaOH (5 x 40 mL). The product, **10**, was isolated as an orange viscous liquid (1.33 g, 6.69 mmol, 97% yield). ^{1}H NMR (400MHz, $CDCl_3$): δ 6.33 (dd, 1H, J_1 = 17.4 Hz, J_2 = 1.6 Hz, CH_2CHAcO), 6.05 (dd, 1H, J_1 = 10.4 Hz, J_2 = 17.4 Hz, CH_2C*H*AcO), 5.73 (dd, J_1 = 1.6 Hz, J_2 = 10.4 Hz, CH_2CHAcO 1H), 4.02 (t, 2H, J = 7.2 Hz, C_2H_3AcOCH_2), 2.94 (m, 2H, N(C*H*Me_2)$_2$), 2.61 (t, 2H, J = 7.2 Hz, *i*Pr_2NCH_2), 0.94 (d, 12H, J = 6.4 Hz, *i*Pr). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 166.2, 130.4, 128.7, 65.3, 49.3, 43.7, 20.8. ESI MS: Expected 199.16, Found 200.0 $[M+H]^+$.

Polymerization data

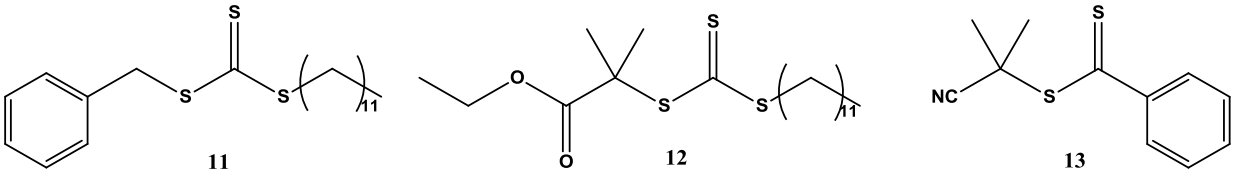


Figure S1. The different CTAs used to polymerize monomer, **10.**

Table S1. Different conditions tried in the attempts to polymerize the monomer **10.**

Entry	CTA	[M]	[AIBN] w.r.t [CTA]	Solvent[a]	Temp / °C	Time / h	Conv / %	M_n (SEC) / kDa	M_w/M_n [b]
1	**11**	60	0.1	DMF	80	24	0	-	-
2	**11**	60	0.1	DMF	80	48	0	-	-
3	**11**	60	0.2	DMF	90	20	0	-	-
4	**11**	60	0.2	DMF	90	44	0	-	-
5	**12**	60	0.1	DMF	80	20	0	-	-
6	**12**	60	0.2	dioxane	70	25	35	2.5	1.32
7	**12**	60	0.2	*bulk*	70	25	41	2.9	2.23
8	**12**	100	0.2	dioxane	70	23	21	2.1	1.33
9	**12**	60	0.3	dioxane	70	23	40	3.0	1.35
10	**12**	60	0.3	dioxane	70	22	38		
11	**12**	60	0.5	dioxane	70	24	57	3.3	1.44
12	**12**	60	0.2	toluene	70	24	25		
13	**12**	60	0.2	dioxane*	70	24	33	2.1	1.43
14	**13**	100	0.3	DMF	90	21	24		

[a] Monomer :solvent1: 1 w/v
* Monomer:solvent 3: 1 w/v
[b] THF SEC, PMMA standards

Table S2. Kinetics of polymerization with CTA **12** with [M]:[**12**]:[AIBN] = 60:1:0.3 at 70°C in dioxane.

Time/ h	Conversion/ %
1	22
2	30
3	36
4	36
5	37
6	36
8	37
22	39
47	39

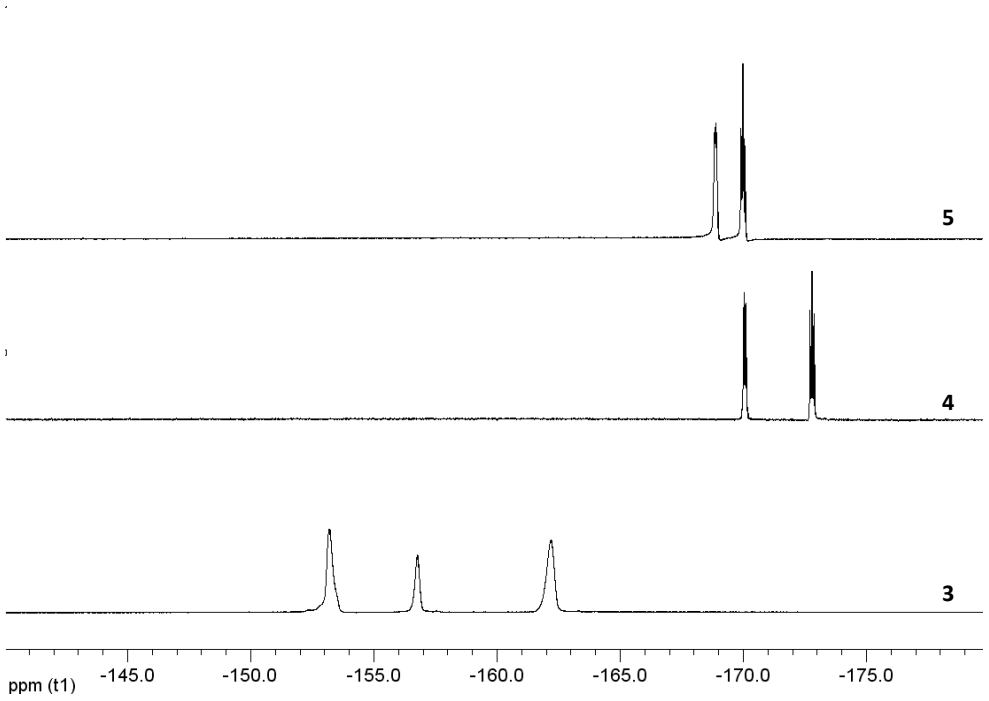


Figure S2. ^{19}F NMR spectra of polymers **3**, **4** and **5** showing the disappearance of the broad polymer peaks and the appearance of the sharp pentafluorophenol peaks upon substitution. Two of the expected three peaks are seen, the third is expected at -185 ppm, which is out of range of the spectrometer.

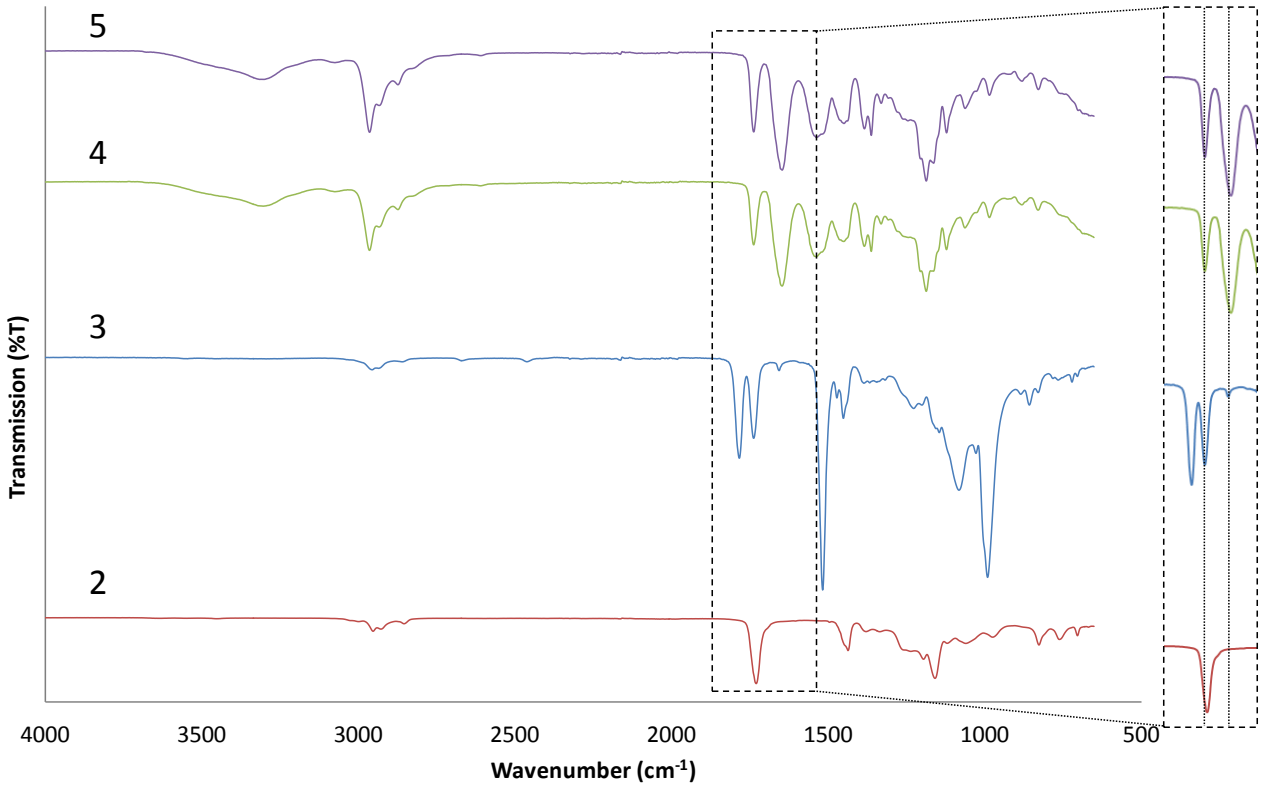


Figure S3. FT-IR data for polymers **2**, **3**, **4** and **5**, with an expansion (1750-1500 cm^{-1}) showing the conversion of the PFPA ester bonds to amide bonds.

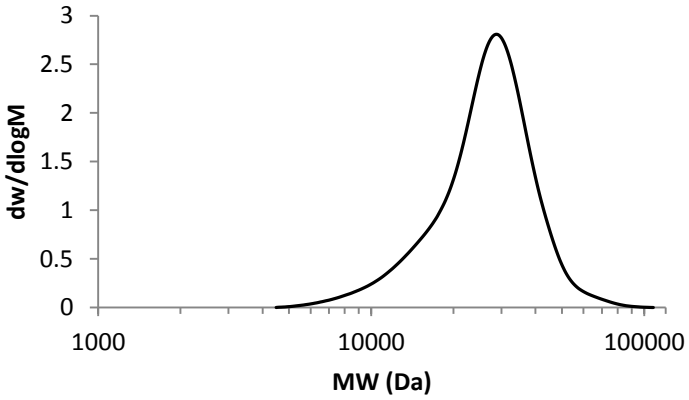


Figure S4. SEC trace (in DMF) for polymer **4.**

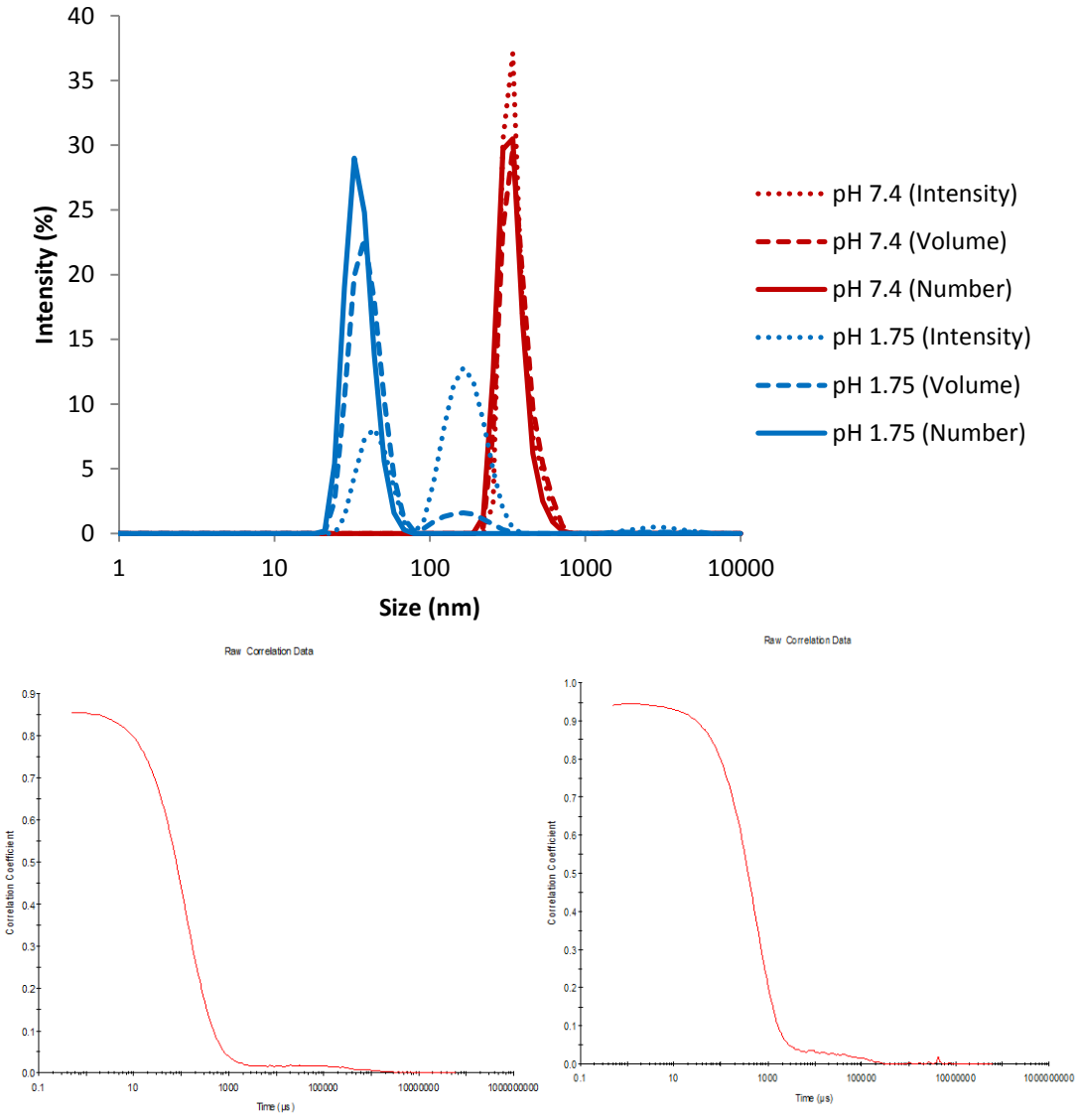


Figure S5. Top) DLS data for self-assemblies formed from polymer **4** at acidic and basic pH values. Bottom left) Raw correlation data for the structures formed at acidic pH and bottom right) raw correlation data for the structures formed at basic pH.

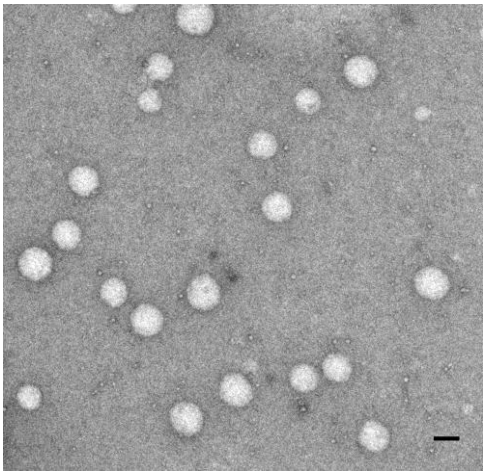


Figure S6. TEM image of polymer **4** self-assembled at basic pH, stained with uranyl acetate, scale bar = 300 nm.

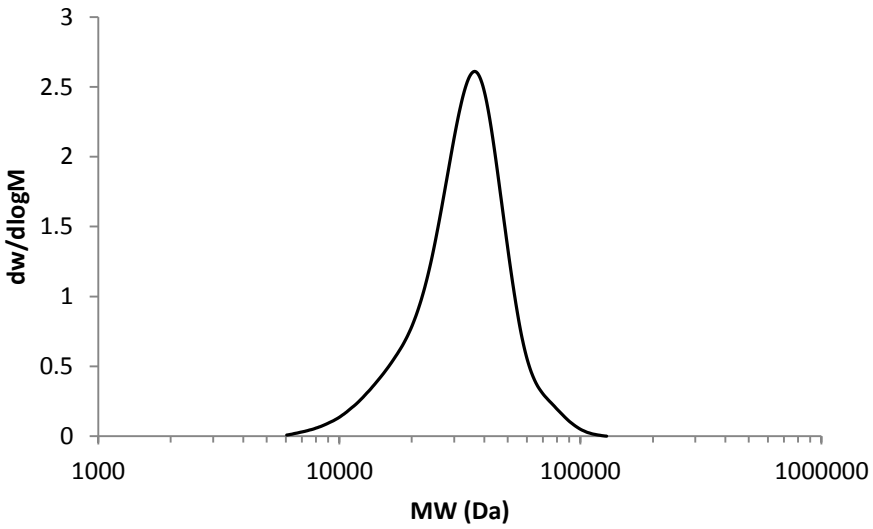


Figure S7. SEC trace (in DMF) for polymer **5**.

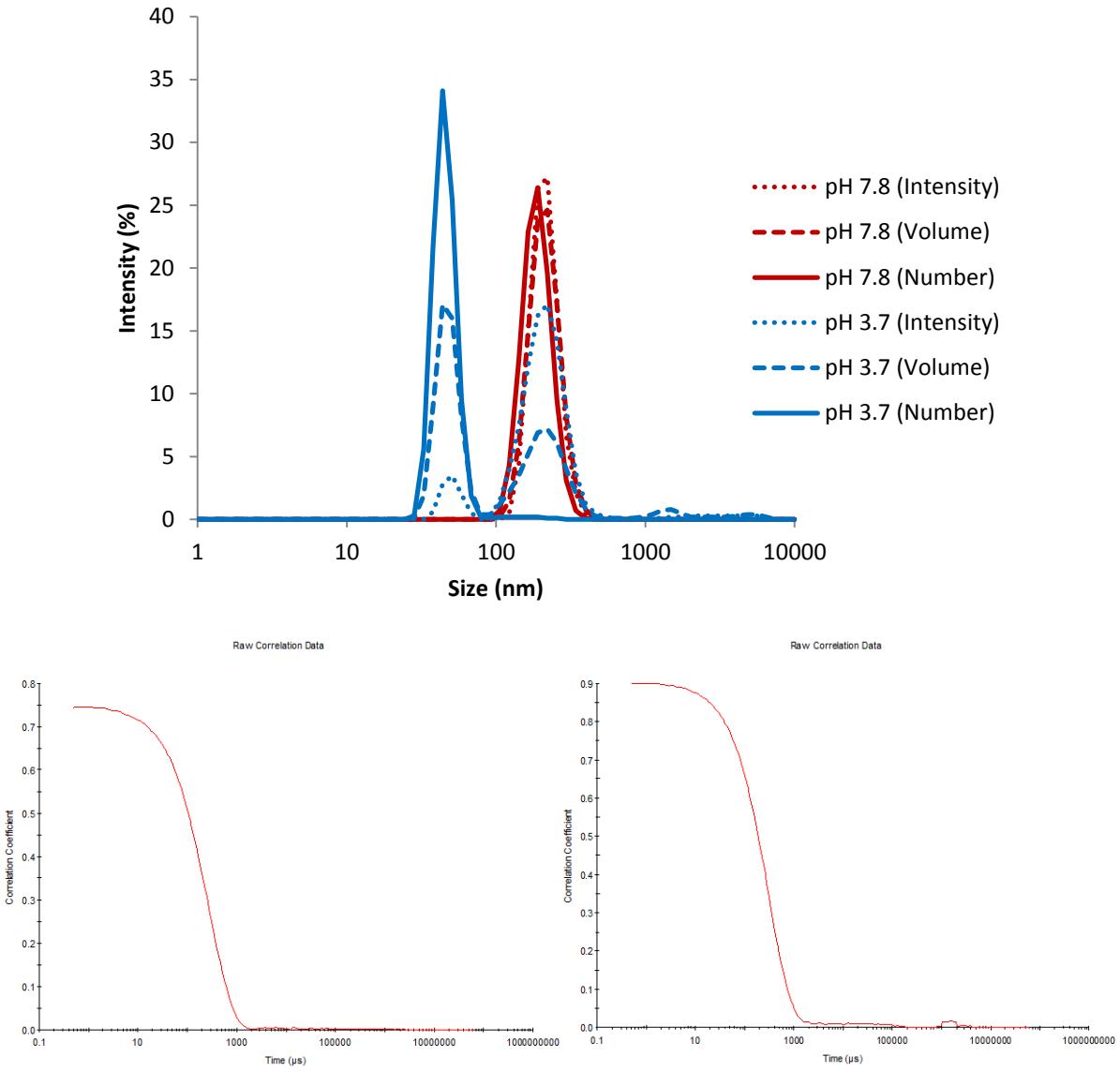


Figure S8. Top) DLS data for self-assemblies formed from polymer **5** at acidic and basic pH values. Bottom left) Raw correlation data for the structures formed at acidic pH and bottom right) raw correlation data for the structures formed at basic pH.

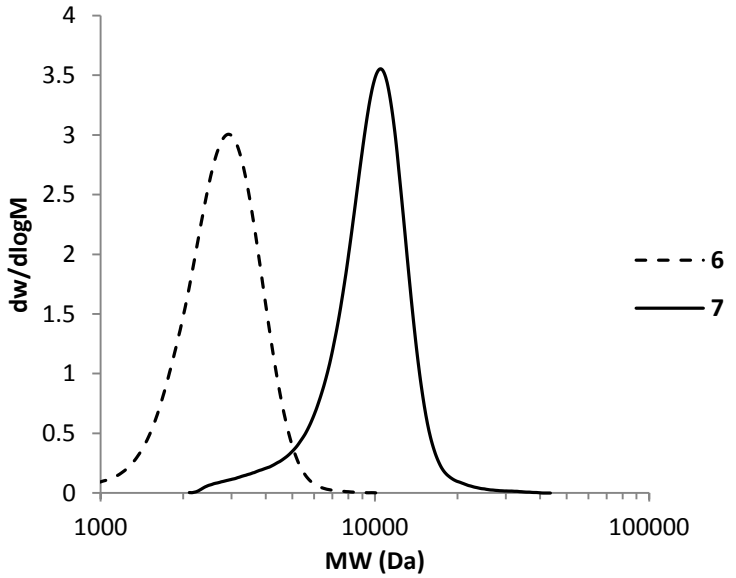


Figure S9. SEC traces (in DMF) showing the chain extension of homopolymer **6** to form diblock copolymer **7**.

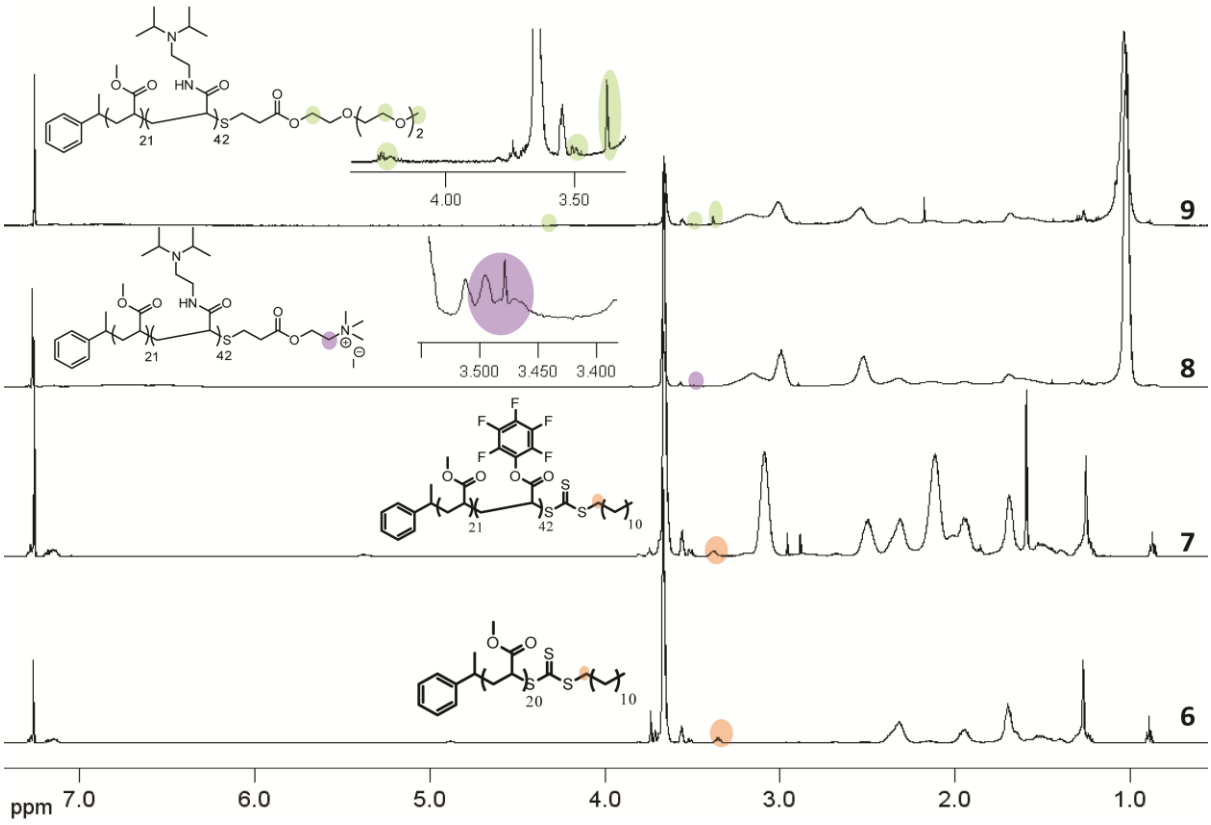


Figure S10. ^{1}H NMR spectra of **6**, **7**, **8** and **9** in $CDCl_3$ with key end group signals highlighted.

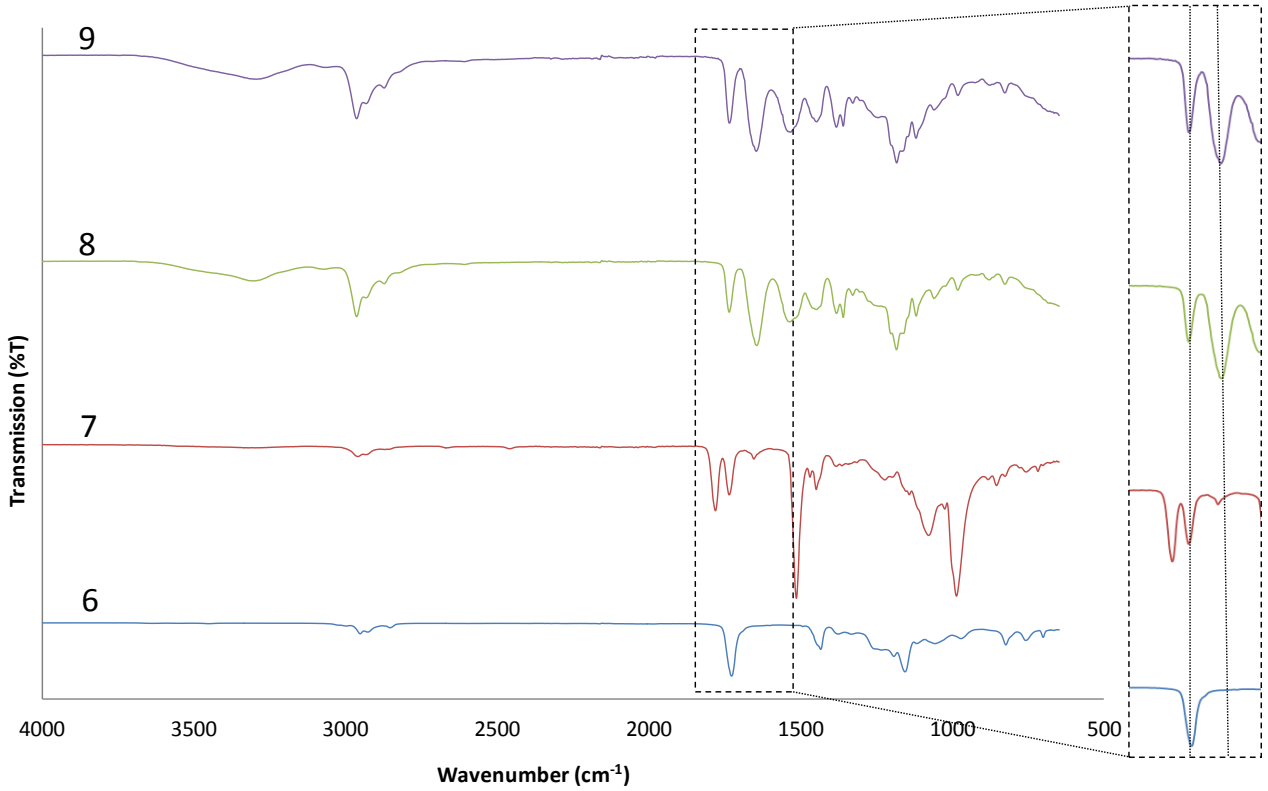


Figure S11. FT-IR data for polymers **6**, **7**, **8** and **9**, with an expansion (1750-1500 cm^{-1}) showing the conversion of the PFPA ester bonds to amide bonds.

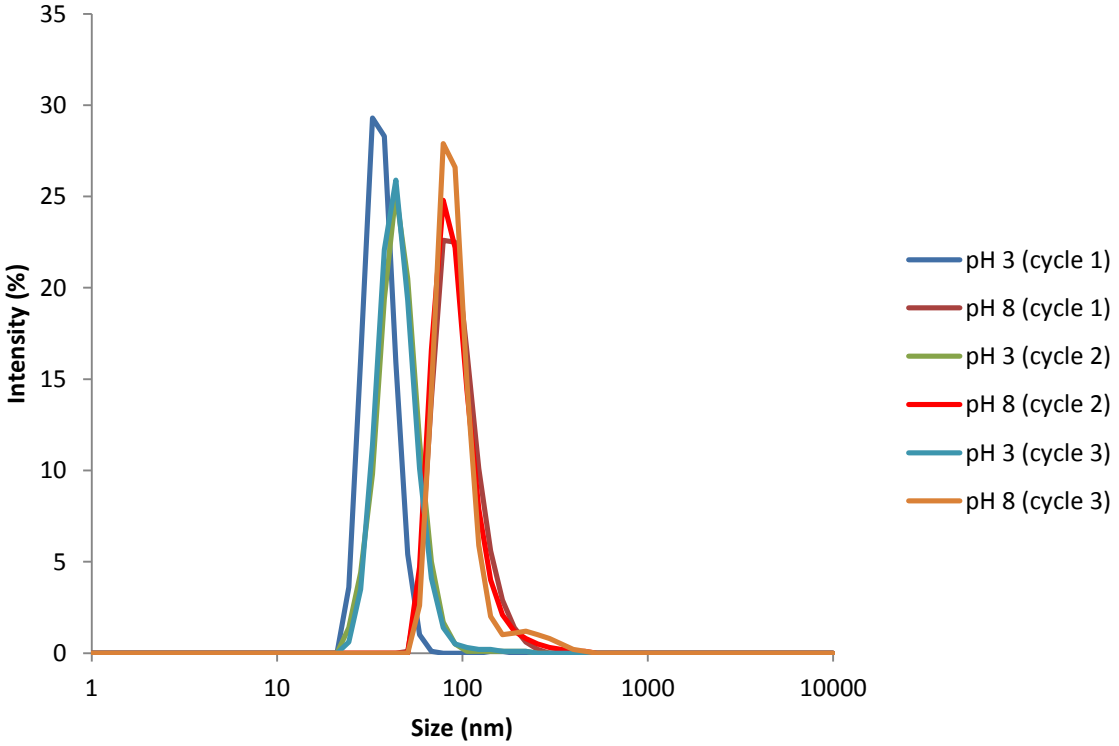


Figure S12. DLS size by number data showing the switching behaviour for polymer **8** for three cycles from pH 3 to pH 8.

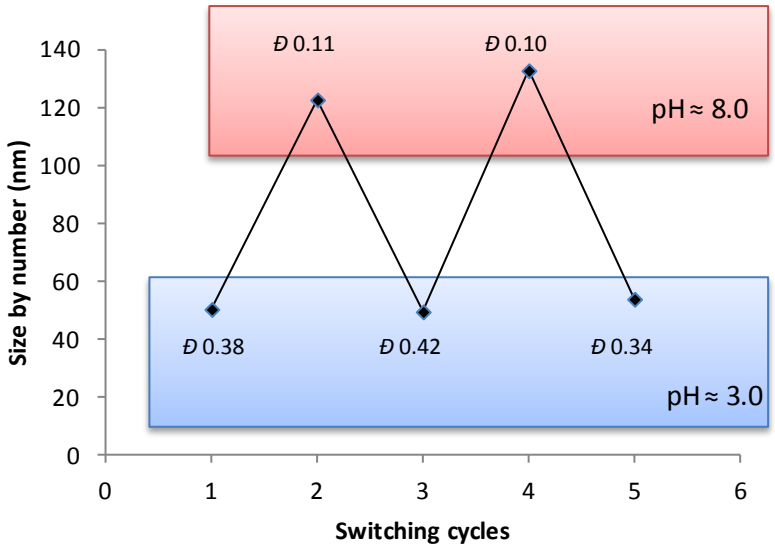


Figure S13. Graph of size by DLS against cycle number to highlight the reversible switching behaviour of **9** with cycling pH values.

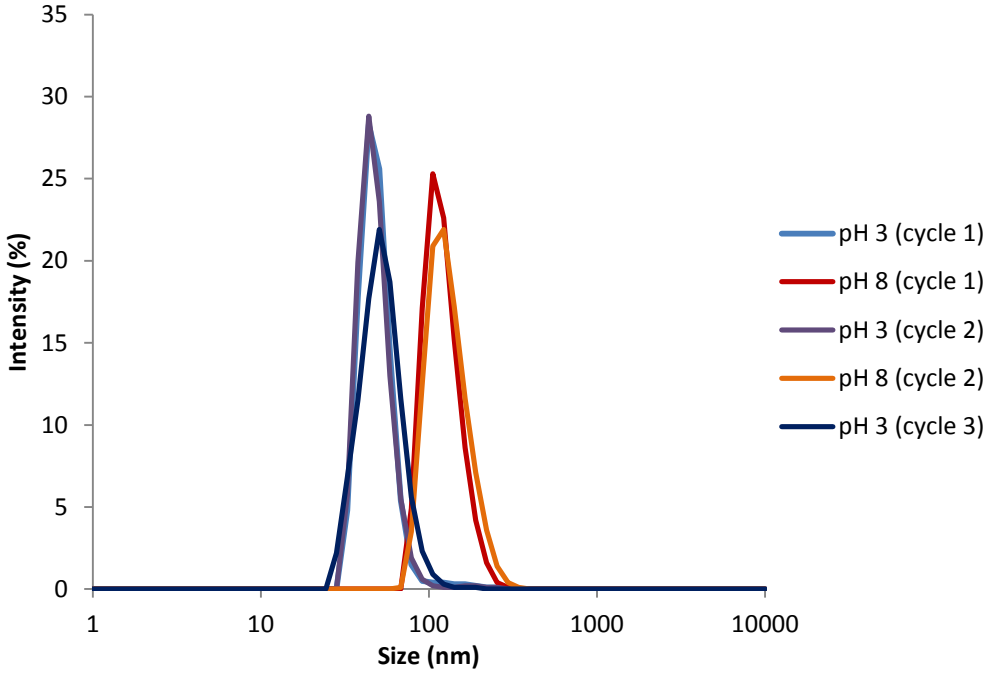


Figure S14. DLS size by number data showing the switching behaviour for **9** for three cycles from pH 3 to pH 8.