Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information on the paper

Gradient and asymmetric copolymers: The role of the copolymer composition profile in the ionization of weak polyelectrolytes

1 Explanation of the process used to select the profiles of D and T

The profiles of the copolymers D and T were selected as simple structures containing only two or three blocks that nevertheless closely mimicked the gradient composition profile. In order to do so, copolymers were designed which matched both the overall composition of the gradient copolymer (50 mol % acrylic acid, AA) and also the average location of AA units within the polymer chain.

The gradient copolymer G has a linear composition profile ranging from 100 mol % AA to 0 mol % AA. Its overall composition is 50 mol % AA. The average position of the acrylic acid units, measured from the AA-rich terminus is given by:

$$\overline{x_G} = \frac{\int_0^1 x(1-x)\,dx}{\int_0^1 (1-x)\,dx} = \frac{1}{3} \approx 0.33$$

D consists of two blocks of equal length, containing 84 and 16 mol % AA respectively. Its overall composition is 50 mol % AA. The average position of the AA units, measured from the AA-rich terminus is given by:

$$\overline{x_D} = \frac{\int_0^{0.5} 0.84x\,dx + \int_{0.5}^{1} 0.16x\,dx}{\int_0^{0.5} 0.84\,dx + \int_{0.5}^{1} 0.16\,dx} = 0.33$$

T consists of two short terminal blocks of poly(acrylic acid) (PAA) and poly(*n*-butyl acrylate) (P*n*BA) respectively, each corresponding to 21 mol% of the total length of the polymer. The central block, corresponding to the remaining 58 mol % of the polymer, is a 50 mol % statistical copolymer of AA and *n*BA. The overall composition of AA is 50 AA%. The average position of the AA units, measured from the AA-rich terminus is given by:

$$\overline{x_T} = \frac{\int_0^{0.21} x\,dx + \int_{0.21}^{0.79} 0.5x\,dx}{\int_0^{0.21} 1\,dx + \int_{0.21}^{0.79} 0.5x\,dx} = 0.33$$

Thus D, T and G share both their overall composition and the average location of AA units in the chain. For comparison, the average location of the AA units in the block copolymer B consisting of equal parts PAA and P*n*BA is

$$\overline{x_B} = \frac{\int_0^{0.5} x\,dx}{\int_0^{0.5} 1\,dx} = 0.25$$

While that of the statistical copolymer containing 50 mol % AA units ($S_{50\%}$) is:

$$\overline{x_S} = \frac{\int_0^1 0.5x\,dx}{\int_0^1 0.5\,dx} = 0.5$$

2. Polymer synthesis

Materials

1,4-dioxane, dichloromethane (DCM), acetone, and methanol were purchased from TCI and used as received. 1,1′-Azobis(cyclohexanecarbonitrile) (ACHN), trifluoroacetic acid (TFA), azobisisobutyronitrile (AIBN), and anisole were purchased from Sigma Aldrich and used as received. *n*-Butyl acrylate (*n*BA) and *tert*-Butyl acrylate (*t*BA) were bought from TCI and stirred with inhibitor remover (purchased from Sigma Aldrich) for 30 minutes before use. Cyanomethyl dodecyl trithiocarbonate (chain transfer agent, CTA) were purchased from Strem Chemicals, lnc. and used as received. Methanol and distilled water were used for polymer precipitation. 1,3,5-trioxane was purchased from Sigma Aldrich and used as received. Deuterated chloroform ($CDCl_3$), deuterated dimethyl sulfoxide (DMSO-d_6), and acetone-d_6 obtained from Eurisotop were used as solvent for proton nuclear magnetic resonance (^{1}H NMR) analysis.

Size Exclusion Chromatography (SEC)

Number-average molar masses (M_n, SEC) and dispersities (*Đ*) of polymers were determined using SEC

SEC system at Laboratoire IMRCP, Université de Toulouse: The SEC analyses were conducted on a system composed of Waters 515 HPLC pump, Agilent 1260 Autosampler, Varian ProStar 500 column valve module, set of three Waters columns (Styragel Guard Column, 20 µm, 4.6 mm × 30 mm, Styragel HR3, 5 µm, 7.8 mm × 300 mm and Styragel HR4E, 5 µm, 7.8 mm × 300 mm), Varian ProStar 325 UV-Vis detector set at 290 nm and Wyatt Optilab rEX differential refractive index detector using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1} (35 °C). The column system was calibrated with poly(methyl methacrylate) (PMMA) standards (ranging from 1120 to 138600 g mol^{-1}). Samples were diluted to a concentration about 2.5 mg mL^{-1} and filtered through 0.45 µm Nylon syringe filters before injection.

SEC system at IOMC, JCSM, Friedrich Schiller University Jena: The measurements were performed on a Shimadzu system equipped with a CBM-20A system controller, an LC-10AD VP pump, a RID-10A refractive index detector and a PSS SDV column. The eluent was a chloroform/isopropanol/trimethylamine (94%/2%/4%, v/v/v) solvent mixture. Samples were run at 1 mL min^{-1} at 40 °C. PMMA standards (molar mass range is ca. 400 – 100000 g mol^{-1}) were used for calibration. Analyzed samples were filtered through a PVDF membrane with 0.22 µm pore size before injection.

a) Synthesis of the P*t*BA-*b*-P*n*BA (B)

Stock solutions for the synthesis of block copolymer B

Stock solution A: CTA (1.27 g, 4.00 mmol) and AIBN (0.066 g, 0.40 mmol) were dissolved in 1,4-dioxane (29.5 g, 28.6 mL, 335 mmol) to yield a solution with a total volume of 30 mL. This stock solution was frozen at 3 °C and melted before use.

Stock solution B: AIBN (0.066 g, 0.40 mmol) was dissolved in 1,4-dioxane (30.8 g, 29.9 mL, 350 mmol) to yield a solution with a total volume of 30 mL. This stock solution was frozen at 3 °C and melted before use.

*n*BA (1.34 g, 1.5 mL, 10.45 mmol) was mixed with stock solution A (1.00 mL, 67 μmol CTA, 6.7 μmol AIBN) in a 15 mL vial, adjusted with 1,4-dioxane (2.5 mL) to 5 mL volume and sealed with a rubber septum. The obtained solution was degassed by sparging with Ar for 15 minutes and immersed into a thermostated heating block at 60 °C for 8 hours. An aliquot was analyzed with ^{1}H NMR to determine the monomer conversion (> 95%), then evaporated under vacuum and analyzed with SEC. The reaction mixture was concentrated under vacuum to remove the unreacted monomer, precipitated in a 10/90 (vol/vol) water/methanol mixture and dried under deep vacuum. This procedure resulted in a near quantitative yield of the originally added *n*BA to polymer. Then, the second monomer *t*BA (1.34 g, 1.5 mL, 10.45 mmol) and stock solution B (1.00 mL, 6.7 μmol AIBN) were added, adjusted with 1,4-dioxane (2.00 mL) to 5 mL volume and polymerized as described above, with > 95% conversion of the *t*BA monomer.

b) Synthesis of gradient copolymers P(*n*BA$_{50\%}$-*grad*-*t*BA$_{50\%}$) (G).

The gradient copolymer was synthesized at 90 °C with ACHN as a thermal initiator. An initial solution of CTA and ACHN in anisole was prepared and degassed by sparging with argon for 30 minutes. Degassed pure *t*BA (7.90 g, 9.0 mL, 61.6 mmol) and *n*BA (4.50g, 5.0 mL, 35 mmol) were added into the reaction mixture via syringe pumps at a total addition rate of 1.75 mL.h^{-1}. At the beginning of the polymerization, 0.875 mL of *n*BA was added in one shot to the reactor. Thereafter, the addition rate of each monomer was adjusted so that the rate of *t*BA addition increased linearly from 0 to 1.75 mL.h^{-1} over 6h, and on the contrary the rate of *n*BA decreased linearly from 1.75 to 0 mL.h^{-1} within 6h. At the final stage of the reaction, 2.63 mL of *t*BA were added during 3 h at 1.75 mL.h^{-1}. See Figure S1 for the addition program. Aliquots of the reaction mixture were taken at predetermined periods of time and analyzed with ^{1}H NMR and SEC (Figure S1) to determine the reaction mixture composition and macromolecular characteristics of the formed polymer. The final product was evaporated under vacuum and analyzed with SEC. The reaction mixture was concentrated under vacuum to remove the unreacted monomer, precipitated in in a 10/90 (vol/vol) water/methanol mixture and dried under deep vacuum. The final composition of the gradient copolymer was 43.9% BA, 56.1% *t*BA, and M_n = 28.9 kg mol^{-1}, $Đ$ = 1.35.

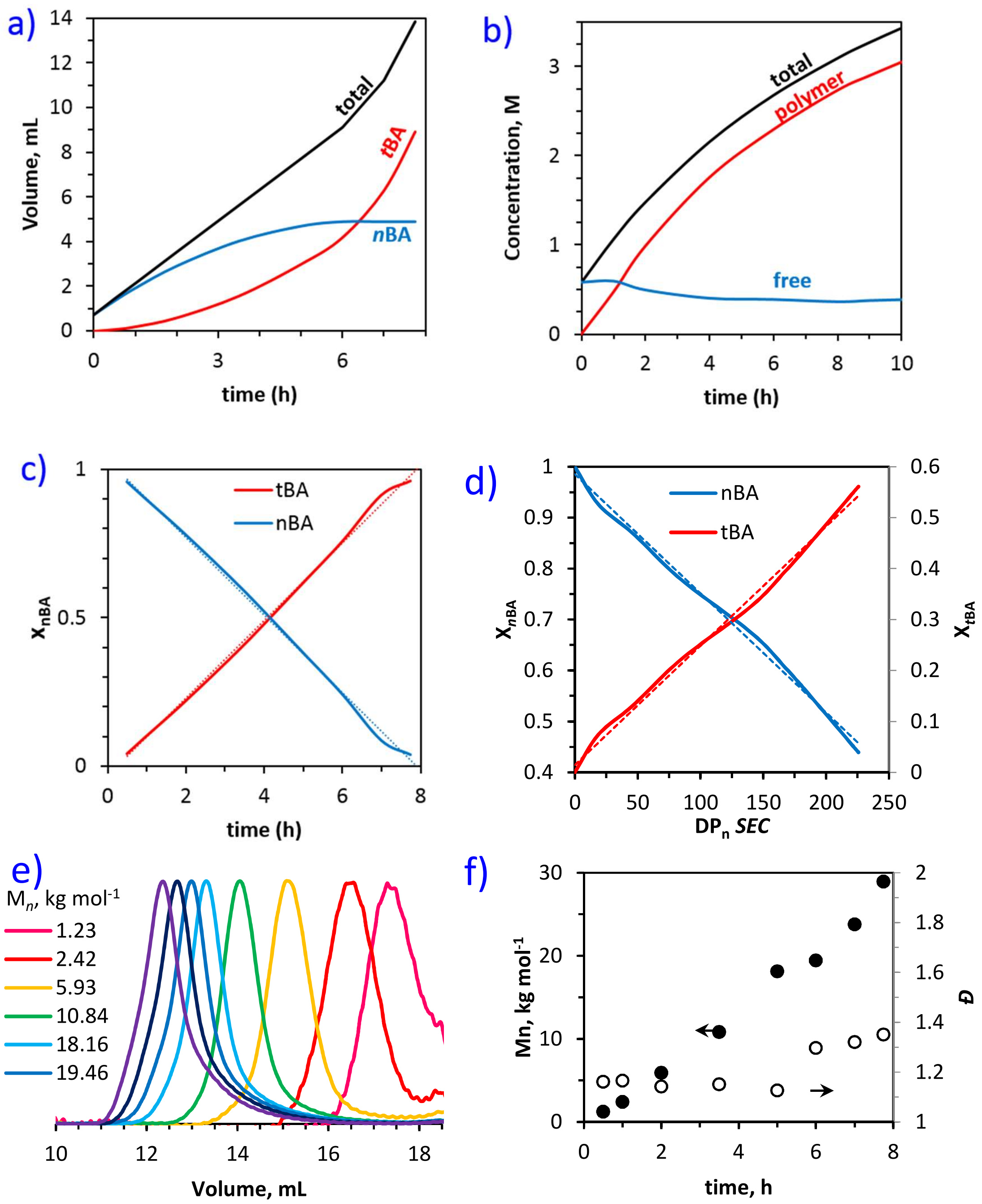

Figure S1. Data for the gradient copolymer poly(tBA$_{50\%}$-*grad*-nBA$_{50\%}$) G20: a) monomer addition program for the synthesis; b) composition of the reaction mixture over the course of the polymerization (molar concentration of nBA units in both monomer and polymer); c) composition of the free monomer mixture over the course of the polymerization; d) cumulative polymer composition of the copolymer; e) SEC traces evolution over the course of the polymerization (samples were analyzed in SEC system at Laboratoire IMRCP, Université de Toulouse); f) evolution of M_n and $Đ$ over the course of the polymerization: final $M_{\text{n,SEC}}$ = 28.9 kg mol^{-1}, $Đ$ = 1.35.

c) Synthesis of asymmetric diblock copolymer P(*t*BA$_{84\%}$-*stat*-*n*BA$_{16\%}$)-*b*-P(*t*BA$_{16\%}$-*stat*-*n*BA$_{84\%}$) (D)

Copolymerizations were performed in a Chemspeed Accelerator SLT automated parallel synthesizer using a sequential reagent addition and similar experimental protocols as reported elsewhere.[1-4]

Experiment for the first block: Stock solutions of CTA (100 mg mL^{-1} in dioxane) and AIBN (0.86 mg mL^{-1} in dioxane) were prepared. These solutions, *t*BA, and *n*BA were transferred into different containers and placed inside the automated synthesizer. Afterwards, aliquots of the prepared stock solution of CTA and AIBN, *t*BA, *n*BA, and solvent were transferred from the containers into the reactor (100 mL) of the synthesizer with the automated liquid handling system to provide the desired concentration of reagents resulting in a final volume of 10 mL (please note that volume change due to mixing of the reagents has been neglected). 1,3,5-Trioxane was added as internal standard at a concentration of 10 mg mL^{-1} of total reaction volume. Once all the reagents were in the reactor, each reaction mixture was subjected to a degassing procedure in parallel by sparging with inert gas (N_2) for 15 min at 0 °C. Thereafter, the reaction mixtures were heated to 60 °C for 11 h. During each polymerization, aliquots were periodically withdrawn under an inert gas flow (4, 6, 8, and 11 h) for ^{1}H NMR (0.075 mL) and SEC (0.05 mL) analysis. Once a molar mass of 10 000 g.mol^{-1} was obtained (76% conversion), the polymerization was stopped by decreasing the temperature to 10 °C. The reaction mixture was used directly for the chain extension without any purification.

Experiment for the second block: The amounts of monomers remaining in the reaction mixture were calculated based on the conversions to deduce the quantities of new monomers required for the chain extension. Thereafter, new batches of monomers (*t*BA and *n*BA) and initiator (AIBN, stock solution of 2 mg.mL^{-1} in dioxane) were added accordingly using the same method as described above. The new reaction mixture was degassed by sparging with inert gas (N_2) for 15 min at 0 °C. Thereafter, the reaction mixture was heated to 60 °C during 4 h. During the polymerization, aliquots were periodically withdrawn under an inert gas flow for ^{1}H NMR (0.075 mL) and SEC (0.05 mL) analysis. Once a molar mass of 19 200 g.mol^{-1} was obtained (conversion = 38%), the polymerization was stopped by decreasing the temperature to 10 °C. After that, the reaction mixture was removed from the reactor and diluted using methanol and precipitated in a water/methanol (1/3, v/v) solvent mixture at least twice to remove all the remaining monomers (checked by ^{1}H NMR) and then dried under deep vacuum.

Experimental details and the characteristics of the polymer are given in Table S1.

Table S1. Experimental conditions used for the synthesis and characterization data of the asymmetric diblock copolymer of 20 kg mol^{-1} (D): P(*t*BA$_{84\%}$-*stat*-*n*BA$_{16\%}$)-*b*-P(*t*BA$_{16\%}$-*stat*-*n*BA$_{84\%}$).

	tBA (mol L^{-1})	*nBA (mol L^{-1})*	*[tBA]:[nBA]:[CTA]:[AIBN]*	*tBA conv.^{a} (%)*	*nBA conv.^{a} (%)*	*$M_{n,th}$^{b} (kg mol^{-1})*	*$M_{n,SEC}$^{c} (kg mol^{-1})*	*Đ^{c}*
1st block	3.36	0.64	121:23:1:0.02	76	77	12.0	10.0	1.12
2nd block	0.48	2.52	27:140:1:0.03	38	38	20.9^{d}	19.2^{d}	1.10

a) Determined by ^{1}H NMR, b) $M_{n,th} = [M]_0 \times p \times M_M/[CTA]_0 + M_{CTA}$, p is the monomer conversion, M_M is the molar mass of monomer, c) Determined by SEC using $CHCl_3$ as an eluent with PMMA standards (SEC system at IOMC, JCSM, Friedrich Schiller University Jena). d) M_n and Đ of the second block represent the overall molar mass and dispersity of the polymer.

d) Typical synthesis of triblock copolymers P*t*BA-*b*-P(*t*BA$_{50\%}$-*stat*-*n*BA$_{50\%}$)-*b*-P*n*BA (T)

Copolymerizations were performed in a Chemspeed Accelerator SLT automated parallel synthesizer using a sequential reagent addition and similar experimental protocols as reported elsewhere.[1-4]

Typical experiment for the first block: Stock solutions of CTA (100 mg mL^{-1} in dioxane) and AIBN (2 mg mL^{-1} in dioxane) were prepared, respectively. These stock solutions and *t*BA were transferred into different containers and placed inside the automated synthesizer. Afterwards, for each investigated triblock copolymer system, aliquots of the prepared stock solution of CTA, stock solution of AIBN, *t*BA, and solvent were transferred from the containers into different reactors (75 mL) of the synthesizer with the automated liquid handling system to provide the desired concentration of reagents resulting in a final volume of 13 mL (please note that volume changes due to mixing of the reagents have been neglected). 1,3,5-Trioxane was added as internal standard at a concentration of 10 mg mL^{-1} of total reaction volume. Once all the reagents were in the reactors, each reaction mixture in each reactor was subjected to a degassing procedure in parallel by sparging with inert gas (N_2) for 15 min at 0 °C. Thereafter, the reaction mixtures were heated to 60 °C for 8 h. During each polymerization, aliquots were taken periodically for ^{1}H NMR (0.075 mL) and SEC (0.05 mL) analysis under an inert gas flow. Once the desired molar masses were obtained (see Table S2), the polymerizations were stopped by decreasing the temperature to 10 °C. Each reaction mixture was used directly for the chain extension without further purification.

In a typical experiment for the second block: The amounts of monomers remaining in the reaction mixture were calculated based on the conversions to deduce the quantities of new monomers required for the chain extension. Thereafter, new batches of monomers (*t*BA and *n*BA) and initiators (AIBN, stock solution of 2 mg mL^{-1} in dioxane) were added accordingly using the same method as described above. The new reaction mixtures were degassed by sparging with inert gas (N_2) for 15 min at 10 °C. Thereafter, the reaction mixtures were heated to 60 °C for 2.5 h. During each polymerization, aliquots were periodically withdrawn under an inert gas flow for ^{1}H NMR (0.075 mL) and SEC (0.05 mL) analysis. Once the desired molar masses were obtained (see Table S2), the polymerizations were stopped by decreasing the temperature to 10 °C. After that, the reaction mixtures were removed from the reactors and diluted using methanol and precipitated in a water/methanol (1/3, v/v) solvent mixture for at least twice to remove all the remaining monomers (checked by ^{1}H NMR) and then dried under deep vacuum.

In a typical experiment for the third block: The obtained polymers from the last step were firstly dissolved in dioxane and then the polymer solutions were transferred from the containers into different reactors (100 mL) of the synthesizer using syringe by hand. The amount of new monomer (*n*BA) required for the third block was calculated based on the amount of polymers added and the targeted conversions. Thereafter, new batches of monomer (*n*BA) and initiators (AIBN, stock solution of 2 mg mL^{-1} in dioxane) were added accordingly using the same method as described above. The new reaction mixtures were degassed by sparging with inert gas (N_2) for 15 min at 10 °C. Thereafter, the reaction mixtures were heated to 60 °C for 3 h. During each polymerization, aliquots were taken periodically for ^{1}H NMR (0.075 mL) and SEC (0.05 mL) analysis under an inert gas flow. Once the desired molar masses were obtained (see Table S2), the polymerizations were stopped by decreasing the temperature to 10 °C. After that, the reaction mixtures were removed from the reactors and diluted using methanol and precipitated in water/methanol (1/3, v/v) at least twice to remove all the remaining monomers (checked by ^{1}H NMR) and then dried under vacuum.

Table S2. Experimental conditions used for the synthesis and characterization data of the triblock copolymers of 10 kg mol^{-1} and 20 kg mol^{-1} (T): P*t*BA-*b*-P(*t*BA$_{50\%}$-*stat*-*n*BA$_{50\%}$)-*b*-P*n*BA.

<table>
<tr><th colspan="9">T10K (Triblock copolymer of 10 000 g mol^{-1})</th></tr>
<tr><th></th><th><i>tBA</i> (mol L^{-1})</th><th><i>nBA</i> (mol L^{-1})</th><th><i>[tBA]:[nBA]:[CTA]:[AIBN]</i></th><th><i>tBA</i> conv.^{a} (%)</th><th><i>nBA</i> conv.^{a} (%)</th><th>$M_{n,th}$^{b} (kg mol^{-1})</th><th>$M_{n,SEC}$^{c} (kg mol^{-1})</th><th>Đ^{c}</th></tr>
<tr><td>1st block</td><td>2.585</td><td>0</td><td>21:0:1:0.02</td><td>73</td><td>-</td><td>2.3</td><td>1.7</td><td>1.10</td></tr>
<tr><td>2nd block</td><td>1.70</td><td>1.70</td><td>33:33:1:0.03</td><td>67</td><td>67</td><td>8.2 ^{d}</td><td>7.8 ^{d}</td><td>1.08 ^{d}</td></tr>
<tr><td>3rd block</td><td>0</td><td>0.741</td><td>0:26:1:0.08</td><td>-</td><td>43</td><td>9.7 ^{e}</td><td>10.0 ^{e}</td><td>1.07 ^{e}</td></tr>
<tr><th colspan="9">T20K (Triblock copolymer of 20 000 g mol^{-1})</th></tr>
<tr><th></th><th><i>tBA</i> (mol L^{-1})</th><th><i>nBA</i> (mol L^{-1})</th><th><i>[tBA]:[nBA]:[CTA]:[AIBN]</i></th><th><i>tBA</i> conv.^{a} (%)</th><th><i>nBA</i> conv.^{a} (%)</th><th>$M_{n,th}$^{b} (kg mol^{-1})</th><th>$M_{n,SEC}$^{c} (kg mol^{-1})</th><th>Đ^{c}</th></tr>
<tr><td>1st block</td><td>3.36</td><td>0</td><td>50:0:1:0.02</td><td>72</td><td>-</td><td>5.0</td><td>4.1</td><td>1.09</td></tr>
<tr><td>2nd block</td><td>1.90</td><td>1.90</td><td>65:65:1:0.03</td><td>56</td><td>55</td><td>14.9 ^{d}</td><td>15.9 ^{d}</td><td>1.07 ^{d}</td></tr>
<tr><td>3rd block</td><td>0</td><td>0.844</td><td>0:50:1:0.08</td><td>-</td><td>43</td><td>17.6 ^{e}</td><td>20.1 ^{e}</td><td>1.07 ^{e}</td></tr>
</table>

a) Determined by ^{1}H NMR, b) $M_{n,th} = [M]_0 \times p \times M_M/[CTA]_0 + M_{CTA}$, p is the monomer conversion, M_M is the molecular weight of monomer, c) Determined by SEC using $CHCl_3$ as an eluent with PMMA standards (SEC system in IOMC, JCSM, Friedrich Schiller University Jena). d) M_n and Đ of the second block, represents the sum of the first two blocks, e) M_n and Đ of the third block, represents the overall molar mass and dispersity of the triblock copolymer.

Acidolysis of block, gradient, diblock and triblock copolymers

Each polymer was first dissolved in 5 mL of DCM, then 5-fold excess (relative to the *t*BA units) of TFA was added at once. The reaction mixture was stirred at room temperature for 72 hours, rotary evaporated, dissolved in 10 mL of 1,4-dioxane and rotary evaporated again, washed with 10 mL of deionized water and dried under vacuum.

e) Synthesis and characteristics of the different statistical $S_{x\%}$ copolymers

The synthesis of $S_{40\%}$, $S_{50\%}$ and $S_{60\%}$ has been reported in a previous paper (they were named MH40, MH50 and MH60 in the previous study).[5, 6] Additional statistical copolymers ($S_{16\%}$, $S_{30\%}$, $S_{70\%}$, $S_{84\%}$) and a sample of PAA homopolymer were prepared according to the following typical procedure (procedure for $S_{30\%}$ is reported).

Stock solutions of cyanomethyl dodecyl trithiocarbonate (55 mg mL^{-1} in dioxane) and AIBN (2 mg mL^{-1} in dioxane) were prepared. These stock solutions, *t*BA (12 mmol, 1.54 g), *n*BA and (28mmol, 3.60 g) were poured into a schlenk tube equipped with a magnetic stirrer. Dioxane was also added until 10 mL. The mixture was degassed by four freeze-pump-thaw cycles and the tube was then filled with argon. The schlenk tube was placed into a pre-heated oil bath at 60 °C for 6h. After this time the polymerization was quenched by immersing the tube in liquid nitrogen. A sample was withdrawn and analysed by ^{1}H NMR and SEC to obtain monomer conversion (69 %) and molar mass (11 700 g.mol^{-1}), respectively. The polymers were purified by two precipitations in a water/methanol (1/3, v/v) solvent mixture.

The characteristics of all statistical copolymers are presented in Table S3.

Acidolysis of $S_{16\%}$, $S_{30\%}$, $S_{70\%}$, $S_{84\%}$ and PAA

Each polymer was first dissolved in 5 mL of DCM, then 5-fold excess (relative to the *t*BA units) of TFA was added at once. The reaction mixture was stirred at room temperature for 72 hours. Afterwards, this mixture was rotary evaporated and subjected to deep vacuum. Then it was dissolved with 10 mL of dioxane and rotary evaporated again. Finally, it was subjected to deep vacuum to eliminate the remaining solvent.

Table S3. Molecular characteristics of the $S_{x\%}$ statistical copolymers of AA and *n*BA.

	Before acidolysis			***After acidolysis***	
Copolymer	*M_n (kg mol^{-1})^a*	*$Đ$ ^{a}*	*tBA mol % ^{b}*	*Expected M_n (g mol^{-1})^c*	*AA mol % ^{d}*
$S_{16\%}$	15.7	1.04	16%	14.6	18%
$S_{30\%}$	11.7	1.05	30%	10.2	31%
$S_{40\%}$	12.5	1.17	40%	10.0	42%
$S_{50\%}$	12.5	1.10	51%	10.0	51%
$S_{60\%}$	13.6	1.34	60%	10.3	61%
$S_{70\%}$	11.7	1.06	70%	9.7	63%
$S_{84\%}$	18.1	1.09	84%	11.4	77%
PAA	18.3	1.04	100%	10.3	83%

a) Determined by SEC in THF calibrated with PMMA standards. For $S_{40\%}$, $S_{50\%}$, and $S_{60\%}$ the analysis was performed on another column calibrated with PS standards,[5, 6] *b) Calculated from molar mass of each block, considering their composition obtained by ^1H NMR, c) M_n expected after acidolysis = M_n(before acidolysis)*(f_{tBA}*(M_{AA}/M_{tBA}) + f_{nBA}), where f_{tBA} and f_{nBA} are the mass fractions of tBA and nBA in the polymer before acidolysis determined by ^1H NMR, d) The number of moles of AA units n_{AA} titrated in a polymer mass m_{pol} ~ 30 mg was determined by potentiometric titration. From that, the AA mol% was deduced as: %AA = $n_{AA}/(n_{AA} + (m_{pol} - n_{AA} \times M_{AA})/M_{nBA})$ where M_{AA} and M_{nBA} correspond to the respective molecular weights of AA or nBA units.*

The theoretical AA content based on the monomer feed composition and conversion of each monomer was consistent with the experimental content determined by potentiometric titration for $S_{16\%}$ to $S_{60\%}$. Significant discrepancies were observed for $S_{70\%}$, $S_{84\%}$ and PAA. We attributed this to the fact that the AA units made the polymer slightly hygroscopic, resulting in the presence of up to 15 wt% of water in these three polymers, causing an underestimation of the AA content by titration. However, since the AA content was recalculated based on the titration experiments in order to plot the evolution of pH and pK_{aeff} as a function of α, this discrepancy only changes the effective AA concentration in the solution. This latter parameter was shown not to affect significantly the titration results (see section 3). All conclusions and interpretations presented in the manuscript therefore remain valid.

3. Control titration experiments

a) Reproducibility and effect of molecular weight

Figure S2 reveals in the particular case of T that the titration curves were reproducible and did not significantly depend on the molar mass of the polymer, at least in the 1-2×10^4 g/mol range.

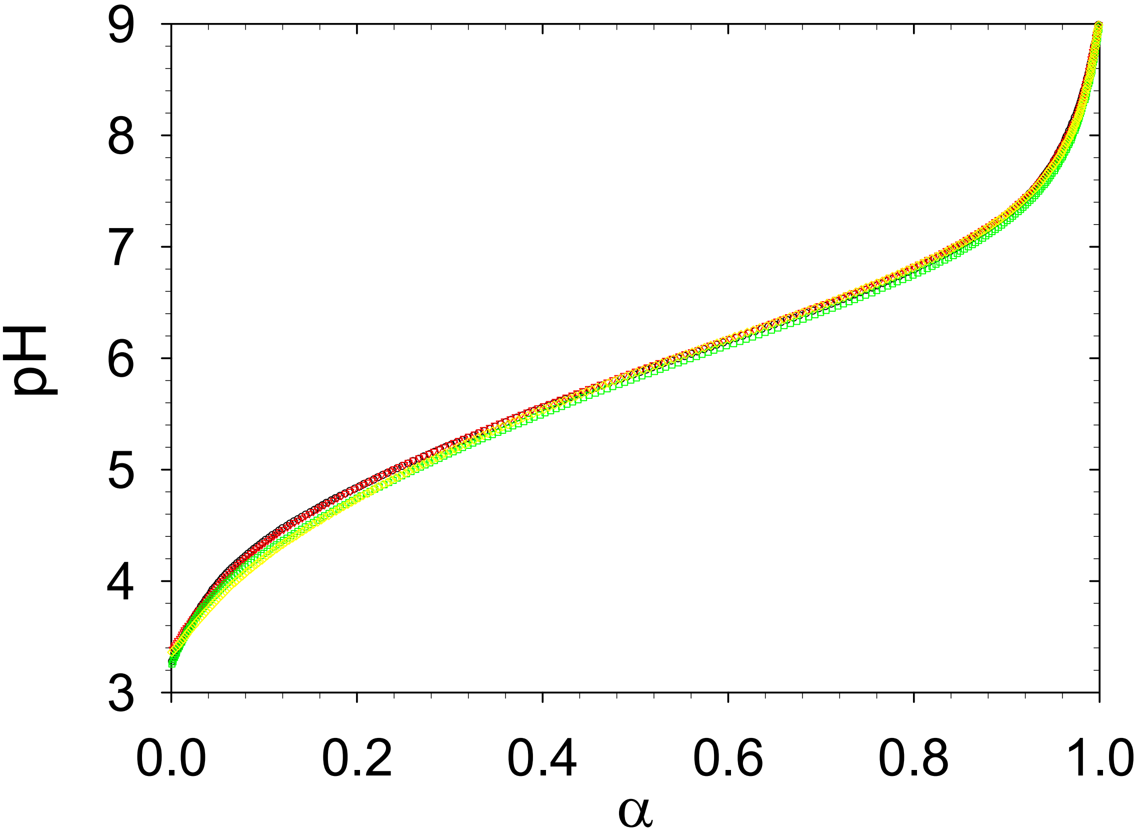

Figure S2. Evolution of the pH as a function of α resulting from titrations conducted from $\alpha = 1$ to $\alpha = 0$ with HCl 0.1 M at a polymer concentration of 1 g.L^{-1} and with 0.1 M NaCl. (○ , ▽) T exhibiting a M_n of 1×10^4 g.mol^{-1}, (□, ◇) T exhibiting a M_n of 2×10^4 g.mol^{-1}. The four sets of symbols, which strongly superimpose, correspond to 4 distinct sets of data.

b) Effect of the [AA] concentration

Figure S3 reveals that in the presence of 0.1 M NaCl, the AA concentration had no significant influence on the titration curves for the concentration range studied here. The differences observed at the two distinct concentrations were slightly more pronounced close to α = 0 or 1 where the determination of α becomes less accurate.

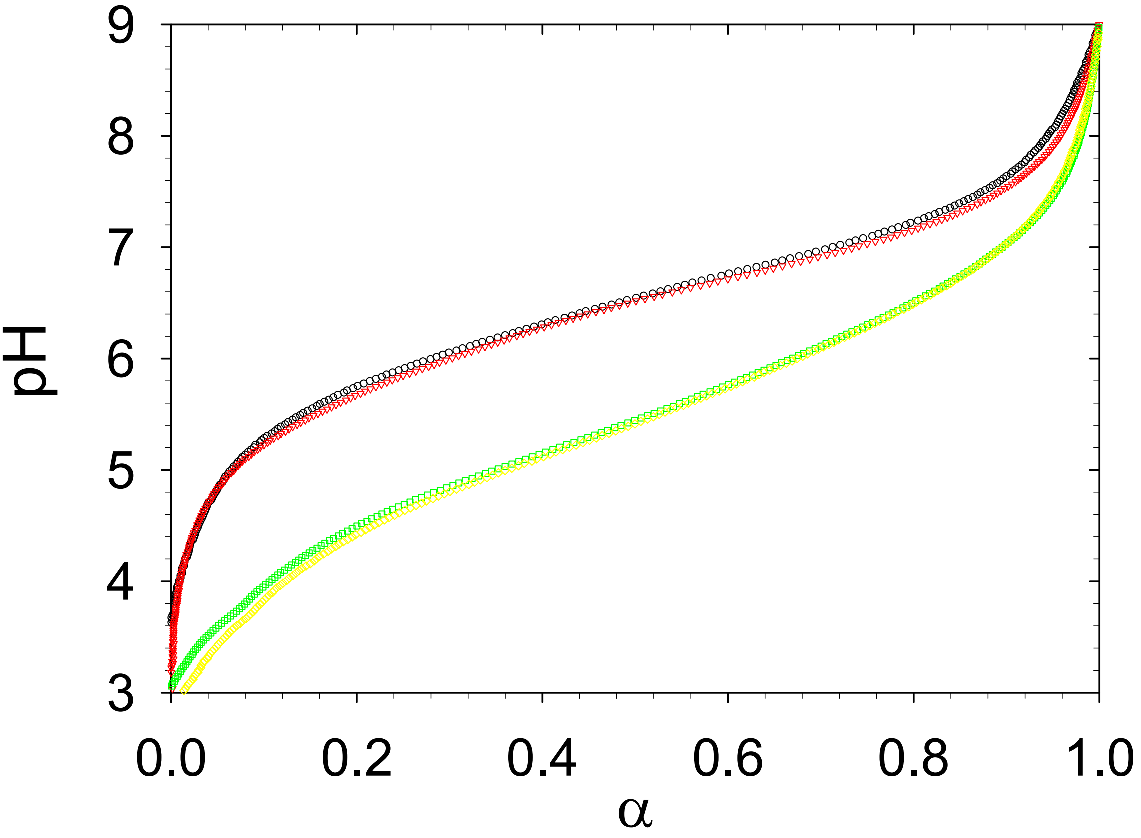

Figure S3. Evolution of the pH as a function of α resulting from titrations conducted from α = 1 to α = 0 with HCl 0.1 M. $S_{30\%}$ at 1 $g.L^{-1}$ (○) and 1.85 $g.L^{-1}$ (▽) corresponding to [AA] = 2.7×10^{-3} or 5.0×10^{-3} $mol.L^{-1}$; $S_{84\%}$ at 1 $g.L^{-1}$ (□) and 0.48 $g.L^{-1}$ (◇) corresponding to [AA] = 10×10^{-3} or 5.0×10^{-3} $mol.L^{-1}$.

4. Raw titration curves and data treatment

Figure S4 presents a typical raw titration curve.

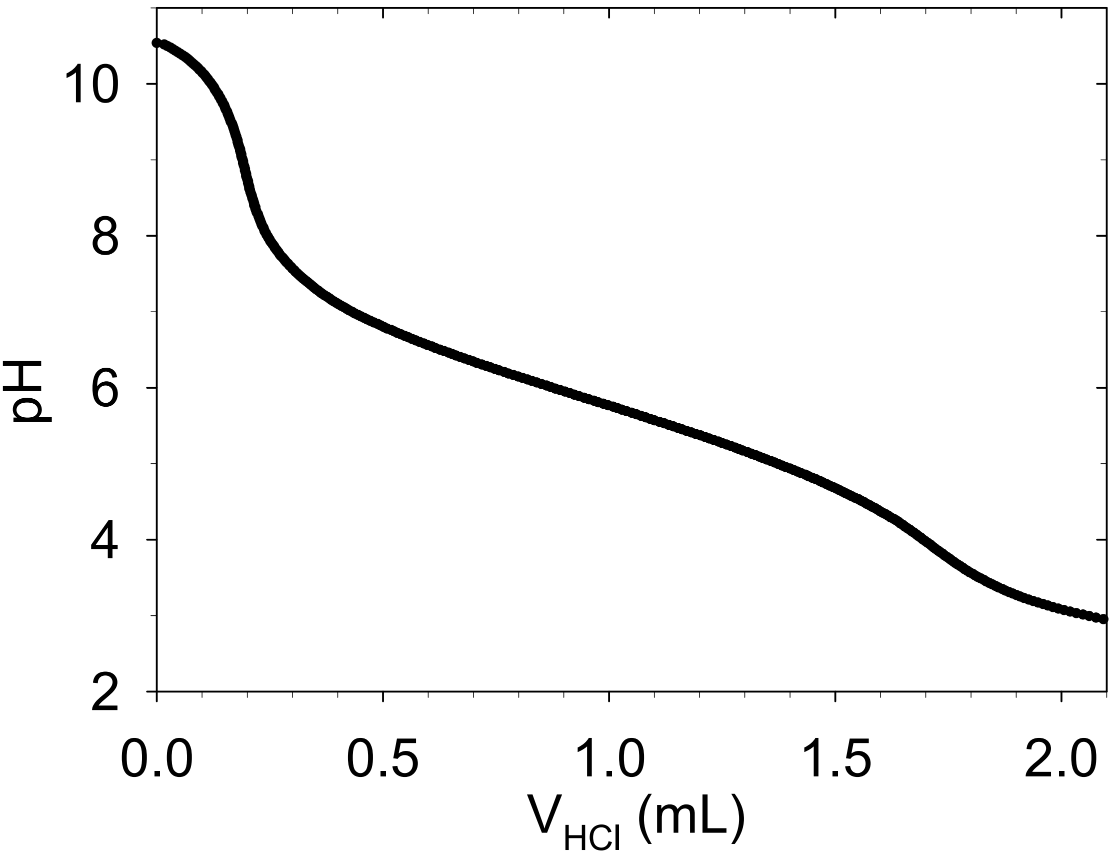

Figure S4. Raw potentiometric titration curve of 30 mg of G ($M_n = 2\times10^4$ g.mol^{-1}) at 1 g.L^{-1} with HCl 0.1 M (addition rate = 0.1 mL.min^{-1}) at a NaCl concentration of 0.1 M and starting with ~10 % excess of NaOH.

The raw titration data were used to deduce the total amount of AA units which could be ionized and to determine the evolution of the ionization degree, α, as a function of the pH value as reported previously.[7]

Briefly, during a titration experiment, HCl could react in three different ways:

1) HCl could react with hydroxide ions according to: $HCl + OH^- \rightarrow H_2O + Cl^-$

This mainly happened at the beginning of the titration with the excess of sodium hydroxide used to ionize the polymer because sodium hydroxide is a strong base (and is therefore more basic than the AA^-,Na^+ units no matter α). The amount of HCl consumed through this reaction was noted n_1.

2) HCl could also react with the AA^-,Na^+ units according to: $HCl + AA^- \rightarrow AAH + Cl^-$

This reaction was the actual titration reaction. The amount n_2 of HCl consumed through this reaction corresponded to the amount of titrated AA^- units which was equal to the amount of AAH formed, n_{AAH}.

3) HCl could finally simply dissociate: $HCl \rightarrow H^+ + Cl^-$

This happened when none of the two former reactions occurred. The amount of HCl consumed through this reaction was noted n_3.

Since HCl is a strong acid, $V_{HCl}.[HCl] = n_1 + n_2 + n_3$, where [HCl] was the starting concentration of HCl and V_{HCl} its added volume.

Assuming that no AA^-,Na^+ units reacted with HCl before the first pH-jump (at V_{eq1} and pH_{Veq1}), corresponding to the end of the titration of the excess of NaOH, n_{AAH} could be calculated from the raw titration data according to the following equation:

$$n_{AAH} = [HCl].\left(V_{HCl} - V_{eq1}\right) - \left[\left(V_{start} + V_{eq1}\right).10^{-14+pH_{Veq1}} - \left(V_{start} + V_{HCl}\right).10^{-14+pH}\right]$$
$$- \left[\left(V_{start} + V_{HCl}\right).10^{-pH} - \left(V_{start} + V_{eq1}\right).10^{-pH_{Veq1}}\right]$$

The total amount of AA units which could be titrated, $n_{AAH\text{-}tot}$, corresponded to the value of n_{AAH} at the plateau for the largest V_{HCl} values.

From $n_{AAH} = f(V_{HCl})$ and from the value of $n_{AAH\text{-}tot}$, $\alpha = f(V_{HCl})$ and then $\alpha = f(pH)$ could be deduced according to the following equation:

$$\alpha = \frac{[AA^-]}{[AAH]+[AA^-]} = \frac{[AA^-]}{[AA]_{total}} = 1 - \frac{n_{AAH}}{n_{AAH-tot}}$$

5. Fits

a) Gaussian fit

Modelling degree of ionization of polymers with a Gaussian distribution of pKa.

For a weak acid, the degree of ionization, α, is given by the equation

$$\alpha = \frac{10^{pH}}{10^{pH} + 10^{pKa}}$$

For a mixture of acids, each with a different pKa, the total degree of ionization is the sum of the degrees of ionization of the individual acids:

$$\alpha = \sum_i f_i . \frac{10^{pH}}{10^{pH} + 10^{pKa_i}}$$

Where f_i is the mole fraction of the acid with pKa = pKa$_i$.

We can extend this to a polyacid with a continuous distribution of pKa, with probability distribution function *f*:

$$\alpha = \int_{-\infty}^{\infty} f(pKa) . \frac{10^{pH}}{10^{pH} + 10^{pKa}} dpKa$$

Assuming that the pKas are normally distributed, with mean μ and standard deviation σ. The degree of ionization is given by:

$$\alpha = \frac{1}{\sigma\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{10^{pH}}{10^{pH} + 10^{x}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} . dx$$

Setting $z = (x- \mu)/\sigma$ gives

$$\alpha = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{1}{1 + 10^{\mu+\sigma z-}} e^{-\frac{z^2}{2}} . dz$$

This equation can be fitted to the data with the help of numerical integration. For nonlinear fitting, the following equations are useful:

$$\frac{\partial\alpha}{\partial\mu} = \frac{-\ln(10)}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{10^{\mu+\sigma z-}}{(1 + 10^{\mu+\sigma z-} \quad)^2} e^{-\frac{z^2}{2}} . dz$$

$$\frac{\partial\alpha}{\partial\sigma} = \frac{-\ln(10)}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{z . 10^{\mu+\sigma z-}}{(1 + 10^{\mu+\sigma z-p} \ )^2} e^{-\frac{z^2}{2}} . dz$$

The pH at 50 % ionization is a reasonable first estimate for μ.

These equations were used to fit the Gaussian model to the experimental degree of ionization data, taking pH as the independent variable and assuming negligible error in this measurement relative to the error in the degree of ionization measurement, using a nonlinear least squares fitting procedure. The fit parameters and an estimate of the standard error in the data points are shown in Table S4.

Table S4. Best fit parameters for Gaussian model (equation 5). The corresponding fits are shown on Figures 2, 3 and S5.

Polymer	Mean pKa (μ)	Standard deviation (σ)	Standard error in fit [a]
$S_{50\%}$	5.92	0.49	0.011
B	5.53	0.86	0.002
G	5.83	0.87	0.004
D	5.65	0.79	0.007
T	5.78	0.89	0.002
$S_{16\%}$	7.05	0.80	0.013
$S_{30\%}$	6.46	0.57	0.013
$S_{40\%}$	6.12	0.45	0.013
$S_{60\%}$	5.69	0.64	0.005
$S_{70\%}$	5.71	0.69	0.011
$S_{84\%}$	5.44	0.97	0.003
PAA	5.43	1.08	0.009

[a] Standard error in fit = $\sqrt{[SSR/(N-2)]}$, where SSR is the sum of squared residuals and N is the number of fitted data points. Roughly 70 % of measured α fall within this distance of the fitted line. The error in measuring pH was assumed to be negligible.

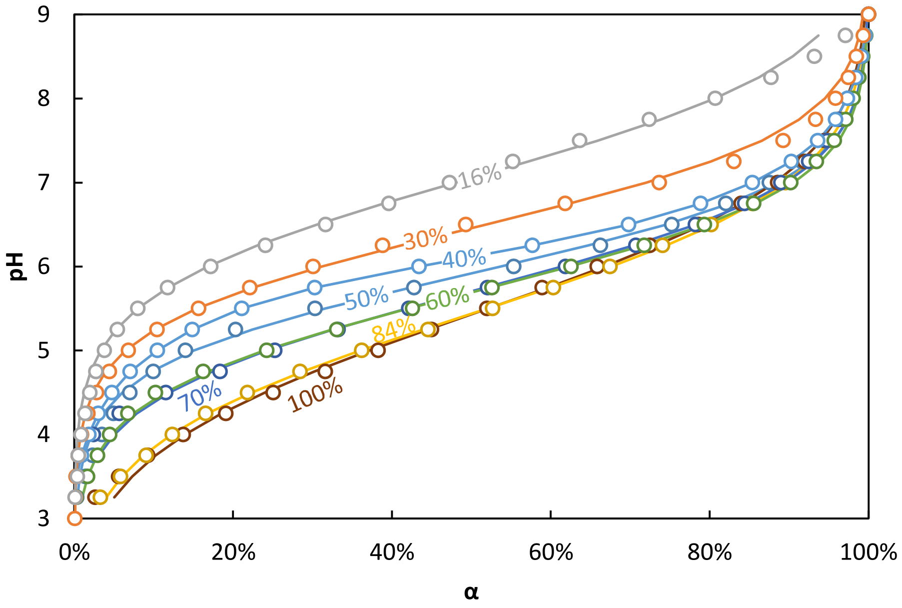

Figure S5: Fits for Gaussian distribution of pKa model to titration data (all statistical polymers)

b) Koper and Borkovec Site Binding model

Koper and Borkovec[8] give a model for a linear polyacid that considers the acidic sites as equally spaced along a chain, and able to interact with each other through pairwise interactions. In the case of an infinitely long chain, the degree of protonation, θ (equal to 1 - α), is given by:

$$\theta = 1 - \alpha = \frac{1 - u + \lambda u}{2 + (\lambda / z)(1 - zu)}$$

In this equation,

$$\lambda = \frac{1 + zu}{2} + \sqrt{z + \frac{(1 - uz)^2}{4}}$$

$$z = Ka_H = 10^{pK - p}$$

$$u = 10^{-\varepsilon}$$

pK is the logarithm of the binding constant for protonation of the fully deprotonated polyacid, and corresponds to the pK_a for dissociation of the final proton from the polyacid. The parameter ε is due to pairwise interactions between the binding sites. The resulting titration curve resembles that of a diprotic acid due to the stability of the state in which every second site is protonated, although the protonation steps are broader.

This equation was fitted to the experimental titration curve (pH vs α) data using nonlinear least squares fitting assuming negligible error in the measurement of pH. Due to the complexity of the equation the partial derivatives ∂α/∂pK and ∂α/∂ε were estimated as:

$$\frac{\partial \hat{\alpha}}{\partial pK} \approx \frac{\hat{\alpha}(1.01 \times pK) - \hat{\alpha}(pK)}{0.01 \times pK}$$

$$\frac{\partial \hat{\alpha}}{\partial \varepsilon} \approx \frac{\hat{\alpha}(1.01 \times \varepsilon) - \hat{\alpha}(\varepsilon)}{0.01 \times \varepsilon}$$

Best estimates for pK and ε are given in Table S5 for PAA and each of the statistical copolymers.

Table S5. Best fit parameters for Koper and Borkovec Site Binding model. Corresponding fits are shown on Figure S6.

Polymer	pK	ε	Standard error in fit[a]
$S_{16\%}$	7.53	1.10	0.011
$S_{30\%}$	6.69	0.52	0.011
$S_{40\%}$	6.25	0.30	0.012
$S_{50\%}$	6.14	0.49	0.012
$S_{60\%}$	6.04	0.79	0.007
$S_{70\%}$	6.09	0.89	0.011
$S_{84\%}$	6.07	1.44	0.013
PAA	6.16	1.66	0.009

[a] Standard error in fit = √[SSR/(N-2)], where SSR is the sum of squared residuals and N is the number of fitted data points. Roughly 70% of measured α fall within this distance of the fitted line. The error in measuring pH was assumed to be negligible.

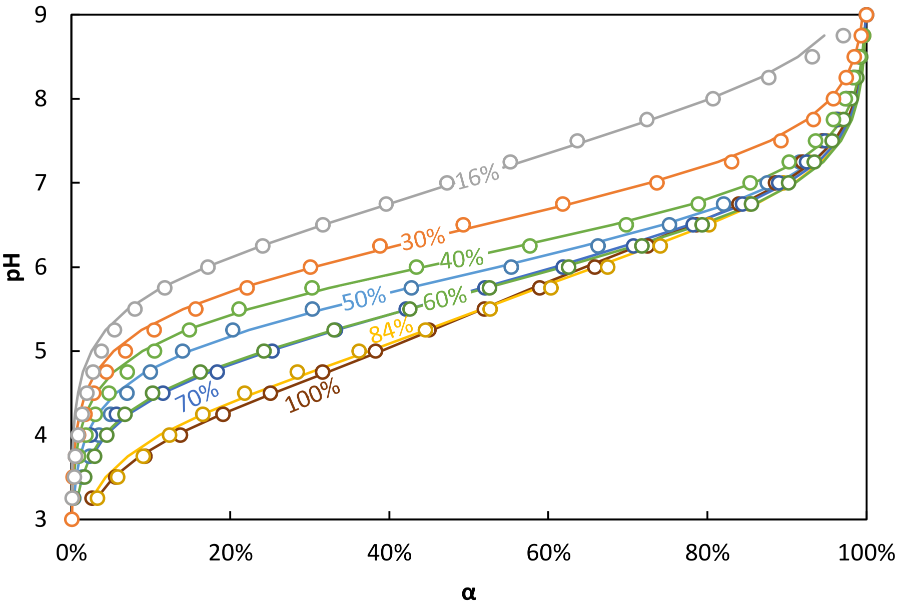

Figure S6. Fits for Koper and Borkovec model to titration data (all statistical copolymers)

6. Mathematical combination of the titration data

To calculate the ionization behavior of the polyelectrolytes exhibiting non homogeneous composition profiles based on that of the $S_{x\%}$ copolymers, we assumed that connecting different blocks covalently did not affect their ionization behavior as compared to when each block is titrated independently. In that case, the following equation can be used to calculate the average ionization degree $\alpha_{\mathrm{average}}$ of the polymer at a given pH value:

$$\alpha_{average} = \sum_{i} f_i \times \alpha_{\mathrm{i}}$$

where, for the chosen pH value, f_i corresponds to the molar fraction of AA units contained in the statistical copolymer i and α_i corresponds to its degree of ionization.

In order to use this equation, the experimental data of each polymer were first interpolated from pH = 3 to 9 with a 0.25 step and $\alpha_{\mathrm{average}}$ was calculated at each pH value. Then, pKa_{eff} was deduced from equation 4 in the manuscript.

The combinations of statistical copolymers used to simulate the ionization behavior of copolymers B, D and T are shown in Table S6

Table S6. Combinations of statistical copolymers used to simulate the ionization behavior of copolymers B, D, and T.

Copolymer	Segment 1	f_1	Segment 2	f_2	Segment 3	f_3	%AA$_{\mathrm{total}}$[a]	$\bar{x}_{AA}$[b]
B	PAA	0.5	P*n*BA[c]	0.5	—	—	50%	0.25
D	$S_{84\%}$	0.5	$S_{16\%}$	0.5	—	—	50%	0.33
T	PAA	0.21	$S_{50\%}$	0.58	P*n*BA[c]	0.21	50%	0.33

[a] overall composition in acrylic acid. [b] average location of acrylic acid units. [c] poly(*n*-butyl acrylate) homopolymer.

The gradient copolymer, G, was simulated using numerous combinations of statistical copolymers, selected in order to maintain an overall composition in acrylic acid of 50 mol%, and an average location of acrylic acid units, $\bar{x}_{AA}$, of 0.33. These combinations are shown in Table S7. Additionally, for each combination the relative contributions of each segment were allowed to vary in order to find the combination of statistical copolymer segments that provided the best fit to the gradient copolymer titration curve, while maintaining an overall composition of 50 mol% AA. These values are also shown in Table S7.

Table S7. Combinations of PAA homopolymer and statistical copolymers used to simulate the titration curve of the gradient copolymer, G.

	Model[a]						Fitted[b]					
	x_1	x_2	x_3	$\%AA_{total}$[c]	$\bar{x}_{AA}$[d]	SSR[e] $\times 10^4$	x_1	x_2	x_3	$\%AA_{total}$[c]	$\bar{x}_{AA}$[d]	SSR[e] $\times 10^4$
PAA/$S_{70\%}$/P*n*BA	0.06	0.63	0.31	0.50	0.33	267	0.00	0.71	0.29	0.50	0.36	240
PAA/$S_{60\%}$/P*n*BA	0.15	0.58	0.27	0.50	0.33	429	0.00	0.83	0.17	0.50	0.42	319
PAA/$S_{50\%}$/P*n*BA	0.21	0.58	0.21	0.50	0.33	132	0.17	0.66	0.17	0.50	0.36	108
PAA/$S_{40\%}$/P*n*BA	0.26	0.59	0.15	0.50	0.33	83	0.25	0.63	0.12	0.50	0.35	77
PAA/$S_{30\%}$/P*n*BA	0.31	0.63	0.06	0.50	0.33	158	0.32	0.60	0.08	0.50	0.33	155
$S_{84\%}$/$S_{70\%}$/P*n*BA	0.13	0.56	0.31	0.50	0.34	329	0.00	0.71	0.29	0.50	0.36	240
$S_{84\%}$/$S_{60\%}$/P*n*BA	0.27	0.46	0.27	0.50	0.34	169	0.20	0.55	0.25	0.50	0.35	132
$S_{84\%}$/$S_{50\%}$/P*n*BA	0.35	0.41	0.24	0.50	0.33	316	0.20	0.66	0.14	0.50	0.38	132
$S_{84\%}$/$S_{40\%}$/P*n*BA	0.40	0.41	0.19	0.50	0.33	219	0.30	0.62	0.08	0.50	0.38	68
$S_{84\%}$/$S_{30\%}$/P*n*BA	0.44	0.43	0.13	0.50	0.33	168	0.38	0.59	0.03	0.50	0.36	69
PAA/$S_{70\%}$/$S_{16\%}$	0.13	0.43	0.44	0.50	0.33	28	0.08	0.51	0.41	0.50	0.35	17
PAA/$S_{60\%}$/$S_{16\%}$	0.19	0.41	0.40	0.50	0.33	71	0.11	0.57	0.32	0.50	0.37	37
PAA/$S_{50\%}$/$S_{16\%}$	0.23	0.43	0.34	0.50	0.33	40	0.20	0.50	0.30	0.50	0.35	32
PAA/$S_{40\%}$/$S_{16\%}$	0.28	0.44	0.28	0.50	0.33	77	0.26	0.51	0.23	0.50	0.34	70
PAA/$S_{30\%}$/$S_{16\%}$	0.32	0.51	0.17	0.50	0.33	190	0.31	0.58	0.11	0.50	0.34	186

[a] Segment lengths x_i selected to maintain $\%AA_{total}$ of 50 mol% and $\bar{x}_{AA}$ of 0.33. [b] Segment lengths varied to minimize SSR. [c] overall composition in acrylic acid. [d] average location of acrylic acid units. [e] sum of squared residuals of fit to titration curve (pH vs α).

Some examples of fits to the titration curves are shown in Figures S7-S9. The best- and worst-fitting combinations are shown from each of the 3 groups of compositions tested (PAA/S$_{30\text{-}70\%}$/P*n*BA; S$_{84\%}$/S$_{30\text{-}70\%}$/P*n*BA; PAA/S$_{30\text{-}70\%}$/S$_{16\%}$).

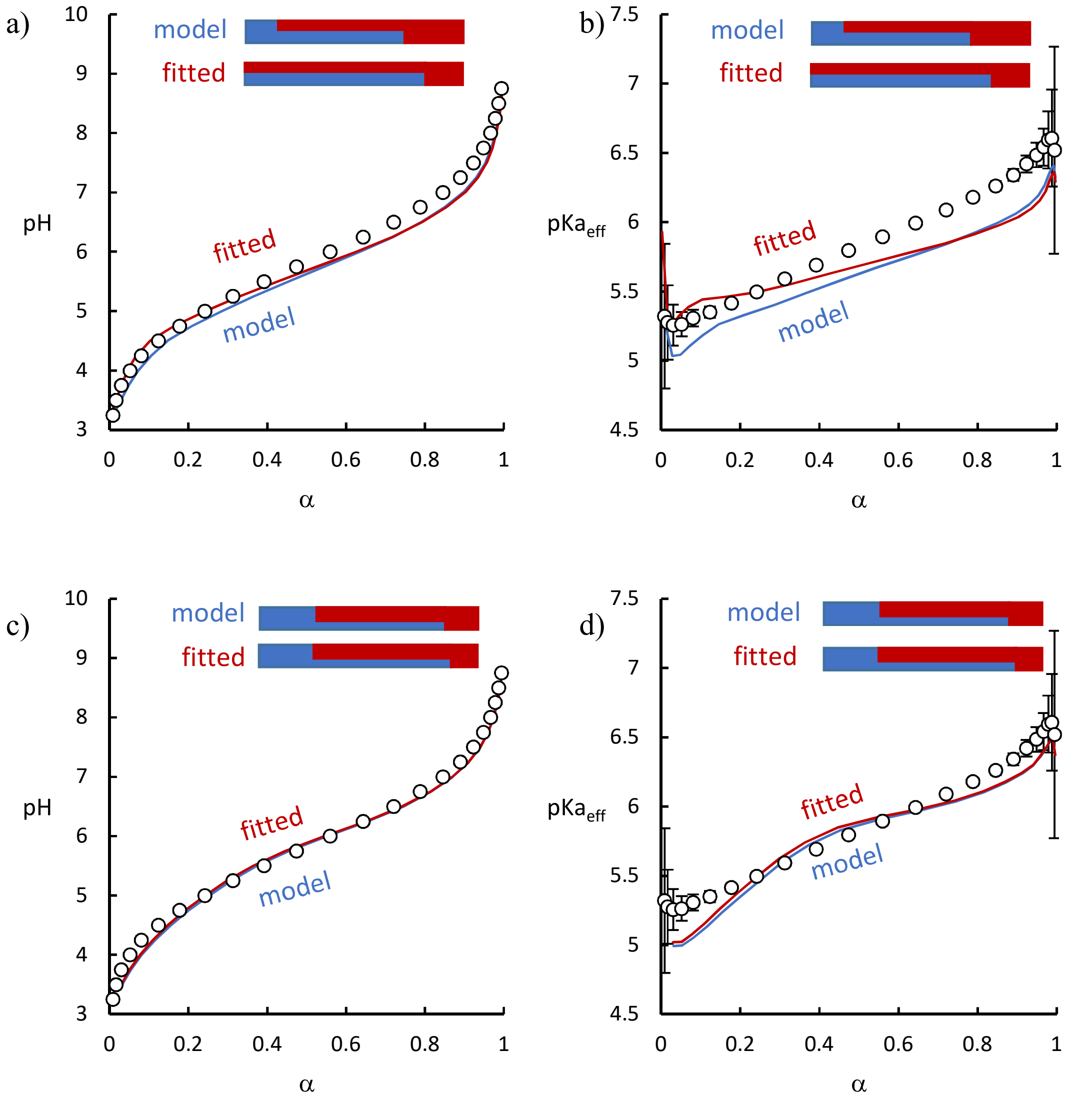

Figure S7. Examples of modeling titration curves (a, c) and pKa_eff *vs.* degree of ionization (b, d) of gradient copolymer G (open circles) using combinations of statistical copolymer segments. (a, b): PAA/S$_{60\%}$/P*n*BA. (c, d): PAA/S$_{40\%}$/P*n*BA. Model: segment lengths selected to match overall composition and average AA location $\bar{x}_{AA}$ of the gradient copolymer. Fitted: Segment lengths allowed to vary while maintaining overall AA composition of 50 mol%. Segment lengths are given in Table S7.

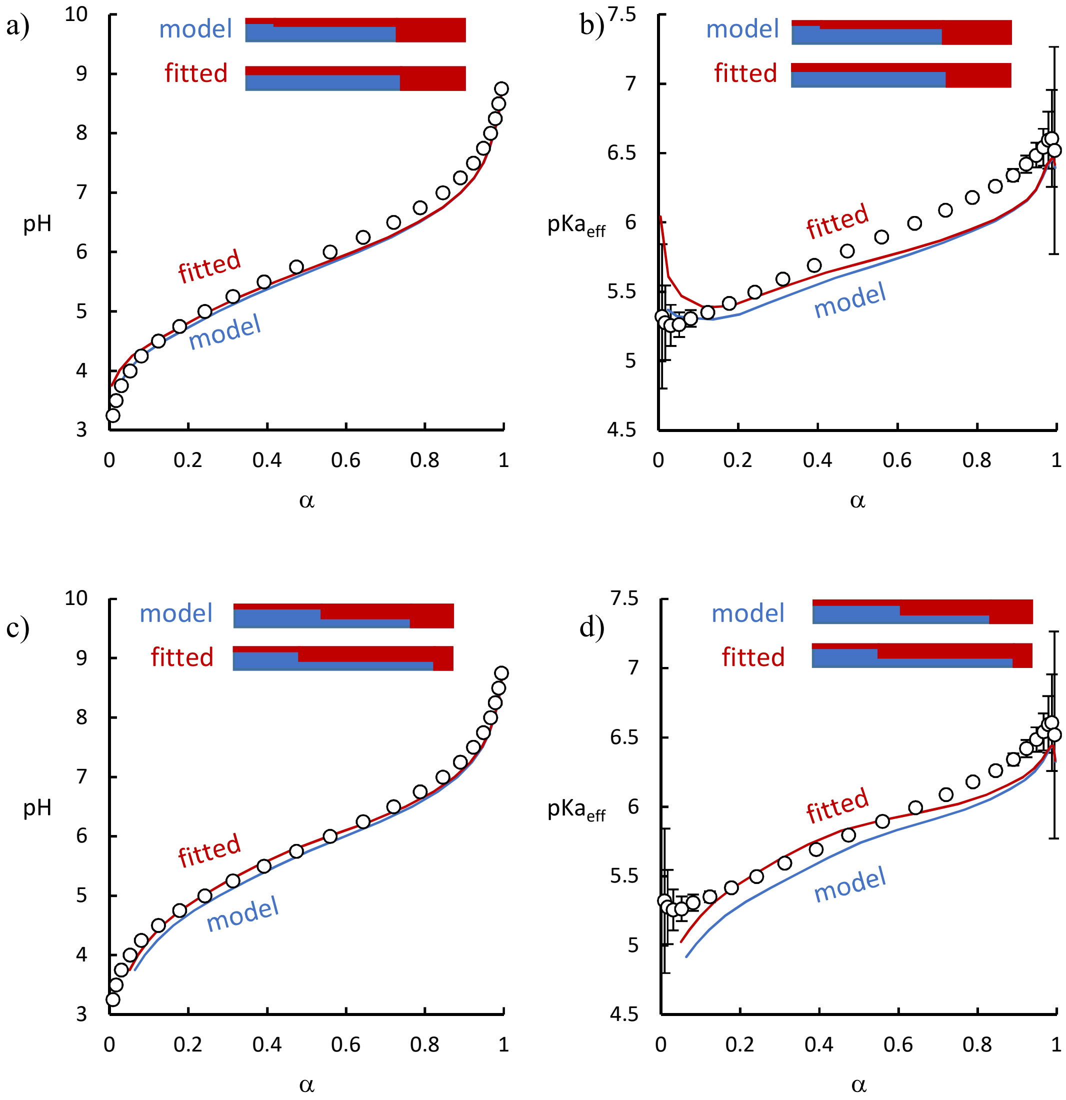

Figure S8. Examples of modeling titration curves (a, c) and pKa_eff *vs.* degree of ionization (b, d) of gradient copolymer G (open circles) using combinations of statistical copolymer segments. (a, b): $S_{84\%}$/$S_{70\%}$/P*n*BA. (c, d): $S_{84\%}$/$S_{40\%}$/P*n*BA. Model: segment lengths selected to match overall composition and average AA location $\bar{x}_{AA}$of the gradient copolymer. Fitted: Segment lengths allowed to vary while maintaining overall AA composition of 50 mol%. Segment lengths are given in Table S7.

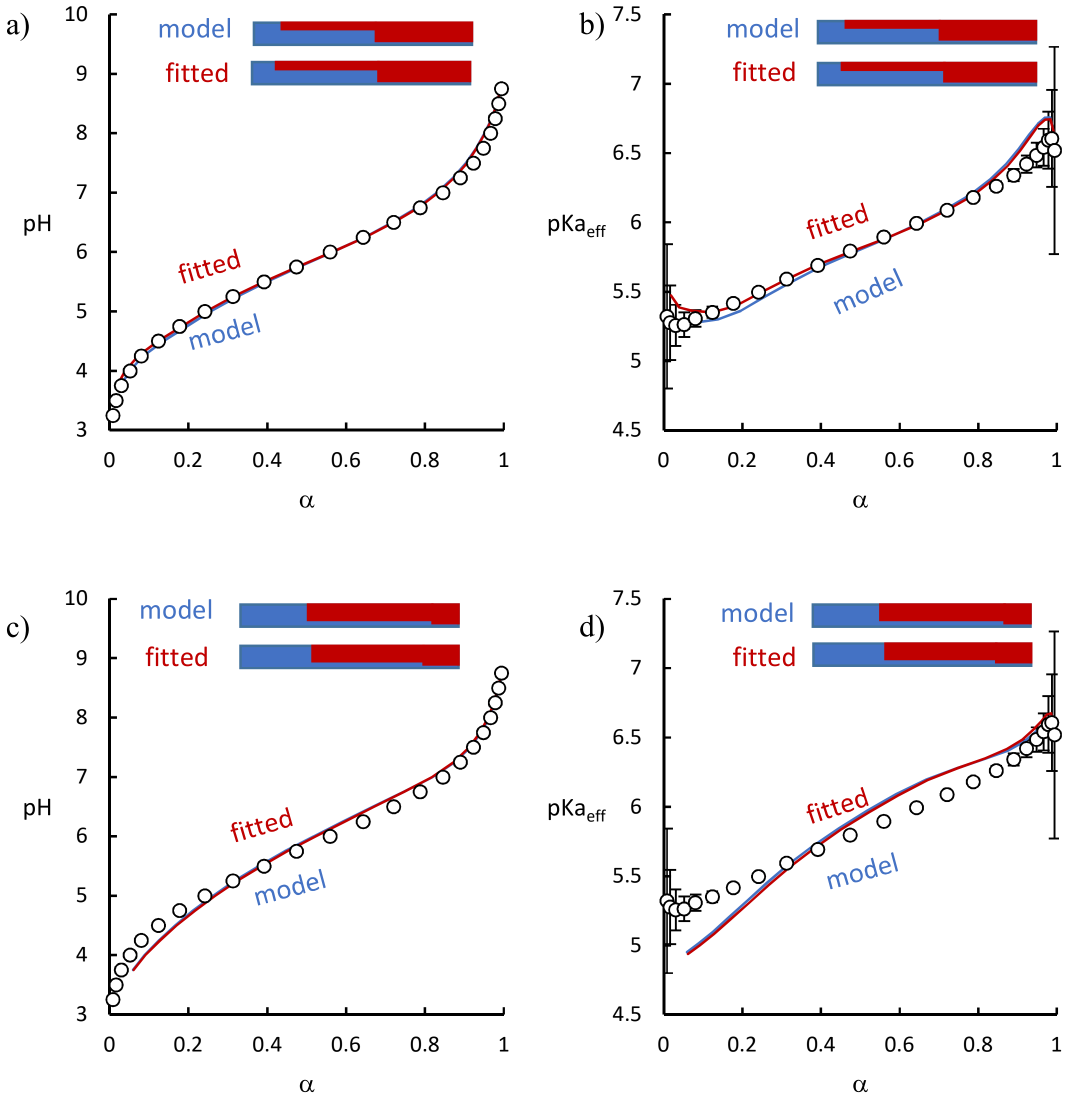

Figure S9. Examples of modeling titration curves (a, c) and pKa_eff *vs.* degree of ionization (b, d) of gradient copolymer G (open circles) using combinations of statistical copolymer segments. (a, b): PAA/$S_{70\%}$/$S_{16\%}$. (c, d): PAA/$S_{30\%}$/$S_{16\%}$. Model (blue line): segment lengths selected to match overall composition and average AA location $\bar{x}_{AA}$of the gradient copolymer. Fitted (red line): Segment lengths allowed to vary while maintaining overall AA composition of 50 mol%. Segment lengths are given in Table S7.

References

1. C. Guerrero-Sanchez, S. Harrisson and D. J. Keddie, *Macromol. Symp.*, 2013, **325–326**, 38–46.
2. J. J. Haven, C. Guerrero-Sanchez, D. J. Keddie and G. Moad, *Macromol. Rapid Commun.*, 2014, **35**, 492–497.
3. J. J. Haven, C. Guerrero-Sanchez, D. J. Keddie, G. Moad, S. H. Thang and U. S. Schubert, *Polym. Chem.*, 2014, **5**, 5236–5246.
4. R. Yañez-Macias, I. Kulai, J. Ulbrich, T. Yildirim, P. Sungur, S. Hoeppener, R. Guerrero-Santos, U. S. Schubert, M. Destarac, C. Guerrero-Sanchez and S. Harrisson, *Polym. Chem.*, 2017, **8**, 5023–5032.
5. L. Lauber, C. Chassenieux, T. Nicolai and O. Colombani, *Macromolecules*, 2015, **48**, 7613−7619.
6. E. Lejeune, M. Drechsler, J. Jestin, A. H. E. Müller, C. Chassenieux and O. Colombani, *Macromolecules*, 2010, **43**, 2667-2671.
7. O. Colombani, E. Lejeune, C. Charbonneau, C. Chassenieux and T. Nicolai, *J. Phys. Chem. B*, 2012, **116**, 7560-7565.
8. G. J. M. Koper and M. Borkovec, *Polymer*, 2010, **51**, 5649-5662.