Supporting information

How dissociation of carboxylic acid groups in a weak polyelectrolyte brush depend on their distance from the substrate

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The supporting information contains 13 pages including 9 figures (S1-S9) and 1 table (S1).

S1: Analysis of the Ellipsometry Data

Optical dispersions of the PAA brushes are described using the empirical Cauchy relation. and Bruggeman effective medium approximation (BEMA) models. Figures S1-S3 demonstrate the modeling data at three different pH values (2.0, 4.75, 9.0) and figures S4-S6 are the results of fitting the same data points to the BEMA model. The difference between the results of the Cauchy model and the BEMA model is smaller than 1 nm.

Fit Results

MSE = 6.735
Thickness # 3 = 46.19 ± 0.237 nm
A = 1.377 ± 0.00037078
B = 0.00329 ± 2.8033E-05
Total Thickness = 149.19 ± 0.237 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **46.19 nm** (fit)
  A = **1.377** (fit) B = **0.00329** (fit) C = 0.0000
  - **Urbach Absorption Parameters**
    k Amplitude = 0.0000 Exponent = 0.00
    Band Edge = 400.0 nm
- Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

Experimental and Model Generated Data Fits

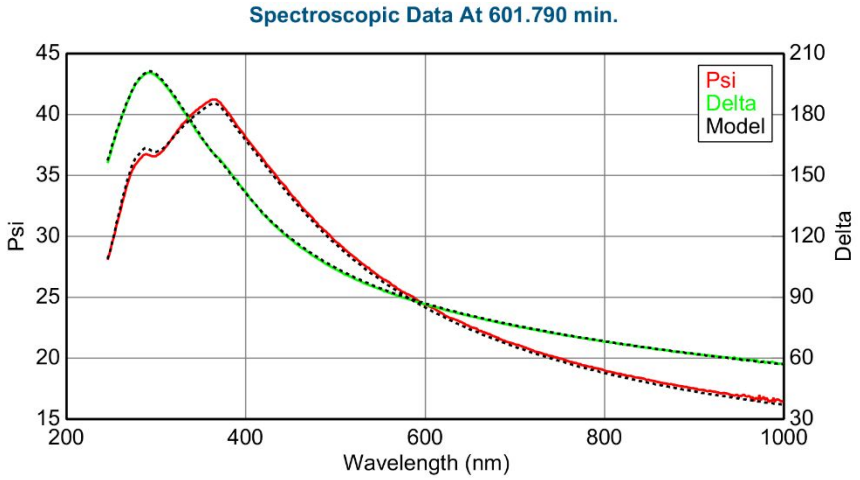

Figure S1. Modelling data from Cauchy relation for the PAA brush at pH 9.0 and an ionic strength of 100 mM.

Fit Results

MSE = 7.235
Thickness # 3 = 37.31 ± 0.256 nm
A = 1.385 ± 0.00055993
B = 0.00347 ± 3.8533E-05
Total Thickness = 140.31 ± 0.256 nm

Optical Model

- Layer # 3 = Cauchy Thickness # 3 = **37.31 nm** (fit)
  A = **1.385** (fit) B = **0.00347** (fit) C = 0.0000
  - **Urbach Absorption Parameters**
    k Amplitude = 0.0000 Exponent = 0.00
    Band Edge = 400.0 nm
- Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

Experimental and Model Generated Data Fits

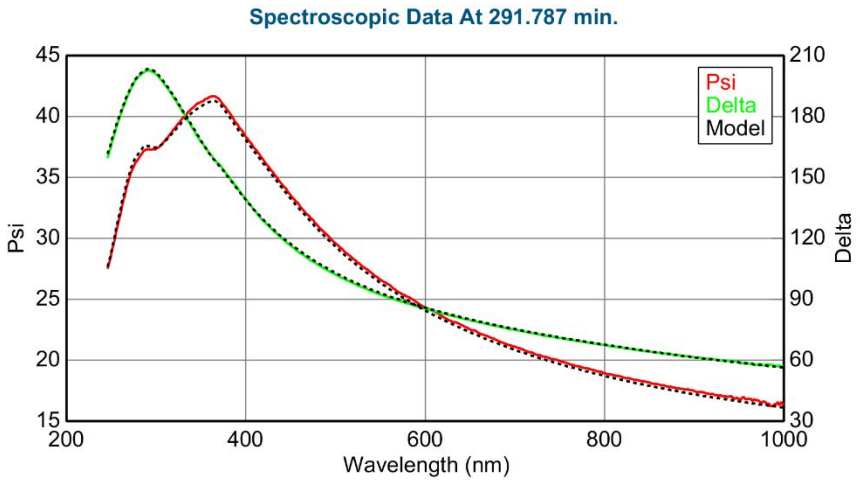

Figure S2. Modelling data from Cauchy relation for the PAA brush at pH 4.75 and an ionic strength of 100 mM .

Fit Results	Optical Model
MSE = 9.023 Thickness # 3 = 26.20 ± 0.280 nm A = 1.412 ± 0.001205 B = 0.00401 ± 7.1765E-05 Total Thickness = 129.20 ± 0.280 nm	- Layer # 3 = Cauchy Thickness # 3 = **26.20 nm** (fit) A = **1.412** (fit) B = **0.00401** (fit) C = 0.0000 - **Urbach Absorption Parameters** k Amplitude = 0.0000 Exponent = 0.00 Band Edge = 400.0 nm Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

Experimental and Model Generated Data Fits

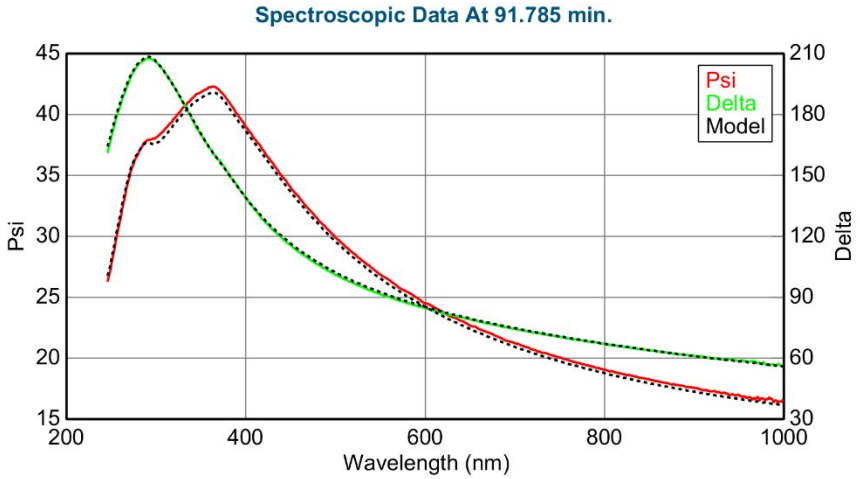

Figure S3. Modelling data from Cauchy relation for the PAA brush at pH 2.0 and an ionic strength of 100 mM.

Fit Results	Optical Model
MSE = 12.532 Thickness # 3 = 46.59 ± 0.417 nm EMA % (Mat 2) = 74.3 ± 0.25 Total Thickness = 149.59 ± 0.417 nm	- Layer # 3 = EMA Thickness # 3 = **46.59 nm** (fit) # of Constituents = 2 - Material 1 = Cauchy A = 1.504 B = 0.00738 C = 0.0000 + **Urbach Absorption Parameters** - Material 2 = Cauchy A = 1.323 B = 0.00327 C = 0.0000 + **Urbach Absorption Parameters** EMA % (Mat 2) = **74.3** (fit) depolarization = 0.333 Analysis Mode = Bruggeman Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

Experimental and Model Generated Data Fits

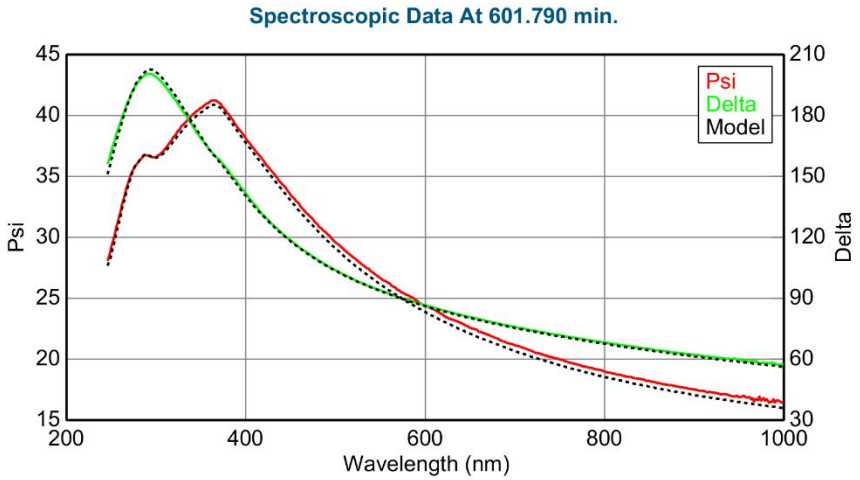

Figure S4. Fitting optical constants according to BEMA model for the PAA brush at pH 9.0 and an ionic strength of 100 mM.

Fit Results	Optical Model
MSE = 11.015 Thickness # 3 = 37.96 ± 0.369 nm EMA % (Mat 2) = 69.9 ± 0.30 Total Thickness = 140.96 ± 0.369 nm	- Layer # 3 = EMA Thickness # 3 = **37.96 nm** (fit) # of Constituents = 2 - Material 1 = Cauchy A = 1.504 B = 0.00738 C = 0.0000 + **Urbach Absorption Parameters** - Material 2 = Cauchy A = 1.323 B = 0.00327 C = 0.0000 + **Urbach Absorption Parameters** EMA % (Mat 2) = **69.9** (fit) depolarization = 0.333 Analysis Mode = Bruggeman Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm Substrate = SI_JAW

Experimental and Model Generated Data Fits

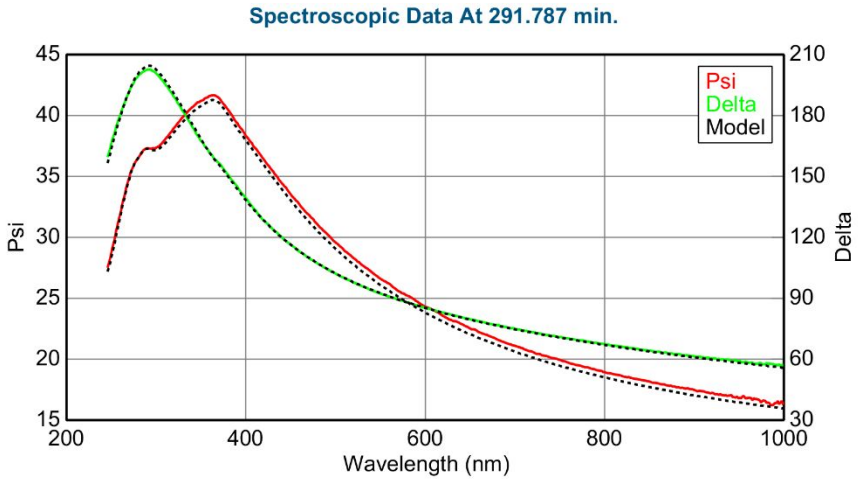

Figure S5. Fitting optical constants according to BEMA model for the PAA brush at pH 4.75 and an ionic strength of 100 mM.

Fit Results

MSE = 10.728
Thickness # 3 = 26.90 ± 0.316 nm
EMA % (Mat 2) = 55.8 ± 0.53
Total Thickness = 129.90 ± 0.316 nm

Optical Model

- Layer # 3 = EMA Thickness # 3 = **26.90 nm** (fit)
  - # of Constituents = 2
  - Material 1 = Cauchy
    - A = 1.504 B = 0.00738 C = 0.0000
    - + **Urbach Absorption Parameters**
  - Material 2 = Cauchy
    - A = 1.323 B = 0.00327 C = 0.0000
    - + **Urbach Absorption Parameters**
  - EMA % (Mat 2) = **55.8** (fit)
  - depolarization = 0.333 Analysis Mode = Bruggeman
- Layer # 2 = SIO2_JAW Thickness # 2 = 102.00 nm
- Layer # 1 = INTR_JAW Thickness # 1 = 1.00 nm
- Substrate = SI_JAW

Experimental and Model Generated Data Fits

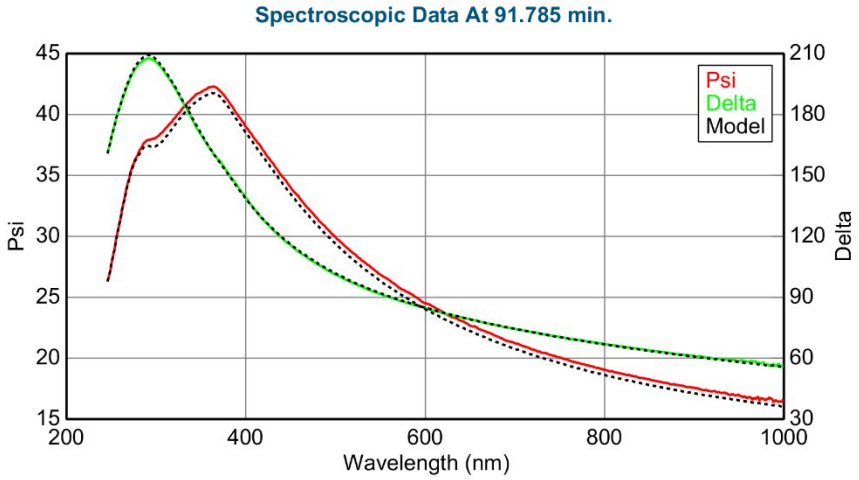

Figure S6. Fitting optical constants according to BEMA model for the PAA brush at pH 2.0 and an ionic strength of 100 mM.

S2: Determination of the sample molecular weight

Molecular weight of the poly (tert-butyl acrylate) synthesized in the solution has been measured by GPC and the grafting density has been calculated assuming that the molecular weight of the polymer chains, which are synthesized in the solution by sacrificial initiator, is equal to grafted chains on the surface. This is not the best assumption since the propagation and termination rate of polymerization in solution might be different from those of polymerization on the surface. To this end, previous studies have shown there will exist a difference between the molecular weight and dispersity of the polymers synthesized in solution and on the surface, respectively.[1,2] However, this assumption has been used in the cases that direct measurement of the molecular weight is not possible due to a limited number of chains on the surface (planar surfaces).[3,4] Further, because the grafting density is not a variable in our work a small uncertainty in the estimated grafting density measurement does not have any influence on the results and conclusions. Figure S7 shows the chain length distribution as a function of retention volume. The relatively low signal to noise ratio is due to the low value of the dn/dc of the poly (tert-butyl acrylate) in THF.

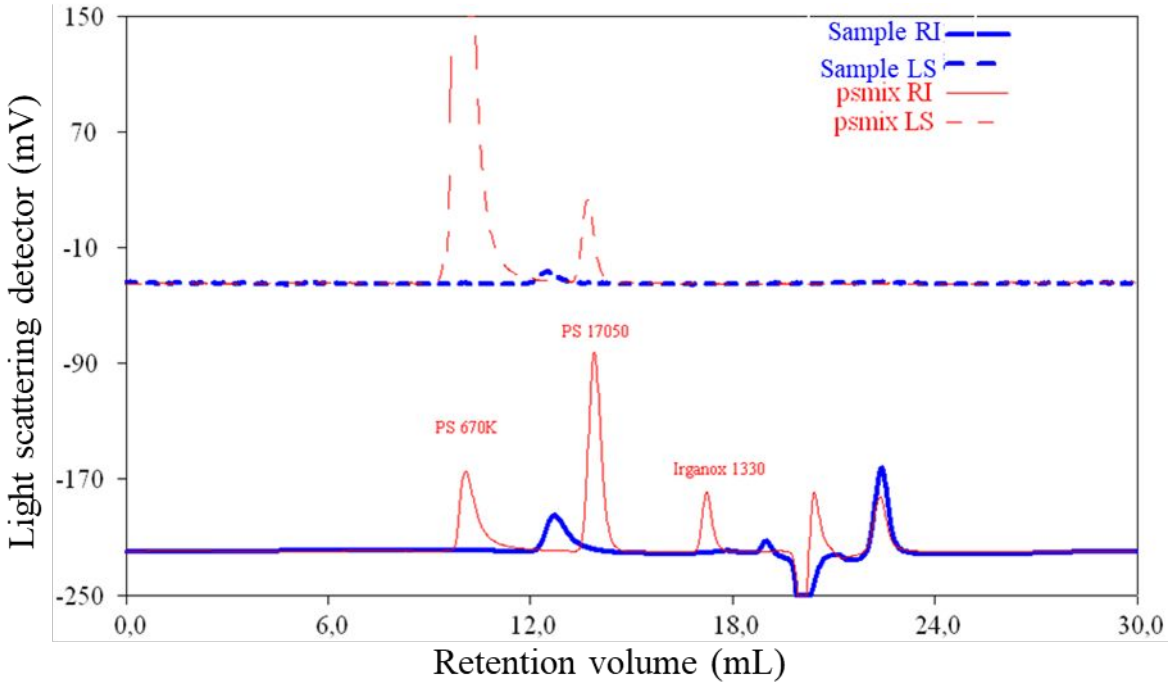

Figure S7. Light scattering signal as a function of retention volume for synthesized PtBA (blue) and poly styrene standards (red)

S3: Conversion-time plot for the controlled radical polymerizatrion

Figure S8 shows the logarithm of the ratio between the initial and current monomer concentration for the tert-butyl acrylate polymerization as a function of time. Approximate linearity of data confirms the controlled radical polymerization mechanism.

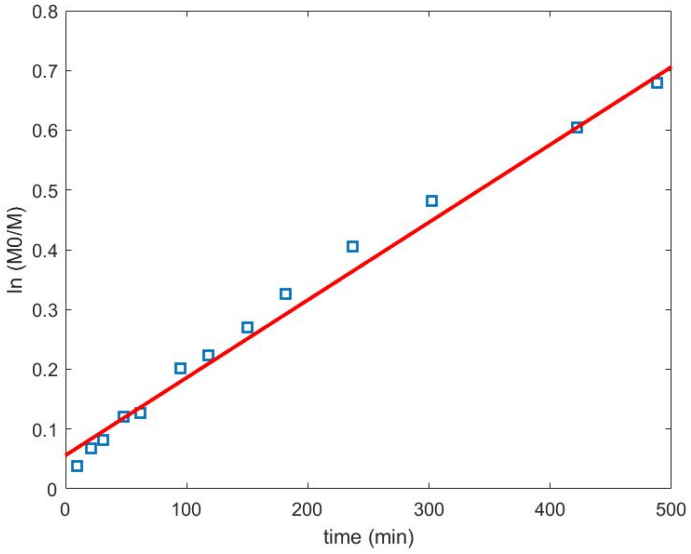

Figure S8. Change in the relative monomer concentration as a function of polymerization time.

S4: Fitting data points to the sigmoid function to find the pKa value

In order to determine pKa value, all experimental data are fitted to a sigmoid function mathematically expressed as:

$$f(x) = \frac{L}{1 + e^{-k(x - x_0)}}$$

Where the function, f, in this case is either brush height, Δf or ΔD; L is the maximum value of f; k is the logistic growth rate; x is the variable – in this case the pH value; and x_0 is the x-value of the sigmoid midpoint – in this case the apparent pKa value.

Fitting results of the dissipation data are presented in table S1.

Table S1- Fitting results of the dissipation data to logistic function.

Ionic strength (mM)	Overtone number	L	k	x_0	R^2
100	3	27.36	3.081	4.145	0.997
100	5	31.99	2.718	4.295	0.998
100	7	35.83	2.496	4.415	0.998
100	9	40.44	2.287	4.554	0.996
100	11	36.09	2.152	4.565	0.996
100	13	35.45	2.362	4.702	0.997
10	3	44.39	2.49	4.372	0.992
10	5	48.24	2.192	4.596	0.995
10	7	51.64	1.971	4.787	0.996
10	9	55.24	1.878	4.964	0.996
10	11	49.56	1.684	5.082	0.994
10	13	48.71	1.829	5.231	0.997
1	3	57.55	1.932	5.000	0.994
1	5	54.26	1.737	5.307	0.994
1	7	53.88	1.532	5.576	0.992
1	9	55.42	1.380	5.847	0.987
1	11	51.18	1.090	6.226	0.986
1	13	52.38	1.048	6.599	0.985

S5: Relative height calculation

The relative height reported in the paper has been defined as follows:

$$Relative\ height = \frac{Brush\ thickness\ (nm)}{Chain\ contour\ length\ (nm)}$$

With the chain contour length calculated as:

$$Chain\ contour\ length = N \times l$$

Where N is the degree of polymerization (measured for polymers which are synthesized in solution – see section S2) and l is the length of each monomer unit in all-trans conformation which is calculated as follows:

$$l = \sqrt{l(C-C)^2 \times (2 - 2\cos{(109.5)})}$$

in which l(C-C) is the length of a carbon- carbon bond (0.15 nm).

S6: Obtaining apparent pKa values from frequency data

In the main manuscript, we used the dissipation data to obtain apparent pKa values of the PAA brush as a function of vertical position. This was done for two reasons. First, the shape of the dissipation data where similar to the shape of the brush height versus pH data obtained with ellipsometry. Secondly, the apparent pKa values obtained from the dissipation data where in overall agreement with the values obtained from the ellipsometry data. Here, we have however performed the same analysis based on the frequency data and although the apparent pKa values differ from the ones obtained from the dissipation and ellipsometry data, all trends are similar to the dissipation. Thus we stress that the discussions and conclusions based on the dissipation data are also valid if one apply frequency instead of dissipation.

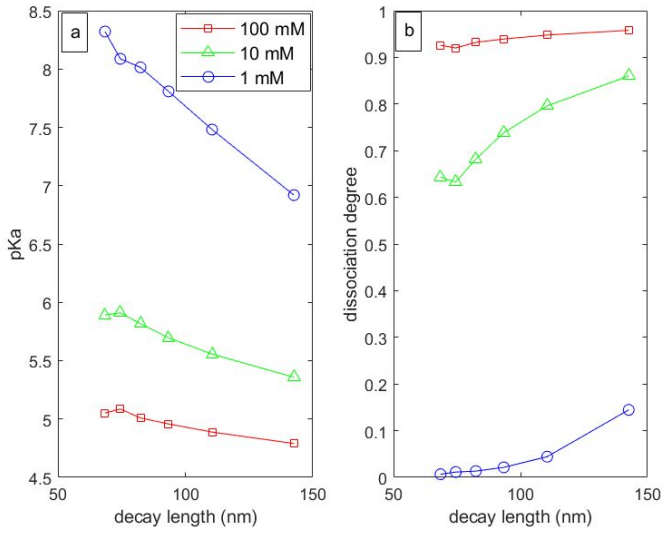

Figure S9. pKa value and dissociation degree as a function of decay length at 1, 10, and 100 mM NaCl solution determined from the QCM-D data presented in fig. 4 b, d and f.

References:

1. Turgman-Cohen, S. & Genzer, J. Simultaneous bulk- and surface-initiated controlled radical polymerization from planar substrates. *J. Am. Chem. Soc.* **2011**, 133, 17567–17569.

2. Kang, C., Crockett, R. & Spencer, N. D. The influence of surface grafting on the growth rate of polymer chains. *Polym. Chem.* **2016**, 7, 302–309.

3. Liao, W. P., Elliott, I. G., Faller, R. & Kuhl, T. L. Normal and shear interactions between high grafting density polymer brushes grown by atom transfer radical polymerization. *Soft Matter* **2013**, 9, 5753–5761.

4. Zhao, B., Yuan, G., Chu, X., Yang, J. & Zhao, J. Response of a permanently charged polyelectrolyte brush to external ions: the aspects of structure and dynamics. *Langmuir* **2018**, 34, 6757-6765.