Supporting Information

Structure of the Electrostatic Complex of DNA with Cationic Dendrimer of Intermediate Generation: The Role of Counterion Entropy

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Determination of the average degree of protonation of PAMAM G4 dendrimer

The charge density of the dendrimer was prescribed by its average degree of protonation (dp), which represents the average number fraction of protonated amine groups of dendrimer. Dendrimers with different dp values were prepared by adding predetermined amounts of 0.1 N HCl into the aqueous solutions of dendrimer. The values of dp were determined from the pH (measured by an ISTEK Model 720P pH meter) of the protonated dendrimer solutions. The molar concentrations of H^+ and OH^- in the solution are given by

$$[H^+] = 10^{-(pH)} \; ; \; [OH^-] = 10^{-(14 - pH)} \qquad \text{(S1)}$$

The molar concentrations of NH_3^+ (protonated primary amine group) and NH^+ (protonated tertiary amine group) in dendrimer can then be obtained via the charge balance [1]

$$[NH_3^+] + [NH^+] + [H^+] = [OH^-] + [Cl^-] \qquad \text{(S2)}$$

where $[Cl^-]$ was calculated from the concentration of HCl added for the protonation. The structural charge per dendrimer molecule is hence given by

$$\text{structural charge} = ([NH_3^+] + [NH^+]) / [G4] \qquad \text{(S3)}$$

where G4 is the molar concentration of PAMAM G4 dendrimer. The dp value is finally calculated via

$$\begin{aligned} dp &= (\text{structural charge})/(\text{total number of amine groups in a G4 molecule}) \\ &= (\text{structural charge})/126 \end{aligned} \qquad \text{(S4)}$$

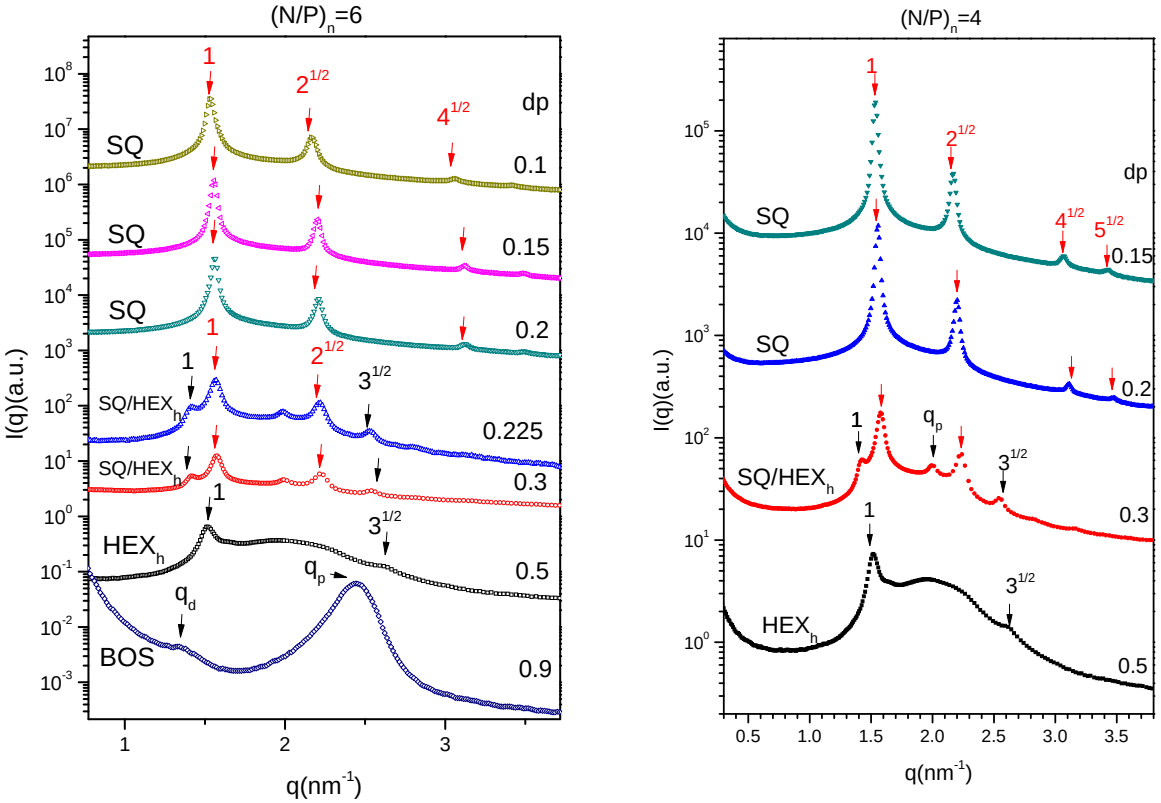
The following Table lists the measured pH and the calculated dp values of the four protonated dendrimer samples.

Sample	pH	structural charge	dp value
dp/0.1	9.08	12.64	0.10
dp/0.3	7.95	37.75	0.30
dp/0.6	5.34	75.56	0.60
dp/0.9	3.44	112.72	0.89

Therefore, PAMAM G4 dendrimers with different dp values were obtained for the subsequent complexation with DNA in this study.

Reference

1. Niu, Y.; Sun, L.; Crooks, R. *Macromolecules* **2003**, 36, 5725.



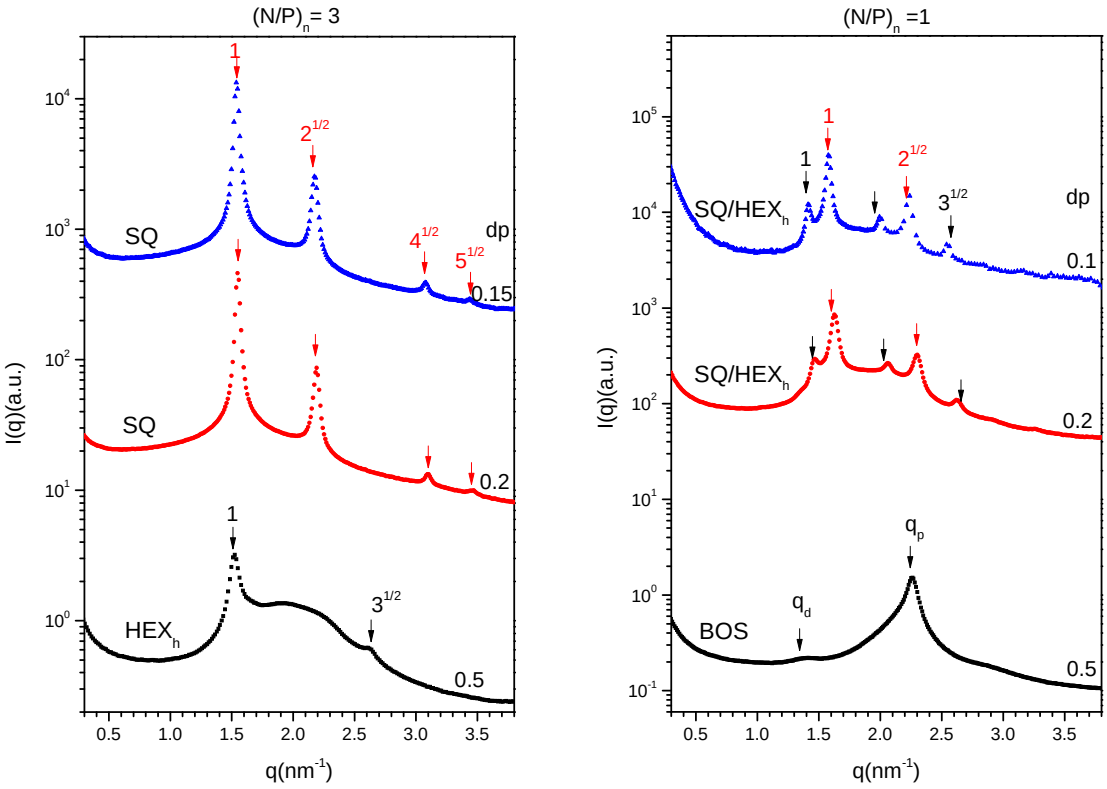


Figure S1. SAXS and SANS profiles of DNA-PAMAM G4 dendriplexes as a function dendrimer dp values under the fixed $(N/P)_n$ ratios marked in the figures.

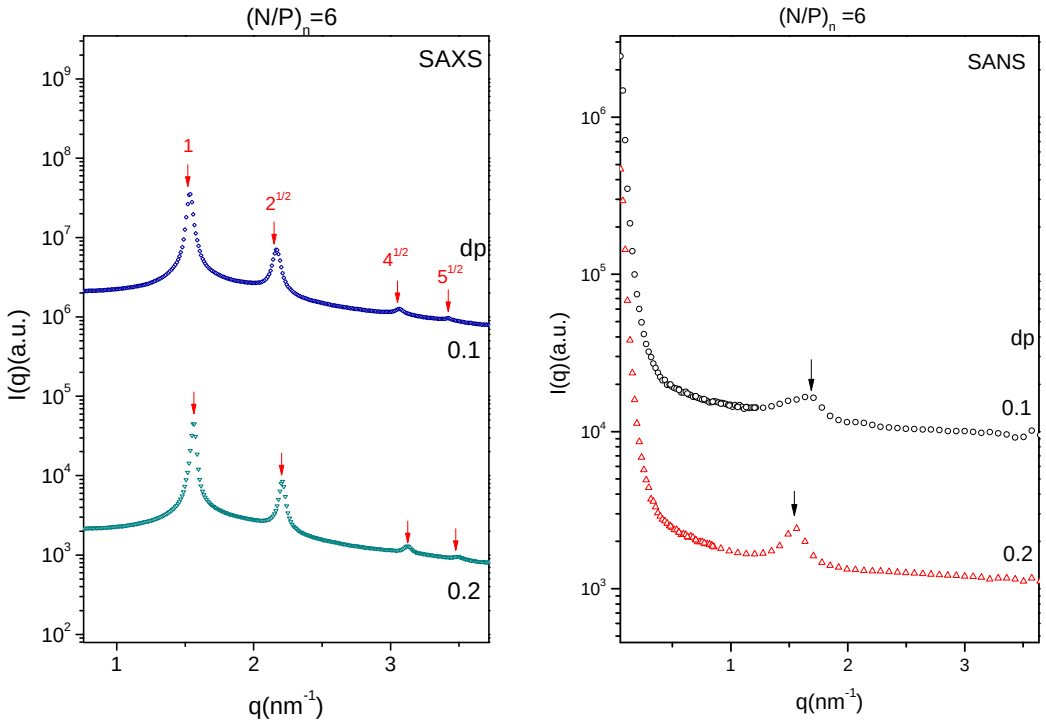


Figure S2. SAXS and SANS profiles of dp/0.1 and dp/0.2 dendrplexes with $(N/P)_n$= 6 to demonstrate that the scattering profiles associated with a given type of structure were virtually the same (except for slight difference in peak position). This implies that a given type of structure was characterized by a well-defined composition or $(N/P)_a$, and the structure with such a composition existed over a certain range of dp.