Notes

Polyelectrolyte Behavior of Astramol Poly(propyleneimine) Dendrimers

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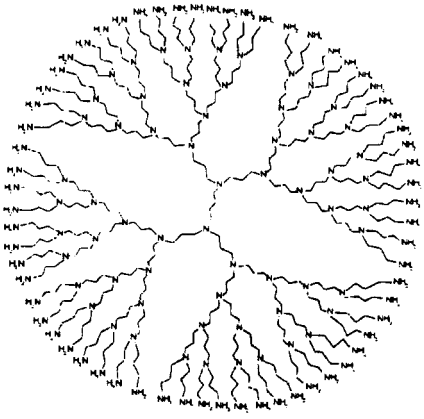
Introduction

The poly(propylenimine) dendrimers, DAB-*dendr*-$(NH_2)_x$, are treelike molecules that are built by starting with a diaminobutane core and adding propylenimine branches to it by an iterative procedure. As a result, a highly symmetric and regular structure is formed, shown below schematically as two-dimensional. The molecular size grows in three dimensions with each additional reaction sequence, called a "generation". The fifth generation dendrimer is shown in I.



(I)

The amine groups of DAB-*dendr*-$(NH_2)_x$ can be protonated, so these peculiar polymers are classified as polyelectrolytes that are positively charged in the protonated form. One of the most important issues in polyelectrolyte chemistry, in particular for DAB-*dendr*-$(NH_2)_x$, relates to the investigation of charging processes that are very sensitive to the structural features of the polymer. The simplest way to study these processes is by potentiometric titration.

Experimental Section

Astramol poly(propylenimine) dendrimers were produced at DSM. They are commercially available from DSM or Aldrich. The synthesis involves a repetitive reaction sequence of Michael additions of acrylonitrile to primary amine end groups followed by catalytic hydrogenation of the nitrile groups. Diaminobutane was used as the core molecule. Detailed information on the synthesis was published elsewhere.[1,2] The Astramol poly(propylenimine) dendrimers of different generations from DAB-*dendr*-$(NH_2)_4$ to DAB-*dendr*-$(NH_2)_{64}$ were used.

The potentiometric titration of the aqueous solutions of dendrimers was performed using a RTS 822 Radiometer titrator with a Sigma glass calomel combination electrode (±0.02 pH) at 20 °C under a nitrogen atmosphere. The 5 mL solution samples containing 0.014 mol/L of dendrimers in distilled water were titrated with 0.1 N HCl. The titrant was added dropwise with continued stirring in 25 μL portions using a micropipet. The time interval to achieve a constant pH value was 2 min.

Results and Discussion

It is important to point out that DAB-*dendr*-$(NH_2)_x$ molecules involve two sorts of amine groups. The primary amine end groups ($-NH_2$) are on the periphery of DAB-*dendr*-$(NH_2)_x$, and their number is equal to 2^{n+1}, with n the generation of dendrimer and x the number of primary amine groups. The tertiary amine groups (>N−) are situated at the branching points in the core of the DAB-*dendr*-$(NH_2)_x$ molecules, and their number is equal to $2^{n+1} - 2$. These two types of amine groups, if isolated, are characterized by different pK values,[3] which are the negative logarithms of the acidic dissociation constant for the protonated primary (pK^p) and tertiary (pK^t) amine groups correspondingly. The basicity of the primary amine group is higher compared with that of the tertiary one, i.e., pK^p > pK^t.

In the case of ionization of polyelectrolytes the effect of electrostatic repulsion between different charged sites plays a very important role. This effect brings about the decrease of the pK value with the increase of the protonation degree, α. This behavior is most clearly observed when the titration is carried out in the absence of a shielding low molecular weight electrolyte. Therefore, the majority of titration experiments were fulfilled in salt-free aqueous solutions of DAB-*dendr*-$(NH_2)_x$.

The potentiometric titration curves for dendrimers of different generations are shown in Figure 1. One can see that the potentiometric curves for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, and DAB-*dendr*-$(NH_2)_{16}$ reveal two clearly distinguishable sections, which correspondingly relate to protonation of primary and tertiary amine groups. The borders between these regions, α_1, for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, and DAB-*dendr*-$(NH_2)_{16}$ are marked by the arrows on the α axis. The titration of primary amine groups proceeds in the interval $0 < \alpha < \alpha_1$, and the titration of tertiary amine groups proceeds in the interval $\alpha_1 < \alpha < 1$. The experimentally obtained ratio $[-NH_2]/[>N-] = \alpha_1/(1 - \alpha_1) = 2/1$ for DAB-*dendr*-$(NH_2)_4$, 1.33/1 for DAB-*dendr*-$(NH_2)_8$, and 1/1 for DAB-*dendr*-$(NH_2)_{16}$, is in an agreement with the ratio between the number of primary and tertiary amine groups as is expected from the chemical structure of DAB-*dendr*-$(NH_2)_x$.

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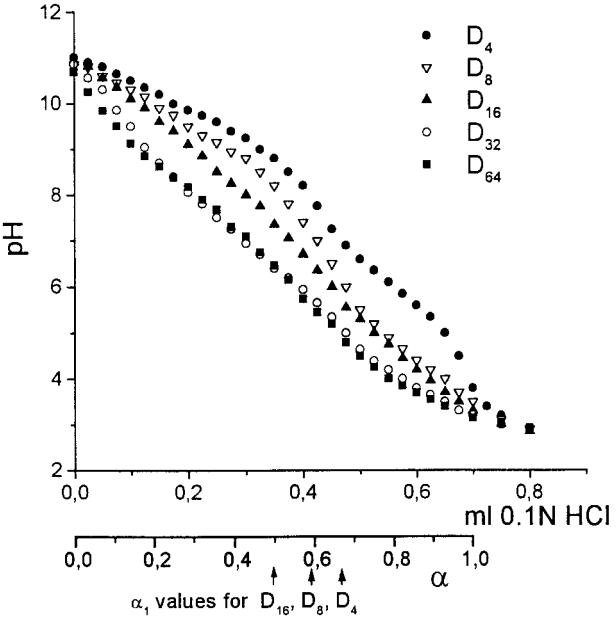

Figure 1. Potentiometric titration curves for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, DAB-*dendr*-$(NH_2)_{16}$, DAB-*dendr*-$(NH_2)_{32}$, and DAB-*dendr*-$(NH_2)_{64}$ in salt-free aqueous solutions; [DAB-*dendr*-$(NH_{2\ bn})_x$] = 0.014 mol/L, V = 5 mL, T = 20 °C.

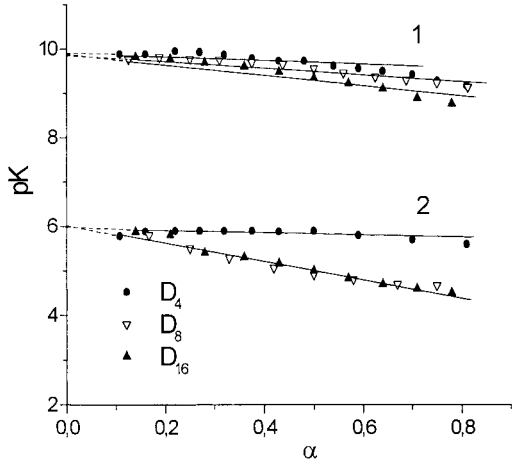

Figure 2. pK^p−α (1) and pK^t−α (2) dependencies for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, and DAB-*dendr*-$(NH_2)_{16}$, obtained from the data in Figure 1.

We analyzed the potentiometric titration data in terms of the modified Henderson−Hasselbach equation:[4]

$$pK = pH + \log \alpha/(1 - \alpha) = pK_o - 0.434\Delta G_{el}(\alpha)/RT \quad (1)$$

where pK_o is the characteristic pK at α → 0 characterizing ionization of the isolated amine group, and $G_{el}(\alpha)$ is the electrostatic free energy of a polyion at a given α. The degree of dissociation, α, was calculated as the molar ratio of the titrant added to the DAB-*dendr*-$(NH_2)_x$ monomer units. The dependence of pK^p (pK^p = pH + log α/(1 − α) in the interval of α from 0 to α_1) and of pK^t (pK^t = pH + log α/(1 − α)) in the interval of α from α_1 to 1) on α for both of these groups is shown in Figure 2 for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, and DAB-*dendr*-$(NH_2)_{16}$. One can see that in the case of DAB-*dendr*-$(NH_2)_4$ the pK values are only slightly dependent on α and therefore pK^p = 9.85 and pK^t = 6.0 for DAB-*dendr*-$(NH_2)_4$ actually represent the dissociation constants of $-NH_3^+$ and $\geq NH^+$ groups electrostatically not much interacting with each other. In the case of DAB-*dendr*-$(NH_2)_8$ and DAB-*dendr*-$(NH_2)_{16}$ a somewhat marked decrease of pK^p and pK^t is revealed with increasing α. The pK^p−α and pK^t−α dependencies are practically linear. Their slopes reflect the influence of the electrostatic potential of the DAB-*dendr*-$(NH_2)_8$ and DAB-*dendr*-$(NH_2)_{16}$ polycations on the amine groups protonation. Therefore, we analyzed the potentiometric data in terms of the modified Henderson−Hesselbach equation (1). The characteristic pK_o^p and pK_o^t were obtained from the intercepts of the straight lines with the pK axis in Figure 2. These values are shown in Table 1.

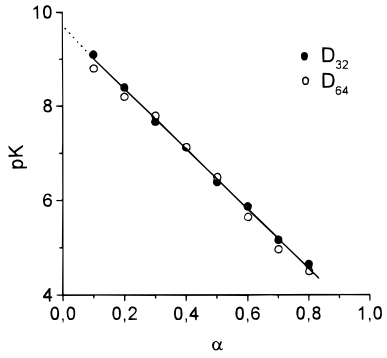

Figure 3. Dependencies pK−α for DAB-*dendr*-$(NH_2)_{32}$ and DAB-*dendr*-$(NH_2)_{64}$ obtained from the data in Figure 1. The correlation coefficient is 0.995.

Table 1. Values of the Characteristic pK_o^p and pK_o^t for DAB-*dendr*-$(NH_2)_x$ Obtained in Salt-Free Aqueous Solutions at [DAB-*dendr*-$(NH_2)_x$] = 0.014 mol/L

DAB-*dendr*-$(NH_2)_x$	pK_o^p	pK_o^t
DAB-*dendr*-$(NH_2)_4$	9.85	6.0
DAB-*dendr*-$(NH_2)_8$	9.80	6.0
DAB-*dendr*-$(NH_2)_{16}$	9.80	6.1
DAB-*dendr*-$(NH_2)_{32}$	9.75	
DAB-*dendr*-$(NH_2)_{64}$	9.75	

It is seen from the data in Table 1 that the pK_o^p and pK_o^t values for DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$, and DAB-*dendr*-$(NH_2)_{16}$ practically coincide.

Up to now we discussed ionization of the lower generations of DAB-*dendr*-$(NH_2)_x$, which are characterized by separate titration of outer shell primary and inner tertiary amine groups. However, both of them are titrated in the manner typical for ordinary polyelectrolytes, i.e., dissociation of primary and tertiary amine groups is described by the apparent dissociation constant K^p or K^t, which increases with the increasing degree of protonation, α.

If we now refer to titration of higher generations DAB-*dendr*-$(NH_2)_x$ (DAB-*dendr*-$(NH_2)_{32}$ and DAB-*dendr*-$(NH_2)_{64}$) in aqueous salt-free solution, we find that these titration curves are smooth and have no clear inflection point (Figure 1, curves 4 and 5). It means that the regions in which the protonation of outer $-NH_2$ and inner >N− groups takes place are considerably overlapping. Indeed, the whole potentiometric curves of DAB-*dendr*-$(NH_2)_{32}$ and DAB-*dendr*-$(NH_2)_{64}$ can be represented as an unresolved combination of contributions approximated by the dependence of pK = pH + log α/(1 − α) on α. In other words, the protonation equilibrium can be described by a single linear function pK(α) shown in Figure 3. The pK_o value for both DAB-*dendr*-$(NH_2)_{32}$ and DAB-*dendr*-$(NH_2)_{64}$ equals 9.75. These values are close to the pK_o^p values (the characteristic pK values

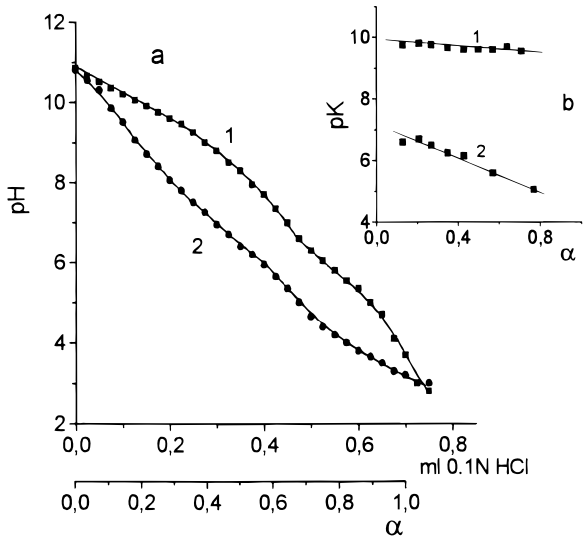

Figure 4. (a) Potentiometric titration curve for DAB-*dendr*-$(NH_2)_{32}$ in 0.02 mol/L NaCl (1) and in salt-free aqueous solution (2) (b) $pK^p-\alpha$ (1) and $pK^t-\alpha$ (2) dependencies for DAB-*dendr*-$(NH_2)_{32}$ in 0.02 mol/L NaCl; [DAB-*dendr*-$(NH_2)_{32}$] = 0.014 mol/L, $V = 5$ mL, $T = 20$ °C.

for the primary amine groups) of DAB-*dendr*-$(NH_2)_4$, DAB-*dendr*-$(NH_2)_8$ and DAB-*dendr*-$(NH_2)_{16}$ (see Table 1).

The behavior revealed for DAB-*dendr*-$(NH_2)_{32}$ and DAB-*dendr*-$(NH_2)_{64}$ is typical for ordinary high molecular weight polyelectrolytes.[4,5] The rather high slope of $pK-\alpha$ dependencies, which is proportional to $\partial G_{el}(\alpha)/\partial\alpha$, reflects the high charge density within these dendrimers. The practically linear decrease of p*K* values with α shows that there are no marked changes in the size of dendrimer molecules due to the increase of their positive charge.

It is well-known that the addition of low molecular weight salts strongly influences ionization of linear polyelectrolytes. In the case of the studied dendrimers it was observed for the potentiometric titration of DAB-*dendr*-$(NH_2)_{32}$ by 0.1 N HCl in 0.02 N NaCl (Figure 4a). As one would expect, the corresponding titration curve is located in the more alkaline pH region as compared with the potentiometric curve of DAB-*dendr*-$(NH_2)_{32}$ in salt-free solution. Moreover, the dependence of p*K* on α for DAB-*dendr*-$(NH_2)_{32}$ is not a single line in terms of eq 1 but shows two distinct regions (Figure 4b) similar to those found for the salt-free solutions of the lower generation dendrimers. In other words, the addition of a simple salt results in effective shielding of Coulomb interactions between the positively charged dendrimer sites that distinguishes between protonation of different types of amine groups.

Our investigations on the potentiometric titration of poly(propylenimine) dendrimers showed that the presence of the two types of amine groups with different basicities and electrostatic interactions of the protonated amine groups (the polyelectrolyte effect) are important factors in the peculiarities of the dendrimer ionization. The presence of the two types of amine groups is strongly manifested in the case of lower generation dendrimers in the form of the two separate pH regions where peripheral primary and inner tertiary amine groups are titrated. The polyelectrolyte effect dominates in the case of higher generation dendrimers. It is manifested in the strong decrease of the p*K*(α) in the course of the protonation of dendrimer amine groups due to the increasing electrostatic potential of the dendrimer polycations. In the latter case, both primary and tertiary amine groups are titrated in the markedly overlapping pH regions. The role of the first effect increases while the role of the second effect decreases when shielding simple salts are added to the aqueous dendrimer solutions.

References and Notes

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