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Intermolecular Interactions between Dendrimer Molecules in Solution Studied by Small-Angle Neutron Scattering

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ABSTRACT: Small-angle neutron scattering has been applied for structural investigations of amine-terminated poly(propylene imine) dendrimer (Astramol) solutions in D_2O as a function of concentration and acidity. The forward scattering, $d\Sigma/d\Omega(Q = 0)$, decreases progressively by increasing dendrimer concentration due to interdendrimer interference, giving rise to a well-defined interference peak. Upon increasing dendrimer concentration, a shift is observed in the peak position, $Q_{\max}$, with the empirical scaling relation $Q_{\max} \sim \phi^{0.55\pm0.05}$, which is significantly larger than that of a simple packing argument $Q_{\max} \sim \phi^{1/3}$. At high Q values, all data sets collapse to a single curve, indicating that the internal structure of the dendrimers are unaffected by interactions between neighboring molecules. Upon addition of acid, the dendrimers become charged, giving rise to a pronounced interference peak. These Coulomb interactions can be screened by addition of either excess acid or salts.

1. Introduction

Dendrimers are synthetic polymeric macromolecules with complex (controlled) architecture.[1,2] Their structure is built by repetitive reaction steps starting from a central multifunctional core under systematic introduction of branching sites. The activity in this field of polymer chemistry has increased considerably in the last decade. Currently, the research activity is shifting from pure synthesis, characterization, and material properties to industrial applications.

The first theoretical treatment of the amine-terminated poly(amido−amine) dendrimers (PAMAM) was presented by de Gennes and Hervet.[3] Considering the problem in the limit of long flexible spacers between the trifunctional monomers, in an athermal solvent, with end groups fully reacted, de Gennes and Hervet predicted a segment distribution function which has the highest density on the periphery with relatively hollow cores.

Lescanec and Muthukumar[4] found, on the contrary, using Monte Carlo simulations, that the density is highest at the center with a decaying profile to the edge of the molecule.

Recently, the molecular structure of poly(propylene imine) dendrimers, DAB-*dendr*-$(NH_2)_{64}$, in dilute solution has been reported by Scherrenberg et al.[5] Small-angle neutron scattering (SANS), viscosimetry and molecular dynamics simulations (MD) techniques were used to characterize the molecular characteristics of the dendrimers. It was concluded that the size of dendrimers varies with the molar mass roughly as $M^{1/3}$, in direct conflict with the theoretical results predicted by de Gennes and Hervet[3] as well as Lescanec and Muthukumar.[4] In addition, the radial density distributions show that the end groups are distributed throughout the dendrimer.

In another recent study, Boris and Rubinstein[6] performed an equilibrium self-consistent mean field (SCMF) calculation and derived a simple analytical equation from Flory theory[7] for the dependence of the radius of gyration of the Starburst poly(amido−amine) dendrimers upon generation. The results show a *good agreement* with both *experiments*[8,9] and *computer simulations*.[4,10,11,12] It was found that the dendrimers have dense, not hollow, cores and the density is greatest at the core and decays to the edge of the molecule. The dendrimer's end groups are distributed throughout the volume of the molecule.

Up to now, only few studies have been carried out in a concentrated regime. Briber et al.[8,9] performed SANS and SAXS (small-angle X-ray scattering) experiments on concentrated poly(amido−amine) dendrimer solutions, and investigated the intermolecular interactions in an acidified medium. They found that the molecules develop *large scale interactions* which can be *screened* by the addition of excess acid or salt.

In this paper, we investigate systematically by SANS the influence of the concentration and the acidity on the intermolecular interactions (i.e., excluded volume and electrostatic interactions) in solutions of the fifth generation poly(propylene imine) dendrimer, DAB-*dendr*-$(NH_2)_{64}$. In addition, a preliminary result of the screening of the interactions by adding the salt to an acidified solution is presented.

2. Experimental Section

2.1. Materials. The Astramol dendrimers are made using diaminobutane as a core. They were synthesized by repetitive reaction sequence of Michael additions of acrylonitrile to the primary amine groups followed by hydrogenation of nitrile groups. More details concerning the synthesis are published elsewhere.[13,14] In the present work, we focus our investigation on the fifth generation dendrimers, DAB-*dendr*-$(NH_2)_{64}$, with 64 amine end groups. These dendrimers have been purified because they contain a very low amount (<1%) of nitrile end groups dendrimers, DAB-*dendr*-$(CN)_{64}$. This impurity can be removed in the following way: In a separation funnel 20 g of DAB-*dendr*-$(NH_2)_{64}$ dissolved in 10 mL of water is washed twice with 25 mL of chloroform. Phase separation into two layers after shaking takes about 6 h. The purified DAB-*dendr*-$(NH_2)_{64}$ is then obtained by removing water with a rotary evaporation for several hours.

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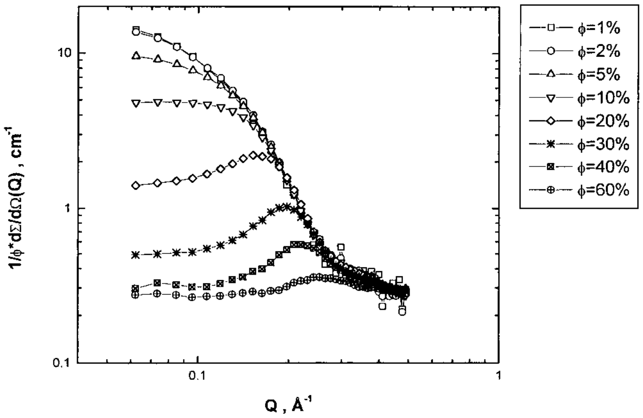

Figure 1. Scattering intensity, in log–log representation, as a function of the dendrimers concentration in D_2O.

2.2. Small-Angle Neutron Scattering (SANS). The small-angle neutron scattering measurements were carried out using the SANS facility at the Risø National Laboratory in Denmark. The covered scattering vectors, defined as $|\mathbf{Q}| = Q = (4\pi/\lambda)\sin(\theta/2)$, vary between 0.002 and 0.5 $Å^{-1}$ with variable neutron wavelength resolution $\Delta\lambda/\lambda$ (λ is the neutron wavelength, θ is the scattering angle, and $\Delta\lambda$ is the full width at half-maximum value of the neutron flux vs wavelength distribution). The neutrons are monochromatized by a mechanical selector, which in the present experiments was set at a wavelength resolution $\Delta\lambda/\lambda = 18\%$. For each sample, the scattering patterns were obtained using two different spectrometer configurations: $\lambda = 3$ Å, $D = 3$ m, and $L = 3$ m and $\lambda = 3$ Å, $D = 1$ m, $L = 1$ m (L is the collimation length and D is the sample–detector distance) corresponding then to two partially overlapping ranges of the scattering vectors **Q**: 0.025–0.2 and 0.06–0.5 $Å^{-1}$, respectively.

The dendrimers were dissolved in deuterated water D_2O (Campro Scientific) in a concentration range from 1% to 60% (v/v). The samples were measured at room temperature in quartz cuvettes (Helma) with path lengths of 1 or 2 mm. The data were radially averaged to reduce the statistical error. The scattering due to the empty cell and the solvent, as well as a calculated incoherent background caused by the protons, was subtracted. Thereafter, the neutron scattering intensity of the raw data is normalized with the scattering of 1 mm of water, H_2O, used as a standard. The water scattering was also used to determine the detector efficiencies. Finally, one obtains the coherent scattering cross-section, $d\Sigma/d\Omega(Q)$, in absolute units (cm^{-1}).

3. Results and Discussion

3.1. Effect of the Concentration. Figure 1 displays a double logarithmic representation of the scattered intensity as a function of dendrimer concentration in D_2O. The scattering patterns were normalized to the concentration in order to allow a direct comparison.

At high Q values, the scattered intensities were found to be independent of the concentration as they *collapse* to a single curve. This regime contains information about the local structure within the dendrimer molecule and implies that the internal structure is not influenced significantly by the intermolecular interactions.[15] At low and intermediate Q values, the scattering curves are identical for low concentrations ($\phi = 1\%$ and 2%) yielding the dendrimers form factor $P(Q)$ whereas the intensity decreases progressively by increasing the concentration ($\phi \geq 5\%$), as the interdendrimer interference (structure factor), $S(Q)$, becomes more pronounced. It is important to notice that the observed scattering function does not show the Q^{-4} variation at large Q which corresponds to the scattering from sharp interface (Porod's law).

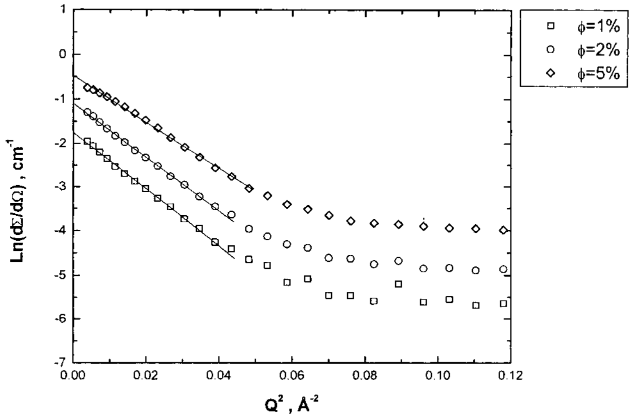

Figure 2. Guinier representation of the scattering intensity from 1%, 2%, and 5% (v/v) dendrimer solutions in D_2O.

The coherent scattering cross-section, $d\Sigma/d\Omega(Q)$, for a monodisperse system can be defined as

$$\frac{d\Sigma}{d\Omega}(Q) = \phi\frac{\Delta\rho^2}{N_A}V_w P(Q)S(Q) \tag{1}$$

Here N_A denotes the Avogadro constant and ϕ the volume fraction of the dendrimers in solution (v/v). V_W is the weight average molar volume of the dendrimers defined as $V_W = M_w/d$, where $M_w = 7156$ g·mol^{-1} is the weight average molar mass of the molecule. The dendrimer density d is approximated to 1 g·cm^{-3}. The quantity $P(Q)$ is the form factor, and $S(Q)$ is the interparticle structure factor. $\Delta\rho^2$ is the contrast factor given by

$$\Delta\rho^2 = \left(\frac{\sum_d b_i}{v_d} - \frac{\sum_s b_i}{v_s}\right)^2 \tag{2}$$

where $\sum_d$ and $\sum_s$ denotes summation of the scattering lengths b_i of the different atoms in the molecules, and v_d and v_s the volumes of the dendrimer and the solvent molecules, respectively. One defines the scattering length density ρ as $\rho = \sum_i b_i/v$, which takes the values $\rho_{D_2O} = 6.40 \times 10^{10}$ cm^{-2} and $\rho_{dendr} = 0.32 \times 10^{10}$ cm^{-2} for D_2O and dendrimer molecules, respectively.

For a quantitative evaluation in the low Q regime, the low concentration data were analyzed by the classical Guinier method in order to determine the radius of gyration R_g. The form factor was approximated by the Guinier formula at small Q:[16]

$$P(Q) = P(0)\exp\left(-\frac{Q^2 R_g^{\,2}}{3}\right) \tag{3}$$

As shown in Figure 2, the radii of gyration were obtained from the slope of the representation ($\ln(d\Sigma/d\Omega(Q))$ vs Q^2) in the Guinier regime defined for low Q R_g.[16] R_g takes the values 13.9, 13.6, and 12.6 Å for concentrations of 1%, 2%, and 5%, respectively, where the reduction in R_g on concentration is due to virial effects. The radius of gyration obtained for the lower concentration (1%), $R_g = 13.9$ Å, is similar to the value found by Scherrenberg et al.[5] and is close to those obtained by the same authors using the molecular dynamic simulations and viscosimetry.

The scattered intensity at low Q values, $d\Sigma/d\Omega(Q = 0)$, is progressively decreased by increasing the concen-

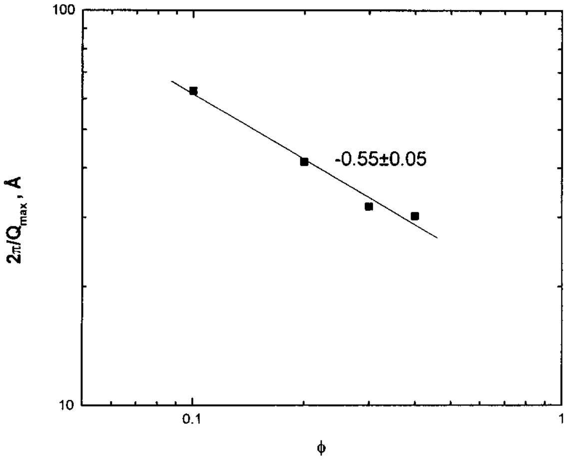

Figure 3. Variation of the mean particle distance $2\pi/Q_{max}$ against the dendrimers concentration in D_2O.

tration due to interdendrimer interferences, i.e., the structure factors.[17,18]

For concentrations $\phi > 5\%$, a single broad peak is observed (Figure 1), centered at a wavevector value Q_{max}, which is shifted toward wider angles with increasing dendrimer concentration. For the highest concentration (60%), which is beyond the overlap concentration ϕ^*, the peak intensity is markedly diminished. This overlap concentration is defined as $V_W/((4\pi/3)R_h^3N_A)$, assuming spherical molecules, and calculated to 36.5%. R_h is the hydrodynamic radius of the DAB-*dendr*-$(NH_2)_{64}$ dendrimers obtained from viscosity measurements ($R_h = 19.8$ Å).[5] The correlations seem to be lost at high concentration as is also observed for many polyelectrolyte,[19] protein,[20,21] and ionic micelle[22] systems. This could be explained by the large interpenetration of the molecules because the medium is filled more and more by the particles as the concentration increases (screening of the excluded volume interactions).

In our case, the ratio R_g/R_h is equal to 0.702. Previous studies on poly(amido−amine) dendrimers (PAMAM)[23] show that the ratio R_g/R_h takes the values 0.74, 0.88, and 1.00 for generations 4, 7, and 8, respectively. Aharoni and Murthy[24] have measured R_g/R_h for poly-(α,ε,L-lysine) by small-angle X-ray methods and have found that the ratio varies between 0.88 and 1.04. For linear chains with Gaussian statistics, $R_g/R_h = 0.67$.[25]

However, the ratio R_g/R_h for a uniform density solid sphere is $(3/5)^{1/2} = 0.775$. Values larger than this could be the result of higher segment density near the exterior of the dendrimers.

Figure 3 shows the concentration dependence of the peak position Q_{max}. An empirical scaling relation is observed for Q_{max} vs ϕ with an exponent 0.55 ($Q_{max} \sim \phi^{0.55\pm0.05}$) in the volume fraction range 10%−40% (v/v). Presently, there is no clear explanation of the exponent 0.55.

For solutions of the hard sphere, the peak position Q_{max} has been interpreted simply as the mean particle distance given by the relation: $D \sim 2\pi/Q_{max} \sim [(4\pi/3)R_{hs}^3/\phi]^{1/3}$, where R_{hs} is the hard sphere radius, i.e., given by the particle number density only. This relation is not correct because Q_{max} is given by a complex function of R_{hs} and ϕ.[26] Inoue and Matsumoto[27] found, for colloidal solutions of globular protein (Ovalbumin and Bovine serum albumin molecules) using small-angle X-ray scattering, the same exponent (0.33) in the variation of Q_{max} at low concentrations, as expected frequently for an uniform particle distribution in solution, while at higher concentrations, Q_{max} scales as ϕ. On the other hand, it was found for other protein systems with ellipsoid shape that the Q_{max} scales as $\phi^{0.27}$ as well as ϕ depending on the concentration range. Willner et al.[28] found a 0.25 exponent for star polymers in solution.

Table 1. Average Distance *D* between the Dendrimer Centers Assuming an Arrangement of Spherical Particles in a Distorted Face-Centered Cubic Lattice

ϕ (% v/v)	Q_{max} (Å^{-1})	D^a(Å)
10	0.1	76.7
20	0.152	50.4
30	0.197	38.9
40	0.208	36.9
60	0.252	30.4

[a] Calculated from SANS measurements via Q_{max} using eq 4.

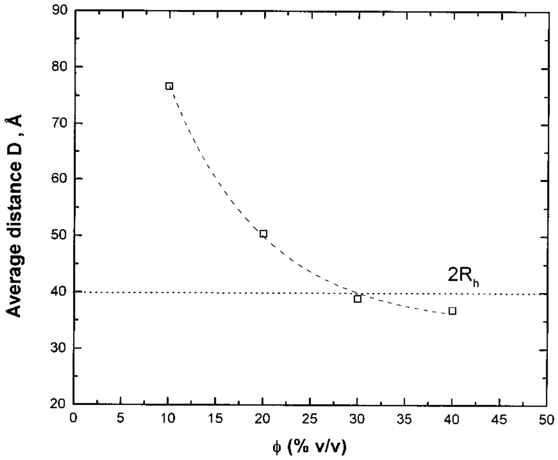

Figure 4. Representation of the average distance *D* between dendrimer centers obtained from eq 4.

In general, the position of the peak depends on the structure of the *arrangement* of the particles and on the particular *structure of each particle* (i.e., interparticle and intraparticle interferences).[16] If we assume the model proposed by Guinier and Fournet,[16] based on the arrangement of particles in a *distorted face-centered cubic lattice*, an average distance *D* between the particle centers is related to the position of the peak Q_{max} via the equation

$$D = 1.22\left(\frac{2\pi}{Q_{max}}\right) \qquad (4)$$

The estimated values of D are listed in Table 1 and plotted in Figure 4. We notice that at the overlap concentration ϕ^*, where the particles approach each other, the mean distance should be approximately $2R_h \sim 40$ Å, yielding a peak position of $Q_{max} \sim 0.19$ Å^{-1}, which is close to the experimental value of about 0.2 Å^{-1}.

We note that this model leads to a $^1/_3$ exponent value in the variation of Q_{max}, regardless of the concentration, which is different from the experimental value. However, it is important to mention that we deal with a *short-range ordered liquidlike* system and not with a crystalline lattice. Such kind of order leads to a scattering which may not be explained by the concept of hard spheres. This method could be used neverthe-

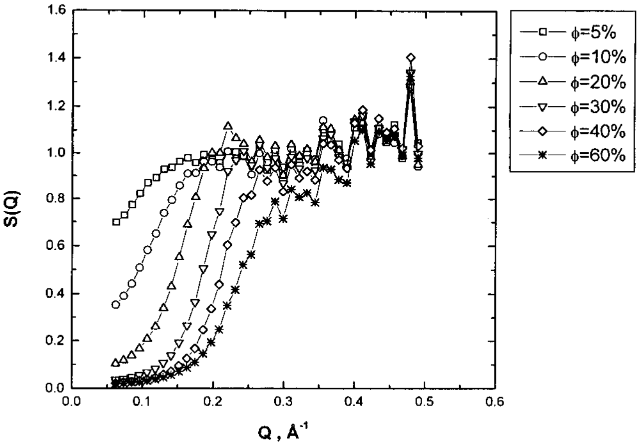

Figure 5. Structure factor S(Q) vs *Q* extracted from the SANS patterns of Figure 1.

less as a first approximation to relate the peak position to an average distance.

Hauber et al.[29] used also this model for star polymers and obtained a good agreement between the hard sphere diameter obtained from the light scattering measurements and the particle distance calculated from eq 4.

Finally, one can evaluate the effect of the concentration via the structure factor S(Q) by dividing the total scattering dΣ/dΩ(Q) by the dendrimer's form factor as can be seen from eq 1. We used the scattered intensity corresponding to $\phi = 2\%$ approximated to the $\phi = 0$ form factor. Obviously, the form factor *P*(*Q*) changes slightly at higher concentration, a phenomenon which can be investigated using the contrast matching method. The obtained structure factor curves, *S*(*Q*), are shown in Figure 5. We observe a marked *correlation hole* in the interdendrimer structure factor at low *Q* due to the decrease in the isothermal compressibility as the concentration increased. The presence of such a small compressibility leading to a depression of *S*(*Q*) at low *Q* without any *peak development* is not obvious. This could be explained by the fact that the form factor *P*(*Q*) dominates in the total scattering dΣ/dΩ(Q). A similar variation of *S*(*Q*) has been observed by Dozier et al.[30] for solutions of polyisoprene stars in cyclohexane. The authors interpreted the lack of the peaks by the "soft-core" nature of the star–star repulsion. This interpretation could also be valid in our case because of the *softness*[31] *of the dendrimer molecules.*

Finally, we note that the existence of a broad scattering peak observed in the total scattering for dendrimer solutions in deuterated water D_2O seems to be a general observed phenomenon for branched and globular solutes (for example, stars, proteins, microgels, etc.) and may be attributed to a spatial arrangement of the molecules.

3.2. Effect of Added Acid at Constant Concentration. Figure 6 shows the typical scattering curves of dendrimers at various HCl concentrations. The amount of 10 M HCl added to the solution is related to the parameter α, called the protonation degree, and defined as the ratio between the number of protons added and the total number of *tertiary* and *primary* amine groups (62 tertiary and 64 primary) in the dendrimer.

Before the SANS measurements, the pH of the solutions was measured for each value of α varying between 0.1 and 4 (Table 2). The total concentration of the solution after adding HCl was maintained constant, equal to 2%. The scattering intensities were compared to the scattering from the dendrimer solution corresponding to α = 0. The latter is taken as a reference scattering in which the correlations are negligible. As mentioned above, the form factor *P*(*Q*) could change significantly by adding acid. Such effect could in principle be investigated further using the contrast matching technique.

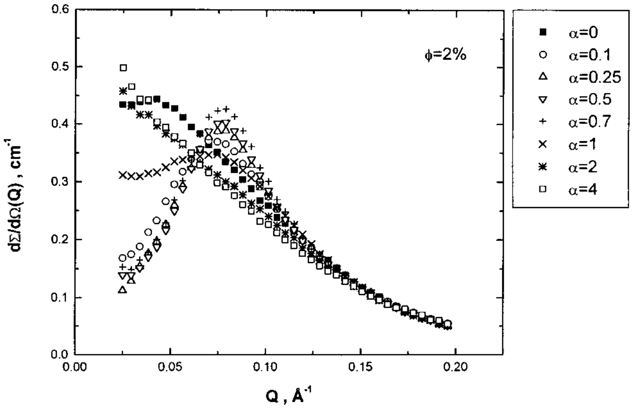

Figure 6. Effect of the addition of acid HCl to the scattering intensity from a 2% dendrimer solution.

Table 2. pH Values of the Solutions as a Function of the Protonation Degree α, Where the Concentration of the Solution Is Maintained Constant Equal to 2%

α	pH	α	pH
0	11.31	1	0.72
0.1	10.03	2	0.03
0.25	9.23	4	−0.37
0.5	5.75	10	−0.95
0.7	4.58		

It can clearly be observed that by adding a very small amount of HCl (α = 0.1), a distinct peak appears in the scattering intensity at $Q_{\max}$ indicating long-range Coulombic interactions due to the charges in the molecules. The interference peak is maximized around α = 0.7 and becomes weaker for the protonation degree *threshold* α = 1 indicating the beginning of the screening effect. The value α = 1 corresponds to the stoichiometric quantity of acid with respect to the total number of amine groups. By adding a large excess of acid to the solution (α = 2 and 4), one enhances screening between charged dendrimers and consequently the correlation peak disappears. One notice that a very small proportion of amino groups can be protonated in solution before adding acid, i.e., dendrimers dissolved in pure D_2O, which does not contribute significantly to the strong Coulombic interactions after addition of acid. Furthermore, with the addition of HCl, the strength of repulsive forces between dendrimers becomes stronger, yielding an increase in the molecule *hardness*.[31]

In accordance with Fournet arguments[32] and using the analogy with the effect of concentration, two characteristics are predicted for the scattering intensity maximum of dense packing hard spheres: (i) a shift of the maximum toward higher *Q* values by increasing the charges in the molecules, due to a decrease of the interference distance; (ii) a more pronounced form of the peak with increasing the charge number. In our case only the second of these two predictions was observed. Indeed, the intermolecular distance between dendrimers is left relatively unchanged (i.e., no significant influence on the position of the maxima within the experimental

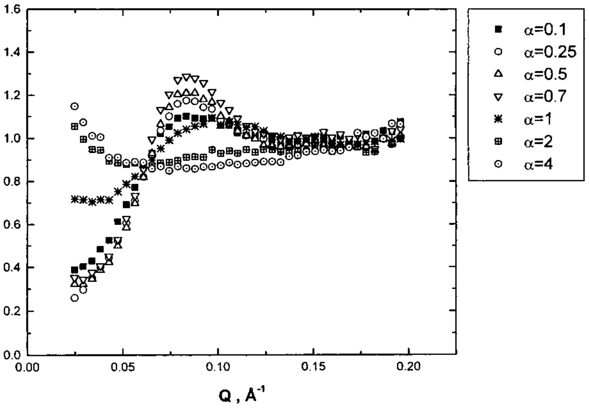

Figure 7. Structure factor $S_{acid}(Q)$ vs Q extracted from the SANS patterns of Figure 5 of the acidified solutions.

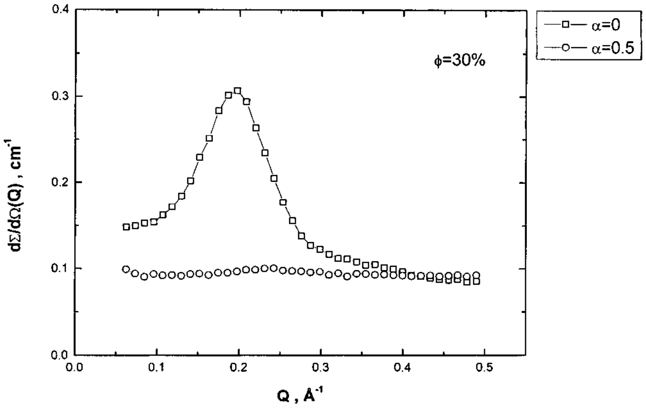

Figure 8. Effect of the addition of acid HCl to the scattering intensity from a 30% dendrimer solution.

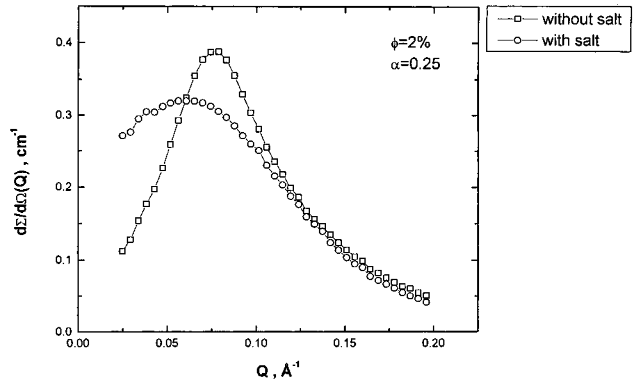

Figure 9. Effect of the addition of salt NaCl to the SANS scattering from a 2% dendrimer solution.

error, $Q_{max} = 0.076$ Å^{-1}), whereas the disorder increases by the addition of acid to the solution below $\alpha = 0.7$. The constancy of Q_{max} is not understood and does not agree with the results found for polyelectrolyte or protein systems.

In attempt to offer a physical explanation of the fact that the maximum of the scattering functions appear at a constant Q value for a system which behaves as a fluid, independent of its number of charges. We assume first that we are dealing with a system of particles in which the peripheral primary amino groups are first charged, followed by the prononation (fixation of proton H^+) of the inner tertiary amino groups. This assumption has been checked for lower dendrimer generation. Second the charges located in the particles are considered as a *fixed* charge. Consequently, the addition of acid leads to an arrangement of the particles characterized by the distance $2\pi/Q_{max}$ equal to the wavelength of the concentration fluctuations. In other words, the parameter $2\pi/Q_{max}$ is considered as the spatial periodicity of the molecules in the solution which would remain the same with an increasing number of charges; i.e., only the concentration fluctuations with the same wavelength $2\pi/Q_{max}$ are favorable. These fluctuations are increased in amplitude for charged dendrimers causing an increase of the scattering intensity at Q_{max}. Such effect is in disagreement with the experimental and the theoretical results obtained for polyelectrolyte systems. As can be seen in Figures 6 and 7, we note that the constancy of the peak position is compensated by the increase of the scattering intensity, regardless the concentration of acid up to the threshold value $\alpha = 1$. Presently, no clear explanation is available for such disagreement.

As discussed above, one can extract the structure factor $S_{acid}(Q)$ from the acidified solutions of 2% concentration (Figure 7). We notice the presence of an interference peak which indicates the repulsive interactions between dendrimers, contrary to the structure factor $S(Q)$ plotted in Figure 4 obtained from the dendrimer concentration dependence in D_2O of the scattering intensities. The long-range interactions seen in $S_{acid}(Q)$ become weaker near the stoichiometric addition of acid ($\alpha = 1$), showing the beginning of the screening effect. The peak which is lower in intensity at this value of α disappears completely after an excess of acid. The upturn appeared in $S_{acid}(Q)$ at low Q for higher values of α may be due to some aggregates formed in the solution. The intensity of the peak in $S_{acid}(Q)$ is approximately 1.3 indicating that the system has only liquidlike ordering[8] while the long-range ordering from crystallization is usually expected to occur when the intensity of the first peak in the structure factor reaches a value close to 2.5.[33]

It is also important to see the effect of acid on a concentrated solution where the interference peak is preexistent. One takes a solution with concentration 30% (Figure 8). After addition of a certain amount of acid, $\alpha = 0.5$, corresponding, by definition, to the protonation of all primary amine groups, one observes a disappearance of the correlation peak. This could be explained by the strong decrease of the interference distance between the molecules (considered as the spatial periodicity) and then the shift of the peak to relatively larger Q, difficult to be detected by the SANS instruments. More systematic studies are necessary in this field.

3.3. Effect of Added Salt at Constant Concentration. The screening of the interactions observed in the acidified solutions with $\alpha \geq 1$ can also be seen by addition of salt (NaCl). Figure 9 shows a preliminary result after addition of NaCl to an acidified solution of concentration 2% ($\alpha = 0.25$). One observes the disappearance of the peak indicating that the interactions are *considerably screened*. Our result is consistent with the common idea in that by adding salt to the solution one enhances screening between the charged particles. Detailed studies in this field will be done soon.

4. Summary and Conclusions

SANS experiments have been performed on solutions of poly(propylene imine) dendrimers, DAB-*dendr*-$(NH_2)_{64}$, in D_2O. When the concentration is increased, a single broad peak appears in the scattering curves centered at a wavevector value $Q_{\max}$, which shifted toward wider angles as observed for many polyelectrolyte systems. The scattering intensity at Q → 0, decreases progressively by increasing the concentration due to the interdendrimer correlations (structure factor). The peak position scales as $\phi^{0.55\pm0.05}$ with an exponent which is difficult to interpret. We note that the observed concentration dependence is clearly larger than that of a packing argument ($\phi^{1/3}$). Other exponent values were found in the literature for different systems. When the concentration is increased, the scattering intensity curves collapse progressively to a single curve at large Q values. The poly(propylene imine) dendrimers behave as *soft* molecules with possible interpenetration at higher concentration. In a condition where the dendrimer molecules are charged by adding acid (HCl), the electrostatic repulsion dominates and correlation peaks were observed in the scattered intensities, indicating a spatial arrangement of the molecules in the acidified medium due to the interaction potential. Therefore, the molecules tend to stretch and behave as *hard* particles (less soft). Furthermore, the peak position from acidified dendrimer solutions remains unchanged whereas its intensity is increased, indicating that the system has a liquidlike ordering. These interactions can be screened by adding an excess of acid or salt (NaCl).

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(15) This regime corresponds to the blob scattering in the case of polymers in semidilute solution (linear, stars, etc.).
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