

Structural properties of methanol-polyamidoamine dendrimer solutions

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We used small angle x-ray scattering to study interparticle structural properties of polyamidoamine starburst dendrimers (PAMAM, with an ethylenediamine central core) in methanol solutions. We have explored the intensity profiles for solutions of starbursts of different generations ($g=2, 3.5, 4$) at various concentrations. We find from the measured spectra that the half-integer generation, $g=3.5$, is characterized by pronounced interparticle correlations also in the very dilute regime. By means of a simple statistical-mechanical model, widely used in charged complex fluids (proteins and ionic micellar solutions), we calculate in this latter case the dendrimer-dendrimer structure factor $S(q)$. The results obtained give clear indication of a partial ionization process which involves the carboxylate ($\text{COO}^- \text{Na}^+$) terminal groups of the dendrimer. The calculated macroion charge number, independent of the solution concentration, is $Z_0 \approx 6$. [S1063-651X(98)09111-9]

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I. INTRODUCTION

“Dendrimers” or “starburst polymers” are a new class of regularly branched macromolecules with unique structural and topological features whose properties are attracting the interest of science and technology. By means of new iterative stepwise synthetic methodologies it is possible to grow, through successive generations, highly branched dendritic structures [1–3]. Starting from simple and low molecular weight compounds, nanoparticles (whose sizes are of the order of some tens of angstroms) with easily controllable properties like dimensions and specific surface functionalization are obtained. More precisely, these macromolecules are constructed from various initiator cores on which radially branched layers, termed generations (g for short), are covalently attached, thus yielding a three-dimensional highly ordered polymeric compound. The final exterior layer may be further chemically modified to provide a variety of terminal functionalities. A remarkable property of this class of compounds, for lower generations ($g < 5$), is their intrinsic monodispersivity. Due to their peculiar molecular arrange-

ment and structure, dendrimers are suitable systems for the development of molecular level synthetic prototypes which are able to mimic organization, highly specific surface recognition processes, and dynamical properties commonly found in complex fluids. In particular they are of interest as model systems for a large variety of biological systems such as liposomes, enzymes, and proteins. Dendrimers represent also a new approach to the control of molecular organization on size scales comparable to those of colloidal suspensions, and for this reason are attractive for studying the self-assembling processes.

Physical properties of dendrimer systems have been studied recently by means of theoretical methods [4], computer simulation [5–8], as well as experimental investigations [9–12], but although new insight has been gained, much remains to be done. For a number of investigations the origin of their structural and dynamical properties, in fact, is partly explained, and for most of them although a qualitative understanding is proposed, a quantitative interpretation is still lacking.

A number of recent investigations mainly focused on the study of the density distribution inside the starburst and in particular in determining the scaling law relating the number of monomers N with the radius R [5–8]. These studies deal with a self-similar behavior in the dendrimer structure. Despite the growing number of computer simulation results,

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experimental studies are still scarce. However, since the behavior of these compounds is related to many physico-chemical properties of the solution, their experimental characterization is of fundamental importance. In fact relevant parameters, for which a starburst presents a particular structural configuration, are solvent properties, temperature, sizes, composition of the basic monomer (e.g., its hydrophilicity or the balance between the hydrophilicity and hydrophobicity of its head groups), chemical potential, interparticle interaction, and so on.

On this basis, in order to have a complete characterization of the polyamidoamine (PAMAM, with an ethylenediamine central core) starburst dendrimers in methanol solution we have carried out a series of small angle x-ray scattering (SAXS) experiments. Such a system has been the object of intensive investigations through different experimental and computer simulation techniques; many of them addressed the self-similarity of structure [5–10]. In particular, size exclusion chromatography [9] has suggested a self-similar morphology (fractality) of their surface and light scattering has given information about the dendrimer hydrodynamic radii [10]. Very recently these suggestions on their fractal nature have been confirmed by the use of the SAXS and small angle neutron scattering (SANS) techniques [11,12]. Data extracted from measured system intensity function [more precisely the particle form factor $P(q)$, where $q=|\mathbf{q}|=(4\pi/\lambda)\sin\theta/2$ (\mathbf{q} is the scattering wave vector, θ is the scattering angle, and λ the wave number)] are in line with the corresponding numerical simulation finding. However, there is not a fairly good agreement between the measured and the proposed fractal dimension d_f .

Besides the internal dendrimer structure, it is of interest to obtain details on the properties related to the interdendrimer interactions in solutions. In such a case the small angle scattering technique can also be successfully used. By studying the scattered intensity of the dendrimer suspension we obtain the corresponding interparticle structure factor $S(q)$, so that it is possible to gain information on the dendrimer-dendrimer structure. As it is well known $S(q)$ is proportional to the Fourier transform of the pair correlation function $g(r)$ [13]. For these systems we identify a ubiquitous and pronounced peak, or an interaction peak, in the measured scattered SAXS intensity distributions. These results are typical of small angle scattering [SAXS, SANS, and small angle light scattering (SALS)] on complex fluids characterized by a mesophase length scale, e.g., a solution of charged polystyrene latex spheres, ionic micelles, and hydrophilic proteins in aqueous solutions [14]. The position of the correlation peak is located at a q value which is approximately 2π times the reciprocal of the mean interparticle separation distance D . These experimental facts imply that in these electrostatically stabilized colloidal suspensions there is a significant local order around a given macroion owing to strong mutual electrostatic interactions, even at fairly low particle volume fractions. The electrostatic Coulomb interaction is screened by small mobile counterions surrounding the macroions, which are necessary to keep the electroneutrality of the solution. As a result the macroion-macroion interaction is dominated by a double-layer repulsive interaction, which, depending on the ionic strength of the solution can be long ranged and of many

$k_B T$ in magnitude at contact (k_B is the Boltzmann constant) [15].

Statistical-mechanical models, applicable in treating scattering data of colloidal suspensions, have been developed in recent years [14,16]. The intermacroion structure factor $S(q)$, which depends on the interparticle interaction (double-layer interaction), the particle diameter σ , and the number density ρ of macroions can be calculated [17,18]. The most successful statistical-mechanical theories of highly asymmetric electrolyte solutions, such as charged colloids, have been based on solving the Ornstein-Zernike (OZ) equation for the total correlation function [19].

On the basis of their globular and monodisperse structure (well defined by the strategy of synthesis), of the molecular weight of some tens of thousands of Daltons (same order of magnitude of lysozyme and other small proteins) and of the characteristic sizes (diameter ranging from about 35 to 50 Å depending on the solvent [11,12]), the polyamidoamine (PAMAM, with an ethylenediamine central core) starburst dendrimers can be classified as colloids. Therefore a better description of their properties can be obtained from SAXS measurements by means of statistical-mechanical models previously developed for charged colloidal suspensions. We show here that such a procedure is successful in obtaining the relevant physical properties of interacting dendrimers. In particular, we can determine the average surface charge of the macromolecule (i.e., the single dendrimer) due to the presence of ionizable terminal groups which are responsible for structural properties of dendrimer solutions.

II. RESULTS AND DISCUSSION

All the data presented in this work were collected at the D22 SAXS station of the LURE DCI synchrotron radiation facility (Orsay-Paris). The chosen angular range provides data from $q=0.005$ to 0.4 \AA^{-1} . The resulting scattering intensities, $I(q)$, were corrected for the incident beam decay, sample thickness, and transmission. The background scattering from the solvent was also subtracted. The optics of the experimental setup were such that no desmearing of the curves was necessary.

For an assembly of monodisperse or nearly nondispersed particles, such as proteins in solutions or the present dendrimers, the scattering intensity distribution $I(q)$ can be written as [20,21]

$$I(q) = \rho_0(\hat{\rho} - \rho_S)^2 V_P^2 \tilde{P}(q) S(q), \quad (1)$$

where ρ_0 is the number density of the particles, $\hat{\rho}$ is the average scattering-length density, ρ_S the scattering-length density of the solvent, and V_P the volume of the particle. $\tilde{P}(q)$ is the normalized particle form factor (normalized to unity at $q=0$) and $S(q)$ is the interparticle structure factor. For spherical scatterers, of diameter σ , $\tilde{P}(q)$ can be written as [21]

$$\tilde{P}(q) = \left[3 \frac{j_1(q\sigma/2)}{(q\sigma/2)} \right]^2, \quad (2)$$

where j_1 is the first-order first-type Bessel function. Thus a Guinier plot of $I(q)$ for dilute solutions would provide σ or

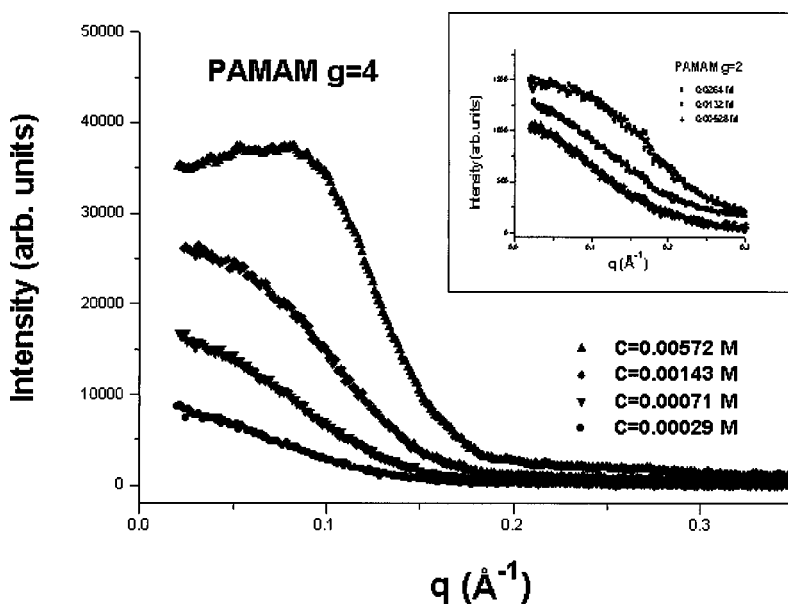


FIG. 1. SAXS profiles of a methanol solution of PAMAM dendrimers (generations $g=2$ and 4). The absence of structural organization allows the determination of the form factor $P(q)$ thus furnishing the values for the starburst dimensions of $R=10 \text{ \AA}$ ($g=2$) and $R=19 \text{ \AA}$ ($g=4$).

equivalently the gyration radius R_G . This is a usual procedure to separate the two contributions, $\tilde{P}(q)S(q)$, from the experimental SAXS spectra, especially when they overlap on the same length scales. Therefore in the low concentration region of the dispersed phase the absence of structural arrangements [$S(q) \sim 1$] allows for an estimation of the dimension R_G of the scattering object. Such a procedure was employed for our scattering data to estimate the dendrimer dimensions.

Figure 1 shows the SAXS spectra obtained for different concentrations C [in molarity (M)], of PAMAM dendrimers (generations $g=2$ and 4) dispersed in methanol solution. The

spectra give an indication that no sensitive structural organization is present in our system at moderate concentration ($C \leq 0.002M$).

A quite different result is obtained, on the other hand, for the PAMAM generation $g=3.5$ (Fig. 2). The presence of visible pronounced peaks in the SAXS spectra, even at concentration as small as $C=3.26 \times 10^{-4}M$, gives an indication that a structural order (structure factor) between dendrimers is present in our samples. The inset in Fig. 2 reports also the calculated structure factor $S(q)$ for the concentration of $C=3.26 \times 10^{-3}M$. This last quantity has been obtained by dividing the scattered intensities obtained, respectively, in the

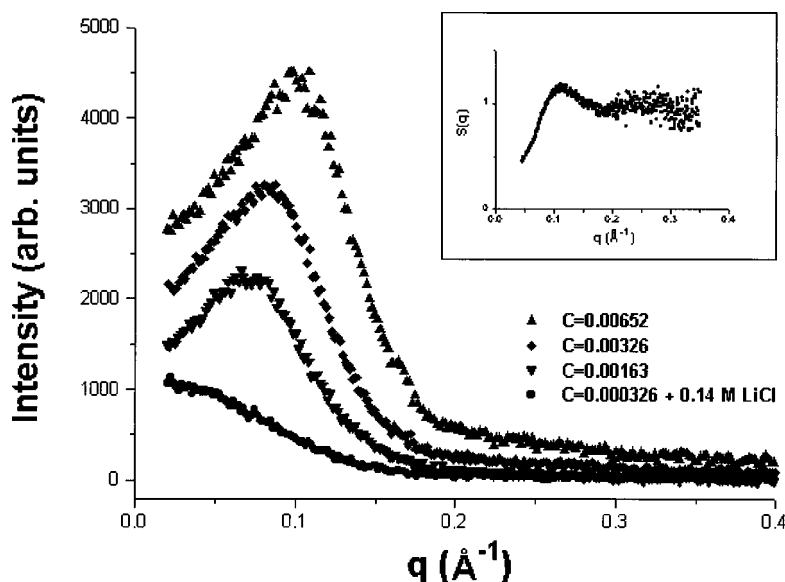


FIG. 2. SAXS spectra for the methanol solution of PAMAM dendrimer generation $g=3.5$, together with the estimation of the structure factor $S(q)$ for the concentration of $C=3.26 \times 10^{-3}M$ (inset). The presence of pronounced peaks in the SAXS spectra, even at concentration as small as $C=3.26 \times 10^{-4}$, gives an indication that a long range structural order (structure factor) between dendrimers is present in the system.

presence and in the absence of interactions. For this purpose, in order to avoid interaction between dendrimers, 0.14M LiCl was added to the less concentrated sample (i.e., $C = 3.26 \times 10^{-4}M$), resulting in a screening effect for the interaction potential, as confirmed by the disappearance of the characteristic peaks.

The observation of the structure factor can be explained with the presence of the carboxylate ($\text{COO}^- \text{Na}^+$) terminal groups in the half-integer generations (i.e., $g = 3.5$) of the starburst. Unlike the amino end groups (NH_2) present in the integer generations (i.e., $g = 2$ and 4), these groups could be partially ionized and, through the generated charge, can exert a long range electrostatic repulsive interaction, leading to a consequent ordering effect throughout the overall structure of the system. The existence of charges on the dendrimer leads, in fact, to intramolecular and intermolecular interactions which may be strong enough to influence both the structural and dynamic properties of the dendrimer solution.

The structure factor for a system of interacting particles can be written as [20]

$$S(q) = 1 + \int_0^\infty 4\pi^2 \rho_0 [g(r) - 1] \frac{\sin(qr)}{(qr)} dr, \quad (3)$$

where $\rho_0 = c/M$ is the particle number density (number of particles per unit volume). This last relation provides a way to relate the structure factor $S(q)$ with the radial pair correlation function $g(r)$ in the system, and then to the interparticle potential.

There is a large literature devoted to the calculation of SANS and SAXS intensities in charged macromolecular and supramolecular solutions [14,17,18,20]. One of the advantages of these techniques is the fact that their cross section can be unambiguously written and computed once the structural model of macroions and the intermacroion interaction are specified [14,17]. Actually, by using proper and sophisticated models, the calculation of the measured structure factor $S(q)$ in terms of the partial structure factors for macroion-macroion, macroion-counterion, and counterion-counterion correlations is possible for these systems considering also combined effects of size and charge polydispersity [17,18].

In practice the interparticle structure factor is too complicated to be calculated in detail when aggregation and charge polydispersity occur [18]. However, $S(q)$ can be calculated analytically for a polydisperse hard-sphere system and polydisperse charged hard-sphere system in a mean spherical approximation (MSA) [16]. These model calculations have shown that $S(q)$ can be well approximated in the vicinity of the first diffraction peak, with a structure factor of an equivalent monodisperse system having an effective diameter σ chosen to preserve the volume fraction of the particles [16–18].

To calculate $S(q)$ we have used the statistical-mechanical approach called the one-component macroion theory (OCM). In order to calculate $S(q)$, using this model (a MSA scheme developed by Hayter and Penfold (HP) [20]), one needs to assign an effective charge Z_0 , and an effective hard-sphere diameter σ to the disperse particle and the particle concentration.

The most successful statistical-mechanical theory of polyelectrolyte solutions, such as the systems treated here, has been based on solving the Ornstein-Zernike equation for the total correlation function $h(r)$ given by

$$h(r) = c(r) + \rho_0 \int c(r') h|r-r'| d^3r. \quad (4)$$

From $h(r)$ one obtains the pair correlation function $g(r) = h(r) + 1$, and then $S(q)$ can be calculated from Eq. (3). To solve the OZ equation it is necessary to impose a closure relation for the direct correlation function $c(r)$. For a charged hard-sphere system the most often used closure relations are hypernetted chain approximation (HNCA) and mean spherical approximation. Both are written in terms of the interparticle potential $U(r)$, for the HNCA:

$$c(r) = -\beta U(r) + h(r) - \ln[h(r) - 1] \quad (5)$$

and for MSA:

$$\begin{aligned} c(r) &= -\beta U(r), & r > \sigma \\ h(r) &= -1, & r < \sigma. \end{aligned} \quad (6)$$

In the above equations, $\beta = 1/k_B T$. HNCA is a nonlinear theory and has to be solved by numerical methods, however, it is known to be the most accurate theory for a charged hard-sphere system [16]. MSA is a linearized less accurate version of HNCA, but with the advantage of having an analytical solution when $U(r)$ is in the Yukawa or screened Coulomb form. MSA is thus a more suitable theory for analysis of small scattering data. The use of the so-called Derjajun-Landau-Verwey-Overbeek double-layer repulsive potential has been customary in small angle scattering literature, since the pioneering work of Hayter and Penfold [20]; it has the following form [15]:

$$U_R(r) = \frac{Z_0 e^2}{4\pi\epsilon(1+\kappa\sigma)^2} \frac{e^{-\kappa(r-\sigma)}}{r}, \quad (7)$$

where Z_0 is the macroion charge number, e is the electron charge, ϵ is the dielectric constant of the solvent, and κ is the Debye-Hückel inverse screening length related to the ionic strength $I(M)$ of the solution in terms of the expression

$$\kappa = \left(\frac{8\pi e^2 N_a I}{\epsilon k_B T \times 10^3} \right)^{1/2}. \quad (8)$$

In general, to have the interaction potential in a complete form, an additional term, A in Eq. (7), is considered, and it is due to a weak short range van der Waals–London attractive contribution coming from interactions between molecules of the colloidal particles. This latter contribution is usually called the Hamaker interaction (A is the Hamaker constant), whose magnitude is of the order $k_B T$ [22]. However, such a contribution in many systems like ionic-micellar solutions, colloidal solutions at low ionic strength, or in the present dendrimer solution without salt addition can be considered negligible in comparison to the strong long range Coulombic repulsive interactions (usually several $k_B T$ at contact). Thus, as far as the calculation of $S(q)$ is concerned, the presence of the Hamaker interaction can be neglected and only the effect of the double-layer repulsion can be considered.

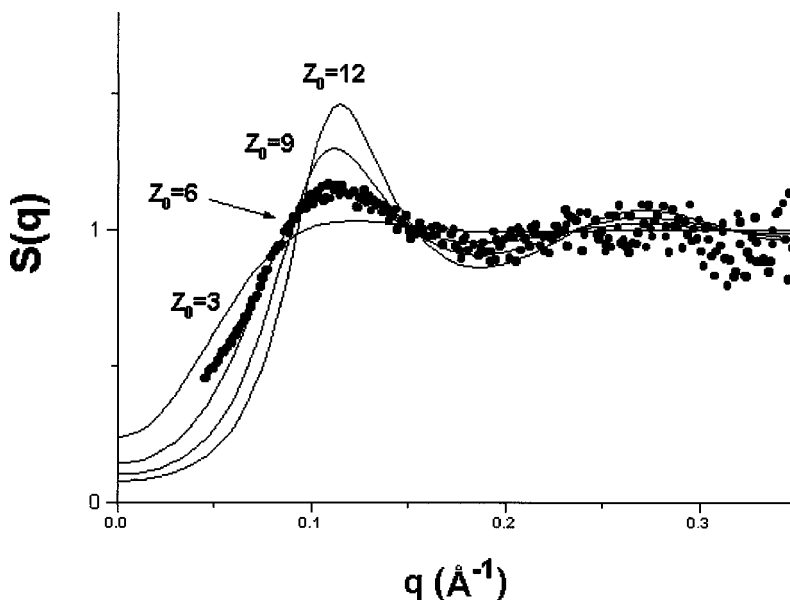


FIG. 3. Computed structure factor $S(q)$ (generation $g=3.5$, particle diameter $\sigma=34 \text{ \AA}$, concentration $0.00326M$) according to the MSA scheme, and for different charge solutions Ze . From the figure it is clear how an effective charge of $Z=6e$ can reproduce quite satisfactorily the findings of the experimentally determined structure factor $S(q)$.

The potential $U_R(r)$ when used in conjunction with the MSA ansatz [Eq. (6)] yields an analytical solution of the OZ equation, and a convenient algebraic form of $S(q)$. This is the HP scheme in the OCM theory. In recent years it has been shown that there is no need to make a MSA ansatz in solving the one-component OZ equation [14,17]. Such a procedure gives an effective one-component OZ equation for the macroions alone; by considering a set of multicomponent coupled OZ equations involving the correlation functions of the macroions and counterions the model leads to the definition of an effective direct correlation function for macroions. The model was named the “generalized one-component macroion” (GOCM) theory. The GOCM theory shows that the DLVO potential used in the current small angle scattering literature is not an “effective interaction potential” between macroions, but the direct correlation function (between macroions) in the dilute regime. Therefore OCM is a limiting case of GOCM, so that the charge extracted from a OCM approach to fit scattering data, at finite concentration, would result in a Z_{OCM} which is larger than that obtained from the use of GOCM, i.e., Z_{GOCM} . At 10% volume fraction of macromolecules, Z_{OCM} is about 5% higher than Z_{GOCM} . On this basis, considering that the aim of the present paper is to show that the half-integer dendrimer generation (as opposed to integer ones) is ionized, for the sake of simplicity we use the OCM scheme to treat the scattering data. OCM of HP gives satisfactory $S(q)$ by using the charge $Z_{\text{OCM}}=Z_0$ in $U_R(r)$ as an adjustable parameter.

Therefore the structure factors of the charged dendrimer solutions are computed, according to the OCM scheme, starting from the knowledge of the particle concentration, the particle diameter σ , and dielectric constant of the solvent ϵ (methanol in our case, with $\epsilon=33$). On the other hand, in the present case both the concentration and the particle diameter [$\sigma=34 \text{ \AA}$ for $g=3.5$ generation as deduced by the fit of $P(q)$ with Eq. (2)] are known quantities. It is sufficient then to compute, according to the OCM scheme, the numerical

structure factor $S(q)$ for different charges Z_0e , and to compare it with the experimentally deduced structure factor. The result of this procedure is presented in Fig. 3 which clearly shows how an effective charge of $Z_0 \cong 6$ can reproduce quite satisfactorily the finding of the experimentally determined structure factor $S(q)$. In order to check for some possible concentration effect the same procedure has been performed for all the available concentrations (Fig. 4). It is clear that the adopted scheme reproduces quite well the experimental results with the same value of the charge ($Z_0=6$). Small deviations are observed in the small q region ($q < 0.07 \text{ \AA}^{-1}$) between experimental and computed $S(q)$ in Figs. 3 and 4. This behavior of $S(q)$ at small wave vector can be attributed to the charge polydispersity, with the size polydispersity being about 5% (in the actual dendrimer it has been estimated to be of the order of 2 \AA). In fact, colloidal solutions with significant charge polydispersity and monodisperse in size show the same behavior [14,16]; for these systems only a proper calculation taking into account the charge polydispersity can exactly reproduce the measured $S(q)$ [18]. On this basis the obtained value of the dendrimer charge must be considered as an average value $\langle Z_0 \rangle$.

Figure 5 gives an estimation of the accuracy in the determination of the dendrimer charge for the half-integer PAMAM generation $g=3.5$. In particular, structure factors calculated for Z_0 ranging from 4 to 8, maintaining fixed values of the remaining parameters, are reported. The inset of Fig. 5 shows the charge values obtained for different dendrimer concentrations; as a result the measured $\langle Z_0 \rangle$ is independent from the concentration.

Furthermore, obtained results give additional indication that the carboxylate terminal groups, in this class of dendrimer-methanol solution, are partially dissociated (COO^-Na^+). On 64 total available carboxylate terminal groups per dendrimer (in the $g=3.5$ generation) only an average number of 6 are dissociated. This partial dissociation is the explanation, in the statistical sense, of the charge poly-

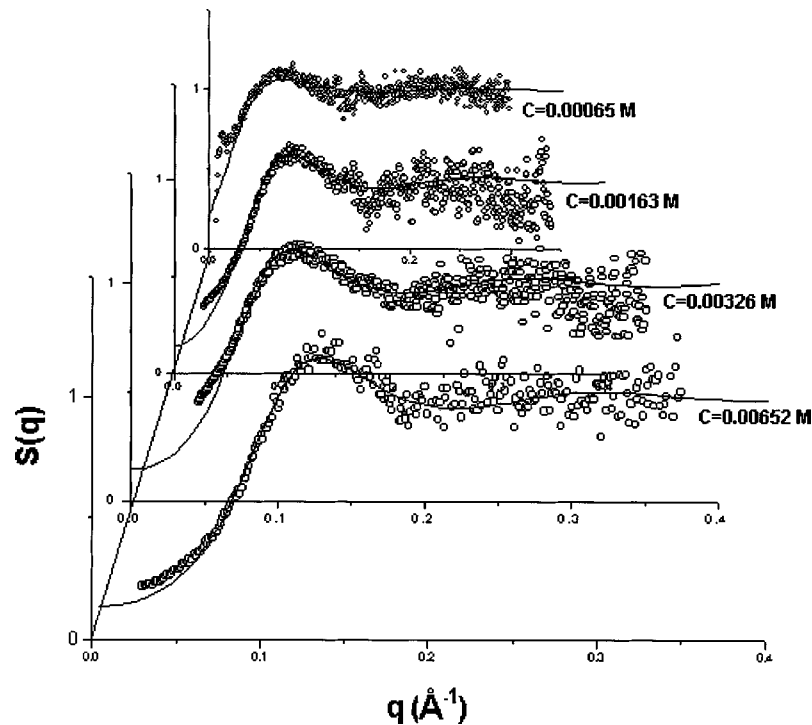


FIG. 4. Comparison between the computed (by means of the MSA scheme) and experimental determined structure factor $S(q)$ for all the available concentrations. As is clear from the figure, the adopted scheme reproduces quite well the experimental results for all the different concentrations and with the same value of the charge $Z=6$ (in unit of e).

dispersity reflected in the difference between the measured and calculated structure factors at small q values.

The dissociation process also has the effect of producing an electrostatic repulsion between the charged polymeric chains belonging to the same dendrimer. This effect determines a swelling of the dendrimer chains and gives rise to a sensitive increase in the overall dendrimer dimensions, as recently observed under different solvent conditions in a recent study of the hydrodynamic properties of PAMAM den-

drimers by means of holographic relaxation spectroscopy (HRS) [10]. More precisely in such a study it has been shown that the hydrodynamic dimensions of the dendrimer molecules increase significantly with increasing polarity of the solvent.

III. CONCLUSIONS

A structural investigation of polyamidoamine starburst dendrimers, of different generations, in methanol solution

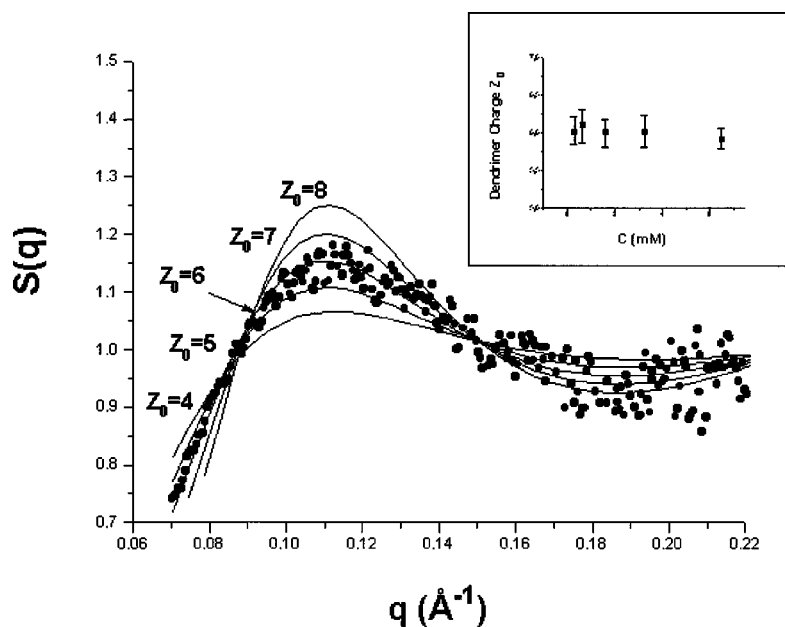


FIG. 5. A zoom into the structure factor $S(q)$ gives a direct estimation of the accuracy in the determination of the dendrimer charge Z , produced by the partial dissociation of the carboxylate surface group.

has been performed by means of the small angle x-ray scattering technique. Obtained intensity profiles give evidence of different behaviors for dendrimers of different generation. More precisely, whereas half-integer generation ($g=3.5$) is characterized by a well defined peak in the structure factor also in the dilute regime ($C \approx 3 \times 10^{-4} M$), integer generations do not evidence any type of structural order in the same concentration interval. The strong interparticle correlation in the half-integer dendrimer can be ascribed to the presence of ionizable carboxylate terminal groups. On the other hand, the presence of pronounced peaks in the intensity profiles, at the experimental q range used, can be ascribed only to a long range order between particles originated by a Coulombic repulsive interaction.

In order to confirm this hypothesis we have analyzed the corresponding experimental structure factor $S(q)$ by using a simple statistical-mechanical model developed for charged macromolecular and supramolecular solutions. More precisely, working in the framework of the MSA scheme by using the one-component macroion theory of current models for charged systems in solution, we can estimate the dissociation degree of the terminal carboxylate groups in this particular dendrimer. The use of such a procedure and the calculated structure factors give a confirmation of the physical picture: dendrimers behave like a charged colloidal solution

and the generation $g=3.5$ undergoes a partial ionization process which involves the carboxylate ($\text{COO}^- \text{Na}^+$) terminal groups of the dendrimer leading to a macroion charge number $Z_0 \approx 6$. The data analysis reveals another remarkable result: in the entire range of concentrations investigated the macroion charge number obtained (inset of Fig. 5) appears to be constant. This finding clearly points out the polyelectrolyte character of the particles.

In conclusion, the present results give an indication, in agreement with molecular computer simulations, that these solutions can be included in the framework of complex fluids. This observation of the presence of a charge distributed inside the polymeric molecule, together with the fractal nature of their structure, prompts us to devote future efforts mainly to the investigation of the physical properties in the region near the interface between the functional groups and the solvent. In this respect, further experiments are in progress in our laboratories in order to better clarify the role of the dendrimer charge and solvent properties.

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