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Scattered intensity from weakly charged cyclic polymer blends in solution

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In this paper, we theoretically investigate the scattering properties of a ternary solution made of two weakly charged cyclic polymers, of different chemical nature. These properties are studied through the total structure factor. The latter is computed using a generalized Zimm single-contact formula. The total structure factor versus the wave-vector is reported for several charge distributions of polyions. Our results are compared to those already observed for solutions of weakly charged linear polymer blends in solution. The main conclusion is that, the weakly charged cyclic polymers scatter better than their linear homologous.

Keywords : Cyclic polymer blends - Phase separation - Scattering properties.

I. INTRODUCTION

The phase behavior of ternary mixtures of two incompatible neutral linear polymers in solution has been the subject of several theoretical investigations using, first, the Random

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Phase Approximation (RPA) [1 – 3], and second, the Renormalization-Group [4 – 6], in order to get a correct phase behavior. Experimentally, the phase behavior of such systems have been studied by light [7, 8] and neutrons scattering techniques [9, 10].

Contrary to neutral polymers, polyelectrolytes possess ionizable groups, which are able to dissociate into charged polymer chains (polyions) and small counterions. Proteins, nucleic acids and super-absorber materials are only a few examples of a large variety of polyelectrolytes.

Linear polyelectrolytes are special polymeric materials, which have received much attention from a theoretical and experimental point of view. This is due to their abundant applications in a wide range of fields [11 – 17], such as physics, chemistry, biology, biochemistry, pharmacology, medicine, etc. Such polymeric systems provide a broad and very important class of materials including most biological and many synthetic polymers. In the last few decades, considerable progresses have been accomplished in the understanding of the behavior of linear polyelectrolytes in solution, in particular, of their structural properties [9, 10, 18 – 22]. The polyelectrolytes were investigated by a number of experimental techniques, in particular, by radiation scattering (light and/or neutrons), and which were revealed to be an useful tool to explore the long- and short-range interactions within polymeric systems, and especially, when these systems are charged. As a matter of fact, the nature of these interactions is noticeably different depending on whether one considers the short-range interactions, which have essentially a thermodynamic origin, or those of long-range, which are determined by electrostatic forces [23 – 27]. On the other hand, linear polyelectrolytes systems are characterized by a peculiar feature, according to which a scattering peak appears. This observation has been fully recognized on the theoretical side as well as on the experimental one.

Before to specify the main purpose of this work, we note that, since the properties of cyclic neutral polymers differ, in many respects, from those of their linear counterparts, it is expected to find some discrepancies between behaviors of weakly charged linear polymers and their cyclic homologous. In the neutral case, these differences have stimulated various investigations for many years [28, 29]. The interest in studying cyclic polymers originates from both applied and fundamental reasons. Furthermore, the compatibility enhancement

of blends of cyclic homopolymers towards phase separation as compared to systems of linear homologous, make them more attractive for some specific applications. From a theoretical point of view, cyclic macromolecules provide a model of polymers that are free from end effects. In some cases, these effects may have important implications, especially when one deals with short chains.

In comparison with linear charged polymers, few investigations have been devoted to similar properties of systems with other architectures. Consequently, this report aims to overcome this handicap by the study of the phase behavior of cyclic weakly charged polymers, and to compare the results with those obtained, in previous studies, for mixtures of linear chains with the same charge distributions [30]. By analogy with considerations mentioned below, the total structure factor of weakly charged cyclic homopolymers is expected to be different from that of linear chains mixtures.

The remainder of presentation proceeds as follows. Sec. 2 is devoted to a review of the theoretical formalism enabling us to apprehend the structural properties of systems under consideration, such as the total structure factor. A detailed discussion of our main results, by specifying the impact of the charge, composition and architecture effects on the total structure factor, is the aim of Sec. 3. Some concluding remarks are drawn in Sec. 4.

II. THEORETICAL BACKGROUNDS

The physical system we consider is a mixture of two weakly charged polymers A and B immersed in a good solvent. We are interested in the determination of the static structure matrix, \mathbf{S} , of the considered ternary mixture. Within the framework of RPA, it has been found [30, 31] that this structure matrix satisfies a generalized Zimm equation [32]

$$\mathbf{S}^{-1}(Q) = \mathbf{S}_0^{-1}(Q) + \mathbf{U}(Q) . \quad (1)$$

This equation gives the inverse total structure matrix for the interacting system as a sum of the inverse bare structure matrix $\mathbf{S}_0^{-1}(Q)$ and the interaction matrix $\mathbf{U}(Q)$, independently on the architecture of chains involved in the polymeric systems under investigation. There, the quantity $Q = |\mathbf{q}|$ stands for the module of the scattering wave-vector (or scattering wave-vector amplitude), which is given by the standard relationship : $Q = (4\pi/\lambda) \sin(\theta/2)$, where

λ and θ are the wavelength of the incident radiation and the scattering angle, respectively.

We note that the bare structure matrix $\mathbf{S}_0(Q)$ has zero off-diagonal elements, and we write

$$\mathbf{S}_0 = \begin{bmatrix} S_a^0 & 0 \\ 0 & S_b^0 \end{bmatrix}, \quad (2)$$

where $S_i^0(Q) = \Phi_i Z_i P_i(Q)$ ($i = a, b$). Here, Φ_i is the concentration of polymer chains of type i , Z_i their polymerization degree, and $P_i(Q)$ their form factor.

The interaction matrix in formula (1) is given by the sum

$$\mathbf{U}(Q) = \mathbf{V} + \mathbf{F}. \quad (3)$$

Here, \mathbf{V} is the ordinary excluded volume matrix whose elements are the excluded volume parameters v_{ij} ($i, j = a, b$)

$$\mathbf{V} = \begin{bmatrix} v_{aa} & v_{ab} \\ v_{ba} & v_{bb} \end{bmatrix}, \quad (4)$$

with

$$v_{aa} = \frac{1}{\Phi_s} - 2\chi_{as}, \quad (5a)$$

$$v_{bb} = \frac{1}{\Phi_s} - 2\chi_{bs}, \quad (5b)$$

$$v_{ab} = v_{ba} = \frac{1}{\Phi_s} - \chi_{as} - \chi_{bs} + \chi_{ab}. \quad (5c)$$

In these expressions, Φ_s represents the volume fraction of solvent, while χ_{is} and χ_{ab} are the polymer i -solvent and polymer A -polymer B Flory-Huggins interaction parameters, respectively. For the sake of simplicity, we assume that the solvent has the same quality for A and B -polymers ($\chi_{as} = \chi_{bs}$), and write

$$v_{aa} = v_{bb} = v_{ab} - \chi \equiv v. \quad (6)$$

We have used the notation : $\chi \equiv \chi_{ab}$.

The long-range electrostatic matrix \mathbf{F} reads

$$\mathbf{F} = \alpha(Q) \begin{bmatrix} f_a^2 & \eta_{ab} f_a f_b \\ \eta_{ab} f_a f_b & f_b^2 \end{bmatrix}, \quad (7)$$

with

$$\alpha(Q) = \frac{4\pi l_B}{Q^2 + \kappa^2}. \quad (8)$$

In this expression, $l_B = e^2/\epsilon k_B T$ accounts for the Bjerrum length, of the order of 7 \AA at room temperature. Here, e is the electron charge, ϵ the dielectric constant of the medium, k_B the Boltzmann's constant and T the absolute temperature. In Eq. (7), $\eta_{ab} = +1$, if monomers A and B have charges of the same sign, and $\eta_{ab} = -1$, otherwise ; $f_a e$ and $f_b e$ represent the charges carried by A and B monomers, respectively. The Debye-Hückel screening length κ^{-1} is as follows

$$\kappa^2 = 4\pi l_B \left(\sum_i \Phi_{ci} + \Phi_{salt} \right). \quad (9)$$

Here, Φ_{ci} is the number density of counterions and Φ_{salt} is that of the added salt (or electrolyte). The sum in the above relation runs over all free-point ions in the system.

With these considerations, the total interaction matrix writes

$$\mathbf{U} = \begin{bmatrix} U_{aa} & U_{ab} \\ U_{ba} & U_{bb} \end{bmatrix}, \quad (10)$$

with

$$U_{aa} = v + \alpha(Q) f_a^2, \quad (11a)$$

$$U_{bb} = v + \alpha(Q) f_b^2, \quad (11b)$$

$$U_{ab} = U_{ba} = v + \chi + \alpha(Q) \eta_{ab} f_a f_b. \quad (11c)$$

Relationships (11a) and (11b) clearly show that the repulsive electrostatic AA and BB -interactions increase the quality of the solvent. On the other hand, relationship (11c) tells us that, if $\eta_{ab} = +1$, the electrostatic repulsion has tendency to increase the incompatibility of A and B polymers, and if $\eta_{ab} = -1$, the electrostatic attraction has as effect to make the mixture more compatible.

Substituting Eqs. (11) and (2) into Eq. (1) yields

$$\mathbf{S}^{-1} = \begin{bmatrix} \frac{1}{S_a^0} + U_{aa} & U_{ab} \\ U_{ab} & \frac{1}{S_b^0} + U_{bb} \end{bmatrix}. \quad (12)$$

Inverting this matrix gives

$$S_{aa}(Q) = \frac{S_a^0(1 + U_{bb}S_b^0)}{\mathcal{D}(Q)}, \quad (13a)$$

$$S_{bb}(Q) = \frac{S_b^0(1 + U_{aa}S_a^0)}{\mathcal{D}(Q)}, \quad (13b)$$

$$S_{ab}(Q) = S_{ba}(Q) = -\frac{U_{ab}S_a^0(Q)S_b^0(Q)}{\mathcal{D}(Q)}, \quad (13c)$$

with

$$\mathcal{D}(Q) = 1 + U_{aa}S_a^0(Q) + U_{bb}S_b^0(Q) + (U_{aa}U_{bb} - U_{ab}^2)S_a^0(Q)S_b^0(Q). \quad (13d)$$

On the other hand, the total structure factor is defined by

$$S_T(Q) = S_{aa}(Q) + S_{bb}(Q) + 2S_{ab}(Q). \quad (14)$$

By using the above explicit forms of S_a^0 , S_b^0 , U_{aa} , U_{bb} and U_{ab} , we find that

$$\frac{S_T(Q)}{Z\Phi} = P(Q) \frac{1 - [2\chi - \alpha(Q)(f_a - \eta_{ab}f_b)^2]x(1-x)\Phi NP(Q)}{\mathcal{D}(Q)}. \quad (15)$$

We assumed that polymers A and B have the same degree of polymerization, Z . Thus, we are concerned with a monodisperse ternary mixture. This implies, in particular, that the two polymers have the same form factor : $P(Q) \equiv P_a(Q) = P_b(Q)$. We have set $\Phi_a = x\Phi$ and $\Phi_b = (1-x)\Phi$, where x is the composition and $\Phi = \Phi_a + \Phi_b$ the total monomer concentration. The denominator $\mathcal{D}(Q)$ appearing in formula (15) can be decomposed as follows

$$\mathcal{D}(Q) = \mathcal{D}_n(Q) + \mathcal{D}_c(Q), \quad (16a)$$

where

$$\mathcal{D}_n(Q) = 1 + v\Phi ZP(Q) - \chi(2v + \chi)x(1-x)\Phi^2 Z^2 P^2(Q) \quad (16b)$$

is the usual contribution, that is in the absence of charges, and

$$\mathcal{D}_c(Q) = \alpha(Q)\Phi ZP(Q) \left[x f_a^2 + (1-x) f_b^2 + v_0 x(1-x)\Phi ZP(Q) \right] \quad (16c)$$

accounts for the contribution of charges. In expression (16c), the parameter v_0 reads

$$v_0 = v(f_a - \eta_{ab} f_b)^2 - 2\eta_{ab} f_a f_b \chi . \quad (16d)$$

Until now, the general formalism reviewed above applies to chains, whatever be their architecture. It is only at this stage that a difference appears in the expressions of their radii of gyration and form factors. For this purpose, we assume that the polyions behave as flexible polymers, and depending on whether chains are linear or cyclic, their form factors are respectively given by Debye [33] and Casassa [34] functions

$$g_D(u_i) = \frac{2}{u_i^2} (e^{-u_i} + u_i - 1) , \quad (17)$$

$$g_C(u_i) = \frac{2}{\sqrt{u_i}} e^{-u_i/4} \int_0^{\sqrt{u_i}/2} e^{t^2} dt . \quad (18)$$

In formulae (17) and (18), u_i represents the dimensionless variable

$$u_i = Q^2 R_{gi}^2 = Q^2 \frac{Z_i \sigma_i^2}{6} , \quad (19)$$

where σ_i is the monomer size, and R_{gi} represents the radius of gyration of a Gaussian linear chain of specie i ($i = a, b$), unperturbed by the excluded volume interactions. Moreover, the radii of gyration of linear chains and their cyclic counterparts are assumed to be governed by excluded volume effects. The calculation of the gyration radius of cyclic chains can be performed using some more recent model [29], according to which the mean-squared distance between two points separated by n monomers along the cyclic chain writes

$$\langle r_n^2 \rangle = n^{1+\zeta} \left(1 - \frac{n}{Z_i} \right)^{1+\zeta} \sigma_i^2 . \quad (20)$$

Combining this relation and the general definition of the radius of gyration of a given polymer yields

$$R_{gc}^2 = Z_i^{1+\zeta} \sigma_i^2 \int_0^1 t^{1+\zeta} (1-t)^{2+\zeta} dt . \quad (21a)$$

Explicitly, we have

$$R_{gc}^2 = Z_i^{1+\zeta} \sigma_i^2 B(2 + \zeta, 3 + \zeta) , \quad (21b)$$

where $B(x, y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$ is the standard Euler's *Beta function* [35]. While in the case of their linear homologous, one obtains [36]

$$R_{gl}^2 = \frac{Z_i^{1+\zeta} \sigma_i^2}{(2 + \zeta)(1 + \zeta)} , \quad (22)$$

with the notation $\zeta = 2\nu - 1$, where $\nu \simeq 0.6$ is the swelling critical exponent. This assumption, which is valid only in the case of weakly charged polymers, means that the conformational properties of chains are dominated by the excluded volume interactions, and the local rigidity due to the electrostatic potential can be neglected. Indeed, if such polymeric systems are highly charged, the chains become strongly extended, and thus, they take configurations similar to that of rods. In addition to the local rigidity, it is interestingly to recall the existence of the overall one due to electrostatic repulsions.

III. RESULTS AND DISCUSSION

A. The scattered intensity

In order to illustrate the angular dependence of the total structure factor $S_T(Q)$, we have plotted it as a function of the renormalized wavenumber QR_g , in various conditions of charge distribution, using the following numerical parameters : $Z = 104$, $\sigma = 2.5 \text{ \AA}$, $R_{gl} = 135 \text{ \AA}$, $R_{gc} = 93 \text{ \AA}$, $\nu = 30 \text{ \AA}^3$ and $l_B = 7 \text{ \AA}$.

It is possible to access directly to the total structure factor $S_T(Q)$, by choosing two polymers whose refraction indices or diffusion lengths are equal. The scattered intensity is then proportional to $S_T(Q)$ of expression (15), namely

$$I(Q) = (a - s)^2 S_T(Q) , \quad (23)$$

where $a - s$ is the contrast factor with respect to solvent molecules.

At fixed Z and monomer concentration Φ , the scattered intensity curve depends on the charges values f_a and f_b and their relative sign (through $\eta_{ab} = -1, +1$).

B. Mixture of a charged and a neutral polymers in solution

We consider a ternary mixture made of a charged polymer A ($f_a = f$), a neutral one B ($f_b = 0$) and a good solvent. The corresponding total structure factor is obtained from general formula (15) setting $f_a = f$ and $f_b = 0$. We find that

$$\frac{S_T(Q)}{Z\Phi} = P(Q) \frac{1 - [\chi - \alpha(Q) f^2/2] \chi_c^{-1}(Q)}{\mathcal{D}(Q)}, \quad (24)$$

with the notation

$$\chi_c^{-1}(Q) = 2x(1-x)\Phi ZP(Q). \quad (25)$$

The angular dependences of the total structure factor, defined in Eq. (24), are plotted in Figs. 1a and 1b, for $f_a = f$ and $f_b = 0$. The first one illustrates the effects of the charge parameter f with a composition fixed to the value $x = 0.8$. Analysis of this figure reveals that, even for a relatively important charge parameter, that is $f = 0.3$, the presence of 20% in neutral polymer is sufficient to provoke practically the disappearance of the scattering peak, whatever be the architecture of chains.

This observation is in agreement with those of Refs. [13] and [24], according to which a peak collapse occurs due to adding a small content in neutral polymer. This phenomenon appears more clearly in Fig. 1b which represents the angular dependence of the total structure factor for $f = 0.1$, $v\Phi Z = 1$, $\chi/v = 0.1$, and several values of the composition x in monomers of specie 1. On the other hand, we observe clearly a peak in the case of a single polyion ($x = 1$), regardless its architecture, but the scattering maximum almost disappears due to adding of only 5% in neutral polymer. Contrary to linear chains systems, for which the scattering peak disappears in the presence of only 5% in neutral polymer, the one corresponding to systems made of their cyclic homologous is significant only for a composition of value $x = 10\%$. These both figures show that the height of the scattering maximum is higher, as compared to that observed in the case of their linear counterparts.

C. Mixture of two charged polymers of the same sign in solution

We consider now two charged polymers A and B , and denote by f_a and f_b the respective non-vanishing charge parameters. The corresponding total structure factor can be obtained

substituting $\eta_{ab} = +1$ into general expression (15)

$$\frac{S_T(Q)}{Z\Phi} = P(Q) \frac{1 - [2\chi - \alpha(Q)(f_a - f_b)^2] x(1-x)\Phi ZP(Q)}{\mathcal{D}(Q)}, \quad (26)$$

where the denominator $\mathcal{D}(Q)$ is given by Eqs. (16a)-(16d), with $\eta_{ab} = +1$.

Firstly, if we fix the composition to the value $x = 0.8$ and neutralize the charge of the second polymer, that is $f_b = 0$, we will have a behavior similar to that illustrated in Fig. 1a. In the second case, the charge parameter of polymer A is maintained constant, namely $f_a = 0$, but that of the second one is increased from 0 to 0.1, with $v\Phi Z = 1$. The behavior of the polymeric system under consideration is depicted in Fig. 2a. This latter shows a progressive reemergence of the peak as the charge parameter f_b increases, and we recover the behavior almost similar to that shown in the single polyion limit, with a small χ -parameter as compared to the electrostatic part.

However, it is interestingly and worthwhile to examine the total structure factor $S_T(Q)$ in the case where both charge parameters f_a and f_b are similar, that is $f_a = f_b = f$. With these considerations, Eq. (26) becomes

$$\frac{S_T(Q)}{Z\Phi} = P(Q) \frac{1 - 2\chi x(1-x)\Phi ZP(Q)}{1 + v_{eff}(Q)\Phi ZP(Q) - \chi[2v_{eff}(Q) + \chi]x(1-x)\Phi^2 Z^2 P^2(Q)}, \quad (27a)$$

with the notation

$$v_{eff}(Q) = v + \alpha(Q) f^2. \quad (27b)$$

At this stage, we remark that, with a modified excluded volume parameter, the expression governing the variations of the total structure factor $S_T(Q)$, has a form similar to that obtained in the neutral limit.

We note that, if $\chi = 0$, Eq. (27a) reduces to that of a single polyion in solution, whose behavior is shown in Fig. 2b. The above observations remain valid for linear chains as well as for their cyclic homologous.

D. Mixture of two charged polymers of different sign in solution

In this case, we find for the total structure factor the expression

$$\frac{S_T(Q)}{Z\Phi} = P(Q) \frac{1 - [2\chi - \alpha(Q)(f_a + f_b)^2] x(1-x)\Phi ZP(Q)}{\mathcal{D}(Q)}, \quad (28)$$

where $\mathcal{D}(Q)$ is given by Eqs. (16a)-(16d), with $\eta_{ab} = -1$.

For this particular system, we have represented, in Fig. 3a, the variations of the total structure factor $S_T(Q)$, as a function of QR_g , for $f_a = 0.1$, $\chi/v = 0.1$, $x = 0.8$, and $v\Phi Z = 1$, and several values of the charge parameter f_b ranging from 0 to 0.3. This figure shows that, as the charge parameter f_b increases, the total structure factor $S_T(q)$ increases substantially at small values of Q . In fact, this originates from strong electrostatic attraction force between polymers of different species, which induces an important scattering signal in that Q 's domain.

Likewise, we show, in Fig. 3b, the variations of the total structure factor versus QR_g for $f_a = f_b = 0.1$ ($\eta_{ab} = -1$), $v\Phi Z = 1$, and $\chi/v = 0.1$, and several values of composition x ranging from 0 to 0.8. Analysis of this figure reveals that the peak disappears rapidly when only 5 % of chains are unlikely charged with respect to the remainder of chains. As expected, we observe that a small quantity in neutral polymer induces a collapse of the scattering peak, because of the significant reduction of the electrostatic repulsion between different polymeric species.

IV. CONCLUSIONS

This paper gives a theoretical framework for the study of structural properties of mixtures of two weakly charged cyclic homopolymers, in solution and their comparison with those corresponding to linear chains systems. This study has been stimulated by several recent reports. However, the present report is voluntarily limited to the examination of the only angular dependence of the total structure factor of polymeric systems under investigation. Various conditions of charge distributions were considered. At this point of view, we note that this latter quantity is readily accessible by radiation scattering measurements, if the contrast factors, with respect to solvent molecules (when neutrons are used) or the increments of refractive indices (in the case of light-scattering) of two monomeric species A and B , are the same.

On one hand, the interactions between two charged monomers are assumed to be governed by an ordinary screened Debye-Hückel potential of the form $\exp\{-\kappa d\}/d$, where d is the distance which separates the centers of two monomeric species. Due to this fact, we are in agreement with the assumptions that the charges are not in a near neighboring each other, and with the fact that the electrostatic interaction is relatively weak. However, in the case where the first hypothesis is not fulfilled, only the excluded volume interaction determines the phase behavior of the considered polymeric system. These features, illustrated clearly by the scattering curves, show that, at small values of the wavenumber Q , the electrostatic interaction predominates, and then, the thermodynamic interaction becomes more and more pronounced as Q increases.

Elsewhere, we have used the Debye and Casassa functions to describe the form factors of Gaussian linear and cyclic chains unperturbed by the excluded volume effects, respectively. Moreover, the radii of gyration of linear chains and cyclic counterparts are assumed to be governed by the excluded volume interactions. For this purpose, the concept of persistence length is not introduced, in such a way that we remain in agreement with our description restricted only to weakly charged polymers. We have also assumed that the small ions, as the counterions, are point-like without any specific contribution to scattering curves or molecular interactions. However, their presence enables to ensure the overall electro-neutrality condition and contributes to the screening of the electrostatic interactions.

In summary, the present model is based mainly on two assumptions. The first one is the RPA which allows to relate the scattering functions for the total system made of a mixture of identical homopolymers in solution. This is introduced through the interaction matrix which, in this case, corresponds to the sum of the bare excluded-volume matrix and the long-range Coulombian one. Meanwhile, we make use of the second approximation according to which the latter matrix is modeled through the Debye-Hückel potential. Strictly speaking, these two approximations apply only far from the overlap polymer concentration (threshold), where the fluctuations of matter are not very strong, so-that the RPA is expected to be reliable. Furthermore, the Debye-Hückel approximation assumes that, even in the absence of salt, it occurs a substantial screening of the electrostatic forces between charged monomers. This requirement is also satisfied in the semi-dilute regime where the counterions, coming

from the dissociation of the polymer, are in large number, because of the electroneutrality condition which needs a concentration of counterions equal to $f\Phi$.

In the light of this study, it appears the following facts : (i) in the neutral limit, the total structure factor $S_T(Q)$ was found to be identical to the one obtained for a homopolymer with a form factor $P(Q)$ and an excluded-volume parameter $v+\chi/2$. Several cases of distributions of charge were examined. (ii) In the case of a mixture of partially charged homopolymers in which the neutral one is isorefractive with respect to solvent molecules, the structure factor shows the same features than those observed for a single polyion system (ordinary polyelectrolyte behavior). This observation was explained by the fact that the whole chains undergo the same repulsions due to the long-range potential. Consequently, the interaction of the polyion is decreased in the presence of polymer B . In other words, this means that an addition of a small quantity of neutral polymer implies a disappearance of the scattering peak. However, if the charges, carried by monomers of species A and B , are of the same sign, the counterions of the second polymer induce a screening of the interaction due to the first one. This implies that, if a small percentage in chains do not contribute to the scattering, the scattering maximum tends to disappear. It has been also observed that, when one passes from a neutral polymer to a charged polymer, the scattering curves decrease substantially, due to the electrostatic interactions which predominate at small values of Q . On the other hand, these curves tell us that cyclic weakly charged polymers scatter better than their linear homologous. This originates from their architectural differences and the fact that the cyclic chains are characterized by a higher segmental density. Elsewhere, we have remarked that the peak location, when it exists, is slightly shifted towards the lower values of Q ; in particular, one observes that the peak, corresponding to cyclic chains, disappears at a value of the charge parameter higher than that referring to the case of their linear counterparts.

In the case of similarly charged monomer species, we essentially found that the results of neutral polymers remain valid with a modified excluded-volume parameter, which becomes Q -dependent, in order to include the effect of long-range electrostatic repulsions. If the two monomer species are oppositely charged, we again found that formulae for neutral polymers could be used, but both the excluded-volume v and the interaction parameter χ should be modified, in order to take into account the long-range electrostatic interactions between

charges within the same species (repulsion) and between different ones (attraction).

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FIGURE CAPTIONS

Fig. 1a : Variations of the reduced total structure factor, $S_T(Q)/Z\Phi$, upon the renormalized wave-number QR_g , for a ternary system made of charged ($f_a \neq 0$) and neutral ($f_b = 0$) homopolymers in solution, at several values of the charge parameter f_a , with no added salt. The solid curves correspond to cyclic chains, whereas the dashed ones represent their linear homologous. From the top, each series of curves corresponds to $f_a = 0$ (neutral polymeric system), 0.075, 0.1, 0.15, 0.2 and 0.3, respectively. In plotting of these curves, we have used the following numerical parameters : $x = 0.8$, $v\Phi Z = 1$ and $\chi/v = 0.1$.

Fig. 1b : Variations of $S_T(Q)/Z\Phi$ upon QR_g , for a polymeric system, similar to that considered in Fig. 1a, for various values of the composition x . The solid curves correspond to cyclic chains, whereas the dashed ones represent their linear homologous. From the bottom, each series of curves corresponds to $x = 1$ (single polyion), 0.95, 0.90, 0.85, 0.80 and 0.50, respectively. The used parameters are : $v = 1$, $v\Phi Z = 1$ and $\Phi_{salt} = 0$ (no added salt).

Fig. 2a : Angular dependence of $S_T(Q)/Z\Phi$ upon the variable QR_g , for a ternary system made of neutral ($f_a = 0$) and charged ($f_b \neq 0$) homopolymers in solution, in the absence of salt and for several values of the charge parameter f_b . The solid curves correspond to cyclic chains, whereas the dashed ones represent their linear homologous. From the top, each series of curves corresponds to $f_b = 0$ (neutral polymeric system), 0.01, 0.03, 0.05, 0.075 and 0.1, respectively. The used parameters are similar to those of Fig. 2a

Fig. 2b : Angular dependence of $S_T(Q)/Z\Phi$ upon the variable QR_g , for a ternary system made of two similarly charged homopolymers ($f_a = f_b \equiv f \neq 0$, $\eta_{ab} = +1$), with $v\Phi Z = 1$, $\chi/v = 0.1$, in the absence of added salt and for several values of the common charge parameter f . The solid curves correspond to cyclic chains, whereas the dashed ones represent their linear homologous. From the top, each series of curves corresponds to $f_a = f_b = 0$ (neutral polymeric system), 0.075, 0.1, 0.15 and 0.2, respectively.

Fig. 3a : Angular dependence of $S_T(Q)/Z\Phi$ upon the variable QR_g , for a ternary system made of two unlikely charged homopolymers ($\eta_{ab} = -1$) for $f_a = 0.1$, $\chi/v = 0.1$, and several values of the charge parameter f_b , with $v\Phi Z = 1$ and no added salt. The solid curves correspond to cyclic chains whereas the dashed ones represent their linear homologous. From the bottom, each series of curves corresponds to $f_b = 0$ (polymer 2 is neutral), 0.075, 0.1, 0.15, 0.2 and 0.3, respectively.

Fig. 3b : Angular dependence of $S_T(Q)/Z\Phi$ upon the variable QR_g , for a polymeric system similar that considered in Fig. 3a, with $f_a = f_b = 0.1$ ($\eta_{ab} = -1$) and several values of the composition x of the mixture. The solid curves correspond to cyclic chains, whereas the dashed ones represent their linear homologous. From the bottom, each series of curves corresponds to $x = 1$ (single polyion system), 0.95, 0.90, 0.85 and 0.8, respectively. The used parameters are : $\chi/v = 0.1$, $v\Phi Z = 1$ and $\Phi_{salt} = 0$ (no added salt).

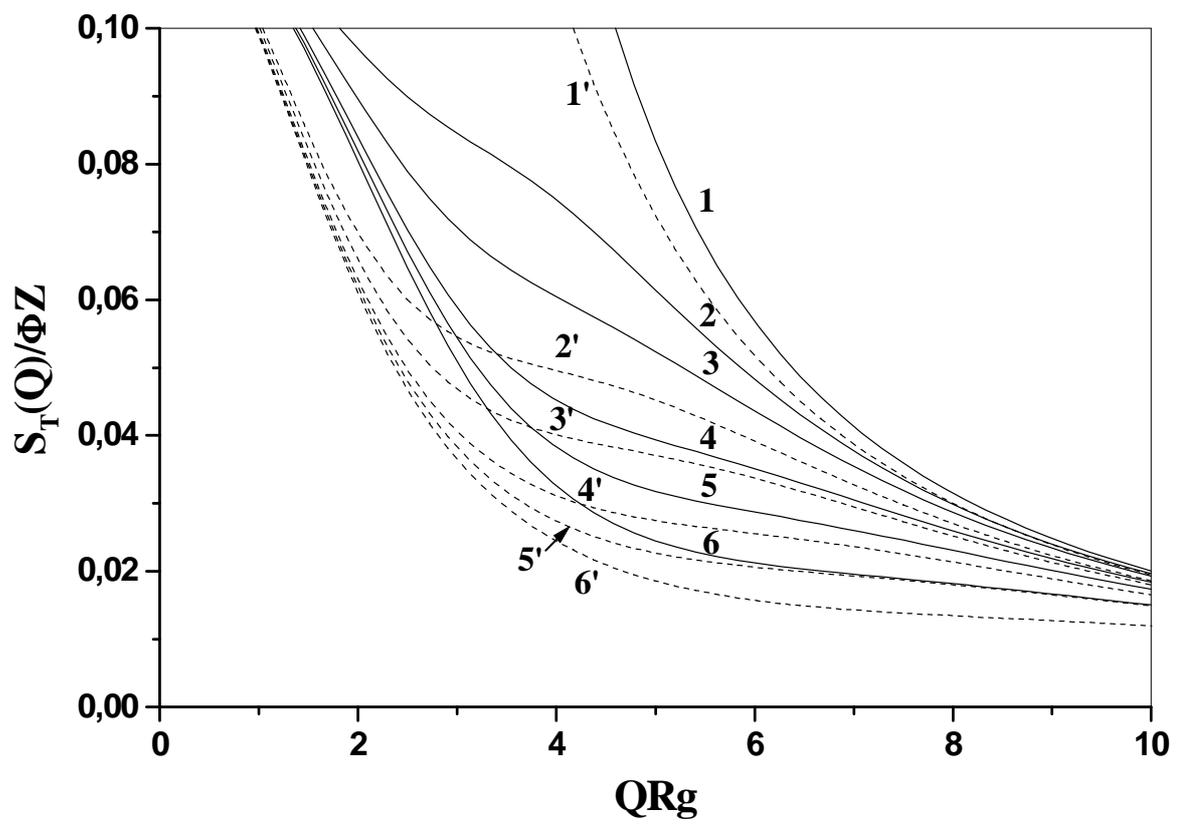


Figure 1a

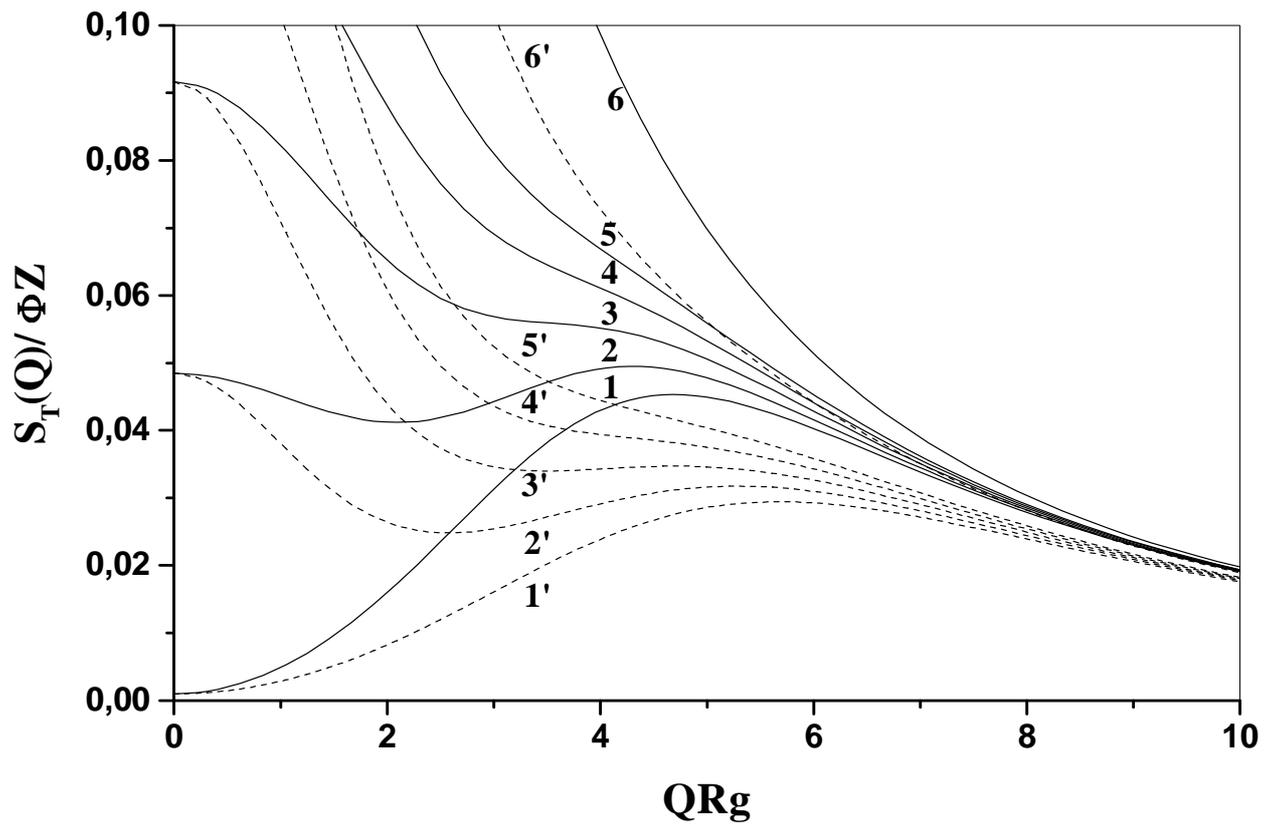


Figure 1b

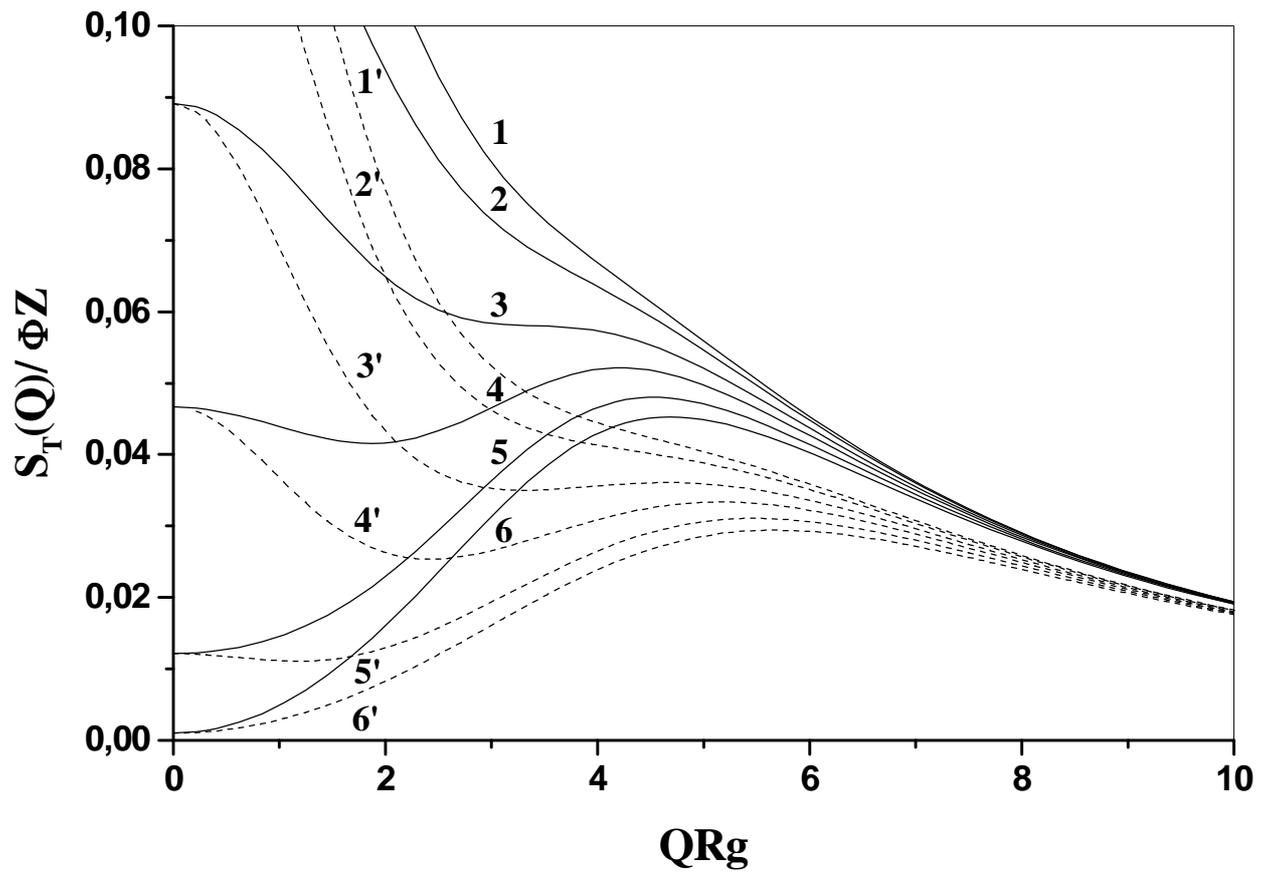


Figure 2a

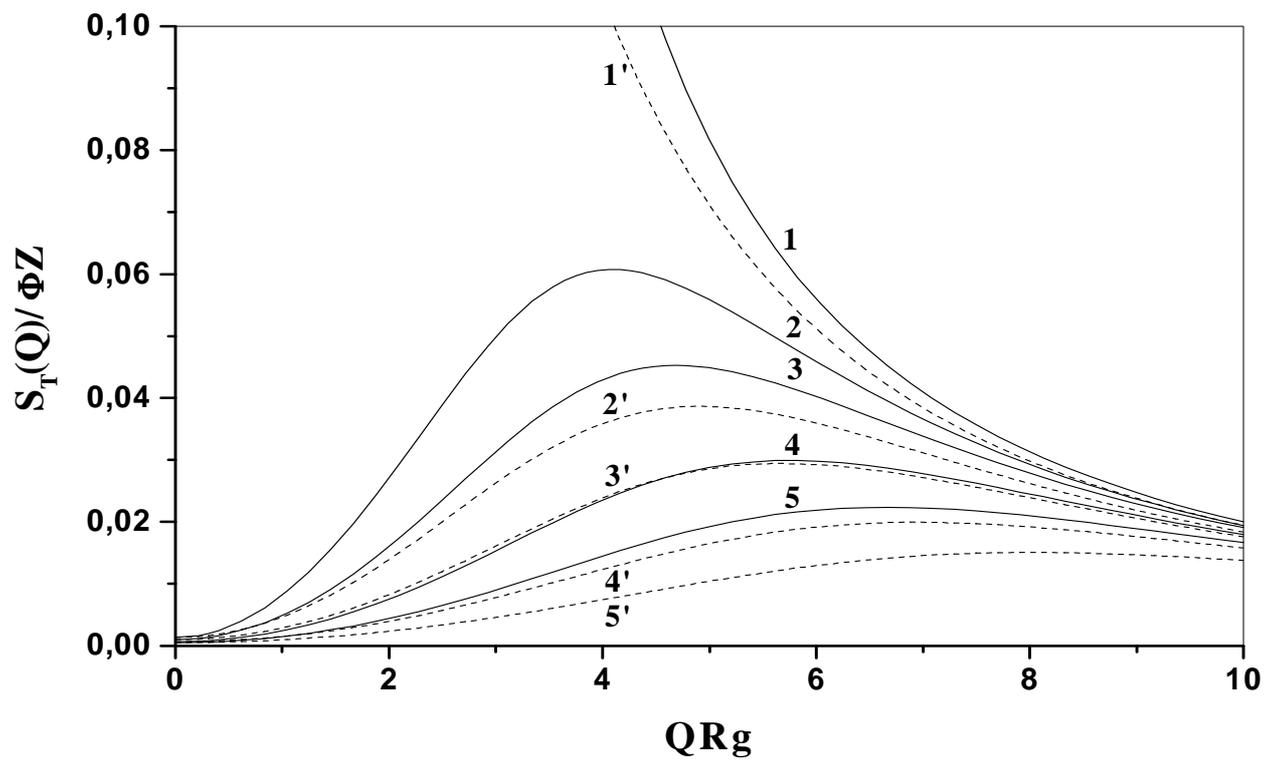


Figure 2b

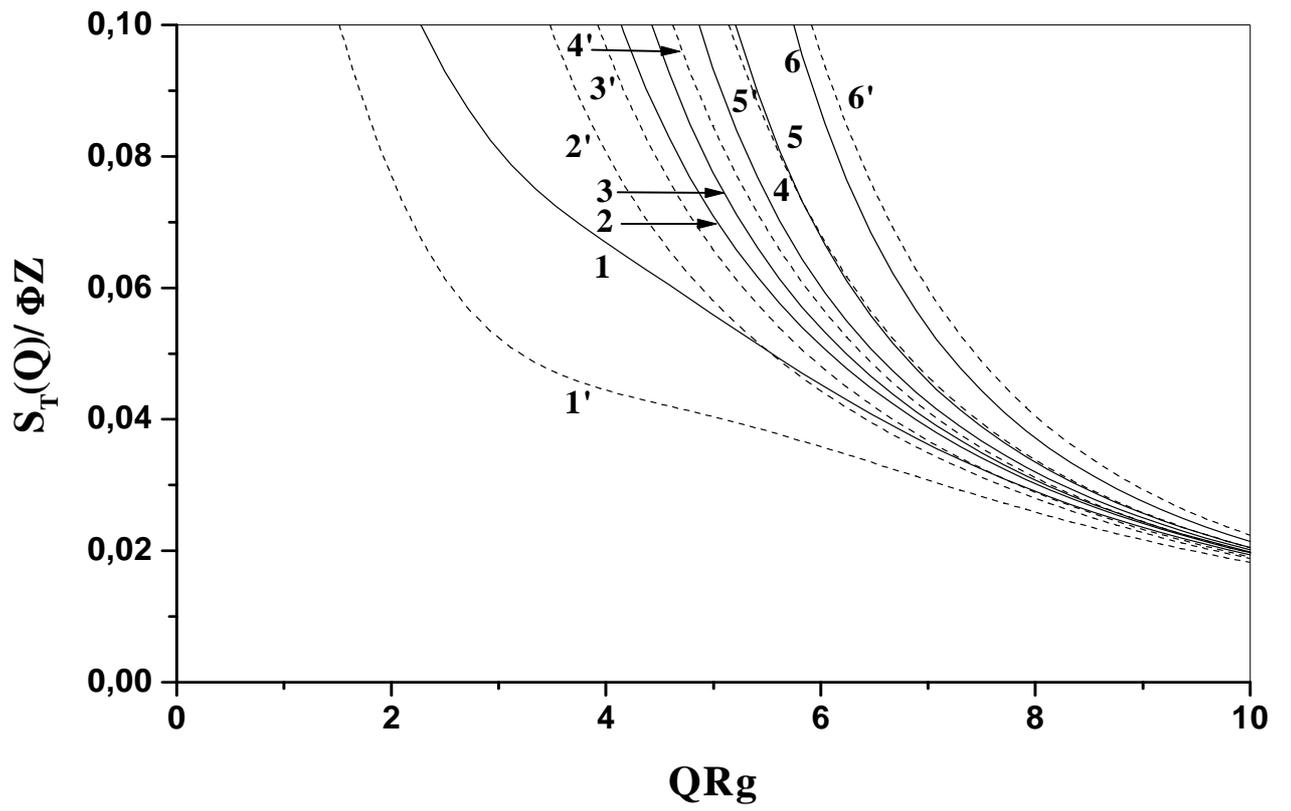


Figure 3a

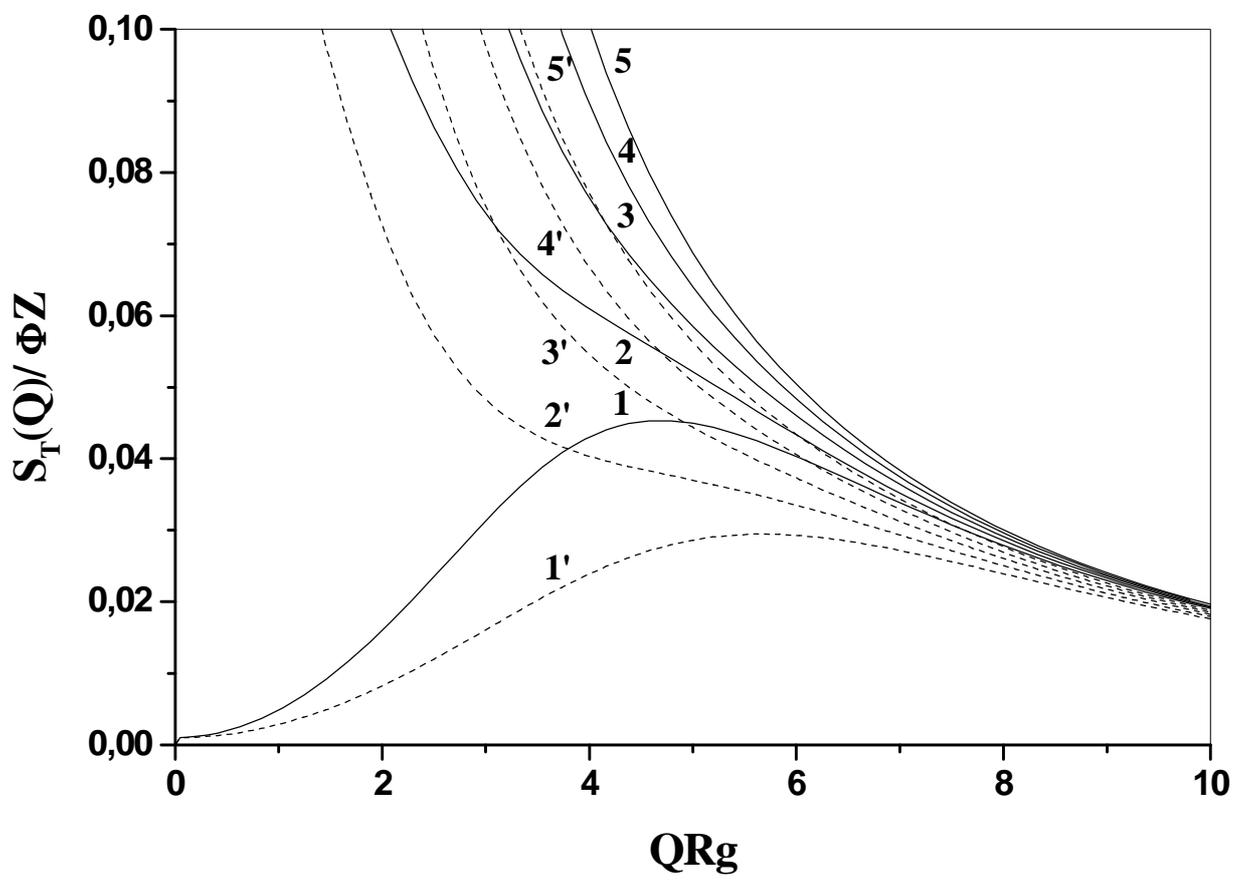


Figure 3b