Macromolecules 1991, *24*, 6418-6425

Static Scattering from Mixtures of Weakly Charged Polymers[†]

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Received March 21, 1991

ABSTRACT: The static scattering properties of mixtures of weakly charged polymers are investigated. The partial structure factors are calculated using the general matrix equation $\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{U}(\mathbf{q})$, where $\mathbf{S}(q)$ and $\mathbf{S}_0(q)$ are the total and bare structure matrices, $\mathbf{U}(q)$ is the interaction matrix, and q is the magnitude of the wave vector. $\mathrm{U}(q)$ is modeled as a sum of the classical excluded volume matrix and the electrostatic interaction matrix. The case of ternary mixtures of two polymers and a solvent is considered. Mixtures of charged and neutral polymers and mixtures of polymers having charges of the same or opposite signs are also investigated. The variations with the wave vector q of various structure factors are examined in some detail in various conditions of charge distribution.

1. Introduction

The properties of charged polymers are the subject of intensive studies from both theoretical and experimental points of view. The combined use of light and neutron scattering techniques has given a better insight into the short- and long-range interaction properties of polymer systems.[1,2] This is particularly true in the case of charged polymers since the nature of interaction is significantly different whether one looks at short-range interactions, which are essentially of thermodynamic nature (or excluded volume), or long-range interactions, which are dominated by electrostatic forces.

The static properties of single-polyion systems have been studied in detail using more or less different models to represent the electrostatic interactions.[3-7] All the representations lead to the same conclusion that the polyion–polyion partial structure factor $S_{11}(q)$ shows a peak at a certain wave vector q_m, and this observation was corroborated by various light and neutron scattering experiments.[2,8] This means that in the low q region, the long-range electrostatic forces determine the behavior of the scattering function whose amplitude decreases significantly as $q \to 0$. The question that we would like to address in this work is how this behavior is changed when one adds another polymer which is either neutral or charged. This question was addressed before where the general formalism for weakly charged polymers was developed and formulas were given in some particular cases of charge distributions.[9] Here we would like to have a closer look at the variations with the wave vector q of various structure factors in order to have a qualitative estimate of the effect of electrostatic interactions.

The general formalism was based on a straightforward extension of the classical Zimm formula written in matrix form[10-12] to charged mixtures. We wrote[9]

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{U}(\mathbf{q}) \tag{1}$$

where $\mathbf{S}(q)$ is the static structure matrix whose elements are $S_{ij}(q)$ $(i, j = 1, 2, ...)$ and $\mathbf{S}_0(q)$ is the bare structure matrix. The interaction matrix $\mathbf{U}(q)$ is a sum of two matrices:

$$\mathbf{U}(\mathbf{q}) = \mathbf{V} + \alpha(\mathbf{q})\mathbf{f}\mathbf{f}^{\mathrm{T}} \tag{2}$$

$\mathbf{V}$ is the excluded volume matrix whose elements are the usual parameters v_{ij}

$$v_{ij} = 1/\phi_s - \chi_{is} - \chi_{js} + \chi_{ij} \tag{3}$$

where ϕ_s is the solvent concentration (number of solvent molecules per unit volume) and χ_{is} and χ_{ij} are the polymer i/solvent and polymer i/polymer j Flory interaction parameters, respectively. The second term in eq 2 describes the electrostatic interaction

$$\alpha(\mathbf{q}) = \frac{4\pi l}{q^2 + \kappa^2} \tag{4}$$

l is the Bjerrum length $\equiv e^2/\epsilon kT$, and κ^{-1} is the Debye–Hückel screening length

$$\kappa^2 = 4\pi l \sum_i \phi_{ci} \tag{5}$$

ϕ_{ci} is the concentration of counterions, and we shall assume in this work that small ions (counterions and co-ions from polymer and added salt) have valence 1 (1:1 electrolyte) for simplicity. $\mathbf{f}$ is a column vector whose elements f_i represent the apparent valences of monomers i (charge fraction $0 \le f_i \le 1$), and $\mathbf{f}^{\mathrm{T}}$ is its transpose. For a ternary mixture of two polyions and a solvent, the bare structure matrix $\mathbf{S}_0(q)$ is a two by two matrix, but only the diagonal terms are nonzero, given by

$$S_i^0(\mathbf{q}) = \phi_i N_i P_i(\mathbf{q}); \quad i = 1, 2 \tag{6}$$

where N_i is the degree of polymerization of polymer i, $\phi_1 = x\phi$, and $\phi_2 = (1 - x)\phi$, x being the fraction of polymer 1 and ϕ the total polymer concentration. $P_i(q)$ is the form factor of polymer i. We shall assume that polyions are flexible polymers and their form factor can be represented by the Debye function

$$P_i(\mathbf{q}) = \frac{2}{\alpha_i^2}[e^{-\alpha_i} + \alpha_i - 1] \tag{7a}$$

$$\alpha_i \equiv q^2 R_{gi}^2 \tag{7b}$$

The radius of gyration R_{gi} is assumed to be governed entirely by the thermodynamic excluded volume interaction, and hence, it can be expressed in terms of N_i and the statistical length of σ_i by[13]

$$R_{gi}^2 = \frac{N_i^{2\nu}\sigma_i^2}{(2\nu + 2)(2\nu + 1)}; \quad \nu = 0.533 \tag{7c}$$

These assumptions mean that the conformational properties of the polymer chains are dominated by the thermodynamic (or excluded volume) interactions and that

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0024-9297/91/2224-6418$02.50/0

the local rigidity which may be due to the electrostatic potential is neglected. This is a reasonable representation for weakly charged polymers, which are the subject of the present investigation. Of course, if one needs to introduce the effect of electrostatic stiffness in $P_i(q)$ and R_{gi}, it is a straightforward matter to do so by using one of the numerous models available and based on the concept of persistence length.[14]

The interaction matrix of eq 2 can be written explicitly in the case of a binary polymer mixture in solution as

$$\mathbf{f}\mathbf{f}^{\mathrm{T}} = \begin{bmatrix} f_1^{\,2} & \epsilon f_1 f_2 \\ \epsilon f_1 f_2 & f_2^{\,2} \end{bmatrix} \tag{8}$$

where $\epsilon = 1$ if monomers 1 and 2 have charges of the same sign and $\epsilon = -1$ otherwise. This paper is organized as follows: In the next section, we discuss the case of a single polyion in solution made of the solvent, counterions, and eventually salt ions. This solution is sometimes referred to simply as the solvent. Only polyions are assumed to contribute to the scattering; small ions (i.e., counterions and co-ions) are assumed to be pointlike and contribute to the screening of electrostatic interaction and to the overall electroneutrality condition. Although this case has been studied before,[2-7] it is useful to reproduce its main results within the present model and compare its predictions with those of a mixture of polyions. In section 3, we discuss various structure factors which are directly measurable in ternary mixtures of two weakly charged polyions 1 and 2 in solution. We consider successively the partial structure for $S_{11}(q)$ which is measured when the contrast (or $\partial n/\partial c_2$) of polyion 2 with respect to the solvent is zero. We also consider the total structure factor $S_{\mathrm{T}}(q)$ which corresponds to the case where the contrasts (or $\partial n/\partial c$) of polyions 1 and 2 are identical. For each structure factor, the following cases are investigated: (i) mixtures of charged and neutral polymers, $f_1 \neq 0, f_2 = 0$; (ii) mixtures of polyions having charges of the same sign, i.e., $f_1 \neq f_2 \neq 0$, $\epsilon = +1$ (the case where $f_1 = f_2 = f$ and $\epsilon = +1$ is also discussed); (iii) mixtures of polyions having charges of opposite signs, i.e., $f_1 \neq f_2 \neq 0$, $\epsilon = -1$ (here also, the case where $f_1 = f_2 = f$ and $\epsilon = -1$ is discussed separately).

In section 4 we briefly examine some static charge correlation functions, and in section 5 we present some concluding remarks.

2. Scattering from a Single Polyion in Solution

In this case, the matrix equation (1) becomes scalar and we have

$$S^{-1}(\mathbf{q}) = S_0^{-1}(\mathbf{q}) + U(\mathbf{q}) \tag{9a}$$

or

$$S(\mathbf{q}) = \frac{S_0(\mathbf{q})}{1 + U(\mathbf{q})S_0(\mathbf{q})} \tag{9b}$$

$$S_0(\mathbf{q}) = N\phi P(\mathbf{q}) \tag{9c}$$

with

$$U(\mathbf{q}) = \upsilon + \alpha(\mathbf{q})f^2 \tag{9d}$$

Substituting eqs 9c and 9d into eq 9b yields

$$\frac{S(\mathbf{q})}{N\phi} = \frac{P(\mathbf{q})}{1 + (\upsilon + \alpha(\mathbf{q})f^2)\phi N P(\mathbf{q})} \tag{10a}$$

It is interesting to write this equation in the reciprocal form and note that it takes the form

$$\frac{N\phi}{S(\mathbf{q})} = \left[\frac{N\phi}{S(\mathbf{q})}\right]_{\text{neutral}} + \alpha(\mathbf{q})f^2 N\phi \tag{10b}$$

with

$$\left[\frac{N\phi}{S(\mathbf{q})}\right]_{\text{neutral}} = \frac{1}{P(\mathbf{q})} + \upsilon N\phi \tag{10c}$$

Let us recall the definitions of some experimental quantities and numerical values used in this work. The second virial coefficient A_2 is related to υ by

$$A_2 = \frac{\upsilon \mathcal{N}_{\text{av}}}{2m_0^{\,2}}$$

where $\mathcal{N}_{\text{av}}$ is Avogadro's number and m_0 is the mass of a monomer. We shall assume that $m_0 = 184$ g/mol for sulfonated polystyrene. The molecular weight is $M = Nm_0$ and the polymer concentration in g/cm^3 is given by

$$c = \phi m_0 / \mathcal{N}_{\text{av}}$$

To illustrate the variation of $S_{11}(q)$ as a function of qR_{g} within the present model as given by eq 10a, we have used the following numerical values, which are also used in the rest of this paper (unless indicated explicitly otherwise): $N = 10^4$; $\sigma = 2.5$ Å; $R_{\mathrm{g}} = 135$ Å; $A_2 = 2.67 \times 10^{-4}$ cm^3/g^2 (or $\upsilon = 30$ Å^3). $l = 7$ Å, which is just an estimate because it corresponds actually to water at 25 °C. Furthermore, if we call ϕ_{salt} the number concentration of salt, the Debye–Hückel screening length κ^{-1} is given by

$$\kappa^2 = 4\pi l(f\phi + \phi_{\text{salt}}) \tag{11}$$

due to the electroneutrality condition.

Figure 1a shows the variation of $S(q)/N\phi$ as a function of qR_{g} for a concentration corresponding to $\upsilon\phi N = 1$ and various values of the charge parameter f. Figure 1b shows a similar plot for a given charge parameter $f = 0.1$ and various concentrations; Figure 1c shows the effect of salt concentration. The behavior of $S(q)/N\phi$ as shown by these three figures is consistent with the results reported earlier by various authors[2-8] either from theoretical or from experimental investigations. The main reason for reproducing these results here is to see how they are modified when adding another polymer which can be neutral, similarly charged, or oppositely charged. This is the subject of the next section.

3. Scattering from Ternary Mixtures of Two Weakly Charged Polymers and a Solvent

The scattering intensity for a ternary mixture of two polymers 1 and 2 in solution is known as

$$I(\mathbf{q}) = (a_1 - s)^2 S_{11}(\mathbf{q}) + (a_2 - s)^2 S_{22}(\mathbf{q}) + 2(a_1 - s)(a_2 - s)S_{12}(\mathbf{q}) \tag{12}$$

where the partial structure factors $S_{ij}(q)$ are the elements of the matrix $\mathbf{S}(q)$ and a_1, a_2, and s are the scattering lengths per monomer 1, monomer 2, and a solvent molecule, respectively (for light scattering $(a_1 - s)$ and $(a_2 - s)$ should be replaced by $(\partial n/\partial c)_1$ and $(\partial n/\partial c)_2$, respectively). For simplicity and without loss of generality, we shall assume that the sizes of both polymers are the same, i.e.

$$N_1 = N_2 = N \quad \text{and} \quad P_1(\mathbf{q}) = P_2(\mathbf{q}) = P(\mathbf{q}) \tag{13a}$$

We also assume that the quality of the solvent is the same for both polymers, which are characterized by a thermodynamic interaction parameter of Flory–Huggins type,

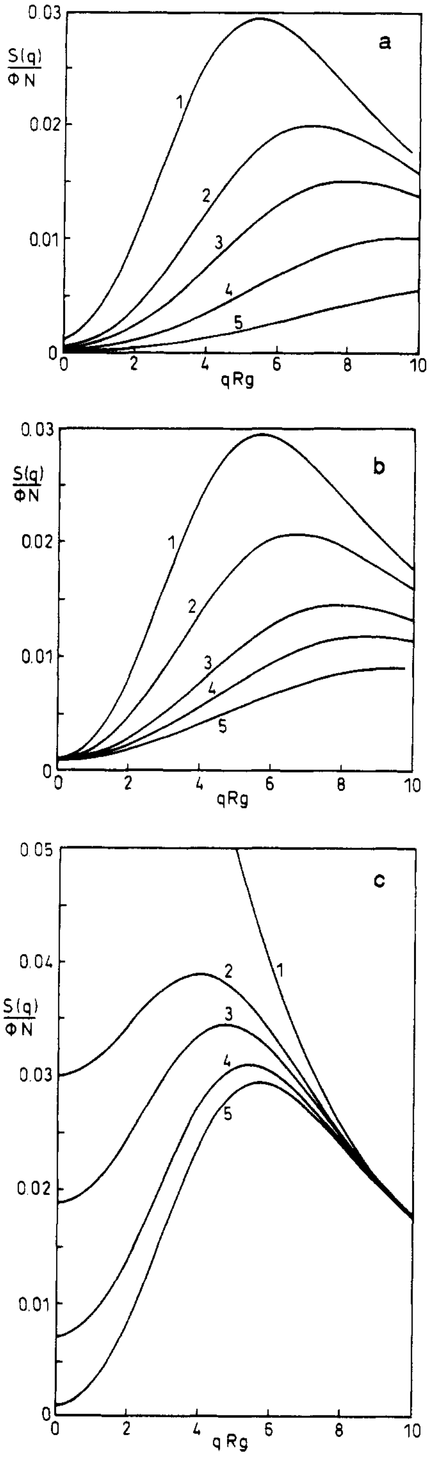

Figure 1. (a) Variation of $S(q)/\phi N$ as a function of qR_g for various values of the charge parameter f (see eq 10a). Curves 1-5 correspond to $f = 0.1$, 0.15, 0.2, 0.3, and 0.5, respectively. The following parameters are chosen: $N = 10^4$, $l = 7$ Å, $v\phi N = 1$; no added salt. (b) Variation of $S(q)/\phi N$ as a function of qR_g for various values of the polymer concentration represented by $v\phi N$ (see eq 10a). Curves 1-5 correspond to $v\phi N = 1$, 2, 4, 6, and 10, respectively. The other parameters are chosen as follows: $N = 10^4$, $l = 7$ Å, $f = 0.1$; no added salt. (c) Variation of $S(q)\phi N$ as a function of qR_g for various values of the salt concentration ϕ_{salt} (see eqs 10a and 11). Curves 1-5 correspond to $\phi_{salt} = 5 \times 10^{-3}$ g/cm^{-3}, 10^{-3}, 6×10^{-4}, 2×10^{-4}, and zero (no salt), respectively.

namely

$$v_{11} = v_{22} = v \quad \text{and} \quad v_{12} = v + \chi \tag{13b}$$

Therefore the base structure factors are

$$S_1^0(\mathbf{q}) = x\phi NP(\mathbf{q}) \quad \text{and} \quad S_2^0(\mathbf{q}) = (1-x)\phi NP(\mathbf{q}) \tag{14a}$$

and the interaction matrix $U(q)$ is given by

$$U(\mathbf{q}) = \begin{bmatrix} v + \alpha(\mathbf{q})f_1^2 & v + \chi + \epsilon\alpha(\mathbf{q})f_1f_2 \\ v + \chi + \epsilon\alpha(\mathbf{q})f_1f_2 & v + \alpha(\mathbf{q})f_2^2 \end{bmatrix} \tag{14b}$$

where $\epsilon = +1$ if the charges carried by monomers 1 and 2 are of the same nature and $\epsilon = -1$ otherwise. It is worthwhile to remember that the solvent comprises small ions (counterions or salt ions) that are assumed to be pointlike and therefore they are structureless; they do not contribute to the scattering intensity and have no specific thermodynamic interaction. Their role is to ensure the global electroneutrality condition and to produce the screening of electrostatic interactions between polyions. We shall now discuss in some detail the variations of $S_{11}(q)$, $S_T(q)$, and $S_I(q)$ with the wave vector q in various conditions of charge distributions.

3.1. The Partial Structure Factor $S_{11}(q)$. This quantity is accessible by scattering experiments if one chooses a polymer 2/solvent such that $a_2 = s$ or $(\partial n/\partial c)_2 = 0$. One finds that the scattering intensity is directly proportional to $S_{11}(\mathbf{q})$, which can be derived from eq 1 using the simplifications described in eqs 13 and 14. The result is

$$\frac{S_{11}(\mathbf{q})}{x\phi N} = \frac{P(\mathbf{q})\{1 + [v + \alpha(\mathbf{q})f_2^2](1-x)\phi NP(\mathbf{q})\}}{\mathcal{D}(\mathbf{q})} \tag{15a}$$

where $x = \phi_1/\phi$ is the fraction of polymer 1 and the denominator $\mathcal{D}$ is obtained as

$$\mathcal{D} = \mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\phi NP(\mathbf{q})\{xf_1^2 + (1-x)f_2^2 + v_e x(1-x)\phi NP(\mathbf{q})\} \tag{15b}$$

$\mathcal{D}_{\text{neutral}}$ is the denominator in the limit of neutral polymers ($f_1 = f_2 = 0$); i.e.

$$\mathcal{D}_{\text{neutral}} = 1 + v\phi NP(\mathbf{q}) - \chi(2v + \chi)\phi^2N^2x(1-x)P^2(\mathbf{q}) \tag{15c}$$

and

$$v_e = v(f_1 - \epsilon f_2)^2 - 2\chi\epsilon f_1f_2 \tag{15d}$$

We note that if $x = 1$ we recover the correct result for the single-polyion case defined by eq 10a. One of the questions to be addressed in this section is to see how the curves in Figure 1 are modified when one adds to polymer 1 a certain amount of polymer 2. For simplicity, we have chosen a polymer that has the same dimensions as 1, but they can be thermodynamically incompatible, and they may have different refractive indices or scattering lengths in addition to different charge distributions. With regards to the latter property, we shall consider the following distributions:

(a) Mixtures of Charged and Neutral Polymers ($f_1 = f$, $f_2 = 0$). Substituting $f_1 = f$ and $f_2 = 0$ in eq 15 yields

$$\frac{S_{11}(\mathbf{q})}{x\phi N} = \frac{P(\mathbf{q})\{1 + v(1-x)\phi NP(\mathbf{q})\}}{\mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})f^2x\phi NP(\mathbf{q})\{1 + v(1-x)\phi NP(\mathbf{q})\}} \tag{16a}$$

which becomes particularly simple and similar to eq 10b when written in the reciprocal form:

$$\frac{x\phi N}{S_{11}(\mathbf{q})} = \left[\frac{x\phi N}{S_{11}(\mathbf{q})}\right]_{\text{neutral}} + \alpha(\mathbf{q})f^2x\phi N \tag{16b}$$

The reason for the similarity between this result and the one in eq 10b valid for the single-polyion system can be understood as follows. This ternary mixture is comparable

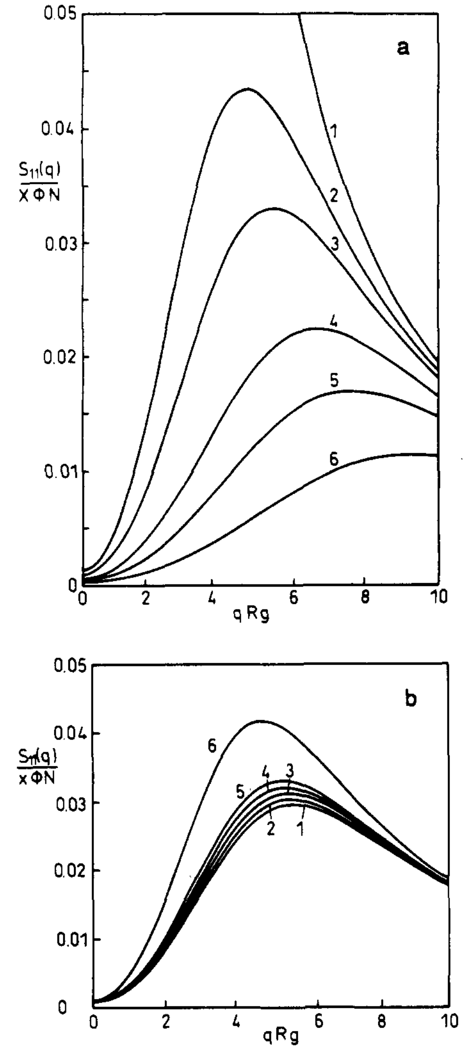

Figure 2. (a) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers and different values of f_1 (see eq 16a). Curves 1–6 correspond to $f_1 = 0$ (neutral mixture), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are chosen as $v\phi N = 1$, $x = 0.8$, and $\chi/v = 0.1$ (no salt). (b) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of neutral ($f_2 = 0$) and charged polymers ($f_1 = 0.1$) for different values of the composition x of polymer 1 (see eq 16a). Curves 1–6 correspond to $x = 1$ (single polyion; see eq 10a), 0.95, 0.9, 0.85, 0.8, and 0.5, respectively. The other parameters are chosen as $v\phi N = 1$ and $\chi/v = 0.1$ (no salt).

to a binary polymer–solvent system in which a fraction of $(1 - x)$ polymers is neutralized ($f_2 = 0$), its scattering contribution is turned off ($a_2 = s$), and an interaction parameter χ is turned on, although its effect is somewhat negligible as compared to the electrostatic interaction in the numerical conditions used here. To illustrate the implications of this procedure on the variations of $S_{11}(q)/Nx\phi$ as a function of qR_g, we have plotted the latter quantity in Figure 2a for $x = 0.8$, $\chi/v = 0.1$, $v\phi N = 1$, and various values of f. One observes that the qualitative behavior of the curves representing the variation of $S_{11}(q)$ is similar to that of the binary system (see Figure 1a). In particular, the peak is not significantly modified as compared to the single-polyion system. This seems to be in contradiction with the conclusions of Joanny and Leibler,[4] who predicted a quick collapse of the peak when a small amount of neutral polymer is added to the charged system. One may note that our eqs 16a,b are similar to their result (see eq 41 of ref 4), with slight differences essentially in the notations. Figure 2b shows $S_{11}(q)/x\phi N$ as a function of qR_g for $f_1 = 0.1$, $f_2 = 0$, $v\phi N = 1$, $\chi/v = 0.1$, and various values of the fraction of charged polymer x ranging from 1 to 0.5. The peak is still present for all values of x, which can be understood easily by a close look at eq 16a. Indeed, one observes that for $N = 10^4$ the charge carried by the polyion has a dominant effect as compared to the thermodynamic excluded volume interaction, which means that the electrostatic part in the denominator $\mathcal{D}$ is very large in the low q range. Actually, this contradiction with the conclusion of Joanny and Leibler is only apparent since one must compare the total structure factor $S_T(q)$ with $S(q)$ for the binary system. One, in fact, finds that the peak of $S_T(q)$ disappears quickly by adding a small amount of neutral polymers (see section 3.2). We shall not discuss the effects of polymer concentrations and added salt because they are qualitatively similar to those shown in parts b and c of Figure 1 for the single-polyion system.

(b) Mixtures of Polymers Having Charges of the Same Sign ($\epsilon = +1$). Let us consider a ternary mixture of two polymers characterized by charge parameters f_1 and f_2 with $\epsilon = +1$ meaning that the charges carried by monomers 1 and 2 are of the same nature (or sign). These two polymers are embedded in a solvent as described earlier. Putting these properties in eqs 15 gives

$$\frac{S_{11}(\mathbf{q})}{x\phi N} = [P(\mathbf{q})\{1 + [v + \alpha(\mathbf{q})f_2^2](1-x)\phi NP(\mathbf{q})\}]/ [\mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})\phi NP(\mathbf{q})\{xf_1^2 + (1-x)f_2^2 + v_e x(1-x)\phi NP(\mathbf{q})\}] \tag{17a}$$

$\mathcal{D}_{\text{neutral}}$ is given by eq 15c, and v_e is

$$v_e = v(f_1 - f_2)^2 = 2\chi f_1 f_2 \tag{17b}$$

The variation of $S_{11}(q)/x\phi N$ as a function of qR_g is illustrated in Figure 3a for $f_1 = 0.1$ and different values of f_2. The concentration is fixed by $v\phi N = 1$, and the interaction parameter is chosen such that $\chi/v = 0.1$. The qualitative behavior of the curves is not really affected by these choices of ϕ and χ. We also assume zero added salt concentration. Interestingly enough, one observes that the peak tends to disappear as f_2 increases from 10^{-2} to 0.1. This can be understood from eq 17a, where one sees that the electrostatic contribution, which is important since N is large, appears both in the numerator and in the denominator $\mathcal{D}$. Therefore there is some sort of cancellation in the small q range. This behavior is even more apparent when one chooses $f_1 = f_2 = f$ with $\epsilon = +1$. It is interesting to note that in this case $S_{11}(q)$ takes a very simple form which is the same as in the neutral case but with a modified excluded volume interaction parameter v which becomes

$$v_{\text{eff}}(\mathbf{q}) = v + \alpha(\mathbf{q})f^2 \tag{18a}$$

Therefore, letting $f_1 = f_2 = f$ in eq 17a yields

$$\frac{S_{11}(\mathbf{q})}{x\phi N} = [P(\mathbf{q})\{1 + v_{\text{eff}}(\mathbf{q})(1-x)\phi NP(\mathbf{q})\}]/ [1 + v_{\text{eff}}(\mathbf{q})\phi NP(\mathbf{q}) - \chi[2v_{\text{eff}}(\mathbf{q}) + \chi]x(1-x)\phi^2N^2P^2(\mathbf{q})] \tag{18b}$$

This result is illustrated in parts b and c of Figure 3.

Figure 3b shows how the variation of $S_{11}(q)$ as a function of the wave vector q is modified when the effective excluded volume parameter $v_{\text{eff}}(q)$ changes from the constant value v to the q-dependent quantity $v + \alpha(\mathbf{q})f^2$ with increasing values of f. In Figure 3c, we have plotted $S_{11}(q)/x\phi N$ as a function of qR_g for $f_1 = f_2 = f = 0.1$ and various values of x. One observes essentially that if 5% of the chains do not contribute to the scattering intensity, the peak tends

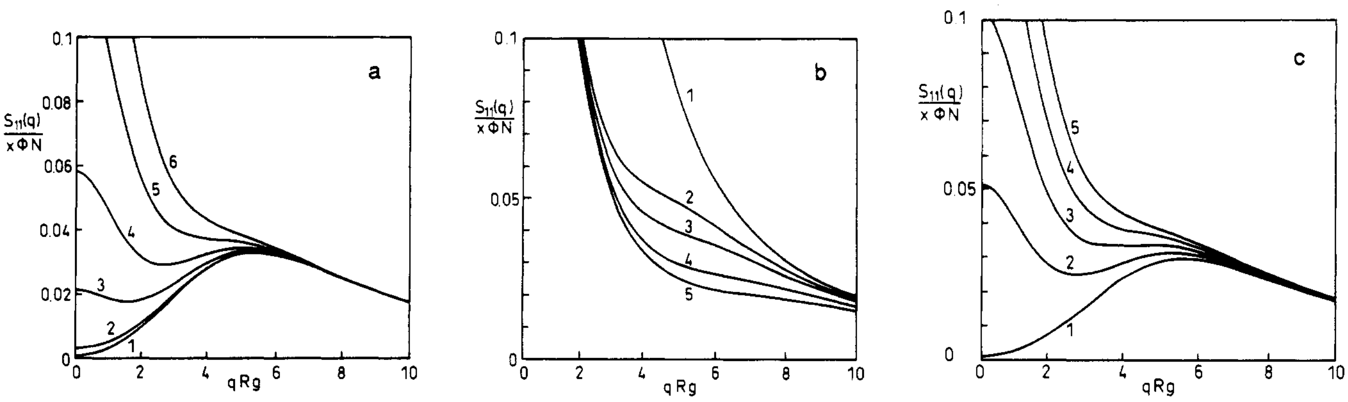

Figure 3. (a) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of charged polymers with $\epsilon = +1$ (charges of the same sign) with $f_1 = 0.1$ and different values of f_2 (see eq 17a). Curves 1–6 correspond to $f_2 = 0$ (polymer 2 is neutral), 0.01, 0.03, 0.05, 0.075, and 0.1, respectively. The other parameters are chosen as $v\phi N = 1$, $x = 0.8$, and $\chi/v = 0.1$ (no salt). (b) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of similarly charged polymers (see eq 18b) and various values of $f = f_1 = f_2$ ($\epsilon = +1$). Curves 1–5 correspond to $f = 0$ (neutral mixture), $f = 0.075$, f 0.1, and $1 \geq f \geq 0.2$, respectively. The other parameters are chosen as $v\phi N = 1$, $x = 0.8$, and $\chi/y = 0.1$ (no salt). (c) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of similarly charged polymers (see eq 18b) and various values of the composition x. Curves 1–5 correspond to $x = 1$ (single polyion system; see eq 10a), 0.95, 0.9, 0.85, and 0.8, respectively. The other parameters are chosen as $f_1 = f_2 = f = 0.1$, $v\phi N = 1$, and $\chi/v = 0.1$ (no salt).

to disappear and the curves are significantly changed. The next question to be addressed is to see how these predictions are modified when $\epsilon = -1$ or when the charges carried by monomers 1 and 2 are of opposite signs.

(c) Mixtures of Polymers Having Charges of Opposite Signs ($\epsilon = -1$). The expression of $S_{11}(q)/x\phi N$ is still given by eq 15a where the denominator $\mathcal{D}$ is unchanged except for v_e which becomes

$$v_e = v(f_1 + f_2)^2 + 2\chi f_1 f_2 \tag{19}$$

To see how this modification can change the shapes of the curves, we have plotted in Figure 4a $S_{11}(q)/x\phi N$ as a function of qR_g for $f_1 = 0.1$ and different values of f_2. Surprisingly enough, one sees that the shapes of the curves are comparable to the ones obtained for similarly charged polymers ($\epsilon = +1$). Therefore, the modification introduced through eq 19 is not really significant. This is due to the fact that we are examining $S_{11}(q)$ and we shall see later that the total structure factor is much more sensitive to the charge distribution than $S_{11}(q)$. In the special case where $f_1 = f_2 = f$ and $\epsilon = -1$, one can easily verify that $S_{11}(q)$ takes the same form as in the neutral limit but with modified q-dependent v and χ parameters. The result is

$$\frac{S_{11}(\mathbf{q})}{x\phi N} = [P(\mathbf{q})\{1 + v_{\text{eff}}(\mathbf{q})(1-x)\phi NP(\mathbf{q})\}]/ [1 + v_{\text{eff}}(\mathbf{q})\phi NP(\mathbf{q}) - \chi_{\text{eff}}(\mathbf{q})[2v_{\text{eff}}(\mathbf{q}) + \chi_{\text{eff}}(\mathbf{q})]x(1-x)\phi^2N^2P^2(\mathbf{q})] \tag{20a}$$

where $v_{\text{eff}}(\mathbf{q})$ is given by eq 18a and $\chi_{\text{eff}}(\mathbf{q})$ is obtained as

$$\chi_{\text{eff}}(\mathbf{q}) = \chi - 2\alpha(\mathbf{q})f^2 \tag{20b}$$

This means that while the excluded volume interaction is enhanced, the interspecies polymer interaction due to a possible incompatibility is reduced by the electrostatic forces. This is clear because the excluded volume interaction is dominated by the intrachain interactions which are enhanced by the electrostatic repulsion while the incompatibility is due to interspecies, interchain interactions. This behavior is illustrated in Figure 4b as far as the variation of $S_{11}(\mathbf{q})$ with the wave vector is concerned. It shows that $S_{11}(q)$ is reduced significantly in the low q range due to the effect of electrostatic attraction, which may be an indication of the compatibilization between the two polymer species. It is useless to mention that $S2_2(q)$ and $S_{12}(q)$ can also be investigated in the same conditions as we did for $S_{11}(q)$. This is perhaps not as useful as the total structure factor $S_T(q)$ or the charge correlation functions which may be directly accessible experimentally and their behavior with q is much more interesting. This study is the subject of the next sections.

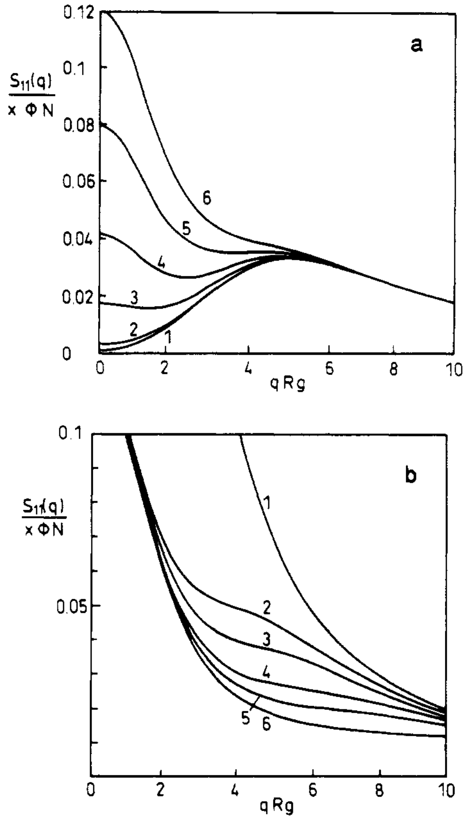

Figure 4. (a) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of polymers having charges of opposite signs (see eqs 15a and 19) for $f_1 = 0.1$ and various values of f_2. Curves 1–6 correspond to $f_2 = 0$ (polymer 2 is neutral), 0.01, 0.03, 0.05, 0.075, and 0.1, respectively. The other parameters are chosen as $v\phi N = 1$, $x = 0.8$, and $\chi/v = 0.1$ (no salt). (b) Variation of $S_{11}(q)/x\phi N$ as a function of qR_g for a mixture of oppositely charged polymers ($f_1 = f_2 = f$; $\epsilon = -1$; see eq 20a) and various values of f. Curves 1–6 correspond to $f = 0$ (neutral mixture), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are $x = 0.8$, $v\phi N = 1$, and $\chi/v = 0.1$ (no salt).

3.2. The Total Structure Factor $S_T(\mathbf{q})$. If the indices of refraction or the scattering lengths of the two polymers

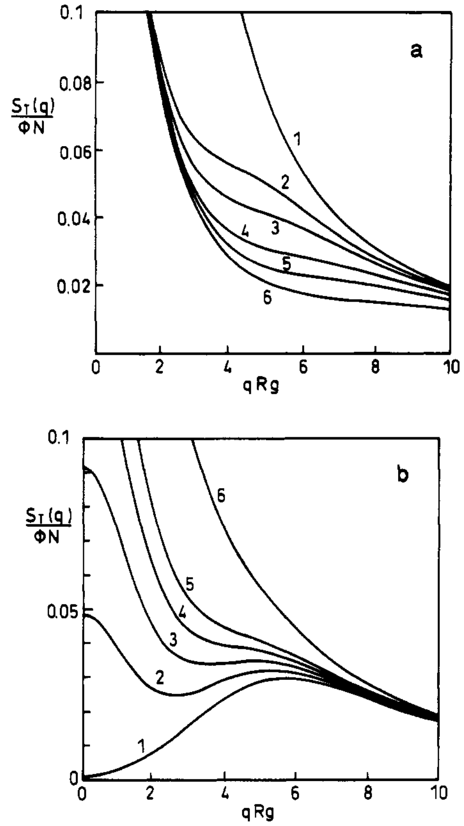

Figure 5. (a) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of charged ($f_1 \neq 0$) and neutral polymers ($f_2 = 0$) and various values of f_1 (see eq 23a). Curves 1–6 correspond to $f_1 =$ 0 (neutral mixture), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are chosen as $x = 0.8$, $\upsilon\phi N = 1$, and $\chi/\upsilon = 0.1$ (no salt). (b) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of charged ($f_1 = 0.1$) and neutral polymers ($f_2 = 0$) and various values of the composition (see eq 23a). Curves 1–6 correspond to $x = 1$ (single polyion system; see eq 10a), 0.95, 0.9, 0.85, 0.8, and 0.5, respectively. The other parameters are as in (a) (no salt).

are equal, then the scattering intensity $I(q)$ is proportional to the total structure factor $S_T(q)$:

$$I(\mathbf{q}) = (a - s)^2 S_T(\mathbf{q}) \tag{21a}$$

where $S_T(\mathbf{q})$ is

$$S_T(\mathbf{q}) = S_{11}(\mathbf{q}) + S_{22}(\mathbf{q}) + 2S_{12}(\mathbf{q}) \tag{21b}$$

In the simplifying assumptions of eqs 13 and 14 one obtains

$$\frac{S_T(\mathbf{q})}{\phi N} = [P(\mathbf{q})\{1 - [2\chi - \alpha(\mathbf{q})(f_1 - \epsilon f_2)^2] \times x(1 - x)\phi NP(\mathbf{q})\}]/\mathcal{D}(\mathbf{q}) \tag{22}$$

where the denominator $\mathcal{D}$ is given by eqs 15. Now, it would be interesting to examine the behavior of $S_T(\mathbf{q})$ in the conditions of charge distributions discussed above in connection with $S_{11}(\mathbf{q})$.

(a) Mixture of Charged and Neutral Polymers ($f_1 = f$, $f_2 = 0$). The total structure factor is obtained from eq 22 as

$$\frac{S_T(\mathbf{q})}{N\phi} = \left[P(\mathbf{q})\left\{1 - \frac{\chi - \alpha(\mathbf{q})f^2/2}{\chi_c(\mathbf{q})}\right\}\right]/[\mathcal{D}_{\text{neutral}} + \alpha(\mathbf{q})f^2x\phi NP(\mathbf{q})\{1 + \upsilon\phi(1 - x)NP(\mathbf{q})\}] \tag{23a}$$

where

$$\chi_c^{-1}(\mathbf{q}) = 2x(1 - x)\phi NP(\mathbf{q}) \tag{23b}$$

is the inverse of the q-dependent critical interaction parameter. The variations of $S_T(q)/\phi N$ as a function of qR_g given by eq 23 is illustrated in Figure 5 for $f_2 = 0$, $\upsilon\phi N = 1$, and $\chi/\upsilon = 0.1$. Figure 5a shows the effect of various values of the charge parameter f_1 for a given value of $x = 0.8$. It shows clearly that with 20% of neutral polymers the peak has completely disappeared even for a relatively large charge parameter $f = 0.3$. This is consistent with the remark of Joanny and Leibler, who noticed that adding a small amount of neutral polymers a "collapse" of the peak. This is more apparent in Figure 5b, where we have plotted $S_T(q)/\phi N$ as a function of qR_g for $f_2 = 0$, $f_1 = 0.1$, $\upsilon\phi N = 1$, $\chi/\upsilon = 0.1$, and various values of the composition x of charged polymers. For the single-polyion limit $x = 1$ and a clear peak is observed. By adding 5% of neutral polymer, the peak almost disappeared.

(b) Mixtures of Polymers Having Charges of the Same Sign ($\epsilon = +1$). Letting $\epsilon = +1$ in eq 22 gives

$$\frac{S_T(\mathbf{q})}{\phi N} = [P(\mathbf{q})\{1 - [2\chi - \alpha(\mathbf{q})(f_1 - f_2)^2] \times x(1 - x)\phi NP(\mathbf{q})\}]/\mathcal{D}(\mathbf{q}) \tag{24}$$

where $\mathcal{D}$ is given by eq 15b and υ_e by eq 17b. To understand the meaning of this quantity, let us assume that we start out with a binary polyion–solvent system as in paragraph 2 where the polyion has a charge parameter $f_1 = 0.1$. Take the fraction of chains $(1 - x)$, say 20%, and modify their charge. If we neutralize completely this charge (i.e., $f_2 = 0$), we get the behavior shown by Figure 5. If starting from $f_1 = 0.1$ and $f_2 = 0$, we increase f_2 keeping f_1 constant with $x = 0.8$ and $\upsilon\phi N = 1$, we obtain the behavior shown by Figure 6a. The peak of $S_T(q)$ reappears progressively as the charge parameter of polymer 2 increases from zero to $f_1 = 0.1$, where we recover almost the behavior of $S(\mathbf{q})$ for a single-polyion system (except for a slight effect of the χ parameter, which is very small as compared to the electrostatic term). It is interesting to write the expression of $S_T(\mathbf{q})$ in the case where $f_1 = f_2 = f$. From eq 24 we have

$$\frac{S_T(\mathbf{q})}{\phi N} = [P(\mathbf{q})[1 - 2\chi x(1 - x)\phi NP(\mathbf{q})]]/[1 + \upsilon_{\text{eff}}(\mathbf{q})\phi NP - \chi[2\upsilon_{\text{eff}}(\mathbf{q}) + \chi]x(1 - x)\phi^2N^2P^2(\mathbf{q})] \tag{25}$$

which is the same form as in the neutral limit with a modified excluded volume parameter consistent with our earlier observation in connection with $S_{11}(q)$ (see eqs 18a and 18b). Note that if $\chi = 0$, eq 25 coincides with eq 10a for a single-polyion system. Therefore the behavior of eq 25 as illustrated by Figure 6b is very similar to the one shown in Figure 1a.

(c) Mixtures of Polymers Having Charges of Opposite Signs ($\epsilon = -1$). Substituting $\epsilon = -1$ in eq 22 gives

$$\frac{S_T(\mathbf{q})}{\phi N} = [P(\mathbf{q})\{1 - [2\chi - \alpha(\mathbf{q})(f_1 + f_2)^2] \times x(1 - x)\phi NP(\mathbf{q})\}]/\mathcal{D}(\mathbf{q}) \tag{26}$$

where $\mathcal{D}$ is given by eq 15b and υ_e by eq 19. The variation of $S_T(\mathbf{q})/\phi N$ as a function of qR_g is plotted in Figure 7a for $f_1 = 0.1$ and various values of f_2 from 0 to 0.3. The composition is chosen as $x = 0.8$, the concentration is fixed by $\upsilon\phi N = 1$, and the interaction parameter $\chi/\upsilon = 0.1$. One observes that $S_T(q)$ increases significantly in the small range of q when the charge parameter increases. This is a consequence of the strong electrostatic attraction between polymers of different species, which leads to a high scattering signal at small q values. This behavior is also clearly apparent if one lets $f_1 = f_2 = f$ and $\epsilon = -1$. In this

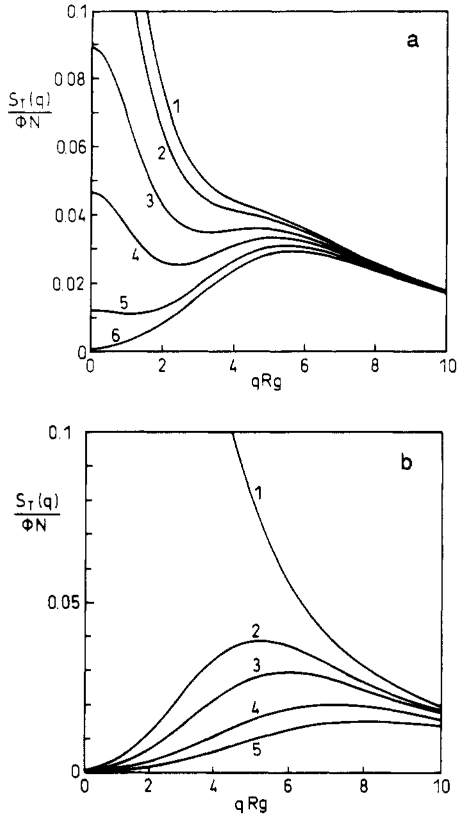

Figure 6. (a) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of polymers having charges of the same sign ($\epsilon = +1$), $f_1 = 0.1$, and various values of f_2 (see eq 24). Curves 1–6 correspond to $f_2 = 0$ (polymer 2 is neutral), 0.01, 0.03, 0.05, 0.075, and 0.1, respectively. The other parameters are $x = 0.8$, $v\phi N = 1$, and $\chi/v = 0.1$ (no salt). (b) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of similarly charged polymers ($f_1 = f_2 = f$, $\epsilon = +1$) and various values of f. Curves 1–5 correspond to $f = 0$ (neutral mixture), 0.075, 0.1, 0.15, and 0.2, respectively. The other parameters are $v\phi N = 1$, $x = 0.8$, and $\chi/v = 0.1$ (no salt) (see eq 25).

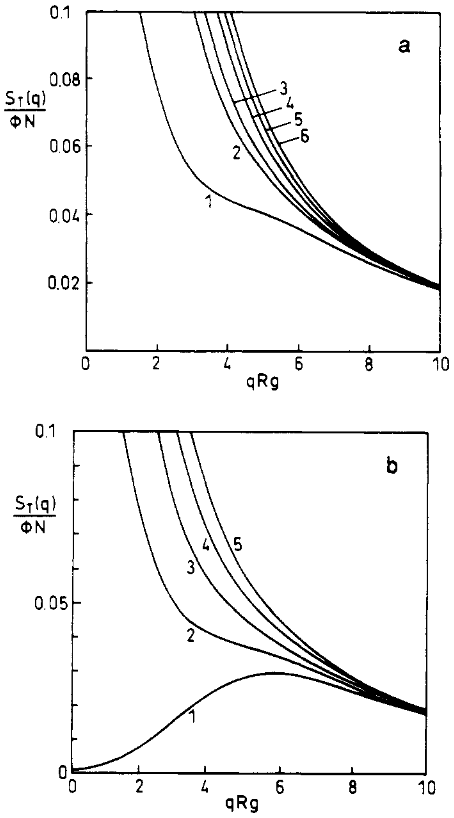

Figure 7. (a) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of polymers having charges of opposite signs ($\epsilon = -1$), $f_1 = 0.1$, and various values of f_2 (see eq 26). Curves 1–6 correspond to $f_2 = 0$ (polymer 2 is neutral), 0.075, 0.1, 0.15, 0.2, and 0.3, respectively. The other parameters are chosen as $x = 0.8$, $v\phi N = 1$, and $\chi/v = 0.1$ (no salt). (b) Variation of $S_T(q)/\phi N$ as a function of qR_g for a mixture of oppositely charged polymers ($f_1 = f_2 = f = 0.1$, $\epsilon = -1$) and various values of the composition x (see eq 27). Curves 1–5 correspond to $x = 1$ (single-polyion system; see eq 10a), 0.95, 0.9, 0.85, and 0.8, respectively. The other parameters are $v\phi N = 1$, and $\chi/v = 0.1$ (no salt).

particular limit, eq 26 becomes

$$\frac{S_T(\mathbf{q})}{\phi N} = [P(\mathbf{q})[1 - 2\chi_{\text{eff}}(\mathbf{q})x(1-x)\phi NP(\mathbf{q})]]/ [1 + v_{\text{eff}}(\mathbf{q})\phi NP(\mathbf{q}) - \chi_{\text{eff}}(\mathbf{q})[2v_{\text{eff}}(\mathbf{q}) + \chi_{\text{eff}}(\mathbf{q})]x(1-x)\phi^2N^2P^2(\mathbf{q})] \quad (27)$$

where $v_{\text{eff}}(\mathbf{q})$ and $\chi_{\text{eff}}(\mathbf{q})$ are defined in eqs 18a and 20b, respectively. This form is consistent with the one written in similar conditions for $S_{11}(q)$ (see eq 20a). Its variation with qR_g is illustrated in Figure 7b for $f_1 = f_2 = f = 0.1$ ($\epsilon = -1$), $v\phi N = 1$, $\chi/v = 0.1$, and various values of x from 1 to 0.8. One observes that the peak disappears quickly as soon as 5% of the chains are charged oppositely to the rest of the polymers. This is of course an expected behavior since even a small amount of neutral polymers produces a collapse of the peak of $S_T(\mathbf{q})$ due to the significant reduction of the electrostatic repulsion between polymers.

In the next section, we shall discuss the possible relationship of these structure factors with charge–charge static correlations.

4. Static Charge Correlation Function

The monomer charge density in a ternary mixture of two charged polymers and a solvent is defined as

$$z(\mathbf{q}) = ef_1\rho_1(\mathbf{q}) + e\epsilon f_2\rho_2(\mathbf{q}) \quad (28)$$

where e is the magnitude of the electron charge and $\rho_1(\mathbf{q})$ and $\rho_2(\mathbf{q})$ are the monomer densities of types 1 and 2, respectively. The partial structure factors are by definition

$$S_{ij}(\mathbf{q}) = \langle \rho_i(\mathbf{q})\rho_j(-\mathbf{q})\rangle \quad (i, j = 1, 2) \quad (29)$$

where the symbol $\langle ...\rangle$ denotes the average with respect to the equilibrium distribution function. The static charge correlation function $S_{zz}(\mathbf{q})$ can be introduced as

$$S_{zz}(\mathbf{q}) = \langle z(\mathbf{q})z(-\mathbf{q})\rangle \quad (30)$$

which by using eq 28 becomes

$$e^{-2}S_{zz}(\mathbf{q}) = f_1^{\,2}S_{11}(\mathbf{q}) + f_2^{\,2}S_{22}(\mathbf{q}) + 2\epsilon f_1f_2S_{12}(\mathbf{q}) \quad (31)$$

The form of this result calls for the following limits:

(i) Charge Correlations in a Mixture of Charged and Neutral Polymers ($f_1 \neq 0$, $f_2 = 0$). Equation 31 becomes

$$e^{-2}S_{zz}(\mathbf{q}) = f_1^{\,2}S_{11}(\mathbf{q}) \quad (32)$$

Therefore $S_{zz}(\mathbf{q})$ is directly proportional to $S_{11}(\mathbf{q})$, which was studied in the third section and part a (see *zz* eqs 16a and 16b parts a and b of Figure 2).

(ii) Charge Correlations in a Mixture of Polymers Carrying the Same Charges ($f_1 = f_2 = f$, $\epsilon = +1$). In this case, we have a charge correlation function that is directly proportional to $S_T(q)$; i.e.

$$e^{-2}S_{zz}(\mathbf{q}) = f^2S_T(\mathbf{q}) \quad (33)$$

where $S_T(\mathbf{q})$ is given by eq 25 and illustrated graphically

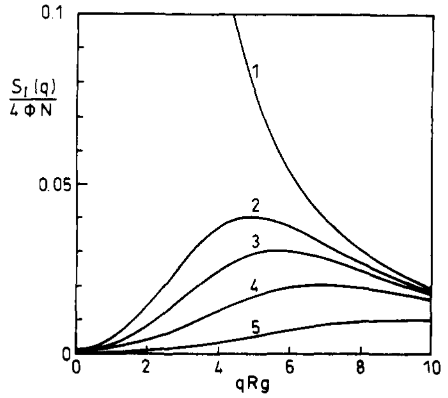

Figure 8. Variation of the charge correlation function $S_I(q)/4N\phi$ as a function of qR_g as given by eq 35 for various values of f ($f_1 = f_2 = f$, $\epsilon = -1$). Curves 1–5 correspond to $f = 0$ (neutral mixture), 0.075, 0.1, 0.15, and 0.2 or higher, respectively. The other parameters are chosen as $x = 0.5$, $\upsilon\phi N = 1$, and $\chi/\upsilon = 0.1$ (no salt).

in Figure 6b.

(iii) Charge Correlations in a Mixture of Polymers Carrying Charges of Opposite Signs ($f_1 = f_2 = f$, $\epsilon = -1$). In this limit we have

$$e^{-2}S_{zz}(\mathbf{q}) = f^2[S_{11}(\mathbf{q}) + S_{22}(\mathbf{q}) - 2S_{12}(\mathbf{q})] \tag{34}$$

This quantity is directly accessible by scattering experiment if one chooses the condition of zero average contrast and $x = 0.5$. Indeed, if we let

$$(a_1 - s)\phi_1 + (a_2 - s)\phi_2 = 0$$

with

$$\phi_1 = \phi_2 = \Phi/2(x = {}^1/_2)$$

one obtains

$$I(q) = (a_1 - s)^2 x^2 S_I(q)$$

$$\frac{S_I(\mathbf{q})}{4N\phi} = [P(\mathbf{q})\{1 + [\upsilon_{\text{eff}} + \chi_{\text{eff}}/2]\phi NP(\mathbf{q})\}]/ \left[1 + \upsilon_{\text{eff}}(\mathbf{q})\phi NP(\mathbf{q}) - \chi_{\text{eff}}(\mathbf{q})[2\upsilon_{\text{eff}}(\mathbf{q}) + \chi_{\text{eff}}(\mathbf{q})]\frac{\phi^2N^2}{4}P^2(\mathbf{q})\right] \tag{35}$$

The variation of this quantity with respect to qR_g for $\upsilon\phi N = 1$, $\chi/\upsilon = 0.1$, and various values of f is represented in Figure 8. It shows a peak even for a small value of f which is an expected result.

5. Conclusion

In this paper, we have examined some static scattering properties of ternary mixtures of two weakly charged polymers and a solvent. This investigation is based upon a generalization of the Zimm single-contact formula[10] to multicomponent polymer mixtures due to Benoit,[11] de Gennes,[17] and Akcasu.[12] This generalization is extended here to weakly charged polymers by a modification of the interaction matrix to include the effect of long-range electrostatic interaction in addition to the thermodynamic excluded volume interaction. The electrostatic part is based on the Debye–Hückel approximation since we have assumed that the interaction between two charged monomers is an ordinary screened potential of the form $\exp(-\kappa r)/r$, where r is the distance between the centers of two monomers. This is of course an approximation which is strictly valid only if the charges are far apart and in the condition where the electrostatic interaction is relatively weak. When monomers are close to each other, the excluded volume interaction becomes dominant. These aspects appear clearly in the scattering curves where we see that in the small q range the electrostatic interaction plays the dominant role and as q increases the excluded volume interaction becomes more and more important.

The other reason for limiting these investigations to weakly charged polymers is that the model does not account for possible ordering of charged molecules when the concentration increases. This phenomenon requires a more refined description which is beyond the scope of this work. We have used the Debye function for the form factor of chains and the radius of gyration without relying on the concept of persistence length in order to be consistent with our description which is restricted to weakly charged polymers. But it should be clear that the latter assumptions are not crucial since one can easily introduce other models for $P(q)$ and R_g that are available for stiff chains either neutral or charged.

Another point which is important to keep in mind is connected with the role of small ions. They are assumed to be pointlike without any specific contribution to the scattering curves or to the molecular interactions. They are present only to ensure the global electroneutrality condition and to produce screening of the electrostatic interaction in addition to the salt. This is of course an approximation which should be reexamined in the case where these ions have large dimensions of the order of q^{-1} for neutron or X-ray scattering and if their contrast with the solvent is not strictly zero.

Acknowledgment. M.B. thanks Professor E. W. Fischer for his kind invitation to the Max-Planck-Institut für Polymerforschung, where this work was completed.

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