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# Compatibility and Phase Behavior in Charged Polymer Systems and Ionomers

**M. G. Brereton**[†] **and T. A. Vilgis***

*Max-Planck-Institut für Polymerforschung, P.O. Box 3148, D-6500 Mainz, FRG.*

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ABSTRACT: In this paper we study the phase behavior of binary blends of charged macromolecules and ionomers. General formulas are given for the density fluctuations in the terms of the monomer and charge structure factors of the individual components, and the stability of the system is examined in detail. Coulombic and ionic interactions among the chains are shown to lead to a renormalization of the classical Flory–Huggins parameters $\chi_0$ and $\chi_F$. The main result is that polyelectrolytes of opposite charges are always compatible, due to the strong long-range Coulombic interaction, which can always overcome the thermodynamic repulsion. In ionomers, where the charges or dipoles are separated by a certain arc length along the chain, a micro phase separation can occur on length scales determined by the charge/ion distribution.

## 1. Introduction

The classical thermodynamic theory of polymer blends shows that is it extremely difficult to mix two or more polymers together, since the critical value of the so-called Flory–Huggins interaction parameter $\chi_0$ is proportional to the inverse of the molecular weight $N^{-1}$ of the polymers. (A physical explanation is given in the text book by de Gennes.[1]) Two polymers, A and B say, are only compatible if the thermodynamic interaction parameter $\chi_F$ between them is *less* than the critical $\chi_0$.

It is now of great interest to modify polymers and polymer blends in such a way that the blends are more compatible over a larger range of concentration and temperature. There are basically two different ways of doing this: first, the whole blend is modified by the addition of a third component and second the polymers themselves can be modified. Consider for example a binary blend of A and B species, which is partially compatible, i.e. in a certain temperature and concentration range. In

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[†] Permanent address: Department of Physics, University of Leeds, Leeds, LS2 9JT, U.K.

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some cases a range of compatibility can be enhanced if a third component is added to the blend. In the simplest case the third component is a diblock copolymer of blocks AB below a critical concentration and molecular weight, i.e. the critical micelle concentration, CMC. It has been shown by experiments[2] and theory[3] that the phase diagrams are altered, that the blend appears morphologically homogeneous, that mechanical properties are improved, etc. Moreover it has been shown by a model calculation that even the use of an arbitrary diblock copolymer XY, where the X and Y parts are not compatible to the homopolymers A and B, might produce better results than the AB block copolymer.[4,5] The shape of such a compatible stablizer is, in industrial applications, more complex than just that of diblock copolymers, since one expects additional effects by topological restrictions, such as entanglements, in very long comblike structures of the copolymers.

As an example of the second possibility to enhance the compatibility of polymer blends by modifying the polymers themselves, consider the case when the polymers A and B contain a few strong attractive monomer units. An extreme case is two polyelectrolytes, A and B, with opposite charges and charge neutrality for the whole blend. A very strong attraction between the two chemically different polymers exists on the length scale of the monomer or on the Kuhn length, and the question arises whether this attraction is so strong that the polymers are always compatible or is there still a point at which phase separation occurs. In this paper we will show that for the case of partially charged polymers, i.e. only a few charges distributed along the chains, the blend can experience a micro phase separation on length scales less than the radius of gyration but remains compatible on larger scales. A similar effect can occur in uncharged blends, which are compatible at high temperatures, then are cross-linked permanently by radiation, and then are cooled below the phase separation temperature. Such a cross-linked blend exhibits a micro phase separation in length scales below the mean distance of the cross-links.[6]

In experimental studies[7] polymer chains have been modified before blending to carry dipoles along the chains. It has been shown by electron microscopy that morphologically the ionic blend looked homogeneous, whereas the pure blend without ionic groups is very inhomogeneous. Such results have been supported by X-ray scattering.

The paper is organized as follows. In the next section we describe the stability of the polymer blends in terms of the response of the average density of each component to a spatially dependent chemical potential. A divergence of the response indicates the limit of stability of the blend. By using a spatially dependent chemical potential, analyzed in terms of its Fourier components, we can detect the spatial scale at which the blend becomes unstable and phase separation occurs. Mean field methods are used to derive the necessary response functions. In section 3 a detailed application is made to polyelectrolytes and ionomers in which we allow for an independent spatial distribution of charge and monomer units. General results are given that show that the stability criterion does depend on a spatial scale, determined by the strength and distribution of the charges. In section 4 specific applications of the general results are considered, including the case where the charge distribution coincides with the monomer distribution (the polyelectrolyte) and the other extreme of only one isolated charge per chain (the ionomer).

## 2. Preliminaries—Stability Criteria and the Mean Field Equations

The mean field method is well-known. We briefly introduce it here mainly to establish precise definitions of the quantities that we will need later. Consider a multicomponent polymer system. The components are labeled by the subscripts $\sigma$ and $\tau$. The chains are labeled by $\alpha$ and $\beta$ and different monomers are denoted by $i$ and $j$. The total energy $U$ is given by

$$U = \sum_{\sigma,\tau} \sum_{\alpha,\beta} \sum_{i,j} V_{\sigma\tau}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}) \tag{1}$$

This can be written in (collective) density variables $\rho_\sigma(\mathbf{q})$ as

$$U = \sum_{\mathbf{q}} \sum_{\sigma,\tau} W_{\sigma\tau}(\mathbf{q})\rho_\sigma(\mathbf{q})\rho_\tau(-\mathbf{q}) \tag{2}$$

with

$$W_{\sigma\tau}(\mathbf{q}) = (\Omega/kT) \int \mathrm{d}^3r\, V(\mathbf{r}) \exp\{i\mathbf{qr}\} \tag{3}$$

and

$$\rho_\sigma(\mathbf{q}) = \frac{1}{\Omega} \sum_{\alpha\in\sigma} \sum_{j} \exp\{i\mathbf{q}\mathbf{r}_{j\alpha}\} \tag{4}$$

and $\Omega$ is the volume of the system. The summation covers all chains belonging to the species $\sigma$. The stability of the system is tested by means of a spatially varying chemical potential for each species, $\mu_\sigma(\mathbf{r}_{i\alpha})$, which can be expressed in terms of the density variables $\rho_\sigma(\mathbf{q})$ as $\sum_{\mathbf{q}} \mu_\sigma(\mathbf{q})\rho_\sigma(-\mathbf{q})$.

The grand canonical partition function is then

$$\mathcal{L} = \int_\sigma \prod \mathcal{D}\rho_\sigma(\mathbf{q}) \exp\{-\sum_{\mathbf{q}} \sum_{\sigma} \mu_\sigma(\mathbf{q})\rho_\sigma(-\mathbf{q}) - \sum_{\mathbf{q}} \sum_{\sigma,\tau} W_{\sigma\tau}(\mathbf{q})\rho_\sigma(\mathbf{q})\rho_\tau(-\mathbf{q})\} \tag{5}$$

The average densities can be generated by the logarithmic functional derivation

$$\langle \rho_\sigma(\mathbf{q}) \rangle = \delta \log \mathcal{L} / \delta\mu_\sigma(-\mathbf{q})|_{\mu_\sigma=0} \tag{6}$$

The stability and hence the compatibility of the blend are monitored by the linear response $\Delta\langle\rho(\mathbf{q})\rangle$ of the average density of each component to a change, $\Delta\mu_\sigma(-\mathbf{q})$, in the chemical potential, i.e.

$$\Delta\langle\rho(\mathbf{q})\rangle = \sum S_{\tau\sigma}(\mathbf{q})\Delta\mu_\tau(-\mathbf{q})$$

where $S_{\sigma\tau}$ is the linear response function. The blend is stable to density fluctuations of a wave vector $\mathbf{q}_0$ if $S_{\sigma\tau}^{-1}(\mathbf{q}_0) > 0$. $q_0^{-1}$ defines a length scale over which the blend can be considered as compatible. For simple homopolymer blends the instability occurs at the macroscopic length scale, $q_0 = 0$. However, as we will show, the addition of an extra structure and interactions in the form of charges can limit the instability to smaller scales, $q_0 > 0$. The response function is derived as

$$S_{\sigma\tau}(\mathbf{q}) = \left.\frac{\delta\langle\rho_\sigma(\mathbf{q})\rangle}{\delta\mu_\tau(-\mathbf{q})}\right|_{\mu_\tau=0} \tag{7a}$$

and with use of (5) and (6) is directly related to equilibrium density fluctuations

$$S_{\sigma\tau}(\mathbf{q}) = \langle\rho_\sigma(\mathbf{q})\rho_\tau(-\mathbf{q})\rangle \tag{7b}$$

Note that this reduces for $\mathbf{q} \to \mathbf{0}$ and $\sigma = \tau$ to the classical expression of the particle number fluctuations, which is related to the compressibility in classical thermodynamics. To calculate the density–density correlation function in (7b), we use the mean field approximation. This involves the replacement of the full interaction energy, (2), by a single chain, $\tau$, in a mean field, $W_{\sigma\tau}(\mathbf{q})\langle\rho_\sigma(-\mathbf{q})\rangle$, due to all the other chains, i.e.

$$W_{\sigma\tau}(\mathbf{q})\rho_\sigma(\mathbf{q})\rho_\tau(-\mathbf{q}) \approx W_{\sigma\tau}(\mathbf{q})\rho_\sigma(\mathbf{q})\langle\rho_\tau(-\mathbf{q})\rangle + W_{\sigma\tau}(\mathbf{q})\rho_\sigma(\mathbf{q})\langle\rho_\tau(-\mathbf{q})\rangle \quad (8)$$

Using this approximation in the grand canonical partition function together with (6) and (7) yields a set of coupled linear equations for the structure factor, i.e.

$$S_{\sigma\tau}(\mathbf{q}) = S^0{}_{\sigma\tau}(\mathbf{q}) - \sum_{\kappa,\lambda} S^0{}_{\sigma\kappa}(\mathbf{q})W_{\kappa\lambda}(\mathbf{q})S_{\lambda\tau}(\mathbf{q}) \quad (9)$$

$S^0{}_{\sigma\tau}(\mathbf{q})$ values are the unperturbed structure factors, i.e. the density correlation function without any interaction, while $S_{\sigma\tau}(\mathbf{q})$ values are the full structure factors.

These equations lead to the standard random phase approximation formulae. Consider for example a one-component system, i.e. $\sigma = \tau$ and $W_{\sigma\tau} = W$. It follows immediately that

$$S = S^0 - S^0WS \quad (10)$$

or

$$S^{-1}(\mathbf{q}) = S^{\mathrm{o}-1}(\mathbf{q}) + W \quad (11)$$

which is de Gennes celebrated formula.

The usual result for a two-component blend[1]

$$S^{-1}(\mathbf{q}) = S^{\circ}{}_{\mathrm{A}}{}^{-1}(\mathbf{q}) + S^{\circ}{}_{\mathrm{B}}{}^{-1}(\mathbf{q}) - 2\Omega l^3\chi_{\mathrm{F}} \quad (12)$$

where the Flory $\chi_{\mathrm{F}}$ parameter is here defined as

$$\chi_{\mathrm{F}} = \lim_{V\to\infty}\{W_{\mathrm{AA}}W_{\mathrm{BB}} - W_{\mathrm{AB}}{}^2\}/W_{\mathrm{BB}} \quad (13)$$

will be derived in the next section as a special case of a more general result. Note that the limit of infinite repulsive potentials corresponds to the incompressibility limit.

The question of stability is now answered.[1] The two-component blend is stable, i.e. in the one phase region, if

$$S^{-1}(\mathbf{q}) > 0 \quad (14)$$

This leads to the usual Flory–Huggins condition $\chi_0 - \chi_{\mathrm{F}} > 0$ for the binary blend in the limit $|\mathbf{q}| \to 0$, where $2\chi_0 = 1/(\phi_{\mathrm{A}}p_{\mathrm{A}}) + 1/(\phi_{\mathrm{B}}p_{\mathrm{B}})$. $\phi_\sigma$ values are the volume fractions, i.e.

$$\phi_\sigma = l^3\rho_\sigma(0)/\Omega \quad (15)$$

where $l$ is the Kuhn length of the polymer, $\Omega$ is the total volume, and $\rho_\sigma(0) = \rho_\sigma(\mathbf{q}{=}0)$, i.e. the mean density of component $\sigma$. $\rho_\sigma$ values are the number of Kuhn steps of the $\sigma$-type chain (degree of polymerization).

## 3. Charged Polymers, Polyelectrolytes, and Ionomers

For simplicity we consider a binary (A, B) blend where both kinds of polymers carry separate charge distributions. The mean field equations (9) require, as input, the unperturbed structure factors $S^0{}_{\mathrm{A}}$ and $S^0{}_{\mathrm{B}}$ and the interaction potentials $V_{\mathrm{AA}}$, $V_{\mathrm{BB}}$, and $V_{\mathrm{AB}}$. However in addition to the usual monomer–monomer structure factors $S^0{}_{\mathrm{A}}{}^{\mathrm{mm}}(\mathbf{q})$ and $S^0{}_{\mathrm{B}}{}^{\mathrm{mm}}(\mathbf{q})$ there are extra structural relations to be accounted for in terms of the spatial arrangements of the charges with respect to each other, i.e. $S^0{}_{\mathrm{A}}{}^{\mathrm{cc}}(\mathbf{q})$ and $S^0{}_{\mathrm{B}}{}^{\mathrm{cc}}(\mathbf{q})$, and with respect to the monomers, i.e. $S^0{}_{\mathrm{A}}{}^{\mathrm{cm}}(\mathbf{q})$ and $S^0{}_{\mathrm{B}}{}^{\mathrm{cm}}(\mathbf{q})$. Correspondingly we have to take into account not only monomer–monomer interactions on and between the A and B chains with interaction terms $V_{\sigma\tau}{}^{\mathrm{mm}}$ but also charge interactions $V_{\sigma\tau}{}^{\mathrm{cc}}$. The precise definitions are given below.

**3.1. The Structure Factors. (a) Monomer–Monomer Structure Factors.** The spatial structure of the monomers with respect to each other is described by

$$S^0{}_{\mathrm{mm},\sigma}(\mathbf{q}) = \frac{1}{\Omega^2}\sum_{\substack{\alpha,\beta\\ i,j}}^{p_{\mathrm{A}},N_{\mathrm{A}}} \langle \exp\{i\mathbf{q}(\mathbf{r}_{i,\alpha}{}^{\mathrm{m}} - \mathbf{r}_{j,\beta}{}^{\mathrm{m}})\}\rangle_0 \quad (16)$$

where the $\mathbf{r}_{i,\alpha}{}^{\mathrm{m}}$ values are the positions of the monomers on the $\alpha$th chain at monomer position $i$. $p_{\mathrm{A}}$ is the chain lengths as before, and $N_{\mathrm{A}}$ is the number of A chains. The label m denotes monomers. $\langle\ \rangle_0$ means an average based on the noninteracting system. Note that in the case of long chains this can be rewritten as

$$S^0{}_{\mathrm{A}}{}^{\mathrm{mm}}(\mathbf{q}) = (1/\Omega)\rho_{\mathrm{A}}{}^{\mathrm{m}}g_{\mathrm{A}}{}^{\mathrm{m}}(\mathbf{q}) \quad (17)$$

where $\rho_{\mathrm{A}}{}^{\mathrm{m}} = N_{\mathrm{A}}p_{\mathrm{A}}/\Omega$ is the monomer density of component A. $g_{\mathrm{A}}{}^{\mathrm{m}}(\mathbf{q})$ is the Debye function coming from the random walk character of the chains, which can be usefully approximated by[8]

$$g_{\mathrm{A}}{}^{\mathrm{m}}(\mathbf{q}) \approx \frac{p_{\mathrm{A}}}{1 + q^2R_{\mathrm{A}}{}^2/2} \quad (18)$$

where $R_{\mathrm{A}}{}^2 = l_{\mathrm{A}}{}^2p_{\mathrm{A}}/6$, i.e. the radius of gyration of the chain in the A component. Similar expressions hold for the B component.

**(b) Charge–Charge Structure Factors.** In a similar way one can define the charge–charge structure factors, i.e.

$$S^0{}_{\mathrm{A}}{}^{\mathrm{cc}}(\mathbf{q}) = \frac{1}{\Omega^2}\sum_{\substack{\alpha,\beta\\ i,j}}^{p_{\mathrm{A}}{}^{\mathrm{c}},N_{\mathrm{A}}} \langle \exp\{i\mathbf{q}(\mathbf{r}_{i,\alpha}{}^{\mathrm{c}} - \mathbf{r}_{j,\beta}{}^{\mathrm{c}})\}\rangle_0 \quad (19)$$

where the $p_{\mathrm{A}}{}^{\mathrm{c}}$ values are the number of charges on the A chain and $N_{\mathrm{A}}$ is the amount of A chains as before. The $\mathbf{r}_{i,\alpha}{}^{\mathrm{c}}$ values locate now the charges on the chain A. This can be written for long chains and for every component $\sigma$ as

$$S^0{}_\sigma{}^{\mathrm{cc}}(\mathbf{q}) = (1/\Omega)\rho_\sigma{}^{\mathrm{c}}g_\sigma{}^{\mathrm{c}}(\mathbf{q}) \quad (20)$$

where $\rho_\sigma{}^{\mathrm{c}}$ is the charge density and $g_\sigma{}^{\mathrm{c}}$ is the structure factor of the charges. Note that $g_\sigma{}^{\mathrm{c}}(\mathbf{q})$ is in general not given by a formula as in eqs 17 and 18. In the simplest case where chains contain only charge per chain, $g(\mathbf{q})$ is a constant: i.e., $g(\mathbf{r})$ is just a delta function locating the charge at a particular point on the chain.

**(c) Charge–Monomer Structure Factors.** The interrelation between monomers and charges is given by

$$S^0{}_\sigma{}^{\mathrm{mc}}(\mathbf{q}) = \frac{1}{\Omega^2}\sum_{\substack{\alpha,\beta\\ i,j}}^{p_\sigma{}^{\mathrm{m}},N_\sigma} \cup \sum_{\substack{\alpha,\beta\in\sigma\\ i,j}}^{p_\sigma{}^{\mathrm{c}},N_\sigma} \langle \exp\{i\mathbf{q}(\mathbf{r}_{i,\alpha}{}^{\mathrm{m}} - \mathbf{r}_{j,\beta}{}^{\mathrm{c}})\}\rangle_0 \quad (21)$$

If we assume that the location of a charge also coincides with the position of a monomer, then selecting any charge and summing over the monomer positions in (21) will produce the term $g_0{}^{\mathrm{m}}(\mathbf{q})$. Hence, the monomer–charge structure factor can be written as

$$S^0{}_\sigma{}^{\mathrm{mc}}(\mathbf{q}) = p_\sigma{}^{\mathrm{c}}N_\sigma g_\sigma{}^{\mathrm{m}}(\mathbf{q})/\Omega^2 \equiv (1/\Omega)\rho_\sigma{}^{\mathrm{c}}g_\sigma{}^{\mathrm{m}}(\mathbf{q}) \quad (22)$$

**3.2. The Interactions. (a) Monomer–Monomer Interactions.** The interaction terms $V_{\sigma\tau}$ are given by eq 3; i.e., we use here explicitly

$$W_{\sigma\tau}{}^{\mathrm{ab}}(\mathbf{q}) = (\Omega/kT)\int \mathrm{d}^3R\ V_{\sigma\tau}{}^{\mathrm{ab}}(\mathbf{R})e^{i\mathbf{qR}} \quad (23)$$

where $\sigma$ and $\tau$ label the components, i.e. A and B, and a and b can be a monomer (m) or a charge (c). The monomer–monomer interactions are taken in the pseudopotential form since the short-range repulsion is a good approximation,[8] i.e.

$$V_{\sigma\tau}{}^{\mathrm{mm}}(\mathbf{R}) = u_{\sigma\tau} l^3 \delta(\mathbf{R}) \tag{24}$$

$l$ is the length of a Kuhn segment, so that $l^3$ is the volume of the statistical segment.

**(b) Charge–Charge Interactions.** We will treat charge interactions and not dipole interactions for reasons of mathematical simplicity. The bare interactions are Coulombic interactions; i.e., they are long-range and pseudopotential approximations cannot be used. The Coulombic potential is

$$V_{\sigma\tau}{}^{\mathrm{cc}}(\mathbf{R}) = \frac{Z_\sigma Z_\tau}{4\pi\epsilon_0}\frac{1}{R} \tag{25}$$

where $Z_\sigma = Z_{\mathrm{A}}$, $Z_{\mathrm{B}}$ are the charges on the A and B chains, respectively. $\epsilon_0$ is the vacuum dielectric constant. In $q$ space the Coulombic interaction is given by

$$W_{\sigma\tau}{}^{\mathrm{cc}}(\mathbf{q}) = \frac{Z_\sigma Z_\tau}{\epsilon_0}\frac{\Omega}{kT}(1/q^2) \tag{26}$$

It is convenient to define intrinsic lengths $\xi_\sigma$ by

$$\xi_\sigma{}^2 = \frac{\epsilon_0 kT}{Z_\sigma{}^2 \rho_\sigma{}^{\mathrm{c}}} \tag{27}$$

so that the electrostatic self-interactions for each chain can be written as

$$W_{\sigma\sigma}{}^{\mathrm{cc}} = (\Omega/\rho_\sigma{}^{\mathrm{c}})(q\xi_\sigma)^{-2} \tag{28}$$

If we neglect second-order effects, such as induced polarizations, higher order quantum effects, etc., we may assume that the charge–monomer interactions are of the same type as that given for the monomer–monomer interactions.

We are now in the position to use the general system of equations (9) in order to calculate the renormalized structure factors, which will lead to the stability conditions in $q$ space.

Finally let us mention that the case of ionomers can be treated in a similar way. We have to replace the Coulombic potential by the corresponding dipole–dipole interaction $\sim 1/R^2$. The Fourier transform of this potential does exist for large distances; i.e., in three dimensions it is $\sim 1/|\mathbf{q}|$. Since the range is finite, it can be cutoff at the range of interaction.

Using the structure factors defined by (16), (19), and (21) and the interaction potentials, we can write out the coupled system of equations (9) in matrix form as

$$\begin{bmatrix} 1 + S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} W_{\mathrm{AA}}{}^{\mathrm{mm}} & S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{AA}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{AB}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} W_{\mathrm{AB}}{}^{\mathrm{mm}} \\ S^0{}_{\mathrm{A}}{}^{\mathrm{mc}} W_{\mathrm{AA}}{}^{\mathrm{mm}} & 1 + S^0{}_{\mathrm{A}}{}^{\mathrm{cc}} W_{\mathrm{AA}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{A}}{}^{\mathrm{cc}} W_{\mathrm{AB}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{A}}{}^{\mathrm{cc}} W_{\mathrm{AB}}{}^{\mathrm{mm}} \\ S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{AB}}{}^{\mathrm{mm}} & S^0{}_{\mathrm{B}}{}^{\mathrm{cc}} W_{\mathrm{AB}}{}^{\mathrm{cc}} & 1 + S^0{}_{\mathrm{B}}{}^{\mathrm{cc}} W_{\mathrm{BB}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{BB}}{}^{\mathrm{mm}} \\ S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} W_{\mathrm{AB}}{}^{\mathrm{mm}} & S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{AB}}{}^{\mathrm{cc}} W_{\mathrm{AB}}{}^{\mathrm{cc}} & S^0{}_{\mathrm{B}}{}^{\mathrm{mc}} W_{\mathrm{BB}}{}^{\mathrm{cc}} & 1 + S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} W_{\mathrm{BB}}{}^{\mathrm{mm}} \end{bmatrix} \cdot$$

$$\begin{bmatrix} S_{\mathrm{AA}}{}^{\mathrm{mm}} \\ S_{\mathrm{AA}}{}^{\mathrm{cm}} \\ S_{\mathrm{AB}}{}^{\mathrm{cm}} \\ S_{\mathrm{AB}}{}^{\mathrm{mm}} \end{bmatrix} = \begin{bmatrix} S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} \\ S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} \\ 0 \\ 0 \end{bmatrix} \tag{29}$$

The problem of finding the density fluctuation $S_{\sigma\tau}{}^{\mathrm{ab}}$ is solved by the inversion of the 4 × 4 matrix in eq 29. In this paper we are primarily concerned with the stability of the charged blend, and this will be decided by the determinant of this matrix. If we symbolically represent the matrix as $(1 + \mathbf{S}^0\mathbf{W})$, then the stability limit is given by

$$\det\,(1 + \mathbf{S}^0\mathbf{W}) = 0 \tag{30}$$

We use (23) for the monomer interactions, so that from (22)

$$W_{\sigma\tau}(\mathbf{q}) = \Omega l^3 u_{\sigma\tau} \tag{31}$$

The evaluation of the determinant is tedious but straightforward and is simplified by writing

$$u_{\sigma\tau} = u_0 + \epsilon_{\sigma\tau} \tag{32}$$

and working in the limit $u_0 \gg \epsilon_{\sigma\tau}$ to ensure incompressibility. Without explicitly writing down the details, it is found that the coefficient of the $u_0{}^2$ term vanishes and hence the leading term in the determinant is of the order $u_0$. Again after some straightforward algebra the coefficient of the $u_0$ term can be written as

$$S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} + S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} - \Omega l^3 2\chi_{\mathrm{F}} S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} + W_{\mathrm{AB}}{}^{\mathrm{cc}} S^0{}_{\mathrm{B}}{}^{\mathrm{cm}} + \\ W_{\mathrm{AA}}{}^{\mathrm{cc}}\{X_{\mathrm{AB}} - \Omega l^3 2\chi_{\mathrm{F}} Y_{\mathrm{AB}}\} + W_{\mathrm{BB}}{}^{\mathrm{cc}}\{X_{\mathrm{BA}} - \Omega l^3 2\chi_{\mathrm{F}} Y_{\mathrm{BA}}\} \tag{33}$$

where

$$X_{\sigma\tau} = S^0{}_\sigma{}^{\mathrm{cc}}\{S^0{}_\sigma{}^{\mathrm{mm}} + S^0{}_\tau{}^{\mathrm{mm}}\} - (S^0{}_\sigma{}^{\mathrm{mc}})^2 \tag{34}$$

$$Y_{\sigma\tau} = S^0{}_\sigma{}^{\mathrm{mm}}\{S^0{}_\sigma{}^{\mathrm{mm}} + S^0{}_\tau{}^{\mathrm{cc}}\} - (S^0{}_\sigma{}^{\mathrm{mc}})^2$$

and

$$2\chi_{\mathrm{F}} = -(1/\Omega l^3) \lim_{u_0\to\infty} \{W_{\mathrm{AA}} W_{\mathrm{BB}} - W_{\mathrm{AB}}{}^2\}/W_{\mathrm{BB}} = \\ 1/kT\{2\epsilon_{\mathrm{AB}} - \epsilon_{\mathrm{AA}} - \epsilon_{\mathrm{BB}}\} \tag{35}$$

which is the usual expression for the Flory χ-parameter. If the charges are removed, i.e. $W_{\sigma\tau}{}^{\mathrm{cc}} = 0$, then the determinant (30) can be written as

$$\det\,(1 + S^0 W) = u_0(S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} + S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} - \Omega l^3 2\chi_{\mathrm{F}} S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} S^0{}_{\mathrm{B}}{}^{\mathrm{mm}}) \tag{36}$$

and the stability criterion becomes

$$\chi_0(\mathbf{q}) - \chi_{\mathrm{F}}(\mathbf{q}) > 0 \tag{36a}$$

where

$$\Omega l^3 \chi_0(\mathbf{q}) = 1/S^0{}_{\mathrm{A}}{}^{\mathrm{mm}} + 1/S^0{}_{\mathrm{B}}{}^{\mathrm{mm}} \tag{37}$$

Using the forms (17) for the structure factors, this is written as

$$\chi_0(\mathbf{q}) = 1/(\phi_{\mathrm{A}} g_{\mathrm{A}}{}^0) + 1/(\phi_{\mathrm{B}} g_{\mathrm{B}}{}^0) \tag{38}$$

where the $\phi$'s are the volume fractions of the two components. This is de Gennes celebrated result.[1]

We have chosen to rewrite the full result (33) in a similar form to (36a), i.e.

$$\chi_0{}^*(\mathbf{q}) - \chi_{\mathrm{F}}{}^*(\mathbf{q}) > 0 \tag{39}$$

where after some rearrangement of (33) we have

$$\chi_0{}^*(\mathbf{q}) = \chi_0\{1 + \Gamma(\mathbf{q})\} \tag{40}$$

$$\chi_{\mathrm{F}}{}^*(\mathbf{q}) = \chi_{\mathrm{F}}\{1 - \Delta(\mathbf{q})\}$$

The additional information concerning the structure of the charge distribution is in the functions Γ and Δ, which introduce a new $q$ dependence and are given by

$$\Gamma(\mathbf{q}) = \frac{g_{\mathrm{A}}{}^{\mathrm{c}}(\mathbf{q})}{(\mathbf{q}\xi_{\mathrm{A}})^2} + \frac{g_{\mathrm{B}}{}^{\mathrm{c}}(\mathbf{q})}{(\mathbf{q}\xi_{\mathrm{B}})^2} - \frac{\rho_{\mathrm{A}}{}^{\mathrm{c}}}{(\mathbf{q}\xi_{\mathrm{A}})^2}\frac{\{g_{\mathrm{A}}{}^{\mathrm{m}}(\mathbf{q}) - g_{\mathrm{B}}{}^{\mathrm{m}}(\mathbf{q})\}^2}{\rho_{\mathrm{A}}{}^{\mathrm{m}} g_{\mathrm{A}}{}^{\mathrm{m}}(\mathbf{q}) + \rho_{\mathrm{B}}{}^{\mathrm{m}} g_{\mathrm{B}}{}^{\mathrm{m}}(\mathbf{q})} \tag{41}$$

$$\Delta(\mathbf{q}) = \frac{g_{\mathrm{A}}^{\mathrm{c}}(\mathbf{q})}{(\mathbf{q}\xi_{\mathrm{A}})^2}\left\{\frac{g_{\mathrm{A}}^{\mathrm{m}}(\mathbf{q})}{g_{\mathrm{A}}^{\mathrm{c}}(\mathbf{q})}\frac{\rho_{\mathrm{A}}^{\mathrm{c}}}{\rho_{\mathrm{A}}^{\mathrm{m}}} - 1\right\} + \frac{g_{\mathrm{B}}^{\mathrm{c}}(\mathbf{q})}{(\mathbf{q}\xi_{\mathrm{B}})^2}\left\{\frac{g_{\mathrm{B}}^{\mathrm{m}}(\mathbf{q})}{g_{\mathrm{B}}^{\mathrm{c}}(\mathbf{q})}\frac{\rho_{\mathrm{B}}^{\mathrm{c}}}{\rho_{\mathrm{B}}^{\mathrm{m}}} - 1\right\} \tag{42}$$

where $\rho_\sigma^{\mathrm{c}}$ is the charge density, i.e. $\rho_\sigma^{\mathrm{c}} = N_\sigma p_\sigma^{\mathrm{c}}/\Omega$.

In deriving these results we have expressed the Coulombic interaction in terms of the screening length $\xi_{\mathrm{A,B}}$ defined in eq 27. This result is very general, since only the structure factors $g_\sigma^{\mathrm{m}}(\mathbf{q})$ and $g_\sigma^{\mathrm{c}}(\mathbf{q})$, the charge density $\rho_\sigma^{\mathrm{c}}$, and the monomer density $\rho_\sigma^{\mathrm{m}}$ of the chains enter into the final stability criterion. In the next section we discuss some simple applications of these results.

## 4. Applications

**4.1. Polyelectrolyte Blends.** If the charges are randomly distributed along the chains so that they can be described as a random walk of step lengths $l_{\mathrm{A}}^{\mathrm{c}}$ and $l_{\mathrm{B}}^{\mathrm{c}}$, then the charge structure factor $g_\sigma^{\mathrm{c}}(\mathbf{q})$ has a form similar to that of the monomer structure factor $g_\sigma^{\mathrm{m}}(\mathbf{q})$. With use of the approximate form (18), we have the structure factors

$$g_{\mathrm{A}}^{\mathrm{m}}(\mathbf{q}) = \frac{p_{\mathrm{A}}^{\mathrm{m}}}{1 + (ql_{\mathrm{A}}^{\mathrm{m}})^2 p_{\mathrm{A}}/12} \tag{43}$$

$$g_{\mathrm{A}}^{\mathrm{c}}(\mathbf{q}) = \frac{p_{\mathrm{A}}^{\mathrm{c}}}{1 + (ql_{\mathrm{A}}^{\mathrm{c}})^2 p_{\mathrm{A}}/12} \tag{44}$$

where $p_{\mathrm{A}}^{\mathrm{m}}$ and $p_{\mathrm{A}}^{\mathrm{c}}$ are the number of monomers and charges, respectively, per chain. Similar expressions hold for the B chain. Since the radius of gyration of the polymer is the same for both the charge and monomer distribution, i.e.

$$p_{\mathrm{A}}^{\mathrm{c}}(l_{\mathrm{A}}^{\mathrm{c}})^2 = p_{\mathrm{A}}^{\mathrm{m}}(l_{\mathrm{A}}^{\mathrm{m}})^2 \tag{45}$$

then

$$g_{\mathrm{A}}^{\mathrm{m}}/p_{\mathrm{A}}^{\mathrm{m}} = g_{\mathrm{A}}^{\mathrm{c}}/p_{\mathrm{A}}^{\mathrm{c}} \tag{46}$$

and the function $\Delta(q)$ given by eq (42) is identically zero ($\Delta \equiv 0$), so that the original Flory–Huggins parameter $\chi_{\mathrm{F}}$ is recovered. The enhancement of the stability of the blend is then entirely contained in the term $\chi_0{}^*$ via the function $\Gamma(\mathbf{q})$. For simplicity we treat only the case of symmetric polyelectrolytes, i.e.

$$g_{\mathrm{A}}^{\mathrm{m}} = g_{\mathrm{B}}^{\mathrm{m}} = g^{\mathrm{m}} \qquad p_{\mathrm{A}}^{\mathrm{m}} = p_{\mathrm{B}}^{\mathrm{m}} = p^{\mathrm{m}}$$

$$g_{\mathrm{A}}^{\mathrm{c}} = g_{\mathrm{B}}^{\mathrm{c}} = g^{\mathrm{c}} \qquad p_{\mathrm{A}}^{\mathrm{c}} = p_{\mathrm{B}}^{\mathrm{c}} = p^{\mathrm{c}} \tag{47}$$

We then find, using eqs 42 and 43

$$\Gamma(\mathbf{q}) = \frac{2g^{\mathrm{c}}(\mathbf{q})}{q^2\xi^2} \tag{48}$$

hence

$$\chi_0(q) = \frac{1}{\phi(1-\phi)}\left\{\frac{1}{g^{\mathrm{m}}(\mathbf{q})} + (p^{\mathrm{c}}/p^{\mathrm{m}})\frac{1}{(q\xi)^2}\right\} \tag{49}$$

and the stability criterion (38) becomes

$$\frac{1}{g^{\mathrm{m}}(\mathbf{q})} + (p^{\mathrm{c}}/p^{\mathrm{m}})\frac{1}{(q\xi)^2} > \phi(1-\phi)\chi_{\mathrm{F}} \tag{50}$$

We see that this is easy to satisfy, at least at small $q$, since the first term diverges. Indeed one needs $(q\xi)^2 > p$ to effect this criterion, and a critical $q$ is of the order of the inverse of the Kuhn step length, where (50) breaks down. Therefore polyelectrolyte blends are always compatible, down to length scales

$$q_0{}^{-1} = \xi\{(p^{\mathrm{m}}p^{\mathrm{c}})\phi(1-\phi)\chi_{\mathrm{F}}\}^{1/2} \tag{51}$$

Using (27) the $\xi$ together with $p^{\mathrm{c}} = p^{\mathrm{m}}$ and estimating $\rho^{\mathrm{m}}$ as $\rho^{\mathrm{m}}l^3 \sim 1$ give

$$\xi^2 = l^2\left(\frac{\epsilon_0 kTlp^{\mathrm{c}}}{Z^2p^{\mathrm{m}}}\right) \tag{52a}$$

Using $l = 10$ Å, a numerical estimate of the values for this critical length scale is given by

$$q_0{}^{-1} = 3.8 \times 10^{-2}l\{(p^{\mathrm{m}}p^{\mathrm{c}})(1-\phi)\phi\chi_{\mathrm{F}}\}^{1/2} \tag{52b}$$

This is less than the Kuhn length, and the blend is compatible on all relevant scales. This result is expected and is somehow trivial, since the strong Coulombic potential cannot be overcome by relatively weak thermodynamic forces. A more interesting case is when we have only a few charges along the chains. We start with the case in which we have only one charge on the chains.

**4.2. Polyelectrolytes and Salt: Debye–Hückel Polyelectrolytes.** In the presence of simple salt counterions the Coulombic interaction becomes screened and is replaced by the screened potential, i.e.

$$W_{\sigma\sigma}{}^{\mathrm{cc}} = (\Omega/\rho_\sigma^{\mathrm{c}})\xi^{-2}/(q^2 + \kappa^2) \tag{53}$$

where $\kappa^{-1}$ is the Debye–Hückel screening length. The only change in the stability criterion is then (see eq 50) the modification

$$\frac{1}{g^{\mathrm{m}}(\mathbf{q})} + (p^{\mathrm{c}}/p^{\mathrm{m}})\frac{1}{\xi^2(q^2+\kappa^2)} > \phi(1-\phi)\chi_{\mathrm{F}} \tag{54}$$

In the same approximations as above we find for the critical $q_0$ value

$$q_0{}^{-2} > \xi^2\frac{(p^{\mathrm{m}}/p^{\mathrm{c}})\phi(1-\phi)\chi_{\mathrm{F}}}{1 - \xi^2\kappa^2\{(p^{\mathrm{m}}/p^{\mathrm{c}})\phi(1-\phi)\chi_{\mathrm{F}}\}} \tag{55}$$

Since the range of $\kappa$ is given by $L^{-1} < \kappa\ l^{-1}$, the critical wave vector, and hence the microphase compatibility of the blend, can be shifted to any desired value by altering either the salt concentration ($\kappa$) or the monomer/charge ratio per chain ($p^{\mathrm{m}}/p^{\mathrm{c}}$).

**4.3. Special Case: One Charge per Chain.** The minimum amount of charges is only one charge per chain. This case can be worked out in a similar fashion. Let us again consider the symmetric case also. For one charge, the charge structure factors are trivial, i.e.

$$g_{\mathrm{A}}^{\mathrm{c}} = g_{\mathrm{B}}^{\mathrm{c}} = 1; \quad p_{\mathrm{A}}^{\mathrm{c}} = p_{\mathrm{B}}^{\mathrm{c}} = 1 \tag{56}$$

and the symmetric chain properties

$$g_{\mathrm{A}}^{\mathrm{m}} = g_{\mathrm{B}}^{\mathrm{m}} = g; \quad p_{\mathrm{A}}^{\mathrm{m}} = p_{\mathrm{A}}^{\mathrm{m}} = p \tag{57}$$

The stability criterion (39) becomes, using the approximate form (18) for the structure factors

$$\chi_0\left\{1 + \frac{2}{q^2\xi^2}\right\} - \chi_{\mathrm{F}}\left\{1 + \frac{l^2p}{6\xi^2(1 + q^2l^2p/12)}\right\} > 0 \tag{58a}$$

This can be rearranged as

$$\frac{\chi_0 - \chi_{\mathrm{F}}}{\chi_0}\left\{q^4 + 2q^2\left(\frac{1}{R^2} + \frac{1}{\xi^2}\right)\right\} > -\frac{4}{\xi^2R^2} \tag{58b}$$

For $\chi_{\mathrm{F}} \leq \chi_0$, the inequality is always satisfied for all $q$ and the system, as expected, is stable. However, when $\chi_{\mathrm{F}} > \chi_0$, the uncharged blend would phase separate, whereas with the presence of one charge per chain the stability criterion (58b) becomes

$$q^4 + 2q^2\left(\frac{1}{R^2} + \frac{1}{\xi^2}\right) > \frac{4}{\xi^2 R^2}\frac{\chi_0}{\chi_F - \chi_0} \tag{58c}$$

and compatibility can still be maintained on scales greater than $q_c^{-1}$, where $q_c$ satisfies (58c) as an equality. When the term $\chi_F - \chi_0$ is small, the $q^4$ term dominates and $q_c$ is given by

$$q_c^{-1} = (R\xi/2)^{1/2}\left\{\frac{\chi_F}{\chi_0} - 1\right\}^{1/4} \tag{59}$$

In other words the compatibility scale for $\chi_F > \chi_0$ is determined by the geometric mean of the Debye length $\xi$ and the radius of gyration $R$ of the polymer chains as well as the closeness to the original phase separation point at $\chi_0 = \chi_F$. The length scale $\xi$ is given by eq 27, and setting $R^2 = Nl^2/6$ gives

$$\xi = R(6\epsilon_0 kTl/Z^2)$$

Hence misciblility of incompatible polymers can be achieved with the addition of one charge $Z$ per chain on a spatial scale greater than

$$q_c^{-1} = R\left\{3\epsilon_0 kTl/(2Z^2)\left(\frac{\chi_F}{\chi_0} - 1\right)\right\}^{1/4} \tag{60}$$

For example, if we take a monomer length scale as $l = 10$ Å, $T = 300$ K, $Z = e = 1.6 \times 10^{-19}$ C, and $\chi_F = 1.1\chi_0$, then the compatibility scale is given as $q_c^{-1} \approx R/10$.

At larger values of the wave vector $q$, i.e. $q^2l^2p/12 \gg 1$, the stability criterion (58) becomes

$$\chi_0\left\{1 + \frac{2}{q^2\xi^2}\right\} - \chi_F\left\{1 + \frac{2}{q^2\xi^2}\right\} > 0 \tag{61}$$

i.e.

$$\chi_0 - \chi_F > 0 \tag{62}$$

which is the usual criterion for uncharged blends. In summary, for the case of one charge per chain it is possible for the blend to be unstable to density fluctuations on wavelength scales smaller than the size of the chain if $\chi_0 < \chi_F$. At the same time the system remains stable on larger scales.

The case of several charges per chain can be treated by the general formulas (40), (41), and (42) for the generalized $\chi^*$ values, i.e. $\chi_0^*$ and $\chi_F^*$. The simplest approach is to say that the charges are nearly equidistantly distributed along the chain. Therefore the charges along the chain can be described by a random walk with another step length $l_\sigma^c$, with $l_\sigma^c \gg l_\sigma^m$, but the same end to end distance as the chain. Thus the distance between the charges introduces a new length scale in the blend, which will be the relevant length scale for the micro phase separation. That means that above $l_\sigma^c$ the blend will be compatible whereas below $l_\sigma^c$ phase separation will take place.

## 5. Conclusion and Discussion

We have presented a mean field theory of charged polymer blends that is formally identical with a generalized A–B copolymer problem, where the species A and B consist of different units. The structure factors and interaction potentials between all the units must be specified, which in the mean field equations leads to four coupled linear equations. In this paper we considered, from the outset, some of these units as charged units and included the possibility of partial screening by additional small molecule counterions. The overall charge neutrality of the system and the charge product nature of the Coulombic potential lead to some simplifications. For a binary blend of homopolymers the usual Flory–Huggins criterion for the phase separation, i.e.

$$\chi_0 > \chi_F$$

is generalized to a $q$-dependent form

$$\chi_0^*(q) > \chi_F^*(q)$$

where the $q$ dependence comes from both the structure and the interactions. In the case of a continuous charge distribution on both species, i.e. polyelectrolytes of opposite charges, we showed that $\chi_F(q) \rightarrow \chi_F$ and that $\chi_0^*(q)$ is enhanced as $q^{-2}$ and compatibility is always ensured. The application of our result to the other extreme of just one charge or dipole per chain, i.e. ionomers, showed that both $\chi_F^*(q)$ and $\chi_0^*(q)$ were $q$ dependent and that if $\chi_0 < \chi_F$, then phase separation would take place on scales smaller than $q_c^{-1}$ determined by the geometric mean of the polymer chain size and the Debye screening length. For reasonable values of the parameters this size is less than the size of the chain. For scales greater than $q_c^{-1}$ the presence of a single charge per chain ensures compatibility for $\chi_F > \chi_0$. Thus the theory predicts a morphological parameter, i.e. the critical $q_c$ value, which gives a compatible length scale. More complicated charge distributions involved more complicated algebra, but the principle result would be the same as that given by the simple charge distributions chosen here.

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