Compatibility Enhancement and Microdomain Structuring in Weakly Charged Polyelectrolyte Mixtures

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ABSTRACT: The phase structure of a mixture of weakly charged polyelectrolytes in the presence of solvent, counterions, and low molecular salt is studied theoretically. The most important contribution to the free energy of this system is connected with the presence of charges and comes from the translational entropy of counterions and ions of low molecular salt. It is shown that the presence of even a small fraction of charges on the polymers leads in many cases to an essential increase of mixture compatibility. This theoretical prediction is confirmed experimentally. Compatibility enhancement is also achieved for the mixture of stiff and flexible macromolecules if one or both components carry some fraction of charged links. On the basis of a more detailed study of this system we conclude that although the region of macrophase separation in the presence of charged links diminishes, the remaining region of the phase diagram is divided into two parts: In one part we have a true molecular compatibility, while in the other part a microdomain structure is formed which is reminiscent of microdomain structures in melts of block copolymer. The physical reason for microdomain formation originates from the translational entropy of counterions and the impossibility of the violation of the condition of total electroneutrality of the system.

1. Introduction

It is well known that in polymer blends involving two polymer components, A and B, there is a strong tendency toward phase separation if the contact of monomeric links A-B is energetically unfavorable, i.e. if the Flory-Huggins interaction parameter[1]

$$\chi = \chi_{AB} - (\chi_{AA} + \chi_{BB})/2 \tag{1}$$

is positive. Even small positive values of χ are enough for a phase separation of a blend.[1-3] The problem of improvement of polymer blend compatibility has been extensively studied.[4-7] Recently it has been shown both theoretically and experimentally that the incorporation of a small fraction of charged links in the chain of one component (say A) enhances the compatibility very effectively.[8] This effect was shown to be quite general; it holds also for the mixtures of stiff and flexible polymers,[9] where the tendency toward phase separation is very pronounced.[10]

Further theoretical studies of polymer blends with one weakly charged component have led to the conclusion[11] that such systems under certain conditions exhibit microdomain structures of the type that is well known for block-copolymer systems (the so-called microphase separation).[12-15] The idea that for polyelectrolyte systems a microdomain structuring is possible was originally put forward by Borue and Erukhimovich,[16] who considered the behavior of weakly charged polyelectrolytes in poor solvents. Recently this phenomenon was studied theoretically for polyelectrolyte mixtures also in the papers of Joanny and Leibler[17] and Brereton and Viglis,[18] which appear independently of our paper.[11]

The present work is aimed primarily at further investigation of the phenomenon of microdomain structure formation in polyelectrolyte mixtures. We will generalize our previous consideration[11] for the case of a mixture of arbitrary number of polyelectrolyte components with a low molecular solvent. We will present the results of calculations both for the case of one charged and one neutral component (which was considered in somewhat different way in ref 11) and for the case of a mixture of two polymers which carry charges of different signs. The explicit consideration of solvent is especially important, because charged groups on polyelectrolyte normally dissociate in water solutions (or in solutions of other polar liquids). Otherwise only formation of ion pairs is possible and specific polyelectrolyte features are lost.

Before going to the original consideration we will briefly recall the main results of the papers[8,9] devoted to the effect of compatibility enhancement. Then we will formulate the model under study and develop the main theoretical formalism. Finally we will present the results obtained regarding the formation and properties of microdomain structures.

2. Compatibility Enhancement in the Mixtures of Weakly Charged Polyelectrolytes

The classical theory of compatibility in polymer blends can be outlined as follows. Let us consider a blend of two polymers A and B having the degrees of polymerization N_A and N_B. In the framework of Flory lattice model the free energy of this system can be written in the form[1,19]

$$\frac{F}{n_0 T} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \chi \Phi_A \Phi_B \tag{2}$$

where Φ_A and Φ_B are volume fractions of the components ($\Phi_A + \Phi_B = 1$), parameter χ is defined by eq 1, T is the temperature expressed in energetic units, and n_0 is the total number of lattice sites in the Flory model (i.e., $n_0 b^3$ is the volume of the system; b is the characteristic spacing of the lattice). By analyzing eq 2 it is possible to find the corresponding equation for spinodal curve:[19]

$$\chi = \frac{1}{2\Phi_A N_A} + \frac{1}{2(1 - \Phi_A)N_B} \tag{3}$$

The dependence $\chi(\Phi_A)$ given by eq 3 for $N_A = N_B = 10^3$ is shown in Figure 1 (curve a). The coordinates of a critical point χ^c and Φ_A^c are[19]

$$\chi^c = \frac{(N_A^{1/2} + N_B^{1/2})^2}{2N_A N_B} \qquad \Phi_A^c = \frac{N_B^{1/2}}{N_A^{1/2} + N_B^{1/2}} \tag{4}$$

From these relations it can be seen that, at $N_A \sim N_B \sim N$, $\chi_c \sim 2N^{-1} \ll 1$, i.e. for long chains ($N \gg 1$) even small values of χ lead to the uncompatibility of the components.

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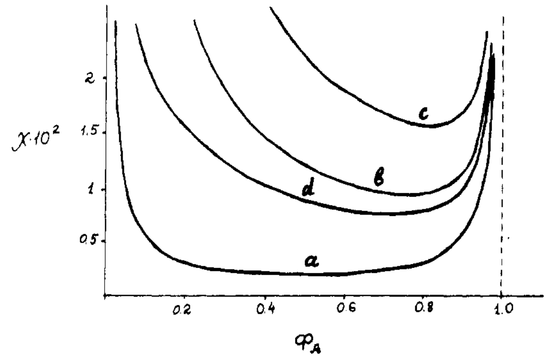

Figure 1. Spinodal curves for the mixture of polymers A and B for the case $N_A = N_B = 10^3$; $n_S = 0$; $f_B = 0$; and $f_A = 0$ (a), 0.01 (b), and 0.02 (c). The influence of the presence of low molecular salt is illustrated by the curve d ($n_S b^3 = 0.01$, $f_B = 0$, $f_A = 0.01$).

The reason for this trend toward phase separation is low values of mixing entropies for polymers. Since monomeric links are connected in the chain, the translational entropy loss due to the phase separation is N times smaller than for low molecular weight substances, while the gain in energy remains the same.

Suppose now that we have slightly modified the system by introducing a small fraction of charged links into the chains A (fN_A charges per chain, $f \ll 1$). Of course, links become charged as a result of dissociation, thus fN_A low molecular weight counterions per each A chain should be present in the system as well, because the system as a whole should be electrically neutral. The conditions for phase decomposition are now essentially modified, because in the case of the phase separation some entropy loss originates from each counterion. This should lead to a significant increase of mixing entropy, and—as a result—to the enhancement of miscibility.

It is not difficult to determine the magnitude of this effect. In the presence of charged links and counterions there are two additional contributions to the free energy arising from the translational entropy of counterions and from the electrostatic interactions. Analysis shows that the latter contribution for the system under consideration is always much smaller than the former. The contribution due to the translational entropy of counterions can be written in the form:

$$\frac{\Delta F}{n_0 T} = f\Phi_A \ln \Phi_A \tag{5}$$

Thus the expression for the free energy $F + \Delta F$ of a mixture of a slightly charged polymer chains A and neutral polymer chains B can be written as follows:

$$\frac{F + \Delta F}{n_0 T} = (1 + fN_A)\frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \chi \Phi_A \Phi_B \tag{6}$$

By comparing expressions 2 and 6 we see that they account for the presence of charges on the chains A from the thermodynamic point of view is equivalent to the renormalization:

$$N_A \rightarrow N_A^{\mathrm{eff}} \equiv N_A/(1 + fN_A) \tag{7}$$

i.e. to the $(1 + fN_A)$ times decrease of the chain length. Thus, the coordinates of the critical point can be determined from formulae 4 with the substitution of eq 7. For the case $N_A \sim N_B \sim N$, $1 \ll fN_A \ll N_A$ we obtain the estimates

$$\chi^c \sim f/2 \qquad 1 - \Phi_A^c \sim (fN)^{-1/2} \tag{8}$$

i.e. the critical point for phase separation shifts toward much higher values of χ in comparison with the mixture of neutral polymers. In Figure 1 phase-separation regions for a blend of neutral polymers with $N_A = N_B = 10^3$ and for the cases when each chain A carries 10 ($f = 0.01$) or 20 ($f = 0.02$) charges are shown. It can be seen that due to the presence of charges we have a very significant compatibility enhancement.

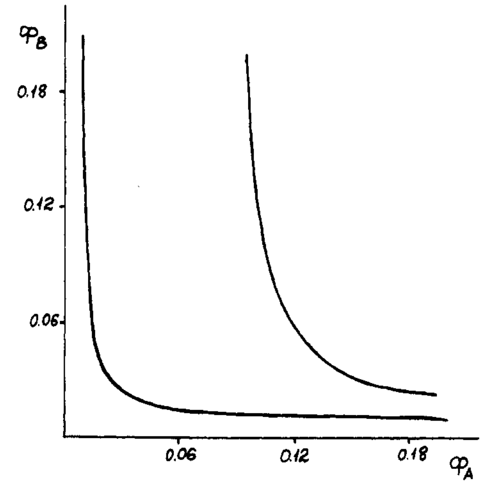

Figure 2. Spinodal curves for the salt-free ternary system: polymer A + polymer B + low molecular solvent S: $N_A = N_B = 10^3$, $\chi_{AB} = 0.05$; $\chi_{AS} = \chi_{BS} = 0$; $f_B = 0$; and $f_A = 0$ (a) and 0.01 (b).

This result was first obtained in ref 8. In refs 9 and 11 it was generalized in several respects.

In particular, in the paper by Nyrkova[11] the spinodal curve for phase separation was calculated in the presence of low molecular weight monovalent 1 – 1 salt of concentration n_s, which creates Debye–Hückel screening. It is to be expected from general considerations that the presence of salt makes the compatibility enhancement effect described above less pronounced. In fact, the spinodal curve for this case has the form (cf. eq 3)[11]

$$\chi = \frac{fN_A + 1}{2\Phi_A N_A} + \frac{1}{2(1 - \Phi_A)N_B} - \frac{fb^3 n_s}{\Phi_A(f\,\Phi_A + 2b^3 n_s)} \tag{9}$$

From eq 9 it can be seen that in the presence of some amount of salt the compatibility improvement effect is less essential than for the salt-free system (when $n_s = 0$) (Figure 1). However, up to the concentration $n_s b^3 \sim f^2 N_A$ (which is fN_A times larger than the characteristic concentration of counterions of the chains A) this effect remains quite substantial (vanishing at $n_s b^3 \sim f^2 N_A$).

Another generalization concerns the accounting for the presence of low molecular weight solvent, i.e. study of the ternary system polymer A + polymer B + solvent S. This has been done already in the paper by Vasilevskaya et al.[8] The spinodal curve equation obtained in ref 8 has the form

$$\left(\frac{fN_A + 1}{\Phi_A N_A} + \frac{1}{\Phi_S} - 2\chi_{AS}\right)\left(\frac{1}{\Phi_B N_B} + \frac{1}{\Phi_S} - 2\chi_{BS}\right) = \left(\frac{1}{\Phi_S} + \chi_{AB} - \chi_{AS} - \chi_{BS}\right)^2 \tag{10}$$

where Φ_S is the volume fraction of a solvent ($\Phi_A + \Phi_B + \Phi_S = 1$), and χ_{AB}, χ_{AS}, and χ_{BS} are the Flory–Huggins parameters of the interaction of corresponding components. In Figure 2 two spinodal curves for this system calculated according to eq 10 at constant values of χ-parameters are shown. It can be seen that for the present case the effect of compatibility enhancement still exists and is very important.

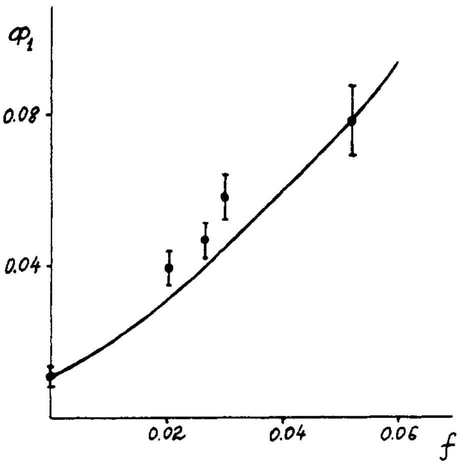

Figure 3. Theoretical (line) and experimental (points) results for spinodal decomposition in ternary system: polymer A + polymer B + low molecular solvent S ($\Phi_A = \Phi_B \equiv \Phi_1$). For explanations see the text of the paper.

To check the results described by eq 10 and Figure 2 some simple experiments were performed, and the results were reported in ref 8. The compatibility of the following system was studied: weakly protonated poly(vinylpyridine) (A)/poly(ethylene oxide) (B)/solvent (methanol–water mixture). The experiments were performed for the conditions, for which $\Phi_A = \Phi_B$. The volume fractions of both polymers in the solvent were gradually increased, and the moment of phase separation of the solution (at $\Phi_A = \Phi_B \equiv \Phi_1$) was registered. The dependence $\Phi_1(f)$ obtained in the experiments is shown in Figure 3 together with the corresponding theoretical curve calculated according to eq 10 for $\Phi_A = \Phi_B \equiv \Phi_1$, $N_A = 1700$, $N_B = 900$, $\chi_{AB} = 0.19$; $\chi_{AS} = \chi_{BS} = 0$ (the values of N_A and N_B were determined from the molecular weight data; the values of χ_{AS} and χ_{BS} were equated to zero because the solvent for both polymers is considered to be a good one; the value of χ_{AB} was used as a fitting parameter). It can be seen that the agreement between the above theory and experimental data is good, and it is reached at reasonable values of the parameters.

Data on similar experimental systems, in which one of the polymeric components is charged, can also be found in literature.[20,21] These data confirm the theory presented above.

The described effect of compatibility enhancement has a quite general character; it is valid not only for the mixtures of two flexible polymers, but also for the mixture of stiff-chain and flexible macromolecules. The corresponding generalization of the theory was performed in ref 9. In the next section we present a brief outline of the consideration of this paper.

3. Compatibility Enhancement for the Mixtures of Stiff and Flexible Polymers

Compatibility of rigid rodlike macromolecules and flexible coils was first studied by Flory and Abe.[10] Their main conclusion was that for such systems phase separation takes place even in the absence of energetic interactions between the species (i.e. even at $\chi = 0$), solely as a result of entropic loss connected with the arrangement of rigid rods surrounded by flexible coils. Stiff-chain macromolecules which demix from flexible coils usually form a nematic phase. The compatibility does not improve even if significant amounts of low molecular weight solvent is added to the system. In ref 10 it is also shown that as soon as phase separation takes place in this system it is practically complete: Flexible polymers usually do not penetrate in significant amounts into the nematic phase, and vice versa. This fact imposes serious limitations on the possibility of incorporation of flexible macromolecules in fibers made of stiff-chain polymers; this goal is of practical importance with respect to the modification of physicomechanical characteristics of such fibers. The method described above can be used for the solution of this problem as well.[9]

Indeed, suppose that we have an athermal ($\chi = 0$) blend of stiff and flexible macromolecules. For the theoretical description of this blend we will adopt the lattice model of Flory and Abe.[10] We will assume that flexible macromolecules can be represented as a random walk on a lattice composed of N_B units (each covering one lattice site); stiff macromolecules are freely jointed chains consisting of N_A rectilinear segments, each covering x_A lattice sites. Let us further assume that either stiff or flexible macromolecules carry charged links, one charge $+e$ per f^{-1} lattice sites covered by a macromolecule (i.e. f is still the fraction of charged links in corresponding chains). Then the number of low molecular weight counterions per each charged macromolecule that should be present in the blend in order to fulfill the total electroneutrality condition is $x_A N_A f$ for the case when stiff polymers are charged and $N_B f$ for the case when the charged links are carried by flexible macromolecules. For simplicity we will assume that all the ions are monovalent, i.e. their charge is $-e$; the self-volume of counterions will be neglected ($\Phi_A + \Phi_B = 1$, where Φ_A and Φ_B are volume fractions of stiff polymer A and flexible polymer B).

Following the method of papers by Flory and Abe[10,22] the free energy F of the system described placed on the lattice containing n_o sites can be written in the form

$$F = F_1 + F_2 + F_3 \qquad (11)$$

where F_1 is the free energy of the corresponding uncharged blend:

$$\frac{F_1}{n_o T} = \frac{\Phi_A}{N_A x_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B - [1 - \Phi_A(1 - y/x_A)] \ln [1 - \Phi_A(1 - y/x_A)] + \frac{\Phi_A}{x_A} [y - 1 - \ln (x_A y^2)] \qquad (12)$$

($y \geq 1$ is the Flory disorientation parameter, which characterizes the degree of orientational ordering of stiff segments;[10] in the isotropic phase $y \equiv x_A$), F_2 is the free energy contribution connected with the translational entropy of counterions:

$$\frac{F_2}{n_o T} = \Phi f \ln \Phi \qquad (13)$$

(In eq 13 $\Phi \equiv \Phi_A$ if stiff chains are charged, and $\Phi \equiv \Phi_B \equiv 1 - \Phi_A$ in the opposite case), F_3 is the free energy of electrostatic interactions, which can always be neglected for the case $f \ll 1$, as it was shown in detail in ref 9.

The expression for F_1 can be written in the form of eq 12 only if we neglect possible orientational ordering of flexible chains in the nematic phase. Although the corresponding effects can be quite substantial[23] they will not be considered in the present paper, because they do not change main conclusions to be formulated below. It should be noted also that in expression 12 some items of the type const × Φ_A, which are unessential for the phase-equilibria calculations, are omitted.

Further calculations with the eqs 11–13 are standard.[9] It is necessary to determine the equilibrium value of y corresponding to a given volume fraction Φ_A from the minimization of the expression in eq 12, then one must

Table I
Volume Fractions of Stiff Polymer Φ_A in Isotropic and Nematic Phases Coexisting at Equilibrium

	Φ_A^{is}	Φ_A^{an}
uncharged polymers	$\exp[N_A[3 \ln x_A - x_A]]$	$\exp(N_B(1 - \ln x_A))$
charged flexible polymer ($N_B^{eff} \sim 1/f$)	$\exp[N_A[3 \ln x_A - x_A]]$	$\exp((1 - \ln x_A)/f)$
charged stiff polymer ($N_A^{eff} \sim 1/(fx_A)$)	$\exp[[3 \ln x_A - x_A]/(x_A f)]$	$\exp(N_B(1 - \ln x_A))$

equate the chemical potentials and pressures in the isotropic and anisotropic phases and determine from this system of equations the region of phase separation $\Phi_A^{is} < \Phi < \Phi_A^{an}$ (Φ_A^{is} and Φ_A^{an} being the concentrations of the stiff component in the coexisting isotropic and anisotropic phases at the point of phase separation, respectively).

In the limits $x_A \gg 1$ and $N_B \gg 1$, the corresponding calculations can be performed analytically. Simple analysis shows that for this case in the whole region $y > 1$ the free energy decreases with the decrease in y. This means that in the liquid crystalline phase we should adopt the value $y \equiv 1$[22,24] (case of perfect orientational ordering).

In this case at $f = 0$ (i.e. in the absence of charges on the chains) it is possible to obtain:

$$\Phi_A^{is} \sim {x_A}^{3N_A} \exp(-x_A N_A(1 - \delta))$$

$$\delta \equiv {x_A}^{-1} + {N_A}^{-1} - (x_A N_A)^{-1}$$

$$1 - \Phi_A^{an} \sim {x_A}^{-N_B} \exp(N_B(1 - \delta)) \exp(-\Phi_A^{is}/x_A N_A) \qquad (14)$$

These are just analytical asymptotic results which follow from the equations obtained in ref 10 (in ref 10 only numerical solutions of these equations was considered).

Now we pass to the case when one of the components is charged ($f \neq 0$). Calculations show that for this case the boundaries of the phase separation region are still described by eqs 14 provided the following substitutions are performed in these equations:

$$N_B \rightarrow N_B^{eff} = \frac{N_B}{1 + fN_B} \quad \text{if flexible chains are charged}$$

$$N_A \rightarrow N_A^{eff} = \frac{N_A}{1 + fN_A x_A} \quad \text{if stiff chains are charged} \qquad (15)$$

It can be seen that charging the flexible component such that $f \gg N_B^{-1}$ leads to an increase of the value of $1 - \Phi_A^{an}$; at the same time the volume fraction Φ_A^{is} practically does not depend on f. If the charges are introduced in the stiff-chain polymer then at $f \gg (N_A x_A)^{-1}$ the value of Φ_A^{is} is considerably increased, while the variation of $1 - \Phi_A^{an}$ is weak. In all the cases charging one of the polymeric component induces the increase of its solubility in the bulk of the other component. These features can be seen, in particular, from Table I, where main exponential asymptotes for the expressions for Φ_A^{is} and $1 - \Phi_A^{an}$ are listed (under the condition that the values of x_A, N_A, $X_A N_A f$, N_B, $N_B f$, and f^{-1} are much larger than unity).

Of course standard numerical analysis of expressions 11–13 for the free energy is also possible. The results of this analysis are shown in Figure 4.[9] In Figure 4b we have plotted also some of the curves obtained with and without the effects of direct electrostatic interactions (using the formulae obtained in ref 9). It can be seen that accounting for these interactions normally leads only to small changes in the final results.

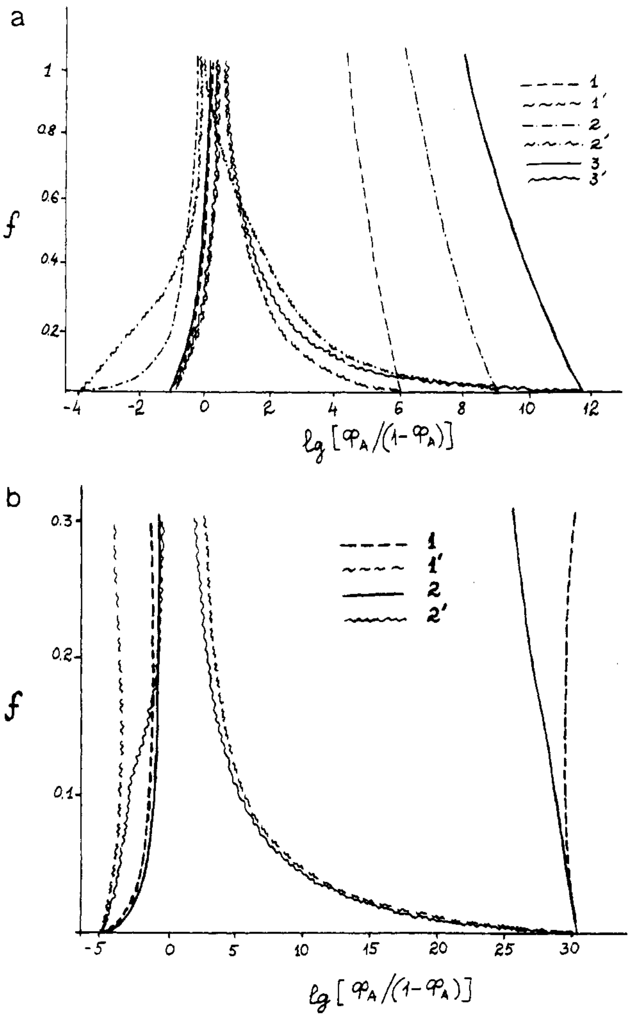

Figure 4. The dependences of volume fraction of stiff polymer Φ_A in isotropic (left lines) and nematic (right lines) phases coexisting at equilibrium on the fraction of charged links f: (a) Electrostatic interactions have been neglected (i.e. the term F_3 is omitted in the sum (eq 11)). $N_B = 10$, $x_A = 10$ (1,1′); $N_B = 10$, $x_A = 20$ (2,2′); $N_B = 20$, $x_A = 10$ (3,3′). For all curves $N_A = 1$. Either stiff chains A (1–3) or flexible chains B (1′–3′) carry electric charges. (b) Electrostatic interactions (F_3) are taken into account. $N_B = 50$, $x_A = 10$, $N_A = 5$ (1,1′); parameter $e^2/\epsilon Tb$ that characterize the intensity fo Coulomb interactions is assumed to be equal to unity (b is the size of lattice site in the Flory model). The curves (2,2′) correspond to the case $F_3 \equiv 0$. Either stiff chains A (1,2) or flexible chains B (1′,2′) carry electric charges.

Thus on the basis of the results presented above it can be concluded that in the mixtures of stiff and flexible macromolecules the introduction of a small fraction of charged monomeric links in one of the components enhances essentially the compatibility (which corresponds to a decrease of the width of the phase separation region $\Phi_A^{is} < \Phi < \Phi_A^{an}$). For the incorporation of some amount of flexible polymer chains into the nematic phase formed by a stiff-chain polymer (i.e. for the increase of the value of $1 - \Phi_A^{an}$) it is most suitable to introduce charges into the flexible macromolecules (see Figure 4 and Table I). On the other hand, if the problem is to obtain the isotropic melt of flexible chains with some small fraction of stiff-chain polymer, then it is necessary to introduce charged links into the stiff chains.

4. Microdomain Structures in Polyelectrolyte Systems

The Model and the Expression for the Free Energy. As already mentioned in the introduction, the idea that the formation of microdomain structures is possible for polyelectrolyte systems was first proposed in ref 16. In a previous paper,[11] we have studied in detail this phenomenon for the blend of two flexible polymers, one of which is sightly charged. It was shown that in this system under certain conditions the formation of microdomain structures is indeed possible. These structures are analogous to those which appear in block-copolymer melts or solutions, but the physical reason for their stability is completely different. In ref 11 the conditions of formation of microdomains and some of the properties of microdomain structures were obtained.

However, from the very beginning it was clear that in order to obtain theoretical predictions which would be useful for experimental studies the consideration of ref 11 should be generalized in two respects. First, it was shown that the effect of microdomain formation is mainly due to the translational entropy of counterions (as the effect of compatibility enhancement described above). Thus this effect can be observed only if the counterions are indeed mobile, i.e. if the true dissociation takes place. However, for the melts of low dielectric constant which were studied in ref 11 mobile charges are usually not encountered due to the formation of ion pairs. The effect of formation of microdomain structures should be more characteristic for polymer mixtures in the presence of highly polar low molecular weight solvent (e.g. water) than for polymer blends. Consequently, it is necessary to generalize the consideration of ref 11 in order to take into account the presence of solvent.

Second, formation of microdomain structures is characteristic not only for the mixture of a charged polymer and a neutral polymer. It is a much more general phenomenon which occurs in various mixtures of polyelectrolyte chains, mainly if both polycations and polyanions are present in the system. It is possible to develop the calculations of ref 11 for this general case.

The generalization of the theory of formation of microdomain structures in the two respects mentioned above is just the aim of the present paper.

Let us consider a mixture of several kinds of polymers (A,B,C,...) and of low molecular weight solvent S. Each of polymer components can be either slightly charged or neutral. Besides that, many small ions are present in the system including counterions which appear as a result of the dissociation of charged groups on polymer chains and ions of low molecular weight salt. Charged species interact by means of Coulomb interactions besides the usual van der Waals interactions between polymer links (or molecules of solvent) which are present as well. For the sake of simplicity we will neglect the self-volume of small ions; we will assume that these small ions interact with the links of polymer chains and solvent molecules only via Coulomb interactions (no energy of interaction of some other type) and that the dissociation of the charged links is complete.

To study the thermodynamic stability of the system with respect to the microphase separation it is necessary to write down its free energy F for an inhomogeneous state in which concentrations of all the components depend on spatial coordinates. In the framework of the lattice Flory–Huggins model in the self-consistent field approximation the expression for F can be written in the following form (cf. refs 11 and 16):

$$\begin{aligned} F/T = \int \mathrm{d}^3r \Biggl\{ & \sum_{\alpha} \frac{\Phi_\alpha}{N_\alpha b^3} \ln \Phi_\alpha + \frac{\Phi_S}{b^3} \ln \Phi_S + \\ & \frac{1}{b^3} \sum\sum_{\alpha<\beta} \chi_{\alpha\beta} \Phi_\alpha \Phi_\beta + \frac{1}{b^3} \sum_{\alpha} \chi_{\alpha S} \Phi_\alpha \Phi_S + \\ & \sum_{\alpha} \frac{l_\alpha^2}{6b^3} [\nabla (\Phi_\alpha(\vec{r}))^{1/2}]^2 + \sum_i n_i \ln n_i + \\ & \frac{1}{2\epsilon T} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \mathrm{d}^3r' \Biggr\} \end{aligned} \tag{16}$$

where $\Phi_\alpha(\vec{r})$ is the volume fraction of polymer component (α = A,B,C,...) at the point $\vec{r}$, $\Phi_S(\vec{r})$ is the volume fraction of the solvent ($\sum_\alpha \Phi_\alpha(\vec{r}) + \Phi_S(\vec{r}) = 1$), N_α is the number of links in the polymer α and l_α is the length of the Kuhn segment of this polymer, b^3 is the volume of elementary lattice site in the Flory model, $\chi_{\alpha\beta}$ are Flory–Huggins interaction parameters between polymer links of the type α and β, $\chi_{\alpha S}$ are polymer α/solvent interaction parameters. In eq 16 ϵ is the dielectric constant of the medium, $n_i(\vec{r})$ is the concentration of the small ions of type i at the point r, and $\rho(\vec{r})$ is the charge density at the point $\vec{r}$:

$$\rho(\vec{r}) = e[\sum_i Z_i n_i(\vec{r}) + b^{-3} \sum_\alpha Z_\alpha \Phi_\alpha(\vec{r}) f_\alpha] \tag{17}$$

where e is an elementary charge, f_α is the fraction of charged links in polymer chain of type α, Z_i and Z_α are valences of the ions of type i and of the charged links of polymer α, respectively. The integration in eq 16 is performed over the volume of the system.

The first two terms in the integrand of eq 16 represent the contributions to the energy from the translational motion entropies of polymer chains and solvent molecules respectively. The third and fourth terms describe the energy of nonelectrostatic interaction of components. The fifth term represents a specific polymeric contribution to the free energy which is connected with the entropy loss due to the inhomogeneous concentration profiles of polymer components (Lifshitz entropy—see refs 25 and 26). The sixth term is due to the translational entropies of small ions, and the seventh term describes the free energy of Coulomb interactions.

Expression 16 for the free energy of the inhomogeneous mixture involves several essential assumptions. First of all, this expression is written in the self-consistent field (SCF) approximation, i.e. the terms connected with fluctuation effects are omitted. The SCF approximation should not be very bad for concentrated systems considered in the present paper; in any case this is a necessary first step toward the understanding of the real situation.

Another assumption is connected with the form of the fifth term in the integrand of eq 16. The expression for this term is strictly valid only if the characteristic scale of inhomogeneities in the system k^{-1} is much larger than b and much smaller than $bN_\alpha^{1/2}$ (α = A,B,C,...).[26] The inequality $k^{-1} \geq b$ will be assumed below. Other restriction $k^{-1} \leq bN_\alpha^{1/2}$ is not important and will not be taken into account, because at $k^{-1} \geq bN_\alpha^{1/2}$ the fifth term in the integrand of eq 16 is anyway much smaller than the first two terms (see ref 11), so its explicit form is not very essential. Thus, eq 16 will be used for the whole region $k^{-1} \geq b$.

Finally, the electrostatic term can be written in the form of the last item in the integrand of eq 16 only if the following three conditions are fulfilled: (i) the dielectric constant ϵ does not depend on $\vec{r}$ (we will consider only conditions for spinodal decomposition, i.e. slightly inhomogeneous mixtures); (ii) $e^2/\epsilon T r_D \ll 1$, where r_D is Debye–Hückel screening radius—in this case the fluctuation part of electrostatic term can be neglected (see ref 11); (iii) polyelectrolytes are slightly charged ($f_\alpha \ll (b\epsilon T/e^2)^2$) and thus the electrostatic stiffening of the chains is absent.

The function $\Phi_\alpha(\vec{r})$ and $n_i(\vec{r})$ in eq 16 are not independent. They are connected because of the condition of electroneutrality of macroscopic regions. To write down this condition we introduce the following notation. If we have some function of spatial coordinates $\gamma(\vec{r})$ (this can be $\Phi_\alpha(\vec{r})$, $n_i(\vec{r})$, $\rho(\vec{r})$, etc.), let us denote

$$\bar{\gamma} = V^{-1}\int_V \gamma(\vec{r})\,\mathrm{d}^3r \qquad \tilde{\gamma}(\vec{r}) = \gamma(\vec{r}) - \bar{\gamma} \tag{18}$$

i.e. $\bar{\gamma}$ is the average value of $\gamma(\vec{r})$, V is the total volume of the system, and $\gamma(\vec{r})$ is the deviation from the average value $\tilde{\gamma}$. Then the electroneutrality condition can be written in the form

$$\bar{\rho} \equiv e\,[\sum_i Z_i \bar{n}_i + b^{-3}\sum_\alpha Z_\alpha \bar{\Phi}_\alpha f_\alpha] = 0 \tag{19}$$

(cf. eq 17).

5. Stability Conditions toward Spinodal Decomposition

In order to investigate the stability of the system described above toward spinodal decomposition it is necessary to determine whether the homogeneous-state functions $\Phi_\alpha(\vec{r}) = \bar{\Phi}_\alpha$, $n_i(\vec{r}) = \bar{n}_i$ correspond to the local minimum of the functional (eq 16). Only in this case will the homogeneous state be stable.

Thus, let us consider the functional (eq 16) for small deviations of the functions $\Phi_\alpha(\vec{r})$ and $n_i(\vec{r})$ from the average values $\bar{\Phi}_\alpha$ and $\bar{n}_i$ ($|\tilde{\Phi}_\alpha| \ll \bar{\Phi}_\alpha$; $|\tilde{n}_i| \ll \bar{n}_i$). The expansion of the free energy $F\,\{\Phi_\alpha(\vec{r}), n_i(\vec{r})\}$ up to the quadratic terms in $\tilde{\Phi}_\alpha$ and $\tilde{n}_i$ has the form:

$$\frac{F}{T} = \left(\frac{F}{T}\right)_{\text{const}} + \frac{1}{2b^3}\int\left\{\sum_\alpha \frac{\tilde{\Phi}_\alpha^2(\vec{r})}{\mathrm{N}_\alpha \bar{\Phi}_\alpha} + \sum_i \frac{b^3\tilde{n}_i^2(\vec{r})}{\bar{n}_i} + \frac{\tilde{\Phi}_\mathrm{S}^2(\vec{r})}{\bar{\Phi}_\mathrm{S}} + 2\sum\sum_{\alpha<\beta} \chi_{\alpha\beta}\tilde{\Phi}_\alpha\tilde{\Phi}_\beta + 2\sum_\alpha \chi_{\alpha\mathrm{s}}\tilde{\Phi}_\alpha\tilde{\Phi}_\mathrm{S} + \sum_\alpha \frac{l_\alpha^2\,(\nabla\tilde{\Phi}_\alpha)^2}{12\quad\bar{\Phi}_\alpha}\right\}\mathrm{d}^3r + \frac{1}{2\epsilon T}\int\int\frac{\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r}\,')\,\mathrm{d}^3r\,\mathrm{d}^3r'}{|\vec{r}-\vec{r}\,'|} \tag{20}$$

where $(F/T)_{\text{const}}$ is the value of (F/T) for $\{\Phi_\alpha(\vec{r}) \equiv \bar{\Phi}_\alpha, n_i(\vec{r}) \equiv n_i\}$.

Now let us perform Fourier transformation of the functions $\gamma(\vec{r}) \equiv \Phi_\alpha(\vec{r})$, $n_i(\vec{r})$ or $\rho(\vec{r})$, i.e. let us introduce the functions

$$\gamma(\vec{k}) = (2\pi)^{-3}\int_V \exp(-i\vec{k}\vec{r})\gamma(\vec{r})\,\mathrm{d}^3r \tag{21}$$

Then expansion 18 can be written in the form:

$$\frac{F}{T} = \left(\frac{F}{T}\right)_{\text{const}} + \frac{(2\pi)^3}{2b^3}\int\left\{\sum_\alpha\left[\frac{1}{\bar{\Phi}_\alpha N_\alpha} + \frac{l_\alpha^2k^2}{12\bar{\Phi}_\alpha}\right]\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\alpha(-\vec{k}) + \sum_i \frac{b^3\tilde{n}_i(\vec{k})\tilde{n}_i(-\vec{k})}{\bar{n}_i} + \frac{\tilde{\Phi}_\mathrm{S}(\vec{k})\tilde{\Phi}_\mathrm{S}(-\vec{k})}{\bar{\Phi}_\mathrm{S}} + 2\sum\sum_{\alpha<\beta}\chi_{\alpha\beta}\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\beta(-\vec{k}) + 2\sum_\alpha \chi_{\alpha\mathrm{S}}\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\mathrm{S}(-\vec{k}) + \frac{4\pi b^3}{\epsilon T}\frac{\tilde{\rho}(\vec{k})\tilde{\rho}(-\vec{k})}{k^2}\right\}\mathrm{d}^3k \tag{22}$$

where $k \equiv |\vec{k}|$.

As already mentioned, the functions $\Phi_\alpha(\vec{r})$ and $n_i(\vec{r})$ (and the functions $\Phi_\alpha(\vec{k})$ and $n_i(\vec{k})$ as well) are not independent. Their average values are connected by condition 19. There is also a correlation between the deviations from the average values $\tilde{\Phi}_\alpha(\vec{k})$ and $\tilde{n}_i(\vec{k})$, because small counterions should rearrange in space in accordance with the given spatial distribution of polymer components $\Phi_\alpha(\vec{r})$. In order to determine the latter correlation it is necessary to find the set of functions $\{\tilde{n}_i(\vec{k})\}$ which minimize functional 22 for an arbitrary set of given functions $\{\Phi_\alpha(\vec{r})\}$. Upon equating to zero the variational derivatives of expression 22 with respect to $\tilde{n}_i(\vec{k})$ we obtain

$$\tilde{n}_i(\vec{k}) = \left(-\frac{\tilde{Q}(\vec{k})}{e\,Z_i}\right)\frac{\varkappa_i^2}{k^2 + \varkappa^2} \tag{23}$$

where $\varkappa_i^2$ and $\varkappa^2$ are the values analogous to the classical Debye–Hückel screening parameter:

$$\varkappa_i^2 \equiv \frac{4\pi e^2}{\epsilon\,T}Z_i^2\bar{n}_i \qquad \varkappa^2 \equiv \sum_i \varkappa_i^2 \tag{24}$$

and $\tilde{Q}(\vec{k})$ is connected with the spatial distribution of charges of the polymer chain:

$$\tilde{Q}(\vec{k}) = \frac{e}{b^3}\sum_\alpha Z_\alpha f_\alpha \tilde{\Phi}_\alpha(\vec{k}) \tag{25}$$

Substituting eq 23 in functional 22 and using the equation $\Phi_\mathrm{S} = 1 - \sum_\alpha \Phi_\alpha$ we obtain

$$\frac{F}{T} = \left(\frac{F}{T}\right)_{\text{const}} + \frac{(2\pi)^3}{2b^3}\int\left\{\sum_\alpha\left[\frac{1}{\bar{\Phi}_\alpha N_\alpha} + \frac{l_\alpha^2k^2}{12\bar{\Phi}_\alpha}\right]\times \tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\alpha(-\vec{k}) + 2\sum\sum_{\alpha<\beta}\chi_{\alpha\beta}\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\beta(-\vec{k}) + 2\sum_\alpha \chi_{\alpha\mathrm{S}}\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\mathrm{S}(-\vec{k}) + \frac{1}{\bar{\Phi}_\mathrm{S}}\sum\sum_{\alpha,\beta}\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\beta(-\vec{k}) + \frac{4\pi b^3}{\epsilon\,T}\frac{\tilde{Q}(\vec{k})\tilde{Q}(-\vec{k})}{(k^2 + \varkappa^2)}\right\}\mathrm{d}^3k \tag{26}$$

It is easy to see that the integrand of eq 26 has the form

$$\sum_\alpha\sum_\beta A_{\alpha\beta}(\vec{k})\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\beta(-\vec{k}) \tag{27}$$

(see eq 25). A homogeneous state of a given system is stable if

$$\det\|A_{\alpha\beta}(\vec{k})\| \geq 0 \tag{28}$$

Thus the analysis of stability conditions can be reduced to the calculation of the determinant of the matrix $\mathbf{A}_{\alpha\beta}(\vec{k})$.

If for a given set of the parameters of the system the inequality 28 is violated for some values of the wave vector $\vec{k}$, the system becomes unstable and the spinodal decomposition begins. If eq 28 is violated for the first time at $k = 0$ we obtain the instability with respect to spinodal decomposition into macrophases. If the inequality 28 is fulfilled at $k = 0$ but is not valid at $k \neq 0$, the spinodal decomposition goes with the formation of microdomain structures of spatial size $\lambda = 2\pi/k_0$.

The results of the stability analysis are given in the next section. Before proceeding to these results it is worthwhile to make the following remark.

The fact that it is possible to convert the sum of two last terms in the integrand of eq 16 to the term $4\pi b^3Q(\vec{k})\cdot Q(-\vec{k})/\epsilon T(\vec{k}^2 + \varkappa^2)$ in the integrand of eq 26 means that instead of simultaneously accounting for both the translational entropy of small ions and direct electrostatic

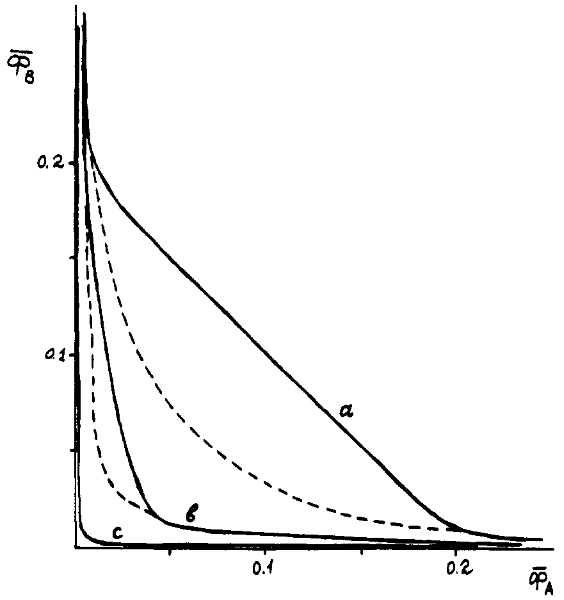

Figure 5. Spinodal curves for the salt-free ($n_S = 0$) mixture of polycation A and polyanion B in θ-solvent ($\chi_{AS} = \chi_{BS} = {}^1/_2$), $\chi_{AB} = 0.5$, $u \equiv e^2/\epsilon Tb = 1$, $N_A = N_B = 10^3$. Macrophase separation spinodals are drawn with solid lines, microphase ones with dotted lines. Linear charge densities of the chains are the following: $f_A = f_B = 0.1$ (a); $f_A = 0.1$, $f_B = 0$ (b); $f_A = f_B = 0$ (c).

interaction it is possible to write down from the very beginning the following "Debye–Hückel" contribution to the free energy:

$$\frac{1}{2\epsilon T}\int\int\frac{\tilde{Q}(\vec{r})\tilde{Q}(\vec{r}')}{|\vec{r}-\vec{r}'|}\exp[-\varkappa|\vec{r}-\vec{r}'|]\,\mathrm{d}^3r\,\mathrm{d}^3r' \qquad (29)$$

where

$$Q(\vec{r}) = \frac{\mathrm{e}}{b^3}\sum_\alpha Z_\alpha f_\alpha \Phi_\alpha(\vec{r}) \qquad (30)$$

This contribution describes not only direct Coulomb interactions but also the rearrangement of small ions at a given polymer density distribution $\{\tilde{\bar\Phi}_\alpha(\vec{r})\}$. It coincides with the well-known expression of the Debye–Hückel theory.[27] Thus the derivation above shows, in particular, that this expression can be used for the general case—the limitation that the number of salt ions should be much larger than the number of counterions is unnecessary. (The value of $\varkappa$ is given by eq 24 which includes the summation over all kinds of small ions—both salt ions and counterions). It is possible to conclude that in the expression for the free energy (eq 16) we have performed the unification of two theoretical approaches, one of which is usually used for salt-free polyelectrolyte solutions (accounting for translational entropy of counterions and for the condition of electroneutrality of macrophases[8]) and another one which is commonly applied for the case of salt dominance (classical Debye–Hückel theory[27]).

6. Spinodals for Macro- and Microphase Separation in Polyelectrolyte Mixtures

We will present the results of the stability analysis of functional 26 vs macro- and microphase separation for the most interesting specific case.

Let us consider a ternary system polymer A + B + solvent S, where polymer A is a weakly charged polycation ($Z_A > 0$ and $f_A \ll 1$) and polymer B is a weakly charged polyanion ($Z_B < 0$ and $f_B \ll 1$). Let us assume further that the valences of all the charges (on chains and in the solvent) are equal to unity ($|Z_A| = |Z_B| = |Z_i| = 1$). For this case the functional 26 can be written in the form

$$\begin{aligned}\frac{F}{T} = \left(\frac{F}{T}\right)_{\text{const}} + \frac{(2\pi)^3}{2b^3}\int\Bigg\{\sum_{\alpha=\mathrm{A,B}}\Bigg[\frac{1}{\bar\Phi_\alpha}\left(\frac{1}{N_\alpha}+\frac{l_\alpha^2k^2}{12}\right) + {}&\\ \frac{1}{\bar\Phi_S} - 2\chi_{\alpha S}\Bigg]\tilde{\Phi}_\alpha(\vec{k})\tilde{\Phi}_\alpha(-\vec{k}) + {}&\\ \left[2\chi_{AB} + \frac{2}{\bar\Phi_S} - 2\chi_{AS} - 2\chi_{BS}\right]\tilde{\Phi}_A(\vec{k})\tilde{\Phi}_B(-\vec{k}) + {}&\\ \frac{4\pi e^2}{\epsilon Tb^3}\frac{[\tilde{\Phi}_A(\vec{k})f_A - \tilde{\Phi}_B(\vec{k})f_B][\tilde{\Phi}_A(-\vec{k})f_A - \tilde{\Phi}_B(-\vec{k})f_B]}{k^2+\varkappa^2}\Bigg\}\mathrm{d}^3k&\end{aligned} \qquad (31)$$

and the stability condition is

$$\begin{aligned}&\left[\frac{1}{\bar\Phi_A}\left(\frac{1}{N_A}+\frac{l_A^2k^2}{12}\right) + \frac{1}{\bar\Phi_S} - 2\chi_{AS} + \frac{4\pi u f_A^2}{b^2(k^2+\varkappa^2)}\right]\times\\ &\left[\frac{1}{\bar\Phi_B}\left(\frac{1}{N_B}+\frac{l_B^2k^2}{12}\right) + \frac{1}{\bar\Phi_S} - 2\chi_{BS} + \frac{4\pi u f_B^2}{b^2(k^2+\varkappa^2)}\right] -\\ &\left[\frac{-4\pi u f_A f_B}{b^2(k^2+\varkappa^2)} + \chi_{AB} + \frac{1}{\bar\Phi_S} - \chi_{AS} - \chi_{BS}\right]^2 \geq 0\end{aligned} \qquad (32)$$

where we have introduced a standard notation

$$u = e^2/\epsilon bT \qquad (33)$$

(for water solution the dimensionless parameter u is usually of the order of unity—see ref 11). In eq 32 the expression for the Debye–Hückel screening parameter $\varkappa$ is (cf. eq 24)

$$b^2\varkappa^2 = 4\pi u(2n_S b^3 + \bar\Phi_A f_A + \bar\Phi_B f_B) \qquad (34)$$

For the sake of simplicity we will present below the results for the solutions of inequality 32 for the case of equal persistent lengths of both components: $l_A = l_B = l$. Moreover, we will assume that both components are flexible and that $l = b$, so for this case we have single microscopic scale, b, in the problem. The generalization for the case $l_1 \neq l_2 \neq b$ is not difficult and does not lead to any new qualitative effects.

After this simplification the following essential parameters remain in expression 32:

$$N_A, N_B, \chi_{AB}, \chi_{AS}, \chi_{BS}, f_A, f_B, u, n_S b^3$$

The diagrams presented below are calculated for the case

$$\chi_{AS} = \chi_{BS} = {}^1/_2$$

(i.e. the solvent corresponds to θ conditions for both components) and $N_A = N_B = 10^3$. We also introduce the notation $\psi_A \equiv \bar\Phi_A/(\bar\Phi_A + \bar\Phi_B)$ for the fraction component A in the A–B mixture.

In Figure 5 the spinodal curves for macrophase (solid lines) and microphase (dotted lines) separation are shown for salt-free solutions ($n_S = 0$), for $\chi_{AB} = 0.5$ and $u = 1$. In the area above the solid lines spinodal decomposition into macrophases takes place, i.e. the inequality 32 is violated at $k = 0$; between the solid and dotted lines spinodal decomposition goes with the formation microdomain structures (i.e. inequality 32 is violated at $k \neq 0$); and the area below these lines is the stability region of a homogeneous phase. The curves in Figure 5 are drawn for the following cases: (a) $f_A = f_B = 0.1$ (mixture of polycation and polyanions with 10% of charged links); (b) $f_A = 0.1$, $f_B = 0$ (mixture of a polyanion and a neutral polymer); and

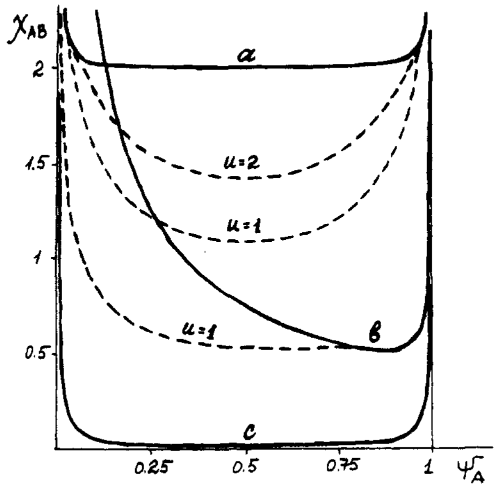

Figure 6. Spinodal curves for the polymer mixture A + B in θ-solvent for the following: $f_A = f_B = 0.1$ (a), $f_A = 0.1, f_B = 0$ (b), $f_A = f_B = 0$ (c), $\psi_A \equiv \bar{\Phi}_A/(\bar{\Phi}_A + \bar{\Phi}_B)$. The values of the parameter u are indicated near the corresponding lines. $\bar{\Phi}_S = 90\%$; $n_S = 0$; $\chi_{AS} = \chi_{BS} = 1/2$; $N_A = N_B = 10^3$.

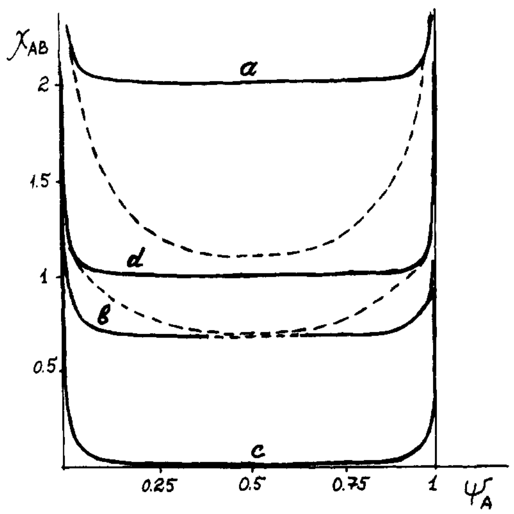

Figure 7. Spinodal curves for the polymer mixture A + B in θ-solvent for the following: $f_A = f_B = 0.1$, $n_S b^3 = 0$ (a); $f_A = f_B = 0.1$, $n_S b^3 = 0.01$ (b); $f_A = f_B = 0$ (c); $\bar{\Phi}_S = 90\%$ (a–c); and $f_A = f_B = 0.1$, $n_S b^3 = 0$, $\bar{\Phi}_S = 80\%$ (d). $u \equiv e^2/\epsilon T b = 1$; $N_A = N_B = 10^3$.

(c) $f_A = f_B = 0$ (mixture of two neutral polymers), in the latter case the region of microphase separation is absent.

Microphase separation phenomena clearly play a significant role in the behavior of the blends under consideration. Further figures are drawn to illustrate the dependences of main characteristics connected with microphase separation on the parameters of the mixture.

Figures 6 and 7 show the dependences of critical Flory–Huggins parameter χ_{AB} of the spinodals on the fraction ψ_A of the polymer component A in the mixture at a constant total polymer concentration. Figure 6 illustrates the influence of the number of charges in the chains and of the value of parameter u on the spinodals. Figure 7 deals with the influence of the total polymer concentration ($\bar{\Phi}_S$ = 90% or 80%) and of the concentrations of additional low molecular salts on the phase diagram.

The dotted lines in Figures 5–7 represent the points for which the expression 32 is valid for all values of k except $k \neq k_0$. For $k = k_0$ this expression is equal to 0. The value of k_0^{-1} characterizes the spatial scale of microdomain structure which appears as a result of spinodal decomposition. The dependence $k_0^2 b^2(\psi_A)$ along the dotted lines in Figures 6 and 7 is shown in Figures 8 and 9. It can be seen that normally

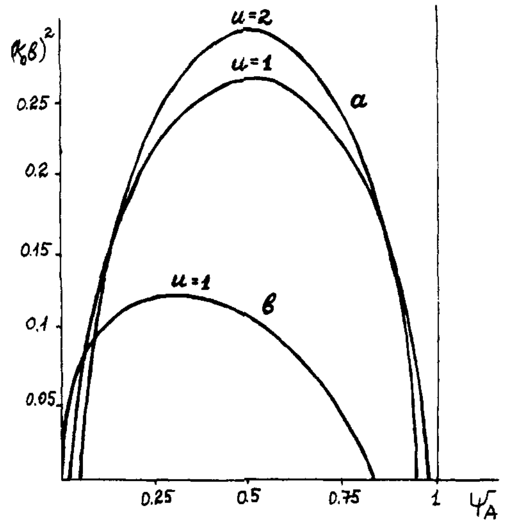

Figure 8. The dependences of characteristics wave vector k_0 on the composition of polymer mixture at the spinodals of microphase separation (dotted lines in Figure 6) for the following: $f_A = f_B = 0.1$ (a); $f_A = 0.1, f_B = 0$ (b); and $\psi_A \equiv \bar{\Phi}_A/(\bar{\Phi}_A + \bar{\Phi}_B)$. The values of the parameter u are indicated near the corresponding lines. $\bar{\Phi}_S = 90\%$; $n_S = 0$; $\chi_{AS} = \chi_{BS} = 1/2$; $N_A = N_B = 10^3$.

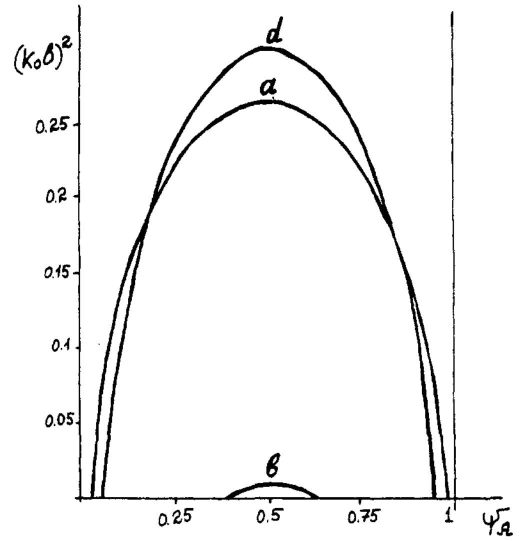

Figure 9. The dependences of characteristics wave vector k_0 on the composition of polymer mixture at the spinodals of microphase separation (dotted lines in Figure 7): $f_A = f_B = 0.1$, $n_S b^3 = 0$ (a); $f_A = f_B = 0.1$, $n_S b^3 = 0.01$ (b); $\bar{\Phi}_S = 90\%$ (a–b); and $f_A = f_B = 0.1$, $n_S b^3 = 0$, $\bar{\Phi}_S = 80\%$ (d). $u \equiv e^2/\epsilon T b = 1$; $\chi_{AS} = \chi_{BS} = 1/2$; $N_A = N_B = 10^3$.

$$k_0^2 b^2 \sim 0.1\text{–}0.3$$

which corresponds to spatial scale of microdomain structure, $\lambda = 2\pi/k_0$, equal to several times the microscopic scale, b (this means $\lambda \sim$ 30–50 Å, thus the best method to determine microdomains might be X-ray scattering). However, near the point of intersection of dotted and solid lines $k_0 \rightarrow 0$, thus the spatial scale of microdomain structure can be very large and it is possible to detect this structure in light-scattering experiments.

By comparing the position of the solid lines in Figure 6 it is possible to conclude that the incorporation of charged links in one or both polymer components leads to an increase in the stability region of the homogeneous phase, in full accord with section 2 of the present paper. At the same time it can be seen that, in a broad region of the $\chi_{AB} - \psi_A$ diagram, a microphase separation takes place. Thus

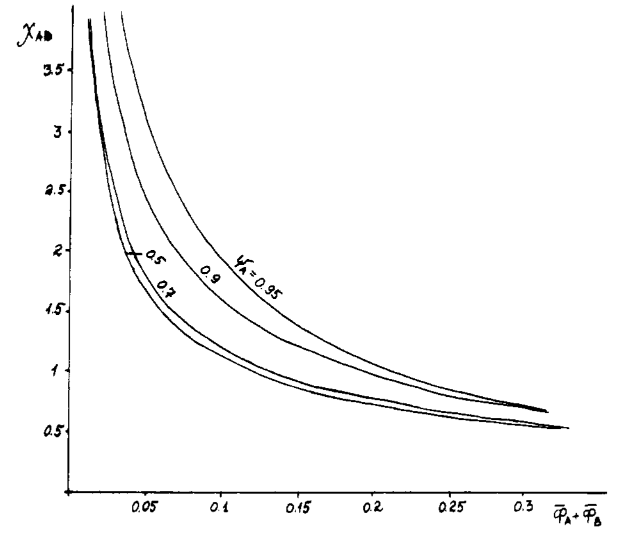

Figure 10. The dependences of the critical value of χ_{AB} at which macro- or microphase separation begins on the dilution of polymer A + B mixture at constant polymer composition (the values of the parameter $\psi_A \equiv \bar{\Phi}_A/(\bar{\Phi}_A + \bar{\Phi}_B)$ are written near the corresponding lines): $f_A = f_B = 0.1$, $n_S = 0$, $\chi_{AS} = \chi_{BS} = {}^1/_2$, $u \equiv e^2/\epsilon Tb = 1$, $N_A = N_B = 10^3$.

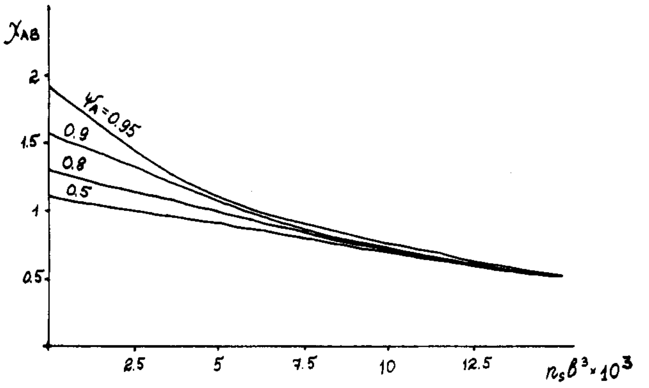

Figure 11. The dependences of spinodals χ_{AB} on the concentration of additional low molecular salt, $n_S b^3$. The values of the parameter $\psi_A \equiv \bar{\Phi}_A/(\bar{\Phi}_A + \bar{\Phi}_B)$ are written near the corresponding lines: $f_A = f_B = 0.1$, $\Phi_S = 90\%$, $\chi_{AS} = \chi_{BS} = {}^1/_2$, $u \equiv e^2/\epsilon Tb = 1$, $N_A = N_B = 10^3$.

the results of ref 11 remain valid for the case of dilute solutions when a large fraction of solvent is present in addition to two polymer components. Moreover, the examination of Figure 7 shows that the region of microdomain structures becomes relatively broader when the polymer volume fractions ($\bar{\Phi}_A + \bar{\Phi}_B$) decrease. At the same time the microdomain scale k_0^{-1} slightly increases with polymer dilution (Figure 9).

Figure 6 also shows that the increase in u (i.e. the decrease of polarity of the solvent) leads to the diminishing of the region of microphase separation. The addition of low molecular salt (Figures 7 and 9) suppresses both the formation of microdomain structures and the effect of compatibility enhancement (cf. eq 9).

Spinodal decomposition curves in other variables are shown in Figure 10. Here we consider a salt-free ($n_S = 0$) solution of polycations and polyanions ($f_A = f_B = 0.1$) with $u = 1$. We fix different compositions of mixture ψ_A and examine the value of χ_{AB} at which micro- or macrophase separation takes place. Thus Figure 10 illustrates the influence of dilution of polymer mixture on the effect under consideration.

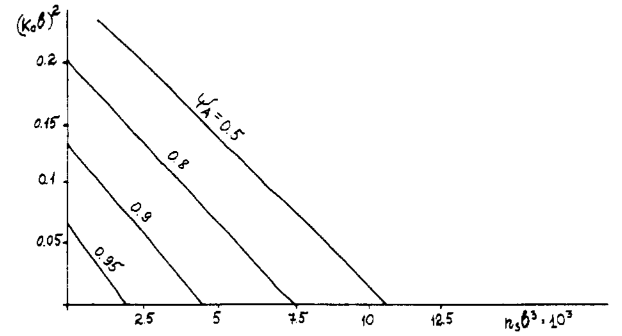

Figure 12. The dependences of the critical wave vector k_0 (which corresponds to the spinodals of microphase separation) on the concentration of additional low molecular salt, $n_S b^3$. The values of the parameter $\psi_A \equiv \bar{\Phi}_A/(\bar{\Phi}_A + \bar{\Phi}_B)$ are written near the corresponding lines: $f_A = f_B = 0.1$, $\Phi_S = 90\%$, $\chi_{AS} = \chi_{BS} = {}^1/_2$, $u \equiv e^2/\epsilon Tb = 1$, $N_A = N_B = 10^3$.

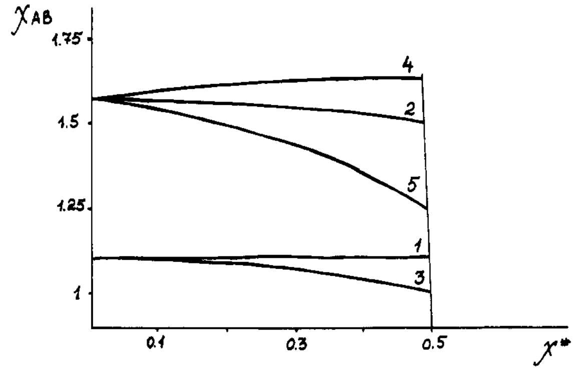

Figure 13. The dependences of spinodals χ_{AB} on the quality of the solvent, χ_{AS} and χ_{BS}: $f_A = f_B = 0.1$, $\Phi_S = 90\%$, $n_S b^3 = 0$, $u \equiv e^2/\epsilon Tb = 1$, $N_A = N_B = 10^3$. For the curves 1 and 2, $\chi^* \equiv \chi_{AS} = \chi_{BS}$, $\psi_A = 0.5$ (1), and $\psi_A = 0.9$ (2). For the curves 3–5, $\chi^* \equiv \chi_{AS}$, $\chi_{BS} = {}^1/_2$, $\psi_A = 0.5$ (3), $\psi_A = 0.1$ (4), and $\psi_A = 0.9$ (5).

Curves in Figures 11 and 12, which are calculated for $f_A = f_B = 0.1$, $u = 1$, and $\Phi_A + \Phi_B = 0.1$, illustrate the influence of low molecular salt on spinodal decomposition curves and characteristic spatial periods of microdomain structures. It can be seen that as the value of $n_S b^3$ is increased, the critical value of χ_{AB} diminishes (i.e. the effect of compatibility enhancement becomes less pronounced—c.f. section 2) and the characteristic scale of microphase separation k_0^{-1} becomes larger.

Figure 13 shows the dependence of spinodal decomposition curves on the quality of the solvent with respect to polymers A and B. For the calculation of curves in these figure we abandon the assumption $\chi_{AS} = \chi_{BS} = {}^1/_2$ and study the dependence on these values of χ-parameters (in a good-solvent interval $0 \leq \chi \leq 0.5$). The main conclusion which can be drawn from Figure 13 (and the corresponding dependence of $(k_0 b)^2$ on χ^*) is that if for both polymers the solvent is reasonably good ($0 \leq \chi \leq 0.5$) the dependence of the effects under consideration on the value of parameters χ_{AS} and χ_{BS} is not very pronounced.

7. Conclusion

It is possible to conclude that in the solutions of immiscible weakly charged polyelectrolytes the spinodal decomposition in many cases takes place with the formation of microdomain structures. The physical reason for this effect is analogous to the cause of the compatibility enhancement effect discussed above. Phase separation with the formation of macroscopic phases is relatively less advantageous due to the translational entropy loss of counterions. At the same time, when microdomain structures are formed the translational entropy loss is small, whereas gain in the contact energy due to the increase of A–A and B–B contact is rather significant.

Microdomain structures can appear not only in the process of spinodal decomposition, but in the equilibrium state as well. In principle, even if the spinodal decomposition takes place with the formation of microdomain structures, these structures can disappear in the final state and usual macroscopic phases can be formed. On the other hand, by analogies with block-copolymer systems it is possible to expect that sometimes the formation of equilibrium lamellar, cylindrical, or spherical microstructures is possible. The fact that such structures really appear in the phase diagrams follows, for example, from the form of spinodal curves shown in Figures 6 and 7: The critical curve for the phase separation into macrophases corresponds to the value of χ_{AB} higher than the χ_{AB}-values at which the mixture is unstable with respect to microphase separation. Thus these latter values are outside the binodal for macrophase separation. In order to obtain the region of equilibrium stability of microdomain structures in the phase diagrams it is necessary to calculate not only spinodal curves, but also phase equilibria curves between structures with different morphologies. This will be the topic of future publications.

It is worthwhile to note also that even for the cases when the equilibrium state corresponds to phase separation between two macroscopically homogeneous phases, the structure appearing in the course of spinodal decomposition can be fixed by rapid cooling with simultaneous glass transition or by rapid cross-linking of polymer chains.

It is important to emphasize that the microstructures appearing in polyelectrolyte mixtures are not completely analogous to that which are formed in the solutions or melts of block-copolymers. In the latter case the interface between two different microregions should be enriched by the junction points between blocks. For the polyelectrolyte case this is not the case since there is no covalent junction between the chains A and B. The characteristic scale of the microstructure for polyelectrolyte mixtures is normally somewhat lower than for block copolymers (see Figures 8, 9, and 12). Finally, for polyelectrolyte systems there are several new parameters (concentration of low molecular salt, pH of the solution, etc.) which are absent for block-copolymer systems. This gives new possibilities for the variation of type and main properties of microdomain structures.

Experimental observation of microdomain structures predicted in the present paper can open the way to the creation of new types of polymeric materials with controlled microstructure.

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