ON THE STATIC SCATTERING FROM TERNARY MIXTURES OF TWO WEAKLY CHARGED LINEAR HOMOPOLYMERS AND THE CORRESPONDING DIBLOCK COPOLYMER

DIFFUSION STATIQUE PAR DES MELANGES TERNAIRES D'HOMOPOLYMERES LINEAIRES FAIBLEMENT CHARGES ET DU COPOLYMERE BISEQUENCE CORRESPONDANT

A. BENSAFI[1], M. BENHAMOU[2], L. BOUZINA[1], S. KHALDI[1], A. BOUSSAID[1]

[a]Université Abou Bekr Belkaid, Faculté des Sciences, Départements de Chimie et de Physique

Bel Horizon, B.P 119, 13000 Tlemcen, Algérie.

E-mail: aeh_bensafi@mail.univ-tlemcen.dz

[c]Laboratoire de Physique des Polymères et Phénomènes Critiques,

Département de Physique, Faculté des Sciences Ben M'Sik, Université Hassan II, Casablanca, Maroc.

RESUME

Il y a plus d'une décennie, Hashimoto et ses collaborateurs étudiaient, pour la première fois, le comportement de phases de mélanges ternaires, formés de deux homopolymères linéaires neutres et du copolymère biséquencé correspondant. Quelques années plus tard, *Benmouna et coll.* ont élargi cette étude à des systèmes similaires composés de chaînes cycliques. Ces auteurs ont mis en évidence que l'effet combiné des transitions de séparations macrophase and microphase dépend non seulement de la concentration en copolymère mais aussi fortement de son architecture. D'autre part, les mélanges, contenant un copolymère cyclique, se caractérisent par une compatibilité bien supérieure à celle observée par *Hashimoto et al.* dans le cas où toutes les chaînes sont linéaires. L'objet de cet article consiste principalement en une analyse du comportement de phases quand les chaînes sont placées totalement ou partiellement dans diverses conditions de distribution de charge et à comparer nos résultats à ceux rapportés par Hashimoto et coll.

ABSTRACT

More a decade ago, Hashimoto and co-workers have first investigated the phase behavior of ternary mixtures made of two neutral linear homopolymers A/B and the corresponding diblock copolymer. A few years later, this study has been extended by *Benmouna et al.* to similar systems composed of cyclic chains. These authors have found that, depending on the concentration of copolymer, the interplay between macrophase and microphase separation transitions can take place. In the other hand, mixtures made of cyclic copolymers exhibit a compatibility enhancement towards phase separation. The main purpose of this paper is to examine how the phase behavior changes when chains are placed totally or partially in various conditions of charge distribution and compare our results to those reported by *Hashimoto et al.*

1. INTRODUCTION

Over the last two decades, the static scattering properties of multi-component polymeric mixtures were the subject of a great deal of attention from the theoretical front as well as the experimental one (*de Gennes*, 1979, *Higgins and Benoît*, 1994). However, only polymers blends and diblock copolymers have received sufficiently attention from the polymer scientists due probably to their simplicity and their importance in the processing of new materials with high performance and specific applications. On this account, Hashimoto and coll. (*Ijichi and Hashimoto*, 1988, *Tanaka and Hashimoto*, 1988) reported a study of the scattering properties and the phase behavior of ternary mixtures made of neutral linear diblock copolymers and parent homopolymers at various compositions.

These authors emphasized that, in the case of the pure linear diblock copolymer A-B, a microphase separation occurs as soon as the interaction parameter χ reaches its critical value χ_s. The corresponding transition induces the appearing of a microstructure, within the system, whose the characteristic size is given by the relation $\lambda^*=2\pi/k^*$, in which λ^* and k^* are the wavelength of the mode of maximum composition fluctuations and the amplitude of the wave-vector at which the scattered intensity shows a peak in the disordered state (i.e. in the homogeneous one-phase region), respectively. Moreover, they have observed a change in the scattering signal and disappearing of the microphase structure when homopolymers A and/or B are added. This behavior originates from a substantial raising in the wavelength λ^* which eventually diverges when k^*

tends to zero. On the other hand, at a temperature T_s (so-called that of macrophase separation), the homopolymers blend A/B separates in two distinct phases via a spinodal decomposition mechanism; however, adjunction of a certain content of copolymer provokes a compatibility enhancement and, hence, the mixture becomes homogeneous. This fact can be proved by light and neutrons scattering measurements through decreasing of the scattered intensity in the thermodynamic limit as the concentration of copolymers raises. In the same order of ideas, such a behavior, observed by others researchers, is well-documented in the literature (*Higgins and Benoît*, 1994). On this account, the main aim of this paper is to attempt a theoretical investigation of these properties for mixtures of weakly charged homopolymers A/B and the corresponding diblock copolymer and compare the results with those reported previously by Hashimoto and others in the case of systems made of their neutral homologous.

This paper is organized as follows. In the second section, we review the theoretical formalism suitable for investigating the scattering properties and phase behavior of polymeric systems under consideration when the both monomeric species are placed in various conditions of charge distributions, whereas the third one is devoted to discussion of the relevant results. Finally, the last section presents some concluding remarks.

2. THEORETICAL BACKGROUND

In order to examine the physico-chemical aspects of polymeric systems under consideration and their structural properties, one can make use of various techniques based upon the scattering of radiations, such as light, neutrons or X-rays. The scattered intensity, $I(k)$, from a system composed of a blend A/B and the corresponding diblock copolymer A-B, can be readily calculated in the framework of the random phase approximation (RPA) [3-6]. By assuming that monomeric species A and B are characterized by an interaction parameter χ and a contrast factor $(\nu a - \nu b)^2$, one gets:

$$\frac{(\nu_a - \nu_b)^2}{I(k)} = \frac{T(k)}{W(k)} - 2\chi \tag{1}$$

where k, being the amplitude of the scattering wave-vector, is related to the wavelength of the incident radiation λ and the scattering angle θ according to the expression $k = (4\pi/\lambda)\sin(\theta/2)$.

Generally, the definitions of $T(k)$ and $W(k)$ depend upon the system under consideration. Due to the fact that this latter involves only two monomer species, it is convenient to introduce a square structure matrix 2x2 whose the elements are the bare partial structure factors Saa (k), Sbb (k) and Sba (k) = Sab (k); by taking account into their definitions, the quantity $T(k)$, corresponding to the sum of the both components of the above structure matrix, writes as follows:

$$T(k) = S_{aa}(k) + S_{bb}(k) + 2S_{ab}(k) \tag{2}$$

whereas W(k), standing for its determinant, reads as:

$$W(k) = S_{aa}(k)S_{bb}(k) - S_{ab}^2(k) \tag{3}$$

where the quantities, appearing in the two above equations, will be defined later in this paper.

Before addressing in detail the predictions of the equation (1), it is worthwhile to note that it corresponds to a well-known relation which was derived, for the first time, by Leibler (*Leibler*, 1980) using the random phase approximation (RPA) in the case of a linear copolymer A-B. This result has been then extended to solutions of copolymers (*Benoît et al.*, 1985), mixtures of homopolymers and copolymers (*Maschke et al.*, 1993, *Benmouna et al.*, 1996, *Benmouna et al.*, 1996, *Benmouna et al.*, 1997, *Benmouna et al.*, 1997, *Benmouna et al.*, 1997, *Bensafi et al.*, 2000).

In the case of weakly charged chains systems (*Zimm*, 1948, *Akcasu and Tombakuglu*, 1990), in addition to the excluded-volume matrix, that of electrostatic interactions, which must be added to the inverse bare matrix S(k), is given by:

$$U(q) = \alpha(k) F \tag{4}$$

where the quantity $\alpha(k)$ describes the electrostatic interaction via the relation:

$$\alpha(k) = \frac{4\pi l_B}{k_B^2 + \kappa^2} \tag{5}$$

in which the Bjerrum length l_B is expressed in terms of the electron charge e, the dielectric constant of the medium ε, the Boltzmann constant k_B and the absolute temperature T according to the relation $l_B \cong e^2/\varepsilon KT$, whereas the quantity κ^{-1}, referring to the Debye-Hückel screening length, in the absence of added salt, is defined following the relationship:

$$\kappa^2 = 4\pi l_B \sum_i \Phi_{ci} \tag{6}$$

where Φ_{ci} is the concentration of counterions; noting that, in equation (4), the matrix F is equal to the product $f f^T$ where f is a column vector, whose elements f_i represent the apparent valences of monomers i or their charge fractions ($0 < f_i < 1$), and f^T is its transpose. Otherwise, it is worthwhile to point out that the off-diagonal elements of the square matrix F can be also expressed according to the relation $Fij = \mu ij f_i f_j$, keeping in mind that f_i is the valence carried by monomer i, with $\mu ij = +1$ if charges i and j are of the same sign and otherwise $\mu ij = -1$.

Here, because of the polymeric systems under consideration involve the homopolymers blend A/B and the corresponding copolymer, the above partial structure factors have hence contributions from the both polymers in the mixture as follows:

$$S_{aa}(k) = \varphi_{ah} Z_{ah} P_{ah}(k) + \varphi_{ac} Z_{ac} P_{ac}(k) \qquad (7a)$$

$$S_{bb}(k) = \varphi_{bh} Z_{bh} P_{bh}(k) + \varphi_{bc} Z_{bc} P_{bc}(k) \qquad (7b)$$

$$S_{ab}(k) = \sqrt{\varphi_{ac} \varphi_{bc} Z_{ac} Z_{bc}}\, P_{abc}(k) \qquad (7c)$$

The subscripts a and b refer to the monomers A and B, while the ones, indicated by h and c, correspond to the homopolymer and copolymer, respectively. For illustration, the respective quantities φ_{ah}, Z_{ah} and $P_{ah}(k)$ are the volume fraction of the homopolymer A, its degree of polymerization and its form factor. The same definitions hold for the other quantities by replacing a to b (monomer B) and h to c (copolymer). Note that $P_{abc}(k)$ is the contribution to the form factor of the copolymer due to the interferences between species A and B belonging to a given copolymer chain (see equation 8 below). Neglecting the effects of excluded volume interactions and assuming Gaussian Statistics, the form factors can be described by the classical Debye function but that one, indicated by $P_{abc}(k)$, is given by the relation:

$$P_{abc}(k) = \frac{(1 - e^{-u_{ac}})(1 - e^{-u_{bc}})}{u_{ac} u_{bc}} \qquad (8)$$

with:

$$u_{ac} = x u_c \qquad (9a)$$

$$u_{bc} = (1 - x) u_c \qquad (9b)$$

$$u_c = k^2 \frac{Z_c a^2}{6} \qquad (9c)$$

$$Z_c = Z_{ac} + Z_{bc} \qquad (9d)$$

where the statistical element length, a, is assumed to be similar for both monomers A and B and $x = Z_{ac}/Z_c$ stands for the composition of the copolymer defined with respect to monomeric specie A. In despite of the fact that the RPA is based upon a mean field theory and not allows to explain the physical laws of systems in the presence of strong fluctuations, it is still possible to benefit it to predict some properties. In particular, the spinodal equation can be readily derived by expressing that the reciprocal scattered intensity is equal to zero at $k=k^*$. This result defines, at the spinodal line, the corresponding interaction parameter χ_s, as:

$$2\chi_s = \frac{T(k = k^*)}{W(k = k^*)} \qquad (10)$$

The wavelength of the mode, leading the system to its critical state, is given by $\lambda^* = 2\pi/k^*$, where k^* is obtained by writing simply that the derivative of the function $(\nu_a - \nu_b)^2/I(k)$ with respect to k is zero. Depending upon the concentration of the copolymer φ_c, k^* is found to be

different from zero in the case of a microphase separation transition, whereas, if the volume fraction φ_c is enough low, the same characteristics is zero and, consequently, a macrophase separation transition occurs.

3. RESULTS AND DISCUSSION

Generally, if the ternary mixture under investigation consists of a weakly charged copolyelectrolyte A-B and the parent homopolymers blend A/B, the corresponding structure matrix reads as follows (*Hakem*, 1997, *Négadi*, 2000, *Bensafi et al.*, 2002, *Bensafi et al.*, 2002)

$$S^{-1}(k) = \begin{pmatrix} \dfrac{S_{bb}}{W} + \alpha f_1^2 & \dfrac{-S_{ab}}{W} + \alpha \mu_{12} f_1 f_2 \\[2ex] \dfrac{-S_{ab}}{W} + \alpha \mu_{12} f_1 f_2 & \dfrac{S_{aa}}{W} + \alpha f_2^2 \end{pmatrix} \qquad (11)$$

3.1 Case of the scattering from a ternary mixture, with $f1 = f2 = f \neq 0$ and $\mu = +1$

In order to illustrate the k-dependence of the scattered intensity from mixtures of neutral polymers and their homologous made of chains having charges of the same sign ($\mu = +1$) at various values of the copolymer concentration φ, we have depicted in figure 1 the variations of the quantity $N_c S(k)/W(k)$ as a function of kR_{gc}. The curves (*a-f*) represent both mixtures of neutral and charged chains; indeed, the charge effect is not perceptible thus meaning that, when the monomeric species A and B are of the same sign and very weakly charged, there is no change in the scattered intensity from the systems under investigation. These curves represent the inverse scattered intensity in the case of ideal systems where the interaction between monomers A and B is zero. These results can be explained as follows. By considering, for example, curve (a) referring to the pure A-B diblock copolymer, the microphase separation transition (MST) takes place at $\chi_s \cong 10.5/N_c$, which result is identical to that reported previously by Leibler (*Leibler*, 1980) This parameter corresponds to a temperature Ts at which the system undergoes substantial composition fluctuations. Curves f (i.e at $\varphi_c = 0$) is for the A/B blend characterized by $\chi_s \cong 4/N_c$, as predicted by classical thermodynamics.

It is important to note that the pure copolymer A-B has $T(k)/W(k) \to \infty$ as $k \to 0$ but adding of a certain content of the homopolymers A and/or B generates that the ratio $T(k=0)/W(k=0)$ is finite, which value decreases as φ_c is lowered. In other words, in the thermodynamic limit (i.e. at $k=0$), the osmotic compressibility is zero for the pure copolymer A-B but not for the mixture under consideration. It should also be noted that the value k_m for the microphase transition shifts to a smaller value with decreasing φ_c and there is a critical volume faction φ_c of the copolymer below from which the microphase transition does not take place.
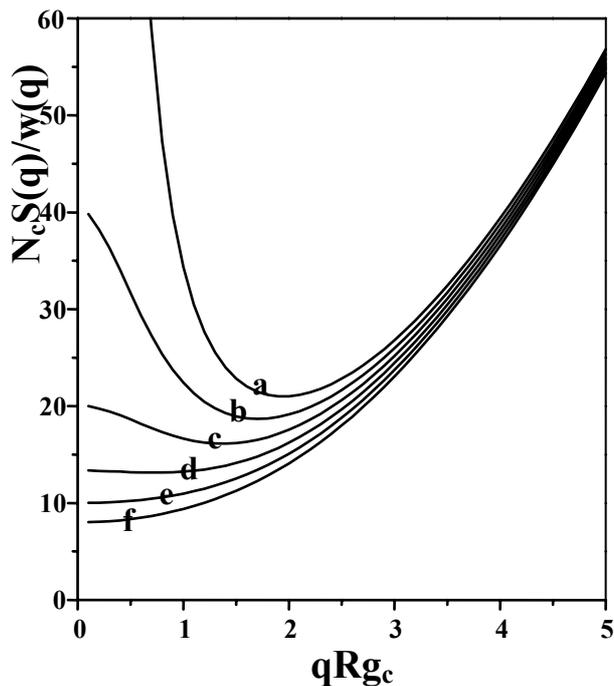
Figure 1: Variation of the normalized reciprocal scattered intensity, NcS(k)/W(k), as a function of kRgc for the polymeric systems under investigation at several values of φc. From the top, the curves are the superposition of the following pairs (a, a'), (b, b'), (c, c'), (d, d') , (e, e') and (f, f') for neutral and charged linear chins and correspond to φc=1, 0.8, 0.6, 0.4, 0.2 and 0. The parameters used in this figure are as follows: N=Nah=Nbh =Nc/2 and Rgah2=Rgbh2=Rgc2/2. This figure shows that the phase behavior of the both polymeric systems are the same due to the weak effect of the charge parameter and the similarity in sign of the charges of monomeric species A and B.

3.2 Case of the scattering from a ternary mixture, with $f1=f≠0$ and $f2 =0$

The results, obtained for the present system, are illustrated in Figure 2 which shows the angular dependence of $N_cS(k)/W(k)$ at six different volume fractions of the copolymers φ_c. The continuous curves (a-f) represent the case of neutral chains whereas the dashed ones (a'-f') refers to those corresponding to mixtures containing a half charged copolymer A- B, charged polymer A and neutral polymer B in similar conditions.

The inverse of scattered intensity is substantially enhanced by the simple fact that only the sequence A of copolymer A-B is charged. This shows clearly a compatibilizing effect due to the electrostatic term. Analyzis of figure 2 shows that the curve a' obtained for the pure half charged diblock copolymer undergoes strong compositions fluctuations at $\chi_s'\cong15.5/Nc$. The interesting observation with respect to present investigation is to realize that in the case of the neutral copolymer (curve a), the MST takes place at a much lower interaction parameter $\chi_s\cong10.5/Nc$. Considering curves b'-f', one observes that they are localized just below the curve a'. In particular, the second mixture investigated (curves b and b'), corresponding to $\varphi_c=0.8$ and

$(\varphi_{ah}+\varphi_{bh}=0.2)$, is deep inside the unstable regime at $\chi_s'\cong15.5/Nc$; indeed, the critical parameter for MST of neutral chains is $\chi_s\cong9.3/Nc$ (curve b) and for charged chains $\chi_s'\cong13.5/Nc$ (curve b'), which is only slightly lower than the corresponding value for a pure charged diblock copolymer as shown by figure a'.
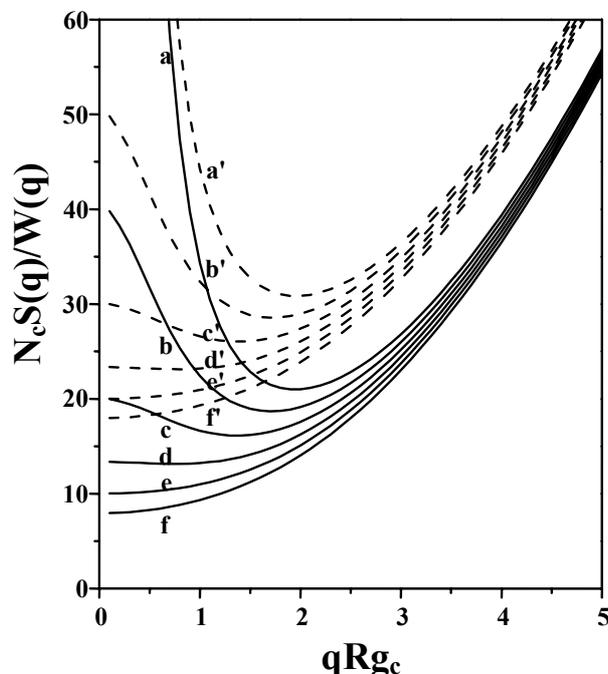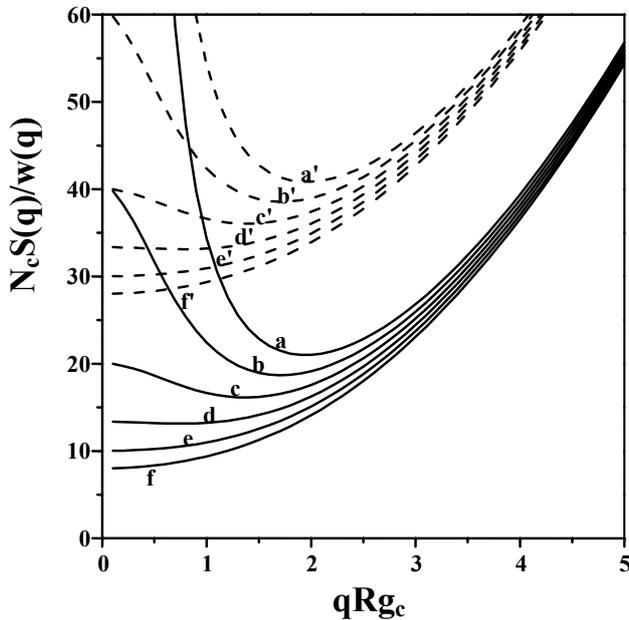

Figure 2 : Variation of the same quantity versus kRgc for a mixture made up of the linear homopolymers blend A/B and the corresponding copolymer. The continuous lines represent the case where all the chains are neutral, whereas the dashed ones correspond to that one where the both chains are half charged.

3.3 Case of the scattering from a ternary mixture, with $f1= f2=f≠0$ and $\mu = -1$

The figure 3 illustrates the variation of $N_cS(k)/W(k)$ as a function of qRg_c for neutral mixture (A-B/A/B) and charged mixture (A-B/A/B). The continuous curves a-f represent the neutral chains whereas the dashed curves a'-f' are corresponding results for charged chains placed in similar conditions.

It shows that the ratio $N_cS(k)/W(k)$ is significantly increased due to the effect of electrostatic attraction, which may be an indication of compatibilization between the two polymer species. This consequence of the strong electrostatic attraction between polymers having charges of opposite signs leads to a low scattering at small q values. Curve a' shows that the charge parameter affects the microphase transition separation; in fact, the copolymer A-B undergoes substantial composition fluctuations at $\chi_s'\cong21/Nc$ which value is higher as compared to that obtained when only one sequence of the copolymer is charged. With regarding to the nature of the phase transitions, one can see that the pure copolymer cannot
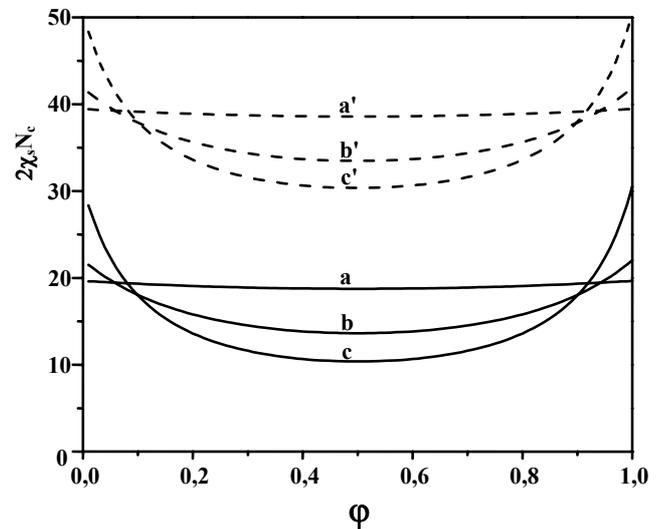
undergo a macrophase separation at any temperature, as expected since the A and B blocks are linked together. However, with even a low amount of homopolymer A and/or B, the mixture can also show a macrophase transition which could be observed at $k=0$ if the temperature is sufficiently high.

than that reported above for the MST. Recalling that it has been shown previously, as one goes from a linear structure to a cyclic one, the phase behavior is dominated by the copolymer, which is not the case in this work although here the neutral copolymer is changed into its charged counterpart.

Figure 3: Variation of NcS(k)/W(k) as a function of qRgc for a neutral mixture of homopolymers A and B and diblock copolymers A-B and charged mixture (A-B/A/B) having charges of opposite signs for several values of φc: (a and a') φc=1.0; (b and b') φc = 0.8; (c and c') φc =0.6; (d and d') φc =0.4; (e and e') φc =0.2; (f and f') φc=0. The continuous lines represent the neutral mixture, whereas the dashed ones correspond to its charged counterpart (f1=f2=f and μ=-1)

Figure 4: Variation of the normalized critical interaction parameter, 2χsNc, as a function of φ for the both ternary mixtures composed of a homopolymers blend A/B and a corresponding diblock copolymer at different values of φc: (a and a') φc=0.8; (b and b') φc=0.4; (c and c') φc=0.2. The continuous curves represent the neutral chains systems, whereas the dashed ones correspond to those made of weakly charged homologous, in the case where μ=-1.

For the sake of illustration another insight on the dependence of the stability limits with the relative composition φ, defined as $\varphi = \varphi_{ah}/(\varphi_{ah}+\varphi_{bh})$, we have depicted in figure 4 the variation of the normalized critical interaction parameter, 2χsNc, as a function of φ at various concentrations of the copolymer φ_c. As indicated in the above figures, the dashed curves represent the results reported previously by Hashimoto et al. (*Ijichi and Hashimoto*, 1988, *Tanaka and Hashimoto*, 1988) in the case of neutral linear chains, while the solid ones correspond to those obtained in this work for weakly charged chains. The pairs of curves (a, a'), (b, b') and (c, c') are plotted by choosing φ_c= 0.8, 0.4 and 0.2, respectively. Analysis of this figure reveals a wide miscibility discrepancy, between neutral and charged chains, which is practically identical for the three values of φ_c. However, for a given charge parameter, the miscibility region decreases as the copolymer concentration is decreased. Otherwise, noting that one observes the interplay of macrophase and microphase separation transitions. On the other hand, as the volume fraction of homopolymers increases, the critical parameter for the macrophase transition decreases faster

4. CONCLUDING REMARKS

This report shows that the scattering properties and phase behavior of ternary mixtures, made of charged homopolymers and copolymers, are clearly different as compared to their neutral linear counterparts. The interplay between macrophase and microphase transitions is clearly sensitive to the concentration of copolymer and the charge distribution. The mixtures containing charged copolymers are characterized by a compatibility much higher than that of their neutral counterparts. The present investigation is an attempt to present a simple formalism, based on the random phase approximation (RPA), which provides some hints on the scattering and phase behavior of the same mixtures than those studied by Hashimoto et al. but containing charged species.

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