2566 *Macromolecules* **1992,** *25,* 2566–2568

Phase Equilibria in the Ternary System Zinc Sulfonated Polystyrene/Poly(ethyl acrylate–4-vinylpyridine)/Tetrahydrofuran

Jian Wang,[†] **Alexei Khokhlov,**[‡]
Dennis G. Peiffer,[§] **and Benjamin Chu***[,†,‖]

Chemistry Department, State University of New York at Stony Brook, Long Island, New York 11794-3400, Physics Department, Moscow State University, Moscow 117234, USSR, Corporate Research Science Laboratory, Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801, and Department of Materials Science and Engineering, State University of New York at Stony Brook, Long Island, New York 11794-2275

Received September 16, 1991
Revised Manuscript Received February 21, 1992

Blends or concentrated solutions of two different polymers often undergo phase separation due to the low entropy of mixing of the polymer components.[1,2] Several methods to improve polymer A–polymer B compatibility have been proposed,[2,3] among which is an introduction of interactive ionic groups into polymer A and polymer B. As a successful example, a bulk polymer blend of ~5 mol % sulfonated polystyrene (SPS) and poly(ethyl acrylate–4 vinylpyridine) (P(EA-*co*-VP)) with ~5 mol % of 4-vinylpyridine in composition was reported to have a single phase as evidenced by a single glass transition, whereas a blend of polystyrene (PS) and poly(ethyl acrylate) (PEA) underwent phase separation.[4] This enhanced compatibility could be attributed to the ionic interactions between the negatively charged sulfonate groups on the PS chains and the protonated nitrogen atoms on the P(EA-*co*-VP) chains. Each nitrogen atom on the polymer chains could possibly trap a positive charge due to its electron-donating nature and thus exhibited a cationlike property. P(EA-*co*-VP) could, therefore, be viewed as a potential polycation. In an aqueous solution of mixtures of polyelectrolytes, where ionic groups could dissociate due to the high dielectric constant of water, the entropy of mixing became pronounced due to the translational entropy of counterions, and consequently the polymer compatibility was improved.[5–8]

It is of interest to investigate the phase behavior of some intermediate situations between the two extreme cases mentioned above, i.e., interactive polymer mixtures in a nonaqueous solution versus polyelectrolyte mixtures in an aqueous solution. Another motivation of this work is to test the theoretical prediction[7,8] on the formation of microdomain structures for mixtures of weakly charged polyelectrolytes analogous to those in block copolymers.

In this paper, we report the phase behavior of mixtures of zinc-sulfonated polystyrene (ZnSPS) and P(EA-*co*-VP) as well as the corresponding "parent" polymers, PS with PEA, in THF solvent at room temperature. The main idea is to show that the compatibility enhancement effect by means of ionic interactions between a polycation and a polyanion can be overcome by a stronger effect which is due to the fact that some ionic groups are not dissociated.

Experimental Section. PEA ($M_w \sim 8.1 \times 10^5$, $M_n \sim 1.8 \times 10^5$) and P(EA-*co*-VP) ($M_w \sim 5.3 \times 10^5$, $M_n \sim 2.0 \times 10^5$, and ~2.4 mol % of vinylpyridine) were prepared by random radical polymerization at low conversion using benzoyl peroxide as an initiator.[9] The polystyrene standard ($M_n \sim 1.1 \times 10^5$) was purchased from Pressure Chemical Co. The preparation of 2 mol % ZnSPS from monodisperse polystyrenes was described in ref 10. Mixture solutions were prepared by dissolving polymer A and polymer B at varying mixing ratios in THF and further clarified by centrifuging the solution at 2000*g* for 2 h. The clarified solution was then transferred to optical cells for turbidity measurements. Each solution was concentrated by evaporating solvent slowly in an oven at 50 °C to a point where another phase appeared visibly. The cloud point was then determined by measuring the turbidity of these solutions at each dilution level.

Results and Discussion. Figure 1 shows the phase-separation diagrams for the PS (polymer A)/PEA (polymer B)/THF system denoted by hollow triangles and for the ZnSPS (polymer A)/P(EA-*co*-VP) (polymer B)/THF system denoted by hollow circles. The phase diagrams are plotted in terms of ϕ_A (volume fraction of component A) versus ϕ_B (volume fraction of component B). The volume fractions were determined by assuming $\phi_i = (W_i/d_i)/\sum(W_i/d_i)$, i = A, B, or S (S = solvent); W_i and d_i are the weight and the density of component i, respectively. The phase-separation region is above and to the right of the curves shown in Figure 1.

An introduction of ionic interactions into the polymer solution mixture leads to a broadening of the phase-separation region. The phase separation for the ionic polymer mixture occurs at lower polymer concentrations than that for the neutral polymer mixture. This observation is consistent with our previous studies[11,12] where a gellike phase appeared upon mixing two interactive polymer solutions up to a certain composition, implying that the thermodynamic stability of the one-phase region could become worse rather than better.[5–8]

A generalized mathematical theory for ternary polyelectrolyte mixtures, i.e., polymer A/polymer B/solvent with charge density $0 \le f_A \ll 1$ and $0 \le f_B \ll 1$ for components A and B, respectively, has been developed recently by one of the authors[8] on the basis of the framework of the Flory–Huggins lattice model. The theory has taken into account the extra contributions to the free energy arising from the translational entropy of counterions and from the electrostatic interactions. The resulting thermodynamic stability condition for a homogeneous single phase is given by[7,8]

$$\left[\frac{1}{\phi_A N_A} + \frac{1}{1-\phi_A-\phi_B} - 2\chi_{AS} + \frac{f_A^{\,2}}{\phi_A f_A + \phi_B f_B}\right] \times \left[\frac{1}{\phi_B N_B} + \frac{1}{1-\phi_A-\phi_B} - 2\chi_{BS} + \frac{f_B^{\,2}}{\phi_A f_A + \phi_B f_B}\right] - \left[\frac{-f_A f_B}{\phi_A f_A + \phi_B f_B} + \chi_{AB} + \frac{1}{1-\phi_A-\phi_B} - \chi_{AS} - \chi_{BS}\right]^2 \ge 0 \quad (1)$$

where N_A and N_B are degrees of polymerization of polymer A and polymer B, f_A and f_B are fractions of charged links in A and B chains, and χ_{AS}, χ_{BS}, and χ_{AB} are Flory–Huggins interaction parameters between the components. When $f_A = f_B = 0$, eq 1 is simply reduced to the Flory–Huggins model. Hence, eq 1 is applicable to polymer A/polymer B/solvent systems whether the polymer components (A and/or B) are charged or not. The theoretical

---

[*] Author to whom all correspondence should be addressed.

[†] Chemistry Department, State University of New York at Stony Brook.

[‡] Moscow State University.

[§] Exxon Research and Engineering Co.

[‖] Department of Materials Science and Engineering, State University of New York at Stony Brook.

0024-9297/92/2225-2566$03.00/0

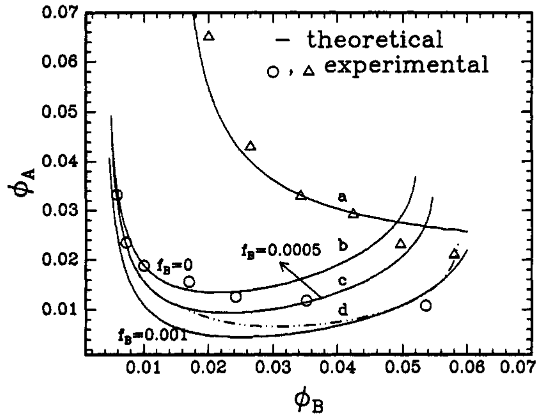

Figure 1. Phase-separation diagrams for ternary mixtures of polymer A/polymer B/solvent at room temperature. ϕ_A, ϕ_B, and ϕ_S are the volume fraction of polymer A, polymer B, and solvent, respectively, with a normalization condition of $\phi_A + \phi_B + \phi_S = 1$. Hollow triangles represent the mixture of PS/PEA/THF (solvent). Hollow circles represent the mixture of ZnSPS/P(EA-*co*-VP)/THF (solvent). Theoretical parameters are as follows: (a) $N_A = 1000$, $N_B = 1400$, $f_A = f_B = 0$, $\chi_{AS} = 0.50$, $\chi_{BS} = 0.50$, and $\chi_{AB} = 0.026$; (b–d) $N_A = 1000$, $N_B = 1400$, $f_A = 0.02$, $\chi_{AS} = 0.50$, $\chi_{BS} = 0.50$, and $\chi_{AB} = -0.36$, with f_B indicated on the curves. The dash–dot–dot line accompanying curve c denotes the theoretical prediction of the microphase separation preceding the macrophase separation (solid line) in accordance with the parameters used in curve c.[16]

fitting curves of the phase-separation behavior in accordance with eq 1 are shown as solid lines in Figure 1. The values $N_A = 1000$ and $N_B = 1400$ for PS and PEA, respectively, were set according to both the molecular weights and the ratio of the molar volume of the smallest polymer repeat unit of PS over that of PEA (~98 and 89 $cm^3\ mol^{-1}$).[13] The charge density for the 2 mol % ZnSPS was taken as $f_A = 0.02$, while the charge density for the P(EA-*co*-VP) with a composition of 2.4 mol % of 4-vinylpyridine was adjusted between 0 and 0.024 because the pyridine groups could only partially be converted into "cations". $\chi_{AS} = 0.5$ was cited from ref 13. As the solubility parameters for PS, PEA, and THF are, respectively, $\delta_A = 9.05$, $\delta_B = 9.16$, and $\delta_S = 9.10$ cal/cm^3 and the difference $|\delta_A - \delta_S|$ between PS and solvent is very close to $|\delta_B - \delta_S|$ between PEA and the solvent, χ_{BS} should have about the same value as χ_{AS}.[14] Therefore, $\chi_{BS} = 0.5$ was presumed. Finally, χ_{AB} was also left as a fitting parameter in order to match the experimental curve. A good fitting was achieved for the neutral polymer mixture (curve a) using the following parameters: $f_A = f_B = 0$, $\chi_{AS} = 0.5$, $\chi_{BS} = 0.5$, and $\chi_{AB} = 0.026$. The fitting of the phase-separation curve for the ionic polymer mixture could be represented by curves b–d, embracing the experimental points in order to account for the uncertainty in the charge density of component B since f_B, as previously discussed, should depend on the chemical environment. The parameters for curves b–d are $N_A = 1000$, $N_B = 1400$, $f_A = 0.02$, $\chi_{AS} = 0.5$, $\chi_{BS} = 0.5$, and $\chi_{AB} = -0.36$, with f_B indicated on the curves. The results show that the f_B value should be small (approximately 0.001). In other words, only a few percent of the 4-vinylpyridine groups are acting as effective associating groups. The small f_B value is comparable with what we observed in our previous studies[11,12] where only a few percent of the base-containing groups on the polymer chains effectively took part in ion-pair interactions with the ZnSPS. The theoretical curve goes down with an increase in the f_B value, predicting a poorer thermodynamic stability for the homogeneous phase with a *larger* fraction of cationlike properties on the polymer B chain in a nonaqueous solution. The fitting curve a demonstrates a polymer–polymer interaction parameter value of $\chi_{AB} = 0.026$, a small positive value which is analogous to a χ_{AB} value of ~0.012 for the blend of polystyrene and poly(methyl methacrylate).[15] As χ_{AS} and χ_{BS} values were not available for the ZnSPS/P(EA-*co*-VP)/THF system, we simply used the same values of χ_{AS} and χ_{BS} as in curve a. The resulting value of $\chi_{AB} = -0.36$ suggests an exothermic mixing, i.e., a negative enthalpy, which is in agreement with our expectation, due to the coordination chemistry based interpolymer interactions. In other words, the interactions are between the Zn counterion on polymer A with the vinylpyridine unit of polymer B. It is noted that the theoretical curve at the higher ϕ_B region deviates appreciably from the experimental points. One possible reason might be attributed to the polydispersity of the component of P(EA-*co*-VP) since the theory deals with strictly monodisperse polymers in terms of molecular weight, composition, degree of branching, and other variables. Nevertheless, the theory, when applied to polydisperse polymers, could serve as a valuable guide for investigating the phase-separation behavior of real polymer mixtures. As a result of the disparity in molecular weight and charge density for the two components, the phase diagram for the ionic polymer mixture is asymmetric.

In refs 7 and 8 it was predicted that in the mixtures of weakly charged polyelectrolytes it should be possible to observe some form of microdomain structure which is analogous to that formed in block copolymer systems. The region of equilibrium stability of this microdomain structure calculated according to eq 32 of ref 8 with the parameters corresponding to curve c is shown between solid and dash–dot–dot lines in Figure 1. Detailed small-angle X-ray scattering (SAXS) experiments aimed to detect the microdomain structure in this region are underway.

Conclusion. A phase diagram for nonaqueous polymer–polymer complex solutions consisting of an ionomer and an amine-containing copolymer was obtained. By comparing this phase diagram with the phase diagram for the corresponding noncharged parent polymer mixture, poorer miscibility associated with polymer complexes was observed after introducing the anions and cations into the polymer chains. This phenomenon is different from the observations obtained in bulk polymer blends having anion–cation interactions. The opposite behavior could be considered as a consequence of the polymer–polymer aggregation phenomenon and poorer solvent quality with respect to the resulting polymer complexes due to the presence of ions. Theoretical estimates of the phase behavior are in agreement with experimental results utilizing reasonable molecular parameters, which could provide us with an insight into the phase diagram. The microdomain structure formation predicted by the theory and preceding the spinodal decomposition has not yet been observed by means of SAXS. Further SAXS studies are underway.

Acknowledgment. B.C. greatly acknowledges the U.S. Army Research Office (Grant DAALO391G0040) for support of this research.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.

(3) Smith, P.; Hara, M.; Eisenberg, A. *Curr. Top. Polym. Sci.* **1987**, *2*, 255.

(4) Eisenberg, A.; Smith, P.; Zhou, Z. *Polym. Eng. Sci.* **1982**, *22*, 17.

(5) Vasilevskaya, V. V.; Starodubtzev, S. G.; Khokhlov, A. R. *Vysokomol. Soedin.* **1987**, *29B*, 390.

(6) Nyrkova, I. A.; Khokhlov, A. R. *Vysokomol. Soedin.* **1989**, *31B*, 575.

(7) Nyrkova, I. A.; Khokhlov, A. R.; Kramarenko, Y. Y. *Vysokomol. Soedin.* **1990**, *32A*, 918. See English translation in: *Polym. Sci. USSR* **1990**, *32*, 852–861.

(8) Khokhlov, A. R.; Nyrkova, I. A. *Macromolecules*, in press.

(9) Gauthier, S.; Eisenberg, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1981**, *22*, 293.

(10) Gabrys, B.; Higgins, J. S.; Lantman, C. W.; MacKnight, W. J.; Pedley, A. M.; Peiffer, D. G.; Rennie, A. R. *Macromolecules* **1989**, *22*, 3746.

(11) Chu, B.; Wang, J.; Peiffer, D. G.; Shuely, W. J. *Macromolecules* **1991**, *24*, 809.

(12) Wang, J.; Peiffer, D. G.; Shuely, W. J.; Chu, B. *Macromolecules* **1991**, *24*, 4349.

(13) Barton, A. F. M. *CRC Handbook of Polymer–Liquid Interaction Parameters and Solubility Parameters*; CRC Press: Boca Raton, FL, 1990.

(14) Paul, D. R. *Polymer Blends*; Academic Press: New York, 1978.

(15) Stockmayer, W. H.; Stanley, H. E. *J. Chem. Phys.* **1950**, *18*, 153.

(16) To plot the dash–dot–dot curve in Figure 1, we assumed that in eq 32 of ref 8 the values of the parameters N_A, N_B, f_A, f_B, χ_{AS}, χ_{BS}, and χ_{AB} are those shown in the caption to Figure 1 and, in addition to this, $l_A = l_B = a$ (both polymers are flexible with approximately equal Kuhn segments), $u = 3$ (which roughly corresponds to the dielectric constant of THF), and $n_s = 0$ (salt-free solution).

CORRECTIONS

Li Zhuomei,* Zhang Xuexin, Chen Yuanpei, and Zhong Yuanzhen: Hydrophobic Interaction of Ionenes in Aqueous Solution. Volume 25, Number 1, January 6, 1992, pp 450–453 .

The authors' names were incorrectly indexed as Zhuomei, L., Xuexin, Z., Yuanpei, C., and Yuanzhen, Z. They should have been indexed as Li, Z. M., Zhang, X. X., Chen, Y. P., and Zhong, Y. Z.