ELSEVIER

Polymer 42 (2001) 1501–1505

polymer

www.elsevier.nl/locate/polymer

Incompatibility of polyelectrolyte solutions — mixed solutions of PSSNa and PVSNa

K. Nishida, M. Shibata, T. Kanaya, K. Kaji*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan

Received 26 April 2000; received in revised form 16 June 2000; accepted 23 June 2000

Abstract

The compatibility of PSSNa and PVSNa in aqueous solution has been studied. PSSNa and PVSNa are compatible when the total concentration is less than 1.0 mol/l, but phase separation occurs when the total concentration exceeds 1.0 mol/l. The cloud point curve is of a typical UCST type. Addition of salt causes a shift of the boundary toward a lower concentration. It may be considered that these new critical phenomena are a reflection of the balance between electrostatic and non-electrostatic interactions. The time evolving processes of the phase separation has also been investigated. The characteristic behavior of spinodal decomposition is observed when the temperature of a mixed solution is jumped down passing through the critical point. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolytes; PSSNa; PVSNa

1. Introduction

Polyelectrolyte solutions, which themselves are very complicated systems, become more complicated when they are mixed with other substances. Although there exist some theoretical approaches for systems [1] such as the mixture of a charged polymer with a non-electrolyte polymer and that of a positively charged and a negatively charged polymer, no theoretical description on the mixture of two like-charged polyelectrolytes is seen as far as the authors are aware. This seems to be quite natural because if these two polyelectrolytes have not only ideally the same charge densities but also the same properties of backbones, they would be identical with respect to intermolecular interactions and so theoretical treatments for this system becomes meaningless. For a mixture of two different real polyelectrolytes, however, such ideal similarity is hardly attained.

For a mixture of a large polyanion (xanthan) with a small polyanion (poly(styrene sulfonate)), as well as a mixture of a high charge density polyanion (xanthan) with a low charge density polyanion (hyaluronate), stochastic mixing does not occur and an existence of some localization of each component is suggested [2]. This interesting result may be rationalized by the difference in the size or charge density of the components, which should cause an asymmetry to the intermolecular interactions. Our interest in this study is focused on the case of a mixture of polyelectrolytes having like charges, the same charge density and a similar backbone.

Poly(styrene sulfonate) (PSS) and poly(vinyl sulfuric acid) (PVS) are typical synthetic polyelectrolytes, and the solutions of their sodium salts (PSSNa, PVSNa) have been often used as model systems for both static and dynamical studies of polyelectrolytes. Thanks to those studies, the structures of PSSNa and PVSNa solutions have been revealed considerably; their behaviors are quite similar in the following points. Both of the polyelectrolyte solutions show a maximum not only in the reduced viscosity versus concentration curve [3,4] but also in the scattering intensity versus scattering vector spectrum measured by various scattering methods, such as small-angle X-ray scattering (SAXS) [5,6], small-angle neutron scattering (SANS) [7,8], and static light scattering (SLS) [9]. Furthermore, when the concentrations are given in molality of the monomer-unit, these maximum positions agree quantitatively with each other in both the relations. It would be quite natural to consider that such phenomenological resemblance must come from the similarity of their structures as long as the electrostatic interactions are not suppressed because both the polyelectrolytes have vinyl type of backbones as well as sulfuric-acid type of dissociation groups.

It is well known that water is a good solvent for both PSSNa and PVSNa. However, we happened to find that

---

* Corresponding author. Tel.: +81-774-38-3140; fax: +81-774-38-3146.
E-mail address: kkaji@scl.kyoto-u.ac.jp (K. Kaji).

PII: S0032-3861(00)00509-7

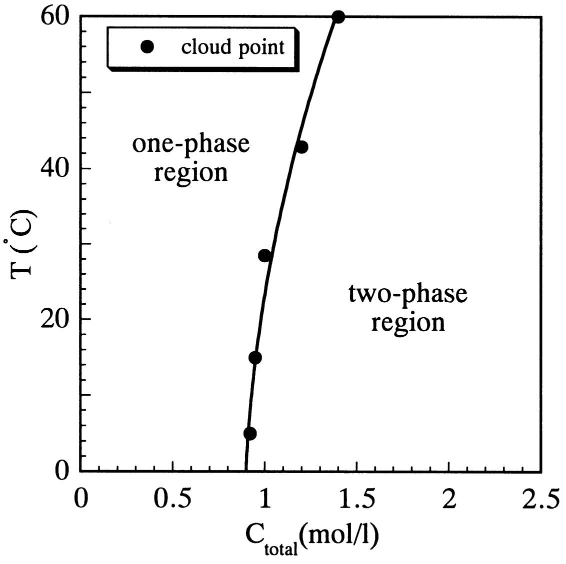

Fig. 1. Phase diagram for aqueous solutions of PSSNa/PVSNa mixture (PSSNa/PVSNa = 1:1). The cloud point temperature T is plotted against the total concentration C_{total}.

the mixtures of their aqueous solutions cause phase separation under certain conditions, which is the motivation of this work. Thus, the purpose of the present study is to clarify the condition where these two polyelectrolytes begin to distinguish one from the other in compatibility; in other words, how a non-electrolyte property comes out in the mixture of actual polyelectrolyte solutions. For this purpose, we construct phase diagrams of a PSSNa–PVSNa–water system. Based on such phase diagrams, the time evolving process of the phase separation is also followed by optical microscopy.

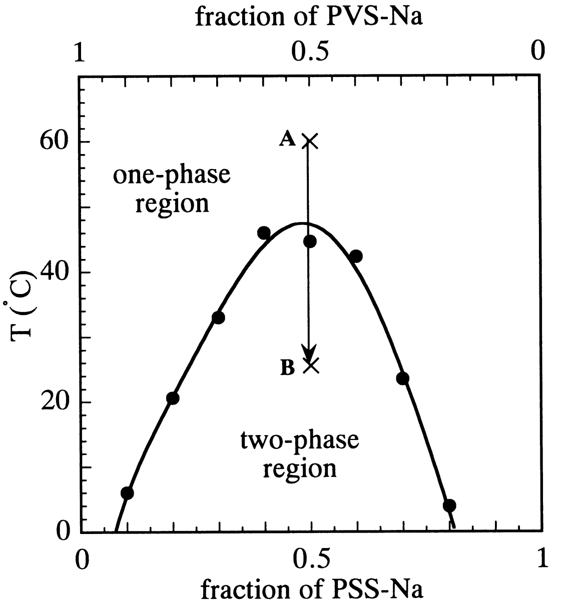

Fig. 2. Phase diagram for aqueous solutions of PSSNa/PVSNa mixture (C_{total} = 1.2 mol/l). The cloud point temperature T is plotted against the molar fraction of PSSNa to PVSNa.

2. Experimental section

A sodium salt of poly(styrene sulfonate) (PSSNa) was prepared from polystyrene (PS) using a conventional method [10]. The parent PS with a degree of polymerization $N \approx 1200$ was purchased from Nacalai Tesque, Inc. A sodium salt of poly(vinyl sulfuric acid) (PVSNa) was obtained using an ion-exchanging procedure from the potassium salt of poly(vinyl sulfuric acid) (PVSK). The PVSK with $N \approx 1500$ was also obtained from Nacalai Tesque, Inc. The cloud point was determined by transmission measurements using He–Ne laser light ($\lambda = 632.8$ nm). The optical microscope observation and its time-evolving recording were carried out using a Nikon Optiphot 2-Pol with a CCD camera and a video recorder.

3. Results and discussion

3.1. Phase diagram

For simplification, the molar proportion of PSSNa to PVSNa in mixed solutions was fixed equally as PSSNa/PVSNa = 1:1. Under this condition, the boundary between the one-phase and two-phase regions was determined as functions of total concentration C_{total} of PSSNa and PVSNa and temperature T (Fig. 1). The boundary exists at around C_{total} = 1.0 mol/l at room temperature, but it shifts to higher concentrations with the rise of temperature. This fact suggests that the co-existing curve is of a UCST type. As will be shown later, a typical mixed solution having a concentration larger than the boundary C_{total} at room temperature is actually separated completely into two transparent macroscopic phases after a sufficient time. According to ^{1}H NMR analysis, the upper and the lower layers are rich in PSSNa and PVSNa, respectively, though precise evaluation of the constituents could not be performed because of the overlapping of their signals.

Continuing the argument, we reason that this new critical phenomenon is a reflection of the balance between the electrostatic and non-electrostatic interactions. As was mentioned in Section 1, PSSNa and PVSNa have the same type of dissociation groups, and hence electrostatic interactions with the same order of magnitude are expected for the both polyelectrolytes. When concentrations are low, the mean separation between the polyions is distant enough to be unaffected by van der Waals interactions and only electrostatic interactions are exerted because the former and the latter are short- and long-range interactions, respectively. In these circumstances, polyions of different species cannot be distinguished from each other. As the concentration increases, counterions are more densely distributed and screen the interpolyion electrostatic interactions more

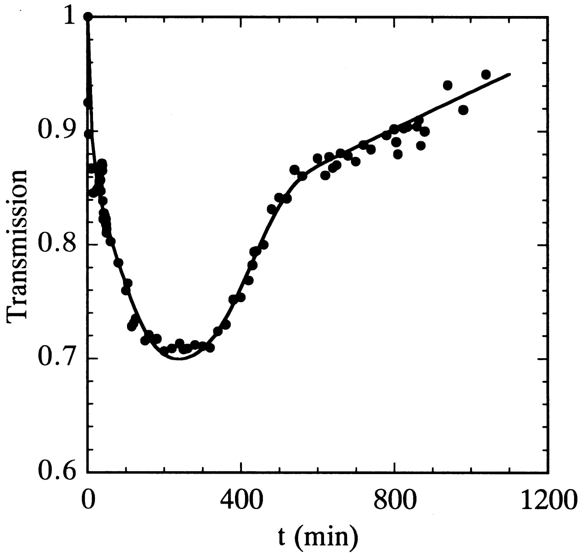

Fig. 3. Time dependence of laser light transmission for aqueous solutions of PSSNa/PVSNa mixture when temperature is jumped from 60 to 25°C; the jumping path is marked with A → B in Fig. 2 ([PSSNa]:[PVSNa] = 1:1 and $C_{\mathrm{total}} = 1.2$ mol/l).

strongly while the van der Waals interactions are more strengthened due to shorter interpolyion distances. When the latter interactions become predominant, PSSNa and PVSNa are no longer compatible and the usual phase separation occurs in accordance with the description of Flory–Huggins theory. The balancing point lies at around 1.0 mol/l at room temperature for the present system. Other investigations [11,12] also support this value; the characteristic features of polyelectrolytes begin to be lost when the concentration of PSSNa exceeds ca. 1.0 mol/l. In this study, we have fixed the total concentration C_{total} at 1.2 mol/l, which is above the boundary concentration at room temperature, and made a phase diagram as functions of temperature T and molar ratio of PSSNa to PVSNa. As seen from Fig. 2, the phase diagram shows a typical UCST type co-existing curve, which was expected in the argument on Fig. 1. It is also noted that the curve is slightly asymmetric around the equi-molar point, meaning that at low temperatures the compatibility is better when a small amount of PVSNa is mixed with a large amount of PSSNa than vice versa.

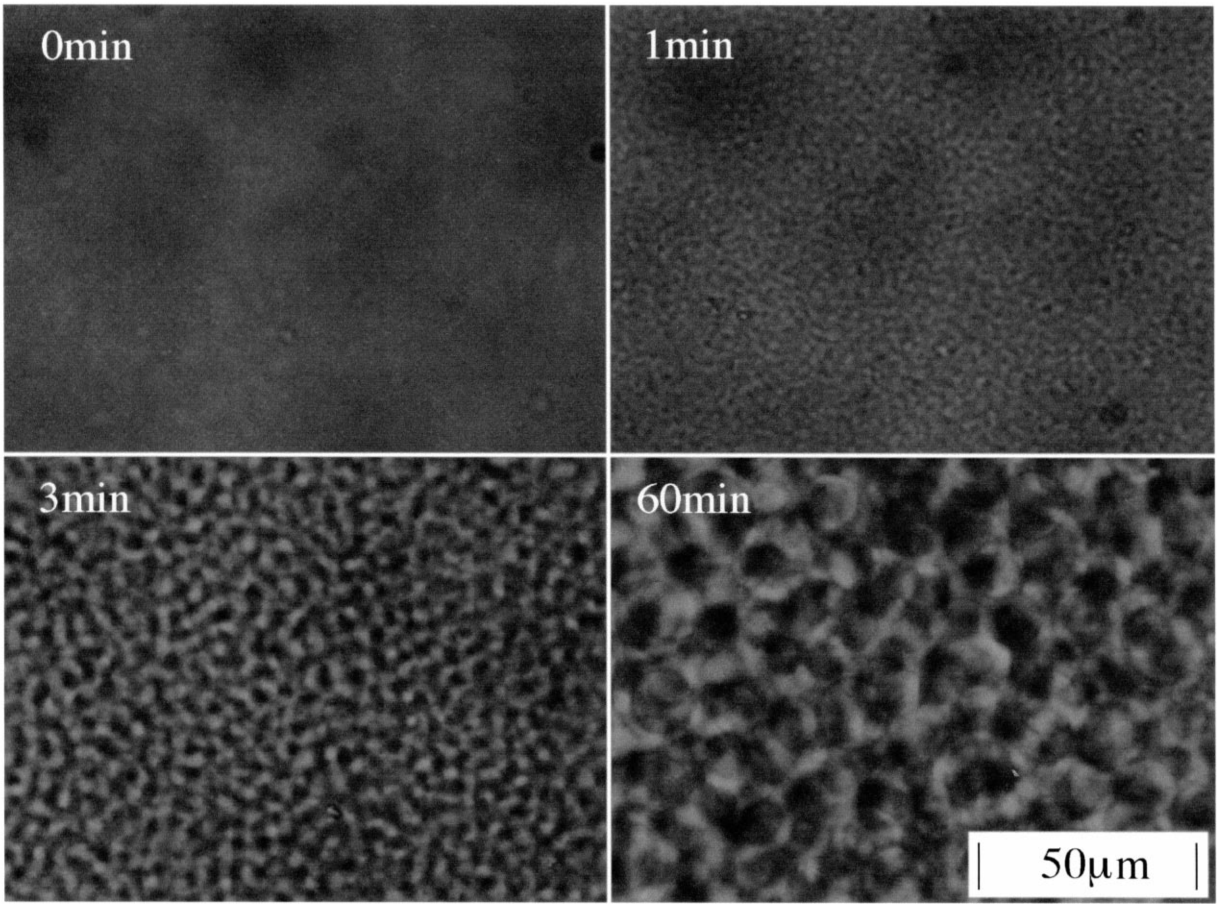

Fig. 4. Optical microscope observation for the time-evolving process of phase separation when temperature is jumped from 60 to 25°C; the jumping path is marked with A → B in Fig. 2 ([PSSNa]:[PVSNa] = 1:1 and $C_{\mathrm{total}} = 1.2$ mol/l).

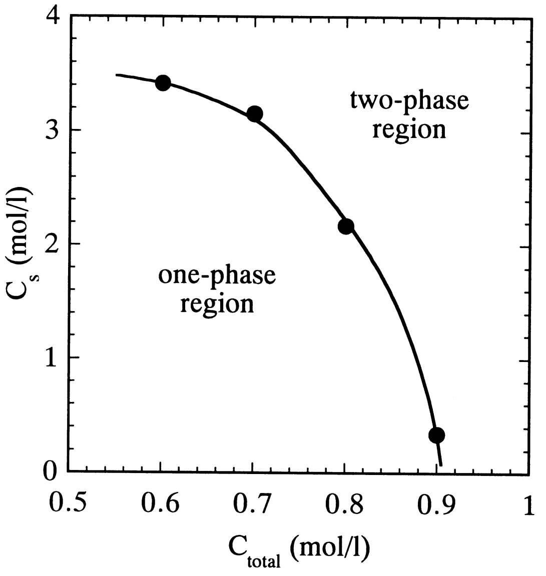

Fig. 5. Added salt effect on the cloud point. The cloud points are plotted as functions of C_{total} and C_s at 25°C ([PSSNa]:[PVSNa] = 1:1).

3.2. Time evolving process of the phase separation

The incompatible conditions between PSSNa and PVSNa could be clarified from the study mentioned above. In this section, the time-evolving process of the phase separation is examined.

Fig. 3 shows the time-evolution of transmission for an aqueous solution of PSSNa/PVSNa = 1:1 at $C_{total} =$ 1.2 mol/l when the solution was quenched from 60 to 25°C. This quenching process passing through the critical point is indicated as A → B in Fig. 2. Immediately after the quenching, the transmission starts to decrease drastically and levels off, reaching a minimum at ca. 200 min. In ca. 300 min it increases again and recovers to almost the initial value in ca. 1000 min. The recovery of the transmission suggests the completion of macroscopic binary phase separation, which can be also confirmed directly by the naked eye.

Fig. 4 shows the time-evolving processes of the phase separation observed by optical microscopy for the same system as in Fig. 3. In ca. 0.5 min, the so-called bicontinuous pattern characteristic of spinodal decomposition [13,14] starts to emerge and increases in intensity with time. After ca. 2 min, the characteristic wavelength of the pattern begins to increase and the bicontinuous pattern changes into the droplet pattern in ca. 50 min. This behavior is qualitatively very common to the process of spinodal decomposition which is well known for polymer blends (see, for example Ref. [15]).

3.3. Added salt effect

We have assumed that the above-described new critical phenomenon is a reflection of the balance between the electrostatic and non-electrostatic interactions as was explained in the first part of this section. In order to confirm this assumption, we have tested if the balancing point shifts when the strength of electrostatic interaction is changed. The adjustment of the electrostatic interaction is usually performed by adding salt because salt weakens the electrostatic interaction [16]. Fig. 5 shows a phase diagram as functions of concentration of added salt C_s and the total concentration C_{total} of the solution, depicting the added salt effect at 25°C. In this experiment, the molar proportion of PSSNa to PVSNa in mixed solutions was equally fixed, and then the cloud point was determined by changing both C_{total} and C_s. As seen from the figure, the critical C_{total} where the phase separation occurs decreases with increasing the amount of added salt, C_s. In other words, the non-electrostatic interaction becomes predominant when the electrostatic interaction is weakened. These facts strongly support our assumption.

The phenomenon of phase separation due to the addition of salt is not related to the precipitation nor to the salting-out of PSSNa and PVSNa, because even if the same quantity of salt is added to a pure solution of each polyelectrolyte, neither precipitation nor phase separation are caused as far as the examined concentration region is concerned.

4. Conclusions

When the polyelectrolyte concentration is low, the shielding effect due to the ionic strength is not effective and the electrostatic interaction is predominant. In this region polyions recognize each other only by the electrostatic interaction. If two species of polyions have the same effective charge density, which is called symmetrical with respect to the strength of electrostatic interaction, then these polyions are compatible.

However, as the concentration increases, the electrostatic interactions begin to be screened and at the same time, the mean separation between polyions becomes shorter, resulting in the short-range forces, namely van der Waals interactions, becoming larger and larger. Above some critical concentration, two species of polyions begin to recognize their individual distinctions and phase separation occurs as seen in usual polymer solutions.

Acknowledgements

We thank Prof. Takenao Yoshizaki, Prof. Fumihiko Tanaka, Prof. Yoshisuke Tsunashima of Kyoto University and Prof. Takahiro Sato of Osaka University for their useful comments and discussion.

References

[1] Benmouna M, Aziz S, Vilgis TA. J Polym Sci B 1993;31:578.

[2] Norwood DP, Benmouna M, Reed WF. Macromolecules 1996;29:4293.
[3] Cohen J, Priel Z, Rabin Y. J Chem Phys 1988;88:7111.
[4] Nishida K, Kanaya T, Kaji K. Polym Prepr Jpn 1990;39:3953.
[5] Kaji K, Urakawa H, Kanaya T, Kitamaru R. J Phys Fr 1988;49:993.
[6] Nishida K, Kaji K, Kanaya T. Macromolecules 1995;28:2472.
[7] Nielich M, Williams CE, Boué F, Cotton JP, Daund M, Farnoux B, Jannink G, Picot C, Moan M, Wolff C, Rinaudo M, de Gennes PG. J Phys Fr 1979;40:701.
[8] Ono M, Okamoto S, Kanaya T, Nishida K, Urakawa H, Kaji K, Kitamaru R. Physica B 1986;138:49.
[9] Krause R, Maier EE, Deggelmann M, Hagenbüchle M, Schulz SF, Weber R. Physica A 1989;160:135.
[10] Vink H. Makromol Chem 1982;182:279.
[11] Takahashi Y, Matsumoto N, Iio S, Kondo H, Noda I, Imai M, Matsushita Y. Langmuir 1999;15:4120.
[12] Nishida K, Kaji K, Kiriyama K, Kanaya T. In: Noda I, Kokufuta E, editors. Polyelectrolytes, Yamada Conference L, 1999. p. 137–40.
[13] Cahn JW, Hilliard JE. J Chem Phys. 1958;28:258.
[14] Cahn JW. J Chem Phys 1965;42:93.
[15] Hashimoto T, Kumaki J, Kawai H. Macromolecules 1983;16:641.
[16] Oosawa F. Polyelectrolytes. New York: Marcel Dekker, 1971.