SHORT COMMUNICATIONS

**Liquid-Liquid Phase Separation and Gelation in the
Poly(vinyl alcohol)–Poly(ethylene glycol)–Water System.
Dependence on Molecular Weight
of Poly(ethylene glycol)**

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(Received July 27, 1985)

KEY WORDS Phase Separation / Gelation / Molecular Weight /
Concentration / Particle /

We recently studied the phase separation of a poly(vinyl alcohol)(PVA)–poly(ethylene glycol)(PEG)–water system, and suggested that the polymer–polymer interaction parameter in the system is a complicated function of PEG molecular weight.¹ In the present work, the concentration regions where liquid-liquid phase separation and gelation occur in the PVA–PEG–water system have been determined, using PEG of different molecular weights ranging from 300 to 5.94×10^5 .

It was found that both phase separation and gelation remarkably depend on the molecular weight of PEG. The phase separation occurred in the mixtures with PEG molecular weights greater than 600, and did not with a PEG molecular weight of 300. The separation-limit concentration curve moved toward the water apex and inclined toward the water-PVA axis in the triangular diagram as the PEG molecular weight increased from 600 to 5.94×10^5 . The gelation-limit concentration curve moved toward the water apex as the PEG molecular weight increased from 300 to 2000, and it moved toward the PVA–PEG axis as the molecular weight increased from 2000 to 5.94×10^5 . The particles in the biphasic mixture were found to be PVA-rich.²

EXPERIMENTAL

Materials

Poly(vinyl alcohol)(PVA), PVA-105 with 98.5 mol% saponification, was kindly donated by Kuraray Co., Ltd. Poly(ethylene glycol) (PEG): average molecular weight ($\bar{M}$), 300, 600, 2000 and 2.00×10^4 manufactured by Kishida Chemical Co., Ltd. and $\bar{M}$, 5.94×10^5 manufactured by Toyo Soda Manufacturing Co., Ltd. were used. PVA and PEG were purified and then PVA was fractionated by the method described previously.¹ Average molecular weights $\bar{M}$ of PEG oligomer samples smaller than 2000 are manufacturer's data calculated from the hydroxyl content. The weight and number-average molecular weights (M_w and M_n) of PVA and PEG of higher molecular weight samples were estimated by gel permeation chromatography (GPC). The characteristics of the samples used are given in Table I.

*Determination of Concentration Regions of
Phase Separation and Gelation*

Concentration regions of the phase separation and gelation were determined in the following way. Both aqueous solutions of PVA

Table I. Molecular weights of the polymer samples

Polymer	$\bar{M}$	M_w/M_n
PVA	3.85×10^4 ^a	1.72
PEG	5.94×10^5 ^a	1.04
PEG	2.00×10^4 ^a	1.10
PEG	2000 ^b	
PEG	600 ^b	
PEG	300 ^b	

^a Weight average molecular weight, M_w .^b Manufacturer's data calculated from the hydroxyl content.

and PEG were combined in a beaker at PEG/PVA ratios of 1/6, 1/2, 1, 2, and 6, and stirred with a glass bar, resulting in a transparent solution. The solution was concentrated step by step to higher polymer concentrations by heating gently at 100°C with continuous stirring. At each step, the mixture was observed with the naked eye 10 min after being cooled to 25°C. The mixture became turbid when the phase separation took place, while the polymer-rich phase or the whole mixture became hard and lost its fluidity or spinnability on gelation. The phase separation point in concentration thus determined was ascertained to be thermodynamical equilibrium value by tracing representative mixtures for additional 5 days. The gel point in concentration determined, though not strictly a thermodynamical equilibrium value, may be useful in revealing aspects of the molecular weight dependence of gelation in the PVA-PEG-water system.

Microscopic Observation

Systems undergoing phase separation were observed microscopically by the following method. The sample was put in a glass cell (20 mm wide $\times$ 1 mm thick $\times$ 30 mm high) and observed from a wide side. This method had several advantages. For example, one could observe clearly the coexistence of upper and lower phases. Also, when the mixture was stirred, one could observe particles appearing in the mixture, and their behavior on terminat-

ing the stirring.

Iodine Coloration

A small amount of 0.02 *N* iodine solution was added to an aqueous PVA solution and stirred, yielding a homogeneous mixture assuming a purple color. Then, the aqueous PEG solution was added to the mixture and stirred. Since PEG assumes a brown color in the presence of iodine, the PEG-rich phase could be distinguished from the purple of PVA-rich phase.

RESULTS AND DISCUSSION

Figure 1 shows the concentration regions of the phase separation and gelation in the PVA ($\bar{M} = 3.85 \times 10^4$)-PEG ($\bar{M} = 2000$)-water system at 25°C and 1 atm. Figure 2 shows the concentration regions of the phase separation and gelation in the PVA ($\bar{M} = 3.85 \times 10^4$)-PEG-water system with PEG of various molecular weights, determined at 25°C and 1 atm in the same way as in Figure 1.

As evident from these figures, both the phase separation and gelation remarkably depend on the PEG molecular weights.

Phase separation occurred in mixtures with a PEG molecular weight greater than 600, and did not with a PEG molecular weight of 300. The separation-limit concentration curve (the boundary between a homogeneous solution region and a phase separation region) moved toward the water apex and inclined toward the water-PVA axis as the PEG molecular weight increased from 600 to 5.94×10^5 .

Gelation occurred in all systems examined. The gelation-limit concentration curve (the boundary between a phase separation region and a gelation region, or the boundary between a homogeneous solution region and a gelation region) moved toward the water apex as the PEG molecular weight increased from 300 to 2000, and it moved toward the PVA-PEG axis as the molecular weight increased from 2000 to 5.94×10^5 . Furthermore, the

Figure 1. The concentration regions of phase separation and gelation in the PVA ($\bar{M}=3.85 \times 10^4$)-PEG ($\bar{M}=2000$)-water system at 25°C and 1 atm. ×, homogeneous solution; O, phase separation; Δ, gelation.

Figure 2. The concentration regions of phase separation and gelation in the PVA ($\bar{M}=3.85 \times 10^4$)-PEG-water system with PEG of various molecular weights; $\bar{M}=300$ (a), 600 (b), 2000 (c), 2.00×10^4 (d) and 5.94×10^5 (e), determined at 25°C and 1 atm in the same way as Figure 1. ----, the boundary between a homogeneous solution region and a phase separation region; —, the boundary between a phase separation region and a gelation region; — · — · —, the boundary between a homogeneous solution region and a gelation region.

gelation-limit concentration curve tended to incline toward the water-PVA axis as PEG molecular weight increased from 300 to 5.94×10^5 . The region of phase separation increased gradually as PEG molecular weight increased from 600 to 5.94×10^5 .

It should be noted that the gelation tended to occur rapidly and completely even at a relatively low polymer concentration in the PVA-PEG-water system with low molecular weight PEG ($\bar{M}=300$ –2000); however, for the system with PEG of $\bar{M}$ higher than 2.00×10^4 , the gelation at low polymer concentrations occurred slowly only in the lower polymer-rich phase.

The effects of PEG molecular weight on the separation-limit concentration curve described above were consistent with our previous data¹ and with Flory-Huggins theory.^{3,4} The theory expects that, for ternary systems consisting of polymer 2, polymer 3 and a solvent (component 1) in which the polymer molecular weight x_2 is fixed but x_3 varied, the binodal moves toward the solvent apex and inclines toward the solvent-polymer 2 axis as x_3 increases.^{1,3,4}

The molecular weight dependence of gelation described above may be explained as follows. Gelation in the PVA-PEG-water system is believed to be generated from both the crystallization of syndiotactic sequences of PVA chains^{5,6} and the complexing between PVA and PEG. In the range of 300 to 2000 of PEG molecular weight, the contribution of complexing to gelation may be prominent and increase with increasing molecular weight, shifting the gelation-limit concentration curve toward the water apex. Our previous work¹ also suggests that the polymer-polymer interaction parameter χ_{23} decreases with increasing PEG molecular weight in the PVA-PEG-water system; that is, the PVA-PEG interaction would increase with increasing PEG molecular weight. In the range of 2.00×10^4 to 5.94×10^5 of PEG molecular weight, the steric hindrance to the crystallization of PVA caused by long PEG chains may become predominant and increase with increasing PEG molecular weight, giving rise to a movement of the gelation-limit concentration curve toward the PVA-PEG axis.

Microscopic examinations revealed that

when stirred gently, particles appeared in mixtures undergoing phase separation. When the stirring was stopped, the particles were observed to settle, join to each other and form a lower polymer-rich phase coexisting with an upper polymer-poor phase. The particles were ascertained to be a PVA-rich phase by iodine coloration. The above results of microscopic examinations are consistent with our previous results, showing that the lower phase is PVA-rich and the upper PEG-rich.¹

Particle size was in the range of 0.1 to 100 μm . It was found that the size and distribution of the particles greatly depend on the composition of the mixture (the PEG/PVA ratio and polymer concentration) rather than the molecular weight of PEG. That is, particle size tends to become smaller and at the same time highly homogeneous (almost monodisperse) as the PEG/PVA ratio deviates from unity or the polymer concentration approaches the phase separation-limit or gelation-limit concentration levels.

Furthermore, when the mixture of polymer-rich (lower) and polymer-poor (upper) phases was cooled slightly, new particles appeared densely in the lower phase. The size of the new particle, which changed from 0.1 to 1 μm

according to the composition of mixture, was almost monodisperse (less than a few percent of diversity) in a lower phase of mixture. The particles could be immobilized together with the matrix of the lower phase by cross-linking with a glutaraldehyde. A further study is now in progress to determine whether the new particles are of the polymer-rich or polymer-poor phase.

Acknowledgements. The authors wish to thank Dr. M. Ueda and Dr. S. Kawai, Kuraray Co., Ltd. for their many helpful comments.

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