Thermodynamic consideration of the sol–gel transition in polymer solutions*

Kazuo Kawanishi, Motoko Komatsu and Takashi Inoue†
Department of Textile and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
(Received 16 September 1986; accepted 27 September 1986)

The thermoreversible sol–gel transition in polymer solutions is discussed in terms of (i) liquid–liquid phase separation by spinodal decomposition, (ii) crystallite formation of polymer chains, and (iii) a hydrogen-bonding type association of the polymer chains. The first two effects can be described by the familiar Flory–Huggins theory and the last by a modern theory of gelation as a result of the site–bond correlated percolation problem. The three equilibrium aspects interpret well our recent results on the sol–gel transition in poly(vinyl alcohol)/water and poly(vinyl chloride)/γ-butyrolactone systems.

(Keywords: sol–gel transition; polymer solution; spinodal decomposition; crystallization; hydrogen bonding; percolation)

INTRODUCTION

It is well known that some polymer solutions lose their fluidity gradually upon cooling. They recover the fluidity on heating. This thermoreversible phenomenon is called a sol–gel transition. Familiar polymer–solvent systems exhibiting the sol–gel transition are poly(vinyl alcohol) in water, gelatin in water, and poly(vinyl chloride) in dibutyl phthalate[1,2]. It is generally agreed that gelation is the result of network formation. However, the nature of the tie points in the network is the subject of some controversy.

Basically, we have three models for the tie points in networks. The classic model by Eldridge and Ferry[3] considers them to be a hydrogen-bonding type association of polymer chains (HBA). The second model is that of polymer crystallite formation (PC). This has been supported by extensive discussions on 'gel melting' behaviour in terms of the thermodynamics of melting-point depression[4–6] and a number of crystallographic studies on the crystallites[7–9]. The third model is associated with liquid–liquid phase separation (LL). The LL model originates from the proposals by Labudzinska *et al.*[10] and Paul[11]. They suggested that gelation is induced by phase separation into polymer-rich and polymer-poor regions. Prins *et al.*[12,13] made the LL model clearer by applying the concept of spinodal decomposition to the gelation process. That is, they interpreted the origin of the network structure in terms of connectivity of the polymer-rich phase. On the same lines as theirs, we have undertaken a more quantitative study on the dynamics of gelation by light scattering, resulting in somewhat different conclusions[14,15].

As will be reviewed in the next section, an important conclusion from our results is that there certainly exists a mode of gelation in which spinodal decomposition takes place at the early stage of gelation; however, the spinodal decomposition (LL) is not only a necessary condition but also a sufficient one for the sol–gel transition. In order to understand the entire mechanism of sol–gel transition, we have to go back once again to the older concepts: HBA and PC.

In this paper, we will first describe the background of sol–gel transition. Then we discuss theoretically the relation between the three aspects, HBA, PC and LL, resulting in a comprehensive understanding of the sol–gel transition.

BACKGROUND

Our experimental results by light scattering[14,15] are reproduced in *Figure 1*. An outline of the experimental procedure is described in Appendix I.

As shown in *Figure 1*, both polymer solutions had an *UCST* (upper critical solution temperature) type phase diagram. The spinodal curve and the sol–gel transition curve divided the phase diagram below the melting-point depression curve into four regions labelled (i) to (iv). In region (i) the solution was a sol. In region (ii), phase separation by spinodal decomposition took place but the solution did not change to a gel. In region (iii), both gelation and spinodal decomposition occurred. In other words, gelation was accompanied by liquid–liquid phase separation through spinodal decomposition. In region (iv), gelation took place without liquid–liquid phase separation.

The presence of region (ii) implies that liquid–liquid phase separation by spinodal decomposition does not always induce gelation. The presence of region (iv) means that spinodal decomposition is not a necessary condition for gelation. However, there exists a region in which gelation accompanies spinodal decomposition. This may correspond to the situation discussed by Labudzinska *et al.*[10], Paul[11] and Prins *et al.*[12–14]

---

* Presented in part at the 35th Annual Meeting of the Society of Polymer Science, Japan, May 1986 (*Polym. Prepr. Jpn.* 1986, 35(4)).
† To whom correspondence should be addressed.

0032-3861/87/060980–05$03.00

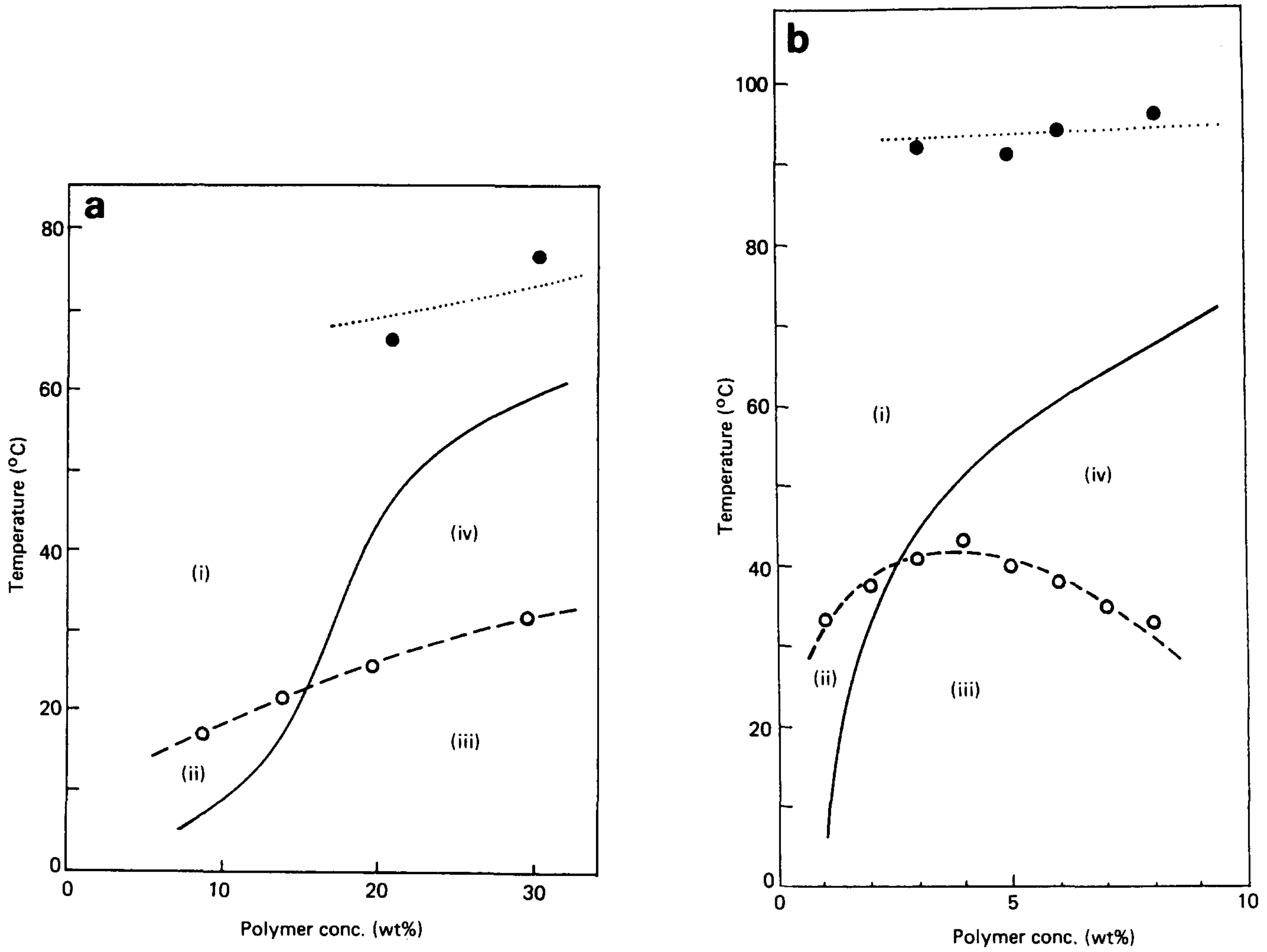

Figure 1 Phase diagrams observed in (a) PVA ($\bar{P}_n = 500$)/water and (b) PVC ($\bar{P}_n = 3200$)/γ-butyrolactone: (———) sol–gel transition curve; (– – –) spinodal curve; and (·····) gel-melting curve

In regions (iii) and (iv), for example, in the PVA system, a broad X-ray diffraction peak at $2\theta = 19.3°$ was observed after a gelation time of more than 20 h. The diffraction peak is assigned to the (010) diffraction from PVA crystallites. That is, liquid–solid phase separation takes place in the late stages of gelation in both regions (iii) and (iv). So the problem is, why are the regions (i) and (iv) separated by the sol–gel transition curve? The presence of region (i) implies that crystallization does not always induce gelation. It is reasonable to think that, although gelation in region (iv) is accompanied by crystallization at a very late stage, it should be induced initially by a mechanism different from crystallization. It may be assigned to a hydrogen-bonding type association of the polymer chains, as will be discussed later.

On the other hand, the sol–gel transition can be discussed in terms of a modern theory developed by Coniglio *et al.*[16] as the site–bond correlation-percolation problem. The sol–gel transition curve predicted by this theory crosses the coexistence (liquid–liquid phase equilibrium) curve, just as is shown in *Figure 1*. That is, speaking qualitatively, the shape of the sol–gel transition curve observed and the positional relation between it and the coexistence curve (instead, spinodal curve in *Figure 1*) in the phase diagram are exactly the same as predicted by the percolation theory.

This encourages us to examine more quantitatively the relation between the sol–gel transition, liquid–liquid phase equilibrium and also crystallization (liquid–solid phase equilibrium). It is expected that these three are not entirely independent but are related to each other through thermodynamic and molecular parameters, such as polymer–solvent interaction, molecular weight and so on. In the next section, we will describe theoretically the relation to answer the above question on the nature of gelation in region (iv).

THEORETICAL

The Flory–Huggins expression for the free energy of mixing ΔG for a binary solution consisting of a solvent (subscript 1) and a polymer (subscript 2) is

$$\frac{\Delta G}{RT}=\frac{\phi_1}{V_1}\ln\phi_1+\frac{\phi_2}{V_2}\ln\phi_2+\chi_{12}\phi_1\phi_2 \qquad (1)$$

where ϕ_i is the volume fraction, V_i is the molar volume and χ_{12} is the interaction parameter[17]. The second derivative of ΔG with respect to ϕ_2 is zero at the spinodal:

$$\frac{1}{V_1\phi_1}+\frac{1}{V_2\phi_2}-2\chi_{12}+2\frac{\partial\chi_{12}}{\partial\phi_2}(1-2\phi_2)=0 \qquad (2)$$

where χ_{12} is assumed to be a function of ϕ_2 and temperature T:

$$\chi_{12}=A+(B/T)+C\phi_2 \tag{3}$$

Here B is the exchange energy parameter defined by

$$B=\frac{zV_1}{2RV_u}(W_{11}+W_{22}-2W_{12}) \tag{4}$$

and z is the coordination number, W_{ij} is the van der Waals interaction energy between component i and j, and V_u is the molar volume of the polymer segment.

The value of W_{ii} may be estimated as $W_{ii}=(2/z)\delta_i^2$, where δ_i is the solubility parameter. When the measured value of the solubility parameter is not available, δ_i is calculated by using Small's molar attraction method[18]. Fitting equation (2) and the critical condition

$$\partial^2\Delta G/\partial\phi_2^2=\partial^3\Delta G/\partial\phi_2^3=0$$

to the observed spinodal curve, one can determine the values of A, B and C in (3). Hence the value of W_{12} in (4) is obtained.

Flory's formulation of the melting-point depression of a polymer due to the presence of a solvent is

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}=\frac{R}{\Delta H_u}\frac{V_u}{V_1}\left[-\frac{\ln\phi_2}{\bar{P}_n}+\left(1-\frac{1}{\bar{P}_n}\right)(1-\phi_2)-\chi_{12}\phi_1^2\right] \tag{5}$$

where ΔH_u is the heat of fusion per mole of polymer segments, T_m° the melting point of pure polymer, T_m the melting point of polymer in the presence of solvent, and $\bar{P}_n$ the degree of polymerization[19].

The values of ΔH_u and T_m° are available in the literature[20,21]. Using the value of χ_{12} obtained by fitting the spinodal curve, we are able to calculate the melting-point depression curve.

In modern theory of gelation developed by Coniglio *et al.*[16] as the site–bond correlated-percolation problem, polymer segments are allowed to interact with each other in two ways: one is by van der Waals interaction, the other by a directional interaction which leads to the tie point in the gel. When an infinite network is formed via the directional interaction, the system is gelled. In our thermoreversible gel, the directional interaction is assumed to be hydrogen bonding. So, the system involves four nearest-neighbour interactions: solvent–solvent ($-W_{11}$), solvent–polymer segment ($-W_{12}$), van der Waals interaction between polymer segments ($-W_{22}$), with weight ρ, and hydrogen-bonding interaction between polymer segments ($-E$) with weight $(1-\rho)$. When the number of interactions per polymer segment and per solvent molecule is equal to 3 (see *Figure 2*) the gelation threshold $\phi_{2,g}$ is given by

$$\phi_{2,g}\simeq\frac{3\bar{P}_nP_Bu^2}{(2\bar{P}_nP_B-1)u^2+(\bar{P}_nP_B-1)^2} \tag{6}$$

where P_B is the probability that the directional interaction is present between two nearest-neighbour polymer segments:

$$P_B=\frac{(1-\rho)\exp(E/RT)}{\rho\exp(W_{22}/RT)+(1-\rho)\exp(E/RT)}$$

and u is

$$u=\left[\rho\exp\left(\frac{W_{11}+W_{22}-2W_{12}}{RT}+f(\phi_2)\right)+(1-\rho)\exp\left(\frac{W_{11}+E-2W_{12}}{RT}+f(\phi_2)\right)\right]^{-2}$$

where

$$f(\phi_2)=\frac{2V_u(A+C\phi_2)}{zV_1}$$

Fitting (6) to the sol–gel transition curve observed, one can estimate the values of E and ρ, since the values of the other parameters are known by the above procedure for the spinodal curve.

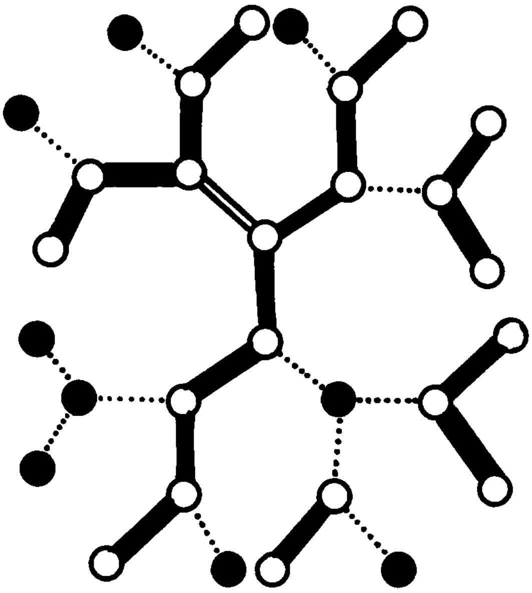

Figure 2 Interactions in the polymer(heavy line)/solvent(closed circle) system: van der Waals interaction (dotted line) and hydrogen-bonding interaction between polymers (double line)

Table 1 Values of various parameters employed for fitting in the PVC/γ-butyrolactone system

Parameter	Value
V_1	76.1 $\mathrm{cm^3\,mol^{-1}}$
V_u	44.6 $\mathrm{cm^3\,mol^{-1}}$
$\bar{P}_n$	3200
δ_1	11.2 $(\mathrm{cal\,cm^{-3}})^{1/2}$ [a]
δ_2	9.6 $(\mathrm{cal\,cm^{-3}})^{1/2}$ [b]
$-W_{11}$	-2.25 $\mathrm{kcal\,mol^{-1}}$
$-W_{22}$	-1.75 $\mathrm{kcal\,mol^{-1}}$
$-W_{12}$	-2.04 $\mathrm{kcal\,mol^{-1}}$
$-E$	-9.23 $\mathrm{kcal\,mol^{-1}}$
ρ	0.9999999
H_u	900 $\mathrm{cal\,mol^{-1}}$ [c]
T_m°	212°C [d]
A	0
B	350 K
C	0.038

[a] Small's method
[b] 'Polymer Handbook'
[c] 858 $\mathrm{cal\,mol^{-1}}$ in ref. 20
[d] See ref. 21

RESULTS AND DISCUSSION

In *Table 1* is shown a set of parameters used in fitting the theoretical curves to the experimental ones for the PVC solution. The calculated curves are shown in *Figure 3*. The situation in *Figure 1* is exactly described in *Figure 3*. It is also noted that the value of E is a reasonable one for the hydrogen-bonding energy. These results suggest that gelation in region (iv) is due to a hydrogen bonding type association of the polymer chains.

Based on these results, we will summarize the mechanism of sol–gel transition. The sol–gel transition pretends to be a complicated phenomenon. However, we believe that the apparent complexity comes from a sequential superposition of three fundamental phenomena: hydrogen-bonding type association, crystallite formation (liquid–solid phase separation) and liquid–liquid phase separation by spinodal decomposition. The mode of superposition may be determined by the kinetics of the individual phenomena, as is typically demonstrated by the following plausible scenario.

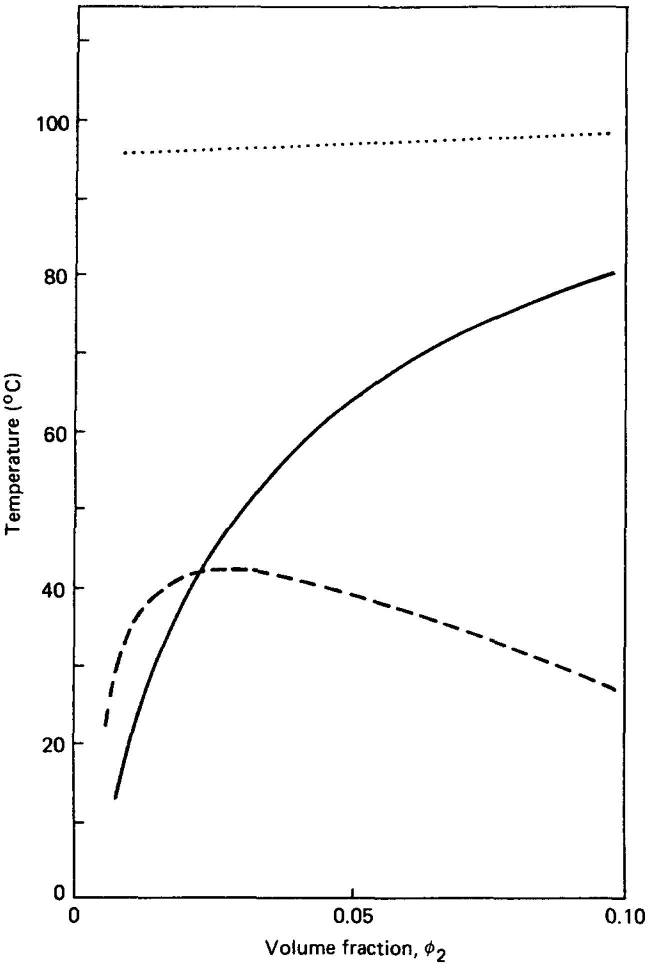

Figure 3 Phase diagram calculated for the PVC ($\bar{P}_n = 3200$)/γ-butyrolactone system: (———) percolation curve; (– – – –) spinodal curve; and (·····) melting-point depression curve

In region (iv), the system is initially gelled by percolation through hydrogen bonding (see *Figure 4a*). Later, network chains are organized into crystallites to form a fringed-micelle type network swollen with solvent (see *Figure 4b*).

In region (iii), spinodal decomposition takes place, resulting in the development of an interconnected structure of polymer-rich and polymer-poor regions (see *Figure 4c*). This is a fast process. Then gelation in the polymer-rich region follows. This gelation may be carried out in a way similar to that in region (iv), i.e. first by hydrogen bonding, then by crystallization*.

In region (ii), spinodal decomposition takes place. However, the system fails to change to a gel, because the connectivity of the polymer-rich region is interrupted, resulting in isolated droplets of polymer-rich phase. This is due to the small volume fraction of polymer-rich phase†, as expected from the location of region (ii) in the phase diagram.

In region (i), the solution does not change to a gel, because the probability of chain association by hydrogen bonding is too low to form an infinite network. Even if crystallites are formed at a very late stage, they might be isolated crystallites, which do not act as tie points of the network.

It is expected that these competitive situations will be clarified in a quantitative way in future. Finally, we will

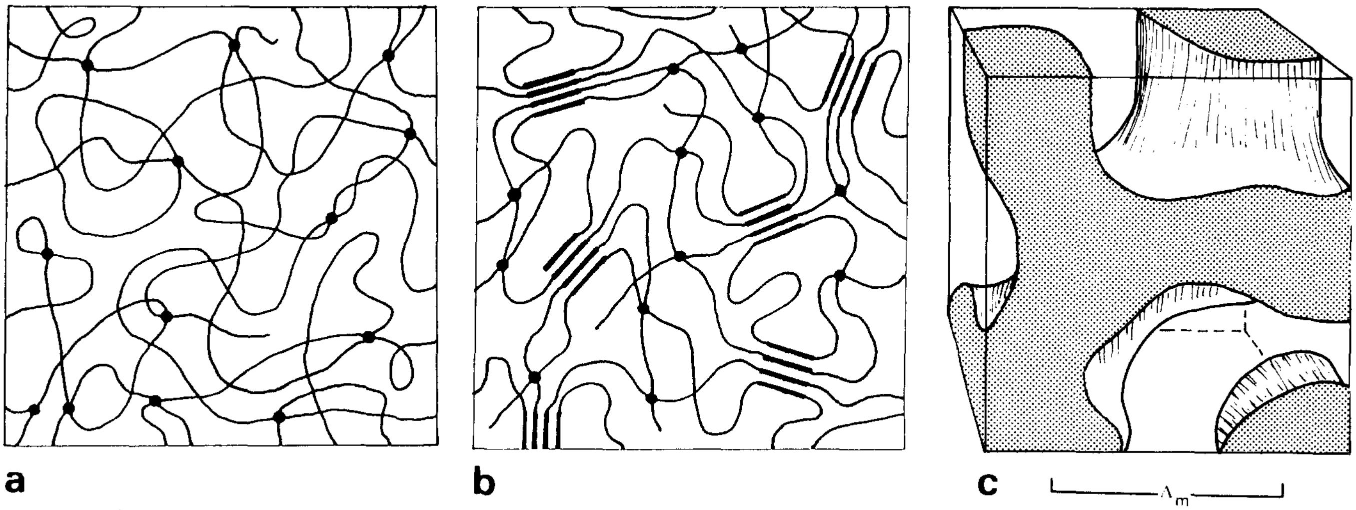

Figure 4 Schematic representations of: (a) a network formed by hydrogen bonding; (b) a fringed-micelle type network swollen with solvent; and (c) the unit cell of the interconnected structure by spinodal decomposition. (In the case of aqueous PVA solution, crystallite size was ~50 Å by X-ray diffraction and the periodic distance Λ_m in the interconnected structure was ~0.3 μm (ref. 14)

---

* The polymer-rich phase is immobilized by gelation. It suppresses further coarsening of the interconnected structure developed by spinodal decomposition. We believe that this type of behaviour must be characteristic of spinodal decomposition in solutions of gel-forming polymers.

† According to the results of computer simulation of spinodal decomposition by Cahn (*J. Chem. Phys.* **42**, 93), the interconnectivity of phases is not accomplished when the volume fraction of minor phase is less than 15%.

demonstrate a possibility that the situation depends on the molecular weight of polymer. This is shown in Appendix II.

APPENDIX I

An outline of the experimental procedures resulting in *Figure 1* (for the case of PVA solution) will be described here.

Aqueous solutions were made up in an n.m.r. tube with inner diameter 6.7 mm by gradual heating to 100°C. The solution was quenched in a water bath kept at constant temperature. After standing for 88 h, the test tube was tilted. When the meniscus deformed under its own weight, we judged that the solution was still a sol. When the meniscus could not be seen to deform, we judged that the system had gelled. Thus, by visual investigations, the sol–gel transition curve was determined.

Similar temperature-drop experiments were carried out in a light scattering photometer. The change in angular distribution of scattered light intensity with time was measured during isothermal phase separation. According to Cahn's linear theory of spinodal decomposition, we obtained the apparent diffusion coefficient $\tilde{D}$. From the temperature dependence of $\tilde{D}$, the spinodal temperature was determined as the temperature at which $\tilde{D}$ is zero.

The gel prepared by standing for a week at 22°C was gradually ($\sim 10^{\circ}\mathrm{C}\ \mathrm{h}^{-1}$) heated up in a water bath keeping the test tube upside down. The gel melting point was the temperature at which the level meniscus began to deform.

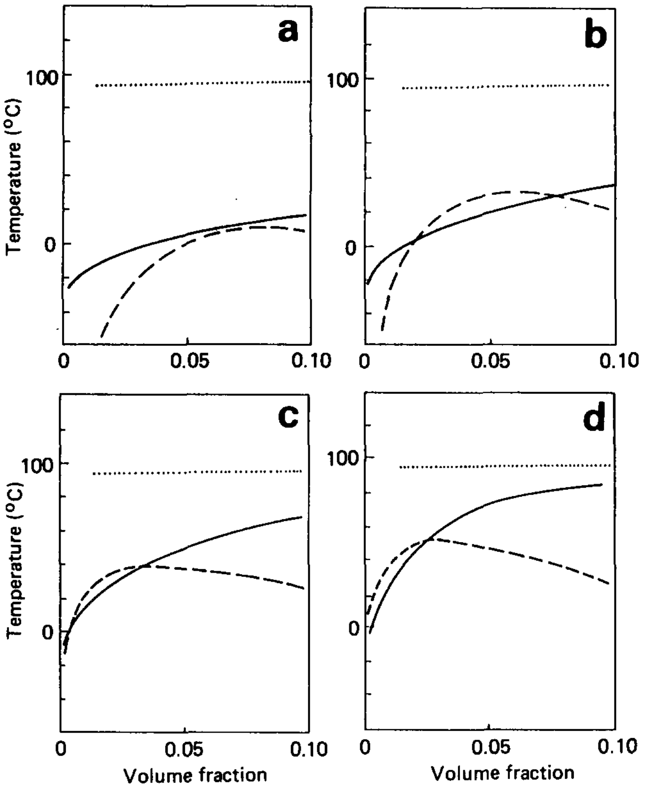

Figure 5 Effect of molecular weight on phase diagram, calculated for the PVC/γ-butyrolactone system: (a) $\bar{P}_n = 200$, (b) $\bar{P}_n = 500$, (c) $\bar{P}_n = 2000$, (d) $\bar{P}_n = 4000$

APPENDIX II

Figure 5 shows the calculated results, demonstrating the effect of molecular weight of PVC on the phase diagram. When $\bar{P}_n$ is very small, the spinodal curve does not cross the percolation curve. On increasing $\bar{P}_n$ the percolation curve became sharp and the *UCST* finally locates below the percolation curves. The system discussed in the text is situated between *Figures 5c* and *5d*. Systems with different phase diagrams may have different modes of sequential superposition.

REFERENCES

1 Harrison, M. A., Morgan, P. H. and Park, G. S. *Eur. Polym. J.* 1972, **8**, 1361
2 Rogovina, L. Z. and Slonimskii, G. L. *Russ. Chem. Rev.* 1974, **43**(6), 503
3 Eldridge, J. E. and Ferry, J. D. *J. Phys. Chem.* 1954, **58**, 992
4 Takahashi, A., Nakamura, N. and Kagawa, I. *Polym. J.* 1972, **3**, 207
5 Matsuzawa, S., Yamaura, K., Maeda, R. and Ogasawara, K. *Makromol. Chem.* 1979, **180**, 229
6 Ogasawara, K., Nakajima, T., Yamaura, K. and Matsuzawa, S. *Colloid Polym. Sci.* 1976, **254**, 982
7 Guerrero, S. J., Keller, A., Soni, P. L. and Geil, P. H. *J. Macromol. Sci. Phys.* 1981, **B20**, 167
8 Guerrero, S. J., Meader, D. and Keller, A. *J. Macromol. Sci. Phys.* 1981, **B20**, 185
9 Guerrero, S. J., Keller, A., Soni, P. L. and Geil, P. H. *J. Macromol. Sci. Phys.* 1981, **B20**, 167
10 Labudzinska, A. and Ziabicki, A. *Kolloid Z. Z. Polym.* 1971, **243**, 21
11 Paul, D. R. *J. Appl. Polym. Sci.* 1976, **11**, 439
12 Prins, E. and Prins, W. *Macromolecules* 1973, **6**, 888
13 Feke, G. T. and Prins, W. *Macromolecules* 1974, **7**, 527
14 Komatsu, M., Inoue, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 303
15 Kawanishi, K., Takeda, Y. and Inoue, T. *Polym. J.* 1986, **18**, 411
16 Coniglio, A., Stanley, H. E. and Klein, W. *Phys. Rev. Lett.* 1979, **42**, 518
17 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953, Chs. 12 and 13
18 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71
19 Garden, J. L. *J. Paint Technol.* 1966, **38**, 43
20 Anagnostopoulos, C. E., Coran, A. Y. and Gamrath, H. R. *J. Appl. Polym. Sci.* 1960, **4**, 181
21 Walter, A. T. *J. Polym. Sci.* 1954, **13**, 207