Solution Properties of Water–Poly(ethylene glycol)–Poly(*N*-vinylpyrrolidone) Ternary System

Isamu INAMURA, Yuji JINBO,^{†,††} Makoto KITAKA, and Ai ASANO

Department of Material Science, Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan

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ABSTRACT: Viscosity and density measurements as well as determination of binodal curves were made for a water–PEG–PVP ternary system. In the system, a hydrodynamic interaction parameter Δb_{23} suggested that a repulsive interaction worked between PEG and PVP molecules and the strength of interaction became strong with increasing molecular weight of the samples. Temperature dependence of partial specific volume $\bar{v}$ could be explained in terms of the amount of hydrated water attracted by each polymer chain. Molecular weight and temperature dependence of binodal curves were obviously related to those of Δb_{23} . Consequently, it is considered that Δb_{23} is closely related to the Flory–Huggins interaction parameter χ_{23} . However, binodal curves were only partially consistent with the Flory–Huggins theory for the solvent 1–polymer 2–polymer 3 ternary system. To explain the binodal behavior, χ_{23} is not only a function of temperature but also a function of polymer-composition as well as that of Δb_{23} . The hydration of each polymer chain relating to interaction parameters χ_{21} and χ_{31} is also an important factor for the binodal behavior.

KEY WORDS Ternary Solution / Viscosity / Partial Specific Volume / Hydration / Liquid–Liquid Phase Separation / Flory–Huggins Theory / Intermolecular Interaction /

We recently reported temperature and/or polymer-composition dependence of the intrinsic viscosity $[\eta]$, Huggins constant k' , hydrodynamic interaction parameter between different polymer species Δb_{23} ,^{1,2} and partial specific volume $\bar{v}$,^{3,4} for various water 1–polymer 2–polymer 3 ternary systems. In these systems, polymer 2 and polymer 3 were chosen from the following water-soluble polymers: poly(ethylene glycol) (PEG), poly(*N*-vinylpyrrolidone) (PVP), poly(vinyl alcohol) (PVA), dextran (Dex), and pullulan (Pul). Generally, $[\eta]$ and $\bar{v}$ reflect a hydrodynamic volume of a polymer chain in solution, k' reflects overall hydrodynamic interactions between polymers in solution,⁵ and Δb_{23} is restricted to interactions between two different polymer species in solution.

Further, we reported binodal curves for a water–PEG–PVA ternary system.^{6,7} In this system, molecular weight dependence of binodal curve was fairly consistent with predictions of the Flory–Huggins theory for the water 1–polymer 2–polymer 3 ternary system.^{8,9} Hefford¹⁰ reported binodal curves for both water–PEG–PVP and water–PEG–Dex ternary systems. However, binodal curves he determined were only partially consistent with the Flory–Huggins theory. He insisted that the disagreement was caused by an abnormal property of PEG in water.

The present study shows the results of molecular weight, polymer-composition, and/or temperature dependence of $[\eta]$, k' , Δb_{23} , and $\bar{v}$ for a water–PEG–PVP ternary system, and details the solution proper-

ties in terms of intermolecular interactions. We also present molecular weight and temperature dependence of binodal curves for the same ternary system, and examine the relation between phase behavior and the results of viscosity and density measurements including our previous results.^{1–4,6,7}

To explain binodal curves, theoretical results of phase equilibrium for the solvent 1–polymer 2–polymer 3 ternary system⁹ are briefly summarized. We deal with the relation between Δb_{23} and the Flory–Huggins interaction parameter χ_{23} , and point out various factors neglected in the Flory–Huggins theory.

FLORY–HUGGINS THEORY FOR THE SOLVENT 1–POLYMER 2–POLYMER 3 TERNARY SYSTEM

This section briefly describes the Flory–Huggins theory for the ternary system consisting of solvent 1, polymer 2, and polymer 3. According to the Flory–Huggins treatment, the change of chemical potential $\Delta\mu_i$ for i component by mixing in the ternary system is expressed as

$$\begin{aligned}\Delta\mu_1 &= RT\{\ln\phi_1 + [1 - (1/x_2)]\phi_2 \\ &\quad + [1 - (1/x_3)]\phi_3 + \chi_{21}\phi_2^2 + \chi_{31}\phi_3^2 \\ &\quad + (\chi_{21} + \chi_{31} - \chi_{23})\phi_2\phi_3\} \\ \Delta\mu_2 &= RT\{\ln\phi_2 + (1 - x_2)\phi_1 \\ &\quad + [1 - (x_2/x_3)]\phi_3 + x_2[\chi_{21}\phi_1^2 + \chi_{23}\phi_3^2]\end{aligned}\quad (1a)$$

[†]To whom correspondence should be addressed (Tel: +81-238-26-3188, Fax: +81-238-26-3177, E-mail: yjinbo@yz.yamagata-u.ac.jp).

^{††}Present address: Graduate School of Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan.

$$+ (\chi_{21} + \chi_{23} - \chi_{31})\phi_1\phi_3\} \quad (1b)$$

$$\begin{aligned} \Delta\mu_3 = RT\{\ln\phi_3 + (1 - x_3)\phi_1 \\ + [1 - (x_3/x_2)]\phi_2 + x_3[\chi_{31}\phi_1^2 + \chi_{23}\phi_2^2 \\ + (\chi_{31} + \chi_{23} - \chi_{21})\phi_1\phi_2]\} \end{aligned} \quad (1c)$$

where RT is the gas constant multiplied by the absolute temperature, and x_i and ϕ_i are the degree of polymerization and volume fraction of i component, respectively. The Flory-Huggins interaction parameter χ_{ij} is expressed by,

$$\chi_{ij} = z\Delta w_{ij}/kT \quad (2)$$

where z and k are the number of neighboring lattice points and the Boltzmann constant, respectively, and Δw_{ij} is an energy change by forming a contact pair of i and j .

When two phases exist at equilibrium, chemical potentials of the components must be the same in the two phases. Then,

$$\Delta\mu'_1 = \Delta\mu''_1 \quad (3a)$$

$$\Delta\mu'_2 = \Delta\mu''_2 \quad (3b)$$

$$\Delta\mu'_3 = \Delta\mu''_3 \quad (3c)$$

Here, single and double primes denote the two phases, respectively.

Scott⁹ calculated the theoretical binodal curve for the ternary system with $x_2 \neq x_3$ by 'dilution approximation' method, *i.e.*, the role of solvent is only to dilute each phase separated in a polymer 2-polymer 3 binary system. Then the volume fraction of solvent in the two phases is the same and the following relations hold:

$$\phi'_1 = \phi''_1 \quad (4a)$$

$$\phi'_2 = \phi''_3 \quad (4b)$$

$$\phi'_3 = \phi''_2 \quad (4c)$$

Substituting these conditions into Eq 1b and let $\chi_{21} = \chi_{31}$ (the interaction of each monomer unit with the solvent is the same regardless of polymer species), binodal curves for the ternary system can be obtained by the following equations:

$$\begin{aligned} \ln\theta'_2 + [1 - (x_2/x_3)]\theta'_3 + x_2\chi_{23}(1 - \phi_1)\theta_3^2 \\ = \ln\theta'_2 + [1 - (x_2/x_3)]\theta'_3 + x_2\chi_{23}(1 - \phi_1)\theta_3^2 \end{aligned} \quad (5a)$$

$$\begin{aligned} \ln\theta'_3 + [1 - (x_3/x_2)]\theta'_2 + x_3\chi_{23}(1 - \phi_1)\theta_2^2 \\ = \ln\theta'_3 + [1 - (x_3/x_2)]\theta'_2 + x_3\chi_{23}(1 - \phi_1)\theta_2^2 \end{aligned} \quad (5b)$$

with $\theta'_2 = \phi'_2/(\phi'_2 + \phi'_3)$ and $\theta'_3 = \phi'_3/(\phi'_2 + \phi'_3)$. Equations 5a and 5b contain only one interaction parameter χ_{23} and the following significant conclusions are obtained.

Table I. PEG and PVP samples used

Sample	$M_w/10^4$	M_w/M_n	Supplier
PEG(2.1)	2.1	1.10	Kishida Chemical Co., Ltd.
PEG(30)	30	—	Aldrich Chemical Company, Inc.
PVP(3.3)	3.28	2.08	Kishida Chemical Co., Ltd.
PVP(4.0)	4.0	—	Kishida Chemical Co., Ltd.
PVP(36)	36	—	Kishida Chemical Co., Ltd.

- (1) When x_2/x_3 is close to 1, the binodal curve in a triangular diagram is symmetric and moves toward the solvent apex with increasing χ_{23} or with increasing molecular weight of two samples.
- (2) When x_2 is fixed but x_3 varied, the binodal curve moves toward the solvent apex and simultaneously inclines toward the solvent 1-polymer 2 axis as x_3 increases.
- (3) When the solution temperature decreases, the binodal curve moves toward the solvent apex due to the temperature term of χ_{23} in Eq 2.

EXPERIMENTAL

Materials

Polymer samples used are listed in Table I. Numbers in parentheses for polymer samples indicate the weight-averaged molecular weight M_w divided by 10^4 . Values of M_w and M_w/M_n (M_n is the number-averaged molecular weight) given by suppliers are shown. All samples were further purified by reprecipitation using a benzene-acetone mixed-solvent for PEG samples and a water-acetone mixed-solvent for PVP samples, respectively.

Viscometry

Viscosity measurements were made at 30 °C using a conventional capillary viscometer of the Ubbelohde type. The polymer mass concentration c (g cm⁻³) of aqueous solutions was determined by a dry method, *i.e.*, each mixed solution and original aqueous solutions of PEG and PVP with a constant volume were dried in vacuum until a constant weight was obtained. The intrinsic viscosity $[\eta]$ and Huggins constant k' for the systems were determined from a common intercept at $c = 0$ and initial slopes of the following plots: η_{sp}/c vs. c , $\ln\eta_r/c$ vs. c , and $[2(\eta_{sp} - \ln\eta_r)]^{1/2}/c$ vs. c plots. Here, $\eta_{sp} (= \eta_r - 1)$ is a specific viscosity.

The intermolecular interaction parameter Δb_{23} was calculated as follows.¹ The specific viscosity $(\eta_{sp})_m$ for a ternary solution with the total mass concentration c_m is,

$$\begin{aligned} (\eta_{sp})_m/c_m = ([\eta]_2w_2 + [\eta]_3w_3) + (k'_2[\eta]_2^2w_2^2 \\ + 2b_{23}w_2w_3 + k'_3[\eta]_3^2w_3^2)c_m \end{aligned} \quad (6)$$

where $[\eta]_i$ and k'_i are the intrinsic viscosity and Huggins constant for the binary system consisting of the solvent and polymer i , respectively, and w_i is the weight fraction of polymer i against total polymer weight. An interaction parameter b_{23} is a complicated parameter in which hydrodynamic, thermodynamic, and other possible intermolecular interactions are included. Assuming the absence of thermodynamic interactions, we evaluate the theoretical intermolecular interaction parameter b^*_{23} by,

$$b^*_{23} = (k'_2 k'_3 [\eta]_2^2 [\eta]_3^2)^{1/2} \quad (7)$$

The interaction parameter Δb_{23} is obtained as,

$$\Delta b_{23} = b_{23} - b^*_{23} \quad (8)$$

The magnitude of Δb_{23} represents the strength of interaction, and its positive or negative sign indicates that the intermolecular interaction between two different polymer species is attractive or repulsive, respectively. When Δb_{23} coincides to zero, it means that polymer 2 and polymer 3 in the ternary system do not affect each other.

Density Measurements

Density measurements were made at 4, 25, 30, and 40 °C using a Lipkin–Devison type pycnometer with 5 cm³ capacity. The specific volume $\bar{v}$ was calculated from the density increment $\partial\rho/\partial c$ at infinite dilution and solvent density ρ_0 as,

$$\bar{v} = [1 - (\partial\rho/\partial c)]/\rho_0 \quad (9)$$

Phase Diagrams

Phase diagrams for the water–PEG–PVP system were obtained as follows. We prepared highly concentrated aqueous solutions of PEG and PVP independently. The mass concentration was determined by the same method as above. Suitable amounts of each PEG and PVP solution were placed in sample tubes with stoppers using a pipette to prepare mixed solutions with an arbitrary PEG/PVP mixing ratio. Fifteen mixed solutions were prepared. Each mixed solution was immersed in a water bath kept at 10 ± 0.04 °C or at 30 ± 0.04 °C for 15 min with stirring and observed whether the solution was turbid due to a liquid–liquid phase separation or transparent by monitoring a mark behind the sample tube. The solution was diluted step by step to a lower polymer concentration by adding water using a burette until it became transparent at equilibrium. Thus, a critical concentration where the liquid–liquid phase separation occurred was determined.

Figure 1. Molecular weight and polymer-composition dependence of (a) the intrinsic viscosity $[\eta]$, (b) Huggins constant k' , and (c) intermolecular interaction parameter Δb_{23} for the water–PEG–PVP ternary system at 30 °C. Unfilled and filled circles indicate data points for the low and high molecular weight systems, respectively.

RESULTS AND DISCUSSION

Figure 1a shows results of $[\eta]$ for the water–PEG–PVP systems at 30 °C. The polymer-composition is denoted by weight-percent of PVP against total polymer weight. Results of $[\eta]$ drastically increase with molecular weight of two polymer samples. In binary systems at both axes, data points increase with $M_w^{0.70}$ for PEG in water and $M_w^{0.72}$ for PVP in water, respectively. These viscosity indices are close to a reference value for PEG in water (0.78)¹¹ and that for PVP in water (0.70)¹² at 30 °C, suggesting that both chains in solution take flexible conformations with an excluded volume effect.¹³ As for the polymer-composition dependence of $[\eta]$, an additivity relationship is retained in both systems. This is reasonable because $[\eta]$ reflects the hydrodynamic volume of a single polymer chain at infinite dilution where any intermole-

cular interactions vanish.

Panel (b) shows results of k' for the same system in Panel (a). As the molecular weight of the system increases, k' slightly decreases at any composition, and the negative deviation from the additivity line represented by each dotted line becomes small so that the data points almost coincide with the additivity line.

Panel (c) shows results of Δb_{23} for the same system in Panel (a). Values of Δb_{23} negatively increase with molecular weight of the samples. This suggests that a *repulsive* intermolecular interaction between PEG and PVP molecule becomes strong with increasing molecular weight. As can be seen for the high molecular weight system, Δb_{23} depends on the polymer-composition, suggesting that other surrounded polymers in the system affect the intermolecular interaction between two different polymer species to some extent. As reported previously,¹ Δb_{23} is a function of temperature. Consequently, the interaction parameter Δb_{23} is at least functions of molecular weight, polymer-composition, and temperature.

Figure 2 shows results of $\bar{v}$ for the water-PEG(2.1)-PVP(4.0) system. Values of $\bar{v}$ for the same polymer-composition increase with solution temperature. We have recently found that $\bar{v}$ for a PVA in water (binary system) has a similar temperature dependence, though it is not shown here. Such temperature dependence of $\bar{v}$ may be caused by reduction of the hydrodynamic volume of polymer chains in solution as the solution temperature increases. Since the hydrodynamic vol-

ume of a polymer in solution reflected on $\bar{v}$ is proportional to the number of solvent molecules excluded by 1 g of the polymer by definition, intermolecular interactions between solvent and polymer may affect on the amount of solvent molecules excluded. That is, when a polymer chain attracts excess solvent molecules from the bulk region at low temperature, the amount of solvent molecules excluded by the polymer reduce and then the hydrodynamic volume or $\bar{v}$ of polymer chain decreases. The density of hydrated water is greater than that of bulk water,¹⁴ indicating that the hydrated water is attracted by polymer from the bulk region. Consequently, as the attractive intermolecular interaction between water and polymer weakens at high temperature, the amount of hydrated water reduces and the value of $\bar{v}$ increases. The amount of hydrated water can be estimated from $\bar{v}$ data if the real volume of a chain is known.

The reduction of hydrodynamic volume of a chain due to reduction of the amount of hydrated water is supported by our previous viscosity result^{1,2} where $[\eta]$ for the water-PEG-PVP system decreases with increasing solution temperature. The hydration effect is correlated to interaction parameters χ_{21} and χ_{31} in Eqs 1a through 1c. Therefore, χ_{21} and χ_{31} should be not only a function of temperature but also a function of the amount of hydrated water.

The additivity relationship for the polymer-composition dependence of $\bar{v}$ was firstly found in the present study. It means that the amount of hydrated water of both polymer species does not change by mixing of PEG and PVP molecules in solution, *i.e.*, χ_{21} and χ_{31} are constant even if two samples are mixed with various compositions. However, we cannot conclude this strongly, because the intermolecular interaction between two different polymers Δb_{23} may affect on χ_{21} and χ_{31} .

Figure 3 shows molecular weight (①, ②, and ③) and temperature (③ and ④) dependence of binodal curves for the water-PEG-PVP system. As molecular weight of polymers increases, ③ to ② and further ② to ①, the binodal curve moves toward the water apex on the triangular diagram, indicating that miscibility of different polymer species decreases with molecular weight. This is consistent with the molecular weight dependence of Δb_{23} , *i.e.*, a repulsive intermolecular interaction became strong and miscibility became poor as molecular weight increases.

It is interesting that our binodal curves are very similar in shape to those obtained by Hefford¹⁰ who determined binodal points by measuring refractive indices of the two phases. Therefore, our simple method is convenient for determining the binodal points qualitatively. Note that the feature of our and Hefford's binodal curves for the water-PEG-PVP system seem to

Figure 2. Temperature and polymer-composition dependence of partial specific volume $\bar{v}$ for the water-PEG-PVP ternary system.

Figure 3. Molecular weight dependence (①, ②, and ③) of binodal curve for the water-PEG-PVP ternary system at 30 °C; combinations of molecular weight divided by 10^4 for PEG/PVP mixtures are ① 30/36, ② 2.1/36, and ③ 2.1/4.0, respectively. Temperature dependence (③ at 30 °C and ④ at 10 °C) of binodal curve for the PEG(2.1)/PVP(4.0) system.

be opposed to the theoretical conclusions (1) and (2) described in the theoretical section. That is, binodal curves always inclined toward the water-PEG axis irrespective of the molecular weight ratio PEG/PVP in the system.

One reason for these disagreements may be the wide molecular weight distribution of the samples used. Results of phase equilibrium are significantly affected by sample's molecular weight polydispersity as compared with other experimental results of viscosity and density presented in this study. Although we purified all samples by reprecipitation, M_w/M_n may be still relatively large and is unknown for three samples. Hefford also used PVP samples with $M_w/M_n = 1.7$ and 2.1. It may be considered that the high molecular weight component in the polydispersed sample moves the binodal curve toward the solvent apex and simultaneously inclines the solvent-other polymer axis. However, the disagreement between theory and experiment cannot be explained only by the molecular weight polydispersity effect, since binodal curves for the water-PEG-PVP system always inclined toward the water-PEG axis even when molecular weight ratio of PEG/PVP is greater than 1 or smaller than 1. The polydispersity effect on the binodal curve is an important problem, which we should clarify in the future.

Hefford found that binodal curves for a water-PEG-Dex system also had a similar features as well as the water-PEG-PVP system, and explained the disagreement between experimental results and the Flory-Huggins theory in terms of large values of the second virial coefficient A_2 for PEG in water (binary system) compared to those for PVP in water and

Dex in water.¹⁰ According to our previous studies,^{6,7} binodal curves in a water-PEG-PVA system are fairly consistent with the Flory-Huggins theory. Nevertheless, A_2 for PVA in water reported elsewhere¹⁵ are almost the same as those for PVP in water. This opposes the argument by Hefford. Therefore, the large difference of A_2 between two different polymer species (χ_{22} and χ_{33} in the ternary system) does not always cause a disagreement between experiment and theory.

Here, it is very interesting that a ternary system where experimental results agree with the Flory-Huggins theory consists of a pair of polymers with a similar chemical composition and monomer unit size, *e.g.*, $[\text{CH}_2\text{CH}_2\text{O}]_n$ and $[\text{CH}_2\text{CH}(\text{OH})]_n$. However, a ternary system where experimental results disagree with the Flory-Huggins theory consists of a pair of polymers with different chemical compositions and monomer unit size. For instance, a monomer molecular weight ratio for PVP/PEG and Dex/PEG is 2.5 and 3.7, respectively. In the latter system the amount of hydrated water attracted by monomer unit should be different for different polymer species. In the case, the assumption $\chi_{21} = \chi_{31}$ considered in the derivation of Eqs 5a and 5b is not valid.

When the solution temperature decreases from 30 °C (③) to 10 °C (④), the binodal curve moves toward the water apex, indicating that miscibility of two different polymer species decreases with decreasing temperature. This is quite consistent with the theoretical conclusion of (3) and Eq 2. The temperature dependence of the binodal curve was consistent with the fact that Δb_{23} for the water-PEG-PVP system negatively increased with decreasing temperature,¹ *i.e.*, the repulsive intermolecular interaction between different polymer species became strong at low temperature. Since, hydrodynamic volumes of PEG and PVP chains in solution increase by the attraction of hydrated water from the bulk with decreasing temperature, change of the amount of hydrated water with temperature should affect the interaction parameter χ_{21} and χ_{31} as well as usual temperature dependence in Eq 2.

Phase equilibrium for the solvent 1-polymer 2-polymer 3 ternary system is theoretically explained by Eqs 5a and 5b using one interaction parameter χ_{23} and binodal curves obtained in this study can be explained by Δb_{23} . Therefore, it seems that χ_{23} and Δb_{23} are closely related. If so, χ_{23} should be also a function of polymer-composition as well as Δb_{23} . This may due to conformational changes of each polymer chain after phase separation. Flexible polymers may change their conformation even at high concentration by the polymer-composition change after phase separation. Polymer-composition dependence of χ_{23} is not considered in the Flory-Huggins theory.

We have dealt with some physical properties of ternary solutions based on the hydrodynamic interaction parameter Δb_{23} . Although Δb_{23} reflects thermodynamic interactions, an entangle effect and other kinetic effects in the fluid make it difficult to deal with thermodynamic interactions quantitatively. Therefore, we should determine the more quantitative thermodynamic intermolecular interaction parameter A_{23} , the second virial coefficient between two different polymer species, by light scattering, sedimentation equilibrium, and osmotic pressure measurement, and should examine the relation among Δb_{23} , A_{23} , and χ_{23} . Interaction parameters A_{23} including A_{21} and A_{31} will help to clarify the physical properties of the water–polymer–polymer ternary system quantitatively.

CONCLUSION

Solution properties for the water–PEG–PVP ternary system were investigated by viscosity and density measurements as well as phase equilibrium measurement. The hydrodynamic intermolecular interaction parameter between two different polymer species Δb_{23} was functions of molecular weight, polymer-composition, and temperature. When Δb_{23} was close to zero, Huggins constants k' for the system negatively deviated from an additivity line tied the data points of each binary system. When Δb_{23} was negatively large and a repulsive interaction is dominant, k' coincided with the additivity line.

The temperature dependence of partial specific volume may be explained by the change of the amount of hydrated water attracted by water-soluble polymers from the bulk region. The hydration effect should reflect on the Flory–Huggins interaction parameters χ_{21} and χ_{31} .

Molecular weight and temperature dependence of binodal curves may be related to Δb_{23} . Therefore, it is considered that the hydrodynamic interaction parameter Δb_{23} was proportional to the thermodynamic parameter χ_{23} . The binodal curve was partially consistent with the Flory–Huggins theory for the water–polymer–polymer ternary system. The disagreement between experimental and theoretical binodal curves was considered due to:

- (1) The molecular weight distribution of the samples used was not sufficiently narrow for the phase

equilibrium experiment in spite of purification.

- (2) When the chemical composition and size of pairing monomer units are considerably different, the amount of hydrated water attracted by each polymer should be more or less different. In that case, χ_{21} may be different from χ_{31} . However, the Flory–Huggins theory assumes $\chi_{21} = \chi_{31}$.
- (3) The interaction parameter χ_{23} should be not only a function of temperature but also a function of the polymer-composition as well as Δb_{23} . This may due to the conformational change of polymer chains after phase separation, since flexible polymers can change their conformation even at high concentration due to the change of polymer-composition by phase separation. This effect on χ_{23} is not considered in the Flory–Huggins theory.

REFERENCES

1. I. Inamura, K. Akiyama, and Y. Kubo, *Polym. J.*, **29**, 119 (1997).
2. I. Inamura, M. Kittaka, T. Aikou, K. Akiyama, T. Matsuyama, M. Hiroto, K. Hirade, and Y. Jinbo, *Macromolecular Research*, submitted.
3. I. Inamura, Y. Jinbo, Y. Akiyama, and Y. Kubo, *Bull. Chem. Soc. Jpn.*, **68**, 2021 (1995).
4. I. Inamura and Y. Jinbo, *Polym. J.*, **23**, 1143 (1991).
5. L. H. Cragg and C. C. Bigelow, *J. Polym. Sci.*, **16**, 177 (1955).
6. I. Inamura, K. Toki, T. Tamae, and T. Araki, *Polym. J.*, **16**, 657 (1984).
7. I. Inamura, *Polym. J.*, **18**, 269 (1986).
8. P. J. Flory, "Principle of Polymer Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953, Chap. XIII.
9. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
10. R. J. Hefford, *Polymer*, **25**, 979 (1984).
11. F. E. Bailey, Jr., J. L. Kucera, and L. G. Imhof, *J. Polym. Sci.*, **1**, 56 (1958).
12. a) W. Scholtan, *Makromol. Chem.*, **7**, 209 (1951).
b) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Interscience Publishers, New York, N.Y., 1966.
13. H. Yamakawa, "Modern Theory of Polymer Solutions," Harper & Row, New York, N.Y., 1971.
14. K. Gekko and H. Noguchi, *J. Phys. Chem.*, **83**, 2706 (1976).
15. a) T. Matsuo and H. Inagaki, *Makromol. Chem.*, **55**, 150 (1962).
b) T. Matsuo and H. Inagaki, *Macromol. Chem.*, **53**, 130 (1962).