Further Study on the Evaluation of Molecular Weight Dependence of χ-Parameter by Phase Equilibrium Experiment on Polystyrene–Methylcyclohexane System

Kenji KAMIDE, Tatsuyuki ABE, and Yukio MIYAZAKI

*Textile Research Laboratory, Asahi Chemical Ind. Co. Ltd.,
Takatsuki, Osaka 569, Japan.*

ABSTRACT: For evaluating the molecular weight dependence of a thermodynamic interaction parameter χ, phase equilibrium experiments on the polystyrene–methylcyclohexane system were carefully carried out. The mathematical phase equilibrium of this polymer–solvent system was determined by taking into account the molecular weight- and concentration-dependences of the χ-parameter, according to the expression $\chi = \chi_{00}(1 + k/X)(1 + pv_{\mathrm{p}})$, where χ_{00} is a constant independent of both polymer molecular weight and concentration, X, the molar volume ratio of the polymer to the solvent, v_{p}, the polymer volume fraction, and k and p are molecular weight- and concentration-dependence coefficients. The partition coefficient σ increased remarkably with $1/X$ and k decreased linearly with an increase in the phase equilibrium temperature T, generally expressed by $k = k_0 (1 - T/\theta)$ (θ is Flory's theta temperature and k_0 is a constant).

KEY WORDS   Phase Equilibrium / Thermodynamic Interaction Parameter / Polystyrene / Partition Coefficient /

In a previous paper,[1] we established a generalized theory for describing the phase equilibrium of multi-component polymer–single solvent systems, by introducing the molecular weight- and concentration-dependences of the polymer–solvent thermodynamic interaction parameter χ into the well-known Flory–Huggins–Fujishiro theory. The χ-parameter is expressed in the form:

$$\chi = \chi_{00}(1 + k/X)(1 + pv_{\mathrm{p}}) \qquad (1)$$

where χ_{00} is a constant independent of both polymer molecular weight and concentration, X, the ratio of the molar volume of the polymer to that of the solvent, v_{p}, the polymer volume fraction, and k and p are molecular weight- and concentration-dependence coefficients, respectively. It should be noticed that eq 1 is a semi-empirical equation and the k- and p-parameters are phenomenological coefficients, although essentially the same expression for χ as a function of X and v_{p} can be readily derived from the refined lattice theory which has a severe limit in applicability to polymer solutions.[1] In eq 1, it is assumed that the k-parameter is independent of the polymer volume fraction and the p-parameter is

independent of molecular weight. This assumption is supported by the following experimental facts: (1) The unique k-temperature relation has been obtained, regardless of v_{p}, for the polystyrene (PS)–cyclohexane (CH) system (Figure 4 of ref 1). A similar observation will be presented in a later section of this paper (see Figure 5). (2) In the strict sense, the χ-parameter is not a linear function of v_{p} but depends also on higher powers of v_{p}. But, in the v_{p} range of phase equilibrium experiments on polymer solutions ($0 \leq v_{\mathrm{p}} \leq 0.5$), χ is reasonably linearly dependent on v_{p} (for example, Figure 1 of ref 2 for the PS–methylcyclohexane (MCH) system). (3) When evaluated from fractionation data on molecular weight distribution (or the molecular weight distribution parameter), the polymer volume fraction in the polymer-rich phase $v_{\mathrm{p(2)}}$ and the volume ratio of the polymer-lean to the polymer-rich phase R, by comparison with the corresponding theoretical values, the values of p coincide well with each other, and are almost constant throughout the fractionation run.[3,4] This strongly implies that a first approximation the p-parameter may be considered as constant throughout temperature and

average molecular weight ranges employed in the fractionation. In addition, the reliability of p estimated from a phase separation study has been confirmed by relevant literature data for the PS–CH system[4] and also by our experimental data on p for the PS–MCH system[2] determined on the basis of other principles, including osmotic pressure, isothermal distillation, vapor pressure, critical miscibility and ultracentrifuge (Table V of ref 3 and Table III of ref 4), in spite of the appreciable differences in average molecular weight and molecular weight distribution of the polymer samples employed. As is evident from the above, eq 1 is sufficiently accurate for describing phase separation phenomena of polydisperse polymer–solvent systems.

The molecular weight dependence of the χ-parameter is closely related to the molecular weight-dependence of the partition coefficient σ of a polymer having X between the polymer-rich and polymer-lean phases (see eq 3).

Using mathematical calculations based on the above theory, we have made a careful study of the effects of the k- and p-parameters on the phase equilibrium and the molecular weight fractionation characteristics of multi-component polymer–single solvent systems.[1] We found that the positive molecular weight dependence of the χ-parameter ($k > 0$) gives rise to a larger polydispersity of the polymers in the polymer-rich and lean-phases, particularly when $k > 3$. In the region of low ρ_p (ρ_p is the weight fraction of the polymer in a polymer-rich-phase relative to the total polymer dissolved), the ratio of the weight- to number-average of X, X_w/X_n, in the polymer-rich phase is remarkably influenced by both p and k. In the region of high ρ_p, the polydispersity of the polymer in the polymer-lean phase is predominantly controlled by k. For PS–CH and PS–MCH systems, k was found by the following means to lie between 0—10: (1) Comparison of the theoretical and experimental relations between σ and $1/X$, (2) osmometric determination of χ as a function of molecular weight and concentration, and (3) comparison of molecular weight distributions (MWD) of the polymer in the two phases with the theoretical curves calculated assuming various values for k. The tendency for k to decrease with an increase in the phase equilibrium temperature, independently of the concentration, was clearly observed. It was also found for

the PS–CH system that k is nearly zero at Flory's theta temperature. Unfortunately, the molecular weight range, in which σ was examined in the previous paper,[1] was too narrow to determine the temperature dependence of k accurately.

In this article we have attempted to carry out further study on the phase equilibrium of the PS–MCH system over a sufficiently wide range of X ($600 \leq X \leq 5000$) and determine the molecular weight dependence of X as a function of temperature. For this purpose, the MWD of polymers partitioned in both phases were evaluated very carefully by high performance liquid chromatography (HPLC) using columns with 12000 theoretical plates each 50 cm in length.

EXPERIMENTAL

Polymer

The same PS sample as that used in previous papers[3–5] was employed here and was characterized as follows: the weight-average molecular weight M_w was 23.9×10^4 by gel permeation chromatography (GPC) in tetrahydrofurane (THF) and 23.2×10^4 by light scattering in benzene at 25°C and a manual extrapolation of the Zimm plot, the number-average molecular weight M_n was 8.6×10^4 by GPC in THF and 8.9×10^4 by membrane osmometry in toluene at 25°C.

This polymer was independently characterized by a polymer group at Essex University (England) using a light scattering technique[6]: $M_w = 23.3 \times 10^4$ by computer analysis program I, 23.8×10^4 by
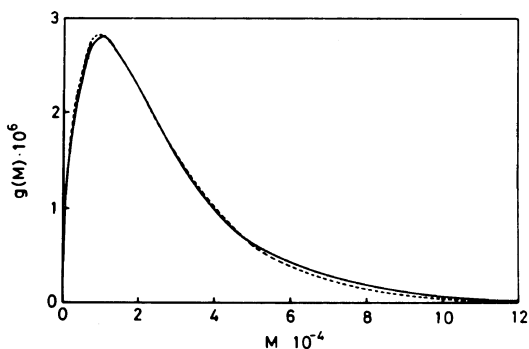

Figure 1. Molecular weight distribution curve $g(X)$ of the polymer sample used for the phase separation experiment: full line, experimental curve; broken line, Schulz–Zimm distribution curve with $M_w = 24.0 \times 10^4$ and $M_w/M_n = 2.8$.

Table I. Phase separation experiments for the polystyrene–methylcyclohexane system

Exptl No.	$v_p^0 \times 100$	T_p/K	ρ_p	R	$v_{p(2)}$	$v_{p(1)} \times 10^3$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	σ_{01}	k
1		328.4	0.11	—	0.178	4.46	38.9	57.8	0.25	2.7
2		325.7	0.31	—	0.199	3.48	32.5	46.4	1.24	11.8
3	0.50	320.9	0.53	97.5	0.263	2.36	27.7	40.3	1.36	11.2
4		312.7	0.80	66.4	0.264	1.01	21.2	33.5	2.32	15.3
5		293.2	0.98	—	0.436	0.10	14.7	27.9	3.03	23.4
6		330.3	0.04	—	0.158	8.29	28.6	53.0	0.69	8.8
7		327.2	0.28	—	0.182	6.29	25.3	42.5	1.41	15.1
8	0.86	322.8	0.57	45.6	0.229	3.80	18.1	29.8	1.64	14.4
9		315.3	0.81	—	0.270	1.68	14.3	27.3	2.23	15.7
10		287.8	0.97	—	0.392	0.26	13.6	26.8	4.39	23.8
11		331.2	0.02	1559	0.140	20.0	28.4	58.2	0.45	7.5
12		329.6	0.22	139	0.150	16.4	22.2	42.1	0.45	6.3
13	2.00	325.9	0.57	14.5	0.179	9.51	20.2	36.0	0.55	5.6
14		318.6	0.82	11.9	0.255	3.85	17.6	32.1	1.25	9.5
15		293.2	0.96	6.6	0.370	0.81	13.4	28.5	3.03	17.8

computer analysis program II and 22.0×10^4 by computer analysis program III, nonlinear least-square program. The M_w values obtained by two computer programs based on two different models for regression analysis are in good agreement with those evaluated by us.

The MWD of the polymer estimated by HPLC was accurately represented by the Schulz–Zimm distribution with $M_w = 24.0 \times 10^4$ and $M_w/M_n = 2.8$, as shown in Figure 1.

Solvent

Reagent grade MCH and THF were distilled immediately prior to use.

Phase Equilibrium Experiments

The PS sample was dissolved in MCH at 70°C to obtain starting solutions. The phase equilibrium experiments were performed accoridng to the procedure described before.[3,4] The experimental conditions, such as initial polymer volume fraction $v_p{}^0$, and phase equilibrium temperature $T_p(K)$, are summarized in the second to fourth columns of Table I. The weight fraction of the polymer in the polymer-rich phase (i.e., fraction size), ρ_p, the volume ratio of the polymer-lean phase to the polymer-rich phase, R, the polymer volume fraction in the polymer-rich phase, $v_{p(2)}$ and that of the polymer-lean phase, $v_{p(1)}$ were determined in the same manner as described before.[3]

Molecular Weight Distributions of Polymers in the Two Phases

Molecular weight distributions (MWD) for polymers separated by the phase equilibrium experiments were determined on a Shimadzu high performance liquid chromatograph model LC-1. The values of M_w and M_n were calculated from the MWD curves obtained. Crosslinked PS (HSG, manufactured by Shimadzu Ltd.) was used as the gel for fractionation. Two columns (50 cm in length) packed with HSG-30 and HSG-50 were connected in series. A theoretical plate number of the columns was 12000/50 cm for acetone at a 1.0 cm³ min⁻¹ flow rate. This instrument was operated using THF as the solvent at 25°C under the following conditions: Concentration of solution, 1.0 wt%; flow rate, 1.0 cm³ min⁻¹; and injection volume, 20 μl; fifteen samples of well-characterized living PS supplied by Pressure Chemical Co. ranging M_w from

600 to 2×10^6 were used as references. Yau and Fleming's method[7] was employed in order to transform the GPC curve to MWD curve. The plot of log M_w vs. elution volume V (cm³) is accurately represented by,

$$\log M_w = 24.26\, V^3 - 1.89_2\, V^2 + 6.44 \times 10^{-2}\, V - 7.89 \times 10^{-4} \quad (2)$$

Partition Coefficient

We denote the heights in the normalized MWD curve $(g(X))$ at X of the polymers in the polymer-rich and -lean phases, by $g_{(2)}(X)$ and $g_{(1)}(X)$, respectively. The partition coefficient σ at X, designated by σ to avoid complication, is defined

$$\sigma = (1/X)\ln\{(v_{p(2)} \cdot g_{(2)}(X))/(v_{p(1)} \cdot g_{(1)}(X))\} \quad (3)$$

In the previous paper[1] on the basis of modified Flory–Huggins theory and eq 1, we derived the relation,

$$\sigma = \sigma_0 + \sigma_{01}/X \quad (4)$$

with,

$$\sigma_0 = \left\{\ln\frac{(1-v_{p(1)})}{(1-v_{p(2)})} + (v_{p(2)} - v_{p(1)}) + \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right)\right\}$$
$$\times \left[2(v_{p(2)} - v_{p(1)}) + 1.5p(v_{p(2)}^2 - v_{p(1)}^2) \right.$$
$$\left. + k\left\{\left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right) + p\left(\frac{v_{p(2)}^2}{X_{n(2)}} - \frac{v_{p(1)}^2}{X_{n(1)}}\right)\right\}\right] \Bigg/$$
$$\left[(v_{p(2)}^2 - v_{p(1)}^2) + p(v_{p(2)}^3 - v_{p(1)}^3) \right.$$
$$\left. + k\left\{\left(\frac{v_{p(2)}^2}{X_{n(2)}} - \frac{v_{p(1)}^2}{X_{n(1)}}\right) + p\left(\frac{v_{p(2)}^3}{X_{n(2)}} - \frac{v_{p(1)}^3}{X_{n(1)}}\right)\right\}\right]$$
$$- \ln\frac{(1-v_{p(1)})}{(1-v_{p(2)})} \quad (5)$$

and

$$\sigma_{01} = k\left\{\ln\frac{(1-v_{p(1)})}{(1-v_{p(2)})} + (v_{p(2)} - v_{p(1)}) + \left(\frac{v_{p(2)}}{X_{n(2)}} - \frac{v_{p(1)}}{X_{n(1)}}\right)\right\}$$
$$\times \left\{(v_{p(2)} - v_{p(1)}) + 0.5p(v_{p(2)}^2 - v_{p(1)}^2)\right\} \Bigg/$$
$$\left[(v_{p(2)}^2 - v_{p(1)}^2) + p(v_{p(2)}^3 - v_{p(1)}^3) \right.$$
$$\left. + k\left\{\left(\frac{v_{p(2)}^2}{X_{n(2)}} - \frac{v_{p(1)}^2}{X_{n(1)}}\right) + p\left(\frac{v_{p(2)}^3}{X_{n(2)}} - \frac{v_{p(1)}^3}{X_{n(1)}}\right)\right\}\right] \quad (6)$$
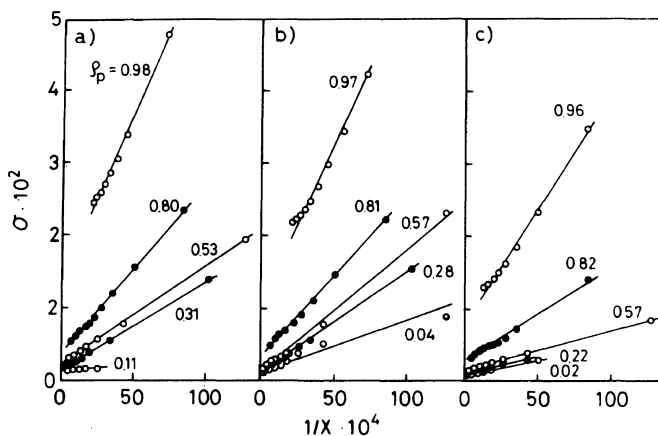
Figure 2. Molecular weight dependence (X=polymer-to-solvent molar volume ratio) of the partition coefficient σ for polystyrene–methylcyclohexane system: a) initial polymer volume fraction $v_p^0=0.50\times10^{-2}$, b) $v_p^0=0.86\times10^{-2}$, and c) $v_p^0=2.0\times10^{-2}$. Numbers on curve are the relative weight fractions ρ_p of polymer in the polymer-rich phase.

Computer Simulation

The mathematical phase equilibrium was undertaken according to the simulative procedure described in the previous paper.[1] The original PS sample was assumed to have a Schulz–Zimm distribution with $X_w=1810$ and $X_w/X_n=2.8$. The p-parameter in eq 1 was experimentally found to be 0.7 by the phase equilibrium,[3] 0.78 by the osmotic pressure,[7] and 0.6 by the cloud point method.[8] In this study, p was taken to be 0.7. The parameter k was varied in the range 0—20. Other parameters including v_p^0 and ρ_p were adapted to the values selected in the actual experiments.

RESULTS AND DISCUSSION

The fifth to ninth columns of Table I show the experimental results for the volume ratio R, the polymer-volume fractions in the two phases, $v_{p(2)}$ and $v_{p(1)}$, and M_w and M_n of the polymer in the polymer-rich phase. Figures 2a—c) show empirical relationship between σ and $1/X$ for the PS/MCH system. Throughout the range of v_p^0 investigated, the plot can be reasonably represented by a straight line, whose slope is equal to σ_{01} defined in eq 4. σ_{01} increases with an increase in ρ_p (*i.e.*, with a decrease in T_p). The σ_{01} values are positive and summarized in the tenth column of Table I. As is evident from the table, the partition coefficient σ depends on the molecular weight.
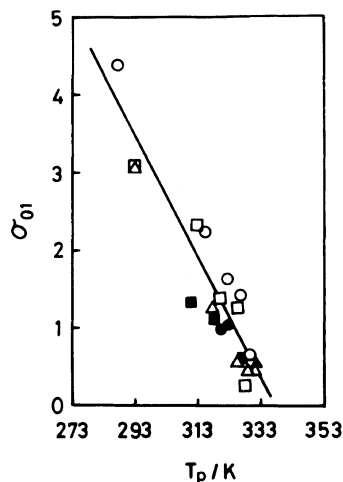

Figure 3. Variation in the parameter σ_{01} in eq 6 with the phase separation temperature T_p; rectangle, initial polymer volume fraction $v_p^0=0.50\times10^{-2}$; circle, $v_p^0=0.86\times10^{-2}$; triangle, 2.0×10^{-2}; open mark, this work; closed mark, data of ref 1; full line, the regression line given by eq 7.

Figure 3 shows the variation in σ_{01} with the phase equilibrium temperature T_p for the PS–MCH system. The figure includes our previous data for the PS–MCH system.[1] In the previous paper,[1] only a few points were available for larger ρ_p in establishing σ vs. the $1/X$ plot, from which σ_{01} was estimated. The previous data for $\rho_p \geq 0.88$ were excluded be-

cause of the considerable uncertainty involved in the estimation of σ_{01}. It can be seen from Figure 3 that the molecular weight dependence of the partition coefficient is a unique function of the temperature, independent of concentration.

The following relation was obtained by the least-square method,

$$\sigma_{01} = 25.3 - 0.75 \ T_p \quad \text{for} \quad \text{PS–MCH} ,$$

$$290\text{K} \le T_p(\text{K}) \le 350\text{K} \tag{7}$$

The theoretical relations between k and σ_{01}, calculated by computer simulation under the same conditions as for actual phase equilibrium experiments, are shown in Figure 4. Using these relations and experimental σ_{01} data in Table I, we were able to evaluate the magnitude of k, and the results are listed in the last column of Table I.
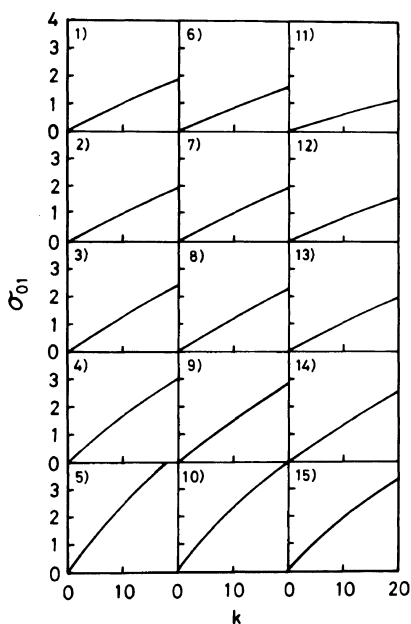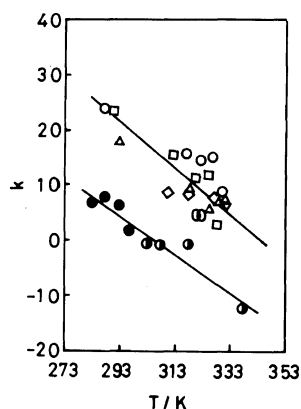
Figure 5. Changes in the k-parameter with temperature T: closed and half-closed mark, PS/CH system; ●, (Kamide–Miyazaki[1]), ◑, (Scholte by light scattering);[9,10] open mark, PS/MCH system; □, $v_p{}^0 = 0.50 \times 10^{-2}$; ◇, $v_p{}^0 = 0.47 \times 10^{-2}$; ○, $v_p{}^0 = 0.86 \times 10^{-2}$; 0, $v_p{}^0 = 0.94 \times 10^{-2}$; △, $v_p{}^0 = 2.0 \times 10^{-2}$; ▽, $v_p{}^0 = 1.86 \times 10^{-2}$.

Figure 4. Theoretical relationships between σ_{01} and the k-parameter: the original polymer (Schulz–Zimm distribution, $X_w = 1810$, $X_w/X_n = 2.8$), $p = 0.7$: 1) $v_p{}^0 = 0.50 \times 10^{-2}$, $\rho_p = 0.11$; 2) $v_p{}^0 = 0.50 \times 10^{-2}$, $\rho_p = 0.31$; 3) $v_p{}^0 = 0.50 \times 10^{-2}$, $\rho_p = 0.53$; 4) $v_p{}^0 = 0.50 \times 10^{-2}$, $\rho_p = 0.80$; 5) $v_p{}^0 = 0.50 \times 10^{-2}$, $\rho_p = 0.98$; 6) $v_p{}^0 = 0.86 \times 10^{-2}$, $\rho_p = 0.04$; 7) $v_p{}^0 = 0.86 \times 10^{-2}$, $\rho_p = 0.28$; 8) $v_p{}^0 = 0.86 \times 10^{-2}$, $\rho_p = 0.57$; 9) $v_p{}^0 = 0.86 \times 10^{-2}$, $\rho_p = 0.81$; 10) $v_p{}^0 = 0.86 \times 10^{-2}$, $\rho_p = 0.97$; 11) $v_p{}^0 = 2.0 \times 10^{-2}$, $\rho_p = 0.02$; 12) $v_p{}^0 = 2.0 \times 10^{-2}$, $\rho_p = 0.22$; 13) $v_p{}^0 = 2.0 \times 10^{-2}$, $\rho_p = 0.57$; 14) $v_p{}^0 = 2.0 \times 10^{-2}$, $\rho_p = 0.82$; 15) $v_p{}^0 = 2.0 \times 10^{-2}$, $\rho_p = 0.96$.
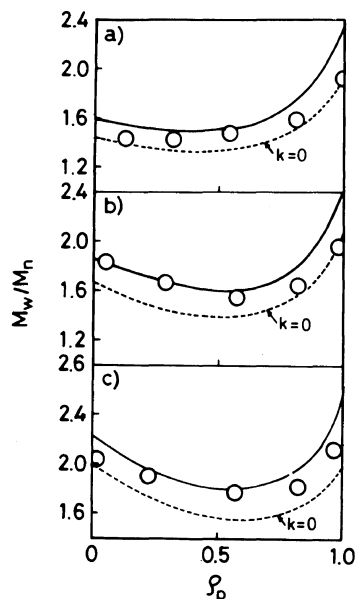
Figure 6. Dependence of the ratio M_w/M_n of polymer in the polymer-rich phase on the relative amount of the polymer (*i.e.*, the fraction size) ρ_p: open circle, experimental data points for PS/MCH system; full line, theoretical curve calculated under the same conditions as those in actual experiments (in this case, temperature dependence of k (see Figure 5) is taken into account); broken line, theoretical curve calculated by assuming $k = 0$ under the same conditions as those in actual experiments, except for k.

Figure 5 shows the temperature dependence of k for the PS–MCH system. In this figure, our previous data for PS–MCH[1] except for $\rho_p \geq 0.88$ and those for PS–CH[1] are shown for comparison. The k-parameter decreases linearly with increasing temperature. In other words, this parameter becomes small as the temperature T approaches Flory's theta temperature. In the previous paper,[1] we demonstrated for the PS–CH system that k vanished at Flory's theta temperature (307 K). For the PS–MCH system, k becomes zero at *ca.* 343 K, which is Flory's theta temperature.[8] Therefore, it may be concluded that the molecular weight dependence of χ changes its sign at Flory's theta temperature θ and that k can be expressed by,

$$k = k_0(1 - T/\theta) \tag{8}$$

k_0 was found to be 129 for PS–MCH and 108 for PS–CH.

The breadth of the MWD of polymers in the polymer-rich phase expressed in terms of M_w/M_n is plotted against ρ_p in Figure 6, were open circles are actual experimental data, the broken lines are the theoretical curves at $v_p^0 = 0.5 \times 10^{-2}$, 0.86×10^{-2}, and 2.0×10^{-2} for $p = 0.7$ and $k = 0$ and the full lines are the theoretical relations calculated for $p = 0.7$ by

taking into consideration the complicated changes in k with phase equilibrium temperature (accordingly ρ_p) (Figure 5). The experimental ρ_p dependence of M_w/M_n in the polymer-rich phase can be reasonably interpreted by considering the molecular weight and concentration dependences of the χ-parameter.

REFERENCES

1. K. Kamide and Y. Miyazaki, *Polym. J.*, **13**, 325 (1981).
2. K. Kamide, K. Sugamiya, T. Kawai, and Y. Miyazaki, *Polym. J.*, **12**, 67 (1980).
3. K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.*, **177**, 485 (1976).
4. K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.*, **9**, 395 (1977).
5. K. Kamide, K. Sugamiya, T. Ogawa, C. Nakayama, and N. Baba, *Makromol. Chem.*, **135**, 23 (1970).
6. K. R. Roberts, J. A. Torkington, M. Gordon, and S. B. Ross-Murphy, *J. Polym. Sci., Polym. Symp.*, No. **61**, 45 (1977).
7. W. W. Yau and S. W. Fleming, *J. Appl. Polym. Sci.*, **12**, 2111 (1968).
8. T. Dobashi, M. Nakata, and M. Kaneko, *Polym. Prepr. Jpn.*, **27**, 1542 (1978).
9. Th. G. Scholte, *Eur. Polym. J.*, **6**, 1063 (1970).
10. Th. G. Scholte, *J. Polym. Sci., A–2*, **9**, 1553 (1971).