Flory Enthalpy Parameter at Infinite Dilution of Polymer Solutions Determined by Various Methods

Kenji KAMIDE, Shigenobu MATSUDA, and Masatoshi SAITO

*Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers,
Asahi Chemical Industry Co., Ltd.,
Hacchonawate 11-7, Takatsuki, Osaka 569, Japan*

(Received July 16, 1987)

ABSTRACT: The Flory enthalpy parameter at infinite dilution κ_0 was evaluated for atactic polystyrene (PS)–cyclohexane (CH) and –*trans*-decalin (D) systems by applying the following four methods from literature data: (1) Temperature dependence of vapor pressure and membrane osmotic pressure, (2) critical solution temperature T_c and critical solution concentration v_p^c for a series of solutions of polymers, (3) temperature dependence of the second virial coefficient in the vicinity of the Flory theta temperature θ , and (4) calorimetry. In method 2, Shultz–Flory, Stockmayer, Koningsveld *et al.* (KKS), and Kamide–Matsuda (KM)'s procedures were applied to estimate θ and the entropy parameter ψ_0 , from which κ_0 was calculated as $\psi_0\theta/T$ (T , temperature). κ_0 values at θ deduced by these methods (in method (2), by KKS and KM treatments) yielded a single master curve against the weight- or number-average molecular weight $\bar{M}_w$ or $\bar{M}_n$; κ_0 (at θ) = $0.924\bar{M}_w^{-0.089}$ for PS–CH system. Excellent agreement (± 0.02) was confirmed between κ_0 values at θ deduced by various methods when $\bar{M}_w$ (or $\bar{M}_n$) of the polymer was the same. This fact strongly supports the validity of the modified Flory–Huggins solution theory, in which the polymer–solvent interaction parameter χ depends on the polymer concentration and its molecular weight.

KEY WORDS Flory Enthalpy Parameter / Polymer Solution / Polystyrene / Chemical Potential / Osmotic Pressure / Light Scattering / Second Virial Coefficient / Critical Solution Point / Calorimetry /

The pair interaction Flory enthalpy parameter κ is defined by the van Laar–Scatchard type relation¹:

$$\kappa = \Delta H_0 / (RTv_p^2) \quad (1)$$

where ΔH_0 is the partial molar heat of dilution with respect to the solvent, R , the gas constant, T , Kelvin temperature, v_p , the polymer volume fraction.

Calorimetry allows direct determination of ΔH_0 , and thus κ . The calorimetric experiments, made by Fujishiro and his students, indicated κ not to be constant independent of T and v_p , which was first assumed in the original Flory–Huggins theory, but a purely phenomenological parameter, which depends on both T and v_p^2 .

$$\kappa = \kappa_0 + \kappa_1 v_p + \kappa_2 v_p^2 + \cdots \quad (2)$$

κ_0 in eq 2 is given by

$$\kappa_0 = \lim_{v_p \rightarrow 0} \{ \Delta H_0 / (RTv_p^2) \} \quad (3)$$

Theoretically, κ or simply κ_0 can be evaluated by various methods, directly or indirectly as will be described later. In other words, if good agreement between κ or κ_0 values evaluated by various methods is confirmed, the theory, on which the principles of the methods are based, is considered thoroughly acceptable to explain all the thermodynamic properties of polymer solutions.

In 1954, Krigbaum³ found that the values of the entropy parameter ψ_0 (see eq 7) (thus, the

enthalpy parameter κ_0 at theta temperature (see eq 6)) for atactic polystyrene (PS)–cyclohexane (CH) system deduced from the critical solution points⁴ (by his expression, the precipitation temperature) by Shultz–Flory method (eq 8) and from intrinsic viscosity⁵ differ from those obtained from the osmotic second virial coefficient A_2 by factors of about 3 and 1/3, respectively. He concluded that the magnitude of the important entropy parameter ψ_0 remains in doubt pending on further refinement of existing theories. Thereafter (in 1955), Krigbaum and Carpenter⁶ attempted to settle this problem by estimating ψ_0 from the temperature dependence of the light scattering second virial coefficient but without success because they obtained for the same polymer–solvent system a surprisingly low ψ_0 , which was considered mainly due to large experimental error inherent in the light scattering measurements.

Up to now, as far as authors know, no further attempt to compare ψ_0 or κ_0 values estimated by various methods has been made. Note that for this purpose κ_0 is preferable to ψ_0 , because the former can be determined directly without using any particular theory of a polymer solution.

We believe that for the past 30 years the situation has dramatically changed and a great deal of progress has been made and among the latest developments are the follows:

(1) the reliability of A_2 determination by the light scattering (LS) method was improved remarkably as a result of well-established experimental techniques and instrumental advance (for example by using laser light) and a sufficient accumulation of the experimental data with high degree of precision for mono-disperse polymer solutions has been made very systematically,

(2) prominent progress was achieved in theory on the critical phenomena of polymer solutions,

(3) advance of calorimetry allowed us to apply it to the polymer solutions, which have

very small partial heats of dilution and have relatively larger viscosities,

(4) it was confirmed that any thermodynamic parameter can not be accurately determined from hydrodynamic properties including the limiting viscosity number for lack of sound theoretical background.

In this article we calculated κ_0 for atactic PS–CH and *trans*-decalin (D) systems by applying various direct or indirect methods to literature data available in order to clarify whether κ_0 values thus evaluated coincide with each other.

THEORETICAL BACKGROUND

κ_0 can be determined by the following methods:

(1) The temperature dependence of vapor pressure and osmotic pressure through use of the relations¹

$$\kappa_0 = \lim_{v_p \rightarrow 0} \{1/(RTv_p^2)\} \{\partial(\Delta\mu_0/T)/\partial(1/T)\}_{P, v_p} \quad (4)$$

and

$$\Delta\mu_0 = RT \ln(P_0/P_0^0) = -\pi/V_0^0 \quad (5)$$

Here, $\Delta\mu_0$ is the chemical potential of the solvent in solution, P_0 , the vapor pressure of the solvent component in solution, P_0^0 , the vapor pressure of the pure solvent, π , the osmotic pressure, V_0^0 , the molar volume of the solvent. The partial differentiation of $\Delta\mu_0/T$ with respect to $1/T$ is carried out under constant pressure and constant composition except the polymer.

(2) The critical phenomena (critical solution temperature T_c and critical polymer concentration v_p^c). κ_0 are related to Flory theta temperature θ and Flory entropy parameter ψ_0 through the definition of θ .¹

$$\kappa_0 = \theta\psi_0/T \quad (6)$$

with

$$\begin{aligned}\psi_0 &= \lim_{v_p^0 \rightarrow 0} (\Delta S_0 - \Delta S_0^{\text{comb}})/(Rv_p^2) \\ &= \lim_{v_p^0 \rightarrow 0} (\Delta\mu_0 - \Delta H_0 - T\Delta S_0^{\text{comb}})/(RTv_p^2)\end{aligned}\quad (7)$$

ΔS_0 is the partial molar entropy of dilution and ΔS_0^{comb} , the combinatorial entropy term.

θ and ψ_0 can be evaluated from T_c (and v_p^c) for a series of solutions of polymers having different molecular weights by the following four methods:

(a) *Shultz and Flory (SF) Method*⁴

Shultz and Flory derived a relation between T_c and the weight-average molar volume ratio of the polymer to the solvent X_w given by

$$1/T_c = (1/\theta\psi_0)(1/X_w^{1/2} + 1/(2X_w)) + 1/\theta \quad (8)$$

The slope of the plot of $1/T_c$ against $(1/X_w^{1/2} + 1/(2X_w))$ gives $1/\theta\psi_0$ and its intercept gives $1/\theta$. It must be noticed that eq 8 is strictly valid only for a monodisperse polymer–single solvent system. Furthermore, the χ -parameter is given in a well-known relation

$$\begin{aligned}\Delta\mu_0 &= RT\{\ln(1-v_p) \\ &\quad + (1-1/X_n)v_p + \chi v_p^2\}\end{aligned}\quad (9)$$

(X_n is the number-average molar volume ratio of the polymer to the solvent) and is assumed to be independent of the polymer molecular weight and the polymer concentration.

(b) *Stockmayer Method*⁷

Stockmayer derived a relation (eq 10) for multi-component polymers–single solvent system, in which the χ parameter is independent of v_p and molar volume ratio of the polymer to the solvent X .

$$\begin{aligned}1/T_c &= (1/(2\theta\psi_0))\{(1/X_w^{1/2} + (X_z/X_w)^{1/2}) \\ &\quad \times (1/X_w^{1/2} + (X_w/X_z)^{1/2})\} \\ &\quad + (1 - 1/(2\psi_0))/\theta\end{aligned}\quad (10)$$

Here X_z is the z -average X . Plot of $1/T_c$ as a function of $\{(1/X_w^{1/2} + (X_z/X_w)^{1/2})(1/X_w^{1/2} + (X_w/X_z)^{1/2})\}/2$ yields $(1/(\theta\psi_0))$ from slope and $(1 - 1/(2\psi_0))/\theta$ as an intercept at

$$\{(1/X_w^{1/2} + (X_z/X_w)^{1/2})(1/X_w^{1/2} + (X_w/X_z)^{1/2})\}/2 = 1/2.$$

Therefore, θ and ψ_0 can be unambiguously determined.

(c) *Koningsveld et al. (KKS) Method*⁸

An alternative expression of neutral equilibrium conditions is given by

$$\begin{aligned}Y &\equiv g_1 - g_2 + 4g_2v_p^c \\ &= \{1/(1-v_p^c)^2 - X_z/(X_wv_p^c)^2\}/6\end{aligned}\quad (11)$$

with

$$g = g_0 + g_1v_p + g_2v_p^2 \quad (12-a)$$

$$= (1/v_0) \int_{1-v_0}^1 \chi d(1-v_0) \quad (12-b)$$

where g is a thermodynamic interaction parameter, related to χ -parameter through eq 12-b, v_0 , volume fraction of the solvent ($=1-v_p$). g_1 and g_2 in eq 11 are calculated from v_p^c , X_w , and X_z by applying the curve fitting method to eq. 11.

g_0 , defined in eq 12-a, is evaluated from g_1 and g_2 , and v_p^c and X_w , using the spinodal equation,

$$\begin{aligned}2g_0 &\equiv 2(g_{00} + g_{01}/T_c) \\ &= 1/(1-v_p^c) + 1/(v_p^cX_w) \\ &\quad + 2g_1(1-3v_p^c) + 6g_2(1-2v_p^c)v_p^c\end{aligned}\quad (13)$$

Plot of g_0 , obtained thus, versus T_0^{-1} enables us to estimate g_{00} and g_{01} . Considering the relation

$$\chi_0 \equiv \lim_{v_p \rightarrow 0} \chi = g_{00} - g_1 + g_{01}/T \quad (14)$$

we obtain the following relations:

$$\psi_0 = 1/2 - g_{00} + g_{01} \quad (15)$$

$$\theta = g_{01}/\psi_0 \quad (16)$$

$$\kappa_0 = g_{01}/T \quad (17)$$

Then, κ_0 can be determined from eq 17.

(d) *Kamide-Matsuda Method*⁹

At the critical point, the following equations can be derived,⁹

$$\begin{aligned} 1/(X_w v_p^c) + 1/(1 - v_p^c) \\ - \chi_0^c (2 + \sum_{j=1} p_j(j+2)v_p^{cj}) = 0 \end{aligned} \quad (18)$$

and

$$\begin{aligned} 1/(1 - v_p^c)^2 - X_z/(X_w v_p^c)^2 \\ - \chi_0^c (\sum_{j=1} p_j j(j+2)v_p^{cj-1}) = 0 \end{aligned} \quad (19)$$

where p_j is the concentration dependence coefficient given in eq 20,

$$\chi = \chi_0 \left(1 + \sum_{j=1} p_j v_p^j \right) \quad (20)$$

Here χ_0 is the concentration independent coefficient and χ_0^c is the critical χ_0 .

χ_0^c is related to T_c , ψ_0 , and θ through the relation

$$1/T_c = \chi_0^c/(\theta\psi_0) + (1/\theta)(1 - 1/(2\psi_0)) \quad (21)$$

First, calculate χ_0^c and v_p^c (theo) by solving eq 18 and 19 with assumed values of p_1 and p_2 . Next determine the most probable p_1 and p_2 as a pair which gives a minimum value of the square average of the difference between v_p^c (theo) and v_p^c (exp). Substituting χ_0^c , calculated for the most probable p_1 and p_2 and the experimental critical temperature T_c (exp) into eq 21, and plotting the relation of $1/T_c$ (exp) vs. χ_0^c (theo), we obtain θ and ψ_0 .

In the former two methods only T_c is necessary and in the latter two methods v_p^c together with T_c are needed for analysis and p_1 and p_2 are obtained simultaneously (g_1 and g_2 , obtained by KKS method, are readily transformed to p_1 and p_2 ⁹). These four methods presume that χ_0^c is independent of X .

(3) Temperature dependence of A_2 by membrane osmometry or light scattering measured in the vicinity of θ temperature (eq 22) via θ and ψ_0 .²

$$\psi_0 = (V_0^0/\bar{v}^2)\theta(\partial A_2/\partial T)_\theta \quad (22)$$

Here $\bar{v}$ is the specific volume of polymer and note that ψ_0 estimated by eq 22 corresponds to the finite molecular weight. θ is determined as the temperature at which A_2 becomes zero. κ_0 can be evaluated by putting θ and ψ_0 into eq 6.

(4) *Calorimetry*

The heat of dilution ΔH and accordingly ΔH_0 ($\equiv (\partial \Delta H / \partial n_0)_{T,p}$, n_0 is the mole number of the solvent) can be directly measured with calorimetry.

Figure 1 demonstrates schematic routes of determination for κ_0 .

APPLICATION TO EXPERIMENTAL DATA

The thermodynamic properties of atactic PS-CH system have hitherto been most thoroughly investigated and the literature data available for this system were chosen for estimating κ_0 . As a supplement the literature data for atactic PS-*trans*-decalin system were also analyzed.

Krigbaum and Geymer¹⁰ estimated the partial molar heat of dilution through use of eq 4 and 5 from the temperature dependence of the osmotic pressure and vapor pressure for a PS sample (the number-average molecular weight $\bar{M}_n = 4.4 \times 10^5$) in CH at 307.2 K (Table V of ref 10). From their data we obtain $\kappa_0 = 0.21$ for $\bar{M}_n = 4.4 \times 10^5$ as shown in Table I. It is noticed that the measurements were made over the temperature range of 34–44°C.

Scholte¹¹ determined the chemical potential of an atactic monodisperse PS ($\bar{M}_n = 1.54 \times 10^5$)-CH system at 303.2, 318.2, and 338.2 K from sedimentation equilibrium in the ultracentrifuge. Using the data in Table V of ref 11 we estimated κ_0 as a function of temper-

ature and κ_0 was found to be 0.32 at 307.2 K ($\approx \theta$ temperature). Scholte discussed the accuracy of determined parameters including $\Delta\mu_0$, concluding that the error in $\Delta\mu_0$ could be estimated to between 5% at low v_p and 10% at high v_p . Then, it is conceivable that κ_0 estimated from Scholte's data is more reliable than that from Krigbaum and Geymer.¹⁰

Koningsveld *et al.*⁸ measured the upper critical point (v_p^c and T_c) for 6 monodisperse PS samples (the weight-average molecular weight $\bar{M}_w = 3.54\text{--}150.0 \times 10^4$) in CH by the phase volume ratio method (see Table I of ref 8) and Kuwahara and his coworkers¹² estimated v_p^c and T_c of the upper critical points for 4 monodisperse PS samples ($\bar{M}_w = 20.0\text{--}68.0 \times 10^4$) and a mixture sample in CH by the diameter method (see, Table I of ref 12). Saeki *et al.*¹³ determined upper cloud point curves for 6 monodisperse PS samples ($\bar{M}_w = 3.7\text{--}270.0 \times 10^4$) in CH. We estimated the critical solution points as the maximum points of their cloud point curves (see, Figure 1 of ref 13). All these three sets of data (in total 16 samples) were, on the whole, analyzed ac-

cording to the methods of SF, Stockmayer, KKS, and KM to estimate θ and ψ_0 (accordingly, κ_0). The plots of three sets of data according to each treatment yielded a single common straight line (for example, see Figure

Figure 1. Routes of calculation of the Flory enthalpy parameter from experimental data of vapor pressure, osmotic pressure, light scattering, and critical solution points.

Table I. Flory θ temperature and entropy parameter ψ_0 at infinite dilution of the upper critical solution point of atactic polystyrene-cyclohexane system

Method		θ — K	κ_0 ($\bar{M}_n$ or $\bar{M}_w \times 10^{-4}$) at 308°C	(Data)
(1) Chemical potential	Membrane osmometry	—	0.21 (44)	(Krigbaum-Geymer) ¹⁰
	Sedimentation equilibrium	—	0.32 (15.4)	(Scholte) ¹¹
(2) Critical point	Shultz-Flory	306.2	0.75 (—)	(Koningsveld <i>et al.</i> , Kuwahara <i>et al.</i> , Saeki <i>et al.</i>) ^{8,12,13}
	Stockmayer	306.5	0.80 (—)	
	Koningsveld <i>et al.</i>	305.2	0.29 (—)	
	Kamide-Matsuda	305.1	0.27 (—)	
			0.26 (∞)	
(3) Second virial coefficient	Membrane osmometry	307.6	0.28 (∞)	[0.28] ^a (Krigbaum) ³ (Krigbaum-Geymer) ¹⁰ (Outer <i>et al.</i>) ¹⁷ (Krigbaum-Carpenter) ⁶ (Schulz-Baumann) ¹⁸ (Kotera <i>et al.</i>) ¹⁹ (Miyaki-Fujita) ^{20,21} (Tong <i>et al.</i>) ²² (Fujihara) ²⁵
		307.6	0.27 (∞)	
	Light scattering	308.0	0.19 (163)	
		308.4	0.19 (320)	
		307	0.39 (17)	
		307.4	0.26 (30)	
		308	0.22 (∞)	
		307.7	0.30 (∞)	
(4) Heat of dilution	Calorimetry	—	0.28 (∞)	

^a Averaged value.

5 of ref 9). In KKS and KM methods, we estimated X_z assuming the Schulz-Zimm type molecular weight distribution for all PS samples of Kuwahara *et al.*¹² and Saeki *et al.*'s¹³ papers. The θ and κ_0 values obtained are summarized in Table I. Application of the KKS method to the above literature data gives $p_1=0.623$ and $p_2=0.308$ and that of the KM method to the same data yields $p_1=0.624$ and $p_2=0.190$, together with θ and ψ_0 . These values are in fairly good agreement with those evaluated by osmotic pressure,^{3,10} isothermal distillation,¹⁰ vapor pressure,¹⁰ phase separation,^{14,15} cloud point curves,¹⁶ and ultracentrifuge.¹¹ Previously Kamide and Matsuda⁹ pointed out that the Shultz-Flory and Stockmayer theories yield incorrectly low v_p^c value: $v_p^c(\text{exp}) > v_p^c(\text{theo})$ and the absolute magnitude of ψ_0 values estimated by methods of Koningsveld *et al.*⁸ and Kamide and Matsuda⁹ are only half or 1/3 those by the SF and Stockmayer methods for PS-CH system.

κ_0 was found to be 0.75 by the SF method and 0.80 by Stockmayer. These values are more than three times larger than those by the other methods. Shultz and Flory⁴ determined precipitation temperature (*i.e.*, cloud point curve) of four PS fractions in CH and obtained $\theta=307.2\text{ K}$ and $\kappa_0=1.055_8$ at θ using their method. They noticed that the parameters deduced from this method appeared to be unacceptable. Saeki *et al.*¹³ evaluated θ and κ_0 at θ to be 486 K and 0.79 by the SF method. Undoubtedly, SF and Stockmayer methods overestimate ψ_0 (accordingly, κ_0). Therefore, the most probable value of κ_0 at θ , estimated from the critical points is an average (0.28) of those (0.29 and 0.27) by Koningsveld *et al.* method and Kamide-Matsuda method (see, the fifth column of Table I).

For atactic PS-CH system, the membrane osmotic pressure (MO) and light scattering (LS) measurements have been carried out to estimate A_2 over a temperature range including θ temperature by Krigbaum (MO),³

Krigbaum and Geymer (MO),¹⁰ Outer *et al.* (LS),¹⁷ Krigbaum and Carpenter (LS),⁶ Schulz and Baumann (LS),¹⁸ Kotera *et al.* (LS),¹⁹ Miyaki-Fujita (LS),^{20,21} and Tong *et al.* (LS).²²

The results of the present analysis for the literature data are assembled in Table II. Here, we constructed the plots of A_2 against T using the literature data, from which $(\partial A_2/\partial T)_\theta$ was estimated. In the table κ_0 at 308 K (*i.e.*, the most probable θ temperature) is demonstrated.

The value of θ for the samples in Krigbaum's study, except sample code H-2-8, is $305.6 \pm 0.4\text{ K}$, which is somewhat lower than those estimated by others for this system. Krigbaum³ ascribed this disagreement to traces of moisture which entered the polymer solutions in the 313.2 K bath. The data for sample code H-2-8 were obtained using adequate precautions to prevent contamination of the solutions with water. The effect of water contamination on κ_0 seems insignificant.

Figure 2 shows κ_0 at θ estimated by the A_2 method for atactic PS-CH system, as function of $\bar{M}_w^{-1}$ or $\bar{M}_n^{-1}$. In the figure the κ_0 value (0.32), obtained from the temperature dependence of the chemical potential by Scholte,¹¹ is shown for comparison.

Least square straight lines a and b in the figure pass through the observed data points of Krigbaum³ (except for sample code H-2-8) and Krigbaum and Geymer,¹⁰ respectively. From these lines, we can evaluate κ_0 at infinite molecular weight to be 0.28 from Krigbaum's data and 0.27 from Krigbaum and Geymer's data (0.28, on average). These values are also presented in Table I for comparison. The κ_0 values obtained from Krigbaum's and by Krigbaum and Geymer's data have a small but significant tendency of decreasing with an increase in $\bar{M}_n$.

It is probably true to say that as early as the mid 1950s the membrane osmometry had been established already as an accurate and reliable method for estimating A_2 , but the light scattering technique remained in 1950s only in em-

Table II. Evaluation of Flory κ_0 parameter from the temperature dependence of the second virial coefficient A_2 by membrane osmometry and light scattering for atactic polystyrene-cyclohexane system

Method	Reporter (Year)	Sample code	$\bar{M}_w(\bar{M}_n)$ $\times 10^{-4}$	Temp range K	$(\partial A_2/\partial T)_\theta$ $\times 10^6 \text{ cm}^3 \text{ mol g}^{-1} \text{ K}$	θ K	κ_0 at 308 K
Membrane osmometry	Krigbaum (1954)	L5-6	(5.05)	303—323	9.53	305.8	0.37
		HA-9	(12.5)		8.72	305.8	0.34
		M2-2	(35.9)		7.84	305.6	0.30
		H1-4	(56.6)		7.22	305.4	0.28
		H2-8	(20.3)		9.14	307.6	0.36
Light scattering	Krigbaum-Geymer (1959)	F-I	(7.2)	313, 322	8.9	307.2	0.35
		F-II	(44.0)	303, 313, 323	7.2	307.9	0.28
	Outer <i>et al.</i> (1950)	B-2	163	300—314.5	4.25	308	0.17
		HB2-3		320	4.76	308.4	0.19
	Krigbaum-Carpenter (1955)	—	17	—	10	307	0.39
	Schulz-Baumann (1961)	—	17	—	10	307	0.39
	Kotera-Saito-Fujisaki (1963)	SMI	30 (15)	303.2—323.2	6.76	307.4	0.26
	Miyaki-Fujita (1981)	IK1500-1	5680	306—323	4.62	307.9	0.18
		IK1500-2	3900	306—323	5.34	307.9	0.21
		BK2500-1	3190	306—328	5.86	307.8	0.23
		BK2500-2	2320	306—323	5.95	307.8	0.23
		BK2500-3	1500	305—328	6.62	308.3	0.26
		BK2500-4	876	305—328	5.58	308.3	0.22
		C1	647	304, 328	6.01	308.2	0.24
		F450	480	303—328	5.43	308.9	0.21
		F288	308	305—328	5.91	307.3	0.23
		F126	134	302—328	7.04	307.3	0.27
	Tong <i>et al.</i> (1984)	F1	1.00	307.7 K ~	8.4	307.7	0.30
		F2	2.15	a value			
		F4	4.36	about 1 K			
		F20	18.1	below the			
		F40	49.8	cloud point			

bryo, being not as precise as the osmotic pressure as Krigbaum and Carpenter noticed.⁶ Therefore, the literature LS data at that time may contain large experimental uncertainty. However, an inspection of Figure 2 leads us to the conclusion that κ_0 values estimated from the classical LS A_2 data by Outer *et al.*, Krigbaum-Carpenter, Schulz-Baumann, and Kotera *et al.* decrease rapidly with an increase in $\bar{M}_w$ and for PS samples with $\bar{M}_w > 10^6$ κ_0 was found to be below 0.20, which is significantly lower than those estimated by MO ($\bar{M}_n = 5.50\text{--}56.6 \times 10^4$). All these classical LS

data except for that by Outer *et al.* do not deviate strongly from a common relation obtained by classical MO and recent LS measurements.

Miyaki and Fujita^{20,21} carried out a tremendously elaborate work in measuring A_2 for ten very high molecular weight atactic PS samples ($\bar{M}_w = 1.34 \times 10^6\text{--}5.68 \times 10^7$) in CH at three to seven different temperatures ranging 309.2 to 328.2 K. Except for a fraction (sample code IK1500-1, $\bar{M}_w = 5.68 \times 10^6$), almost the constant value of κ_0 ($= 0.23 \pm 0.01$, at 308 K) was obtained over a wide range of $\bar{M}_w$ ($8.76 \times$

Figure 2. Molecular weight dependence of Flory enthalpy parameter at infinite dilution κ_0 , evaluated by the temperature dependence of the chemical potential and of the second virial coefficient A_2 in vicinity to theta temperature and by calorimetry for atactic polystyrene-cyclohexane system: ●, Krigbaum³ (membrane osmometry (MO)); ■, Krigbaum-Geymer¹⁰ (MO); ○, Scholte¹¹ (ultracentrifuge); △, Krigbaum-Carpenter⁶ (light scattering (LS)); ▽, Schulz-Baumann¹⁸ (LS); ◇, Kotera *et al.*¹⁹ (LS); ○, Outer *et al.*¹⁷ (LS); □, Miyaki²¹ (LS); ⊙, Fujihara²⁵ (calorimetry). Solid line, master curve of all data; broken line a, drawn pass through the data points of Krigbaum; b, Krigbaum-Carpenter. Inserted figure, enlarged plots of Miyaki *et al.* data. Broken line c, drawn pass through the data points of Miyaki *et al.*

10^5 — 6.47×10^6) as shown in Table II. The figure inserted in Figure 2 shows the enlarged plots in the lower $\bar{M}_w^{-1}$ region. κ_0 values thus determined by Miyaki and Fujita scatter fairly largely, probably due to experimental difficulty of LS measurements of solutions of polymers with $\bar{M}_w \sim 10^7$. $\kappa_0 = 0.22$ at 308 K was obtained for $\bar{M}_w = \infty$ from line c in the figure, constructed by the least-squares method. Tong *et al.*²² determined A_2 of five monodisperse PS samples in the temperature range from 307.7 K to about 1 K above the cloud point and they found A_2 for monodisperse PS in CH below θ to be independent of M , within the ranges of T and M studied. Since unfortunately the A_2 values were not described in their paper, we estimated $(\partial A_2 / \partial T)_\theta$ from the initial slope of the plot of $-A_2$ vs. T^{-1} (Figure 4 of ref 22), to

be 0.30.

Table I contains θ and κ_0 values estimated from the temperature dependence of A_2 . Plural samples were employed in the studies of Krigbaum,³ Krigbaum-Geymer,¹⁰ Miyaki-Fujita,^{20,21} and Tong *et al.*²² The κ_0 value at infinite molecular weight for each study is shown in the table.

If all the data points in Figure 2 are treated equally, although they scatter markedly, we can conclude that κ_0 decreases slightly with increasing $\bar{M}_w$ or $\bar{M}_n$ or can be roughly regarded as constant up to $\bar{M}_w$ or $\bar{M}_n < \sim 1 \times 10^6$ and further, the molecular weight dependence of κ_0 tends to become remarkably large for polymer with $\bar{M}_w$ or $\bar{M}_n > 3 \times 10^7$. It is particularly noteworthy that κ_0 extrapolated to $\bar{M}_w = \infty$ ($\kappa_0(\infty)$) depends definitely on the molecular weight range, over which the experimental data points were obtained and from which the extrapolation was made.

Amaya and Fujishiro²³ reported the heat of dilution ΔH , obtained with a calorimetry specially designed and constructed, for five CH solutions of an atactic PS (unfractionated sample, $X = 275$) at 303.2 K. From Table I of ref 23 we can calculate κ_0 at 298.2 K to be 6.0. This value is unbelievably large. In this case the measurements were carried out almost 4–5 K below the θ temperature and Amaya and Fujishiro²³ pointed out that it may be reasonable to suppose that in the solution at 303.2 K there remains more or less aggregations of polymers. Schulz and Horbach²⁴ measured ΔH directly for nine atactic PS fractions (the viscosity-average molecular weight $\bar{M}_v = 400$ — 1.7×10^4) in CH at 296.2 K and for two PS sample ($\bar{M}_v = 1200$ and 1.1×10^4) they obtained ΔH_0 as a function of the polymer concentration v_p . κ , calculated by eq 1 from the experimental ΔH_0 (Table 7 of ref 24), indicated a strong negative molecular weight dependence. From these data, however, we cannot evaluate an accurate κ or κ_0 at infinite molecular weight in θ solvent (≈ 307.5 K). For example, we obtained $\kappa_0 = 0.9$ for PS with

$\bar{M}_v = 1.1 \times 10^4$, but this value is almost 2.5 times larger than that (0.4) estimated from Fujihara's data²⁵ for monodisperse PS with $\bar{M}_w = 1.02 \times 10^4$ at 307.2 K. The difference in temperature of measurements provides at least a partial explanation of this great difference. From Abb. 4 of ref 24 for atactic PS ($\bar{M}_w = 6.8 \times 10^4$), in CH (the polymer concentration 10%) (cited from Cantow's data²⁶) it is shown that the κ value at θ is nearly half that at 297.2 K.

By overcoming numerous experimental difficulties encountered in calorimetry Fujihara²⁵ succeeded in measuring directly ΔH_0 of four monodisperse PS samples ($\bar{M}_w = 6.2 \times 10^3$ — 1.07×10^5) in CH at 307.2 K. According to him, the PS-CH system is a large endothermic solution, decreasing ΔH_0 with increasing $\bar{M}_w$. First we constructed the plot of κ against v_p for each sample from the data in Table I of ref 25 and estimated κ_0 as an intercept of the above plot. Figure 3 shows the molecular weight dependence of κ_0 determined thus. κ_0 decreases noticeably with an increase in $\bar{M}_w$. The data points except for the highest $\bar{M}_w$ sample can be reasonably represented by a straight line, yielding $\kappa_0 = 0.33$ at $\bar{M}_w = \infty$. If all the data points are taken into consideration of the extrapolation procedure, we obtain $\kappa_0 = 0.28$ at $\bar{M}_w = \infty$.

The molecular weight range covered by calorimetry is somewhat shifted to a side lower than that used for MO and LS experiments, due to ease in conducting the experiments. κ_0 values for the two highest $\bar{M}_w$ samples by calorimetry are plotted for comparison in Figure 2. It is noted that the chemical potential method and calorimetry give almost the same κ_0 value with those by A_2 method for the same $\bar{M}_w$ polymer. κ_0 was found by the chemical potential method¹¹ for $\bar{M}_n = 15.4 \times 10^4$ to be 0.32 and by calorimetry²⁵ for $\bar{M}_w = 10.7 \times 10^4$ to be 0.31, which should be compared with 0.34 by A_2 method (Krigbaum³) for $\bar{M}_w = 12.5 \times 10^4$ and 0.32 by A_2 method (Tong *et al.*²²) for $\bar{M}_w = 1$ — 18.1×10^4 . Tong *et al.*'s

Figure 3. Plots of Flory enthalpy parameter at infinite dilution κ_0 , evaluated directly by Fujihara²⁵ using calorimetry, atactic polystyrene-cyclohexane system at 308.2 K.

experimental findings that $(\partial A_2/\partial T)_\theta$ is practically independent of $\bar{M}_w$ can be accepted by inspecting Fig. 2 because they employed PS samples in the $\bar{M}_w$ range of 1— 18.1×10^4 , in which all literature data points of ψ_0 (and κ_0) can be considered as nearly constant. It is probably true to say that at the limit of $\bar{M}_w$ (or $\bar{M}_n$) $\rightarrow \infty$ both ψ_0 and κ_0 at θ approach zero concurrently (see eq 28).

Although all the methods proposed so far for analyzing the critical solution points assume that χ -parameter is independent of the polymer molecular weight, this assumption is not often realistic. For example, from analysis on the molecular weight distribution of polymers partitioning in a polymer-rich phase and a polymer-lean phase, both in equilibrium, Kamide *et al.*^{27,28} determined for the PS-CH system the partition coefficient σ , concluding the χ -parameter to be slightly dependent of the polymer molecular weight and χ_0 in eq 20 can be expressed semi-empirically over the limited X_w range by

$$\chi_0 = \chi_{00} \{1 + (k_x/X_n)\} \quad (23)$$

with

$$k_x \simeq k_0 \{1 - (\theta/T)\} \quad (24)$$

k_x was shown to decrease noticeably with increase in T , vanishing at θ . The absolute magnitude of k_0 has unavoidably large experimental uncertainty.

The spinodal equation and equation of

neutral equilibrium condition were derived by Kamide *et al.*,¹⁶ for the case where χ and χ_0 were given by eq 20 and 23, respectively. The results are:

$$\begin{aligned} & 1/(X_w v_p) + 1/(1 - v_p) \\ & - \chi_{00} \{ 1 + k_\chi (1 + 1/X_n - X_w/X_n) \} \\ & \times \left\{ 2 + \sum_{i=1} p_i (i+2) v_p^i \right\} = 0 \end{aligned} \quad (18')$$

$$\begin{aligned} & 1/(1 - v_p)^2 - X_z/(X_w v_p)^2 \\ & - \chi_{00} \{ 1 + k_\chi (1 + 1/X_n - X_w/X_n) \} \\ & \times \left\{ \sum_{i=1} p_i i (i+2) v_p^{i-1} \right\} = 0 \end{aligned} \quad (19')$$

By putting k_χ , X_n , and X_w into eq 18' and 19' we obtain v_p^c and χ_{00}^c (χ_{00} at the critical point), together with p_1 and p_2 , for a given polymer in solvent.

χ_0 is related to ψ_0 and κ_0 through the relation

$$1/2 - \chi_0 = \psi_0 - \kappa_0 \quad (25)$$

and ψ_0 and κ_0 , corresponding to χ_0 , given by eq 23, can be approximately represented by eq 26 and 27, respectively.

$$\psi_0 = \psi_{00} (1 + k_\psi / X_n) \quad (26)$$

$$\kappa_0 = \kappa_{00} (1 + k_\kappa / X_n) \quad (27)$$

Figure 2 provides experimental support to confirm the validity of eq 26 and 27 over the range of $\bar{M}_w$ below 10^6 , but eq 26 and 27 are shown to be not fully satisfactory when a very large molecular weight range is considered. κ_{00} is an apparent value extrapolated to $\bar{M}_w$ (or $\bar{M}_n$) = ∞ from the data points in the limited $\bar{M}_w$ range. So κ_{00} is similar to the values at the intercept of lines a, b, and c in Figure 2. κ_{00} does not necessarily mean a true κ_0 value at infinite molecular weight.

Equation 21 can be modified into

$$1/T_c = \chi_{00}^c / (\theta \psi_{00}) - (1/(\theta \psi_{00})) (1/2 - \psi_{00}) \quad (21')$$

Then, a graph of $1/T_c$ as a function of χ_{00}^c

Figure 4. Effect of the molecular weight dependence coefficient k_0 (eq 24) on Flory theta temperature θ and Flory entropy parameter at infinite dilution ψ_0 , both evaluated by the Kamide–Matsuda method (eq 18 and 19) from the critical solution points data, for the atactic polystyrene–cyclohexane system.

enables θ and ψ_{00} to be evaluated from the intercept and the slope simultaneously.

In order to clarify the effect of the molecular weight dependence of χ on ψ_{00} we calculated θ and ψ_0 using eq 21' assuming k_0 for literature data.^{8,12,13} The results are shown in Figure 4. At $k_\chi = 0$, $\psi_{00} = 0.27$ and $\theta = 305.1$ K are obtained. As noted previously,²⁹ θ values estimated by the Koningsveld *et al.* method and by the Kamide–Matsuda method are by a few degrees lower than the temperature at which A_2 vanishes. Provided that underestimation of θ by these two methods is entirely due to undue neglect of the molecular weight dependence of the χ -parameter and eq 23 and 24 hold their validity over an whole X_w range including infinite molecular weight, ψ_{00} (and accordingly κ_{00} at θ) and k_0 corresponding to the true θ are considered to be the most probable values. From Figure 4, we obtain $\psi_{00} = 0.26 \pm 0.01$ and $k_0 = -4.6$, corresponding to $\theta = 307.5 \pm 0.01$ K for PS–CH system. It is noteworthy that the ψ_{00} (accordingly, κ_{00} at θ) value is equivalent to that extrapolated from the data points in the range of $\bar{M}_w = 3.45 \times 10^4$ – 270.0×10^4 . The former value should be compared with 0.27, which was derived assuming that χ -parameter is molecular weight independent.

Figure 2 indicates that except for the points

Figure 5. Log-log plot of Flory enthalpy parameter at infinite dilution κ_0 , evaluated by the temperature dependence of the chemical potential and second virial coefficient A_2 in the vicinity of the theta temperature and by calorimetry versus the reciprocal weight- (or number-) average molecular weight $\bar{M}_w$ ($\bar{M}_n$) for the atactic polystyrene-cyclohexane system: ●, Krigbaum³ (membrane osmometry (MO)); ■, Krigbaum-Geymer¹⁰ (MO); ●, Scholte¹¹ (ultracentrifuge); △, Krigbaum-Carpenter⁶ (light scattering (LS)); ▽, Schulz-Baumann¹⁸ (LS); ◇, Kotera *et al.*¹⁹ (LS); ○, Outer *et al.*¹⁷ (LS); □, Miyaki²¹ (LS); ⊙, Fujihara²⁵ (calorimetry). Solid line, the equation $\kappa_0 = 0.92 \bar{M}_w^{-0.089}$.

by Schulz and Baumann¹⁸ and by Krigbaum³ (sample code H-2-8), all the data points estimated by numerous researchers using various methods seem to be represented by a single master curve, which very gradually decreases with $\bar{M}_w$ above $\bar{M}_w > 10^6$. In order to obtain a better understanding of the molecular weight dependence of κ_0 , a log-log plot of κ_0 against $\bar{M}_w^{-1}$ or $\bar{M}_n^{-1}$ for atactic PS-CH system at 307.2 K is shown in Figure 5. All available data points yielded a straight line given by

$$\kappa_0 (\equiv \psi_0) = 0.924 \bar{M}_w \text{ (or } \bar{M}_n)^{-0.089} \quad (28)$$

Equation 28 is valid over the entire experimentally accessible molecular weight range from 6.2×10^3 to 5.680×10^7 and of course eq 28 has much wider applicability than eq 27. Equation 28 is represented by the full line in Figure 2. Therefore, we can conclude that the most probable κ_0 value is, in a strict sense, dependent on $\bar{M}_w$ (or $\bar{M}_n$), irrespective of the method employed and that if eq 28 can be expanded its applicability to $\bar{M}_w = \infty$ κ_0 at

Table III. The Flory θ temperature and entropy parameter κ_0 at infinite dilution for the upper critical solution point of the atactic polystyrene-*trans*-decalin system

Method	θ /K	κ_0 at θ
Critical point		
Shultz-Flory	293.7	0.95
Kamide-Matsuda	292.7	0.33
Second virial coefficient		
Light scattering	296.8	0.32

infinite molecular weight may be zero. This is an experimental indication that both the randomness in the mixing of a polymer and solvent and the spacial homogeneity of the polymer segment density in solution are expected to be realized in dilute solutions of polymer with infinitely large molecular weight (*i.e.*, $\Delta S_0 = \Delta S_0^{\text{comb}}$). The fact that methods (1)–(4) give essentially identical κ_0 value within ± 0.02 for a given PS sample in CH, strongly supports the validity of the modified Flory-Huggins theory.

For the atactic PS-*trans*-decalin system, upper critical solution points and temperature dependence of the second virial coefficient were reported in literature. Nakata *et al.*³⁰ determined v_p^c and T_c for four monodisperse PS samples ($\bar{M}_w = 3.7\text{--}270 \times 10^4$) in *trans*-decalin. In the previous paper,²⁹ we estimated θ and ψ_0 from the above data according to the Shultz-Flory, Kamide-Matsuda methods. The results are shown in Table III, where κ_0 values at θ calculated from ψ_0 are shown.

Inagaki and his coworkers³¹ measured the light scattering second virial coefficient A_2 of four well-fractionated PS samples ($\bar{M}_w = 14.3\text{--}112 \times 10^4$) in *trans*-decalin over temperatures ranging 291.2 to 349.2 K and evaluated θ and $(\partial A_2 / \partial T)_\theta$ (Table III of ref 22), from which we calculated ψ_0 and κ_0 at θ assuming $(V_1/\bar{v}^2) = 183.82 \text{ g}^2 \text{ cm}^3 \text{ mol}^{-1}$, regardless of temperature. The results are summarized in Table IV. From the plot of κ_0 vs. $1/\bar{M}_w$ (Figure 6), κ_0 at infinite molecular

Table IV. Evaluation of Flory κ_0 parameter from the temperature dependence of the second virial coefficient A_2 by light scattering for atactic polystyrene-*trans*-decalin system

Method	Reporter (Year)	Sample code	$\bar{M}_w$ $\times 10^{-4}$	Temp K	$(\partial A_2/\partial T)_\theta$ $\times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$	θ K	κ_0 at θ^a
Light scattering	Inagaki <i>et al.</i> (1966)	G-2	14.3	291.2—343.2	1.43	296.8	0.78
		J-4	22.2	295.5—302.1	1.14	296.8	0.62
		J-10	51.3	295.2—300.1	1.11	296.7	0.61
		P-4	112	295.2—302.8	0.69	296.8	0.38

^a $(V_1/\bar{v}^2) = 183.82$ **Figure 6.** The molecular weight dependence of Flory enthalpy parameter at infinite dilution κ_0 , evaluated by Inagaki *et al.*³¹ from the temperature dependence of the second virial coefficient A_2 , for the atactic polystyrene-*trans*-decalin system.

weight was found to be 0.32 (Table III). κ_0 can also be experimentally represented by

$$\kappa_0 = 31.5 \bar{M}_w^{-0.312} \quad (29)$$

The κ_0 value from the critical point by Kamide-Matsuda treatment (0.33) for the atactic PS-*trans*-decalin system agrees fairly well with that from $(\partial A_2/\partial T)_\theta$ (0.32) because the molecular weight ranges of these two sets of data overlap fairly well.

Summarizing, this article clarified the reliability of κ_0 in Flory theta solvent experimentally estimated and a molecular weight dependence of κ_0 for typical non-polar polymer-non-polar solvent systems. Then, we come to the conclusion that the modified Flory-Huggins theory, derived by introducing the molecular weight- and the concentration-dependences of the χ parameter into the original theory, can be regarded as valid and

sufficiently accurate to express any thermodynamic property of a polymer solution.

REFERENCES

1. See, for example, P. J. Flory, "Principle of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953.
2. See, for example, A. Kagemoto, S. Murakami, and R. Fujishiro, *Bull. Chem. Soc. Jpn.*, **39**, 15 (1966).
3. W. R. Krigbaum, *J. Am. Chem. Soc.*, **76**, 3785 (1954).
4. A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).
5. T. G. Fox, Jr. and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1915 (1951).
6. W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).
7. W. H. Stockmayer, *J. Chem. Phys.*, **17**, 588 (1949).
8. R. Konigsveld, L. A. Kleintjens, and A. R. Shultz, *J. Polym. Sci., A-2*, **8**, 1261 (1970).
9. K. Kamide and S. Matsuda, *Polym. J.*, **16**, 825 (1984).
10. W. R. Krigbaum and D. O. Geymer, *J. Am. Chem. Soc.*, **81**, 1859 (1959).
11. Th. G. Scholte, *J. Polym. Sci., A-2*, **8**, 841 (1970).
12. N. Kuwahara, N. Nakata, and M. Kaneko, *Polymer*, **14**, 415 (1973).
13. S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 246 (1973).
14. K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.*, **177**, 485 (1976).
15. K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.*, **9**, 395 (1977).
16. K. Kamide, S. Matsuda, T. Dobashi, and M. Kaneko, *Polym. J.*, **16**, 839 (1984).
17. P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
18. G. V. Schulz and H. Baumann, *Makromol. Chem.*, **60**, 120 (1963).

Flory Enthalpy Parameter of Dilute Polymer Solutions

19. A. Kotera, T. Saito, and N. Fujisaki, *Rep. Progr. Polym. Phys. Jpn.*, **6**, 9 (1963).
20. Y. Miyaki and H. Fujita, *Macromolecules*, **14**, 742 (1981).
21. Y. Miyaki, PhD. Dissertation, 1981, Osaka Univ.
22. Z. Tong, S. Ohashi, Y. Einaga, and H. Fujita, *Polym. J.*, **15**, 835 (1983).
23. K. Amaya and R. Fujishiro, *Bull. Chem. Soc., Jpn.*, **31**, 19 (1958).
24. G. V. Schulz and A. Horbach, *Z. Phys. Chem. Neue Folge*, **22**, 377 (1959).
25. I. Fujihara, PhD. Dissertation, 1979, Osaka City Univ.
26. H. J. Cantow, *Z. Phys. Chem. Neue Folge*, **7**, 58 (1956).
27. K. Kamide and Y. Miyazaki, *Polym. J.*, **13**, 325 (1981).
28. K. Kamide, T. Abe, and Y. Miyazaki, *Polym. J.*, **14**, 355 (1982).
29. K. Kamide, S. Matsuda, and M. Saito, *Polym. J.*, **17**, 1013 (1985).
30. M. Nakata, S. Higashida, N. Kuwahara, S. Saeki, and M. Kaneko, *J. Chem. Phys.*, **64**, 1022 (1976).
31. H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, *J. Phys. Chem.*, **70**, 1718 (1966).