agreement between the two expressions for H_m in the region of intermediate z (ca. $z = 0.5$), where both are practical.

The result of the contour deformation, appropriate transformation of the Bessel functions from real to imaginary arguments, and considerable rearrangement, is

$$H_m = \frac{2|z|}{\pi} \int_\kappa^\infty \frac{(BC - AE)}{C_2 + E^2} \exp(-R|z|)\, \mathrm{d}R \qquad \text{(A2)}$$

where

$$A = J_m(R)J_m(S\rho); \quad S \equiv (R^2 - \kappa^2)^{1/2}; \quad a = 1$$

$$B = -J_m(R)Y_m(S\rho)$$

$$C = DJ_m(R)SJ_m'(S) - D_0J_m(S)RJ_m'(R)$$

$$E = -DJ_m(R)SY_m'(S) + D_0Y_m(S)RJ_m'(R)$$

$$BC - AE \rightarrow (2D/\pi)[J_m(R)]^2 \text{ as } \rho \rightarrow a = 1$$

Equation A2 also requires certain precautions in the numerical integration, because of the rapid variation of the integrand in the vicinity of the zeros of $J_m(R)$. For small z the integrand converges slowly, the integral must be extended to large z, and a great many zeros require special treatment.

Our procedure was to use eq A2 for m up to 10, and to supplement these values with the asymptotic form, eq A1, when necessary for the smaller values of z.

We now return to the possible poles of g_m in the k plane. We are indebted to Professor Ira Bernstein for suggesting the lines of our argument. In eq II.6, let $D(\rho)$ be replaced by a continuous function of arbitrary steepness, and the interval $(0,\infty)$ by a finite interval. At the right boundary g_m vanished, and at the left $\mathrm{d}g_m/\mathrm{d}\rho$ vanishes. Then

$$(\mathcal{L} + k^2)g_m = 4\pi\delta(\rho - a)/aD(\rho) = s(\rho) \qquad \text{(A3)}$$

where

$$\mathcal{L}g_m \equiv -\frac{1}{\rho D(\rho)} \frac{\partial}{\partial\rho}\left(\rho D(\rho) \frac{\partial g_m}{\partial\rho}\right) + \left(\kappa^2(\rho) + \frac{m^2}{\rho^2}\right)g_m \qquad \text{(A4)}$$

The operator $\mathcal{L}$ is self-adjoint and positive definite for a scalar product defined with weight function $\rho D(\rho)$. Consequently $\mathcal{L}$ has a complete set of eigenfunctions f_i and positive eigenvalues λ_i, and the source and Green's function may be expanded as follows:

$$s(\rho) = \sum s_i f_i; \quad g_m = \sum s_i f_i/(k^2 + \lambda_i) \qquad \text{(A5)}$$

it follows that g_m can have only imaginary poles. These generate a branch cut as the limits on ρ are extended to zero and infinity.

References and Notes

(1) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).
(2) F. H. Westheimer and J. G. Kirkwood, *J. Chem. Phys.*, **6**, 513 (1938).
(3) F. P. Buff, N. S. Goel, and J. R. Clay, *J. Chem. Phys.*, **63**, 1367 (1975).
(4) D. L. Beveridge and G. W. Schnuelle, *J. Phys. Chem.*, **79**, 2562 (1975).
(5) F. R. Harris and S. A. Rice, *J. Chem. Phys.*, **25**, 955 (1956).
(6) T. L. Hill, *Arch. Biochem. Biophys.*, **57**, 229 (1955).
(7) G. Manning, *Biophys. Chem.*, **7**, 95 (1977), and earlier work cited there.
(8) A. D. MacGillvray, *J. Chem. Phys.*, **57**, 4071, 4075 (1972), and earlier work cited there.
(9) J. Skolnick, Ph.D. Thesis, Yale University, 1978.
(10) M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", Dover Publications, New York, N.Y., 1972. We use their notation for all Bessel functions, *J, Y, I, K*.
(11) J. A. Stratton, "Electromagnetic Theory", McGraw-Hill, New York, N.Y., 1941, p 204, eq 20.
(12) J. M. Bailey, *Biopolymers*, **12**, 559 (1973).

Pressure Dependence of Upper Critical Solution Temperatures in the System Polystyrene–Cyclopentane

Maki Ishizawa,[1a] Nobuhiro Kuwahara,*[1b] Mitsuo Nakata,[1a]
Wataru Nagayama,[1a] and Motozo Kaneko[1a]

Department of Polymer Science, Faculty of Science, Hokkaido University,
Sapporo, Japan, and Department of Polymer Science, Faculty of Technology,
Gunma University, Kiryu, Japan.

Received April 26, 1978

ABSTRACT: The pressure dependence of the upper critical solution temperature (ucst) in solutions of polystyrene in cyclopentane has been measured over the pressure range of 0.1 to ~70 MPa. The values of $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ for the ucst of polystyrene ($M_w \times 10^{-4} = 67$ and 200) in cyclopentane are negative (−0.398 and −0.480 deg MPa^{-1}). The magnitude of $(\mathrm{d}T/\mathrm{d}P)_c$ at constant composition gradually decreases with increasing pressure over 0.1 to ~70 MPa. The pressure dependence of the ucst in the polystyrene–cyclopentane is examined through the χ_1 parameter derived by Patterson and Delmas in conjunction with the equations of state by Flory.

The recent theories of polymer solution thermodynamics by Patterson[2-6] and Flory[7-10] qualitatively predict both the upper critical solution temperature (ucst) and the lower critical solution temperature (lcst). The importance of the free volume effect or "equation of state" contribution in the polymer solution has been recognized because of the general appearance of the lcst in nonpolar polymer solutions,[11-18] the pressure dependence of the ucst and lcst,[19-25] the negative excess volume of mixing,[26-32] and the composition dependence of χ.[27-31,33-36]

Saeki et al.[15] found a pair of the θ_u and θ_l in a convenient temperature range in the system polystyrene–cyclopentane. Since contribution of the free volume term to χ_1 is beyond 40% at the θ_u,[15] a considerable lowering of the ucst with increase of pressure is expected even in the temperature region of the ucst. Examinations of the pressure dependence of the ucst and lcst under high pressure are of great importance in understanding thermodynamic properties of polymer solutions. The present work was done to supply the (P, T, composition) phase diagram for

0024-9297/78/2211-0871$01.00/0

Table I
Upper Critical Solution Temperatures at Different Pressures for the Polystyrene–Cyclopentane System

$M_w \times 10^{-4}$	ucst (K) at pressure (MPa)					
	1	10	20	40	60	70
67	286.0	283.0	280.6	277.8	276.3	276.0
200	291.0	287.3	284.9	282.0	280.3	280.1

the ucst of polystyrene solutions in cyclopentane over the pressure range of 0.1 to ~70 MPa. Experimental values of $(dT/dP)_c$ have been examined in the light of the recent theories of polymer solution thermodynamics[2-10] by use of the experimental ν, τ, and π parameters.

Experimental Section

Polystyrene samples were obtained from the Pressure Chemical Co. The samples used in this work are characterized by $M_w/M_n < 1.15$ for $M_w \times 10^{-4} = 67$ and $M_w/M_n < 1.30$ for $M_w \times 10^{-4} = 200$. Cyclopentane was reagent grade and was further purified before use. The solvent was dried over anhydrous potassium carbonate and fractionally distilled by use of a column of 100-cm length and 10-mm diameter packed with glass rasching rings. Several solutions in cyclopentane prepared from each sample in the concentration range of 1 to ~7 wt % were stirred for 1 day and then sealed inside the solution cells by a mercury seal. Preparation of all the samples was carried out in a dry box under an atmosphere of dry nitrogen.

The apparatus for determination of the cloud point under pressure consisted of three parts: a pressure generator, a calibrated Bourdon-type pressure gauge, and a high-pressure vessel made of stainless steel with a holder for the solution cell and two windows for passage of the He–Ne laser beam. The stainless-steel vessel of high pressure was immersed into a water bath controlled within ±0.001 °C, pressure was raised, and then the temperature of the water bath was very slowly lowered at 0.0005 to ~0.001 °C min^{-1} under an applied pressure. By the aid of the pattern of He–Ne laser beam fully described elsewhere,[37] the cloud point for solutions near the critical concentration was determined with an accuracy of ±0.001 MPa and ±0.002 °C by use of a calibrated Bourdon-type pressure gauge of 45-cm diameter (Heise Co., to 5 MPa) over the pressure range of 0.1 to ~5 MPa and with an accuracy of ±0.1 MPa and ±0.01 °C with a calibrated Bourdon-type pressure gauge of 30-cm diameter (Heise Co., to 160 MPa) over the pressure range of 0.1 to ~70 MPa. For solutions with concentration far from the critical one the determination of the cloud point was less accurate because of a relatively weak scattering of the laser beam by the solutions.

The thermal pressure coefficient γ of cyclopentane was measured with an accuracy of ±0.003 MPa deg^{-1}. The method of determination of γ is described in detail elsewhere.[25] The value of γ over the temperature range of 10 to ~45 °C for cyclopentane was represented by the relation

$$\gamma(\text{MPa deg}^{-1}) = 1.175 - 8.04 \times 10^{-3}t + 4.50 \times 10^{-5}t^2$$

where t is in degrees Celsius.

Results

Typical cloud-point curves at different pressures of 0.1 to ~70 MPa for solutions of polystyrene of $M_w \times 10^{-4} = 67$ in cyclopentane are shown in Figure 1. The scattering of the experimental points is due to a slight trace of water in the solution leading to the considerable rise of the precipitation temperature. The cloud-point temperature is lowered and the miscibility region is extended with increase of pressure. Although the maximum point of the cloud-point curve is not the critical mixing point, the difference of the maximum temperature from its critical mixing temperature should be quite small[38] because of the small deviation from unity of M_w/M_n for the samples in this work. The critical mixing temperatures at pressures of 0.1 to ~70 MPa for the ucst are listed in Table I. No pressure dependence of the critical composition along the critical locus was observed within experimental error.[20]

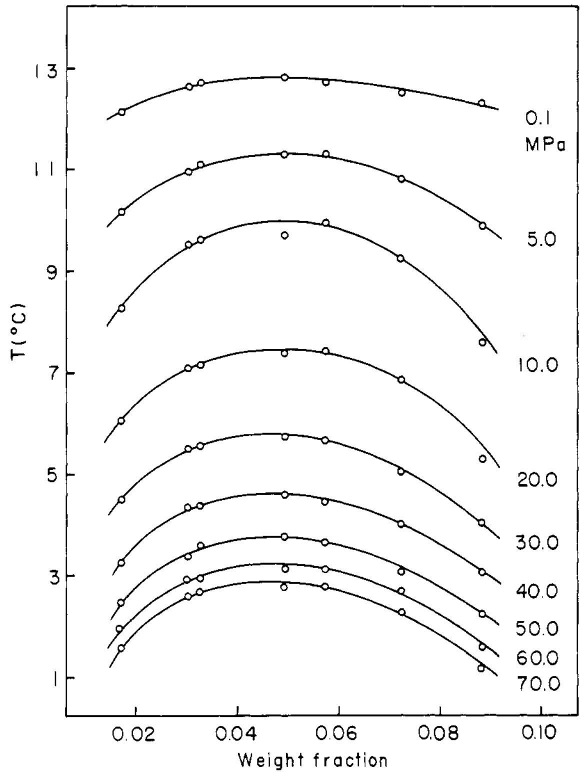

Figure 1. The (temperature, weight fraction) phase diagram for the polystyrene ($M_w \times 10^{-4} = 67$)–cyclopentane system at pressures indicated in MPa.

The pressure dependence of the ucst at a constant composition close to the critical concentration for polystyrene in cyclopentane is shown in Figure 2 for the pressure range of 0.1 to ~5 MPa and in Figure 3 for 0.1 to ~70 MPa. The results in the T_c vs. P_c plot are characterized by convex downward curves. The observed values of $(dT/dP)_{c,P=0}$ were determined from a two-parameter least-squares fit by use of the data over the pressure range of 0.1 to ~5 MPa in Figure 2. The pressure dependence of T_c over 0.1 to ~5 MPa is fitted to

$$T_c(\text{K}) = 286 - 0.398P_c + 0.97 \times 10^{-3}P_c^2 \qquad (1)$$

for the solution of polystyrene of $M_w \times 10^{-4} = 67$ and to

$$T_c(\text{K}) = 291 - 0.480P_c + 1.38 \times 10^{-3}P_c^2 \qquad (2)$$

for $M_w \times 10^{-4} = 200$. The molecular weight dependence of $(dT/dP)_{c,P=0}$ in the polystyrene–cyclopentane system is characterized by the increasing absolute value of $(dT/dP)_{c,P=0}$ with an increase of the molecular weight of polymer and its tendency is in accordance with the result for the system polystyrene–*tert*-butyl acetate.[25]

Discussion

The pressure dependence of the critical solution temperature under the critical condition is related to the ratio of the second derivatives of volume and enthalpy per mole of mixture with respect to composition

$$(dT/dP)_c = \lim_{T\to T_c, w_2\to w_{2c}} [T(\partial^2 V/\partial w_2^2)_{T,P}/(\partial^2 H/\partial w_2^2)_{T,P}] \qquad (3)$$

where w_2 is the weight fraction of polymer. By assuming χ independent of concentration, eq 3 can be written as

$$(dT/dP)_c = -(\partial\chi_1/\partial P)_{T_c}/(\partial\chi_1/\partial T)_{P_c} \qquad (4)$$

The Patterson and Flory theories of polymer solution thermodynamics predict the pressure dependence of the ucst and its variation with the molecular weight of polymer. By use of a van der Waals dependence of the configura-

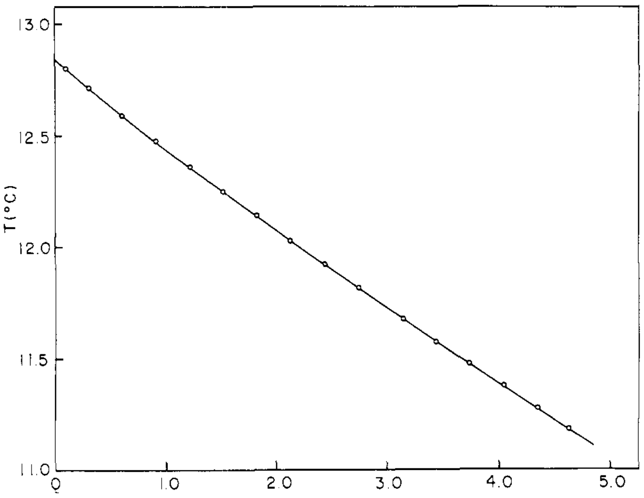

Figure 2. The (P,T) isopleth over the pressure range of 0.1 to 5 MPa for the sample close to the critical concentration in the polystyrene ($M_w \times 10^{-4} = 67$)–cyclopentane system.

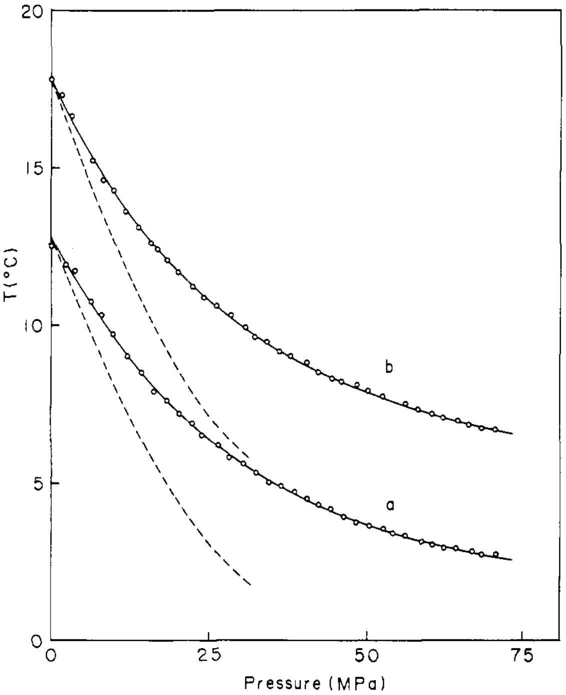

Figure 3. The (P,T) isopleths over the pressure range of 0.1 to 70 MPa for the samples close to the critical concentration: (a) data for polystyrene of $M_w \times 10^{-4} = 67$ in cyclopentane; (b) data for polystyrene of $M_w \times 10^{-4} = 200$ in cyclopentane. Dotted lines are calculated.

tional energy on volume, Flory derived the equation of state in the reduced form[7]

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - \tilde{V}^{-1/3})^{-1} - (\tilde{V}\tilde{T})^{-1} \tag{5}$$

where $\tilde{P}$, $\tilde{V}$, and $\tilde{T}$ are respectively the reduced variables of pressure, volume, and temperature. The χ_1 parameter for the van der Waals model derived by Patterson and Delmas is given by[5]

$$\chi_1/c_1 = (-\tilde{U}_1/\tilde{T}_1)\nu^2 + (\tilde{C}_{p,1}/2)[\tau + (\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1)\pi]^2 \tag{6}$$

with

$$\tilde{U}_1 = -\tilde{V}_1^{-1}$$

$$\tilde{C}_{p,1}^{-1} = [1 - (2/3)\tilde{V}_1^{-1/3}] - 2(1 - \tilde{V}_1^{-1/3})/(\tilde{P}_1\tilde{V}_1^2 + 1)$$

and

$$\tilde{\beta}_1\tilde{P}_1/\tilde{\alpha}_1\tilde{T}_1 = \tilde{P}_1\tilde{V}_1^2/(\tilde{P}_1\tilde{V}_1^2 + 1)$$

Table II
Parameters and Pressure Dependence of Critical Solution Temperatures

$M_w \times 10^{-4}$	$\tilde{V}_1$	$(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$, deg MPa^{-1}		
			calcd	
		obsd	$\pi = -6.03 \times 10^{-2}$	$\pi = 0$
67	1.2566	−0.398	−0.612	−0.429
200	1.2643	−0.480	−0.706	−0.503

where c_1, $-\tilde{U}_1$, and $\tilde{C}_{p,1}$ are respectively the one-third total number of external degrees of freedom, the reduced vaporization energy, and the configurational heat capacity of the solvent, and $\tilde{\alpha}_1$ and $\tilde{\beta}_1$ are respectively the reduced thermal expansion coefficient and isothermal compressibility of the solvent. The ν parameter is related to the difference of cohesive energy and size between the solvent molecule (1) and polymer segment (2). The τ parameter is a measure of the difference in degrees of thermal expansion coefficient or free volumes of two components

$$\tau = 1 - T_1^*/T_2^*$$

and the π parameter expresses a difference in pressure reduction parameters of the two components

$$\pi = P_1^*/P_2^* - 1$$

The quantities T^* and P^* are respectively characteristic parameters of temperature and pressure. The relations for the first derivtives of χ_1 on temperature and pressure by the Patterson theory are represented by

$$[\partial(\chi_1/c_1)/\partial\tilde{T}_1]_{\tilde{P}=0} = [\tilde{V}_1^{2/3}/(4\tilde{V}_1^{-1/3} - 3)] \times [-\nu^2/(1 - \tilde{V}_1^{-1/3})^2 + 6\tau^2/(4\tilde{V}_1^{-1/3} - 3)^2] \tag{7}$$

$$-[\partial(\chi_1/c_1)/\partial\tilde{P}_1]_{\tilde{T}_c} = [3\tilde{V}_1^2/(4\tilde{V}_1^{-1/3} - 3)][-\nu^2 + (1 - \tilde{V}_1^{-1/3}) \times (14\tilde{V}_1^{-1/3} - 9)\tau^2/(4\tilde{V}_1^{-1/3} - 3)^2 - \tau\pi] \tag{8}$$

Values of $(\partial^2 H/\partial w_2^2)_c$ must be negative for the ucst of the endothermic condition and positive for the lcst of the exothermic condition. The value of $[\partial(\chi_1/c_1)/\partial\tilde{T}]_{\tilde{P}=0}$ is negative in the region of the ucst as the ν^2 term is dominant, while it is positive in the region of the lcst as the τ^2 term contributes more than the ν^2 term. Saeki et al. determined molecular parameters ν and τ from the molecular weight dependence of the ucst and lcst.[15] The τ^2 term contributes to χ_1 by almost the same amount as the ν^2 term in the vicinity of the ucst for the solution of polystyrene in cyclopentane. A negative value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst and a negative excess volume of mixing ($V_E < 0$) is expected for the system polystyrene–cyclopentane with a large contribution of the τ^2 term.

The critical interaction parameter χ_1(crit) at zero pressure is given as a function of the $\tilde{V}_1$ by[13]

$$\chi_1(\mathrm{crit}) = c_1\nu^2/(1 - \tilde{V}_1^{-1/3}) + c_1\tau^2/2[(4/3)\tilde{V}_1^{-1/3} - 1] = (1/2)(1 + r^{-1/2})^2 \tag{9}$$

where r is the ratio of molar volumes of the polymer and solvent. The value of $\tilde{V}_1$ at zero pressure in the second column of Table II was obtained from eq 9 with $c_1\nu^2 = 0.022$, $c_1\tau^2 = 0.100$, and r. The calculated $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ by use of $\tilde{V}_1$, $\nu^2 = 0.0312$, $\tau^2 = 0.142$, and $\pi = -0.0603$ is given in the fourth column of Table II. $P_1^* = 513.8$ MPa at 25 °C obtained from this work and $P_2^* = 546.79$ MPa at 25 °C by Flory et al.[39] were used for evaluation of π. The calculated $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ with an assumption of a zero value of the π parameter gives much better agreement with experiment and is given in the fifth column. It is noted from inspection of eq 7 and 8 that the discrepancy of the calculated $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ from the observed one is attributed to the overestimation of the τ^2 term.

The $\tilde{T}_1$ under pressure was obtained from eq 5 and 6 with $P_1^* = 513.8$ MPa, $\pi = -0.0603$, and molecular parameters by Saeki et al.[15] by assuming a constant value for $(1/2)(1 + r^{-1/2})^2$. The calculated (P,T) critical lines are given by the dotted lines in Figure 3. The agreement between the calculated and observed lines is satisfying in the region of low pressure and the dependence of $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ on the molecular weight is in semiquantitative agreement with theoretical prediction.

Acknowledgment. The authors thank the Ministry of Education in Japan for supporting them with a grant.

References and Notes

(1) (a) Hokkaido University; (b) Gunma University.
(2) G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **57**, 79 (1962).
(3) J. M. Bardin and D. Patterson, *Polymer*, **10**, 247 (1969).
(4) D. Patterson, *Macromolecules*, **2**, 672 (1969).
(5) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).
(6) D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, **49**, 98 (1970).
(7) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507, 3515 (1964).
(8) P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(9) R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6822 (1967).
(10) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).
(11) P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).
(12) J. M. G. Cowie, A. Maconnachie, and R. J. Ranson, *Macromolecules*, **4**, 57 (1971).
(13) K. S. Siow, D. Delmas, and D. Patterson, *Macromolecules*, **5**, 29 (1972).
(14) S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 246 (1973).
(15) S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, *Macromolecules*, **6**, 589 (1973).
(16) N. Kuwahara, S. Saeki, T. Chiba, and M. Kaneko, *Polymer*, **15**, 777 (1974).
(17) S. Konno, S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Macromolecules*, **8**, 799 (1975).
(18) S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **17**, 685 (1976).
(19) J. Ham, M. C. Bolen, and J. K. Hughes, *J. Polym. Sci.*, **57**, 25 (1962).
(20) P. Ehrlich and J. J. Kurpan, *J. Polym. Sci., Part A*, **1**, 217 (1963).
(21) G. Allen and C. H. Baker, *Polymer*, **6**, 181 (1965).
(22) C. D. Myrat and J. S. Rowlinson, *Polymer*, **6**, 645 (1965).
(23) L. Zeman, J. Biros, G. Delmas, and D. Patterson, *J. Phys. Chem.*, **76**, 1206, 1214 (1972).
(24) S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **16**, 445 (1975).
(25) S. Saeki, N. Kuwahara, and M. Kaneko, *Macromolecules*, **9**, 101 (1976).
(26) C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).
(27) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035, 2053, 2061, 2066 (1968).
(28) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968).
(29) P. J. Flory and H. Höcker, *Trans. Faraday Soc.*, **67**, 2258 (1971).
(30) H. Höcker and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2270 (1971).
(31) H. Höcker, H. Shih, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2275 (1971).
(32) R. A. Orwoll and J. A. Small, *Macromolecules*, **6**, 755 (1973).
(33) N. Kuwahara, T. Okazawa, and M. Kaneko, *J. Polym. Sci., Part C*, **No. 23**, 543 (1968).
(34) P. J. Flory and H. Shih, *Macromolecules*, **5**, 761 (1972).
(35) K. Sugamiya, N. Kuwahara, and M. Kaneko, *Macromolecules*, **7**, 66 (1974).
(36) M. Nakata, S. Higashida, N. Kuwahara, S. Saeki, and M. Kaneko *J. Chem. Phys.*, **64**, 1022 (1976).
(37) S. P. Lee, W. Tscharnuter, B. Chu, and N. Kuwahara, *J. Chem. Phys.*, **57**, 4240 (1972).
(38) R. Koningsveld, *Discuss. Faraday Soc.*, **49**, 144, 180 (1970).
(39) H. Höcker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.*, **67**, 2251 (1971).

Upper and Lower Critical Flocculation Temperatures in Sterically Stabilized Nonaqueous Dispersions

Melvin D. Croucher* and Michael L. Hair

Xerox Research Centre of Canada Limited, Mississauga, Ontario L5L 1J9 Canada.
Received April 3, 1978

ABSTRACT: The preparation and partial characterization of poly(acrylonitrile) latex particles stabilized by poly(α-methylstyrene) in n-butyl chloride have been described. It was observed that these sterically stabilized particles flocculated both on heating and on cooling. The upper and lower critical flocculation temperatures were found to correlate qualitatively with the Θ temperatures associated with the LCST and the UCST, respectively. Consideration of a temperature-dependent excluded volume integral allows the χ parameter, and hence the free energy of interpenetration of the stabilizing chains, to be predicted as a function of temperature. These temperature-dependent functions predict that, in principle, all nonaqueous sterically stabilized dispersions should show both enthalpic and entropic stabilization provided that a large enough temperature range can be scanned. It is suggested that flocculation at the LCFT can be largely ascribed to the contact energy dissimilarity between the stabilizing polymer and the dispersion medium, while flocculation at the UCFT is dominated by the free volume dissimilarity between the stabilizing moiety and the dispersion medium.

The steric stabilization of colloidal dispersions using polymeric surfactants is a subject of considerable scientific interest[1] and technological importance.[2] This method of stabilizing particles against coagulation has been found to be effective in aqueous and nonaqueous media. It is especially useful in nonaqueous media of low dielectric constant where electrostatic stabilization appears to be comparatively ineffective.

Three types of experiment involving sterically stabilized dispersions have been reported in the literature. They are incipient flocculation,[3] stability in polymer melts,[4] and measurement of the repulsive interactions between stable particles.[5,6] Incipient flocculation has been the most extensively reported measurement, and can be induced by changing the solvent quality of the dispersion media relative to that of the stabilizing polymer. This can be carried out through addition of nonsolvent or by changing the temperature (or pressure) of the system.[7] It has been observed that incipient instability is a reversible phenomenon[7] and that spontaneous redispersion occurs if the solvency of the disperse medium is improved with respect to the stabilizing polymeric moiety.

0024-9297/78/2211-0874$01.00/0