Lower Critical Solution Temperature in Linear Polyethylene—n-Alkane Systems

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ABSTRACT: The molecular weight dependence of the lower critical solution temperature (LCST) of linear polyethylene in n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16} and n-C_8H_{18} was determined and theta temperature Θ_L was obtained according to Shultz—Flory's equation. Observed values of Θ_L were compared with the values calculated by using equation-of-state parametes based on the theories on polymer solution developed by Flory and Patterson.

KEY WORDS   Lower Critical Solution Temperature / Polyethylene / Normal Alkane / χ Parameter / Equation of State /

It is common that the mutual solubility of a non-polar polymer with a polar or other poor solvent increases with increasing temperature until complete miscibility is reached at an upper critical solution temperature (UCST). There are, however, a few systems composed of a polar polymer and a polar solvent for which the mutual solubility increases with decreasing temperature and in which complete miscibility is attained at a lower critical solution temperature (LCST). These are, almost without exception, aqueous solution of a polar polymer, such as poly(ethylene oxide),[1] poly(propylene oxide),[1] partly acetylated poly(vinyl alcohol),[2,3] partly formalized poly-(vinyl alcohol),[2,3] methyl cellulose,[4] and poly-(vinyl methyl ether).[5] Such a LCST is found only for solutions in which both components are highly polar, and is usually below the boiling temperature of the solvent. Another type of solution which shows a LCST was found for systems composed of a non-polar polymer and a non-polar solvent,[11] for example, polystyrene—benzene,[6] polyisobutylene—n-pentane,[7] and poly-ethylene—n-alkane.[8-11] The LCST of these systems is usually found at higher temperature than the boiling temperature of the solvent and, moreover, negative heat of mixing is found near the LCST. The latter LCST has rather recently been noticed because it lies above the boiling temperature of the solvent, but seems to be a completely general phenomenon for polymer solutions.

Conventional theory of polymer solution by Flory—Huggins[12] failed to explain this LCST but the new thermodynamic theories on polymer solutions developed by Flory[9,13,14] and Patterson[17,18] can explain very well the new LCST phenomenon as discussed later.

The value of LCST is dependent on the molecular weight of polymers and decreases with increasing molecular weight, in contrast to the case of UCST. From the molecular weight dependence of LCST we can obtain the theta temperature Θ_L[8] by extraporating the values of LCST at various molecular weights to infinite molecular weight, in the same manner as to obtain the theta temperature Θ_U from UCST.[12]

Two of the authors[8] (A. N. and F. H.) have determined the molecular weight dependence of LCST for linear polyethylene fractions in n-pentane, and n-hexane and obtained Θ_L.[8] In this paper, we have further determined the molecular weight dependence of LCST for linear polyethylene fractions in n-heptane and n-octane and will discuss the observed values of Θ_L for polyethylene in n-alkanes in connection with the carbon number of n-alkanes. We have carried out some calculations to obtain Θ_L of polyethylene in n-alkanes from theoretical considerations basically developed by Flory and Patterson. Thus observed values of Θ_L are compared with calculated ones.

EXPERIMENTAL

Sample

A linear polyethylene Sholex 6009 (polyethylene of Marlex 50 type, manufactured by Japan Olefin Chem. Co.) was fractionated into 10 fractions in a column designed by us.[19] The polymer percipitated on Celite (No. 545) by cooling from xylene solution, was eluted at 127°C with mixtures of xylene and butyl cellosolve with increasing solvent concentration. The fractions were collected in methanol and filtered and dried under vacuum at 95°C for 8 hr. The molecular weight of linear polyethylene fractions was calculated from intrinsic viscosity in decalin at 135°C using eq 1.[20]

$$[\eta] = 6.2 \times 10^{-4} \, M_w^{0.70} \qquad (1)$$

Four n-alkanes, n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16} and n-C_8H_{18}, were used as solvents for the determination of LCST. n-C_5H_{12} and n-C_8H_{18} were obtained from Phillips Petroleum Co., and the purities were 99.6% and 99%, respectively. n-C_6H_{14} and n-C_7H_{16} were spectrograde reagents. These solvents were used without further purification.

Measurements of Precipitation Temperature

Each of the polymer fractions with different molecular weights was sealed in a small glass tube, under nitogen, together with solvent containing 10 ppm of 2, 6-di-*tert*-butyl-*p*-cresol. The mixtures were heated to an elevated temperature to dissolve the polymer completely: then the precipitation temperature was determined by visual observation to detect the temperature at which the solution becomes turbid upon slow heating. This temperature was in accord, within 0.2°C, with the temperature at which the turbidity disappears upon slow cooling. The critical precipitation temperature for each fraction was determined as the minimum point of the precipitation temperature vs. concentration curve.

RESULTS AND DISCUSSION

Flory and Patterson recently have developed thermodynamic theories on polymer solution using parameters in the equation of state. According to Flory,[13] chemical potential of solvent component relative to the pure solvent is

$$\frac{\mu_1 - \mu_1^0}{RT} = \left[\ln(1-\varphi_2) + \left(1 - \frac{x_1}{x_2}\right)\varphi_2 \right]$$
$$+ x_1 c_1 \left\{ 3 \ln\left(\frac{\tilde{v}_1^{1/3}-1}{\tilde{v}^{1/3}-1}\right) - \frac{(\tilde{v}_1 - \tilde{v})\tilde{v}_1^{1/3}}{\tilde{v}(\tilde{v}_1^{1/3}-1)} \right\}$$
$$+ \left(\frac{x_1\beta_{12}}{T\tilde{v}}\right)\varphi_2^2 \qquad (2)$$

where φ_2 is the segment fraction for polymer, x_1 and x_2 are the number of segments in solvent and polymer, respectively, $\tilde{v}_1$ and $\tilde{v}$ are the reduced volume of solvent and solution, respectively, and β_{12} is related to the exchange interaction parameter P_{12}^*. φ_2, $\tilde{v}_1$, $\tilde{v}$, and β_{12} are defined by

$$\varphi_2 = 1 - \varphi_1 = \frac{x_2 v_2^*}{x_1 v_1^* + x_2 v_2^*} \qquad (3)$$

$$\tilde{v}_1 = \frac{v_1}{v_1^*} \qquad (4)$$

$$\beta_{12} = \frac{p_{12}^* v^*}{R} = \left(\frac{p_\infty^* v_1^* b'}{R}\right)\left(\frac{1}{x_1} - \frac{1}{x_2}\right)^2 \qquad (5)$$

where v_1^* and v_2^* are the core volume per mole of segment of solvent and solution, respectively, p_∞^* is the characteristic pressure p^* of n-alkane with infinite number of carbon atoms and b' is assumed as constant for all n-alknanes.

The series expansion of the chemical potential given by eq 2 can be written as

$$\frac{\mu_1 - \mu_1^0}{RT} = -\left(\frac{x_1}{x_2}\right)\varphi_2$$
$$- \left(\frac{1}{2}\right)\left[1 - \frac{3x_1 c_1\left(1 - \frac{T_1^*}{T_2^*}\right)^2}{1 - \frac{4\tilde{v}_1 T}{T_1^*}} - \frac{2x_1\beta_{12}}{T\tilde{v}_1}\right]\varphi_2^2$$
$$+ 0(\varphi_2^3) \qquad (6)$$

where $3c_1$ is the number of external degrees of freedom per segment of solvent, and T_1^* and T_2^* are the characteristic temperatures of solvent and polymer. c_1 is defined by

$$c_1 = \frac{p_1^* v_1^*}{RT_1^*} \qquad (7)$$

From eq 6, we have the expression for interaction parameter.

$$\chi = \left(\frac{1}{2}\right)\left[\frac{3x_1 c_1\left(1 - \frac{T_1^*}{T_2^*}\right)^2}{1 - \frac{4\tilde{v}_1 T}{T_1^*}} + \frac{2x_1\beta_{12}}{T\tilde{v}_1}\right] + 0(\varphi_2) \qquad (8)$$

Also χ may be expressed by a series in powers of segment fraction φ_2.

$$\chi = \chi_1 + \chi_2\varphi_2 + \chi_3\varphi_2^2 + \cdots \quad (9)$$

Therefore, from eq 8 and 9, we have

$$\chi_1 = \left(\frac{1}{2}\right)\left[3x_1c_1\frac{\left(1-\dfrac{T_1^*}{T_2^*}\right)^2}{1-\dfrac{4\tilde{v}_1T}{T_1^*}}+\frac{2x_1\beta_{12}}{T\tilde{v}_1}\right] \quad (10)$$

The first term in the right hand side of eq 10 is an equation-of-state term (free volume term) and increases with increasing temperature while the second term is the contact energy term and decreases with increasing temperature. We confine present consideration to liquid—liquid miscibility. From the condition for critical miscibility,

$$\left(\frac{\partial\mu_1}{\partial\varphi_2}\right)_{T,p}=0$$

$$\left(\frac{\partial^2\mu_1}{\partial\varphi_2^2}\right)_{T,p}=0$$

Denoting χ for critical condition by χ_c, we have

$$\chi_c = \left(\frac{1}{2}\right)(1+x^{-1/2})^2 \quad (11)$$

where x is the ratio of the molar volumes of polymer and solvent. Since critical concentration, however, occurs at a very small volume fraction of polymer[12], χ_c is nearly equal to χ_{1c}, which is χ_1 at critical temperature. Therefore from eq 10 and 11, we have

$$(1+x^{-1/2})^2 = \frac{3x_1c_1\left(1-\dfrac{T_1^*}{T_2^*}\right)^2}{1-\dfrac{4\tilde{v}_1T_c}{T_1^*}}+\frac{2x_1\beta_{12}}{T_c\tilde{v}_1} \quad (12)$$

This equation shows the dependence of the critical solution temperature on the molecular weight of polymer. For infinite x, we can get

$$\frac{3x_1c_1\left(1-\dfrac{T_1^*}{T_2^*}\right)^2}{1-\dfrac{4\tilde{v}_1T_c}{T_1^*}}+\frac{2x_1\beta_{12}}{T_c\tilde{v}_1}=1 \quad (13)$$

This equation immediately predicts the occurrence of Θ_L in the mixture of n-alkane with polyethylene. With complete generality, the excess chemical potential of solvent may be expressed by neglecting higher terms of solute concentration by the following equation,

$$(\mu_1-\mu_1^0)_E = RT(\kappa_1-\psi_1)v_2^2 = RT(\chi_1-\tfrac{1}{2})v_2^2 \quad (14)$$

Where κ_1 and ψ_1 are heat and entropy parameter such that

$$\Delta\bar{H}_1 = RT\kappa_1v_2^2$$

$$\Delta\bar{S}_1 = R\psi_1v_2^2 \quad (15)$$

If we assume that the theta temperature Θ is expressed by

$$\Theta = k_1T/\psi_1 \quad (16)$$

we can get

$$(\mu_1-\mu_1^0)_E = -RT\psi_1\left(1-\frac{\Theta}{T}\right)v_2^2 \quad (17)$$

From eq 14, 17, and 12, we have

$$-\psi_1\left(1-\frac{\Theta}{T}\right)=\chi_{1c}-\frac{1}{2}=x^{-1/2}+\frac{1}{2x} \quad (18)$$

$$\frac{1}{T_c}=\left(\frac{1}{\Theta}\right)\left[1+\left(\frac{1}{\psi_1}\right)\left(x^{-1/2}+\frac{1}{2x}\right)\right] \quad (19)$$

where T_c is the critical solution temperature, which is obtained from the phase diagram of polymer—solvent system. If ψ_1 is in dependent
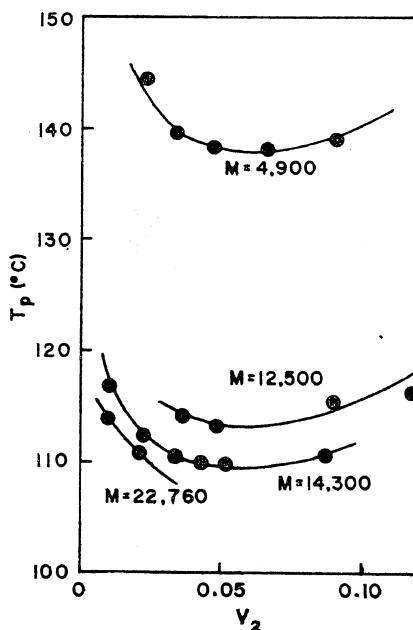

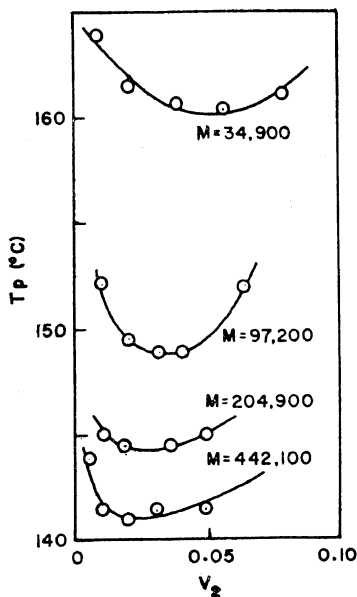**Figure 1.** Phase diagrams for polyethylene fractions in n-pentane.

Figure 2. Phase diagrams for polyethylene fractions in *n*-pentane.

Figure 3. Phase diagarms for polyethylene fractions in *n*-heptane.
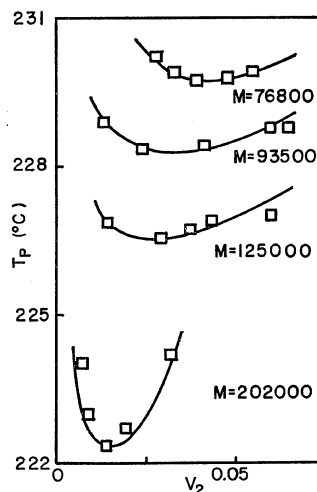

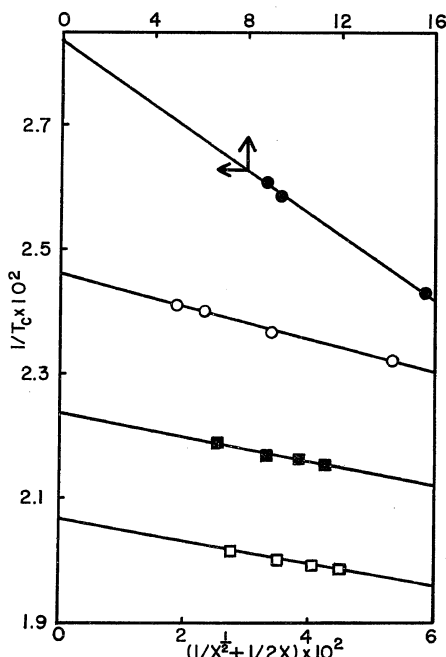**Figure 4.** Phase diagrams for polyethylene fractions in *n*-octane.

Figure 5. Plots of the reciprocal critical temperature against the molecular size function for polyethylene fractions in *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane.

of temperature we can get Θ and ϕ_1 from the plot of reciprocals of T_c against the function $x^{-1/2} + 1/2x$ according to Shultz—Flory method.

Thermodynamic theory of polymer solutions using the equation-of-state parameter shows that generally ϕ_1 is dependent on temperature[15,16], and eq 16 is not valid. Therefore theta temperature, Θ obtained by Shultz-Flory method is

not strictly correct. In this paper, however, we obtained experimentally theta temperature by Shultz—Flory method and the observed values of Θ was compared with the values calculated

by eq 13.

Precipitation temperature T_p for polyethylene fractions in $n\text{-}C_5H_{12}$, $n\text{-}C_6H_{14}$, $n\text{-}C_7H_{16}$, and $n\text{-}C_8H_{18}$ is plotted against the volume fraction v_2 of polymer in Figures 1, 2, 3, and 4, respectively. LCST decreases with increasing molecular weight of polyethylene in contrast to the case of UCST. Critical volume fraction decreases with increasing molecular weight in similar way with the case of UCST.

The plot of reciprocals of the lower critical solution temperature, T_c obtained from these curves against the function $x^{-1/2}+1/2x$ is shown in Figure 5, from which the theta temperature Θ_L, and entropy parameter ψ_1 were determined. These were shown in Table I together with the enthalpy parameter κ_1 at 130°C. Θ_L increases with increasing the number of carbon atoms in the n-alkane. Both ψ_1 and κ_1 show negative

Table I. Experimental values of Θ_L, ψ_1, and κ_1 for polyethylene—n-alkane systems

	$n\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	$n\text{-}C_7H_{16}$	$n\text{-}C_8H_{18}$
Θ_L, °C	*ca.* 80	133.3	173.9	210.0
ψ_1	−1.3	−1.0	−1.2	−1.1
κ_1 at 130°C	−1.1	−1.0	−1.1	−1.0

Table II. Calculated values of Θ_L for polyethylene—n-alkane systems

	$n\text{-}C_6H_{14}$	$n\text{-}C_8H_{18}$
Θ_L, °C (from eq 13)	133.0	215.4
β_{12}, °K		6.58	3.82
Θ_L, °C (from eq 20)	164.2	230.3

signs and, moreover, are nearly equal independent of the number of carbon in the n-alkane, at least from $n\text{-}C_5H_{12}$ to $n\text{-}C_8H_{18}$.

The calculated values of Θ_L of polyethylene—n-alkane systems by eq 13 were shown on first line of Table II. Numerical calculations have been carried out using the equation-of-state parameter shown in Table III with $b'=0.40$ and $x_1=n+1^{13}$, where n is the number of carbon atoms of n-alkane. These equation-of-state parameters were taken from the experimental values by Orwall and Flory[9] and selected data from the literature.[21] The thermal pressure coefficient, γ of $n\text{-}C_8H_{18}$ at theta temperature was obtained by extraporating the value of γ of $n\text{-}C_8H_{18}$ in 21° − 150°C to theta temperature. Since values of $n\text{-}C_5H_{12}$ and $n\text{-}C_7H_{16}$ at theta temperature were not available in literature and it was not possible to calculate the theta temperature of $n\text{-}C_5H_{12}$ and $n\text{-}C_7H_{12}$ by eq 13. Parameter β_{12} for polyethylene—n-alkane systems was shown on the second line of Table II. Calculated values of Θ_L agree with experimental value of Θ_L rather well.

Patterson[22] also has shown that Θ_L can be calculated by eq 20 together with the reduced equation-of-state of eq 21.

$$\tilde{P}_1=\frac{1+C_1\tau^2(1+x^{-1/2})^{-2}-\frac{4}{3}\tilde{V}_1^{-1/3}}{1-C_1\tau^2(1+x^{-1/2})^{-2}-\frac{2}{3}\tilde{V}_1^{-1/3}}\tilde{V}^{-2} \qquad (20)$$

$$\tilde{T}_1=(\tilde{P}_1\tilde{V}_1+\tilde{V}_1^{-1})(1-\tilde{V}_1^{-1/3}) \qquad (21)$$

where $\tilde{V}_1$ is the reduced volume per mole of solvent, C_1 is the number of external degrees of freedom of solvent molecule and τ is defined by

Table III. Equation-of-state parameters used in calculating Θ_L from eq 13

(a) n-alkane[9,21]

Liquids	t_c, °C	v_{sp}, cc g^{-1}	$\alpha\times10^3$, deg^{-1}	γ, cal cc^{-1} deg^{-1}	$\tilde{v}$	v^*, cc mol^{-1}	T^*, °K	P^*, cal cc^{-1}	xc
C_6H_{14}	133.0	1.840[19]	2.303[19]	0.086[9]	1.5651	14.454	4579	85.53	0.9511
C_8H_{18}	215.4	1.9547[19]	2.630[19]	0.0624	1.6745	14.798	5183	85.47	1.1052

(b) Polyethylene[9]

	t_c, °C	$\alpha\times10^3$, deg^{-1}	γ, cal cc^{-1} deg^{-1}	$\tilde{v}$	T^*, °K	P^*, cal cc^{-1}
	133.0	0.718	0.177	1.2430	7212	110.80
	215.4	0.768	0.126	1.2983	7612	103.95

Table IV. Equation-of-state parameters used in calculating Θ_L from eq 20

(a) n-alkane[9,21]

Liquids	t_c, °C	v_{sp}, cc g^{-1}	$\alpha \times 10^3$ deg^{-1}	γ, cal cc^{-1} deg^{-1}	$\tilde{v}$	v^*, cc mol^{-1}	T^*, °K	P^*, cal cc^{-1}	c
C_6H_{14}	164.2	1.9956[19]	3.018[19]	0.0614[9]	1.6832	14.577	4614	76.01	0.8459
C_8H_{18}	230.3	2.0331[19]	2.923[19]	0.0578	1.7209	14.976	5227	86.12	1.1176

(b) Polyethylene[9]

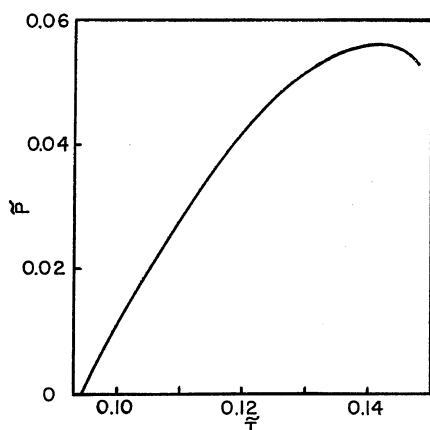| t_c, °C	$\alpha \times 10^3$, deg^{-1}	$\tilde{v}$	T^*, °K
164.2	0.727	1.2608	7406
230.3	0.785	1.3104	7646

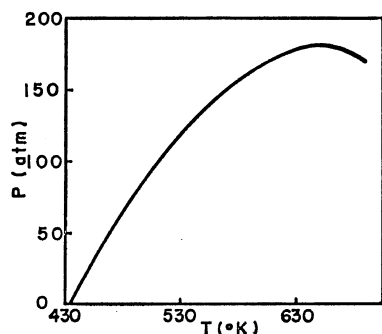**Figure 6.** Plot of $\tilde{P}$ against $\tilde{T}$ for polyethylene in n-hexane.

Figure 7. Plot of P against T for polyethylene in n-hexane.

$$\tau = 1 - \frac{T_1^*}{T_2^*} \qquad (22)$$

From eq 20 and 21, we can derive a relation between $\tilde{P}_1$ and $\tilde{T}_1$ and the extraporation of T to $P=0$ yields Θ_L. As an example, the relation between $\tilde{P}_1$ and $\tilde{T}_1$ for polyethylene with n-hexane is shown in Figure 6 and that between P and T is shown in Figure 7, from which we can obtain Θ_L. These values obtained for Θ_L are shown on the forth line of Table II. The equation-of-state parameters used in this calculation are shown in Table IV. These equation-of-state parameters were taken from experimental values by Orwall and Flory[9] and selected data from the literature.[21] Since γ values of n-C_5H_{12} and n-C_7H_{16} at theta temperature were not available in literature and it was not possible to calculate thata temperature of n-C_5H_{12} and n-C_7H_{12} by eq 20 and 21.

As shown in Table II, the value of Θ_L calculated by Patterson's method is considerably larger than that of observed Θ_L. Such results may be well explained in the following way.

Evidently from procedure above mentioned, Θ_L calculated by Patterson's method corresponds to temperature which satisfies a following equation.

$$1 + C_1\tau^2(1+x^{-1/2})^{-2} - \tfrac{4}{3}\tilde{V}_1^{-1/3} = 0 \qquad (23)$$

We can derive eq 23 from Flory's equation 13 with $\beta_{12}=0$ and together with the reduced equation of state (eq 21) at $P=0$. If the second term of the left hand side in eq 13 is neglected, the calculated value of Θ_L becomes larger. Therefore the disagreement of value of Θ_L calculated by Patterson's method with observed value of Θ_L with decreasing number of carbon atom of n-alkane is obvious considering that

we can't neglect β_{12} because of the end effect of the n-alkane with a small number of carbon atoms.

We obtained Θ_L by Shultz—Flory's methods as mentioned above, but Θ_L should be obtained by considering equation-of-state term. Also it must be noted that entropy parameter ψ_1 and enthalpy parameter κ_1 obained by Shultz—Flory's method are higher than those obtained by osmotic pressure measurement on dilute solutions[12]. These factors will be discussed in a subsequent publication.

REFERENCES

1. G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).
2. F. F. Nord, N. Bier, and S. N. Timasheff, *J. Amer. Chem. Soc.*, **73**, 289 (1951).
3. I. Sakurada, Y. Sakaguchi, and N. Ito, *Kobunshi Kagaku* (*Chem. High Polymers, Japan*), **14**, 41 (1957); Y. Sakuguchi, and N. Ito, *Ibid.*, **15**, 635 (1958).
4. K. Uda and G. Meyerhoff, *Macromol. Chem.*, **47**, 168 (1961).
5. C. E. Shildknecht "Vinyl and Related Polymers," Willy, New York, N. Y., 1952.
6. H. Tompa, *J. Polym. Sci.*, **8**, 51 (1952).
7. C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 215 (1962).
8. A. Nakajima and F. Hamada, *Rep. Progr. Polym. Phys. Japan*, **9**, 41 (1966).
9. R. A. Orwall and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967).
10. D. Patterson, G. Delmas, and T. Somcynsky, *Polymer*, **8**, 503 (1967).
11. P. I. Freeman and J. S. Rowlinson, *ibid.*, **1**, 20 (1960).
12. P. J. Flory, "Principle of Polymer Chemistry," Cornell University Press, New York, N. Y., 1953.
13. P. J. Flory, R. A. Orwall and A. Vrij, *J. Amer. Chem. Soc.*, **86**, 3507 and 3515 (1964).
14. P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).
15. B. E. Eichinger, *J. Chem. Phys.* **53**, 561 (1970).
16. B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).
17. G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **52**, 79 (1962).
18. D. Patterson, *Macromolecules*, **2**, 672 (1969).
19. S. Hayashi, F. Hamada, A. Saijo, and A. Nakajima, *Kobunshi Kagaku* (*Chem. High Polymers, Japan*), **24**, 769 (1967).
20. R. Chiang, *J. Phys. Chem.*, **69**, 1645 (1965).
21. S. Young, recorded by J. Timmermans, "Physico-Chemical Constants of Pure Organic Constants", Vol. 1, Elsevier Publishing Co., New York, N. Y., 1968.
22. D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1968).