Studies on the Interaction Parameter in Polysiloxane Solutions

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ABSTRACT: The thermodynamic properties of solutions of polydimethylsiloxane and silicon resin in non-polar solvents have been studied in a moderate concentration range at temperatures from 26 to 40°C. Applying Flory's theory, the interaction parameter χ_1 was calculated from the activity of solvent, which was determined from the lowering of its vapor pressure. It was found that the value of χ_1 and its temperature dependency are characteristic of the interaction of polysiloxane with solvent. The heat term (ΔW_h) and the entropy term (ΔW_s) in χ_1 were calculated from the temperature dependency of χ_1 at the average temperature. It was confirmed that the obtained relation between ΔW_h and ΔW_s is represented by a smooth curve, independent of concentration and solvent which goes nearly through the origin.

KEY WORDS Polydimethylsiloxane / Silicone Resin / Thermodynamics / Interaction Parameter / Polymer Solution /

The Flory—Huggins equation (eq 1) has been widely used in interpreting the thermodynamic properties of polymer-liquid mixtures.

$$\Delta \mu_1 = RT[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2]$$
$$(1)$$

where $\Delta \mu_1$ is the difference in the chemical potential between the solvent in a polymer solution and the pure solvent, x is the ratio of the molecular volumes of polymer and solvent, v_2 is the volume fraction of polymer in the solution, and χ_1 is defined as a free energy parameter to characterize a given polymer—solvent pair at a specified temperature.[1]

χ_1 has been obtained by measuring the vapor pressure of solvent on polymer solution[2,3] or the osmotic pressure of solution.[4] The vapor pressure method is the most adequate to measure the χ_1 in a moderately concentrated solution of either linear or branched polymer.

The natural rubber—benzene system has been studied first. The χ_1 in the system is found to be independent of the concentration over a wide range.[5] However, generally speaking, χ_1 depends on the concentration. For example, it has been shown[6] that the χ_1 for polystyrene solution increased in methylethylketone, but decreased in toluene, with increasing polymer concentration.

The separate contributions of the heat component and the entropy component have been studied by many workers.[7] Recently, C. Booth and coworkers[8] obtained the values of ΔW_h and ΔW_s from the values of χ_1 at two temperatures for natural rubber in acetone, methyl ethyl ketone and ethyl acetate, and showed these obtained values of ΔW_h and ΔW_s were positive and increased with increasing polymer concentration. Takenaka has shown that the relation between ΔW_h and ΔW_s in a nitrocellulose—acetone system gives a straight line which goes through the origin.[9]

In this report, the thermodynamic properties of a solution of polysiloxanes in various non-polar solvents were investigated in terms of the interaction parameter χ_1, and of the heat and entropy components in χ_1.

THEORETICAL

As a general representation of the free energy of mixing n_1 solvent molecules with n_2 polymer molecules to form a solution containing a volume fraction v_2 of polymer, the following equation has been given

$$\Delta F_M = kT[n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 n_1 v_2]$$
$$(2)$$

χ_1 is a parameter which characterizes the free energy change in the standard state, $kT\chi_1 n_1 v_2^1$,

which has been assigned to the process, in which pure polymer and pure solvent are converted to the contact state of the two components in the solution.[10]

The entropy change, ΔS_M, and the heat of mixing, ΔH_M, are given by

$$\Delta S_M = - (\partial F_M / \partial T)p$$
$$= \Delta S_M{}^* - k[\partial \chi_1 T)/\partial T]n_1 v_2 \qquad (3)$$

and

$$\Delta H_M = - T^2[\partial(\Delta F_M/T)/\partial T]_p$$
$$= - kT^2(\partial \chi_1/\partial T)n_1 v_2 \qquad (4)$$

where $\Delta S_M{}^*$ is the configurational entropy change of mixing in the ideal case,[1] that is

$$\Delta S_M{}^* = - k(n_1 \ln v_1 + n_2 \ln v_2) \qquad (5)$$

and the term $- k[\partial(\chi_1 T)/\partial T]n_1 v_2$ represents the standard state entropy change.[11] Representing the heat term and the entropy term in χ_1 with ΔW_h and ΔW_s, respectively, the following equation is defined, on the assumption that ΔW_h and ΔW_s are independent of temperature.[1]

$$RT\chi_1 = \Delta W_h - T\Delta W_s \qquad (6)$$

In this report, the value of χ_1 was calculated by using eq 1 from the activity of the solvent, which was obtained by measuring the vapor pressure p of solvent over the polymer solution, relative to that p_0 over pure solvent, in equilibrium.

EXPERIMENTAL

Material

Polydimethylsiloxane (I) and silicone resin (II) were synthesized by the ordinary method and were treated to cut low molecular portions by precipitation in methyl alcohol from a tetrachloro methane solution. The above silicone resin was poly(dimethyldiphenylsiloxane) with branched chains, in which the ratio of the methyl group to the phenyl group was 1.74. Their molecules were shown to be flexible and noncrystalline by literature already published.[12] The molecular weight was found to be 88000 for sample I by the intrinsic viscosity method,[13] and 4200 for sample II by ebullioscopy with toluene. Their densities, which were shown in Figure 1,

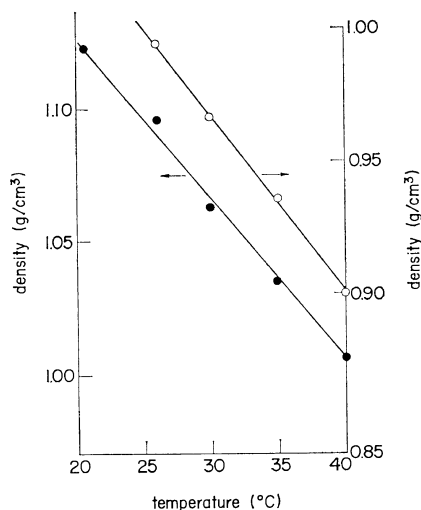were measured by means of a picnometer.

Figure 1. Density of polydimethylsiloxane (—○—) and silicone resin (—●—).

Solvents used in this experiment were nonpolar solvents, that is, benzene, toluene, ethyl benzene, n-hexane, and n-octane. They were purified by distillation from commercial reagents and their purity was checked by gas chromatography. Their densities were referred from published data.[14] Prepared solutions were left until mixing reached a uniform state. In particular, solutions in relatively higher concentrations were left for a few days to make sure they were completely uniform. Incomplete solutions could be checked by abnormal values of the ratio of p/p_0.

Measurement of Vapor Pressure

It was found, in the measurement of the ratio of p/p_0, that a large part of the error arose from the deviation of the temperature at which p were measured from that at which p_0 were measured. So as to compensate for this, differential manometry was used according to the same principle described by Gee and Treloar.[2] The manometer immersed in the constant temperature bath was controlled within an accuracy of $\pm 0.01^\circ$C and the head of mercury was read to 0.005 cm by a cathetometer. The relations of p/p_0 vs. v_2 at measuring temperatures are shown in Figures 2 and 3.
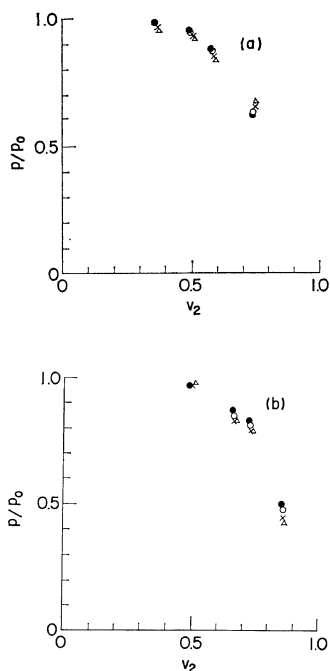
Figure 2. Concentration (volume fraction) dependence of the activity of solvent in the solution of polydimethylsiloxane; examples of n-hexane (a), and benzene (b).
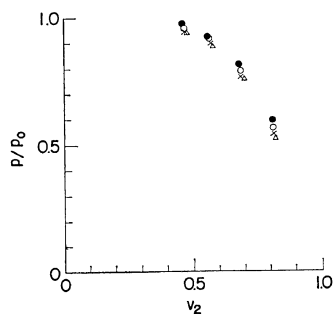

Figure 3. Concentration (volume fraction) dependence of the activity of solvent in the solution of silicone resin; an example of toluene.

CALCULATION OF χ_1

The values of χ_1 were calculated by eq 1, where the term $1/x$ was neglected as it was far less than unity. The values of v_2, assuming that no volume change occurred on mixing, were calculated at each temperature from the following equation

$$v_2 = \frac{1}{\dfrac{W_1}{W_2} \times \dfrac{\rho_2}{\rho_1} + 1}$$

where ρ_1, ρ_2 are the densities of solvent and solute, respectively.
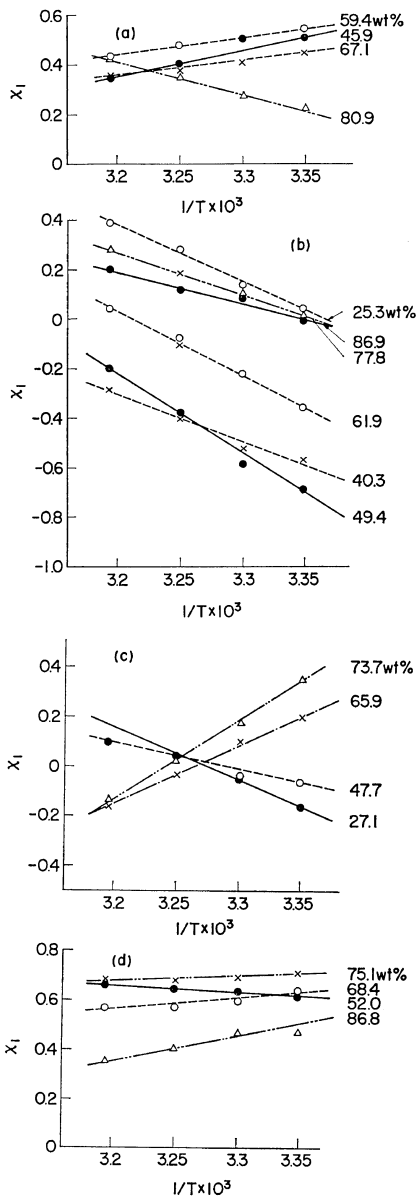

Figure 4. Temperature dependence of the interaction parameter χ_1 for polydimethylsiloxane—solvent systems: (a) n-hexane, (b) n-heptane, (c) n-octane, (d) benzene, (e) toluene, and (f) ethylbenzene.

Figure 4. (continued)

Figure 5. Temperature dependence of the interaction parameter χ_1 for silicone resin—solvent systems: (a) n-octane, (b) benzene, and (c) toluene.
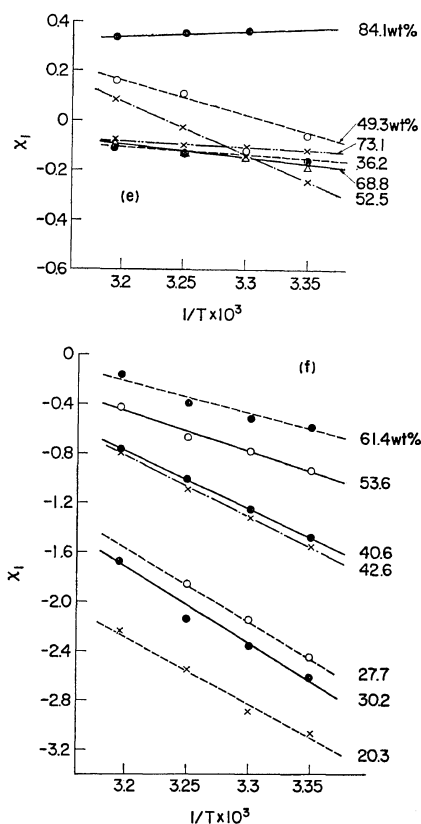
On the assumption that the volume fraction of solute in a solution was constant in the range of temperature studied, the χ_1 values were plotted against $1/T$ in Figures 4 and 5. The obtained graph was found to be a straight line relation. Then, using eq 6, the resolution of χ_1 into ΔW_h and ΔW_s terms was made from the slope and intercept, respectively. ΔW_h and ΔW_s obtained are listed in Tables I and II. Furthermore, ΔW_h was plotted against corresponding ΔW_s and a curve was obtained to show the relation between them.

DISCUSSION

The dependence of the activity of solvent on the polymer concentration has been estimated from the activity *vs.* volume fraction curves.[15] The theoretical curve of the activity *vs.* volume fraction has been given by M. L. Huggins,[15] on the assumption that the interaction parameter
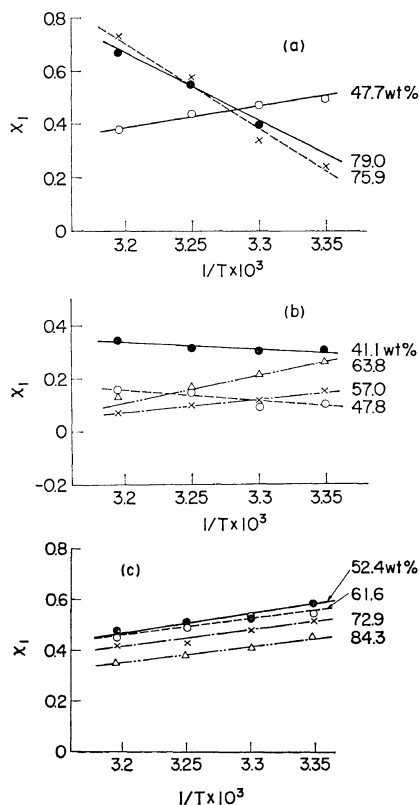
χ_1 is independent of concentration at a constant temperature. An example of such a system is the solution of natural rubber in benzene investigated by G. Gee and L. R. G. Treloar.[2] But such a solution as the interaction parameter being independent of concentration is rather fortuitous. For example, natural rubber in acetone, methyl ethyl ketone, or ethyl acetate, showed concentration dependency in its interaction parameter.[8] If the interaction parameter depends on concentration, the relation of the activity with concentration should deviate from the above theoretical relation curve.

In this experiment, the relations of the activity with concentration were shown in Figures 2 and 3. Since these relations showed that the activities of solvent decreased non-uniformly as the polymer concentration increased, the interaction parameter in the studied solution depends on the concentration. These figures show also

Table I. ΔW_h and ΔW_s in polydimethylsiloxane solutions at 33°C

Solvent, n-hexane

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.367	0.46	0.35	2.1	6.3
0.499	0.51	0.44	1.3	3.6
0.582	0.42	0.36	1.2	3.1
0.746	0.28	0.42	−2.6	−9.5

Solvent, n-heptane

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.194	0.15	0.39	−4.5	−15.8
0.315	−0.49	−0.29	−3.8	−12.0
0.413	−0.54	−0.20	−6.4	−20.7
0.535	−0.23	0.05	−5.3	−17.5
0.712	0.10	0.28	−3.4	−11.8
0.825	0.06	0.20	−2.6	−9.1

Solvent, n-octane

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.215	−0.05	0.17	−4.2	−14.1
0.400	−0.08	0.11	−2.2	−7.4
0.585	0.09	−0.36	8.4	28.4
0.672	0.19	−0.14	6.3	21.1

Solvent, benzene

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.496	0.62	0.66	−0.74	−3.7
0.664	0.61	0.56	−0.93	−4.1
0.731	0.70	0.68	0.40	−0.036
0.857	0.46	0.35	2.0	6.0

Solvent, toluene

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.338	−0.14	−0.11	−0.58	−1.7
0.467	0.02	0.17	−2.8	−9.6
0.499	0.14	0.09	−4.3	−14.4
0.664	−0.15	−0.09	−1.1	−3.4
0.700	−0.11	−0.09	−0.42	−1.2
0.827	0.36	0.34	0.42	0.70

Solvent, ethylbenzene

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.187	−2.83	−2.26	−10.8	−41.3
0.381	−1.26	−0.76	−9.3	−28.8
0.401	−1.31	−0.80	−9.8	−30.6
0.510	−0.79	−0.45	−6.5	−20.3
0.589	−0.48	−0.21	−4.8	−15.5

Table II. ΔW_h and ΔW_s in silicone resin solutions at 33°C

Solvent, benzene

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.366	0.26	0.35	−1.6	−5.8
0.430	0.11	0.12	−0.21	−0.92
0.522	0.12	0.07	0.94	2.8
0.593	0.21	0.11	1.9	5.9

Solvent, toluene

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.473	0.54	0.46	1.5	4.1
0.567	0.52	0.46	1.1	2.8
0.687	0.48	0.41	1.3	3.6
0.814	0.41	0.35	1.2	3.4

Solvent, n-octane

v_2	χ_1 30°C	χ_1 40°C	$\Delta W_h \times 10^{-3}$	ΔW_s
0.421	0.47	0.39	1.6	4.4
0.675	0.38	0.72	−6.4	−22.4
0.714	0.42	0.68	−5.1	−18.2

that the temperature-dependency of the activity of solvent hardly appeared at all in some concentrations.

The relations between the interaction parameter χ_1 and the reciprocal of absolute temperature gave straight lines, as shown in Figures 4 and 5. The heat term (ΔW_h) and the entropy term (ΔW_s) in χ_1 obtained from these graphs are shown in Tables I and II.

Recently, B. E. Eichinger and P. J. Flory have pointed out that a part of the standard state free energy change arises from the contribution of the equation-of-state, which is responsible for almost all of the concentration dependence of χ_1.[16] And it has been found that polysiloxane chains, which are coiled into helices[12] in the pure state, are easily deformable in the dissolved state.[17,18] Then, the polysiloxane solution is subject to the contribution from the equation-of-state, characteristic of the kind of solvent.

The values of χ_1 in the system of ethyl benzene for polydimethylsiloxane depended markedly on concentration. This system, in which ΔW_h and ΔW_s were found both in large negative values, exhibits a lower critical solution temperature in a wide range of concentrations.[19] It is expected in such a solution that χ_1 contains the large negative contribution from the equation-of-state.[20]

On the other hand, in the systems of n-hexane, n-octane, benzene and toluene for polydimethyloxane, χ_1 was found to be independent of concentration at and near the middle temperature observed, 33°C. In these systems, absolute values of ΔW_s are small, and the value of ΔW_s varies in proportion to the variation of ΔW_h with concentration. Namely, corresponding ΔW_h and ΔW_s are plotted on an almost straight line in the vicinity of origin, as shown in Figure 6. Then, the variations of ΔW_h and $T\Delta W_s$ with concentration may compensate one another.

The same relation in the silicone resin solution is apparently a straight line, as shown in Figure 7, and this result accounts for the concentration-independence of χ_1 near 33°C.

The benzene solution indicates that the negative value of ΔW_h in lower concentrations inverts its sign at higher concentrations. The
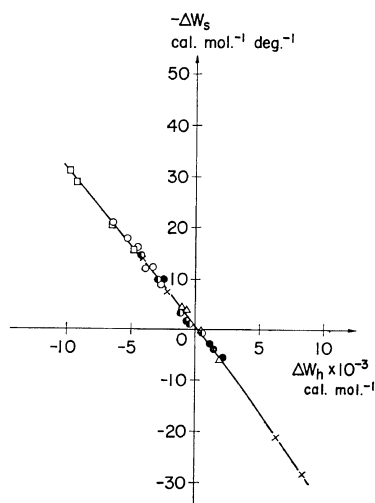

Figure 6. Relation between ΔW_h and ΔW_s for polydimethylsiloxane—solvent systems: (●) n-hexane, (○) n-heptane, (×) n-octane, (△) benzene, (◑) toluene, and (□) ethylbenzene.
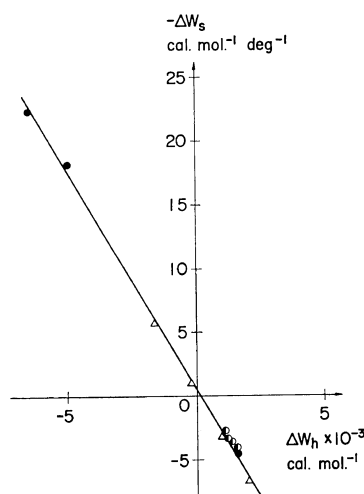

Figure 7. Relation between ΔW_h and ΔW_s for silicone resin—solvent systems: (●) n-octane, (△) benzene, and (◑) toluene.

same trend has been found in the polyisobutylene solution in cyclohexane[21] and n-pentane.[20] However, the positive values of ΔW_h at higher concentrations of this solution are too uncertain to enable conclusions to be drawn.

The large positive values of ΔW_h, as found in the solution of polydimethylsiloxane in n-hexane and in that of silicone resin in n-octane,

predict the limited miscibility that agrees with the observed phase separation in lower concentrations.

The graph, in which ΔW_h are plotted against the corresponding ΔW_s, shows a curve for the polydimethylsiloxane solution, whereas it shows a straight line for the silicone resin solution. However, the relations between ΔW_h and ΔW_s may be considered to be a straight line in the range of small ΔW_h and ΔW_s, either in the solution of polydimethylsiloxane or in that of silicone resin. The above graphs show readings nearly through the origin. This trend agrees with Takenaka's data.[9]

Takenaka has obtained the above data which were independent of the molecular weight of nitrocellulose.[9] It is confirmed in this experiment, that the said relations between ΔW_h and ΔW_s are independent of the solvent, although non-polar, and of concentration.

CONCLUSION

The thermodynamic properties of two types of polysiloxane in non-polar solvent systems were studied. It was found that the values of χ_1 and its temperature dependency are characteristic of the combination of polysiloxane and solvent. The relation between the heat term ΔW_h and the entropy term ΔW_s was represented with a smooth curve for each polysiloxane solution. The said relations were confirmed to be independent of the concentration and the kind of solvent, although the said solvents are limited to being non-polar. It was found, furthermore, that the said curve goes nearly through the origin, for each polysiloxane solution.

REFERENCES

1. P. J. Flory, "Principles of Polymer Chemistry" Cornell University Press, Ithaca, N. Y., 1953, Chapter 12.
2. G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).
3. S. Prager, E. Bagley, and F. A. Long, *J. Amer. Chem. Soc.*, **75**, 2742 (1953).
4. P. J. Flory and H. Daoust, *J. Polym. Sci.*, **25**, 429 (1957).
5. G. Gee, *J. Chem. Soc.*, **1947**, 280.
6. C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 677 (1950).
7. C. Booth, G. Gee, M. N. Jones, and W. D. Tayler, *Polymer*, **5**, 353 (1964).
8. C. Booth, G. Gee, G. Holden, and G. R. Williamson, *Polymer*, **5**, 343 (1946).
9. H. Takenaka, *J. Polym. Sci.*, **24**, 321 (1957).
10. See footnotes of P. J. Flory, "Principle of Polymer Chemistry", Cornell University Press, Ithaca, 1953, p 510.
11. E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).
12. H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 1401 (1947); E. C. Warrick, M. J. Hunter, and M. J. Barry, *ibid.*, **44**, 2196 (1952); S. M. Ohlberg, L. E. Alexander, and E. L. Warrick, *J. Polym. Sci.*, **27**, 1 (1958); E. G. Rochow, "An Introduction to the Chemistry of the Silicones" John Wiley and Sons, Inc., New York, N.Y., 1947, Chapter 4, p 60.
13. J. Barry, *J. Appl. Phys.*, **17**, 1020 (1946).
14. Deutshen Chemischen Gesellschaft, "Beilsteins Hundbuch der Organischen Chemie", Band 1 (1928) u. Band 5 (1930), Erstes Ergänzungswerk, Julius Springer, Berlin.
15. M. L. Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943).
16. B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).
17. P. J. Flory, L. Mandelkern, J. B. Kinsinger, and W. B. Schultz, *J. Amer. Chem. Soc.*, **74**, 3364 (1952).
18. M. J. Newing, *Trans. Faraday Soc.*, **46**, 613 (1950).
19. C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *Polymer*, **3**, 213 (1962).
20. B. E. Eichinger and P. J. Flory, *Trans. Farady Soc.*, **64**, 2066 (1968).
21. B. E. Eichinger and P. J. Flory, *ibid.*, **64**, 2061 (1968).