eq. 1, well within the range of their uncertainty, could bring about agreement. Such modification would not affect the interpretation or general magnitude either of the isomerization energies or of the shift in bond distances.

Of the alternative factors responsible for the difference between hydrocarbons and the diamond, purely electrostatic effects should be small. It seems unprofitable to invoke second-order hyperconjugation because effects of first-order hyperconjugation are not clearly evident in a variety of recently determined ground state structures of molecules. Similarly, it appears unnecessary to attribute the differences to a change of hybridization possibly associated with the 3° difference in the C–C–C angles. The relationship between bond angles and hybridization seems less direct than popularly supposed, presumably because of bond bending due to non-bonded repulsions. It is interesting to note, in this connection, that in the *n*-hydrocarbons (tetrahedral bonds) the C–C–C angles, which are increased by steric strain, are almost the same as in isobutene (trigonal bonds) where the Me–C–Me angle is decreased by steric strain, and where the C–C bond is appreciably shorter.[7] According to the scheme of Dunitz and Schomaker,[8] the bending of the bonds in *n*-hydrocarbons should have a negligible effect on the C–C distance.

The *n*-hydrocarbon C–C distance of 1.533 ± 0.003 Å. appears in some respects a more suitable reference for saturated molecules than the diamond distance. It should be pointed out, however, that neither distance seems a satisfactory reference for conventional estimations of bond orders in conjugated systems with trigonal bonds. A single bond distance of about 1.48 Å. for cases in which both C atoms participate in double bonding is suggested by the value of 1.506 Å. for the single bond in isobutene.[7] For reasons to be discussed elsewhere,[7] we prefer to regard the single bond in isobutene as a pure single bond, shortened by effects of hybridization and relaxation of non-bonded repulsions but altered very little by hyperconjugative effects.

Much of the present work on internuclear distances is inaccurate or confused by the different operational definitions of bond lengths associated with various spectroscopic and diffraction methods, so that an extensive comparison now is difficult. Preliminary comparisons indicate that the above approach may prove generally useful in correlating precise molecular structures as well as energies of formation.

MORE ADDED IN PROOF.—It is now apparent that the dependence on r assumed above for the H–H term is too extreme and, accordingly, the result for the *trans–gauche* energy difference is somewhat fortuitous. An improved potential function to be described elsewhere, coupled with corrections for deformation and zero-point effects, has led to a better value of the energy difference.

AMES, IOWA

[7] R. A. Bonham and L. S. Bartell (to be published).

[8] J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

Variation of the Thermodynamic Ideal Temperature in the Polystyrene–Cyclohexane System[1]

BY DONALD MCINTYRE, J. H. O'MARA AND B. C. KONOUCK

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The second virial coefficients of cyclohexane solutions of several fractions of polystyrene prepared in slightly different ways have been determined by light scattering and osmometry near the theta, or ideal, temperature. The results indicate that the ideal temperature is increased as the molecular weight is decreased. The larger increase is due to small but increasingly effective chemical interactions when an *n*-butyl mercaptan group is incorporated in the chain. A much smaller effect appears to exist even when the chain is apparently uniform.

According to the earlier theories of Flory,[2] for solutions of all molecular weights of a given polymer in a particular solvent there is a temperature, called the theta temperature, at which the solvent–polymer segment interaction allows the penetration of polymer segments among each other freely. Consequently the equations relating the experimental quantities of osmotic pressure, turbidity and concentration gradient in centrifugation to the molecular weight and concentration at the theta temperature would be written without the second virial term in equations 1, 2 and 3. The terms are the same as those used by Flory.[2] In

$$\pi/c = RT/M + A_2c + \ldots \quad (1)$$

$$Hc/\tau = 1/MP(\theta) + 2A_2c + \ldots \quad (2)$$

$$(H_u/RT)(c_x/(\mathrm{d}c/\mathrm{d}x)) = 1/M_x + 2A_2c_x + \ldots \quad (3)$$

this case the osmotic pressure yields the familiar van't Hoff relation which would correspond to an ideal solution. In this sense the theta temperature may also be referred to as an ideal temperature.

By working under these ideal conditions the measurement of the molecular weights of high polymers can be facilitated. Thus in an effort to determine accurate molecular weights of fractions of polystyrene, samples were prepared under conditions best suited to obtaining large amounts of fractions in various molecular weight ranges. These fractions of polystyrene then were studied under ideal conditions by equilibrium ultracentrifugation, light scattering and osmometry on the assumption that the ideal temperatures would be identical for all of the fractions when they were dissolved in cyclohexane. However, it was discovered that the

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[1] Presented at the 132nd Meeting of the American Chemical Society in New York, N. Y., on September 9, 1957.

[2] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XII.

ideal temperatures were not the same for all of the fractions.

In the meantime, Orofino and Flory[3] presented a new theoretical calculation which predicted that the theta temperature might be different for different molecular weights if the terms in the heat of mixing did not have certain explicit numerical values simultaneously. The observed change of the theta temperature with the molecular weight was much larger than this theory could predict. As a consequence, additional fractions of polystyrene were prepared and studied in order to differentiate between the possible effects of chemical structure on the theta temperature and effects of the molecular weight alone. This work indicates that the large differences that can be observed in the theta temperature are due to internal chemical differences rather than to differences in molecular weight. In addition, there still remains a very small effect of molecular weight on the theta temperature.

Experimental

Materials. Polymer A.—Vacuum-distilled styrene (Eastman) was polymerized in bulk at 70° for 2.5 hours with 1 mole % benzoyl peroxide as initiator and 0.2 mole % *n*-butyl mercaptan (Eastman) as transfer agent. The reaction mixture was poured into methanol and later precipitated by the addition of water. The viscosity–average molecular weight of the whole polymer was 34,000. Fractionation of the sample began with an initial concentration of 0.6% in methyl ethyl ketone–acetone mixture (1:1) using methanol as a precipitant. Twelve fractions ranging from 110,000 to 5,500 finally were obtained.

Polymer B.—Vacuum-distilled styrene (Eastman) was polymerized in bulk with 0.05 mole % benzoyl peroxide as initiator at 70° for 18 hours. The reaction mixture was poured into methanol with vigorous stirring. Fractionation of the sample was started with an initial concentration of 0.48% polystyrene in methyl ethyl ketone. This was followed by a recombination and subsequent fractionation at a concentration of 0.1% in methyl ethyl ketone. Twenty-five fractions were obtained in this fashion with molecular weights ranging from 1,000,000 to 108,000.

Polymer O.—Vacuum-distilled styrene (Eastman) was polymerized in a dilatometer in bulk by thermal initiation at 180°. Within a few minutes the dilatometer was removed from the hot oil-bath and cooled quickly to room temperature. The conversion to polymer was about 30% complete, and the viscosity–average molecular weight of the bulk polymer after precipitation in methanol was about 51,000. The precipitation and fractionation were the same as described above for polymer A.

Cyclohexane.—Reagent-grade cyclohexane (Fisher) was used throughout the work. The absence of benzene was confirmed by the absence of change in refractive index on elution of the cyclohexane through silica gel.

Since previous workers[4,5] had shown that water had a pronounced effect on the virial coefficients in the polystyrene–cyclohexane system all the cyclohexane that was used, except on one occasion, was distilled from a column packed with glass helices. On one occasion the cyclohexane was distilled over sodium with rigid exclusion of water vapor from the system.

Procedures. Refractive Index Increment.—Refractive index increments were determined in a thermostated Hilger Rayleigh interferometer using the 546-mμ light from an AH-3 mercury arc and Corning filters 3484, 5120 and 4303. Each compartment of the cell was entirely closed except for an access hole to insert the hypodermic syringe. This prevents volatilization, isothermal distillation or creep of the liquids over the partitions.

Light Scattering.—Light scattering measurements were made in a Phoenix light-scattering photometer whose receiver optics, cell holder and entrance slits, as well as power supply and amplifier, had been replaced to produce a better defined optical instrument and a more stable signal. The acceptance angle (half-angle), defined by the aperture stop, was 2.8° using a telecentric receiving system with a field stop that viewed a 6.8 × 2.7-mm. field at the center of the cell. The light was vertically polarized, and the beam constancy was checked repeatedly with a slightly turbid glass prism as well as with a sample of benzene. This instrument was calibrated by the use of fraction B-II-3 whose molecular weight had been measured previously using an equilibrium ultracentrifuge.

The constant-temperature cell housing maintained the temperature constant within ±0.05° of the desired value. The housing was supplied by water pumped from a constant-temperature bath. The cell was weighed before and after each run to observe any volatilization losses, which never changed the concentration by more than 2 parts in 1000. The dissymmetry method was used in calculating the molecular weight.

The refractive index correction for the instrument was applied to all of the results and is included in the constant term. A cylindrical cell was used throughout the work.

Equilibrium Ultracentrifugation.—A Svedberg equilibrium centrifuge manufactured by LKB Produkter was used, as described elsewhere.[6]

Osmometry.—The osmometric results were obtained with a block osmometer designed and constructed at the National Bureau of Standards and also with Stabin[7] osmometers. The membranes were "never-dried" gel cellophane, No. 600.[8] All of the measurements were equilibrium osmotic pressures and required about 5 days to come to equilibrium.

Preparation of Solutions.—All solutions were prepared on a weight basis from freeze-dried polymer samples whose remaining solvent was less than 0.5%, as determined by high-vacuum drying experiments above the glass temperature. The light-scattering solutions were prepared by filtration through ultra-fine glass filters–all filtrations being conducted inside a thermostated box. Concentration dependence was determined by serially diluting or occasionally serially concentrating solutions. The serial dilution was simpler and gave no different results in terms of the turbidity or dissymmetry. All experimental concentrations are expressed in g./dl., except the values of d*n*/d*c*, which are customarily expressed as ml./g.

Experimental Results

Light Scattering. Measured Refractive Index Increment.—Table I lists the refractive index increment, d*n*/d*c*, calculated at different temperatures from the equation $dn/dc = 0.1693 + 3.10 \times 10^{-4} (t - 30)$, where t is the centigrade temperature. This equation best represents the experimental data at 28.9, 34.0, 38.6 and 53.5° for the interferometrically measured d*n*/d*c* of polystyrene in cyclohexane in the concentration range of 0.1 to 0.4 g./dl. The concentration for each temperature was calculated by assuming that the concentration of a solution made up at 30° could be used for the other temperatures by correcting for the change in specific volume of the solvent only.

Table I

Refractive Index Increment and Thermal Correction Factor for c/τ' for Polystyrene in Cyclohexane

Temp., °C.	d*n*/d*c*	*F*
30	0.1693	0.988
35	.1708	1.000
40	.1724	1.012
45	.1739	1.023
50	.1755	1.035
55	.1770	1.046

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[3] T. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

[4] W. R. Krigbaum, This Journal, **76**, 3758 (1954).

[5] H.-J. Cantow, *Z. physik. Chem.* (*Frankfurt*), **7**, 58 (1956).

[6] L. Mandelkern, L. C. Williams and S. G. Weissberg, *J. Phys. Chem.*, **61**, 271 (1957).

[7] J. V. Stabin and E. H. Immergut, *J. Polymer Sci.*, **14**, 209 (1954).

[8] Supplied through the courtesy of the American Viscose Company.

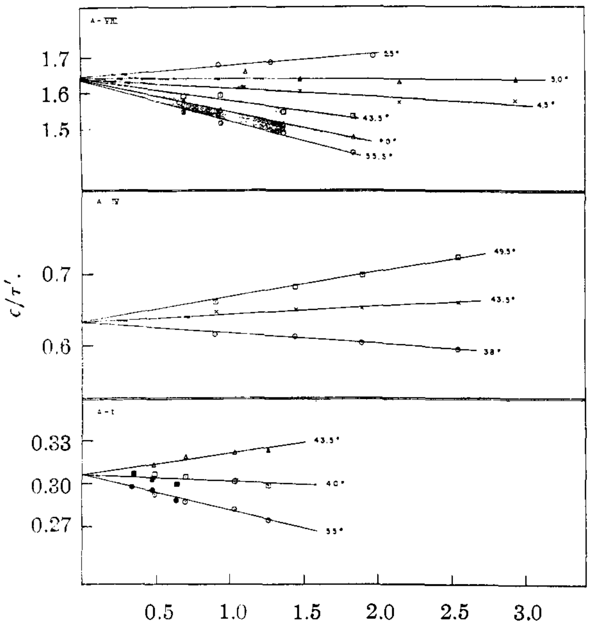

Fig. 1.—Light-scattering measurements on "A fractions" of polystyrene in cyclohexane at different temperatures.

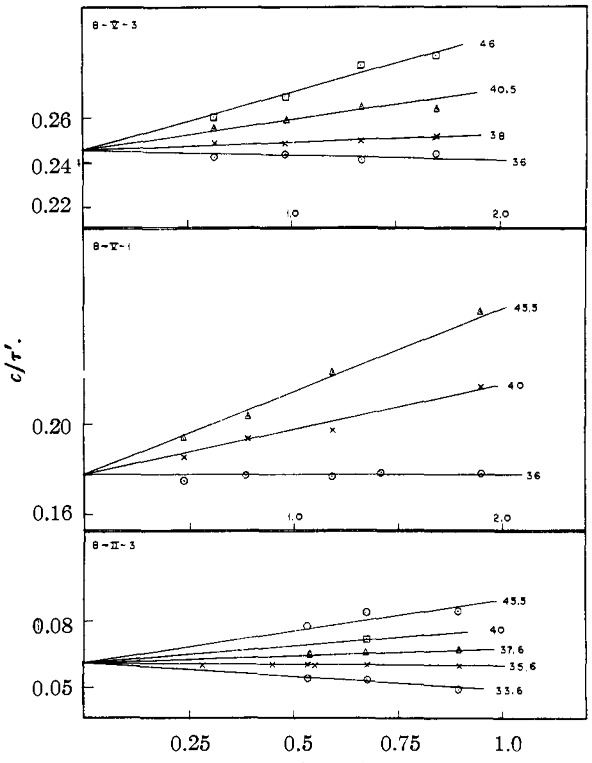

Fig. 2.—Light-scattering measurements on "B fractions" of polystyrene in cyclohexane at different temperatures.

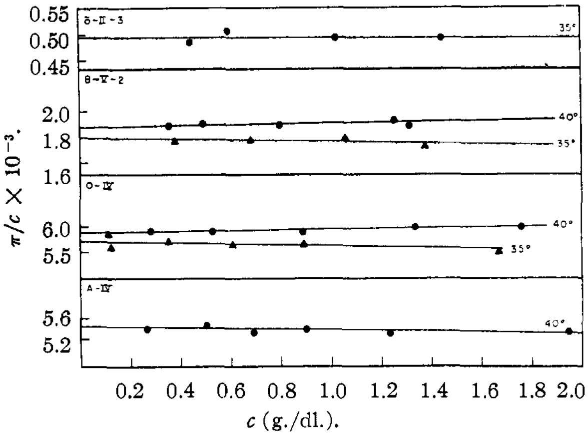

Fig. 3.—Osmotic-pressure measurements on fractions of polystyrene in cyclohexane at different temperatures.

Experimental Turbidity Measurements.—The graphs of Figs. 1 and 2 show the experimental data for the temperature dependence of the scattered light with the A and B fractions, respectively. The curves at different temperatures have a common intercept because the temperature dependence of (dn/dc), n and c have been removed from the c/τ' plot by applying the correction factor, F, in Table I to the experimental data. The correction factor is the ratio of the quantity $[c(dn/dc)^2]$ at temperature t to its value at 35°. This factor arises because $K = (4\pi^2/N_0\lambda^4)n^2(dn/dc)^2$ and $R_{90} = 0.0765n^2\tau'$ are temperature dependent. n refers to the refractive index of solution and 0.0765 represents geometrical and optical instrument constants. Thus the intercepts are directly related to the molecular weights when corrected for the dissymmetry of scattering, and the slopes are related to the virial coefficients. Table II summarizes the virial coefficients derived from the data in Figs. 1 and 2. $(Kc/R_{90})_{35°} = 3.56 \times 10^{-5} (c/\tau')$ and $(Kc/R_{90})_{t°} = F(Kc/R_{90})_{35°}$.

TABLE II

LIGHT-SCATTERING SECOND VIRIAL COEFFICIENTS

Fraction	Mol. wt.	Temp., °C.	$A_2 \times 10^4$, moles cm.^{3}/g.^{2}
A-VIII	21,700	55	0.415
		50	0
		45	−0.31
		43.5	−0.75
		40	−1.17
		35.5	−1.53
A-IV	55,900	49.5	0.44
		43.5	.14
		38	− .19
A-1	115,000	43.5	.19
		40	− .06
		35	− .32
B-V-3	145,000	46	.33
		40.5	.17
		38	.047
		36	− .034
B-V-1	207,000	45.5	.47
		40	.25
		36	.0
B-II-3	640,000	45.5	.38
		40	.20
		37.6	.09
		35.6	0
		33.6	−0.14

Osmotic Pressure.—Figure 3 presents the salient data from the osmotic pressure measurements of several fractions of polystyrene in cyclohexane, and Table III summarizes the virial coefficients and molecular weights for all of the fractions that have been analyzed in this manner.

TABLE III

OSMOTIC-PRESSURE VIRIAL COEFFICIENTS

Fraction	Mol. wt.	Temp., °C.	$A_2 \times 10^4$, moles cm.^{3}/g.^{2}
A-IV	47,840	40	−0.33
	49,100	45	− .07
O-IV	45,000	35	− .20
	44,400	40	.26
	45,100	45	.44
B-V-2	144,000	35	− .07
	139,200	40	.19
B-V-1	208,800	35	.04
	196,500	40	.74
B-II-3	519,000	35	.0

Discussion

Variation of the Ideal Temperature.—Figure 4 is a plot of the second virial coefficients derived from the light-scattering data as a function of temperature. From this plot the ideal temperature, namely, the temperature at which the virial coefficient is zero, can be found for each fraction. In a similar manner the ideal temperature could be found for the fractions which were studied osmometrically. However, the osmotic pressure results, except in one case, were obtained at only two temperatures, so the ideal temperature located in this manner has much greater uncertainty. Fraction O-IV, in which measurements were obtained at three temperatures, has been treated in the same manner as the light-scattering data. Table IV compares the ideal temperatures derived from osmotic pressures and those from light scattering. The number in parentheses represents the approximate value of the molecular weight.

TABLE IV

IDEAL TEMPERATURES

Fraction		Light scattering	Osmotic pressure
A-VIII	(22,000)	~49	
A-IV	(50,000)	41	46
O-IV	(50,000)		37
A-1	(115,000)	40	
B-V-3	(145,000)	37	
B-V-2	(150,000)		36
B-V-1	(200,000)	36	35
B-II-3	(600,000)	36	35

The estimated error in the location of the ideal temperature from light-scattering results is ±0.5° while that from the osmotic-pressure results may be more than ±1°. Additional data from light scattering at 436 mμ gives the same results within ±0.5° as the 546 mμ data except for A-IV which has a theta temperature of 43.5° compared to 41° for 546 mμ. Nevertheless, the agreement for the various fractions that have been studied by the two methods is on the whole encouraging. It enables more confidence to be placed in the light-scattering results than otherwise might be the case. For example, it could be argued that the refraction corrections, thermostatting effects, the depolarization factors, or other instrumental uncertainties are blurring the effects seen in the light-scattering experiments, but in view of the over-all agreement with the osmotic pressure experiments these items are not considered to be serious general objections to the present work.

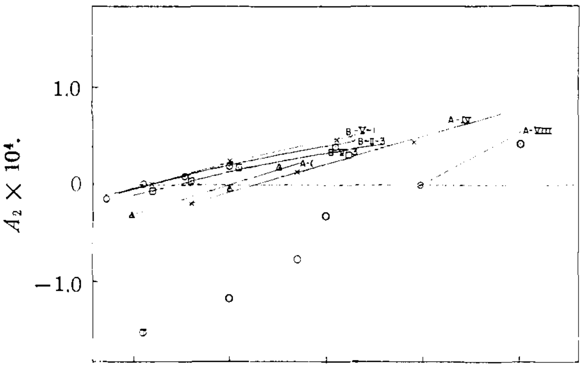

Fig. 4.—Virial coefficients (A_2) of polystyrene fractions in cyclohexane as a function of temperature.

Table IV indicates that the ideal temperatures of the A fractions are as a group higher than those of the other fractions and also increase with decrease in molecular weight. The only difference between these polymers should be that the A series has a mercaptan group incorporated in the polymer chain since *n*-butyl mercaptan was used as a transfer agent. Such a marked effect of presumably small internal structural differences on the virial coefficient had not been expected. In retrospect it seems reasonable to assume that if such small chemical changes are ever going to manifest themselves it should be in the vicinity of the theta temperature where a very close balance between solvent–polymer and polymer–polymer interactions exists.

In a similar manner the effects of small impurities in the solvents might also account for some of these effects. In all of this work it was realized that very high purity could not be maintained in the cyclohexane for all of the many operations that have to be carried out in light scattering, osmometry and ultracentrifugation. The cyclohexane would unquestionably pick up small amounts of water and other trace impurities. For this reason a purposeful attempt was made to avoid the gradual change of the solvent through the absorption of water vapor, not by distilling the solvent from a pot containing sodium, but rather by distilling the solvent without the presence of drying agents so that an equilibration with the water vapor in the air would occur during the distillation. However, the appearance of such a high ideal temperature for some of the fractions made it necessary to check again on the solvent, especially since both Cantow and Krigbaum had noticed that theta temperature had decreased when water was present in cyclohexane. Thus fraction A-IV was rerun using water-free cyclohexane. The virial coefficients were the same within experimental error as those reported in Table II. In view of the many experiments that have been conducted in the past two years in this Laboratory without any apparent difficulties from the solvent, it seems that the solvent preparations described are sufficient to ensure adequate reproducibility.

Table V lists the manner of preparation of the polymers and the theta temperatures that have been determined by other workers for the polystyrene–cyclohexane system. It should be noted that the results of the present work as listed in Table IV are in good agreement at the higher molecular weights.

TABLE V

LITERATURE VALUES FOR THE POLYSTYRENE–CYCLOHEXANE SYSTEM

Author	Method	Preparation	Mol. wt.	Ideal temp.
Krigbaum[9]	L.S.	Thermal initiation	3,200,000	35
Krigbaum[4]	O.P.	Benzoyl peroxide initiation	203,000	34.4
Outer[10]	L.S.	Benzoyl peroxide initiation	1,610,000	35
Cantow[5]	L.S.	Benzoyl peroxide initiation, polymn. carried out with solvent	68,700	35

The data in Table IV also seem to indicate beyond experimental error that the ideal temperature does increase slightly as the molecular weight is decreased when the mercaptan effect is not present. A conservative estimate based qualitatively on the light-scattering value for B-V-3 compared to other light-scattering values of the ideal temperature for higher molecular weights, and the osmotic-pressure value for O-IV compared to other osmotic values for higher molecular weights clearly has to be that the ideal temperature does increase, perhaps as much as 1°. In addition, the equilibrium ultracentrifuge indicates that an increase in the theta temperature of perhaps 0.5° occurs in going from B-II-3 to B-V-2, that is, from 600,000 to 150,000 in molecular weight. The centrifuge method, because of its manner of distributing a varying concentration along the cell, appears to be the most sensitive of all the methods used in detecting deviations from exact ideal conditions. The effects have not been fully analyzed, but a very small difference from the ideal condition, say 0.5°, makes a very large difference in the curvature of the plot of equation 3.

The fractions seem to be reasonably sharp, judging from the ratio of the weight-average to number-average molecular weights. These values are tentative and await the resolution of just what the absolute weight-average molecular weight is, but they indicate that the fractions are sharp enough so that extreme difficulties should not arise from the different manner in which the virial coefficients are weighted in the various techniques. For the same reason any systematic change of the virial coefficient with molecular weight due to a change in heterogeneity of the fractions seems unlikely with these fractions.

This small variation in the ideal temperature with molecular weight which has been observed in this work was not found to be significant in the work of Krigbaum.[4] Actually, as he mentioned, there appeared to be a spreading of the theta temperature, but the spread was within the experimental error in which his theta temperature was located by plotting a curve through the virial coefficients at 30, 40 and 50°. Although the data in Table V show no variation of the "ideal" temperature with molecular weight, it is doubtful whether such a small effect could be seen with different solvents, polymers and apparatus.

The theory of Orofino and Flory[3] expresses the free energy of mixing (ΔF_m) as

$$\Delta F_m = kT\{n_1 \ln v_1 + n_2 \ln v_2 + xn_2 [\chi_0 \sum_{i=1} (\chi_i/i)v^i{}_2]\} \quad (4)$$

where n is the number of molecules, v is the volume fraction, and x is the ratio of molar volumes of solute and solvent, designated 2 and 1, respectively. χ_i is a polymer–segment interaction term expressed as a power series whose running index i has no relation to solvent or solute of the volume fraction. From this expression the chemical potential of the solvent (μ_1) can be expressed as

$$\mu_1 - \mu_1{}^0 = RT[\ln(1 - v_2) + (1 - 1/\chi)v_2 + \sum_{i=1} \chi_i v_2{}^{i+1}] \quad (5)$$

or

$$= RT\,[v_2/\chi + (1/2 - \chi_i)v_2{}^2 + (1/3 - \chi_2)v_2{}^3 + \ldots] \quad (5a)$$

From the expression for the free energy of mixing, Orofino and Flory have calculated the excluded volume in dilute solution and have been able to derive equation 6 representing a convenient closed form for the virial coefficient, A_2.

$$A_2 = (2^{5/2}\pi N/3^3\,\phi)([\eta]/M) \ln [1 + (\sqrt{\pi}/4)X_1 + (\sqrt{\pi}3^{3/2}/32)X_2] \quad (6)$$

where

$$X_1 = (3^3\phi/2^{1/2}\pi^{3/2}N)(v^2/V_1)(M/[\eta])(1/2 - \chi_1) \quad (6a)$$

and

$$X_2 = 3(3^{3/2}\phi^2/\pi^3 N^2)(\bar{v}^3/V_1)(M/[\eta]^2)(1/3 - \chi_2) \quad (6b)$$

ϕ is a constant (approximately 2.2×10^{21}) defined by equation 7, relating the intrinsic viscosity $[\eta]$ in dl./g., to the root mean square end-to-end distance $<\bar{r}^2>^{1/2}$ in cm., and the molecular weight M. $\bar{v}$/ml./g., is the partial specific volume of polymer, and V_1, ml./g. mole, is the molar volume of solvent.

$$[\eta] = \phi <\bar{r}^2>^{3/2}/M \quad (7)$$

For polystyrene in cyclohexane at 35° equation 6 can be expressed as

$$A_2 = 180([\eta]/M) \ln [1 + 4.34 \times 10^{-5}(M/[\eta])(1/2 - \chi_1) + 3.88 \times 10^{-7}(M/[\eta]^2)(1/3 - \chi_2)]$$

Thus a value of χ_2 derived from osmotic-pressure or vapor-pressure measurements of the solvent activity at moderate concentrations of polymer would allow a comparison of this theory with the observation that the theta temperature increases with a decrease in molecular weight. For the polystyrene–cyclohexane system there is only Schmoll and Jenckel's work[11] on the vapor pressures of concentrated solutions and some recent unpublished activity measurements by Krigbaum and Geymer.[12]

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(9) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).

(10) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

(11) K. Schmoll and E. Jenckel, *Z. Elektrochem.*, **60**, 756 (1956).

(12) W. R. Krigbaum and D. O. Geymer, private communication, to be published.

The nature of most vapor-pressure measurements is such that only the very high polymer concentrations yield precise solvent activities so that an estimate of χ_2 from these data is difficult to make because the larger interactions at higher concentration have already become important in the expression for the chemical potential. However, Krigbaum and Geymer made osmotic pressure measurements at 34.4° with moderate concentrations of polystyrene in cyclohexane and found that $\chi_2 = {}^1/_3$, but that χ_3 was significant.

Equations 6 may be analyzed to determine what values of χ_2 would be required to make the theta temperature change by the observed amount. If it is assumed that the ratio of the X_1 and X_2 terms in equation 8 is such that the X_2 term is negligible compared to the X_1 term for a high molecular weight, then it may be considered that the X_1 term is zero for all fractions at the temperature corresponding to theta conditions for the high molecular weight. The intrinsic viscosities and the

$$X_2/X_1 = (1.5 \times 10^{-2})(v/[\eta])[(1/3 - \chi_2)/(1/2 - \chi_1)] \tag{8}$$

calculated ratio of X_2/X_1 for two fractions of polystyrene in cyclohexane are listed in Table VI.

TABLE VI

INTRINSIC VISCOSITIES AND RATIO OF X_2/X_1

Fraction	$[\eta]$ (temp.)	$[\eta]$ (theta)	$(X_2/X_1) \times \frac{({}^1/_2 - \chi_1)}{({}^1/_3 - \chi_2)}$
B-II-3	0.629 (35°)	0.629 (35°)	0.022
O-IV	.178 (35°)	0.180 (37°)	0.078
	.185 (45°)		
	.191 (55°)		

If fraction O-IV may then be considered to have X_1 equal to zero at 35°, it is found that the experimentally measured $A_2(2 \times 10^{-5})$, when substituted in equation 6 and solved for $({}^1/_3 - \chi_2)$, demands that $({}^1/_3 - \chi_2)$ be negative, and equal to −0.049. This requires that χ_2 be equal to +0.38. In fact it would require that any increase in the theta temperature be accompanied by a χ_2 greater than ${}^1/_3$.

Flory and Daoust[13] point out that it is not possible to have a value for χ_2 greater than ${}^1/_3$ if the critical concentration of a very high molecular weight fraction is zero. The experimental data of Flory and Shultz[14] indicate strongly that the critical concentration of a very high molecular weight fraction is zero. Thus it is quite probable that the higher terms in the expression for the free energy of mixing are important for polystyrene–cyclohexane solutions.

Differences Due to Structure.—The differences due to the incorporation of the mercaptan group are difficult to interpret in any specific way. The results of Walling[15] indicate a very high transfer constant for the transfer of *n*-butyl mercaptan to the growing polymer radical. In consequence, it is to be expected that there will be one mercaptan group at the end of each polymer molecule.

There always exists the possibility of branching reactions occurring even at a conversion of 30% but Thurmond and Zimm[16] found no change in the ideal temperature in a mixed solvent for polystyrene fractions that had been crosslinked by the addition of a small amount of divinylbenzene in the polymerization mixture. In view of this work it seems tentatively reasonable to assume that small chemical changes in the backbone of the chain can be detected by carefully scanning the region of the theta temperature. No more than this can be said without much further work using well-known materials.

Summary

The ideal or theta temperature of a series of polystyrene fractions appears to increase as the molecular weight decreases. The change in the theta temperature is very small for a large change in the molecular weight and is probably the result of the increased segment density in the zone of interaction between two chain molecules as discussed by Flory. This effect appears to be different from that predicted by Flory and Orofino, although this difference may be due to their omission of higher interaction terms which are significant even at low concentrations in the polystyrene system.

There also is a large increase in the theta temperature when fractions of polystyrene prepared by the use of *n*-butyl mercaptan as a transfer agent are compared to fractions of polystyrene prepared without the use of transfer agent. In addition these mercaptan transferred polymers also give an increase in theta temperature as the molecular weight is decreased. The differences seen in the comparison of mercaptan and non-mercaptan polymers are believed to be due to the small chemical differences near the chain ends which have a large effect in poor solvents.

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WASHINGTON, D. C.

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(13) P. J. Flory and H. Daoust, *J. Polymer Sci.*, **25**, 429 (1957).

(14) A. R. Shultz and P. J. Flory, THIS JOURNAL, **74**, 4760 (1952).

(15) C. Walling, *ibid.*, **70**, 2561 (1948)

(16) C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 477 (1952).