racy of the low temperature work was within ± 2%. The reliability of the present work can only be inferred, since data for comparison are limited.

The smooth curves which can be drawn through the low and high temperature data can be taken as evidence that the new thermostat introduced no unsuspected bias in the high temperature data. A review of the basic principles of the hot-wire technique has revealed no reason for expecting progressive deviations from true values at higher temperatures, except perhaps from convection. Results presented earlier (*1*) indicated no convection, even with materials as fluid as chloroform. As the apparatus used in the present work was the same, the factor which would have the most significant contribution to convection would be viscosity. At the highest temperatures used, the viscosity of the most fluid compound considered only approached that of chloroform. Thus, there appears to be no cause for believing that convection was a factor in the present measurements.

Biphenyl and its chlorinated and alkylated derivatives show very little change in thermal conductivity with increasing temperature (see Table I). Phosphate, carboxylate, and silicate esters (see Figures 2 through 5) all show a steady decrease in thermal conductivity with increasing temperature.

A similar decrease is observed with Dowtherm A (Dow Chemical Co.) (Figure 6), considering the experimental data determined in this work to complement the work of Woolf and Sibbitt (*3*).

Available data on density and viscosity variations with temperature failed to show correlations which would have predicted this difference in behavior. Sakiadis and Coates (*2*) predict that positive, negative, and zero temperature coefficients of thermal conductivity are possible, but sufficient data on the heat capacity, velocity of sound, and intermolecular spacing in the liquid state were not available for the present compounds to permit use of their theoretical equation. The equation of Sakiadis and Coates predicts a linear variation of thermal conductivity with temperature. The curved lines which were obtained over wide temperature ranges, particularly with di-2-ethylhexyl sebacate, point up the need for modification of their treatment to explain these results.

The temperature coefficient data for Aroclor 1248 and Dowtherm A should be useful in the design of heat exchangers utilizing these important heat transfer fluids.

CONCLUSIONS

The success of this present work has shown that thermal conductivity values can be easily measured at high temperatures. If suitable liquids for the vapor bath and silver-soldered or spot-welded leads are used, the method discussed should be applicable at higher temperatures.

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Received for review July 13, 1956. Accepted November 3, 1956.

Heats of Solution of Polyindene

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The physical-chemical behavior of high polymer–solvent systems has received a great deal of attention in recent years. On the other hand, the behavior of low molecular weight polymer solutions has not received much attention in spite of their commercial importance. The present study was undertaken to investigate the nature of the interaction of a low molecular weight polyindene type of polymer with solvents or plasticizers. Solubility measurements of this polymer have been reported elsewhere (*10*). Precise measurements of the heat of solution of polyindene are reported here and form the basis for a thermodynamic study of polyindene-solvent systems.

The usual expression for the energy of mixing of nonelectrolytes is given by the equation

$$\Delta E^M = V_m B\, V_2(1 - V_2) \tag{1}$$

where V_m is the volume of solution in cubic centimeters, V_2 is the volume fraction of polymer, and B is given by the expression:

$$B = (S_1 - S_2)^2 \tag{2}$$

where S_1 and S_2 are the solubility parameters of solvent and polymer, respectively. The volume change on mixing may be considered to be negligible at low concentrations, so that the heat of mixing is equal to the energy of mixing. According to Equation 1 a plot of $\Delta E^M/V_m$ vs. $V_2(1 - V_2)$ should give a straight line with slope B. Since B is a squared term, it must be positive and thus this theory predicts that the heat of mixing of two nonelectrolytes must be endothermic. However, where specific interactions occur, the experimental value of B is not realized by Equation 2 but becomes more complex and often negative. Equation 1 may, however, still be applicable.

EXPERIMENTAL

Materials. Polymer. The polymer used in this study was a coumarone indene resin manufactured by the Pennsylvania Industrial Chemical Corp. Previous work in this laboratory on the molecular weight distribution, viscosity, and solubility of this resin (*5, 6, 10*) has been reported. [This resin corresponds to Pieski's (*5*) Resin II and to Vanderryn's (*10*) Resin IV.] The resin was fractionated into four fractions

Table I. Polymer Properties

Molecular weight	749	(cryoscopic)
	765	(No. average)
	1023	(wt. average)
Softening point	105 °C.	(ring and ball)
	86 °C.	(capillary)
Density	1.09	grams/cc.
Chemical analysis	91.5%	carbon
	7.9%	hydrogen
	0.6%	oxygen

Fractions	Density, Grams/Cc.	Mol. Wt. (Cryoscopic)	Softening Pt., °C. (Capillary)
X-1	1.09	1790	162
X-2	1.09	1350	135
X-3	1.09	842	94
X-5	1.15	401	27

by Pieski and Zettlemoyer (*5, 6*) and the molecular weight fractions prepared by them were used in the present study. Pertinent properties of the polymer and its fractions are listed in Table I. The chemical analysis shows that the resin contains little or no coumarone since its oxygen content is quite low. Thus it will be referred to as a polyindene polymer.

Solvents. The organic solvents were reagent grade chemicals, dried over anhydrous magnesium sulfate, and distilled. The benzene was washed with concentrated sulfuric acid, dried over sodium, and distilled.

Methods. Heat of Solution. The thermistor calorimeter which was used to measure the heats of solution has been described previously (*9, 11*). Sample bulbs were blown from 8-mm. borosilicate glass tubing. Finely powdered resin was weighed into the bulbs, which were then sealed off and placed in the sample holder of the calorimeter. Two hundred milliliters of solvent was added to the Dewar flask, the system was allowed to equilibrate, and the sample bulb was broken under the liquid. The detailed procedure used is reported elsewhere (*9*). The calculated calorimeter error, excluding the heat of breaking, was about ±2%. Blank runs, made to determine the heat effect produced in breaking the sample bulb, gave average values of − 0.02 cal. for solvents boiling above 100 °C. and + 0.25 cal. for more volatile solvents. In the latter case the reproducibility was not very good, the average deviation being 0.04 cal. This relatively large deviation is in agreement with the findings of Bartell and Suggitt (*1*). The heat of solution measurements were made at 26 °C.

RESULTS

Unfractionated Polymer. The results of the heat of solution measurements for most of the solvents (cyclohexane, 1-nitropane, nitrobenzene, ethyl acetate, methyl ethyl ketone, benzene, methylchloroform, carbon tetrachloride, bromobenzene, chlorobenzene, butyl chloride, *sym*-tetrachloroethane, and chloroform) are presented in Figures 1 to 3, where integral heats of solution of polymer in cal. per 200 ml. of solvent are plotted versus volume fraction, V_2, of polymer. V_2 has been used instead of $V_2(1 - V_2)$ because in this concentration range $V_2 \simeq V_2(1 - V_2)$. The pertinent data for all the solvents which were used are listed in Table II, which gives average values for the heat of solution per gram per 200 ml. of solvent, per base mole (monomer unit) per 200 ml. solvent; B values for Equation 1 taken from the slopes of the curves of Figures 1 to 3; dipole moments and solubility parameters for the solvents; and calculated B values assuming a solubility parameter of 9.15 for the polymer. The value 9.15 was determined previously (*10*) and coincides with the parameter for benzene. This result is in agreement with Equation 1 since the heat of solution in benzene is approximately zero.

The heat of solution per gram or per base mole was constant (average deviation in ΔH per gram was 5%) over the concentration range used in this study. On a mole fraction basis the solutions were extremely dilute—e.g., the highest concentration which was used (methyl ethyl ketone, run 24) corresponded to a polymer mole fraction of 1.91×10^{-3}. Higher concentrations were not used in this study because of (*a*) the difficulty of rapidly dissolving the polymer, (*b*) the high viscosity of the resulting mixture, and (c) the physical limitations of the calorimeter.

Intrinsic viscosities for solutions of unfractionated polymer in benzene, ethyl acetate, 1-nitropropane, carbon tetrachloride, chlorobenzene, and *sym*-tetrachloroethane were determined. The best values for the intrinsic viscosity, $[\eta]$, are listed in Table III along with the B values obtained from the heat of solution measurements. Figure 4 illustrates the relation between B and $[\eta]$.

Fractionated Polymer. The heats of solution of fractions *X*-1, *X*-2, *X*-3, and *X*-5 in chloroform, chlorobenzene, and 1-nitropropane were measured and the values in cal. per gram per 200 ml. are listed in Table IV. The value for the unfractionated polymer is listed for comparison.

Table II. Heats of Solution of Resin IV (Polyindene)

Solvent	Dipole Moment	S_1[a]	ΔH/Gram Cal./200 Ml.	ΔH/Base Mole Cal./200 Ml.	B, Cal./Ml., Exptl.	B, Cal./Ml., Calcd.
Cyclohexane	0	8.2	3.52	407	3.96	0.9
1-Nitropropane	3.3	10.7	2.01	232	2.22	2.4
Nitrobenzene	4.1	10.0	1.09	127	1.25	0.7
Ethyl acetate	1.8	9.1	1.00	116	1.14	0
Anisole	1.35	(8.5)	0.49	57	0.5	0.4
Methyl ethyl ketone	2.8	9.3	0.46	53	0.5	0.02
n-Heptyl chloride	1.85	...	0.36	42	0.4	...
Benzene	0	9.15	−0.01	− 1	0	0
Ethyl benzoate	1.8	(7.8)	−0.16	− 19	−0.2	1.8
Ethylbenzene	0.5	8.8	−0.33	− 39	−0.37	0.1
Methylchloroform	1.6	8.5	−0.42	− 48	−0.44	0.4
Carbon tetrachloride	0	8.6	−0.59	− 68	−0.63	0.3
Bromobenzene	1.7	(8.9)	−0.92	−107	−1.01	0.06
Chlorobenzene	1.7	9.5	−0.93	−108	−1.01	0.1
Butyl chloride	2.0	(8.4)	−0.96	−112	−1.06	0.6
Benzonitrile	4.1	8.4	−1.04	−121	−1.1	0.6
Pyridine	2.2	10.7	−1.61	−187	−1.42	2.4
Dimethylaniline	1.6	(8.4)	−1.95	−226	−2.1	0.6
sym-Tetrachloroethane	1.6	(9.7)	−4.48	−519	−2.9	0.3
Chloroform	1.0	9.3	−4.80	−558	−5.2	0.02

[a] Parantheses indicate approximate values.

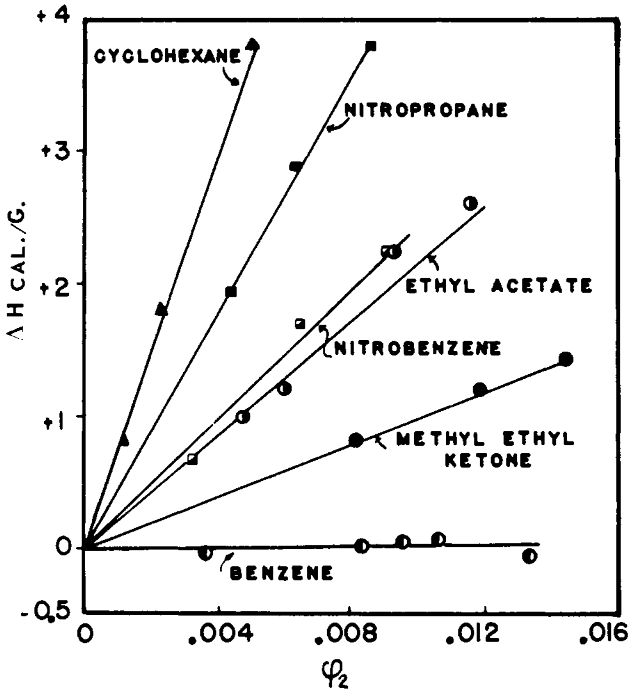

Figure 1. Heat of solution of polyindene in various solvents

DISCUSSION

Figures 1, 2, and 3 show that within the limits of experimental error the integral heat of solution varies linearly with the volume fraction of polymer as predicted by Equation 1. The only exception to this is carbon tetrachloride above 0.01 volume fraction of polymer. Inspection of Table II shows, however, that the experimental value of B is not at all in agreement with the theoretical value as predicted from the solubility parameters by Equation 2. The experimental positive values of B are, in general, larger than the predicted theoretical values.

The graph of B values versus intrinsic viscosity in Figure 4 indicates that the polymer molecules tend to uncurl in the exothermic solvents and remain in a compact form in the endothermic solvents. The shape of the curve is almost identical to that obtained by Daoust and Rinfret (2) for solutions of poly (vinyl acetate). The curve shows that the maximum intrinsic viscosity, and thus the apparent maximum length of the polymer chain, is attained at relatively low exothermic heats of solution. A higher exothermic heat apparently does not tend to increase further the effective length of the molecule in solution, and thus the increased exothermicity of solvents such as chloroform is not due to physical effects but must result from chemical interactions. Similarly, at low endothermic heats the polymer molecule is in a compact form preferring intrapolymer contacts; again larger endothermic heats probably do not cause further configurational changes.

The usual explanation for exothermic heats is given as the occurrence of specific interactions in the mixture such as solvation. For example, the exothermic heats of solution of poly(vinyl acetate) in chloroform have been explained on the basis of "acid-base" interaction between the "acid" hydrogen of the chloroform and the "basic" carbonyl oxygen of the polymer (2). No functional groups as such exist in the polyindene molecule and thus such a straightforward explanation cannot be offered.

Table III. Intrinsic Viscosities

Solvent	B, Cal./Ml.	$[\eta]$
sym-Tetrachloroethane	− 4.9	0.053
Chlorobenzene	− 1.01	0.056
Carbon tetrachloride	− 0.63	0.054
Benzene	0.00	0.032
Ethyl acetate	1.14	0.027
1-Nitropropane	2.22	0.026

Table IV. Heats of Solution of Polyindene Fractions
(Heats in cal. per gram per 200 ml.)

Fraction	Solvent Chloroform	 Chlorobenzene	 1-Nitropropane
X-1	− 13.5	− 11.0	− 9.6
X-2	− 11.3	− 8.0	− 5.7
X-3	− 3.7	− 1.0	1.2
X-5	− 4.6	− 0.3	1.3
Unfractionated	− 4.80	− 0.93	2.01

However, it is instructive to compare the results of Hellfritz (4) on the heat of solution of polystyrene and those of Daoust and Rinfret (2) on poly(vinyl acetate) with the results obtained in this study. In Figure 5 the results obtained by Hellfritz and by Daoust and Rinfret are plotted versus the results obtained in this study for solvents which were common to both studies. In both cases the values for toluene were compared to the values for ethyl benzene obtained in this study. The units were used as they were reported in the literature: ΔH per gram for polystyrene and B values for poly(vinyl acetate). Inspection of Figure 5 shows that there is a regular relationship between the heats of solution of polystyrene and polyindene except for chloroform. The heat of solution of polyindene in chloroform is much more exothermic than would be expected from the polystyrene data. On the other hand, the chloroform and *sym*-tetrachloroethane data for poly(vinyl acetate) and polyindene seem to follow a regular relationship. This comparison suggests that there may be a similarity in the mechanism of the interaction of chloroform and *sym*-tetrachloroethane with low molecular weight polyindene and with poly(vinyl acetate).

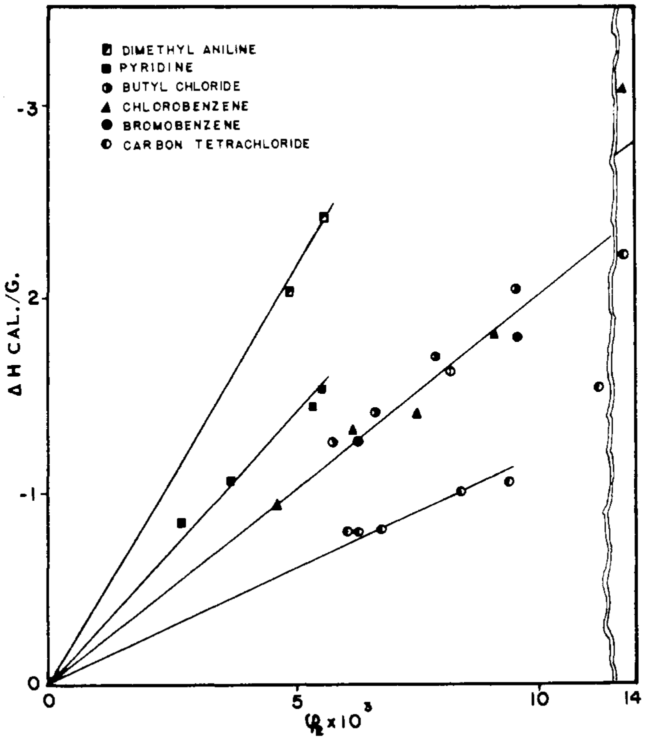

Figure 2. Heat of solution of polyindene in various solvents

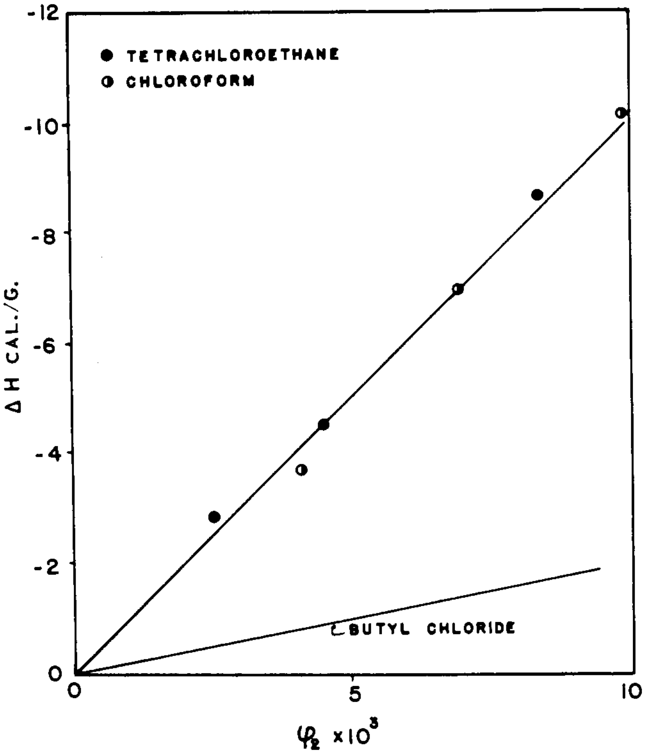

Figure 3. Heat of solution of polyindene in tetrachloroethane and in chloroform

This mechanism apparently does not operate or is not present to any noticeable extent in the case of polystyrene (molecular weight, 20,000).

An inspection of the values for the heats of solution of polyindene in chloroform, *sym*-tetrachloroethane, methylchloroform, and carbon tetrachloride indicates that the compounds containing "acid" hydrogens (chloroform and *sym*-tetrachloroethane) bring about high exothermic heats while carbon tetrachloride and methyl chloroform, which contain no "acid" hydrogen atoms, exhibit markedly lower exothermic heats of solution. The "basic" or electron donor groups, which must be present for interaction with the acid hydrogen, may exist in the form of terminal double bonds in the polyindene molecule (polyindene contains one terminal double bond per molecule). Polystyrene of a high molecular weight has very few terminal double bonds and thus does not exhibit this interaction to an appreciable extent. On the other hand, the low molecular weight polyindene has many more double bonds available for interaction. Thus the high exothermic heats of solution of polyindene in chloroform and *sym*-tetrachloroethane are tentatively attributed to "acid-base" interaction. Further investigation of this phenomenon using infrared absorption spectrophotometry is in progress.

The experimental heats of solution for most of the other solvents may be qualitatively explained on the basis of structure and the chemical nature of the solvent molecules. Cyclohexane exhibits a high endothermic heat of solution. This molecule has no polar groups available for solvent-solute interaction and is not easily polarized. It is a poor solvent for the type of polymer used in this study and thus energy must be supplied in order to bring about the solution process. On the other hand, benzene is very similar in structure to the polymer, has a highly polarizable conjugated double bond structure and yet no polar groups, and has a solubility parameter equal to that of the polymer. Thus it is not surprising that the solution process is athermal.

The molecules which contain oxygen all exhibit endothermic or very low exothermic heats. These compounds are not strongly "acidic" or "basic," in some cases may exhibit some association in the pure liquid state, have relatively high dipole moments (especially the nitro compounds and methyl ethyl ketone), and have large polar groups. Steric effects and the fact that both the oxygens and the polymer are electron donors would thus prevent polymer-solvent interaction. Within this group of solvents the influence of the aromatic versus aliphatic structure is evident. In the pairs nitrobenzene-nitropropane and ethyl benzoate-ethyl acetate, the aromatic derivative exhibits a lower endothermic heat because of structural similarity to the polymer. The importance of the length of the aliphatic chain is evident by comparing the value for heptyl chloride, which exhibits a low endothermic heat, with butyl chloride, which is exothermic.

Effect of Molecular Weight. The increasing exothermic heats of solution with increasing molecular weight may be explained by considering the state of the polymer at room temperature. A polymer below its second-order transition temperature, T_m, is in a thermodynamically unstable state (*7*) and can be considered a supercooled liquid. When the polymer is placed in solution, in effect the transition temperature is lowered, which liberates the excess free energy of the unstable state. In other words, the polymer is in a higher energy state in the bulk "solid" than it is in solution.

Ueberreiter and Kanig (*8*) have shown that the second-order transition temperature of polystyrene varies linearly with the degree of polymerization, P, according to the equation:

$$\frac{1}{T_m} = a + \frac{b}{P} \qquad (3)$$

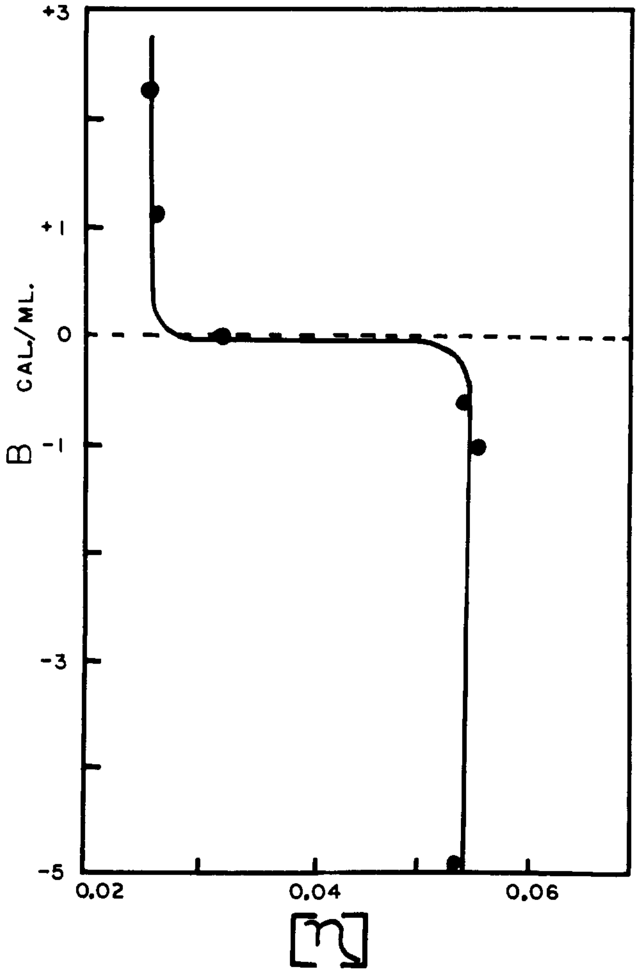

Figure 4. Heat of solution vs. intrinsic viscosity

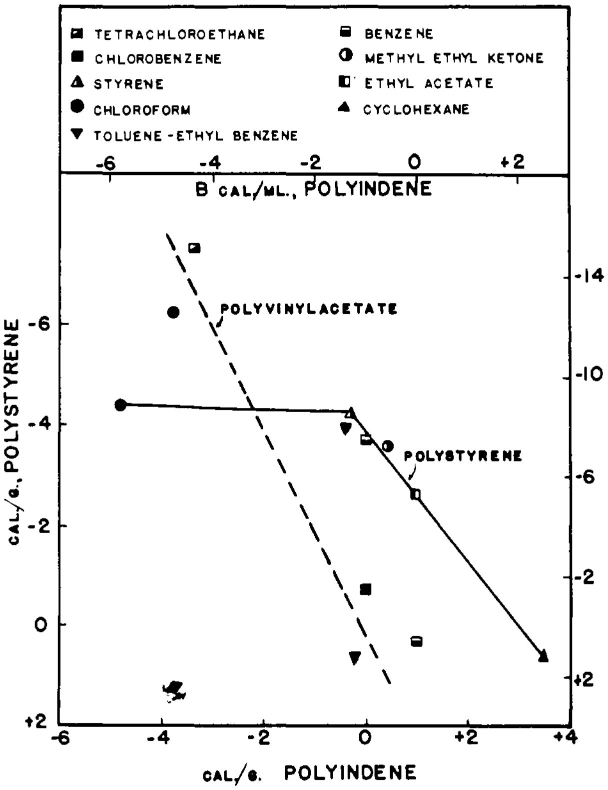

Figure 5. Heat of solution of polyindene vs. polystyrene (4) and poly(vinyl acetate) (2)

where *a* and *b* are constants. Von Gunner and Schulz (3) have recently applied this concept quantitatively and have developed the following equation for the heat of solution of a polymer:

$$\Delta H = \frac{-\Delta C_p}{a} \frac{(P)}{(P + b/a)} + T\,\Delta C_p + W_w \qquad (4)$$

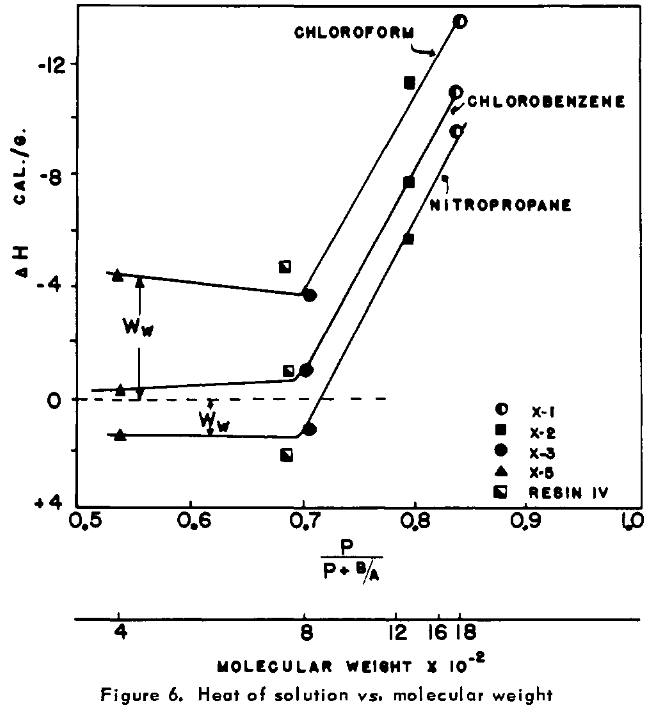

Figure 6. Heat of solution vs. molecular weight

where ΔC_p is the difference in heat capacity of the polymer above and below T_m, and W_w is the chemical interaction energy between polymer and solvent. The heat of solution of a polymer below the second-order transition point is thus composed of a "physical" (first two terms on right-hand side of Equation 4) and a chemical (W_w) heat term. Above T_m the heat of solution is given by

$$\Delta H = W_w \qquad (5)$$

A preliminary test of this theory by Von Gunner and Schulz (3) has shown that Equations 4 and 5 are applicable to the heats of solution of polystyrene in various solvents over a range of *P* values from 30 to 100, using values for *a*, *b*, and ΔC_p from the literature. The values of their constants *a*, *b*, and ΔC_p are not available for polyindene. Figure 6 shows a plot of ΔH vs. $\frac{P}{P + b/a}$ for polyindene (see Table IV) assuming a value of 2.98 for b/a. The actual value of b/a does not affect the shape of the curves in Figure 6 but only serves to shift them along the abscissa.

These results support the work of Von Gunner and Schulz. Inspection of Figure 6 shows that the curves obtained for the three solvents are parallel lines drawn through the data for the three highest molecular weight fractions and level off sharply for the lowest molecular weight fraction. Since the lowest molecular fraction (*X*-5) is a viscous liquid, more dense than the higher molecular weight fractions which are "solids," its second-order transition temperature must be below room temperature. Furthermore, the values of T_m are usually somewhat below the softening point of the polymer which is 27°C. for fraction *X*-5 (Table I). Equation 5 must thus be used for the heat of solution of fraction *X*-5, while Equation 4 applies to the other fractions. Thus, the heat of solution of fraction *X*-5 is due only to chemical interactions, whereas the heats of solution of fractions *X*-1 and *X*-2 are a result of both chemical and physical contributions.

The higher exothermic heat of solution of fraction *X*-5 in chloroform as compared to fraction *X*-3 is explained by the fact that *X*-5 has more double bonds available for interaction with the "acid" hydrogen of the chloroform. This effect is not evident in solutions of chlorobenzene and nitropropane, because these solvents do not have any "acid" hydrogen atoms.

It has thus been shown that the theory of the "solid" state of polymers explains the change in heat of solution with molecular weight and is able to differentiate between the "physical" and chemical contributions to the heat of solution.

ACKNOWLEDGMENT

This work was supported by Kentile, Inc., Brooklyn, N.Y.

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Received for review July 5, 1956. Accepted December 3, 1956.

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