Product Isolation. All the reactions were terminated by introducing a few drops of methanol into the reaction vessel. The total reaction mixture was first dissolved in a minimum amount of benzene (10-15 ml) and stirred for 30 min until all of the product was dissolved. The benzene solution was then added dropwise to 50-60 ml of methanol in a 200-ml beaker and vigorously stirred by means of a magnetic stirrer. After complete addition of benzene solution to methanol, the contents of the beaker were further stirred for 30 min. In most of the cases, the polymer precipitated out in methanol as a solid, but in some cases, it was found to be a heavy oil. In the former case the polymer was separated by simple filtration, while in the latter case a separatory funnel was used. In all cases the polymer was purified by redissolving in benzene and reprecipitating in methanol as described above. The last traces of solvents from the polymer were removed by drying the polymer under high vacuum at room temperature for 24 hr. In all cases the final state of the polymer obtained was solid unless stated otherwise.

Polymerization Characterizations. All melting points of tosylate monomers and softening points of polymers were measured on a Fisher-Johns melting point apparatus. A double-beam Perkin-Elmer 257 spectrophotometer was used to obtain infrared spectra of the polymeric products. Most of the infrared spectra were obtained as KBr pellets, but where appropriate an NaCl cell was used. Number-average molecular weights were obtained by the vapor-pressure depression method on a Hitachi Perkin-Elmer Model 115 molecular weight apparatus using 0.09-0.10 g of the polymer sample dissolved in 25 ml of benzene at 30°. Perkin-Elmer Model DSC-1B differential scanning calorimeter was used for determining melting points of monomers and polymers and for determining rate behavior of the polymerization reactions at various temperatures.

Photomicrography of Benzyl Tosylate Crystals. Large crystals were grown from a dilute solution of benzyl tosylate in anhydrous ether by cooling the solution slowly to −10°. These crystals were dried under vacuum at 0°. A single large crystal was mounted on the stage of the polarizing microscope, and a 35-mm camera was adjusted within the focus of the crystal image as viewed from the eyepiece. Photographs of the morphological change in the crystal were taken at a magnification of 200× at room temperature at known time intervals.

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Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. II. Semicrystalline Polymer Systems

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ABSTRACT: A gas chromatographic (GC) method has been developed to measure solubility isotherms of a low molecular weight solvent in a semicrystalline polymer. This method depends on the elution of the injected solvent on a concentration plateau of the same solvent in nitrogen carrier gas. The measured solubility in the amorphous phase is used to calculate the vapor-solid equilibrium ratio ($\Omega = a_1/w_1$), along with the polymer-solvent interaction parameter χ, as a function of solution composition. The following polymer-solvent systems have been studied: high-density polyethylene with *n*-hexane and hexane-isopropyl alcohol azeotrope at 80° and with cyclohexane at 100°; and stereoregular polypropylene with hexane at 80°. The Ω values range from about 4.5 to 5.5.

This study is an extension of a new gas chromatographic (GC) method for measuring the thermodynamic properties of polymer solutions into the area of semicrystalline polymers such as high-density polyethylene and stereoregular polypropylene. The application of this method to amorphous polymer solutions has been reported in part I,[2a] along with many experimental details. Other investigators[2b,3] have reported their GC measurements of activity coefficients and vapor-polymer equilibrium ratios at infinite dilution. We have determined solubility isotherms, polymer-solvent interaction parameters, and activity coefficients rationalized by weight fraction (Ω) for high-density polyethylene and polypropylene with selected hydrocarbon vapors constituting up to 60 mol % of the carrier gas.

There have been numerous studies of vapor sorption and diffusion in semicrystalline polymers. Rogers *et al.*[4] report on the sorption of about a dozen different organic vapors in three samples of polyethylene, including high-density polyethylene, at room temperature and below. The sorption of propane and propylene in branched polyethylene has been studied from −30 to +30°.[5] Some of the sorption studies have been primarily concerned with the effects of various forms of pretreatment of the polymer with solvent.[6-8] Since practically all of these earlier studies used a gravimetric method to measure the degree of sorption, they provide an independent check on the accuracy of the new GC method.

Theory

Most of the theoretical framework that applies for GC studies on completely amorphous polymers also applies in the case of semicrystalline polymers. This framework has been discussed in the literature,[2a,9-12] so that only the main differences will be covered here.

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(1) (a) Research and Development Department, Amoco Chemical Corporation; (b) Research and Development Department, Standard Oil Company (Indiana).

(2) (a) N. F. Brockmeier, R. W. McCoy, and J. A. Meyer, *Macromolecules*, **5**, 464 (1972); (b) D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).

(3) R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, **76**, 1492 (1972).

(4) C. E. Rogers, V. Stannett, and M. Szwarc, *J. Phys. Chem.*, **63**, 1406 (1959).

(5) M. L. Santos and D. M. Leitao, *J. Polym. Sci., Part A-2*, **10**, 769 (1971).

(6) D. A. Blackadder and J. S. Keniry, *J. Appl. Polym. Sci.*, **16**, 1261 (1972).

(7) R. F. Baddour, A. S. Michaels, H. J. Bixler, R. P. de Filippi, and J. A. Barrie, *J. Appl. Polym. Sci.*, **8**, 897 (1964).

(8) A. S. Michaels, W. Vieth, A. S. Hoffman, and H. A. Alcalay, *J. Appl. Polym. Sci.*, **13**, 577 (1969).

(9) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **64**, 1505 (1968).

(10) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **64**, 3100 (1968).

(11) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **65**, 824 (1969).

(12) J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, **65**, 839 (1969).

The presence of a crystalline phase requires one change in the equation for the solubility isotherm, because only the amorphous fraction of the polymer will sorb the solvent to a significant extent. The solubility isotherm at pressure P is given by the integral

$$q(P) = \frac{j}{\alpha V_2}\int_0^{y_0} \frac{V_R - V_M}{1 - \psi}\mathrm{d}c \qquad (1)$$

where α, the amorphous fraction of polymer, has been added to the original equation of Conder and Purnell.[11] The vapor–polymer equilibrium ratio Ω is given by the solvent activity divided by the weight fraction sorbed in the amorphous polymer, the same as for amorphous systems[2]

$$\Omega = \frac{a_1}{w_1} = \frac{P_1}{P_1{}^0 w_1}\exp\left[\frac{PB_{11}}{RT} - \frac{P_1{}^0(B_{11} - \bar{V})}{RT}\right] \qquad (2)$$

The terms in the exponential are corrections for nonideality using the second virial coefficient B_{11}. These corrections are usually less than 1% at the low pressures and moderate temperatures we have used.

The other major change is in the form of the Flory–Huggins equation, which is modified because the crystalline regions of the polymer are inaccessible to solvent. These regions act somewhat as cross-links to limit the swelling of the amorphous regions. Rogers[13] shows that for polymers with moderate to high crystallinity, the expression for the solvent activity takes the following semiquantitative form

$$\ln a_1 = \ln \phi_{1a} + \phi_{2a} + \mu_1 \phi_{2a}{}^2 + \frac{\rho_a \bar{V}}{M_c}\phi_{2a}{}^{1/3} \qquad (3)$$

where ϕ_{1a} and ϕ_{2a} refer to the amorphous phase volume fractions of solvent and polymer, respectively. The μ_1 is the Flory–Huggins interaction parameter. The quantity ρ_a is the density of the unswollen amorphous polymer; $\bar{V}$ is the molar volume of the solvent; and M_c is the molecular weight of amorphous polymer between crystalline cross-links. The use of eq 3 permits a direct comparison of our GC thermodynamic measurements with those of other investigators. If χ is defined by the following

$$\chi = [\ln (a_1/\phi_{1a}) - \phi_{2a}]/\phi_{2a}{}^2 \qquad (4)$$

then eq 3 can be rearranged to solve for χ

$$\chi = \mu_1 + \frac{\rho_a \bar{V}}{M_c}\phi_{2a}{}^{-5/3} \qquad (5)$$

The two unknowns in eq 5, μ_1 and M_c, are determined by plotting χ as a function of $\phi_{2a}{}^{-5/3}$ and finding the y intercept and the slope. The χ value for infinite dilution is calculated with ϕ_{2a} equal to unity. The calculation of χ from the GC retention data has been discussed in part I of this series.[2a] In order to calculate volume fractions based solely on the amorphous phase, the following relation is used

$$\phi_{1a} = \frac{1}{1 + r/q(P)M_1} = 1 - \phi_{2a} \qquad (6)$$

where r is the ratio of the specific volume of the amorphous polymer to that of the solvent at the operating temperature. This assumes the additivity of volumes as the solvent penetrates the amorphous polymer.

Table I
Description of Gas Chromatographic Columns[a]

Column No.	Polymer	Mesh Size	Polymer Loading %	Polymer Loading GM	Length (ft)
1	High-density polyethylene	70–80	1.52	0.1280	5
2	High-density polyethylene	80–100	0.834	0.0726	5
3	High-density polyethylene	80–100	1.78	0.3336	10
4	High-density polyethylene	80–100	0.834	0.1552	10
5	High-density polyethylene		0.994	0.1749	10
6	Stereoregular polypropylene	80–100	2.68	0.4828	10

[a] ¼-in o.d. copper tubing.

Experimental Section

The experimental apparatus used in this study is essentially the same as that described in part I.[2a] The reader is referred to that source for details. The procedures used are also essentially the same, except that the GC oven temperature was held below that of the crystalline melting points of the polymers. The characteristics of the GC columns are summarized in Table I. The first four high-density polyethylene columns were coated in the manner described in part I, using precipitation and filtration (in fact, columns 3 and 4 are the same columns as were used in part I). For the fifth high-density polyethylene column about 300 g of xylene was brought to reflux under nitrogen in a 1-l. flask equipped with a stirrer. Polymer (0.5 g) (Amoco Chemicals 680-B4-HDPE of 13 melt index) was then added to the flask and refluxing was continued until the polymer dissolved completely. The flask was cooled enough to break the reflux and 49.5 g of Chromosorb W support was added slowly, with stirring. The resultant slurry was slowly cooled to ambient temperature and placed in a vacuum oven to remove the xylene. The last traces of solvent were removed at 170° under vacuum. With this technique, only a negligible amount of polymer was lost. The isotherm from column 5 matched the one from columns 1–4.

For polypropylene, the polymer (nominally 6 melt flow rate Amoco Chemicals 1016 material) was dissolved in 350 g of decalin. The procedure was the same as for high-density polyethylene, except the resultant packing slurry was filtered at 40–60° to remove the bulk of the solvent before being dried in a vacuum oven.[2a]

Columns 1–6 were conditioned overnight with nitrogen in the GC instrument at 175° and then cooled at about 1°/min to 60° before use. Cooling either bulk high-density polyethylene or polypropylene at these relatively slow rates will allow these polymers to crystallize to the normal extent of 70%, as calculated from densities measured in our laboratory. We have assumed that the crystallinity of these polymers as coated on the Chromosorb support and operated at 80° is 70%. The work on semicrystalline systems was completed (part II) before columns 3 and 4 were used at the higher temperatures of part I.

One normally expects that solvent adsorption on the solid support will contribute to errors in measuring the retention volume, especially at the very light loadings used in this study. This source of error was checked by running the same experiment on three columns of 0.5, 1.5, and 2.7 wt % high-density polyethylene. The measurements yielded essentially identical isotherms from the three columns, so we concluded that adsorption of hexane on the support caused negligible error at the conditions used in this study. For details regarding other sources of error, see part I.[2a] In the case of the isopropyl alcohol azeotrope, there probably was adsorption of the isopropyl alcohol, but the steady supply of azeotropic vapor should have saturated the packing and restored the desired carrier gas plateau composition. A small injection of

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(13) C. E. Rogers, in "Engineering Design for Plastics," E. Baer, Ed., Reinhold, New York, N. Y., 1968, Chapter 9, p 609.

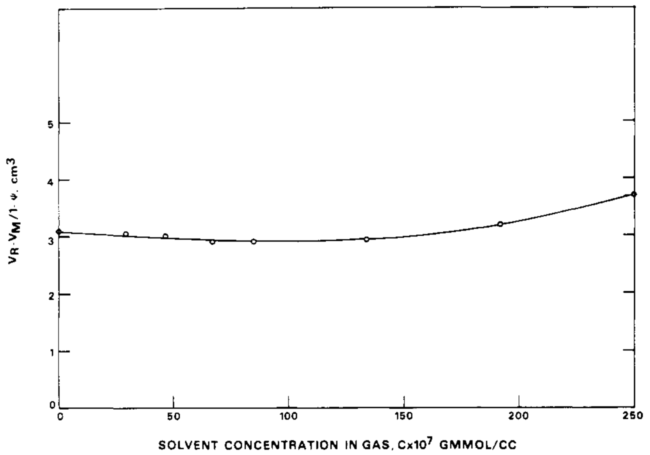

Figure 1. Retention volume difference as a function of plateau solvent concentration for hexane–high-density polyethylene (HDPE) at 80°.

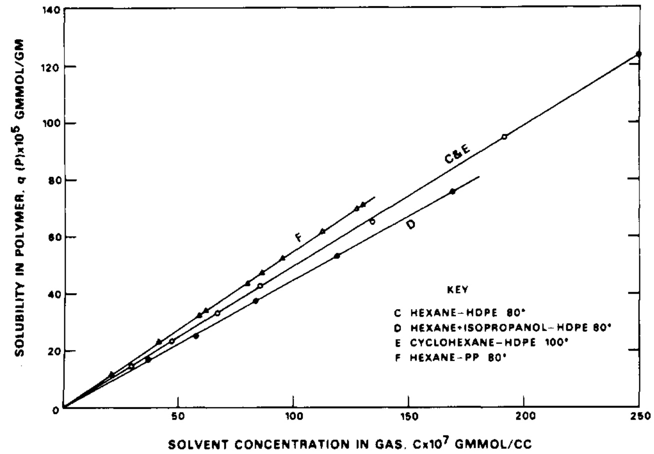

Figure 2. Solubility isotherms for semicrystalline polymers based on amorphous fraction.

pure hexane was used to probe the system. We believe that this technique correctly measured hexane volatility in the polymer containing the azeotrope.

There is at least one additional adsorption mechanism available in semicrystalline polymers that is not present in amorphous polymers: that of adsorption of the crystalline interface. We believe that the results from the loading experiment above indicate that this mechanism contributes negligible error—that we are measuring results typical of the bulk properties of the polymer.

Figure 1, which is typical of the results for semicrystalline polymers, shows how the primary data from these experiments are used. The retention volume difference ($V_R - V_M$) is corrected for the sorption effect ($1 - \psi$) and plotted as a function of the corrected plateau concentration of the solvent in the mobile phase. The area under the curve in Figure 1 is proportional (eq 1) to the solubility at each value of the plateau concentration. The curved line in Figure 1 will lead to a very slightly sigmoidal isotherm, hardly distinguishable from a straight line because of the choice of scale. However, the nonlinearity of Figure 1 will generally show in plots of χ and Ω.

Results and Discussion

Solubility. Figure 2 shows the solubility isotherms we determined for four different systems listed in Table II: *n*-hexane in high-density polyethylene (C), *n*-hexane and isopropyl alcohol in high-density polyethylene (D), cyclohexane in high-density polyethylene (E), and *n*-hexane in polypropylene (F). Two of the systems, C and E, yielded an identical isotherm, so only the data points for system C are placed on the middle curve to prevent crowding. The maximum solvent concentration shown, 2.5×10^{-5} mol/cm^3, corresponds to a carrier gas composition plateau of 0.557 mol fraction hexane. At this concentration there is some evidence that the isotherm is beginning to curve upward in a fashion characteristic of sorption with Van der Waals type forces. However, the curvature is insignificant in comparison with that of the iostherms measured for completely amorphous polymers in part I.[2a]

The fairly close agreement between the 80° isotherms (C and F) for *n*-hexane in high-density polyethylene and polypropylene was not surprising in view of the similarity between these two polymers. The hexane solubility in polypropylene was expected to be slightly higher than in high-density polyethylene because polypropylene has more space between chains. The slightly reduced solubility in the case of the azeotrope (curve D) was less pronounced than expected, judging from the polar nature of the isopropyl alcohol used in the vapor mixture. The coincidence of the isotherms for systems C and E occurred because the higher temperature reduced the somewhat higher solubility of the higher boiling cyclohexane.

Polymer–Solvent Interaction. The theoretical treatment of solvent interaction in polymers with moderate to high crystallinity is given semiquantitatively by eq 3-5. The assumption is that only the amorphous fraction partakes in sorption. As more solvent is sorbed, the amorphous polymer swells, but the extent of swelling is limited by crystalline cross-links. Therefore, we expect the interaction χ to increase as these cross-links are stretched by the swelling. The gradient of χ should be related to the chain length or molecular weight of the amorphous polymer between tie points M_c and a function of composition $(\phi_{2a}^{-5/3})$.

Figure 3 compares the values of χ measured at 0 and 30° by vapor sorption[4] with the values measured at 80° by the new GC method for the solution of *n*-hexane in high-density polyethylene. Although this comparison is only qualitative, the two sets of data at 30 and 80° are displaced downward to a greater extent as the temperature is increased in this range. The slopes of all three lines are about the same—thus the M_c values are comparable. Figure 4 shows that the χ values measured for the remainder of our systems are similar to those for hexane in high-density polyethylene at 80°.

The curvature observed in χ at very low solvent fraction (1% based on whole polymer, 4% based on amorphous fraction only) is quite similar to that observed by Blackadder and Keniry using a quartz spring balance.[6] The curvature of our system C in Figure 3 is comparable with their curves for interaction of *p*-xylene in pretreated high-density polyethylene films at 50°. They have discussed this behavior in terms of the change in M_c and the creation and subsequent destruction of solvent micelles with changes in the sorption level.[6] The behavior of our systems is consistent with their results though not as pronounced. Our GC column conditioning procedure probably eliminated the effects of pretreatment that might have persisted from our solution method of coating the GC packing.

Table II lists the values for M_c calculated from a linear approximation to the χ curves in Figures 3 and 4. Our value of 94.3 for M_c in system C falls between the values reported for hexane–high-density polyethylene at lower temperatures (systems A and B). A slight upward trend in M_c is expected with increasing temperature, with a large increase in M_c at the melting point of the crystalline phase.

Table II also lists the values calculated for μ_1. Equation 5 indicates that in the limit of pure solvent, χ approaches μ_1. These μ_1 values compare well with literature values measured by vapor sorption.[4] However, these negative values of μ_1 do not correspond at all to the generally positive values measured for amorphous polymer–solvent systems.[2,3] This disagreement is an illustration of one of the

Table II
Parameters for the Polymer-Solvent Systems

Polymer Sample	Vapor	Temp (°C)	$\bar{V}$ (cm^3/mol)	ρ_a (g/cm^3)	M_c (g/mol)	μ_1	System No.
HDPE[a] (Phillips Marlex 100)	*n*-Hexane	0	126	0.83	83	−0.52	A
HDPE (Amoco 680 Br4)		30	132	0.83	100	−0.47	B
HDPE (Amoco 680 Br)	*n*-Hexane	80	142.7	0.821	94.3	−0.87	C
HDPE (Amoco 680 B4)	*n*-Hexane–isopropyol alcohol azeotrope	80	127.1	0.821	67.9	−1.17	D
HDPE (Amoco 680 B4)	Cyclohexane	100	120.3	0.810	63.3	−1.21	E
PP[b] (Amoco 1016)	*n*-Hexane	80	142.7	0.780	80.8	−1.13	F

[a] HDPE = high-density polyethylene; PP = polypropylene.

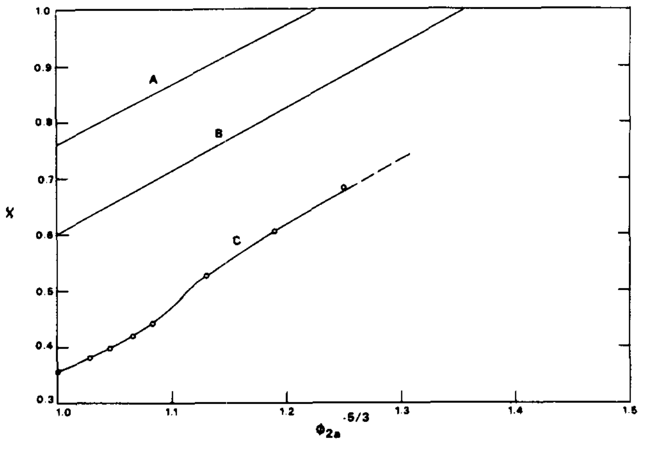

Figure 3. Interaction parameters for hexane in high-density polyethylene; A at 0°, B at 30°, and C at 80° (lines A and B from ref 4).

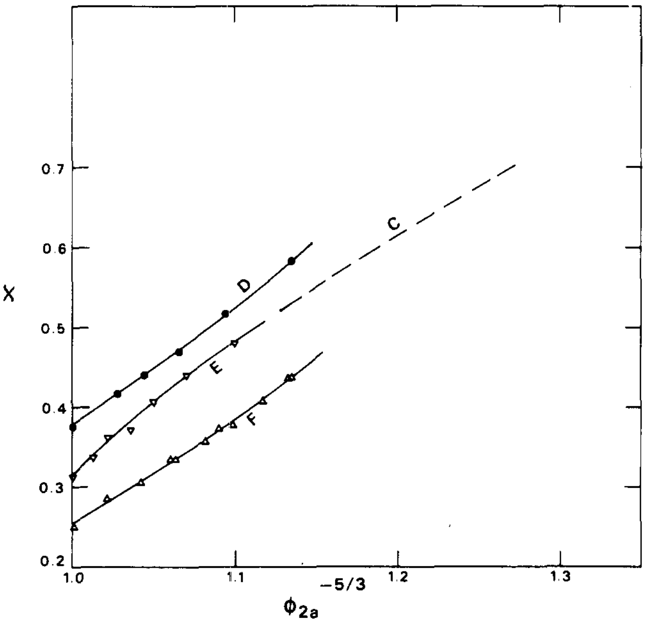

Figure 4. Interaction parameters as a function of composition.

problems of extrapolating eq 3, which is intended for a system with crystalline cross-links, into the pure solvent regime where the crystalline phase no longer can exist. In the limit of pure solvent, eq 3 and 5 probably have no meaning.

Vapor–Polymer Equilibrium. Figure 5 shows the equilibrium ratio Ω of *n*-hexane as a function of the weight per cent of solvent sorbed in the amorphous regions of the polymer. The Ω values are comparable with those measured for completely amorphous polymers.[2,3] There are interesting similarities between these four systems—all of the Ω values tend to increase as the plateau concentration of solvent is increased. This contrasts with the behavior of Ω for completely amorphous polymers (part I).[1a] The increase over the range from 0 to 4% solvent is especially noticeable when contrasted with the solid curves generated by substituting the appropriate constants from Table II into eq 3. Unless additional terms are included in eq 3, it will normally yield an Ω curve that decreases monotonically to unity as the composition approaches pure solvent. We believe that the Ω values that fall below the theoretical curve reflect the same changes in M_c and the configuration of the sorbed solvent that are reflected in the χ curves in Figures 3 and 4. The theory is not detailed enough to describe this sorption behavior exactly. A plot of Ω *vs.* the composition based on whole polymer would have qualitatively the same slope.

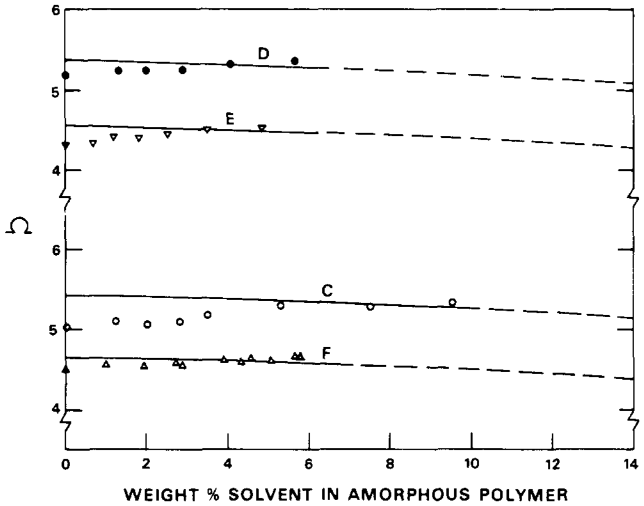

Figure 5. Equilibrium ratios based on amorphous fraction of polymer.

The main purpose for studying the azeotropic system (D) was to see whether the presence of the alcohol would boost the vapor equilibrium ratio of the *n*-hexane. Calculations of the apparent equilibrium ratio from another study indicated some promise for this phenomenon, at least in polypropylene.[14] For computation purposes the azeotrope was assumed to be a pure compound with molar-averaged properties. The results for systems C and D in Figure 5 indicate little effect, if any, caused by addition of 2-propanol to hexane in the high-density polyethylene system. We believe that polypropylene would not act differently than high-density polyethylene. One expla-

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(14) L. Basel and E. Gray, *Chem. Eng. Progr.*, 58, 67 (1962).

nation for the high Ω from the literature is that an inert gas diluted the vapor stream, thereby improving the solvent removal.

The data in Figure 5 indicate that Ω is equal to 5.0 ± 10% for all of the semicrystalline polymer–solvent systems in this study. Earlier work with nonpolar amorphous polymer–solvent systems also yields about the same values of Ω,[2,3] at least at infinite dilution. This unexpected result can be rationalized by examining the equation for Ω at infinite dilution from part I[2a]

$$\ln \Omega^\infty = -\ln r + 1 + \chi \qquad (7)$$

At the temperatures chosen for the convenience of good GC retention volume measurements, the ratio of specific volumes r has been larger for those systems which had a larger χ. If temperatures were held constant, the Ω^∞ for a homologous series of alkanes should decrease as molecular weight increases.

Conclusions

The results of our study indicate that the GC method of elution on a plateau can be used to determine the solubility isotherms of polymer–solvent systems, including semicrystalline polymers. The accuracy of this new method is almost comparable with that of vapor sorption using a quartz spring balance, but the new method is quite a bit faster to perform. Furthermore, the nature of the GC method allows measurements on essentially pure polymer, a limit which almost no other method can reach. This feature permits the investigator to cover a wider range of compositions and allows a more complete test of the implications of any solution theory.

Acknowledgments. The authors thank Amoco Chemicals Corporation for permission to publish these results.

Appendix

Nomenclature

a_1	Solvent activity over the stationary phase
B_{11}	Second virial coefficient of pure solvent at column temperature, cm^3/mol
c	Solvent concentration in mobile phase, mol/cm^3
j	Correction factor for gas compressibility and nonideality
M_1	Solvent molecular weight, g/mol
M_c	Molecular weight of amorphous polymer between cross-links, g/mol
P	Mean total pressure in GC column, atm
P_1	Solvent partial pressure, atm
P_1^0	Solvent vapor pressure at oven temperature, atm
q	Moles of solvent sorbed per unit mass of polymer in stationary phase, mol/g
r	Ratio of specific volumes, amorphous polymer to solvent
R	Gas constant
T	Temperature, °K
$\bar{V}$	Molar volume of solvent, cm^3/mol
V_M	Gas holdup (measured with helium) cm^3
V_R	Sample retention volume, cm^3
V_2	Mass of polymer in stationary phase, g
w_1	Weight fraction solvent sorbed in amorphous polymer
y_0	Mole fraction of solvent in outlet gas from column.

Greek Letters

α	Amorphous fraction of polymer
ψ	Corrected gas-phase mole fraction of solvent
χ	Polymer–solvent interaction parameter defined in eq 4
Ω	Vapor-polymer equilibrium ratio, a_1/w_1
ϕ	Volume fraction in polymer solution
μ_1	Flory–Huggins interaction parameter
ρ_a	Density of amorphous polymer, g/cm^3

Subscripts

1	Refers to solvent
2	Refers to polymer
a	Refers to amorphous fraction
i	Refers to inlet
0	Refers to outlet