Study of Polymer–Solute Interactions by Gas Chromatography

Olav Smidsrød[1] **and J. E. Guillet**

Department of Chemistry, University of Toronto, Toronto 5, Canada.

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ABSTRACT: The interaction of acetic acid, butyl alcohol, α-chloronaphthalene, naphthalene, and hexadecane with poly(N-isopropylacrylamide) was investigated by gas chromatography using the polymer as the stationary phase. The results showed that the partial molar excess free energy of mixing of the solutes became increasingly less favorable in the above order. At 100° only the two first solutes were absorbed by the bulk polymer phase. By using solutes interacting weakly with the polymer, the glass transition temperature of the polymer could be determined with the same degree of accuracy as in a differential scanning calorimeter. Above the glass transition temperature, all solutes penetrated the polymer, whereas below this temperature, adsorption on the polymer surface seemed the main sorption mechanism for the solutes with the most unfavorable free energy of mixing. For solutes interacting more strongly with the polymer, probably *via* hydrogen bond formation, the partial molar excess enthalpy and entropy of mixing could be determined even at temperatures far below the glass transition temperature. It is concluded that gas chromatography is a valuable tool for studying the structure of polymers and their interaction with compounds of lower molecular weight.

The gas chromatograph has now become an indispensable analytical instrument in the chemical laboratory. However, its power as an analytical tool has tended to obscure the fact that much more information can be obtained from it than just the composition of an unknown mixture. The development of gas chromatographic theory by the classic work of Purnell and others[2] has permitted the determination of vapor pressures, adsorption isotherms, activity coefficients, solvent–solute interactions, and many other thermodynamic quantities from gas chromatographic data. In fact, the ease with which such experiments can be carried out suggests that this procedure should supplant many of the more conventional methods of obtaining such data.

The application of gas chromatography to polymers has been relatively recent. Because of their negligible vapor pressure they cannot be employed as the moving phase, but have, from the earliest days, been used extensively as stationary phases. Typical examples are silicone oils, polyethylene, polyethylene oxides, and polyesters, but little attention was paid to information obtained thereby about the properties of the stationary phase. Later it was discovered[3] that polymers which thermally depolymerize or give reproducible thermal cracking products could be analyzed by pyrolysis gas chromatography. Reviews on the subject have recently been published by Guillet[4] and Alishoev and Berezkin.[5]

In the course of an investigation of the solution properties of poly(N-isopropylacrylamide) it seemed appropriate to use gas chromatography with the polymer as the stationary phase to study solvent–polymer interactions. Because the simplest application of theory gives activity coefficients at infinite dilution of the moving phase,[6,7] one is effectively studying properties relating to those of solvent molecules isolated in pure polymer, and one might expect to find effects relating to the physical state and structure of the material. First-order transitions (melting) in polymers have already been observed[5] in the gas chromatograph. For polyethylene[8] and polyethyleneglycol[9] a peak maximum in the temperature dependence of the retention volume was found close to the melting temperature. Second-order transitions (*e.g.*, glass transition) have so far not been detected in the gas chromatograph although solid–solid transitions in inorganic crystals have been reported by this method.[10]

In the present paper some preliminary results obtained using poly(N-isopropylacrylamide) as the stationary phase will be reported, and it will be shown that by appropriate choice of the moving phase, one may obtain a sharp determination of the glass transition, as well as thermodynamic data relating to the interaction of the polymer with various solvents.

Method

A gas chromatographic column is usually filled with a solid support material which contains a layer of the stationary phase. The retention of a moving solute then depends on the partition of the solute between this stationary phase and the moving gas phase. This partition is dependent mainly on the saturation vapor pressure of the solute at the column temperature and on the tendency of the stationary phase to sorb the solute molecule.[2] A detailed discussion of the influence of the carrier gas on this partition has been given by Cruickshank, *et al.*[6,7] In the present study the carrier gas is assumed to behave "ideally," that is, any

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[1] Norwegian Institute of Seaweed Research, N.T.H., Trondheim, Norway.

[2] H. Purnell, "Gas Chromatography," John Wiley & Sons, Inc., New York, N. Y., 1962.

[3] J. E. Guillet, W. C. Wooten, and R. L. Combs, *J. Appl. Polym. Sci.*, **3**, 61 (1960).

[4] J. E. Guillet, *Soap Chem. Specialties*, **41**, 145 (1965).

[5] V. R. Alishoev and V. G. Berezkin, *Russ. Chem. Rev.*, **36**, 545 (1967).

[6] A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, *Proc. Roy. Soc.* (London), **A295**, 259 (1966).

[7] A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, *ibid.*, **A295**, 271 (1966).

[8] V. R. Alishoev, V. G. Berezkin, and Yu. V. Mel'nikova, *Zh. Fiz. Khim.*, **39**, 200 (1965).

[9] A. G. Altenu, R. E. Kramer, D. J. McAdoo, and C. Merrit, *J. Gas Chromatog.*, **3**, 96 (1966).

[10] B. T. Guran, L. B. Rogers, *ibid.*, **5**, 574 (1967).

imperfections in the gas are disregarded, also, any corrections for the interaction between the solute molecules in the gas phase and the carrier gas molecules are neglected. The experimental results of Cruickshank, *et al.*, indicate that these are good approximations when hydrogen is the carrier gas and the operating pressure of the column is low, as is generally the case in this study.

Since high polymers lie somewhat between conventional crystalline solids and ordinary liquids with respect to viscosity and the diffusivity of small molecules in the polymer phase, one must consider two main mechanisms for the sorption of solutes: (1) absorption of solutes in the bulk–polymer phase, and (2) adsorption of solutes on the polymer surface.

Although attempts have been made to evaluate data where both mechanisms are operating simultaneously in the gas chromatograph[11] a quantitative treatment of the data is best carried out when absorption is the dominant mechanism. When the solute is held back by absorption only, the retention volume is directly proportional to the amount of polymer on the column (the liquid loading). In the case of adsorption, proportionality between retention volume and surface area should be observed. The surface area is not generally proportional to the weight of the polymer, so by using columns of different liquid loadings, one can determine if absorption dominates. If a direct proportionality exists between retention volume and liquid loading, one may also rule out adsorption on the column wall, and on uncovered parts of the surface of the solid support. A discussion of such effects is to be found in a review article by Ross and Tolles.[12]

When absorption in the bulk polymer is the dominating mechanism, the theory of gas–liquid partition chromatography may be applied to the results to calculate various thermodynamic quantities. The vapor pressure p_1 of compound **I** above a binary solution can generally be expressed as

$$p_1 = \gamma_1 x_1 p_1^0 \tag{1}$$

where γ_1 is an activity coefficient, x_1 is the mole fraction of compound **I** (the injected solute), and p_1^0 is the saturation vapor pressure of the same component. In ideal solutions γ_1 equals unity, in real solutions γ_1 is different from unity and dependent on x_1. The concentration of solute in a gas chromatographic column is not known, but often is so low that Henry's law, stating that γ_1 is a constant independent of x_1, explains the results. For polymers as stationary phase one can not always expect such behavior. This does not impose a serious problem since one can do experiments with different sample sizes and extrapolate to zero concentration using the relation

$$p_1 = \gamma_1^\infty x_1 p_1^0 \tag{2}$$

where γ_1^∞ is the activity coefficient at infinite dilution.

This equation can be rewritten so that the activity coefficient may be expressed in terms of gas chromatographic and saturation vapor pressure data.[2] In

$$\gamma_1^\infty = \frac{273R}{V_g p_1^0 M_1} \tag{3}$$

eq 3, R is the universal gas constant, M_1 is the molecular weight of the solvent in the stationary phase, and V_g represents the specific retention volume (per gram of solvent) reduced to the standard state (0°, 1 atm) as defined in eq 4.

$$V_g = \frac{273 V_R}{TW} \tag{4}$$

In this equation T is the column temperature, W is the weight of the stationary phase in the column, and V_R is the retention volume corresponding to that measured at the column temperature, corrected for gas holdup in the column and for pressure drop from the inlet to the outlet of the column.[2] The partial molar excess free energy of mixing may now be found[13] from the relation

$$\overline{\Delta G_m} = RT \ln \gamma_1^\infty \tag{5}$$

If measurements are conducted at different temperatures one may also determine the partial molar enthalpy of mixing

$$\overline{\Delta H_m} = R\frac{\partial(\ln \gamma_1^\infty)}{\partial(1/T)} \tag{6}$$

and the corresponding partial molar excess entropy of mixing

$$\overline{\Delta S_m} = \frac{\overline{\Delta H_m} - \overline{\Delta G_m}}{T} \tag{7}$$

The value of M_1 which should be used for polymeric solvents is not entirely clear. In the present case involving sorption of small molecules in bulk polymers, it might be expected that the activity of the polymer phase will depend on some parameter relating to segment length. In the absence of such information we equate the value of M_1 with the number average molecular weight of the polymer.

Experimental Section

A. Preparation of Poly(N-isopropylacrylamide). A mixture of 10 g of N-isopropylacrylamide, 0.35 g of lauroyl peroxide, and 50 ml of chloroform was prepared, and the oxygen was removed by passing nitrogen through the reaction vessel for 30 min. The polymerization was carried out at 60° for 3 hr with continuous stirring. The viscous solution was then precipitated by pouring the mixture into a large excess of toluene. After filtration and repeated washing with toluene, the polymer was dried under vacuum at 120° to constant weight. The yield of polymer was 9.1 g.

B. Preparation of Gas Chromatographic Columns. The columns were 0.25-in. aluminum tubing and approximately 5 ft long. The solid support was Chromosorb G, which had been washed with acid and treated with dimethyldichlorosilane. The support was covered with the polymer by mixing a weighed amount of the support with a solution of the polymer in chloroform. The solvent was then evaporated by passing nitrogen through the solution. To

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(11) D. Cadogan and J. H. Purnell, paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

(12) S. Ross and E. D. Tolles, "The Solid–Gas Interface," Vol. 2, A. Flood, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, pp 647.

(13) H. J. Purnell and S. H. Langer, *J. Phys. Chem.*, **67**, 263 (1963).

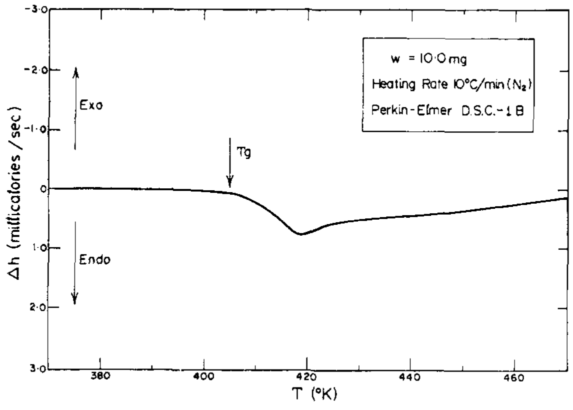

Figure 1. Differential thermogram for poly(N-isopropylacrylamide) showing glass transition T_g at 130°.

allow the solid support to be in constant contact with the polymer solution, the solution was stirred continuously during the evaporation period. The particles were then dried under vacuum at 120° to constant weight, and the amount of polymer on the support was found by weighing.

The columns were filled with the covered particles and packed by using a mechanical vibrator. The amount of the covered support in the filled column was found by weighing, and the corresponding amount of polymer could then be calculated. Two columns were prepared, column 1 containing 0.715 g and column 2 containing 1.65 g of the polymer.

C. Determination of Specific Retention Volumes. The gas chromatograph was an Aerograph Autoprep 700, equipped with flow meter, pressure gauge, and a thermal conductivity detector. Temperature control was obtained by means of a circulating air oven. The temperature of the column varied within ±1° of the control temperature. The samples were injected by a 1- or 10-μl Hamilton syringe. Naphthalene was injected as a liquid using hot syringes or in solution. The retention time was always found as the difference between the position of the maxima of the air and solute peaks. In this way the holdup in the column was correctly accounted for.[2] The flow of the carrier gas was measured by a soap bubble flow meter. The gas was hydrogen except for some few introductory experiments. The room temperature and barometric reading were recorded to allow a calculation of the flow speed corresponding to 760 mm and 0° required to calculate the specific retention volume. The pressure drop in the column was measured by a pressure gauge prior to the gas chromatographic experiments, and a series of calibration curves relating the pressure drop at different temperatures to the flow speed was made. The pressure drop was usually considerably less than 0.1 atm, but corrections were made using the well-known equation of Purnell[2] when necessary.

D. Determination of the Glass Transition Temperature, T_g. A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used. The temperature range from 50 to 250° was scanned and the glass transition T_g was found by adjusting the slope of the output to zero below the glass transition, and taking T_g as the temperature where the first change in slope was observed.[14] A typical differential thermogram is shown in Figure 1. An average of six determinations gave a value of T_g = 130 ± 3°.

The existence of the glass transition was confirmed by heating a small sample of the polymer in *n*-hexadecane. There was no sign of solvation or swelling up to 200°, but a sharp transition occurred at 130° from a hard brittle solid to an elastic rubber. The change was reversible and showed no difference after repeated temperature cycles through T_g. The polymer is amorphous and has no melting point. It begins to flow at about 160–170°.

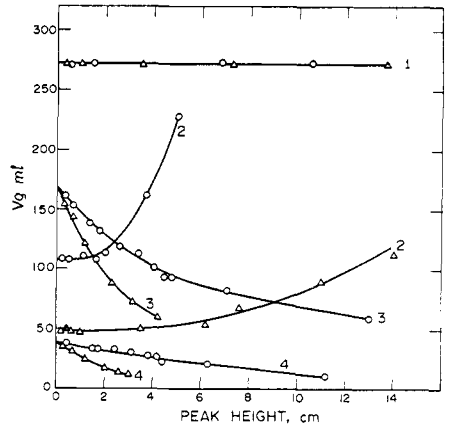

Figure 2. Specific retention volume as a function of peak height at 100°: curve 1, butyl alcohol (hydrogen); curves 2, hexadecane (hydrogen); curves 3, ethanol (nitrogen); curves 4, acetone (nitrogen); ○, column 1; △, column 2.

E. Solubility. The polymer was completely soluble in acetic acid, ethanol, acetone, and butanol at room temperature and above. There was no evidence for solution or swelling in paraffinic hydrocarbons such as *n*-hexadecane up to 200°.

F. Molecular Weight. The number average molecular weight of the polymer was determined in tetrahydrofuran solution using a Mechrolab automatic membrane osmometer. The value obtained was $\overline{M}_n$ = 50,100 ± 2000. Analysis on a Waters Ana-Prep chromatograph in THF solution indicated that the distribution was somewhat broader than normal.

G. Solvents. The solvents were Eastman White Label or Fisher Certified grades used without further purification. The gas chromatograph indicated better than 99% purity in all cases. The *n*-hexadecane was a gas chromatograph standard supplied by Beckman Instruments Inc.

Results

Preliminary experiments were made with the column at 100°. Injection of a series of aliphatic hydrocarbons with normal boiling points less than 200° resulted in retention times close to zero. The peaks could not be separated from the air peak. Acetone and a series of alcohols gave retention times too long to be measured. The high-boiling hydrocarbon, hexadecane, gave measurable retention times.

In all cases the retention volume depended significantly on the amount of the injected solute. In Figure 2 the specific retention volumes at 100° are plotted as a function of the peak height in centimeters. Some of the experiments (ethanol and acetone) were carried out with nitrogen as the carrier gas. In these cases the detector system was unable to measure samples of less than 0.2 μl with good definition of the peak maxima. The sample sizes therefore ranged from 0.2 to 5 μl. Figure 2 shows that the extrapolation to zero peak height in this case is curved and therefore not very accurate. The results with *n*-butyl alcohol were obtained using hydrogen as the carrier gas. Because of the greater difference in thermal conductivity, the range

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(14) B. Ke in "Newer Methods of Polymer Characterization," B. Ke, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, p 347.

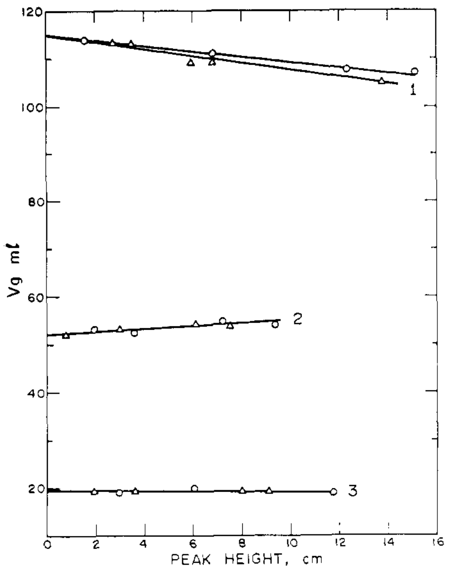

Figure 3. Specific retention volume as a function of peak height at 185°: carrier gas, hydrogen; curve 1, acetic acid; curve 2, hexadecane; curve 3, butyl alcohol; ○, column 1; △, column 2.

of sample sizes could now be kept as low as 0.01-0.2 μl, and the straight line extrapolation is quite accurate.

Before comparing the results obtained for the two columns, it may be noted that for ethanol and acetone the retention volume decreased with increasing sample size. From eq 3 it is evident that this corresponds to an increase in γ, with an increase in sample size; in other words, these solutes show a negative deviation from Raoult's law. A positive deviation is seen to be the case for hexadecane (curves 2). Qualitative information concerning this type of deviation may also be obtained directly by inspecting the asymmetry of the peaks.[2] Hexadecane gave peaks with a diffuse leading edge and a sharp tail, whereas ethanol and acetone gave sharp leading edges and diffuse tails, which is in accordance with the deviations from Raoult's law predicted from gas chromatography theory.

A comparison of the results obtained with columns 1 and 2 shows that for acetone, butyl alcohol, and ethanol the specific retention volumes at zero peak height are independent of the liquid loading. These results therefore strongly indicate that these solutes are held back exclusively by absorption in the bulk polymer phase. Hexadecane, on the other hand, gave specific retention volumes 2.2 times higher for column 1 than for column 2. Since the weight ratio of the polymer in column 2 and 1 is 2.3, the retention volume is almost independent of the liquid loading, suggesting an adsorption mechanism.

In Figure 3 similar results at 185° (well above the flow temperature of the polymer phase) are given for acetic acid, butyl alcohol, and hexadecane. A markedly different behavior of hexadecane is now observed. The specific retention volume is the same for the two columns, indicating that at this temperature hexadecane is absorbed by the polymer phase. The two other solutes also show the same behavior.

Measurements were carried out for five different

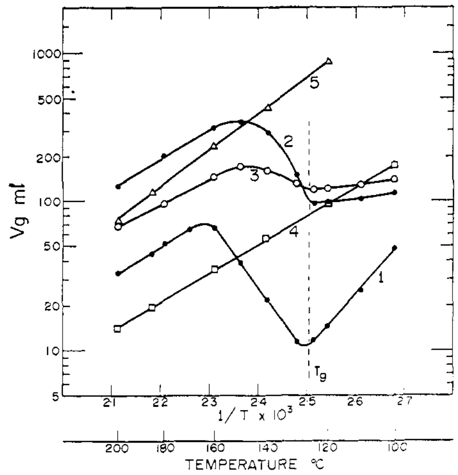

Figure 4. Specific retention volume as a function of reciprocal absolute temperature: curve 1, hexadecane; curve 2, α-chloronaphthalene; curve 3, naphthalene; curve 4, butyl alcohol; curve 5, acetic acid.

solutes at a series of temperatures between 100 and 200°, and the logarithm of the specific retention volume was plotted *vs.* $1/T$ as shown in Figure 4. Acetic acid and butyl alcohol yield straight lines over the whole temperature region. Hexadecane on the other hand shows a completely different behavior. Above 180° the line is straight, with a slope similar to the other solutes, between 170 and 160° the slope changes from positive to negative, this negative slope continues down to between 125 and 130° where it changes back to positive. The two other hydrocarbon solutes in Figure 4, naphthalene and α-chloronaphthalene, show a similar behavior. The peak maximum is, however, broader than for hexadecane and is moved toward lower temperatures. The minimum is also less sharp, but does occur between 130 and 125°. This temperature range is the same as that reported above for the glass transition temperature.

There seems to be no correlation between the specific retention volumes of the solutes in the high temperature range and the shape of their curves in Figure 4. Since the retention volume is dependent both on the saturation vapor pressure of the solutes and the solubility of the solute in the polymeric phase (represented by γ_1^{∞}), saturation vapor pressure data were used[15] to calculate the activity coefficients. As shown in Figure 5, the solutes differ widely in solubility behavior. Hexadecane has by far the highest activity coefficient and acetic acid the lowest.

By using the results in Figure 5 and eq 5, 6, and 7, the partial molar excess free energy of mixing (at 200°) and the corresponding enthalpy and entropy values in the given temperature ranges were calculated. The results are shown in Table I. It is seen that the large negative excess free energy of mixing of acetic acid is due to a favorable enthalpy term, whereas the other solutes have favorable entropy terms but unfavorable enthalpy terms.

(15) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958.

Table I
Thermodynamic Data at 200°

	$\overline{\Delta G_m}$, cal/mol	$\overline{\Delta H_m}$, cal/mol	$\overline{\Delta S_m}$, cal/deg mol
Acetic acid	−6740	−2400	+9.2
Butyl alcohol	−5390	+1100	+13.7
Naphthalene	−4360	+3900	+17.5
α-Chloronaphthalene	−4010	+3600	+11.3
n-Hexadecane	−1760	+2200	+8.4

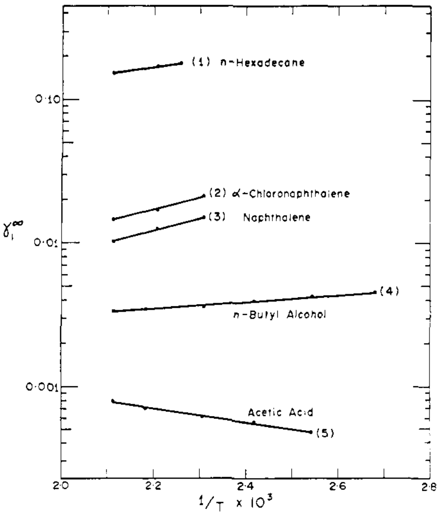

Figure 5. Infinite dilution activity coefficients (γ_1^∞) as a function of reciprocal temperature: curve 1, hexadecane; curve 2, α-chloronaphthalene; curve 3, naphthalene; curve 4, butyl alcohol; curve 5, acetic acid.

Discussion

The advantage of the gas chromatographic technique compared to classical static equilibrium methods for obtaining thermodynamic data for the mixing of polymer and solutes lies mainly in the speed of obtaining data. It must be stressed, however, that by the present method only data at infinite dilution of the solute may be obtained and that it is of particular importance to study the effect of the liquid loading on the specific retention volume at infinite dilution before a quantitative interpretation of the data is made. The results in Figure 2 show clearly that hexadecane at 100° is not absorbed in the bulk of the polymer, and correlating the observed retention volumes to the mixing process would in this case be meaningless. The same holds for α-chloronaphthalene and naphthalene in the lower temperature region, below T_g for the polymer.

The thermodynamic data calculated here (Table I) are all from the straight-line portion of the curves at high temperatures for hexadecane, naphthalene, and α-chloronaphthalene, and for the whole temperature range for acetic acid and *n*-butyl alcohol. In these cases, the specific retention volumes were independent of the liquid loading, and the calculation is therefore justified.

Because of the possible errors in extrapolation and the measured experimental error these values can be considered accurate only to within ±10%.

It would be desirable to compare such data with that obtained by more established methods. Unfortunately no data for the mixing of poly(N-isopropylacrylamide) with low molecular weight compounds in the temperature region used here are available.

The excess free energy of mixing at infinite dilution of the solute appears to be related to the solubility of the polymer using the same solute as a solvent. For example, the solutes with the lowest excess free energy of mixing (hexadecane, α-chloronaphthalene, and naphthalene) are nonsolvents for the polymer. Butyl alcohol and acetic acid are solvents, and these compounds also have more favorable excess free energy of mixing.

The values for the enthalpy of mixing are rather high, both negative and positive. It is known[16] that poly(N-isopropylacrylamide) is soluble only in solvents capable of hydrogen bond formation. This suggests that the polymer in the solid state is held together, at least partly, by hydrogen bonds between the amide groups. Since the enthalpy change upon hydrogen bond formation is usually in the order of 3–5 kcal/mol,[17,18] one may assume that two amide groups held together by two hydrogen bonds should have a strength of about 6–10 kcal/mol. The mixing of a solute into such a structure must involve breaking and formation of hydrogen bonds, and the rather large enthalpy changes are therefore reasonable.

The trend in the variation of the enthalpy values may be accounted for by the tendency of the solutes to form hydrogen bonds with the amide group. Acetic acid shows a negative excess enthalpy of mixing, and it is well known that acetic acid can form strong hydrogen bonds. The difference between the other solutes is less pronounced, but again *n*-butyl alcohol with its capability of hydrogen bond formation, gives the smallest positive enthalpy.

The excess entropy of mixing is in general a function of the size of the solute and the excess enthalpy of mixing. Lettler and Grundwald[19] suggested that for chemically related compounds, a linear plot will result from the correlation of $\overline{\Delta H_m}$ *vs.* $\overline{\Delta S_m}$. With only five solutes, such a plot is not conclusive, but the results in Table I show some tendency for a simultaneous increase in both $\overline{\Delta H_m}$ and $\overline{\Delta S_m}$. Measurements with a series of solutes differing only slightly in chemical structure may yield more valuable information of this kind.

The rather unusual temperature dependence of the retention volume for hexadecane, naphthalene, and α-chloronaphthalene requires some further discussion. A full explanation for this behavior probably would require measurements of diffusion coefficients and adsorption isotherms, but a tentative explanation may be given.

It is evident from the results shown in Figures 2 and 3

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(16) M. Heskins and J. E. Guillet, *J. Macromol. Sci., Part A*, in press.

(17) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(18) D. E. Martire and P. Riedl, paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968.

(19) J. E. Leffler and E. M. Grundwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.

that hexadecane is absorbed in the bulk of the polymer at 185°, and that sorption on the polymer surface is dominant at 100°. Below the glass transition temperature the retention volume is linear with $1/T$ (Figure 4). It was also found that at all temperatures below T_g the observed retention volume was independent of the liquid loading. These results strongly indicate that adsorption on the polymer surface dominates at all temperatures below T_g. The transition range between 160 and 130° may then be explained by a nonequilibrium sorption mechanism. Such a mechanism would occur if the diffusion of hexadecane is so slow that only part of the polymer is "available" for this solute. The amount of "available" polymer would decrease with temperature, and the drop in retention volume with a decrease in temperature would be explained. When the glass transition temperature is reached, the hexadecane molecules must diffuse in an essentially frozen polymer structure, most probably characterized with a higher activation energy,[20-22] and adsorption on the polymer surface becomes the dominating sorption mechanism.

It is evident from these experiments that the change in the sign of the slope around T_g occurs for the three substances with the smallest excess free energy of mixing. This may be related to the large size of the hexadecane, naphthalene, and α-chloronaphthalene molecules, and more experiments are needed to clear up this point. It seems likely, however, that acetic acid and *n*-butyl alcohol with their ability to form hydrogen bonds may diffuse in the polymer by another mechanism, and this is why these solutes are able to penetrate the polymers even below the glass transition temperature.

Regardless of what the detailed explanation for the behavior around the glass transition may be, the effect is pronounced and, at least for hexadecane, very sharp and easily detected, and it seems likely that this effect may be a general one for polymer substrates interacting with a "nonsolvent" solute.

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(20) R. J. Kokes, F. A. Long, and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

(21) Ch. A. Kumines and J. Roteman, *J. Polym. Sci., Part A-1*, 527 (1963).

(22) J. L. Duda and J. S. Vrentas, *ibid., Part A-1*, **6**, 675 (1968).

Pyrolysis–Gas Chromatographic Investigation on the Structure of Chlorinated Poly(vinyl chlorides)

Shin Tsuge, Tadaoki Okumoto, and Tsugio Takeuchi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa ku, Nagoya, Japan. *Received February 27, 1969*

ABSTRACT: The distributions of the chlorine atoms in the chain of chlorinated poly(vinyl chlorides) were studied by means of pyrolysis–gas chromatography over a wide range of degree of chlorination. In addition to vinyl chloride, 1,2-dichloroethylene, and vinylidene chloride units, which up to now were regarded as the only possible microstructures of chlorinated poly(vinyl chloride), the presence of 1,1,2-trichloroethylene units was confirmed. The estimated concentration of the new unit amounted to up to 10% at a high degree of chlorination.

The chemical and physical properties of poly(vinyl chloride) (PVC) vary with the degree of after-chlorination. Chlorinated poly(vinyl chloride) (CPVC) generally shows improved thermal stability. As CPVC is a nonuniform polymer and the distributions of the chlorine atoms along the chain of the polymer are complex, various authors[1-4] have reported conflicting results regarding its molecular structure. Germar[1] has presented ir spectroscopic work on the microstructure of CPVC. He found that chlorination of the methylene groups is favored to form $-CHClCHCl-$ and that $-CH_2CCl_2-$groups are present up to 20% at most. Fredriksen and Crowo,[2] who also used ir spectra, found that the ratio of the chance for chlorination of $-CH_2-$ and $-CHCl-$ is about 2:1. Using nmr spectra of CPVC, Petersen and Rånby[3] and Tho and Berticat[4] determined the concentration of $-CH_2CHCl-$, $-CHClCHCl-$, and $-CH_2CCl_2-$. According to the results, $-CHClCHCl-$ is formed preferentially at the initial stage of chlorination. This is in fairly good agreement with ir results, but the reported high content[3] (up to 34%) of $-CH_2CCl_2-$ rather disagrees with the result (up to 20%) by ir analysis.[1] Generally, the authors[1-4] interpreted the microstructure of CPVC by assuming that only two chlorine atoms could be contained at most in a monomer unit by after-chlorination and that the original PVC has a regular head-to-tail structure. Consequently, only the three units mentioned above were taken into consideration.

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(1) H. Germar, *Makromol. Chem.*, **86**, 89 (1965).

(2) O. Fredriksen and J. Crowo, *ibid.*, **100**, 231 (1967).

(3) J. Petersen and B. Rånby, *ibid.*, **102**, 83 (1967).

(4) R. Q. Tho and P. Berticat, *Eur. Polym. J.*, **4**, 265 (1968).