deed, the 1.0 Å gaps within the *Valonia* coupled with the H1 distortion gave better agreement than the perfect crystallite for the relative intensities of the $1\bar{1}0$ and 110 reflections. This reversal of intensities is of interest since such differences in these relative intensities and slight differences in the positions of the three strong reflections have been observed for unoriented specimens of native cellulose from different sources. It is also interesting to note that insertion of one water molecule per chain between faces of the elementary fibril would produce an expansion of approximately 1 Å. As an analogy, conversion of anhydrous β-chitin to the monohydrate increases the lateral lattice parameter from 9.3 to 10.3 Å.[25] An imperfect layer of water molecules between the elementary fibrils would thus be an acceptable distortion.

The defects within the microfibril could be modeled more closely by Hosemann type two (H2) distortions,[12] incorporating possible turns about the fiber axis. The H2 distortions would have the effect of broadening the reflections with increasing scattering angle, but for a system as nearly perfect as *Valonia* cellulose, the use of H1 model is probably adequate. For less ordered systems such as cotton cellulose the reflections are much broader and it is likely that H2 distortions will need to be incorporated. Such studies are currently in progress for cotton, where the higher layer line data are also being used to investigate elementary fibril displacements parallel to the fiber axis.

Acknowledgment. This research was supported by NSF Grant No. GH34227 and N.I.H. Research Career Development Award No. AM80642 (to J. Blackwell).

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The Effect of Surface Adsorption on Gas Chromatographic Measurements Near Polymer Melting Transitions

G. Courval and D. G. Gray*

Pulp and Paper Research Institute of Canada, and the Department of Chemistry, McGill University, Montreal H3C 3G1, Canada. *Received January 25, 1975*

ABSTRACT: The extension of gas chromatographic methods to studies on the interaction of polar polymers and vapors is complicated by adsorption at the polymer–vapor interface. Some effects of this adsorption were examined using water and *n*-propyl alcohol as probes with a poly(ethylene oxide) stationary phase coated onto an inert fluorocarbon support. The measured retention volumes depended markedly on the surface-to-volume ratio of the stationary phase, in a manner consistent with independent surface and bulk contributions to the retention mechanism. Using an extrapolation procedure, the true bulk retention volumes for poly(ethylene oxide) above and below its melting point were determined. The crystallinity of the polymer, estimated from these data, was found to be in good agreement with previously reported values. It is concluded that in order to interpret correctly GLC retention data near a polymer melting region, both exclusion of the vapor from crystalline regions and surface adsorption must be considered.

The application of gas chromatography to physicochemical measurements [1,2] has proven useful in several areas of polymer science.[3] Perhaps the most fruitful area has been the derivation of thermodynamic information on polymer–solvent interactions at low solvent concentrations.[3,4] For relatively nonpolar vapors and polymers, at temperatures substantially above the melting point or glass transition temperature, equilibrium thermodynamic parameters may be derived with some confidence from appropriately corrected[1] gas chromatographic data.

Gas chromatography has also been used to study polymer phase transitions. The GC retention volume[1–3] reflects the interaction of a "probe" vapor with the polymer; changes in the polymer structure which occur at the melting point or the glass transition temperature should therefore exert a marked effect on the retention volumes. Sharp discontinuities have been detected in the variation of retention volumes with temperature for hydrocarbons on columns containing polyethylene and polypropylene near the polymer melting points.[5] This work was extended by Guillet and coworkers who determined melting points, degrees of crystallinity, and crystallization kinetics for polyolefins by GC.[6] Glass transition temperatures of poly(*N*-isopropyl acrylamide),[7] poly(styrene), poly(vinyl chloride), poly(methyl methacrylate),[8] polycarbonates[9] and poly(acrylonitrile)[10] were also detected by this method. Gas chromatographic evidence has been presented for a second-order transition other than the glass transition in cellulose acetate.[11] Phase transitions of organic compounds and liquid crystals have also been widely dealt with in the gas chromatographic literature, mainly with a view to their possible usefulness in improving separations.[12] In particular, the melting of poly(ethylene oxide), a common stationary phase, has received attention.[13–16]

Despite the high surface-to-volume ratio of the stationary phase in GC experiments, it is usually assumed that the vapor interacts uniformly with the bulk of the polymeric stationary phase, and that surface adsorption is only important below the glass transition temperature. However, many polymers are very polar in comparison with the usual analytical GC stationary phases, and it has long been recognized that in polar systems, adsorption on the surface of the stationary phase may contribute significantly to the retention in the column.[17,18] The purpose of this paper is to emphasize the importance of such adsorption on polymer surfaces, and to draw attention to the effect it may have on the temperature dependence of the retention volume near the melting temperature of crystalline polymers. Surface effects near the glass transition will be considered in a subsequent publication.

Adsorption on Stationary Phase Surface

The standard approach to adsorption on liquid stationary phases is to assume that bulk and surface processes make independent contributions to the measured retention volume[17–19]

$$V_N = K_B V_L + K_S A_L \tag{1}$$

when V_N is the measured net GC retention volume, corrected for column hold-up and pressure drop,[2] K_B and K_S are the bulk and surface partition coefficients respectively, V_L is the volume of stationary phase, and A_L is the surface area of the stationary phase. The separate contributions to the retention mechanism may thus be evaluated by varying V_L and plotting V_N/V_L against $1/V_L$. Extrapolation to $1/V_L = 0$ gives the value of the bulk partition coefficient K_B, and K_S can also be evaluated if A_L is known as a function of V_L. It is assumed in eq 1 that other retention mechanisms, such as adsorption at the stationary phase–support interface, may be neglected. The size of the injected vapor sample is assumed to be so small that V_N, K_B, and K_S are independent of its size. In fact K_S and hence V_N are often dependent on vapor sample size; in this case it has been suggested[19] that in experiments where V_L is varied, the vapor sample size should be varied, so that the effective surface concentration remains constant.

Much of the interest in factoring retention volumes into bulk and surface components has been to obtain true bulk partition coefficients from GC retention data in order to determine the thermodynamics of the interaction between the bulk stationary phase and the vapor. Applications in the polymer field include the data reduction applied to GC retention volumes for organic solvents in polystyrene[20] and poly(ethylene oxide)[21] stationary phases. However, it is evident that information on the concurrent surface adsorption process should in principle also be available. As mentioned previously, adsorption on the surface of polymer melts is expected to become significant when the polymer is polar and the vapor is relatively nonpolar. The vapor may thus have a relatively low solubility in the polymer, so that the importance of surface contributions to the retention mechanism is correspondingly greater. Surface adsorption may also be important when both vapor and polymer are polar, because of strong dipole–dipole interactions or hydrogen bonds between the solute and the melt surfaces.[18]

Model for the Effects of Phase Transitions on Chromatograms

The effect of surface contributions to retention mechanisms at polymer phase transition temperatures will be considered using a simple model. The first assumption is that surface and bulk mechanisms make additive contributions to the GC retention volume, as indicated by eq 1. It is often convenient to convert the column retention volume V_N to specific retention volume V_g,[2] the retention volume per gram of stationary phase, measured at 273.2°K. In this case, the retention volume may be divided into surface and bulk contributions

$$V_g = V_g^b + V_g^s \tag{2}$$

where

$$V_g = (V_N/w)(273.2/T) \tag{3}$$

and the bulk and surface contributions to the specific retention may be expressed in terms of the partition coefficients

$$V_g^b = (K_B/\rho)(273.2/T) \tag{4}$$

$$V_g^s = (K_S A_L/w)(273.2/T) \tag{5}$$

where ρ is the density of the polymer at temperature T and w is the weight of stationary phase in the column. It should be emphasized that unequivocal theoretical or experimental justification of this approach has not yet been presented, so that eq 1 and 2 are best viewed as useful empirical approximations.

Having factored the retention volume into surface and bulk components, the temperature dependence of these components is next considered. For bulk retention, the temperature dependence of the retention volume is often written as

$$\partial \ln V_g^b/\partial(1/T) = \Delta H^b/R \tag{6}$$

where ΔH^b is an enthalpy of vaporization of the vapor probe from infinitely dilute solution in the stationary phase. This equation predicts a linear dependence of $\ln V_g^b$ on $1/T$ if the temperature dependence of ΔH^b is neglected. (This relation also implies a neglect of the effect of gas phase imperfections;[2] inclusion of corrections is necessary for thermodynamic calculations, but would unnecessarily complicate this qualitative model.) A similar equation may be written for purely surface adsorption

$$\partial \ln V_g^s/\partial(1/T) = \Delta H^s/R \tag{7}$$

where ΔH^s is an enthalpy of vaporization of the probe at effectively zero coverage from the surface of the polymer. If the total measured retention volume is expressed as the sum of the surface and bulk contributions, then the slope of the retention diagram at any temperature must consequently be given by

$$\frac{\Delta H}{R} = \frac{\partial \ln V_g}{\partial(1/T)} = \frac{\partial \ln (V_g^b + V_g^s)}{\partial(1/T)} = \frac{V_g^b}{V_g^b + V_g^s}\,\frac{\Delta H^b}{R} + \frac{V_g^s}{V_g^b + V_g^s}\,\frac{\Delta H^s}{R} \tag{8}$$

The slope of the retention diagram for the total retention at a given temperature is thus equal to a weighted sum of the slopes of the surface and bulk retention diagrams. It should be noted that the weighting factors are temperature dependent, so that even if ΔH^b and ΔH^s are assumed to be temperature independent, the overall ΔH is not necessarily so, and the assumption that enthalpy contributions may be linearly combined over a range of temperatures may not be generally valid. However, inspection of eq 8 shows that $\partial(\ln V_g)/\partial(1/T) = \Delta H/R$ will approach temperature independence if V_g^b and V_g^s are different in magnitude, or if ΔH^b and ΔH^s are very similar in magnitude. This latter condition is often satisfied, as both ΔH^b and ΔH^s are usually close to ΔH_{vap}, the latent heat of vaporization of the pure liquid probe.

Melting Transitions

GC retention volumes on polyolefin stationary phases change markedly at the polymer melting point.[5] Stein and Guillet[6] proposed that below the melting point, the vapor probe could only penetrate the amorphous regions of the polymer, and suggested that the crystallinity could be estimated directly from the retention volumes. The behavior is illustrated schematically in Figure 1. The linear relationship between ln V_g and $1/T$ for an amorphous polymer is shown in line I. If, however, a fraction C of the polymer crystallizes, leaving a fraction $(1 - C)$ of the polymer available to interact with the probe, then the retention volume will be reduced by a factor of $(1 - C)$

$$V_g = (1 - C)V_g^b \tag{9}$$

where V_g^b is the retention volume for a totally amorphous polymer, extrapolated from the region above the melting temperature T_B using eq 6. Curves II and III indicate the expected shapes for $C = 0.33$ and 0.67, respectively. It is assumed that the enthalpy of vaporization from the amorphous regions below the melting temperature is the same as that from the amorphous melt above T_B, that the degree of crystallization remains constant below some temperature T_A, and that no new retention mechanism such as adsorption on crystalline surfaces is operative. Thus the curves I, II, and III are parallel straight lines below T_A. Curve IV illustrates the behavior of a completely crystalline polymer where $V_g^b = 0$ below T_A. The crystallinities of polyethylene and polypropylene calculated in this way using hydrocarbon vapors agreed well with estimates based on differential scanning calorimetry.[6]

This agreement suggested that there was no need to consider surface adsorption of hydrocarbon probes on polyolefins. However, surface adsorption may well occur on more polar crystallizable polymers. In this case, combining the above assumptions on surface retention and the effect of crystallinity, the measured retention volume may be written as:

$$V_g = (1 - C)V_g^b + V_g^s \tag{10}$$

The total surface and bulk retention volume will still show a discontinuity at the melting point, but the surface contribution will result in an apparent crystallinity which is *less* than the true value. This is illustrated schematically in Figure 2. Curve II represents the bulk retention diagram for a polymer with crystalline fraction $C = 0.5$ for $T < T_A$. Curve I represents the surface contribution, where it is assumed that ΔH^s remains the same above and below the melting region. Curve III is the sum of the two contributions. Because ΔH^s is assumed to be greater than ΔH^b, the portions of curve III above and below the transition region are slightly curved. More importantly, because the surface retention is proportionately greater below the crystallization temperature, the crystalline fraction appears in this case to be 0.36 rather than 0.5. Thus GC measurements on semicrystalline polymers may be seriously in error if surface adsorption is significant. The underestimation of crystallinity will be largest for thin layers of polar crystalline polymers where the relative surface contribution is greatest.

These predictions on the importance of surface adsorption when interpreting GC results on polymers will be illustrated by some results for the interaction of hydrogen bonding sorbates on low molecular weight poly(ethylene oxide), PEO, near its melting point. This polymer was chosen because it is relatively polar, has a convenient melting transition temperature, and is a widely used stationary phase for analytical gas chromatography. The marked change in retention volume as PEO passes through its melting point has often been noted in the literature and has generally been attributed[13,14,16] to a change from gas-liquid partitioning above the melting point to gas-solid adsorption below the melting point. This interpretation is thus different from that proposed for polyolefin melting transitions.[6] The only adsorption site considered in the proposed model is the polymer-vapor interface. However, adsorption may also occur at the stationary phase-support interface,[1] and significant effects have been reported for very thin layers of poly(ethylene oxide) on inorganic supports.[22] A fluorocarbon support was selected in order to minimize this column retention mechanism.

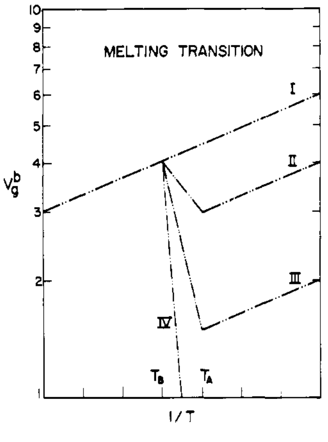

Figure 1. Illustration showing the effect of degree of crystallinity on the GC retention diagram. Curves I, II, III, and IV represent 0, 33, 66, and 100% crystallinity, respectively. Melting commences at temperature T_A and is complete at T_B.

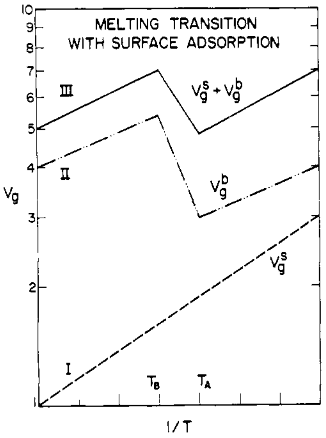

Figure 2. Diagram illustrating the addition of surface (curve I) and bulk (curve II) retention volumes to give the actual retention diagram (curve III) for a semicrystalline polymer.

Experimental Section

A sample of poly(ethylene oxide) (Carbowax 20M, Union Carbide Co.) was used as received. The PEO was coated from solution in acetone onto Fluoropak 80 (The Fluorocarbon Co.), an inert fluorocarbon support, then packed into 0.25 in. O.D. polypropylene tubes of about 1 m in length. The fluorocarbon support and the polypropylene columns were chosen to ensure that the water retention would be due solely to interaction with the PEO, and not with any other column materials. The columns were heated to about 100°, then quickly quenched in an ice-water bath. They were then allowed to equilibrate, with a steady stream of helium carrier gas passing through them, in a water bath which permitted temperature control to ±0.03°. The detection system employed was a Carle Model 100 thermistor detector. Peak retention times for distilled water and reagent grade *n*-propyl alcohol were mea-

Table I
Characteristics of Carbowax 20M Columns

Column % loading	Weight of support (s), g	Weight of PEO (w), g
0.4	17.475	0.069
2.0	14.426	0.290
2.4	13.301	0.327
3.7	14.674	0.574
7.5	14.246	1.149

sured directly from the chart paper on the recorder. The column characteristics are summarized in Table I.

At temperatures more than 20° below the melting point of the polymer (62°), the retention times were no longer independent of the peak height. The "infinite dilution" retention volumes were therefore obtained by plotting peak height against retention time, and extrapolating to zero peak height. Specific retention volumes were then calculated using the formula

$$V_g = 273.2 \frac{(t_r - t_m)F_0 j}{T_R w} \frac{(p_0 - p_w)}{p_0}$$

where t_r is the measured retention time, t_m is the time required for an inert vapor (air) to pass through the column, F_0 is the volume flow rate of the carrier gas measured at the column outlet and at room temperature T_R, j is the correction factor for pressure drop across the column,[1-3] p_0 is the atmospheric pressure, p_w is the vapor pressure of water at T_R, and w is the weight of PEO in the column.

The specific retention volume, V_g, is conventionally reported as milliliters of carrier gas (measured at 273.2°K) per gram of stationary phase. Carrier gas flow rates, which were usually about 40 ml/min, were measured using a soap-bubble flow meter.

Results and Discussion

The effect on retention volumes of using columns with different proportions of stationary phase to support is shown in Figures 3 and 4 for n-propyl alcohol and water, respectively. All the retention diagrams show the expected sharp maxima at the polymer melting point, but in contrast to the results with polyolefins,[6] the shape of the retention diagram is markedly affected by the column loading. It is evident that the higher the surface-to-volume ratio of the poly(ethylene oxide) stationary phase, the higher the retention volume. The increase in retention volume is most marked below the melting transition, but remains in evidence above T_m. It is also obvious that the apparent crystallinity, as given by eq 9, decreases drastically as the surface-to-volume ratio increases. The most reasonable interpretation is that the retention is more properly given by eq 10, and that surface adsorption is perturbing the shape of the retention diagrams as illustrated in Figure 2 and thus decreasing the apparent crystallinity.

In order to measure the true crystallinity of the sample, it is necessary to separate the surface from the bulk contribution to retention both above and below the melting transition. This involves changing the proportion of stationary phase to support in the GC column, and extrapolating to "infinite loading", where the surface contribution is negligible. To make the extrapolation, it is convenient to rewrite eq 10 in the form

$$V_g = (1 - C)V_g^b + V^s A(s/w) \qquad (11)$$

where V^s is the retention volume, measured at 0°, per square centimeter of stationary phase surface, A is the area of the stationary phase per gram of *support*, and s is the number of grams of support in the column. The true bulk retention $(1 - C)V_g^b$ may then be found by extrapolating a plot of V_g against (s/w) to infinite thickness of stationary phase (i.e., $s/w = 0$). Figure 5 shows the effect of column loading on the retention volumes for water and n-propyl alcohol at 70°. A reasonably linear relationship at high loadings allows extrapolation to $(s/w) = 0$, which should correspond to the bulk retention component V_g^b at 70°, since $C = 0$ above the melting point. A similar extrapolation of the retention data at 45° is shown in Figure 6, enabling (1 −

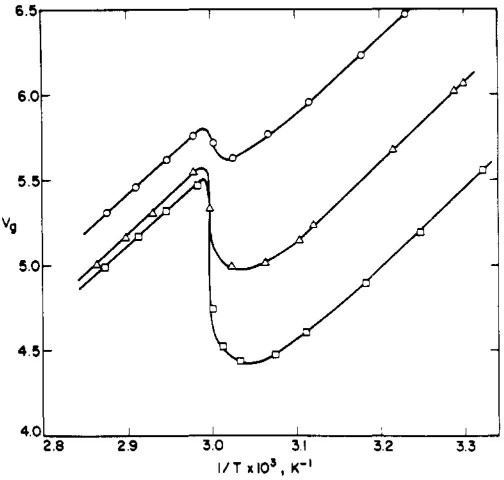

Figure 3. Retention diagram of n-propyl alcohol on poly(ethylene oxide) for 0.4% (○), 2.5% (△), and 7.5% (□) loadings.

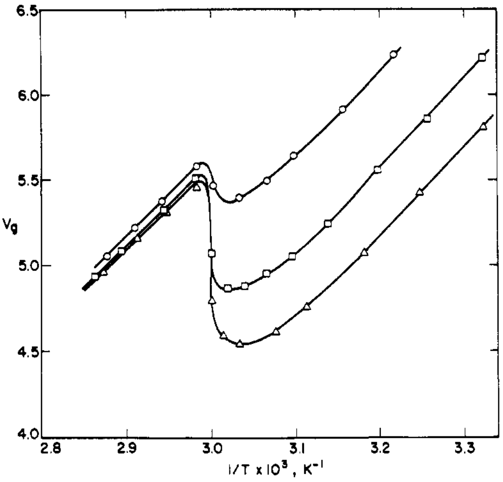

Figure 4. Retention diagram of water on poly(ethylene oxide) for 0.4% (○), 2.5% (□), and 7.5% (△) loadings.

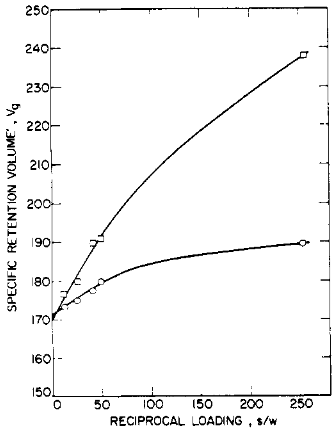

Figure 5. Plot of specific retention volume (milliliters per gram) vs. reciprocal loading for water (○) and n-propyl alcohol (□) on poly(ethylene oxide) at 70.0°.

Table II
Enthalpies of Vaporization (kJ/mol) for Water and *n*-Propyl Alcohol with Carbowax 20M

	Water	*n*-Propyl alcohol
$\Delta H(63–80°)$	40 ± 1	38 ± 4
$\Delta H(20–40°)$	43 ● 3	39 ± 2
$\Delta H_{vap}(70°)^a$	42.0	45.3
$\Delta H_{vap}(40°)^a$	43.2	47.4

[a] Data from "Handbook of Physics and Chemistry", 10th ed, McGraw-Hill, New York, N.Y.

$C)V_g^b$ to be determined. An estimate of V_g^b at 45° is thus required to obtain the crystallinity C. As in the previous work,[6] an extrapolation of retention data from the temperatures above T_m may be used. It is evident from Figures 3 and 4 that above T_m the retention diagrams are parallel lines. The average slope of these lines, converted to enthalpy units, is given in Table II. Using the slopes obtained in the high-temperature region, together with the values of V_g^b at 70°, the values of V_g^b at 45° may be obtained. The value for $V_g^b(1 - C)$ at 45° is known so that C at 45° is readily calculated. Values for the crystalline fraction of 0.83 ± 0.03 and 0.86 ± 0.05 were obtained using the data for water and *n*-propyl alcohol, respectively. This agreement is within experimental error, despite the differing chemical nature of the two vapors, and is in accord with the values quoted by Bergmann[23] of 0.9 and 0.8 for PEO samples of molecular weights 300,000 and 8,000, respectively, which were derived by NMR and X-ray methods. It should be noted that without correcting for surface adsorption, apparent crystallinities of from 0.40 to 0.74 were obtained, depending on the column loading. Correction for surface adsorption is thus necessary for reliable estimates of the crystallinity of more polar polymers by GC methods.

Errors in the calculation of crystallinity by this method stem from three main sources. These are errors in the measured GC retention volumes, uncertainty in the extrapolations used to eliminate surface effects, and errors introduced when extrapolating amorphous retention data from above T_m to below T_m. Considering each source of error in turn, the retention volumes for the temperatures above 40° were the average of at least three injections, and were reproducible to within 2.5%. The peak retention volumes appeared independent of peak height for the smallest injection sizes, but the peaks did exhibit marked tailing, presumably due to poor column performance or to extracolumn factors. As mentioned in the Experimental Section, a dependence of retention volume on peak size became apparent at temperatures below about 40°. A linear extrapolation was therefore used to determine the retention volume at zero peak height resulting in diminished precision below 40°. The retention volumes are thus presumed to be at "infinite dilution", rather than at some finite concentration as suggested by Condor et al.[19] Poly(ethylene oxide) is widely used above its melting point as a stationary phase for analytical GC, so the accuracy of the retention volumes should be further indicated by comparison with literature values. No data on water retention were found in the literature; for *n*-propyl alcohol, Castello and D'Amato[24] recently reported a retention volume at 100° of 58.9 ml/g on a column loaded with 20% Carbowax 20M on a Chromosorb W support. By linear extrapolation of our data, using V_g^b at 70° and ΔH for the range 63–80°, a value of 58.6 ml/g for the bulk retention value at 100° was obtained. The excellent agreement is probably fortuitous in view of the two extrapolation procedures necessary to compare results. However, agreement within 3% is also found with the GC data of Roberts and Hawkes[25] for *n*-propyl alcohol. In neither case were the literature data corrected for surface retention, but the loadings were higher than in the current work.

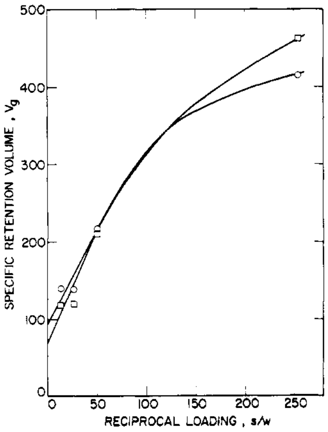

Figure 6. Plot of specific retention volume (milliliters per gram) vs. reciprocal loading for water (○) and *n*-propyl alcohol (□) on poly(ethylene oxide) at 45.0°.

The extrapolation procedure used to obtain V_g^b is a second source of error. According to eq 11, if A (the area of stationary phase per gram of support) is independent of the amount of PEO stationary phase in the column, then these plots should be linear. For example, if the PEO forms a thin continuous layer on the support, then A should be approximately equal to the specific surface area of the uncoated Fluoropak support. In many cases a more complex variation of the stationary phase surface area is predicted.[19] Figures 5 and 6 show deviations from linearity at lower loadings, possibly because the film of PEO does not wet the fluorocarbon support, and so it becomes discontinuous as the loading is reduced. However, the curvature at low loadings does not interfere with the extrapolation to $s/w = 0$; the major source of error here is the scatter due to difficulties in measuring the weight of PEO accurately at low loadings. This, combined with the very steep dependence of retention volume on loading below the melting point (Figure 6), reduces the precision of the $(1 - C)V_g^b$ values to ±15% at 45°.

A third source of error results from the calculation of V_g^b values below T_m using the V_g^b values obtained from the data above T_m together with the enthalpy data above T_m. According to the model, if the measured retention volume can be factored into bulk and surface components, then the measured enthalpy $\Delta H/R = \partial \ln V_g/\partial(1/T)$ may also be factored into bulk and surface components (eq 8). Consequently, the measured enthalpy values above and below T_m (Table II) are not attributable to bulk and to surface processes, respectively, as has been assumed,[14] but rather should be viewed as composite values. To obtain ΔH^b, the temperature dependence of V_g^b above T_m should be obtained by extrapolating V_g vs. loading plots to infinite loading at several temperatures above T_m. However, it is evident from Figures 3 and 4 that the plots above and below T_m are effectively parallel. Thus, to a first approximation, the measured slope of ΔH may be taken equal to ΔH_b in order to estimate values for V_g^b below T_m. The enthalpies listed in Table II were therefore determined by averaging the slopes of the retention diagrams, as shown in Figures 3 and 4, over the indicated temperature intervals. The errors listed are the 90% confidence limits. The uncertainty in the enthalpies, together with the uncertainties in the value of V_g^b at 70°, result in a precision in V_g^b at 45° of

5%. When C is large, the crystallinity determined by eq 10 is relatively insensitive to the previously discussed precision in measuring $V_g^b(1 - C)$ so that the overall precision in measuring C is of the order of 5%.

In conclusion, it is evident that with relatively polar polymers and sorbate vapors, GC retention data depend on the surface-to-volume ratio of the polymer in the column. This effect is quite marked at polymer transition temperatures. The simplified model presented here, which considers the effect of surface adsorption together with the exclusion of the sorbate vapor from the crystalline regions of the polymer, predicts a crystallinity for poly(ethylene oxide) in accord with recent literature data. The model also clarifies earlier results in the GC literature for retention of PEO below its melting temperature.

On a more speculative level, if it proves possible to characterize quantitatively the variation in polymer surface area with loading, then this GC technique may have some novel possibilities. For example, below T_m, a more detailed interpretation of the dependence of the retention volume on s/w should indicate whether very thin layers of the polymer exhibit different crystalline properties from the bulk polymer. Above T_m, the factoring of solution properties of thin layers into bulk and surface contributions may allow the surface excess concentration of solute in a polymer to be measured.[17,18] Thus, in principle, the GC method may be extended from studies on the adsorption of vapors on polymers where bulk absorption is negligible[26] to studies of adsorption with concurrent solution in the polymer.

Acknowledgement. One of us (G.C.) thanks the National Research Council of Canada for a Graduate Studentship.

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Morphological Characterization of Polyester-Based Elastoplastics

R. W. Seymour,[*1a] **J. R. Overton,**[1a] **and L. S. Corley**[1b]

Research Laboratories, Tennessee Eastman Company, Divison of Eastman Kodak Company, Kingsport, Tennessee 37662, and Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts. *Received January 8, 1975*

ABSTRACT: Morphological and structural characterization of a series of elastoplastic materials based on a semicrystalline poly(tetramethylene terephthalate) hard segment and a poly(oxytetramethylene) soft segment have been performed. Results from low angle laser light scattering and polarized light microscopy demonstrate the presence of a spherulitic superstructure over a wide range of compositions. The direction of the optic axis within the spherulite is dependent on the average hard block length and sample preparation method. Evidence for chain folding within the lamellae has been obtained by the chemical etching technique. Mechanical relaxation measurements suggest that the noncrystalline soft phase is a mixed phase of the polyether soft segment and uncrystallized polyester hard segments. The response of this structure to uniaxial extension has also been determined using low angle laser light scattering. The spherulites deform into ellipsoids having their major axis in the stretch direction. This deformation is only partially recoverable on release of the load. The proposed model differs from the two-phase domain microstructure generally assumed for block copolymer systems, being more closely related to the structure of semicrystalline homopolymers.

Elastoplastics, or thermoplastic elastomers, are a class of materials in which an attempt is made to combine certain desirable properties of elastomers (primarily recovery and energy absorption) with those of plastics (modulus and strength). This has been done by block copolymerization, combining alternating segments of rigid "hard" polymer and flexible "soft" polymer. A level of rigidity, structural integrity, and thermal resistance are imparted by the hard segment, while elastic recovery is provided by the soft segment. Such polymers contain no chemical cross-links, and thus may be processed as conventional thermoplastics.

The most widely studied of these systems has been the styrene–butadiene–styrene and styrene–isoprene–styrene triblock copolymers. Here it was determined that the hard