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Inverse Gas Chromatography for Polymer Surface Characterization above and below T_g

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ABSTRACT: Inverse gas chromatographic experiments (IGC) with a styrene–butadiene rubber (SBR) as the stationary phase have been conducted at temperatures on either side of the polymer T_g and at carrier gas flow rates up to 60 mL/min. Above the T_g retention volumes decrease with rising carrier flow rate, attaining equilibrium values at high flow rates. The equilibrium values are interpreted as being due solely to surface interactions, calculations having shown that under these carrier gas flow rates dwell times of probe molecules at the polymer surface are too short to permit diffusion into the bulk. In this manner it is possible to use IGC for surface characterizations of polymers above their T_g. The chromatographic data also allow the maximum size of vapor molecules able to diffuse into the polymer bulk to be estimated.

Introduction

There is rising awareness of the importance attached to interfacial interactions in polymer systems, notably to their influence on a range of system properties. When materials at interfaces are not bonded chemically, then surface, interface, and interphase properties are determined by physical forces. These may be separated into ubiquitous dispersion forces, caused by fluctuating dipoles, and into nondispersive or specific forces. The latter, though not universal, can be of great importance and include acid/base interactions, hydrogen bond forces, etc. Present trends favor the summing of all nondispersion forces into acid/base terms,[1,2] making it important to characterize components of polymer systems as electron donors and/or acceptors. Experimental approaches to that objective have generated much interest, recent emphasis being on inverse gas chromatography (IGC) as a viable route. IGC has seen use as a method for the determination of acid/base parameters for polymers, fibers, and fillers, among other constituents of polymer systems.[3-7] The method offers several advantages, frequently described in detail;[3] salient among these is the ease of data acquisition, particularly in comparison with normal calorimetric methods.

Balancing the attractions of the IGC technique are several difficulties, some not wholly resolved. Our attention is drawn to the question of surface vs bulk characterization of interaction properties. This has been debated for several years: Lichtenthaler et al.[8] concluded that polymer–solvent interactions measured by the IGC experiment report on the character of the surface, in view of the large surface/volume ratio in packed columns. In contrast, Gray and Courval[9] argued that film thicknesses in packed columns are sufficiently large to allow for the diffusion of vapor probe molecules, so that bulk properties contribute to measurements made by the packed column technique. Again, Pawlisch and co-workers[10] drew attention to the diffusion of vapor molecules into the stationary phase in IGC, by using a capillary column with thick, uniform coatings. They concluded that there was good agreement between thermodynamic properties obtained by the capillary column and packed column techniques, suggesting that molecular diffusion was a factor in both cases. The work of Guillet and co-workers,[11] which measured the crystallinity of polymers using the packed column technique, also supports the relevance of IGC data to the bulk properties of polymers.

The pertinence of IGC measurements to bulk properties clearly depends on whether or not the vapor molecules can diffuse into the bulk to a significant extent in the course of the experiment. Temperature becomes a vital question. It is generally agreed that IGC data collected above the T_g of a stationary phase are the sum of surface and bulk sorption. Below T_g it is assumed that surface effects predominate sufficiently to neglect contributions from bulk sorption. Various expressions for diffusion variables and for their temperature dependence have been suggested.[12-16] The recent review by Schlotter and Furlan[17] of small molecule diffusion into polyolefins is of special interest to the present work, these researchers having observed that the diffusion process could be used as a measure of molecular interactions between adsorbent and adsorbate. We shall return to this subject later in this presentation.

The above background defines the motivation for the present report. Our interest is to characterize the specific, acid/base interaction potential of polymer surfaces above their T_g, using the packed-column IGC method. The vehicle for our work was a water-based polymer latex. The temperature scanned in the work was sufficient to traverse the T_g of the latex polymer. We report an experimental protocol which appears to satisfy the demand, at the same time elaborating on the effect of acid/base interactions (i.e., molecular interactions of ref 17) on molecular diffusion processes. The experimental procedure also seems able to specify the maximum dimension of molecules able to diffuse into the bulk polymer.

IGC Measurements at Infinite Dilution of the Vapor Phase

It is well known now that IGC at infinite dilution of the mobile phase is based on the equilibrium partitioning of probe molecules between vapor and stationary phases. The fundamental quantity of the experiment, describing the equilibrium state of partitioning, is the net retention volume, V_n. This is, in principle, independent of the probe concentration and depends on its interaction energy with the stationary phase.[18,19] Below the T_g of the stationary phase, V_n provides information on the adsorption of probe molecules on the surface of the stationary phase. This interaction concept may be made quantitative by applying

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the well-known arguments of Fowkes,[2,20] which show an analogy between the work of adhesion W_A, and the free energy of adsorption, ΔG, for adsorbent/adsorbate pairs. When the molecules of the vapor phase can exert only dispersion forces, then the chromatographic information yields the dispersive (Lifshitz/van der Waals, or L/W) component of the adsorption free energy. When the vapor-phase adsorbates are "polar", that is, able to act as electron donors or acceptors, then in addition to L/W interactions, the IGC experiment also takes into account specific, and acid/base, interactions through the function ΔG^{ab}. Formally we write[3,6]

$$\Delta G^{ab} = RT \ln V_n - RT \ln(V_n)_{ref} \qquad (1)$$

where the reference subscript designates the retention characteristics of L/W probes, and the experimental data are placed on an x axis which takes into account the surface area of the vapor probe, a, and its dispersion-force surface energy, $(\gamma_l)^d$. When the temperature of the experiment exceeds T_g, then, as already noted, the thermodynamic quantity combines information on adsorption and absorption into the bulk of the stationary phase. Under these conditions, however, accurate evaluations of surface properties cannot be obtained from the IGC data.

Donor/Acceptor Concepts

The selection of polar probes requires a choice to be made between contemporary theories of Lewis acidity/basicity. Most favored are the four-parameter approach of Drago[21] and the simpler two-parameter approach due to Gutmann.[22,23] The latter has been used in our work, but in awareness of difficulties inherent in the Gutmann hypothesis. This characterizes organic probe molecules by acceptor and donor numbers, AN and DN, but uses definitions resulting in different units for these parameters. Thus, while use of the Gutmann concept leads to a convenient statement for the ΔG^{ab} of two interacting species via

$$-\Delta G^{ab} = (AN_1)(DN_2)/100 \qquad (2)$$

the thermodynamics significance of the statement is compromised by the asymmetry of units. The problem, discussed recently in some detail by Panzer and Schreiber,[24] can be avoided by resorting to the empiricism implicit in eq 1. A more formal solution to the problem has been suggested by Riddle and Fowkes,[25] who introduced a modified acceptor number, AN*, with the same units (kJ/mol) as DN. The original Gutmann AN value may be linked with the redefined version by[25]

$$AN^* = 0.288(AN - AN^d) \qquad (3)$$

where AN^d is the dispersive contribution to the overall acidity parameter of the chemical. Use of the modified parameters has been illustrated in ref 24 to obtain the acid/base rating for polycarbonate resins. In this paper a comparison is made between the interaction numbers of a latex polymer when these are evaluated by the modified Gutmann procedure both below and above the polymer T_g.

Experimental Section

Materials and Procedures. The polymer used in this study was a water-borne, random copolymer of styrene–butadiene (SBR) latex kindly supplied by the Dow Chemical Co., Midland, MI. The supplier reported that the polymer also contained an unspecified amount of carboxylation, and that DSC determinations showed the T_g to be 93 °C. On this basis, the polymer was judged to be predominantly polystyrene, with a calculated mole fraction of 0.97. The polymer was deposited from a diluted aqueous dispersion onto a Chromosorb G support (AW/DMCS treated, 60/80 mesh size), and packed in previously degreased, washed, and dried stainless steel tubing 0.4 m in length and 0.6 cm in diameter. Standard ashing procedures[19] showed the weight of supported polymer to be 7.0% of the total solids.

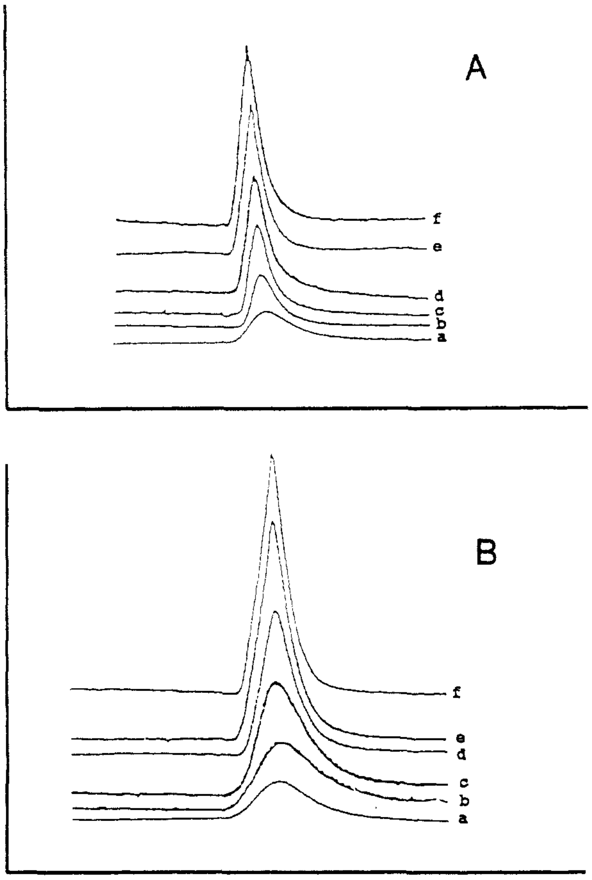

Figure 1. (A) Chromatographic peak shapes of n-heptane at flow rates (a) 10 mL/min, (b) 20 mL/min, (c) 30 mL/min, (d) 40 mL/min, (e) 50 mL/min, and (f) 60 mL/min. T = 105 °C. (B) Chromatographic peak shapes of chloroform at flow rates (a) 10 mL/min, (b) 20 mL/min, (c) 30 mL/min, (d) 40 mL/min, (e) 50 mL/min, and (f) 60 mL/min. T = 105 °C.

The vapors used were normal alkanes from hexane through decane, representing probes able to interact through L/W forces only. Designated bases[25] were diethyl ether (DEE) and tetrahydrofuran (THF); the acids[25] were ethyl acetate (EtAc), chloroform, and benzene. Acetone was used as a bifunctional (amphoteric) vapor. All of these were reagent grade materials, used without further purification.

Chromatographic measurements were made with a Varian 3400 unit, equipped with both thermal conductivity and flame ionization detectors. The flow rates of He carrier gas were in the range 10–60 mL/min, corrected for pressure drop along the column, and for temperature variations between the column and a monitoring soap-bubble flow meter. The rationale for the unusually wide range of flow rates used in this work will be discussed in succeeding sections. Measurements were made at temperatures between 55 and 115 °C, traversing the reported T_g value of the SBR specimen. Upper temperature and gas flow rate limits were set by experimental exigencies. Above the stated limits, net retention times were reduced to a point where experimental uncertainties exceeded ±8%, and were deemed unacceptable for this investigation. The stationary phase was conditioned at 120 °C for 24 h prior to data collection, in order to remove physisorbed water and to place the SBR sample into a reproducible reference state. Extremely small amounts of vapor were injected into the system via 1-μL Hamilton syringes, with both air and methane used as markers. At all of the carrier gas flow rates, both above and below the polymer T_g, symmetric elution peaks were obtained. Figure 1 illustrates this for

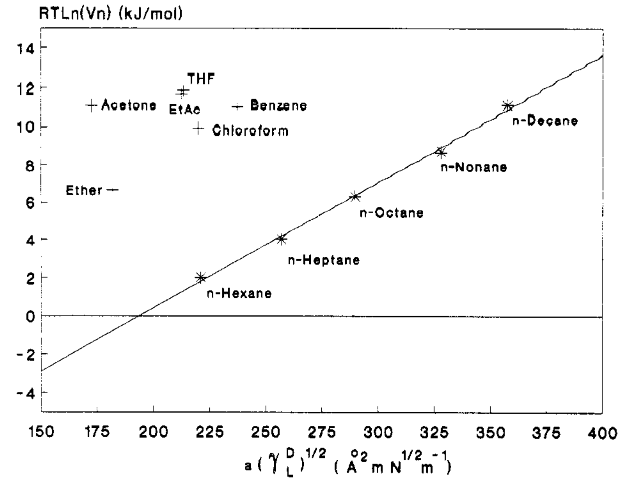

Figure 2. Representation of inverse gas chromatography data for the SBR polymer at 55 °C.

n-heptane and chloroform injections at 105 °C, above the polymer T_g.

Results and Discussion

As already stated, and reported in recent literature,[6,26] the net retention volume, V_n, can be expressed conveniently as a function of the probe molecule's cross-sectional area a, and its dispersion surface energy $(\gamma_l)^d$:

$$RT \ln V_n = 2Na[(\gamma_l)^d]^{1/2}[(\gamma_s)^d]^{1/2} + \text{const} \qquad (4)$$

where N is Avogadro's number and $(\gamma_s)^d$ is the L/W component of the solid's surface energy. Thus, when the left-hand side of the equation is plotted against the product $a[(\gamma_l)^d]^{1/2}$ for L/W vapors, such as the present set of *n*-alkanes, a linear relationship is expected, the slope yielding a value of $(\gamma_s)^d$. Of course, when the stationary phase is able to act as electron donor and/or acceptor, then retention data for acid/base probes will fall above the "reference" line. By the arguments advanced above, empirical values of AN and DN then may be obtained for the solid phase. A more formal approach to calculating acid and base interaction parameters for polymer surfaces has been proposed by Papirer and by Schultz and coworkers.[26,27] The quantities K_a and K_b are calculated from the temperature dependence of the ΔG^{ab} datum, introduced above.

An example of the pattern of results obtained is given in Figure 2 for the isotherm at 55 °C, well below the reported T_g of the SBR. The excellent linearity produced by the alkanes justifies the use of eq 4, and allows for the determination of the dispersion surface energy for the SBR sample. As noted previously,[28] in view of the extreme dilution of probe molecules, it is probable that these adsorb preferentially on high-energy sites within the solid's site energy distribution. The $(\gamma_s)^d$ obtained by this experiment may therefore be greater than values obtained from macroscopic sampling of the surface, e.g., from contact angle measurements.

The retention data for other probes are well removed from the alkane line. Since both acidic and basic vapors follow the trend, the solid is considered to be interactive as both electron donor and acceptor.

The excellent linearity of alkane isotherms was followed at each of the temperatures used in this study. An example of this is shown in Figure 3, the isotherm at 105 °C now being above the reported polymer T_g. Similar consistent trends were displayed in the placement of the acidic and basic probes, as illustrated in the graph. The normal distance for each polar probe datum from the corresponding point on the alkane line, defined as ΔG^{ab} in eq 1, is a function of temperature, and the variation is illustrated in Figure 3 for the ether probe. All other vapors, polar and nonpolar, followed general trends similar to that shown. The coordinates in Figure 4 are stated so as to allow for evaluation of the specific (acid/base) interaction enthalpy from the slope of linear portions. That linearity is excellent at lower temperatures, but an important deviation occurs near 94 °C. The departure from linearity is assumed to mark the initial absorption of the probe molecules into the bulk of the stationary phase, and therefore identifies its glass transition range. The T_g of the SBR obtained in this manner was 94 + 2 °C, in excellent accord with the DSC evaluation reported by the supplier.

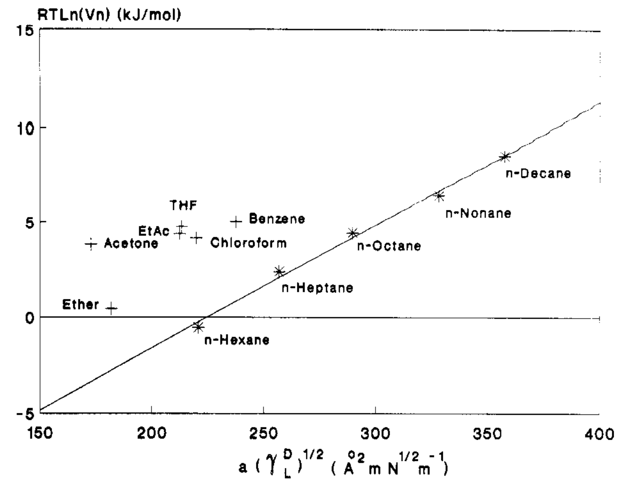

Figure 3. Representation of inverse gas chromatography data for the SBR polymer at 105 °C.

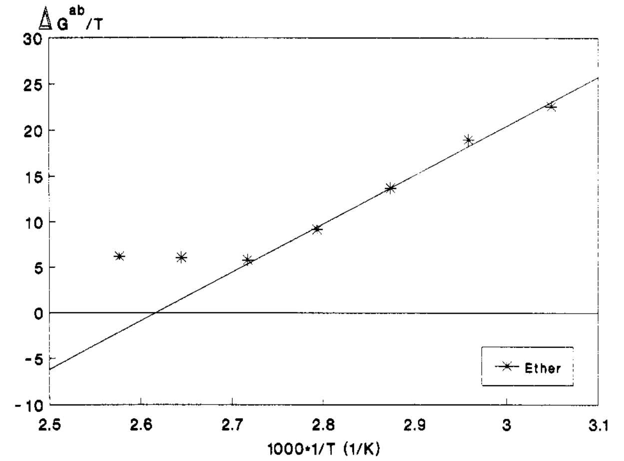

Figure 4. Temperature dependence of the adsorption free energy due to acid/base interaction between the SBR polymer and diethyl ether.

Table I. Dispersive Component of Surface Free Energies (mJ/m^2)

temperature (°C)	55	65	75	85	95	105	115
polymer $(\gamma_s)^d$	30.2	25.8	21.3	15.0	24.1	23.5	20.5

The dispersion surface energies of the SBR, calculated from the slopes of alkane reference lines, are summarized in Table I. A consistent trend is noted at temperatures below T_g, the $(\gamma_s)^d$ varying inversely and systematically with T, as expected. An extrapolation to room temperature indicates a dispersive component of surface energy equal to about 38 mJ/m^2, in good agreement with expectations for a polymer with the present overall composition. The established trend is interrupted above the glass transition, where the slopes of the alkane function increase significantly. Again this is taken as evidence for the penetration

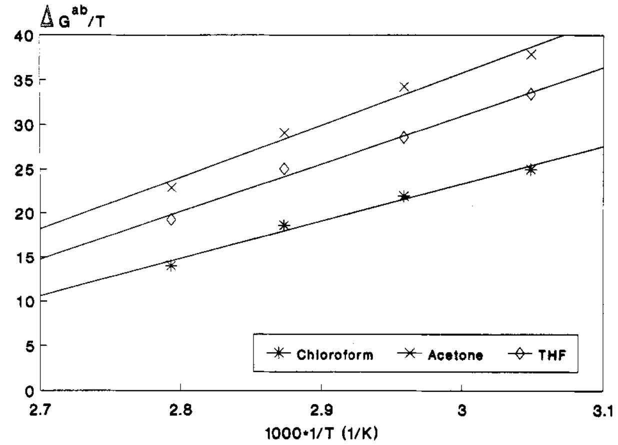

Figure 5. Acid/base interaction between SBR and vapor probes as a function of T below the polymer glass transition.

of the vapor probes into the bulk of the polymer, a process which perturbs the chromatographic retention datum and consequently compromises the value of the information as an indicator of surface properties. The issue will be elaborated in the next section of the paper.

Acid/base parameters for the polymer may be obtained directly from representations such as those of Figures 2 and 3, the value ΔG^{ab} representing the net acidity and basicity of the polymer as sensed by the designated acid and base vapor probes. The empirical acid/base parameters are shown in Figure 5, as a function of the temperature. For simplicity, only the data for chloroform, THF, and acetone have been used to construct the figure. Chloroform and THF are selected as reference acid and base probes, respectively, and their positions define the relative acid/base properties of the stationary phase. Acetone, an amphoteric molecule according to the Gutmann classification,[23] is used to show whether or not acid and base sites on the polymer surface are accessible to the amphoteric probe. The results in the figure confirm earlier qualitative statements: The SBR is bifunctional, with a moderate "skew" toward surface acidity, as indicated by the relative position of curves for THF and chloroform. The skew is more evident at temperatures below T_g, where these curves diverge. Above the glass transition a gradual approach of the acid and base curves is observed. The result suggests that a change in the overall polymer composition occurs when going from the polymer surface to the interphase separating the surface and bulk. The surface acidity may be ascribed to the presence of carboxyl groups, and may result from the preferred interaction of these groups with the water environment from which the polymer is recovered. This would indicate a surface depletion of styrene moieties, since earlier research has shown polystyrene to be basic.[2,29] The increasing basicity above T_g may arise from an increase in the concentration of PS chains as the probe molecule senses composition further removed from the surface alone. The implied disparity among surface, interphase, and bulk compositions, driven by surface energy demands, is consistent with the theory developed by Lipatov.[30] Finally, the results for the acetone molecule confirm the postulate of surface/bulk variations in composition and/or chain orientation. If both acid and base sites of the SBR were fully accessible, then ΔG^{ab} of the amphoteric molecule should equal the sum of the values for chloroform and THF. Instead the acetone values fall relatively close to those of the THF. The acetone probe therefore senses the acidic sites of the SBR surface, but detects only a fraction of the basic sites.

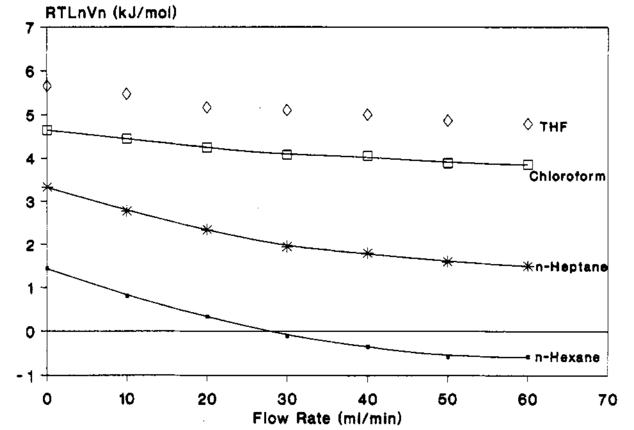

Figure 6. Variation of retention volume with carrier gas flow rate at 105 °C.

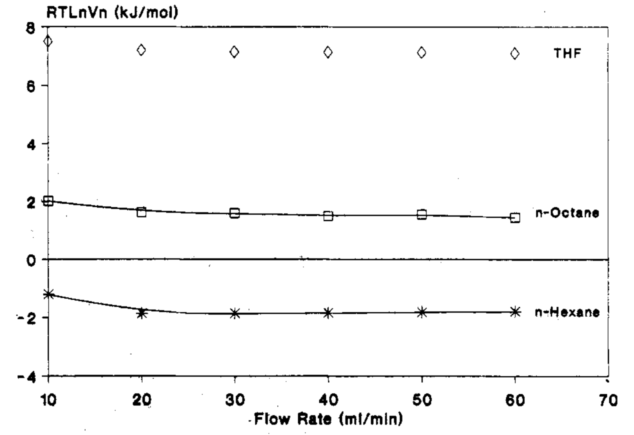

Figure 7. Variation of retention volume with carrier gas flow rate at 55 °C.

Surface Characteristics above T_g. The evidence for bulk penetration by probe molecules makes it difficult to obtain information on surface properties when the IGC experiment is carried out above the T_g of the stationary phase. Molecular diffusion is the most likely mechanism for this penetration.[31,32] The ability of a typical probe molecule to diffuse through the free volume of the stationary phase depends on the dimensions of the accessible volume and on the time during which the probe molecule remains in contact with the adsorbent. The latter variable may be controlled in the IGC experiment, through control over the carrier gas flow rate. Thus, it seems possible to reduce or eliminate the diffusion process above T_g, by increasing the flow rate to a point where retardation of the probe molecule is again due solely to the effects of surface-localized interactions. The hypothesis was tested empirically, with relevant results shown in Figures 6 and 7. The isotherm in Figure 6, at 105 °C, is above the T_g value of about 94 °C; that in Figure 7, at 55 °C, is below the glass transition. In Figure 7, the retention data are independent of the carrier gas flow rate in the *normal* range of operation, typically 5–20 mL/min. Above T_g, however, the retention data are sensitive to flow rates in this range, attaining plateaus of V_n only at elevated flow rates, generally in the vicinity of 50 mL/min.

The minimization of diffusion effects at high carrier gas flow rates appears to be reasonable in light of the very short contact times between probes and surface sites. A rough calculation is presented by way of illustration.

The surface area of a typical probe molecule is of the order of 50×10^{-16} cm^2. For a spherical molecule this corresponds to a diameter of about 8×10^{-8} cm. For present

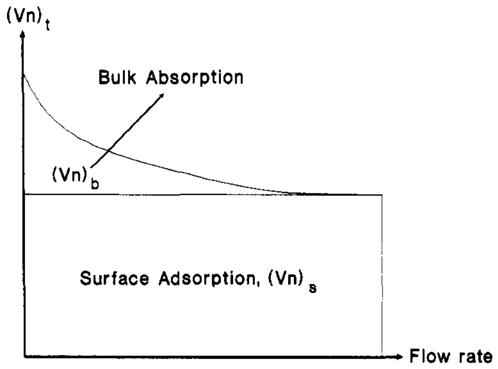

Figure 8. Schematic diagram applicable to polymers above T_g, defining probe volumes retained by the polymer bulk and by its surface.

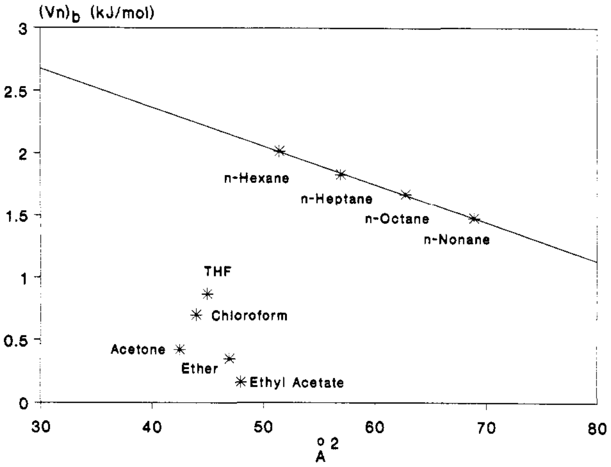

Figure 9. Retention by the SBR polymer bulk of vapors as a function of their areas of cross-section; T = 105 °C.

purposes it is assumed that this also corresponds to the diameter of a typical surface adsorption "site". At flow rates of 50 mL/min, the net retention time of probes is in the range of 5 s, and this is required to traverse a column with an overall length of 40 cm. It follows that the contact time between the site and probe molecule is in the range of 5×10^{-9} s. This is near or below the limits of diffusion coefficients for small molecules penetrating olefinic polymers,[17] and may be taken as roughly indicative of molecular diffusion in thermoplastics generally. At low flow rates, e.g., 10 mL/min, retention times increase into the 10^2-s range, thus also increasing some 20-fold the contact time at the probe/solid site interface. Diffusion-controlled penetration into the bulk polymer becomes feasible under these conditions.

The pattern of results in Figure 6 leads to the definition of two critical V_n values when $T > T_g$. The point is elaborated with the aid of the model shown in Figure 8. The plateau datum at high flow rates evaluates the contribution to V_n due to *surface interactions*, and is labeled $(V_n)_s$. The extrapolation to the ordinate intercept evaluates the total retention volume, taking into full account both surface and bulk contributions. The bulk retention, $(V_n)_b$, is then given by

$$(V_n)_b = (V_n)_t - (V_n)_s \tag{5}$$

The characteristics of $(V_n)_b$ at 105 °C are shown in Figure 9 as a function of the probe molecule area of cross-section. We note first the excellent linearity produced by the n-alkane data. Bulk retention decreases systematically with increasing size of the probe molecule. The alkane data are recast, using the number of carbons in the alkane chain as the x axis, with the result shown in Figure 10.

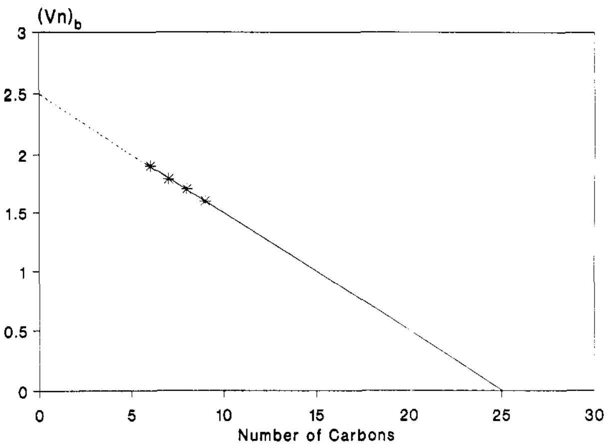

Figure 10. Retention by the SBR polymer bulk of n-alkane probes as a function of chain carbons; T = 105 °C.

Here the linearity is retained, as might be expected, but the main point of interest is the abscissa intercept. On the basis of this we conclude that neutral (L/W) molecules larger than C_{24} cannot be retained by the SBR (at the temperature in question). In other words, the intercept may be used to infer a limiting surface area for molecules able to initiate diffusion. In the present case this is about 650 Å^2. If one were to make assumptions about the geometry of voids within the bulk polymer, then an explicit evaluation of free volume in the polymer may also be attempted from the chromatographic information.

Returning to Figure 9, it seems surprising at first to find acid and base probes generating bulk retention volumes which are significantly lower than those of L/W probes of similar size. The result, however, is reasonable when viewed in terms of the surface composition of the SBR polymer. As inferred earlier, the surface layer's relative acidity is due to an excess presence of carboxyl groups. In turn this is the result of the polymer having been deposited from an aqueous medium, where minimization of the interfacial tension between the continuous phase and the polymer would promote the presence of these groups. The carboxyl groups will tend to interact with polar probes through acid/base forces, and thus trap the molecules in the surface region long enough to reduce their ability to diffuse into the bulk. Were this rationalization to be tenable, then the $(V_n)_b$ data should correlate with the strength of acid/base interactions between solid/vapor pairs. It is possible to estimate a pair interaction parameter using the available acid/base numbers. In this work, the parameter $I_{sp}{}^*$ has been calculated from the expression

$$I_{sp}{}^* = (K_a)(\mathrm{DN}_v)^{1/2} + (K_b)(\mathrm{AN}^*{}_v)^{1/2} \tag{6}$$

Here K_a and K_b are the acid and base interaction constants for the stationary phase, while the vapor interaction parameters are given by the AN* and DN indices. The asterisk of AN_v indicates that revised acidity indexes are employed. The definition of eq 6 is empirical, but follows the precedent of recent publications in which pair interaction parameters were used successfully to rationalize adhesion and mechanical properties of polymer systems.[27,29]

A test of the above hypothesis is found in Figure 11. This introduces an excess bulk retention datum, $(\Delta V_n)_b$, obtained from the representations shown in Figure 9. $(\Delta V_n)_b$ is the difference, at constant molecular size, between the position on the line defined by the L/W probes and the position of the point for a given polar probe. The reasonable linearity between the excess volume parameter

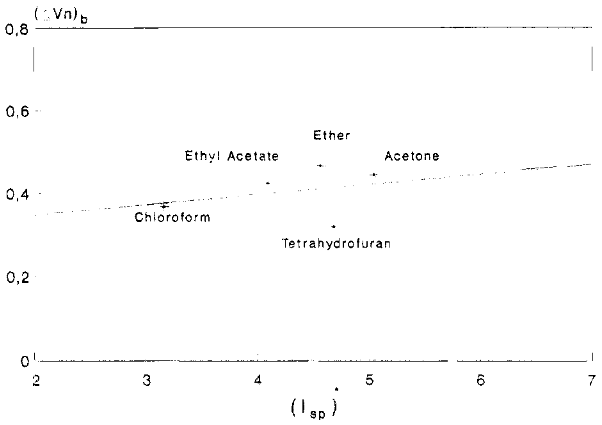

Figure 11. Excess bulk retention volume by SBR of nondispersion probes as a function of the acid/base pair interaction parameter; T = 105 °C.

Table II. Surface K_a, K_b, and Dispersion Energies of the SBR Polymer above T_g

T (°C)	K_a	K_b	$(\gamma_s)^d$ (mJ/m^2)
55			30.2^a
65			25.8^a
75	2.33	1.66	21.3^a
85			15.0^a
95			17.0 (24.1)^b
105			23.1 (23.5)^b
115	1.63	1.85	18.2 (20.5)^b

^{a} From Table I. ^{b} From Table I, calculated from V_n uncorrected for bulk absorption.

and I_{sp}* appears to leave little doubt that acid/base forces acting at polymer surfaces will retard the diffusion of vapors (and perhaps of fluids) able to act as electron donors and/or acceptors. Moreover, the magnitude of the retardation seems adequately stated by the pair interaction number, as given by eq 6.

Finally, returning to the matter of surface characterization above T_g, the apparent ability to separate bulk and surface effects from IGC data collected above that temperature permits such estimates to be made. The $(V_n)_s$ data, determined as noted, were used to calculate corrected $(\gamma_s)^d$ data and values of the acid/base parameters K_a and K_b. The results are entered in Table II. This also reports acid/base parameters below T_g, and for ease of comparison repeats the surface energy results from Table I. Since acid/base parameters are obtained from the slopes of ΔG^{ab} vs $1/T$ relationships, the K values in the table are averages for the ranges 55–85 and 95–115 °C. The rising importance of basic interactions at $T > T_g$ is evident. In the surface energy values, reported for defined temperatures, some irregularity remains above the glass transition due mainly to the datum at 105 °C. Further confirmation of this result is to be sought. The large discontinuity in $(\gamma_s)^d$ observed in the T_g region when using data uncorrected for bulk penetration, however, is much reduced.

Conclusions

The following may be concluded.

IGC has been used to evaluate dispersion surface energies and acid/base interaction data for a SBR latex polymer. The polymer was found to be amphoteric with slight prevalence of surface acidity.

The IGC method used at high carrier gas flow rates and above the polymer T_g is able to separate the net retention volume of probe molecules into components of surface and bulk retention. Results suggest that the polymer composition varies from the surface to the bulk. For the SBR specimen of this research, in the temperature range 95–105 °C, the variation of bulk retention with the size of n-alkane probes has led to a definition of the maximum molecular dimension able to diffuse into the bulk polymer.

Vapors able to interact with the polymer by nondispersion (acid/base) forces are more strongly retained by the surface above T_g than are dispersion force molecules of similar dimensions.

The excess surface retention of acidic or basic probe molecules correlates well with an acid/base pair interaction parameter calculated on the basis of acceptor and donor indices from the Gutmann theory.

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