Study of the Glass Transition of Poly(ethylene Terephthalate) by Gas Chromatography

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Synopsis

The technique of gas chromatography is used to detect the temperature (T_g) at which the solubility of organic solutes in poly(ethylene terephthalate) (PET) becomes detectable, when the temperature is raised from below to above the glass transition temperature. For a given solute, T_g varies with the structure of PET. For a given structure of PET, T_g varies with the nature of the solute.

INTRODUCTION

It is customary in gas chromatography to use a liquid stationary phase. The specific retention volume V_g of the solute is then primarily due to its bulk partitioning in the stationary phase, although under certain circumstances sorption at interfaces may become important.[1] The negative temperature coefficient of V_g that is obtained in equilibrium partitioning means that the heat of evaporation from the stationary phase is positive. Thus, as the temperature increases, the solute spends relatively less time in the stationary phase and travels through the column more quickly.

The normal materials that constitute the stationary phase undergo transition from the liquid to the glassy state at a temperature (T_g) that is below the usual operating range in chromatography, so that their sorption behavior in the glassy state is not observed. Recently, polymers having glass transitions at temperatures easily observable under normal operating conditions have been employed as the stationary phase.[2,3] Typically, three regions are observed in the plot of ln V_g versus $1/T$ (see Fig. 1). At low temperatures, the polymeric stationary phase exists as a glass, and sorption of solute at glass surfaces is responsible for V_g. At sufficiently high temperatures, the stationary phase exists as a liquid, and partitioning in the bulk of the polymer is primarily responsible for V_G. In both regions, distribution of the solute between the gas and polymer phases is presumed to be an equilibrium phenomenon, and the temperature coefficient of V_g is negative.

Between these two ranges of temperature, however, a nonequilibrium region exists in which solute converts from surface sorption to bulk partitioning. Initially, at low temperatures near and just above the glass transition, the polymer segmental jump rate is too slow to permit bulk partitioning to be

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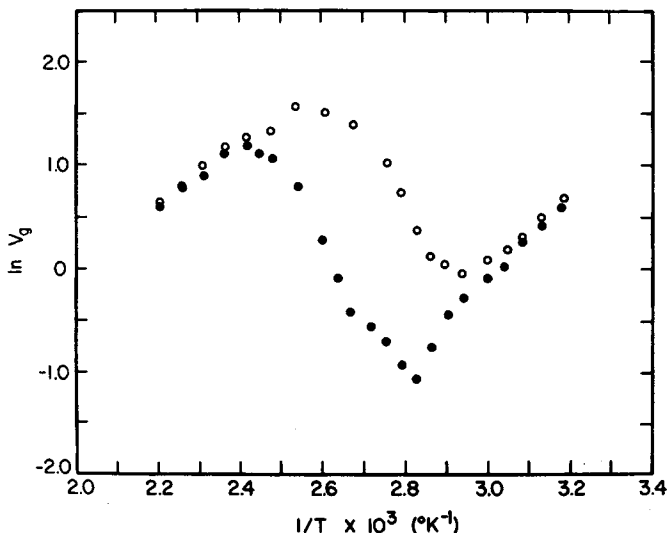* Present address: 5015 Nantucket Rd., College Park, Maryland 20740.

Fig. 1. ln V_g vs $1/T$; benzene on amorphous PET (O), semicrystalline PET (●) (column II).

achieved at the flow rate of carrier gas maintained in the column. The onset of bulk partitioning is taken as the temperature at which the contribution of bulk partitioning to V_g becomes detectable, and this temperature, which occurs at the minimum of the ln V_g versus $1/T$ plot, is identified in this paper as T_g. Because the contribution of bulk partitioning to V_g increases with temperature, the nonequilibrium region is marked by a positive temperature coefficient of V_g.

Since T_g is taken as the temperature at which the solubility of solute becomes detectable, the nature of the solute becomes an important determinant of the location of T_g. A second influence is the degree crystallinity of the polymer.[4] This paper deals with the effect of the nature of the solute and the structural state of the polymer on the glass transition of poly(ethylene terephthalate) (PET) as revealed by the technique of gas chromatography. That organic solutes affect the morphology of polymers, especially PET,[5,6] has been well established. In the present system, the size of the sample of solute injected onto the polymeric stationary phase was extremely small so that any change in morphology was considered negligible.

EXPERIMENTAL

Column Preparation

A weighed amount of stationary phase (PET) was dissolved at 140–150°C in a mixture of phenol and 1,1,2,2-tetrachloroethane (1:1 by volume). Acid-washed and dimethyl dichlorosilane-treated Chromosorb W, previously sieved to 100–120 mesh, was mixed with the polymer solution. Most of the solvent was removed on a rotating evaporator under vacuum. Residual solvent was removed by heating overnight at 170–180°C under vacuum.

A straight piece of stainless steel column (⅛ in. O.D.) was rinsed with methanol, bathed with steam for 20 min, and dried with nitrogen gas. The

columns, designated column II (8 ft) and column III (10 ft), were packed with the stationary phase using a hand vibrator. The loading of the stationary phase was determined to be 15% by extraction of a portion of the column packing using trifluoroacetic acid. The thickness of the stationary phase was calculated to be about 0.13 μ.

Materials

PET was obtained in the form of chips (column II) and ribbon (column III) from American Enka Company with intrinsic viscosities respectively of 0.64 and 0.65 at 25°C in a solvent of phenol/tetrachloroethane 1/1 by weight. The number-average molecular weight was calculated to be 1.77 × 10^4 for the chip and 1.81 × 10^4 for the ribbon.[7]

The organic liquids used as solutes were reagent grade in quality.

Determination of Specific Retention Volume

The Perkin-Elmer Model 990 gas chromatograph provides regulated flow of He carrier gas to dual sample injectors, an air-circulating oven for control of column temperature, and a thermal conductivity detector. To obtain the column temperature accurately, the thermocouple tip of a digital thermocouple thermometer was placed close to the instrument thermocouple tip that senses the oven temperature. Oven temperature was found to be constant within 0.1°C.

A mercury manometer, connected in the He flow line to observe the inlet pressure at the entrance to the column, was read to within 0.1 in. Hg. A mercury barometer was employed to measure the outlet pressure (atmospheric) to within 0.01 in. Hg. The volume flow rate was determined at the column exit by a soap bubble flowmeter.

The specific retention volume V_g was calculated from the following equation:

$$V_g = J \cdot \frac{P_0 - P_w}{P_0} \cdot \frac{V_0}{W} \cdot \frac{273.2}{T_r} \cdot (t_R - t_A)$$

where $J = [3(P_i/P_0)^3 - 1]/[2\,(P_i/P_0)^2 - 1]$ is a correction to the measured volume flow rate V_0; P_i and P_0 are the inlet and outlet pressures, respectively; P_w, the water vapor pressure at room temperature T_r, corrects for the vapor pressure of water inside the soap bubble flowmeter; W is the mass of the stationary phase; t_A is the measured retention time for the noninteracting reference sample, air; and t_R is the measured retention time for the solute. Times were measured from zero time at injection to the time corresponding to the peak-maximum of the eluted substance.[8]

The sample size was varied from 0.02 μl to 0.2 μl. Three to four injections were made with each solute at each temperature. The value of t_R was plotted against peak height, which was taken as a measure of sample size. A straight line was drawn by inspection and the intercept at zero height was used to calculate V_g. With some of the solutes, symmetrical elution peaks were obtained and t_R was independent of sample size. Most of the solutes gave nonsymmetric peaks having sharp front profiles and diffuse rear profiles, the shapes of which were attributed to isotherms that are nonlinear ex-

cept at very low solute concentrations.[9] The peaks tended to become more symmetrical with decreasing sample size.

Ideally, V_g is calculated under conditions of zero sample size and zero flow rate. From the first condition, it follows that Henry's law is obeyed; from the second, that equilibrium partitioning of solute occurs. The extrapolation procedure required to achieve the latter condition is not feasible, however.[10] When the loading of stationary phase is sufficiently low, e.g., near 15%, the stationary film is relatively thin and the influence of flow rate (or ratio of P_i to P_0) on retention volume becomes small.[11] In this study, plots of V_g versus P_i/P_0 were relatively flat above the P_i/P_0 value of 1.6. The value of this ratio was therefore maintained between 1.6 and 2.0, producing flow rates from 3 to 8 cm^3/min.

RESULTS AND DISCUSSION

Bulk Partitioning and the Glass Transition

Behavior typical of amorphous PET when it is used as the stationary phase for the solute benzene is illustrated in Figure 1. That portion of the plot between the maximum and the minimum represents the nonequilibrium region. The temperature at the minimum was taken as T_g. The data on either side of the minimum were used to establish a simple, local quadratic response function, and the position of the minimum was calculated by regression analysis.[12,13] This procedure for obtaining T_g was followed throughout the work.

Not every solute is capable of detecting T_g, as may be seen by referring to cyclohexane in Figure 2 or to carbon tetrachloride in Figure 3. As was pointed out earlier, T_g is assumed to be the temperature at which the bulk solubility of the solute is detectable in V_g. If the heat of mixing liquid solute with liquid polymer is endothermic, as is the case with the present system, the
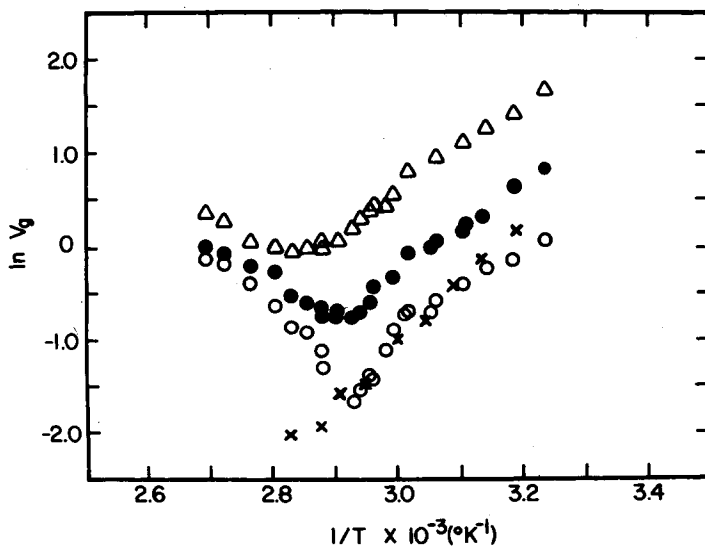

Fig. 2. ln V_g vs. $1/T$; cyclopentene (O), cyclohexene (●), cycloheptene (▲), on amorphous PET (column III); cyclohexane (×) on amorphous PET (column II).
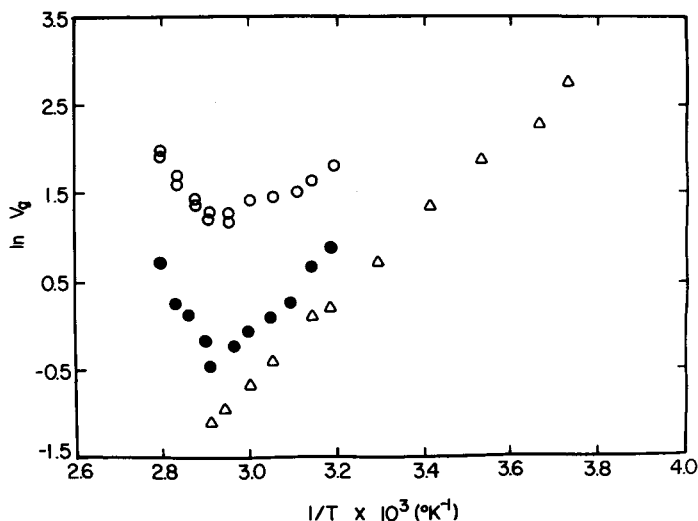
Fig. 3. ln V_g vs. $1/T$; methylene chloride (O), chloroform (●), on amorphous PET (column II); carbon tetrachloride (△), on amorphous PET (column III).

higher the temperature, the greater the solubility of solute in the polymer. Eventually, a temperature is reached at which the contribution of bulk partitioning to V_g is sufficiently great to cause the temperature coefficient of V_g to become positive, even with very weakly soluble solutes, producing a minimum at T_g. Volatile solutes such as cyclohexane and carbon tetrachloride with respective boiling points of 80.8°C and 76.8°C are driven from the polymer before this temperature can be reached, i.e., the difference in retention time between the air (reference) and solute peaks becomes extremely small and V_g tends toward zero. It ought to be possible to detect the onset of bulk partitioning with these solutes in a pressurized column, however.

Even volatile compounds may be used to detect T_g if their solubility in PET is large enough. In this case, the interaction between PET and solute presumably involves specific forces such as induction and orientation forces. The unsaturated solutes of Figure 2 probably interact through induction forces: a single unsaturated bond in five-, six-, and seven-membered rings is sufficient to produce a positive temperature coefficient of V_g. The polar solutes of Figure 3 are capable of interaction through orientation forces. The example of methylene chloride is especially interesting: the T_g associated with it is approximately 20°C higher than its boiling point, and although it is the most volatile of the solutes shown, its specific retention volume is the greatest.

The Effect of Crystallinity

Since the crystalline part of the polymer is inaccessible to the solute, the contribution of bulk partitioning to V_g decreases with increasing crystallinity, and T_g may become more difficult to detect. A more critical effect on T_g arises from the constraint that the crystallites impose on the amorphous polymer.[14] Rotational barriers near the crystallites are raised, and a higher temperature must be reached to achieve the glass transition. This is illustrated in Figures 1, 4, and 5 for the solutes benzene, cyclohexene, and meth-
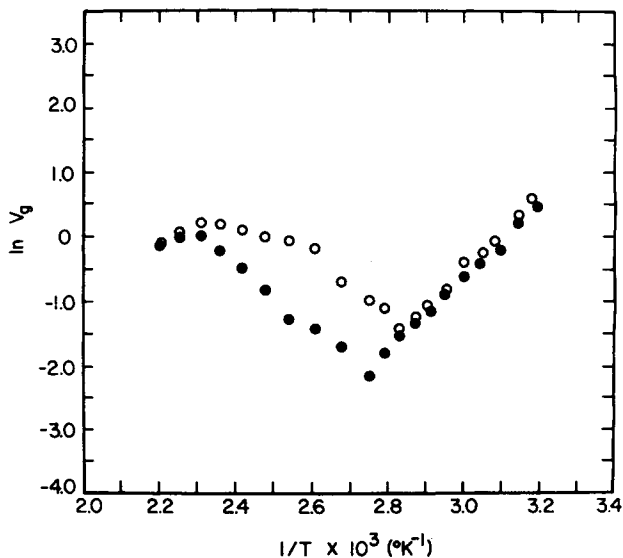
Fig. 4. ln V_g vs. $1/T$; cyclohexene on amorphous PET (O); semicrystalline PET (●) (column II).

ylene chloride on PET stationary phase that had been previously crystallized by annealing in the column for 2 hr at 180°C. Its weight fraction crystallinity was estimated by the procedure of Guillet and Stein[15] to be 0.501 from the equation

$$X_w = \frac{V_g{}^\circ - V_g}{V_g{}^\circ}$$

where $V_g{}^0$ is the specific retention volume of solute (benzene) on the molten polymer at 180°C, obtained by extrapolation of data obtained on molten
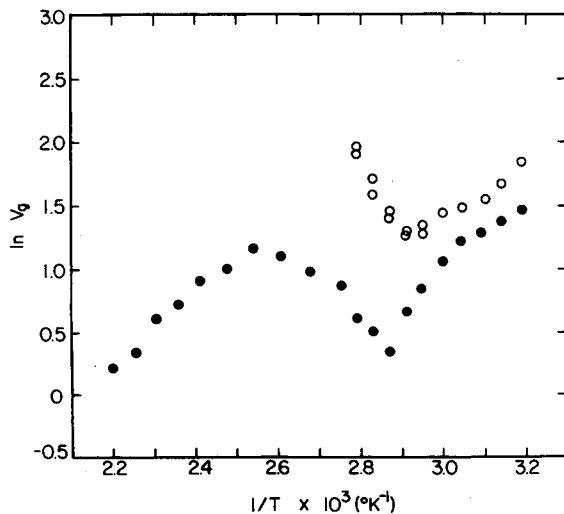

Fig. 5. ln V_g vs. $1/T$; methylene chloride on amorphous PET (O); semicrystalline PET (●) (column II).

TABLE I
Effect of Crystallinity of PET on T_g. Polymer Annealed 2 hr at 180°C

		T_g, °C
Column II		
Benzene	amorphous	62.5
Benzene	semicrystalline	78.1
Cyclohexene	amorphous	79.6
Cyclohexene	semicrystalline	94.6
Chloroform	amorphous	66.0
Chloroform	semicrystalline	80.6
Methylene chloride	amorphous	61.8
Methylene chloride	semicrystalline	76.4
Perchloroethylene	amorphous	64.4
Perchloroethylene	semicrystalline	82.0
Column III		
Ethylcyclohexane	amorphous	91.8
Ethylcyclohexane	semicrystalline	104.7
n-Propylcyclohexane	amorphous	94.4
n-Propylcyclohexane	semicrystalline	107.0

polymer, and V_g is the specific retention volume on the annealed polymer at 180°C. It may be seen from Table I that the effect of crystallinity varied somewhat from one solute to another, but the increase in T_g was generally in the neighborhood of 15°C.

Below T_g, the segmental motion of the polymer chain is too restricted to permit penetration and mixing of large solute molecules in the bulk of the polymer. It is interesting that the curves for amorphous and semicrystalline PET below T_g nearly coincide for benzene and cyclohexene (Figs. 1 and 4). This was also found to be the case with cyclohexane, chloroform, and perchloroethylene. The number of available sites for adsorption presumably is the
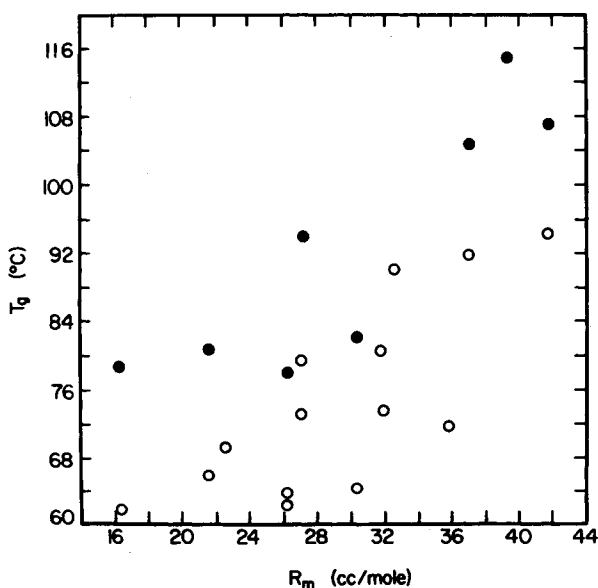

Fig. 6. Relation between glass transition temperature of PET (columns II and III) and molar refraction of various solutes: (O) amorphous PET; (●) semicrystalline PET.

same for the glassy and semicrystalline states. In any event, these solutes are unable to distinguish between the two states. Methylene chloride, alone among the various solutes that were investigated at temperatures below T_g, appears to "see" a difference between amorphous and semicrystalline PET (Fig. 5). The methylene chloride molecule may be small enough to penetrate to some degree into regions of the amorphous glass from which larger solute molecules are excluded.

The plots of ln V_g versus $1/T$ for amorphous and semicrystalline PET coincide for all the solutes that were investigated at temperatures above the maximum for the semicrystalline polymer (see Figs. 1 and 4). Since crystallization occurs at finite rates above T_g, it may be concluded that amorphous polymer is converted to semicrystalline polymer during chromatographic measurement, the conversion being essentially complete at temperatures exceeding that which marks the maximum.

Solute Size and the Glass Transition

The volume required to accommodate a solute molecule increases with its molecular size. The additional mode of expansion acquired in the form of segmental motion by amorphous polymer above its T_g by an endothermic process allows the polymer to reach at successive temperatures the "free volume" accommodation state of successively larger solute molecules. Since partitioning of the solute in the bulk of the polymer is the experimental measure by which the transition from glassy to liquid-like behavior is recognized in this work, T_g may be expected to increase both with size of solute and with heat of mixing.

The molar refraction R_m, which may be used as a measure of size,[16] was calculated at 20°C for each of the solutes from the equation

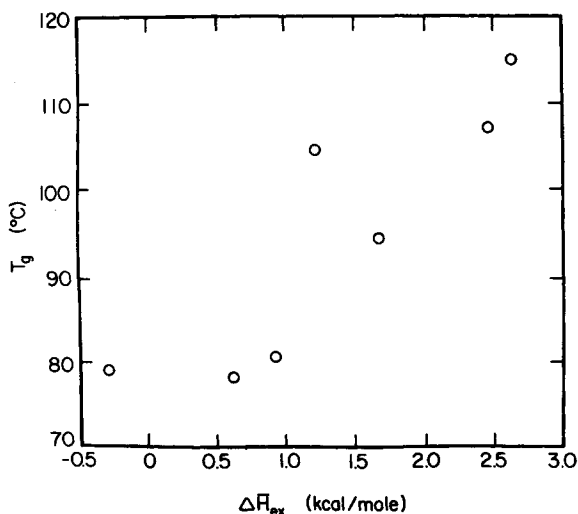$$R_m = \frac{n^2_D - 1}{n^2_D + 2} \frac{M}{\rho}$$

Fig. 7. Relation between glass transition temperature of semicrystalline PET (columns II and III) and partial molar excess heat of mixing of various solutes.

where n_D is the refractive index using the sodium D line,[17] ρ is the density, and M is molecular weight.

Results were obtained showing the relation between the glass temperature of PET and molar refraction of the following solutes: on semicrystalline PET, methylene chloride, chloroform, percholoroethylene, cyclohexene, benzene, ethylcyclohexane, n-propylcyclohexane, and n-octane; on amorphous PET, methylene chloride, chloroform, perchloroethylene, benzene, ethylbenzene, methylcyclohexane, ethylcyclohexane, n-propylcyclohexane, cyclopentene, cyclohexene, cycloheptene, and 1-methylcyclohexene. From Figure 6, it may be seen that as the solute becomes larger, the glass transition temperature of PET tends to increase.

The partial molar excess heat of mixing liquid solute at infinite dilution into liquid polymer, $\Delta \bar{H}$ex, may be obtained from the variation with temperature of the activity coefficient of solute:

$$\frac{d \ln \gamma_w{}^\infty}{d\, 1/T} = -\frac{\Delta \bar{H}_{\text{ex}}}{R}$$

where R is the molar gas constant and T is the absolute temperature; $\gamma_w{}^\infty$ in turn may be calculated at each temperature from experimental data of specific retention volume. In the limiting case in which the volume fraction of polymer in the mixture approaches unity, the activity coefficient of solute, using weight fraction as the reference function, may obtained[18] as

$$\gamma_w{}^\infty = \ln \frac{273.2R}{M_2 V_g{}^a P_2{}^\circ}$$

where $V_g{}^a$ is the specific retention volume based on the weight of amorphous polymer and $P_2{}^0$ is the saturation vapor pressure of solute. Values of $P_2{}^0$ were taken from Dreisbach[19] and Zwolinski and Wilhoit.[20] The use of $P_2{}^0$ instead of $f_2{}^0$, the fugacity in the pure liquid state, implies ideal behavior in the vapor state. Corrections for nonideal behavior were not applied.

$\Delta \bar{H}$ex was determined for the semicrystalline polymer previously annealed 2 hr at 180°C, at temperatures greater than the temperature of the maximum of the plot of ln V_g versus $1/T$. In this range of temperature, equilibrium bulk partitioning is presumed to be attained and to be responsible for the excess heat of mixing. The results, which are plotted in Figure 7, indicate that the glass transition temperatures tends to increase as the partial molar excess heat of mixing increases.

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