Molecular Probes in the Study of Polymer Structure

J. E. Guillet[a]

[a] Department of Chemistry, University of Toronto, Toronto, Ontario

PLEASE SCROLL DOWN FOR ARTICLE

NEW INTERPRETATIONS

Molecular Probes in the Study of Polymer Structure

Recent experiments in our laboratories [1-3], have shown that the technique of gas chromatography may be utilized to obtain extensive information about polymer structure and interactions in the solid phase. Although it might appear logical to apply the name "gas chromatography of polymers" to such experiments, the terminology is misleading in that the polymer is obviously not in the gas phase, nor is it undergoing a chromatographic separation. The terms GLC (gas-liquid chromatography) and GSC (gas-solid chromatography) appear to be equally inapplicable for similar reasons. In fact, the nature of the experiment has more in common with the molecular beam technique for gaseous reactions and we prefer therefore to refer to these as studies on polymers using "molecular probes."

In essence, the experiment involves sending a pulse of molecules along a narrow tube which has a thin coating of the polymer to be investigated covering the inner wall (Fig. 1). The probe molecules will undergo random diffusional motion in all directions, upon which is superimposed a velocity U in the forward direction maintained by a flow of inert carrier gas. In general each of the probe molecules will have a velocity component U_p perpendicular to the flow direction which will cause them to impinge on the polymer surface at the wall. If collision with the wall involves no interaction, there will be no alteration in the component of velocity U_f in the forward direction. On the other hand, any interaction with the polymer will result in a retardation of the net translational velocity of the probe molecules along the tube direction. The strength and nature of the interaction can be deduced from this change in velocity by application of rather simple physicochemical considerations.

The apparatus required for such experiments is simple, consisting of a tube coated with a thin film of polymer, or alternatively a short column packed with an inactive material containing the polymer dispersed as a thin film on the surface. A uniform flow of inert carrier gas is maintained through the column and a pulse of probe molecules injected at one end and detected at the other by a suitable detector. A small pulse of non-interacting gas may also be injected with the probe molecules to aid in
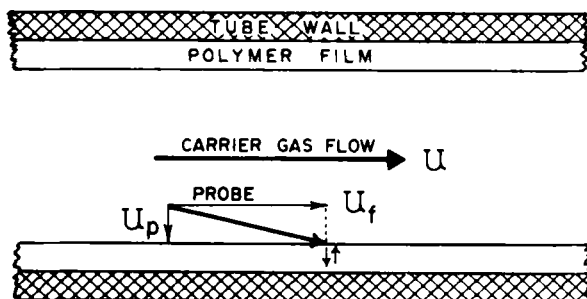
Fig. 1. Schematic representation of molecular probe experiment.
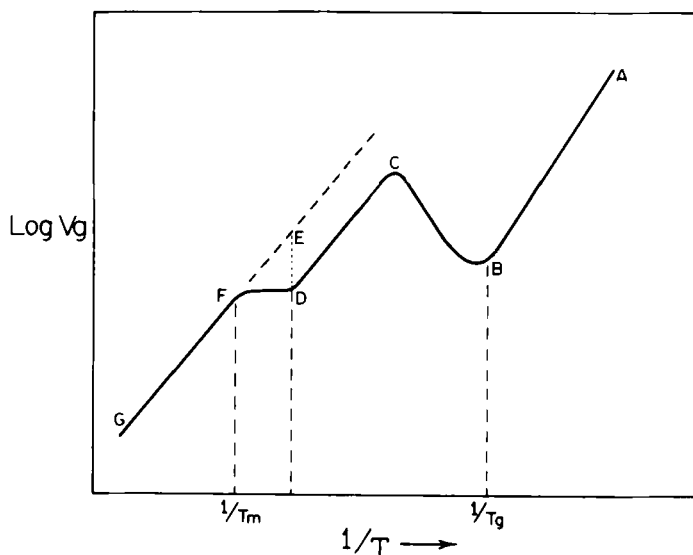
Fig. 2. Generalized retention diagram for semicrystalline polymer.

detection of the carrier gas front. As in conventional gas chromatography it is convenient to express the results of the experiment in terms of the retention volume V_r, defined as the volume of carrier gas required to elute the probe molecules, rather than the net translational velocity U_f. The fundamental quantity from which the various interactions may be deduced is the specific retention volume V_g which is defined by the expression:

$$V_g = \frac{273}{T} \cdot \frac{V_r}{w}$$

where T is the temperature of the system (in °K), V_r is the retention volume, and w is the weight of the polymer film.

In a typical experiment the value of V_g for a particular probe molecule (e.g., hexadecane) is determined for a specified polymer at a series of temperatures. The data are plotted in a generalized retention diagram in the form of log V_g as a function of the reciprocal of absolute temperature (1/T). A typical curve [2, 3] for a semicrystalline polymer with probe molecules having weak molecular interaction is shown in Fig. 2. Such a curve would be expected for polypropylene and crystalline polystyrene using hydrocarbon probe molecules such as the linear alkanes, except that for experimental reasons it is unlikely that a single linear alkane could be used over such a wide temperature range. If the vapor-pressure-temperature relationship is accurately known for the probe molecules, and suitable corrections are made for pressure drop along the column, concentration effects, and nonideality of the gas phase [4], a great deal of valuable information can be obtained from such curves.

In the temperature region corresponding to the segment of the Curve A-B, the polymer is below its glass transition and penetration of the probe molecule into the bulk of the polymer phase is precluded. Retention in this case is due to the sum of terms due to condensation and adsorption on the polymer surface. The curve approximates a straight line, the slope of which at any point is equal to $(\Delta H_v - \Delta H_a)/2.3R$, where ΔH_v is the latent heat of vaporization of the probe molecule and ΔH_a is the enthalpy of adsorption. If the surface area of the polymer film is known, the latter quantity may then be determined with some degree of accuracy.

From the modification of the shape of the concentration pulse of the probe molecules one may also determine the adsorption isotherms using the theory already well developed in GSC [5]. The deviation from linearity represented by point B can be related to the glass transition temperature of the polymer [1, 2]. The Region BC corresponds to nonequilibrium absorption of the probe molecules in the polymer phase. The molecules begin to penetrate the bulk phase but the rate of diffusion is still low, so that until Point C is reached, absorption through the complete film thickness is not attained during the time of the pulse. From this region of the curve it is possible in principle to obtain information regarding the diffusion coefficient D and its temperature coefficient for the probe molecule in the polymer. Similar information can be obtained for any portion of the total temperature range by determining the height equivalent to a theoretical plate (HETP) at various flow rates and applying the Van Deemter equation [6]. Experimental studies of this type will be the subject of a future communication from this laboratory [7].

Table 1

	Process	Enthalpy term
(1)	Condensation on the surface	$\Delta H_c = \Delta H_v$
(2)	Surface adsorption [a]	$\Sigma b_i \Delta H_{a_i}$
(3)	Solution in the polymer phase	ΔH_m

[a] There are now at least two terms relating to the two surfaces accessible to the probe molecules, i.e., the polymer-gas interface and the polymer-support interface. Additional terms may come from interfaces between crystalline and amorphous regions in the polymer. The b_i coefficients relate to the proportion of retention due to adsorption at each interface. These factors can be evaluated experimentally [13] and are related to the surface-to-volume ratio for the polymer film. For thick films it may be possible to ignore these terms.

Equilibrium absorption of the probe molecules in the amorphous phase of the polymer occurs in the Region CD. Retention in this region is caused by three processes (Table 1). The slope of the linear portion of this curve is given by $(\Delta H_v - \Sigma b_i \Delta H_{a_i} - \Delta H_m)/2.3R$. One may also calculate activity coefficients if the vapor pressure of the probe molecule is known. These may be either infinite dilution values (1) or at finite concentrations using the procedures described by Conder and Purnell [8]. From the activity coefficients and the temperature coefficients one may determine the partial molal excess free energy of mixing $\overline{\Delta G_m}$, the partial molal excess entropy of mixing $\overline{\Delta S_m}$, and the enthalpy of mixing $\overline{\Delta H_m}$.

Thermodynamic quantities determined in this way may be used to test various solution theories. For example, if simple Flory-Huggins' theory is applicable, the partial molal excess enthalpy of mixing $\overline{\Delta H_1}$, determined from the slope of the generalized retention diagram, may be used to estimate the interaction parameter χ from the relation [9];

$$\overline{\Delta H_1} = RT\chi v_2^2$$

At infinite dilution of the probe molecules this reduces to

$$\overline{\Delta H_1} = RT\chi$$

which permits a direct determination of the Flory-Huggins interaction parameter.

Similarly, if regular solution theory is applicable to this situation these values of χ may be used to estimate cohesive energy densities for the polymer from the relation [10]:

$$\chi = \frac{\overline{\Delta H_1}}{RT} = \frac{v_1}{RT} (\delta_1 - \delta_2)^2$$

$$\overline{\Delta H_1} = v_1 (\delta_1 - \delta_2)^2$$

where δ_1^2 is the cohesive energy density of the probe molecule, δ_2^2 is the cohesive energy density of the polymer, and v_1 is the molar volume of the probe molecule. Since the cohesive energy density is known or easily calculable for most probe molecules, this represents in principle a method for determining such values for the polymer.

In the Region DF of the curve, the polymer is undergoing a melting transition. If, as seems likely for most noninteracting probe molecules, the crystalline phase is impermeable, this curve gives information about the size and distribution of crystalline regions, and the per cent crystallinity at any point during the melting process [3]. This is done by extrapolating the linear portion of the Curve GF to lower temperatures. This represents the curve for 100% amorphous polymer. Since the quantity V_g is proportional to the weight of the absorbing phase, the per cent crystallinity corresponding to, say, Point D is given by

$$\left(1 - \frac{(V_g)_D}{(V_g)_E} \right) \times 100$$

Experiments with polyethylene show that the results obtained using decane as the probe molecule compare quite well with those estimated from density measurements [3].

The Region FG, which should approximate a straight line, corresponds to equilibrium absorption in the total molten amorphous phase of the polymer. The same considerations apply as for Section CD and one may therefore obtain similar thermodynamic parameters for this temperature range. The accuracy of the thermodynamic measurements has yet to be tested in polymer systems; however, in recent studies using smaller molecules [11] the accuracy appears to be quite as good as for static measurements, and

the simplicity of the technique makes the experiment accessible to any laboratory having a gas chromatograph.

Although the molecular probes discussed in this paper are primarily those with weak interactions such as hydrocarbons, it is obvious that almost any stable molecule having the correct vapor pressure range can be used in the experiment. Stronger interactions involving complex formation have already been studied in hydrocarbon solvents by Cadogan and Purnell [12], and there is no reason why a similar technique cannot be used for polymers. The use of more polar molecular probes can be used to estimate strong interactions such as hydrogen bonding at the surface or the interior of the polymer film. Such experiments would have particular relevance to fundamental processes in adhesion to polymer substrates.

Because of the wealth of information that can be obtained in a single study of this type, we suggest that the "molecular probe" experiment will soon be widely used as a method of determining structure and interactions in macromolecular systems.

REFERENCES

[1] O. Smidsrφd and J. E. Guillet, *Macromolecules,* **2**, 272 (1969).

[2] A. Lavoie and J. E. Guillet, *Macromolecules,* **2**, 443 (1969).

[3] A. N. Stein and J. E. Guillet, *Macromolecules,* **3**, 102 (1970).

[4] J. H. Purnell, *Gas Chromatography,* Wiley, New York, 1962, pp. 30, 67.

[5] W. J. de Wet and V. Pretorius, *Anal. Chem.,* **30**, 325 (1958).

[6] Ref. 4, p. 128.

[7] D. G. Gray and J. E. Guillet, In preparation.

[8] J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.,* **64**, 3100 (1968); **65**, 824, 839 (1969).

[9] P. J. Flory, *Principles of Polymer Chemistry,* Cornell Univ. Press, Ithaca, New York, 1953, p. 512.

[10] D. E. Martire and J. H. Purnell, *Trans. Faraday Soc.,* **62**, 710 (1966).

[11] A. J. B. Cruickshank, M. L. Windsor, and C. L. Young, *Proc. Roy. Soc., Ser. A.,* **295**, 271 (1966).

[12] D. F. Cadogan and J. H. Purnell, *J. Chem. Soc., A,* **1968**, 2133.

[13] J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.,* **73**, 700 (1969).

J. E. Guillet

Department of Chemistry
University of Toronto
Toronto 181, Ontario