Notes

Comments on the Paper "Polymer-Solvent Interactions from Gas–Liquid Chromatography with Capillary Columns" by R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz

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Recently Lichtenthaler, Liu, and Prausnitz[1] reported the use of capillary columns to measure polymer–solute interactions by gas chromatography. The advantage of capillary over packed columns was to provide an increase in film thickness, approximating the conditions prevailing in the bulk material.

Lichtenthaler et al.[1] claimed that the film thicknesses achievable with capillary columns exceeded those of packed columns by two orders of magnitude, typically 10^4–10^5 Å as compared to 10^2–10^3 Å. It should be pointed out that their packed columns consisted of high surface area inert supports (Chromosorb W and P) at rather moderate loadings (10 to 20% w/w). Furthermore, the film thicknesses were computed from the specific surface area of the inert supports as quoted by the manufacturer, about 2.5 and 5 m^2/g for Chromosorb W and P, respectively.[2] Such figures are questionable when considering coverage of an inert support by bulky macromolecules.

It was shown by Perret and Purnell[3] that the specific surface area of Chromosorb P for adsorption by acetone vapors was only 2 m^2/g as opposed to 4 m^2/g for an inert gas. This is explained by the presence of numerous pores in the complex structure of such diatomaceous earths which are inaccessible to bulkier molecules. In the case of the considerably larger polymer molecules it has been found[4] that for coverage by polystyrene (M_v = 120,000) the effective surface area of Chromosorb G was about 0.1 m^2/g, as compared with the quoted 0.5 to 1.0 m^2/g for nitrogen adsorption.[2] As a result, the coating thicknesses achieved with packed columns can be comparable to those of capillary columns. For example, we estimate an average film thickness of 1.0×10^4 Å for a 10% (w/w) loading of polystyrene on Chromosorb G. Even thicker polymer films could be obtained at higher loadings without much change in column performance. Thus the film thickness in packed columns may be only an order of magnitude less than for capillary columns.

However, the use of very thick films, while desirable to alleviate possible orientation effects of the support, can be detrimental to the chromatography of polymer stationary phases. This is illustrated in Figure 1 representing the variation of specific retention volumes with coating thickness (plotted as log V_g vs. log of reciprocal of mass of polymer in column, w_L) for n-hexadecane at 128° on polystyrene packings covering three orders of magnitude of coating thickness.[4] If one assumes that the errors in bulk retention data are solely due to the occurrence of surface retention contributions, then as one increases the thickness (or mass) of the stationary phase the surface contributions should become negligible, as indicated by the dashed line in Figure 1. In fact, as the thickness is increased, the retention volumes tend rapidly toward zero, while becoming strongly flow-rate dependent. This is because diffusional equilibrium is no longer achieved during the passage of the solute peak through the column. As the thickness of the stationary phase increases this factor becomes even larger. In the case of capillary columns which are usually characterized by high linear velocities of carrier gas and thick polymer films, most retention data must therefore be obtained from lengthy and necessarily less precise extrapolation procedures.[1] It is thus questionable whether such disadvantages justify the use of capillary columns.

The magnitude of this flow-rate dependence is directly related to the glass transition temperature, T_g, and the nature of the polymer stationary phase. Usually at temperatures exceeding T_g by 50° or more, equilibrium retention volumes are observed with most polymers in packed columns. A notable exception is polyisobutylene, as indicated by its generalized retention diagram shown in Figure 2. Although the T_g of polyisobutylene is at −70°, equilibrium bulk sorption can only be established at temperatures largely above +50°, or even higher if very thick stationary films or high carrier gas flow rates are used. The reason for this abnormally long region of "glassy" behavior for polyisobutylene is not understood at present, but it does appear

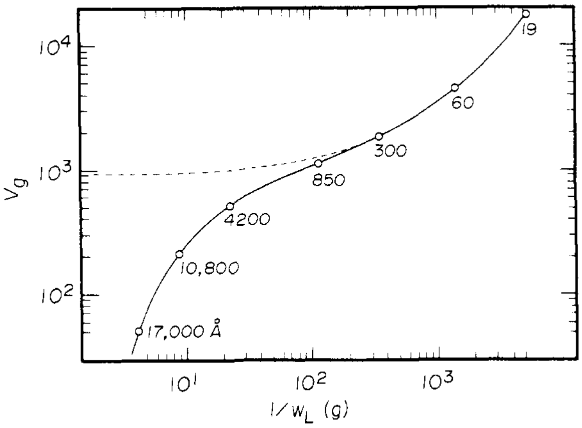

Figure 1. Variation of specific retention volumes (V_g) with coating thickness of stationary phase for n-hexadecane on polystyrene at 128°. Dashed line represents ideal behavior. The numbers indicate the approximate film thickness in Å.

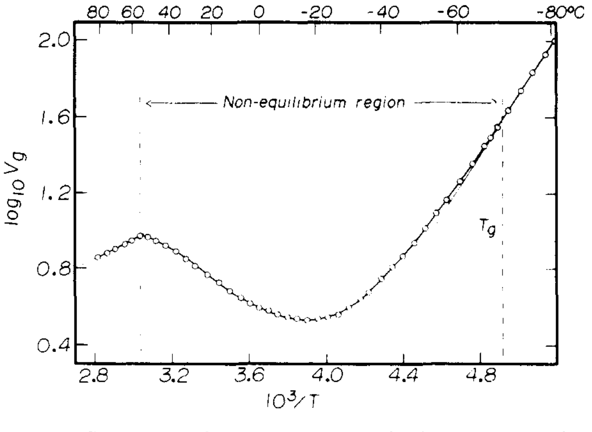

Figure 2. Retention diagram for 2-methylbutane on polyisobutylene (1.07 g of Vistanex L-100, 13.9% on Chromosorb G, AW DMCS, 70/80). Estimated film thickness, 1.5×10^4 Å.

to be unique among the many amorphous polymers we have investigated.

It is quite unfortunate that polyisobutylene was chosen in numerous studies[1,5-9] to investigate the validity of GLC-derived polymer–solute interactions as compared to the more conventional static measurements. As reported earlier by Hammers and DeLigny,[5] it is usually necessary to perform extrapolations of retention volumes to zero flow rate, even in the 50–100° temperature range, thereby introducing a certain degree of imprecision. Due to the magnitude of this flow-rate dependence, results obtained below this range are less reliable. Only at a much higher temperature (T_g +150°) can equilibrium measurements be made directly, and these we believe are the only data with sufficient reliability to afford a satisfactory comparison with static data.

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References and Notes

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Some Solution Properties of Poly(bicycloheptene sulfone) (PBCHS)

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The solution properties of poly(bicycloheptene sulfone) (PBCHS) have not been reported in the literature although solution data are available for at least six other fractionated poly(olefin sulfones).[1] The constants in the Mark–Houwink equation ($[\eta] = KM^{-a}$) have been determined for these polysulfones in Θ solvents permitting calculation of the polymer unperturbed dimensions. In this study, we have investigated the solution properties of PBCHS which included refractive index increment measurements and a study of polymer fractions by light scattering, viscometry, and gel permeation chromatography. From these measurements the Mark–Houwink constant, the mean square end to end distance, and the characteristic ratio of the polysulfone chains were estimated.

The free radical initiated copolymerization of bicycloheptene with sulfur dioxide was carried out at −10° in a 2 l. glass lined Parr stirring-type stainless-steel pressure reactor. The yield of polymer ("whole polymer") was 15 g (47.5%). The polymer was fractionated in CHCl$_3$–methyl alcohol. Four fractions and a whole polymer were used for the GPC, refractive index, light scattering, and viscometry measurements.

A modified Waters Associates GPC model 200 with five 4-ft fractionating columns having permeability limits ranging from 5 × 10^6 to 5 × 10^3 Å was used in this work.

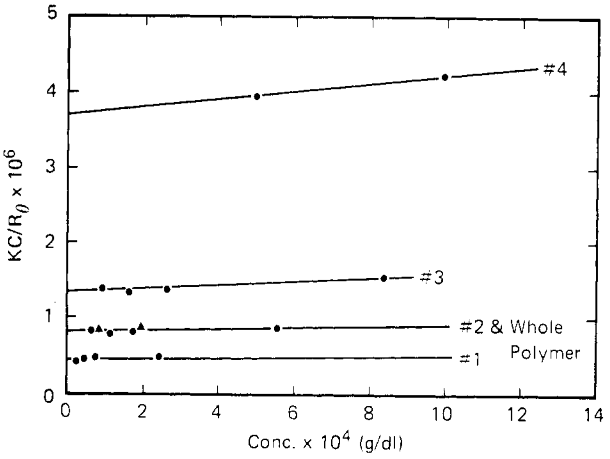

Figure 1. Plot of KC/R_Θ versus concentration of PBCHS in CHCl$_3$ at 25° and at 4° angle of observation.

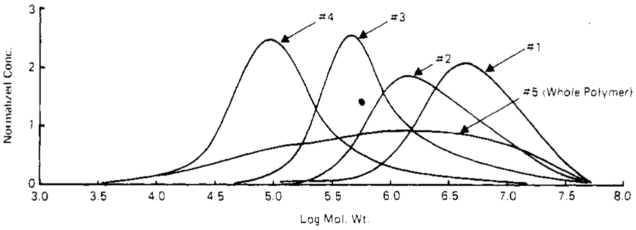

Figure 2. Normalized apparent differential molecular weight distribution (MWD) of the whole PBCHS polymer and its different fractions.

The instrument used for the weight average molecular weight measurement was a recently developed high precision low angle laser light scattering photometer (LALLS)[2,3] by the Beckman Instrument Co.

The sample solutions were prepared in CHCl$_3$ and also in cyclohexanone (chromatographic grades) and diluted to different concentrations in 25 ml volumetric flasks. The solutions were filtered through a 0.2 μ millipore filter before direct injection into the sample cell. The molecular weight was calculated from the intercept of the plot of KC/R_Θ versus concentration such as that shown in Figure 1. K is the polymer constant which is dependent on the refractive index of the solvent (n) and the refractive index increment, $\Delta n/\Delta c$. In CHCl$_3$, n and $\Delta n/\Delta c$ were determined to be 1.446 and 0.1025 ml/g, respectively. This gives a value of 8.98 × 10^{-8} for K at 4° angle of observation using a helium–neon laser (6328 Å) light source. The correction due to an interference effect was estimated to be less than 3% ($P(\Theta) > 0.97$) for the highest molecular weight fraction. Consequently, no correction was considered necessary for the lower molecular weight fractions. Light scattering data for sample 2 were also obtained in cyclohexanone; n and $\Delta n/\Delta c$ were found to be 1.451 and 0.112 ml/g, respectively. The $\Delta n/\Delta c$ of PBCHS in CHCl$_3$ and cyclohexanone were measured using the Brice-Phoenix differential refractometer which was calibrated using a potassium chloride solution. The molecular weight obtained in cyclohexanone was 1.10 × 10^6 compared with 1.25 × 10^6 in CHCl$_3$. The good agreement in the light scattering data helps support our contention that there is no appreciable association of the polymer with itself.

A Fica Viscomatic viscometer with a Haake temperature controller was used to measure the solution and solvent ef-