

CHROM. 5061

GEL PERMEATION CHROMATOGRAPHY

DIFFUSIONAL PHENOMENA IN DILUTE POLYMER SOLUTIONS
FLOWING IN CAPILLARIES*

AUGUSTUS C. OUANO AND JOSEPH A. BIESENBERGER**

IBM Research Laboratory, San Jose, Calif. 95114 (U.S.A.)

SUMMARY

This work is concerned with the dispersion of high-molecular-weight solutes in dilute solutions flowing through empty capillary tubing, such as that which is found between chromatographic columns and detectors, etc., in gel permeation or liquid chromatographs.

Residence time distributions of solvent as well as solutes were measured simultaneously. This was done for both pulse and step solution inputs using a two-cell detection system. The solutes, *o*-nitrotoluene and narrow-distribution polystyrene (gel permeation chromatographic standards), were monitored with an ultraviolet detector while hexane (hexane-chloroform (20:80) was used to dissolve the polymer solutes) was monitored with a refractometer in a chloroform mobile phase. Polystyrene concentrations were 0.20 percent and 0.15 percent. Three tubing lengths and two flow rates were studied.

The results indicate that polymer molecules have residence time distributions which are different from those of small molecules. This lends support to our belief that molecular entanglements occur among the polymer molecules which causes radial concentration non-uniformities and virtual two-phase flow.

INTRODUCTION

All fluid solutions which are transported through capillaries by bulk flow have a radial velocity distribution which, in the total absence of molecular diffusion, gives rise to dispersion which is rather broad and extremely unsymmetrical. We have named this extreme case the segregated flow regime¹.

Only when radial molecular diffusion is permitted to occur to a sufficient degree does this dispersion become symmetrical or Gaussian. This phenomenon has been studied by TAYLOR and is called TAYLOR diffusion. We have named the symmetrical case the TAYLOR regime².

The region between these extremes is of special importance in all types of chro-

* For a preliminary report, see *J. Polym. Sci., A2*, in press.

** Stevens Institute of Technology, Hoboken, N.J., U.S.A.

matography employing liquid solutions, and in particular gel permeation chromatography (GPC) because the latter involves polymeric solutes which have very low molecular diffusion coefficients.

In our previous studies^{1,3} we have shown that, while maintaining capillary tubing as short as possible causes dispersion to remain narrow in width, the capillary tubing also gives rise to severe skewing, even with small solute molecules and certainly with polymeric solutes. On the other hand, long tubing tends to reduce skewing while increasing the width of dispersion. It is clear that skewed chromatograms are not desirable, since they do not conform to most theories in chromatography which assume Gaussian behavior.

We have also shown that not only can skewing perhaps never be totally eliminated in polymer solutes flowing in capillaries, but that polymer dispersion does not exhibit the behavior expected of small molecules. Rather, polymer solutes exhibit anomalous dispersion and give rise to bimodal chromatograms. Moreover, some recent preliminary studies with recycle GPC have shown that skewness, rather than disappearing with increasing number of recycles, is severely compounded with polymer solutions in the recycle mode.

As a possible explanation of the anomalous dispersion behavior of polymer solutes in capillaries, we have proposed that molecular entanglements occur among the polymer molecules. These entanglements cause them to aggregate near the tube center and to have residence time distributions which are different from those of the solvent, as well as any other small molecule solutes which might be present in solution.

We are in essence proposing that something similar to two-phase flow exists in which polymer clusters behave virtually like a separate phase, independent of the remaining solution consisting of small-molecule solutes and solvent.

If this picture is accurate, then the solvent residence time distribution, which is equivalent to a newtonian, parabolic velocity profile in the segregated flow regime, should be different from that of the polymer solute. Similarly, TAYLOR diffusion among the small-molecules in the TAYLOR regime should proceed more or less independently of the polymer solute.

Thus, we believe that the results of the present study, which consist of simultaneous measurement of polymer solute and solvent residence time distributions, contribute new experimental evidence in support of our interpretation of the anomalous flow phenomenon.

EXPERIMENTAL PROCEDURE

The independent measurement of the elution time (or elution volume) of a polymer solute and solvent through a small diameter tubing with no packing, was done using a standard DuPont Model 820LC liquid chromatograph which was equipped with an ultraviolet (UV) photometer (254 nm) connected in series to a Fresnel Type refractometer (RI) detector (UV ahead of RI). Polystyrene dissolved in a mixture of hexane-chloroform (20:80) is a good choice of solvent, since both hexane and chloroform have very low UV extinction coefficients (at 254 nm) relative to polystyrene. The RI detector, on the other hand, can be made insensitive to polystyrene by using a much higher concentration of hexane (relative to polystyrene) in the polystyrene-hexane-chloroform solution. Consequently, when the polystyrene solution containing hexane is injected into a chloroform mobil phase, the UV and the

RI detectors become specific for monitoring the elution of polystyrene and hexane, respectively.

The chromatographic column of the DuPont 820LC was replaced with stainless steel tubing by modifying the septum injection port. The modification consisted of replacing the chromatographic column with a 2 in. \times 1/4 in. O.D. brass tubing with an I.D. of 0.047 in. To the brass tubing, 4 in. \times 1/16 in. O.D. tubing with an I.D. of 0.047 in. was silver-soldered to act as the connector for the 0.047 in.-I.D. tubing being tested.

Polystyrene (Pressure Chemical Co., \bar{M}_w/\bar{M}_n of 1.02–1.10 with molecular weights of 600, 10,000, 20,400, and 97,200) and *o*-nitrotoluene were each dissolved in a 20–80 (5:95 for step input) by volume hexane–chloroform solvent mixture to 0.2% (0.15% for step input) solutions. Lower concentrations of hexane and polystyrene were necessary for the step input to prevent the recorder from going off scale at the highest detector attenuation.

For the pulse input mode, two tubing lengths (39 in. and 146 in.) and flow rates (1.9 ml/min and 1.0 ml/min, respectively) were used. The test conditions covered both segregated flow and TAYLOR diffusion dispersion ranges. Sample volume injected was between 4 to 6 μ l. For the step input mode, only the segregated flow dispersion region was studied. This corresponds to 17 in. of tubing at 1.0 ml/min flow rate.

In order to accommodate a large amount of solution in the injection port which is required for the step injection mode, the septum type sample injection port was replaced by the Waters Associates' six-port sample injection valve. The regular 2 ml sample loop which comes as standard equipment with the Waters' sample injection valve was replaced by a 7 ml sample loop.

DISCUSSION OF RESULTS

Fig. 1 shows the elution curves of 20,400 and 97,200 molecular-weight polystyrene (PS) solutions along with the corresponding elution curve of hexane, which was

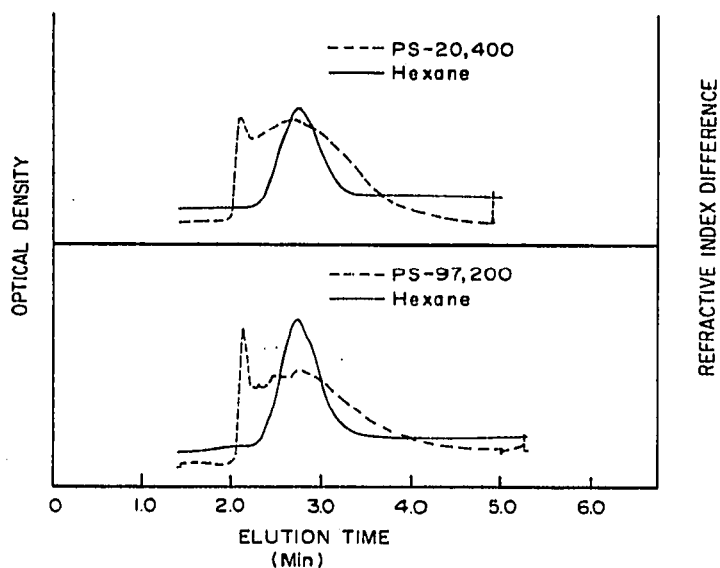


Fig. 1. Pulse input elution curve of PS-97,200 and 20,400 through a 146 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. ---, UV optical density; —, refractive index difference.

injected with the polymer into the chloroform solvent stream through 146 in. of 0.047 in. I.D. stainless steel tubing. It is evident that the bimodal anomaly occurs in the polystyrene elution, but not in hexane. Furthermore, the hexane elution curve approaches the Gaussian shape which agrees with the theoretical curve based on TAYLOR diffusion² in tubing.

The possibility of a malfunctioning UV photometer cell, which can cause anomalies in the elution curve of polystyrene, was checked by substituting PS-600 and *o*-nitrotoluene for high-molecular-weight polystyrene. Fig. 2 shows the elution curve of *o*-nitrotoluene and PS-600 (detected by the UV photometer) to be free of the bimodal anomaly. The elution curve of PS-10,000, however, is beginning to show the anomaly. This indicates that the bimodal elution curve of high-molecular-weight polystyrene is not an artifact but is highly dependent on the molecular weight of the solute.

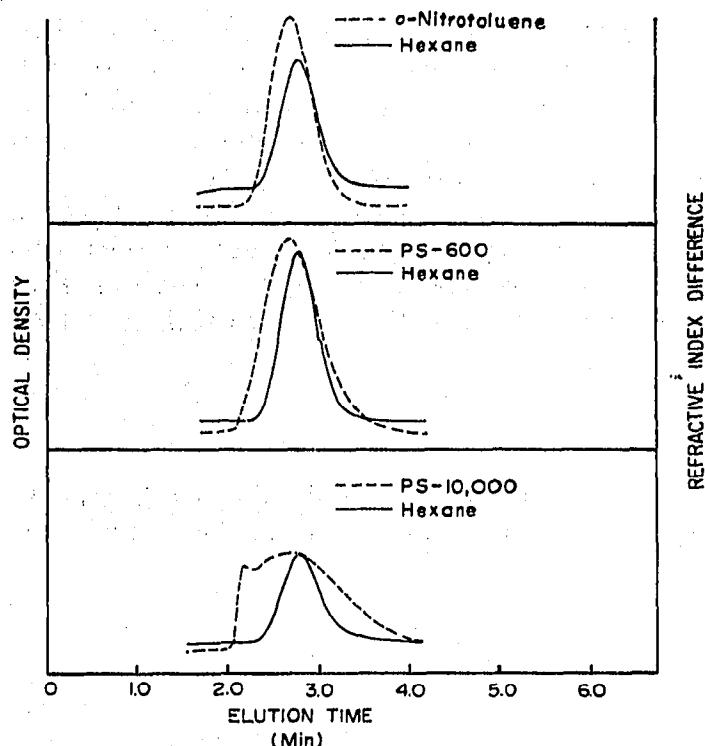


Fig. 2. Pulse input elution curve of PS-10,000, PS-600 and *o*-nitrotoluene through a 146 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. - - -, UV optical density; —, refractive index difference.

For a better comparison of the elution curves of hexane, *o*-nitrotoluene, and the various molecular weight polystyrenes, a normalized curve is presented in Fig. 3. It shows that elution curves of *o*-nitrotoluene and hexane fall within the shaded area, which is Gaussian as predicted by a model based on TAYLOR diffusion³. Since the elution curves of high-molecular-weight polystyrene and hexane were measured independently in the solution, the difference in their elution curves indicates that a two-phase flow in dilute polystyrene solution may actually be taking place. This flow condition may be similar to that of a dilute pulp slurry (0.1 %) flowing in pipes⁴. In the pulp suspension experiment, it was observed that the pulp fibers tend to flow

as an entangled mass with a velocity profile considerably flatter than the water suspending medium. The pulp fibers were also observed to concentrate at the axis of the pipe. This phenomenon can perhaps be more directly shown if shorter tubing length and higher flow rates are used such that the segregated flow condition is met.

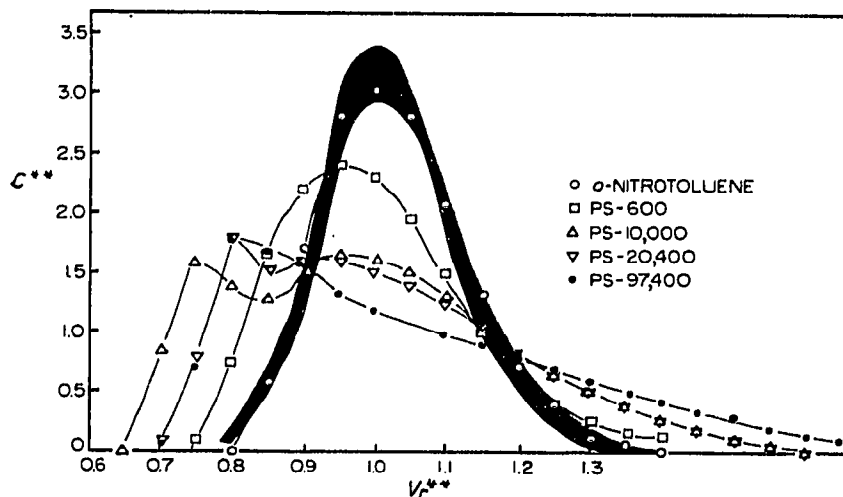


Fig. 3. Normalized pulse input elution curve of high- and low-molecular-weight polystyrenes and *o*-nitrotoluene through a 146 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate.

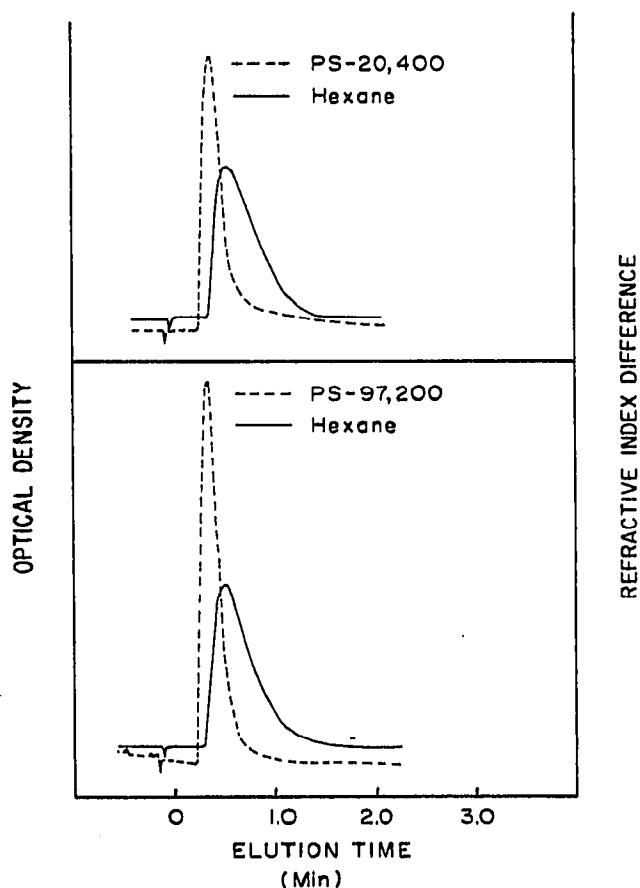


Fig. 4. Pulse input elution curve of PS-97,200 and PS-20,400 through a 39 in. long \times 0.047 in. I.D. stainless steel tubing at 1.9 ml/cm flow rate. - - - -, UV optical density; ———, refractive index difference.

Figs. 4 and 5 show the elution curves of PS-97,200, PS-20,400, PS-10,000, PS-600 and *o*-nitrotoluene through a 39 in. stainless steel tubing. The dependence of the elution curve on molecular weight is again apparent. The higher molecular weight polystyrenes show a sharper elution curve than that of hexane and *o*-nitrotoluene. The shape of the elution curves of high-molecular weight polystyrenes seems to approach a sharp spike (pulse response to pulse input), which is associated with a "plug-like" velocity profile. The contrast in the shape of polystyrene and hexane elution curves is more readily seen in Fig. 6, which is a normalized elution curve of PS-97,200, PS-600 and *o*-nitrotoluene and hexane. The shaded area in Fig. 6 includes the data points for hexane and *o*-nitrotoluene.

The elution curves (for a step input of solutions) of PS-97,200, PS-20,400,

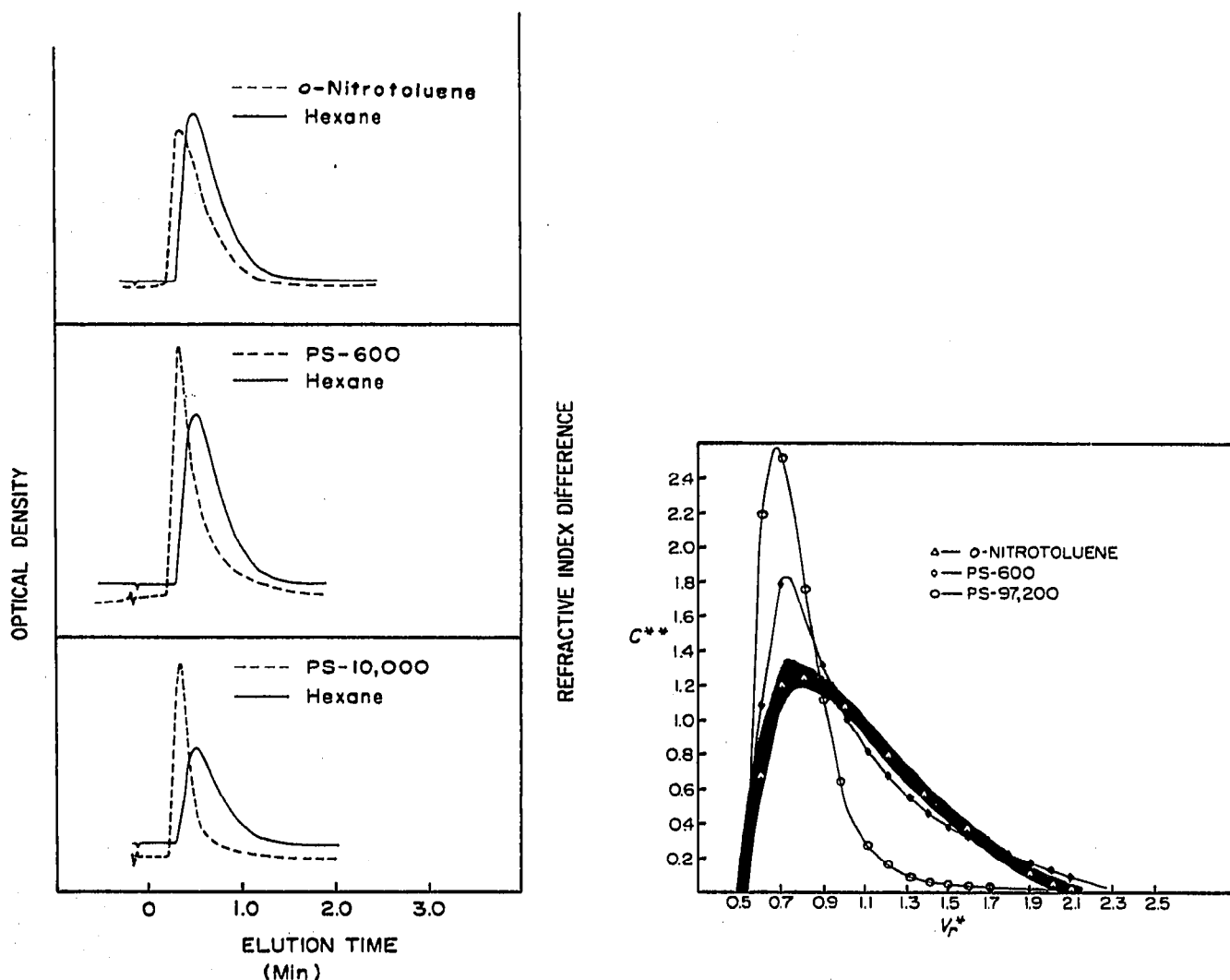


Fig. 5. Pulse input elution curve of PS-10,000, PS-600 and *o*-nitrotoluene through a 39 in. long by 0.047 in. I.D. stainless steel tubing at 1.9 ml/min flow rate. - - - , UV optical density; ———, refractive index difference.

Fig. 6. Normalized pulse input elution curve of high- and low-molecular-weight polystyrene and *o*-nitrotoluene through a 39 in. by 0.047 in. I.D. stainless steel tubing at 1.9 ml/min flow rate.

PS-600 and *o*-nitrotoluene through stainless steel tubing (17 in.) are shown in Figs. 7 and 8. The plug-like flow of the high-molecular-weight polystyrene is again evident. The "step-like" elution curve of high-molecular-weight polystyrene reveals its "plug-like" velocity profile. An elution curve of a model based on parabolic velocity profile (segregated flow condition) along with normalized experimental curves for PS-97,200, PS-600 and *o*-nitrotoluene are shown in Fig. 9. It is clear in this plot that the elution curve of high-molecular-weight polystyrene does not reflect a parabolic velocity profile, since it is much steeper than the model curve. The deviation of the *o*-nitrotoluene elution curve from the model curve can perhaps be explained by molecular diffusion of *o*-nitrotoluene (small, but nevertheless finite), for which the segregated flow model does not account (assumes molecular diffusivity to be zero).

If one assumes plug flow for the high-molecular-weight solute and parabolic

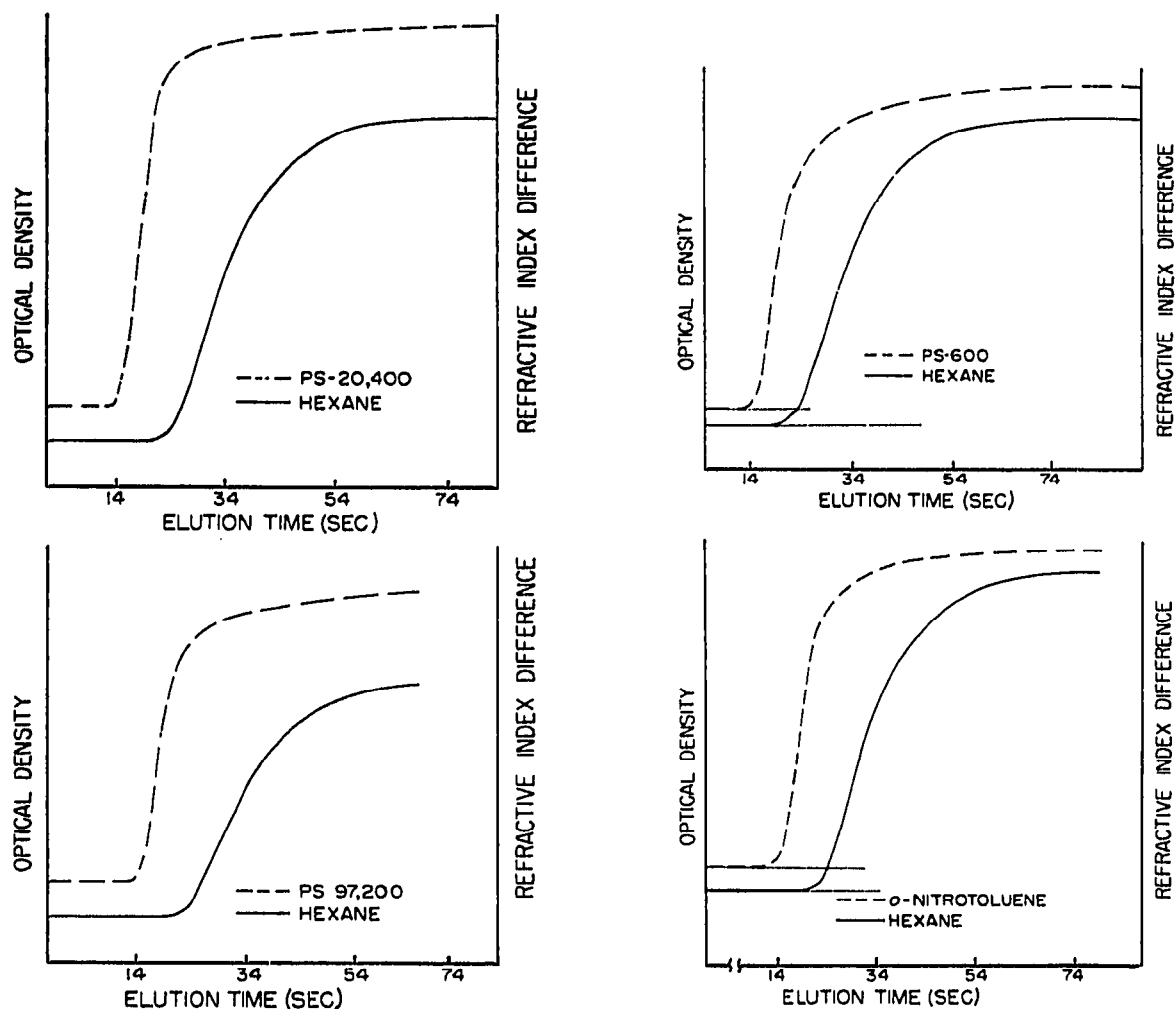


Fig. 7. Step input elution curve of PS-97,200 and PS-20,400 through a 17 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. - - - -, UV optical density; ———, refractive index difference.

Fig. 8. Step input elution curve of PS-600 and *o*-nitrotoluene through a 17 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. - - - -, UV optical density; ———, refractive index difference.

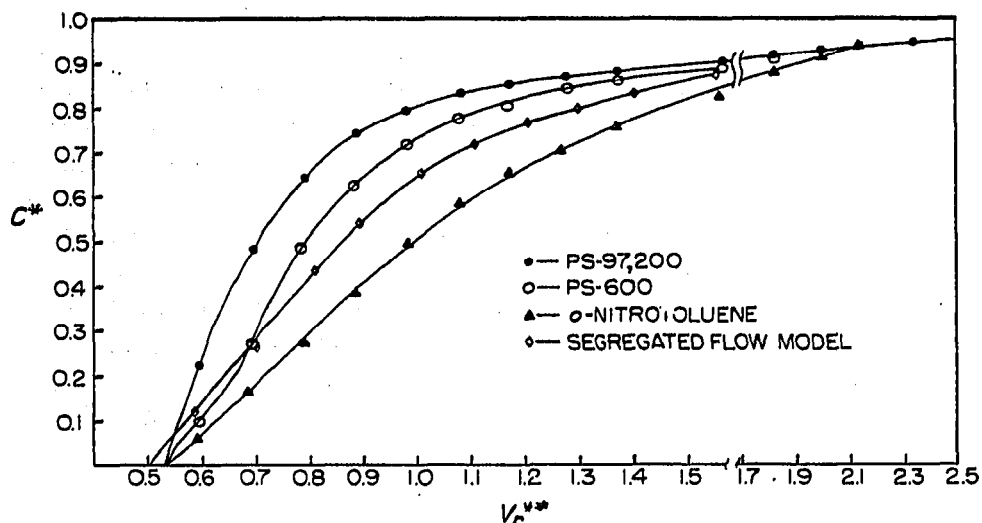


Fig. 9. Normalized step input elution curve of high- and low-molecular-weight polystyrene and *o*-nitrotoluene through a 17 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate.

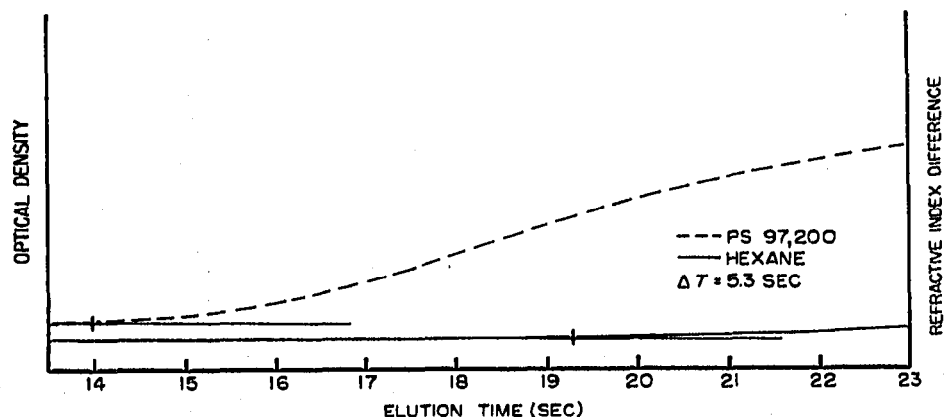


Fig. 10. High speed (recorder speed = 1 in./sec) recording of the step input elution curve of *o*-nitrotoluene and hexane through a 17 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. ---, UV optical density; —, refractive index difference.

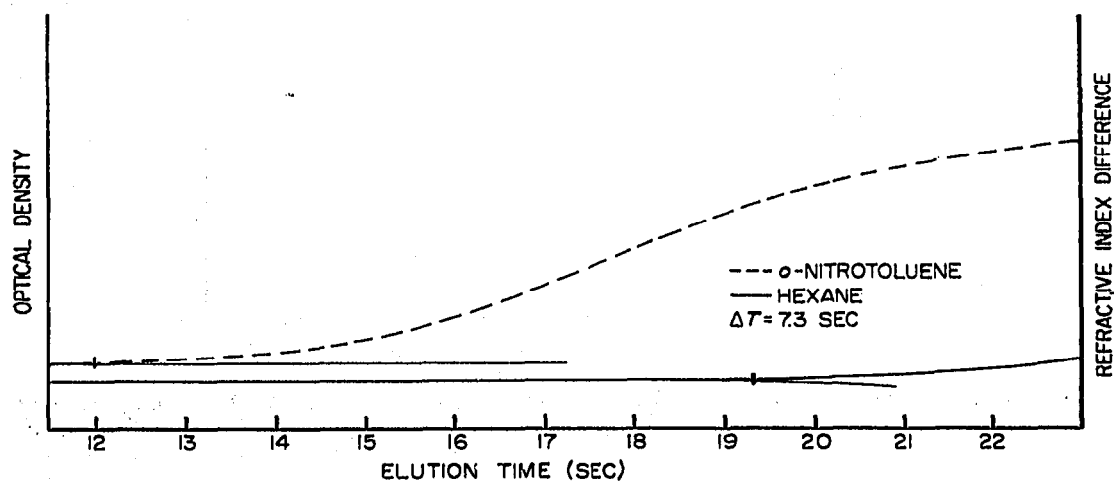


Fig. 11. High speed (recorder speed = 1 in./sec) recording of the step input elution curve of PS-97,200 and hexane through a 17 in. long by 0.047 in. I.D. stainless steel tubing at 1 ml/min flow rate. ---, UV optical density; —, refractive index difference.

flow for the solvent, then a difference in minimum elution time between the polystyrene and hexane curves should exist. The hexane/*o*-nitrotoluene difference is due to detector configuration only, while that of hexane/PS-97,200 is due to detector configuration and velocity profile difference. This difference has been observed directly by comparing the difference between the minimum elution time of *o*-nitrotoluene/hexane and PS-97,200/hexane solutions. This difference is illustrated in Figs. 10 and 11. Although the difference in elution times of *o*-nitrotoluene/hexane and PS-97,200/hexane is only 2 sec, this is significant when one considers the length of the tubing used, which was 17 in.

A summary of the experimental evidence presented in this paper suggests that there is some inhomogeneity in the flow of dilute polymer solutions in small-diameter tubing. It also indicates that a two-phase flow similar to that observed in dilute pulp slurries flowing in pipes⁴ may take place in dilute solutions of polymers with sufficiently high molecular weight. Although a good molecular model which can explain this anomalous behavior is at the moment not available, a qualitative speculation as to its cause is perhaps in order.

When a polymer solution is injected into a solvent stream, it is thought that intermolecular interaction between polymer solute molecules causes them to flow with a "plug-like" velocity profile. It is also proposed that, because of the shear gradient in laminar flow, a polymer solute molecule is more highly perturbed by a neighboring polymer molecule which is closer to the tubing axis than another neighboring polymer molecule which is closer to the tubing wall. This results in a radial migration of polymer solute toward the tubing axis. Furthermore, there is a critical radial distance, R , which is a function of shear rate, polymer concentration and molecular weight, from the tubing axis where the polymer solute is essentially unperturbed by the neighboring polymer molecules (no radial migration). The net result of the above proposal is a polymer solute concentration profile which has a maximum near the tube axis and a minimum in an annular region (R distance from the tubing axis). If the above explanation is accepted, the bimodal elution curve becomes evident when one superimposes the velocity profile with the above distorted concentration profile.

APPENDIX

- A = Area of elution curve
 C_o = Concentration of injected sample
 \bar{C} = Instantaneous concentration at the cell
 C^* = \bar{C}/C_o = dimensionless concentration (step input)
 C^{**} = $\frac{\bar{C}V_e}{A}$ = dimensionless concentration (pulse input)
 V = Detector cell volume
 V_t = Volume of tubing
 V_e = $V_t + V$ (total system volume)
 V_r = Retention volume
 V_r^{**} = $\frac{V_r}{V_t}$

ACKNOWLEDGEMENTS

The authors wish to extend appreciation to Mrs. B. Dawson who helped in obtaining most of the data in this paper and to Drs. R. J. GRITTER and T. L. SMITH for their helpful suggestions in reviewing this manuscript.

REFERENCES

- 1 J. A. BIESENBERGER AND A. C. OUANO, *J. Appl. Polymer Sci.*, 14 (1970) 471.
- 2 G. I. TAYLOR, *Proc. Roy. Soc. (London)*, A219A (1953) 186.
- 3 A. C. OUANO AND J. A. BIESENBERGER, *J. Appl. Polym. Sci.*, 14 (1970) 483.
- 4 J. W. DAILY AND G. BUGLIARELLO, *Ind. Eng. Chem.*, 51 (1959) 887.

J. Chromatog., 55 (1971) 145-154