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FLOW RATE DEPENDENCE OF SEPARATION AND
BROADENING EFFECTS IN GPC

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ABSTRACT *

The primary objective of this work is an investigation of the separation and zone brodening effect in columns packed with porous and nonporous materials, and estimation of the accuracy of the broadening parameter, h , obtained by a reverse flow method. In order to study the separation and dispersion phenomenon in the mobile phase, and that caused by a mass-transfer process, columns packed with smooth glass beads and porous silica columns were used.

INTRODUCTION

In GPC, the relationship between the experimental chromatogram $F(v)$ and the chromatogram after the correction

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for zone broadening $W(y)$ is given by the Tung's integral equation (1)

$$F(v) = \int_{-\infty}^{\infty} W(y) G(v-y) dy \quad (1)$$

where both v and y represent the elution volume, and the function $G(v-y)$ represents the overall zone broadening, which is thought to have come from several sources: (a) broadening caused by mixing outside the packed columns, (b) broadening caused by mixing (diffusional and convective) in the mobile phase within the packed columns, and (c) broadening caused by the process of transfer of solute between the mobile and stationary phases in the columns. The effect of (a) has been shown to be small (2). The effect of (b) and (c) have been shown to give Gaussian broadening for conventional chromatography,

$$G(v-y) = \frac{h}{\sqrt{\pi}} \exp[-h^2 (v-y)^2] \quad (2)$$

where h is a parameter describing the degree of the broadening and is related to the standard deviation of a Gaussian distribution by

$$h = \frac{1}{\sigma\sqrt{2}} \quad (3)$$

In order to use Tung's integral equation, the parameter h , as a function of elution volume, must first be determined

experimentally for each calibration standard and column combination. There are two techniques that can be used to determine the h value: the reverse flow technique (3) and the recycle technique (4-5). Using the reverse flow method, Tung has found that the parameter h , as a function of elution volume, passes through a minimum. This is the result of combined effects of the extent and rate of permeation. In the present work, the separation ability and broadening effect in mobile phase, the flow rate dependence of the elution volume on porous silica columns, and the flow rate dependence of the function $h(K)$, where K is the solute distribution coefficient, were determined by means of a reverse flow or recycle method. The accuracy of the h value obtained by the reverse flow method was also estimated.

EXPERIMENTAL

1) Equipment

GPC Unit, Model SNJ-75-1, with a four-port valve (for reverse flow technique) and two six port valves (one for injection of the sample and the other for recycle technique) was used in this study. A differential refractometer and a UV detector were used to monitor the solute concentration in the eluent.

2) Columns

Five porous silica columns of 2000, 1200, 350, 150 and 100 angstrom mean pore sizes were used, each being 1m long with 10 mm i.d.

TABLE 1
Standard Polystyrene Samples

Sample -----	Molec. Weight -----
PS-1	2350
PS-2	8500
PS-3	3.5×10^4
PS-4	1.1×10^5
PS-5	2.0×10^5
PS-6	4.7×10^5
PS-7	2.7×10^6
PS-8	3.7×10^6

Four columns, 1 m x 10mm i.d. were packed with nonporous glass beads of 44-53 micron particle size.

3) Samples -----

The polystyrene standards were obtained from Waters Associates and are listed in Table I. In addition to the above samples, a polystyrene NBS-706 sample, four PMMA samples, two PVC fractions, a SBS TR-1101 copolymer and benzene were used.

4) Experimental Conditions -----

All measurements were performed at room temperature, THF was used as solvent, flow rate 0.5-5.0 ml/min. The injection volume was 1.3 ml for porous silica columns and 0.5 ml for glass bead columns.

RESULTS AND DISCUSSION

1) Separation Ability and Zone Broadening Effect in the Mobile Phase.

It was considered that the mobile phase caused only the broadening of the solute zone but did not separate solutes with different molecular weights. Yau (6) used columns packed with nonporous glass beads and found no separation between a styrene monomer and a polystyrene sample, and, by means of this observation, indicated that separation by flow in the mobile phase was not an effective mechanism in GPC. Our experimental results for PS and PVC samples and benzene on nonporous glass bead columns are listed in Table II. This shows that the peak elution volume, V_p , depends upon the molecular weight of the samples. V_p decreases with increasing molecular weight, though the variation is small. In order to further confirm this effect, the recycle

TABLE 2
Elution Vol., V_p , & Broadening Parameters h and h' .

Sample	MW	V_p	h	h'

Benzene	78.1	38.09	2.46	2.41
PS-1	2350	38.07	2.17	2.04
PS-4	1.1×10^5	38.00	1.93	1.78
PS-6	4.7×10^5	37.87	1.89	1.79
PS-7	2.7×10^6	37.60	1.45	1.21
PVC-B	1.18×10^5	38.01	1.89	1.58

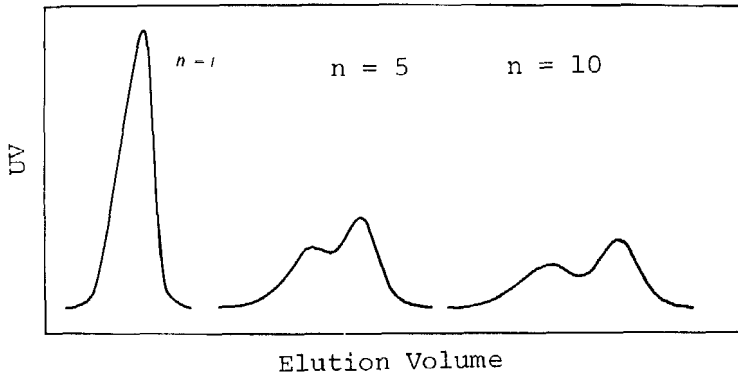


Figure 1. Separation of mixture (PS-1 + PS-7) on nonporous glass bead columns

technique was used; this served the same purpose as the lengthening of the column. Figure 1 shows the recycle chromatogram of a mixed polystyrene sample (PS-1 and PS-7), n is the number of cycles. At the first cycle there was only a single peak of the mixed sample, but after several cycles the peak was split into two. The first two peaks were further separated from each other with increasing cycle number. Thus, the separation ability of the columns was well confirmed. Flow rate dependence of V_p is shown in Figure 2. V_p of both samples increase with increasing flow rate, and the slopes of both curves are almost the same. This result could not be explained in terms of separation by flow and separation by steric exclusion because, in both cases, the flow rate independence of V_p is usually expected (7). Explanation by restricted diffusion theory is not possible either; it would predict that the elution volume should decrease with increasing flow rate and that the

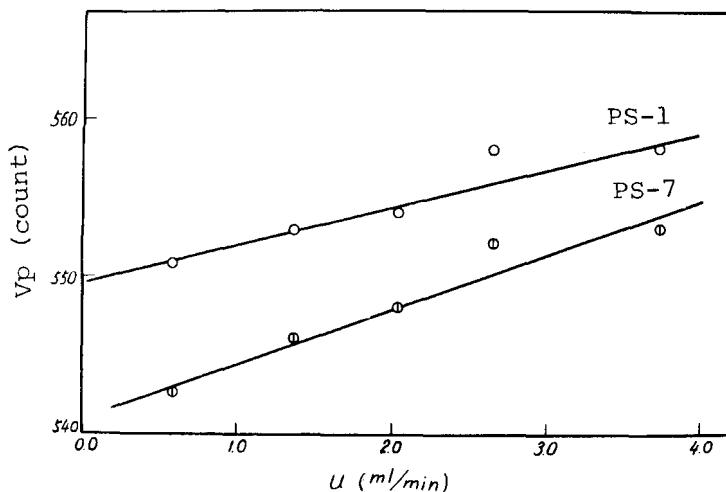


Figure 2. Variation of V_p with flow rate on nonporous glass bead columns

elution volume of low molecular weight compounds should be influenced by a variation of flow rate to a lesser extent (B).

According to Kelley and Billmeyer(9) the plate height equation describing dispersion in the mobile phase with a velocity profile model is expressed by equation (4)

$$H_m = 2\phi D_m U^{-1} + 2\lambda dp + \frac{2kRc^2}{\phi D_m U^{-1} + \lambda dp} \quad (4)$$

where H_m is the mobile phase plate height, U is the interstitial velocity, D_m is the diffusion coefficient for the solute in the mobile phase, ϕ is the tortuosity factor ($\phi = 2/3$), λ is an eddy diffusion proportionality factor ($\lambda = 1/11$), dp is the effective particle diameter, k is a velocity profile constant, and Rc is the column radius.

Thus H_m is composed of molecular diffusion, eddy diffusion, and velocity profile terms. The molecular diffusion contribution to dispersion is ignored. This was supported by the experimental results of Copper (10). The eddy diffusion term is a function of particle size only, being independent of molecular weight of solute molecules. The third term, the velocity profile effect, is related to MW through D_m in the denominator.

In this work, the broadening parameter h (or h' , the broadening parameter obtained from a straight-through flow chromatogram) is used to describe the dispersion effect. The relationship between H_m and h is

$$H_m = L (2V_p^2 h^2)^{-1} \quad (5)$$

where L is the column length. The values of h and h' obtained from reverse flow and straight through flow chromatograms respectively for several PS, PVC-B and benzene are listed in Table 2. The fact that h' decreases with increasing MW is qualitatively in agreement with the prediction of the velocity profile model. But in equation (4) there was no factor related to the MWD of the solute. As mentioned above, the samples could be separated according to their MW's in the mobile phase, so we considered that a factor reflecting the solute MWD should be added to equation (4). This deduction was supported by the data of Table II. The narrow-distribution PS-4 and the broad-distribution PVC-B ($M_w/M_n = 2.9$) have almost the same values of V_p and h , but their h' values are obviously different from each other.

Here, similar h values mean that the broadening caused by polydispersity has been almost cancelled by the flow reversal, and the difference in h' simply reflects the effect of polydispersity of the sample.

2) Effect of Reverse Flowing Process on Zone Broadening on Nonporous Glass-Packing Columns

As the low MW solute benzene is monodisperse in molecular weight, the broadening parameters h and h' should have the same value. The h and h' for benzene were determined from reverse flow and straight-through flow chromatograms. Figure 3 shows the flow rate dependence of Δ

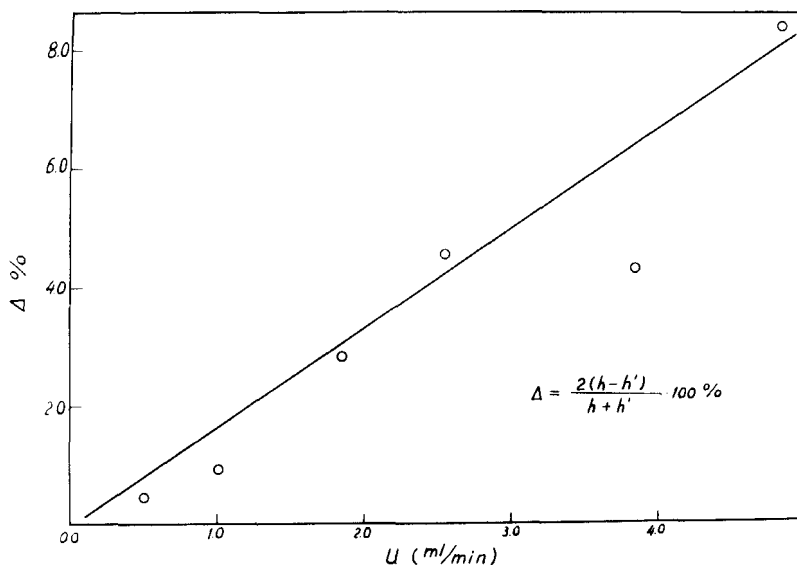


Figure 3. Variation of Δ for benzene with flow rate on nonporous glass bead columns

($\Delta = 2(h-h')/h+h'$). The fact that $h > h'$ could be explained by the following assumption: According to Kelley and Billmeyer's velocity profile model, while the fluid is flowing in some fixed direction on the column, the velocity profile is formed and the solute zone disperses to some extent. During the reverse flowing process, the fluid changes its flow direction in a very short time; thus, the velocity profile should be disturbed. After this time, a new velocity profile is established and the solute zone further dispersed. However, the extent of dispersion of this reverse flowing experiment should be less than that of the straight through flowing experiment, in which the velocity profile is not disturbed. Therefore, the value of h becomes larger than that of h' . It is expected that the extent of disturbance is dependent upon the flow rate as shown in Figure 3.

3) Flow Rate Dependence of Elution Volume on Porous Silica Columns

The dependence of peak elution volume on flow rate has been reported by several authors giving conflicting results. Yau (11) observed that the elution volume of PS high molecular weight decreased with increasing flow rate in the range from 0.1 to 10.0 ml/min. Little (12), on the other hand, found V_p was independent of flow rate in the same range. Spatorico (13) reported that a negligible dependence of V_p on U was obtained in porous glass-bead packing studies, whereas a small increase in V_p was observed with

increasing flow rate in the range of 0.2 to 1.0 ml/min on polystyrene gel studies. Recently Aubert and Tirrell (14) and Gudzinowicz and Alden (15) came to the conclusion that the elution volume increased with increasing flow rate in a range of 1.0 to 3.0 ml/min on porous silica columns, and offered an explanation based upon a flow-rate dependent equilibrium distribution coefficient. Moreover, Boni et al. (16) reported that the observed V_p passed through a maximum as flow rate was increased (0.2 - 2.0 ml/min). Mori (17), on the other hand, found an opposite result, i.e., that the observed elution volume passed through a minimum as flow rate was increased on Microstyrigel columns in the range of 0.5 to 4.0 ml/min. This problem was investigated in the present work with porous silica columns. A siphon was used to collect the effluent liquid for the purpose of monitoring the flow and the elution volume. The volume of discharged liquid was corrected as follows. The weight per count of collected liquid, A , at flow rate, U , was weighed. The relationship between A and U is given in Figure 4. The calibration curve may be expressed by a linear equation.

$$A = A_0 + \alpha U \quad (6)$$

and the corrected elution volume V_p may be calculated using equation (7)

$$V_p = (V_p)_{app} \left(1 + \frac{\alpha}{A_0} U \right) \quad (7)$$

where $(V_p)_{app}$ is the experimentally measured elution volume at the flow rate U . A_0 and α could be obtained from the

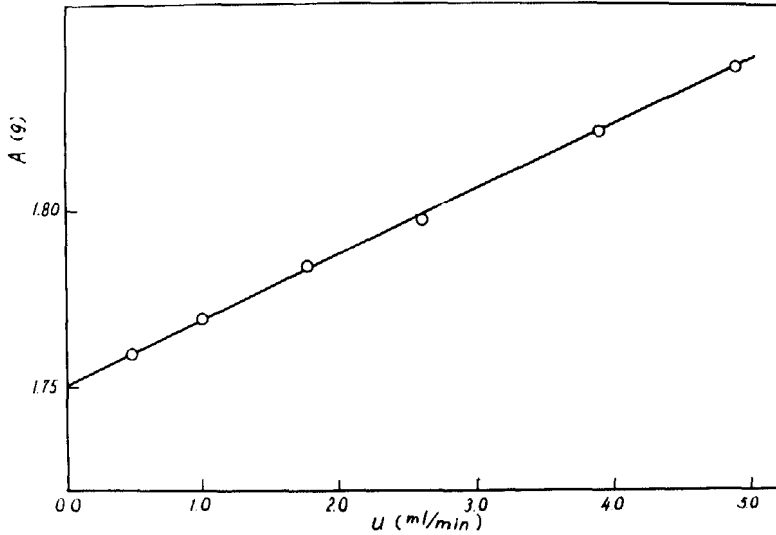


Figure 4. Flow rate dependence of discharged efflux

calibration curve. As the evaporation rate in the siphon chamber of the solvent used (THF) was very small (less than 0.4 ml/24 hr), its effect on elution is ignored. It was found that the corrected elution volume is independent of flow rate for all samples used, in the range of 0.5 to 5.0 ml/min on porous silica columns, as shown in Figure 5.

The GPC calibration curve is given in Figure 6, from which the void volume is obtained ($V_0 = 68.5$ count). The total permeation volume, $V_0 + V_i$, is equal to the elution volume of benzene ($V_0 + V_i = 150.1$ count). Thus, the pore volume V_i is equal to 81.6. Using these data, the distribution coefficient K for all standards were calculated.

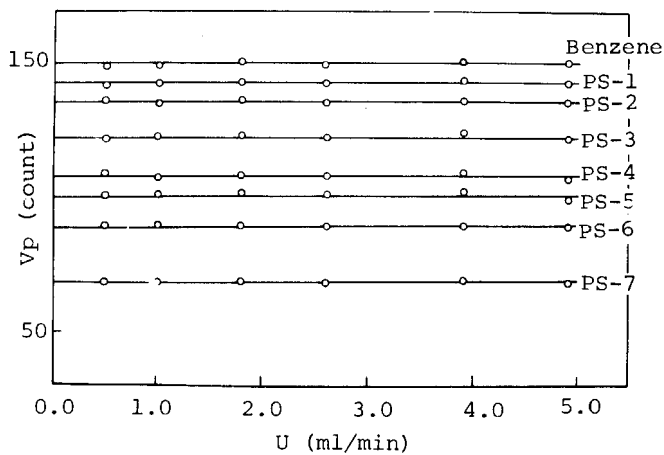


Figure 5. Flow rate dependence V_p on porous silica columns

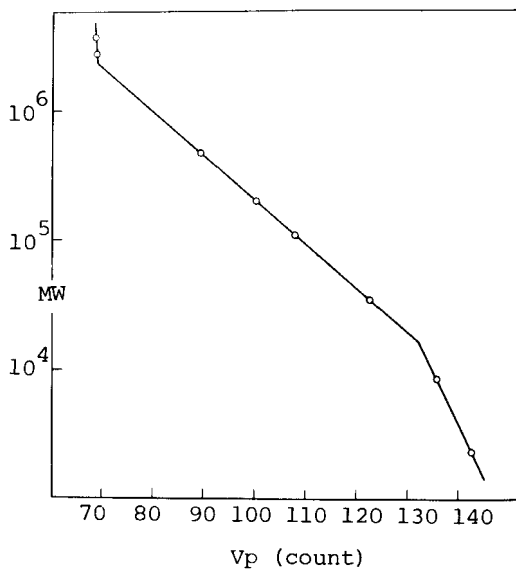


Figure 6. GPC calibration curve of porous silica columns

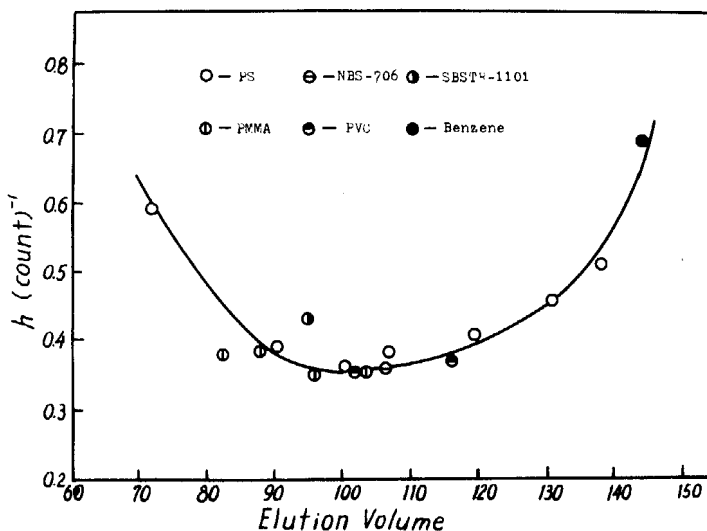


Figure 7. Variation of parameter h with elution volume

4) Zone Broadening Effect on Porous Silica Columns

The broadening parameter h of seven PS standards, four PMMA samples, two PVC fractions, a broad MWD sample PS NBS-706, a SBS TR-1101 copolymer and benzene were determined by using reverse flow method. Figure 7 shows the observed h parameter as a function of elution volume. All points fall on a single curve. This is in agreement with Tung's experimental result (3) that the relationship between h and V_p is universal, independent of chemical structure and MWD of samples.

The relationship between parameter h and distribution coefficient K was determined at different flow rates as shown in Figure 8. It shows that the value of h is strongly dependent upon flow rate. However, these curves are very

similar in shape for different flow rates except for smallest two. This means that $h(V_p)$ (or $h(K)$) functions are defined primarily by pore structure of the packing materials. Recently Wenner and Halasz reported the result of a study of the relationship between the zone broadening effect and pore size distribution of stationary phase. These authors found that the plots of plate height vs relative molecular weight, and of pore volume frequency vs

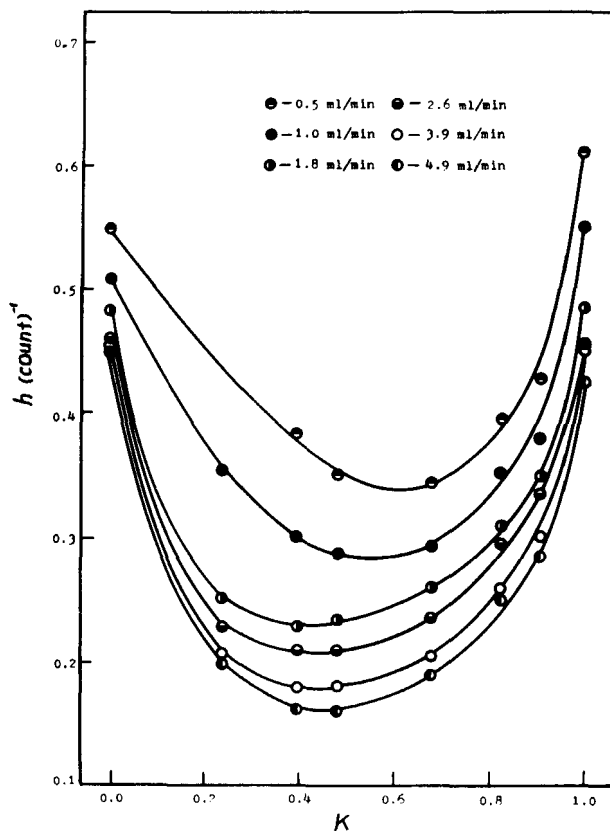


Figure 8. Flow rate dependence of $h(K)$

pore diameter showed very good agreement. The results of that paper and of the present work complement each other.

5) Effect of Reverse Flowing Process on Zone Broadening with Porous Silica Columns

As described above, for the nonporous glass bead columns, the parameters h and h' for benzene on porous silica columns were determined from reverse flow and straight through flow chromatograms obtained at different flow rates. For all flow rates $h > h'$ are obtained, and Δ as a function of flow rate U is given in Figure 9. It reveals that the difference between h and h' decreases with

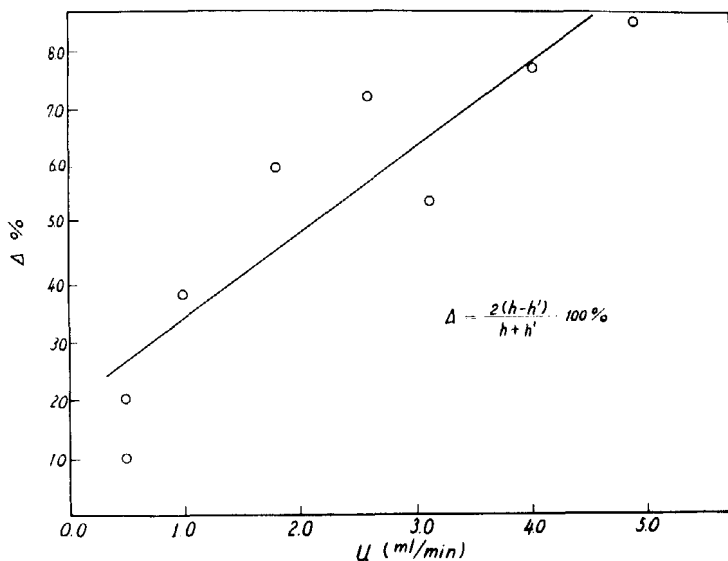


Figure 9. Variation of Δ for benzene with flow rate on porous silica columns

decreasing flow rate in agreement with the result obtained for nonporous glass bead columns. Therefore the explanation based upon the assumption of velocity profile disturbance during the reverse flowing process is valid in this case. The inequality of h and h' obtained for benzene ought to be expected for polymer samples. The fact that $h > h'$ indicates that the use of the h value obtained from the reverse flow method to correct the zone broadening effect may lead to slight underestimation. However, this effect may be ignored when experiments are run at low flow rate.

CONCLUSION

The experimental results show that polymer samples may separate in the mobile phase of GPC columns according their molecular weights; thus, a factor reflecting a sample's polydispersity ought to be added to the plate height equation describing mobile phase dispersion. After correcting for the syphon volume, the elution volume is independent of flow rate in the range of 0.5 to 5.0 ml/min on porous silica columns. The relationship between h and V_p (or K) is universal, independent of chemical structure and MWD of polymers. The curves of h (K) are similar in shape for different flow rates. The broadening parameter, obtained from a reverse-low chromatogram, h , is larger than that obtained from a straight-through-flow chromatogram h' for benzene on both nonporous and porous packing columns. This fact indicates the use of the h value obtained from the reverse-flow method may lead to slight underestimation of

the zone broadening effect in GPC. But this influence may be ignored when the GPC experiments are run at low flow rates.

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