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The Effects of Flow Rate and Column Combination on the Separation Efficiency in Multicolumn Gel Permeation Chromatography

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Synopsis

Using general-purpose multicolumn sets, it was found that separations could be increased by increasing analysis time, either by decreasing flow rate or increasing column length. Several examples are shown illustrating the influence of these system variables. The generation of linear calibration curves over extended molecular weight ranges is discussed. In particular, the desirability of using high molecular weight standards to extend the calibration curve and eliminate extrapolation of the curve is shown. Not using all available gel porosities, i.e., gapped column sets, is shown to be detrimental to the resolution of molecular species. It was found that with the use of sufficiently long column lengths and low flow rates, accurate molecular weights of both narrow and broad molecular weight distribution samples are directly calculable from the chromatogram without the need for peak spreading corrections.

INTRODUCTION

Gel permeation chromatography (GPC) has found widespread acceptance as a characterization tool because of the speed with which it can generate a visual picture of the molecular weight distribution (MWD) of a sample from which molecular weights can be calculated through the proper calibration of the columns used. Because of the attractive rapid analysis time, much of the research work done with GPC has dealt with possible ways to decrease analysis time, usually by increasing flow rate or by decreasing column legth. However, it has been our experience that more information can be obtained by increasing analysis time and, conversely, that decreasing the analysis time by the usual means produces often misleading and sometimes useless data.

It has been shown that reducing the flow rate can greatly improve resolution.[1,2] However, many of the flow rate studies reported in the literature have been done on short columns with narrow porosity ranges, usually to allow a more fundamental interpretation of the results connected to the gel porosity. As a consequence, it is difficult for the GPC user to ascertain *a priori* the extent to which general-purpose, multicolumn sets will respond to changes in the flow rate. In addition, how the multicolumn set is best assembled to perform specific sepa-

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rations has received scant attention in the literature. One example is a study by Slagowski and co-workers[3] who found a column set which had a linear calibration of at least 10^7 g/mole for polystyrene samples of narrow molecular weight distribution.

Because of these disparities, we feel it appropriate to comment here on our approach to the use of GPC to fulfill our characterization needs. Specific examples will be shown where, although the analysis time is increased relative to that of so-called "normal" conditions, system variables such as flow rate and column combination are tailored to optimize the GPC separation.

EXPERIMENTAL

The Waters Ana-Prep, 100, 200, and 501 gel permeation chromatographs were used with up to twelve 4-ft Styragel columns. The porosities of these columns ranged from 50 to 10^7 Å. The solvent used was either tetrahydrofuran or chloroform at a temperature of 25° or 40°C. The detectors used were the Waters UV and differential refractometer instruments. Solution concentrations were 0.25% (w/v) or less. Flow rates of 0.25 and 1 ml/min were used. Full-loop (2 ml) injections were made. The Ana-Prep instrument was equipped with a 5-ml syphon, while the other instruments had 2.5-ml syphons. These syphons were covered and the syphon chambers saturated with solvent vapor in order to minimize solvent evaporation at the 0.25 ml/min flow rate.

A seven-column set with a porosity range from 2×10^3 to 5×10^6 Å was used to obtain most of the data presented in this paper. This column combination had a plate count of 750 ppf at the 1 ml/min flow rate and a value of 950 ppf for the 0.25 ml/min flow rate.[4]

Column calibrations were carried out with commercial polystyrene standards and polystyrenes synthesized and characterized in these laboratories.[5] Other polystyrenes[6] and the poly(α-methylstyrene), polybutadiene, and poly(n-butyl isocyanate) samples were synthesized and characterized in these laboratories[5,6] and at the National Bureau of Standards.[6,7] In the main, these samples were obtained from termination-free anionic polymerization systems.

The synthetic polyisoprene was the Natsyn 2200, a commercial material prepared by a Ziegler–Natta catalyst. Hence, this sample may contain some branched material. The microstructure was virtually 100% *cis*-1,4.

The oligomeric ($<3 \times 10^2$ g/mole) polybutadienes were separated by vacuum distillation under high vacuum from commercial, polydisperse low molecular weight polybutadienes. The molecular weights of these fractions were determined by the MC-2 mass chromatograph (Chemalytics Crp.).[8]

Polystyrene, PS-6, was synthesized using a difunctional initiator made from 2,4-hexadiene and lithium.[9] Some termination probably took place at the outset of the polymerization thus causing the development of a bimodal molecular weight distribution.

DISCUSSION

Generation of Linear Calibration Curves

Figure 1 shows a calibration curve constructed with the usual commercial polystyrene standards. For the typical four-column set used here, the familiar

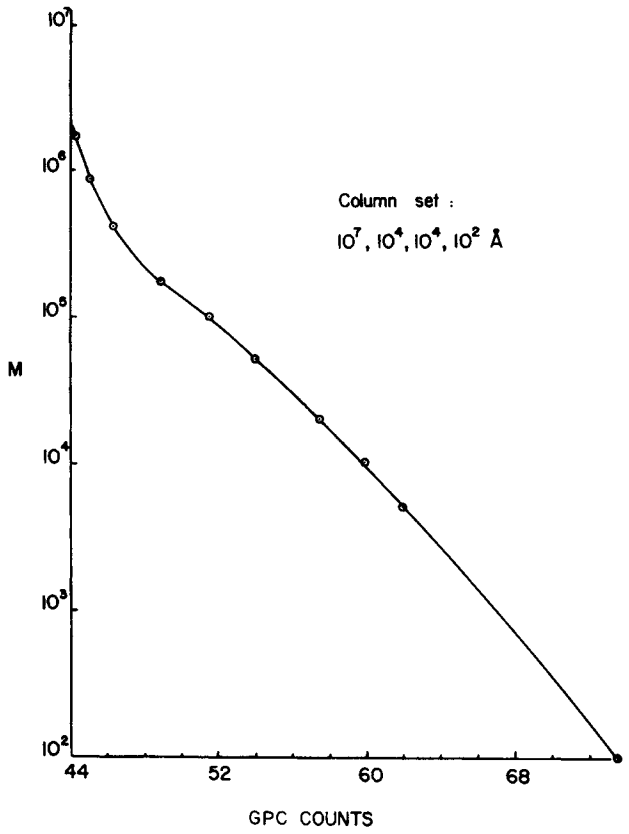

Fig. 1. S-Shaped Polystyrene Calibration Curve for a "gapped" four-column set (1 count represents 2.5 ml). Flow Rate, 1 ml/min.

S-shaped calibration is obtained where resolution is lost at both high and low molecular weights. This degree of resolution is usually sufficient if rather average samples are analyzed which elute within the region of optimum resolution between 50 and 64 counts. But if the sample elutes in the high molecular weight region of 44 to 50 counts, or in the low molecular weight region of 64 to 74 counts, resolution will be reduced, as suggested by the more vertical slopes. What can be done in these cases is to change the column set to concentrate more on the specific molecular weight range to be fractionated. That is, the idea is to flatten out the calibration curve by increasing the resolution. For example, a column set was assembled specifically for high molecular weights. In Figure 2, the column set can be seen to maintain adequate resolution clear up to 10^7 g/mole and possibly beyond.

Since the slopes above and below 10^6 g/mole are the same, this illustrates that it is possible to get as good a resolution for the high molecular weight species as is normally obtained at lower molecular weight. The asymptotic region of Figure 1 is extended to a much higher molecular weight region. However, to accomplish this, a rather cumbersome ten-column set was needed which was weighted heavily to the high-porosity packings. This increased the analysis time, but the resolution range was greatly extended. Resolution in the low molecular weight region is possible also. In Figure 3, a special twelve-column set designed to enhance

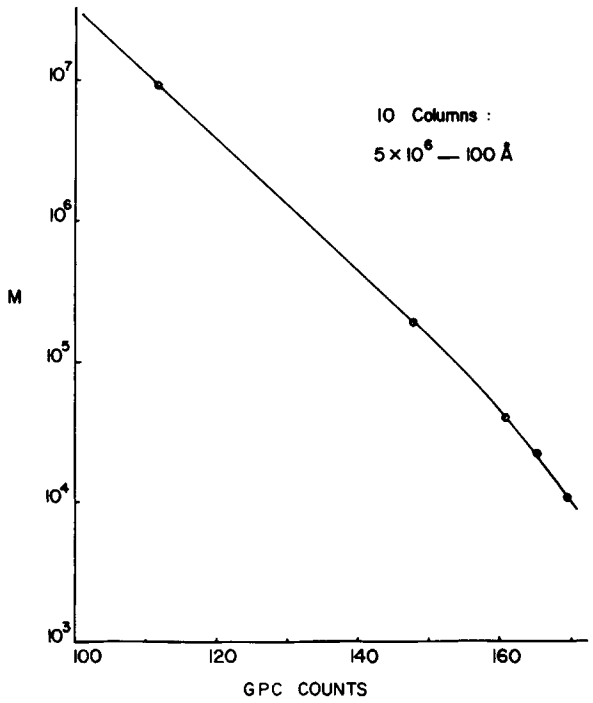

Fig. 2. Polystyrene calibration curve for a ten-column set (1 count represents 2.5 ml). Flow rate, 1 ml/min.

the oligomeric range had a linear calibration curve down to 160 g/mole. The slope of the line is the same over the entire molecular weight range, indicating a constant degree of resolution.

Use of High Molecular Weight Standards

The ability to separate high molecular weight components is demonstrated in Figure 4. A commercial high molecular weight, broad molecular weight distribution polyisoprene was fractionated on a column set similar to that of Figure 2. Inserted on the high molecular weight end of the chromatogram are the polyisoprene molecular weights at four different retention volumes. It was apparent that this sample had a large percentage of high molecular weight material. However, with the use of high molecular weight standards, much more of the chromatogram was explicitly defined than if the 2×10^6 molecular weight polystyrene standard were the highest standard used. This point deserves some further comment here. Most GPC workers do not use high molecular weight standards but rather rely on extrapolation of a calibration curve from the available low molecular weight (2.6×10^6) data points into the region of higher molecular weight (e.g., an extension of a calibration line such as in Fig. 1). Extrapolation in this region is risky, especially if the calibration curve is curving upward rapidly as it usually is. This is because extrapolation procedures are usually based on fitting data points eluting in one region to some mathematical function, even though the behavior of this function in another region outside of the data points (where resolution may be decreasing) is not necessarily related

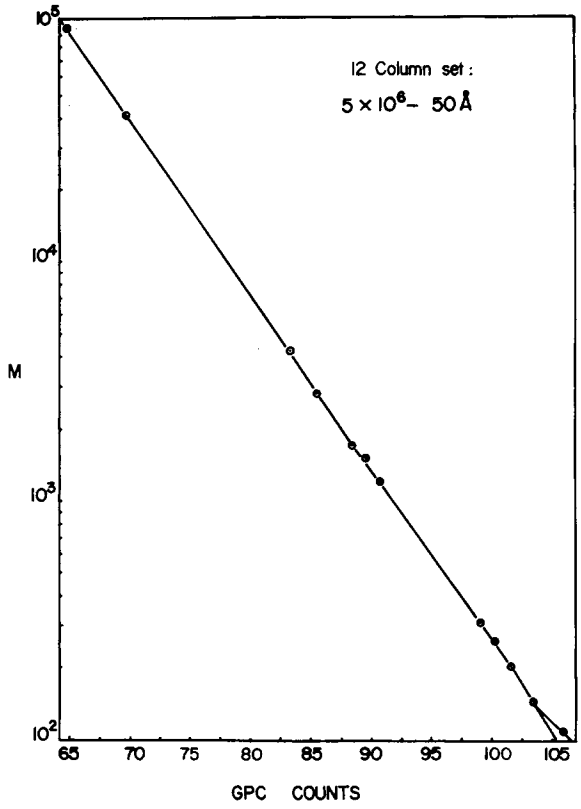

Fig 3. Polybutadiene calibration curve for a 12-column set in the low molecular weight region (1 count represents 2.5 ml). Flow rate, 1 ml/min.

to that of the interpolated function. Hence, it is relatively ineffective to eliminate the drawback of curvature in the calibration by building a linear calibration to fractionate higher molecular weights if there is no means to calibrate this high molecular weight region. It is useful to use high molecular weight standards as data points. This allows interpolation instead of extrapolation of the calibration curve. In this way, the entire chromatogram of Figure 4 is defined.

Both points, linear calibration curves *and* high molecular weight standards,

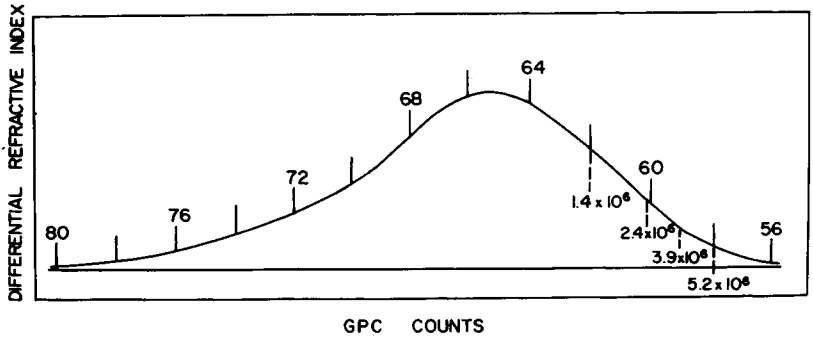

Fig. 4. Chromatogram of a high molecular weight synthetic polyisoprene (1 count represents 2.5 ml). Flow rate, 1 ml/min.

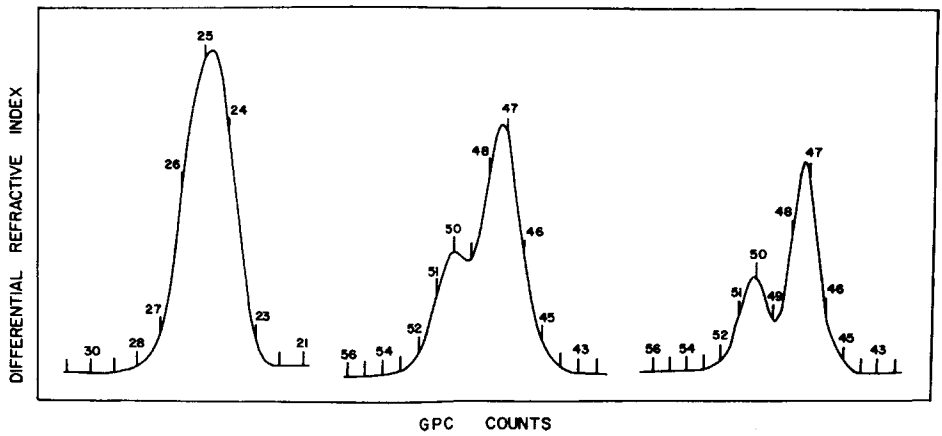

Fig. 5. Chromatograms of bimodal polystyrene, PS-6. The third chromatogram was obtained at a flow rate of 0.25 ml/min; (1 count represents 5 ml).

illustrate that column sets must be tailored to the specific separation to be done. To get the most out of the separation, long column sets are needed. Time will have to be sacrificed to achieve these types of separations, but it can be done if so desired. The accuracy of the calibration curve can be improved by developing linear calibration curves and using high molecular weight standards to extend the interpolation of the calibration curve.

Effects of Column Combination, Column Length, and Flow Rate

To obtain an adequate molecular weight separation, the molecular weights of the separated species must be properly matched to the pore size of the gel packing. High molecular weight polymers cannot be fractionated by tight-porosity packings nor can oligomers be separated by the high-porosity packings. In the same context, when assembling a multicolumn set, if a continuous transition of gel packings is not achieved by linking all the available gel packings together, "gaps" are created in the column set. Using a "gapped" column set as a general-purpose column set, e.g., Figure 1, can lead to misleading results, especially when analyzing narrow molecular weight distribution samples that would have been fractionated by the missing column porosities. To illustrate what could happen, the first two chromatograms of Figure 5 are the GPC curves of the same polystyrene sample, PS-6, run on two different column sets at the same flow rate. The first column set (with the same column arrangement shown in Fig. 1) was gapped, and the chromatogram appeared at first glance to be fairly monodisperse with a slight shoulder on the low molecular weight side of the peak. When the sample was chromatographed on the second column set (seven columns with a porosity range of 5×10^6 to 2×10^3), this one not gapped, separation of two species was clearly indicated in the second chromatogram. To be sure, to some extent the improvement in separation was due to the longer column length of the second column set and to the switch from chloroform to tetrahydrofuran, but the important variable here was the influence that gapping made. What probably happened in generating the "one-peak" chromatogram was that the sample was of a molecular weight range that was above the permeation limit of

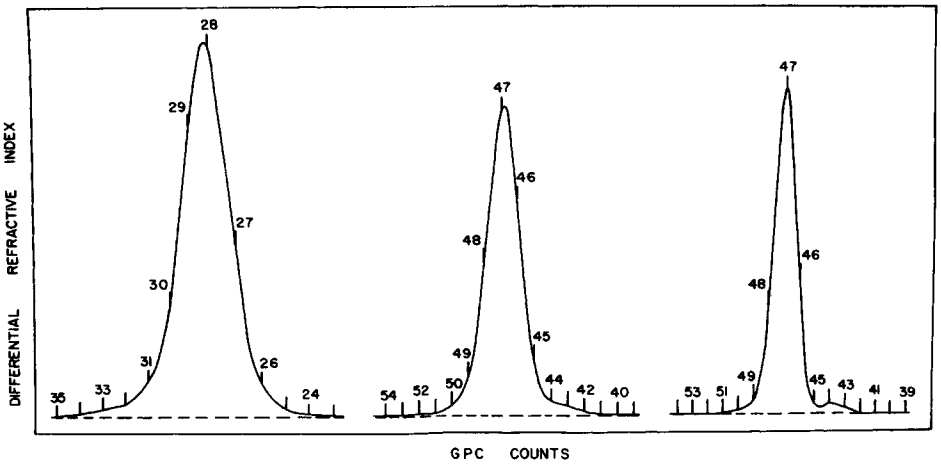

Fig. 6. Chromatograms of the NBS 705 polystyrene. The third chromatogram was obtained at a flow rate of 0.25 ml/min; (1 count represents 5 ml).

the small porosity columns and yet was capable of total permeation in the high-porosity columns. There was no column available to perform an adequate separation on this sample. This seriously inhibited the separation of this narrow MWD sample, and would be expected to influence the chromatograms of broad MWD samples as well.

Consider now the effect that the column length has on the separation. By increasing the column length, resolution usually increases. For example, Figure 6 shows three chromatograms of polystyrene standard NBS 705. The first chromatogram was obtained on a four-column set (no gaps), while the second was from a seven-column set (both at 1 cc/min). The presence of a high molecular weight component was indicated on the chromatogram from the longer column set. (The third chromatogram, obtained by lowering the flow rate of 0.25 cc/min on the seven-column set,[10] revealed a clearly resolved component of twice the molecular weight of the main peak.) Resolution was increased by increasing the column length. This effect is to be expected. The equation for the plate count of a column,

$$P = \frac{16}{f}\left(\frac{x}{d}\right)^2 \tag{1}$$

is widely used as an indicator of the performance of a column or column set, where P is the resolution factor in plates/foot, f is the column length, x is the elution volume of the eluted peak, and d is the width of the eluted peak. When the column length f is doubled while P is held constant, the length of the interval between the void volume and total permeation volume (the width of the calibration curve) is doubled, as is x. When this happens, d increases only by $\sqrt{2}$, the net effect being that the width of the peak becomes effectively narrower and an increase in resolution is indicated. Thus, just by increasing the column length, resolution is improved. This is one way to increase the accuracy of molecular weight calculations from GPC measurements, even for narrow MWD samples. The need for resolution corrections can be minimized or even eliminated in this way.[11]

The first two chromatograms of Figures 5 and 6 were both generated at a flow rate of 1 ml/min. It is clear that the elimination of gaps in the porosity range covered markedly enhanced resolution. One other way[1,2] to increase resolution is to decrease the flow rate. In the third chromatograms of Figures 5 and 6, the flow rate was lowered to 0.25 ml/min. A further increase in resolution is indicated. The high molecular weight component (counts 42–45) seen in the chromatogram of the NBS 705 corresponds to an $\langle M_n \rangle$ of 3.3×10^5 g/mole and an $\langle M_w \rangle$ of 3.5×10^5 g/mole. This "dimer" of the parent material may be the result of the presence of carbon dioxide or oxygen during the termination of this anionically prepared polystyrene. These species can cause the coupling of organolithium compounds.[12,13]

It is germane to note that recently published chromatograms[14] of the NBS 705 polystyrene fail to show the coupled product present in the two chromatograms of Figure 6. This is probably due to the fact that too few columns were used in the analysis by the National Bureau of Standards.

Thus, it is apparent that multicolumn sets are sensitive to changes in flow rate. These findings are not new,[1,2] but Figures 5 and 6 serve to illustrate the importance of using not only the proper column set and the proper gel packings but also the improvement of resolution that can be achieved by a decrease in the flow rate. Hence, GPC separations can be improved by optimizing either one or both of these techniques. An increase in analysis time will result, but more information and, more importantly, more correct information will be obtained.

A general view has been established that GPC data can only be rendered accurate after suitable dispersion corrections have been performed. As a result, corrections for imperfect resolution in GPC have been developed.[15–17] An outcome of our work has been the result that accurate data can be generated on near-monodisperse and polydisperse samples without the need for dispersion corrections. This can be achieved through the proper choice of column length, porosity combination, and rate of flow.

McCrackin[11] (using polystyrene chromatograms generated on our seven-column set) has calculated the p factor (which represents the resolving power for a set of columns) to be 0.98 at a flow rate of 1 ml/min, while at the 0.25 ml/min flow rate the value of p is 0.99. For ideal resolution, p is equal to 1. Hence, McCrackin's analysis demonstrates that corrections of the molecular weight averages obtained by integrating the chromatograms obtained from the seven-column set are of a trivial nature. His conclusions are fortified by the good agreement between the values of $\langle M_n \rangle$ and $\langle M_w \rangle$ in Table I obtained from GPC and absolute measurements for a series of polystyrenes. These GPC results were obtained from chromatograms generated by the seven-column set. The samples cover a molecular weight distribution range of <1.1 to 2.1.

The synthesis of the polydisperse S-1 through S-6 polystyrenes was accomplished by the use of *tert*-butyllithium. We have found,[4] as has Hsieh,[22] that this initiator reacts slowly with styrene. The claim has been advanced[23] that highly purified *tert*-butyllithium will react rapidly with styrene. However, our work with the purified initiator consistently reveals that this organolithium reacts slowly with styrene in hydrocarbon solvents.[24]

It should be noted that the chromatograms of samples 28, 30, 31, and 31D were symmetrical. No bimodal character in the molecular weight distribution was found. The presence of a bimodal molecular weight distribution was a possibility

TABLE I
Molecular Weights of Polystyrene Samples

Sample[a]	Absolute molecular weight measurements				GPC molecular weights			
					0.25 ml/min		1 ml/min	
	$\langle M_n \rangle \times 10^{-3}$, g/mole	$\langle M_v \rangle \times 10^{-3}$ g/mole	$\langle M_w \rangle \times 10^{-3}$ g/mole[b]	$\langle M_w \rangle \times 10^{-3}$ g/mole[c]	$\langle M_n \rangle \times 10^{-3}$ g/mole	$\langle M_w \rangle \times 10^{-3}$ g/mole	$\langle M_n \rangle \times 10^{-3}$ g/mole	$\langle M_w \rangle \times 10^{-3}$ g/mole
28	149	197.7[d]	203	235	—	—	151	225
30	547.2	717.5	700	820	—	—	550	800
31	80.2	82.7	88	102	—	—	81	100
31D	88.8	82.7	89	102	—	—	85	95
S-6	27	42[e]	45	—	24	46	24	46
S-3	57	103	120	—	55	113	55	112
S-4	90	145	148	—	90	147	88	145
S-7	97	97	98	—	96	97	95	97
S-1	185	272	320	—	184	318	175	320
S-2	190	296	327	—	195	337	190	350
S-5	380	550	540	—	384	530	370	540
NBS-705	170.9	173[d]	179.3	189.8	169	179	167	179
NBS-706	<136.5	216	257.8	288.1	140	290	137	287

[a] Samples 28 to 31D were prepared by sodium naphthalene in tetrahydrofuran[6]; S-1 to S-6 by *t*-butyllithium in cyclohexane;[4] S-7 by *s*-butyllithium in cyclohexane;[4] NBS-705 by *n*-butyllithium in benzene;[18,19] NBS-706 by thermal polymerization in bulk.[20] The absolute molecular weights in this table are from references 4, 7, 18, 19, and 20.

[b] By light scattering.

[c] From sedimentation equilibrium.

[d] $[\eta]^{35°C}_{\text{cyclohexane}} = 8.5 \times 10^{-4} M^{0.5}$ (ref. 21).

[e] $[\eta]^{30°C}_{\text{benzene}} = 8.5 \times 10^{-5} M^{0.75}$ (ref. 21).

in view of the fact that the initiator, sodium naphthalene, will form difunctional chains. Partial termination would then lead to the creation of a contingent of active chains growing at one end only.

It was found that there is a molecular weight dependence of the change in elution volume with a change in flow rate. As can be seen in Figure 7, high molecular weight polymers will remain in the GPC longer at low flow rates than at higher flow rates; but at lower molecular weights, no change in retention volume is found. This gives some insight into the GPC separation mechanism.[25] A slower linear velocity of the polymer molecules down the column allows a longer residence time in front of each gel pore and provides a greater opportunity for the molecule to enter the gel pore only on the merits of its hydrodynamic size. At faster flow rates, molecules may be swept past a gel pore before they can enter it. Thus, the slower flow rate allows more of the molecules of the same molecular weight to follow the same paths through the column uninfluenced by extraneous effects caused by the linear velocity. This results in a narrowing of the peak due to a narrowing of the distribution of path lengths. All of these samples had $\langle M_w \rangle / \langle M_n \rangle$ of less than 1.1.

Other System Variables

There are other variables that can be utilized to improve resolution. For ex-

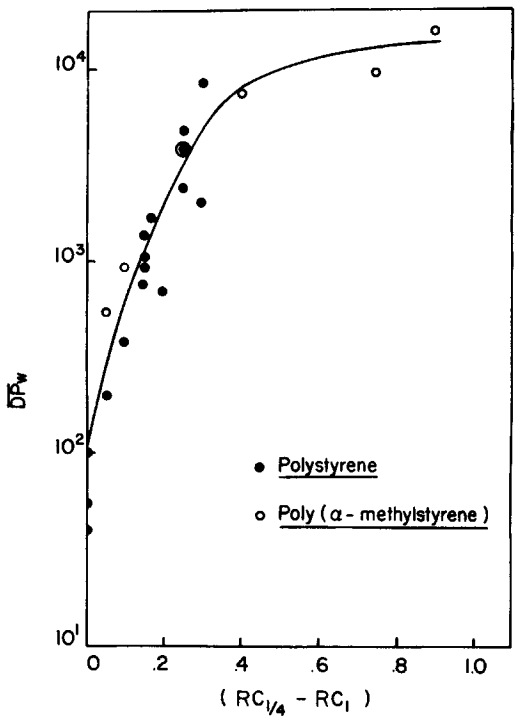

Fig. 7. Dependence of retention count (RC) on flow rate.

ample, the solvent plays a major role in the GPC separation. When all else is equal, it has been our experience that THF provides better resolution than chloroform, and toluene allows even less resolution. This has been pointed out by Cooper and co-workers.[1,2] Presumably this is related to the viscosity of the solvent (or perhaps to the solvent polarity and its influence on solute–gel packing adsorption). Resolution can also be increased by raising the temperature, thereby reducing the viscosity of the solvent. Another way of increasing resolution is by increasing the solvent power for the polymer. An increase in the Mark–Houwink coefficient a will result in a flatter molecular weight calibration curve.

Another variable influencing resolution is the posture of the polymer. For example, poly(n-butyl isocyanate)(PBIC) has the peculiar property of being a rigid rod (a = 2.0)[7,26] at molecular weights below 10^5; but at higher molecular weights, PBIC attains sufficient flexibility to warrant its description as a non-Gaussian, worm-like chain with a = 0.5. Thus, the conformation of PBIC is molecular weight dependent. For this reason, it was of interest to construct a calibration curve for this polymer in order to evaluate the effect that conformational changes can exert. Figure 8 is the PBIC calibration obtained[25] on the seven column set over a molecular weight range of 2.5×10^4 to 1.2×10^7. In Figure 8, the molecular weight calibration curve is seen to dramatically flatten for the more rigid PBIC chains, indicating an increase in resolution. For comparison, the dashed linear line represents the polystyrene calibration for this seven-column set. Parenthetically, it should be noted that the low molecular weight PBIC materials do not fit[27] the GPC universal calibration.[28] This

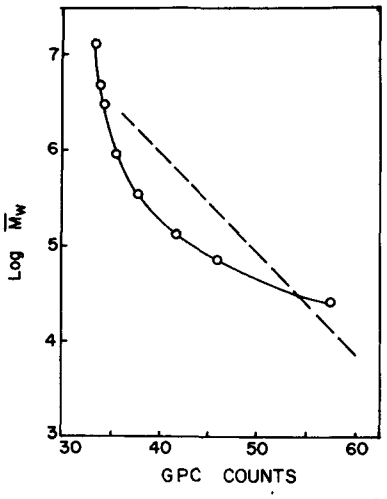

Fig. 8. Calibration curve for poly(*n*-butyl isocyanate) in tetrahydrofuran (1 count represents 5 ml). Flow rate, 1 ml/min.

finding[25,27] seemingly demonstrates that $M[\eta]$ can serve as a universal calibration parameter only when the molecular geometries involved are similar.

The effect of chain geometry regarding resolution in GPC can be seen in Figure 9, which contains the chromatograms of a rigid PBIC sample and a flexible polystyrene (Waters Associates 25168) possessing similar molecular weights and molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle$ less than 1.1). As can be seen, these two polymers exhibit radically different chromatograms even though both eluted in the same region. This aspect of the resolution question has not been emphasized in the past in the literature. Usually, this property is not one that can be altered or optimized, but it does contribute to the separation process.

Because of the rod-like shape of PBIC, part of this species is retained on the seven-column set for a longer time than the polystyrene. This leads to an increase in resolution and a decrease in the slope of the calibration curve (Fig. 8). However, at the same time, the PBIC shows a broad peak, relative to the polystyrene, for a sample with a narrow molecular weight distribution.[26] Obviously, increased rigidity has caused peak spreading. The elution behavior of this rigid species can be rationalized as follows. When the flow field in the columns pre-

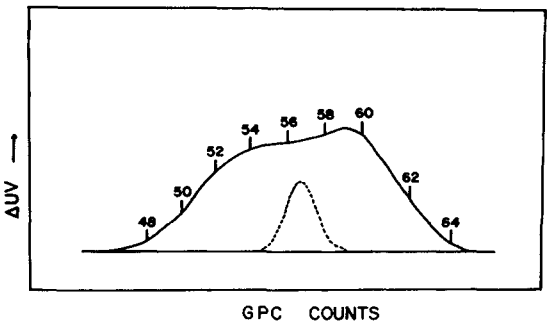

Fig. 9. Chromatograms of rod-like poly(*n*-butyl isocyanate) and polystyrene of the same molecular weight. Polystyrene $\overline{M}_w = 20.8 \times 10^3$; PBIC $\overline{M}_w = 25 \times 10^3$ (1 count represents 5 ml). Flow rate, 1 ml/min.

sents a rigid polymer to the entrance of a pore, the molecule can do one of three things, to wit: (a) enter the Styragel pore structure and become permanently stuck or held for a long period of time; (b) enter the pore structure and flow through; or (c) enter the pore structure, travel partly through, and then come back out. A combination of these three steps will thus place these rigid molecules at the next position in the column at different times, i.e., they will be spread out in the column. This is, in reality, the mechanism of peak spreading in all chromatographic separation processes whereby different molecules end up taking different paths through the column. Based on the chromatogram in Figure 9, it would appear that the stiffness of a chain affects the GPC separation mechanism to a significant degree. Hence, it would be expected that the more rigid the species, the greater the probability that (a) and (c) will occur; but with increasing flexibility, the probability of (b) occurring becomes much greater. This would then lead to less peak spreading. This has been observed[25,26] for PBIC chromatograms as the molecular weight and flexibility of this polyisocyanate increase.

CONCLUSIONS

All of the separate experiments presented herein contribute to the overall view that increasing the analysis time—either by increasing column length, increasing the number of pertinent columns used, or decreasing the flow rate—will increase the resolution. Multicolumn sets can be used advantageously for many types of separations by following these generalities. The use of linear calibration curves, high molecular weight standards, and long column lengths can improve the accuracy of the GPC experiments to the point that the GPC data can directly represent the polymer without the need for mathematical resolution corrections.

It should also be noted that the μ-Styragel columns afford an alternative route to enhanced resolution. Our experience with the PS-6 sample has apparently shown that a six-column μ-Styragel set with a porosity range of 10^2 to 10^6 Å and a flow rate of 1 ml/min is equal in resolving power to the seven-column set at the same rate of flow. The addition of a recycling step would doubtlessly lead to increased resolution from the μ-Styragel column set.

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