

Practical Applications of GPC of Interest to the Polymer Chemist

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Synopsis

Five examples are discussed showing how gel permeation chromatography was applied to studies of polymer systems. The calculation of molecular weights from the curves was not pertinent to the studies. The only requirement was that the separation be a size separation and the results be reproducible.

INTRODUCTION

Gel permeation chromatography (GPC) was first introduced in the form of a commercial instrument a little over two years ago. Nearly thirty papers have been presented or published on the subject since that time. Mostly these papers are concerned with one of the following three subjects: Comparison of the GPC distribution curve with one obtained by a solution technique;¹⁻³ Mathematical treatment for bringing GPC data in closer agreement with other solution techniques;⁴⁻⁶ Explanation as to the nature of the separation and the effect of variables on the separation.⁷⁻⁹ All of these are valuable contributions to the proper understanding and use of the GPC technique. However, there are valuable uses of the technique which do not require the curve to be exactly correct nor do they require the calculation of any molecular weight average. All that is required is the separation be a size separation and the results be reproducible. Moore and Hendrickson¹⁰ give experimental proof of size separation in their paper "The Nature of the Separation." More recently, Smith and Kollmansbueger¹¹ offered evidence to indicate that the molecular volume is the important parameter influencing the degree of separation. Hill¹² has shown that the standard deviation for 18 determinations on a polymeric system was 1.03% for M_w and 6.8% for M_n . Different column combinations were employed. We made a reproducibility study on an ethylene-propylene terpolymer. Six runs were made using manual injection and seven runs using automatic injection. The standard deviation was 1.2% for M_w and 3.1% for M_n . Five columns ranging from 10^2 to 10^6 Å. were used for all runs.

Examples of five studies are discussed. The studies contributed information of practical use to our polymer research staff.

EXPERIMENTAL

A. Study of the Mastication of Elastomers

A study was made of the changes that occur in molecular weight distribution during the mastication of natural and SBR rubber. The changes were then compared with stress relaxation data and mill processing behavior. Part of this work has been reported by Jacobs and Harmon.¹³

Pike and Watson¹⁴ studied the cold mastication of natural rubber. They concluded that "degradation is caused by mechanical rupture of primary carbon-carbon bonds to give polymer radicals (R·). The radicals are stabilized by oxygen to give degraded polymer molecules." This has been verified spectroscopically. Angier, Chambers, and Watson¹⁵ cold-masticated natural rubber and determined a viscosity-molecular weight relationship. They also advanced a mechanism of rupture above a critical molecular weight.

The GPC curves for natural rubber are shown in Figure 1. As the polymer is milled the distribution is narrowed and the peak molecular weight shifts lower and lower. However, there is only a relatively small change in peak from sample C (38 min.) to sample F (76 min.). The low end of the distribution remains nearly unchanged. The appearance of the hump in sample B is best explained as follows. There is a gel fraction in natural rubber which is removed in the process of filtering sample A. The large molecules are preferentially broken. The hump in B is the result of breaking these "gel molecules" to a low enough size to pass the filter. As more and more are broken the peak gets larger and begins to shift down scale as

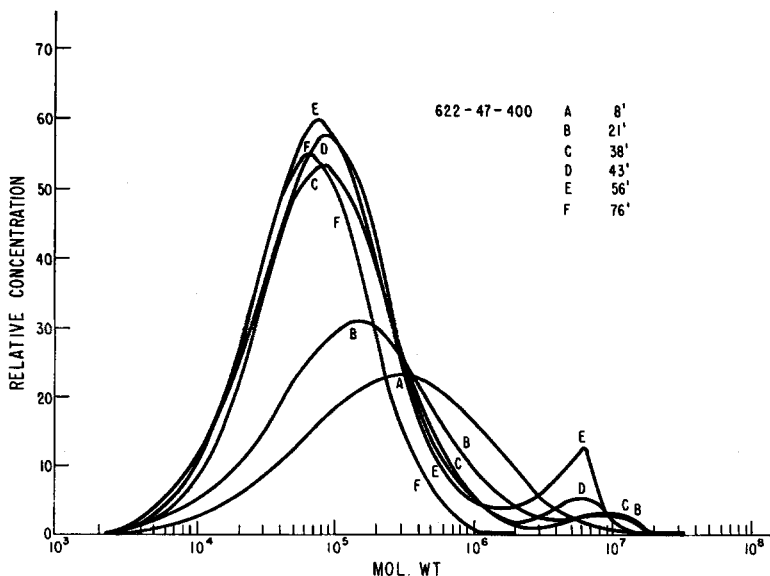


Fig. 1. GPC distribution curves on natural rubber as a function of milling time.

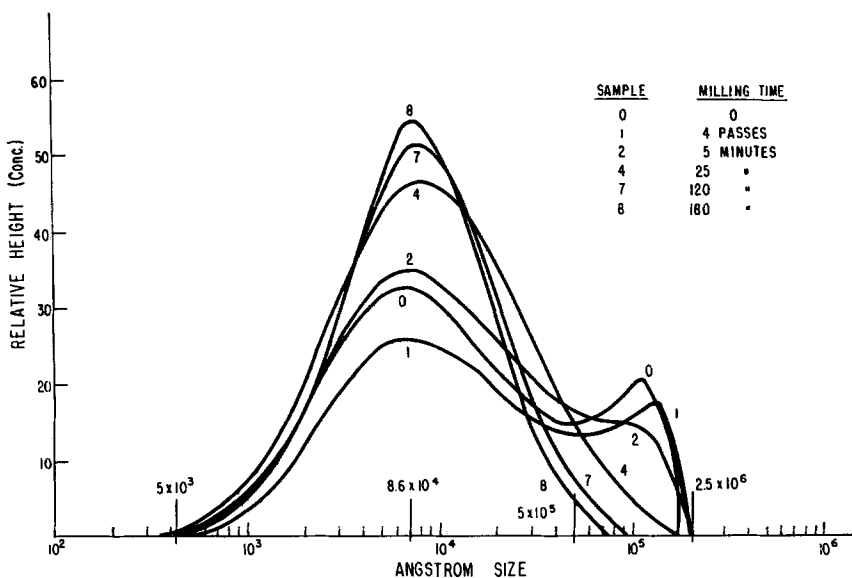


Fig. 2. GPC distribution curves of SBR as a function of milling time.

more than one break is introduced per original gel molecule. Finally, in sample F all of the molecules have been broken to the point that they fall within the main peak.

Frenkel¹⁶ deduced that a polymer chain length greater than a critical value, X_0 , becomes extended when sheared and eventually ruptures at a bond near the center section to give segments of length $X_0/2$. Molecules less than X_0 are not considered ruptured under a given set of shear conditions. Support for Frenkel's theory is the similarity in shape and near coincidence of the low molecular weight half of the distribution curve. It is also interesting to note that the peak and angstrom size from A to B represents a decrease by a factor of about 2 as does the size difference from B to C.

Examination of the GPC curves obtained on a series of milled SBR samples reveals striking differences from the curves of natural rubber. (Fig. 2). Milling conditions were the same as for natural rubber. The gap was about $1/8$ in. and no heat was applied. In the case of SBR the batch heated up to 210°F. after 180 min. of milling. The original sample of SBR (O) shows a hump at the high end after filtering in contrast to no hump for natural rubber. As milling progresses the hump gets smaller until it finally disappears (sample 4, 25 min.). There is very little shift in the peak and what there is seems to indicate the peak first goes up then down. In comparison natural rubber shows a steady decrease in peak position.

It is apparent in both cases that the large molecules are preferentially broken. The data shows the distribution of the SBR to be less affected by milling than that of natural rubber. The critical molecular weight or

length of SBR may be above the peak weight of the sample while that of natural rubber was below the peak weight. In the case of SBR, oxygen may be playing less of a role in termination than in natural rubber. Therefore, chances for recombination are greater and could account for the slight increase in peak position. While natural rubber contains its own stabilizers, SBR has stabilizer added during polymerization. This could cause a difference in the effect of oxygen.

B. Use of GPC to Make Controlled Distributions by Blending

Two samples of SBR were analyzed as to molecular weight distribution by use of GPC. One was medium high Mooney viscosity polymer (A) and the other a low Mooney viscosity polymer (D). (Fig. 3). Two blends were prepared. The first (B) was 75% A and 25% D. The second (C) was 50% A and 50% D. The distributions of B and C were first calculated from the GPC curves for A and D. The actual curves were then run and compared with the calculated curves (Figs. 4 and 5). It is seen that

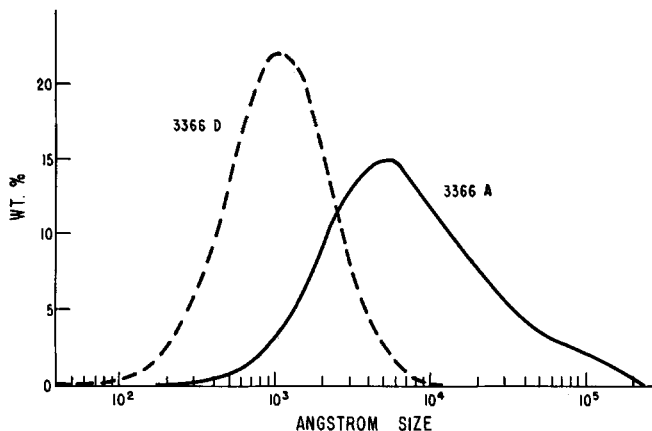


Fig. 3. GPC distribution curves of a high and a low Mooney SBR.

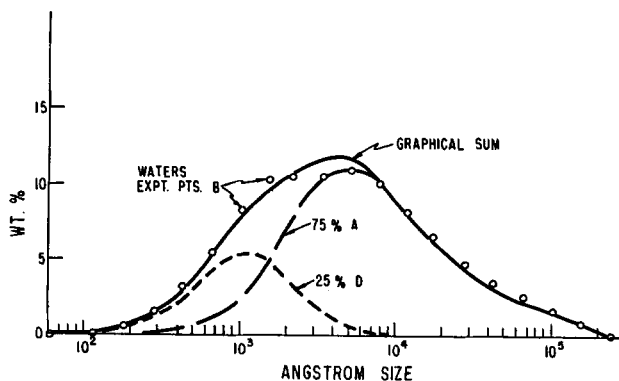


Fig. 4. Experimental and calculated GPC curve for a 75A/25D SBR blend B.

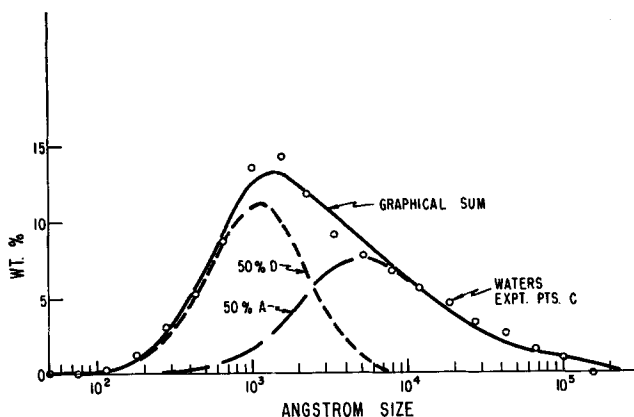


Fig. 5. Experimental and calculated GPC curve for a 50A/50D SBR blend C.

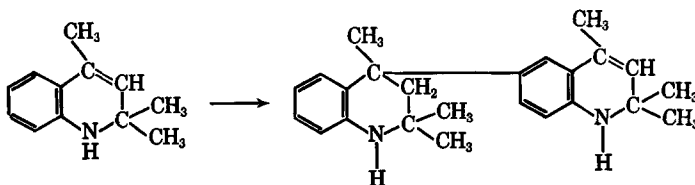
there is good agreement between the calculated and measured curves. Table I shows the agreement between some of the calculated and measured values. This technique permits preparation of blends of polymers with certain desired distributions. These blends will then be studied as to their processing behavior and cured physical properties. While blending to obtain a specified Mooney or limiting viscosity number has always been possible, one could not control the width or shape of the distribution curve.

TABLE I
Comparison of Calculated and Measured Weight Distributions of Polymer Blends

Wt. distribution	A		B		C		D
	Exp.	Exp.	Calc.	Exp.	Calc.	Exp.	
10^2 - 10^3 Å.	6	19	$18\frac{1}{2}$	31	31	57	
10^3 - 10^4	65	57	60	53	$54\frac{1}{2}$	43	
10^4 - 10^5	28	23	$20\frac{1}{2}$	16	14	0	
10^5 - 10^6	1	1	1	0	$\frac{1}{2}$	0	
Mooney 4 ft./212°	74	19		14		1	

C. The Effect of Molecular Weight Distribution on the Melting Point of Poly-2,2,4-trimethyl-1,2-dihydroquinoline

Several companies produce an antioxidant which is formed by the polymerization of 2,2,4-trimethyl-1,2-dihydroquinoline (TMDHQ). The polymerization has been shown to proceed primarily through the transfer of hydrogen.



Melting points have been reported on the commercial products ranging from about 80–120°C. The molecular weight distribution was analyzed in an attempt to gain some insight into the reasons for the differences. Monomer (M.W. = 173) and dimer were mixed with a laboratory-prepared polymer. The mixture was put through three GPC columns of 500, 100,

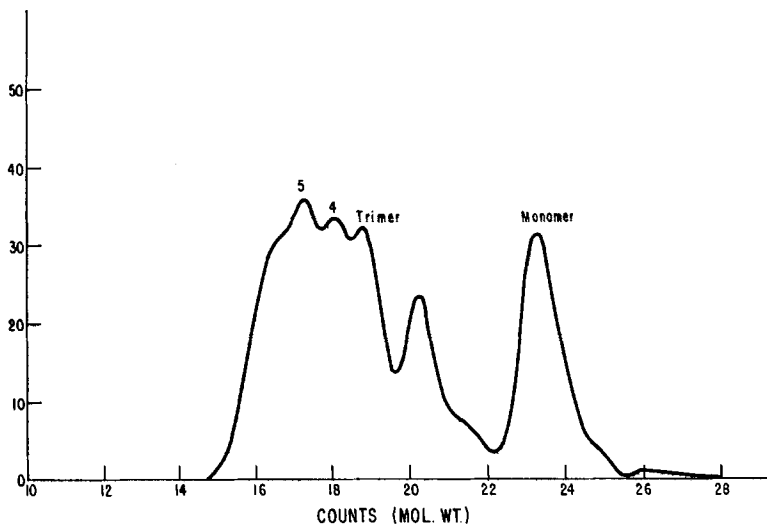


Fig. 6. GPC curve on calibration mixture monomer, dimer, and polymerized TMDHQ.

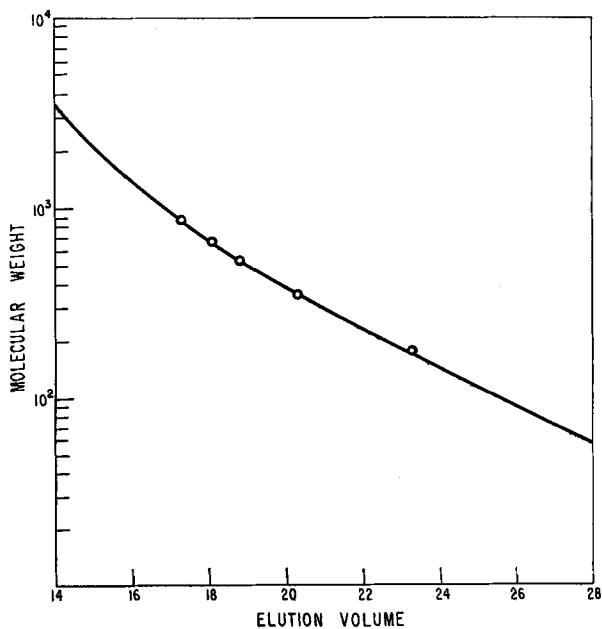


Fig. 7. Calibration curve for TMDHQ. Molecular weight vs. elution volume.

and 40 Å pore size. Each succeeding peak was considered as the next higher degree of polymerization (Fig. 6). A calibration curve was prepared from this data (Fig. 7). The curve is nearly linear.

A production sample of TMDHQ was then analyzed. The sample had a softening point of 79–80°C. The sample was found to consist of an appreciable amount of monomer and dimer (curve A, Fig. 8). Stripping off the low molecular weight material resulted in a product with a softening point of 110–113°C. (curve B, Fig. 8). The stripped polymer contained 40% less monomer and dimer than the original sample.

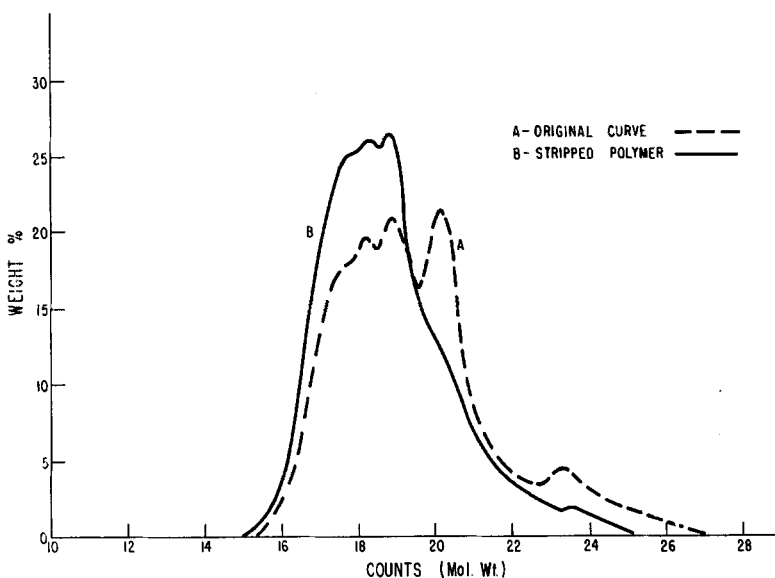


Fig. 8. GPC curves on production TMDHQ before and after stripping.

D. The Effect of Addition of Hydrogen on the Molecular Weight Distribution of an Experimental Copolymer

Polymerization of an ethylene-propylene copolymer resulted in a material containing a high amount of gel and poor processing characteristics. Hydrogen had been employed as a molecular weight modifier. Measurement of the molecular weight distribution by GPC revealed a hump at the high end of the curve. (Fig. 9, sample 657-3). The hump is characteristic of polymers containing molecules too large to be separated by the columns. The highest column used was a 10⁶ Å. A distribution curve which did not contain the hump resulted from increasing the rate of addition of hydrogen (657-8). The peak of the curve was shifted toward lower molecular weight. Further increase in the rate of hydrogen addition resulted in a further shift toward low molecular weight (657-13). The molecular weight values calculated from the curves are given in Table II. Hydrogen addition resulted in a lowering of the molecular weight and a narrow-

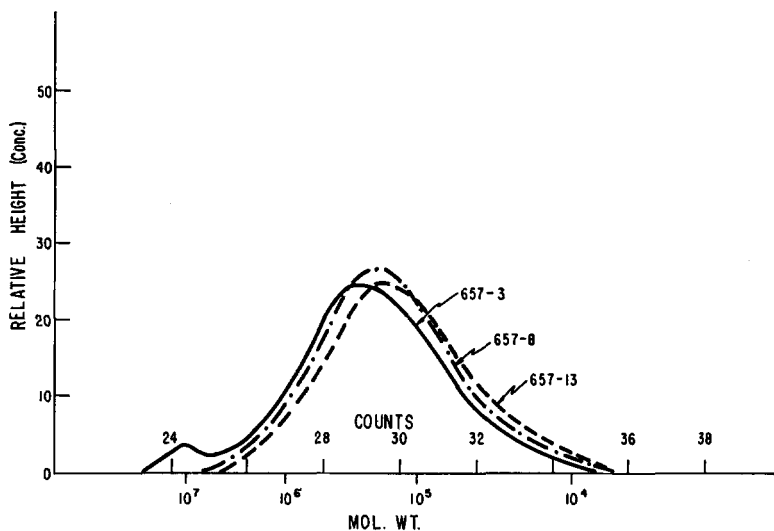


Fig. 9. Effect of rate of hydrogen addition on the GPC distribution curve of an EP copolymer.

ing of the distribution. The formation of extremely large molecules apparently was inhibited.

TABLE II
Effect of Rate of Hydrogen Addition on the
Weight Distribution of an Ethylene-Propylene Copolymer

H ₂ increasing rate →	657-3	657-8	657-13
$M_w \times 10^3$	746	380	334
$M_n \times 10^3$	117	98	87
Peak $\times 10^3$	293	247	231
M_w/M_n	6.41	3.89	3.85
Per cent ethylene	66	66	66
DSV	3.09	2.57	2.32

E. Examination of Extended Polymer by GPC

In the course of studies on "extended" polymers a question arose as to the actual increase being achieved in molecular weight. An "extended" polymer is one in which the molecular weight has been increased by capping growing chains with reactive end groups and the causing the end groups to react with other chains.

In one system studied it was believed that there was one reactive species formed which should give rise to a doubling of the molecular weight. A series of polymers were made in which molecular weight extension was encouraged. A control was made which consisted of polymer prepared exactly as the others except the reactive sites were quenched.

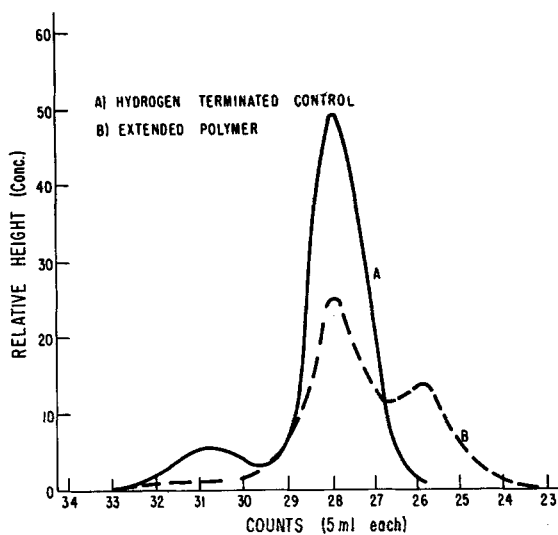


Fig. 10. GPC distribution curves on hydrogen terminated control (A) and extended polymer (B).

Molecular weight distribution analysis by GPC revealed a dual peak for the extended polymers. The original polymer is revealed by a single peak at a count of 28 (Fig. 10) while the peak at 25 represents the extended polymer. The small low peak at a count of 31 is probably polymer terminated at low molecular weight during the course of the original polymerization. Molecular weight of the extended peak is three times that of the original peak. It seems that the reaction results in at least two reactive sites on the end of the polymer chain. Table III illustrates this point.

TABLE III
 M_w Values for the Main Peaks in Extended Copolymers

Sample No.	M_w low peak	M_w high peak	$3 \times$ low peak
468 No. 1	9,900	28,000	29,700
468 No. 3	15,000	46,800	45,000
468 No. 4	19,500	60,000	58,500
470 No. 1	13,700	40,000	41,100
470 No. 3	28,000	81,000	84,000
480 No. 3	125,000	390,000	375,000

In Figure 11, three phases of a reaction designed to double the molecular weight are shown. The first phase is the original polymer showing a sharp peak at 31,000. The second phase shows partial conversion to a molecular weight of 59,000. The final phase shows near complete conversion to a polymer of approximately double the molecular weight of the original.

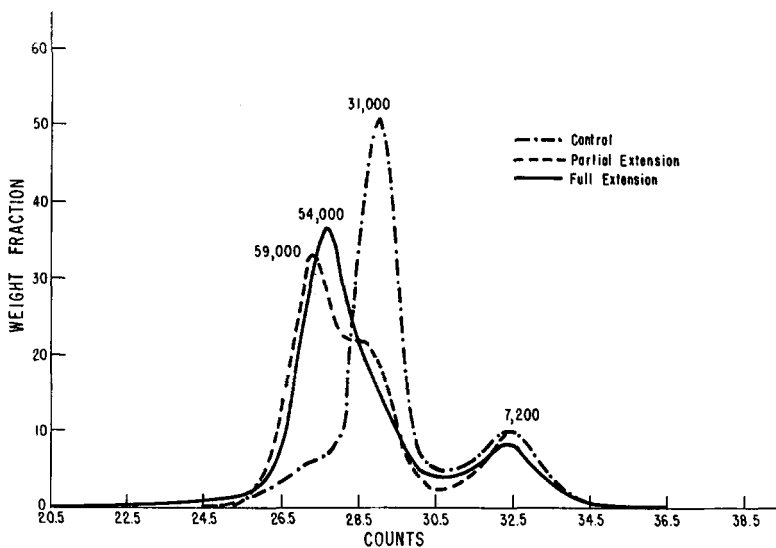


Fig. 11. GPC distribution curve for a double extension reaction.

CONCLUSIONS

Five examples have been presented of how GPC was used to give information of practical interest to polymer chemists and physicists. The only requirement was that the separation actually be by size and that the results be reproducible. The data obtained in most cases could have been obtained in no other way. The examples illustrated the versatility of gel permeation chromatography as a technique for the study of high polymers.

I wish to take this opportunity to acknowledge the works of Thomas Reed, Howard Jacobs, and Dr. Frank Donat from whose studies three of the examples were taken, and to thank them for their contributions. This work was sponsored in part by the Goodrich-Gulf Chemical Company.

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Résumé

Cinq exemples ont été décrits montrant comment la chromatographie par perméation sur gel était appliquée à l'étude de systèmes polymériques. Le calcul des poids moléculaires au départ des courbes ne se rapportait pas à ces études. L'unique exigence était que la séparation soit une séparation de grandeur et que les résultats soient reproductibles.

Zusammenfassung

Fünf Beispiele für die Anwendung der Gelpermeationschromatographie auf die Untersuchung polymerer Systeme werden diskutiert. Eine Molekulargewichtsberechnung aus den Kurven war für die Untersuchungen nicht wesentlich. Das einzige Erfordernis war eine Trennung nach der Grösse und eine Reproduzierbarkeit der Ergebnisse.

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