

## Fractionation of Polymers on a Preparative Scale by Precipitation Chromatography

J. F. HENDERSON and J. M. HULME,  
*Research and Development Division, Polymer Corporation Limited,  
Sarnia, Ontario, Canada*

### Synopsis

A preparative-scale elution chromatographic column is described which will fractionate 45 g. of polymer in a single operation. The size of the column is kept to manageable dimensions by reducing the temperature differential from 50 to 10°C. along the length of the temperature-gradient section. It appears that this change limits the range of molecular weights that are in this section of the column at any one time which leads to a more uniform distribution of a polymer along the column. The net result is that the ratio of polymer load to cubic capacity of the column as a whole can be increased about tenfold over that for the conventional analytical column. It is shown that the equation derived by Caplan is valid under a variety of conditions and that this equation supports the arguments which lead to a reduced temperature differential in the column.

### INTRODUCTION

Fractionation of polymers by precipitation chromatography has been confined almost entirely to operations on an analytical scale, polymer samples up to about 1 g. in weight being used.<sup>1-8</sup> Cantow and co-workers<sup>9</sup> describe a multiple column unit capable of handling 30-50 g. of polyisobutylene with molecular weights ranging up to  $1.66 \times 10^5$ , the design and operating conditions of which were based on experience with small-scale columns. Analytical scale fractionations have been undertaken in these laboratories,<sup>8</sup> but it was found necessary to increase the scale of operations to prepare fractions weighing up to 5 g. One of the major problems in changing from analytical to preparative-scale fractionations is the low ratio of acceptable polymer load  $W_p$  to cubic capacity of the column  $V_c$ . In analytical work this ratio is usually about 2 g./l., with the result that a column suitable for operations on a 50-g. scale would be very large.<sup>8</sup> Other workers<sup>5,10</sup> have also found that column loadings in excess of 2-4 g./l. lead to poor fractionation. The purpose of this investigation was to discover a means of increasing the ratio,  $W_p/V_c$ , and hence to design a column suitable for fractionation of 50-g. samples of polymer.

## EXPERIMENTAL

### Apparatus

Two columns were employed for the fractionations. Both may be visualized as consisting of two units, the constant-temperature heated zone to which the polymer is charged initially and the temperature-gradient

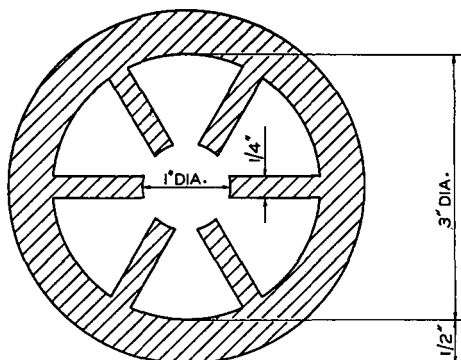


Fig. 1. Column cross-section.

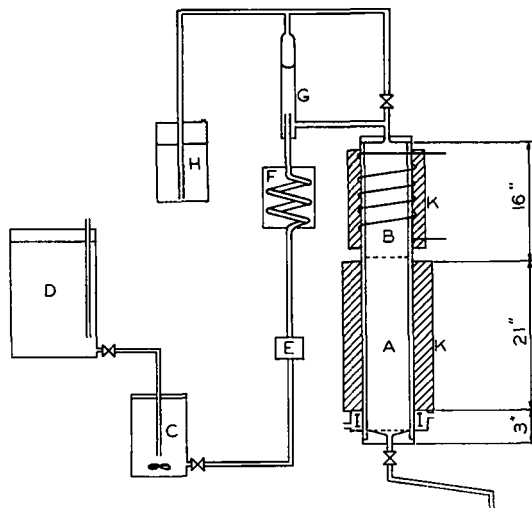


Fig. 2. Preparative-scale fractionation apparatus: (A) temperature gradient zone, cross section as shown in Fig. 1; (B) constant-temperature zone; (C) mixing vessel; (D) solvent reservoir; (E) pump; (F) preheater; (G) vent; (H) hydrostatic head equalizer; (I) water jacket.

section where the polymer is subjected to several stages of precipitation and dissolution. The first column was for analytical fractionation and had dimensions of  $30 \times 2.4$  cm. with a nominal capacity of 0.3 g. when the temperature gradient was  $50^{\circ}\text{C}$ . This equipment has been described

in a previous paper.<sup>8</sup> Based on further studies with this apparatus, a second column with a cubic capacity of 2 liters and capable of fractionating 40–50 g. of polymer was designed. The length of such a column depends upon the maximum tolerable cross-sectional area which, in turn, depends upon the degree of temperature control that is required. Assuming that the maximum allowable temperature deviation across the column is  $\pm 0.1^\circ\text{C}$ ., it was shown that the diameter of the column could not exceed 1 in. Consequently, a single 2-liter column would be about 15 ft. long which could be inconvenient for laboratory work. The idea of several such columns in parallel was rejected because of the possibility of variable back-pressures in the columns preventing eluant from a common feed source from being distributed evenly between the columns. This difficulty was overcome by constructing a section of column from aluminum so that no part of the substrate was more than 0.50 in. from a metal surface (Fig. 1). Tests on this section showed that it fulfilled the specification regarding temperature control. A detailed description of the column dimensions and auxiliary equipment is given in Figure 2.

### Raw Materials

Phillips Petroleum Company "Pure" grade *n*-heptane and isooctane containing 0.02 g./100 ml. Naugawhite antioxidant supplied by Naugatuck Chemicals Division, U.S. Rubber Co., were used as eluant components. The ethanol used in the polymer recovery procedure for the large-scale column was of commercial grade and was used as received. The temperature-gradient section and the heated zone of the column were packed with glass beads having a size range of 105–149  $\mu$  and with Chromosorb P (Canadian Johns-Manville Co., Ltd., Celite Division), respectively (Fig. 2).

### Procedures

The procedures used for the fractionations on the small column have been described in an earlier publication.<sup>8</sup> The conditions used in these runs are listed in Table I, together with those used for the experiments on the large column. Included in this table are the conditions employed for the fractionation of a sample of polystyrene prepared by an emulsion polymerization process and of a sample of a commercial grade of butyl rubber. Both were fractionated on the large column after it had been shown to give a satisfactory result with polybutadiene. The procedures used in the large-column fractionations of polybutadiene are as follows.

Polymer (44 g.) was dissolved in 500–600 ml. of *n*-heptane and mixed with 400 g. of Chromosorb. The mixture was placed in a steam-jacketed column, 35  $\times$  7 cm., fitted with a coarse 6-cm. fritted disk at the bottom. A stream of hot nitrogen was passed through the fritted disk into the column until all the solvent was evaporated, leaving a film of dry polymer deposited on the Chromosorb. Two liters of isooctane were added to

TABLE I  
Conditions Used in Fractionations

Sample	Sample size, g.	Eluant components		Initial charge to mixing vessel		Solvent/precipitant ratio in reservoir		Temperature gradient, °C.	Flow rate, ml./hr.
		Solvent	Precipitant	Solvent, ml.	Precipitant, ml.	Solvent	Precipitant		
Polybutadiene 1	0.3	<i>n</i> -Heptane	Isooctane	—	125	45	55	50	125
"	1.6	"	"	—	525	"	"	"	"
"	3.3	"	"	—	1000	"	"	10	"
"	43	"	"	—	7000	45	55	10	2300
Polybutadiene 2	43	"	"	—	"	50	50	"	"
Polystyrene	43	Cyclohexane	Methyl cyclohexane	—	"	70	30	"	"
Polysar Butyl PB-301	45	Isooctane	Methyl isobutyl ketone	1500	6000	48	52	"	"
Polysar Butyl PB-301, Fractions	0.3	"	"	75	175	46	54	50	125

the column through the bottom outlet, care being taken to ensure that air bubbles were eliminated. The temperature of the cooling water flowing through the jacket (I) was then adjusted to 40°C. and the temperature of the constant-temperature zone (B) to 50°C. (Fig. 2). The dried polymer-Chromosorb mixture was packed into the hot zone of the column, and the column was completely filled with isooctane, again care being taken to eliminate air bubbles. The cap of the column was then screwed on and the feed lines were connected.

The mixing vessel (C, Fig. 2) was filled with 7 liters of isooctane and the solvent reservoir (D, Fig. 2) with 20 liters of a mixture of *n*-heptane and isooctane. For polybutadiene sample 1 this mixture contained 45 ml. of *n*-heptane/100 ml. and for polybutadiene sample 2, 50 ml. of *n*-heptane/100 ml. of the mixture. The pumping rate was adjusted to 2.3 l./hr., and the preheater was set to heat the mixture to 50°C.

Elution of the polymer was commenced after a wait of 10–15 min. to allow the column temperatures to return to their equilibrium values. The column discharge was collected in cuts of approximately 600 ml. each in a fraction collector operated by a time switch. The fractions were recovered by combining consecutive cuts to give a volume of 2–4 liters, depending upon the expected concentration of polymer in the eluant. Ethanol (1–2 liters) was added to the combined cuts, and the whole was stirred vigorously until the precipitated polymer was coagulated. After settling and decanting off of the excess solvent, the polymer was washed and kneaded with ethanol until most of the solvents were removed. The fractions were then dried to a constant weight at 50°C. in a vacuum oven which was periodically flushed with nitrogen to ensure the absence of air. Recovery of the polymer was usually about 95% of that initially charged to the column, the main source of loss being attributed to poor coagulation of the lowest molecular weight fractions which were usually in the form of a thick syrup.

## RESULTS

Preliminary experiments were carried out on the small column under the conditions shown in Table I. The results of these experiments indicated that when the temperature gradient was 10°C., a charge of 3.3 g. gave results substantially in agreement with those obtained when a 0.3 g. charge was fractionated with a 50°C. gradient. (Fig. 3). However, when a charge of 1.6 g. was fractionated with a 50°C. gradient, reversal at high molecular weight was observed which indicates the occurrence of local overloading in the column.<sup>8</sup> Based on these findings, the large-scale column was designed and several 45-g. samples of polymers were fractionated by using a 10°C. gradient. The limiting viscosity numbers of the fractions produced in three of these experiments suggest that the degree of fractionation was satisfactory (Table II). Furthermore, the results of an analytical-scale fractionation of polybutadiene 1 are shown to be in good agreement with those from the large-scale run (Fig. 4).

TABLE II  
Results of Large-Scale Fractionations

Fraction no.	Polybutadiene 1			Polybutadiene 2			Polystyrene		
	Fraction weight, g.	Recovery, wt.-% (cumulative)	$[\eta]$	Fraction weight, g.	Recovery, wt.-% (cumulative)	$[\eta]$	Fraction weight, g.	Recovery, wt.-% (cumulative)	$[\eta]$
1	2.35	5.4	0.84	4.60	10.4	0.67	2.28	5.1	0.37
2	2.47	10.9	1.33	4.13	19.8	0.95	2.25	12.3	0.52
3	2.60	16.9	1.76	5.53	33.2	1.30	3.56	20.2	0.68
4	5.19	28.6	2.20	3.62	47.2	2.10	5.13	31.6	1.22
5	7.13	44.9	2.42	4.10	58.4	2.32	4.52	41.7	1.50
6	7.36	61.6	2.92	5.06	69.9	2.65	5.20	53.2	1.98
7	5.97	75.2	3.11	4.02	79.0	3.12	3.82	61.8	2.34
8	4.28	84.8	4.02	3.48	87.0	3.76	4.33	71.4	2.67
9	2.43	90.5	5.07	1.77	90.9	4.95	3.56	79.4	3.08
10	1.61	94.0	5.94	1.49	94.4	6.22	2.38	84.5	3.21
11	0.33	94.4	6.62				1.56	88.0	3.41

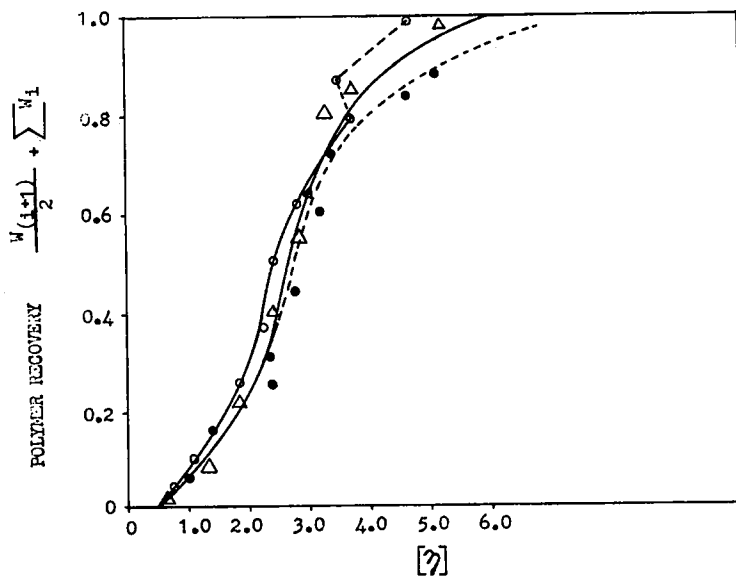


Fig. 3. Comparison of results from the fractionation of polybutadiene sample 1 on the analytical-scale column: (●) 0.3 g. sample, 50°C. temperature gradient; (Δ) 3.3 g. sample, 10°C. temperature gradient; (○) 1.6 g. sample, 50°C. temperature gradient.

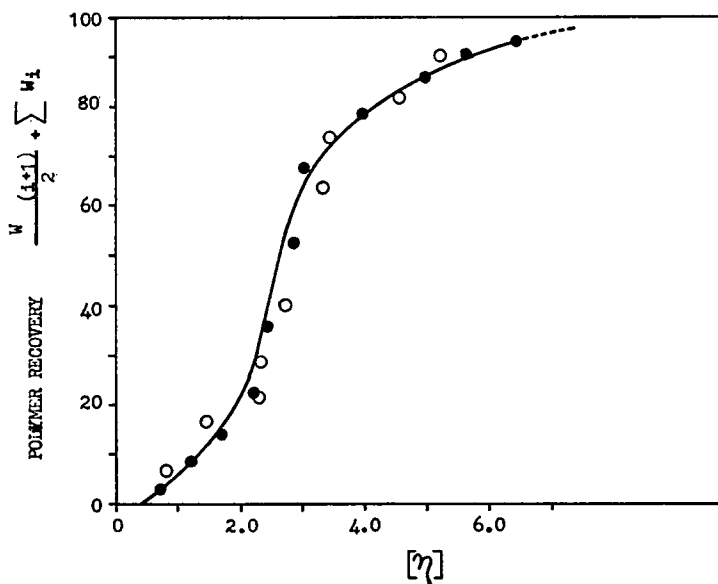


Fig. 4. Comparison of results of polybutadiene sample 1 fractionations: (●) large-scale run with 10°C. temperature gradient; (○) analytical-scale run with 50°C. temperature gradient.

To evaluate the large column further, three adjacent fractions of butyl rubber having limiting viscosity numbers of 1.02, 1.67, and 2.44 in diisobutylene at 30.2°C. were selected from a large-scale fractionation of this copolymer and were fractionated both with the small column and by the precipitation curve technique.<sup>11</sup> The refractionation results are shown in Figure 5, and the ratios  $\bar{M}_w/\bar{M}_n$  for the fractions were estimated to be 1.1, 1.2, and 1.3, respectively, by using the relation,  $[\eta] = 3.6 \times 10^{-4}M^{0.64}$ .

Due to the observed influence of the temperature gradient on the fractionations, the effect of temperature on the precipitation of *cis*-polybu-

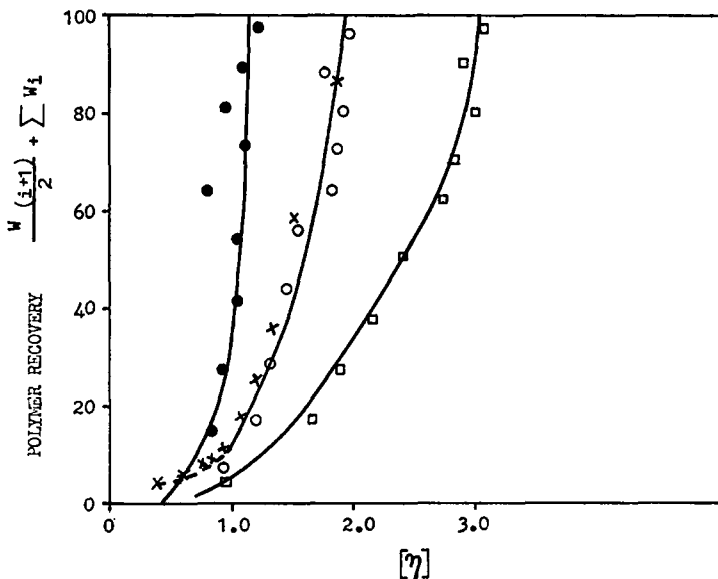


Fig. 5. Analytical-scale fractionation of butyl fractions from the large column: (●)  $[\eta] = 1.02$ ; (○)  $[\eta] = 1.67$  (fractionation by chromatographic technique); (×)  $[\eta] = 1.67$  (fractionation by precipitation-curve technique); (□)  $[\eta] = 2.44$ .

tadiene from *n*-heptane-isooctane mixtures was investigated further. *n*-Heptane solutions of *cis*-polybutadiene fractions at 40, 50, and 90  $\pm$  0.1°C. were titrated with isooctane to the point of incipient precipitation. The onset of cloudiness as detected visually was taken to be the end point, and the reproducibility was  $\pm 1\%$  or less, except at the lowest molecular weights where the end point was difficult to observe. The polymer concentration in solution was between 0.1 and 0.2 g./100 ml. The results are shown in Figure 6.

## DISCUSSION

The experiments carried out with both the small and large columns demonstrate that the capacity of precipitation chromatographic columns



as measured by the weight of charged polymer relative to the volume of the column can be increased markedly by reducing the temperature gradient from 50 to 10°C. Furthermore, this finding appears to be independent of the structure of the polymer being fractionated. From the practical point of view, reduction of the temperature gradient increases the ease of fractionating large polymer samples greatly. It is therefore relevant to examine the role of the temperature gradient in greater detail.

Other workers have demonstrated that failure to fractionate polymer under certain conditions is due to the lack of attainment of equilibrium

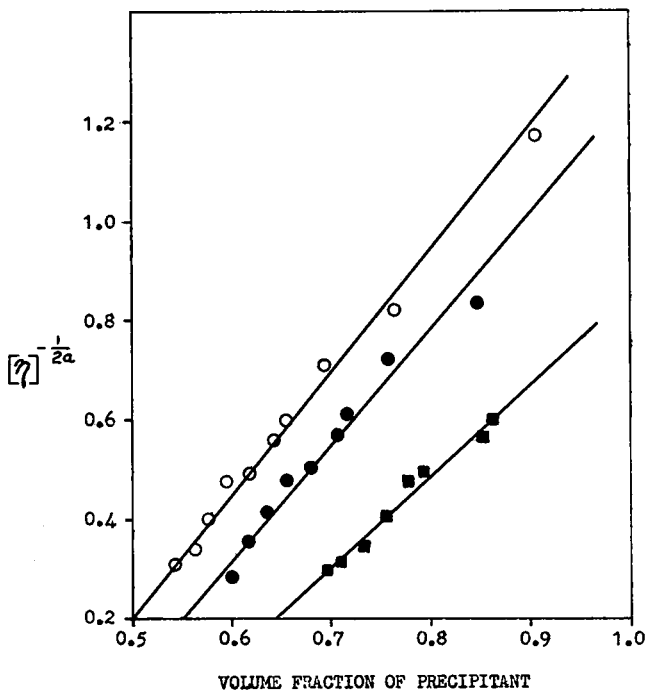


Fig. 6. Relation between the limiting viscosity numbers of fractions of polybutadiene sample 1 and volume fraction of the precipitant at the cloud point: (O) 40°C.; (●) 50°C.; (■) 90°C.

between the static precipitated polymer and the moving polymer solution in the column.<sup>12-14</sup> The establishment of this equilibrium is enhanced by ensuring that the weight of polymer charged to the column is not excessive and that the precipitated polymer is distributed as uniformly as possible along the length of the column. A very non-uniform distribution of precipitated polymer can lead to a local overloading of polymer in the column, unless the amount of polymer charged to the column initially is very small. From the fractionation results, it appears that decreasing the temperature gradient causes the distribution of precipitated polymer along the column to become more uniform, which permits

the polymer charge to be increased. This is reasonable, considering the fact that the precipitation temperatures of polymer fractions in a given solvent or solvent/precipitant mixture increase with increasing molecular weight. Hence, the distance separating two given fractions in a chromatographic column at equilibrium will become greater as the temperature gradient becomes smaller and the distribution of precipitated polymer along the length of the column will thus be more uniform.

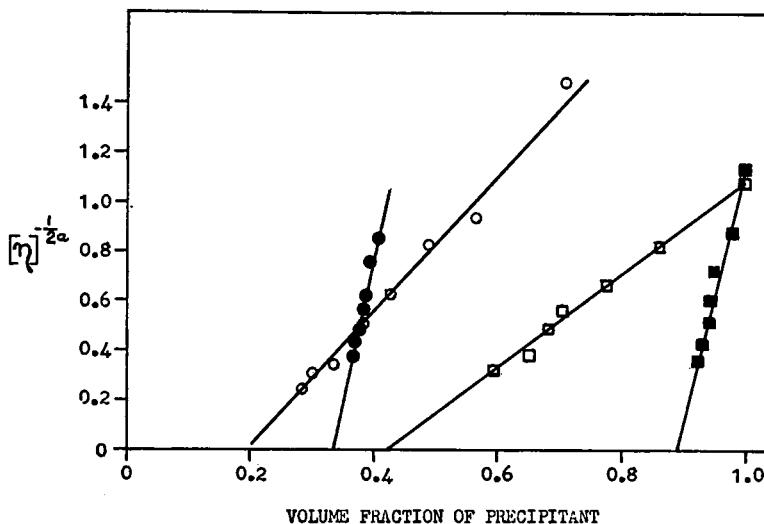


Fig. 7. Relation between the limiting viscosity number of the fraction and the volume fraction of precipitant for several systems of polymers, solvents and precipitants at 40°C.: (O) styrene-butadiene copolymer, 28% styrene, isooctane-methyl isobutyl ketone; (□) polybutadiene sample 1, *n*-heptane-isooctane; (●) polybutadiene sample 1, toluene-*n*-propanol; (■) polybutadiene sample 1, toluene-isooctane.

Caplan<sup>2</sup> has observed that the molecular weights of fractions eluted from a chromatography column are related to the elution temperature by the equation

$$M = \{KT/[\sigma(1 - v) + r - T]\}^2 = [KT/(c - T)]^2 \quad (1)$$

where  $T$  is the elution temperature,  $r$  is the Flory  $\Theta$  temperature of the solvent,  $\sigma$  is the difference between the Flory  $\Theta$  temperatures of the solvent and precipitant,  $v$  is the volume fraction of solvent in the eluant at any instant, and  $K$  is related to the polymer-solvent thermodynamic interaction parameters. Equation (1) can be arranged to give

$$[\eta]^{-1/2a} = [\sigma(1 - v) + r - T]/K'T \quad (2)$$

where  $a$  is the exponent in the Mark-Houwink equation. The results in Figures 6 and 7 show that eq. (2) is obeyed by polybutadiene in a variety

of solvent-precipitant systems at several temperatures and by a styrene-butadiene copolymer.

If a column is now considered for which the temperatures at the top and bottom are  $T_1$  and  $T_2$ , respectively, we obtain

$$M_1 - M_2 = [KT_1/(C_1 - T_1)]^2 - [KT_2/(C_2 - T_2)]^2 \quad (3)$$

where  $M_1$  and  $M_2$  are the molecular weights of fractions in equilibrium at the top and bottom of the column at any instant of time. The difference,  $M_1 - M_2$ , will become larger as  $T_1 - T_2$  increases, which will promote an accumulation of precipitated polymer in the column assuming that the column length is kept constant. This accumulation will inhibit the rapid attainment of equilibrium in the column with the result that large samples of polymer can be fractionated by a conveniently sized apparatus only when the temperature gradient is small.

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### Résumé

Une colonne chromatographique par élution à des fins préparatives est décrite qui permet de fractionner 45 g. de polymère en une seule opération. La grandeur de la colonne est maintenue à des dimensions accessibles en réduisant la différentielle de température de 50 à 10°C tout le long de la section du gradient de température. Il semble que cette modification limite le domaine des poids moléculaires qui sont dans cette section de la colonne à chaque moment et permet une distribution plus uniforme du polymère le long de la colonne. Le résultat net est que le rapport de la charge moléculaire à la capacité cubique de la colonne dans son entièreté peut être augmenté d'environ dix fois par rapport à celui pour la colonne analytique conventionnelle. On montre que l'équation dérivée par Caplan est à valable dans diverses conditions et que cette équation confirme les arguments qui amènent à une température différentielle réduite dans la colonne.

### Zusammenfassung

Eine präparative Elutionschromatographiesäule zur Fraktionierung von 45 g Polymerem in einem einzigen Vorgang wird beschrieben. Die Grösse der Säule wird durch Reduzierung des Temperaturdifferentials von 50°C auf 10°C längs des Temperaturgradientenabschnittes auf handlichen Dimensionen gehalten. Es scheint, dass diese Änderung den zu einer beliebigen Zeit in diesem Säulenabschnitt befindlichen Molekulargewichtsbereich einschränkt, was zu einer einheitlichen Verteilung im Polymeren entlang der Säule führt. Das Nettoergebnis besteht darin, dass das Verhältnis von Polymerbeladung zur Volumskapazität der Säule als Ganzes gegenüber demjenigen der konventionellen analytischen Säule auf etwa das zehnfache erhöht werden kann. Es wird gezeigt, dass die von Caplan abgeleitete Gleichung unter verschiedenartigen Bedingungen gültig ist und dass diese Gleichung eine Stütze für die Argumente für ein reduziertes Temperaturdifferential in der Säule bildet.

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