This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Phase Distribution Chromatography (PDC) of Polystyrene

R. H. Casper[a]; G. V. Schulz[a]
[a] INSTITUT FÜR PHYSIKALISCHE CHEMIE DER UNIVERSITÄT MAINZ, MAINZ, WEST GERMANY

To cite this Article Casper, R. H. and Schulz, G. V.(1971) 'Phase Distribution Chromatography (PDC) of Polystyrene', Separation Science and Technology, 6: 2, 321 — 329

To link to this Article: DOI: 10.1080/00372367108058965

URL: http://dx.doi.org/10.1080/00372367108058965

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE, 6(2), pp. 321–329, April, 1971

Phase Distribution Chromatography (PDC) of Polystyrene*

R. H. CASPER and G. V. SCHULZ

INSTITUT FÜR PHYSIKALISCHE CHEMIE DER UNIVERSITÄT MAINZ
MAINZ, WEST GERMANY

Summary

Phase distribution chromatography is a new chromatographic method of fractionating polymers. The separation is achieved by partitioning the sample between the solvent and a polymer phase, in the case a noncross-linked polystyrene of very high molecular weight, which is coated as a thin layer on small glass beads. The temperature must be held below the θ-temperature of the sample. The separation increases sharply with decreasing temperature. The theory of this method is presented and compared with experimental results. The agreement is very good.

INTRODUCTION

In ordinary gel permeation chromatography, the elution volume increases with decreasing sample molecular weight. It is easy to modify this method in such a way that this relation is inverted. For this purpose, only the cross-linking of the gel phase must be omitted. Then the high molecular species dissolve in the gel phase to a higher extent than those of lower molecular weight and therefore leave the column later. The theory of this effect seems to be simpler than that of GPC, it is similar to the Baker-Williams method (*1*, *2*), but again considerably simpler.

EXPERIMENTAL

The main parts of the apparatus are sketched in Fig. 1. The sample column (a glass tube 100 × 3 cm) was filled with glass

---

* Presented at the ACS Symposium on Gel Permeation Chromatography sponsored by the Division of Petroleum Chemistry at the 159th National Meeting of the American Chemical Society, Houston, Texas, February, 1970.

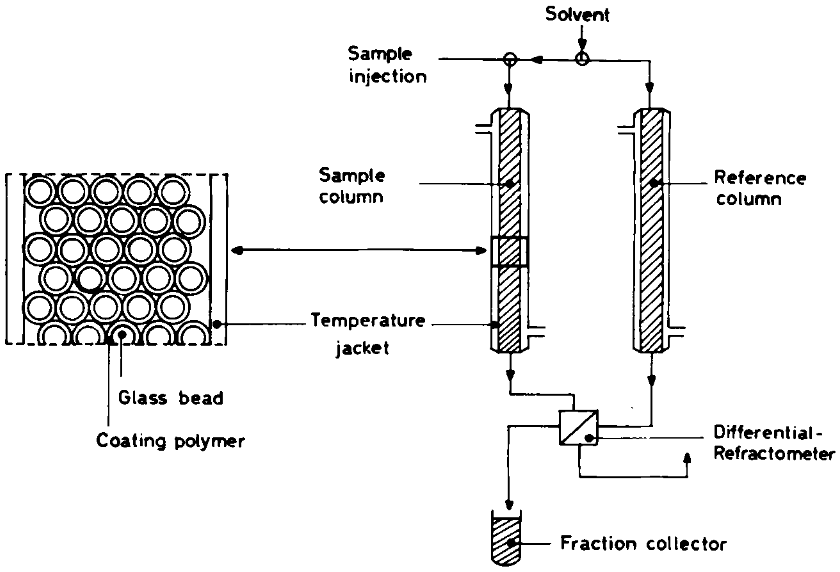

FIG. 1. Scheme of the PDC apparatus.

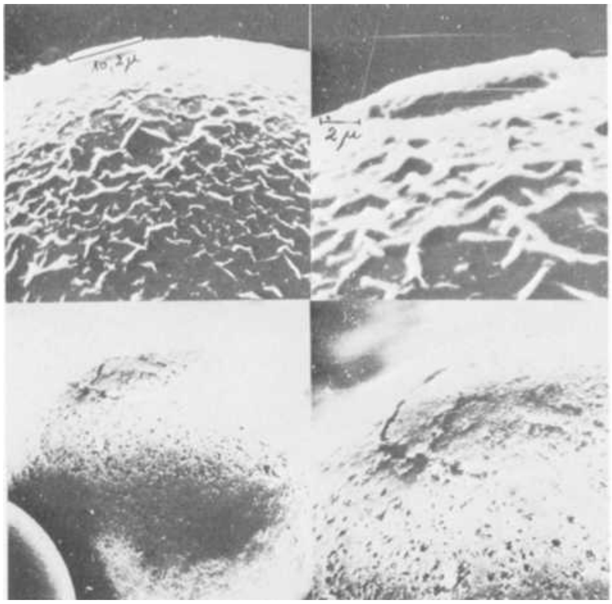

FIG. 2. Surface of the glass beads coated by PS (top) and uncoated (bottom).

beads (ballotines, diameter 0.1 mm) which were covered with a layer of a well-fractionated tritium-labeled polystyrene of very high molecular weight ($M_w = 8 \times 10^6$). The coating polymer was practically insoluble in the solvent used in our experiments (cyclohexane below the θ-temperature of 35°C. The layer of the swollen polymer had a thickness of nearly 3000–4000 Å. It was extracted at 28°C until the solvent leaving the column contained less than 1 mg/liter (as measured by radioactivity). An electron micrograph of the coated and uncoated glass beads is shown in Fig. 2.

The separation efficiency of the column and its dependence on temperature is demonstrated by the experiments represented in Fig. 3.

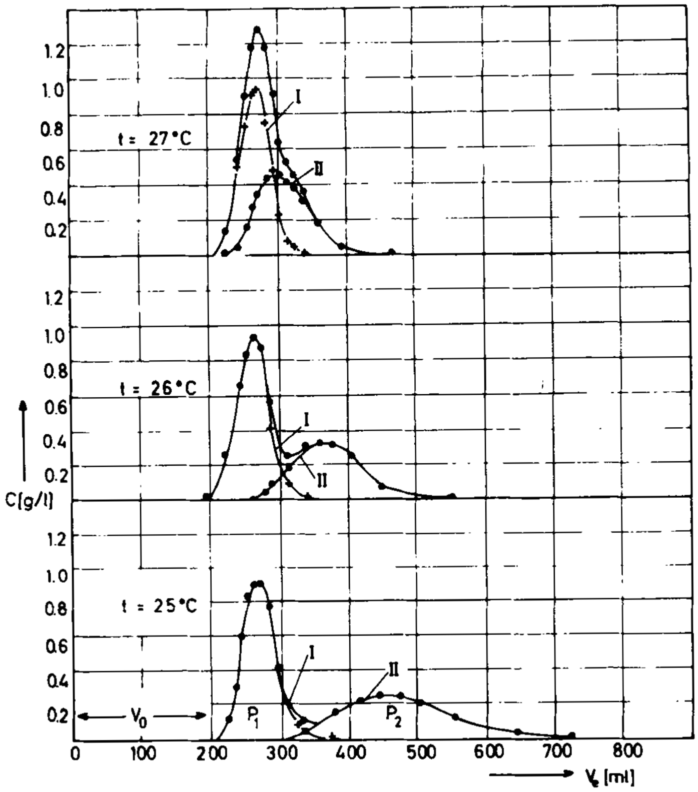

FIG. 3. Elution curve of a 1:1 mixture of two samples of anionically prepared polystyrenes; $\bar{M}_w = 135{,}000$ (I) and 415,000 (II) (300 mg in 20 ml cyclohexane).

A 1:1 mixture of two samples of anionically prepared PS was dissolved in 20 ml of cyclohexane and passed through the column with a flow rate of 10 ml/hr. The sample with the molecular weight 4.15×10^5 was labeled with tritium; thus, the amount of this polymer could be determined in each collected fraction. One can see that with decreasing temperature, the separation efficiency increases sharply as the elution volumes of the higher molecular weight samples become larger while those of low molecular weight remain nearly constant. Some preliminary experiments were published elsewhere (*3*).

THEORY OF THE METHOD

The elution volume V_e is controlled by the distribution coefficient $K(P)$ which defines the distribution of a species with the degree of polymerization P between the two phases

$$K(P) = \Phi_{\text{gel}}/\Phi_{\text{sol}} \qquad (1)$$

Φ_{gel} and Φ_{sol} are the volume fractions of the sample polymer P in the two phases. The ratio of the volumes V_{sol} and V_{gel} of the phases in the column is

$$r_v = V_{\text{sol}}/V_{\text{gel}} \qquad (2)$$

Applying the usual transport equation for a chromatographic process, we obtain

$$V_e = V_e^0[1 + K(P)/r_v] \qquad (3a)$$

and

$$K(P) = r_v(V_e/V_e^0 - 1) \qquad (3b)$$

where V_e^0 is the void volume of the column.

With these equations, one can predict the elution volume if the distribution coefficient is known from thermodynamic calculations or, in turn, one can calculate the distribution coefficient from the measured elution volume. The required condition of working close to equilibrium can be easily controlled by varying the flow rate. Equilibrium is established if the elution volume does not depend on the flow rate. This condition was maintained in our experiments.

Elution experiments were performed with some anionically prepared polystyrene samples of narrow molecular weight distributions in order to determine experimentally the relation of the distribution coefficient with the degree of polymerization and with temperature. The DP covered the range from 300 up to 4000, and the

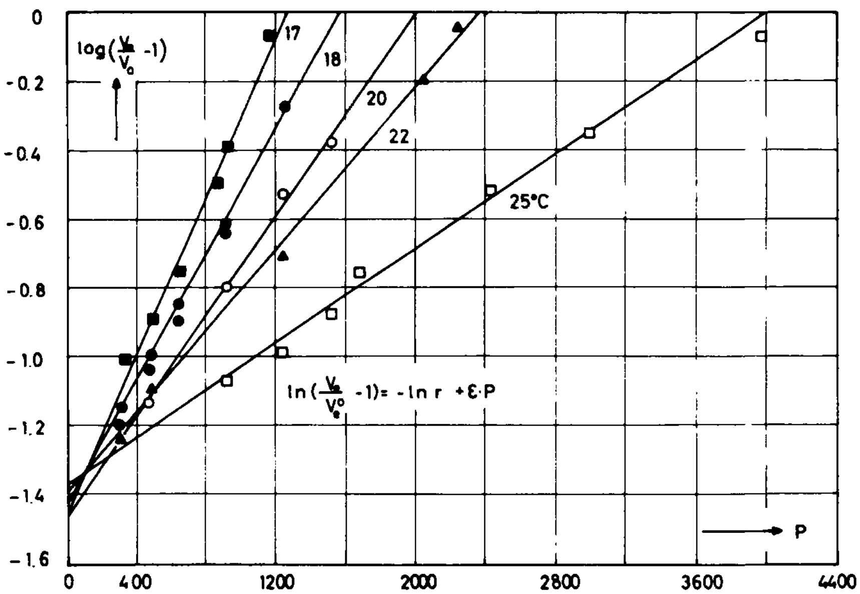

FIG. 4. Elution experiments Log $(V_e/V_e^0 - 1)$ as a function of the degree of polymerization P at different temperatures. Polystyrene in cyclohexane below the θ-temperature (35°C).

temperature was 10–18°C below the θ-temperature (35°C). Figure 4 shows that the relation between the elution volume V_e and the degree of polymerization P can be described by

$$\log\,[(V_e/V_e^0) - 1] = -a + bP \tag{4}$$

Comparison of Eq. (4) with Eq. (3b) reveals that

$$a = \log r_v \tag{5}$$

and

$$\log K(P) = bP \tag{6a}$$

On the average, a has a value of 1.4; hence, $r_v \approx 30$. This agrees satisfactorily with independent swelling experiments performed with the high molecular polystyrene.

Equation (6a) is identical with the following relation which was first introduced by Brönsted (*4*)

$$K(P) = \exp\,(\epsilon P) \tag{6b}$$

Equation (6b) had previously been used by one of us to evaluate experimental results of polymer fractionation in terms of its mechanism (*5, 6*). A theoretical treatment of the Baker-Williams column was based (*1, 2*) on the same equation. This treatment could be experimentally confirmed (*2*).

We call $v_{p,s}$ the volume of the polymer solution which is injected at the top of the column. The solution drains into the interstitial volume between the glass beads and comes in contact with a certain amount of the stationary gel layer of the volume $v_{p,g}$. Obviously the total volume which contains the sample is given by

$$v_p = v_{p,s} + v_{p,g} \tag{7}$$

The composition of the two phases can approximately be described by a quaternary system consisting of the solvent and three polymer components with the molecular weights M_1, M_2, and M_3. The "polydisperse" low molecular weight polymer mixture is represented by M_1 and M_2, and the high molecular weight component by M_3. The "molecular weight distribution" of the low molecular weight mixture can be characterized by the ratio of mass m_1/m_2. Its total amount is $m_1 + m_2$.

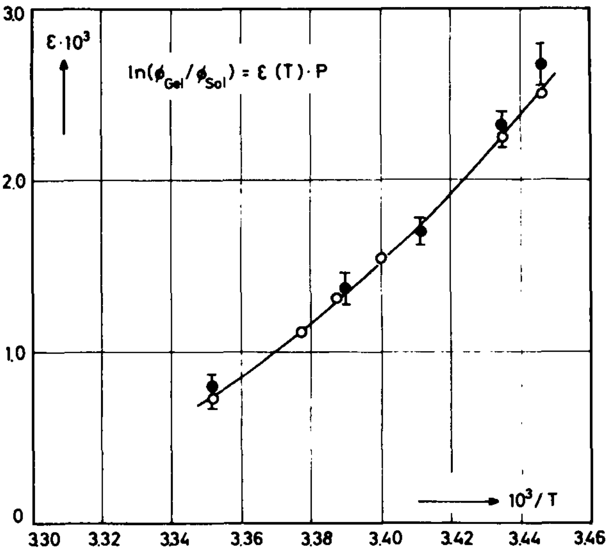

FIG. 5. Brönsted coefficient ϵ in Eq (6b) as a function of the temperature: ○, calculated according to Koningsveld; ●, experimental points (slope of elution curves in Fig. 4).

The dependence of the Huggins interaction coefficient χ on the temperature and on the concentration in the system cyclohexane polystyrene was measured by Koningsveld (*7*) and Rehage (*9–11*). Assuming that phase equilibrium has been established, the composition of the adjacent phases as well as the distribution coefficients for M_1, M_2, and M_3 can then be calculated on the basis of the Flory-Huggins relation for the free enthalpy of mixing of polymer solutions (*8*). The good agreement of measured and calculated ϵ values, as shown in Fig. 5, proves that our theory of the PDC method is complete and correct.

On this theoretical basis, model calculations were made, the results of which are listed in Tables 1–3.

Three conclusions can be drawn from Table 1:

(a) The high molecular sample of polystyrene which forms the gel phase 10°C below the θ-temperature is practically insoluble in the sol phase.

(b) The distribution coefficients $K(P)$ of the two lower samples (P_1 and P_2) of polystyrene are completely independent from their concentrations and also with good approximation from the ratio of their masses.

(c) At lower concentrations the elution volumes of the different

TABLE 1

Distribution Coefficient, Elution Volume, and the Ratio of Phase Volumes $r_v = v_{p,s}/v_{p,g}$ Calculated as a Function of the Mass of Three Samples of Polystyrene with Various Degrees of Polymerization; $P_1 = 1{,}300$; $P_2 = 4{,}000$; $P_3 = 80{,}000$. Total Interstitial Volume ca. 250 ml; Temperature 25°C. $v_{p,s} = 20.0$ ml; $m_3 = 124.5$ mg

m (mg)		$K(P) = \Phi_{sol}/\Phi_{gel}$			V_e/V_e^0		
1	2	1	2	3	1	2	r_v
0.5	0.5	0.380	0.0512	1.5×10^{-26}	1.093	1.690	28.3
5.0	5.0	0.380	0.0512	1.5×10^{-26}	1.096	1.711	27.5
50.0	50.0	0.380	0.0512	1.5×10^{-26}	1.119	1.889	22.0
500.0	500.0	0.381	0.0512	1.5×10^{-26}	1.178	2.319	14.8
1.0	9.0	0.379	0.0506	1.2×10^{-26}	1.097	1.727	27.2
3.0	7.0	0.380	0.0509	1.3×10^{-26}	1.096	1.720	27.3
5.0	5.0	0.381	0.0511	1.5×10^{-26}	1.096	1.711	27.5
9.0	1.0	0.382	0.517	1.8×10^{-26}	1.094	1.696	27.8

TABLE 2

Distribution Coefficients and Elution Volume as a Function of the Degree of Polymerization at 25°C (Calculated for a Quaternary System).
$m_1 = m_2 = 5$ mg; $m_3 = 124.5$ mg; $v_{p,s} = 20$ ml

Degree of polymerization			Φ_{sol}/Φ_{gel}			V_e/V_e^0	
1	2	3	1	2	3	1	2
500	4000	80,000	0.69	0.0512	1.6×10^{-26}	1.05	1.71
1,300	4000	80,000	0.38	0.0511	1.5×10^{-26}	1.10	1.71
2,500	4000	80,000	0.16	0.0509	1.4×10^{-26}	1.24	1.72
3,500	4000	80,000	0.07	0.0506	1.2×10^{-26}	1.50	1.73
11,000	4000	80,000	3.0×10^{-4}	0.0502	1.0×10^{-26}	142.1	1.75

species are independent from each other. At higher concentrations the elution volume is more or less influenced by changes of the relation r_v caused by the local enlargement of the gel phase.

In Table 2 the molecular weight of Component P_1 was varied up to a factor of 22. One sees that the mutual influence of the components at the conditions given here is very small and that neighboring degrees of polymerization (e.g., 3500 and 4000) are well separable. The large difference of the distribution coefficients of the samples with DP of 11,000 and 80,000, respectively, suggests that a polymer can be used as the gel-forming component in the PDC column for a sample, the molecular weight of which is smaller by less than one order of magnitude.

Table 3 shows the very large influence of temperature.

TABLE 3

Calculated Distribution Coefficients of Three Degrees of Polymerization as a Function of Temperature (θ = 35°C)

	Φ_{sol}/Φ_{gel}			V_e/V_e^0	
T (°C)	DP = 500	4000	80,000	500	4000
17	0.28	4.3×10^{-5}	0	1.085	566
21	0.46	2.2×10^{-3}	0	1.061	17.97
23	0.57	1.2×10^{-2}	10^{-39}	1.055	3.684
25	0.69	5.1×10^{-2}	10^{-26}	1.053	1.709

CONCLUSIONS

The PDC method has two aspects: it allows determination of the thermodynamic parameters, e.g., distribution coefficients in phase equilibria. On the other hand, it is a new method for the determination of molecular weight distributions. It seems that the fractionating efficiency for polymers can be considerably improved if one makes use of a programmed temperature increase. Experiments in this direction are under way.

Acknowledgment

This work was supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AIF).

REFERENCES

1. G. V. Schulz, P. Deussen, and A. G. R. Scholz, *Makromol. Chem.*, **69,** 47 (1963).
2. G. V. Schulz, K. C. Berger, and A. G. R. Scholz, *Ber. Bunsenges. Phys. Chem.*, **69,** 856 (1965).
3. R. H. Casper and G. V. Schulz, *J. Polym. Sci., Part A-2,* **8,** 833 (1970).
4. J. N. Brönsted, *Z. Phys. Chem.* (*A*), **155,** 343 (1931); **168,** 381 (1934).
5. G. V. Schulz, *Z. Phys. Chem.* (*B*), **46,** 137 (1940); **47,** 155 (1940).
6. G. V. Schulz and E. Nordt, *J. Prakt. Chem.*, **155,** 115 (1940).
7. R. Koningsveld and A. Staverman, *J. Polym. Sci., Part C,* **16,** 1775 (1967); *Part A-2,* **6,** 305, 325, 349, 367, 383 (1968).
8. R. H. Casper, Dissertation, University of Mainz, 1970.
9. G. Rehage and R. Koningsveld, *J. Polym. Sci., Part B,* **6,** 421 (1968).
10. G. Rehage and D. Möller, *J. Polym. Sci.*, **16,** 1787 (1967).
11. G. Rehage, J. Palmen, D. Möller, and W. Wefers, IUPAC Symposium on Macromolecules, Toronto, 1968.

Received by editor July 15, 1970