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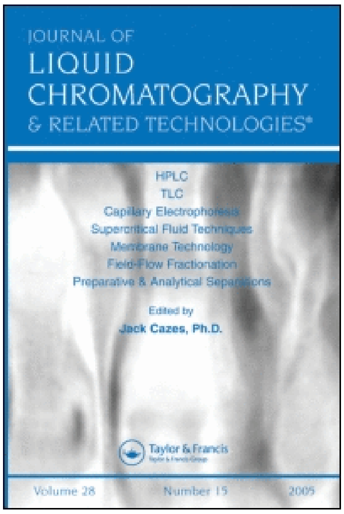

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Characterization of Polyvinylchloride by Size Exclusion Chromatography. I. Concentration Dependence of Axial Dispersion Observed in Size Exclusion Chromatography Coupled With Light Scattering

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CHARACTERIZATION OF POLYVINYLCHLORIDE BY SIZE EXCLUSION CHROMATOGRAPHY. I. CONCENTRATION DEPENDENCE OF AXIAL DISPERSION OBSERVED IN SIZE EXCLUSION CHROMATOGRAPHY COUPLED WITH LIGHT SCATTERING

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ABSTRACT

A comparative study on the axial dispersion in size exclusion chromatography was carried out on sample solutions with narrow molar mass distribution of polyvinylchloride (M_w=12000-96300 g/mol; M_w/M_n=1.14-1.25) and polystyrene (M_w=9000-1130000 g/mol M_w/M_n=1.04-1.08) in tetrahydrofuran. Determination of the axial dispersion parameter σ was accomplished by two independent methods for simultaneous calibration of separation and axial dispersion. For polystyrene, a slight dependence of σ on the peak elution volume was found as postulated in literature. At low concentration, there is a good agreement between σ measured for polystyrene (PS) and polyvinylchloride (PVC). Raising the concentration by a factor of 3, an increase of σ by about 25 % was found for PVC. The method of universal calibration proved to be applicable independent of concentration, when $[\eta]=1.6 \times 10^{-4} M^{0.706}$ dl/g for PS and $[\eta]=1.6. \times 10^{-4} M^{0,77}$ dl/g for PVC is used.

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INTRODUCTION

Due to the great technical importance of polyvinylchloride (PVC), there exists a great number of studies by size exclusion chromatography (SEC) on this homopolymer(1), revealing that commercial PVC samples usually have a molar mass distribution close to the most probable distribution with $M_w/M_n \cong 2$.With the PVC standard samples made available by Polymer Standards Services (Mainz, FRG), it appeared to be interesting to carry out a comparative study on polystyrene (PS) and PVC samples of narrow molar mass distribution.

In this study, the procedures for simultaneous calibration of separation and axial dispersion of He et al.(2) and of Billiani et al.(3) were applied. In this way, both the applicability of the universal calibration and the volume dependence of the axial dispersion are investigated.

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EXPERIMENTAL

Samples:

The polystyrene standards (PS1-PS6) were obtained from Polymer Laboratories Ltd. (Church Stretton, Shropshire, UK), the polyvinylchloride standards (PVC1-PVC6) from Polymer Standard Service GmbH (Mainz, FRG). For average values of molar mass confer to Tab. 1.

THF analytical grade (Merck, Darmstadt, FRG) was used as an eluent.

TABLE 1

Polystyrene (PS) and polyvinylchloride (PVC) samples of narrow molar mass distribution; weight average molar mass, M_w, and number average molar mass, M_n, as given by the supplier. $[\eta]$ calculated from peak molar mass, M_p, by eq. 6.

Sample	M_w [g/mol]	M_n [g/mol]	M_w/M_n	M_p [g/mol]	$[\eta]$ [dl/g]
PS1	9000	8650	1.04	8800	0.083
PS2	34500	32800	1.05	33600	0.231
PS3	68000	64100	1.06	66000	0.435
PS4	170000	163000	1.04	166000	0.823
PS5	500000	462000	1.08	480000	1.599
PS6	1130000	1060000	1.06	1090000	2.833
PVC1	12000	14000	1.16	12900	0.285
PVC2	17000	21000	1.25	18800	0.324
PVC3	32000	37000	1.15	34000	0.622
PVC4	43000	49000	1.14	45900	0.634
PVC5	65000	73000	1.12	68000	1.095
PVC6	80300	96300	1.16	88000	1.238

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Apparatus:

The measurements were carried out at ambient temperature. The SEC system consisted of a HPLC-pump Modell 510 (Waters Associates, Milford, Mass, USA), an injection valve with 25 µl loop (Knauer, Berlin, FRG), a PL mixed gel column (Polymer Laboratories Ltd., Church Stretton, Shropshire, UK) of 60 cm length and 10 µm particle size and a PS-4000 column (Cat. No. 50059 Lichrogel, E. Merck, Darmstadt, FRG). A low angle laser light scattering (LALLS) photometer (model KMX-6, LDC/Milton Roy, Hasselroth, FRG) and a RI detector (Multiref. 90 L, Optilab, Vällingby, Sweden) were connected in series. The flow rate (1 ml min^{-1}) was occasionally verified by measuring the mass of the eluent.

SEC data were collected by a personal computer (IBM PC-XT) equipped with a 4 channel high speed data acquisition system of 12 bit resolution. The computer programs used for data acquisition and interactive processing including graphical selection of baseline and calculation of e(v) and E(v) were developed in our laboratory by one of us (J.B.). The computer programs for the simultaneous calibration of separation and axial dispersion including peak broadening correction developed by Rois (4) were used in connection with a VAX 11-750 microcomputer.

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RESULTS AND DISCUSSION

The eluogram e(v) of the polystyrene and the polyvinylchloride sample solutions (concentration as shown in Tab. 3) are given in Fig. 1 and Fig. 2 respectively, with e(v) defined by

$$e(v) = \frac{s(v)}{\int s(v)\,dv} \qquad \text{1a}$$

where s(v) = signal of the RI detector in arbitrary units (proportional to concentration) as a function of elution volume v,

and $$\int e(v)\,dv = 1\ . \qquad \text{1b}$$

From the light scattering signal E(v) defined by (5):

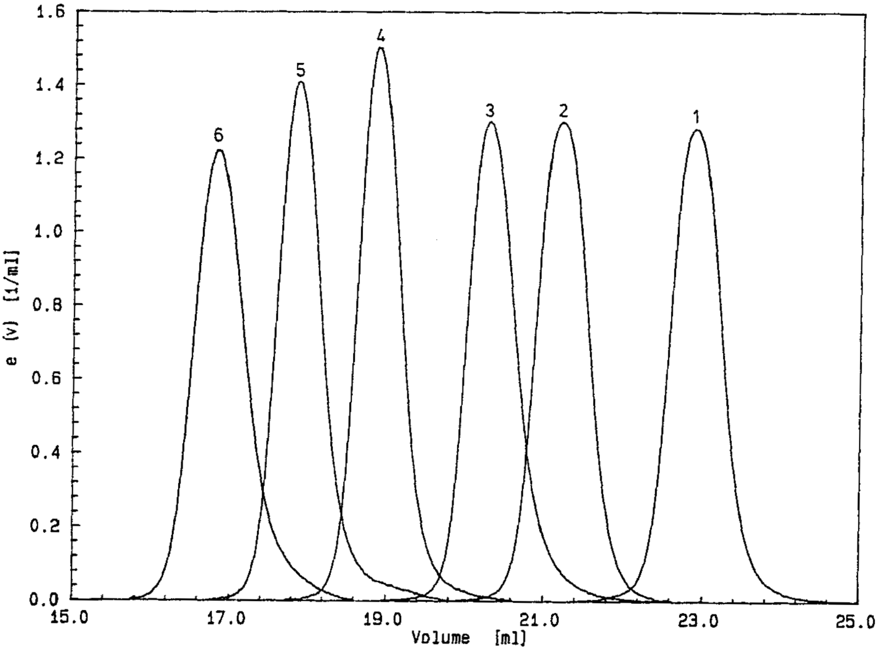

FIGURE 1

Eluogram of polystyrene samples of narrow molar mass distribution (cf. Tab. 1). For definition of e(v) see eq. 1a

$$E(v) = \frac{R_\theta(V)}{K\ m} \tag{3}$$

where R_Θ = reduced scattering intensity extrapolated to $c=0$ with $A_2=4 \times 10^{-3}$ ml mol g^{-2},

m = injected mass of polymer=c v_1 (c=concentration of sample solution, cf. Tab. 3, v_1=injected volume=25×10^{-6}l),

and

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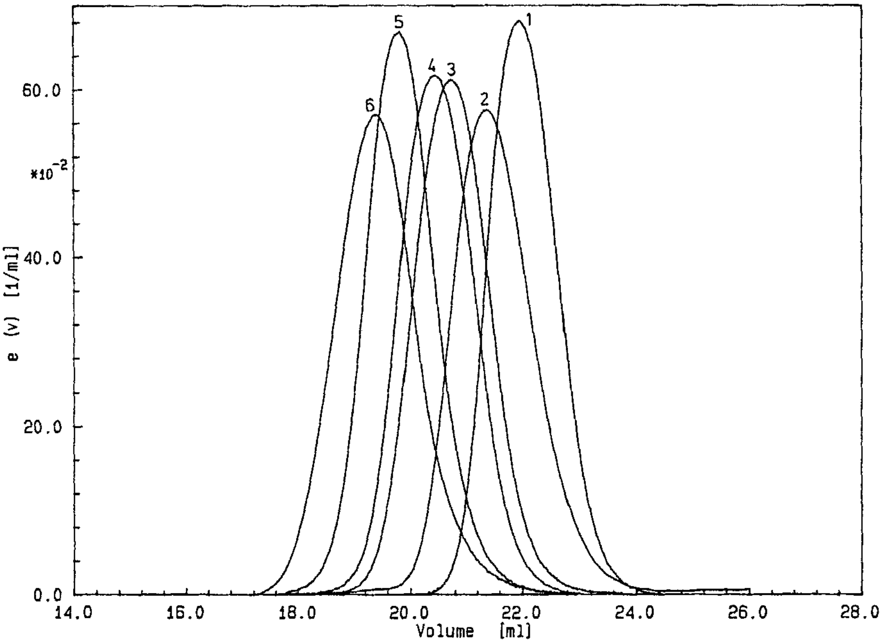

FIGURE 2

Eluogram of polyvinylchloride samples of narrow molar mass distribution (cf. Tab. 1.). For definition of e(v) see eq. 1a.

$$K= \frac{2\pi^2 n^2}{\lambda^4 N} (dn/dc)^2 (1-\cos^2\theta) \quad , \qquad 3a$$

with n = refractive index of solvent=1.404 for THF at 25°C

λ = wave lenght=632.4 nm,

N = Avogadro's number,

dn/dc = refractive index increment=0.185 cm^3/g for PS and 0.103 cm^3/g for PVC, and

2θ = scattering angle=4.6°,

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the weight average molar mass in the detector cell, $M_w(v)$, is calculated by

$$M_w(V) = \frac{E(v)}{e(v)} \quad , \qquad 4$$

taking into account the volume lag between LALLS and RI detector of 70 µl as determined by the procedure of Billiani et al.(6).

Fig. 3 shows the eluogram e(v) together with the molar mass function $M_w(v)$ of the sample PVC5 for two different concentrations of sample solution. From such data, simultaneous calibration of separation and axial dispersion can be accomplished by the iterative procedure developed in our laboratory(3,7).

Hereby the dispersion parameter σ is defined according to Tung's equation

$$e(v) = \int w(V_p)\ D(v-V_p)\ dV_p \quad , \qquad 5$$

where $w(V_p)$ = mass distribution of the peak elution volume V_p

and $$D(v-V_p) = \frac{1}{\sigma\ (2\pi)^{0.5}} \exp\left[(v-V_p)^2/2\sigma^2\right] ,$$

with σ = axial dispersion parameter,
and log $M(V_p)$ is assumed to be a linear function of V_p.

The "uncorrected values" of M_w and M_n in Tab. 2 were calculated on the basis of the calibration function $M(V_p)$ determined by our iterative procedure and the eluograms e(v) shown in Fig. 1 and Fig. 2 without correction for peak broadening. To calculate the

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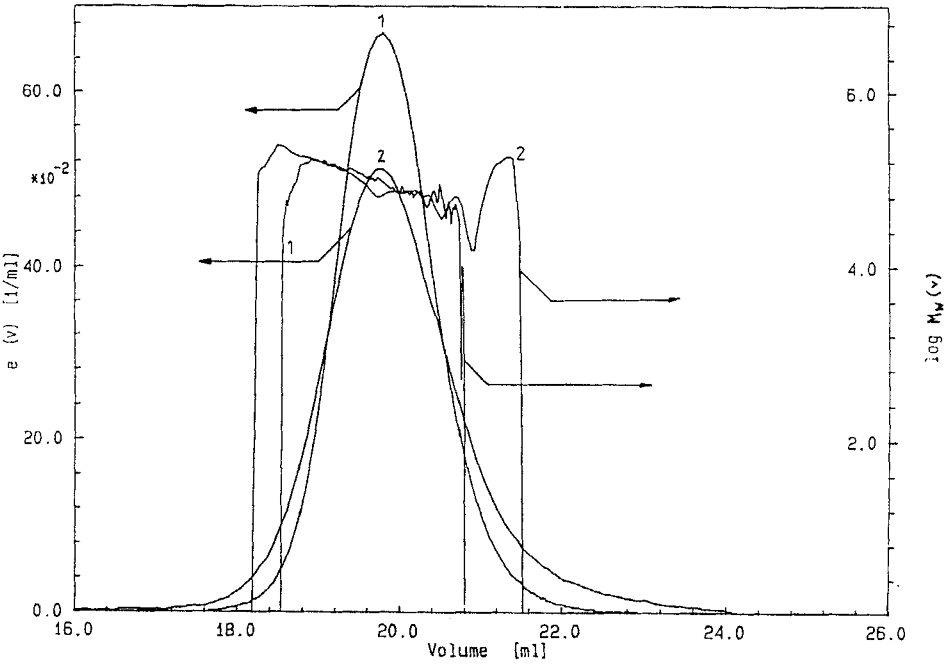

FIGURE 3

Eluogram, e(v), and weight average molar mass in the detector cell, $M_w(v)$, of sample PVC5 determined by SEC/LALLS. 1: c=2.024 [g/l] ; 2: c=0.750 [g/l]. For definition of e(v) and M_w (v) see eq. 1a and 4, respectively.

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"corrected values" of M_w and M_n, the widely used method 2 of Ishige(8) was applied to e(v), assuming a constant value of $\sigma = 0.25$ ml for PS and of $\sigma = 0.30$ ml for PVC prior to the respective integration.

With polystyrene, comparison of the data in Tab. 1 and Tab. 2 shows a very good agreement between the values of M_w, M_n and M_w/M_n given by the supplier and those obtained by these SEC/LALLS measurements; correction for peak broadening led to a small decrease

TABLE 2

Weight and number average molar mass, M_w and M_n, of narrow PS- and PVC-samples (cf. Tab. 1), determined by SEC/LALLS, uncorrected and corrected for peak broadening

	"uncorrected values"			"corrected values"		
Sample	M_w [g/mol]	M_n [g/mol]	M_w/M_n	M_w [g/mol]	M_n [g/mol]	M_w/M_n
PS1	7970	7400	1.07	7940	7500	1.05
PS2	31800	29600	1.07	31400	29700	1.06
PS3	64500	59000	1.09	64300	55900	1.08
PS4	215000	203000	1.06	214700	205100	1.04
PS5	476000	429600	1.11	484600	438000	1.10
PS6	1115000	1014800	1.09	1108500	1023700	1.08
PVC1	15300	12300	1.24	15140	12500	1.20
PVC2	24800	16300	1.46	23500	16900	1.39
PVC3	44900	33700	1.33	44200	34200	1.29
PVC4	55500	42500	1.31	54700	43200	1.26
PVC5	92900	70900	1.31	91500	72000	1.27
PVC6	127300	85070	1.49	125700	86300	1.46

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of M_w (except with PS5), to a small increase in M_n and to an improved agreement of M_w/M_n with the data given by the supplier.

With PVC, comparison of the data in Tab. 1 and Tab. 2 shows rather a good agreement for the values of M_n but considerable disagreement for M_w, which increases with molar mass. This might be due to the different procedures applied for the preparation of sample solutions. The supplier of the narrow PVC samples is taking special precautions to avoid aggregation in samples with $M_w > 50000$ by dissolving the sample at 60°C in a pressurized tube for several hours and subsequent fast cooling prior to light scattering measurements(9). As with polystyrene, correction for peak broadening led only to a small decrease of M_w and to a small increase of M_n; even after correction for peak broadening, the values of M_w/M_n in Tab. 2 are considerably larger than in Tab. 1, which is mainly due to the differences in M_w probably caused by the different procedures of sample preparation mentioned above.

Since all the eluograms in Fig. 1 and Fig. 2 closely resemble a Gaussian and the calibration curve log $M_w(v)$ gives a straight line, the peak molar mass M_p was approximated by

$$M_p = (M_w\ M_n)^{0.5} \qquad 6$$

inserting M_w and M_n from Tab. 1. Calculating $[\eta]$ from these M_p values according to

$$[\eta] = 1.6 \times 10^{-4}\ M^{0.706}\ \text{dl/g} \quad \text{for polystyrene (10)} \qquad 7a$$
$$[\eta] = 1.6 \times 10^{-4}\ M^{0.770}\ \text{dl/g} \quad \text{for PVC (11)} \qquad 7b$$

we arrived at the universal calibration curve shown in Fig. 4.

Fig. 4 shows that the calibration curve of PVC agrees very well with that of polystyrene. From these findings there is no indication for special effects caused by aggregation of PVC. However, this might be due to the fact that eq. 7b used for PVC was originally determined via universal calibration with narrow polystyrene standards applying a procedure for the preparation of PVC sample solutions similar to ours.

As can be seen from Fig. 3, there is a profound influence of concentration on the eluogram e(v) of PVC5; there is however hardly any influence of concentration on the peak elution volume and on the function log $M_w(v)$. It is therefore rather obvious that the

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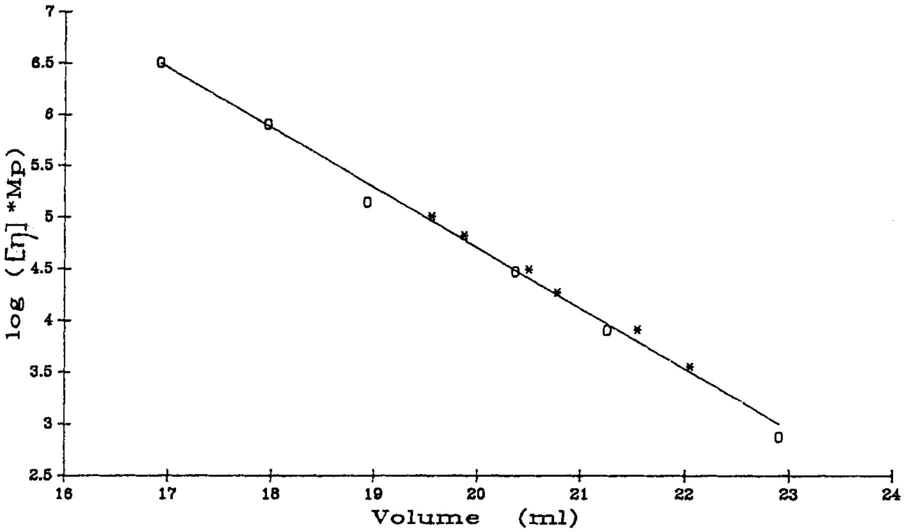

FIGURE 4

Universal calibration with narrow PS- and PVC-samples. O PS, * PVC; [η] and M_p from Tab. 1, V_p from Tab. 2.

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change in e(v) with increasing concentration is mainly due to an increase of the dispersion parameter σ. This is clearly demonstrated by the values of σ shown in Tab. 3, irrespectively whether the iterative procedure of Billiani et al.(3) or the algebraic approximation of He et al.(2) is chosen for simultaneous calibration of separation and peak broadening.

In most cases, three independent SEC/LALLS experiments were carried out with one sample solution, Tab. 2 and Tab. 3 presenting the arithmetic mean of M_w, M_n and σ. Fig. 5 shows the individual values of σ in the plot σ^2 vs. V_p, as suggested by Cheng et al. (12). For polystyrene a decrease of σ^2 with increasing peak elution volume is observed as suggested in the literature (12). A larger scatter in σ^2 and a higher

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TABLE 3

Peak elution volume, V_p, concentration of sample solution, c, and axial dispersion parameter, σ, calculated according to Billiani et al.(3), σ_B, or to He et al. (2), σ_H, of narrow PS- and PVC-samples (cf. Tab. 1); σ^* from measurements with c=0.75 g/l

Sample	V_p ml	c g/l	σ_B ml	σ_H ml
PS1	22.90	0.728	0.260	0.243
PS2	21.25	0.738	0.240	0.261
PS3	20.37	0.677	0.226	0.255
PS4	18.93	0.492	0.245	0.262
PS5	17.96	0.524	0.268	0.301
PS6	16.92	0.523	0.260	0.285
PVC1	22.04	2.027	0.313	0.343
PVC2	21.53	2.043	0.266	0.312
PVC3	20.77	2.004	0.314	0.325
PVC4	20.50	1.975	0.311	0.358
PVC5	19.86	2.024	0.301 $\sigma_B^*=0.24$	0.312 $\sigma_H^*=0.26$
PVC6	19.55	1.978	0.314	0.368

value of σ^2 is observed for PVC solutions with c=2 g/l than in the case of PS solutions with c=0.49-0.74 g/l. However, the values of σ measured with PVC at lower concentration (c=0.75 g/l) agree very well with the σ-values found with PS. In contradiction to an earlier publication(6), additional measurements could not prove the pronounced increase of σ^2 with V_p found from the first data points measured with PVC at c=2.0 g/l. Also given in Fig. 5 is the range of V_p where according to Cheng $\sigma^2(V_p)$ should reach its maximum; this range of V_p is described by eq. 8:

$$V_{p,\sigma^2_{max}} = V_e + \frac{1}{e\,B} , \qquad 8$$

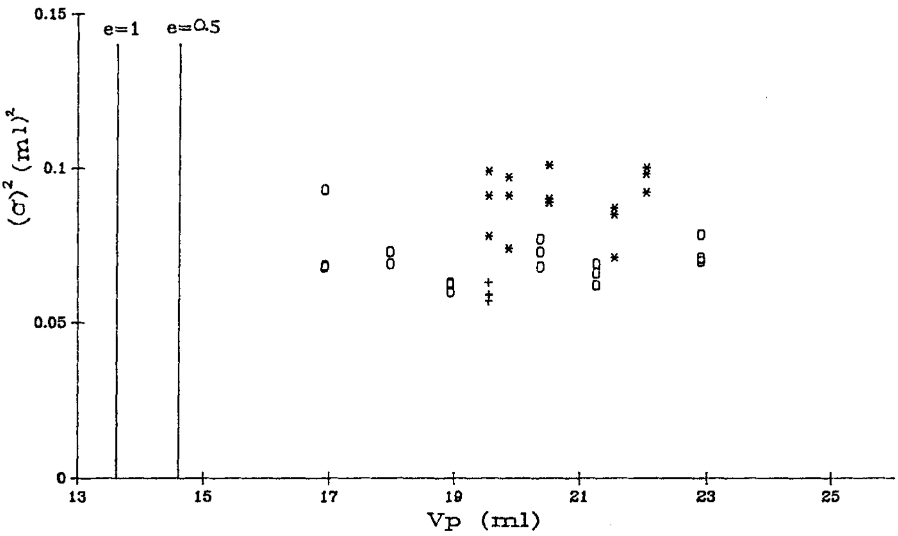

FIGURE 5

Dispersion parameter σ as a function of peak elution volume V_p in the plot of σ^2 vs V_p according to Cheng et al.(12). O PS, * PVC, + PVC5 with c=0.75 [g/l] (cf. Tab. 3). For definition of parameter e see text (eq. 8).

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with V_e = exclusion volume of the columns used,

B = slope of the calibration line ln $M(V_p)$, and

e = a parameter, varying between 1 and 0.5.

The results of the iterative procedure of Billiani et al.(3) and the method of He et al.(2) agree very well only in those cases where e(v) is well described by a Gaussian. This is to be expected, since the applicability of the latter method is limited to the case of a Gaussian eluogram e(v) combined with a linear calibration function log $M(V_p)$.

These findings indicate that the axial dispersion parameter σ is not always a function of the peak elution volume V_p only, but may in certain cases, e.g. PVC, also strongly depend on concentration. For determination of molar mass distribution on an absolute scale, individual SEC/LALLS runs on homopolymers should therefore always be evaluated by simultaneous calibration of separation and axial dispersion. In this way, any change of the axial dispersion and separation will be recorded and can be corrected for, whether it is due to special effects of the sample or to changes in the quality of the columns.

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REFERENCES

1. Lyngaae-Jorgensen, J., J. Polymer Sci. Polym. Symp. 33, 39, 1971
2. He, Z. D., Cheng, R. S., Zhang, X. Ch., J. Liq. Chromatog. 5, 1209, 1982
3. Billiani, J., Rois, G., Lederer, K., Chromatographia 26, 372, 1988
4. Rois, G., Diplomarbeit, Montanuniversität Leoben, 1988
5. Kaye, W., Havlik, A. J., Appl. Optics 12, 541, 1973

6. Billiani, J., Amtmann, I., Mayer T., Lederer K., J. Liq. Chromatog. (in print)

7. Lederer, K., Imrich-Schwarz, G., Dunky, M., Appl. Polym. Sci. 32, 4751, 1986

8. Ishige, T., Lee, S. I., Hamielec, A. E., J. Appl. Polym. Sci. 15, 1607,1971

9. Kilz, P., Polymer Standards Service, Mainz, FRG, private communication 1990

10. Alliet, D. F., Pacco, J. M., 6th International GPC Seminar 274, 1968, as cited in 1988 Annual Book of ASTM Standards, Vol. 08.03, 145

11. Goedhart P., Opschoor, A., J. Polymer Sci. Polym. Phys. Ed. 8, 1227, 1970

12. Cheng, R.-S., Wang, Z.-L., and Zhao, Y., ACS Sym. Series 352, 281, 1987

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