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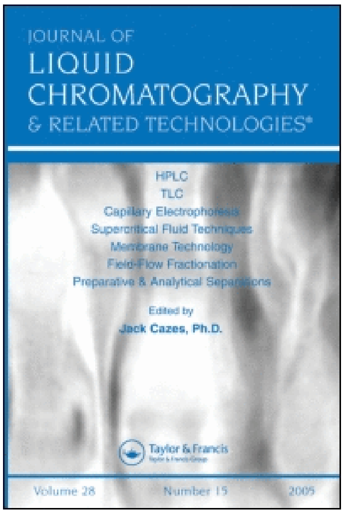

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SIZE-EXCLUSION CHROMATOGRAPHY OF LOW MOLECULAR WEIGHT POLYMERS

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ABSTRACT

To overcome the difficulty of the determination of the molecular-weight characteristics by size exclusion chromatography in the low-molecular-weight region ($M < 10^4$), the Sadron-Rempp relationship was used both for the construction of dependence of the universal calibration parameter on elution volume and for the tranformation of chromatographic data to molecular characteristics. Numerical values of constants of the above relation between intrinsic viscosity and molecular weight, which were calculated for some polymer-eluent systems on the basis of literature data, are given.

INTRODUCTION

Size exclusion chromatography (SEC) is suitable for the characterization of low-molecular-weight polymers since the product of intrinsic viscosity and molecular weights $[\eta]M$ determines their hydrodynamic retention.[1-4] Direct determination of molecular weight M is mostly excluded because of insufficient sensitivity of light scattering to short macromolecules. Therefore a calibration of the separation system is not avoidable. The concept of "universal calibration", i.e. the dependence of the parameter $[\eta]M$ on elution volume V, makes possible characterization of any polymer,[1] for which a set of molecularly uniform standards is not available. For this purpose the relations between $[\eta]$ and M both for calibrants and for polymers under study are needed. The frequently used Mark-Houwink-Sakurada equation is not appropriate for most polymer-good solvent systems if $M<10^4$. For this range of molecular weights, other two-parameter equations were suggested.[5-7] The Dondos-Benoit equation was already used for interpretation of SEC data.[6,8-11] In this paper a more general three-parameter equation suggested by Sadron and Rempp[12] was applied

$$[\eta] = A_1 + A_2 M^a \tag{1}$$

to demonstrate the determination of molecular weight distribution of small polymers by SEC.

MATERIALS AND METHODS

Polymers

Polystyrene (PS), poly(oxyethylene) (POE), polyisobutylene (PIB), and polybutadiene (PB), were purchased from Chrompack and Polymer Laboratories, Serva and Fluka, Polymers Standard Service, and Polyscience, respectively. Poly(1-decene), poly(1-decene), poly(methyl methacrylate) were prepared by ionic polymerization.

Methods of Measurement

High-speed SEC was performed using an HP 1084 B (Hewlett Packard, U.S.A.) liquid chomatograph with differential refractometric detection (Knauer 2025/50, FRG) and with columns (7.5/600 mm) packed with PL-GEL 10 μm 500 Å and 100 Å (Polymer Laboratories, GB). Tetrahydrofuran (THF, flow rate 1 cm^3 min^{-1}) was the mobile phase. Under chosen separation conditions the axial dispersion was neglected.

Osmotic measurements (VPO) were performed with a Hitachi Perkin-Elmer vapour pressure apparatus M 115 in chloroform at 37°C (cf. 13).

Viscosity of solutions of some polymers in THF was measured at 25°C with an Ubbelohde capillary viscometer adapted for gradual dilution. Viscometric data were evaluated by Heller's extrapolation method.

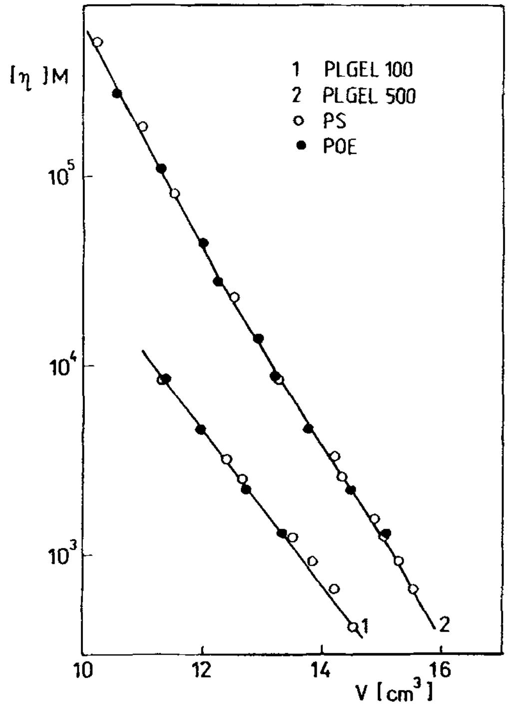

Figure 1. Dependence of universal calibration parameter $[\eta]M$ on elution volume V for two separation systems

RESULTS AND DISSCUSSION

PS and POE standards were subjected to SEC to obtain their elution volumes V. An experimental "universal calibration" (Fig. 1)

$$\log([\eta]M) = f(V) \qquad (2)$$

was constructed using osmometrically checked molecular weights and intrinsic viscosities calculated according to eq.(1). Parameters of this equation determined on the basis of literature data are summarized in Table 1. (In addition to A_1, A_2, and a for PS and POE in THF, constants for calibrants in other solvents widely used as SEC eluents are listed).

Table 1

The Parameters* of Sandron-Rempp Equation[1] for Various Polymer-Eluent Systems Determined at 25°C in the Molecular-Weight Range $(0.3\text{-}30)\mathrm{x}10^3$

Polymer	Eluent	A_1	A_2 $\mathrm{x}10^2$	a	Ref.
PS	Tetrahydrofuran	0.73	2.22	0.65	21, 23
PS	Toluene	0.94	1.33	0.70	22, 23
PS	Chloroform	0.28	4.52	0.59	6, 22
POE	Tetrahydrofuran	0.50	4.75	0.65	24
POE	Dioxane	0.05	4.00	0.70	12, 25
POE	Dimethylformamaide	1.03	5.93	0.63	25
POE	Chloroform	-1.10	18.80	0.55	6, 26
POE	Methanol	0.51	7.74	0.60	12, 25
POE	Water	1.47	4.84	0.66	12, 25, 26
PMMA	Tetrahydrofuran	0.91	3.19	0.60	10, 14
PIB	Tetrahydrofuran	---	5.00	0.60	16
PB	Tetrahydrofuran	---	4.87	0.68	17, 18

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* The values of $[\eta]$ atr in $\mathrm{cm}^3\mathrm{g}^{-1}$.

Poly(methyl Methacrylate)

For $M<10^4$ the double logarithmic plot of $[\eta]$ against M for PMMA in good solvents[14] deviates upwards. This behaviour of PMMA in THF can be described well by eq.(1) with respective constants given in Table 1. To transform the chromatographic data to molecular weight distribution (MWD), eqs (1) and (2) were combined

$$f(V) = \log\left(A_1 M + A_2 M^{(a+1)}\right) \qquad (3)$$

Using Newton's method of successive approximation the values of M along the chromatogram were calculated from eq.(3). Then the calculated M_i and w_i (weight fraction of polymer at V_i) appeared in summations giving weight-average and number-average molecular weight as well as intrinsic viscosity,

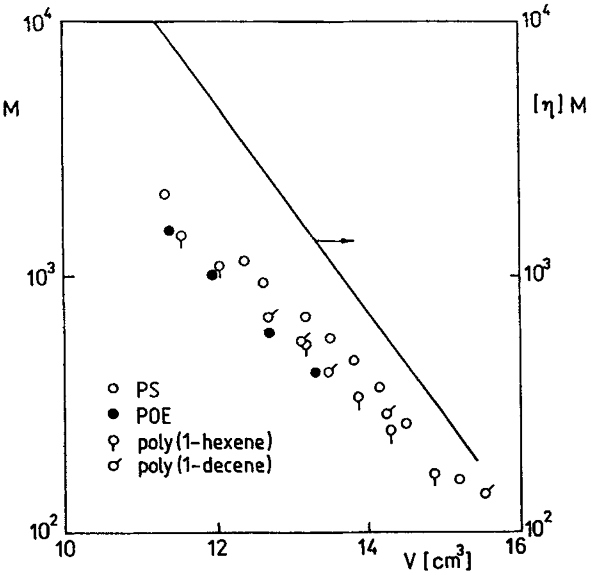

Figure 2. Plot of log $[\eta]$ vs. log M. The lines represent Mark-Houwink-Sakurada relations in the high-molecular-weight region.

Table 2

Comparison of Molecular Weights Obtained by Different Methods for PMMA and PIB Samples

Polymer	**VPO**	**SEC**			
		SR eq.		**MHS eq.**	
	M_n	M_n	M_W/M_n	M_n	$M_W M_n$
PMMA	2700	2780	1.50	3930	1.35
PMMA	3400	3550	1.77	4790	1.57
PMMA	4600	4620	2.46	6130	2.05
PIB	550	---	---	596	1.12
PIB	1500	---	---	1610	1.24

$M_W = \Sigma w_i Mi$, $M_n = (\Sigma w_i / Mi)^{-1}$ and $[\eta] = \Sigma w_i f(V_i) M_i^{-1}$. Characteristics of three PMMA samples obtained by the described way are compared in Table 2 with those calculated using the MHS relation derived for high-molecular-

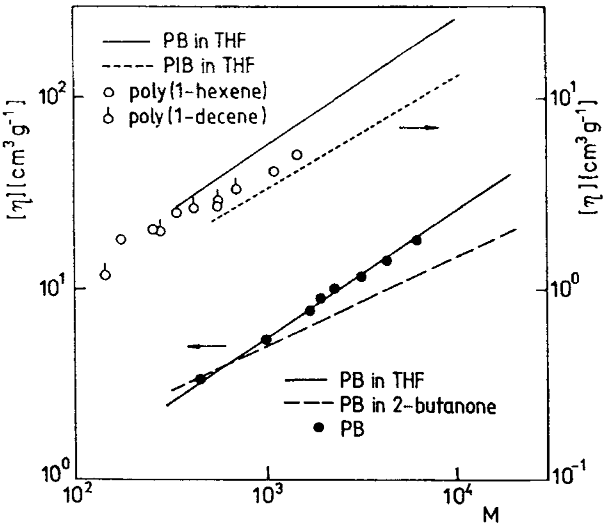

Figure 3. Elution behaviour of different low-molecular-weight polymers in separation system PLGEL 100.

weight region.[15] M_n increassed up to 30-40%, i.e. the nonuniformity became lower (Table 2), when not taking into account specific hydrodynamic behaviour of low PMMA's.

Polyisobutylene and Polybutadiene

For the system PIB-THF the range of validity of the MHS relation[16] can be extended to very low molecular weights, since reliable molecular weight parameters with admissible errors were obtained as shown in Table 2. The same conclusion was drawn from evaluation of the SEC data of PB in THF.[17,18] As this statement contradicts the literature data,[9] the evidence is given in Figure 2. The experimental points with coordinates $[\eta]$ and M follow the MHS dependence[17] satisfactorily.

Poly(1-alkene)'s

Only little is known about hydrodynamic behaviour of these oligomers/polymers in solution. Using the "universal calibration" concept, it was possible to obtain missing data. The $[\eta]$ value was calculated from the $[\eta]$M value corresponding to the elution volume in the maximum of a chromatographic curve[19] as demonstrated in Figure 3. Individual low oligomers in multimodal chromatograms were identified by reverse phase liquid chromatography[20] and 75 eV impact mass spectrometry. Other necessary M_n values were measured by osmometry. In Figure 2 the dependences of $[\eta]$ on M for poly(1-hexene) and poly(1-decene) in THF are compared with those for PIB and PB.

CONCLUSION

It was shown that disregarding specific hydrodynamic behaviour of polymers in low-molecular-weight region ($M<10^4$) becomes the cause of possible errors in molecular characterization by SEC. This phenomenon must be taken into account both in construction of universal dependence (eq.1) using molecularly uniform standards and in recalculation of SEC data to MWD by means of the "universal calibration" principle. On the other hand, SEC in combination with an independent measuring method (e.g. VPO) can be used for estimation of hydrodynamic behaviour of short polymer molecules.

REFERENCES

1. Z. Grubisic, P. Rempp, H. Benoit, J. Polym. Sci., **B5**, 573 (1967).

2. B. G. Belenkii, J. A. Vakhtina, O. G. Tarakanov, Vysokomol. Soedin., **B16**, 507 (1974).

3. J. Aurenge, Z. Gallot, A. J. De Vries, H. Benoit,, J. Polym. Sci., **C52**, 217 (1975).

4. M. R. Ambler, J. Polym. Sci., Polym. Lett. Ed., **14**, 683 (1976).

5. J. E. Hearst, J. Chem. Phys., **40**, 1506 (1964).

6. A. Dondos, H. Benoit, Polymer, **18**, 1161 (1977).

7. M. Bohdanecký, Macromolecules, **16**, 1483 (1988).

8. A. Dondos, V. Skordilis, J. Polym. Sci., Polym. Phys. Ed., **23**, 615 (1985).

9. K. Ito, T. Saito, T. Aoyama, Polymer, **28**, 1589 (1987).

10. C. Tsitsilianis, G. Mitsiani, A. Dondos, J. Polym. Sci., Polym. Phys. Ed., **27**, 763 (1989).

11. C. Tsitsilianis, A. Dondos, J. Liq. Chromatogr., **13(15)**, 3027 (1990).

12. C. Sadron, P. Rempp, J. Polym. Sci., **29**, 127 (1958).

13. L. Mrkvičková, S. Pokorná, J. Appl. Polym. Sci., **30**, 1211 (1985).

14. Y. Fujii, Y. Tamai, T. Konishi, H. Yamakava, Macromolecules, **24**, 1608 (1991).

15. J. M. Evans, Polym. Eng. Sci., **13**, 401 (1973).

16. L. Mrkvičková, P. Lopour, S. Pokorná, J. Janča, Angew. Makromol. Chem., **182**, 445 (1981).

17. G. Kraus, C. J. Stacy, J. Polym. Sci., **A2**, 10, 657 (1972).

18. L. Mrkvičková, I. Kuchaříková, S. Pokorná, J. Čermák, Plaste Kautsch., **34**, 17 (1987).

19. A. E. Hamielec, A. C. Ouano, J. Liq. Chromatogr., **1(1)**, 111 (1978).

20. L. Mrkvičková, J. Kuklík, B. Porsch, will be published.

21. C. Tsitsilianis, G. Staikos, J. Appl. Polym. Sci., **33**, 3081 (1987).

22. R. Kwiewske, W. M. Kulicke, Makromol. Chem., **184**, 2173 (1983).

23. Y. Einaga, Y. Miyaki, H. Fujita, J. Polym. Sci., Polym. Phys. Ed., **17**, 2103 (1979).

24. J. Horský, Polym. Commun., **32**, 346 (1991).

25. H. G. Elias, Makromol. Chem., **103**, 214 (1967).

26. C. Rossi, C. Cuniberti, J. Polym. Sci., Polym. Lett. Ed., **2**, 689 (1964).

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