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GPC Calibration for Poly(Methyl Acrylate)

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SUMMARY

The methods of GPC calibration proposed by WEISS and COHN Ginsberg (1969) and by MAHABADI and O'DRISCOLL (1977) has been applied. Their restriction and a possibility to overcome it has been demonstrated.

INTRODUCTION

Preparation and characterizing of narrow standards of each kind of polymer of interest for GPC is not always feasible. The calibration of GPC columns is performed most often with commercial narrow polystyrene standards. A direct evaluation of a chromatogram on the base of such a calibration leads to the distribution of effective hydrodynamic volumes of a polymer sample in the solvent used as eluent. Then it has to be converted into its molecular mass distribution.

The conversion is easily performed if we do have a reliable pair of K,α coefficients for the Mark-Houvink equation (where for moderately flexible polymers $0.5 < \alpha < 1.0$) expressing the relation between the molecular masses of the polymer and its intrinsic viscosities in the same solvent and temperature in which the GPC experiment has been performed, and for the proper range of molecular masses. In tetrahydrofurane (THF), which is a commonly used eluent in the GPC, they are very often unknown.

In this case the calibration may be performed with unfractionated polymer samples by several methods: from intrinsic viscosity measurements in the solvent of interest and GPC chromatograms of at least two samples of the polymer (WEISS, COHN-GINSBERG, 1969), from viscosity measurements of several samples of the polymer in two solvents for one of which the coefficients are given (COLL, GILDING 1970), or from viscosity measurements and a chromatogram of one polymer sample if its one or two average molecular masses (M_w and/or M_n) are known (WEISS, COHN-GINSBERG, 1969, 1970, BELENKII, NEFEDOV 1972, MAHABADI, O'DRISCOLL 1977, KATO, TAKAMATSU et al. 1977, PARK, GREASLEY 1977). Some of these methods are restricted by specific demands such as the shape of the molecular mass distribution (WEISS, COHN-GINSBERG 1970), θ-conditions of measurements (KATO, TAKAMATSU et al. 1977) or linearity of the calibration curve (BELENKII, NEFEDOV 1972).

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The methods of WEISS and COHN-GINSBERG (1969) and of (MAHABADI and O'DRISCOLL 1977) have no such demands and they seem to be valid for a broad range of molecular masses. But their precision is reduced by possible errors in the molecular masses and viscosity measurements. These errors being of oder of 5 - 10 % (STRAZIELLE, BENOIT 1970) may be considerable if they come to superposition.

Substantial in these methods is to find a value of the parameter α (stepping by 0.01 within the interval of 0.50 - 1.00) for which the difference between right and left sides of the following equations is minimized:

$$[\eta]_1/[\eta]_2 = \sum_i w_{1i} J_i^{\alpha/(\alpha+1)} \Big/ \sum_i w_{2i} J_i^{\alpha/(\alpha+1)} \qquad (1)$$

$$[\eta] M_n = \sum_i w_i J_i^{\alpha/(\alpha+1)} \Big/ \sum_i w_i / J_i^{1/(\alpha+1)} \qquad (2)$$

where w_i is a weight fraction of molecular species of the sample, $J_i = [\eta]_i M_i$ is a universal calibration parameter (effective hydrodynamic volume), M_i, $[\eta]_i$ - are the molecular mass and the intrinsic viscosity of the species, respectively.

The value of the coefficient K may be evaluated from the same chromatogram, the same calibration curve and the experimental value of $[\eta]$, M_n or M_w.

EXPERIMENTAL

The number average molecular masses of 8 samples of poly(methyl acrylate) have been determined by osmometry measurements in benzene.* The viscosity average molecular masses of three of them have been determined by measurements in benzene at 25 °C with the parameters K,α of GUZMAN (1956). Intrinsic viscosities of 7 samples have been determined in THF in 25 °C. The results of these determinations are presented in Table I.

The GPC measurements were performed on a Waters liquid chromatograph ALC/GPC - 201 type equipped with a set of 5 μ-styragel columns in THF, with flow speed of 1.5 ml/min at room temperature (25 ± 2 °C).

The calibration of the μ-styragel columns has been performed with 17 polystyrene standards of Waters and Sas & Son.

The calculations were performed on a Hewlett Packard 4825 A type calculator.

RESULTS AND DISCUSSION

The equation (1) was applied for quotients of $[\eta]_t/[\eta]_1$ where $t = 3, \ldots, 8$ is the serial number of the sample.

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*The samples have been prepared (by polymerization in benzene and in dimethylformamide at 50 °C) and the osmotic measurements performed by E.Boros Gyevi in our laboratory.

Table I

Serial number	PMA samples	$[\eta]_{C_6H_6}$	$[\eta]_{THF}$	$\bar{M}_n \cdot 10^{-3}$ (osmometry)	$\bar{M}_v \cdot 10^{-3}$ (viscometry)	GPC molecular masses computed: from equation 1 for coincidence better than 1%			GPC molecular masses computed: for parameters $K = 3.88 \cdot 10^{-5}$ dl/g $\alpha = 0.82$		
						$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$
	polymerized in benzene										
1	1	-	0.55	66	-	61	103	101	62	104	109
2	2	0.85	-	82	207	-	-	-	82	181	202
3	6	1.65	1.70	182	451	171	446	472	173	433	479
4	7	-	1.43	251	-	239	454	485	234	413	436
5	8	-	2.06	253	-	280	565	625	265	567	610
6	10	2.06	1.78	359	583	432	631	710	358	577	601
	polymerized in DMF										
7	143	-	1.68	341	-	425	606	612	339	545	569
8	144	-	1.18	238	-	253	418	450	211	357	374

Performing the calculations according to both formulas (1) and (2) we have experienced a broad spread of the values of α obtained for the best agreement (which was always better than 1%) between the left and the right sides of the equations. The value of α diverged in the interval of 0.72 - 0.95 with an average 0.82. The value of K belonging to this α was $3.88 \cdot 10^{-5}$ (see relation (3) below).

For an uncertainty of 2% in the results of extrapolation of viscosity measurements, which seems to be quite reasonable, the quotient of two intrinsic viscosities will suffer of already 4% of uncertainty. Similarly, for uncertainty of 10% in molecular masses determination by osmometry the uncertainty of the product of $M_n[\eta]$ may have an error of 12%.

We have repeated the calculations of the parameters K,α with a condition of only ±10% for the agreement of the two sides of the equations (1) and (2). Independently on the deviations between the two sides of the equations all the K,α values belonging to each other proved to be related by a logarythmic expression of the type:

$$\log K = C - B\alpha \qquad (3)$$

That can be seen in Figure 1, where the line A presents the least squares fit for all the K,α pairs computed for 7 samples of poly(methyl acrylate) by equations (1) and (2) with different requirements (better than 1% and 10%) for the agreement of the two sides of the equations. The number and weight average molecular masses computed from the same chromatogram for any of K,α pairs belonging to this relation are not very sensitive for the choise of this pair. For two pairs obtained for α as different as 0.77 and 0.88 the values of M_n and M_w will differ from one another by about 1% and 6% respectively.

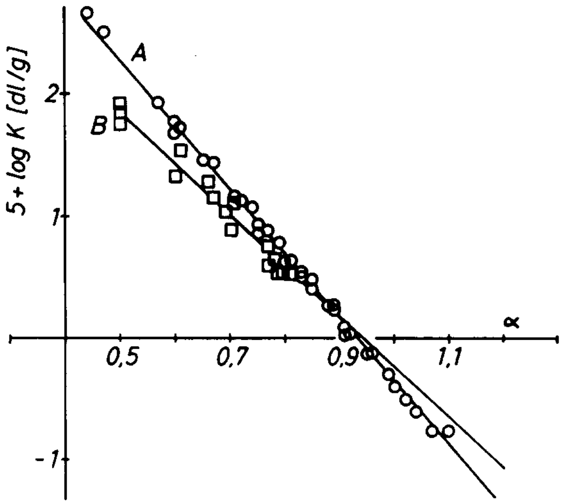

Figure 1. Log K - vs. α relationship for poly(methyl acrylate) o - values determined from equation (1) and (2) for samples in THF (C = -0.113, B = 5.24; □ - values compiled in Polymer Handbook (BRANDRUP, IMMERGUT 1975), (C = -1.07, B = 4.17).

It was shown elsewhere (AHARONI 1977), that despite of the considerable scatter of the K,α pairs their values obtained empirically for the same polymer by different investigators in different solvents and temperatures cluster about a line represented by a relation similar to the relation (3). Furthermore, one can obtain a K_θ value which is a characteristic quantity of each polymer by extrapolation of the log K versus α plots to $\alpha = 0.5$ even in case, where experimental $\alpha \gg 0.5$.

AHARONI has collected the data of K,α pairs for 22 different polymers and represented them graphically and as a table of constants C and B.

These constants must of course be quite different for poly(methyl acrylate) than ours, because they give a relation between real average hydrodynamic volumes of the polymer samples among different conditions and their average molecular masses, including the hydrodynamic volumes in the θ point (line B in Figure 1).

Our relation represents the reality in one point only. It is obvious that this point should be approximated by the intersection of the two lines. It can be seen that our average K,α pair lays indeed not far from it. It doens't deviate more from the line B than the points marking it out.

We have repeated the procedure in the case of two PVC samples. Their characteristic is presented in Table II. K,α pairs have been accounted by the equation (2) (see Figure 2). In this case the intersection point of the two lines is also in good

Table II. PVC samples characterization

	$[\eta]_{THF}$	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$
Solvic*	0.819	38	84
PVC-470	1.066	54	97

*Averages of the data of determinations published by STRAZIELLE and BENOIT (1971).

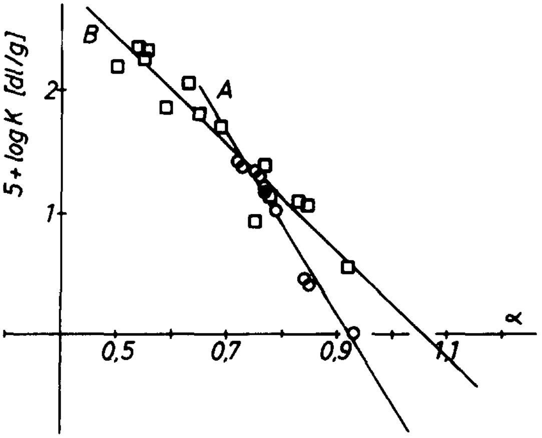

Figure 2. Log K - vs. α relationship for poly(vinyl chloride);
o - values determined from equation (2) for two samples in THF
($C = 1.915$, $B = 7.51$);
□ - values compiled in Polymer Handbook (BRANDRUP, IMMERGUT 1975),
($C = -0.373$, $B = 4.38$)

agreement with the pair of $K = 1.5 \cdot 10^{-4}$, $\alpha = 0.77$, which has been obtained (BOHDANECKY, SOLC et al. 1967) from direct measurements of molecular masses and intrinsic viscosities in THF of fractionated PVC samples and was applied (KOLINSKY, JANCA 1974) to construct a GPC calibration curve for PVC with good results.

On this base we consider the K,α parameters' pair obtained as average for the system poly(methyl acrylate) - tetrahydrofurane as reliable and suitable for constructing a GPC calibration curve for this material.

The number average and viscosity average molecular masses of the samples used for the calibration as measured by osmometry and viscometry, respectively, and computed from chromatograms applying equation (1) are compared in Figure 3. See also Table I.

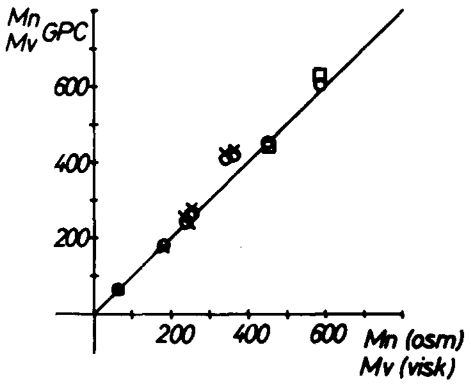

Figure 3. Comparison of average molecular masses measured by osmometry (x) and viscometry (□) with values computed from chromatograms according to equation (1). The circles mean the computations performed for only 10% of coincidence between the two sides of the equations. The other signs concern computations performed for the best coincidence.

Figure 4 compares the number and viscosity average molecular masses of several samples of PMA (also the samples used for the calibration) measured by osmometry and viscometry and by GPC for $K = 3.88 \cdot 10^{-5}$, $\alpha = 0.82$ parameters' pair mentioned above.

In the first case the values computed from GPC measurements deviate from the osmometry and viscosity data on an average 10% with maximum 24%. In the second case they deviate on an average 7% with maximum 20%. The deviations do not show any particular tendency.

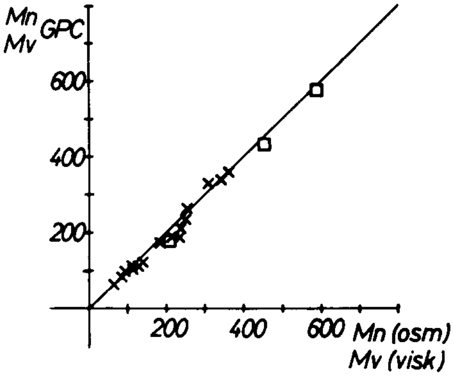

Figure 4. Comparison of average molecular masses measured by osmometry (x) and viscometry (□) with values determined from GPC unversal calibration curve in THF for parameters $K = 3.88\cdot10^{-5}$, $\alpha = 0.82$.

REFERENCES

AHARONI,S.M.: J.Appl.Pol.Sci., 21, 1323 (1977)
BELENKII,B.G. and NEFEDOV,P.P.: Vysokomol.Soed. A14, 1658 (1972)
BOHDANECKY,M., SOLC,K., KRATOCHVILL,P., KOLINSKY,M., RYSKA,M. and LEM,D.: J.Pol.Sci., A-2, 5, 343 (1967)
BRANDRUP,J and IMMERGUT,E.H. (eds.): Polymer Handbook, 2nd edition New York, London, Sydney, Toronto, Wiley Interscience (1975)
COLL,H. and GILDING,D.K.: J.Pol.Sci. Part A-2, 8, 89 (1970)
GUZMAN,G.M.: Anales Real.Soc.Espan.de Fiz.Quim. 52-B, 377 (1956)
KATO,Y., TAKAMATSU,T., FUKUTOMI,M., FUKUDA,M. and HASHIMOTO,T.: J.Appl.Pol.Sci., 21, 577 (1977)
KOLINSKY,M. and JANCA,J.: J.Pol.Sci. Polym.Chem.Ed. 12, 1181 (1974)
MAHABADI,H.K. and O'DRISCOLL,K.F.: J.Appl.Polym.Sci., 21, 1283 (1977)
PARK,W.S. and GREASSLEY,W.W.: J.Polym.Sci. Polym.Phys.Ed. 15, 71 (1977)
STRAZIELLE,C. and BENOIT,H.: IUPAC Intern.Symp.on Macromol. (1970) Leiden, Main and Survey Lectures, London, Butterworths, 1971, p. 451
WEISS,A.R. and COHN-GINSBERG,E.: J.Pol.Sci. Part B, 7, 379 (1969)
WEISS,A.R. and COHN-GINSBERG,E.: J.Pol.Sci. Part A-2, 8, 148 (1970)

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