Characterization of Commercial Polyvinylbutyral by Gel Permeation Chromatography

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Synopsis

Fractions of commercial polyvinylbutyral "Movital" were investigated by the "off-line" combination of gel permeation chromatography and viscometry. Parameters of the Mark–Houwink equation were determined for polyvinylbutyral in tetrahydrofuran at 25°C. Real values of the molecular parameters were obtained by the evaluation of chromatographic data using the principle of universal calibration.

INTRODUCTION

Polyvinylbutyral (PVB) is a product of the simultaneous hydrolysis of poly(vinyl acetate) and acetalization of the poly(vinyl alcohol) thus formed with butyraldehyde. The reaction may proceed not only intramolecularly, but also intermolecularly; in other words, long chain branching may also take place. As the polymeranalogous transformation is not complete, PVB is a copolymer which, in addition to butyral rings, possesses also hydroxyl groups. The latter form intermacromolecular hydrogen bonds,[1] which especially with respect to light scattering impedes the molecular solubility of PVB. This is why the behavior of PVB in dilute solutions is poorly reproducible, and the interpretation of experimental data is questionable. Also, reported data concerning the determination of some molecular parameters and the study of the thermodynamic and hydrodynamic behavior of PVB are subject to discussion.[2,3]

Most frequently, the method of gel permeation chromatography (GPC) is used in the determination of the individual average molecular weights and molecular weight distributions. In practice, it may be employed in the "off-line" combination with viscometry in the determination of parameters of the Mark–Houwink–Kuhn–Sakurada (MHKS) equation,[4] if the system of separation columns has the so-called "linear universal calibration" [5]:

$$[\eta]M = A_1 e^{-A_2 V_e} \tag{1}$$

Here $[\eta]$ is intrinsic viscosity, M is molecular weight, A_1, A_2 are the calibration constants, and V_e is the elution volume. By combining eq. (1) and the MHKS relation with parameters K and a, the relation

$$[\eta] = (K^{1/a} A_1)^{a/(a+1)} \exp\left(-A_2 \frac{a}{a+1} V_e\right) \tag{2}$$

is obtained. From the slope and intercept of the experimental dependence log $[\eta]$ vs. V_e (elution volume in the maximum of the chromatographic curve), the

parameters K and a needed for a standard treatment of GPC data can be calculated using universal calibration.

The paper demonstrates the application of the method of Weiss and Cohn-Ginsberg[4] in the characterization of PVB. At the same time, attention is drawn to the possibility of the GPC analysis of this product, widely used for industrial purposes.

EXPERIMENTAL

Materials. Commercial polydisperse "Movitals" (Hoechst) were used in the analysis and fractionation; they contain on the average 70% of monomer units of saponified poly(vinyl acetate) transformed into butyral, the remaining monomer units (30%) being present as vinyl alcohol.

The column elution method was used in the fractionation: the polymer deposited over the whole column packing was gradually extracted with solvent–precipitant mixtures containing increasing contents of solvent. Since PVB possesses an extraordinary adhesion to glass (almost irreversible adsorption), stainless steel coils (2 × 2 mm) had to be used as the elution column packing. The sample was deposited by precipitating PVB from a 3.5% solution (mixture isopropyl alcohol–heptane, 1:1), by cooling to −40°C. The mixture of solvents was gradually replaced with heptane, and the coils covered with PVB were dried at room temperature. Chloroform and n-heptane were used as solvent and precipitant, respectively, in the extraction which proceeded at room temperature. The individual fractions were isolated by evaporation of the extraction mixture *in vacuo*.

METHODS

GPC measurements were carried out with an apparatus built at this Institute, with a flow differential refractometer R-403 (Waters) used for detection. Four separation columns of standard dimensions (8 × 1200 mm) were packed with a styrene–divinylbenzene gel "Styragel" (Waters) with pores of various sizes so as to obtain a "linear" dependence of the calibration plot in the system. The flow rate of tetrahydrofuran (THF) was 0.35 cm^3·min^{-1}; c. 1.64 cm^3 of the solution of the analyzed polymer was injected at concentrations approximately 0.25% (w/v). The universal calibration dependence was constructed by means of polystyrene standards (Waters) for which $[\eta] = 1.17 \times 10^{-2} M^{0.717}$. The molecular parameters of PVB samples were calculated using this universal calibration and the Mark–Houwink equation derived for PVB in THF at 25°C. Under the chosen experimental conditions of separation, the interfering dispersion was almost suppressed; the chromatograms were therefore not corrected for axial dispersion of the chromatographic curve.

The viscosities of PVB were measured with an Ubbelohde viscometer in THF at 25°C. The light scattering measurements were performed with a FICA photogoniodiffusometer in vertically polarized light, with wavelength 546 and angular range 30–150°. The experimental techniques and method of evaluation will be reported elsewhere.[6] The weight average molecular weight M_w was determined in a mixture of isopropanol with 25 vol % water at room temperature.
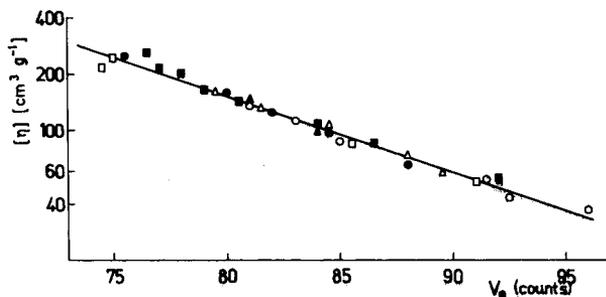
Fig. 1. Dependence described by eq. (2) for fractions prepared by fractionation of maternal polyvinylbutyral: (O) A/1; (△) A/2; (●) B/1; (□) B/2; (▲) C/1; (■) C/2.

A Brice-Phoenix differential refractometer was used for measurements of the refractive index increments dn/dc, which served as optical constants in the evaluation of scattering data, and as a criterion of the weight content of the individual components in the copolymer PVB (the composition was measured in methyl alcohol).

Osmometric measurements in methyl alcohol were carried out at 30°C with an automatic membrane osmometer Knauer.

RESULTS AND DISCUSSION

The advantage of the Weiss–Cohn-Ginsberg method consists of the fact that the analyzed polymers may be polydisperse. A sufficient condition for a simple application of this method is the Schultz–Zimm molecular weight distribution with a width not exceeding the so-called normal distribution $M_w/M_n \lesssim 2$ (cf. Refs. 7, 8). In such a case we have

$$\log [\eta]M_v \simeq \log [\eta]M_w = f(V_e) \tag{3}$$

Under these conditions, a polymer fraction having molecular weight identical with the weight average of the analyzed polydisperse sample (M_w) separates in the maximum of the chromatographic curve (at V_e). In the case of the Schultz–Zimm distribution, the experimental error given by combination of the measuring methods used exceeds the effect due to the difference between the M_w and M_v (viscosity average molecular weight) values on the accuracy of determination of the Mark–Houwink parameters using eq. (2).

The experimental dependence log $[\eta]$ vs. V_e of a large number of PVB fractions is shown in Figure 1. The scatter of experimental points is minimal, although the fractions were obtained by six independent fractionations (three commercial samples A, B, C were fractionated, and fractionation of each of the samples was moreover reproduced). The fact that also in the range of the lowest V_e's the experimental dependence keeps its linear character rules out any "long chain branching" of the analyzed maternal PVB. In the case of branching, the $[\eta]$ value would systematically decrease with decreasing V_e or increasing M of the fractions. The character of the plot of experimental points in Figure 1 could also be unfavorably affected by the heterogeneity (if any) in the chemical composition of maternal copolymers.[3] No heterogeneity was detected by differential refrac-

TABLE I
Characteristics of Fractions of Commercial Polyvinylbutyral

Sample	dn/dc (cm^3·g^{-1})	Values obtained by absolute methods				Values obtained by GPC		
		$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$[\eta]$ (cm^3·g^{-1})		$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$[\eta]$ (cm^3·g^{-1})
4-A/1	—	2.7	—	43		2.6	2.2	46
3-B/2	0.158	3.3	—	52		3.3	2.6	54
4-A/2	0.158	4.3	3.4	59		4.1	3.1	67
7-A/1	—	6.1	4.2	89		6.5	4.9	97
4-B/1	0.157	6.8	5.0	98		7.7	5.7	111
7-C/2	—	7.4	6.0	108		7.4	5.4	107
8-A/1	—	8.3	6.3	127		8.9	6.1	124
8-C/2	—	11.8	8.2	150		12.0	8.3	157
7-B/2	0.155	13.6	6.0	—		13.4	7.2	169
9-C/2	—	15.0	—	183		14.7	9.5	185
7-B/1	0.160	27.1	14.6	250		26.7	13.7	293

tometry, however, as indicated within the limits of experimental error by the identical refractive index increments dn/dc of some fractions (Table I).

The MHKS relation for PVB in THF at 25°C calculated using eq. (2)

$$[\eta] = 1.4 \times 10^{-2} M^{0.8} \tag{4}$$

was used in the evaluation of GPC data, i.e., in the calculation of the individual average molecular weights and their distribution.   The experimental differential distribution curves of some analyzed fractions are demonstrated in Figure 2. These curves are compared here with those calculated for the Schulz–Zimm distribution type with the same parameters M_n and M_w.   For narrow fractions ($M_w/M_n \leq 1.5$) the maxima of both curves compared with each other overlap completely.   In the case of fractions of the highest molecular weight and of the largest width ($M_w/M_n \leq 2$), the position of the maximum of the experimental curve is much closer to the maximum of the Schulz–Zimm distribution type than to that of the logarithmic-normal distribution. Within the whole range of M of the analyzed PVB fractions condition (3) was satisfactorily fulfilled; hence,
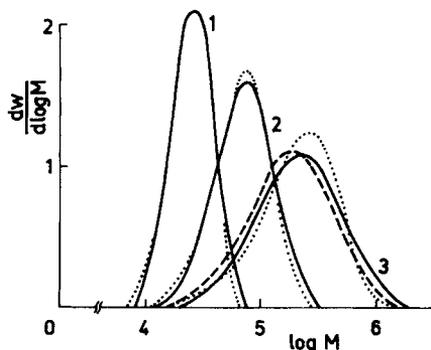
Fig. 2. Differential distribution curves: (——) experimental, (·· · ·) calculated using Schultz–Zimm; (- - -) calculated for logarithmic normal distribution; (1) fraction 4-A/1; (2) fraction 7-C/2; (3) fraction 7-B/1 (cf. Table I).
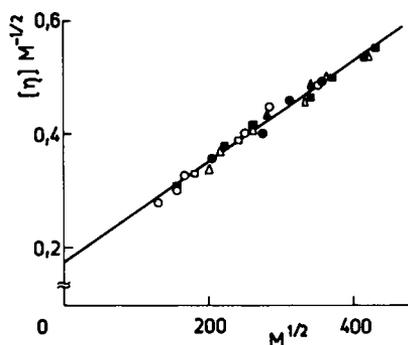
Fig. 3. Stockmayer–Fixman–Burchard plot. Experimental points denoted as in Figure 1.

distortion of the experimental dependence log $[\eta[$ vs. V_e in Figure 1 due to a different type of the distribution curve is negligible.

The real character of $[\eta]$, M_w values calculated from GPC data were verified by application of the Stockmayer–Fixman–Burchard equation.[9] Extrapolation of a linear relation obtained by plotting of $[\eta]M^{-0.5}$ vs. $M^{0.5}$ to $M^{0.5} = 0$ (Fig. 3) gave the length of unperturbed chains $[(L^2)_0/P]^{0.5}$ (L is the statistical average end-to-end distance of the unperturbed chain, and P is the degree of polymerization). This length is 0.68 nm, in good agreement with the reported data.[2,3] Reliability of the GPC analysis was also demonstrated by comparison with the M_w and M_n values determined by absolute methods, i.e., by light scattering and membrane osmometry (Tables I and II). It should be pointed out that in simple solvents PVB has a strong trend to aggregation, which makes the determination of M_w by light scattering virtually impossible. The ability of hydroxyl groups to form intermacromolecular hydrogen bonds was successfully eliminated in a mixture of isopropanol and water.[6] Osmometric measurements had to be carried out in thermodynamically less good solvents with respect to PVB; otherwise, the determination of M_n is complicated due to the nonlinear character of the dependence of reduced pressure on concentration (e.g., in THF). The M_w and M_n values obtained from GPC data and by absolute methods are in good agreement within the limits of experimental error. This concerns both characteristics of fractions (Table I) and characteristics of commercial polydisperse PVB (Table II).

TABLE II
Characteristics of Commercial Polydisperse Polyvinylbutyrals

Sample	Values obtained by absolute methods			Values obtained by GPC		
	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$[\eta]$ $(cm^3 \cdot g^{-1})$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$[\eta]$ $(cm^3 \cdot g^{-1})$
A	15.2	6.4	185	14.9	6.1	174
B	21.8	8.9	206	20.4	8.4	256
C	15.6	7.9	178	13.9	7.6	174
D	17.8	7.4	—	17.6	7.4	206
E	16.3	8.4	198	15.2	7.7	186
F	15.0	5.4	187	15.0	6.5	182
G	20.0	—	197	20.6	6.4	209

Results of the analysis of molecular parameters obtained from GPC data as described above allow us to recommend gel permeation chromatography with the styragel packing of separation columns and tetrahydrofuran as eluent as a tool for the evaluation of industrially produced polyvinylbutyral. The M_w, M_n, and $[\eta]$ values can then be calculated using the principle of universal calibration and the Mark–Houwink parameters determined in this study.

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