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USE OF GEL-PERMEATION CHROMATOGRAPHY IN THE DETERMINATION OF THE COMPOSITION OF TWO-POLYMER MIXTURES

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SUMMARY

The possibility of evaluating with acceptable accuracy the composition of a two-polymer mixture that is well separated by gel-permeation chromatography was studied by using mixtures of high-molecular-weight polybutadiene ($\bar{M}_w = 4.5 \times 10^5$) and low-molecular-weight polyisobutylene ($\bar{M}_n$ ca. 10^3). It was concluded that a satisfactory evaluation of the composition of a polymer mixture can be achieved, provided that the variations of the refractive index with the molecular weight are taken into account for the low-molecular-weight polymer (the polyisobutylene).

INTRODUCTION

The existence of a proportionality coefficient between the concentration of a single solute in a solution c and the increase of the refractive index of the latter, Δn, with respect to that of the pure solvent, allows differential refractometry to be used for measuring the concentration of a compound eluted by gel permeation chromatography (GPC).

If the eluted solute is a pure compound (not a mixture) or a homogeneous polymer, this coefficient is constant since all the molecules are identical, and is analogous to the gas chromatographic (GC) detection coefficient which is, in a given concentration range, related only to the nature of the detected compound. The situation is different when the solute is a heterogeneous polymer, in which the macromolecules may have various molecular weights, because the proportionality coefficient becomes related to the molecular weight. In GPC, in which molecules are separated according to their size (*i.e.*, for a given polymer, according to their molecular weight), a given elution volume is associated both with a concentration and a molecular weight so that Δn is a continuous function of two variables. Fortunately, the variations of the refractive index of a polymer with its molecular weight are negligible as long as the latter is sufficiently high. Thus, for a solution of a high polymer the proportionality between its concentration and Δn is valid without restriction, irrespective of the molecular weight distribution. On the other hand, the influence of the molecular weight on the refractive index is considerable in the low-molecular-weight range, as will be seen below, and it is not possible to neglect it. In this case,

$$n_S - n_s = \Delta n = Kcf(M) \tag{1}$$

where n_S and n_s are the refractive indices of the solution and the solvent, respectively, M is the molecular weight, and K is a proportionality coefficient.

If this influence were neglected, the heights read on a chromatogram would be associated with incorrect concentration values so that the calculation of the amount of polymer corresponding to the elution peak would be wrong, as would also be the calculation of the number-average and the weight-average molecular weights. If GPC is to be used to determine the composition of a mixture of two polymers, one of them will inevitably be a low-molecular-weight polymer since they must be well separated. The amount of a low-molecular-weight polymer must be calculated from the chromatogram of the mixture and the above considerations become important. These aspects are developed in the present paper.

THEORETICAL: CALCULATION OF THE AMOUNT OF A LOW-MOLECULAR-WEIGHT POLYMER IN A TWO-POLYMER MIXTURE

This amount, q, will be calculated by integrating the elution peak:

$$q = \int_v^V c \cdot dv \tag{2}$$

where c is the concentration and v is the elution volume ($V > v$).

As emphasized above, the concentration, c, of an elementary slice, the width of which is dv, cannot be simply related to its height on the chromatogram by a proportionality coefficient.

Eqn. 1 for the pure polymer can be written as

$$n_p - n_s = K\rho f(M) \tag{3}$$

where n_p is the refractive index of the pure polymer and ρ is its specific gravity.

From eqns. 1 and 3 follows

$$\Delta n = \frac{c}{\rho}(n_p - n_s) \tag{4}$$

ρ and n_p being functions of the molecular weight. Therefore

$$\rho = \rho(M) \tag{5}$$

$$n_p - n_s = \psi(M) \tag{6}$$

The GPC apparatus records a signal, i.e., a height h on the chromatogram, which is proportional to the Δn value detected by its differential refractometer:

$$\Delta n = kh \tag{7}$$

(k is a constant factor of the apparatus depending on the sensitivity used).

From eqns. 4 and 7 follows

$$c = k \cdot \frac{h\rho(M)}{\psi(M)} \tag{8}$$

and therefore:

$$q = k \int_{v}^{V} \frac{h\rho(M)}{\psi(M)} \cdot dv \tag{9}$$

On the other hand, for a given polymer, the relation between the elution volume and the molecular weight

$$v = \varphi(M) \tag{10}$$

can be differentiated to give

$$dv = \varphi'(M) \cdot dM \tag{10a}$$

Thus the amount of polymer can be calculated from the expression

$$q = k \int_{M}^{m} \frac{\rho(M)h(M)\varphi'(M)}{\psi(M)} \cdot dM \tag{11}$$

It is clear that $\varphi(M)$ is the inverse function of the well known calibration function $M = \xi(v)$, the latter being universally accepted to be:

$$M = \exp(a - bv) \tag{12}$$

In fact, experimental confirmation of eqn. 12 is observed only when M is neither too high nor too low. Indeed, if the macromolecules are larger than the pore diameter of the gel, they will be eluted in the interstitial volume of the column, the so-called "exclusion volume", whatever their molecular weight may be. If they are too small, the pores produce no more segregation between them so that they are eluted in the same volume, the so-called "penetration volume" (interstitial volume + pore volume), whatever their molecular weight may be.

Hence, eqn. 12 is applicable only to a high polymer in which the higher molecular weights are not too high. Moreover, in this case, eqn. 11 is simpler since the refractive index and the specific gravity of such a polymer do not depend on its molecular weight.

Finally, the respective amounts, q_1 and q_2, of the low polymer and the high polymer are given by the expressions:

$$q_1 = k \int_{M_1}^{m_1} \frac{\rho_1(M)h_1(M)\varphi'_1(M)}{\psi_1(M)} \cdot dM \tag{13}$$

$$q_2 = k \cdot \frac{\rho_2}{n_2 - n_s} \int_{M_2}^{m_2} h_2(M)\varphi'_2(M) \cdot dM \tag{14}$$

Theoretically, this calculation is valid whatever the number of polymers in the mixture. Nevertheless, it must be kept in mind that not only is it difficult to achieve a good separation of more than two very polydispersed polymers by GPC, but even these two polymers must have very different average molecular weights.

EXPERIMENTAL: MIXTURES OF LOW-MOLECULAR-WEIGHT POLYISOBUTYLENE AND HIGH-MOLECULAR-WEIGHT POLYBUTADIENE

Our experimental work was concerned with mixtures of low-molecular-weight polyisobutylene and high-molecular-weight cis-1,4-polybutadiene.

In the first part, the functions $\rho(M)$, $\psi(M)$ and $\varphi(M)$ were studied for polyisobutylene and verified to be constant for polybutadiene, using samples that were as monodispersed as possible.

The second part of this work was intended to check the calculation method proposed above. We applied the latter to twelve mixtures of polyisobutylene and highly polydispersed polybutadiene, the composition of which was known.

Specific gravity and refractive index measurements were carried out at 30°C with a pycnometer and an Abbe refractometer, respectively, according to classical methods. The GPC experiments were carried out on a GPC 100 apparatus (Waters Associates), the four columns of which had porosities of 1.5×10^6, 1.5×10^5, 5×10^4 and 3×10^3 Å.

After 2 ml of a 0.5 % solution of the sample in tetrahydrofuran (THF) had been injected, the elution was carried out with THF at a flow-rate of 1 ml/min.

RESULTS AND DISCUSSION

Study of the $\rho(M)$, $\psi(M)$ and $\varphi(M)$ functions

Polyisobutylene. In addition to the oligomers of isobutylene, diisobutylene, triisobutylene and tetraisobutylene, we used three samples of polyisobutylene, the polydispersities of which were between 1.2 and 1.5 and the number-average molecular weights of which were 460, 1250 and 2500, and a rather polydispersed sample prepared in the laboratory for which $\bar{M}_n$ was 14 000. This latter polymer, which was difficult to handle, was not used for the specific gravity measurements and was replaced by a butyl rubber with a higher molecular weight (about 35000).

The results are given in Table I. Figs. 1, 2 and 3 show the behaviour of $\rho_1(M)$, $\psi_1(M)$ and $M = \xi_1(v)$ for polyisobutylene. Neither of the functions $\rho_1(M)$, $\psi_1(M)$

TABLE I

CHARACTERISTIC FUNCTIONS FOR POLYISOBUTYLENE AT 30°C

$n_{THF} = 1.4025$ at 30°C.

$\bar{M}_n$	$\rho_1(M)$	v (number of siphon volumes)	n_1	$\psi_1(M) = n_1 - n_{THF}$
112	0.707	36.7	1.4062	0.0037
168	0.755	36.3	1.4275	0.0250
224	0.790	36.0	1.4465	0.0440
460	0.843	35.5	1.4708	0.0683
1 250	0.892	33.9	1.4968	0.0943
2 500	0.900	32.5	1.5015	0.0990
14 000	a	28.5	1.5055	0.1030
35 000	0.906			

a Impossible to measure accurately.

can be considered to be constant so long as $M < 5000$, and for $M < 1000$ the calibration curve $\xi_1(v)$ is no longer a straight line because of the penetration phenomenon described above.

Although the considerable polydispersity of the sample prepared in the laboratory ($\bar{M}_n = 14000$) does not alter in any way the behaviour of $\psi_1(M)$ in this range, it certainly produces an error in the left-hand part of the curve $M = \xi_1(v)$. Never-
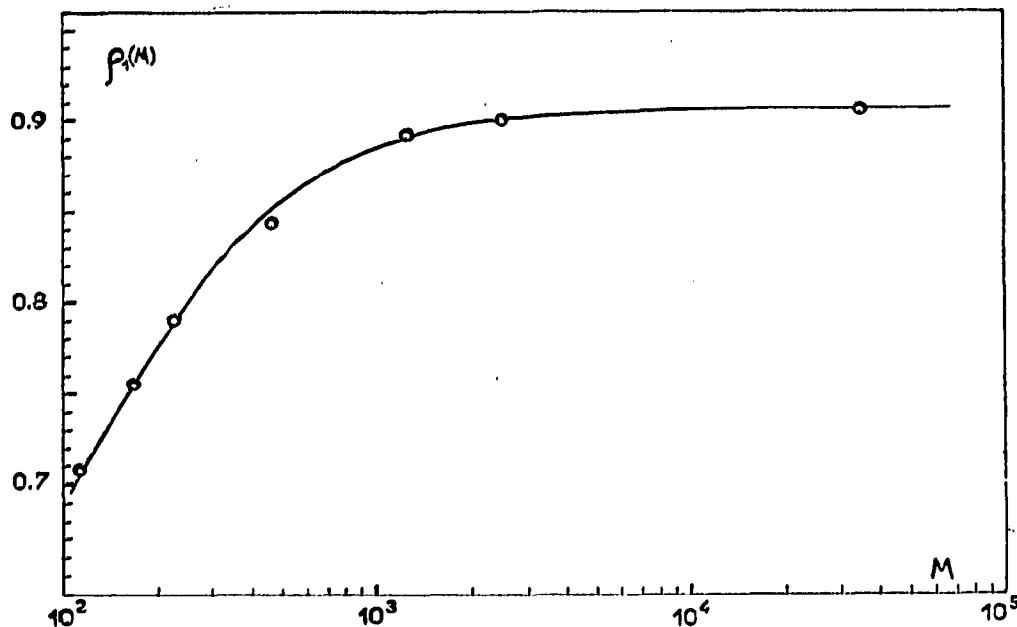
Fig. 1. Variations of the specific gravity of polyisobutylene with the molecular weight in the low-molecular-weight range at 30°C.
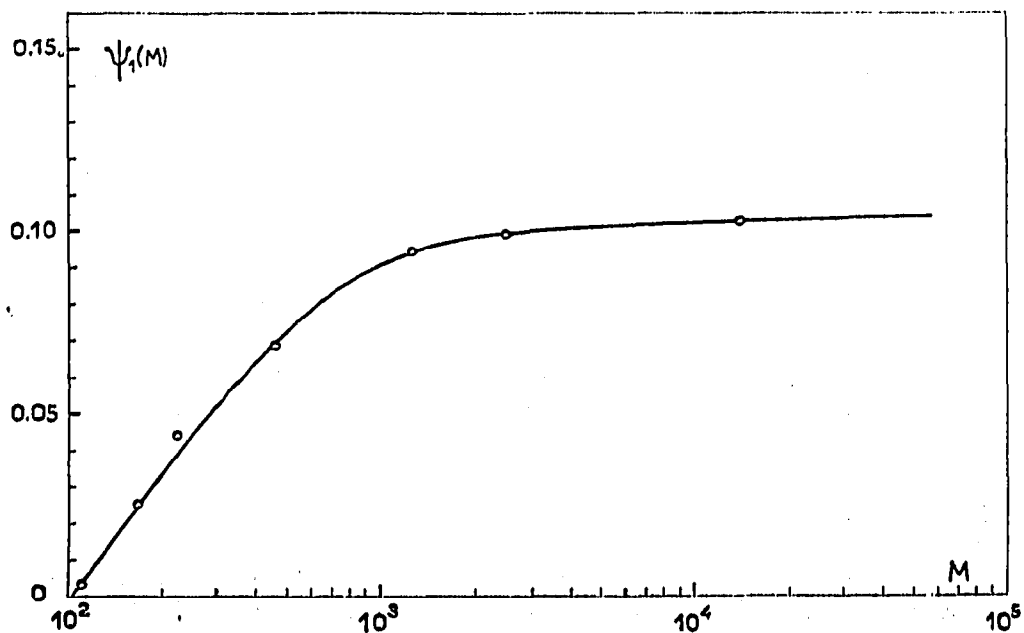
Fig. 2. Variations of the difference $n_p - n_{THF}$ with molecular the weight for polyisobutylene in the low-molecular-weight range at 30°C.

theless, this part will be used only for a very small fraction of the eluted polyiso-butylene so that the error will be concerned only with this small fraction.
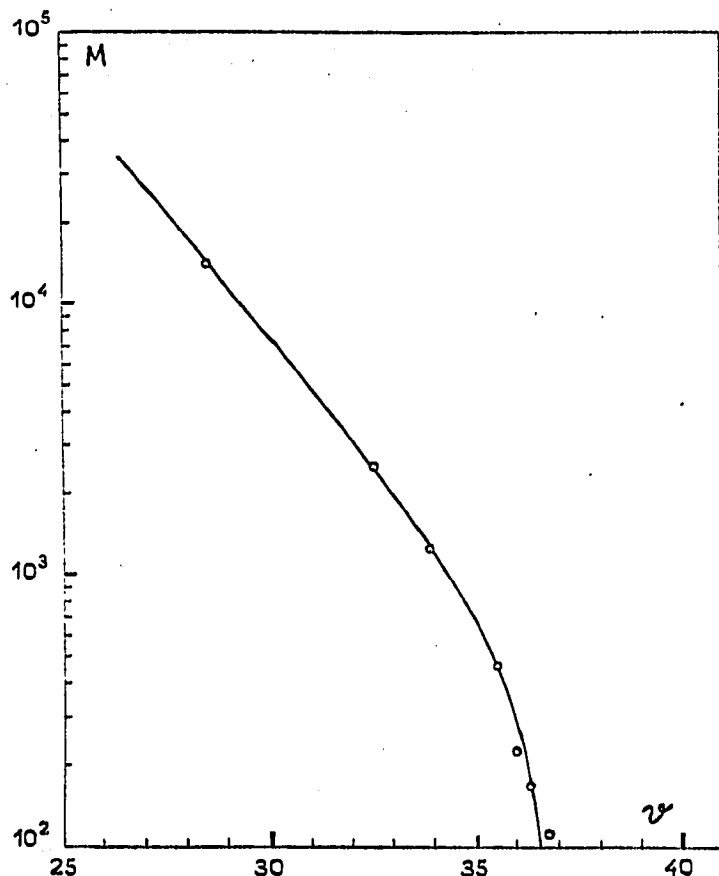

Fig. 3. GPC calibration in THF at 30°C for polyisobutylene in the low-molecular-weight range.

Polybutadiene. We used a series of fractions, the residual polydispersities of which were between 1.3 and 1.7. The molecular weights corresponding to the tops of the elution peaks of these fractions have been calculated using FRANCK's method[1] which takes their residual polydispersity into account. The values so obtained verified satisfactorily the universal calibration according to which, in the elution of macro-molecules, the involved volume of the eluting solvent is closely related to their hydro-dynamic radii[2-4]. In Fig. 4, where $[\eta]M$ is plotted against the elution volume, it can be seen that the points corresponding to very weakly polydispersed polystyrenes and those corresponding to the polybutadiene fractions are fairly well situated on a single straight line ($[\eta]$ is the limiting viscosity number). This law associated with the viscosity law of polybutadiene in THF at 30°C established from the same fractions gave $\varphi_2(M)$:

$$v = \varphi_2(M) = 47.75 - 4.38 \log_{10}M$$

It was not possible to measure accurately the specific gravities of the fractions because most of them were sticky. We only measured that of a very polydispersed high-molecular-weight polybutadiene ($\bar{M}_n = 90000$); we obtained a value of 0.885 for the specific gravity.

The results obtained for the refractive indices of the fractions as well as the corresponding values of $\psi_2(M)$ are shown in Table II.
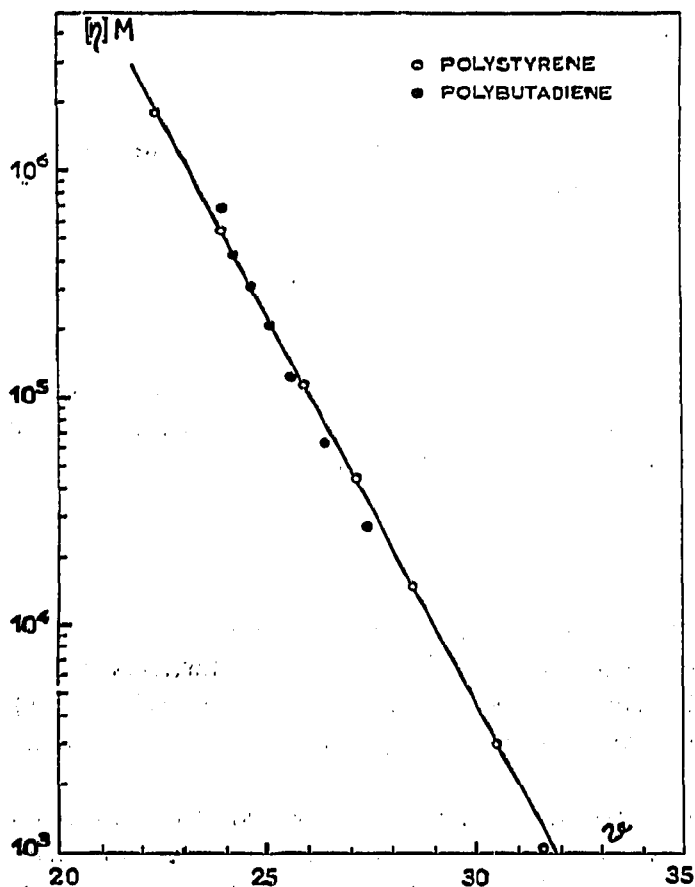

Fig. 4. Universal calibration in THF at 30°C established with polystyrene. Behaviour of polybutadiene. O—O, polystyrene; ●—●, polybutadiene.

TABLE II

REFRACTIVE INDEX OF POLYBUTADIENE AT 30°C

n_{THF} = 1.4025 at 30°C.

$\bar{M}_n \times 10^{-5}$	n_2	$\psi_2(M) = n_2 - n_{THF}$
0.24	1.5202	0.1177
0.61	1.5199	0.1174
0.94	1.5201	0.1176
1.19	1.5202	0.1177
1.43	1.5200	0.1175

From Table II, it is clear that the refractive index of polybutadiene is constant at least as long as M is higher than 2×10^4. Referring to the results obtained for polyisobutylene, it can be assumed that $\rho_2(M)$ is constant above this value of M; this assumption is reasonable since ψ and ρ are both closely related to the molecular volume. Since the proportion of polymer with molecular weights below 2×10^4 is very low in a high polymer, even in the very polydispersed polybutadiene we used

to check the method, we maintained the following values: $\psi_2 = 0.1176$ and $\rho_2 = 0.885$.

Checking of the method

In the theoretical calculation presented above, it was logical to assign the role of independent variable to the molecular weight; however, in the practical evaluation, a summation will be carried out from the chromatogram on a peak divided into p slices of arbitrary width Δv, so that the independent variable will always be the elution volume:

$$q_1 = \Delta v \sum_{i=1}^{p} c_i = k\Delta v \sum_{i=1}^{p} \frac{\rho_i h_i}{\psi_i}$$

Therefore, for each slice, h_i and v_i being read on the chromatogram, M_i must be deduced from $v = \varphi_1(M)$ (Fig. 3). The corresponding values of ρ_i and ψ_i must then be read on Figs. 1 and 2. For the high polymer, the summation reduces to:

$$q_2 = k\Delta v \frac{\rho_2}{\psi_2} \sum_{i=1}^{p} h_i$$

We applied the method to twelve mixtures of very polydispersed high-molecular-weight polybutadiene ($\bar{M}_w = 450000$; $\bar{M}_w/\bar{M}_n = 3.5$) and the moderately polydispersed polyisobutylenes which we had already used in the study of $\rho_1(M)$, $\psi_1(M)$ and $\varphi_1(M)$ and of which the number-average molecular weights were 460, 1250 and 2500, respectively.

It is necessary to explain how the chromatograms of these twelve mixtures were evaluated, because when the molecular weight of polyisobutylene was very low ($\bar{M}_n = 460$), the peak interfered with those of THF impurities, leading to consider-
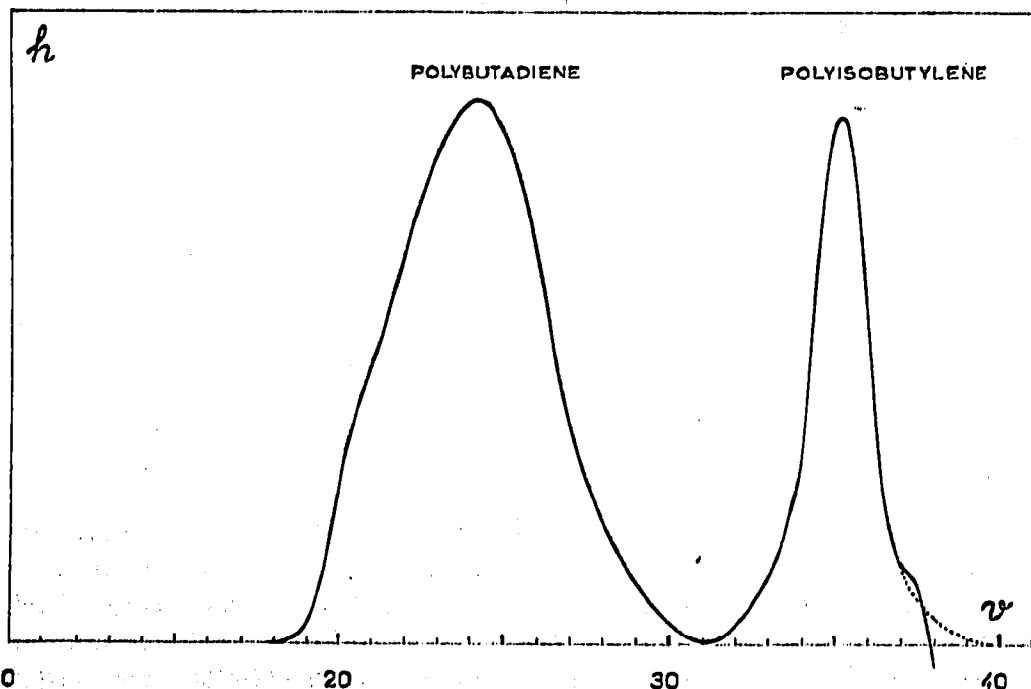

Fig. 5. Chromatogram obtained for one of the checking mixtures (sample No. 4).

able errors. As an illustration, Fig. 5 shows the chromatogram obtained for sample No. 4 and it can be seen that the polyisobutylene peak can be appreciably altered in its low-molecular-weight region. In order to ascertain the importance of the resulting error, we calculated the polyisobutylene content of each mixture, $q_1/q_1 + q_2$, by integrating the whole peak on the one hand, and by integrating only the non-altered half of the peak on the other. The two corresponding sets of results are given in the fourth and fifth columns of Table III. It appears that the integration can lead to values of the polyisobutylene content clearly higher than the actual ones if carried out on the whole polyisobutylene peak. Also, it is obvious that the higher the impurity level in THF, the higher will be the discrepancies. As expected, the latter diminish as the molecular weight of polyisobutylene increases (see Table III). Therefore, it seemed reasonable to calculate q_1 by integrating only the non-altered half of the polyisobutylene peak, that is its high-molecular-weight half. The results given in the last three columns of Table III correspond to this kind of integration.

TABLE III

COMPARISON OF THE COMPOSITIONS OBTAINED BY GPC WITH THE ACTUAL COMPOSITIONS

Weight fraction of polyisobutylene.

Sample No.	$\bar{M}_n$ (polyiso-butylene)	Actual fraction	Fraction calculated according to the theory from the whole peak	Fraction calculated from the non-altered half of the peak		
				According to the theory	$\rho_1(M)$ constant	Neglecting the variations of Δn
I	460	0.147	0.156	0.152	0.156	0.0996
2	460	0.198	0.258	0.202	0.207	0.159
3	460	0.257	0.316	0.244	0.250	0.195
4	460	0.370	0.397	0.349	0.357	0.288
5	460	0.477	0.468	0.445	0.457	0.374
6	1250	0.0386	0.0289	0.0314	0.0318	0.0258
7	1250	0.0747	0.0819	0.0756	0.0763	0.0629
8	1250	0.184	0.216	0.181	0.182	0.153
9	1250	0.266	0.271	0.258	0.260	0.223
10	1250	0.376	0.395	0.394	0.393	0.349
11	2500	0.0742	0.0839	0.0811	0.0814	0.0687
12	2500	0.122	0.140	0.137	0.137	0.117

Fig. 6, in which the results in the fifth column of Table III have been plotted against the actual polyisobutylene content for the twelve mixtures, shows the accuracy level of the method. Although the accuracy is not excellent, it can be seen that the points are quite near the diagonal and this accuracy, which is not lower than that of methods such as infrared spectroscopy, may be adequate for many applications.

If the variations of Δn with the molecular weight were neglected, the asymptotic values ρ_1 and ψ_1 of $\rho_1(M)$ and $\psi_1(M)$ would have to be used and the polyisobutylene content of the mixtures would be obtained simply as a ratio of peak areas, $A_1/(A_1 + 0.855\,A_2)$ where 0.855 is the ratio of $\rho_2\,\psi_1$ to $\psi_2\,\rho_1$. The results which would be thus obtained are shown in the seventh column of Table III.
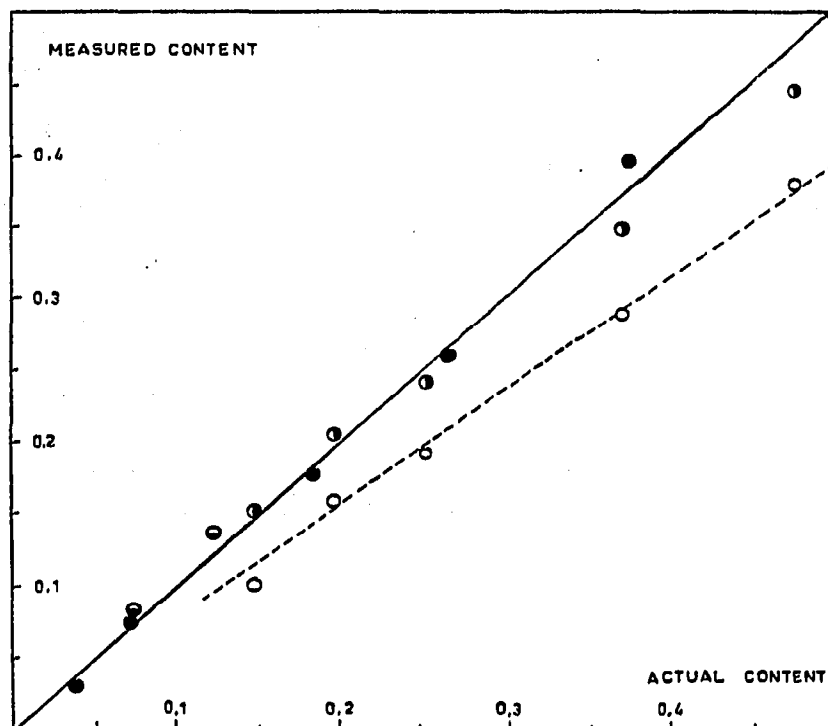
Fig. 6. Checking of the method with twelve mixtures of known composition. ◑, $\bar{M}_n = 460$; ●, $\bar{M}_n = 1,250$; ◒, $\bar{M}_n = 2,500$. O———O, results which would be obtained if the variations of Δn with the molecular weight were neglected, for the mixtures corresponding to $\bar{M}_n = 460$.

In the sixth column of Table III are given the results which would be obtained if, taking the variations of $\psi_1(M)$ into account, those of $\rho_1(M)$ were neglected, *i.e.*,

$$q_1 = k \Delta v \rho_1 \sum_{i=1}^{p} \frac{h_i}{\psi_i}$$

From comparisons of the fifth column with the seventh and the sixth, respectively, the following conclusions may be drawn:

Neglecting the variations of the refractive index with the molecular weight leads to too low values of the polyisobutylene content, as illustrated by Fig. 6 in the case of the polyisobutylene of lowest molecular weight ($\bar{M}_n = 460$). When increasing $\bar{M}_n$, the extent of these discrepancies decreases since $\psi_1(M)$ approaches its asymptotic value (it clearly appears in Table III).

On the other hand, the variations of $\rho_1(M)$ could be neglected as the differences between the results of the fifth and the sixth columns in Table III are clearly lower than the errors inherent in the method, even for $\bar{M}_n = 460$. This is not surprising because $\rho_1(M)$ can vary only between 0.7 and 0.9.

It must be kept in mind that the relation $v = \varphi_1(M)$ was established with samples of weak but not negligible and not identical polydispersities, to which we did not apply FRANCK's correction[1], and that, in general, we have neglected the overlapping of the chromatographic elution bands corresponding to the different molecular weights, as taken into account by EVREINOV *et al.*[5]. Lastly, it must be noted that all the GPC experiments were probably slightly altered by a constant overload effect,

owing to the injected amount (10 mg), which decreases the resolving power; in spite of this, the separation of the two polymers was very good, as can be seen in Fig. 5.

GPC may thus be used to determine with acceptable accuracy the composition of a two-polymer mixture provided that the variations of the refractive index with the molecular weight are taken into account for the low-molecular-weight polymer.

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