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*Molecular Weights by Gel Permeation Chromatography:
Unperturbed Dimensions Calibration for Polyisoprene*

In a recent paper¹, it was proposed that the unperturbed dimensions $\langle L^2 \rangle$ of a polymer can be used as the universal calibration parameter in gel permeation chromatography (GPC). Our experimental studies in chloroform gave the same molecular weight calibration for fractions of polystyrene, poly(methyl methacrylate) and poly(dimethyl siloxane). These polymers have very similar unperturbed dimensions. When literature calibration data²⁻⁷ are placed on an unperturbed dimensions plot, reasonable universal curves are obtained¹. To check the proposed procedure further, we have studied the calibration of polystyrene and polyisoprene which have different values for the unperturbed dimensions.

A Waters Associates GPC instrument with chloroform as solvent was used as described previously¹. The injected weight for both polystyrene and polyisoprene was 5 mg. The polystyrene samples were the calibration standards supplied by Waters Associates. A smooth curve drawn through the peak molecular weight and elution volume (counts) data for polystyrene is shown on a semi-logarithmic plot in *Figure 1*. The microstructure of the polyisoprene samples 60, 66, 67 and 78, determined by nuclear magnetic resonance (n.m.r.), was 70-75 per cent *cis*-1,4-units, the remainder being almost entirely *trans*-1,4-units. The polyisoprene GPC elution curves are shown in *Figures 2* and *3*. Number average molecular weight \bar{M}_n measurements were made with a Mechrolab membrane osmometer, using toluene as solvent at 37°C. Weight average molecular weight \bar{M}_w measurements were made with a Sofica light scattering instrument, using cyclohexane as solvent at 30°C.

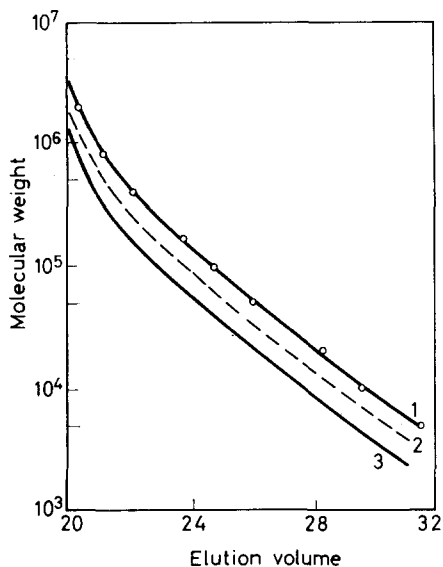
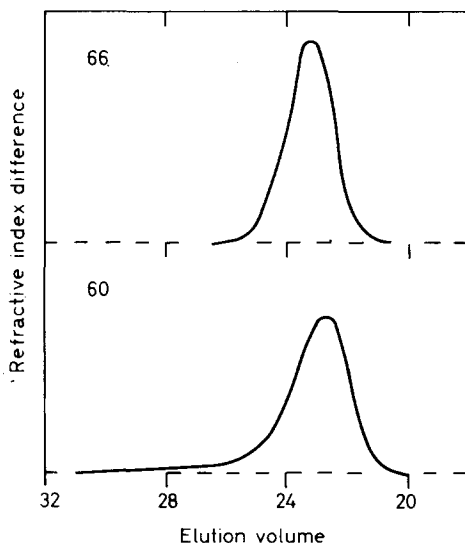


Figure 1—Calibration curves: 1 (full line) obtained experimentally with polystyrene standards, 2 (broken line) obtained from curve 1 using equation (1), 3 (full line) obtained from curve 1 using extended chain length as the universal parameter

Figure 2—Chromatograms of polyisoprenes 60 and 66



The molecular weight calibration for the polystyrene standards was used to calculate average molecular weights for the chromatograms in *Figures 2 and 3*. The computer programme of Pickett, Cantow and Johnson⁸ was employed. For all samples the computed molecular weights, shown in *Table 1*, are much higher than the experimental values obtained by osmometry and light scattering. The molecular weights calculated from the chromatograms depend on the choice of chromatogram baseline. The error takes values up to ten per cent. A molecular weight calibration for polyisoprene can be obtained from the polystyrene curve, if one

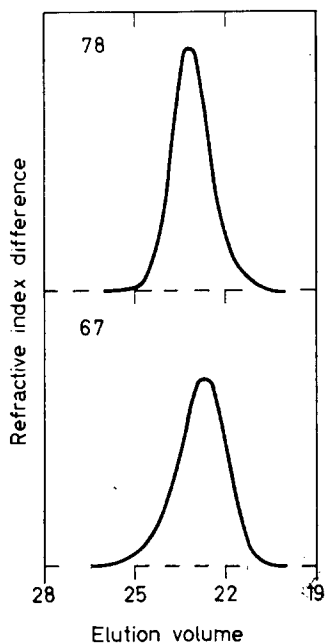


Figure 3—Chromatograms of polyisoprenes 67 and 78

assumes the unperturbed dimensions to be the GPC universal parameter. At a given elution volume the relation between the two curves is

$$\log M_{PI} = \log M_{PS} + \log \left[\frac{\langle L_0^2 \rangle}{M} \right]_{PS} \left[\frac{M}{\langle L_0^2 \rangle} \right]_{PI} \quad (1)$$

where M_{PI} and M_{PS} are the molecular weights for polyisoprene and polystyrene respectively. Literature values⁹ of $[\langle L_0^2 \rangle / M]^{1/2}$ for polystyrene, 100 per cent *cis*-1,4-polyisoprene and 100 per cent *trans*-1,4-polyisoprene are 0.67, 0.81 and 0.97 Å respectively. In view of the microstructure of

Table 1. Molecular weight data for different calibration curves

Sample	Experiment	GPC (curve 1)	GPC (curve 2)	GPC (curve 3)
Polymer 60				
\overline{M}_w	174 500 ± 5%	257 000	161 000	105 000
\overline{M}_n	95 000 ± 2%	138 000	87 000	56 000
Polymer 66				
\overline{M}_w	122 000 ± 5%	214 000	135 000	88 000
\overline{M}_n	89 500 ± 5%	182 000	115 000	74 500
Polymer 67				
\overline{M}_w	177 000 ± 5%	283 000	177 000	116 000
\overline{M}_n	124 000 ± 6%	225 000	140 000	91 500
Polymer 78				
\overline{M}_w	173 500 ± 5%	243 000	153 000	100 000
\overline{M}_n	128 000 ± 4%	211 000	133 000	86 000

our polyisoprene samples, we have arbitrarily taken $[\langle L_0^2 \rangle / M]_{PI}^{1/2}$ as 0.85 Å. The molecular weight calibration for polyisoprene is, therefore, related to that of polystyrene by a vertical shift of $\log 0.621$, giving the dashed curve 2 in *Figure 1*. This polyisoprene calibration was used with the computer programme to calculate average molecular weights for samples 60, 66, 67 and 78. The results are shown in *Table 1*. Molecular weights obtained from the unperturbed dimensions calibration are in reasonable agreement with the experimental values. Alternatively, the projected extended chain length can be used as the universal parameter^{10,11}. The molecular weight per Ångström unit has values of 41.0 and 16.8 for polystyrene and polyisoprene respectively. Then, the vertical shift in molecular weight at a given elution volume is $\log 0.409$, giving the calibration curve 3 in *Figure 1*. Molecular weights calculated by computer with curve 3 are given in *Table 1*. It is clear that the extended chain length calibration underestimates polyisoprene molecular weights. A similar situation was found by Harmon¹² for *cis*-1,4-polybutadiene.

The above results illustrate the convenience of the unperturbed dimensions procedure for calibrating a broad molecular weight range, when well characterized narrow fractions of the polymer to be studied are not available. We have made no attempt to correct for possible chromatogram distortion caused by the lack of infinite GPC resolution and by the choice of operating variables such as flow rate and sample concentration, since none of the methods proposed for the correction of distortion are completely adequate^{13,14}. Although the GPC molecular weights are, therefore, liable to error, we feel the results demonstrate the applicability of the unperturbed dimensions calibration procedure.

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ANNOUNCEMENTS

GEL PERMEATION CHROMATOGRAPHY— FORTHCOMING SEMINAR

The Seventh International GPC Seminar will be held at the Palais des Congrès in Monaco, 12–15 October 1969. In addition to papers on recent advances in polymer characterization by gel permeation chromatography, this Seminar will include panel discussion groups. For further information contact Mr R. L. FENWICK, Waters Associates (Instruments) Ltd, Meadow Mills, Water Street, Portwood, Stockport, Cheshire.

FIFTEENTH CANADIAN HIGH POLYMER FORUM

The Fifteenth Canadian High Polymer Forum will be held at Queen's University in Kingston, Ontario on 3–5 September. The Forum is sponsored by the Macromolecular Division of the Chemical Institute of Canada and the National Research Council of Canada and is concerned with all aspects of polymer science. The Chairman of the Forum is Dr D. M. WILES, Applied Chemistry Division, National Research Council of Canada, Ottawa, Ontario.

The Forum Lecturer, Dr A. CHAPIRO, will deal with 'Recent developments in radiation initiated polymerizations'.

In connection with the Fifteenth Forum there will be a one-half day Symposium on Methods of Polymer Characterization. The speakers and their topics are as follows: Dr J. E. GUILLET, 'Determination of polymer physical properties by gas chromatography'; Mr. S. T. BALKE, 'Gel permeation chromatography'; Dr H. J. HARWOOD, 'Methods for determining sequence length distributions in copolymers'; and Dr R. J. SAMUELS, 'Methods for determining morphology and chain conformation in bulk polymers'.

Persons wishing to contribute papers on any aspect of polymer science to the Fifteenth Forum, or to attend personally, should immediately contact Dr J. F. HENDERSON, Research and Development Division, Polymer Corporation Ltd, Sarnia, Ontario.