

Notes to the Editor

Molecular weight characterization of poly(vinyl chloride): reference materials and universal calibration

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INTRODUCTION

A set of reference materials of poly(vinyl chloride) (PVC) certified^{1,2} as to molecular weight*, has been made available from this Laboratory. The materials were produced³ by fractionation by preparative gel permeation chromatography (g.p.c.) in 1,2-dichlorobenzene at 135°C, and their certification involved, in part, analytical g.p.c. under those conditions, unconventional for PVC. It seemed important, therefore, to investigate and report their behaviour on g.p.c. in the solvent, tetrahydrofuran, more usual for that polymer. The molecular weights measured by classical techniques, membrane osmometry for the number-average, \bar{M}_n , and light scattering photometry for the weight-average, \bar{M}_w , are collected in Table 1, together with data for three commercially available whole polymer reference materials. The samples were of PVC produced above ambient temperature.

EXPERIMENTAL

A Waters 200 gel permeation chromatograph was used at 35°C with tetrahydrofuran containing 0.05% by mass Santonox R (Monsanto) as antioxidant. Five columns (1.2 m × 1 cm) were used, packed with Styragel (Waters Associates) of exclusion limits: 35, 5 × 10², 5 × 10³, 7 × 10⁴ and 5 × 10⁵ nm. The flow rate was 1 cm³/min, and 2 cm³ of solution 0.3% by mass were injected. The effect of heat was studied with solutions degassed and sealed *in vacuo* in glass tubes. Thirty minutes elapsed between the end of heat treatment (1 h at 200°C) and injection.

* The term 'molecular weight' replaces the more correct 'relative molecular mass'

RESULTS AND DISCUSSION

Absolute calibration

Gel permeation chromatography of PVC in tetrahydrofuran is complicated by aggregation⁴. There is evidence⁵ that aggregates can be destroyed by sufficient heat treatment, and heating above the normal boiling point of tetrahydrofuran may be necessary to ensure a molecularly dispersed solution. Chromatograms of the sample of highest molecular weight, and therefore⁶ the most likely to aggregate, were not affected significantly by heating the solution in an evacuated sealed tube at 200°C for 1 h before injection. A similar result was found² in 1,2-dichlorobenzene, so that aggregation could be neglected.

The relation between elution volume and molecular weight was established as follows. Envelopes of linear calibrations consistent with each of the molecular weights certified for the NPL reference materials and the chromatograms in tetrahydrofuran were calculated by Frank's method⁷. An estimated common tangent was drawn and average

molecular weights, $(\bar{M}_n)_{g.p.c.}$ and $(\bar{M}_w)_{g.p.c.}$ were calculated with it from the chromatograms. The elution volumes corresponding to those molecular weights were then plotted against the classical values and an improved calibration was found (linear least squares). Further iteration made no significant difference to the calibration, and there was no deviation from linearity. That calibration was then used to calculate average molecular weights from chromatograms of all the samples listed in Table 1, where the values are compared with those measured classically. The estimated uncertainty of the classical measurements was ±10% and the g.p.c. results were reproducible to ±5%. The absolute calibration established in tetrahydrofuran with the NPL samples was therefore consistent with the elution behaviour of the commercial samples in that solvent.

Universal calibration

Production of reference materials suitable for calibration in g.p.c. is difficult, and much attention has been given to universal calibrations, namely semi-empirical means of deriving calibrations for other materials from that for polystyrene. It was of interest to relate the elution behaviour of the PVC

Table 1 Molecular weight characterization of reference materials

Sample	Molecular weights measured				
	Classically		By g.p.c.		
	\bar{M}_n 10 ³	\bar{M}_w 10 ³	\bar{M}_n 10 ³	\bar{M}_w 10 ³	\bar{M}_o 10 ³
400-2 ^a	25.5	68.6	26.4	63.4	47.1
400-3 ^a	41.0	118	46.4	107	73.9
400-4 ^a	54.0	132	57.3	143	92.0
PVC 30 ^b	30.5		30.3	52.2	40.5
PVC 50 ^b	50.1		48.6	98.0	68.9
PVC 83 ^b	82.7	143	88.6	158	110
PVC 122 ^b	122		113	222	153
PVC 175 ^b	175	271	155	275	189

^a Supplied by ArRO laboratories;
^b NPL certified reference materials

reference materials to that of a polystyrene sample^{8,9} of broad molecular weight distribution ($\bar{M}_w/\bar{M}_n = 3.4$) made available by this Laboratory as a means of calibration in g.p.c. In order to do so, account must be taken of dispersion, which is important for samples with $\bar{M}_w/\bar{M}_n < 2$, but can be neglected for the polystyrene reference material.

Some estimate of dispersion is possible from chromatograms of samples of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.1$). Smith's¹⁰ 'molecular weight correction factors' were calculated from chromatograms of some commercial polystyrene reference materials (Pressure Chemical Company) of that sort, and lay between 1.06 and 1.09 for the elution volume range of the PVC samples. Since the difference is within the error of that determination, dispersion was taken to be symmetrical and invariant with elution volume. There is evidence¹¹ that dispersion is independent of polymer type under a given set of experimental conditions, and the result was assumed to hold for PVC.

For each of the PVC samples a linear calibration consistent with the classical number- and weight-average molecular weights was found by Frank's⁷ method; $(\bar{M}_w)_{g.p.c.}$ was used for the three samples without measured weight-average molecular weights. The effect of symmetrical dispersion is to rotate such a calibration about the peak molecular weight, M_0 , so that the molecular

weight identified in that way is invariant with dispersion. The M_0 values found are given in *Table I*; the values for the NPL samples are within 10% of $(\bar{M}_n \bar{M}_w)^{1/2}$, so that by Berger and Schulz's criterion¹² the molecular weight distribution of those samples are close to log-normal. The same result was found¹³ for a series of polypropylene reference materials produced in the same way. The peak molecular weights found in that way for the PVC samples were found to be directly proportional to the M_0 values found from the chromatograms and the polystyrene calibration established with the broad reference material; regression analysis gave a straight line through the origin with no residual exceeding 3% and no systematic deviation with molecular weight and sample source. The calibrations for polystyrene and PVC were therefore parallel, as is consistent with ample evidence^{14,15} that tetrahydrofuran is a good solvent for both polymers. In that case the unperturbed dimensions can serve¹⁶ as universal calibration parameters, and the slope of the relation described is given by the ratio of the root mean square end-to-end distances, $(\langle r_0^2 \rangle / M)^{1/2}$, of the two polymers. With an averaged value¹⁶ of that parameter for polystyrene (67 nm) under these conditions, the observed slope gives 84 nm for PVC. The agreement with a value (79 nm) determined¹⁷ viscometrically is good, considering the approximations in both treatments.

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Changes in electric conductivity during the process of methyl methacrylate polymerization

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INTRODUCTION

As soon as the process of polymerization starts in the monomer, various quantities become functions of time i.e. the mass of the molecule, the number of free radicals, and the concentration of free admixture ions. This leads to

variations in the macroscopic properties of the material undergoing polymerization¹⁻³.

In this paper, results are reported on changes in the electrical conductivity of methyl methacrylate (MMA) during the polymerization process at constant temperature and constant illumination. Moreover, the feasibility of inducing an electret effect when polymerizing MMA in static electric field is considered.

EXPERIMENTAL

MMA polymerization was initiated in chemically pure MMA using benzoyl peroxide. A special liquid condenser, filled with MMA, was placed in a thermostat at constant temperature. On partial polymerization of the material, a d.c. electric field was applied to the condenser and the current was measured over 10 days (*Figure 1*, switch K in position 1). Next, the field was removed, the system was short circuited, and the thermally stimulated discharge (TSD) current was measured when heating the sample at a constant rate.

* Polish Pat. Application P-190261 (8 June 1976)