

NOTES

Mark-Houwink Relationship of the System PVC/N-Methylpyrrolidone (NMP)

INTRODUCTION

The use of N-methylpyrrolidone (NMP) as a solvent for poly(vinyl chloride) (PVC) has gained considerable attention in the past few years. Traditionally, solvents such as tetrahydrofuran (THF) and cyclohexanone have been widely accepted as powerful solvents for PVC, and as a result the great majority of polymer-solvent interaction studies done on PVC have dealt with solutions in one or the other of these two solvents. Almost all gel permeation chromatography studies of PVC have been carried out in THF solutions. Molecular weight determinations by various methods have been reported using solutions in THF or cyclohexanone. Viscosity $[\eta]$ -molecular weight M relationships for PVC solutions are known only for very few solvents.¹

N-Methylpyrrolidone is a very powerful solvent for PVC as well as many other polymers.² Despite this fact, the literature contains no information about the system PVC-NMP except for a patent disclosing the use of NMP as an industrial solvent for cleaning PVC reactors.³ In such applications where large volumes of solvent are being handled, NMP offers many advantages over THF since it is considerably less hazardous to use both from toxicity and inflammability viewpoints. This solvent has low vapor pressure and a high flash point (96°C); it is also neither a primary skin irritant nor a sensitizer.²

With the increasing awareness of the high dissolving power and safe handling features of NMP, its use is being extended to cover other applications such as polymer characterization and, in particular, gel permeation chromatography (GPC). In order to use a solvent in GPC for molecular weight analysis of a specific polymer, the relationship between polymer molecular weight M and solution limiting viscosity number $[\eta]$ must be known. Such a relationship, known as the Mark-Houwink relationship, is given by

$$[\eta] = KM^a \quad (1)$$

where K and a are the Mark-Houwink constants, to be evaluated experimentally. It is evident that K and a for the system PVC-NMP should be evaluated to make eq. (1) useful for molecular weight analysis.

Precise determination of K and a requires measuring $[\eta]$ for several monodisperse standards of known molecular weights. Such narrow PVC standards are usually not available commercially. Alternatively, the narrow standards can be prepared in reasonable quantities by such procedures as precipitation fractionation, but this is a lengthy and tedious operation. Fractionation can also be accomplished by other means such as gel permeation chromatography (GPC). The main drawback of the GPC method is that the material in each fraction is present in a very small quantity, which could possibly result in some error when measuring $[\eta]$. Nevertheless, this method was used in this study due to its simplicity and in order to obtain a working, first-approximation relationship.

A sample of a broad PVC standard was fractionated into ten narrow fractions by gel permeation chromatography with THF as solvent. The solvent was then evaporated from each fraction and replaced by NMP. The NMP solutions of the narrow fractions were then characterized for limiting viscosity numbers $[\eta]$ with a capillary tube viscometer.

EXPERIMENTAL

PVC Standard

This was a broad suspension resin standard supplied by ARRO Laboratories Inc., with $M_n = 54,000$ (osmometry) and $M_w = 132,000$ (light scattering), where M_n is number-average molecular weight and M_w is weight-average molecular weight.

Gel Permeation Chromatography

A Waters ALC/GPC Model 100 with six 3-foot columns (4.0×10^6 , 1.2×10^6 , 4.0×10^5 , 100×10^3 , 50×10^3 , and 30×10^2 molecular weight polystyrene) was used. Carrier solvent was THF at room temperature; flow rate, $2 \text{ cm}^3/\text{min}$; sample concentration, 1.0 wt-%; size, 2 ml. The solution was heated in a sealed ampoule at 100°C for 10 min.⁴ This procedure was undertaken to disintegrate the PVC aggregates usually found in dilute PVC solutions which may lead to erroneous results. The columns were calibrated using narrow polystyrene standards.

A nonlinear polystyrene calibration curve was developed in the form

$$M_{\text{PS}} = D_1 \exp(D_2 t + D_3 t^2 + D_4 t^3)$$

where M_{PS} is molecular weight of polystyrene, t is retention time, and D_1 to D_4 are constants. A PVC calibration curve could then be obtained by applying the concept of hydrodynamic volume and converting M_{PS} to M_{PVC} (molecular weight of PVC) using literature values of Mark-Houwink constants for both polystyrene and PVC in THF. The above procedure, however, does not correct for axial dispersion in the GPC columns. Alternatively, the error due to axial dispersion can be substantially reduced by developing an effective PVC calibration curve.⁵ Such an effective curve was obtained by applying a search technique to find the best K and a values for PVC in THF to minimize the objective function (F) defined as

$$F = |\Delta M_w| + |\Delta M_n|$$

where $|\Delta M_w|$ and $|\Delta M_n|$ are the absolute values of the differences between the calculated and the actual weight-average and number-average molecular weights of the PVC standard, respectively. The search resulted in calculated M_w and M_n of about 134,000 and 55,000, respectively, thus indicating that the error in molecular weight measurements is probably less than 2%. Naturally, the accuracy of the developed calibration curve depends on the correctness of the actual M_w and M_n of the PVC standard. The figures given by the supplier were assumed correct, and no further confirmation of M_w and M_n by independent methods was carried out. The effective PVC calibration curve was used in calculating molecular weight distribution of the broad standard and also molecular weights of fractions.

Ten fractions were collected (Fig. 1). The weight of polymer in each fraction was kept more or less constant by collecting the fractions at intervals corresponding to approximately one tenth of the chromatogram area. The solvent (THF) was then evaporated from the fractions by placing them in a vacuum oven at 40°C overnight. Two cm^3 of NMP was then added to the solid resin left in each fraction. After complete dissolution in NMP, the solutions were heat treated again as described above shortly before viscosity measurements.

The retention time t_i^w , corresponding to the weight-average molecular weight of the polymer in fraction number i , was calculated following the method proposed by Goedhart and Opschoor⁶:

$$t_i^w = t_i + \frac{2h_{i+1} + h_i}{3h_{i+1} + 3h_i} (t_{i+1} - t_i) \quad (2)$$

where t_i , t_{i+1} and h_i , h_{i+1} represent the retention times and chromatogram heights at the beginning and at the end of fraction i , respectively. The weight-average molecular weights were then calculated from the calibration curve.

Viscometry

A small Ubbelohde-type viscometer was employed. Flow times ranged from 99 to 117 sec. All measurements were made at 25°C .

Limiting viscosity numbers $[\eta]$ were calculated from the single-point determination by applying Huggins' equation:

$$\eta_{\text{sp}} = [\eta]c + k'[\eta]^2 c^2 \quad (3)$$

where η_{sp} is the specific viscosity given by

$$\eta_{\text{sp}} = (\theta_i - \theta_s)/\theta_s \quad (4)$$

where θ_i and θ_s are flow times of solution i and solvent (NMP), respectively, and c is the concentration given by

$$c = (A_i/A)(w/V_i) \quad (5)$$

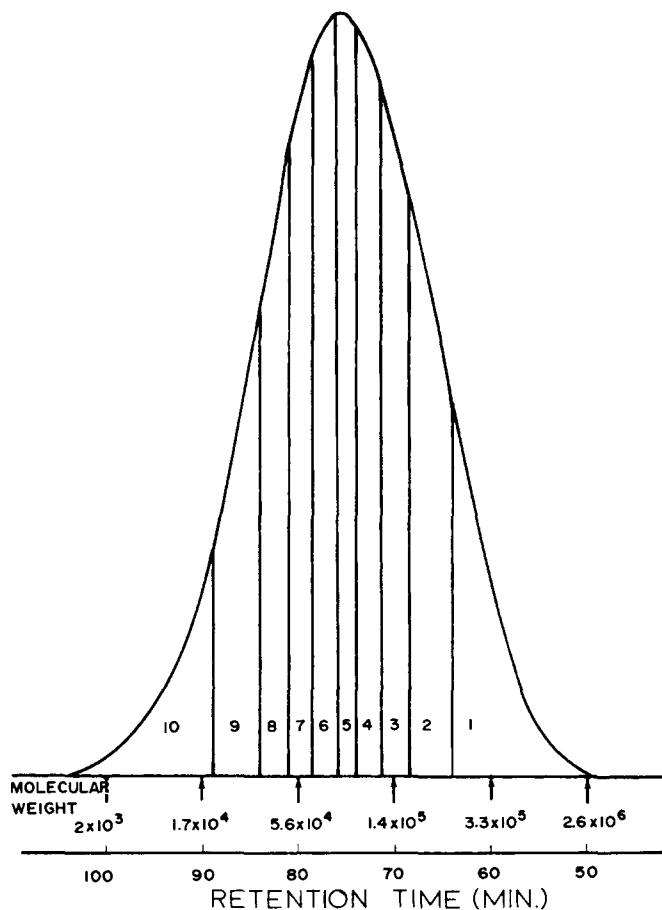


Fig. 1. GPC chromatogram of the PVC standard.

Further, A_i is the area under the GPC chromatogram corresponding to fraction i , A is the total chromatogram area, W is the total mass of polymer injected, and V_i is the volume of NMP added to fraction i , 2 ml. Finally, k' is the Huggins constant, for which a value of 0.409 was used.⁷ No kinetic energy correction was attempted. The solvent (NMP) is a Newtonian liquid, and the solutions were assumed Newtonian due to the very low concentration. Such assumption is consistent with other experimental findings.⁷

RESULTS

The molecular weight distribution of the standard is shown in Figure 1. As can be seen from the figure, fractions 1 and 10 are fairly broad; accordingly, they were discarded because of the low accuracy associated with both ends of the distribution. The weight-average molecular weight M_w and the limiting viscosity number of each fraction are listed in Table I. The measured limiting viscosity number of the whole polymer is also given.

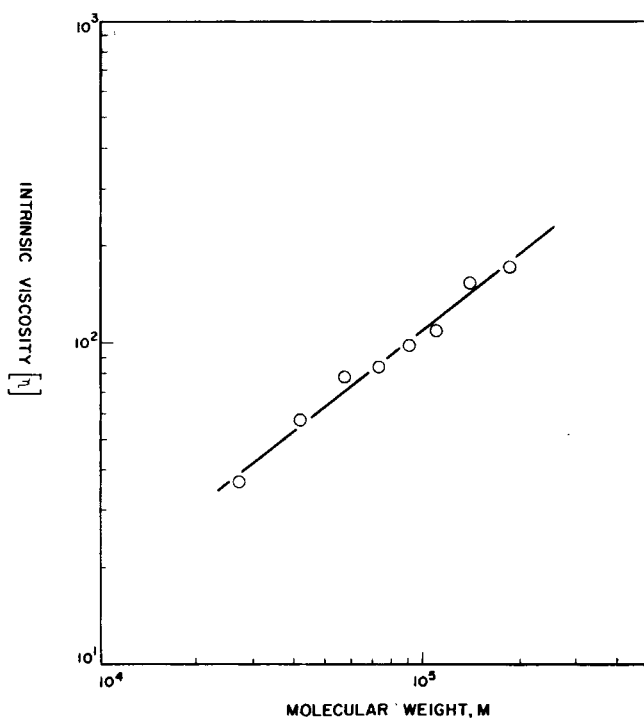
Figure 2 shows the Mark-Houwink plot of the data. The least-squares linear fit yielded the following expression:

$$[\eta]_{\text{NMP}}^{25^\circ\text{C}} \approx 1.66 \times 10^{-2} M_w^{0.76} \quad \text{cm}^3/\text{g} \quad (6)$$

The relatively high value of the exponent a reflects the high dissolving power of N-methylpyrrolidone. In order to obtain some quantitative assessment of the degree of approximation of eq. (6), the estimated Mark-Houwink constants were used to calculate the limiting viscosity number of the whole polymer as follows:

TABLE I
 M - $[\eta]$ Properties of Fractions

Fraction no.	Molecular weight M_w	$[\eta]_{25}$, cm ³ /g
1	—	—
2	185 000	164.7
3	140 000	144.2
4	110 000	104.8
5	90 000	94.8
6	73 000	80.4
7	57 000	76.4
8	42 000	56.3
9	27 000	36.3
10	—	—
Whole polymer		134.3

Fig. 2. $[\eta]$ - M relationship.

The viscosity-average molecular weight of the whole polymer (M_v) was calculated from the molecular weight distribution $W(M)$:

$$M_v = \left[\int_0^{\infty} W(M) M^{0.76} dM \right]^{1/0.76} = 121,000 \quad (7)$$

from which

$$[\eta]_{\text{whole}} = 0.0166[(121,000)^{0.76}] = 121.1 \text{ cm}^3/\text{g} \quad (8)$$

This value is in reasonable agreement with the measured value of 134.3 cm³/g, which suggests that the error resulting from using eq. (6) is probably small.

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