

**Estimation of Molecular Weight by Gel Permeation Chromatography and Viscometry**

A calibration curve, i.e., the relationship between molecular weight and elution volume, is necessary to calculate average molecular weights of polymer samples from GPC data. Generally, the calibration curve is difficult to obtain directly with the samples under study. Therefore, the methods of obtaining calibration curves have been investigated by making use of the concept that the product of intrinsic viscosity ( $\eta$ ) and molecular weight  $M$  is a universal calibration parameter. Coll and Gilding have proposed a method of converting the universal calibration curve established by measuring a series of narrow-distribution polystyrene standards, for example, into a calibration curve for the polymer of interest using the Mark-Houwink-Sakurada equation:<sup>1</sup>

$$[\eta] = KM^a \tag{1}$$

The use of this method is, however, restricted to the sample for which eq. (1) is known in the same conditions employed for GPC measurements. Weiss and Cohn-Ginsberg have shown that one can obtain  $a$  and  $K$  in eq. (1) from GPC and viscosity data of two samples in conjunction with a universal calibration curve.<sup>2</sup> This method has been demonstrated to be very effective for the sample for which eq. (1) is not known in advance.<sup>3,4</sup> This method is as follows:  $[\eta]$  and number-average and weight-average molecular weights  $M_n$  and  $M_w$  can be written as eqs. (2) – (4) for the sample comprising species  $i$  whose molecular weights, intrinsic viscosities, and weight fractions are  $M_i$ ,  $[\eta]_i$ , and  $w_i$ , respectively:

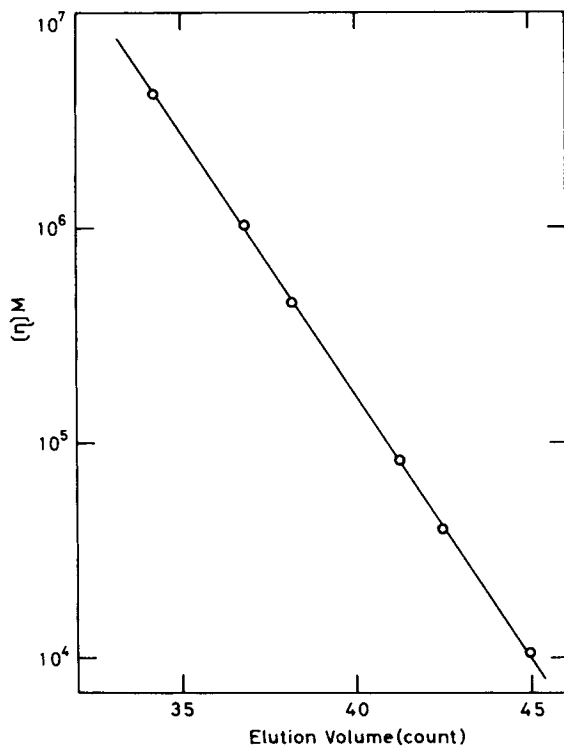


Fig. 1. Universal calibration curve for the column set.

TABLE I  
Results of Viscosity, Osmotic Pressure, and GPC Measurements for Polychloroprene

Sample	Viscometry	Osmometry	GPC and Viscometry	
	$[\eta]$ , dl/g	$M_n \times 10^{-4}$	$M_n \times 10^{-4}$	$K \times 10^8$
PCR-1	0.350	8.74	8.89	1.12
PCR-2	0.375	10.3	9.99	1.13
PCR-3	0.424	13.1	13.4	1.11

$$[\eta] = K^{1/(a+1)} \sum w_i J_i^{a/(a+1)} \quad (2)$$

$$M_n = K^{-1/(a+1)} / \sum (w_i / J_i^{1/(a+1)}) \quad (3)$$

$$M_w = K^{-1/(a+1)} / \sum w_i J_i^{1/(a+1)} \quad (4)$$

where  $J_i$  is a universal calibration parameter defined as follows:

$$J_i = [\eta]_i M_i \quad (5)$$

If  $a$  and  $K$  are known,  $[\eta]$ ,  $M_n$ , and  $M_w$  can be calculated from eqs. (2) - (4) using  $w_i$ 's from the GPC chromatogram and  $J_i$ 's from the universal calibration curve. Although  $a$  and  $K$  are unknown in this case,  $a$ - $K$  pairs are obtained at first so that  $[\eta]$  calculated by substituting proper values into  $a$  and  $K$  in eq. (2) coincides with  $[\eta]$  from direct viscosity measurements. Unique values of  $a$  and  $K$  can then be determined from the  $a$ - $K$  pairs observed for two samples. Subsequently,  $M_n$  and  $M_w$  are able to be calculated from eqs. (3) and (4) using the values of  $a$  and  $K$  so obtained.

If the measurements are performed under theta condition for the sample under study,  $K$  is determined from GPC and viscosity data for only one sample as  $a$  equals 0.5. Moreover, as  $a$  is exactly known in advance,  $K$  and the average molecular weights are expected to be estimated more accurately. In this report, therefore, GPC and viscosity measurements are made for polychloroprenes under theta condition; namely, in methyl ethyl ketone (MEK) at 25°C,<sup>5</sup> and  $M_n$  values calculated from the results are compared with  $M_n$  determined by osmometry to assess the accuracy of this approach.

The samples were three fractions obtained by fractionating a commercial chloroprene rubber by the column elution technique. Narrow molecular weight-distribution polystyrene standards purchased from Pressure Chemical Co. were used to establish the universal calibration curve.

GPC measurements were carried out at 25°C on a Shimadzu gel permeation chromatograph, Type 1A, equipped with five TSK-GEL columns, G7000S, G6000S, G5000S, G4000S, and G3000S. Nominal porosities of these columns were  $10^7$ ,  $10^6$ ,  $10^5$ ,  $10^4$ , and  $10^3$  Å, respectively. The theoretical plates of the column set was 1,700 plates/ft. Reagent-grade MEK was used as the solvent without further purification. The flow rate was 1 ml/min. The sample concentration and the injection volume of the solution were 0.5 mg/ml and 2 ml, respectively.

Intrinsic viscosities were determined in MEK at 25°C with an Ubbelohde capillary viscometer.

Number-average molecular weights were determined with a high-speed membrane osmometer (Hewlett-Packard, Mechrolab Model 502) at 35°C using MEK as a solvent.

The universal calibration curve for the column set is linear over a wide range of molecular weight as shown in Figure 1. The linearity of the calibration curve is important for accurate computation.  $[\eta]$  and  $M_n$  determined by viscometry and by osmometry are summarized in Table I.  $M_n$  and  $K$  calculated from GPC chromatogram and  $[\eta]$  of the sample together with the universal calibration curve are also listed in Table I. Agreement of  $M_n$  estimated from the two methods is within  $\pm 3\%$ , indicating that the method employed in this work is very promising for accurately estimating the average molecular weights of the polymer samples. Moreover, the values of  $K$  in Table I are in good agreement with the value in Mark-Houwink-Sakurada eq. (6) for polychloroprene in MEK at 25°C reported by Kawahara et al.:<sup>5</sup>

$$[\eta] = 1.13 \times 10^{-3} M_w^{0.5} \quad (6)$$

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