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ANALYSIS OF LOW MOLECULAR WEIGHT POLYMERS WITH GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

Intrinsic viscosities and gel permeation chromatography (GPC) elution times were determined in toluene on commercially available standards of polystyrene (PSTY) and polymethyl methacrylate (PMMA) having M_n in the range of 10^3 to 10^5 and 10^4 to 10^6, respectively. In addition, elution times were determined on the discrete GPC peaks of dimer, trimer, tetramer, etc. as seen in lower molecular weight PSTY and PMMA. Intrinsic viscosities of oligomers were estimated by extrapolation of the Mark–Houwind–Sakurada equations determined from our data, and the results were used to establish a universal calibration curve over a wide range of molecular weights. A similar approach was taken by using literature data for the intrinsic viscosities of PSTY and PMMA in tetrahydrofuran. It was verified by proton NMR that the universal calibration curve so constructed is useful at M_n values as low as 300. No correction was necessary for chain length dependence of the detector response.

INTRODUCTION

In recent years there has been considerable interest in making low molecular weight polymers and oligomers by free-radical polymerization [1–6]. We consider here polymers having chain lengths in the approximate range of 2 to 100. Both the chemical properties and processing behavior of these low molecular weight polymers may depend critically on the molecular weight distribution, which is usually characterized by gel permeation chromatography (GPC). The calibration of GPC for very low molecular weight cannot readily be done using standards, either because of the absence of standards of narrow molecular weight distribution having known molecular weight or because of the experimental difficulties associated with using osmotic pressure or vapor-phase osmometry with polymers of molecular weight in the range of interest. Therefore, in this paper we present our work using the universal calibration curve (UCC) on low molecular weight polystyrene (PSTY) and polymethyl methacrylate (PMMA).

Construction of a reliable UCC requires the determination of GPC elution times for samples of known intrinsic viscosity $[\eta]$ and known molecular weight (MW); preferably the samples will have a narrow molecular weight distribution (MWD). The anionically polymerized, commercially available PSTY samples commonly used as standards do have a reasonably narrow MWD at higher MW, but in our experience the lower MW samples (MW $<$ 4000) have a rather broad distribution. For this reason we have taken advantage of the fact that low MW PSTY and PMMA reveal distinct peaks in the GPC chromatogram which correspond to the dimer, trimer, tetramer, etc. which provide the elution time for very low molecular weight polymers (oligomers) of precisely calculable MW. The $[\eta]$ values for these oligomers were estimated by extrapolations of the Mark-Houwink-Sakurada (MHS) equation

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

whose parameters are determined from available polymers of somewhat higher MW. In doing so, it is important to note that the exponent a in the MHS equation is not constant over a wide range of molecular weight, but approaches 0.5 at very low molecular weight. This is in accord with the Flory-Fox treatment of polymers in a θ solvent [7], since short polymers will have a more rodlike than coil shape and their size will be unperturbed by a good solvent. On the other hand, larger polymers chains will be swollen by solvent and a will typically have values of 0.7 ± 0.1.

EXPERIMENTAL

Intrinsic Viscosity

An Ubbelohde suspended level Cannon viscometer was used to measure the viscosity of dilute solutions of PSTY and PMMA in toluene at 25 °C. It was assumed that viscosity is proportional to efflux time, that the kinetic energy correction and variation in temperature are negligible, and that there is no adsorption of polymer on the capillary wall.

The flow time for HPLC grade toluene was 172.3 seconds. In the case of PSTY of MW $< 10^4$, the error in measuring $[\eta]$ from a single sample was relatively high because the time difference between solvent and solution efflux was relatively small. In order to minimize the error, for each low molecular weight polymer sample three starting solutions having the same concentration were independently prepared. After viscosity measurements at various dilutions were performed on each of the starting solutions, all the obtained results were plotted on one graph and $[\eta]$ was estimated by a linear regression analysis. Error in measurement of the efflux time is random; therefore, based on the central limit theorem, as the number of independent measurements increases the estimation becomes more accurate; i.e. three starting solutions or more will result in a better estimation of $[\eta]$.

Figure 1 shows plots of typical data according to the Huggins and Kraemer equations [8]. From the intercepts of such plots we estimated the $[\eta]$ values shown in Table 1 for the PSTY and PMMA standards used in this work.

GPC

The GPC measurements were performed with a Waters Associates apparatus equipped with a 590 GPC pump, a TCM temperature controller unit, a UV detector model 441 using a 254-nm cut-off filter, and a differential refractometer (DRI) model R-401. The detectors were linked to an Apple-IIGC microcomputer through an ISAAC interface for data acquisition. A set of PL-gel columns (Polymer Laboratories, Shropshire, UK) with pore sizes of 10^5, 10^3, and 10^2 and a bead size of 10 μm were used at the operating temperature of 25 °C.

Toluene and tetrahydrofuran (THF) were used as eluants where the flow rate was kept at 1.0 mL/min. The HPLC-grade toluene was used without further purification. THF was refluxed over potassium for 24 h, distilled, and stabilized with butylhydroxytoluene (BHT) to prevent formation of peroxides.

The polystyrene standards were obtained from Pressure Chemical Co. (Pittsburgh, Pennsylvania, USA) and the PMMA standards were received from Polymer Laboratories. In Fig. 2 the GPC chromatograms in THF of PSTY standards having $M_p = 519$ and 20,400 are shown along with that of a PMMA synthesized in this work whose M_n of 332 was determined as described below.

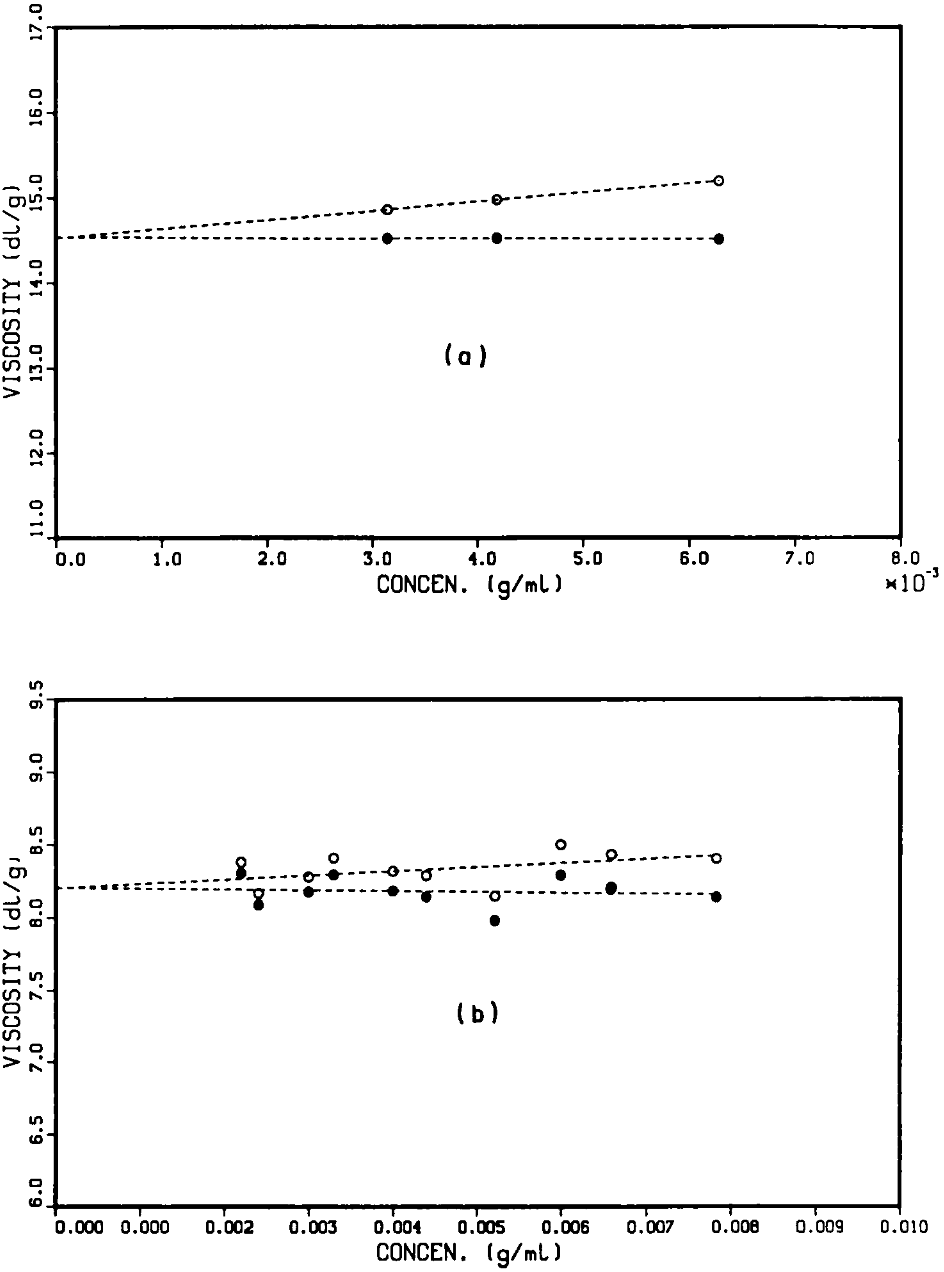

FIG. 1. Typical back-extrapolation of Huggins (solid circles) and Kraemer (open circles) equations for PSTY in toluene. (a) MW = 20,400; (b) MW = 9000.

TABLE 1. Intrinsic Viscosity of PSTY and PMMA in Toluene at 25°C

PSTY, MW	[η], dL/g	PMMA MW	[η], dL/g
233,000	87.703	1,600,000	184.820
97,200	45.502	400,000	79.879
50,000	26.585	265,000	62.370
20,400	14.531	185,000	51.680
9,000	8.203	107,000	39.110
4,000	5.581	64,000	22.063
2,000	4.260	27,000	13.180
1,050	2.926	19,700	11.408
		7,800	6.540

NMR

The NMR spectra were taken with a high precision 250-MHz FT-NMR spectrometer at 130°C using *o*-dichlorobenzene-d_4 as solvent (≈10% w/v solution) and 0.1% w/v tetramethyl silane as internal reference.

RESULTS

Intrinsic Viscosity–Molecular Weight Relation

When the data of Table 1 for PSTY are plotted as in Fig. 3, they may be represented by two intersecting straight lines with the intersect at MW = 10,069. However, the point with MW = 9000 statistically belongs to both lines. Equation (1) is nonlinear and, in general, linearization of a nonlinear model leads to a poor parameter estimation, an improper error structure, and an inaccurate estimate of the error. In the past, linearization was preferred because of its simplicity, whereas now, with the availability of statistical packages for nonlinear parameter estimation, the proper route should be chosen. K and a were estimated from the data in Table 1 and tabulated in Table 2 for PSTY and PMMA in toluene at 25°C by using a linear and a nonlinear regression.

In a recent publication [9] the intrinsic viscosity of very low molecular weight polystyrene (MW from 266 to 10,100) was carefully determined in benzene at 25°C. Their results in benzene are almost identical with the low molecular weight results obtained from this work (a = 0.472).

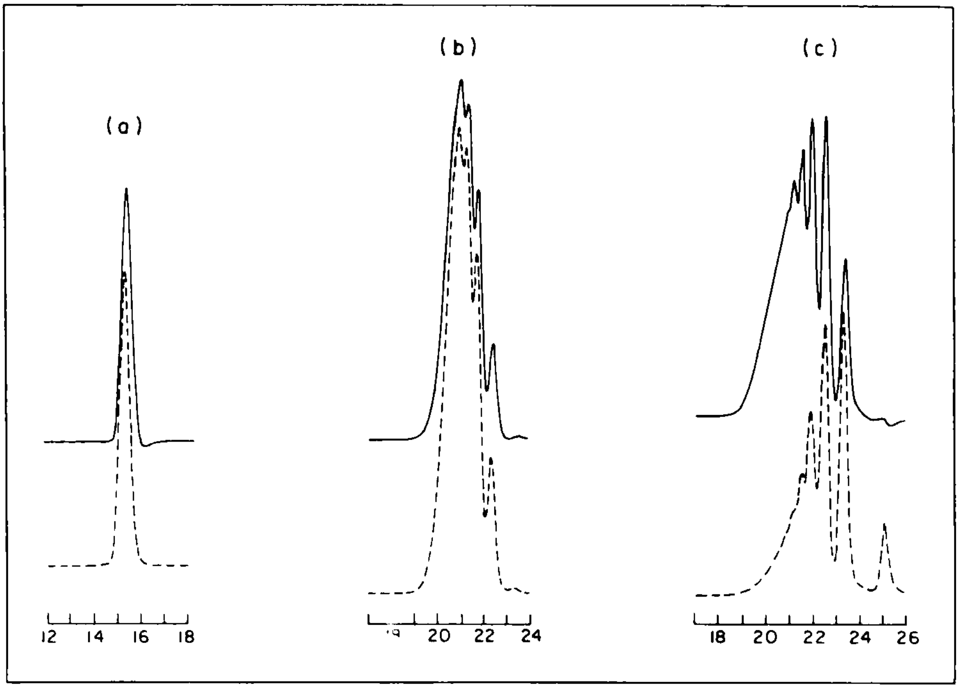

FIG. 2. GPC trace: (——) DRI detector and (---) UV detector. (a) PSTY standard with M_p = 20,400, (b) M_p = 519, and (c) PMMA with M_n = 332.

In another publication [10] an empirical relationship for intrinsic viscosity was proposed and is shown below. This relationship can predict the intrinsic viscosity of PSTY and PMMA in THF with molecular weights ranging from a few hundreds up to 100,000.

$$\text{For PSTY:} \quad [\eta]^{-1} = -0.018 + 12.3M^{-1/2} \tag{2}$$

$$\text{For PMMA:} \quad [\eta]^{-1} = -0.00877 + 12.1M^{-1/2} \tag{3}$$

Construction of Universal Calibration Curve

The GPC elution volumes of PSTY and PMMA standards were measured in toluene. In order to ensure that the deviation between PMMA and PSTY is not due to secondary separation, the UCC must be established. The elution times and intrinsic viscosities of individual samples

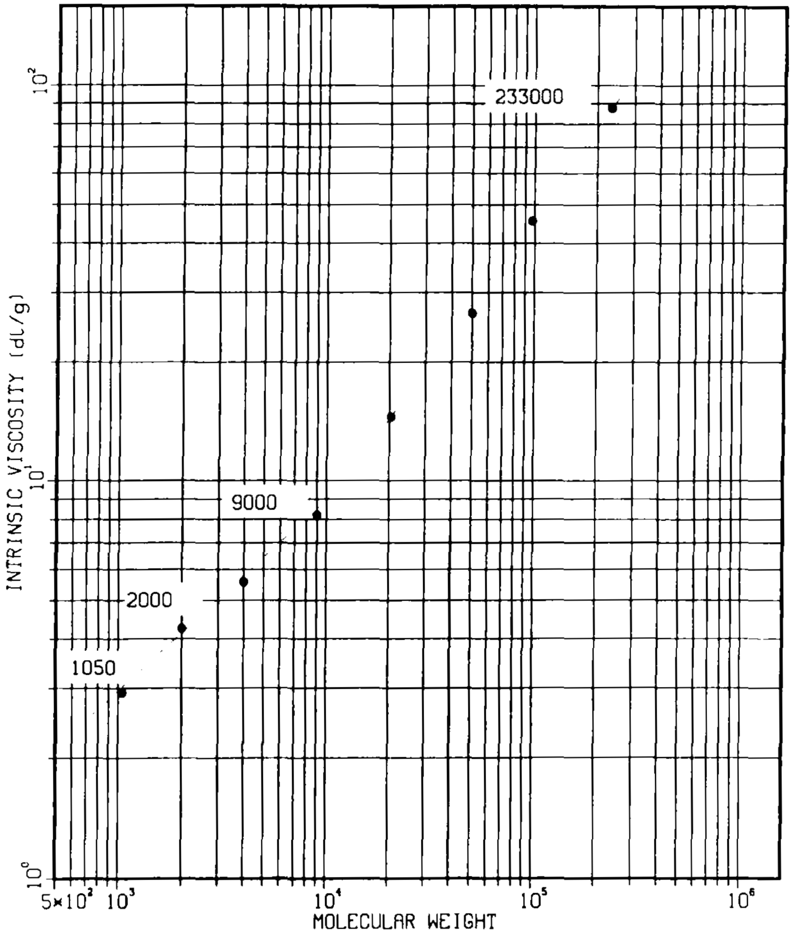

FIG. 3. Intrinsic viscosity of PSTY in toluene.

are known, and the intrinsic viscosities of low molecular weight polymers were extrapolated by use of the MHS equation to predict the intrinsic viscosity of oligomers. Figure 4 presents a universal calibration curve in terms of hydrodynamic volumes (V_H) for PMMA and PSTY standards in toluene. The open circles are the elution volumes (V) of the oligomers corresponding to the discrete peak maxima shown for the low MW PSTY standard sample. The MW corresponding to the peak maxima, M_p, was

TABLE 2. *K* and *a* values for PSTY and PMMA in Toluene

	Linearized model		Nonlinearized model	
	K	*a*	*K*	*a*
PSTY:				
MW ≤ 9000	1.142×10^{-3}	0.470	1.220×10^{-3}	0.462
MW ≥ 9000	1.059×10^{-4}	0.728	7.974×10^{-5}	0.753
PMMA:				
MW ≥ 7800	2.081×10^{-4}	0.640	3.421×10^{-4}	0.602

reported by the manufacturer to be 519; thus, the highest peak was assigned as pentamer, the second highest peak after was tetramer, then trimer, and the last peak in the MWD was dimer. The hydrodynamic volume of the styrene oligomers and of the PSTY and PMMA standards belong to the same curve; therefore, the UCC can be extended into the very low molecular weight region. The addition of oligomers to the UCC has significantly improved the precision of measurement at the low end of the MW scale. The curve shown in Fig. 4 is best represented as a virial equation of the form

$$\log (V_H) = C_0 + C_1 V + C_2 V^2 + C_3 V^3 \tag{4}$$

When THF was used as the eluant in GPC, the elution times were slightly changed due to the change in the hydrodynamic volumes. The intrinsic viscosity of polymers in THF were estimated by using Eqs. (2) and (3). A new UCC was constructed and extended to very low molecular weights by using oligomers of PSTY and MMA (Fig. 5).

Low molecular weight PMMA was prepared via free radical polymerization of MMA in the presence of a catalytic chain transfer agent [11]. These polymers had a double bond at the end group; therefore, they exhibit a strong UV absorption due to the conjugated double bond (Fig. 2).

In the GPC measurements the DRI detector measures the mass concentration of the PMMA in the eluant while the UV detector measures the corresponding molar concentration. Hence the MWD derived from the DRI detector is a weight distribution, while that from the UV detector is a number distribution. The two distributions should be convertible

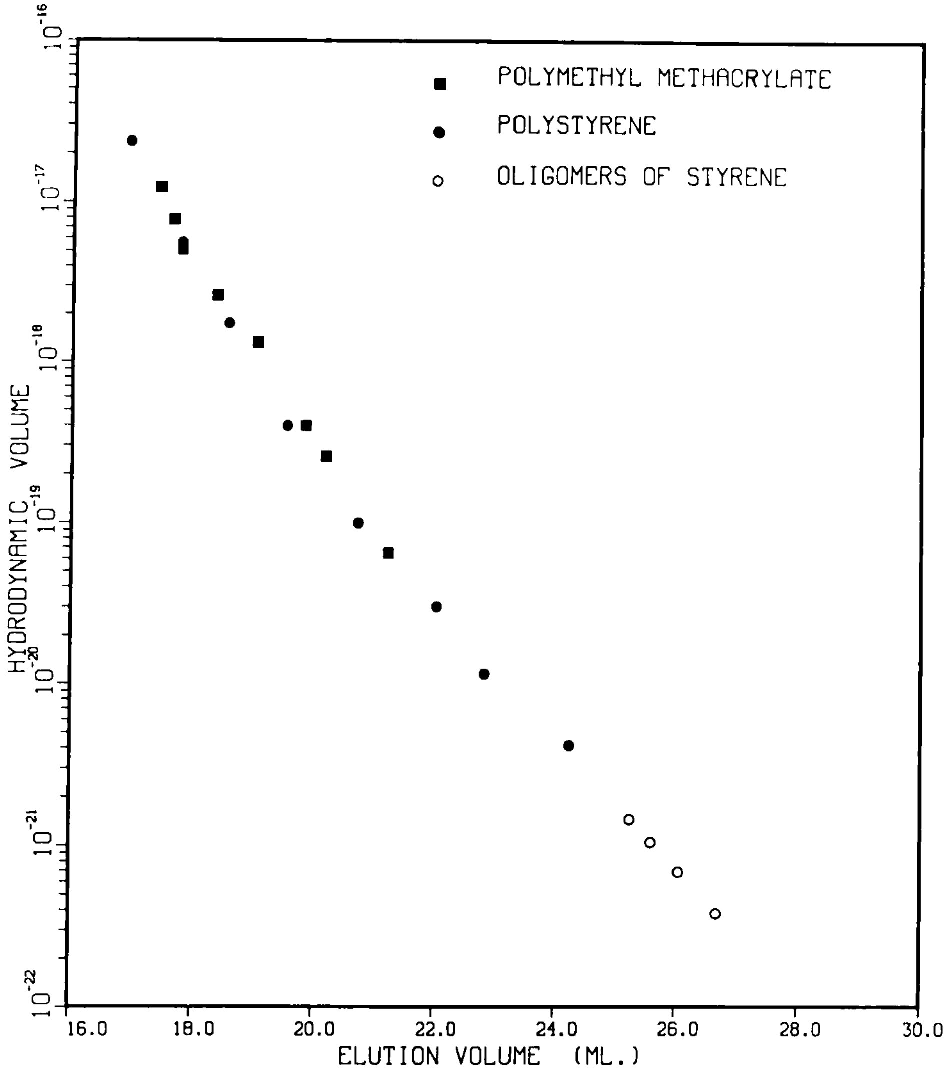

FIG. 4. Universal calibration curve in toluene.

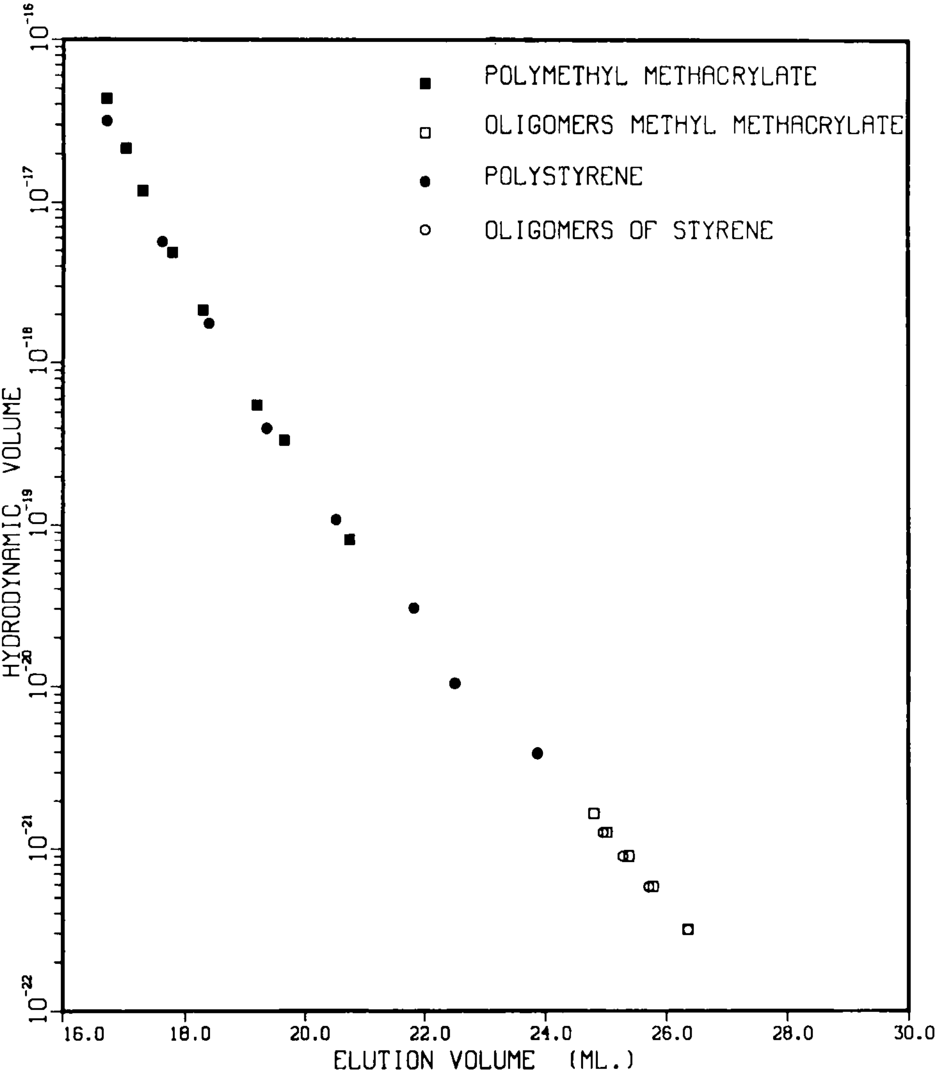

FIG. 5. Universal calibration curve in THF.

to each other. In addition, we have measured the proton NMR of these polymer samples (details are contained in Ref. 11) and, because of the terminal double bond, are able to calculate their M_n from the NMR spectra. For comparison, the values of M_n determined by UV, DRI, and NMR are given in Table 3.

During our experimental work we were aware that properties such as refractive index increment and UV absorbancy might be a function of MW, especially at very low MW where the end groups' contribution to molar refraction or absortivity may differ importantly from that of the polymer repeating unit. However, the fact that our approach has worked at MW values as low as 200 to 300 suggests that this problem is either numerically unimportant or fortuitously canceled by some other error for which we have not accounted. By way of example, we offer some calculations based on our own observations and on some literature data which suggest that this problem is numerically unimportant.

The use of dual detectors (DRI and UV) in our GPC measurements on the PSTY samples makes it possible to estimate the variation of the refractive index of PSTY with chain length. At the very low concentrations of polymer in GPC eluant, we may assume that the DRI signal, S_{DRI}, is proportional to the polymer concentration c_p and to the difference between the refractive index of polymer and that of the solvent, $(n_p - n_s)$, while the UV signal, S_{UV}, is simply proportional to the polymer concentration:

$$S_{\mathrm{DRI}} = K_{\mathrm{DRI}} c_p (n_p - n_s) \tag{5}$$

TABLE 3. Estimated MW from GPC and NMR

$M_{n(\mathrm{UV})}$	$M_{n(\mathrm{DRI})}$	$M_{n(\mathrm{NMR})}$	M_w/M_n (DRI)
1573	1682	1580	1.84
1455	1668	1454	1.91
1172	945	1105	1.79
716	882	894	1.65
419	401	472	1.46
344	352	355	1.45
341	332	408	1.35
312	310	334	1.33

$$S_{\mathrm{UV}} = K_{\mathrm{UV}} c_p \tag{6}$$

Therefore, the ratio of the two signals is proportional to the difference of the refractive indices and may be a function of chain length. If we assume the UV absorbancy, K_{UV}, is not a function of chain length, we can calculate from the GPC signals for PSTY standards at each peak maxima the corresponding refractive index (n_p). We have done so and find that the values so determined, listed in Table 4, can be expressed as a function of either the inverse chain length or the inverse square root of chain length as suggested by Candau et al. [12]. Linear least-squares analyses of the data in Table 4 give

$$n_p = 1.5879 - \frac{0.06741}{X_n} \tag{7}$$

or

$$n_p = 1.5941 - \frac{0.05122}{X_n^{0.5}} \tag{8}$$

The square of the correlation coefficient is 0.9233 for Eq. (7) and 0.9921 for Eq. (8).

These equations can be used to predict the effect of the chain length dependence of n_p on a given MWD determined by GPC in a given sol-

TABLE 4. Chain Length Dependence of Refractive Index of PSTY

X_n	n_p
2	1.5592
3	1.5639
4	1.5669
5	1.5713
10	1.5788
38	1.5861
87	1.5869
196	1.5916
481	1.5920

vent. We have done the necessary calculation for an assumed, most probable distribution of PSTY in THF. From the calculation we find the effect would cause the uncorrected M_n to be approximately 2% too high in the range of $M_n = 2000$ if Eq. (7) is used and 3% too high if Eq. (8) is used. Details of these calculations will be published elsewhere [13].

The change in the refractive index increment (*dn/dc*) with chain length for PSTY having cumyl end groups has been reported in the literature [12]. Calculations similar to those above can be done with the *dn/dc* values given for PSTY in benzene [12], which suggest the uncorrected M_n would be 8 and 4% too high with the analogs of Eqs. (7) and (8), respectively.

CONCLUSION

Comparison of the PMMA GPC results shown in Table 3 with the NMR-based computation of M_n indicates that the use of the universal calibration curve in GPC gives acceptable results. To achieve this, we needed information about the elution volumes for the lowest oligomers (dimer, trimer, etc.) and a valid relationship between intrinsic viscosity and molecular weight. The former can be obtained by observation of the discrete peaks corresponding to the oligomers, while the latter has proven to be possible either by extrapolation of the MHS equation where $a \approx 0.5$ or by use of another empirical relation established with low MW polymers.

In doing this work, we observed no consistent discrepancies for either our PSTY or PMMA oligomers in the UCC (Figs. 4 and 5) or for the PMMA samples in comparison of the GPC with the NMR results (Table 3). The estimated impact of a correction for the chain length dependence of n_p or *dn/dc* for PSTY on the M_n value is much less than 10%. Therefore, we believe a correction for the chain length dependence of refractive index is not necessary.

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