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Characterization of Homopolymers and Copolymers by the Coupling of Gel Permeation Chromatography and Automatic Viscometry

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Synopsis

An improvement in gel permeation chromatography for polymer characterization has been effected by combining it with an automatic viscometric technique. This allows not only determination of the molecular weight distribution but also the intrinsic viscosity for any kind of homopolymer. Moreover, it permits determination of the viscosity-molecular weight relationship for linear polymers and the degree of branching for branched polymers. The use of this technique, coupled with UV or IR spectrometric measurements, provides information with respect to composition and molecular weight distribution in the case of copolymers. It is thus possible to characterize copolymers from the double point of view of composition and molecular weight polydispersity.

INTRODUCTION

In previous publications on the techniques of gel permeation chromatography[1,2] the use of the method of universal calibration to obtain the molecular weight distributions of various samples was reported. It was shown that the utility of the technique could be considerably improved by the determination of the intrinsic viscosity of each fraction obtained from GPC. Preliminary results showed that such measurements were possible and useful, despite the very low concentrations of polymer present in the fractions. Results of a similar nature have since been published by other workers.[3]

The present study describes the results from further studies which more firmly establish the utility of this technique.

EXPERIMENTAL

The classical Waters Associates GPC apparatus having a 5-ml syphon and with columns being 10^7, 10^5, 10^4, 250, 50/80 Å porosity, as designed by the manufacturer, has been used. In all experiments, tetrahydrofuran

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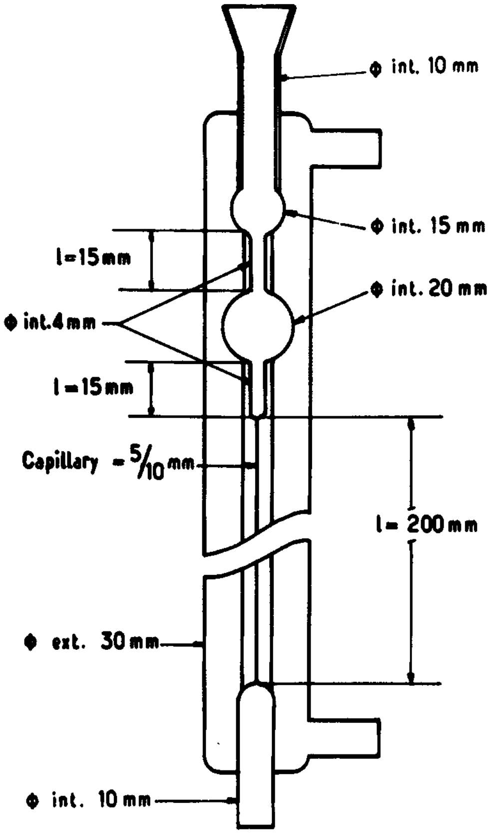

Fig. 1. Diagram of capillary viscometer coupled with GPC.

was used as the solvent. The solutions were introduced into the chromatograph through a 2-ml loop without filtering, since Millipore filters retain high molecular weight species and the filtration results in a lowering of the concentration of the solution. The flow rate of the solvent was adjusted to 1 ml/min at room temperature. The outlet of the syphon was connected to an automatic viscometer having a capillary of 0.5 mm in diameter and a length of 20 cm (Fig. 1). The diameter and the length of the capillary were selected so as to have a flow time shorter than the time required for the consequent filling of the syphon. The temperature of the viscometer was controlled at 10.01°C. The flow times were determined by an automatic device which has been commercialized by Fica.[4] The volume of the bulbs in the viscometer were slightly greater than the volume of the syphon in the GPC apparatus. This was required in order to avoid bubble formation during the filling of the viscometer from the syphon. Tubes with an inner diameter of 4 mm were employed at the ends of the two bulbs used in the viscometer. This device thus provides a means to obtain a recording of the flow time of each syphon count. A typical set of

TABLE I
Recorded Set of Flow Times

t_0	99.177
	99.177
	99.175
	99.173
	99.172
	99.176
	99.179
t	99.188
	99.345
	100.025
	101.576
	102.029
	100.150
	99.358
	99.211
	99.191
	99.186
t_0	99.177
	99.179
	99.174
	99.179
	99.170
	99.179
	99.179

observations is given in Table I, where the initial values correspond to the flow times of the pure solvent. It can be seen from this record that the reproducibility in solvent flow time is better than 0.01 sec. The apparatus is thus of sufficient precision to yield accurate values of the specific viscosities of each GPC fraction.

It is also apparent from Table I that the values of the flow time rise appreciably when the polymer is being eluted from the columns of the GPC. At the end of the elution, the solvent flow times are again recorded. The device is sensitive enough to detect impurities in tetrahydrofuran introduced with the sample.

Intrinsic Viscosity Measurements

The specific viscosity is given by the relation

$$\eta_{sp} = \frac{t}{t_0} - 1$$

with the assumption that kinetic energy corrections are negligible. Then in order to obtain the reduced viscosity, it is necessary to have the concentration C_i of the polymer at each syphon count. Such information can be obtained simply from the refractometer of GPC which gives a signal proportional to the instantaneous concentration of the solute. The total area of the chromatograms is directly proportional to the amount m of the polymer injected. Then the area S_i corresponding to the syphon content is proportional to the amount m_i of polymer in that fraction:

$$\frac{m_i}{m} = \frac{S_i}{S}. \tag{1}$$

Since the volume of the syphon v is known, the above equation can be written as

$$C_i = \frac{S_i}{S} \times \frac{m}{v}. \tag{2}$$

Hence the specific viscosity is given by the following equation:

$$\frac{\eta_{sp}i}{C_i} = \frac{t_i - t_0}{t_0} \times \frac{1}{C_i} = \frac{t_i - t_0}{t_0} \times \frac{S}{S_i} \times \frac{v}{m}. \tag{3}$$

One has to take into account the correction due to the dead volume between the refractometer and the syphon in order to obtain the real value of S_i corresponding to the measured viscosity and hence the real value of C_i. We measured the value of dead volume, which was found to be 1.9 ml for our system.

The usual practice in the use of reduced viscosity data is to determine the intrinsic viscosity $[\eta]$ by means of a plot of η_{sp}/C versus C. Such a technique is not possible with the present method, nor indeed is it necessary. At the very low concentrations of polymer present in the GPC fractions, the difference between the measured reduced viscosity and the extrapolated values which would yield the intrinsic viscosity can be shown by means of the Huggins equation[5]

$$\eta_{sp}/C = [\eta] + K[\eta]^2C \tag{4}$$

to be such as to yield in the most unfavorable cases an error of the order of 1.5%.

Check of Experimental Device

The utility of the device can be checked by applying the equation

$$[\eta] = \Sigma[\eta]_i\gamma_i$$

where $[\eta]_i$ is the limiting viscosity number of a fraction i having a weight fraction of polymer of γ_i. If the polymer was completely eluted and the viscosity measurements were correct, the value of $[\eta]$ obtained on the application of the above equation should correspond to the value of $[\eta]$ directly measured.

The above equation can be rewritten as

$$[\eta] = \frac{\Sigma[\eta]_iC_i}{\Sigma C_i} \tag{5}$$

TABLE II
Comparison of Viscosities Obtained

Samples	Direct measurement	$[\eta]$ From eq. (3)	From eq. (6)
PS (linear)	127.6	121.8	121.8
	66.4	64.3	64.3
	46.0	42.0	41.1
	24.5	22.5	22.5
	11.5	11.8	10.9
PVAc (linear)	80.4	81.7	81.6
	51.6	53.7	53.9
	36.9	37.9	37.9

This equation, on the assumption that the viscosity number of a fraction $\eta_{sp}i/C_i$ is equal to its limiting viscosity number $[\eta]_i$, can be written as

$$[\eta] = \frac{\Sigma(t_i - t_0)}{t_0} \times \frac{V}{m}. \tag{6}$$

The value of the limiting viscosity can easily be calculated from known values of m, V, and given values of $\Delta t = t_i - t_0$. It is seen from the above equation that in the concentration range used, the value of $[\eta]$ is independent of the actual concentration C_i. In other words, the value $[\eta]$ is not dependent on the results given by the refractometer and the measurements of the areas on the chromatogram.

A close agreement between the value of $[\eta]$ obtained from such measurements and the value directly determined on whole polymer would be a good test of the validity and applicability of the proposed device. Some results of such tests for a number of different polymers are given in Table II and clearly show this agreement.

The limiting viscosity numbers are, however, slightly lower than those obtained by direct measurements. This could be due either to a slight retention of polymer on the chromatographic support or to the fact that we have assumed, following Waters, that the volume of the loop, i.e., the volume of solution injected in the columns, was exactly 2 ml. In order to verify this latter assumption, we determined this quantity by the following procedure. Each loop was filled with a PS solution of known concentration and was disconnected from the GPC apparatus. The solutions from the loops were collected in a 25-ml volumetric flask, and the final volume was adjusted to 25 ml. The concentration of polymer in this solution was estimated by means of UV spectrophotometry. The estimation thus provided the concentrations of the solutions and the volumes of the loops. These results are given in Table III. It is seen from the table that the volume depends on the loop used. Assuming 2 ml, instead of the correct values, introduces an error which can be as large as 4.5%.

TABLE III
Loop Volumes

Loop no.	Volume, ml
1	1.91
2	1.97
3	1.97
4	2.01
5	2.08
6	1.97

Since during the course of this work we did assume 2 ml, not noting which loop was used, it is impossible to make a correction in the current data.

The Limits of Applicability

Molecular Weight. In order to determine the lower limit of molecular weight of the samples which could be studied by means of the present device, a polystyrene having a molecular weight about 14,000 and polydispersity of 1.3 was injected in GPC. Five counts showed flow times different from that for the pure solvent, the differences in flow time varying from 0.2 to 1.3 sec. The estimated value of the limiting viscosity number along with that determined directly by classical methods is given in Table IV. The excellent agreement between these values distinctly points out that the device is adaptable even to samples of very low intrinsic viscosity. Thus, the lower accuracy in estimating the limiting viscosity number for low molecular weight samples does not prevent the applicability of the proposed device.

Effect of Polydispersity of the Fractions. The fractions which are collected in the syphon and measured in the viscometer are not mono-

TABLE IV
Comparison of Intrinsic Viscosities and Weight-Average Molecular Weights Obtained by Several Methods[a]

Sample	$[\eta]_{\text{Ubbelohde}}$	$\bar{M}_{wLS}$	$[\eta]_{\text{GPC}}$	$\bar{M}_{w\text{GPC}}$
PS (linear)	11.5	14,500	11.8	15,400
	66.4	173,000	64.3	182,000
PVAc (linear)	36.9	66,500	37.9	73,700
	51.6	109,000	53.7	109,800
	63.6	143,000	61.2	158,000
	80.4	192,000	81.7	195,000
PVAc (branched)	31.2	48,000	26.1	51,700
	33.1	60,400	32.0	59,400
	89.5	318,000	85.5	269,000
	112.0	500,000	111.7	501,300

[a] Ubbelohde viscometer, light scattering (LS), and the proposed technique in case of homopolymers.

disperse since elution volume is a function of molecular weight. In a given syphon, the molecular weights correspond to a difference in elution volume of about 5 ml. In order to be precise, the average molecular weight of the corresponding fraction should be used. Since its evaluation is not easily accomplished, we took as the elution volume of the fraction, and therefore as the molecular weight, the value corresponding to the abcissa of the vertical line cutting the chromatogram between two successive counts into two equal areas.

Another error due to axial dispersion should also be taken into account. Because of the axial dispersion, the elution volumes as seen from the chromatogram correspond to a molecular weight distribution and not to a unique molecular weight as assumed. It is sometimes believed that such axial dispersion could introduce a large error in estimating the viscosity-molecular weight relationship and that precise determination of the values of K and a in the classical viscosity equation $[\eta] = KM^a$ by this method would be impossible. It is evident that if a perfectly monodisperse sample is injected, the axial dispersion will give fractions of the same viscosity at different elution volumes, and at the limit it would result in a zero value for a. The effect of axial dispersion on the estimation of the values of K and a in viscosity-molecular weight relation is an interesting and difficult problem. It will be discussed in details in a forthcoming paper.[6]

APPLICATIONS AND DISCUSSION

Homopolymers

Test of Validity of Method. During the studies on universal calibration for GPC, the effects of the polydispersity were not taken into account. The present device provides a means to calculate these effects. It enables one to estimate the limiting viscosity number $[\eta]$ for each fraction from eq. (3) and subsequently M_i from the universal calibration. The average molecular weight thus obtained for a sample should, in principle, correspond to that measured directly from light scattering.

Results of such determinations on a number of linear anionic polystyrenes and on fractions of linear as well as on branched poly(vinyl acetate) are given in Table IV where $[\eta]$ GPC values are calculated by means of either eq. (5) or (6). The agreement between values of molecular weights and limiting viscosity numbers obtained by different methods is most satisfactory, and it is seen from the results that the discrepancies seldom exceed 5%. This error could perhaps be attributed to the overestimated values of the injection volume of the loops.

Viscosity–Molecular Weight Relationship. As pointed out in our earlier communication,[7] this device also enables one to determine viscosity–molecular weight relationships for both linear and branched polymers. The viscosities obtained for fractions can be plotted against their corre-

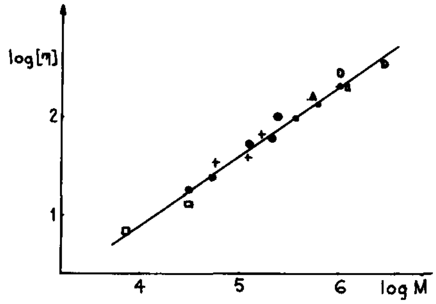

Fig. 2. Intrinsic viscosity vs. molecular weight: (D) M_w = 2,145,000; (△) M_w = 867,000; (●) M_w = 411,000; (◑) M_w = 173,000; (+) M_w = 98,200; (○) M_w = 40,000; (□) M_w = 14,500.

sponding molecular weights on a log–log scale. Such results for the middle fractions obtained from the chromatogram for narrow molecular weight samples of polystyrene are shown in Figure 2.

The least-squares line drawn corresponds to the following equation:

$$[\eta] = 1.18 \times 10^{-2} M^{0.709}.$$

The relation is in satisfactory agreement with that found previously[8]:

$$[\eta] = 1.41 \times 10^{-2} M^{0.7}.$$

However, due to the axial dispersion, the slope of the plot of log $[\eta]$ versus log M for the fractions should be smaller than the slope obtained for the least-squares line for various samples. This is true only for the higher molecular weight samples, suggesting that the axial dispersion is predominant for high molecular weight samples only.

Copolymers

Estimation of Molecular Weight Distribution. The estimation of molecular weight distributions in the case of copolymers have been, to date, very difficult to obtain. The difficulty arises from the fact that the exact relations between the elution volume from GPC of a sample along with molecular weight were not available. In the present studies, however, we have successfully characterized di- and triblock copolymers of polystyrene–polyisoprene (PS–PIP) (kindly made available by J. Terrisse, Ecole d'Application des Hauts Polymères, 67, Strasbourg, France) and a diblock copolymer of polystyrene–poly(methylmethacrylate) (PS–PMMA) (Fig. 3), all of them prepared by an anionic technique.

In case of azeotropic or strictly alternating copolymers, where the composition fluctuations with respect to their molecular weights are generally negligible, the problem of the estimation of molecular weight distribution is similar to that of linear or branched homopolymers. The concentration of each fraction is proportional to the indication given by the refractometer. The data can thus be analyzed in the same way as those of the homopolymers.

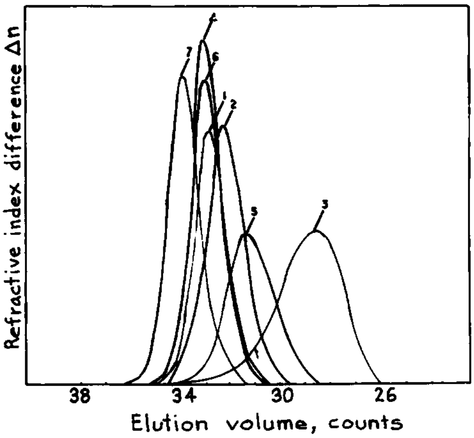

Fig. 3. GPC distribution curves of copolymer samples.

In case of copolymers, where structure and composition polydispersity is present, the fractions collected from the chromatograph have different compositions, and thus the response obtained from the refractometer is not only proportional to the instantaneous concentration since it depends also on the composition. However, compositional polydispersity can be obtained with the help of UV spectrometric measurements for the polystyrene sequences in each fraction.

The additivity of the refractive index increment was assumed, and has been checked and found to be valid for different copolymers. Thus, the refractive index increment for a copolymer can be written as

$$(dn/dc)_{AB} = (dn/dc)_A x + (dn/dc)_B (1 - x)$$

where $(dn/dc)_A$ and $(dn/dc)_B$ are the refractive index increments for the corresponding homopolymers A and B, respectively, and x is the weight fraction of A units in the copolymer. The refractometer response h can be written as

$$h = Kc\, dn/dc$$

and is not directly proportional to concentration due to the variations of dn/dc.

Let us designate $(dn/dc)_0$ as the value of the index increment corresponding to the whole sample with average composition x_0. In order to obtain a quantity proportional to the concentration, it is sufficient to correct this value multiplying it by the factor $(dn/dc)_0/(dn/dc)_i$ leading to

$$h_{cor}' = h_i (dn/dc)_0/(dn/dc)_i.$$

The results before and after such a correction are shown in Figure 4 and Table V for one of the samples studies (PS–PIP 3).

The corrected values of the refractometer response then can be used to obtain the corresponding limiting viscosity numbers, which, in their turn,

TABLE V

Example of the Correction of Refractometer Response for Copolymer Sample PS–PIP-3[a]

Fraction	Weight, %	PS, %	dn/dc	h_i	$h_{i\,\mathrm{corr}}$	$[\eta]_i$	$[\eta]_i M_i$	$M_i \times 10^{-5}$
A	0.75	—	—	5.0	—	2188.0	5.2×10^9	23.766
B	11.85	75.9	0.183	34.5	31.7	645.8	1.9×10^9	29.720
C	29.36	61.2	0.174	63.5	61.5	424.1	6.7×10^8	15.798
D	28.63	52.5	0.168	59.0	59.0	321.1	2.1×10^8	6.570
E	17.14	40.9	0.161	36.5	38.0	270.1	9.3×10^7	3.443
F	7.72	31.2	0.155	16.0	17.34	226.6	3.8×10^7	1.676
G	3.58	26.9	0.152	6.0	6.63	222.0	1.47×10^7	0.662
H	0.94	—	—	2.5	—	164.9	5.2×10^6	0.315
I	0.03	—	—	1.0	—	78.3	2.15×10^6	0.274

[a] $M_{w\mathrm{LS}} = 1074{,}000$: $[\eta]_{\mathrm{Ubbelohde}} = 414$; $[\eta]_{\mathrm{GPC}} = 371$; $M_{w\mathrm{GPC}} = 1147{,}000$; $M_{n\mathrm{GPC}} = 375{,}200$; $M_w/M_n = 3.0$.

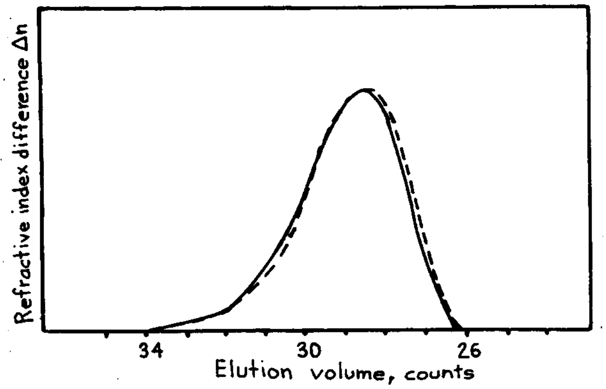

Fig. 4. Uncorrected (- - -) and corrected (——) GPC distribution curve for copolymer PS–PIP-3.

provide one with sufficient information to calculate various average molecular weight values. Molecular weights obtained with the help of this correction along with those obtained directly, from classical methods, are given in Table V.

It has been well established that the compositional heterogeneities in copolymers present difficulties in measuring their true molecular weight by light scattering. The molecular weights obtained by the use of the classical light-scattering equation

$$M_w^{-1} = (2\pi^2/\lambda^4 N_a R_b) n_b^2 (dn/dc)^2 I_b \left(\frac{c}{I_0}\right) \qquad \begin{matrix} c = 0 \\ \theta = 0 \end{matrix}$$

for such copolymers is different depending on the solvent used. According to the Bushuk and Benoit equation for light scattering by copolymer solutions,[9] the molecular weights calculated are apparent values which are related to the true molecular weight for given samples by the following equation:

$$M_{\text{app}} = M_w + 2P\{(dn/dc)_{\text{A}} - (dn/dc)_{\text{B}}\}/(dn/dc)_{\text{AB}} + Q\{(dn/dc)_{\text{A}} - (dn/dc)_{\text{B}}\}/(dn/dc)_{\text{AB}}$$

The determination of the molecular weight for a copolymer in different solvents, which give different refractive index increments, would result in a parabola when M_{app} is plotted against $\{(dn/dc)_{\text{A}} - (dn/dc)_{\text{B}}\}/(dn/dc)_{\text{AB}}$. The intercept on the Y − axis of such plot yields the true molecular weight. The results obtained from light-scattering measurements on samples 3 and 4 in six solvents are given in Table VI.

The plots of apparent molecular weights versus $\{(dn/dc)_{\text{A}} - (dn/dc)_{\text{B}}\}/(dn/dc)_{\text{AB}}$ are shown in Figure 5. The values of M_w thus obtained are given in Table VII along with the values of M_n obtained with an automatic Mechrolab 502 osmometer in toluene using Schleicher-and-Shuell membranes. In the same table, the values of the average molecular weights

TABLE VI
Apparent Weight-Average Molecular Weight of PS–PIP-2 and PS–PIP-3 in Different Solvents

	PS–PIP-2		PS–PIP-3	
Solvent	$\frac{(dn/dc)_A - (dn/dc)_B}{(dn/dc)_{AB}}$	M_{app}	$\frac{(dn/dc)_A - (dn/dc)_B}{(dn/dc)_{AB}}$	M_{app}
Tetrahydrofuran	0.34	160,000	0.33	1450,000
Carbon tetrachloride	0.53	169,000	0.49	1200,000
Toluene	1.07	169,000	1.05	1640,000
Benzene	1.50	182,000	1.55	1960,000
Cyclohexane	0.39	163,000	—	—
Chlorobenzene	—	—	2.23	2600,000
Bromonaphtalene	1.08	156,000	—	—

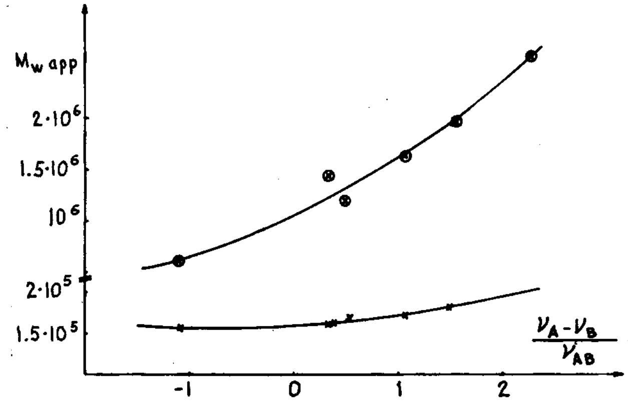

Fig. 5. M_{app} vs. $[(dn/dc)_A - (dn/dc)_B]/(dn/dc)_{AB}$ for PS–PIP-3 (⊗) and PS–PIP-2 (×).

obtained with help of this device coupled with an UV spectrophotometer are also given.

The good agreement between the various results indicates that the present device is suitable for such studies. However, it should be mentioned that the values of the limiting viscosity number differ beyond the experimental error for PS–PIP-3. The difference can perhaps be attributed to the fact that the sample has a very broad distribution in heterogeneity as well as in molecular weight.

***P* and *Q* Parameters.** Since the true molecular weights of the samples and the composition for each fraction are known, it would be interesting to calculate the values of the P and Q parameters suggested by Bushuk and Benoit for the light scattering of copolymer solutions where P and Q are defined as follows:

$$P = \Sigma M_i C_i (x_i - x_0)/C$$

TABLE VII
Comparison of Viscosities and Molecular Weights Obtained by Classical Methods and by GPC Viscosities Measurements of Copolymers

Sample	PS_{UV}, %	$\bar{M}_{wLS}$	$\bar{M}_{nOSM}$	$\bar{M}_{wGPC}$	$\bar{M}_{nGPC}$	$[\eta]_{Ubbelohde}$	$[\eta]_{GPC}$
PS–PIP-1	11.0	101,000	95,800	104,000	84,000	82	75
PIP–PS-2	52.7	159,000	137,700	167,500	136,200	103	100
PS–PIP-3	53.8	1074,000	—	1147,000	375,200	414	371
PIP–PS-4	93.4	114,000	88,100	124,500	89,000	57	54
PS–PMM-5	49.7	404,000	345,000	442,000	268,900	101	104
PS–PIP–PS-6	75.3	119,000	107,600	132,000	105,000	64,0	60,7
PS–PIP–PS-7	77.4	69,000	61,100	74,000	59,000	42,0	39,7

and

$$Q = \Sigma M_i C_i (x_i - x_0)^2 / C.$$

The values of P and Q obtained in this study can be compared with those obtained from the plot of M_{app} versus $[(dn/dc)_A - (dn/dc)_B]/(dn/dc)_{AB}$. These are given in Table VIII.

TABLE VIII
P and *Q* Values

Sample	P LS	P GPC	Q LS	Q GPC
PS–PMM-5	3.4×10^3 -6.7×10^3 [a]	-7.9×10^3	3.1×10^3 9.1×10^3 [a]	6.2×10^2
PS–PIP-3	2.4×10^5	1.1×10^5	7.9×10^4	2.4×10^4
PS–PIP-2	3.8×10^3	-1.3×10^4	4.4×10^3	1.0×10^4

[a] Calculated from the equations

$$P = x(1 - x)\,[M_w^A - M_n^A - (M_w^B - M_n^B)]$$

and

$$Q = x(1 - x)[(1 - x)(M_w^A - M_n^A) + x(M_w^B - M_n^B)].$$

The values of P and Q obtained by GPC are seen to be systematically smaller than those obtained from classical light-scattering measurements. However, Lamprecht and co-workers[10] have pointed out that the classical light-scattering measurements give higher values of P and Q than those obtained from sedimentation equilibrium measurements. Thus, the results obtained from GPC measurements appear to be more significant and more precise than the results of classical light-scattering measurements.

In the case of PS–PIP-2, the values of P obtained from GPC and light-scattering measurements have opposite signs. This is due to the very low value of P which causes it to be rather difficult to estimate precisely. The value of P/M_w for this sample is of the order of 0.02, which is perhaps beyond the limit for an accurate determination of the value of P.

CONCLUSION

In the present work, some possible uses of a device which couples GPC with an automatic viscometer are presented. Such coupling provides more information with respect to the molecular weight distribution for both homopolymers and copolymers. From the present results as well as from those previously published, this method appears promising and should enable faster and more precise characterization of polymers in solution.

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