On the molecular weight determination of bisphenol-A polycarbonate

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In order to assess the reliability of absolute molecular weights of bisphenol-A polycarbonate samples measured by size exclusion chromatography, the results obtained from two experimental systems and two calibration methods are compared with each other as well as with data provided by light scattering determinations. The interest of coupling a light scattering detector to the chromatographic system is discussed.

(Keywords: bisphenol-A polycarbonate; size exclusion chromatography; light scattering; viscometry; universal calibration)

INTRODUCTION

Size exclusion chromatography (SEC) has become a widespread technique for assessing molecular weights and their distributions. However, the use of SEC for measuring *absolute* molecular weights remains somewhat controversial due to the indirect nature of the method. Moreover, the agreement between results obtained in various laboratories is often poor.

In the particular case of bisphenol-A polycarbonate [poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)] (PC), the precise measurement of molecular weights by SEC is complicated by two major problems: the absence of monodisperse molecular weight standards and the variety of viscosity equations described in the literature for the same solvent[1-4]. On the other hand, the measurement of molecular weights by light scattering techniques (LS) does not require any calibration. However, LS gives only the second moment of the distribution ($\bar{M}_w$) and is very sensitive to the presence in the polymer of any heterogeneity, even at very low concentrations: branched molecules, microcrystals, microgel, etc.

The main purpose of this publication is to demonstrate the interest of coupling SEC and LS in order to combine the information provided by both techniques. It will also be shown that reliable absolute molecular weights can be obtained by SEC, provided that broad primary standards characterized by LS are available or Mark–Houwink relations valid within the molecular weight range of interest are known.

Since PC is commercially available only in a limited range of molecular weight (MW), high molecular weight fractions and oligomers synthesized in the laboratory were used to extend the calibration range. Various viscosity relations reported in the literature for PC in methylene chloride and tetrahydrofuran (THF)[2-4] were checked by comparison between the results obtained by LS, viscometry and SEC (universal calibration).

EXPERIMENTAL

Samples

A high MW PC sample was synthesized by interfacial polycondensation of 4,4′-dihydroxydiphenyl-2,2-propane and phosgene in a mixture of 72% methylene chloride and 28% aqueous sodium hydroxide (45% NaOH). Triethylamine was used as acid acceptor[2]. The sample obtained by this method was fractionated. The fractional precipitation was carried out with methylene chloride as solvent and methanol as precipitant, giving six fractions (referred to as PC1 F1 to PC1 F6).

Commercial PC samples were supplied by Bayer (PC2, 6, 7 and 11), General Electric (PC3 and 4) and Aldrich (PC5, 8, 9 and 10).

A mixture of PC oligomers having the following structural formulae

$$\phi[\text{OCOO}-\phi-\text{C}(\text{CH}_3)_2-\phi]_n-\text{O}-\text{CO}-\text{O}-\phi$$

were synthesized by transesterification of bisphenol-A diphenyl carbonate following a procedure described by Bailly, Legras and Mercier[5].

Techniques

Viscometry. Intrinsic viscosities were measured in THF using a Fica Viscomat. The intrinsic viscosity values were determined by the usual double extrapolation of the reduced and inherent viscosities at zero concentration.

Light scattering. Light scattering measurements were obtained in THF at 546 nm (vertically polarized light)

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using a Fica 50 instrument. The solutions were annealed either for 15 h at 36°C or for 48 to 64 h at 50°C before centrifugation at 25 000 *g* for 90 min.

Size exclusion chromatography. Two experimental systems were used for measuring the MW distributions by SEC. The first system comprised a set of two Shodex ABOM columns (10 μm particle size) providing a good separation between 3×10^3 and 3×10^6 (PS equivalent MW). Distilled and filtered THF was used as the mobile phase at a 1 cm^3 min^{-1} flow rate. The detector was a Shodex SE-11 differential refractometer. Preliminary calibration of the columns was obtained with 12 narrow PS standards (MW ranging between 1500 and 3.6×10^6). The viscosity relation for linear PS in THF at 25°C, LS is[6]:

$$[\eta] = 14 \times 10^{-3}\, M^{0.70}\, (\mathrm{cm^3 g^{-1}})$$

During SEC–LS coupling experiments, a LS detector was inserted between the columns and the differential refractometer. The experimental device and the analysis of the data have been described in a previous publication[7].

The second experimental system comprised a set of six Waters Ultrastyragel columns (10^6, 10^5, 10^4, 10^3, 500 and 100 Å porosities). This set of columns is suited to the separation of MW ranging from 50 to 10^7 (PS equivalent MW). The mobile phase was methylene chloride, used at a 1 cm^3 min^{-1} flow rate. The detector was a Hewlett-Packard 1036A UV detector (254 nm). An internal standard (sulphur) was used to correct for small variations of the flow rate[8]. This method was found to enhance significantly the reproducibility of the results. Data acquisition and analysis were carried out on a Trivector Trilab 2000 system.

Ethylbenzene and 19 narrow PS standards ($\bar{M}_w$ between 800 and 1.75×10^6) were used to construct the calibration curve. The viscosity relation chosen for PS in methylene chloride at 25°C is

$$[\eta] = 6.1 \times 10^{-3}\, M^{0.74}\, (\mathrm{cm^3\, g^{-1}})$$

which was determined in the Polymer Laboratory of the Federal Polytechnic, Lausanne[9].

RESULTS

Viscometry

The six fractions obtained from sample PC1 (PC1 F1 to PC1 F6) were characterized by viscometry in THF at 25°C. Viscometric average MW ($\bar{M}_v$) were calculated by using the Mark–Houwink relation proposed by Schnell[2]:

$$[\eta] = 39.9 \times 10^{-3}\, \bar{M}_v^{0.70}\, (\mathrm{cm^3\, g^{-1}})$$

The results are summarized in *Table 1*.

LS and SEC–LS coupling

The weight average MW ($\bar{M}_w$) of all samples were determined by LS. The Zimm plot of unfractionated PC1 presents an anomalous angular distribution of scattered intensity (*Figure 1*). The strong curvature observed at small angles could *a priori* be explained by a high polymolecularity of the sample. However, since the heterogeneity index calculated by SEC is 2.1, this curvature is more likely to arise from the presence of aggregated particles in solution (microcrystals or insoluble residual fraction). The presence of a very high MW fraction in sample PC1 was confirmed by the SEC–LS coupling.

Table 1 Fractionation of sample PC1

Fraction	Weight (g)	Cumulative weight fract. (%)	$[\eta]$ (cm^3 g^{-1})	$\bar{M}_v$[a]
PC1 F6	0.3	1.90	109	82 200
PC1 F5	1.9	16.00	152	130 400
PC1 F4	2.1	41.65	193	183 500
PC1 F3	2.0	70.60	218	218 500
PC1 F2	1.3	89.05	255	273 000
PC1 F1	0.2	98.70	295	340 000
PC1 (unfract.)	7.9	100	230	235 000
PC1 (after fract.)	7.8	98.7	200	195 000

[a] Viscometric average MW ($\bar{M}_v$) calculated from the viscosity relation proposed by Schnell[2] for PC in THF

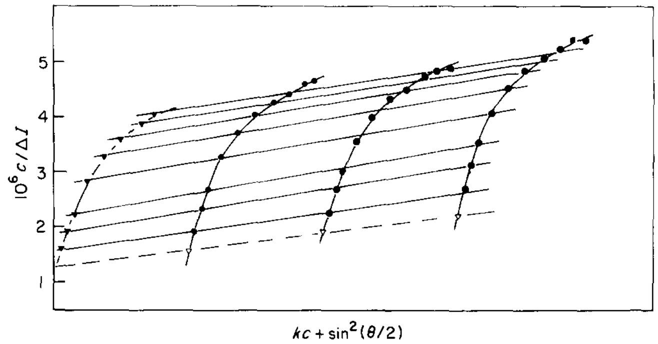

Figure 1 Zimm plot for sample PC1 in THF at 25°C

The fractions PC1 F2 to PC1 F6 were analysed by SEC–LS coupling after the solutions had been annealed for 15 h at 36°C. *Figure 2* shows the refractive index (ΔC) and scattered light (ΔI) curves for fractions PC1 F5 and PC1 F2. Only one peak is found by both detectors for sample PC1 F5 whereas a second one (A) is observed by the LS detector for sample PC1 F2. This latter peak must arise from the presence of very high MW particles, in very low concentration since the refractive index shows no departure from the baseline in this region. The same observation was made for PC1 F3. For these two samples, the SEC–LS coupling data were analysed by considering only the main peak (referred to as 'P' in *Figure 2*).

The presence of the secondary peak in PC1 F2 and F3 indicates that the solution contains aggregated particles which may result in an overestimation of $\bar{M}_w$ as measured by LS. In order to favour the dissolution of these particles, solutions of samples PC1 F2 and F3 were submitted to more severe annealing conditions. Results of LS measurements on the annealed solutions are presented in *Table 2*. The two samples react differently to the thermal treatment since only for PC1 F2 are the $\bar{M}_w$ values obtained by LS and SEC–LS identical, within experimental error, after 64 h at 50°C. Because of the imprecise value of $\bar{M}_w$ measured by LS for samples PC1 F2 and F3, only the MW measured by SEC–LS will be considered for these samples.

Table 3 summarizes the results obtained by viscometry, LS and LS–SEC coupling in THF for all the samples. The agreement between LS and SEC–LS coupling is excellent, except for PC1 F3, as explained above.

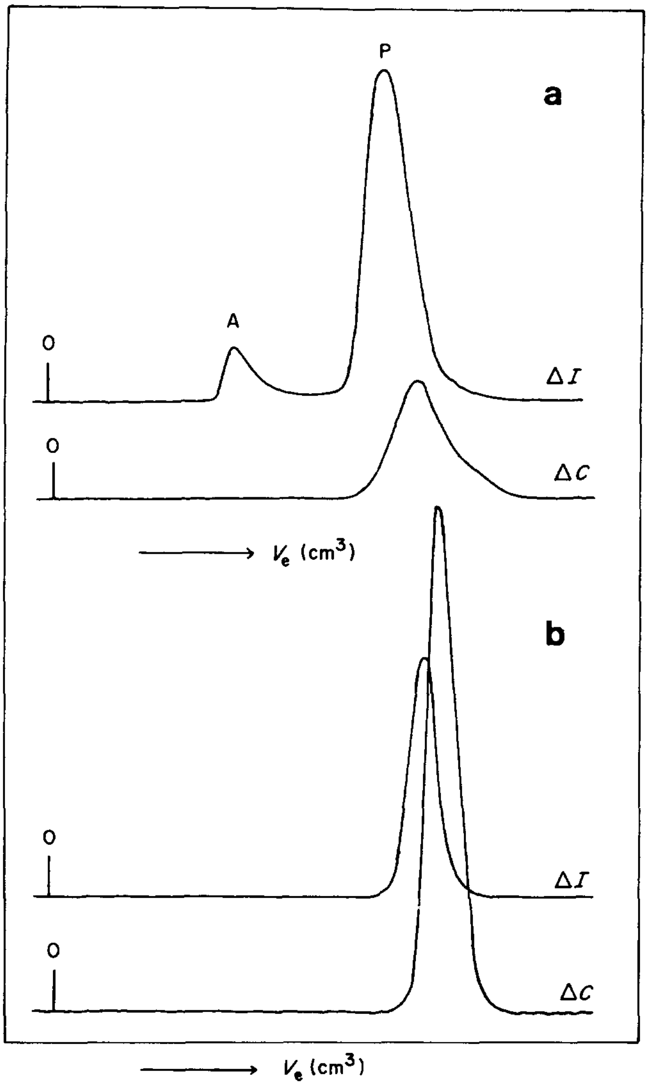

Figure 2 SEC–LS coupling; ΔC (refractive index) and ΔI (scattered intensity) curves. (a) PC1 F2, (b) PC1 F5

The calculated second virial coefficient values (A_2) are rather high (ranging from 7×10^{-4} to $27\times10^{-4}\,\mathrm{mol\,cm^3\,g^{-2}}$) and decrease with increasing MW, following the relation:

$$A_2=4.73\times10^{-2}\,\bar{M}_w^{-0.33}\,(\mathrm{mol\ mg\ g^{-2}})$$

The results of the SEC–LS coupling were corrected to take into account the effect of A_2:

$$\frac{1}{M_w^i}=\frac{1}{M_w^{*i}}-2A_2C_i$$

where M_w^i is the corrected MW of the fraction eluting at time *i*, C_i is the instantaneous concentration and M_w^{*i} is the uncorrected MW obtained directly from the chromatograms:

$$\frac{1}{M_w^{*i}}=K\frac{\Delta C_i}{\Delta I_i}$$

This correction is taken into account in *Tables 2* and *3*. *Figure 3* shows the distribution obtained for sample PC1 F5, as an example of the calculations.

Mark–Houwink relations in THF

Several viscosity relations are found in the literature for PC in THF at 25°C:

$$[\eta]\,(\mathrm{cm^3\,g^{-1}})=39.9\times10^{-3}\,M_v^{0.7}\qquad(\text{Schnell}^2)$$
$$[\eta]\,(\mathrm{cm^3\,g^{-1}})=38.9\times10^{-3}\,M_v^{0.7}\qquad(\text{Sitaramaiah}^3)$$

$$[\eta]\,(\mathrm{cm^3\,g^{-1}})=49.0\times10^{-3}\,M_v^{0.67}\qquad(\text{Moore}^4)$$

The viscosity relation obtained by Moore significantly differs from those proposed by Schnell and Sitaramaiah. Moreover, these relations were established in a rather narrow range of MW (between 9×10^3 and 9×10^4). Schnell's and Moore's viscosity laws are shown in *Figure 4*, along with the experimental relation obtained in the present work (*Table 3*).

From our data, the following relation can be deduced for MW ranging from 10^4 to 3×10^5, a significantly broader range than previously reported:

$$[\eta]\,(\mathrm{cm^3\,g^{-1}})=41.2\times10^{-3}\,M_w^{0.69}$$

This relation is very similar to the one proposed by Schnell, which will be used subsequently in this work.

Universal calibration method

All the samples were characterized by SEC, using methylene chloride or THF as the mobile phase. The average MW were calculated with the help of the universal calibration method or a PC calibration. The universal calibration was obtained from a PS calibration and the Mark–Houwink laws summarized in *Table 4*.

Two series of standards were used to determine the PC calibration: (i) samples characterized by LS (except PC1 F1 and F2)—the peak MW (M_p) of these samples was assimilated to $\bar{M}_w$; (ii) PC oligomers with MW ranging from 214 to 1992. Both calibration curves were expressed as a third-degree polynomial.

SEC in methylene chloride. By using the universal and PC calibration curves shown in *Figure 5*, the average MW of the samples could be recalculated. *Table 5* summarizes the results. As can be observed from *Figure 5* and *Table 5*, the agreement between both calibration methods is excellent. This confirms the validity of the viscosity relations used for PC and PS in methylene chloride (*Table 4*). It should be noted that the use of other viscosity relations such as the ones proposed by Abbas[10] can result in large discrepancies between the universal and PC calibrations. Moreover, SEC gives $\bar{M}_w$ values very close to those obtained by LS for MW lower than 10^5. The peak and weight average MW are identical, within

Table 2 Influence of annealing of samples PC1 F3 and PC1 F2

Fraction	$\bar{M}_w$ (SEC–LS)[a]	Thermal treatment	$(\bar{M}_w)_{LS}$[b]
PC1 F3	238 000	15 h at 36°C	490 000
		24 h at 50°C	376 000
		64 h at 50°C	312 000
PC1 F2	299 000	15 h at 36°C	592 000
		24 h at 50°C	410 000
		64 h at 50°C	290 000

[a] Coupling between SEC and LS
[b] LS alone

Table 3 Molecular characterization of PC samples in THF by LS, SEC–LS coupling and viscometry

	Light scattering			SEC–LS coupling			
Sample	$\bar{M}_w$[a]	$\bar{M}_w$[b]	$A_2 \times 10^4$	$\bar{M}_w$	$\bar{M}_n$	H	$[\eta]$ (cm^3 g^{-1})
PC3	–	10 000	27.0	–	–	–	23.5
PC4	–	165 000	20.7	–	–	–	35.3
PC6	26 700	25 700	14.2	–	–	–	47.0±0.5
PC5	–	25 800	–	–	–	–	–
PC2	–	26 600	13.9	28 100	13 300	2.10	59.0
PC8	38 100	28 600	13.6	–	–	–	54.0±0.5
PC7	34 500	35 000	14.0	–	–	–	57.0±1
PC9	47 900	38 600	17.2	–	–	–	–
PC1 F6	–	78 700	10.0	80 600	76 400	1.05	109.0
PC10	–	94 300	–	–	–	–	–
		90 000[d]	12.3				109.0[d]
PC1 F5	–	124 500	12.0	124 000	114 000	1.08	152.0
PC1 F4	–	192 000	9.0	190 000	146 000	1.30	193.0
PC1 F3	–	312 000[c]	7.6	238 000	164 000	1.45	218.0
PC1 F2	–	290 000[c]	7.0	299 000	137 000	2.17	258.0

[a] As given by the manufacturer

[b] This work

[c] After annealing

[d] After dissolution and reprecipitation

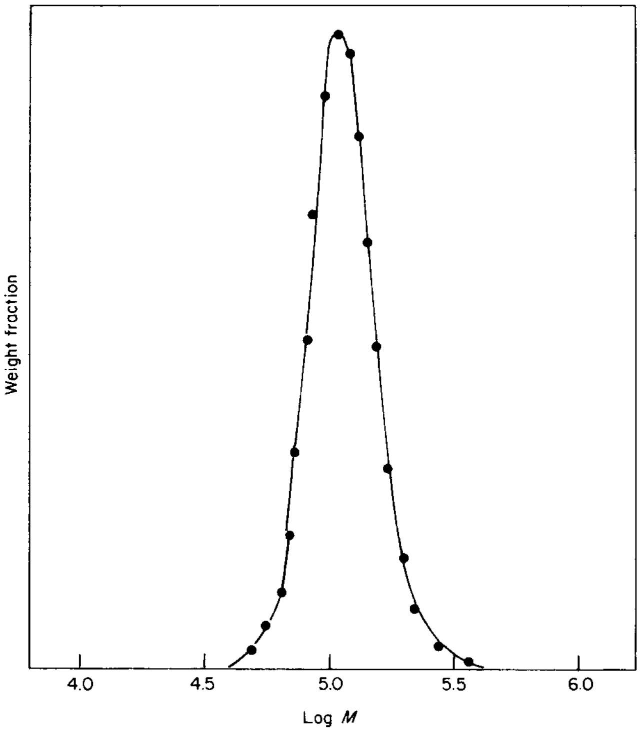

Figure 3 Molecular weight distribution of sample PC1 F5 as obtained from SEC–LS coupling ($\bar{M}_w = 124\,000$; $\bar{M}_n = 114\,000$)

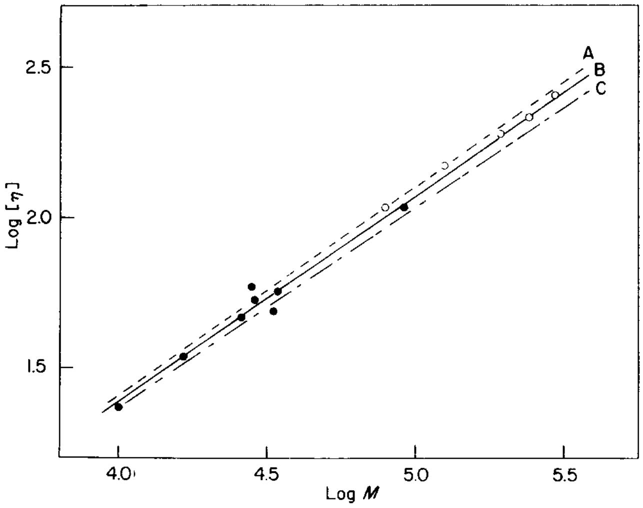

Figure 4 Mark–Houwink relations for PC in THF at 25°C: A, proposed by Schnell; C, proposed by Moore; C, this work. ○, fractionated samples; ●, unfractioned samples

experimental error, confirming the validity of the assumption made to obtain the PC calibration curve. The two calibration curves diverge for MW lower than 1500. Although this discrepancy has no influence on the $\bar{M}_w$ values of our samples, it can lead to significant differences in $\bar{M}_n$ when $\bar{M}_w$ is below 10 000. This highlights the interest of including PC oligomers in the calibration curve when precise determinations of $\bar{M}_n$ and the molecular weight distributions are required. *Figure 6* illustrates this point by showing the number and weight average MW distributions of sample PC3. The high resolution of the column set used shows up oligomers with MW below 2000. Moreover, the precision of the PC calibration curve allows a positive identification of the species[11].

SEC in THF. A similar study was carried out, using THF as the mobile phase. The Shodex column set chosen was found to be less selective in the low molecular weight region than the Ultrastyragel set, as expected from the specifications of the columns. The universal and PC calibration curve are shown in *Figure 7*. The MW values recalculated using them are summarized in *Table 6*. It is observed that the two calibration curves diverge at low molecular weights (below 1500) but also, slightly, in the high molecular weight range (above 8×10^4). This behaviour is confirmed by the $\bar{M}_w$ and $\bar{M}_n$ values obtained by both calibrations (*Table 6*).

Comparison between SEC results in THF and methylene chloride. The comparison between *Tables 5* and *6* and between *Figures 6* and *7* shows that, independently of the nature of the mobile phase, the universal and PC calibrations give very similar average MW for samples having a $\bar{M}_w$ below 10^5. Moreover, the $\bar{M}_w$ values obtained by LS and SEC are close together in the same MW region. For samples of higher MW, the PC calibration in THF seems to give results closer to LS determinations than the other methods.

However, it is dangerous to draw conclusions concerning the reliability of both calibration methods in the high MW range. Owing to the lack of PC standards above 250000, calibration curves become imprecise above this value. This means that the $\bar{M}_w$ of samples PC1 F3 to F5, the distributions of which start at MW as high as 1.5×10^6, 8.5×10^5 and 5×10^5 respectively, cannot be measured precisely by the PC calibration method. The same limitation also applies to the universal calibration since the viscosity relations used for PC are strictly valid only below 2.5×10^5.

In the low MW range (below 1500), the universal and PC calibrations diverge significantly. It is clear that for MW as low as 10^3 the concept of hydrodynamic volume, whereon the universal calibration method rests, is no longer valid.

Table 4 Mark–Houwink relations used in this work

	$[\eta]$ (cm^3 g^{-1})	
Solvent	Polystyrene	Polycarbonate
CH_2Cl_2	$6.1\times10^{-3}M_v^{0.74}$ (ref. 9)	$11.9\times10^{-3}M_v^{0.80}$ (ref. 2)
THF	$14.0\times10^{-3}M_v^{0.70}$ (ref. 6)	$39.9\times10^{-3}M_v^{0.70}$ (ref. 2)

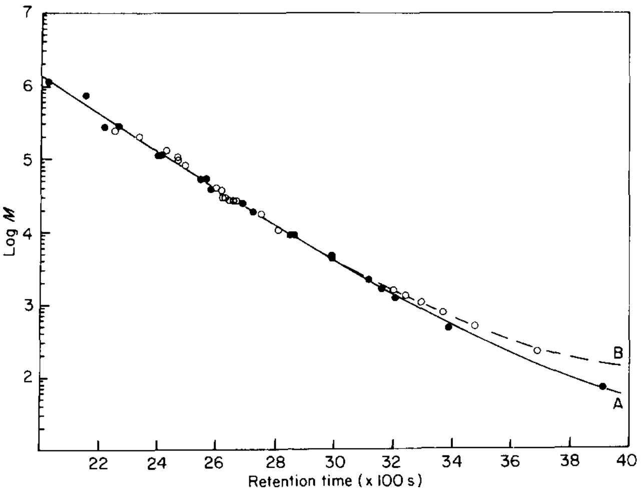

Figure 5 Calibration curves for PC obtained from the universal (curve A (●)) and PC (curve B (○)) calibrations in methylene chloride. See text for further details

Table 5 Molecular characterization of PC samples in methylene chloride by LS and SEC

Sample	$(\bar{M}_w)_{LS}$	Calibration[a]	$\bar{M}_w$	$\bar{M}_n$	M_p	H
PC3	10000	1	10800	5200	11300	2.08
		2	10900	5600	11400	1.95
PC4	16500	1	15100	6200	15600	2.44
		2	15200	6700	15700	2.27
PC6	25700	1	25100	11200	27500	2.14
		2	25100	11800	27400	2.13
PC5	25800	1	27600	10300	29800	2.69
		2	27600	11000	29000	2.51
PC2	27200	1	29900	13400	31500	2.23
		2	29900	14000	31400	2.14
PC8	28600	1	31000	10800	33300	2.88
		2	31000	11600	33200	2.67
PC7	35000	1	34400	16800	34900	2.05
		2	34400	17400	34800	1.98
PC9	38600	1	38600	12400	38400	3.12
		2	38700	13400	38400	2.88
PC1 F6	78700	1	74200	61800	71900	1.20
		2	74400	61800	71900	1.20
PC1 F5	124500	1	105900	76100	104900	1.39
		2	106500	76300	105300	1.40
PC1 F4	192000	1	174800	119900	178000	1.46
		2	177000	120500	179800	1.47
PC1 F3	238000[b]	1	282100	152400	311300	1.85
		2	288200	153600	317300	1.84

[a] 1 = Universal calibration. 2 = PC calibration
[b] SEC–LS coupling

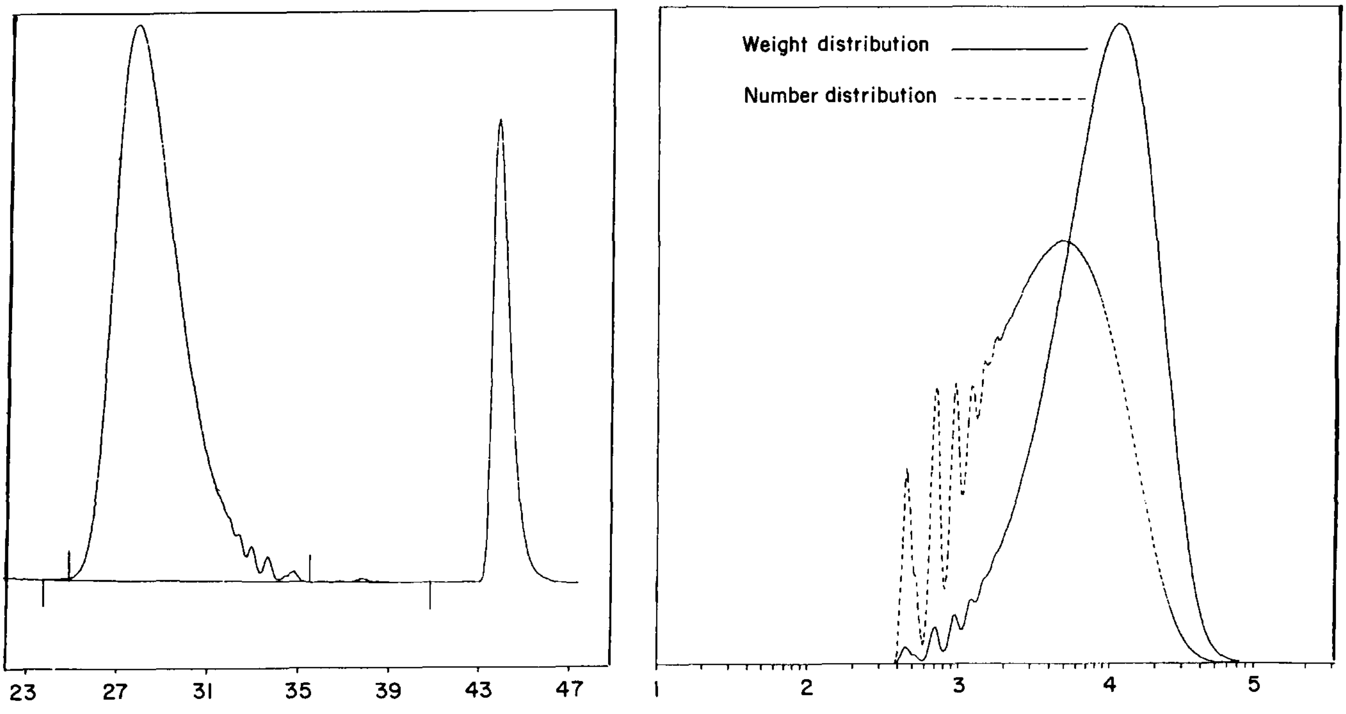

Figure 6 Chromatogram (left) and distribution curves (right) of sample PC3 in methylene chloride

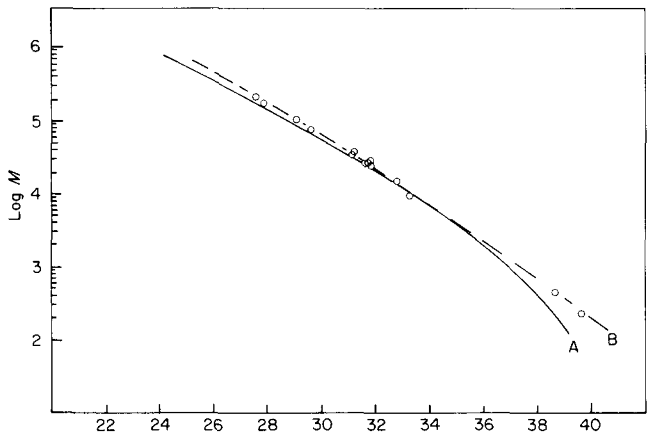

Figure 7 Calibration curves for PC obtained from the universal (curve A) and PC (curve B) calibrations in THF. See text for further details

It would be interesting to use molar volumes instead[12,13]. On the other hand, delayed elution of the PC oligomers resulting from a reversible adsorption on the columns cannot be excluded since Bailly *et al.*[11] have shown that the elution volume of PC oligomers varies significantly as a function of the nature of the chain ends.

CONCLUSIONS

It has been shown that SEC in methylene chloride or THF is a reliable method to obtain accurate average MW of PC samples with $\bar{M}_w$ lower than 10^5. If the universal calibration is used, it is advisable to calibrate the MW range below 1500 with PC oligomers. For samples above $\bar{M}_w = 10^5$, the lack of PC standards above $\bar{M}_w = 2.5 \times 10^5$ makes both PC and universal calibrations imprecise.

The presence of very high MW particles in some samples (aggregates, microcrystals, microgel, etc.) was shown seriously to affect the validity of LS determinations of $\bar{M}_w$. The problem was solved by coupling a LS detector to a conventional SEC system. By this method, the aggregated particles can be separated from the main distribution. SEC–LS coupling also provides a convenient way to obtain absolute MW by SEC. However, while this method is perfectly adapted for MW higher than 10 000, it lacks sensitivity when it comes to lower MW owing to the low level of the scattered intensity.

Table 6 Molecular characterization of PC samples in THF by LS and SEC

Sample	$(\bar{M}_w)_{LS}$	Calibration[a]	$\bar{M}_w$	$\bar{M}_n$	M_p	H
PC3	10 000	1	–	–	–	
		2	11 500	5 500	10 300	2.10
PC4	16 500	1	15 800	7 000	15 600	2.26
		2	16 100	5 900	15 980	2.70
PC6	25 700	1	–	–	–	–
		2	28 400	11 600	26 200	2.40
PC5	25 800	1	29 000	10 700	27 500	2.70
		2	27 500	9 600	27 000	2.80
PC2	27 200	1	32 400	14 200	28 500	2.29
		2	28 650	12 300	27 540	2.33
PC8	28 600	1	–	–	–	–
		2	28 900	10 500	27 500	2.76
PC7	35 000	1	35 700	13 900	32 800	2.57
		2	33 400	16 100	30 500	2.07
PC9	38 600	1	39 700	12 700	37 200	3.13
		2	38 100	11 700	36 800	3.25
PC1 F6	78 700	1	85 900	72 500	80 800	1.18
		2	78 800	66 500	73 700	1.18
PC1 F5	124 500	1	123 000	92 600	112 900	1.33
		2	109 000	85 700	99 600	1.28
PC1 F4	192 000	1	224 000	147 000	182 000	1.52
		2	178 000	124 000	157 000	1.43
PC1 F3	238 000[b]	1	273 000	150 000	252 300	1.82
		2	237 000	140 500	190 000	1.69

[a] 1 = Universal calibration. 2 = PC calibration
[b] SEC–LS coupling

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