Viscometric constants for small polystyrenes and polyisobutenes by gel permeation chromatography

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Using an on-line, continuous, single-capillary viscometer and a refractometer in gel permeation chromatography (g.p.c.), two sets of polymer standards (polystyrene and polyisobutene) of narrow distribution and low/median molecular weight were investigated for their intrinsic viscosities. The experimentally obtained intrinsic viscosity *versus* molecular weight relations of the polystyrenes conform well to the Mark–Houwink–Sakurada (MHS) equation and the Dondos–Benoit (DB) equation in the molecular-weight ranges considered. The deduced viscometric constants were found to be very close to the values reported in the literature. By using both number-average and weight-average molecular weights, the experimental intrinsic viscosity *versus* molecular weight relations of the polyisobutenes were found to conform to the MHS equation or the DB equation in the molecular-weight range studied. This characteristic of the polyisobutenes provides easy access to the indirect g.p.c. calibration introduced by Dondos.

(Keywords: viscometric constants; molecular-weight standards; gel permeation chromatography)

INTRODUCTION

The relationship between intrinsic viscosity and molecular weight is very important in calculating the molecular-weight distribution of a polymer sample in gel permeation chromatography (g.p.c.) using universal calibration[1,2]. This relation is commonly represented[3–5] by the Mark–Houwink–Sakurada (MHS) equation:

$$[\eta]=KM^{\alpha}$$

or the empirical equation proposed by Dondos and Benoit (DB equation) if in the low-molecular-weight region:

$$\frac{1}{[\eta]}=-A_2+\frac{A_1}{M^{1/2}}$$

where $[\eta]$ is the intrinsic viscosity, M is molecular weight, and K, α, A_1 and A_2 are constants for a defined condition, which are related to the particular polymer–solvent system, temperature and the molecular-weight range employed. In order to deduce these useful constants for g.p.c. under a particular experimental condition, we need to measure the intrinsic viscosities independently[6–8] under the same conditions if an on-line viscometer in g.p.c. is not available (a very commonly used Ubbelholde-type viscometer, for example). Finally the standards should be submitted to g.p.c. to obtain their experimental elution volumes to constitute a practical universal calibration curve, generally expressed by:

$$\log([\eta]M)=f(V_e)$$

where $f(V_e)$ is a mathematical function of the elution volumes.

With the advent of commercialized on-line viscometry in g.p.c.[9–11], it is possible, with a refractometer, to estimate the intrinsic viscosity of a polymer sample, and at the same time obtain the experimental elution volume, thus producing universal calibration. Using a g.p.c. equipped with an on-line, continuous, single-capillary viscometry detector and a concentration detector, the intrinsic viscosity can be obtained experimentally by:

$$[\eta]=\sum W_i[\eta]_i=\frac{\sum C_i\eta_i}{\sum C_i}$$

where W_i is the weight fraction of molecule i possessing intrinsic viscosity $[\eta]_i$, and is equal to the concentration fraction $C_i/\sum C_i$ by means of a concentration detector. The principles and the special features of employing such an on-line viscometer have been detailed in refs 9 and 10.

Recently, the intrinsic viscosities of two sets of narrow-distribution, low/median-molecular-weight polymer standards (polystyrene and polyisobutene) were investigated. Under the experimental conditions, the intrinsic viscosities obtained conformed perfectly with the MHS equation and the DB equation using the molecular weights provided. The deduced constants are in good accord with those reported in the literature.

EXPERIMENTAL

Polymer standards

A set of 10 narrow-distribution polystyrene (PS) standards, prepared by anionic polymerization, were

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purchased from Tosoh Corporation (Japan). Their molecular weights ranged from 2500 to $\sim 1 \times 10^6$ g mol^{-1}. A set of eight polyisobutene (PIB) standards were obtained from Polymer Standard Service (PSS, Germany), with molecular weight ranging from 730 to 67 600 g mol^{-1}. These standards are detailed in *Table 1*. The intrinsic viscosity values listed in the table were obtained experimentally by the g.p.c. method described below.

Viscometry detector

The viscometry detector consisted principally of a capillary viscometer, which was a 6 inch ($\sim$15 cm) length of stainless-steel tubing ($\sim$1.6 mm o.d., $\sim$0.35 mm i.d.) and a sensitive pressure transducer (Millipore Waters, USA; abbreviated by Waters hereafter). They were arranged between the column system and the differential refractometer detector, on the inside of the thermostated Waters 410 refractometer chamber held at 40°C. The inter-detector volume was calculated on the basis of the physical volumes of the connecting tubing.

Gel permeation chromatography

A Waters 590 programmable h.p.l.c. pump with 10 supplementary pulse damping units, a Waters 715 Ultra Wisp automatic sample processor and a Waters 410 differential refractometer were used. All the data were converted to digital data with a Keithley 199 System Scanner and processed by an AT type computer (Compaq 286e).

The columns employed were (i) a linear column (Waters), (ii) a 10^3 Å column (Waters), (iii) a 500 Å column (Waters), (iv) a 100 Å column (Waters) and (v) a KF-801 column (Shodex, available from Waters). They were linked together. The total effective molecular-weight separation range was from very low up to 4×10^6 g mol^{-1} expressed by polystyrene. The column system was thermostated at 40°C in two column chambers controlled by the Waters 410 refractometer.

The mobile phase was tetrahydrofuran (THF) stabilized by 0.025–0.04% dibutyl-2,6-methyl-4-phenol, and was degassed continuously with helium. The flow rate was 1 ml min^{-1}. The sample concentration was adjusted for each run according to $[\eta]C \approx 0.05$ to minimize the concentration effect[12]. The concentration range was between 0.01% and 2×10^{-4} g ml^{-1}. The injection volume was 400 μl. The sample solutions were prepared 24 h before analysis. A large vessel was employed in order to keep solvent exactly the same for the whole set of samples, which were analysed by a single run with a computer program. All the chromatographic data were stored and treated after the whole run was finished.

Table 1 Molecular weights (number-average M_n and weight-average M_w) and experimental intrinsic viscosities ($[\eta]$) of employed polystyrene (PS) standards (Tosoh Corp.) and polyisobutene (PIB) standards (available from PSS)

Sample reference[a]		M_w (g mol^{-1})	M_n (g mol^{-1})	$[\eta]$ (ml g^{-1}), 40°C, THF
PS	A-2500 (TS-134)	2 710	2 460	4.97
	A-5000 (TS-64)	5 240	5 110	7.16
	F-1 (TS-203)	9 830	9 610	10.31
	F-2 (TS-159)	19 100	18 900	15.83
	F-4 (TS-202)	37 200	36 900	25.87
	F-10 (TS-144)	98 900	98 300	49.25
	F-20 (TS-140)	189 000	181 000	81.96
	F-40 (TS-85)	354 000	344 000	127.3
	F-80 (TS-201)	707 000	676 000	207.2
	F-128 (TS-206)	1 110 000	1 030 000	300.5
PIB	1	820	730	3.36
	2	2 040	1 560	5.24
	3	5 000	4 000	8.22
	4	15 800	13 500	17.46
	5	36 100	31 500	27.47
	6	53 400	46 000	36.71
	7	61 000	45 800	41.88
	8	80 400	67 600	49.65

[a] Batch numbers given in parentheses

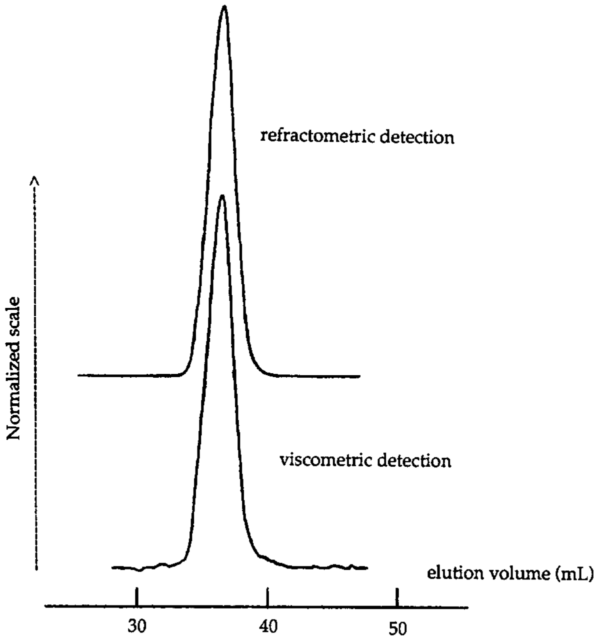

Figure 1 The normalized chromatograms experimentally obtained from polystyrene A-2500 ($M_w/M_n = 1.10$). The separation system consists of four Waters columns (linear, 10^3 Å, 500 Å and 100 Å) and a KF-801 column (Shodex, available for Waters). The injection volume was 400 μl

RESULTS AND DISCUSSION

The experimentally obtained intrinsic viscosities under the indicated chromatographic conditions are gathered in *Table 1* for the polystyrenes and polyisobutenes. For all the studied polymer standards, no evident lag between the viscometric and the refractometric chromatograms was observed. Unlike the refractometer, the viscometer is sensitive not only to sample concentration but also to sample molecular weight. There is a certain mismatch for chromatograms obtained by different detectors, which has been observed by Pang and Rudin[13]. However, this mismatch of sensitivities was negligible in our case since the employed polymer standards have quite limited molecular weights and polydispersities. On the other hand, we also found that this mismatch is less visible while polydispersity becomes weak. In the experiment, there was no difference between the normalized viscometric and refractometric chromatograms for the polystyrenes. The chromatogram obtained for the polystyrene of largest polydispersity in the set ($M_w/M_n = 1.10$, PS A-2500) is shown in *Figure 1*. When the normalized chromatograms of PIB 2 (largest polydispersity in the set, $M_w/M_n = 1.31$) are compared (*Figure2*), it is seen that the chromatograms from the viscometer and the refractometer were highly compatible. In fact, the chromatograms in *Figure 2* were the worst pair in the polyisobutene set.

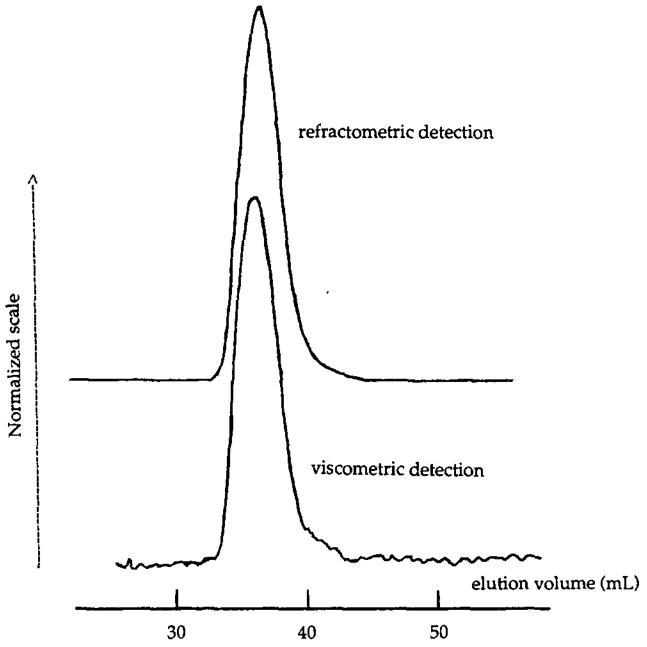

Figure 2 The normalized chromatograms experimentally obtained from polyisobutene 2 ($M_w/M_n = 1.31$). The separation system consists of four Waters columns (linear, 10^3 Å, 500 Å and 100 Å) and a KF-801 column (Shodex, available from Waters). The injection volume was 400 μl

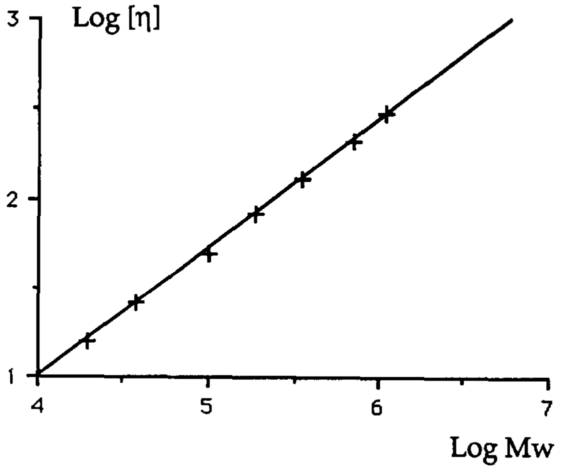

Figure 3 The Mark–Houwink–Sakurada (MHS) relation of the polystyrene standards from F-2 to F-128 ($19\,100 \leqslant M_w$ (g mol^{-1}) $\leqslant 1.11 \times 10^6$); experimental intrinsic viscosity ([η]) in ml g^{-1} and weight-average molecular weight (M_w)

Using the reported weight-average molecular weights (M_w) of the polystyrene standards, a graph of $\log[\eta]$ *versus* $\log M_w$ and a graph of $1/[\eta]$ *versus* $1/M_w^{1/2}$ were established to deduce the constants in the Mark–Houwink–Sakurada (MHS) and the Dondos–Benoit (DB) equations. It was found that the MHS relation could be applied to the standards ranging from F-2 to F-128 ($19\,100 \leqslant M_w$ (g mol^{-1}) $\leqslant 1.11 \times 10^6$, *Figure 3*), the high-molecular-weight part in the set. The Dondos–Benoit relation could be applied to the standards from A-2500 to F-4 ($2710 \leqslant M_w$ (g mol^{-1}) $\leqslant 37\,200$, *Figure 4*), the low-molecular-weight part in the set. The relationship between intrinsic viscosity and molecular weight changes from the MHS equation to the DB equation when we go to the smaller molecular-weight region. This phenomenon relating to conformational changes has been observed by several authors[2–4,14], not only for the polystyrene–tetrahydrofuran system but also for some other polymer–solvent systems. The deduced constants for the MHS relation are quite close to the values reported in the literature[15], shown in *Table 2*, but a difference of experimental temperatures was observed (40°C for ours instead of 25°C in the literature). The constants for the DB equation were also very close to the values reported in ref. 3. They are also gathered in *Table 2*.

However, we noted that there are certain differences to the constants of the DB equation in ref. 4:

$$A_1 = 9.9\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}} \qquad A_2 = 0.008\,\mathrm{g\,ml^{-1}}$$

obtained at 38°C for the molecular-weight range $800 \leqslant M$ (g mol^{-1}) $\leqslant 6 \times 10^5$. The apparently important differences reported are that the polystyrene standards used in ref. 4 were prepared by radical polymerization instead of anionic polymerization, and the considered molecular-weight range was larger.

In the universal calibration procedure, Hamielec and Ouano[16] demonstrated, experimentally and theoretically, that the correct universal calibration parameter in g.p.c. is the product of the intrinsic viscosity and the number-average molecular weight, $[\eta]M_n$. As a logical consequence, it would be adequate if the empirical constants

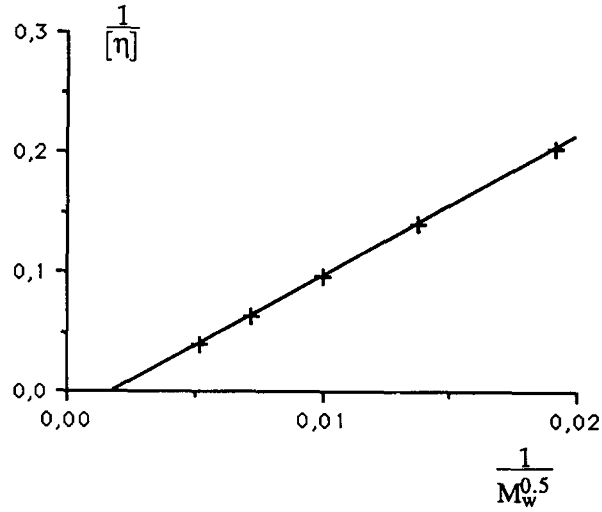

Figure 4 The Dondos–Benoit (DB) relation of the polystyrene standards from A-2500 to F-4 ($2710 \leqslant M_w$ (g mol^{-1}) $\leqslant 37\,200$); experimental intrinsic viscosity ([η]) in ml g^{-1} and weight-average molecular weight (M_w)

Table 2 Experimentally deduced viscometric constants of employed polystyrene standards and the values reported in the literature. The molecular weights are in g mol^{-1} and the intrinsic viscosities are in ml g^{-1}

	MHS equation	DB equation
M_w–[η], 40°C, THF	$K = 0.0131$ $\alpha = 0.719$ $1.91 \times 10^4 \leqslant M_w \leqslant 1.11 \times 10^6$	$A_1 = 11.6\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}}$ $A_2 = 0.0206\,\mathrm{g\,ml^{-1}}$ $2710 \leqslant M_w \leqslant 37\,200$
M_w–[η], reported in literature	$K = 0.0136$ $\alpha = 0.714$ 25°C $2.04 \times 10^4 \leqslant M_w \leqslant 1.81 \times 10^7$ Ref. 15	$A_1 = 12.3\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}}$ $A_2 = 0.018\,\mathrm{g\,ml^{-1}}$ 25°C $4000 \leqslant M \leqslant 1.1 \times 10^5$ Ref. 3
M_n–[η], 40°C, THF	$K = 0.0158$ $\alpha = 0.706$ $5110 \leqslant M_n \leqslant 1.03 \times 10^6$	$A_1 = 10.79\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}}$ $A_2 = 0.0144\,\mathrm{g\,ml^{-1}}$ $2460 \leqslant M_n \leqslant 1.81 \times 10^5$

(or experimental constants) in MHS and DB equations used in the experimental universal calibration were deduced by the M_n values with the experimental $[\eta]$ of the standards. On this basis, the application showed that the polystyrene standards from A-2500 to F-20 ($2460 \leqslant M_n$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 1.81 \times 10^5$) followed the DB equation (*Figure 5*). On the other hand, those larger than A-500 (up to F-128) ($5110 \leqslant M_n$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 1.03 \times 10^6$) agreed well with the MHS equation (*Figure 6*). The obtained constants are listed in *Table 2*.

In the case of polyisobutene standards, the intrinsic viscosity results and the number-average molecular weights conformed very well both to the MHS equation and the DB equation shown in *Figures 5* and *6* respectively. The obtained constants are:

for the MHS equation ($[\eta]$ in $\mathrm{ml\,g^{-1}}$)

$$K = 0.0647 \qquad \alpha = 0.593$$

and for the DB equation

$$A_1 = 8.29\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}} \qquad A_2 = 0.0125\,\mathrm{g\,ml^{-1}}$$

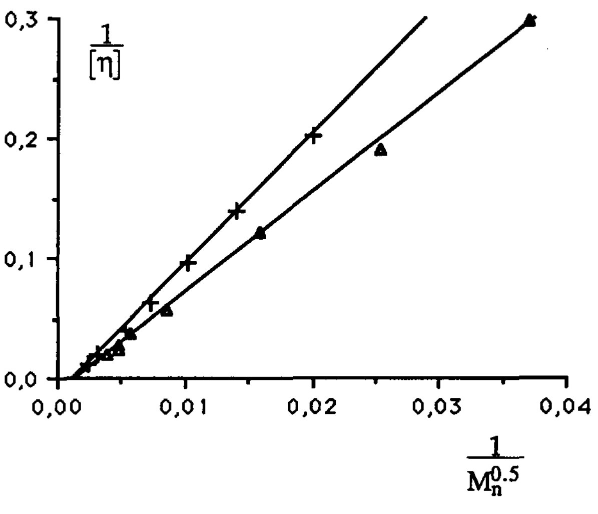

Figure 5 The Dondos–Benoit (DB) relations of the polystyrene standards (+) from A-2500 to F-20 ($2460 \leqslant M_n$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 1.81 \times 10^5$) and the polyisobutene standards (Δ); experimental intrinsic viscosity ($[\eta]$) in $\mathrm{ml\,g^{-1}}$ and number-average molecular weight (M_n)

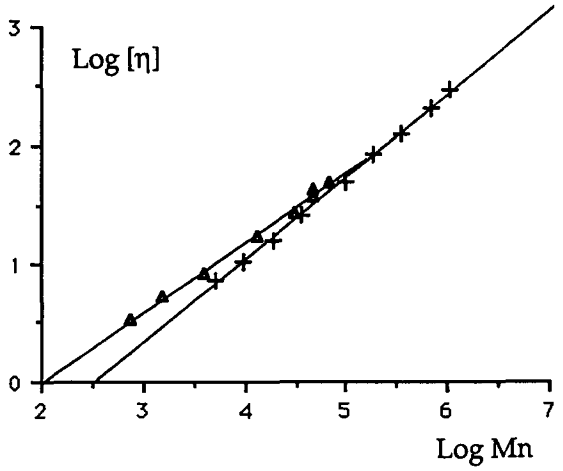

Figure 6 The Mark–Houwink–Sakurada (MHS) relations of the polystyrene standards (+) from A-5000 to F-128 ($5110 \leqslant M_n$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 1.03 \times 10^6$) and the polyisobutene standards (Δ); experimental intrinsic viscosity ($[\eta]$) in $\mathrm{ml\,g^{-1}}$ and number-average molecular weight (M_n)

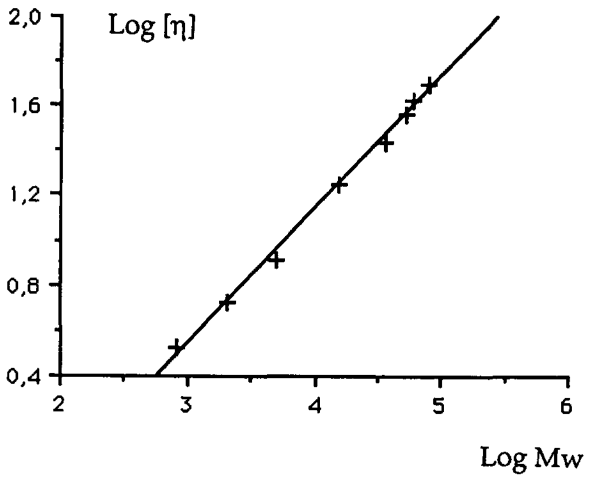

Figure 7 The Mark–Houwink–Sakurada (MHS) relations of the polyisobutene standards; weight-average molecular weight ($820 \leqslant M_w$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 80\,400$) and experimental intrinsic viscosity ($[\eta]$) in $\mathrm{ml\,g^{-1}}$

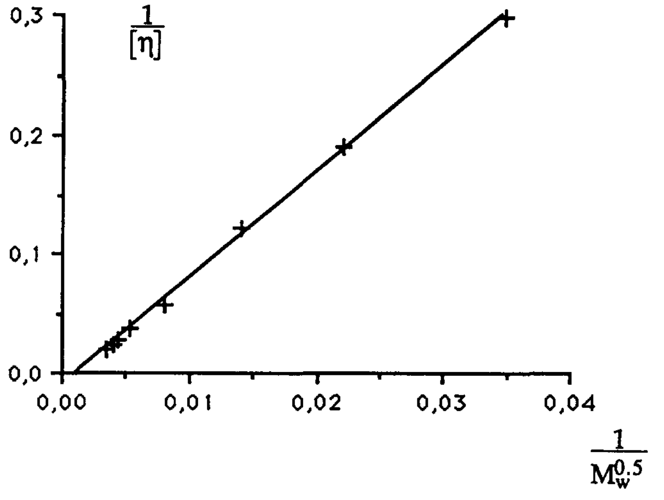

Figure 8 The Dondos–Benoit (DB) relation of the polyisobutene standards; weight-average molecular weight ($820 \leqslant M_w$ ($\mathrm{g\,mol^{-1}}$) $\leqslant 80\,400$) and experimental intrinsic viscosity ($[\eta]$) in $\mathrm{ml\,g^{-1}}$

for number-average molecular weight ranging from 730 to $67\,600\,\mathrm{g\,mol^{-1}}$. When weight-average molecular weights were considered ($820 \leqslant M_w$ ($\mathrm{g\ mol^{-1}}$) $\leqslant 80\,400$), both the MHS and DB equations were available, too. Thus we obtained the following constants:

for the MHS equation ($[\eta]$ in $\mathrm{ml\,g^{-1}}$)

$$K = 0.0579 \qquad \alpha = 0.593$$

and for the DB equation

$$A_1 = 8.94\,\mathrm{g^{3/2}\,ml^{-1}\,mol^{-1/2}} \qquad A_2 = 0.0107\,\mathrm{g\,ml^{-1}}$$

The graphs for molecular weight and intrinsic viscosity are shown in *Figures 7* and *8* respectively.

Dondos *et al.*[2] used an indirect g.p.c. calibration method for the low-molecular-weight region. On application of the DB equation for both polymer sample and polymer standard, they deduced a formula to transform molecular weight from polymer standard expression to polymer sample expression as an indirect calibration method:

$$AM_p^{3/2} + BM_p^{1/2} - C = 0$$

with

$$A = A_{1s} - A_{2s} M_s^{1/2}$$
$$B = A_{2p} M_s^{3/2}$$
$$C = A_{1p} M_s^{3/2}$$

In the above, A_{1s}, A_{2s}, A_{1p} and A_{1p} are constants for the polymer standard (marked s) and polymer sample (marked p), respectively. On the same theoretical basis, if polymer samples can be described by the MHS equation with constants K and α in the studied molecular-weight range, the formula introduced by Dondos to transform the molecular-weight expression becomes much simpler and easy to resolve:

$$M_p = \left(\frac{M_s}{A_1 K / M_s^{1/2} - A_2 K} \right)^{1/(\alpha+1)}$$

The case for the polyisobutenes studied here provides this interesting and special feature.

CONCLUSIONS

In g.p.c. experiments, the on-line viscometer can provide an easy, rapid approach to estimate the intrinsic viscosities of polymer standards of narrow distribution and low/median molecular weight. The advantage is that the necessary constants in the universal calibration procedure under some special polymer/solvent/temperature conditions can be obtained directly and experimentally.

Application to polystyrene standards shows a very close result to the values reported in the literature. We also found that both MHS and DB equations are applicable for polyisobutenes in the studied molecular-weight range, when either number-average or weight-average molecular weights were considered under the experimental conditions. Thus it provides easier access to the indirect g.p.c. calibration introduced by Dondos.

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