Solution viscosity – molar mass relationships for poly(butylene succinate) and discussion on molar mass analysis

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Abstract. Poly(butylene succinate) (PBS) is currently developing due to its biodegradability and the similarity of its mechanical properties to those of polyolefins. Relationships between the number average molar mass, $\overline{M}_n$, and solution viscosity such as $[\eta]$ and η_{red} were derived for this aliphatic polyester. $\overline{M}_n$ values were determined by end-group analysis and size exclusion chromatography (SEC). Mark-Houwink-Sakurada (MHS) parameters were proposed in two solvents and for the different molar masses and viscosity measurement methods. As an example, the MHS equations were respectively, $[\eta] = 6.4 \cdot 10^{-4} \cdot \overline{M}_n^{0.67}$ in chloroform and $[\eta] = 7.1 \cdot 10^{-4} \cdot \overline{M}_n^{0.69}$ in 50/50 wt% 1,2-dichlorobenzene/phenol at 25°C for molar masses measured by SEC in hexafluoro isopropanol (HFIP) with poly(methyl methacrylate) (PMMA) standards. Empirical relationships were also suggested to derive $\overline{M}_n$ directly from reduced viscosity, η_{red} , which is much easier to determine than intrinsic viscosity. With these data, the number average molar mass of PBS can be conveniently estimated from a single viscosity measurement. In addition, it was shown that PBS contains 1–2 wt% of cyclic oligomers produced during esterification and that molar masses determined by taking this fraction into account or not were significantly different, especially for long chains.

Keywords: biopolymers, poly(butylene succinate), molar mass, cyclic oligomers

1. Introduction

Poly(butylene succinate) (PBS) is one of the ‘old’ polyesters which regains interest because of the current preoccupation with the environment [1–3]. It is biodegradable and can be bio-based. Its thermal and mechanical properties are close to those of polyolefins and its processability is excellent while its durability is much lower due to possible hydrolysis. Indeed it recently drew attention from academia and industry [4–9] and now, the producers are trying to find applications in agriculture, fishery, forestry,

civil engineering and other fields in which recycling of materials is challenging.

Poly(butylene succinate) is not a new polymer however it was not developed commercially in the 1950s or 1960s as was done with commodity polymers. As a consequence research has not been very active until now and basic data on PBS may be missing. Here we will focus on the topic of molar mass determination of PBS.

There are several ways to determine the number and weight average molar masses ($\overline{M}_n$, $\overline{M}_w$) of a

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polymer such as end-group analysis by titration or by $^1\text{H-NMR}$ spectroscopy ($\overline{M}_n$), size exclusion chromatography (SEC) ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$), ($\overline{M}_n$), membrane osmometry ($\overline{M}_n$), light-scattering (M_w), and viscometric method ($\overline{M}_v$) [10, 11].

Viscometry is a quick and simple method if dispersity data are not needed. It involves measuring the viscosity of dilute solutions of the polymer, from which the molar mass may be calculated since the relationship between the intrinsic viscosity, $[\eta]$, and the viscosity-average molar mass, $\overline{M}_v$, can be described by the well-known Mark-Houwink-Sakurada (MHS) equation (Equation (1)):

$$\eta = k \cdot \overline{M}_v^a \quad (1)$$

where k and a are constants for a given well-defined polymer-solvent-temperature system. In general, $\overline{M}_v$ is not experimentally accessible, and in most reports, different average molecular masses ($\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$), instead of the viscosity-average molar mass $\overline{M}_v$, are substituted in the MHS equation, ignoring dispersity effects [12–14]. For poly(butylene succinate) k and a parameters are poorly defined in the literature [15–17].

On the other hand only size exclusion chromatography provides information on the molar mass distribution but it is not an easy technique for aromatic polyesters due to their poor solubility in commonly used SEC eluents. Aliphatic polyesters are more soluble but other difficulties arise. As an example, PBS is soluble in chloroform at room temperature but the refractive indexes of the polymer and the solvent are very close to each other ($dn/dc \sim 5 \cdot 10^{-2} \text{ mL} \cdot \text{g}^{-1}$) so inaccuracies are observed. The above comment illustrates one of the reasons why the determination of molar mass by SEC with a refractive index or light scattering detector for polyesters is controversial in chloroform. Several authors have recently highlighted that polystyrene-calibrated SEC measurements in chloroform overestimate the real $\overline{M}_n$ by at least 50% in the range above $10^4 \text{ g} \cdot \text{mol}^{-1}$ for poly(ϵ -caprolactone), polylactide and related copolyesters [18–24]. For these reasons, researchers have used complementary techniques such as MALDI-TOF mass spectrometry [19, 25]. Also, commercial polyesters often contain a fraction of cyclic oligomers, which may significantly affect the calculation of $\overline{M}_n$. These inaccuracies are

especially critical if the actual molar mass is needed with the aim of modelling polymerization or chemically modifying end-groups.

In this context, the objectives of this work were to provide information on the uncertainties attached to molar mass determination of PBS and develop a methodology to conveniently determine it. To this end, a series of linear PBS was synthesized, different methods for molar mass determination were explored, and the impact of the oligomer content on the data was estimated.

2. Experimental

2.1. PBS synthesis

A series of PBS samples with increasing molar mass were synthesized from succinic acid (SA) (99% min, GADIV Petrochemical Ind., Haifa, Israel) and 1,4-butanediol (BDO) (99%, Sigma-Aldrich, Saint-Quentin-Fallavier, France) via a two-step melt polycondensation reaction described in detail elsewhere [26]. Titanium (IV) *n*-butoxide (97%, Sigma-Aldrich, Saint-Quentin-Fallavier, France) was used as the catalyst with 400 ppm of Ti present in the final polymer.

Seven PBS samples were collected. The pellets were dried and stored in sealed aluminium bags. The first, PBS1, was collected after the esterification step. The others, denoted PBS2 to PBS7, were collected when the stirring torque variation reached 0.1, 0.5, 1, 3, 16, and 22.5 Nm, respectively. They are numbered PBS1 to PBS7 in the order of increasing molar mass.

2.2. Intrinsic viscosity and reduced viscosity determination

An automated viscometer (AVS310, Schott Geräte, Hofheim, Germany), was used to determine the intrinsic viscosities of the PBS samples at $25 \pm 0.05^\circ\text{C}$ in 50/50 wt% 1,2-dichlorobenzene/phenol (solvent for the standard DIN53728) and in chloroform. The capillary diameter was 0.84 mm for the analysis in 50/50 wt% 1,2-dichlorobenzene/phenol and 0.36 mm in chloroform in order to have sufficient accuracy for the flow time data. The PBS samples were solubilized at room temperature in both solvents. The solution viscosities were measured for four PBS concentrations varying from 2.5 to $10 \text{ g} \cdot \text{L}^{-1}$ in quadruplicate. The reduced viscosity, η_{red} , is the viscosity measured with a concentration equal to $5 \text{ g} \cdot \text{L}^{-1}$.

2.3. Molar mass determination by size exclusion chromatography (SEC)

Polymer molar mass was assessed by size exclusion chromatography coupled to a UV detector (UV-272) and a refractive index (RI) detector (RI-1100) (Agilent, Germany, Waldbronn). 1 g·L⁻¹ samples were eluted at a flow rate of 0.75 mL·min⁻¹ with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The average molar masses $\bar{M}_n$ and $\bar{M}_w$ were determined with calibration method using poly(methyl methacrylate) (PMMA) standards. Calculation of the average molar masses was done using two methods, integrating low molar mass species between 100 and 1000 g·mol⁻¹ or not.

2.4. Molar mass determination by hydroxyl and carboxyl end-group contents

Hydroxyl and carboxylic end-group concentrations, N_{HC} and N_{CC} , were determined by ¹H NMR spectroscopy. A liquid state NMR spectrometer equipped with a BBFO+ probe at 25°C was used (Avance III 400 MHz, Bruker, Wissembourg, France). Polymer samples were dissolved in deuterated chloroform containing tetramethylsilane (TMS) before analysis and trifluoroacetic anhydride (TFAA) was added to shift the CH_2OH and CH_2COOH signals of the hydroxyl and carboxylic end-groups (down-field shift of ~0.6 ppm) [18]. The number of scans was 256.

2.5. Oligomer extraction and characterization

To assess the quantity of the oligomers, 5 g of PBS samples were dispersed in 40 g of tetrahydrofuran (THF) over a period of three days under stirring. The dissolved oligomers were collected and the amount was quantified after evaporation at 25°C until a constant weight.

PBS oligomers were first analyzed by SEC (Shimadzu, DGU-20A3 + LC-20AD, Japan) with THF as the eluent. 5 g·L⁻¹ samples were injected in three 5 μm columns containing Waters Styragel HR2THF, HR1THF and HR0.5THF at 1 mL·min⁻¹. $\bar{M}_n$ and $\bar{M}_w$ were determined with a calibration method using polystyrene standards.

To compare the molar masses and to identify the nature (cyclic or linear) of the oligomers, the samples extracted with THF were analyzed by MALDI-TOF mass spectroscopy. All MALDI-TOF mass spectra were obtained with a Voyager-DE PRO (Applied Biosystems, Framingham, MA) equipped

with a nitrogen laser emitting at 337 nm with a 3 ns pulse duration. The instrument was operated in reflector mode. The ions were accelerated under a potential of 20 kV. The positive ions were detected in all cases. The mass spectra were the sum of 300 shots and external mass calibration of the mass analyzer was used (a mixture of peptides, Sequazyme, Applied Biosystems, Framingham, MA). Samples were prepared by mixing 10 μL of 2-(4'-hydroxyphenylazo) benzoic acid (HABA) at 0.1 M in chloroform/THF 50/50 v/v with 10 μL of sample (at 5 g·L⁻¹ in THF). The resulting mixtures (0.5 μL) were spotted on the MALDI sample plate and air-dried.

3. Results and discussion

3.1. Intrinsic viscosity determination

The intrinsic viscosity was determined for the seven PBS samples by two different methods:

1. At different concentrations, then extrapolation to infinite dilution.
2. *Via* the single-point method based on the solution's specific viscosity, η_{sp} , and reduced viscosity, η_{rel} , at only one specific concentration ($C = 5 \text{ g·L}^{-1}$).

3.1.1. Method using different concentrations

The flow time of the pure solvent, t_0 , and of four different PBS concentrations, t , was measured. Based on these time values, the specific viscosity η_{sp} and the relative viscosity η_{rel} were calculated using Equations (2) and (3):

$$\eta_{\text{rel}} = \frac{t}{t_0} \quad (2)$$

$$\eta_{\text{sp}} = \frac{t - t_0}{t_0} = \eta_{\text{rel}} - 1 \quad (3)$$

The intrinsic viscosity can be determined when η_{sp} and η_{rel} are known (Equation (4) and (5)):

$$[\eta] - k_1[\eta]^2 C = \frac{\eta_{\text{sp}}}{C} \quad (4)$$

$$[\eta] - k_2[\eta]^2 C = \frac{\ln \eta_{\text{rel}}}{C} \quad (5)$$

where k_1 and k_2 are the Huggins and Kramer coefficients, respectively and C is the concentration of the polymer solution in g·L⁻¹.

For each PBS, η_{sp}/C and $(\ln \eta_{\text{rel}})/C$ were plotted against the concentration C (Huggins and Kramer

Figure 1. A typical Huggins-Kramer dual extrapolation plot for PBS7 ($M_n = 55,550 \text{ g}\cdot\text{mol}^{-1}$ by SEC in HFIP versus PMMA standards) in 50/50 wt% 1,2-dichlorobenzene/phenol at 25°C. (♦) $(\eta_{sp})/C$, (■) $(\ln \eta_{rel})/C$.

plots) and the intrinsic viscosity was obtained by extrapolating the plots to infinite dilution [27]. An example of such a graph for PBS 7 is given in Figure 1.

The intrinsic viscosity data of PBS samples at 25°C in 50/50 wt% 1,2-dichlorobenzene/phenol and in chloroform are listed in Table 1.

3.1.2. Method using a single-point

The intrinsic viscosity, $[\eta]$, can be estimated with the measurement of specific viscosity, η_{sp} , and relative viscosity, η_{rel} , for a single concentration with Equations (6), (7) and (8) [28–30]:

$$\text{Solomon and Ciuta: } [\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{C} \quad (6)$$

$$\text{Kuwahara: } [\eta] = \frac{\eta_{sp} + 3 \ln \eta_{rel}}{4C} \quad (7)$$

$$\text{Rao and Yaseen: } [\eta] = \frac{\eta_{sp} + \ln \eta_{rel}}{2C} \quad (8)$$

The previous method of Huggins and Kramer at different concentrations and the single-point method play two separate roles in characterizing the molar mass of polymers. The method of Huggins and Kramer is employed for procuring accurate information on the intrinsic viscosity, while the single-point method is fast for a reasonable estimation but is widely criticized in the literature. Both methods are consistent for some polymer-solvent couples but only if the solution has a low concentration ($\leq 0.2\%$) and low specific viscosity between 0.15 and 0.30 [27–32]. In most published studies where viscosity measurements were performed with PBS, these measurements were carried out in chloroform at 25 or 30°C [25, 33–35]. Some use the method developed by Huggins and Kramer [25, 33] while others prefer the single-point method. In this case, the most used equation is the one of Solomon and Ciuta [33, 34]. The concentration used for the single-point method was $2.5 \text{ g}\cdot\text{L}^{-1}$. Viscosity data extracted with the two methods are shown in Table 1.

Table 1. Comparison of $[\eta]$ of PBS determined from the Huggins and Kramer plots and from the single-point method determined in 50/50 wt% 1,2-dichlorobenzene/phenol and chloroform at 25°C

Solvent	PBS sample	$[\eta] \text{ (dL/g)} (\pm 0.01 \text{ dL}\cdot\text{g}^{-1})$			
		Huggins-Kramer dual extrapolation	Single point method ^{a)}		
			Solomon and Ciuta	Kuwaraha	Rao and Yaseen
50 :50 1,2-dichlorobenzene/phenol	PBS1	0.11	0.11	0.11	0.11
	PBS2	0.33	0.33	0.33	0.34
	PBS3	0.67	0.67	0.66	0.68
	PBS4	0.81	0.83	0.82	0.84
	PBS5	1.30	1.29	1.28	1.33
	PBS6	1.50	1.48	1.46	1.53
	PBS7	1.62	1.62	1.60	1.68
Chloroform	PBS1	0.08	0.08	0.08	0.08
	PBS2	0.25	0.25	0.24	0.25
	PBS3	0.50	0.50	0.49	0.50
	PBS4	0.57	0.57	0.57	0.58
	PBS5	0.89	0.89	0.89	0.91
	PBS6	0.99	0.99	0.99	1.01
	PBS7	1.07	1.08	1.07	1.10

^{a)} data determined for a concentration of $2.5 \text{ g}\cdot\text{L}^{-1}$.

The data suggest that estimating $[\eta]$ of PBS using single-point calculation fits quite well with more than 97% accuracy recorded at relatively low concentrations and when the specific viscosity η_{sp} is not higher than 0.2.

3.2. Molar mass determination by end-groups analysis

To calculate the equivalent Mark-Houwink-Sakurada parameters, the next step was to determine the molar mass of the PBS samples. Two methods were accessible: end-groups analysis and size exclusion chromatography. Both were done with and without an estimation of the cyclic oligomers fraction. End-groups analysis is presented first.

3.2.1. End-groups analysis (without cyclic oligomers)

The molar masses of PBS samples can be calculated if the chain end-groups content is known (Equation (9)):

$$\bar{M}_n = \frac{1}{\frac{N_{CC} + N_{HC}}{2}} \quad (9)$$

where N_{HC} is the hydroxyl end group content, and N_{CC} is the carboxylic acid end group content, both measured by $^1\text{H-NMR}$ and expressed in $\text{mol}\cdot\text{g}^{-1}$.

The carboxylic end-group concentration cannot be determined with a simple analysis in chloroform containing TMS because their signals superimpose to the 2.6 ppm peak which corresponds to the succinic acid methylene groups inserted in the chains. The addition of trifluoroacetic anhydride (TFAA) which reacts quantitatively with both hydroxyl and carboxylic acid end-groups is necessary. As a consequence of that reaction, the peak corresponding to hydroxyl end-groups shifts downfield from 3.6 to 4.4 ppm (H5), and two peaks corresponding to carboxylic end-groups appear at 2.7 ppm (H2) and 2.9 ppm (H3) (Figure 2).

The N_{HC} and N_{CC} end-group concentrations were calculated using Equations (10) and (11):

$$N_{HC} = \frac{\frac{I_{H5}}{2}}{\sum I_{PBS}} \cdot \frac{2}{M_{PBS}} \quad (10)$$

$$N_{CC} = \frac{\frac{I_{\text{COOH at 2.9 ppm}}}{2}}{\sum I_{PBS}} \cdot \frac{2}{M_{PBS}} \quad (11)$$

where M_{PBS} is the molar mass of the repeat unit ($172 \text{ g}\cdot\text{mol}^{-1}$). I_{H5} is the integral of trifluoroacetylated PBS hydroxyl end-groups at 4.4 ppm

Figure 2. $^1\text{H-NMR}$ spectrum of a sample of a trifluoroacetylated PBS (solvent: CDCl_3) at 25°C

($-\text{CH}_2\text{OCOCF}_3$) and ΣI_{PBS} is the sum of the integrals from all monomer units in the chains of PBS (Equation (12)):

$$\Sigma I_{\text{PBS}} = \frac{I_{\text{H3}}}{2} + \frac{I_{\text{H5}}}{2} + \frac{I_{\text{H1}}}{4} + \frac{I_{\text{H4}}}{4} \quad (12)$$

where I_{H1} is the integral at 2.6 ppm, referring to the methylene groups of succinic acid units in PBS and the peak at 4.2 ppm, referring to butanediol units in PBS.

N_{HC} , N_{CC} data and the resulting molar masses of the PBS series are detailed in Table 2.

3.2.2. End-groups analysis taking into account cyclic oligomers

As reported in the literature, the synthesis of PBS may produce a non negligible amount of oligomers, especially cyclic species [18, 19]. Most of the time, in scientific studies, PBS is purified to get rid of these species but commercial PBS clearly contains oligomers since dissolution/precipitation steps are not performed. In some cases it may be of importance to be able to account for their presence.

Equation (9) is not adapted for calculating the molar mass of a polymer that contains cycles. Indeed cyclic oligomers do not contain chain-ends, thus the molar mass derived with Equation (9) is overestimated since cycles monomer units are considered as being integrated into the linear chains population. It is possible to modify Equation (9) to account for cyclic oligomers only if their fraction and molar mass are known.

To this purpose, the mass fraction of cyclic oligomers, w_{cyclic} , of PBS samples was evaluated by extraction in THF and was found to be equal to 1–

2 wt% (Table 2). The SEC analysis of the extractible fraction clearly shows four main elution peaks corresponding to species with estimated molar masses of 355, 487, 630 and 801 $\text{g}\cdot\text{mol}^{-1}$ (Figure 3a). These four populations corresponding to cyclic oligomers could be discriminated more accurately by MALDI-TOF mass spectrometry: C2 (367.1 m/z), C3 (539.2 m/z), C4 (711.3 m/z), and C5 (883.3 m/z) corresponding respectively to Na^+ cationized cyclic oligomers composed of 2, 3, 4 and 5 repeat units, i.e. $\text{DPn} = 4, 6, 8$ and 10 (Figure 3b). The average molar mass, $\bar{M}_{\text{cyclic}}$, was calculated with the help of SEC and MALDI-TOF mass spectrometry data (Table 2). The cyclic oligomer content, N_{c} , may be expressed in $\text{mol}\cdot\text{g}^{-1}$ with Equation (13):

$$N_{\text{c}} = \frac{w_{\text{cyclic}}}{\bar{M}_{\text{cyclic}}} \quad (13)$$

Then a corrected value of $\bar{M}_{\text{n}}$ which includes cycles may be calculated with Equation (14):

$$\bar{M}_{\text{n cor}} = \frac{1}{\frac{w_{\text{cyclic}}}{\bar{M}_{\text{cyclic}}} + \frac{N_{\text{CC}} + N_{\text{HC}}}{2}} \quad (14)$$

where $\bar{M}_{\text{n}}$ values calculated with Equation (14) are listed in Table 2.

3.3. Molar mass determination by size exclusion chromatography

In addition to $^1\text{H-NMR}$, $\bar{M}_{\text{n}}$ was also measured by SEC with HFIP as the eluent and calibration with PMMA standards. It is necessary to note that polyester samples were not purified after synthesis. In order to get an idea of the influence of the small chains fraction, the molar mass was then calculated

Table 2. End-group concentrations and cycles fraction of PBS. $\bar{M}_{\text{n}}$ data of PBS determined using two methods, SEC and NMR (by taking cyclic oligomers into account or not)

PBS	$N_{\text{CC}}/N_{\text{HC}}^{\text{a}}$ [$\mu\text{eq}\cdot\text{g}^{-1}$]	$w_{\text{cycles}}^{\text{b}}$ [wt%]	$\bar{M}_{\text{n of cycles}}^{\text{c}}$ [$\text{g}\cdot\text{mol}^{-1}$]	$[\eta]$ [$\text{dL}\cdot\text{g}^{-1}$]		$\bar{M}_{\text{n}}$ [$\text{g}\cdot\text{mol}^{-1}$]		$\bar{D}^{\text{d}}$	$\bar{M}_{\text{n with cyclic}}^{\text{e}}$ [$\text{g}\cdot\text{mol}^{-1}$]		Number of cycles per PBS chain ^h
				CHCl_3	D/P^{d}	SEC ^e	$^1\text{H-NMR}$		SEC ^e	$^1\text{H-NMR}$	
PBS1	812/1 060	1.9	484	0.08	0.11	1 150	1 070	2.6	1 150	1 030	0.046
PBS2	62/362	2.1	473	0.25	0.33	10 300	4 710	1.7	5 120	3 890	0.52
PBS3	27/216	0.9	442	0.50	0.67	25 000	8 260	1.8	8 300	7 080	0.51
PBS4	18/107	1.1	432	0.57	0.81	29 950	16 000	1.8	9 400	11 500	0.77
PBS5	21/48	1.4	450	0.89	1.30	48 550	28 900	1.9	11 600	15 000	1.53
PBS6	46/12	1.6	466	0.99	1.50	55 250	34 100	2.0	12 300	15 600	1.93
PBS7	43/6	2.0	459	1.07	1.62	55 550	40 400	2.0	11 300	14 400	2.46

^a)Carboxylic and hydroxyl end-groups concentrations, ^b)Cycles mass fraction, ^c)SEC versus PS standard and with THF as the eluent, ^d)In 50/50 wt% dichlorobenzene/phenol, ^e)SEC versus PMMA standards and with HFIP as the eluent, ^f)Dispersity, ^g)Average molar mass including the contribution of cyclic oligomers, ^h)Data calculated from w_{cycles} , $\bar{M}_{\text{n cycles}}$ and $\bar{M}_{\text{n SEC}}$ (see text)

Figure 3. Analysis of the THF soluble fraction of PBS samples, (a) SEC in THF and (b) positive MALDI-TOF mass spectrum obtained in reflector mode (HABA matrix). Peaks at m/z 511.2 and 683.3 correspond to $CH_2=CHCO(C_8H_{12}O_4)_{DP}O(CH_2)_4OH$ with $DP=6$ and 8 , respectively.

by integrating the chromatograms excluding or not the molar mass range corresponding to oligomers ($100\text{--}1000\text{ g}\cdot\text{mol}^{-1}$) (Table 2).

3.4. Comparison of molar mass data obtained by ^1H -NMR and SEC

The number-average molar mass of PBS2 to PBS7 obtained via chain-ends quantification by ^1H -NMR was significantly lower than that measured by using SEC (both without correction for cyclic oligomers). This confirms the trend reported for polylactones and polylactides by several authors. Hiltunen *et al.* [20] measured molar masses 2–3 times smaller by titration than by SEC. Kowalsky *et al.* [21] and Save

et al. [23] reported the same feature and found that the error depends on the chemical structure of the polymer and its mass range. They proposed a correction factor ranging from 0.54 to 0.58 depending on the polymer. For PBS, Lahcini *et al.* [19] found that measurements by SEC in chloroform calibrated with polystyrene standards caused an overestimation of the molar mass by 80–100% compared to universal calibration. Actually, the values determined by SEC can vary significantly depending on the detector and/or on the calibration for PBS samples. In the present study, the values determined by SEC overestimated the real $\overline{M}_n$ by at least 50%, partly due to SEC calibration using PMMA hydro-

dynamic volumes which are different from those of the PBS and partly because of baseline errors due to oligomers.

Note that the molar mass determined by $^1\text{H-NMR}$ or by SEC by taking cyclic oligomers into account was much different from that with no correction. Although the oligomers represent a small mass fraction of the polymer ($w_{\text{cyclic}} \approx 0.9$ to 2.1 wt%), the number of these cycles is high in comparison with the number of linear chains. As an example the number of moles of cycles in 1 g of PBS 5 is $n_{\text{cycles}} = w_{\text{cycles}}/M_{\text{n cycles}} \sim 0.003$ mole and the number of moles of long chains is $n_{\text{chains}} = (100 - w_{\text{chains}})/M_{\text{n chains}} \sim 0.002$ mole (w_{cycles} is the mass percentage of cycles). Thus it is roughly estimated to be 1.5 cyclic molecule per PBS linear chain for PBS with $\bar{M}_{\text{n}} \sim 48\,550\text{ g}\cdot\text{mol}^{-1}$ (the data for other PBS is listed in Table 2). As a consequence, the corrected $\bar{M}_{\text{n}}$ is much lower than the data derived without considering cyclic oligomers. Indeed, this is particularly true for samples with a high molar mass.

Finally, despite the experimental inaccuracies linked with the elution of low molar mass compounds, SEC technique and $^1\text{H-NMR}$ provided consistent $\bar{M}_{\text{n}}$ results when cyclic oligomers were integrated into the calculation.

3.5. Correlation between intrinsic viscosity and molar mass.

Figure 4 and Figure 5 show the plot of $\ln[\eta]$ versus $\ln\bar{M}_{\text{n}}$ for PBS samples in 50/50 wt% 1,2-dichlorobenzene/phenol and in chloroform respectively, where $\bar{M}_{\text{n}}$ values were determined by the different methods presented previously (SEC and $^1\text{H-NMR}$), and $[\eta]$ is the average of the Huggins and Kramer dual extrapolation values. The linear relationship between $\ln[\eta]$ and $\ln\bar{M}_{\text{n}}$ was obtained by the least squares linear regression method. The values of equivalent a and k were obtained from the slope and intercept of the axis, respectively.

The values of equivalent k and a are presented in Table 3 as a function of the solvent used to determine the intrinsic viscosities and the method used to measure the molar mass.

Equivalent a and k values can be compared to those obtained by Imaizumi *et al.* [15] in chloroform at 40°C , $[\eta] = 2.75 \cdot 10^{-4} \cdot \bar{M}_{\text{n}}^{0.75}$. Molar masses were determined by SEC with polystyrene standards calibration. On the other hand Liu *et al.* [16] proposed $[\eta] = 1.706 \cdot 10^{-4} \cdot \bar{M}_{\text{n}}^{0.79}$. They determined the MHS

Figure 4. Relation between $\ln[\eta]$ and $\ln\bar{M}_{\text{n}}$ for PBS samples in 50/50 wt% 1,2-dichlorobenzene/phenol at 25°C with $[\eta]$ in $\text{dL}\cdot\text{g}^{-1}$ and $\bar{M}_{\text{n}}$ in $\text{g}\cdot\text{mol}^{-1}$. $\bar{M}_{\text{n}}$ determined ($\diamond$) by SEC in HFIP, ($\blacksquare$) end-group analysis and ($\blacktriangle$) end-group analysis considering cyclic oligomers.

Figure 5. Relation between $\ln[\eta]$ and $\ln\bar{M}_{\text{n}}$ for PBS samples in chloroform at 25°C with $[\eta]$ in $\text{dL}\cdot\text{g}^{-1}$ and $\bar{M}_{\text{n}}$ in $\text{g}\cdot\text{mol}^{-1}$. $\bar{M}_{\text{n}}$ determined ($\diamond$) by SEC in HFIP, ($\blacksquare$) end-group analysis and ($\blacktriangle$) end-group analysis considering cyclic oligomers.

parameters in 50/50 wt% phenol/tetrachloroethane with $\bar{M}_{\text{n}}$ values obtained by SEC measurements in chloroform with polystyrene calibration ($\bar{M}_{\text{n}} < 100\,000\text{ g}\cdot\text{mol}^{-1}$). Recently Garin *et al.* [17] proposed $[\eta] = 39.94 \cdot 10^{-5} \cdot \bar{M}_{\text{n}}^{0.71}$ in chloroform at 30°C with molar mass determined by SEC with a triple detection system. $[\eta]$ is expressed in $\text{dL}\cdot\text{g}^{-1}$.

3.6. Correlation between reduced viscosity and molar mass

The Mark-Houwink-Sakurada parameters are largely used in order to calculate molar masses from intrinsic viscosity measurements but the methodology requires the analysis of several concentrations of one polymer. In routine characterization only the reduced viscosity, η_{red} , of polyesters is measured

Table 3. Equivalent k and a parameters in chloroform and 50/50 wt% 1,2-dichlorobenzene/phenol to calculate the molar mass for different method of determination. $[\eta]$ in $\text{dL}\cdot\text{g}^{-1}$.

Solvent used for determining viscosity	Method for molar mass determination	Range of $\bar{M}_n$ [g/mol]	Equivalent Mark-Houwink-Sakurada relation ^{a)}
50/50 wt% 1,2-dichlorobenzene/phenol	SEC in HFIP ^{b)}	1 150–55 550	$[\eta] = 7.1 \cdot 10^{-4} \cdot \bar{M}_n^{0.69}$
	End-group analysis without considering cyclic oligomers	1 070–40 400	$[\eta] = 6.4 \cdot 10^{-4} \cdot \bar{M}_n^{0.74}$
	End-group analysis considering cyclic oligomers	1 030–15 600	$[\eta] = 1.2 \cdot 10^{-4} \cdot \bar{M}_n^{0.97}$
Chloroform	SEC in HFIP ^{b)}	1 150–55 550	$[\eta] = 6.4 \cdot 10^{-4} \cdot \bar{M}_n^{0.67}$
	End-group analysis without considering cyclic oligomers	1 070–40 400	$[\eta] = 6.1 \cdot 10^{-4} \cdot \bar{M}_n^{0.71}$
	End-group analysis considering cyclic oligomers	1 030–15 600	$[\eta] = 1.2 \cdot 10^{-4} \cdot \bar{M}_n^{0.93}$

^{a)} k parameter determined with $[\eta]$ in $\text{dL}\cdot\text{g}^{-1}$; ^{b)}versus PMMA standards, without taking cycles into account

because obtaining this data is much less time consuming. Only one polyester solution is prepared and analyzed. In the polyester industry, it is common practice to calculate $\bar{M}_n$ with the help of simple linear empirical relationships between molar mass and reduced viscosity. As an example, very helpful equations have been proposed by Gantillon *et al.* [36] for poly(ethylene terephthalate). In the same way, it is possible to apply this approach to PBS and plot $\bar{M}_n$ values versus η_{red} . The example

Figure 6. Number average molar mass versus reduced viscosity η_{red} measured for a 5 $\text{g}\cdot\text{L}^{-1}$ PBS solution in 50/50 wt% dichlorobenzene/phenol at 25°C. Molar mass determined by ^1H -NMR without correction for the cyclic oligomers.

depicted in Figure 6 is the most reliable one, for which we have the more data; the different relationships for obtaining $\bar{M}_n$ data are summarized in Table 4

4. Conclusions

The determination of the molar mass of polyesters is a difficult task. Here a series of PBS samples was synthesized with molar masses ranging from 1000 to 40 000 $\text{g}\cdot\text{mol}^{-1}$. They contained a fraction of cyclic oligomers produced during the esterification step of the synthesis process. This fraction was deliberately not removed by purification in order to evaluate its effect. The characterization of the solution viscosity of these polymers was performed in chloroform, a typical solvent for PBS and in a mixture of dichlorobenzene/phenol, a classical solvent for semi-aromatic polyesters. The molar mass of the polymers was determined using different techniques. The first one was an easily available method but did not provide an absolute value of $\bar{M}_n$. More reliable data were obtained using ^1H -NMR spectroscopy. In addition a correction was proposed to account for the presence of PBS cyclic oligomers with a number average degree of polymerization, $\text{DP}_n = 4, 6, 8$ and 10. The proposed sets of Mark-Houwink-Sakurada parameters and empirical relationships were

Table 4. Empirical relationship for determining $\bar{M}_n$ from reduced viscosity measurements. η_{red} in $\text{dL}\cdot\text{g}^{-1}$. Concentration of the solution for the viscosity measurement = 5 $\text{g}\cdot\text{L}^{-1}$.

Solvent used for determining η_{red}	Range of $\bar{M}_n$ [g $\cdot\text{mol}^{-1}$]	$\bar{M}_n = f(\eta_{\text{red}})$	$\bar{M}_n$ value corresponds to that measured by:
50/50 wt% 1,2-dichlorobenzene/phenol	1 150–55 500	$\bar{M}_n = 29\,000 \cdot \eta_{\text{red}} + 700$	SEC in HFIP ^{a)}
	1 070–40 400	$\bar{M}_n = 20\,600 \cdot \eta_{\text{red}} - 2580$	End-group analysis without considering cyclic oligomers
	1 030–15 600	$\bar{M}_n = 7\,500 \cdot \eta_{\text{red}} + 1700$	End-group analysis considering cyclic oligomers
Chloroform	1 150–55 550	$\bar{M}_n = 47\,000 \cdot \eta_{\text{red}} - 1300$	SEC in HFIP ^{a)}
	1 070–40 400	$\bar{M}_n = 33\,000 \cdot \eta_{\text{red}} - 4500$	End-group analysis without considering cyclic oligomers
	1 030–15 600	$\bar{M}_n = 12\,000 \cdot \eta_{\text{red}} + 1100$	End-group analysis considering cyclic oligomers

^{a)}versus PMMA standards, without taking cycles into account

very helpful to calculate $\overline{M}_n$ either from the determination of the intrinsic viscosity or with a simple measurement of the reduced viscosity, η_{red} .

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