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Comparison of calibration with poly(propylene glycol) and poly(styrene) standards in size exclusion chromatography measurements for characterization of oligo(lactone) macromonomers

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Summary

The calibration of size exclusion chromatography (SEC) measurements for determination of the molecular weights of oligo(lactone) macromonomers was carried out by use of poly(propylene glycol) (PPG) and poly(styrene) (PS) standards. The results are compared with those obtained by end-group analysis with ^{1}H-NMR as well as those calculated from the molar ratio of lactone and initiator in the initial mixture regarding the conversion of lactone. Clearly, calibration with PPG standards results in a better correspondence of molecular weights from SEC measurements with those of end-group analysis and calculated ones compared to calibration with PS standards.

Introduction

The ring-opening polymerization of various lactones initiated by ionic or coordination catalysts often proceeds as a „living“ reaction (1). In these cases, the molecular weights of the poly(lactone)s are given by the ratio of monomer molecules converted per initiator molecule, and the poly(lactone)s are characterized by a low polydispersity index (PI) of their molecular weights. For determination of the latter, the use of PS standards for SEC calibration is quite common (1,2). However, in some cases it has been shown that the molecular weights obtained by calibration with PS standards are significantly higher than those calculated and those obtained by end-group analysis (3-10). We observed this effect with various oligo(lactone) macromonomers (4). The latter were synthesized by initiating the oligomerization of a lactone, e.g. lactide, by a 2-hydroxyalkyl methacrylate, e.g. bisphenol-A-bis(2-hydroxypropyl) methacrylate (BisGMA), as described in (3,4) and shown in the following reaction scheme.

The "living" mechanism of this oligomerization reaction was demonstrated by kinetic studies (4). However, the molecular weights of the macromonomers as determined by calibration of SEC with PS standards differed from the calculated ones by a factor of about 1.5. This has to be expected because both the chemical constitution and the architecture of the PS standard and the macromonomers are completely different.

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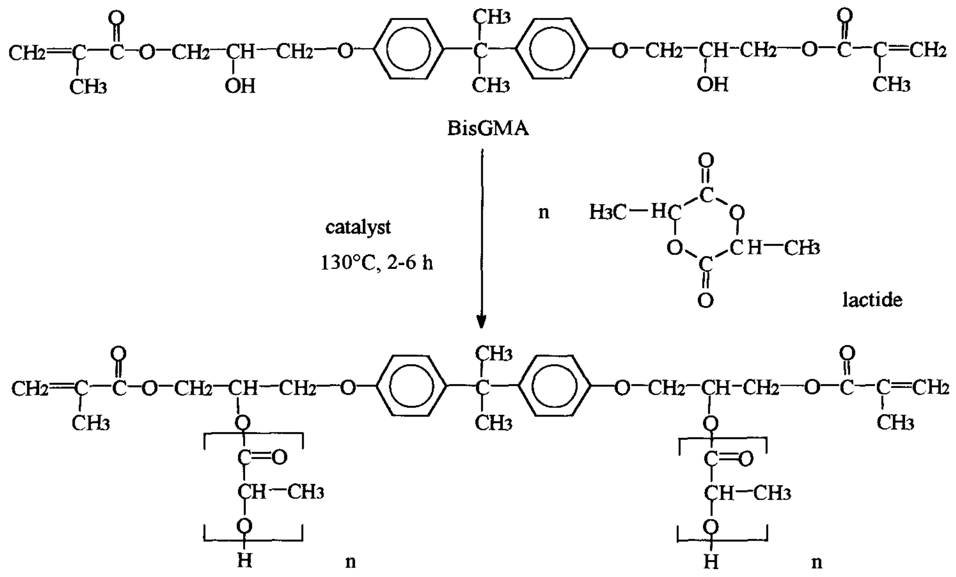

Reaction scheme of BisGMA initiated L-lactide oligomerization.

RAFLER (11) used poly(lactide) instead of PS standards for SEC calibration to determine the molecular weights of lactide copolymers which correspond well both with those calculated and those measured by membrane osmosis. However, the suitability of poly(lactide) as a standard may be questionable because of its sensitiveness to degradation by hydrolysis. Poly(propylene glycol) (PPG) has been seemed to us to be a suitable calibration standard because it contains oxygen atoms in the chain like the polylactones. The results of these studies using PPG standards are reported here.

Experimental Part

Materials

Bisphenol-A-bis(2-hydroxypropyl) methacrylate (BisGMA) was synthesized as described in (12). L-lactide (Boehringer Ingelheim KG) was stored over P_4O_{10} in vacuo. Ionol (2,6-di-tert-butyl-4-methylphenol) (Merck-Schuchardt), Sn(II) octoate ($Sn(oct)_2$) (Sigma Chemical Co.), 6-caprolactone and 5-valerolactone (both Fluka) were used as received. Tetrahydrofuran (THF) was distilled over a 20 cm Vigreux-column.

The PS standards (M_n = 510 - 7000 g mol^{-1}) were purchased from Shodex, Showa Denko KK, Tokio (S-Series, SL-105, Lot. No. 21103), the PPG standards (M_n = 76 - 5430 g mol^{-1}) from Polymer Standards Service, Mainz (no specification).

Synthesis of macromonomers

The macromonomers were synthesized by reaction of BisGMA and lactone in the presence of the catalyst $Sn(oct)_2$ (BisGMA:$Sn(oct)_2$ = 1:0.02 mol/mol) and of 0.1 wt % Ionol as an inhibitor under stirring at 130°C until a conversion of lactones of more than 95 % was achieved. Cooligomerizations of 5-valerolactone and 6-caprolactone, respectively, with lactide were performed both as parallel reactions and as step reactions, the latter reaction with addition of lactide after attaining a conversion of more than 95 % of the first lactone.

Analysis

Monitoring of the reaction course, i.e. determination of the degree of conversion of lactones as well as the determination of the molecular weights of the macromonomers was performed by SEC on a Knauer, Berlin, device equipped with a Knauer differential refractometer. Three Hibar RT-columns (LiChrogel) provided by Merck were used: PS 1 100-2000, PS 4 100-5000 and PS 20 100-20000 g mol^{-1}. THF served as eluent at a flow rate of 1 ml per minute. 20 µl of a solution of 50 to 100 mg of the macromonomer in 5 ml THF were injected after filtering the solution.

The conversions of lactide and the other lactones were determined from the peak height in their chromatograms by calibration with different concentrations of the corresponding substances.

The software GPC-PRO, version 3.13 (1994) by Viscotek Corp., Porter, TX and Polymer Standards Service (PSS), Mainz, respectively, was used for measurements, calibration and analysis.

The ^{1}H-NMR spectra of macromonomers were recorded with a Varian Gemini 300 or 2000 (both 300 MHz) at room temperature (13). The number average molecular weights (M_n) were calculated from the relative intensity ratio of the CH signals of lactide at 5.1 ppm and of the CH_3 signals of the methacrylate group at 1.9 ppm.

Results and discussion

The SEC calibration curve with ten PS standards was fitted by a second order polynom and that with seven PPG standards was fitted by a third order polynom (both *Figure* 1) resulting in the following equations : $\log M = 19.66 - 2.325\ V_e + 0.080 V_e^2$ (R = 0.99024, SD = 0.05562) for PS calibration and $\log M = 25.57 - 4.436\ V_e + 0.300 V_e^2 - 0.007 V_e^3$ (R = 0.99933, SD = 0.02371) for PPG calibration.

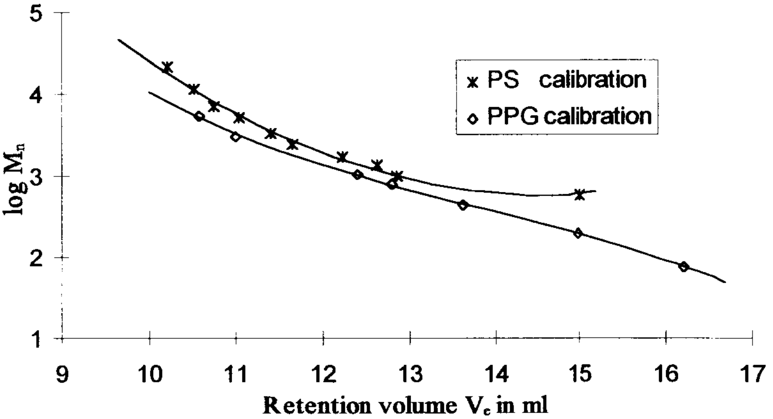

Figure 1 : Calibration plots for SEC measurements based upon PS and PPG standards

The calculation of the theoretical molecular weights of the macromonomers $M_{n,calc.}$ is based on the initial molar ratio of lactone and BisGMA considering the conversion $x_{lactone}$ of the lactone(s) according to the following equation :

$$M_{n,calc.} = M_{BisGMA} + \frac{[lactone] \cdot M_{lactone} \cdot x_{lactone}}{[BisGMA]}$$

where M_{BisGMA} is the molecular weight of BisGMA and $M_{lactone}$ is the molecular weight of the corresponding lactone.

The increasing molecular weights determined by both calibration methods during the L-lactide oligomerization initiated by BisGMA and the calculated values are compared in *Table* 1. The different values of M_n are clearly visible : $M_{n,PS} > M_{n,calc.} > M_{n,PPG}$. The polydispersity index PI differs between both calibrations and is lower with the PPG calibration. The similar effect is also observed for cooligomerizations of different lactones initiated by BisGMA, for instance for the step oligomerization of 6-caprolactone and L-lactide as shown in *Table 2*. A worse correspondence between $M_{n,PPG}$ and $M_{n,calc.}$ in *Table* 1 compared to *Table* 2 is noticeable. It may be caused by the partial sublimation of L-lactide during its homooligomerization with BisGMA as apparent from the lower M_n values determined at higher conversions by SEC compared with $M_{n,calc.}$ (*Table* 1). This sublimation has never been observed in the presence of 6-caprolactone or 5-valerolactone.

Table 1 : Molecular weights of the macromonomer from BisGMA:LL = 1:8 mol/mol

Reaction time min	$M_{n,calc}$* g mol^{-1}	PS calibration M_n g mol^{-1}	PS calibration PI	PPG calibration M_n g mol^{-1}	PPG calibration PI
30	1368	1878	1.17	1340	1.10
60	1551	2094	1.17	1435	1.12
90	1636	2068	1.21	1448	1.13
120	1631	2062	1.20	1412	1.14
150	1608	2061	1.20	1434	1.13

* M_n calculated for 100% conversion = 1664 g mol^{-1}

The molecular weights based on PPG calibration correspond relatively well with the calculated molecular weights for various macromonomers after almost complete conversion of used components (*Table* 3). In most cases the calculated molecular weights lie in the range between M_w and M_n of the macromonomer measured by SEC. Differences between parallel and step reactions of the same sample are obvious. The worse correspondence of calculated and found values of M_n for parallel reactions is caused by lactone losses when taking samples during the long reaction times necessary for these reactions compared with step reactions.

Table 2 : Molecular weights of the macromonomer from BisGMA:CL:LL = 1:2:8 mol/mol (step reaction, L-lactide added at 120 min reaction time)

Reaction		PS calibration		PPG calibration	
time	$M_{n,\,calc}$*	M_n	PI	M_n	PI
min	g mol^{-1}	g mol^{-1}		g mol^{-1}	
30	658	824	1.06	589	1.07
60	713	897	1.09	644	1.10
90	726	936	1.12	674	1.11
120	734	953	1.12	679	1.12
150	1226	1608	1.17	1154	1.13
180	1469	1991	1.19	1391	1.12
210	1632	2212	1.22	1521	1.14
240	1685	2430	1.22	1667	1.14
270	1753	2558	1.22	1709	1.12
300	1804	2594	1.21	1742	1.13
330	1828	2672	1.20	1795	1.11
360	1830	2653	1.23	1800	1.12

* M_n calculated for 100% conversion = 1892 g mol^{-1}

Table 3 : Calculated and experimentally found molecular weights of various macromonomers

Sample	Conversion			PPG calibration		^{1}H-NMR
BisGMA:CL:LL	CL	LL	$M_{n,\,calc}$	M_w	M_n	M_n
	%	%	g mol^{-1}	g mol^{-1}	g mol^{-1}	g mol^{-1}
1 : 10 : 0	88	-	1511	1705	1304	1500
1 : 8 : 0 *	88*	-	1220	1573	1150	1330
1 : 0 : 8	-	95	1609	1615	1434	-
1 : 0 : 24	-	100	3968	4598	3999	4120
1 : 0 : 31	-	100	4976	4997	4714	5120
1 : 0 : 40	-	100	6272	5587	4988	6120
1 : 2 : 6 p	83	99	1552	1549	1361	-
1 : 2 : 6 s	96	98	1578	1777	1546	-
1 : 2 : 8 p	73	100	1831	1748	1542	1900
1 : 2 : 8 s	95	95	1828	2015	1800	-
1 : 2 : 6 p*	89*	98	1530	1500	1370	1560
1 : 2 : 6 s*	85*	98	1530	1660	1420	1540
1 : 4 : 6 p*	98*	100	1580	1870	1550	1700
1 : 2 : 8 p*	82*	98	1810	1840	1630	1940

p = parallel / s = step reaction * VL used instead of CL

The obtained molecular weights using PPG calibration furthermore correspond well with those derived from ^{1}H-NMR spectra, as already noticed for some samples in (13) and also shown in *Table* 3.

In order to compare old and new results and to convert old results into new ones a mathematical correlation between the molecular weights of the different calibrations has been established for the molecular weight range from 600 to 14000 g mol^{-1} ($M_{n,PS}$) and is shown in *Figure* 2 with $y = 2E\text{-}09x^3 - 5E\text{-}05x^2 + 0.798x - 28.138$ ($R = 0.99926$, $SD = 35.32$), where $x = M_{n,PS}$ and $y = M_{n,PPG}$.

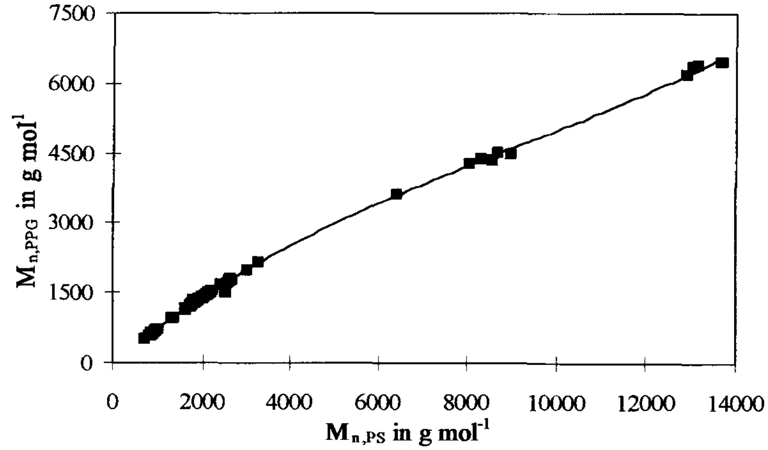

Figure 2 : Correlation between $M_{n,PPG}$ and $M_{n,PS}$ of various macromonomers

The differences in both calibrations can be explained by the different proportions of hydrodynamic volume to mass for the calibration standards used. PS chains have a higher hydrodynamic volume than PPG has at the same molecular weight, because of the steric hindrance of the PS chains by the bulky phenyl substituents. These differences between both polymers may be represented by the steric factor $\sigma = r_o/r_{of}$, where r_o and r_{of} are the end-to-end distances in the unperturbed and in the freely rotating state of the chains, respectively, with $\sigma_{PS} = 2.22 \pm 0.5$ and $\sigma_{PPG} \approx 1.6$ (14). Since the separation process in SEC depends on the hydrodynamic volume, PS standards pass the columns faster than PPG standards with the same molecular weight. Therefore, the molecular weights based on PS standards are too high for our samples which are sterically and with respect to their polarity more similar to PPG.

Conclusions

As a result of our investigations we can strongly recommend to use PPG standards instead of PS standards for SEC characterization of cooligomer lactone macromonomers. The molecular weights of oligo(lactone) macromonomers determined with PPG standards are considerably lower than those determined with PS standards and the PPG based values correspond much better with the calculated values.

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