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Syntheses of Poly(butylene succinate) by Means of Non-Toxic Catalysts

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The usefulness of bismuth, calcium, magnesium and zinc salts for the preparation of poly(butylene succinate), PBSu, was studied. Two different approaches were compared. Firstly, 1,4-butanediol (or in a few experiments ethanediol) dimethyl succinate were condensed at temperatures up to 240°C in the presence of Bi_2O_3. Regardless of the feed ratio, only low molar mass polyesters having two diol endgroups were obtained. Secondly, 1,4-butanediol and succinic anhydride were polycondensed in refluxing decalin with azeotropic removal of water. $BiCL_3$, $BiBr_3$, BiI_3, and Bi-triflate were used as catalyst and the monomer/catalyst ratio was varied. The highest molar masses were achieved with $BiCl_3$. Analogous polycondensations catalysed with $ZnCl_2$, Zn-triflate, $MgCl_2$, Mg-triflate and $CaCl_2$ were unsuccessful. Yet the $BiCl_3$, decalin method was also successfully applied to the combination of succinic anhydride and 1,5-pentanediol.

Keywords: Bismuth, polyester, polycondensation, succinic acid

1 Introduction

Aliphatic polyesters are the most widely studied and most frequently produced group of biodegradable materials. According to their chemical structure aliphatic polyesters may be subdivided into two classes: polyesters derived from hydroxy acids and polyesters based on alkanediols and aliphatic dicarboxylic acids. Whereas, the first class of polyesters is usually prepared by ring-opening polymerization, the second class is usually prepared by polycondensation processes. Three different polycondensation methods were explored in the past. First, transesterification between aliphatic diols and dimethylesters of decarboxylic acids; second, esterification of aliphatic diols with dicarboxylic acids; and third, polycondensation of alkanediols with dicarboxylic acid dichlorides in solution. The latter approach is versatile, but too expensive for upscaling.

Poly(butylene succinate), PBSu, is a particularly important technicaly produced biodegradable polyester for three reasons. Firstly: succinic acid is a biogenic monomer, or in other words, a monomer based on renewable resources. Secondly: the rates of hydrolysis of polysuccinates are higher than those of polyesters derived from higher aliphatic dicarboxylic acids. Thirdly: the melting temperature, and thus, the heat distortion temperature of PBSu (Tm = 120°C) is the highest of all polysuccinates derived from α,ω-alkanediols. Synthese of polysuccinates were described by several research groups (1–18) beginning with the work of Carothers (1,2). The preparation of high molar mass PBSu (M_ns = 10 000 Da) is plagued by the high tendency of 1,4-butanediol to form tetrahydrofuran, THF. At temperatures above 120°C even the acidity of SuAc suffices to catalyze this process. Stronger acids catalyze the cyclization already around 100°C. When an excess of 1,4-butanediol is used to compensate for the loss of THF, polycondensations with SuAc at temperatures up to 240°C in bulk only yield low molar mass PBSu ($M_n < 4\ 000$ Da) having two diol endgroups. Higher molar mass (M_n's up to 13 000 Da) were obtained when an excess of 1,4-butanediol was used in combination with titanium tetrabutoxide as catalyst (17), the alternative approach chain extension with 1,6-hexamethylene diisocyanate, and commercial PBSu (e.g. from Aldrich Co.) is indeed prepared in this way. Higher molar mass PBSu can also be prepared by a one-step

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*Address correspondence to: Hans R. Kricheldorf, Institute für Technische und Makromoleculare Chemie, Bundesstr. 45, D-20146 Hamburg, Germany; E-mail: kricheld@chemie.uni-hamburg.de procedure using refluxing decalin as reaction medium. In the first description of this method (5) highly toxic dibutyltin compounds served as catalysts. More recently it was reported (18) that far less toxic (19-21) bismuth salts may also serve as catalysts, but the procedure was not optimized. In this context the present work had to purposes. Firstly, two different synthetic methods should be compared. Secondly, in combination with the better method the usefulness of different non-toxic catalysts should be explored.

2 Experimental

2.1 Materials

1,4-butanediol, ethandiol, 1,5-pentanediol, 1,3-propanediol dimethyl succinate (DMSu), succinic anhydride (SuAh), decalin, BiO_3, $BiCl_3$, $BiBr_3$, BiI_3, Bi-triflate, Bi-Subsalicylate, $MgCl_2$, Mg-triflate, $ZnCl_2$, and Zn-triflate were all purchased from Alfa Aesar (Karlsruhe, Germany). All diols and decalin were distilled in vacuo prior to use.

2.2 Polycondensations

2.2.1. *Transesterification of DMSu*

A) Procedure A (No. 6, Table 1): 1,4-butanediol (120 mmol), DMSu (100 mmol), and BiO_3 (0.2 mmol) were weighed on a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet and outlet tubes, the reaction vessel was placed into an oil bath preheated to 100°C. After rapid heating to180°C the following temperature-time program was applied: 180°C/1 h, 200°C/0.5 h, 220°C/0.5 h, 240°C/1 h plus 240°C for 1 h with vacuum. The cold reaction product was dissolved in dichloromethane and precipitated into methanol.

B) Procedure B (No. 7, Table 1): The following temperature-time program was used, 180°C/1 h, 200°C/0.5 h, 220°C/1 h, plus 220°C for 3 h with vacuum.

Table 1. Bi_2O_3-catalyzed polycondensations of dimethylsuccinate, (DMSu) with ethanediol (Nos 1–4) or 1,4-Butanediol (Nos 5–8)

Exp. No.	*Diol*	*Excess of Diol (mol%)*	*Procedure*	*Yield (%)*	η^a_{inh} *(dL/g)*
1	Ethanediol	10	A	58	0.09
2	Ethanediol	20	A	63	0.13
3	Ethanediol	20	B	60	0.08
4	Ethanediol	50	A	60	0.14
5	1,4-Butanediol	10	A	60	0.13
6	1,4-Butanediol	20	A	65	0.13
7	1,4-Butanediol	20	B	68	0.11
8	1,4-Butanediol	50	A	61	0.11

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.

Table 2. Polycondensations of 1,4-Butanediol and SuAh in decalin catalyzed by Bi-halides

Exp. No.	*Catalyst*	*SuAh/Cat.*	*Yield (%)*	η^a_{inh}*(dL/g)*
1	$BiCl_3$	250	91	0.57
2	$BiCl_3$	500	89	0.59
3	$BiCl_3$	1000	88	0.61
4	$BiCl_3$	2000	88	0,58
5	$BiCl_3$	5000	87	0.33
6	$BiBr_3$	1000	88	0.54
7	BiI_3	1000	88	0.36

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.
[b]SEC measurements in chloroform calibrate with polystyrene.

2.2.2. *Polycondensation of SuAh*

A)With 1,4-butanediol (No. 3, Table 2) 1,4-butanediol (60 mmol), SuAh (60 mmol), and $BiCl_3$ (0.12 mmol) were weighed into a 250 ml round bottom flask equipped with magnetic stirring bar and a Dean-Stark Trap. The reaction vessel was placed into an oil bath preheated to 120°C and stirred for 1 h. Decalin (60 ml) was then added and the reaction mixture was stirred and refluxed at a bath temperature of 215–220°C for 24 h. After cooling the solid product was dissolved in chloroform and precipitated into diethylether.

The polycondensations of Table 3 and 4 were conducted analogously with $ZnCl_2$, Zn-triflate, $MgCl_2$, Mg-triflate, $CaCl_2$ instead of $BiCl_3$.

B) With ethanediol (No. 2, Table 5)

Ethanediol (103 mmol), SuAh (100 mmol) and $BiCl_3$ (0.2 mmol) were weighted into a 250 ml round bottom flask equipped with Dean-Stark trap and magnetic bar and polycondensed as described above for A).

In the case of 1,3-propanediol and 1,5-pentanediol equimolar amounts of diol and SuAh were used.

2.3 Measurements

The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20°C. The 400 MHz ^{1}H-NMR spectra was recorded on a Bruker "Avance 400" FT NMR spectrometer in 5 mm o,d,e sample tubes. $CDCl_3$ containing TMS served as solvent. The

Table 3. Polycondensations of 1,4-Butanediol and SuAh in decalin catalyzed by Zn-salts

Exp. No.	*Catalyst*	*Mon/Cat.*	*Yield (%)*	η^a_{inh}*(dL/g)*
1	$ZnCl_2$	250	82	0.36
2	$ZnCl_2$	500	80	0.37
3	$ZnCl_2$	1000	81	0.36
4	Zn-triflate	500	0	0
5	Zn-triflate	1000	0	0
6	Zn-triflate	2000	44	0.16

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.

Table 4. Polycodensations of 1,4-Butanediol and SuAh in decalin catalyzed by Mg-salts

Exp. No.	*Catalyst*	*Mon/Cat.*	*Yield (%)*	η^a_{inh}*(dL/g)*
1	$MgCl_2$	500	80	0.24
2	$MgCl_2$	1000	80	0.24
3	$MgCl_2$	2000	81	0.25
4	$MgCl_2$	4000	80	0.24
5	Mg-triflate	1000	84	0.28
6	Mg-triflate	2000	82	0.28

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.

SEC measurements (Table 8) were performed on a PSS apparatus equipped with Shodex RI 101 refractive index detector and a Viscotik viscosity detector 250 (operating at 30°C). The chloroform solutions containing chlorobenzene as interval standard were filtered through a 0.45μm PTFE membrane and passed at 35°C through 3 PSS 5μ SDV-gel columns (10^5, 10^3, 50A°, BX 300 mm each) at a flow rate of 1 ml/min. The raw data were processed using the PSS Win 6 PC Unity software package of PSS (Mainz, Germany). Commercial polystyrene standards served for calibration. The elution curves were evaluated from 400 Da up-words: The MALDI-TOF (MT) mass spectra were measured with a Bruker "Smartbeam" mass spectrometre in the reflection mode and with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solution with DCTB as matrix and K-trifluroacetate as dopant. The calculated masses of the reaction products discussed in this work are sammarized in Tables 6 and 7.

3 Results and Discussion

3.1 Transesterification of DMSu

In a previous study (22) polycondensations of 1,4-butanediol (in excess) with dimethylterephthalate were conducted in bulk at temperatures up to 240°C. Several commercial bismuth salts (e.g. Bi_2O_3, $BiCl_3$, Bi(III)acetate or Bi-SS) were compared to each other and to other numerous metal salts with regard to their usefulness as transesterification catalysts. It was found that the bismuth salts were less effective than the best and long known catalyst $Ti(OBu)_4$ but Bi_2O_3 caused lower side reactions than all other catalysts. The reaction products consisted almost exclusively of telechelic polyesters terminated by two diol units. Furthermore, clean telechelic polyesters were also obtained when dimethyl adipate or dimethylsebacate were polycondensed with excess ethanediol in the presence of BiO_3, or Bi hexanoate (23).

Table 5. Polycodensations of SuAh with various alkanediols in decalin catalyzed by $BiCl_3$

Exp. No.	*Diol*	*Molar excess of Diol(%)*	*Yield (%)*	η^a_{inh}*(dL/g)*
1	Ethanediol	0	85	0.32
2	Ethanediol	3	81	0.32
3	Ethanediol	6	82	0.30
4	1,3-Propanediol	0	84	0.35
6	1,5-Pentanediol	0	88	0.65

[a]Measured at 20°C with c = 2 g/L in CH_2Cl_2.

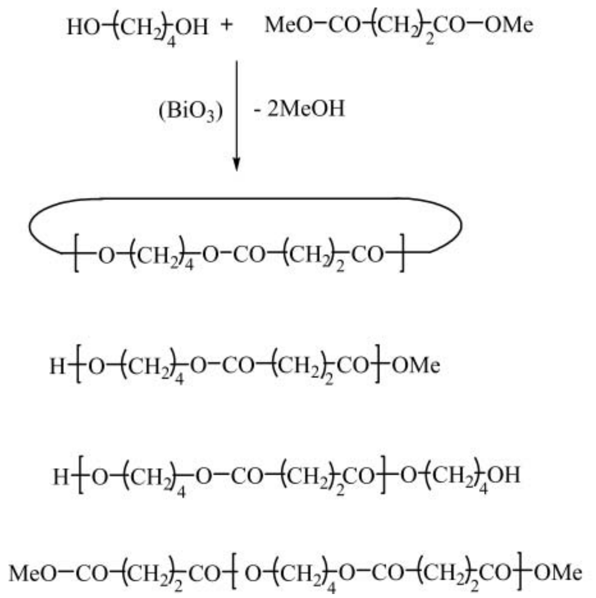
Table 6. Calculated masses (incl, K-doping) of the reaction products discussed for polycondensations of 1,4-butanediol and SuAh or DMSu

DP	*C*	*La*	*Lb*	*Lc*	*Ld*	*Le*
5	900	932	990	1046	918	1018
6	1072	1104	1162	1218	1090	1190
7	1244	1276	1334	1390	1262	1362
8	1416	1448	1507	1562	1434	1535
9	1589	1621	1679	1735	1607	1707
10	1761	1793	1851	1907	1779	1879
15	2622	2654	2712	2768	2640	2740
20	3483	3515	3573	3629	3501	3601

In the present work, DMSu was polycondensed with ethanediol and 1,4-butanediol in bulk at temperatures up to 240°C. BiO_3 were used as catalysts and the excess of the diol was varied. The results summarized in Table 1 allowed the following conclusions. The inherent viscosities and thus, the molecular weights were low regardless which catalyst or diol were used. Since, ethanediol and 1,4-butanediole gave almost identical viscosity data the relatively low molecular weights were not caused by dramatic loss of 1,4-butanediol in the form of THF. This conclusion is supported by the observation that a larger excess of the diol does not significantly improve the molecular weight. The MALDI-TOF mass specta of the PBSu samples revealed that the diol terminated polyester chains (**Lb** in Scheme 1) were the predominant reaction products followed by chains having one CH_2OH and one CO_2CH_3 endgroup (**La** in the Scheme 1). Cycles and linear chains containing two CO_2CH_3 endgroups were almost absent. In summary, it may be

Table 7. Calculated masses (incl, K-doping) of the reaction products discussed for polycondensations of 1,5-pentanediol and SuAh

DP	*C'*	*La'*	*Lb'*	*Lc'*	*Ld'*	*Le'*
5	970	1002	1060	1116	988	1088
6	1156	1188	1246	1302	1174	1274
7	1342	1375	1433	1489	1360	1461
8	1529	1561	1619	1675	1547	1647
9	1715	1747	1805	1861	1733	1833
10	1901	1933	1991	2047	1919	2019
15	2832	2864	2922	2978	2850	2950
20	3763	3795	3853	3909	3781	3881



Sch. 1. Potential reaction products of polycondensation of DMSu with 1,4-butanediol.

concluded that both Bi-catalysts were not effective enough to reach high conversion.

3.2 Polycondensations of SuAh with 1,4-butanediol

In a previous publication (18), it was demonstrated that polycondensations of 1,4-butanediol and SuAh in refluxing decalin around 200°C gave twice or three times higher molecular weights than polycondensations in bulk at 80°C, although, the much higher temperature favors formation of THF. Furthermore, it was found that Bi-triflate and $BiCl_3$ had a catalytic effect even a catalyst/monomer ratio was performed, and such on optimization was now studied in the present work. The viscosity-data listed in Table 2 indicates that a monomer/$BiCl_3$ ratio around 1000/1 is close to the optimum. At the same monomer/catalyst ratio $BiBr_3$ and BiI_3 yielded lower molecular masses. With Bi-triflate monomer/catalyst ratios of 500/1, 1000/1 and 2000/1 were examined, but all three polycondensation only yielded black tars, and therefore, these experiments were not listed in Table 2. In summary, $BiCl_3$ proved to be the best of the four acidic Bi-catalysts studied in this work.

The finding that the "Ueda" or "decalin" method yielded considerably higher molar masses than the transesterification method prompted us to explore the usefulness of other non-toxic metal salts as catalysts. At first $ZnCl_2$ and Zn-triflate were used, and again the monomer/catalyst ratio was varied. The inherent viscosities listed in Table 3 evidenced that no solution viscosity above 0.40 dL/g was achieved. Yet as demonstrated previously (18) and by Ueda et al. (5) such inherent viscosities can also be obtained without addition of catalyst, because the CO_2H groups of succinic acid catalyze the esterification themselves at high temperature. In other words, both $ZnCl_2$ and Zn-triflate were ineffective as catalysts. Analogous polycondensation were conducted with $MgCl_2$ and Mg-triflate. It was found again that regardless of catalyst and feed ratio, no catalytic effect was detectable. Three more polycondensations (not listed in a table) were performed with $CaCl_2$ at monomer/catalyst ratios of 500/1, 1000/1 and 2000/1. The inherent viscosities of the reaction products fell into the range of 0.25–0.28 dL/g in agreement with the analogous experiments conducted with $MgCl_2$ (Table 4). In other words, among the four non toxic metal chlorides studied in this work only $BiCl_3$ proved to be useful catalyst.

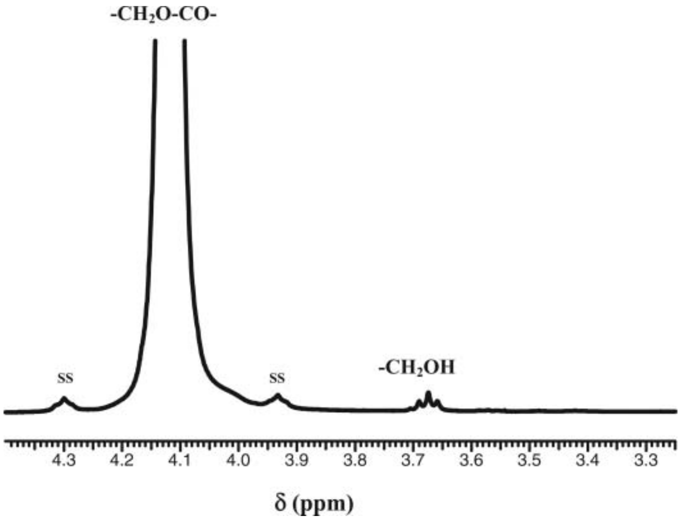


Fig. 1. 400MHz ^1H spectrum of a poly(1,4-butylene succinate) prepared by means of $ZnCl_2$ in refluxing decalin (No. 3, Table 3).

The reaction products of the metal chloride catalyzed polycondensation were characterized by ^1H-NMR spectroscopy and MT mass spectrometry to find out which factors are responsible for the poor results obtained from Mg, Ca and Zn Chlorides. The ^1H-NMR spectra revealed that none of the polyesters listed in Tables 2–4 contains ether groups. The triplet signal of CH_2OH endgroups (Figure 1) was more intensive in the $ZnCl_2$, $MgCl_2$ and $CaCl_2$-"catalyzed" polyesters (e.g. No. 3, in Tables 4+5) than in the best product prepared with $BiCl_3$ (No. 3, Table 2) suggesting lower conversions. This suggestion was confirmed by MT mass spectra as exemplarily illustrated in Figures 2 and 3.

In the case of the $BiCl_3$-catalyzed sample No. 3, Table 2 the peaks of cyclic polyesters are the most intensive peaks at masses below 4000 Da quite analogous to the mass spectrum presented in Figure 3. At higher masses the peaks of **Lb**, **Ld** and **Le** chains (defined in Scheme 2) were prevailing, but peaks of unknown byproducts were not detectable. A high content of cycles is in agreement with clean polycondensations and high conversion according to the theory of Gordon et al. (24), Stepto et al. (25) and Kricheldorf (26, 27). However, in the MT mass spectra of the $ZnCl_2$,

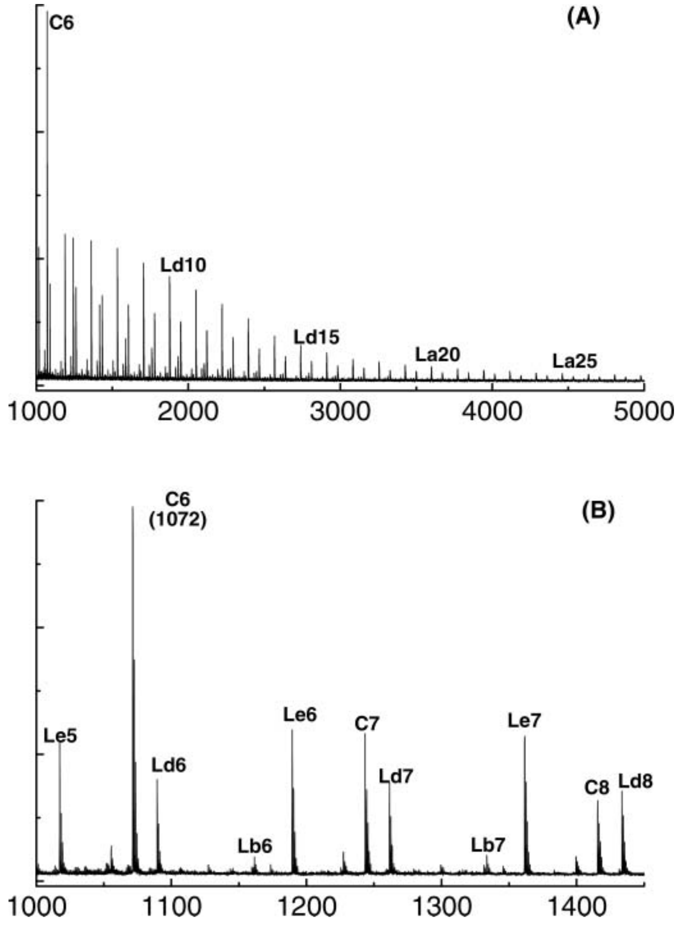


Fig. 2. MALDI-TOF mass spectrum of a poly(1,4-butylene succinate) prepared by means of $MgCl_2$ in refluxing decalin (No. 2, Table 4).

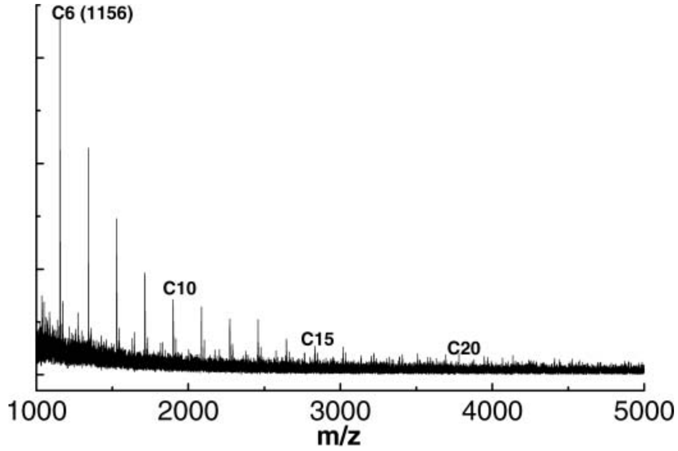


Fig. 3. MALDI-TOF mass spectrum of a poly(1,5-pentylene succinate) prepared by means of $BiCl_3$ in refluxing decalin (No. 6, Table 5).

$MgCl_2$ or $CaCl_2$ "catalyzed" polyesters the peaks of linear chains (**Lb**, **Ld**, **L**e or K-salts of **Ld** and **Le**) were most intensive over the full mass range and the peaks of cycles were weak (Figure 2). Peaks of unexpected byproducts were again not detectable. Hence, it may be concluded that the relatively low molar masses of the $ZnCl_2$, $MgCl_2$ and $CaCl_2$-"catalyzed" polyesters in the consequence of relatively low conversions, indicating a low catalytic reactivity of those metal chlorides.

3.3 Polycondensations of SuAh with Various Alkanediols

The success of the "decalin (Ueda) method" depends on the insolubility of the reaction products in the reaction medium because dissolution favours cyclization at the expense of chain growth due to the Buggli-Ziegler dilution principale. Hence, the $BiCl_3$-decalin method should also be useful for polycondensations of SuAh with other short alkanediols. Therefore, several polycondensations were conducted with ethanediol, 1,3-propanediol and 1,5 pentanediol. The polyesters of longer alkanediols were expected to be soluble in decalin. Furthermore, polycondensations of SuAh with longer alkanediols were successfully conducted in bulk at 80°C using $BiCl_3$ as catalyst (18).

Since ethanediol is the most volatile diol, three polycondensation were performed with variation of the feed ratio (Nos. 1–3, Table 5). An excess of ethanediol should not only compensates for the loss by distillation but also for the loss of CH_2OH groups by ether formation. However, an excess of ethanediol did not prove advantageous and only moderate viscosity values were obtained. An analogous polycondensation of 1,3-propanediol was not better, whereas the polycondensation of 1,5-pentanediol was a full success, the inherent viscosity of this polyester (No. 5) was almost twice as high as that obtained from Bi-triflate-catalyzed polycondensation of 1,5-pentanediol and SuAh in bulk (18). The successful polycondensation of 1,5-pentanediol is reflected in the MT mass spectrum (Figure 3) which displays intensive mass peaks of cyclic polyesters up to 4000 Da.

3.4 Determination of the Molecular Weights

In a recent study dealing with syntheses of various poly(alkylene succinate), Mn values of a few PBSu samples were also reported. The correlation of η_{in} and M_n values deviated largely from that reported by Ueda et al. (5), but this discrepancy was not discussed.

In the present work, it was taken into account that several research groups (25–31) reported for several polylactones that direct comparison with polystyrene standards in chloroform overestimates the real molecular weights by 50–80% (depending on chemical structure and mass range). This overestimation corresponds to correction factors in the range of 0.55–0.67. In this work, when the SEC measurements of three PBSu samples were evaluated via the universal calibration method (Table 8) it was found that

Table 8. SEC measurements (chloroform at 35°C) of three poly(1,4-butylene-succinate) samples evaluated without and with universal calibration

	Direct Calibration		*Universal Calibration*			
Origin of PBSu	η^{a}_{inh} *(dL/g)*	M_n *(dDa)*	M_w *(kDa)*	M_n *(kDa)*	M_w *(kDa)*	*MSH*[b]
Aldrich Co	0.41	20	34	11.5	18.0	7.8
No. 3, Table 3[c] this work	0.61	34	58	18.0	29.0	15.5
No. 3, Table 6[d] in Ref. (18)	0.98	49	95	23.5	44.0	34.0

[a] Measured at 20°C with c = 2 g/L in CH_2Cl_2.
[b] Calculated from eq. $M_n = 3.29^* [\eta]^{1,54}$ in chloroform (17).
[c] Catalyzed by $BiCl_3$ in refluxing decalin.
[d] Catalyzed by $SnCl_2$ in refluxing decalin.

the direct calibration with polystyrene causes an overestimation of M_n and M_w by 80–100%. However, these results do not explain yet the discrepancy between our M_n values and those of Ueda et al.

For PBSu samples having inherent viscosities around 0.95–100 dL/g (in CH_2Cl_2 at 20°C) Ueda et al. reported M_ns around 200 kDa, whereas, for sample No 3, Table 6 in ref.18 Mn values of 49 kDa (Table 8) or 61 kDa (18) were measured without correction. The only explanation we can offer for this discrepancy (factor of 4!) are different starting points used for the evaluation of the elution curves. In the case of polycondensation the maximum of the frequency distribution is usually the dimeric species (regardless if linear or cyclic). Therefore, polycondensates contain a high molar fraction of oligomers, which is important for the calculation of M_n even when their mass fraction is low. If the evaluation of the elution curve begins with the mass of the dimer (around 400 Da) with a mass of 2000 Da or with a mass of 5000 Da may result in a variation of M_n by a factor of 10, whereas the influence on M_w is small. Therefore, M_n values of polycondensates published without definition of the mass range used for their calculation are absolutely meaningless. Taking also into account that the viscosity/molecular weight correlation presented in Tables 8 agree well with those of other polyesters (33) it may be concluded that the molecular weight data presented in this work and in ref. (18) are much closer to the reality than the high values reported by Ueda et al (5). This conclusion is also supported by the molecular weight data reported by Bikaris and Achilias (17) who used the Mark Houwink-Sakurada equation cited in foot note "c" of Table 8. The M_n's calculated via this equation and presented in the last column of (Table 8) deviate from those determined via universal calibration, but they belong to the same order of magnitude.

4 Conclusions

The results elaborated in this work allow for three interesting conclusions. First, the direct polycondensation of 1,4-butanediol with succinic anhydride (or succinic acid) in refluxing decalin is superior to a Bi_2O_3 catalyzed polycondensation of 1,4-butanediol and dimethyl succinate. Secondly, for polycondensations via the "decalin method" $BiCl_3$ proved to be a more useful catalyst than other Bi-salts, and $BiCl_3$ also proved superior to other non toxic catalysts such as $ZnCl_2$, Zn-triflate, $MgCl_2$, Mg-triflate or $CaCl_2$. Third, realistic molecular weight data may be obtained by polystyrene-calibrated SEC measurements when the universal calibration method is applied and the evaluation of the elution curves begins at 400-500 Da. Without universal calibration, the M_n values are overestimated by 80%, quite analogous to those of other aliphatic polyesters.

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