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Hafnium Chloride Catalyzed Polycondensation of α, ω-Alkanediol with Dicarboxylic Acids or Succinic Anhydride

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Three different kinds of polycondensation were preformed and the usefulness of $HfCl_4$.2THF as estrification and polycondensation catalyst was evaluated. It was compared with $HfCl_4$, $BiCl_3$, $LaCl_3$ and $SnCl_2$. In polycondensations of 1,6-hexandiol, and 1,10-decandiol with various dicarboxylic acids all catalysts failed to give satisfactory results. However, in polycondensations of 1,4-butanediol with succinic anhydride in refluxing decalin good results were obtained, and $HfCl_4$.2THF was the most effective catalyst after $SnCl_2$. The MALDI-TOF mass spectra revealed that cyclization made a significant contribution to the limitation of the chain growth.

Keywords: Polyester, polycondensation, hafnium, cyclization

1 Introduction

Over the past twenty years aliphatic polyesters have attracted much interest as biodegradable materials. Their syntheses can be realized by two different strategies, either by ring-opening polymerization of cyclic esters or by polycondensation of α, ω-alkanediols with aliphatic dicarboxylic acids (ADAs), their dimethyl esters and dichlorides. Polycondensation of alkanediols with ADA dichlorides in solution at temperature $\leq 20°C$ is the most versatile approach, which allows one to include secondary diols and unsaturated diols. However, this approach is expensive and unfavorable for upscaling because dry solvents and moisture sensitive ADA dichlorides are needed. Polycondensation of alkanediols with dimethyl esters of ADAs in bulk requires temperatures up to 240°C conditions which are unfavorable for low boiling monomers and thermolabile monomers. When volatile diols are used in excess, a careful and time consuming removal of this excess at high temperatures is required to achieve number average molecular weights (Mn's) above 10000 Da. Polycondensation of alkanediols with ADAs in bulk at temperature up to 240°C involves side reactions (e.g. formation of ether groups) and usually produces low molar mass polyesters (1,2). An exception concerning syntheses of poly(1,4-butylene succinate) is discussed below in more detail. Recently, low temperature polycondensations of alkanediols and ADAs were published by several research groups (3–8). Catalysts of moderate acidity such as diphenylammoniume triflate (4), various metal trifaltes (5–10), and hafnium chloride THF complex (i.e., $HfCl_4$.2THF) (11) were proposed as polycondensation catalysts. $HfCl_4$.2THF was reported to be an extraordinarily good catalyst for the esterification of alcohol and carboxylic acids. Only a few polycondensation were mentioned including one single polycondensation of an alkanediol and an aliphatic dicarboxylic acid A Mn of 20000 Da was given, but without precise description how the SEC curves were calibrated and evaluated. However, Mn data of polycondensates are meaningless if the oligomers are not included in the evaluation and the usefulness of the calibration is not established. Furthermore, no comparison with other catalyst was reported. Therefore, it was the purpose of this study to find out, if $HfCl_4$.2THF (which has meanwhile been commercialized) is an exceptional catalyst for polycondensation of alkanediols and aliphatic or aromatic dicarboxylic acids.

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2 Experimental

2.1 Materials

1,4-butanediol, 1,6-hexanediol and 1,10-decanediol were purchased from Aldrich Co. (Steinheim, Germany) and distilled in vacuum prior to use. Adipic acid, sebacic acid, isophthalic acid, and succinic anhydride (SuAh) were also purchased from Aldrich Co. and used as received. $HfCl_4$.2THF, $HfCl_4$, $BiCl_3$, $LaCl_3$ and $SnCl_2$ were again purchased from Aldrich Co. and used as received. The synthesis of 3,5-bis(3-phenylpropenyloxy) terephthalic acid was described previously (12).

2.2 Polycondensation

2.2.1. *Hexandiol and sebacic acid (No.1, Table 1), Method A*

1,6-hexanediol (50 mmol), sebacic acid (50 mmol) and $HfCl_4$.2THF (0.5 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer, gas inlet and outlet tubes. The reactor was placed into an oil bath preheated to 80°C. The reaction mixture was stirred for 1 h without vacuum, then vacuum of a membrane pump was then gradually applied and finally a vacuum of approx. 1 mbar was applied for 48 h. The resulting polyester was dissolved in approx. 100 ml of dichloromethanen and precipitated into methanol. The experiments Nos.2-8 in Table 1 were conducted analogously.

2.2.2. *1,10-decanediol and isophthalic acid (IPA) (No.9 Table 1), Method B*

1,10-decanediol (50mmol), IPA (50 mmol) and $HfCl_4$.2THF (0.5 mmol) were weighed into a 250 mL round bottom flask equipped with a magnetic bar and a Dean-Stark trap. Decalin (60 mL) was added and the reaction mixture was stirred for 1 h at 120°C. Afterwards, the temperature was rapidly raised to 220°C and maintained for 24 h. After cooling, the decalin was decanted and the product dissolved in chloroform.

2.2.3. *1,10-decanediol and isophthalic acid (IPA) (No.11, Table 1), Method C*

1,10-decanediol (40 mmol), IPA (40 mmol) and $HfCl_4$.2THF (0.4 mmol) were weighed into a 150 mL round bottom flask equipped with a magnetic stirring bar and a Dean-Stark trap. *o*-Xylene (40 mL) was added and the reaction mixture was refluxed for 24 h with azeotropic, with water removed. After decantation of the o-Xylene, the product was dissolved in chloroform and the soluble part was precipitated into methanol.

2.2.4. *1,4-butanediol and succinic anhydride (No.1 Table 2)*

1,4-butanediol (60 mmol), SuAh (60 mmol) and $HfCl_4$.2THF (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 other experiments of Table 2 were performed analogously.

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 MALDI-TOF mass spectra were measured with a Bruker "Smartbeam" mass spectrometer equipped with smart beam laser. All mass spectra were measured in the reflection

Table 1. Polycondensation of 1,6-hexanediol or 1,10-decanediol with various aliphatic or aromatic dicarboxylic acids

Exp. No	*Diol*	*Dicarboxylic acid*	*Method*^{a}	*Catalyst*	*Final Temp (°C)*	*Yield (%)*	η^b_{inh} *(dl/g)*	*Remarks*
1	1,6-hexanediol	Adipic	A	$HfCL_4$.2THF	80	0	—	—
2	1,6-hexanediol	Sebacic	A	$HfCL_4$.2THF	80	0	—	—
3	1,6-hexanediol	Sebacic	A	$HfCL_4$.2THF	100	0	—	—
4	1,6-hexanediol	Sebacic	A	Hf-triflate	80	93^c	0.35^c	Fibrous product
5	1,6-hexanediol	BPPT	A	$HfCL_4$.2THF	120	61	0.05	Fine powder
6	1,6-hexanediol	BPPT	A	Sm-triflate	120	69	0.06	Fine powder
7	1,10-decanediol	Isophthalic	A	$HfCL_4$.2THF	120	30	Partial insol	Fine powder
8	1,10-decanediol	Isophthalic	A	$SnCl_2$	120	34	Partial insol	Fine powder
9	1,10-decanediol	Isophthalic	B	$HfCL_4$.2THF	220	0	Partial insol	Fine powder
10	1,10-decanediol	Isophthalic	B	$SnCl_2$	220	24	Partial insol	Fine powder
11	1,10-decanediol	Isophthalic	C	$HfCL_4$.2THF	180	20	Partial insol	Fine powder

[a] See procedures in the Experimental part.

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

[c] Data taken from Ref. 7.

Table 2. Polycondensation of 1,4-butanediol and succinic anhydride in refluxing decalin

Exp. No	*Catalyst*	*Mon/cat*^{a}	*Yield (%)*	η^b_{inh} *(dl/g)*	M_n *(SEC) (Da)*
1	$HfCl_4$.2THF	1000/1	82	0.54	—
2	$HfCl_4$.2THF	2000/1	86	0.66	37 000
3	$HfCl_4$.2THF	2000/1	86	0.52	—
4	$HfCl_4$.2THF	4000/1	78	0.52	—
5	$HfCl_4$	1000/1	83	0.42	21 000
6	$HfCl_4$	2000/1	84	0.46	23 000
7	$BiCl_3$	1000/1	76	0.53	—
8	$BiCl_3$	2000/1	70	0.48	—
9	$BiCl_3$	4000/1	82	0.47	—
10	$LaCl_3$	1000/1	80	0.35	18 000
11	$SnCl_2$	2000/1	84	1.25^d	56 000
12	$SnCl_2$	10000/1	91^e	0.96^e	49 000

^{a}Molar feed ratios based on the sum of both monomers.
^{b}Measured at 20°C with $c = 2$ g/dl in CH_2Cl_2.

mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solution with dithranol as matrix and K-Trifluroacetate as dopant. The calculated masses of the reaction products of SuAh (Scheme 2) are listed in Table 3.

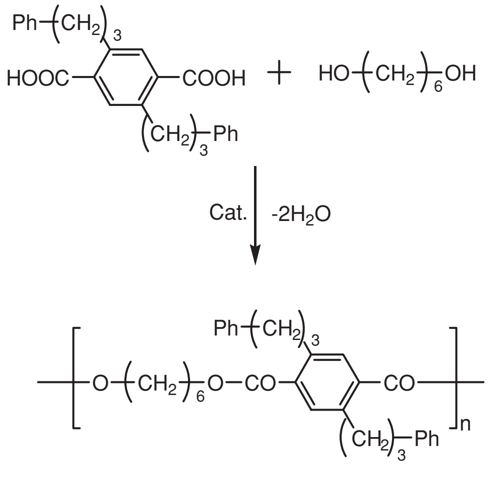
3 Results and Discussion

3.1 Polycondensation of Dicarboxylic Acids

The experiments of this work may be subdivided into two groups, polycondensation of dicarboxylic acids with α, ω-alkanediols and polycondensation of succinic anhydride (SuAh). Polyesters of succinic acid play an outstanding role as biodegradable polyesters, but at first, polycondensations of dicarboxylic acids should be discussed. Three experiments were conducted with 1,6-hexanediol and adipic acid or sebacic acid as reaction partners (Nos 1–3, Table 1). These polycondensation were performed in bulk with removal of the liberated water in vacuum. Numerous such polycondensations were recently studied based on metal triflates as catalyst (5–10). With bismuth or samarium trifalte inherent viscosity around 0.6 dL/g were obtained (7,8). The reaction mixtures resulting from $HfCl_4$.2THF catalyzed polycondensation of this work did not even yield low molar mass polyester when precipitated into methanol. A significantly better result was achieved with Hf-triflate (No. 4 Table 1) confirming that for polycondensation of α, ω-alkanediol and ADAs in bulk metal triflates are far superior to $HfCl_4$.2THF as catalyst. Furthermore, polycondensation were performed with aromatic dicarboxylic acids. BPPT (see Scheme 1) was used instead of unsubstituted terephthalic acid to obtain a homogenous reaction mixture at temperatures below 150°C with terephthalic acid homogenization below 200°C was not expected. Using 1,6-hexanediol as comonomer homogeneous reaction mixtures was indeed obtained at 120°C (Nos. 5+6, Table 1). Yet only low oligomers were formed regardless if $HfCl_4$.2THF or Sm-triflate were used as catalysts. A higher temperature did not significantly raise the molecular weight. Finally, the combination of 1,10-decanediol plus isophthalic acid was used for five experiments because this combination was also used by Ishihara et al.(11). Three different sets of reaction conditions were studied, namely polycondensation in bulk with vacuum (as in all experiments before, method A), polycondensation in refluxing decalin with azeotropic removal of water (Nos. 9 and 10) and finally polycondensation under conditions resembling the procedure given in the science article (11). In two experiments, $SnCl_2$ was used as catalyst for comparison. Regardless of catalyst and method low yield of a fine powder were obtained, what means that only oligomers were formed. A small amount of solid particles were detected in CH_2Cl_2 solutions which prevent exact viscosity measurements. After filtration, this solid material was identified by IR and 1H-NMP spectroscopy as unreacted isophthalic acid. Nonetheless, all experiments listed in Table 1 may be summed by saying that $HFCl_4$.2THF was useless as catalyst for polycondensation of dicarboxylic acids and α, ω- alkanediol.

Table 3. Mass calculated (incl. Na-doping) for the reaction products of SuAh and 1,4-butanediols (for symbols see Scheme 2)

DP	*C*	*La*	*Lb*	*Lc*
5	883.9	901.9	973.9	1001.9
6	1056.1	1074.1	1146.1	1174.1
7	1228.3	1246.3	1318.3	1346.3
8	1400.5	1418.5	1490.5	1518.5
9	1572.6	1590.6	1662.6	1690.6
10	1744.8	1762.8	1834.8	1862.8



Sch. 1. Polycondensation of 1,6-hexanediol and BPPT.

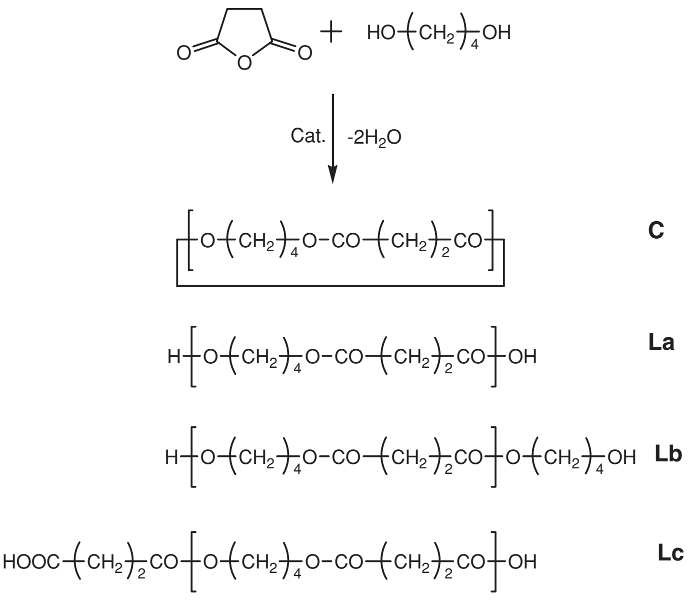
Concerning the procedure presented by Ishihara et al. (11), it should be mentioned that it was described by quantities of 10 mmol of each monomer in combination with 2 ml of o-xylene as reaction medium. This procedure does not allow for upscaling in the usual way, because the amount of solvent does not suffice to use the standard equipment for the removal of water, namely a dean-stark trap in combination with a reflux condenser. Furthermore, the large amount of the extremely expensive HfCl4.2THF needed for this procedure is prohibitive for any upscaling.

3.2 Polycondensation of 1,4-butanediol and SuAh

Poly(butylenes succinate) is an important and commercially available polyester for three reasons. First, succinic acid is a monomer which can technically be produced from renewable resources. Second, its rate of hydrolytic, (bio)degradation is higher than that of all polyesters derived from longer dicarboxylic acids. It is thus comparable to that of polylactide. Third, it's melting temperature (120°C) and thus it's distortion temperature is higher than those of polysuccinates of all other α, ω-alkanediol and higher than that of all aliphatic polyesters derived from longer dicarboxylic acids. Commercial poly(butylenes succinate) (e.g. the product offered by Aldrich Co) is prepared by chain extension of telechelic oligomers with 1,6-hexamethylene diisocyanate. A simple procedure leading to high molar mass poly(butylenes succinate) in one step is thus highly desirable. Previous studies have shown that polycondensations of 1,4-butanediol succinic acid or SuAh in refluxing decalin may give excellent results (13). Ueda et al., who described this procedure for first time, achieved high molecular weights (η_{inh} around 0.9–1.1 dl/g in CH_2Cl_2) but they used highly toxic tin catalyst such as $SnCl_2$ or distannoxanes. Quite recently, it was found that the non-toxic $BiCl_3$ yields polyesters having η_{inh} values up to 0.6 dl/g (10). In this work, $HfCl_4.2THF$ catalyzed polycondensation were compared with $HfCl_4$, $BiCl_3$, $LaCL_3$ and $SnCl_2$catalyzed ones under identical conditions (see Table 2). When the monomer/catalyst ratio was varied (Nos. 1–4. Table 2) the viscosity values passed flat maximum at 2000/1. The experiments Nos 7–9 confirmed previous results which evidenced a flat maximum of the viscosity value of $BiCl_3$-catalyzed polycondensations at 1000/1. Interestingly, the inherent viscosities resulting from $HfCl_4$-catalyzed polycondensation were lower than those achieved with $HfCl_4.2THF$. this observation agrees with data reported by Ishihara et al. who also found a slightly higher esterification activity of $HfCl_4.2THF$. The highest viscosity value was achieved with $SnCl_2$ as catalyst in agreement with previous experiment (10). In other words, the catalytic activity of the metal chlorides used in this work decreased in the following order:

$$SnCl_2 > HfCl_4 \cdot 2THF > BiCl_3 > HfCl_4 > LaCl_3$$

Finally, MALDI-TOF mass spectra of two samples having almost identical viscosity values (Nos 1 and 7) were measured to compare the extent of cyclization. According to the theory of Stepto (14), Gordon (15) and Kricheldorf (16,17) the extent of cyclization (and the molecular weight) increase with conversion. Therefore, two polycondensation of identical structure and identical molecular weight should contain identical fractions of cycles. A deviation from this simple correlation was found for metal triflate catalyzed polycondensation of α, ω-alkanediol and SuAh (10) or citraconic anhydride (19). Sm-triflate yielded larger fraction of cycles than other metal triflates. Since such polycondensations involve both esterification and transestrification reactions different activities of catalyst in both reactions may be responsible for a different extent of cyclization.



Sch. 2. Potential reaction product of polycondensation of 1,4-butanediol and succinic anhydride.

The MT mass spectra of samples No 1 and 7 were almost identical and the spectrum of sample No 1 is presented in Figure 2. The mass peaks of cyclic polyesters were predominant below 4000 Da, but weak peaks of **La** and **Lc** chains (for definition see Scheme 2) were also observable. In contrast, The MT mass spectrum of sample No 10 presented in Figure 1 displays intensive peaks of **La** and **Lc** chains (with Na and K doping), whereas the peaks of the cycles were weak. The peaks of **Lb** chains were particularly weak in the spectra of Figures 1 and 2, because small amounts of 1,4-butanediol were lost from the reaction mixture after cyclization to THF as discussed prviously (10). In the case of the high molar mass sample No 11 (Table 2) only peaks of cycles are detectable below 4000 Da in the MT mass spectrum. Therefore, the comparison of Figures 1, 2 and 3 illustrates the correlation cited above: the extent of cyclization increases with conversion and molecular weight. These mass spectra also suggest that for polyester having inherent viscosites above 0.5 dl/g cyclization made a significant contribution to the limitation of the chain growth.

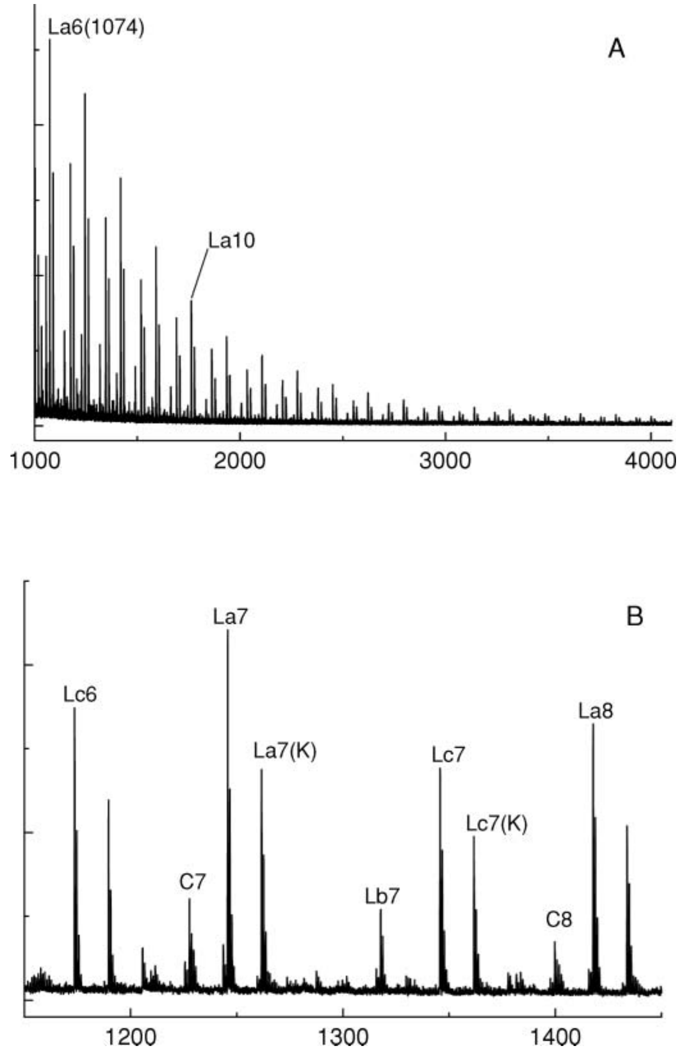


Fig. 1. MALDI-TOF mass spectrum of the poly(butylene succinate) prepared by means of $LaCl_3$ (No. 10, Table 2).

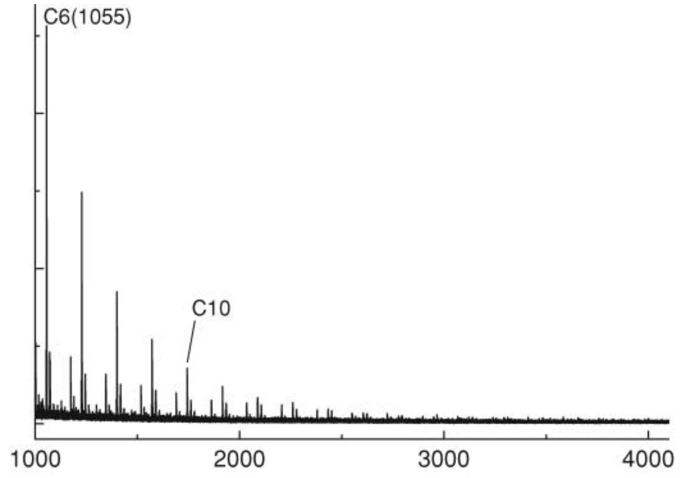


Fig. 2. MALDI-TOF mass spectrum of the poly(butylene succinate) prepared by means of $HfCl_4.2THF$ (No. 1, Table 2).

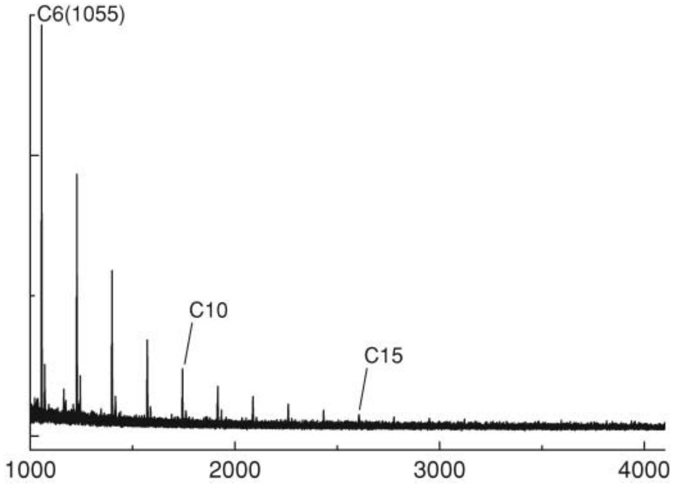


Fig. 3. MALDI-TOF mass spectrum of the poly(butylene succinate) prepared by means of $SnCl_2$ (No. 11, Table 2).

Concerning the number average molecular weights (M_n‘s) presented in Table 2 it should be mentioned that polystyrene-calibrated SEC measurements overestimate the real M_n’s by 50–80%. This correlation has been found by numerous researchbgroups using a variety of analytical methods. By means of the universal calibration method we have recently found that (19) that the overestimation of approximately 80% is also true for poly(butylene succinate). Using a correlation factor of 0.6 the real M_n of sample No 10 (Table 2) should be close to 11 000 Da, the real M_n of No 2 (Table 2) close to 22 500 Da and the real M_n of No 11 (Table 2) around 34 000 Da.

4 Conclusions

The results of the present work clearly demonstrate that $HfCl_4.2THF$ is not the exceptionally good catalyst for polyester syntheses suggested by the paper of Ishihara, et al., in polycondensation of α, ω-alkanediol with dicarboxylic acids it is totally ineffective and inferior to metal triflates. In polycondensation of SuAh, according to the decalin method, $HfCl_4.2THF$ gives satisfactory results, but the molecular weights are considerably lower than those obtained with $SnCl_2$, and $BiCl_3$ which gives lower molecular weight and has the advantage of lower toxicity.

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