Aliphatic Polyesters by Bismuth Triflate-Catalyzed Polycondensations of Dicarboxylic Acids and Aliphatic Diols

Pavel Buzin,[†] Mohammed Lahcini,[‡] Gert Schwarz,[§] and Hans R. Kricheldorf*[,§]

Institute of Problems of Chemical Physics (IPCP RAS), Acad. Semenov av. 1, Chernogolovka, Moscow region 142432, Russian Federation, Laboratoire de Chimie Bioorganique et Macromoléculaire, Faculté des Sciences et Techniques Marrakech, Bld Abdelkarim Khattabi, 40000 Marrakech, Maroc, and Institut für Technische and Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, Germany

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ABSTRACT: Polycondensations of aliphatic dicarboxylic acids (ADAs) with 1,4-butane or 1,6-hexane diol were conducted in bulk at 80 or 100 °C. Temperature and monomer/catalyst ratio were varied. With bismuth triflate, $Bi(OTf)_3$, as catalyst, number average molecular weights (M_n's, uncorrected SEC data) up to 30 000 Da were obtained. Analogous polycondensations were performed with the triflates of sodium, magnesium, aluminum, zinc, tin(II), scandium, and hafnium, but the highest M_n values were achieved with $Bi(OTf)_3$. Polycondensations and model experiments proved that most triflates catalyzed the formation of tetrahydrofuran from 1,4-butane diol above 100 °C. Therefore, polycondensations of 1,4-butane diol required temperatures ≤100 °C. Polycondensations of 1,4-butene diol or 1,4-butyne diol were unsuccessful, because of side reactions. All polycondensations involved rapid equilibrations, and the content of cyclic oligo- and polyesters increased with the conversion.

Introduction

Polyesters derived from aliphatic diols and aliphatic dicarboxylic acids (ADAs) are crystalline, biodegradable materials, which represent an alternative to biodegradable polyesters derived from lactones or cyclic diesters. The major problem is to find a convenient, inexpensive synthetic method avoiding toxic catalysts. The three standard methods known for the preparation of aliphatic polyesters have the following characteristic disadvantages. First, transesterification of diols with dimethyl esters of ADAs requires high temperatures (up to 240 °C) for high conversions.[1] At such high temperatures, the volatility of numerous monomers such as ethane diol or dimethyl esters of succinic and adipic acid is a serious problem, and depending on the catalyst ether groups may be formed.[1] Furthermore, the aliphatic polyesters are sensitive to oxidation by traces of oxygen. Second, the acid-catalyzed polycondensations of diols and ADAs with azeotropic removal of water by aromatic solvents[2−4] favor cyclization due to dilution and may yield high fractions of ether groups by proton-catalyzed reaction of two alcohols. Third, polycondensations of diols with dicarboxylic acid dichlorides require dry inert solvents. Furthermore, the ADA dichlorides are expensive and sensitive to hydrolysis and prone to side reactions such as β-elimination of HCl. Finally, due to polycondensation in solution, the chain growth is limited by cyclization.[5]

A relatively new approach working under mild conditions is the enzymatic polycondensation of ADAs and diols by means of nonspecific lipases.[6−8] However, rather large amounts (e.g., 1 wt %) of an expensive enzyme are required, and this catalyst needs to be separated from the reaction product at the end of the polycondensation.

Another new method allowing for the direct polycondensation of ADAs under mild conditions (e.g., 35 °C) was reported by Takasu et al.[9,10] Those authors condensed mixtures of methyl succinic acid with various diols by means of scandium-triflate ($Sc(OTf)_3$) in bulk and removed the liberated water by applying vacuum for a period of 3 days. This method is not applicable to most polyesters of unsubstituted ADAs, because they are crystalline with melting temperature (T_m's) ≥ 50 °C. Furthermore, number average molecular weights (M_n's) in the range of 1000−14 000 Da were reported determined by polystyrene-calibrated SEC measurements. Yet, those authors ignored that this method overestimates the M_n's of aliphatic polyesters by at least 50% above 10^4 Da and up to 100% below 10^4 Da[11−16] (see discussion below). This means that the real molecular weights fall into the range of 600−8000 Da, which is too low for most applications.

The present work served the following purposes. First, reaction conditions allowing for the preparation of crystalline aliphatic polyesters should be elaborated. Second, the usefulness of Bi triflate should be elucidated, because the $Bi^{3\oplus}$ ion is the least toxic heavy metal ion.[17−19] This property is particularly important, when applications of the polyesters in pharmacy, human, or veterinarian medicine and in agriculture are considered. Third, formation of ether groups should be kept on a low level. Fourth, real M_n's around or above 10 000 Da should be achieved. Numerous applications of Bi triflate in organic syntheses including acetylation of various alcohols by acetic anhydride were recently reviewed.[20]

Experimental Section

Materials. 1,4-Butane diol, 1,4-butene diol, 1,4-butyne diol, 1,6-hexane diol, 1,4-cyclohexane diol, 4-(hydroxymethyl) benzyl alcohol, succinic, adipic, suberic, sebacic, and 1,10-decane dicarboxylic acid were all purchased from Alpha Aesar (Karlsruhe, Germany) and used as received. Triflic acid and the metal triflates listed in Table 3 were also purchased from Alpha Aesar and used as received. Bis(β-hydroxyethyl) terephthalate was prepared by transesterification of dimethyl terephthalate with an excess of ethylene glycol as described in the literature.[21] Its purity was checked by ^{1}H NMR spectroscopy.

Polycondensations. 1,6-Hexane diol (50 mmol), sebacic acid (50 mmol), and Bitriflate (0.5 mmol) were weighed in a cyclindrical glass reactor equipped with a mechanical stirrer and gas-inlet and outlet tubes. Dioxane (5 mL) was injected to accelerate the homogenization of the reaction mixture. The reaction vessel was

* Corresponding author. E-mail: kricheld@chemie.uni-hamburg.de.
† Institute of Problems of Chemical Physics.
‡ Laboratoire de Chimie Bioorganique et Macromoléculaire.
§ Universität Hamburg.

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Table 1. Polycondensations of Sebacic Acid and 1,6-Hexane Diol in Bulk with Variation of Temperature and Time[a]

expt. no.	temperature (°C)	time (h)	yield (%)	η_{inh}[b] (dL/g)	M_n[c](SEC)	M_n[d](corrected)	PD
1	80	8	87.0	0.27			
2	80	24	90.0	0.43			
3	80	48	93.0	0.55	29 000	19 500	1.64
4	80	72	93.5	0.56	29 500	20 000	1.65
5	100	48	95.0	0.39	20 000	13 500	1.75
6	120	48	93.5	0.32	16 700	11 100	1.75
7	140	48	88.0	0.21	11 000	7400	1.50
8	160	48	86.0	0.10			

[a] Molar monomer catalyst ratio = 200/1. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] Polystyrene-calibrated SEC measurements. [d] SEC data multiplied by 0.67.

Table 2. Polycondensations of Sebacic Acid and 1,6-Hexane Diol in Bulk with Variation of the Molar Monomer/Catalyst Ratio[a]

expt. no.	mon/cat	yield (%)	η_{inh}[b] (dL/g)	M_n[c] (SEC)	M_n[d] (corrected)	PD
1	1000/1	92.2	0.30	16 000	11 000	1.75
2	600/1	93.5	0.35			
3	400/1	94.4	0.40	20 000	13 500	1.75
4	200/1	92.8	0.55	29 000	19 500	1.65
5	150/1	95.0	0.50	25 000	16 700	1.75
6	100/1	94.0	0.40	21 000	14 000	1.75
7[e]	150/1[e]	95.2	0.24	12 000	8100	1.85
8[e]	100/1[e]	96.5	0.26			

[a] Reaction conditions: 80 °C, 48 h. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] Polystyrene-calibrated SEC measurements. [d] SEC data multiplied by 0.67. [e] Scandium triflate was used as catalyst.

Table 3. Polycondensations of 1,6-Hexane Diol and Sebacic Acid in Bulk with Variation of the Catalyst[a]

expt. no.	catalyst	pH[b]	yield (%)	η_{inh}[c] (dL/g)
1			0	
2	NaOTf	10.15	0	
3	$Mg(OTf)_2$	4.15	0	
4	$Zn(OTf)_2$	5.95	89.0	0.15
5	$Al(OTf)_3$	3.90	93.5	0.43
6	$Sc(OTf)_3$	3.15	93.0	0.30
7	$Sn(OTf)_2$	1.80	92.0	0.27
8	$Bi(OTf)_3$	1.05	94.0	0.57
9	$Hf(OTf)_4$	<0.97	93.0	0.35
10	triflic acid	<0.50	96.5	0.22

[a] Reaction conditions: 80 °C, 48 h. Monomer/catalyst ratio: 200/1. [b] Metal triflate concentration = 0.05 mol/L at 20 °C. [c] Measured at 22 °C with c = 2 g/L in CH_2Cl_2.

placed into an oil bath preheated to 80 °C, and the reaction mixture was stirred for 0.5 h at normal pressure. Afterward, vacuum was gradually applied, so that dioxane and water were slowly removed. Finally, a vacuum of approximately 1 mbar was applied for 48 h. The highly viscous reaction product was dissolved in CH_2Cl_2 and precipitated into methanol. In the case of higher reaction temperatures (Table 1), the temperature was raised, after evacuation at 80 °C for 0.5 h.

Model Experiments with 1,4-Butane Diol. 1,4-Butane diol (50 mmol) and a catalyst (Table 6, 0.25 mmol) were weighed into a 50 mL Erlenmeyer flask, and a magnetic bar was added. The reaction vessels were closed with glass stopper and steel spring and immersed into an oil bath preheated to 120 °C. After 1 h, the reaction mixture was cooled and a ^{1}H NMR spectrum was recorded.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostatted at 20 °C. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker "Avance 400" FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent. The MALDI-TOF (MT) mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All spectra were recorded in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and potassium trifluoroacetate as dopant. The SEC measurements were performed on an apparatus of Polymer Laboratories equipped with a RI detector "Shodex RI 101". A combination of three PC mixed bed columns was used with chloroform as eluent (flow rate 1.0 mL/min). Commercial polystyrene standards served for calibration. The pH measurements were performed with a HANNA instrument HI 991001 equipped with a pH probe HI 1296 D. The pH meter was calibrated with buffer solutions prior to the measurements.

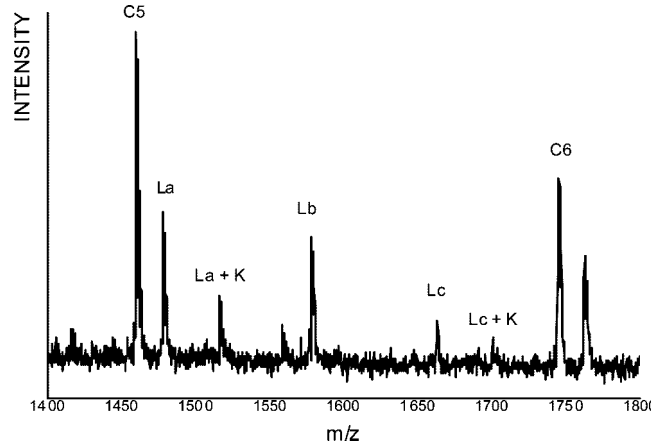
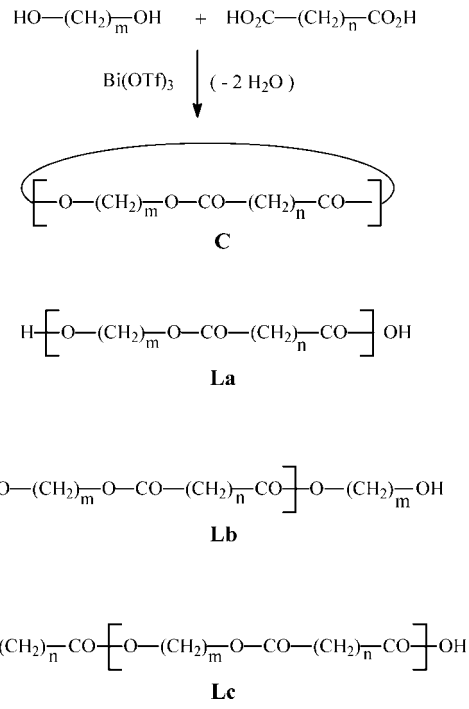


Figure 1. MALDI-TOF mass spectrum of the poly(hexane diol sebacate) prepared with $Bi(OTf)_3$ at 80 °C/8 h (no. 1, Table 1). The peak assignments are explained in Scheme 1.

Results and Discussion

Most polyesters based on alkane diols and aliphatic dicarboxylic acids (ADAs) are crystalline and possess melting temperatures (T_m's) ≤ 80 °C. Therefore, 80 °C was used as the minimum reaction temperature in this work. A low reaction temperature has the additional advantage that the significant loss of diols is avoided, when vacuum is applied to remove the liberated water. To find optimum reaction conditions, a first series of polycondensations was conducted with variation of time at 80 °C (nos. 1−4, Table 1). The highest molecular weight was achieved at the longest time, but the difference between the 48 h and the 72 h experiments was so small that all further experiments were performed with a reaction time of 48 h. As illustrated by the MT mass spectrum of Figure 1, significant amounts of cyclic oligoesters were already formed after 8 h at least in the mass range below 3000 Da. Furthermore, the three peaks of linear chains having CH_2OH and/or CO_2H endgroups (**La**, **Lb**, **Lc** in Scheme 1) were present as expected for a normal "$a_2 + b_2$" polycondensation. Two additional weaker peaks represented the potassium salts of **La** and **Lc** chains and were labeled **LaK** and **LcK** in Figure 1. The potassium salts resulted from reactions of the polymers with the excess of potassium trifluoroacetate used as dopant. With higher conversions, the peak intensities of the cyclic polymers increased at the expense of the "linear peaks", and in the case of sample nos. 3 and 4, the cycles were detectable up to 7000 Da, the technical limit of these measurements. This observation also means that cyclization had a significant influence on the limitation of the chain growth. When the temperature was varied at a fixed time of

Scheme 1. Reaction Products of $Bi(OTf)_3$-Catalyzed Polycondensations of Alkane Diols and Dicarboxylic Acids



48 h (nos. 5−8, Table 1), the lowest temperature (i.e., 80 °C) was surprisingly found to yield the highest molar mass, although the conversion was not complete at 80 °C after 48 or 72 h as indicated by the MT mass spectra. Apparently, higher temperatures accelerate side reactions. This interpretation was supported by the observation that the polyesters prepared at 120, 140, and 160 °C turned grayish and finally black. Redox reactions of the Bi^{3+} cation yielding elementary bismuth might be responsible for this effect.

In a second series of polycondensations, the monomer catalyst ratio was varied (Table 2), whereby the maximum molecular weight (M_n = number average) was achieved at a M/C ratio of 200/1. Therefore, this M/C ratio was used for all further polycondensations of this work. Two polycondensations of Table 2 were performed with Sc-triflate to find out how this previously recommended catalyst[5] compares to Bi triflate. Both polycondensations (nos. 7 + 8) yielded significantly lower molecular weights, indicating that $Bi^{3\oplus}$ combines two advantages: a lower toxicity and a higher efficiency as esterification catalyst. This conclusion was confirmed by a third series of polycondensations, which was designed to compare Bi triflate with a broader variety of catalysts (Table 3). In addition to the catalyst-free control experiment no. 1, the polycondensations doped with sodium or magnesium triflate failed to yield a polyester. Four more results are worth noting. First, the highest molar mass was achieved with the Bitriflate-catalyzed polycondensation (no. 8, Table 3). This experiment is not identical to experiment no. 2 in Table 1. Experiment no. 8, Table 3 was conducted by another co-worker to check the reproducibility of polycondensation no. 2, Table 1, which was found to be satisfactory. Second, another experiment with Sc-triflate (no. 6, Table 3) confirmed that Bitriflate is the more efficient catalyst. Third, because the experiments of Takasu et al. evidenced that Sc-triflate is a more efficient esterification catalyst than samarium, yttrium, and ytterbium triflate, the experiments indirectly include a comparison of Bitriflate with those three metal triflates. Fourth, the pH values of all triflates were measured in water around 20 °C at a concentration matching their concentration in the polycondensation experiments. The experiments listed in Table 3 were listed according to these pH values to find out if the efficiency of the catalysts directly parallels their acidity. Such a correlation was indeed found as an overriding trend, but interesting deviations from this trend were also observed. For instance, $Zn(OTf)_2$, although more basic than $Mg_2(OTf)$, yielded a polyester, and the molar mass obtained with the most acidic triflate (i.e., Hf triflate) was significantly lower than that achieved with Bi triflate. Apparently, the reaction mechanism is not only based on a simple proton-catalyzed esterification mechanism, but involves complexation of monomers by metal ions. However, the poor performance of triflic acid may be ascribed to its volatility.

On the basis of the optimized reaction conditions, 1,6-hexane diol was successfully polycondensed with various α,ω-dicarboxylic acids (Table 4). Because of the higher melting temperatures of polyesters derived from succinic acid, the reaction temperature of experiment no. 1 was raised to 120 °C. Regardless of the reaction temperature, the ^1H NMR spectroscopic characterization of the isolated polyesters indicated the absence of ether groups. At this point, it should also be mentioned that in all experiments a small amount of dioxane was added to the monomer mixture to accelerate the homogenization (i.e., dissolution of the dicarboxylic acid).

In a fifth series of experiments, sebacic acid was polycondensed with a variety of diols (Table 5). 1,4-Butane diol (no. 1) was selected, because it is sensitive to an acid-catalyzed dehydration yielding tetrahydrofuran. It was previously demonstrated[12] that $BiCl_3$ catalyzed this cyclization above 120 °C. However, the polycondensation at 80 °C was successful, and in a model experiment (stirring neat 1,4-butane diol with Bitriflate at 80 °C for 24 h) no THF was detectable. In this connection, the results of Takasu et al. need discussion. Those authors reported relatively high M_n's (20 000 and 30 000 Da; uncorrected SEC data) for Sc-triflate-catalyzed polycondensations of 1,4-butane diol with succinic acid at 160 or 180 °C. These polycondensations were not reproducible in our hands, and the reason for this failure is explained by the results of model experiments listed in Table 6. Various metal triflates and triflic acid were added to neat 1,4-butane diol at a concentration corresponding to that in the polycondensation experiments. The evaluation of the virgin reaction mixtures by ^1H NMR spectroscopy revealed that Sc-triflate like Al-triflate and all more acidic catalysts produced THF in large quantities after 1 h at 120 °C. Not unexpected, the highest conversion was observed for triflic acid (Figure 2). As illustrated in Figure 3 for the Bitriflate-catalyzed reaction, all acidic metal triflates yielded complex reaction mixtures containing cyclic and/or linear oligoethers in addition to THF. Regardless of the exact composition of the reaction mixtures, the model experiments compiled in Table 6 clearly indicate why acid-catalyzed polycondensations of 1,4-butane diol at temperatures above 100 °C are unsuccessful.

Bitriflate-catalyzed polycondensations of sebacic acid with 1,4-butene diol or 1,4-butyne diol also proved to be unsuccessful even at 80 °C (nos. 2 + 3, Table 5). Black tars were obtained in both experiments. Black viscous oils were also obtained with triflic acid as catalyst (not listed in Table 5), and thus the failure of these polycondensations is not characteristic for Bi triflate, but seems to be typical for acid-catalyzed polycondensations of these unsaturated diols.

Under acidic conditions, terephthalyl alcohol easily yields benzyl (tropylium) cations, which may cause side reactions such as formation of ether groups and alkylation of the benzene ring. Therefore, the formation of a gel in experiment no. 4 (Table 5) was not surprising. 1,4-Cyclohexane diol yielded a polyester, but the molecular weight was low. Obviously the lower reactivity of the secondary alcohol group played an important

Table 4. Polycondensations of Hexane Diol with Different Dicarboxylic Acids in Bulk[a]

expt. no.	dicarboxylic acid	yield (%)	η_{inh}[b] (dL/g)	M_n[c] (SEC)	M_n[d](corrected)	PD
1[d]	succinic acid[d]	95.2	0.35	18 500	12 400	1.75
2	adipic acid	93.4	0.38	19 000	12 800	1.70
3	sebacic acid	92.8	0.55	29 000	19 500	1.55
4	dodecandicarboxylic acid	96.8	0.46	24 000	16 000	1.79

[a] Reaction conditions: 80 °C, 48 h. Monomer/catalyst ratio: 200/1. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] Polystyrene-calibrated SEC measurements. [d] SEC data multiplied by 0.67.

Table 5. Polycondensations of Sebacic Acid with Various Diols in Bulk[a]

expt. no.	diol	yield (%)	η_{inh}[b] (dL/g)
1	butane-1,4-diol[c]	93	0.30[c]
2	2-butene-1,4-diol		black liquid
3	2-butyne-1,4-diol		black liquid
4	1,4-cyclohexane diol[d] (cis/trans: 1/1)	84.5	0.18[d]
5	4-(hydroxymethyl)- benzylalcohol		gel
6	bis(β-hydroxy ethyl) terephthalat	89.0	0.25

[a] Reaction conditions: 80 °C, 48 h. Monomer/catalyst ratio: 200/1. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] $M_n = 16\,000$, PD = 1.70 (uncorrected SEC data). [d] $M_n = 3500$, PD = 1.40.

Table 6. Formation of Tetrahydrofuran (THF) from 1,4-Butane Diol after 1 h at 120 °C

expt. no.	catalyst	pH at 22 °C	THF (mol %)	linear ether groups
1	Na-triflate	10.15	≈0	−
2	Zn-triflate	5.95	≈0	−
3	Mg-triflate	4.45	≈0	−
4	Al-triflate	3.90	∼45	+
5	Sc-triflate	3.15	∼35	+
6	Sn-triflate	1.80	∼35	+
7	Bitriflate	1.05	∼35	+
8	Hf-triflate	0.95	∼50	+
9	triflic acid	<0.50	∼35	+

role, but a realistic mechanistic concept explaining this result in more detail cannot be forwarded at this time. In the last experiment of this series, bis(2-hydroxyethyl) terephthalate served as reaction partner of sebacic acid. A clean polycondensation without transesterification should result in a crystalline copolyester having an alternating sequence of the different dicarboxylic acids. As demonstrated previously,[21] the ^{1}H NMR signals of the O−CH_2 protons allow a straightforward differentiation between alternating and random sequences. The ^{1}H NMR spectrum of sample no. 6 (Table 5) indicated a nearly perfect random sequence as expected for a polycondensation involving reversible esterification/hydrolysis reactions. This result also means that this new synthetic procedure allows for the preparation of numerous random copolyesters from mixtures of different ADAs and for mixtures of different diols.

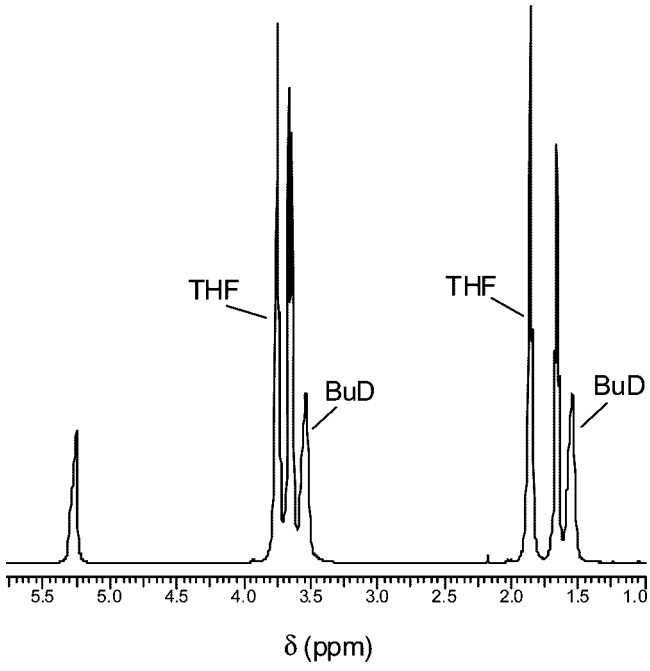


Figure 2. 400 MHz ^{1}H NMR spectrum of 1,4-butane diol after heating with trifluoroacid for 1 h at 120 °C.

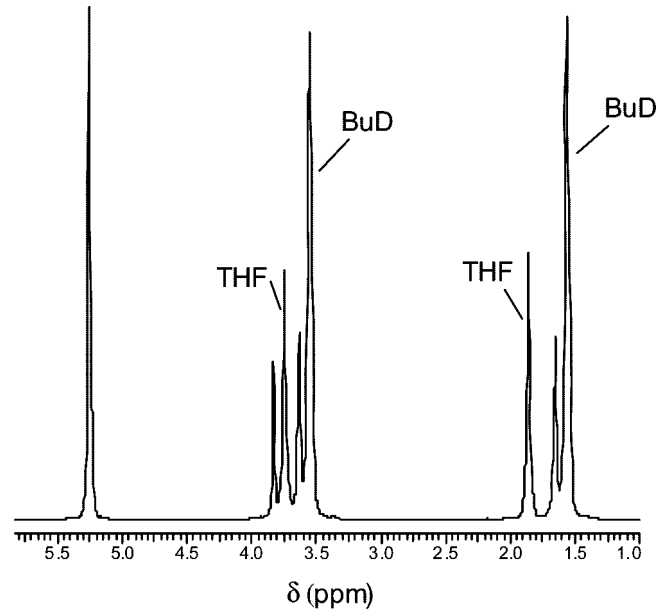


Figure 3. 400 MHz ^{1}H NMR spectrum of 1,4-butane diol after heating with $Bi(OTf)_3$ for 1 h at 120 °C.

Finally, the molecular weight measurements need a short discussion. It is known from the work of several research groups[11−16] that polystyrene-calibrated SEC measurements overestimate the real molecular weights of aliphatic polyester (e.g., poly ε-caprolactone) by at least 50% for M_n's above 10^4 Da and up to 80% for M_n's below 10^4 Da. Therefore, two series of M_n data were listed in Tables 1, 2, and 4, the original SEC measurements and "corrected" M_n's. These "corrected" M_n's were derived from the original M_n's by multiplication by a correction factor of 0.67, eliminating an overestimation of 50%. This overestimation means that the hydrodynamic volume of unsubstituted aliphatic polyesters is higher and the coil density lower than in the case of polystyrene. However, the hydrodynamic volume of cyclic polymers is lower (and the coil density higher) than that of the corresponding linear polymers. Hence, the overestimation of the molecular weights resulting from calibration with polystyrene is reduced, when a significant fraction of cycles is present. In other words, the real M_n's of the polyesters presented in this work are somewhat higher than the corrected M_n's. Yet, the content of cycles varies from sample to sample, and a routine method allowing for the quantification of cycles is not available, and thus modification of M_n values with regard to the content of cyclic polyesters was not feasible. Anyway, it is a satisfactory result of this work that both series of M_n values indicate that most polyesters possess molar masses above 10^4 Da, which justifies the label polymer according to the definition of Staudinger. Regardless of definitions, flexible

tough films were obtained, when the corrected M_n's of the aliphatic polyesters reached values around or above 13 000 Da. The finding that all polyesters gave polydispersities (PDs) below 2.0 is a consequence of the fact that upon precipitation part of the oligomers remained in solution.

Conclusion

The results of the present work demonstrate that Bi triflate is a useful catalyst for the preparation of aliphatic polyesters by polycondensation of α,ω-alkane diols with aliphatic dicarboxylic acids. Number average molecular weights (corrected M_n's) in the range of 10 000−20 000 Da can be obtained, which form coherent films. Because commercial chemicals may be used without further purification or drying, the procedure is so simple that it allows for upscaling to a technical production.

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