Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 6433–6439 **6433**
DOI: 10.1021/ma9009356

Isomerization-Free Polycondensations of Maleic Anhydride with α,ω-Alkanediols

Hans R. Kricheldorf,*,† Takao Yashiro,†,‡ and Steffen Weidner§

†*Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, D-20146 Hamburg, Germany,* ‡*JSR Corporation, Miyukigaoka 25, Tsukuba, Ibaraki, 305-0841 Japan, and* §*Bundesanstalt für Materialforschung u. – prüfung (BAM), Fed. Inst. Material Research and Testing, 1.35 "Polymer Analysis", Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany*

Received May 18, 2009; Revised Manuscript Received July 9, 2009

ABSTRACT: Maleic anhydride (MaAh) was polycondensed with 1,6-hexanediol in bulk at 60, 100, or 140 °C. The triflates of lanthanum, samarium, magnesium, aluminum, scandium, tin(II), and bismuth were used as catalysts, whereby the acidity of the catalysts increased in the given order. At 60 °C, low molar masses (number average, M_n < 5 kDa) were obtained, but side reactions such as formation of ether groups and fumarate units were avoided. At 100 °C, weak side reactions were detectable for all acidic catalysts, but the highest molar masses of this work (M_n up to 12 kDa) were achieved at this temperature. With the exception of the basic La triflate, all catalysts caused an intensive side reaction at 140 °C. The MALDI-TOF mass spectra of the best products obtained at 100 °C revealed a high extent of cyclization that made a significant contribution to the limitation of the chain growth, which was pronounced when 1,6-hexanediol was replaced by 1,4-butanediol. The observed side reactions and activities of the catalysts suggest that the reaction mechanism involves complexation of carboxylic groups by metal ions and that Bi triflate causes side reactions of the C−C double bond.

Introduction

Unsaturated polyesters are an important class of technically produced specialty polymers that are used for coatings and insulating laquers.[1−3] The most widely used unsaturated monomer is maleic anhydride (MaAH), which partially isomerizes to fumaric ester units when the polycondensations are performed at temperatures in the range of 150−200 °C (as usual). These unsaturated moieties are decisive for an efficient curing process at moderate temperatures (typically <180 °C). To study the properties of stereochemically uniform polyesters of maleic acid and fumaric acid, a French/Yugoslavian research group prepared such polyesters by polyalkylation of potassium or cesium maleate or fumarate (Scheme 1) at temperatures <120 °C.[4−13] At these relatively low temperatures and in the absence of strong acids or strong bases, isomerization was totally avoided when *N*-methylpyrrolidone was used as solvent. Those authors studied various properties of homo- and copolyesters including solution and melt viscosities. It was found that the viscosities of polymaleates are considerably lower than those of polyfumarates having identical molar masses. For certain applications (e.g., as insulating lacquers), a low melt viscosity is advantageous and, thus, polyesters of maleic acid almost free of fumaric acid are not only of academic interest. However, any technical application requires a solvent-free, inexpensive synthetic procedure and the method elaborated by the French/Yugoslavian group does not meet these requirements.

A few years ago, Takasu reported[14,15] that Sc triflate catalyzes polycondensations of methyl succinic acid and various α,ω-alkanediols at temperatures as low as 35 °C, so that polyesters having corrected number average molecular weights (M_ns, see Results and Discussion below) in the range of 800 to 8000 Da can be obtained. More recently, Kricheldorf and coworkers found[16,17] that Bi triflate catalyzes polycondensations of α,ω-alkanediols and aliphatic dicarboxylic acids or succinic anhydride at 80 °C, so that polyesters with corrected M_ns up to 20000 Da were accessible. With samarium triflate, even slightly higher molar masses were achieved.[18] Regardless of the performance, bismuth has the important advantage of being the least toxic heavy metal.[19−21] On the basis of these results it was the purpose of the present work to find out if $Bi(OTf)_3$ also catalyzes polycondensations of alkanediols and MaAh, so that without significant isomerization polyesters having M_ns up to 10000 Da are formed (Scheme 2). A comparison with other metal triflates was also included in this study.

Experimental Section

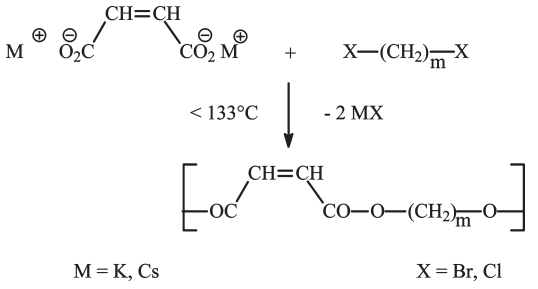
Materials. Maleic anhydride (MaAh, purity 98+ %) and the triflates of Bi^{3+}, Mg^{2+}, Al^{3+}, Sn^{2+}, Sc^{3+}, La^{3+}, and Sm^{3+} were purchased from Alpha Aesar (Karlsruhe, Germany) and used as received. Another batch of MaAh (purity 99%) was kindly supplied by Elantas Ag (Hamburg, Germany). 1,6-Hexanediol (purity 99%) and 1,4-butanediol (purity 98%) were purchased from Aldrich Co. The 1,4-butanediol was distilled in vacuo prior to use.

Polycondensations. (*1*). *1,6-Hexanediol and MaAh* (*No. 2, Table 3*). 1,6-Hexanediol (60 mmol), MaAh (60 mmol), and $Sm(OTf)_3$ (0.3 mmol) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer and gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 100 °C. The reaction mixture was stirred for 10 h under a slow stream of nitrogen, and afterward vacuum was gradually applied for a period of 1 h. The reaction mixture was then stirred for 22 h in a vacuum of 11−12 mbar. The crude yellowish, transparent reaction product was characterized.

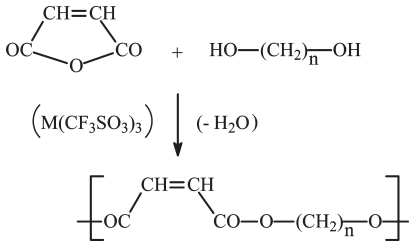
*Corresponding author. Tel.: 040-49-42838-3168. Fax: 040-49-42838-6008. E-mail kricheld@chemie.uni-hamburg.de.

Published on Web 08/13/2009

Scheme 1. Syntheses of Polyesters of Maleic Acid Free of Fumaroyl Units According to Refs 4−13



Scheme 2. Syntheses of Polyesters of Maleic Acid Free of Fumarate Units by Metal Triflate-Catalyzed Polycondensations of MaAh and Aliphatic Diols



In experiment Nos. 3 and 9, Table 3, the vacuum of 11−12 mbar was applied for 46 h. The polycondensations of Tables 2 and 5 were conducted analogously at 60 or 140 °C. In Table 4, the concentration of Sm triflate was lowered from 0.5 mol % to 0.33 or 0.25 mol % (Nos. 1−3) and the excess of 1,6-hexanediol was varied from 0 to 4 mol % (Nos. 4−6).

(*2*). *1,4-Butanediol + MaAh* (*No. 1, Table 6*). 1,4-Butanediol (60 mmol), MaAh (60 mmol), and Sm triflate (0.3 mmol) were weighed into a cylindrical glass reactor and stirred at 80 °C for 1 h without vacuum. Vacuum (down to 20 mbar) was gradually applied for 1 more hour and finally a vacuum of 11 mbar was applied for 22 h.

Measurements. The inherent viscosities were measured in CH_2Cl_2 using an automated Ubbelohde viscometer thermostatted at 20 °C. The 400 MHz ^{1}H NMR spectra were recorded in a Bruker "Avance 400" FT NMR spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent. The MALDI-TOF mass spectra were measured with a Bruker "Autoflex Smartbeam" mass spectrometer equipped with a smart beam laser.

All mass spectra were measured 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 calculated masses of all reaction products of 1,6-hexanediol discussed in this work were listed in Table 1. The SEC measurements were performed on a homemade chromatograph equipped with a RI detector Shodex RI 101 and 4 SDV PSS aluminum housing pore size of 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} Å. THF used as an eluent at a flow rate of 1 mL/min. Commercial polystyrene standard used for calibration. The pH values were measured with a Hanna instrument HI 991001 equipped with a pH probe HI 1296 D. The pH meter was calibrated with two buffer solutions immediately before the measurements

Results and Discussion

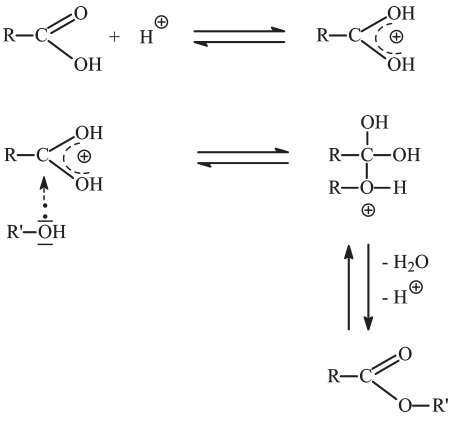
Polycondensations with 1,6-Hexanediol at 60 °C. In previous studies dealing with metal triflate-catalyzed polycondensations of 1,6-hexanediol with sebacic acid[16−18] or succinic anhydride[17] it was found that the lowest temperature, namely, 80 °C, gave the highest molar masses. Due to the rapid crystallization of the saturated polyesters lower reaction temperatures were not applicable. Because the unsaturated polyesters prepared in this work were amorphous, it was feasible to explore the usefulness of reaction temperatures below 80 °C. Furthermore, the influence of the temperature on molecular weight, isomerization of the maleic units and on the formation of ether groups should be studied. Therefore, three series of polycondensations were conducted, the first one at 60 °C and the second and third series at 100 and 140 °C, respectively. At each temperature the catalysts were varied so that metal triflates of different acidity were compared. The acidities were measured in the form of pH values in water at a concentration comparable to that in the reaction mixture. It should be elucidated if the condensation mechanism exclusively obeys the classical proton-catalyzed esterification mechanism (Scheme 3) or if complexation of the monomers by the metal ion plays an important role as speculatively formulated in Scheme 4.

Table 1. Calculated Masses (Incl. K^+ Doping) of the Reaction Products Observed in the MALDI-TOF Mass Spectra Prepared from 1,6-Hexanediol and Maleic Anhydride[a]

DP	C	C′	La	Lb	Lc
5	1030.1	1130.2	1048.1	1148.2	1146.1
6	1228.3	1328.5	1246.3	1346.4	1344.4
7	1426.5	1526.7	1444.5	1544.6	1542.6
8	1624.7	1724.9	1642.7	1742.8	1740.8
9	1823.0	1923.1	1841.0	1941.1	1939.0
10	2021.2	2121.3	2039.2	2139.3	2137.3
15	3012.3	3112.5	3030.3	3130.4	3128.4
20	4003.4	4103.6	4021.4	4121.5	4119.5
25	4994.5	5094.7	5012.5	5112.6	5110.6

[a] In the case of 1,4-butanediol, the mass values of **C**, **C′**, and **Lb** are lower by 28 Da.

Scheme 3. Proton-Catalyzed Esterification of Carboxylic Acids (and Hydrolysis of Ester Groups)



At first a model experiment was conducted by stirring an equimolar mixture of MaAh and 1,6-hexanediol for 1 h at 60 °C without addition of a catalyst. The ^{1}H NMR spectrum of the reaction mixture indicated a partial reaction of MaAh. The polycondensations performed with addition of catalysts were compiled in Table 2. All polycondensations of this work were conducted in such a way that after stirring for 1 h without vacuum, vacuum was gradually applied, so that the pressure was lowered to approximately 20 mbar within 1 h. Finally, a vacuum of 11−12 mbar was maintained for a period of 22 (or 46) h. The metal triflates and pH values listed in Table 2 indicate that the acidities of these catalysts varied over a broad range including a basic (La triflate) and a neutral (Sm triflate) species. However, the inherent viscosities were low in all cases and the SEC measurements suggest that the number average molecular weights (M_ns) were all

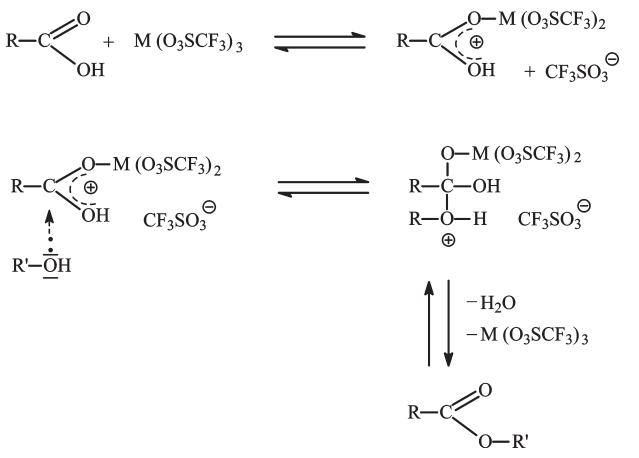
below 4000 Da. In agreement with low conversions, relatively intensive end group signals were observed in the ^{1}H NMR spectra. As demonstrated in Figure 1 for a sample of Table 3, the CH_2OH end groups give a triplet signal at 3.7 ppm and a terminal maleic acid (half ester) gives a doublet of doublets around 6.3 ppm. Ether groups are detectable by a triplet signal at 3.39 ppm and the singlet signal of fumarate units at 6.84 ppm, whereas the signal of the maleate units appears at 6.24 ppm. The ^{1}H NMR spectra of all polyesters listed in Table 2 had in common that the signals of fumarate and ether groups were absent.

Furthermore, MALDI-TOF (MT) mass spectra were recorded. As exemplarily illustrated in Figure 2 by the MT mass spectrum of sample No. 2, Table 2, mass peaks of cyclic oligomers were strong below 2000 Da despite the low conversion, indicating a high cyclization tendency. However, numerous peaks of expected linear chains (e.g., **La**, **Lb**, **Lc**, Scheme 5) and unexpected linear species (e.g., K-salts of **La** and **Lc** chains) were also present in agreement with the low conversion. Finally, it should be noted that the Bi triflate-catalyzed polycondensation was repeated twice (No. 6, A−C) to check the reproducibility of the results.

Polycondensation with 1,6-Hexanediol at 100 °C. A second series of polycondensations was performed at 100 °C, whereas all other parameters were identical with those used for the 60 °C experiments. The results summarized in Table 3 allowed for the following interesting conclusions and interpretations. First, the model experiment conducted without catalyst revealed complete reaction of MaAh. Yet, only low oligomers were formed and no precipitation occurred from diethyl ether or methanol. The same negative result was found when magnesium triflate was added (No. 4, Table 3). Second, in contrast, the basic La triflate yielded a polyester with medium molecular weight and the highest M_n was achieved with the neutral Sm triflate (Nos. 2−4, Table 3). Besides Mg triflate Bi triflate gave the low inherent viscosities (No. 8, A,B), although this triflate was the most acidic catalyst. Therefore, these results clearly demonstrate that the catalytic effect of these metal triflates is based on complexation of the substrate (most likely a complexation of CO_2H groups) and not on a simple proton catalysis according to Scheme 3. It fits in with this interpretation that the efficiency of the catalyst depends on the chemical structure of the dicarboxylic acids or their anhydrides. For instance, Bi triflate proved the best catalyst in polycondensations of 1,6-hexanediol with succinic anhydride,[17] whereas it was a poor catalyst for MaAh. Third, the higher reaction temperature had the consequence that isomerization of maleate to fumarate units occurred, but the extent of this isomerization was ≤1.5 mol %. Fourthly, the formation of ether groups was found, and here a clear trend became detectable, namely, increasing fraction or ether groups with higher acidity of the catalyst. All these results are exemplarily illustrated in the ^{1}H NMR spectrum of Figure 1.

At this point it should be mentioned that the experiments No. 7 in Table 2 and Nos. 2 and 9 in Table 3 were repeated to check the reproducibility. Furthermore, a new, seemingly purer batch of MaAh became available at the end of this work, and with this new MaAh, the experiment Nos. 2 and 7 of Table 2 were repeated and listed as Nos. 3 and 8 in Table 2. The experiments Nos. 2 and 9 of Table 3 were also repeated and listed as Nos. 3 and 10 in Table 3. The new MaAh gave indeed slightly higher viscosity values, and the polyester with the highest molar mass was obtained in this way using Sm triflate as catalyst (No. 10, Table 3). These reproducibility tests were necessary because, in a quite recently published

Scheme 4. Metal Triflate-Catalyzed Esterification of Carboxylic Acids



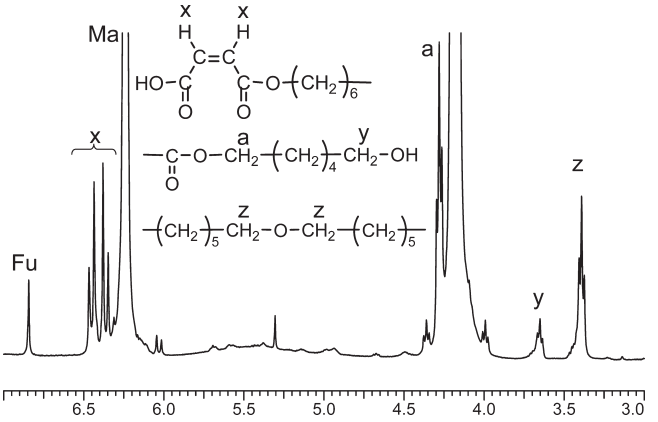


Figure 1. ^{1}H NMR (400 MHz) spectrum of polyester No. 8, Table 3, prepared with bitriflate at 100 °C (24). The signals a, b, and, c represent the CH_2 groups of the hexanediol units.

Table 2. Polycondensation of MaAh with 1,6-Hexanediol in Bulk at 60°C/24 h. Variation of Catalysts

exp. No.	catalysts;[a] triflate of	pH	$\eta_{inh.}$ (dL/g)	fumarate or ether (mol %)[b]	CH_2OH (mol %)	CH-CO_2H (mol %)
1	lanthanum	7.80	0.12	0	7	6
2	samarium	6.95	0.12	0	6	7
3[d]	samarium	6.95	0.13[d]	0	7	6
4	aluminum	3.90	0.14	0	7	7
5	scandium	3.15	0.13	0	6	6
6	tin(II)	1.80	0.15	0	4	4
7	bismuth	1.05	0.13[c] (0.11, 0.12)	0	2.0	2.5−3.0
8[d]	bismuth	1.05	0.14[d]	0	2.0	2.0

[a] Molar feed ratio monomers/catalyst = 200/1. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] This experiment was repeated twice. [d] MaAh of Elantas AG was used.

Table 3. Polycondensations of MaAh with 1,6-Hexanediol in Bulk at 100°C: Variation of Catalysts

exp. No.	catalysts;[a] triflate of	pH	total time (h)	$\eta_{inh.}$ [b] (dL/g)	fumarate (mol %)	ether (mol %)	CH_2OH or CH-CO_2H
1	lanthanum	7.80	24	0.20	< 1.0	0	2.0
2	samarium	6.95	24	0.25 (0.26)[c]	< 1.0	~1.0	< 1.0
3[d]	samarium	6.95	24	0.31[d,e]	< 1.0	~1.0	< 1.0
4	samarium	6.95	48	0.26	< 1.0	~ 1.0	< 1.0
5	magnesium	4.15	24	0.04			
6	aluminum	3.90	24	0.24	1.5	2.0	~1.0
7	scandium	3.15	24	1 s	< 1.0	1.0	~ 1.0
8	tin(II)	1.80	24	0.23	< 1.0	~1.0	~1.0
9	bismuth	1.05	24	0.17 (0.16)[c]	1.5	3.0	~1.0
10[d]	bismuth	1.05	24	0.19[d]	1.5	2.5	~1.0
11	bismuth	1.05	48	0.18	3.0	6.5	~1.0

[a] Molar feed ratio monomers/catalyst = 200/1. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] These experiments were repeated. [d] MaAh of Elantas AG was used. [e] M_n = 13 000 Da, PD = 2.6.

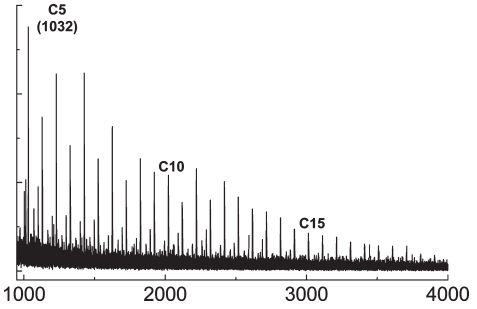


Figure 2. MALDI-TOF mass spectrum of the polyester No. 2, Table 2, prepared with Sm triflate at 60 °C. C5 means cyclic pentamer (see also Scheme 5).

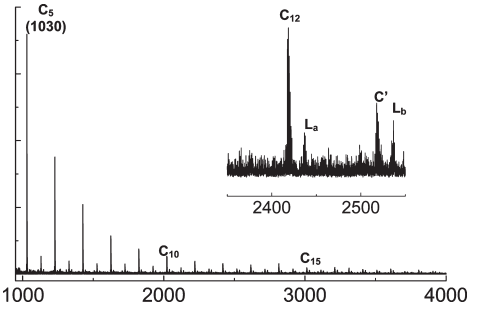
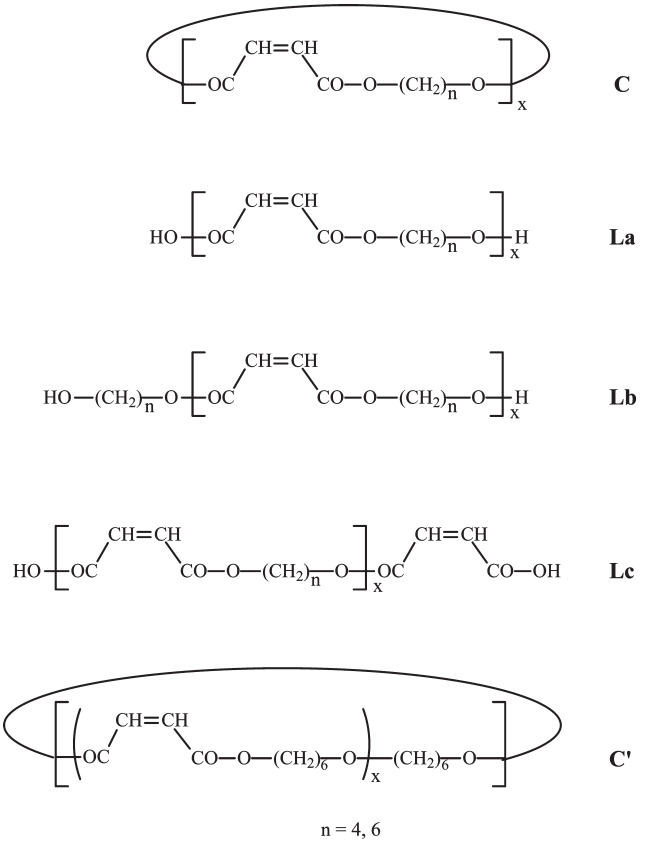


Figure 3. MALDI-TOF mass spectrum of the polyester No. 2, Table 3, prepared with Sm triflate at 100 °C. C5 means cyclic pentamer (see also Scheme 5).

Scheme 5. Potential Reaction Products of Polycondensation of MaAh with 1,4-Butanediol or 1,6-Hexanediol



thesis,[22] Bi triflate was reported to be the best catalyst for polycondensations of MaAh. Furthermore, it was concluded in the same thesis that meta triflate-catalyzed polycondensations of MaAh are exclusively catalyzed by protons, whereas the results presented in this work demonstrate (in agreement with previous publications)[16−18] that the metal ions are involved in the polymerization process.

The MT mass spectra revealed that the higher conversions with the higher molecular weights (relative to the 60 °C experiments) also had the consequence of more efficient cyclization as illustrated by comparison of Figures 2 and 3. The mass peaks of the cyclic polymers were the prominent peaks up to masses above 4000 Da (Figure 3). Particularly interesting is the presence of the mass peaks labeled **C′**. The mass difference relative to the **C** peaks amounts to 100 Da (see Table 1) corresponding to one hexamethylene oxide unit. Therefore, this peak was assigned to structure **C′** in Scheme 5. If the intensities of the **C** and **C′** mass peaks are added, it is evident that all cycles together present the vast majority of all reaction products at least below 5000 Da.

When it became clear that the highest molar masses were achieved with Sm triflate (Nos. 2 and 3, Table 3), a further optimization of the reaction conditions was performed. These experiments were listed in Table 4. At first, the concentration of the catalyst was varied maintaining a reaction time of 24 h (Nos. 1−4). The viscosity data showed that decreasing catalyst concentration results in lower molar masses. The MT mass spectra revealed that lower conversions were responsible for this correlation. Furthermore, it was taken into account that the formation of ether groups means consumption of CH_2OH groups with ensuing stoichiometric imbalance. Therefore, three more polycondensations were conducted using an excess of 1,6-hexanediol (Nos. 4−6, Table 4). The inherent viscosities decreased with increasing excess of the diol and proved that the equimolar feed ratio was close to optimum despite formation of ether groups. The ^{1}H NMR spectra evidenced increasing intensities of the CH_2OH end group signal, and the MT mass spectra indicated larger fractions of **Lb** chains with higher feed ratios of

Table 4. Samarium Triflate-Catalyzed Polycondensations of MaAh and 1,6-Hexanediol in Bulk at 100°C/24 h: Variation of Feed Ratio and Catalyst Concentration

exp. No.	$\frac{\text{mon.}^a}{\text{cat.}}$	excess of diol (mol %)	$\eta_{\text{inh.}}{}^b$(dL/g)	fumarate (mol %)	M_n (Da)	PD ^{c}	$M_p{}^c$ (Da)
1	200/1	0	0.25	< 1.0	12 500	2.3	21 000
2	300/1	0	0.18	< 1.0	8000	2.1	14 000
3	400/1	0	0.10	< 1.0	4500	2.1	9000
4	200/1	1	0.23	< 1.0	11 500	2.5	20 000
5	200/1	2	0.20	< 1.0	10 000	2.4	18 000
6	200/1	4	0.16	< 1.0			766+ 15 000

[a] Sum of both monomers. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] SEC measurements in chloroform calibrated with polystyrene.

Table 5. Polycondensation of MaAh with 1,6-Hexanediol in Bulk at 140°C/24 h: Variation of Catalysts

exp. No.	catalysts;[a] triflate of	pH	$\eta_{\text{inh.}}{}^b$ (dL/g)	fumarate (mol %)	ether gr. (mol %)	CH_2OH (mol %)
1	lanthanum	7.80	(0.42)[c]	4.5	2.0	
2	samarium	6.95	0.16	5.0	4.5	
3	aluminum	3.90	0.14	11.0	3.5	
4	scandium	3.15	(0.32)[c]	4.5	2.5	< 1.0
5	tin(II)	1.80	0.05	total degradation		
6	bismuth	1.05	0.05	total degradation		

[a] Molar feed ratio monomers/catalyst = 200/1. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] When this experiment was repeated, gel particles were detected in the chloroform solution.

1,6-hexanediol chain growth. A comparison of the polyesters listed in Table 3 with polyesters prepared from 1,6-hexanediol and succinic anhydride under similar reaction conditions[17] suggests that the *cis*-structure of the maleate units considerably favors the formation of rings. This suggestion agrees with the studies of another research group,[4−15] which found lower melt and solution viscosities for aliphatic polyesters of maleic acid relative to those of fumaric acid. A higher coil density of the polymaleates means shorter end-to-end distances which, in turn, favor cyclization. The MT mass spectra also indicated that in agreement with the theory of Gordon[23] an Kricheldorf[24,25] cyclization made a significant contribution to the limitation of the chain growth, when the polycondensations of MaAh were performed under nearly optimum conditions.

Polycondensations with 1,6-Hexanediol at 140 °C. With exception of magnesium triflate the same catalysts already used at 60 and 100 °C were also used at 140 °C (Table 5). For comparison with the experiments presented in Tables 2 and 3 the reaction time was limited to 24 h. These experiments provided a couple of unexpected results. First, the inherent viscosities scattered over a broad range and the lowest values resulted from Sn- and Bi-triflate-catalyzed experiments. Second, the most acidic catalysts, Sn and Bi triflate caused a broad structural variation and degradation of the reaction products. This conclusion is not only based on the low inherent viscosities but also on the ^{1}H NMR spectra. Figures 4 and 5 allow for a comparison of the correct structure obtained with the basic catalyst La triflate and the strange mixture of products resulting from the Sn-triflate-catalyzed polycondensation. The ^{1}H NMR spectrum presented in Figure 5 also revealed that the signal intensity of the maleate units had dramatically decreased, mainly to isomerization to fumarate units (signal at 6.84 ppm). However, the relatively low intensity of both signals also indicated further side reactions of the double bond, for instance, addition of CH_2OH groups. The multitude of "aliphatic signals" supports this assumption but radical reactions may also be involved. The ^{1}H NMR spectra of the Sm-, Sc-, and Al-triflate-catalyzed polyesters resembled largely that of the La-catalyzed product presented in Figure 4, but several weak signals indicating side reactions were also present. The relatively high viscosity values of the La- and Sc-triflate-catalyzed experiments were only observed in one

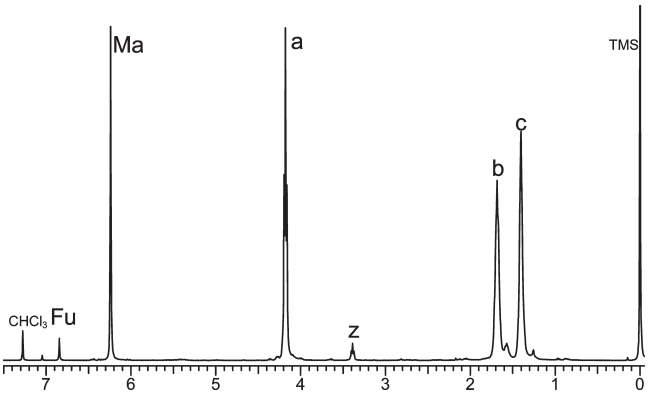


Figure 4. ^{1}H NMR (400 MHz) spectrum of polyester No. 1, Table 5, prepared with La triflate at 140 °C. The signals a, b, and c represent the CH_2 groups of the hexanediol units.

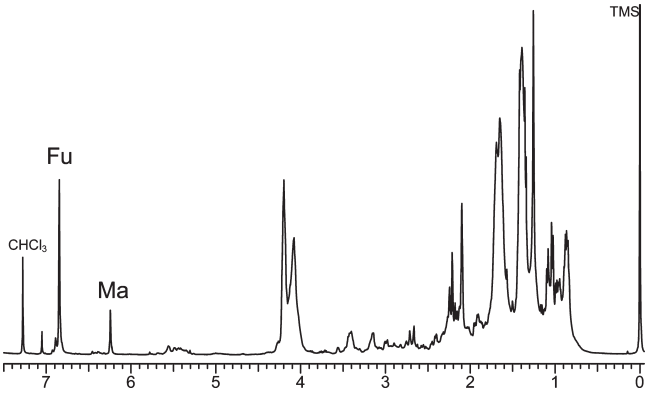


Figure 5. ^{1}H NMR (400 MHz) spectrum of polyester No. 5, Table 5, prepared with tin triflate at 140 °C.

out of three experiments. In two experiments, gel particles were observed in the $CHCl_3$ solutions. Therefore, it may suspected that the relatively high viscosities given in brackets in Table 5 resulted from branching or from formation of nanogel particles. In summary, temperatures above 110 °C are certainly not favorable for preparative purposes (as already observed for polycondensations of sebacic acid and

Table 6. Polycondensation of MaAh and 1,4-Butanediol in Bulk at 80°C

exp. No.	catalysts;[a] triflate of	pH	yield (%)	$\eta_{inh.}$[b](dL/g)	fumarate (mol %)	ether gr. (mol %)	CH_2OH (mol %)	CO_2H (mol %)
1	samarium	6.95	76.0	0.23	0	0	0	0
2	aluminum	3.90	77.5	0.20	0	0	~1	~1
3	scandium	3.15	67.0	0.22	<1	<1	~1	~1
4	bismuth	1.05	68.5	0.15	~1	~1	~2	~2

[a] Molar feed ratio monomers/catalyst = 200/1. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2.

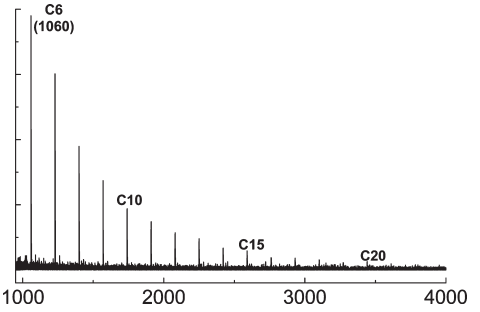


Figure 6. MALDI-TOF mass spectrum of polyester No. 1, Table 6, prepared with Sm triflate at 80 °C. C6 means cyclic hexamer (see also Scheme 5).

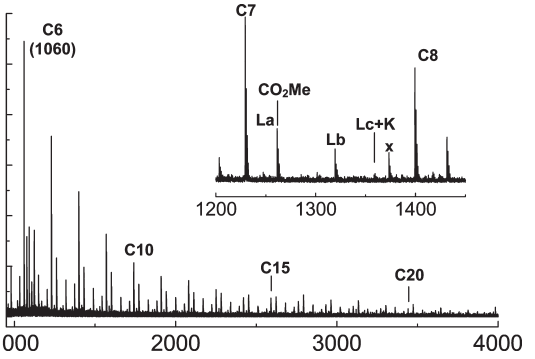


Figure 7. MALDI-TOF mass spectrum of polyester No. 3, Table 6, prepared with Sc triflate at 80 °C. C6 means cyclic hexamer (see also Scheme 5).

1,6-hexanediol),[16−18] and highly acidic catalysts are particularly prone to cause considerable degradation.

Polycondensations of 1,4-Butanediol at 80 °C. The successful polycondensations of 1,6-hexanediol suggested to extend these studies to other alkanediols. 1,4-Butanediol was selected for two reasons. First, it is the least expensive diol besides 1,2-ethanediol. Second, it is particularly difficult to use 1,4-butanediol in combination with acidic catalysts, because it rapidly generates THF when heated above 100 °C with a protic acid or Lewis acid.[16] Therefore, the reaction temperature was lowered to 80 °C. As demonstrated by the data compiled in Table 6, inherent viscosities above 0.20 dL/g were obtained in the first three experiments when the precipitated polyesters were measured. When it is considered that the butanediol is shorter than 1,6-hexanediol, the inherent viscosities suggest that the degrees of polymerizations of the polyesters of Tables 3 and 6 are quite similar. In other words, the polycondensation of 1,4-butanediol proceeded without significant loss of THF. Furthermore, ^{1}H NMR signals of fumarate units or ether groups were almost absent as expected for the relatively low reaction temperature.

Two more aspects are worth noting. First, Bi triflate yielded again the lowest molecular weight. Together with the results presented in Tables 3 and 5, these findings clearly indicate that Bi triflate is not an attractive catalyst for polycondensations of MaAh, whereas it is proven to be a good catalyst when saturated monomers were used.[16−18] Second, the ^{1}H NMR spectrum of the Sm-catalyzed sample (No. 1, Table 6) did not display any end group signals, although the inherent viscosity was not extraordinarily high. The MT mass spectrum revealed that this sample almost exclusively consisted of cycles at least up to masses around 4000 Da, the technical limit of these measurements (Figure 6). The peaks of cycles were also largely prevailing in the MT mass spectra of the other three samples (Figure 7), but Sm triflate gave the cleanest polycondensation with the highest conversion. This finding also suggests that the chain growth was mainly limited by cyclization, and the cyclization tendency was higher than for polycondensations of 1,6-hexanediol. This suggestion is supported by the consideration that the positive influence of the *cis*-structure of the maleate units on the cyclization tendency will decrease with greater lengths of the alkanediols.

SEC Measurements. At this point the SEC measurements deserve a short discussion. From saturated aliphatic polyesters such as ε-caprolactone or polylactide it is known[26−32] that polystyrene-calibrated SEC measurements overestimate the real molecular weights by at least 50%. The extent of overestimation is higher for masses below 10000 Da and it is higher in chloroform than in the weaker solvent tetrahydrofuran. This overestimation indicates that the hydrodynamic volume of the polyesters is higher, with their coil density lower than those of polystyrene. Yet, in the case of polycondensations, the *cis*-structure of monomeric units favors a higher coil density than that of saturated polyesters and the lower solution and melt viscosities relative to the corresponding polyfumarates is an indirect proof of this assumption. Furthermore, the hydrodynamic volume of cyclic polymers amounts to approximately 2/3 that of the corresponding linear polymers. Considering that the high molecular weight samples of this work (e.g., η_{inh} > 0.20 dL/g) contain a significantly fraction of cycles it may be concluded that the PS-calibrated SEC measurements of these polymaleates come close to the real values.

The SEC data presented in Table 4 (and in the footnote of Table 3) deserve the following comment. All elution curves were measured from virgin reaction products, so that all cyclic and linear oligomers were present. All elution curves displayed a weak maximum around 900 Da the area of which amounted to approximately 5% relative to that of the main maximum. As discussed previously,[24] such a weak maximum in the low molar mass range is characteristic for polycondensates containing a high fraction of cyclic oligomers The number average molecular weight (M_n) and polydispersity (PD) data listed in Table 4 (and in the footnote of Table 3) were determined for the main maximum. The M_n data indicate that for samples having inherent viscosities around 0.20 dL/g M_n values around 10000 Da were achieved. In the case of sample 6 (Table 4), the elution curve consisted of two equally intensive maxima, and thus, M_n and PD were not calculated. Finally, it should be mentioned that PD values above 2.0 are quite normal for virgin polycondensates containing significant amounts of cyclic oligomers and polymers.[23] However, branching by addition of CH_2OH groups onto C−C double

bonds may also contribute to a broadening of the molecular weight distribution.

Conclusion

To the best of our knowledge, this study presents for the first time a successful polycondensation of MaAh yielding polyesters almost free of fumarate units. In contrast to saturated polyesters, Bi triflate was a relatively poor catalyst, and the best results were obtained with Sm triflate. Furthermore, it was found that the basic La triflate yielded satisfactory results, whereas the more acidic Mg triflate was inactive. These findings suggest that the polycondensation mechanism involves complexation of the monomers by metal ions and not only a simple proton-catalyzed esterification according to Scheme 3. Under optimum conditions the conversions were so high that the chain growth was mainly limited by cyclization. The highest molecular weights achieved in this work may be too high for coating applications, but regulation to lower values can easily be achieved by standard measures, such as lower reaction temperatures (Table 2), shorter times, stoichiometric imbalance (Table 4), or addition of a chain stopper. Lower catalyst concentration will also lower the molecular weights (Table 4) and has the additional benefit that the relatively high costs of Sm triflate are reduced. The simplicity of the procedure allows for upscaling and technical production.

Acknowledgment. We wish to thank Prof. M. Schmidt and Dipl.Ing. E. Wächtersbach (University of Mainz, Germany) for the SEC measurements.

References and Notes

(1) Malik, M.; Choudhary, V.; Varma, I. K. *Rev. Macromol. Chem. Phys.* **2000**, *C40*, 139–165.
(2) Penczek, P.; Czub, P.; Pielichowski, J. *Adv. Polym. Sci.* **2005**, *184*, 1–95.
(3) Andreis, M.; Meic, Z.Veksli, Z. *Polymer* **1983**, *24*, 2611–2616.
(4) Lacoudre, N.; Leborgne, A.; Sepulchre, M.; Spassky, N.; Djonlagic, J.; Jácovic, M. S. *Macromol. Chem.* **1986**, *187*, 341–350.
(5) Jácovic, M. S.; Djonlagic, J.; Sepulchre, M.; Sepulchre, M.-O.; Leborgne, A.; Spassky, N. *Makromol. Chem.* **1988**, *189*, 1353–1362.
(6) Djonlagic, J.; Sepulchre, M.-O.; Sepulchre, M.; Spassky, N.; Jacovic, M. S. *Makromol. Chem.* **1988**, *189*, 1485–1492.
(7) Djonlagic, J.; Sepulchre, M.-O.; Sepulchre, M.; Spassky, N.; Dunjic, B.; Jacovic, M. S. *Makromol. Chem.* **1990**, *191*, 1529–1543.
(8) Sepulchre, M.-O.; Moreau, M.; Sepulchre, M.; Djonlagic, J.; Jacovic, M. S. *Makromol. Chem.* **1990**, *191*, 1739–1758.
(9) Sepulchre, M.-O.; Sepulchre, M.; Spassky, N.; Djonlagic, J.; Jacovic, M. S. *Makromol. Chem.* **1991**, *192*, 1073–1084.
(10) Jacovic, M. S.; Djonlagic, J.; Sepulchre, M.; Sepulchre, M.-O.; Spassky, N. *Makromol. Chem.* **1992**, *193*, 2113–2122.
(11) Jacovic, M. S.; Dunjic, B.; Djonlagic, J.; Spassky, N.; Sepulchre, M.; Sepulchre, M.-O. *Polym. Bull.* **1992**, *28*, 621–626.
(12) Djonlagic, J.; Dunjic, B.; Sepulchre, M.; Sepulchre, M.-O.; Spassky, N. *J. Serbian Chem. Soc.* **1993**, *58*, 299–309.
(13) Dunjic, B.; Sepulchre, M.-O.; Sepulchre, M.; Spassky, N.; Djonlagic, J. *Macromol. Chem. Phys.* **1998**, *199*, 1051–1055.
(14) Takasu, A.; Oishi, Y.; Ito, Y.; Imai, Y.; Hirabayashi, T. *Macromolecules* **2003**, *36*, 1772–1774.
(15) Takasu, A.; Ito, Y.; Oishi, Y. *Macromolecules* **2003**, *38*, 1048–1050.
(16) Buzin, P.; Lahcini, M.; Schwarz, G.; Kricheldorf, H. R. *Macromolecules* **2008**, *41*, 8491–8495.
(17) Yoshiro, T.; Kricheldorf, H. R.; Weidner, S. M. *Macromol. Chem. Phys.* **2009**, in press.
(18) Garaleh, M.; Lahcini, M.; Kricheldorf, H. R.; Weidner, S. M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *47*, 170–177.
(19) Gao, Z.; Sadler, P. J. *Angew. Chem.* **1999**, *111*, 1610; *Angew. Chem., Int. Ed. Engl.* **1999**, *28*, 1512−1531.
(20) Briand, G. C.; Burford, N. *Chem. Rev.* **1999**, *99*, 2601–2657.
(21) Rodilla, V.; Miles, A. T.; Jenner, W.; Harksworth, G. M. *Chem. Biol. Interact.* **1998**, *115*, 71–83.
(22) www.chemie.uni-hamburg.de/bibliothek2008/DissertationSchellenberg.pdf (published without permission of the first author).
(23) Gordon, M.; Temple, W. B. *Makromol. Chem.* **1972**, *160*, 263.
(24) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359–381.
(25) Kricheldorf, H. R. *Macromol. Rapid Commun.* **2008**, *29*, 1695–1704.
(26) McLain, S. J.; Drysdale, N. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (1), 174–175.
(27) Pasch, H.; Rode, K. *J. Chromatogr., A* **1995**, *699*, 21–28.
(28) Hiltunen, K.; Härkönen, M.; Seppälä, J. V.; Väänen, T. *Macromolecules* **1996**, *29*, 8677–8682.
(29) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114–2122.
(30) Kricheldorf, H. R.; Eggerstedt, S. *Macromol. Chem. Phys.* **1998**, *199*, 283–290.
(31) Kricheldorf, H. R.; Rost, S. *Polymer* **2005**, *46*, 3248–3256.
(32) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 884–899.