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Polycondensations of Substituted Maleic Anhydrides and 1,6-Hexanediol Catalyzed by Metal Triflates

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Polycondensations of methylmaleic anhydride (citraconic anhydride, CiAh), bromomaleic anhydride (BMaAh), and dichloromaleic anhydride (DCMaAh) with 1,6-hexanediol were conducted in bulk. For polycondensations of CiAh, the triflates of aluminum, bismuth, lanthanum, magnesium, samarium, and scandium were used as catalysts and the best results were obtained with Bismuth triflate. MALDI-TOF mass spectra indicated that the chain growth was limited by cyclization and incomplete conversion, but temperatures above 100°C were not advantageous due to side reactions. Bismuth and samarium triflate catalyzed polycondfensations of BMaAh and DCMaAh were less successful than polycondensations of CiAh. For polycondensations of CiAh, BMaAh, and DCMaAh, only a low extent of isomerization to trans isomers (1–3%) was observed at 100°C, but considerably higher extent at 140°C.

Keywords: Bismuth, citraconic anhydride, polyesters, polycondensation, cyclization

1 Introduction

Unsaturated polyether based on polycondensations of maleic anhydride (MeAh) and aliphatic diols are technically produced in large quantities, and play an important role as components of coatings and lacquers (1–3). The technical polycondensations are usually performed at temperatures up to 180°C and have the consequence that usually 30–60% of the maleate units isomerizes to the fumarate moieties. Stereochemically uniform polyethers of maleic or fumaric acid were prepared by a French/Yugoslavian research group (4–10) and their chemical and physical properties were studied in much detail, it was found that the hydrodynamic volume of the polymaleates is significantly lower (the coil density higher) than that of the corresponding polyfumarates. Hence, both melt and solution viscosities of polymaleates are lower, an interesting advantage for coating and lacquers applications.

The synthetic method used by that research group is based on polycondensation of α, β-dibromoalkanes with the potassium or cesium salts of maleic and fumaric acid (Scheme 1). However, the method is far too expensive for a technical production. Quite recently, it was found (11) that polymaleats almost free of fumarate units can be prepared by polycondensation of MaAh with α, ω-alkanediol in bulk at temperature around 100°C. Metal triflates used as catalysts whereby the lightest molar masses were achieved with samarium triflate. Bismuth triflate gave relatively poor results, although it proved to be a good catalyst for synthesis of saturated polymers (12, 13). These results suggested that the bismuth triflate catalyzed side reaction of C-C double bonds either due to addition of CH_2OH groups or due to redox-reactions. Yet, Bi-salts are particularly interesting as catalysts, because bismuth is the least toxic heavy metal (14–16).

The present work served two purposes. Firstly, it should be found out, if the new synthetic approach is also successful with substituted maleic anhydrides. Secondly, it should be elucidated how electron rich and electron poor double bonds respond to a comparison of Bi triflate and Sm triflate. In a quite recently published thesis (17), it was reported that dimethylmaleic anhydride does not react with hexanediol at 100°C in contrast to dichloromaleic anhydride. Therefore, methylmaleic anhydride (citraconic anhydride, CiAh), bromomaleic anhydride (BMaAh), and dichloromaleic anhydride (DCMaAh) were used as comonomers of 1,6-hexanediol in this work.

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Table 1. Polycondensation of citraconic anhydride (CiAh) with 1,6-hexanediol in bulk at 100°C

Expt. No.	*Triflate cat.*	*pH*[a]	*Trans Isomer (%)*	*Time (h)*	η^{b}_{inh} *(dL/g)*	*mol% ether*	*Mn n*[c] *(Da)*	*PD*[c]
1	Lanthanium	7.80	<1.0	24	0.10	<1.0	3100	3.3
2	Lanthanium	6.50	<1.0	24	0.11	<1.0	3700	3.0
3	Samarium	6.95	~ 1.0	24	0.22	~ 2.0	6000	3.5
4	Samarium	6.95	~ 1.0	48	0.18	~ 2.0	3100	3.9
5	Magnesium	4.15	0.0	24	0.03	0.0	800	2.3
6	Aluminum	3.90	<1.0	24	0.16	~ 1.0	4900	3.5
7	Scandium	3.15	~ 2.0	24	0.13	~ 2.0	3400	3.5
8	Tin(II)	1.80	<1.0	24	0.21	~ 1.0	4400	4.9
9A	Bismuth	1.05	~ 2.0	24	0.26	~ 1.5	7500	3.9
9B	Bismuth	1.05	~ 2.0	24	0.32	~ 2.0	8500	4.9
10	Bismuth	1.05	14.0	48	0.18	~ 9.0	3300	6.2

[a] Measured at 20°C with c=0.05mol/L in H_2O.
[b] Measured at 20°C with c=2 g/L in CH_2Cl_2.
[c] SEC measurements in chloroform at 25°C calibrated with polystyrene.

2 Experimental

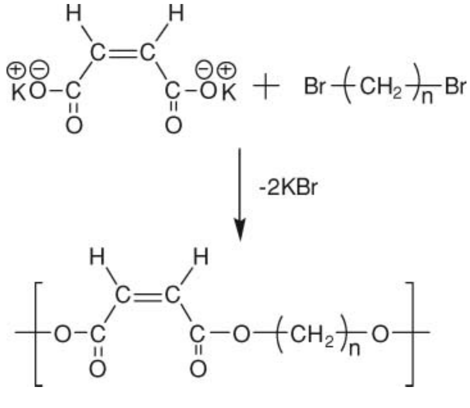
2.1 Materials

CiAh, BMaAh, and DCMaAh were purchased from Aldrich Co. (Steinheim, Germany). CiAh was distilled *in vacuo* prior to use, whereas the other anhydrides were used as received. 1,6-Hexanediol (purity 99%) was also purchased from Aldrich Co. and distilled *in vacuo*. The triflates of aluminum, magnesium, lanthanum, samarium, and tin(II) were purchased from Alpha Aesar (Karlsruhe, Germany) and used as received. Triflates of bismuth, lanthanum, and scandium were also purchased from Aldrich Co.

2.2 Polycondensations

2.2.1. *Table 1; No. 2*

1,6-Hexane diol (60 mol), CiAh (60 mmol) and Sm triflate (0.6 mmol) were weighed into a cylindrical glass reactor equipped with glass-stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 100°C and the reaction mixture was stirred for 1 h without vacuum. The vacuum was gradually applied over a period of 1 h and a vacuum of approximately 11–12 mbar was then maintained for 22 h. Finally, the cold reaction product was characterized. All other polycondensations listed in Table 1, 2, and 4 were conducted analogously, but in the cases of No. 3 and No. 9 in Table 1, the total reaction time was extended to 48 h, and in the case of Table 2, all experiments were conducted at 140°C.



Sch. 1. Polycondensation of potassium maleats with α,ω-dibromoalkanes.

2.2.2. *Table 4; No. 7*

1,6-Hexane diol (60 mol), DCMAh (60 mmol), and Bi triflate (0.6 mmol) were weighed into a cylindrical glass reactor equipped with glass-stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 120°C and the reaction mixture was stirred for 1 h without vacuum. The vacuum was gradually applied over a period of 1 h and a vacuum of approximately 11–12 mbar was then maintained for 22 h. Finally, the cold reaction product was characterized. All other experiments of Table 4 were conducted analogously with variation of the temperature.

Table 2. Metal triflate-catalyzed polycondensations of CiAh with 1,6-hexanediol at 140°C

Expt. No.	*Triflate cat.*	*pH*[a]	η^{b}_{inh} *(dL/g)*	*Trans Isomer (%)*	*mol% ether*
1	Lanthanum	7.80	0.10	<1.0	<1.0
2	Samarium	6.95	0.22	~ 1.0	~ 2.0
3	Tin(II)	1.80	0.21	<1.0	~ 1.0
4	Bismuth	1.05	–	Black tar (decomposition)	

[a] Measured at 20°C with c=0.05mol/L in H_2O.
[b] Measured at 20°C with c=2 g/L in CH_2Cl_2.

Table 3. Polycondensation of bromomaleic anhydride with 1,6-hexanediol in bulk at 100°C

Expt. No.	*Triflate cat.*	*pH*^{a}	*Trans Isomer (%)*	*Time (h)*	η^b_{inh} *(dL/g)*	*mol% ether*
1	Lanthanum	7.80	6.8	24	0.15	1.2
2	Samarium	6.95	7.9	24	0.18	1.2
3	Tin(II)	1.80	2.2	24	0.12	2.0
4	Bismuth	1.05	4.3	24	0.14	1.7

[a] Measured at 20°C with c=0.05mol/L in H_2O.
[b] Measured at 20°C with c=2 g/L in CH_2Cl_2.

2.3 Measurements

The inherent viscosities were measured in dichloromethane using an automated Ubbelohde viscometer thermostated at 20°C. The 400 MHz ^{1}H-NMR spectra and the 100.25 MHz ^{13}C-NMR spectra were recorded on a Bruker "Avance 400" FP spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent. The MALDI-TOF mass spectra were recorded on a Bruker "SmartBeam" mass spectrometer equipped with a smartbeam laser. All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions using dithranol as matrix and potassium trifluoroacetate. The calculated mass of the potassium-doped reaction products are listed in Tables 5 and 6. The SEC measurements were performed on an apparatus of Polymer Laboratories (PL) equipped with a refractive index detector "Shodex Ri 101". A calibration of these PL mixed-bed columns was used and chloroform served as solvent at an elution rate of 1mL/min. Commercial polystyrene standards were used for calibration. The pH measurements were performed in distilled water at a concentration of 0.005 mol/L with a HANNA instrument HI 991001 equipped with a pH probe HI 12960. With exception of the La-triflate all pH value listed in Table 1 were measured at 20°C as reported previously (12, 18). For this work, a La-triflate of Alpha Aesar and La-triflate of Aldrich Co. were measured at 23°C and pH value of 7.80 and 6.50 (±0.05), respectively were determined. The pH meter was calibrated with buffer solutions of pH 4 and pH 7 immediately before the measurements.

Table 4. Sm and Bi triflate-catalyzed polycondensations of DCMaAh with 1,6-hexanediol in bulk with variation of the temperature

Expt. No.	*Triflate cat.*	*Temp (°C)*	η_{inh} *(dL/g)*^{a}	*mol% ether*
1	Samarium	80	0.02	0.0
2	Samarium	100	0.06	0.0
3	Samarium	120	0.12	<1.0
4	Samarium	140	0.09	~ 1.5
5	Bismuth	80	0.03	0.0
6	Bismuth	100	0.23	~ 1.0
7	Bismuth	120	0.18	~ 2.0
8	Bismuth	140	0.09	~ 2.5

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

Table 5. Calculated masses (incl. K^+doping) of the reaction products of CiAh and 1,6-hexanediol^a

DP	*C*	*Ce*	*La*	*Lb*	*Lc*
5	1100.3	1200.5	1118.3	1218.5	1230.4
6	1312.6	1412.7	1330.6	1430.7	1442.7
7	1524.8	1625.0	1542.8	1643.0	1654.9
8	1737.1	1837.2	1755.1	1855.2	1867.2
9	1949.3	2049.5	1967.3	2067.5	2079.4
10	2161.6	2261.7	2179.6	2279.7	2291.7
15	3222.8	3322.9	3240.8	3341.0	3352.9
20	4284.0	4384.2	4302.0	4402.2	4414.1

[a] mass of the repeat unit: 212.246.

3 Results and Discussion

3.1 Polycondensations of CiAh

Firstly, when two different commercial samples of La triflate having different pH values were used as catalyst, almost identical results were obtained regardless of the acidity. Secondly, both La triflates and the neutral Sm triflate yielded polyesters, whereas the more acidic Mg triflate did not. These findings clearly support the previously discussed hypothesis that the esterification (condensation) mechanism is not exclusively based on the catalytic effect of protons (resulting from liberated triflic acid) but involves complexation of the monomers by metal ions.

From polycondensations of MaAh and 1,6-hexanediol (11), it was learned that a temperature of 60°C was too low to achieve satisfactory molecular weights, whereas a temperature of 100°C had proven to come close to the optimum. Therefore, a first series of polycondensations of CiAh was performed at 100°C with variation of the catalysts. In analogy to previous studies (11–13, 18), the experiments

Table 6. Calculated masses (incl. K^+doping) of the reaction products of DCMaAh and 1,6-hexanediol^a

DP	*C*	*Ce*	*La*	*Lb*	*Lc*
4	1107.8	1207.8	1125.8	1225.7	1292.7
5	1374.5	1474.5	1392.5	1492.5	1559.4
6	1641.6	1741.6	1659.6	1759.6	1826.8
7	1908.8	2008.8	1926.8	2026.8	2093.8
8	2175.9	2275.9	2193.9	2293.9	2360.8
9	2443.0	2543.0	2461.0	2561.0	2627.9
10	2710.1	2810.1	2728.1	2828.1	2895.0
15	4045.6	4145.6	4063.6	4163.6	4230.5
20	5381.2	5481.2	5399.2	5499.2	5566.1

[a] mass of the repeat unit: 267.112.

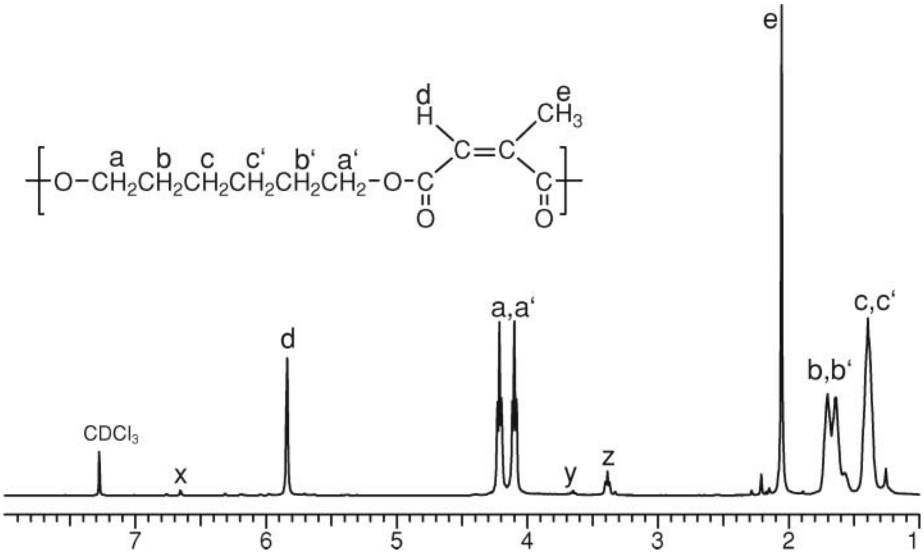


Fig. 1. 400 MHz ^{1}H-NMR spectrum of the polyester prepared by Sm-triflate catalyzed polycondensation of CiAh and 1,6-hexanediol (No. 3, Table 1).

listed in Table 1 were ordered according to the acidities of the catalysts. Three results were remarkable. The third interesting result concerns the good performance of Bi triflate which was the best catalyst of this study. In the case of MaAh, Bi triflate showed a poor performance due to intensive side reactions with the double bond. These side reactions are partially based on redox reactions with the p-electrons playing the role of the reducing agent. Furthermore, Bi triflate catalyzes the addition of CH_2OH groups onto the double bond since the double bond of CiAh possesses a higher electron density (i.e., lower elctrophilicity), it is obvious that the good performance of Bi triflate results from a lower frequency of addition reactions. This interpretation is supported by the ^{1}H-NMR spectra which do not display additional signals in the region below 4.5 ppm.

To detect further side reactions, the ^{1}H-NMR spectra of the polycondensation products were analyzed with respect to the formation of ether groups and with respect

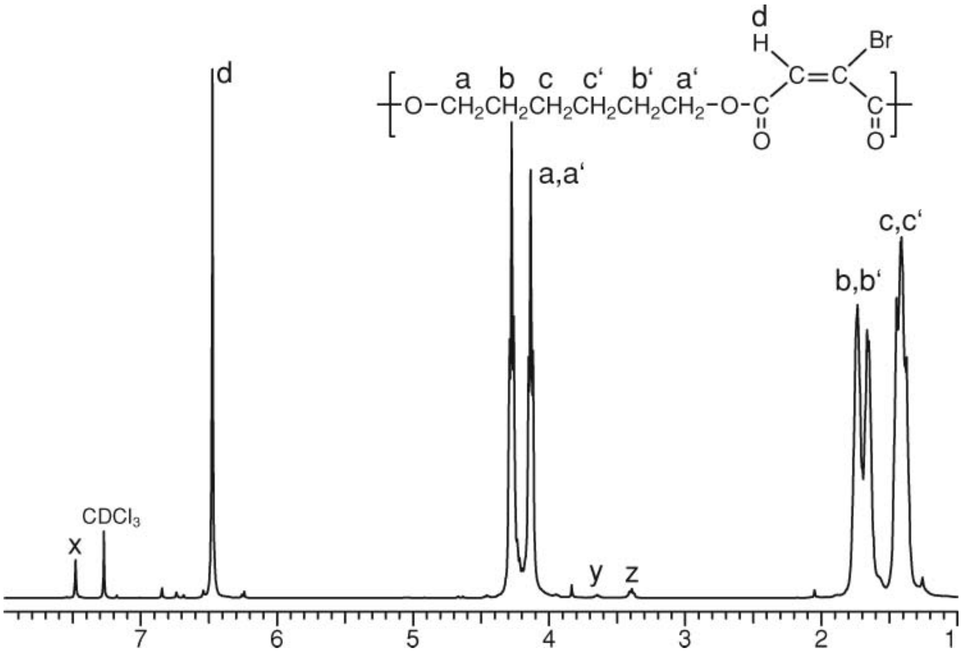


Fig. 2. 400 MHz ^{1}H-NMR spectrum of the polyester prepared by La-triflate catalyzed polycondensation of BMaAh and 1,6-hexanediol (No. 1, Table 3).

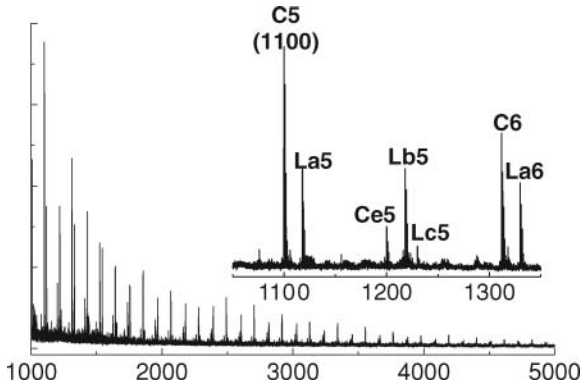


Fig. 3. MALDI-TOF mass spectrum of polyester prepared by Sm-triflate catalyzed polycondensation of CiAh and 1,6-hexanediol (No. 3, Table 1, for the symbols see Scheme 2).

to cis/trans isomerization. The formation of trans isomers was detectable from a weak singlet signal at 6.85 ppm of the olefinic protons (signal x in Figure 1) and from the singlet signal of the CH_3 group at 2.11 ppm. The corresponding signals of the citraconate moieties appeared at 5.85 and 2.05 ppm, respectively as demonstrated in Figure 1. At 100°C, the extent of isomerization was low quite analogous to the polycondensations of MaAh under identical conditions. Again, in agreement with the polycondensations of MaAh, formation of ether groups was observed (signal z in Figure 1). Finally, it should be mentioned that a longer reaction time (48 h in the case of No. 3 and 10, Table 1) did not significantly raise the molecular weights, while the extent of isomerization was higher. The presence of unreacted CH_2OH groups was evident from signal y (Figure 1).

A few polycondensations were conducted at 140°C to elucidate the consequences of higher temperatures. As expected from previous studies (12–14), the molecular weights did not increase, whereas the side reactions became more intensive. With Bi triflate, a black tar was obtained (No 4), whereas tin(II) triflate generated a high extent of etherification and isomerization as documented by the ^{1}H-NMR spectrum of Figure 2. The lowest level of side reactions and the highest viscosity values were found, when the neutral Sm triflate was used as catalyst.

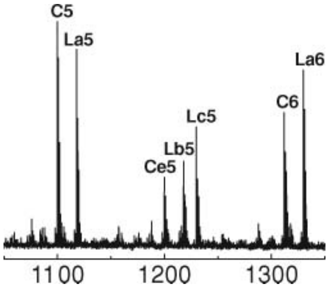
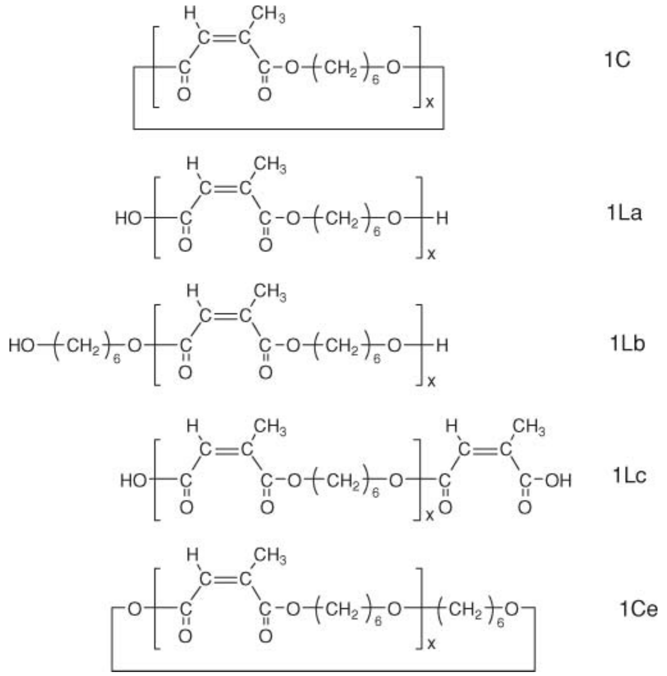


Fig. 4. MALDI-TOF mass spectrum of polyester prepared by Bi-triflate catalyzed polycondensation of CiAh and 1,6-hexanediol (No. 9A, Table 1, for the symbols see Scheme 2).



Sch. 2. Reaction products of CiAh and 1,6-hexanediol

The MT mass spectra (exemplarily illustrated in Figures 3 and 4) gave the following results. The polyesters prepared at 100°C displayed the four signals of the main reaction products, which may be expected from a clean polycondensation (**1C**, **1La**, **1Lb**, and **1Lc** in Scheme 2). Furthermore, a weak peak representing cyclic polyesters with one ether group (**1Ce** in Scheme 2) was detectable in agreement with the existence of ether groups in the ^{1}H-NMR spectra (signal z in Figure 1). In summary, these mass spectra evidenced that the chain growth was mainly limited by cyclization and incomplete conversion and not so much by side reactions destroying functional groups. Considering the moderate conversions, it is surprising that longer reaction times did not improve the molecular weights. Either deactivation of the catalysts or slow diffusion of the water out of the viscous melt is the limiting factors. Nonetheless, the obtained molecular weights are sufficient for coating or lacquer applications.

At this point, it should be mentioned that the virgin reaction products were used for SEC measurements and the evaluation of the elution curves was started at 200Da including all oligomers. When the evaluation of the elution curves was started at 1000Da concentrating on the main "peak", the number average molecular weights (M_n) of samples 9A and 9B on Table 1 increased to 11000 and 12000Da, respectively. The high polydispersities mainly result from the presence of cycles as discussed previously (19), but branching due to addition of CH_2OH endgroups onto double bonds may also contribute to high polydispersities.

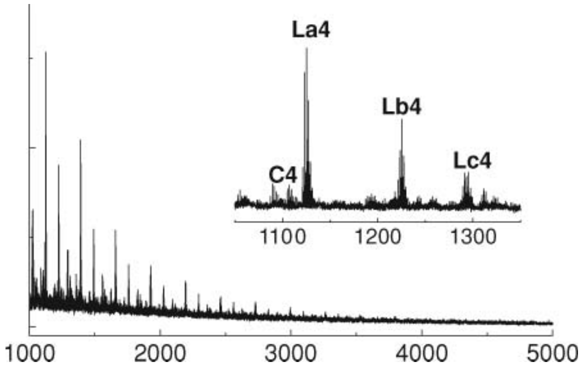


Fig. 5. MALDI-TOF mass spectrum of polyester prepared by Sm-triflate catalyzed polycondensation of CiAh and 1,6-hexanediol (No. 2, Table 4, for the symbols see Scheme 3).

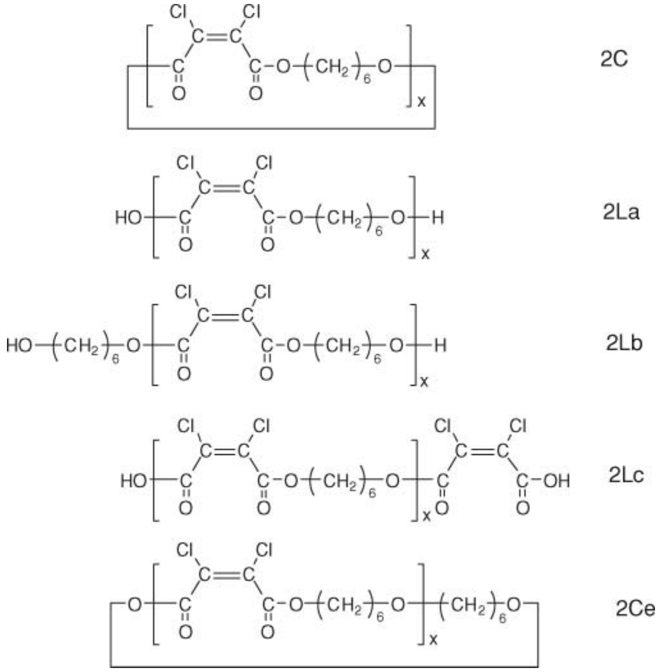
3.2 Polycondensation of BMaAh

Four polycondensations of BMaAh were conducted at 100°C with variation of the catalysts. Polyesters were isolated from all four polymerizations (Table 3) and two interesting results were obtained. Sm triflate gave the highest viscosity value, but the basic La triflate gave a slightly better result than the highly acidic Bi triflate. These findings clearly confirm the conclusion presented above, namely the metal ions are directly involved in the condensation mechanism.

The ^{1}H-NMR spectrum presented in Figure 4 is characteristic for all four polycondensations and it is analogous to the spectrum of the CiAh-based polyesters shown in Figure 1. In addition, of the four signals of the repeat units, three weak signals (labeled x, y, and z) were detected which indicate a low-level of isomerization (x), CH_2OH endgroups (y), and formation of ether groups (z). The extent of isomerization was slightly higher than in the case of CiAh. Remarkable, is the low concentration of CH_2OH endgroups in spite of low viscosity values. This combination of properties might result from a high content of cyclic oligomers and polymers. Unfortunately, samples 1 and 2 of Table 3 didn't give useful MT mass spectra possibly due to side reactions of the Br-C bond with the dopant.

3.3 Polycondensations of DCMAh

Polycondensations of the expensive DCMAh were restricted to the comparison of Bi triflate and Sm triflate. This comparison was of interest for two reasons. First, Sm triflate was the only neutral catalyst and Bi triflate, the most acidic one in this work. Second, it was found in our previous study of polycondensations of MaAh that Sm triflate gave the highest and Bi triflate the lowest molecular weights (due to side reactions with the C-C double bond). The temperature was varied from 80 to 140°C in steps of 20°C. The following trends were observed. A reaction temperature of 100°C was optimum in the case of Bi triflate (No 7, Table 4), whereas 120°C was the optimum for Sm triflate-catalyzed polycondensations. The molecular weights obtained with Bi.triflate were considerably higher than those achieved with Sm triflate. The ^{1}H-NMR spectra proved the formation of ether groups, but surprisingly without significant temperature gradient. The MT mass spectra (illustrated by Figure 5) indicated the formation of the five reaction products formulated in Scheme 3. Even the polyester with the highest viscosity value (No 6, Table 4) displayed mainly mass peaks of linear chains (**2La**, **2Lb**, **2Lc**, Scheme 3), what means, that the low viscosity and molecular weight values were above all a consequence of relatively low conversions. This finding and the extremely low viscosities obtained at 80°C indicate that the reactivity of DCMAh is lower than those of MaAh or CiAh contrary to our expectations. In addition to the steric hindrance caused by two Cl atoms, electronic effects may play a predominant role. If the lone electron pairs of the Cl atoms are delocalized to the double bond, they exert a positive mesomeric effect which overcompensates the negative inductive effect of their electronegativity, and thus, reduce the electrophilicity of the CO groups.



Sch. 3. Reaction products of DCMA and 1,6-hexanediol

Furthermore, it should be mentioned that three polyesters (No. 2, 6, and 8 on Table 3) were subjected to ^{13}C-NMR spectroscopy to detect isomerization to dichlorofumarate groups. However, in all three cases, only two signals of the dichloromaleate units were observed at 130.50 and 161.3ppm. Considering the lower signal-to-noise ratio of the ^{13}C-NMR spectra, it may be concluded that isomerization, if it happened at all, was certainly below a level of 5%. Finally, it should be noted that all polyesters prepared in this work were amorphous, and therefore, characterization by X-ray and DSC measurements was not performed.

4 Conclusions

The results obtained in this work allow for the following interesting conclusions. First, in contrast to analogous polycondensations of MaAh, Bi triflate proved to be the best catalyst for polycondensations of CiAh or DCMAh in bulk at 100°C. Second, the chain growth was, in all experiments, mainly limited by incomplete conversion and not by side reactions destroying fuctional groups, but surprisingly, neither longer reaction times nor higher temperatures gave significantly higher molecular weights. The third unexpected result was the relatively low reactivity of DCMAh which may be ascribed to a positive mesomeric effect of the free electron pairs of the Cl atoms. Due to the amorphous character with glass transitions <20°C and due to the low or moderate molar masses, the polyesters prepared in this work are useless as engineering plastics or fiber forming materials. Yet, the polyesters of citraconic acid may be useful as components of coatings and lacquers allowing for radical branching or crosslinking.

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