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Telechelic Poly(butylene terephthalate)s by Means of Bismuth Catalysts

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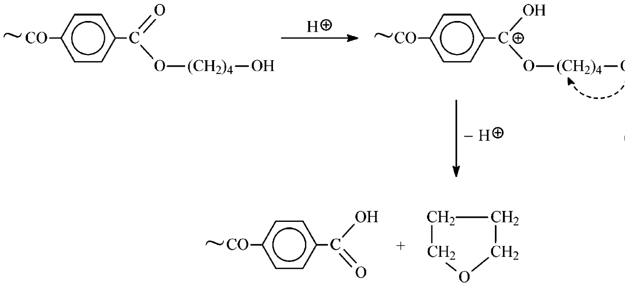
ABSTRACT: Dimethyl terephthalate was polycondensed in bulk with a 300 mol % excess of 1,4-butanediol in bulk up to 250 °C. The following catalysts were used Bi_2O_3, $BiCl_3$, Bi−subsalicylate, bismuth(III) acetate, ZnO, $ZnCl_2$, SnO, $SnCl_2$, Y_2O_3, YCl_3, La_2O_3, $LaCl_3$, Sb_2O_3/manganese(II) acetate, and $Ti(OBu)_4$. The highest molecular weights were obtained with $Ti(OBu)_4$. The MALDI−TOF mass spectra revealed that cycles were the main reaction products below 5000 Da. Clean telechelic oligo- and polyesters having two OH end groups were obtained with Bi_2O_3 and bismuth(III) acetate. With $BiCl_3$, almost clean telechelics having two dimethyl terephthalate end groups were obtained. All other catalysts yield complex reaction mixtures containing cycles and linear chains having CH_2OH methyl ester and/or CO_2H end groups. At a final reaction temperature of 280 °C, formation of cycles, of CO_2H, end groups and of bis(4-oxybutyl) ether units was favored.

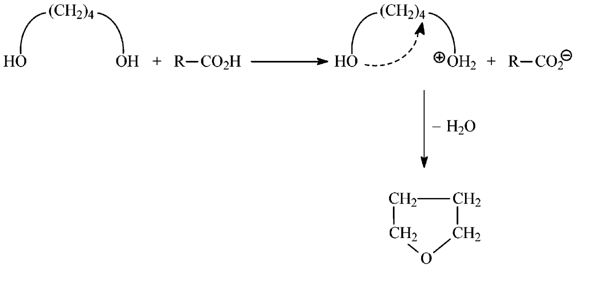
Introduction

Poly(butylene terephthalate), PBT, is an important engineering plastic, which over the past 50 years was mainly produced by polycondensation of dimethyl terephthalate with an excess of 1,4-butanediol.[1,2] PBT has a moderately high melting temperature of around 225 °C, which allows easy processing from the melt. This property, rapid crystallization, and the ability to modify the mechanical properties by additives or by blending rendered PBT a particularly useful thermoplastic material. Furthermore, PBT blocks proved to be attractive as crystalline blocks of thermoplastic elastomers[3,4] because of their rapid crystallization.

All syntheses of PBT in the melt (as it is typical for the technical production) are plagued by side reactions such as the thermal β-elimination (Scheme 1) by acid-catalyzed formation of tetrahydrofuran[2,5,6] (eqs 1 and 2) and by acid-catalyzed formation of dibutyl ether units (eq 3). These side reactions limit, of course, the chain growth, and thus, it is a permanent challenge to find better catalysts which allow for a reduction of the reaction time and of the extent of side reactions. The most successful and most widely used catalysts for syntheses of PBT and related block copolymers are titanium tetraalkoxides, mainly $Ti(OBu)_4$. A slight reduction of the reaction time was recently reported by using cocatalysts such as La(acac)s,[7] $Hf(acac)_3$,[7,8] or NaH_2PO_4.[9] However, a significant enhancement of the molecular weight was not mentioned. A considerable enhancement of the molecular weight (by a factor of 2 or 3) may be achieved by solid-state polycondensation of PBT at temperatures around 210−220 °C[2] with the disadvantage of long and expensive reaction times. A second approach to enhance the molecular weight is the addition of di- or trifunctional coupling agents. Yet, the success of this method requires that most PBT chains possess CH_2OH or CO_2H end groups. Therefore, it was the first purpose of this work to study the influence of various catalysts on nature and number of end groups. In the ideal case, clean telechelic oligo-/poly PBT chains should be obtained.



(1)



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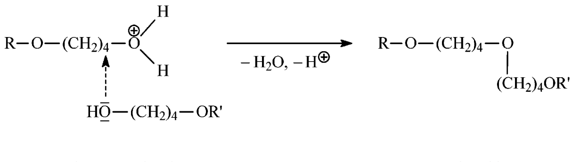

(3)

It was the second purpose of this study to obtain more information about the extent of cyclization by means of MALDI−TOF mass spectrometry. The role of cyclization was not included in previous studies of side reactions.[1,2,5,6] Yet, it is well-known that a few percent of cyclic oligoesters are formed when PBT is synthesized by transesterification reactions in the melt. When PBT is exposed to transesterification catalysts at high temperature and low concentration, even large amounts of cyclic oligoesters can be produced[10] in agreement with the Jacobson−Stockmayer theory.[11] However, to the best of our knowledge a detailed mass spectroscopic study of how the reaction conditions influence the formation of cyclic oligo- and polyesters has not been published yet. The presence of sizable amounts of cycles hinders the calculation of number-average molecular weights (M_ns) from end group analyses, reduces the

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Scheme 1

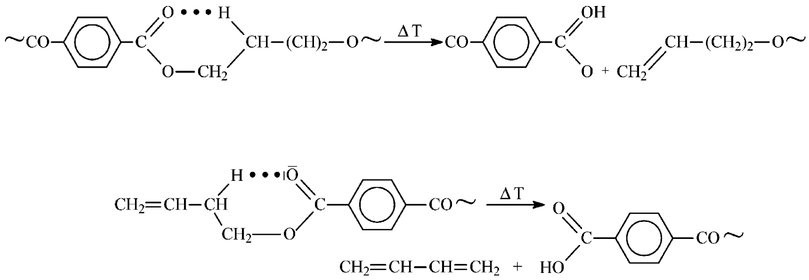


Table 1. Polycondensations of Dimethyl Terephthalate with 1,4-Butanediol Using Various Catalysts

expt no.	catalyst	η_{inh}[a] (dL/g)	reaction products (MALDI−TOF)[b]
1	ZnO	0.17	**La**, **Lb**, **Lc**, (**C**)
2	$ZnCl_2$	0.10[c]	**Lc**, **Lf** (**La**)
3	SnO	0.61	**Lb** + **C** (up to 2000 Da)
4	$SnCl_2$	0.68	**Lb** + **C**
5	Y_2O_3	0.08	**La**, **Lc**, **Lb**, **C**, **Ld**
6	YCl_3	0.12	**La**, **Ld**, **Lb**, **C**
7	La_2O_3	0.10	**La**, **Lb**, **Lc**, **C**
8	$LaCl_3$	0.12	**La**, **Lc**, **Lb**, **C**, **Ld**
9	Sb_2O_3 + $MnAc_2$	0.19	**La**, **Lc**, **Lb**, **C**
10	$Ti(OBu)_4$ + NaH_2PO_4	0.92[d]	**C**
11	$Ti(OBu)_4$	1.00	**C**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (4:1 by volume). [b] Symbols in parentheses mean that only traces of this species were detectable. [c] $M_n \sim 300$ Da, $M_w \sim 600$ Da. [d] $M_n \sim 23\,000$ Da, $M_w \sim 51\,000$ Da by SEC measurements.

Table 2. Bismuth-Catalyzed Polycondensations[a] of Dimethyl Terephthalate with 1,4-Butanediol

expt no.	catalyst	final temp (°C)	time (h)	η_{inh}[b] (dL/g)	reaction products (MALDI-TOF)[d]
1	Bi_2O_3	250 + vacuum	2.0	0.36[c]	**Lb**
2	Bi_2O_3	250 + vacuum	5.0	0.53	**Lb**, (**C**)
3	Bi_2O_3	240 + vacuum	0.5	0.28	**Lb**
4	Bi_2O_3	240 + vacuum	1.0	0.47	**Lb**
5	Bi_2O_3	240 + vacuum	2.0	0.62	**Lb**, (**C**)
6	Bi_2O_3	240 + vacuum	5.0	0.53	**Lb**, (**C**)
7	$Bi(OAc)_3$	250 + vacuum	1.0	0.36	**Lb** (**Lb′**)
8	BiO salicylate	250 + vacuum	1.0	0.24	**Lb**, **Ld**, **C** (**Lc**)
9	$BiCl_3$	250 + vacuum	1.0	0.28	**Lc** (**Lc′**)

[a] Up to the final reaction temperature, the same time/temperature program was used for all polycondensations. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (4:1 by volume). [c] Repetition of the experiment gave $\eta_{inh} = 0.34$ dL/g. For this sample $M_n \sim 2000$ Da and $M_w \sim 7000$ Da was found by SEC. [d] Symbols in parentheses mean that only traces of this species were detectable.

Table 3. Polycondensations of Dimethyl Terephthalate with 1,4-Butanediol Using Various Catalysts (Final Temperature: 280 °C)

expt no.	catalyst	η_{inh}[a] (dL/g)	reaction products (MALDI-TOF)[b]
1	Bi_2O_3	0.27	**C**, **Le**, **Ld**, **C′**
2	Sb_2O_3 + $Mn(OAc)_2$	0.43	**C**, **Le**, **Ld**, **C′**
3	$SnCl_2$	0.76	**C**, **Le**, **Ld**
4	$Ti(OBu)_4$	0.64	**C**, **Le**, **Ld**, **C′**

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [b] Symbols in parentheses mean that only traces of this species were detectable.

efficiency of chain extension, and affects the melt rheology. Unfortunately, the MALDI−TOF mass spectrometry alone does not allow for a quantification of individual reaction products, but it allows for a straightforward comparison of polymers prepared under various reaction conditions.

Experimental Section

Materials. Dimethyl terephthalate was kindly supplied by DSM Research (Geleen, The Netherlands) and used as received. 1,4-Butanediol and all catalysts were purchased from Aldrich Co. (Milwaukee, WI), whereas the catalysts were used as received. 1,4-Butanediol was azeotropically dried with toluene and distilled in a vacuum of 10^{-1} mbar.

Polycondensations. A. Final Temperature: 240 °C (Nos. 1 and 2, Table 2). Dimethyl terephthalate (50 mmol), 1,4-butanediol (200 mmol), and the catalyst (0.05 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 onto an oil bath preheated to 150 °C. The following temperature/time regime was then applied: 180 °C (0.5 h), 190 °C (0.5 h), 220 °C (0.5 h), and 240 °C (0.5 h with vacuum). The evolved methanol and 1,4-butanediol were removed with a slow stream of dry nitrogen before vacuum was applied. The crude reaction products were characterized.

In an analogous polycondensation, vacuum was applied at 240 °C for 1 h.

B. Final Temperature: 250 °C (Tables 1 and 2). Dimethyl terephthalate (50 mmol), 1,4-butanediol (200 mmol), and catalyst (0.05 mmol) 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 150 °C, and the following temperature/time program was applied: 180 °C (0.5 h), 190 °C (0.5 h), 200 °C (0.5 h), 220 °C (0.5 h), 240 °C (0.5 h, plus vacuum for 15 min), and 250 °C (1.0 h with vacuum). The liberated methanol and the excess 1,4-butanediol were removed with a slow stream of dry nitrogen before vacuum was applied. The crude reaction products were characterized.

C. Final Temperature 280 °C (Table 3). Dimethyl terephthalate (50 mmol), 1,4-butanediol (210 mmol), and catalyst (0.05 mmol) were polycondensed in a cyclic glass reactor using the following time−temperature program: 190 °C (1.0 h), 200 °C (1.0 h), 240 °C (1.0 h), 260 °C (1.0 h), 280 °C (1.0 h with vacuum). The crude reaction products were characterized.

Cyclization of 1,4-Butanediol with $BiCl_3$. Dry 1,4-butanediol (500 mmol) and $BiCl_3$ (1 mmol) were slowly heated to 240 °C in a round-bottom flask equipped with a distillation head. At a bath temperature of approximately 140−150 °C, a colorless liquid began to distill. Up to 180 °C, more than 50% of the original liquid had distilled and was identified by ^1H and ^{13}C NMR spectroscopy as rather pure tetrahydrofuran. In a second experiment, the reaction mixture was refluxed for 10 min prior to distillation. In this case, the distillation of THF began at a bath temperature around 110−120 °C (1,4-butanediol has a boiling point of 230 °C). In a parallel experiment, BF_3OEt_2 (1 mmol) was used as catalyst, and again THF was isolated as the main product.

Measurements. The inherent viscosities were measured in dichloromethane containing 20 vol % of trifluoroacetic acid (TFA) with an automated Ubbelohde viscometer thermostated at 20 °C.

The MALDI−TOF mass spectra were recorded on a Bruker Biflex III mass spectrometer equipped with a nitrogen laser

($\lambda = 337$ nm). All spectra were measured in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from hexafluoro-2-propanol with dithranol as matrix and K−trifluoroacetate as dopant. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker "Avance 400" spectrometer in 5 mm o.d. sample tubes. A mixture of $CDCl_3$/TFA (4:1 by volume) containing TMS served as solvent and shift reference, respectively.

The SEC measurements were performed with a Hewlett-Packard 1090M2 liquid chromatograph equipped with four detectors: a UV-DAD detector combined with Tri SEC 3.0 software, a RI detector HP 1047, a differential viscometer Visutek H 5023 combined with a data manager DM 400, and a light-scattering detector working with a scattering angle of 90°. A set of three PPS "PFG linear XL" columns was used thermostated at 35 °C. Hexafluoro-2-propanol containing 0.1 mol % of potassium trifluoroacetate served as eluent at a flow rate of 0.4 mL/min.

Results and Discussion

Polycondensations Using Various Catalysts. All polycondensations were conducted in bulk with a 300 mol % excess of 1,4-butanediol relative to DMT. The catalysts were added in a molar ratio of 1/1000 relative to DMT. For the first series of polycondensations (summarized in Table 1), 11 different catalysts were selected. $Ti(OBu)_4$ was selected because it is the most widely used catalyst for the technical production of PBT and also used for syntheses of poly(ethylene terephthalate), PET (frequently in combination with other catalysts such as Sb_2O_3). An addition of NaH_2PO_4 (no. 10, Table 1) was recommended in a recent publication.[9] The combination of Sb_2O_3 and manganese(II) acetate is again another catalyst which has found application in the technical production of PET. Furthermore, four elements were selected, salts of which are known to be good transesterification catalysts and efficient initiators of ring-opening polymerizations of lactones. The salts of these elements were selected, so that a relatively basic catalyst (oxide) and a relatively acidic catalyst (i.e., the chloride) could be compared.

All polycondensations listed in Table 1 were performed with the same temperature/time program and the maximum temperature was limited to 250 °C. This temperature is slightly higher than the melting temperature of PBT, and thus, the reaction mixtures were permanently kept in the molten state.

The inherent viscosities and the SEC measurements of three selected samples (see footnotes of Tables 1 and 2) revealed that high molar mass PBT was only obtained with $Ti(OBu)_4$ (nos. 10 and 11, Table 1). Moderately high molar masses were obtained with SnO and $SnCl_2$ (nos. 3 and 4, Table 1), whereas all other catalysts listed in Table 1 yield low molar mass products. MALDI−TOF mass spectrometry was used for the structural characterization of the virgin reaction products because it allows for the detection of cyclic polymers and of individual end group combinations in contrast to ^{1}H or ^{13}C NMR spectroscopy. The mass peaks of the MALDI−TOF MS presented in Figures 1−4 and 6 were labeled according to the structures summarized in Scheme 2. The same symbols were also used in Table 1 (and Tables 2 + 3).

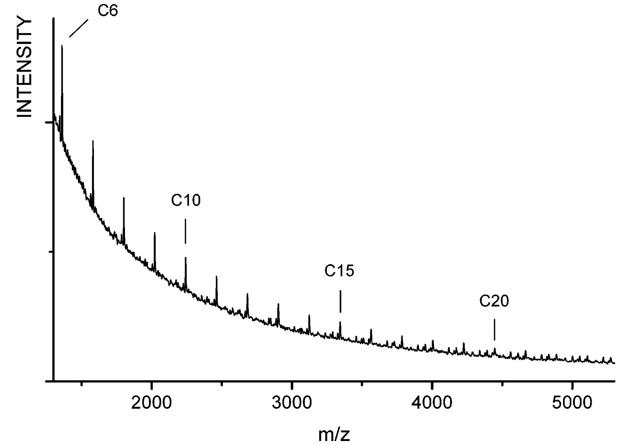


Figure 1. MALDI−TOF mass spectrum of the PBT obtained by $Ti(OBu)_4$-catalyzed polycondensation (no. 11, Table 1).

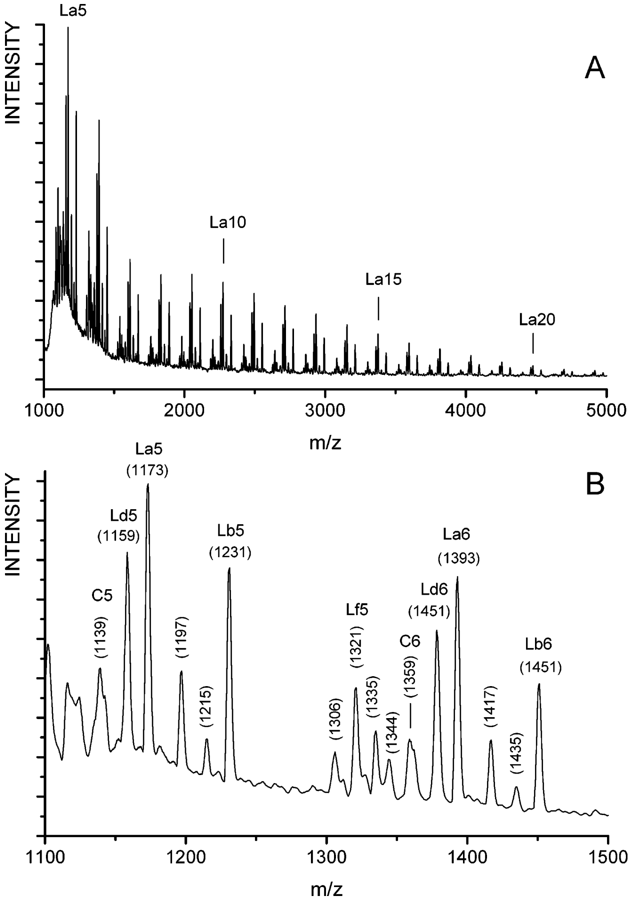


Figure 2. MALDI−TOF mass spectrum of the PBT obtained by YCl_3-catalyzed polycondensation (no. 6, Table 1).

Unfortunately, the high molar PBT samples prepared with $Ti(OBu)_4$ gave, as expected, MS with rather poor signal-to-noise ratio. The reason for this nonsatisfactory result is the fact that in the case of most polar polymers, chains with masses above 10 000 or 15 000 Da are barely detectable by the MALDI−TOF method (using the reflection mode). In high molar mass polymers, the fraction of chains having masses below 10 000 or 15 000 Da is relatively low and the signal-to-noise ratio is therefore low. Nonetheless, the MS of samples nos. 10 and 11 revealed that cyclic polyesters were the main products in the mass range below 5000 Da (Figure 1). Similar MS were obtained for the SnO- and $SnCl_2$-catalyzed PBT samples. The formation of small amounts of cyclic oligomers (~ 3 wt %) were predicted by Jacobsen and Stockmayer for all thermodynamically controlled polycondensations (TCPs). TCP means that rapid equilibration reactions (including backbiting) establish thermodynamically controlled chain−chain, ring−chain, and ring−ring equilibria at any stage of a

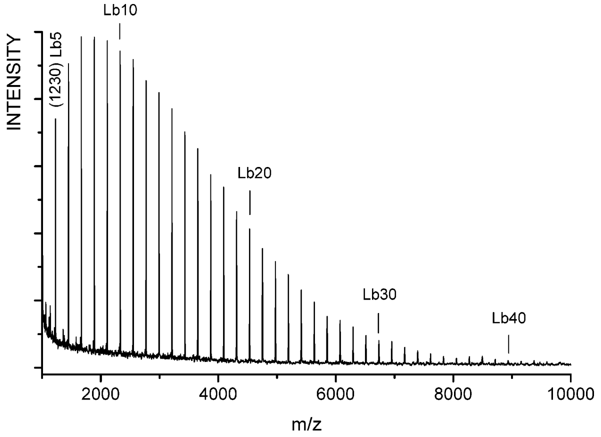


Figure 3. MALDI−TOF mass spectrum of the PBT obtained by Bi_2O_3-catalyzed polycondensation (no. 3, Table 2).

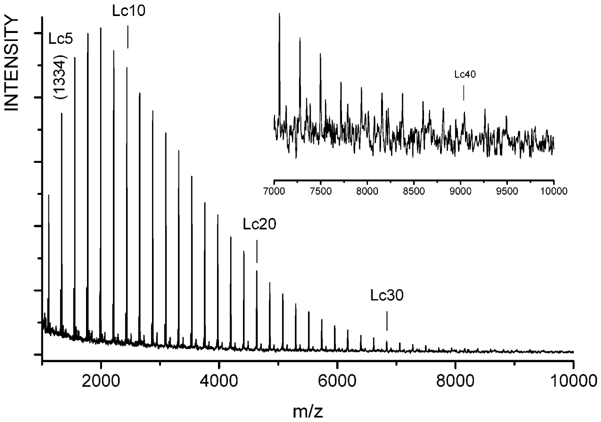
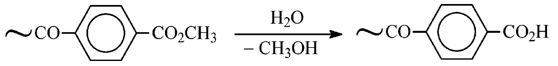


Figure 4. MALDI−TOF mass spectrum of the PBT obtained by $BiCl_3$-catalyzed polycondensation (no. 9, Table 2).

polycondensation. In a recent modification of this theory, Kricheldorf has postulated[12] that the content of cycles steadily increases with the conversion and finally reaches 100% at 100% conversion. The results of this study satisfy this hypothesis, because cyclic oligomers and polymers proved to be the main products when the best transesterification catalysts were used and when the highest molar masses (and thus conversions) were achieved.

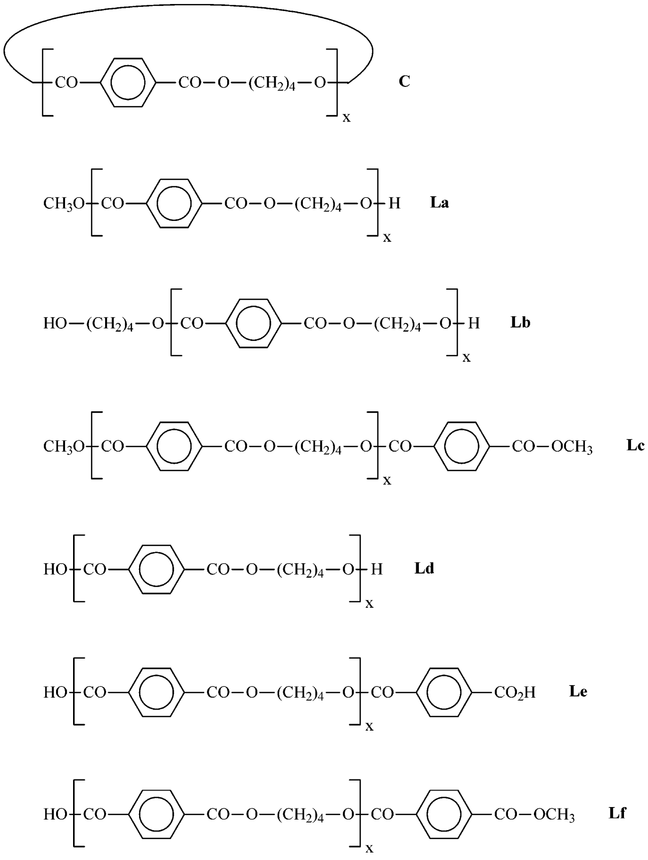
The reaction products obtained from all other catalysts were complex mixtures of linear chains with a low content of cycles. The MS presented in Figure 2 is an exemplary illustration of this result. The simultaneous presence of methyl ester end groups and CH_2OH end groups proves that the conversions were far from complete. Free CO_2H groups (**Ld**, **Le**, **Lf**) are a consequence of a rapid formation of tetrahydrofuran. The CO_2H groups were either formed by the direct cyclization of butanediol ester end groups (eq 1) or via the intermediate formation of water (eqs 2 and 4).



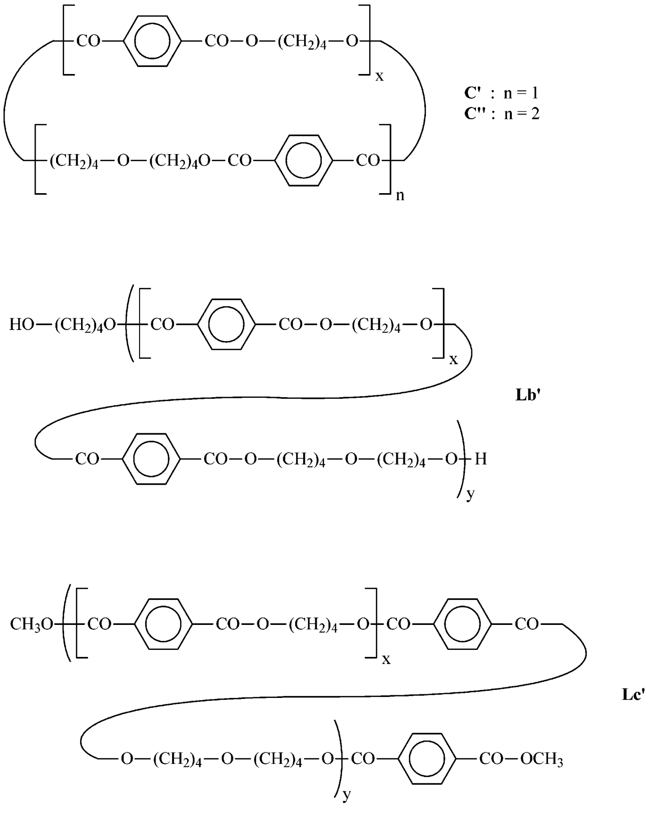
(4)

Polycondensations Using Bismuth Catalysts. The original screening of various transesterification catalysts (Table 1) included Bi_2O_3 and $BiCl_3$. Yet, the surprising results obtained with both catalysts prompted a somewhat more detailed study and a separate discussion. When the PBT prepared with Bi_2O_3 up to 250 °C (nos. 1 and 2, Table 2) was analyzed by MALDI−TOF mass spectrometry, an almost clean telechelic polyester of structure **Lb** was found after 2 h, as evidenced by Figure 3. A longer reaction time had the consequence

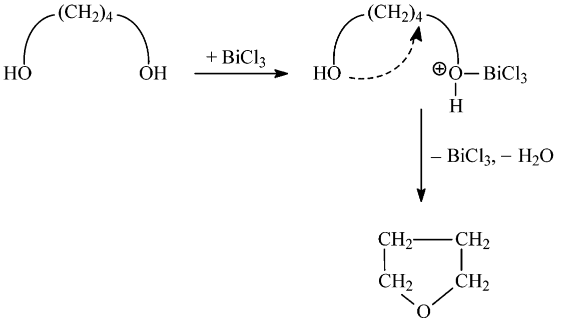
Scheme 2. Potential Reaction Products of PBT Syntheses



Scheme 3. PBT Species Containing Bis(4-butyl) Ether Units



that a higher molecular weight was obtained and a small amount of cycles was formed. Reduction of the final reaction temperature to 240 °C and variation of time with vacuum allowed for a broader variation of the molecular weight (nos. 3−6) but the reaction products were the same. At longer reaction times (≥2 h), traces of cycles became detectable (nos. 5 and 6). When a "250 °C polycondensation" was performed with bismuth(III) acetate as catalyst (no. 4), again almost perfect telechelics of **Lb** structure were found. With bismuth subsalicylate (no. 8), the **Lb** structure was still prevailing, but large amounts of **Ld** chains having one CH_2-OH and one CO_2H end group were also present. Furthermore, cycles containing one ether group (formally: +THF) and traces of **Le** chains were detectable. With $BiCl_3$ as catalyst, rather clean telechelics of structure **Lc** were obtained as demonstrated by the MS of Figure 4. Weak peaks of **Lc′** chains (Scheme 2) containing one ether group were also observable. The totally different result obtained with $BiCl_3$ may be explained by its role as Lewis acid favoring the formation of tetrahydrofuran and bis(4-hydroxybutyl) ether from 1,4-butanediol. The rapid formation and distillation of tetrahydrofuran causes an imbalance of the stoichiometry, so that the initial excess of butanediol is converted into an excess of DMT. This hypothesis was confirmed by heating neat 1,4-butanediol with $BiCl_3$ (molar ratio 500:1) or with BF_3, whereby large amounts of tetrahydrofuran were isolated. Quite surprising is the selectivity of this process, because the absence of CO_2H groups proves that tetrahydrofuran was formed according to eq 5, and hydrolysis of ester groups was not catalyzed. The result obtained with $BiCl_3$ cannot be explained by a catalytic effect of liberated HCl alone, because other metal chlorides which also can liberate HCl gave different results (Table 1).



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The structures of the telechelics **Lb** and **Lc** obtained by catalysis with Bi_2O_3, bismuth(III) acetate, or $BiCl_3$ were confirmed by ^1H NMR spectroscopy. In the ^1H NMR spectra of the samples nos. 1−4 (Table 2) a multiplet signal of the CH_2OH end groups was detectable around 3.8 ppm (measured in $CDCl_3$ + TFA, volume ratio 8:1). Characteristic for this end group is its rapid reaction with trifluoroacetic anhydride which shifts the OCH_2 signal about 0.5 ppm to lower field where it overlaps with the signal of the repeat units. In the case of sample no. 6 (see Figure 5), a singlet signal of the methylester end groups is observable at 4.05 ppm (signal c) and a weak triplet signal at 3.75 ppm (signal x) resulting from the protons of the $-CH_2-O-CH_2-$ groups.

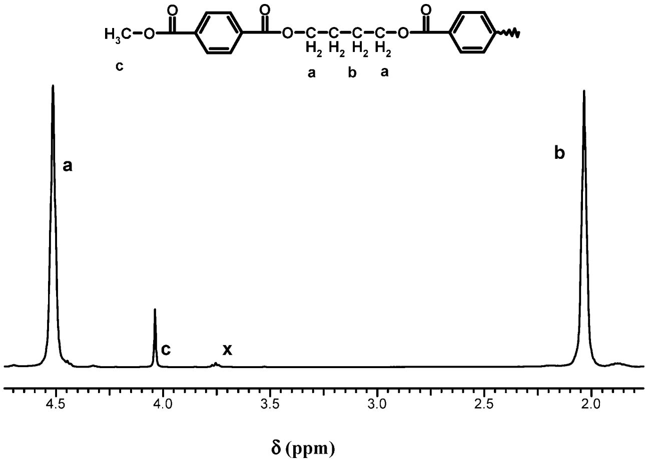

Figure 5. 400 MHz ^1H NMR spectra of the PBT obtained by $BiCl_3$-catalyzed polycondensation (no. 9, Table 2).

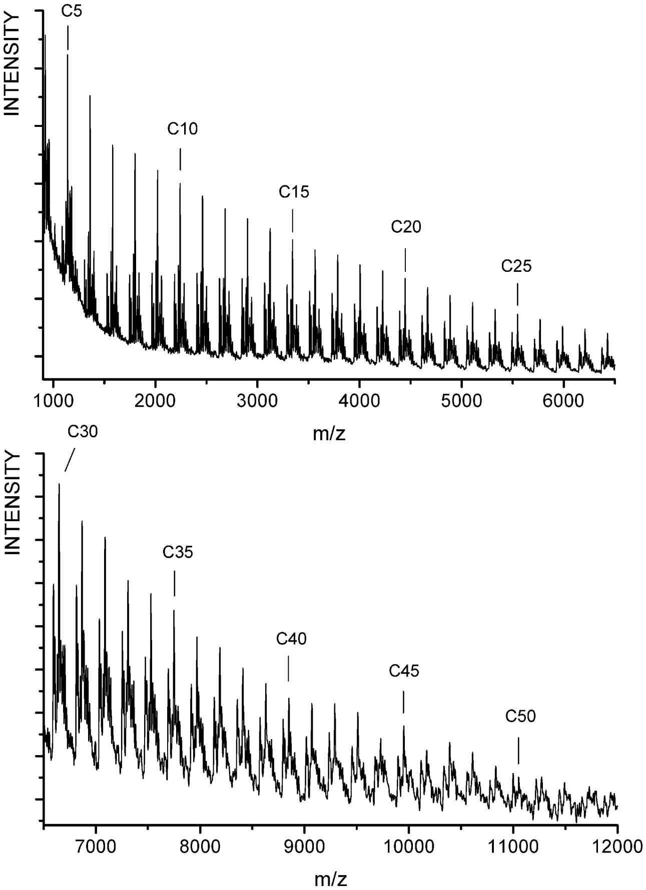

Figure 6. MALDI−TOF mass spectrum of the PBT catalyzed by Sb_2O_3 + $MnAc_2$ (up to 280 °C, no. 2, Table 3).

Finally, the influence of higher polycondensation temperatures was studied for Bi_2O_3 and three other catalysts (Table 3). In the case of Bi_2O_3, the **Lb** telechelics had completely vanished whereas the content of cycles was considerably higher. Furthermore, weak peaks of the ether containing **C′** were detected. Moreover, **Le** chains (two CO_2H end groups) and four more peaks of unidentified byproducts were observable. The same trend was found for the other three polycondensations listed in Table 3. The content of cycles and of linear chains containing ether groups (**Lb′** and **Lc′**) or CO_2H end groups (**Le**) was higher. Particularly interesting proved the MS of the sample prepared with Sb_2O_3/$MnAc_2$ (Figure 6) which from the technical point of view was the best mass spectrum of this work, and thus, particularly informative. The cyclic oligo- and polyesters of structure **C** were the main products up to masses around 12 000 Da, clearly proving that the formation of cycles in syntheses of PBT is not limited to oligomers. Furthermore, mass peaks of cycles containing one ether unit (**C′**) were found as minor byproduct. The main representative of the linear chains had the structure **Le** with two CO_2H end groups. Furthermore, **Lf** and **Lc** chains were detected. The existence of large amounts of CO_2H end group corresponds to an efficient elimination of tetrahydrofuran either according to eq 1 or eq 2. Four more weak peaks were detectable having masses of 16, 22, 38, and 55 Da above the mass of cycles. These species were not identified, but all mass peaks together demonstrate that syntheses of PBT at high temperatures involve a complex pattern of side reactions.

Conclusions

The screening of various transesterification catalysts with respect to their usefulness in the preparation of PBT yielded two interesting results. First, bismuth salts were unexpectedly found to allow for syntheses of rather clean telechelic PBTs. The relatively basic oxide and the acetate yielded OH-terminated polyesters (**Lb**), whereas the acidic $BiCl_3$ yields telechelics terminated by two methyl ester groups (**Lc**). Particularly surprising is the high selectivity of the transesterifications catalyzed by Bi_2O_3 and $Bi(OAc)_3$. It is only the alcoholytic transesterification of the methyl ester groups of DMTA which is promoted, whereas the "backbiting equilibration" (and probably the ester-ester interchange) is not catalyzed at temperatures ≤ 240 °C. The **Lb** telechelics generated by means of Bi_2O_3 are useful starting materials for syntheses of A−B−A triblock copolymers and multiblock copolymers (e.g., thermoplastic elastomers) and for a variety of chain extension reactions. With regard to biomedical applications it is noteworthy that bismuth is seemingly the least toxic heavy metal. Second, it was found that the content of cyclic oligo- and polyesters increases with the efficiency of transesterification and with higher conversion. This finding complies to our theory of thermodynamically controlled polycondensation which postulates that the weight fraction of cycles (and their ring size) steadily increases with the conversion and approaches 100% for quantitative conversion of the functional groups.[12]

Further studies of syntheses of telechelic polyesters using bismuth-based catalysts are in progress and yielded promising results in the field of biodegradable aliphatic polyesters.[13]

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References and Notes

(1) Pilati, F. Polyesters. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: Oxford, U.K., 1989; Vol. 5, pp 275−315.
(2) Van Berkel, R. W. M.; Van Hartingsveldt, E. A. A.; Van der Sluijs, C. L. Polybutylene Terephthalate. In *Handbook of Thermoplastics*; Olabisi, O., Ed.; Marcel Dekker Inc.: New York, Basel, and Hong Kong 1997; Chapter 20.
(3) Adams, R. K.; Hoeschele, G. K.; Witsiepe, W. K. Thermoplastic Poly(ether ester) Elastomers. In *Thermoplasatic Elastomers*, 2nd ed.; Holden, G., Legge, N. R., Quirk, R., Schroeder, H. E., Eds.; Hanser Publ.: New York, 1996; Chapter 8.
(4) Van Berkel, R. W. M.; Borggreve, B. J. M.; van der Sluijs, C. L.; Werumeus-Baning, C. H. W. In *Polyester-Based Thermoplastic Elastomers*" in *Handbook of Thermoplastics*; Olabishi, O., Ed.; Marcel Dekker: New York, 1997; Chapter 17.
(5) Passalacqua, V.; Pilati, F.; Zamboni, V.; Fortunato, B.; Manaresi, P. *Polymer* **1976**, *17*, 1044.
(6) Lum, R. M. *J. Polym. Chem. Ed.* **1979**, *17*, 203.
(7) Banach, T. E.; Buti, C.; Colonna, M.; Fioroni, M.; Marianucci, E.; Messori, M.; Pilati, F.; Toselli, M. *Polymer* **2001**, *42*, 7511.
(8) Banach, T. E.; Colonna, M. *Polymer* **2001**, *42*, 7514.
(9) Colonna, M.; Banach, T. E.; Berti, C.; Fioroni, M.; Marianucci, E.; Messori, M.; Pilati, F.; Toselli, M. *Polymer* **2003**, *44*, 4773.
(10) Hubbard, P. A.; Brittain, W. J.; Mattice, W. L.; Brunelle, D. J. *Macromolecules* **1998**, *31*, 1518.
(11) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(12) Kricheldorf, H. R. *Macromolecules* **2003**, *36*, 2302.
(13) Kricheldorf, H. R.; Behnken, G.; Schwarz, G. *Polymer*, submitted.

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