Biodegradable Hyperbranched Aliphatic Polyesters Derived from Pentaerythritol

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ABSTRACT: Pentaerythritol (PENT) was polycondensed with dimethyl sebacate (DMS) in bulk at 240 °C. With $Ti(OBu)_4$ as the catalyst, an equimolar feed ratio resulted in gelation even when no vacuum was applied. When the PENT/DMS ratio was raised to 1.2/1.0, soluble viscous resins were obtained, but despite the excess of PENT, the conversion of methyl ester groups never exceeded 92%. With bismuth(III) *n*-hexanoate ($BiHex_3$) as the catalyst and an 1.0/1.0 feed ratio, nonviscous polyesters were obtained with conversions <75%. When $BiHex_3$ was used in the beginning and $Ti(OBu)_4$ was added at a later stage, soluble viscous resins were obtained even at 1.0/1.0 feed ratio. Further polycondensations were conducted with higher PENT/DMS ratios. The reaction products were characterized by viscosity measurements, ^{1}H NMR spectroscopy, and MALDI-TOF mass spectrometry. These measurements indicated the formation of hyperbranched polyesters almost free of cycles and ether groups. Furthermore, acylations with acetic or methacrylic anhydride were studied and quantitative conversions of the CH_2OH groups were achieved.

Introduction

The present work deals with polycondensations of pentaerythritol and dimethyl sebacate. This work should serve two purposes. From the viewpoint of material science, this work belongs to a broader study of synthesis, characterization and application of biodegradable polyesters. With pentaerythritol as tetrafunctional (b_4) monomer, two structural features should be realized, namely, (hyper)branching and functionalization with numerous hydroxy groups. These groups allow for a further modification by acylation or alkylation, and they render these polyesters good adhesives forming H-bonds to a variety of polar surfaces.

On the other hand, polycondensations of pentaerythritol and dicarboxylic acids (or their derivatives) are representative examples of "$a_2 + b_4$" polycondensations also known as "three-dimensional" polycondensations.[1] The first example of an "$a_2 + b_4$" polycondensation was reported by Flory,[1,2] who studied acid catalyzed polycondensations of dicarboxylic acids with pentaerythritol in the melt to prove his theory of step-growth polycondensations. He had defined a branching factor "α", which (for feed ratios of 2:1 and in the absence of side reactions) was connected to the functionality of the "b_n" monomer by eq 1 and to the conversion by eq 2. Under ideal conditions and in the absence of cyclization reactions, gelation should set in at a conversion above 57.5%. Flory found that gelation occurred at a conversion above 60% and attributed the difference in his theoretical calculations to the existence of a few cyclization reactions. However, at that time, high resolution NMR-spectroscopy did not exist, and the acid-catalyzed formation of ethers from primary alcohol groups (eq 3) was not distinguishable from the cyclization of main or side chains via ester groups as schematically formulated in eq 4. Cyclization such as that of eq 4 occur in competition to chain growth in any kind of two- or three-dimensional polycondensations[3] and are unavoidable, whereas side reactions such as that of eq 3 depend on the reaction conditions, on the reaction mechanism, and on the catalyst.

In this context, the present work served two purposes. On one hand, biodegradable OH-functionalized polyesters could be prepared, which might be useful as adhesives with or without additional modification. On the other hand, an "$a_2 + b_4$" polycondensation could be studied, which is complementary to the work of Flory in two directions. First, transesterification reactions without addition of acidic catalysts could be used as synthetic method to avoid acid-catalyzed formation of ether groups, and second, a feed ratio of 1:1 could be used to avoid gelation and to obtain linear and hyperbranched polyesters. In this context, it should be mentioned that several "$a_2 + b_4$" polycondensations based on either a 1:1 feed ration[4−6] or a 2:1 feed ratio[7−15] were previously reported by Kricheldorf and coworkers. Recently, an "$a_2 + b_4$" polycondensation that yielded a soluble multicyclic oligomer called "noria" was published by Nishikubo et al.[16]

Experimental Section

Materials. Pentaerythritol, bispentaerythritol, and dimethyl sebacate (purity ≥ 99%) were purchased from Aldrich (USA) and used as received. Dimethyl sebacate (purity 94%) was also purchased from ACROS Organics (Geel, Belgium) and used as received. Titanium tetrabutoxide ($Ti(OBu)_4$) and bismuth(III)acetate were purchased from Aldrich Co. Bismuth(III) *n*-hexanoate, $BiHex_3$, was prepared from bismuth acetate and *n*-hexanoic acid as described previously.

A. Polycondensation with $Ti(OBu)_4$ Alone (no. 4, Table 1). DMS (50 mmol) and pentaerythritol (60 mmol) were weighed into a cyclindrical glass reactor equipped with mechanical glass stirrer and gas-inlet and gas-outlet tubes. A 0.5 M solution of $Ti(OBu)_4$ in toluene (0.5 mL) was added. The reactor was purged with nitrogen and placed into an oil bath preheated to 280 °C. After a few minutes, when the reaction mixture began to homogenize, the temperature was lowered to 260 °C. When the homogenization was complete (after approximately 1 h), the temperature was lowered to 240 °C and maintained for 4.5 h. Vacuum was then applied for 15 min. After cooling, the crude reaction product was characterized. The β-experiment was performed to check the reproducibility of the α-experiment.

B. Polycondensation with a Second Addition of $Ti(OBu)_4$ (no. 7, Table 1). DMS (50 mmol) and pentaerythritol (60 mmol) were polycondensed as described above, but after 10 min at 260 °C, a 0.5 M solution of $Ti(OBu)_4$ (0.5 mL) was added again. After 4.5 h at 240 °C, vacuum was applied for 3 min, because evacuation resulted in gelation (nos. 5 and 6, Table 1).

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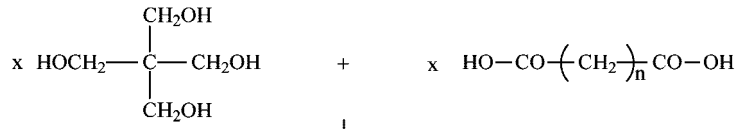
$$\alpha = \frac{1}{f - 1} \quad (1)$$

f = number of functional groups of the b_n monomer (i.e. its functionality)

$$a = p^2 \quad (p = \text{conversion}) \quad (2)$$

$$2\ R{-}CH_2OH \xrightarrow[-H_2O]{(H^{\oplus})} R{-}CH_2{-}O{-}CH_2{-}R \quad (3)$$



$$- 2\,x\ H_2O \quad (4)$$

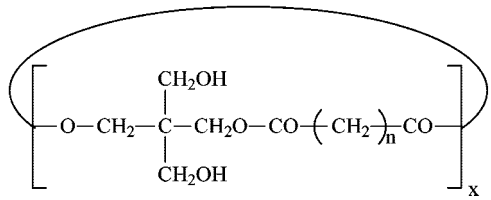


Table 1. $Ti(OBu)_4$ Catalyzed Polycondensations[a] of Pentaerythritol with Dimethyl Sebacate

expt. no.	procedure[b]	PENT[c]/DMS	time of vacuum (min)	conversion (%)	η_{inh}[d] (dL/g)	properties
1α	A	1.0/1.0	0	~85	gelation	
1*β*	A	1.0/1.0	0	~85	gelation	
2	A	1.0/1.0	0	81	0.06	yellowish, viscous, slightly turbid
3	A	1.2/1.0	0	84	0.07	yellowish, viscous, slightly turbid
4α	A	1.2/1.0	15	0.88	0.12	yellowish, viscous, slightly turbid
4*β*	A	1.2/1.0	15	87	0.12	yellowish, viscous, slightly turbid
5	B	1.2/1.0	15	gelation		
6	B	1.2/1.0	10	gelation		
7α	B	1.2/1.0	3	(80) [e]91	0.12	yellowish, turbid, highly viscous
7*β*	B	1.2/1.0	3	(78) [e]91	0.13	yellowish, turbid, highly viscous

[a] Reaction condition: 280 °C/5 min, 260 °C/1 h, 240 °C/4.5 h + time under vacuum as listed above. [b] A: $Ti(OBu)_4$ was added only once before heating. B: $Ti(OBu)_4$ was added twice, before heating and after heating to 260 °C (1 h). [c] Molar feed ratio. [d] Measured at 25 °C with $c = 2$ g/L in DMSO. *e*. [e] Measured before vacuum was applied.

Table 2. $BiHex_3$ Plus $Ti(OBu)_4$-catalyzed Polycondensations[a] of Pentaerythritol with Dimethyl Sebacate

expt. no.	PENT[b]/DMS	time of vacuum (min)	conversion of CO_2CH_3(%)	η_{inh}[c] (dL/g)	properties
1	1.0/1.0	45	gelation	-	solid
2	1.0/1.0	30	gelation	-	solid
3	1.0/1.0	15	84	0.08	transparent highly viscous
4	1.1/1.0	30	83	0.08	yellowish, viscous
5	1.2/1.0	30	82	0.07	greyish, turbid highly viscous
6	1.3/1.0	30	81	0.06	greyish, turbid highly viscous

[a] Procedure C with temperatures decreasing from 280 to 260 °C and finally to 240 °C. [b] Molar feed ratio. [c] Measured at 20 °C with $c = 2$ g/L in DMSO.

C. Polycondensation with a Combination of $BiHex_3$ and $Ti(OBu)_4$ no. 5. Table 2 DMS (50 mmol) and pentaerythritol (60 mmol) were weighed into a cyclindrical glass reactor and a 0.5 M solution of $BiHex_3$ in toluene (0.5 mL) was added. The reaction vessel was placed into an oil bath preheated to 280 °C, and after a few minutes when the homogenization process has begun the temperature was lowered to 260 °C. After 10 min, a 0.5 M solution of $Ti(OBu)_4$ in toluene (0.5 mL) was added, and the homogenization was continued at 260 °C for 1 h. The temperature was then lowered to 240 °C for 4.5 h and finally vacuum was applied for 30 min (see Table 2).

A. Acylations with Acetic Anhydride. The polyester no. 4, Table 1 (2.5 g) was dissolved in dioxane (25 mL), and acetic anhydride (30 mmol = 100% excess relative to CH_2OH groups) and pyridine (60 mmol) were added to the solution. After stirring for 24 h at 20−22 °C, the reaction mixture was precipitated into water. After a few hours, the syrupy reaction product sticked completely to the glass walls of the beaker. Water was decanted, and the remaining product was washed with fresh water and dried at 40 °C in vacuo.

B. Acylations With Methacrylic Anhydride. The polyester no. 4, Table 1 (2.5 g) was dissolved in dry dioxane (25 mL), and methacrylic anhydride (30 mmol = 100 mol% excess relative to CH_2OH) and pyridine (60 mmol) were added to the solution. The reaction mixture was stirred for 20 h at 50−55 °C and finally precipitated into cold methanol. The syrupy product was isolated after decantation of methanol and washed with methanol. It was dried at 60 °C in vacuo and characterized without reprecipitation.

Table 3. Masses Calculated with K-doping for the Reaction Products in Scheme 1

n	C + K	La + K	Lb + K	Lc + K	Ld + K	Le + K	Lf + K
1	341.4	373.4	477.5	571.7	770.0	968.2	505.4
2	643.7	675.7	779.8	874.0	1072.3	1270.5	807.7
3	946.0	978.0	1082.1	1176.3	1374.6	1572.8	1110.0
4	1248.3	1280.3	1384.4	1478.6	1676.9	1875.1	1412.3
5	1550.6	1582.6	1686.7	1780.9	1979.2	2177.4	1714.6
6	1852.9	1884.9	1989.0	2083.2	2281.5	2479.7	2016.9
7	2155.2	2187.2	2291.3	2385.5	2583.8	2782.0	2319.2
8	2457.5	2489.5	2593.6	2687.8	2886.1	3084.3	2621.5
9	2759.8	2791.8	2895.9	2990.1	3188.4	3386.6	2923.8
10	3062.1	3094.1	3198.2	3292.4	3490.7	3688.9	3226.1
11	3364.4	3396.4	3500.5	3594.7	3793.0	3991.2	3528.4
12	3666.7	3698.7	3802.8	3897.0	4095.3	4293.5	3830.7
13	3969.0	4001.0	4105.1	4199.3	4397.6	4595.8	4133.0
14	4271.3	4303.3	4407.4	4501.6	4699.9	4898.1	4435.3
15	4573.6	4605.6	4709.7	4803.9	5002.2	5200.4	4737.6
16	4875.9	4907.9	5012.0	5106.2	5304.5	5502.7	5039.9
17	5178.2	5210.2	5314.3	5408.5	5606.8	5805.0	5342.2
18	5480.5	5512.5	5616.6	5710.8	5909.1	6107.3	5644.5
19	5782.8	5814.8	5918.9	6013.1	6211.4	6409.6	5946.8
20	6085.1	6117.1	6221.2	6315.4	6513.7	6711.9	6249.1

Radical Polymerization of Methyl Methacrylate (MMA). MMA (50 mmol), the methacrylate of polycondensates no. 3, Table 1 (see also procedure B, 200 mg), and dibenzoyl peroxide (0.02 mmol) were weighed into a 25 mL Erlenmeyer flask in an atmosphere of dry nitrogen. The closed reaction vessel was immersed into an oil path preheated to 80 °C. After 24 h, a glassy transparent mass was obtained, insoluble in CH_2Cl_2 and other organic solvents. In a parallel experiment with neat MMA, soluble PMMA was obtained.

Cross-Linking with Diisocyanates. Polycondensate no. 3, Table 1 (2.5 g) was suspended in dry CH_2Cl_2 (25 mL). 1,6-Hexamethylene diisocyanate (2 mmol) was the added, and the reaction mixture was stirred for 24 h at 20 °C, whereby one lump of insoluble material was formed.

In a parallel experiment with isomeric toluene diisocyanates, the formation of an insoluble lump occurred within 0.5 h.

Measurements. ^{1}H NMR spectra were recorded with a Bruker Avance 400 FT NMR spectrometer in 5 mm o.d. sample tubes. DMSO-d_6 containing 10 vol % of C_6D_6 and 0.3 vol % of TMS served as the solvent. The conversion of methyl ester groups was calculated from the singlet signal at 3.57 ppm. The MALDI-TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode using an accelerator voltage of 20 kV. The irradiation targets were prepared from trifluoroethanol solutions using dithranol as matrix and potassium fluoroacetate as dopant. The calculated masses of the reaction products **C**, **La**, **Lb**, **and Lc** are listed in Table 3. Inherent viscosities were measured in DMSO using an automated Ubbelohde viscometer thermostatted at 20 °C.

Results and Discussion

Polycondensations Catalyzed by Ti(OBu)$_4$ Only. Ti(OBu)$_4$ is known as the most efficient catalyst for syntheses of polyesters from alkane diols and dimethylesters of dicarboxylic acids and has been proved in our recent study on comparison of several transesterification catalysts.[4] Therefore, this catalyst is widely used for research activities in the field of polyesters and also for the technical production of poly(butylene terephthalate).[5–8] Consequently, the first series of experiments of this work were performed with Ti(OBu)$_4$ as catalyst (see Table 1). In the first four experiments, the catalyst was added once in the beginning of the polycondensation. All polycondensations were conducted in such a way that the monomer−catalyst mixture was shortly heated to 280 °C and afterward for 1 h to 260 °C to achieve a complete homogenization of the reaction mixture. The polycondensation was then continued at 240 °C, because it is known from degradation studies[9] and previous syntheses[10] that in the case of aliphatic polyesters temperatures above 240 °C may cause severe side reactions. The first polycondensation was performed with an equimolar feed ratio, but gelation occurred before the reaction time of 4.5 h was over. The β-experiment confirmed the reproducibility of the α-experiment. With the assumption that gelation was caused by formation of ester groups and not by ether links, the high conversion of ester groups was responsible for cross-linking. Therefore, the feed ratio was enhanced to 1.2/1.0 (no. 3, Table 1), but a melt of low viscosity was only formed after 4 h. When vacuum was

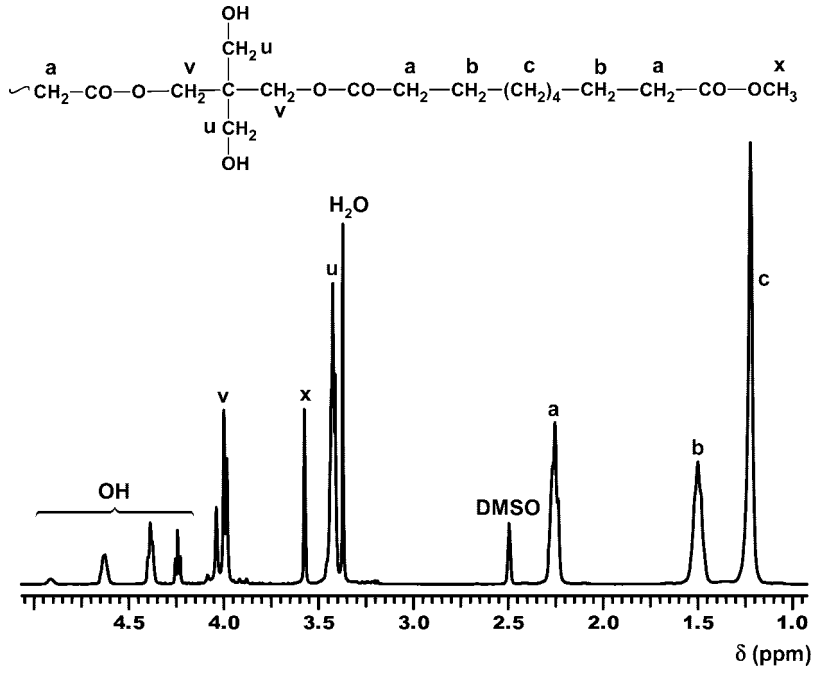


Figure 1. 400 MHz ^{1}H NMR spectrum of the polyester prepared with a PENT/DMS ratio of 1.0/1.0 and one addition of Ti(OBu)$_4$ (procedure A, no. 2, Table 1).

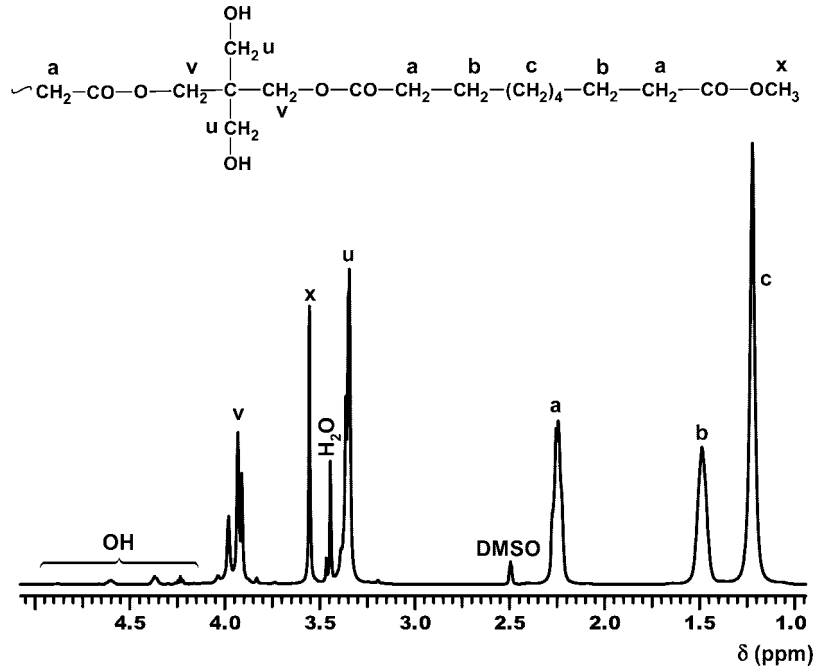


Figure 2. 400 MHz ^{1}H NMR spectrum of the polyester no. 2, Table 1 (see Figure 1) after treatment with D_2O in DMSO-d_6 solution.

applied for 15 min, the higher feed ratio prevented gelation, but the molecular weight increased (no. 4, Table 1, the β-experiment proved the reproducibility). The conversion of the methyl ester groups as determined by ^{1}H NMR spectroscopy from the singlet signal at 3.57 ppm (signal X in Figures 1 and 2) reached 88 ± 1%.

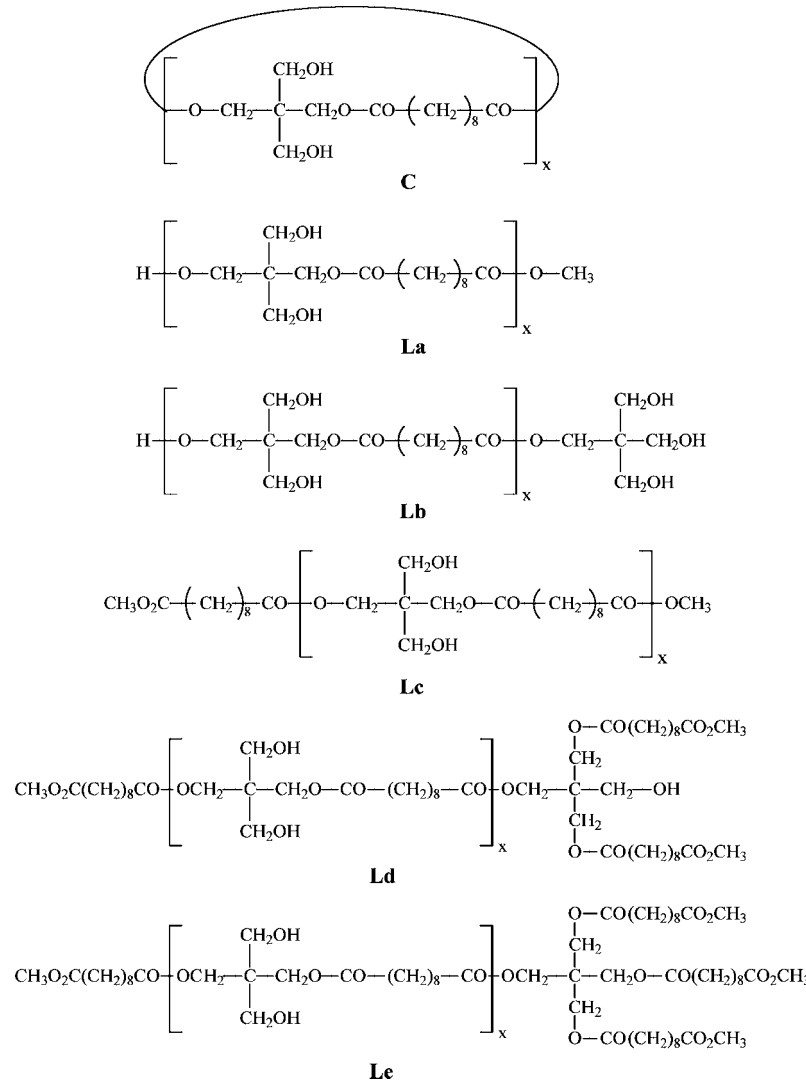
To obtain unambiguous assignments of all signals in DMSO-d_6, three steps were taken. First, the ^{1}H NMR spectrum of neat dimethyl sebacate was measured which displayed the signals x, a, b, and c (Figures 1, 2, and 5). Second, to identify the H_2O peak, a trace of 4-toluene sulfone acid was added which shifted this peak to higher ppm values (downfield). Third, the solution of a polyester in DMSO-d_6 was shaken with D_2O and the excess of D_2O and H_2O were removed by azeotropic distillation with toluene. As demonstrated by Figure 2, the intensities of all signals between 4.1 and 5.0 ppm were strongly reduced, indicating that they originate from OH groups. Fourth, the spectrum of commercial bis-pentaerythritol was measured to identify the signal of the ether ($-CH_2OCH_2-$) groups. Such ether groups were not detected in the polycondensates of this work.

Another interesting aspect of the ^{1}H NMR spectra concerned the splitting of the CH_2O signal around 4.0 ppm into three peaks (3.97, 4.00, and 4.04 ppm) with an intensity ratio around 1:2:1. Furthermore, a weak peak at 4.09 ppm was detectable. These peaks may be assigned to mono-, di-, tri-, and tetra-acetylated PENT units. In other words, the peak at 3.97 ppm represents PENT endgroups (e.g., structure **Lb** in Scheme 1), the peak at 4.00 ppm represents the PENT repeat units, and the peaks at 4.04 and 4.05 ppm indicate the branching points of tri- and tetra-substituted PENT units. This interpretation is supported by the ^{1}H NMR spectrum of the fully acetylated polyester (Figure 5 and discussion below), which displays only one sharp signal for fully acylated PENT groups at 4.09 ppm. The intensity ratio of the first three peaks suggest a statistical mono-, di-, and trisubstitution with one branching point for two repeat units.

The MT mass spectrum presented in Figure 3 gave the following information. Only negligible amounts of cyclic oligoesters (labeled **C** in Scheme 1 and in all Figures) were detectable. Therefore, the MT mass spectra confirm that the polyesters of this work possess an open hyperbranched structure (see also Figure 4 and discussion below). The most intensive mass peaks resulted from chains having methyl ester endgroups (**La** and **Lc** in Scheme 1) or two PENT endgroups (**Lb** in Scheme 1). Hence, this mass spectrum agrees with the ^{1}H NMR spectra in that the conversion of methyl ester groups was far from complete despite the rather harsh reaction conductions and despite an enormous excess of CH_2OH groups. The solubility of the products nos. 3 and 4 (Table 1) obtained from an excess of PENT and the absence of polyesters containing ether groups in the mass spectrum confirmed that under the given conditions the formation of ether groups did not play a significant role, although small amounts might have been formed. However, somewhat different results were obtained when a DMS of ACROS Organics with a purity of 94% was used. The ^{13}C NMR spectrum indicated the presence of CO_2H groups either in the form of free sebacic acid or its monomethyl ester. When this less pure DMS was used, the gelation occurred at lower conversions and the MT mass spectra of the soluble products indicated the presence of ether groups.

In four additional experiments, a second charge of $Ti(OBu)_4$ was added at 260 °C based on the speculation that most of the initially added $Ti(OBu)_4$ had decomposed at 280 °C. With this larger amount of catalyst, partial gelation had occurred after 15 min of evacuation and also after 10 min (nos. 5 and 6, Table 1). Yet, when vacuum was applied for only 3 min, a soluble viscous polyester was obtained and this experiment was reproducible (nos. 7α and 7β). The ^{1}H NMR spectra indicated that the conversion was around 78−80% before and around 91% after subject to vacuum. These results evidenced that the evacuation step was necessary to obtain high conversion, but all experiments also proved that this polycondensation is highly sensitive to slight variations of the reaction conditions. The MALDI-TOF mass spectra of the polyesters nos. 7α and 7β (Table 1) did not provide more information than the mass spectrum presented in Figure 3. All soluble products had in common that the solution viscosities were rather low and quite similar. Such a result was expected, because the conversion of ester groups did never exceed 91% and also because the hyperbranched polymers may have low solution viscosities despite rather high molar masses.

Scheme 1. Potential Reaction Products of Equimolar Polycondensations of Pentaerythritol with Dimethyl Sebacate



Polycondensations Catalyzed by $BiHex_3$ + $Ti(OBu)_4$. A major problem of the procedures A and B discussed above is the high initial reaction temperature required for homogenization of the reaction mixture. Furthermore, it is well-known from technical syntheses of poly(butylene terephthalate)s and had beenconfirmed by a recent study[11]) that $Ti(OBu)_4$ causes several side reactions in polycondensations of alkane diols above 220 °C. On the other hand, it was demonstrated[11,12] that Bi_2O_3 and Bi(III) carboxylates are less reactive as transesterification catalysts but cause significantly fewer side reactions. Therefore, a third procedure (C) was tested in the present work based on a sequential addition of two catalysts. The first condensation and homogenization step at 280 °C was catalyzed by $BiHex_3$ and after lowering of the temperature to 260 °C $Ti(OBu)_4$ was added. Finally, the polycondensation was continued at 240 °C and vacuum was applied at the end of the entire polymerization process (see Table 2).

When the "vacuum time" was varied with a constant feed ratio of 1.0/1.0 (no. 3, Table 2), it was found that a soluble product was only obtained at the shortest vacuum time, whereas longer times yielded gelation. Yet, at the short vacuum time, the conversion of methyl ester groups stagnated at 84% (no. 3). In further polycondensations, the PENT/DMS ratio was increased and gelation could be avoided, despite a vacuum time of 30 min (nos. 4−6). Despite of the higher content of CH_2OH groups in the reaction mixture, the conversion of methyl ester groups did not increase, whereas the molecular weights slightly decreased. When the MT mass spectrum of the polyester no. 4, 5, or 6, Table 2 (exemplarily illustrated in Figure 4) was compared to that of no. 3, Table 1, two slight differences were observed. First, peaks of cyclic products were absent and a higher content of **Lc** and **Le** chains was found at higher masses. Yet, in summary, these results allow the conclusion that procedure C was not more successful than procedures A and B.

Chemical Modifications. Acylations of the polyester no. 3, Table 1 were studied using acetic anhydride or methacrylic anhydride. These modification experiments were performed to find out if the free CH_2OH groups of the PENT units are available for quantitative substitution and for introduction of new functional groups. Several experiments with variation of reaction time and excess of acetic anhydride gave the result that quantitative acetylation is feasible at 20−22 °C when a 100% molar excess of acetic anhydride is used in combination with a large excess of pyridine. The ^1H NMR spectrum presented in Figure 5 demonstrated that all signals attributed to CH_2OH groups (see Figures 1 and 2) had disappeared, whereas one strong signal at 4.09 ppm summarized all CH_2O groups acylated by acetic or sebacic acid.

In an analogous experiment with methacrylic anhydride quantitative acylation was again achieved, when the reaction

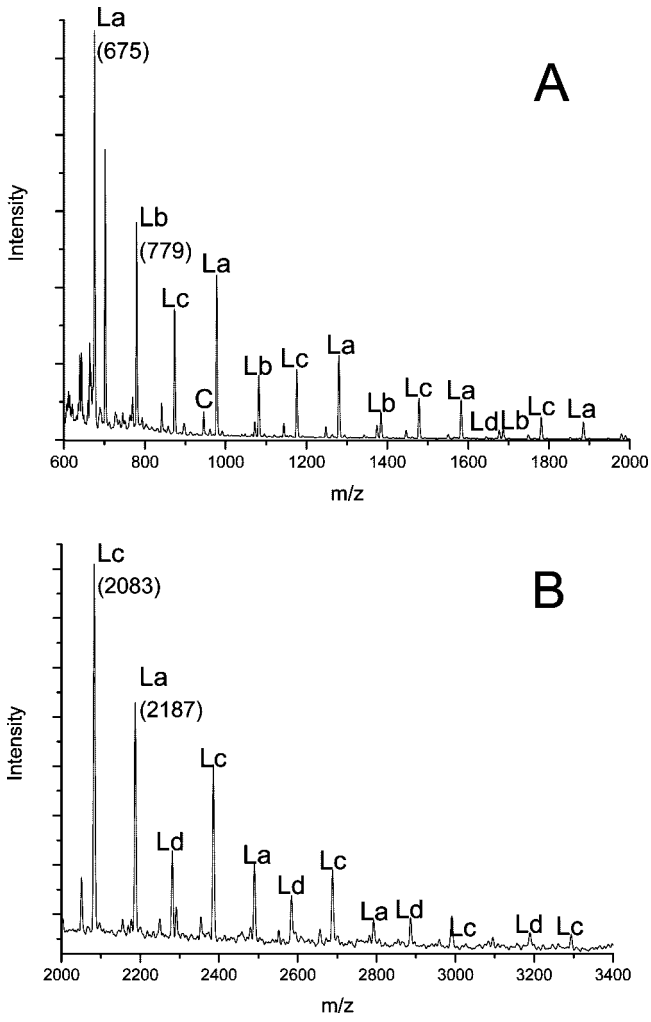


Figure 3. MALDI-TOF mass spectrum of the polyester prepared with a PENT/DMS ratio of 1.2/1.0 and one addition of $Ti(OBu)_4$ (procedure A, no. 3, Table 1).

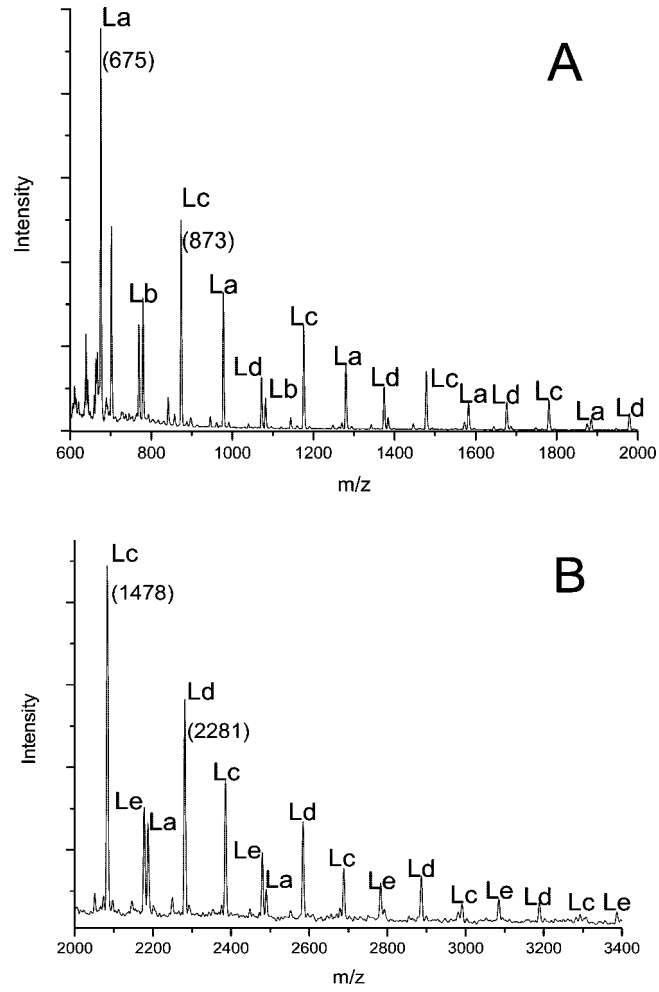


Figure 4. MALDI-TOF mass spectrum of the polyester prepared with a PENT/DMS ratio of 1.0/1.0 and a combination of $BiHex_3 + Ti(OBu)_4$ (no. 3, Table 2).

temperature was raised to 50−55 °C with 100 mol % excess of the anhydride. The incorporation of the methacrylate groups was evident from two equally intensive broad singlet signals at 5.67 and 6.03 ppm. Unfortunately, the reaction product was again a syrupy, sticky material which was difficult to handle. None-the-less, a 5 wt % solution in methyl methacrylate was obtained and polymerized at 100 °C with dibenzoylperoxide (0.5 wt %) as initiator. After a few minutes, a gel was formed, whereas in a parallel experiment with neat methyl methacrylate, no gelation occurred. In other words, the methacrylate-modified polyester played the expected role of a cross-linker.

Whereas the acylated poly(PENT sebacate) were only soluble in DMSO or acidic solvent such as hexafluoroisopropanol, the acylated derivatives were completely soluble in chloroform and, thus, allowed for SEC measurements. These measurements gave $M_n \approx 2\,800$ Da and $M_w \approx 7\,000$ Da for acetyl derivative and $M_n \approx 3\,000$ Da with $M_w \approx 7\,500$ Da for the methacrylate, when calibrated with polystyrene. Approximately 25% of the elution curve resulted from chains with molecular weights above 10 000 Da. Therefore, the polyesters having inherent viscosities around 0.12 dL/g or higher may be classified as low molar mass polymers.

Finally, it should be mentioned that cross-linking of the virgin poly(PENT sebacate) was performed with 1,6-hexamethylene diisocyanate or toluene diisocyanate in suspension at 20−22 °C without addition of a catalyst. Such cross-linking reactions are, of course, quite normal for a multifunctional alcohol. None-the-less, these experiments confirm that these (hyper)branched polyesters may be useful as components of biodegradable coatings.

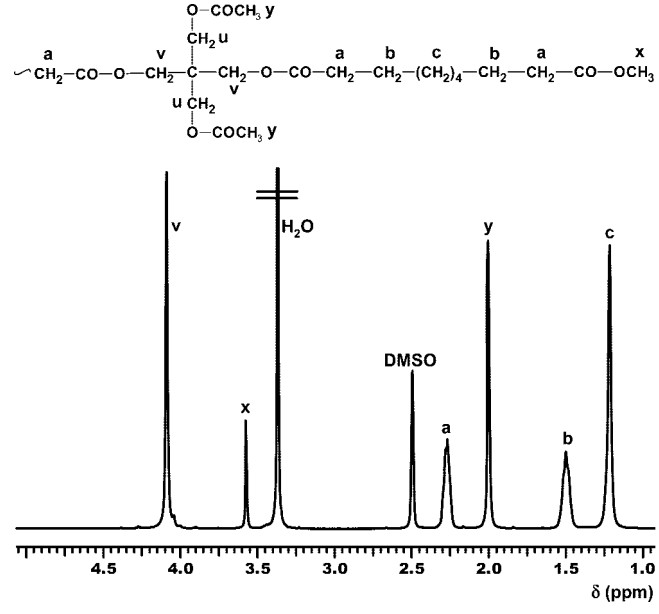


Figure 5. 400 MHz ^1H NMR spectrum of the polyester no. 4, Table 1 (see Figure 1) after acetylation with an excess of acetic anhydride and pyridine.

Conclusions

The results of this work demonstrate that soluble (hyper) branched polyesters can be prepared by polycondensations of pentaerythritol and dimethyl sebacate in bulk. Despite high reaction temperature, gelation is avoidable for equimolar feed ratios (and PENT/DMS ratios >1.0), when the reaction conditions are optimized, so that the conversions of methyl ester groups stay $\leq 91\%$. Both ^{1}H NMR and MT mass spectra indicate formation of (hyper) branched polyesters almost free of cyclic structures and with a low content of ether groups, despite high reaction temperatures. Chemical modification of these polyesters is feasible by acylation of the CH_2OH groups, and with a large excess of acetic or methacrylic anhydride, even quantitative acylation can be achieved. Functionalization with methacrylate groups yields materials which may act as biodegradable super cross-linkers in radical polymerizations of methacrylates. Such an application may allow, for instance, modification of the mechanical properties of bone cements based on the polymerization of methyl methacrylate. The virgin polyesters having numerous CH_2OH groups can easily be cross-linked by means of diisocyanates and, thus, may serve as biodegradable components of coatings.

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