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Cyclic hyperbranched polyesters derived from 4,4-*bis*(4′-hydroxyphenyl)valeric acid[☆]

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Abstract

Three monomers were prepared from 4,4-*bis*(4′-hydroxyphenyl)valeric acid (BHVA) namely its methylester (BHVAM), its bis-acetylated methylester (BAVAM) and its 4,4-*bis*(4′-acetoxyphenyl)valeric acid (BAVA). All three monomers were polycondensed in bulk at various temperature profiles using $Ti(OBu)_4$, $Co(OAc)_2$, $Mn(OAc)_2$, $Sn(OAc)_2$ or $Bu_2Sn(OAc)_2$ as transesterification catalysts. The structure of the resulting 'hyperbranched' polyesters were characterized by ^1H NMR spectroscopy, MALDI-TOF mass spectroscopy and in selected cases by SEC. Regardless of the reaction conditions only low oligomers almost free of cycles were obtained from the methylesters BHVAM and BAVAM. Higher molecular weights and high contents of cycles were obtained from polycondensations of BAVA. The content of cycles increased with the conversion. Hyperbranched polyesters with cyclic core were detected up to masses around 10,000 Da. The reactivities of the three hyperbranched monomers were compared with those of bisphenol-A plus dimethyl sebacate or acetylated bisphenol-A plus sebacic acid in 'linear polycondensations' and close analogies were found.

Keywords: 4,4-Bis(4′-hydroxyphenyl)valeric acid; MALDI-TOF; Macrocycles

1. Introduction

Polymers having a hyperbranched structure are an invention of the evolution in the form of polysaccharides such as glycogen. Prior to any successful synthesis of hyperbranched polymers Flory [1] developed the so-called 'cascade theory' predicting the formation of hyperbranched polymers from polycondensations of 'ab_n' monomers (with 'a' and 'b' as functional groups which can exclusively react with each other). In his cascade theory Flory did neither differentiate between kinetically controlled polycondensations (KCPs) and thermodynamically controlled ones (TCPs) nor did he consider a significant influence of cyclization reactions. From this point of view the cascade theory was a logic consequence of Flory's theory of linear polycondensations [2], which also ignored a distinction between KCP and TCP and ignored the impact of cyclization. Somewhat later Jacobson and Stockmayer [3] demonstrated that the equilibration reactions characteristic for TCPs involve the formation of cyclic oligomers and polymers by 'back-biting degradation'. However, for polycondensations conducted in bulk the weight fraction of cycles was predicted to be as low as 2.5–3.5% at 100% conversion [1].

Quite recently, we have presented a new theory of TCPs [4]. This theory says that the molar ratio of cycles versus linear species increases with higher conversions until 100% cycles are formed at 100% conversion. The ring–ring equilibria limit the chain growth as illustrated by Eqs. (1)–(3). This theory should in principle also apply to TCPs of ab_n monomers. Typical representatives of TCPs are syntheses of polyesters at high temperatures (eg. ≥100 °C) in the presence of transesterification catalysts. Numerous syntheses of hyperbranched polyesters under the conditions of a TCP have been reported [5–23] but only in three cases [14,18,20] the formation of cycles was detected by means of MALDI-TOF mass spectroscopy. However, the masses of the identified cycles were limited to mass range below 5000 Da, the influence of the conversion on the content of cycles was not investigated and validity or usefulness of the cascade theory were not challenged.

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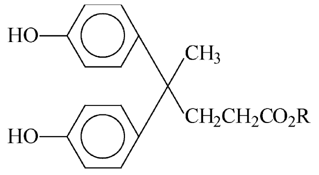
Furthermore, a paper of Chu et al. [22] reported on the basis of endgroups analyses that polycondensations of the alkyl or phenyl esters **1a–d** did not involve cyclization. At first glance these results look like a contradiction to our theory of TCPs. Moreover, Moore and coworkers [23] reported on syntheses of high molar mass hyperbranched polyesters from monomer **2**, but their study did not include the aspect of cyclization. This situation prompted us to reinvestigate the polycondensations of monomers **1a** and **2**. Monomer **3** was also included in this work.

$$\mathrm{C[M]}_x + \mathrm{C[M]}_y \Rightarrow \mathrm{C[M]}_{x+y} \tag{1}$$

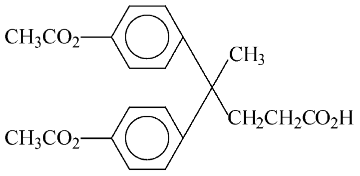
$$\mathrm{K_c} = \frac{\mathrm{C[M]}_{xy}}{\mathrm{C[M]}_x \mathrm{C[M]}_y} \tag{2}$$

$$\overline{\mathrm{DP}} = \frac{1}{1 - p(1 - x^{-Kc})} \tag{3}$$



a: R = CH_3
b: R = CH_2CH_3
c: R = $CH_2CH_2CH_3$
d: R = C_6H_5

1 a-d



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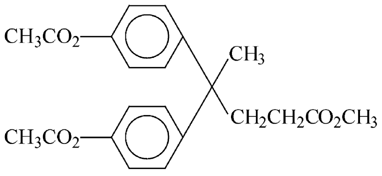

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2. Experimental

2.1. Materials

4,4-*Bis*(4′-hydroxyphenyl)valeric acid (BHVA) was purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. Cobalt(II)acetate, manganese(II)acetate, titanium tetrabutoxide, tin(II)acetate and dibutyltinbisacetate were also purchased from Aldrich Co. and used as received. The acetylated BHVA (i.e. the synthesis of BAVA) was performed according to the literature [23]. The melting point (154–156 °C) agreed with the literature data [23].

2.2. Methyl 4,4-bis(4′-hydroxyphenyl)valerate (BHVAM) (1a)

BHVA (0.5 mol) was dissolved in dry methanol (1.0 l) and cooled to approximately −10 °C. Distilled thionylchloride was added dropwise, so that the inner temperature was kept below −5 °C. After complete addition the reaction mixture was stirred for 1 h without cooling and refluxed for 2 h. All volatile compounds were then removed in vacuo and the rest was dissolved in THF:ethylacetate (1:3) and extracted with water. The remaining crude product was recrystallized from toluene.

M.p. 127–128 °C, yield: 76%, analyses calcd for $C_{18}H_{20}O_4$ (300.3), C: 71.98, H: 6.71, found C: 71.81, 6.75%. ^{1}H NMR (DMSO-d_6/TMS), $\delta = 1.46$ (s, 3H), 2.00–2.04 (t, 2H), 2.21–2.27 (t, 2H), 3.53 (s, 3H), 6.64–6.66 (d, 2H), 6.93–6.95 (d, 2H), 9.2 (s, 2H) ppm.

2.3. Acetylation of 1a (synthesis of BAVAM, 3)

BHVAM (**1a**, 0.2 mol) was dissolved in a mixture of dry dichloromethane (700 ml) and dry dioxane (175 ml). Acetic anhydride (0.6 mol) and pyridine (30 ml) were added and this mixture was refluxed for 6 h. After cooling dichloromethane (1 l) was added and the organic phase was extracted twice with 500 ml portions of 0.5 M HCl, with one 500 ml portion of 1 M aqueous Na_2CO_3 and twice with 500 ml portions of water. The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The product was isolated by distillation over a short-path apparatus at bath temperature of 240–250 °C in a vacuum of 10^{-2} mbar.

Yield: 77%, analyses calcd for $C_{22}H_{24}O_6$ (384.3), C: 68.74, H: 6.29, found C: 68.61, H: 6.14. ^{1}H NMR ($CDCl_3$/TMS), $\delta = 1.6$ (s, 3H), 2.10–2.15 (t, 2H), 2.27 (s, 6H), 2.42–2.46 (t, 2H), 3.61 (s, 3H), 6.98–7.00 (d, 2H), 7.18–7.20 (d, 2H) ppm.

2.4. Polycondensations of BHVAM (1a)

BHVAM (20 mmol) and catalyst (100 mg) were polycondensed according to the procedure given in Ref. [22] (see Table 1).

Table 1
Polycondensations of BHVAM (**1a**) in bulk

Exp. no.	Catalyst	Temperature (°C)	Time (h)[a]	Yield (%)	η_{inh}[b] (dl/g)
1	$Ti(OBu)_4$	120, 190V, 225V	2, 1, 2V	87	0.04
2	$Co(OAc)_2$	120, 190V, 225V	2, 1, 2V	76	0.04
3	$Bu_2Sn(OAc)_2$	120, 190V, 225V	2, 1, 2V	78	0.05
4	$Sn(OAc)_2$	120, 190V, 225V	2, 1, 2V	75	0.05
5	$Ti(OBu)_4$	150, 190, 225V, 250V	2, 1, 2V, 1V	82	0.06
6	$Co(OAc)_2$	150, 190, 225V, 250V	2, 1, 2V, 1V	72	0.05
7	$Bu_2Sn(OAc)_2$	150, 190, 225V, 250V	2, 1, 2V, 1V	88	0.06
8	$Sn(OAc)_2$	150, 190, 225V, 250V	2, 1, 2V, 1V	79	0.07

[a] V means: vacuum was applied.
[b] Measured at 20 °C with $c = 2$ g/l in THF.

2.5. Polycondensations of BAVAM (3), No. 1, Table 2

BAVAM (20 mmol) was weighed into a two-necked 100 ml glass flask having silanized glass walls. The reaction vessel was placed into an oil bath preheated to 100 °C and dry nitrogen was slowly bubbled through the reaction vessel. After 10 min, the catalyst (0.2 mmol) was added to the mobile melt of the monomer, and the temperature was rapidly raised to 200 °C. After 1 h the temperature was raised to 225 °C, after 1 h to 250 °C for another hour and finally vacuum was applied for 10 min at 250 °C. The cold product was dissolved in dichloromethane, filtered and precipitated into diethyl ether. All other experiments of Table 2 were conducted analogously.

2.6. Polycondensations of BAVA (2), No. 3, Table 3

BAVA (20 mmol) was weighed into a two-necked 100 ml glass flask having silanized glass walls. The reaction vessel was placed into an oil bath preheated to 160 °C and dry nitrogen was slowly bubbled through the reaction vessels. The catalyst (0.2 mmol) was then added to the molten monomer and the temperature was rapidly raised to 200 °C. After 1 h, the temperature was raised to 225 °C and finally to 250 °C. After 1 h at 250 °C, vacuum was applied for additional 10 min. Finally, the cold polyester was dissolved in dichloromethane, filtered and precipitated into diethyl ether.

2.7. Measurements

The inherent viscosities were measured in tetrahydrofuran or dichloromethane with an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MHz ^1H NMR spectra were recorded on a Bruker Avance 400 FT NMR spectrometer in 5 mm O.D. sample tubes using $CDCl_3$/TMS or DMSO-d_6 as solvent and shift reference. The MALDI-TOF mass spectra were recorded on a Bruker Biflex III, equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were measured in the reflection mode with an acceleration ratio voltage of 20 kV. The irradiation targets were prepared from THF solutions with dithranol as matrix and potassium trifluoroacetate as dopant.

The SEC measurements were performed on a home-made apparatus consisting of a Waters HPLC pump (Md 515), a degasser ERC 3114, a column oven 'ERC croco-cil' thermostated at 40 °C, a 'Waters 2387' UV detector and a 'Waters 2410' RI detector. Four '112-SD plus' columns with pore sizes of 10^3, 10^4, 10^5 and 10^6 Å were used and tetrahydrofuran served as eluent at a rate of 1 ml/min.

3. Results and discussion

3.1. Polycondensation of BHVAM (1a)

All polycondensations of BHVAM were conducted in bulk, and the results were summarized in Table 1. Three

Table 2
Polycondensations of monomer BAVAM (**3**) in bulk

Exp. no.	Catalyst	Temperature (°C)	Time (h)[a]	Yield (%)	η_{inh}[b] (dl/g)
1	$Ti(OBu)_4$	200, 225, 250	1, 1, 1, 10 minV	83	0.15
2	$Bu_2Sn(OAc)_2$	200, 225, 250	1, 1, 1, 10 minV	61	0.05
3	$Co(OAc)_2$	200, 225, 250	1, 1, 3, 10 minV	80	0.04
4	$Ti(OBu)_4$	200, 225, 250	1, 1, 3, 10 minV	77	0.15
5	$Bu_2Sn(OAc)_2$	200, 225, 250	1, 1, 3, 10 minV	67	0.08
6	$Ti(OBu)_4$	200, 225, 250, 275	1, 1, 3, 1, 10 minV	82	0.15
7	$Bu_2Sn(OAc)_2$	200, 225, 250, 275	1, 1, 3, 1, 10 minV	81	0.16

[a] V means: vacuum was applied.
[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

experiments (Nos. 1–3) were performed with variation of the catalyst under the conditions described by Chu et al. [22] However, the initial temperature was raised to 150 °C, because the melting point of monomer **1a** is 128 °C. Therefore, an initial temperature of 120 °C mentioned in a general procedure in Ref. [22] does not make any sense for **1a** (in contrast to **1b** or **1c**), because **1a** does not melt and does not react at 120 °C. In a second series (Nos. 5–8) the final reaction temperature was higher, but without significant influence on the molecular weights. All eight polycondensations have in common that only low oligomers were obtained. This conclusion is based on four analytical methods including viscosity measurements. The ^{1}H NMR spectra displayed a strong signal of the methylester endgroups, which allowed for the calculation of a maximum degree of polymerization ($\overline{DP}$), which fell into the range of 4–6. The MALDI-TOF m.s. exclusively displayed the signals of linear oligomers having the structure **La** (Scheme 1)

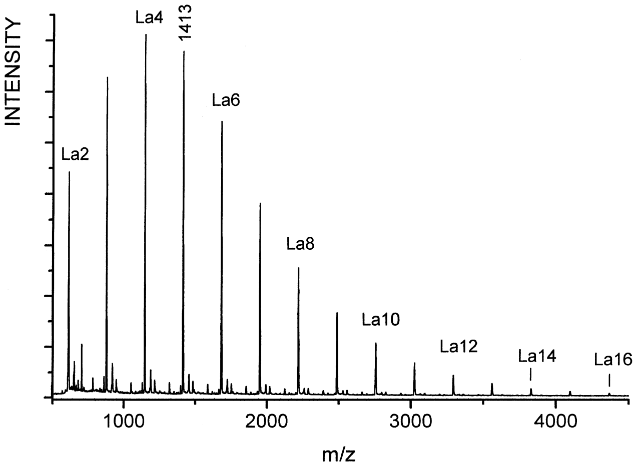
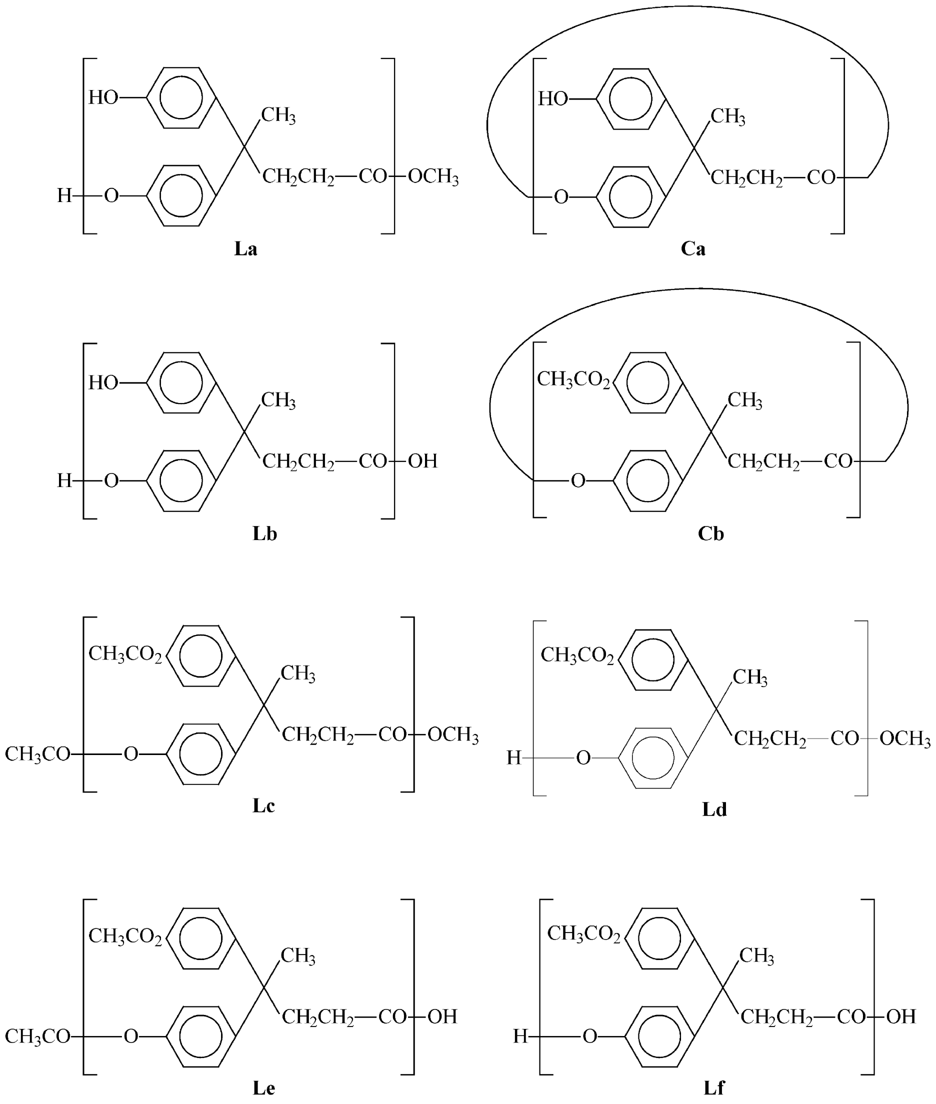


Fig. 1. MALDI-TOF mass spectrum of the oligoester **La** prepared by Ti(OBu)$_4$ which catalyst catalyzed polycondensation of monomer **1a** (No. 1, Table 1).



Scheme 1.

with a maximum around a $\overline{\mathrm{DP}}$ of 4 (Fig. 1). The mass peaks of cycles (**Ca**) or of linear polymers having masses above 5000 Da were absent. These results were confirmed by SEC measurements, as exemplarily illustrated in Fig. 2. The SEC elution curve shows well resolved peaks of oligomers, but no fraction of high molar mass polymers. Therefore, these findings agree with the conclusion of Chu et al. [22] in that no cyclization was indeed detectable, but this result is a necessary consequence of the low conversion (75–80%).

Chu et al. [22] reported high weight average molecular weights, M_ws, (typically 18,000–128,000 Da), but unfortunately, they did not give viscosity values, number average molecular weights (M_ns) or polydispersities. Therefore, it was of interest to correlate the poor results obtained from the polycondensations of BHVAM (**1a**) with analogous polycondensations of linear monomers. For this purpose, three polycondensations of bisphenol-A with dimethyl sebacate (Eq. (4)) were conducted. The catalysts, times and temperatures paralleled those used for the polycondensations of **1a**. Regardless of the catalyst liquid reaction mixtures of low viscosity were obtained (($\eta_\mathrm{inh} = 0.02$–0.03 dl/g in THF at 20 °C). The ^{1}H NMR spectra indicated a low conversion and no polymers precipitated from methanol or diethyl ether. Therefore, the failure of the ‘linear polycondensation’ according to Eq. (4) agrees well with the poor results obtained from monomer **1a**. As discussed below significantly better results were achieved from polycondensations of acetylated bisphenol-A (Eq. (5)) and from polycondensations of monomer **2**:

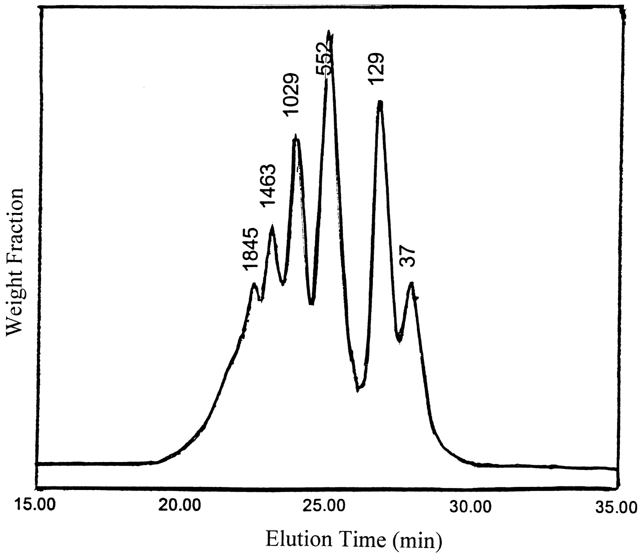
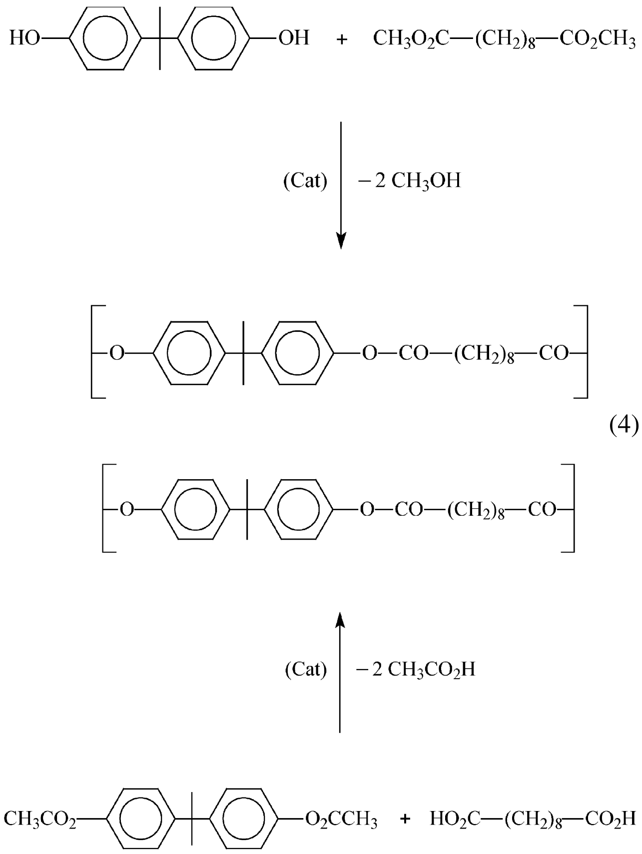


Fig. 2. SEC elution curve of the oligoester **La** prepared by Ti(OBu)$_4$-catalyzed polycondensation of monomer **1a** (No. 1, Table 1).



(4)

(5)

For comparison bisphenol-A bis-acetate (BABA) was polycondensed with sebacic acid at the same temperature/time profile (Eq. (5) and Table 4). Significantly higher viscosity values were obtained, at least when a catalyst was used. These findings are in a good agreement with the well-known fact that polyesters of diphenols are best prepared by polycondensation of acetylated diphenols with dicarboxylic acids and not by transesterification of diphenols with alkyl esters of dicarboxylic acids. Hence, the low molecular weights obtained from the methylester **1a** and the much higher molecular weights from monomer **2** (see Section 4.1 below) are in perfect agreement with analogous polycondensations of ‘linear monomers’, so that the polycondensations of the ab$_2$ monomers used in this work do not represent any exception.

3.2. Polycondensations of BAVAM (3)

The polycondensations of monomer **3** (BAVAM) were conducted with three different transesterification catalysts and with two different maximum reaction temperatures. The results of these seven polycondensations were compiled in Table 2. From these results the following conclusions may be drawn. First, Ti(OBu)$_4$ proved to be the best catalyst. Second, only with Ti(OBu)$_4$ the inherent viscosities (and thus, the molar masses) were slightly higher than those obtained with monomer **1a**. Third, methylester endgroups were detected in the ^{1}H NMR spectra indicating low $\overline{\text{DP}}$s. Fourth, only traces of cycles having the structure **Cb** were detectable in the MALDI-TOF mass spectra. These mass spectra also revealed several mass peaks with **Lc** and **Ld** chains being the main reaction products (Fig. 3). In summary, these polycondensations proved that monomer **3** is not suited for syntheses of high molar mass polyesters free of side reactions.

3.3. Polycondensations of BAVA (2)

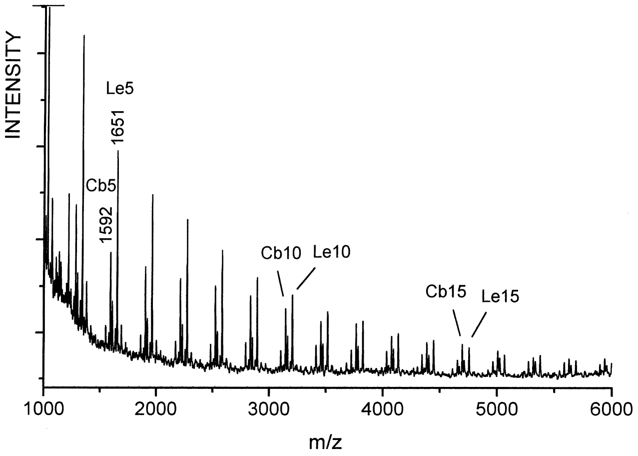


Fig. 4. MALDI-TOF mass spectrum of the polyester prepared by polycondensation of neat monomer **2** (No. 1, Table 3).

Monomer **2** was polycondensed in bulk with variation of catalyst, temperature and time (Table 3). When BAVA was polycondensed under the conditions reported in the literature [23] (No. 2, Table 3) a soluble polymer with an inherent viscosity of 0.43 dl/g (in CH_2Cl_2 at 20 °C) was isolated in good agreement with the literature data ($\eta = 0.45$ dl/g in THF at 30 °C) [23]. Such a polycondensation was repeated with a shorter time (2 h, No. 1, Table 3) to study the influence of the conversion on the structure and composition of the reaction product. As illustrated in Fig. 4 for the 2 h product, the MALDI-TOF m.s. revealed indeed the formation of cyclic hyperbranched polyesters, but the tree-shaped species **Le** was clearly the main product. After 6 h (No. 2, Table 3) the fraction of cycles had increased, but additional peaks of byproducts had appeared, the structure of which was not elucidated. Obviously, the long reaction time favored side reactions. Therefore, additional experiments were performed at higher temperatures and short reaction times. Transesterification catalysts were added to accelerate the polycondensation and to reduce the influence of side reactions. This strategy proved to be successful when the maximum temperature was limited to 250 °C (Nos. 3, 5, 7, Table 3). Although the molecular weights were lower than that of sample No. 2, the MALDI-TOF m.s. proved a clean polycondensation process. As illustrated in Fig. 5, only two reaction products were detectable, namely the tree-shaped polyesters of structure **Le** and the hyperbranched polyesters with cyclic core (**Cb**). At higher masses, the cyclic polyesters seem to become the predominant species.

When the final temperature of the polycondensation was raised to 275 °C (Nos. 4, 6, 8, Table 3) the molecular weights did not increase. The MALDI-TOF m.s. exhibited numerous mass peaks of byproducts indicating that

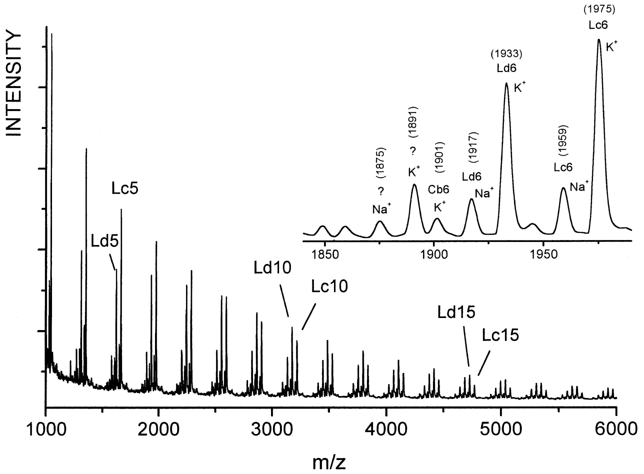


Fig. 3. MALDI-TOF mass spectrum of the polyester prepared by $Ti(OBu)_4$-catalyzed polycondensation of monomer **3** (No. 1, Table 2).

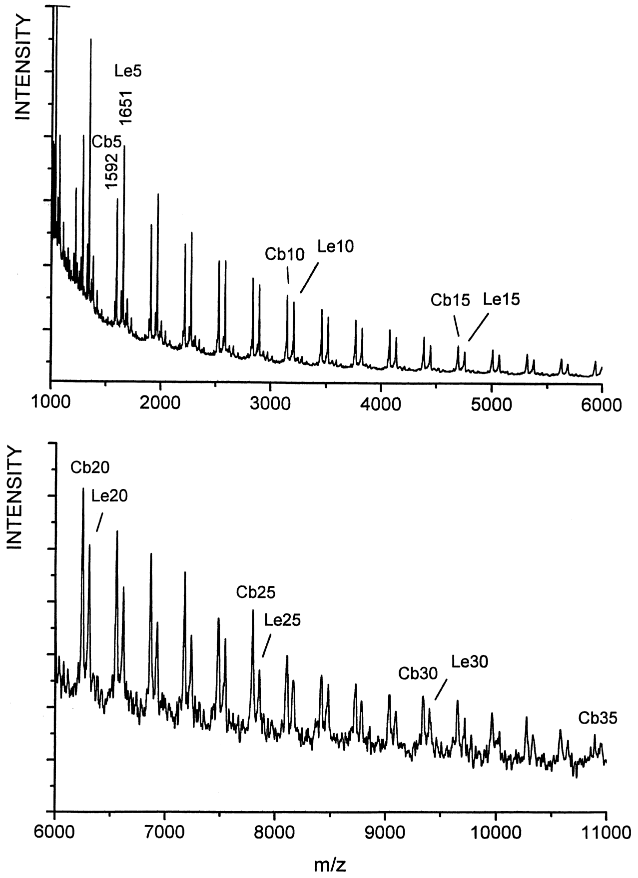


Fig. 5. MALDI-TOF mass spectrum of the polyester prepared by $M_n(OAc)_2$-catalyzed polycondensation of monomer **2** (No. 3, Table 3).

Table 3
Polycondensations of monomer BAVA (**2**) in bulk

Exp. No.	Catalyst	Temperature (°C)	Time (h)[a]	Yield (%)	η_{inh}[b] (dl/g)
1	–	210, 210 V	2, 2V	76	0.33
2	–	210, 210 V	2, 6V	85	0.43
3	$Mn(OAc)_2$	200, 225, 250	1, 1, 1 + 10 minV	79	0.34
4	$Mn(OAc)_2$	200, 225, 250, 275	1, 1, 1, 1 + 10 minV	87	0.17
5	$Co(OAc)_2$	200, 225, 250	1, 1, 1 + 10 minV	86	0.28
6	$Co(OAc)_2$	200, 225, 250, 275	1, 1, 1, 1 + 10 minV	90	0.25
7	$Sn(OAc)_2$	200, 225, 250	1, 1, 1 + 10 minV	68	0.32
8	$Sn(OAc)_2$	200, 225, 250, 275	1, 1, 1, 1 + 10 minV	70	0.20

[a] V means: vacuum was applied.
[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

intensive side and degradation reactions had occurred in all three experiments. A detailed study of these side reactions was not intended in this work. Hence, these results clearly prove that 250 °C is the upper limit temperature for clean polycondensations of monomer **2**.

For comparison with the polycondensations of monomer **2** and polycondensations of bisphenol-A (Eq. (4)) several polycondensations of acetylated bisphenol-A with sebacic acid were performed in bulk (Eq. (5)). For most polycondensations (Nos. 1–5, Table 4) the same temperature/time profile as for monomer **1a** was used. In the absence of a transesterification catalyst no significant conversion was observed. After addition of catalysts polyesters of low or moderate molecular weight were formed which were isolated by precipitation of the crude reaction products into diethyl ether (Table 4). When the maximum temperature was raised from 225 to 250 °C a higher molecular weight was obtained (No. 6, Table 4) indicating that the temperature profile used for **1a** are not the optimum reaction conditions for polycondensations of acetylated bisphenol-A. In summary, the data compiled in Table 4 prove that polycondensations of acetylated bisphenol-A with free sebacic acid are far more successful than polycondensations of free bisphenol-A (Eq. (4)). This finding agrees with the well known fact that polyesters of diphenols are usually best prepared by polycondensations of their bis-acetates with dicarboxylic acids. The MALDI-TOF m.s. of the poly(bisphenol-A sebacate)s indicated the formation of cyclic oligo- and polyesters, and the highest fraction of cycles was found for the sample with the highest molecular weight. In summary, all results obtained from 'linear polycondensation' agree well with those obtained from monomers **1a** and **2**.

4. Conclusion

4.1. Discussion

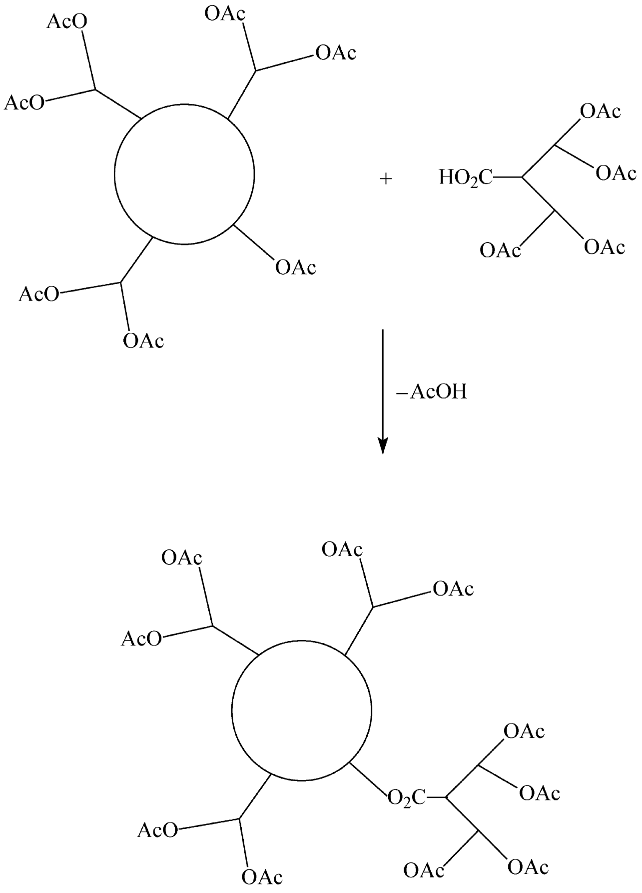
The results presented above allow the following conclusions. In agreement with the report of Chu et al. [22], no cyclization was observed for polycondensations of monomer **1a** (BHVAM). However, very low conversions were found to be responsible for the absence of cycles. Similarly, negative results were obtained from monomer **3** (BAVAM). Low conversion and side reactions hindered the formation of significant amounts of cycles. Only polycondensations of monomer **2** (BAVA) were clean at temperatures ≤250 °C and short reaction times, so that hyperbranched polyesters of moderate molecular weight were obtained. In agreement with our new theory of TCPs, the formation of cycles increased with conversion (and average molecular weight). Hyperbranched polyesters were detected up to masses around 10,000 Da. However, in contrast to cyclizations of linear chains the masses of cyclic hyperbranched polymers do not say anything about the

Table 4
Polycondensations of acetylated bisphenol-A and sebacic acid in bulk (Eq. (5))

Exp. no.	Catalyst	Temperature (°C)	Time (h)[a]	Yield (%)	η_{inh}[b] (dl/g)
1	–	120, 190, 225	2, 1, 2 + 0.2 V	0	–
2	–	120, 190, 225 V	2, 1, 2 V	0	–
3	$Co(OAc)_2$	120, 190, 225	2, 1, 2 + 0.2 V	52	0.12
4	$Bu_2Sn(OAc)_2$	120, 190, 225	2, 1, 2 + 0.2 V	46	0.11
5	$Mn(OAc)_2$	120, 190, 225	2, 1, 2 + 0.2 V	45	0.16
6	$Mn(OAc)_2$	120, 190, 225, 250	2, 1, 2, 1 + 0.2 V	48	0.25

[a] V means: vacuum was applied.
[b] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2.

ring-size of the cycles. When a cyclic core has been formed the ‘chain growth’ can continue according to Eq. (6). This growth reaction has the consequence that even a few cycles suffice, such that at high conversion (>99.9%) almost all molecules will have a cyclic core.



(6)

The failure of monomer **1a** to yield hyperbranched polyesters and the more successful polycondensations of monomer **2** are paralleled by ‘linear polycondensations’ (Eqs. (4) and (5)). This means that the different reactivities of **1a** and **2** are not unusual properties of these ab_2 monomers, but they are in line with the different reactivities of bisphenol-A and acetylated bisphenol-A in analogous model polycondensations.

Another important consequence of these results and those of other authors [14,18,20] concerns Flory’s cascade theory. This is not a true theory explaining the formation of hyperbranched polymers in real experiments. The cascade theory is in fact a largely misleading hypothesis which does not correctly predict the final structure of the reaction products, because it ignores cyclization and the growth reaction of Eq. (6). Furthermore, it makes wrong predictions about the dependence of molecular weight and polydispersity on the conversion, because the formation of cycles clearly limits both chain growth and polydispersity.

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