Multicyclic Polyesters by Polycondensation of 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane with Dicarboxylic Acid Dichlorides

Hans R. Kricheldorf,* Kirstin Bornhorst, and Gert Schwarz

Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, D-20146 Hamburg, Germany

Received July 25, 2006; Revised Manuscript Received November 14, 2006

ABSTRACT: 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI) was polycondensed with 2 equiv of sebacoyl chloride or 1,6-hexanediol bischloroformiate. Although the monomer concentration was varied by a factor of 10, partially or totally cross-linked polyesters were obtained in all experiments. Analogous polycondensations of TTSBI were conducted with double molar amounts of α,ω-bis(4-chlorocarbonylphenoxy)-alkanes or α,ω-bis(3-chlorocarbonylphenoxy)alkanes. Depending on concentration and structure of the dicarboxylic acid dichlorides, either gels or soluble multicyclic polyesters were obtained and characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF, and FAB mass spectrometry. SEC measurements revealed broad molecular weight distributions, and DSC measurements indicated an amorphous character of all multicycles.

Introduction

The present work is part of a broader study of "$a_2 + b_4$" polycondensations meaning polycondensations of difunctional with tetrafunctional monomers. Whereas "$a_2 + b_3$" including polycondensations have a long tradition beginning with the work of Kienle et al.,[1−3] Flory,[4] and recent contributions of numerous research groups, little is known about "$a_2 + b_4$" polycondensations. However, "$a_2 + b_4$" polycondensations are interesting because they allow, in principle, for syntheses of various architectures, and these architectures may be realized in different classes of polymers such as polyesters, polyethers, or polyamides. For instance, equimolar polycondensations of "$a_2 + b_4$" monomers should yield (hyper)branched polymers having numerous functional groups. Equifunctional polycondensations (involving one b_4 and two a_2 monomers) may yield insoluble gels or multicyclic polymers depending on the efficiency of cyclization reactions. Further architectures may be obtained from copolycondensations with additional monomers or telechelic blocks.

Another aspect of "$a_2 + b_4$" polycondensations is the classification into reversible (thermodynamically controlled) polycondensations and into irreversible (kinetically controlled) ones. This classification may be applied to any kind of chemical reaction, but in the field of vinyl polymerizations thermodynamically controlled polymerizations do not exist, and thus, this aspect is usually not discussed in textbooks of polymer science. However, we have recently demonstrated that soluble multicyclic oligomers and polymers can be prepared by thermodynamically controlled "$a_2 + b_4$"polycondensations.[5−7] Furthermore, two classes of multicyclic polyethers were synthesized by irreversible "$a_2 + b_4$" polycondensations.[8,9] In this context, the present work should serve three purposes. First, the polycondensations should be based on a nucleophilic "b_4" monomer, namely on a tetraphenol. Second, our studies of "$a_2 + b_4$" polycondensations should be extended to polyesters. Third, our work should represent a parallel or complementary study of experiments conducted by Flory.[10,11] Flory investigated the formation of hyperbranched and cross-linked pentaerythritol and dicarboxylic acid in the melt. Unfortunately, the experimental description of that study is poor. Yet, it was reported that gelation occurred at a conversion around 58%, slightly higher than calculated from the theory. The difference was ascribed to a few cyclization reactions. Flory also calculated and measured that the number-average molecular weights (M_ns) of the (hyper)-branched soluble reaction products immediately before or around the gel point is low (M_n < 3000 Da). Therefore, it was of great interest to see if the polyesterifications studied in this work allow us to avoid gelation even at conversions >99% and to obtain multicyclic polyesters having M_ns > 3000 Da. In the present work 5,5′,6,6′-tetrahydroxy-3,3′,3,3′-tetramethylspirobisindane (TTSBI) was selected as "b_4" monomer because it was hoped that its steric structure favors cyclization. In a future study a different tetraphenol should serve as "b_4" monomer for comparison.

Experimental Section

Materials. 1,6-Hexanediol bischloroformiate (HDBC) was kindly supplied by Bayer AG (Uerdingen, Germany) and used after distillation in vacuo. Sebacoyl chloride was purchased from ACROS Organics (Geel, Belgium) and used after distillation in vacuo. Ethyl 3-hydroxybenzoate, methyl 3-hydroxybenzoate, or methyl 4-hydroxybenzoate and various α,ω-dibromoalkanes were all purchased from ACROS Org. and used as received. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI) was purchased from ABCR Chemicals (Karlsruhe, Germany) and used as received. 1,4-Dioxane was refluxed and distilled over sodium. Dichloromethane was distilled over P_4O_{10}.

1,5-Bis(3-Chlorocarbonylphenoxy)pentane (6, *n* = 5). *A. Synthesis of the Diethyl Ester*. Ethyl 3-hydroxybenzoate (0.4 mol) and potassium *tert*-butoxide (0.4 mol) were dissolved in dry DMF, and 1,5-dibromopentane (0.2 mol) was added. The reaction mixture was stored for 2 h at 23−25 °C and for 4 h at 100 °C. The reaction mixture was then concentrated in vacuo to ∼50% of its original volume and poured into cold water. Since crude diethyl ester did not crystallize, it was extracted with three 500 mL portions of ethyl acetate. The combined extracts were twice washed with water and dried over sodium sulfate. The ethyl acetate was removed in a rotatory evaporator and finally in a vacuum of 10^{-1} mbar at 60 °C. The remaining brown syrup was characterized (yield 98%). Elemental analyses calcd for $C_{23}H_{28}O_6$ (400.47 Da): C 68.98, H 7.05; found: C 68.96, H 7.23%. ^{1}H NMR ($CDCl_3$/TMS): δ = 7.63 (d, J = 8.0 Hz, 2H), 7.56 (s, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.35−4.40 (m, 4H), 4.01−4.06 (q, J = 7.5

10.1021/ma061675a CCC: $37.00
Published on Web 12/24/2006

Table 1. Yields and Properties of α,ω-bis(3-Chlorocarbonylphenoxy)Alkanes (6)

			elemental analyses				
n	yield (%)	mp (°C)		C	H	Cl	^{13}C NMR chemical shifts δ (ppm) (in $CDCl_3$/TMS)
5	51	67−69	calcd	59.86	4.76	18.60	168.3, 159.3, 134.3, 129.9, 124.0, 122.3, 116.0, 68.1, 28.8, 22.7
			found	59.84	4.88	18.78	
6	82	103−106	calcd	60.77	5.10	17.94	168.4, 159.3, 134.4, 129.9, 124.0, 122.3, 116.0, 68.2, 29.0, 25.8
			found	60.48	5.25	18.18	
8	48	79−81	calcd	62.42	5.71	16.75	168.4, 159.4, 134.4, 129.8, 124.0, 122.4, 116.0, 68.4, 29.3, 29.1, 25.9
			found	61.98	5.85	16.70	
10	59	63−65	calcd	63.86	6.25	15.71	168.4, 159.4, 134.4, 129.8, 124.0, 122.4, 116.0, 68.4, 29.3, 29.1, 25.9
			found	63.49	6.38	15.83	

Table 2. Polycondensations of TTSBI with Sebacoyl Chloride or 1,6-Hexanediol Bischloroformate (HDBC)

expt no.	a_2 monomer	concn[a] (mol/L)	results
1	sebacoyl	0.20	gel
2	sebacoyl chloride	0.10	gel
3	sebacoyl chloride	0.07	gel
4	sebacoyl chloride	0.04	gel
5	sebacoyl chloride	0.02	partially cross-linked
6	HDBC	0.04	partially cross-linked
7	HDBC	0.02	partially cross-linked

[a] Initial TTSBI concentration in mol/L.

Table 3. Polycondensations of TTSBI with α,ω-Bis(4-hydroxyphenoxy)alkanes

expt no.	a_2 monomer	concn[a] (mol/L)	yield (%)	η_{inh}[b] (dL/g)	M_n[c] (kDa)	PD[c]
1	**5a** ($n = 5$)	0.44	gel			
2	**5a** ($n = 5$)	0.22	92	0.14[b]	10	4.1
3	**5b** ($n = 6$)	0.04	gel			
4	**5b** ($n = 6$)	0.22	98	0.17[c]	12	5.0

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

Table 4. Polycondensations of TTSBI with α,ω-Bis(3-hydroxyphenoxy)alkanes

expt no.	a_2 monomer	concn[a] (mol/L)	yield (%)	η_{inh}[b] (dL/g)	M_n[c] (kDa)	PD[c]	T_g (°C)
1	**6a** ($n = 5$)	0.08	gel				
2	**6a** ($n = 5$)	0.04	94	0.13	5.3	3.6	171
3	**6b** ($n = 6$)	0.04	92	0.16	6.7	4.2	167
4	**6c** ($n = 8$)	0.04	93	0.21	7.3	5.0	148
5	**6d** ($n = 10$)	0.08	gel				
6	**6d** ($n = 10$)	0.04	gel				
7	**6d** ($n = 10$)	0.02	92	0.12	6.0	3.8	116

[a] Initial concentration of TTSBI. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] SEC measurements in $CHCl_3$ calibrated with polystyrene. [d] DSC measurements with a heating rate of 20 °C/min second heating.

Hz, 4H), 1.85−1.92 (m, 4H), 1.66−1.72 (m, 2H); 1.41−1.36 ppm (t, $J = 7.5$ Hz, 6H). ^{13}C NMR ($CDCl_3$/TMS): $\delta = 166.6$, 159.0, 131.8, 129.3, 121.8, 119.6, 114.7, 67.9, 61.1, 29.0, 22.7, 14.3 ppm.

B. Saponification. The diethyl ester (0.2 mol) was dissolved in dioxane (300 mL) and refluxed with portionwise addition of 4 N sodium hydroxide (200 mL) for 4 h. The reaction mixture was brought to dryness by means of rotatory evaporator, and the residue was dissolved in 300 mL of hot water. After cooling, 4 N HCl was added dropwise with stirring; the precipitated EDA was isolated by filtration, washed with water, and dried in vacuo at 60 °C (yield: 82%); mp 211−215 °C. Elemental analyses calcd for $C_{19}H_{20}O_6$ (344.4 Da): C 66.27, H 5.85, found: C 65.79 H 5.50%. ^{13}C NMR ($CDCl_3$/TMS): $\delta = 167.0$, 158.5, 132.1, 129.6, 121.4, 119.3, 114.4, 67.5, 28.3, 22.1 ppm.

C. Chlorination. EDA (0.2 mol) and distilled thionyl chloride (300 mL) were refluxed for 2 days. After the first 4 h, a solution of DMF (1 mL) in chloroform (10 mL) was added dropwise. The thionyl chloride was then completely removed by distillation under reduced pressure. The remaining crystalline EDA dichloride was dissolved in dry toluene (100 mL) and filtered from sodium chloride under exclusion of moisture. The filtrate was concentrated in vacuo to ∼50% of its original volume, and ligroin (10−20 mL) was added. After storage in a refrigerator for 24 h, the crystallized product was isolated by filtration, washed with ligroin, and dried in vacuo. Yields and properties are listed in Table 1.

All other EDA dichlorides were prepared analogously.

For the p-EDA **5**, $n = 4$, a mp of 95−97 °C and for **5**, $n = 6$, a mp of 84−86 °C (82 °C in ref 12) were found.

Polycondensations. *A. With Sebacoyl Chloride (Table 2).* TTSBI (4.0 mmol) was dissolved in dry dioxane (85 mL), and sebacoyl chloride (8.02 mmol) was added. A solution of dry pyridine (32 mmol) in dry dioxane (10 mmol) was then added dropwise with stirring. The reaction mixture was stored for 20 h at 22−25 °C and refluxed for 2 h. The reaction mixture was then concentrated in vacuo (to ∼30 mL) whereby gelation occurred.

B. With 1,6-Bis(4-chlorocarbonylphenoxy)hexane (No. 4, Table 3). TTSBI (4.0 mmol) and the dichloride **5b**, $n = 6$ (8.02 mmol), were dissolved in dry dioxane (85 mL), and a solution of dry triethylamine (17 mmol) in dry dioxane (10 mL) was added dropwise with stirring. The reaction mixture was stored for 20 h at 22−25 °C and refluxed for 2 h. Approximately 50% of the dioxane was then distilled off under reduced pressure, and the remaining solution was then precipitated into methanol. Yield: 98%. Elemental analyses calcd for $C_{61}H_{60}O_{12}$ (985.1): C 74.37%, H 6.14%, found: C 73.89, H 6.21%.

C. With 1,5-Bis(3-chlorocarbonyl phenoxy)pentane (No. 2, Table 4). TTSBI (4.0 mmol) and the dichloride **6a** (8.02 mmol) were dissolved in dry dioxane (85 mL) and polycondensed as described before. Yield: 94%. Analyses calcd for $C_{60}H_{58}O_{12}$ (971.1): C 74.21%, H 6.02%, found: C 73.88, H 6.13%.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C.

The 400 MHz ^{1}H NMR spectra and the 100.4 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent. The DSC measurements were performed on a Mettler Toledo Md 821 with a heating rate of 20 °C/min. The fast atom bombardment (FAB) mass spectra were measured with a VG/70-205 spectrometer of VG-Analytical using *m*-nitrobenzyl alcohol as matrix. 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 recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solution using dithranol as matrix and potassium trifluoroacetate as dopant. The SEC measurements were performed with an apparatus of Polymer Laboratories containing a RI detector "Shodex RI 101". A combination of three PL mixed-bed columns was used with chloroform as eluent (flow rate 1.0 mL/min). Commercial polystyrene standards served for calibration. The lower limit for the evaluation of the elution curves was 650 Da.

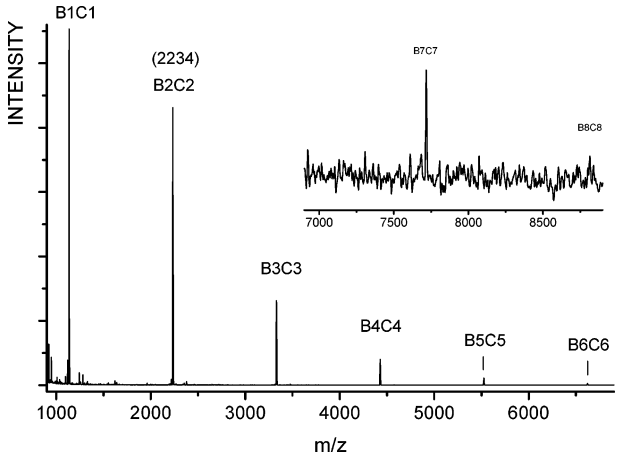


Figure 1. MALDI-TOF mass spectrum of the multicyclic polyester of structure **3**, $n = 5$ (no. 2, Table 3).

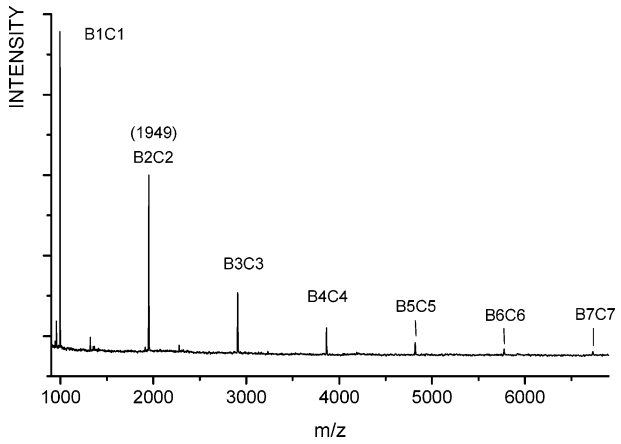


Figure 2. MALDI-TOF mass spectrum of the multicyclic polyester of structure **4**, $n = 5$ (no. 2, Table 4).

Results and Discussion

Syntheses of New "Ether Dicarboxylic Acid" (EDA) Dichlorides. For the syntheses of the polyesters **2** and **3**, the "ether dicarboxylic acid" (EDA) dichlorides **5** and **6** were needed. All these dichlorides were prepared in the same way. At first, a commercial ethyl- or methylhydroxy benzoate was reacted with an α,ω-dibromoalkane according to the so-called "Williamson's ether synthesis" outlined in eq 4. The resulting diethyl or dimethyl esters were saponified (eq 5), and the crude dicarboxylic acids were dried. Because of their poor solubility in organic solvents, they were not fully characterized. The dicarboxylic acids were then chlorinated in refluxing thionyl chloride (eq 6). This reaction pathway is fully described for ethyl 3-hydroxybenzoate and 1,5-dibromopentane in the Experimental Section. The EDAs and their dichlorides derived from 4-hydroxybenzoic acid were described by several research groups in the literature,[12−14] and therefore, a detailed characterization is not provided in the present work. However, the EDAs and their dichlorides based on 3-hydroxybenzoic acid were not described in the literature, and thus, the yields and properties of all *m*-EDA dichlorides used in this work were compiled in Table 1.

Terminology of "$a_2 + b_4$" Multicycles. Prior to the discussion of experimental results, the terminology of multicycles used in the text, in Figures 1−3, and in Table 5 should shortly be explained. This terminology is consistent with that used for the multicycles of "$a_2 + b_3$" polycondensations in previous publications. In the symbols B*n*C*N*, C stands for cycle and B for bridging unit (resulting from "a_2" monomers). The letter *N* stands for the degree of polymerization and *n* for the number of bridging units connecting two cycles or bridging one cycle. Multicycles meeting the conditions $n = N$ are free of functional (end) groups and may be considered to be the ideal reaction products of a clean "$a_2 + b_4$" polycondensation conducted with perfect 2:1 stoichiometry and conversions up to almost 100%. Imbalance of the stoichiometry has the consequence that multicycles having one or more functional groups are formed. As illustrated in Schemes 1 and 2, the perfect B*n*C*n* (or B_NCN) multicycles may exist in the form of various isomers the number of which increases exponentially with *N*.

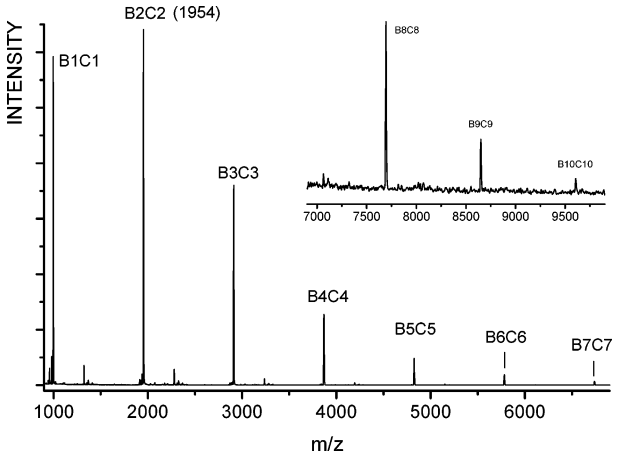
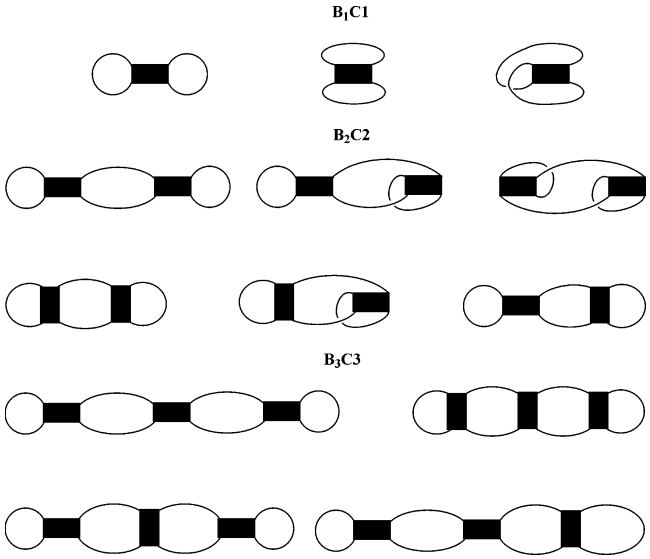


Figure 3. MALDI-TOF mass spectrum of the multicyclic polyester of structure **4**, $n = 10$ (no. 6, Table 4).

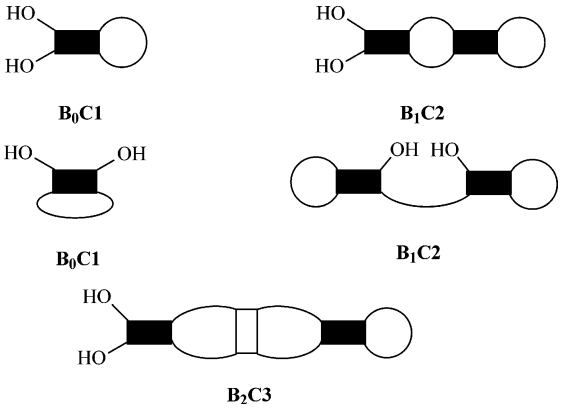
Table 5. Masses (Da, Including K^+) of Multicyclic Polyesters Derived from TTSBI

multicycle	**1** (X−CH_2)	**2** (X=O)	**3**	**4**
B_1C_1	712.0	719.9	1080.3	1080.3
B_2C_2	1384.8	1400.6	2121.6	2121.6
B_3C_3	2057.7	2081.3	3162.8	3162.8
B_4C_4	2730.5	2762.0	4204.1	4204.1
B_5C_5	3403.4	3442.8	5245.3	5245.3
B_6C_6	4076.2	4123.5	6286.6	6286.6
B_7C_7	4749.1	4804.3	7327.8	7327.8
B_8C_8	5421.9	5485.0	8369.1	8369.1
B_9C_9	6094.8	6165.7	9410.3	9410.3
$B_{10}C_{10}$	6767.7	6846.5	10451.6	10451.6

Scheme 1. Selected Isomers of B_nCn (B_NCN) Multicycles Derived from TTSBI

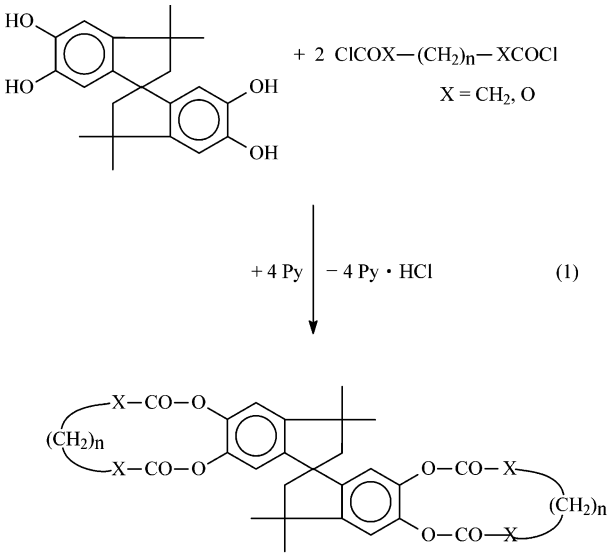


Scheme 2. Selected Isomers of Multicyclic Polymers $B_{n-1}Cn$ ($B_{N-1}CN$) Derived from TTSBI



The MALDI-TOF mass spectroscopy does, of course, not allow for an identification of individual isomers.

Polycondensations with Sebacoyl Chloride or HDBC. Sebacoyl chloride was selected as comonomer of TTSBI because it is a relatively long and relatively inexpensive acid chloride and because it is chemically more stable than shorter aliphatic dicarboxylic acid dichlorides. Dioxane was selected as reaction medium because TTSBI is not well soluble in other inert solvents such as dichloromethane, toluene, or ethyl acetate. The monomer concentration was varied from 0.20 to 0.02 mol/L (see Table 2). Yet, regardless of this variation, all reaction products were completely or partially cross-linked. From the samples 4 and 5 (Table 2), MALDI-TOF mass spectra were measured which evidenced that these samples contained a soluble fraction. These MS exclusively displayed the peaks of multicyclic polyesters of structure **1** (for the masses see Table 5).



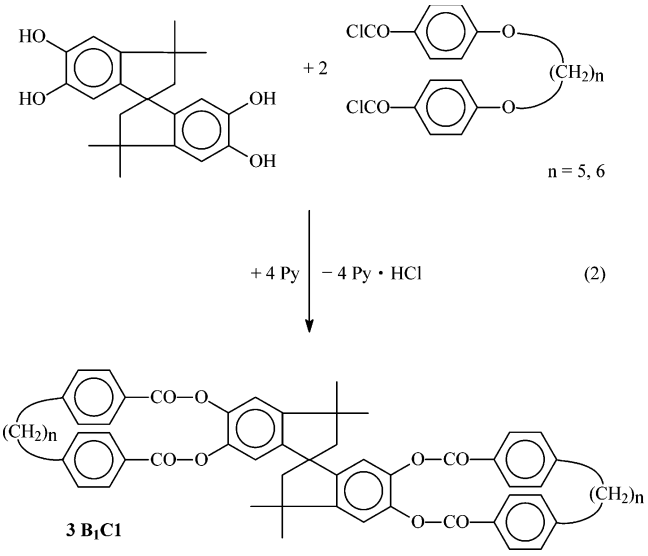
1 B_1C1 : X = CH_2

2 B_1C1 : X = O

+ Multicyclic Oligo- and Polyesters

HDBC was selected as second aliphatic comonomer of TTSBI because its length is identical with that of sebacoyl chloride and because it possesses two $O-CH_2CH_2$ groups. It is well-known from aliphatic polyethers that $O-CH_2CH_2$ groups favor gauche conformations, whereas the energetically most favorable conformation of alkane chain is the all-trans conformation. Gauche conformations favor in turn cyclization reactions for both thermodynamic and kinetic reasons. Nonetheless, the polycarbonates prepared at low concentrations (nos. 6 + 7, Table 2) were partially cross-linked. Nonetheless, several attempts were made to obtain MALDI-TOF MS of the soluble fractions. However, these MS had poor signal-to-noise ratios and displayed numerous weak peaks, most of which were difficult to interpret. In summary, the experiments with HDBC did not evidence a higher cyclization tendency than those performed with sebacoyl chloride.

Polycondensations with Aromatic Dicarboxylic Acid Dichlorides. A first series of polycondensations were conducted using the para-functional dichlorides **5**, $n = 5$ and 6 (see Table 3). At a TTSBI concentration of 0.04 mol/L both polycondensations ended with gelation. Yet, reduction of the concentration by a factor of 2 sufficed to avoid cross-linking, and completely soluble multicyclic polyesters were obtained in high yields (nos. 2 + 4, Table 3). The MALDI−TOF m.s. presented in Figure 1 proves their structure and suggests high conversions. It is interesting to note that even B_1C1 cycles were formed which correspond to the spirocyclic structure outlined in eq 2. The formation of these spirocycles was confirmed by fast atom bombardment (FAB) mass spectrometry.



Analogous experiments with the meta-functional dichlorides **6** (summarized in Table 4) gave the following results. With a pentamethylene spacer gelation occurred at a TTSBI concentration of 0.08 mol/L (no. 1), but soluble multicycles were obtained at 0.04 mol/L. At this concentration the dichlorides possessing six or eight CH_2 groups also yielded soluble multicycles. These findings indicate that the cyclization tendency of the dichlorides **6**, $n = 5$ and 6, is higher than that of the para compounds **5**, $n = 5$ and 6. The MALDI-TOF MS presented in Figures 2 and 3 demonstrate that rather clean polycondensations with high conversions were achieved.

The polycondensations using the dichloride **6** with a decamethylene spacer gave a somewhat unexpected result. Initially, it was expected that this dichloride is the most flexible monomer and, thus, particularly prone to cyclization. Therefore, the first polycondensation with this dichloride was performed at a TTSBI concentration of 0.08 mol/L. Yet, gelation occurred not only at 0.08 mol/L but also at a concentration of 0.04 mol/L: Soluble multicycles were finally obtained at a concentration of 0.02 mol/L. This finding can be rationalized considering that the energetically most favorable conformation of alkane chains is

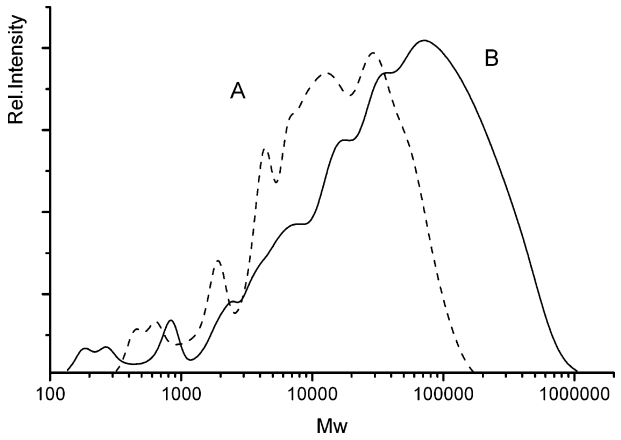
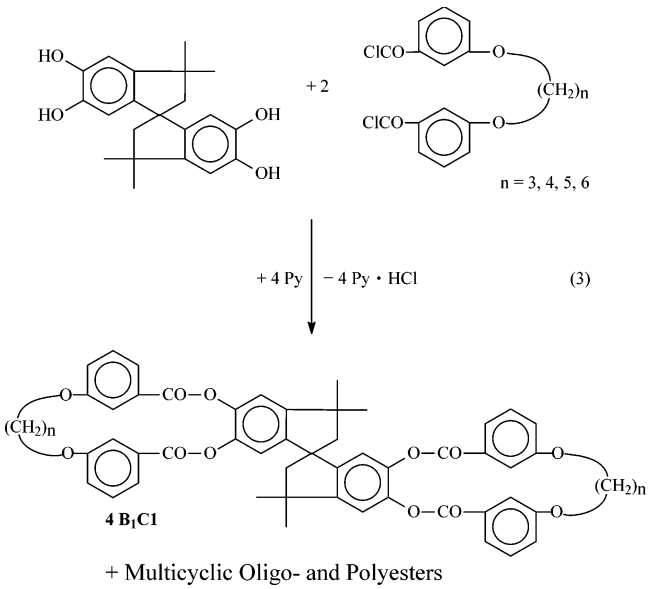


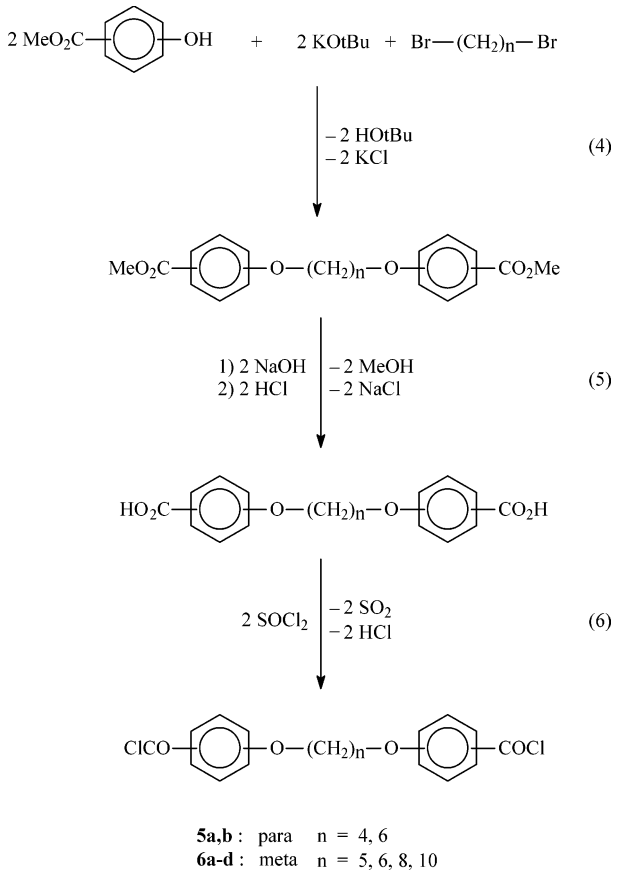
Figure 4. SEC measurements of (A) multicyclic polyester no. 7, Table 4, and (B) multicyclic polyester no. 2, Table 3.

the all-trans conformation which is unfavorable for cyclization. When the spacers of the dichlorides **6** (or **5**) are shorter, the percentage of gauche conformations resulting from the O−CH_2-CH_2 groups is higher. These factors seemingly dominate the competition between cyclization and chain growth. This interpretation also agrees with the failure of sebacoyl chloride to yield soluble multicycles.



+ Multicyclic Oligo- and Polyesters

SEC Measurements. Although the multicyclic polyesters of this work were insoluble in tetrahydrofuran, they proved to be soluble in chloroform and, thus, allowed us to perform SEC measurements. The usual calibration with polystyrene does certainly not yield accurate molar mass data, but the order of magnitude should be correct. The data listed in Tables 3 and 4 indicate that the number-average molecular weights (M_ns) of all samples are higher than 5000 Da. The high polydispersities are typical for all multicyclic polymers we have synthesized so far, and they are also typical for "$a_2 + b_2$" polycondensates, when a high extent of cyclization is involved.[15] The elution curves (exemplarily illustrated in Figure 4) also suggest that the samples with the highest weight-average molecular weights (M_ns) contain a sizable fraction around 10^5 Da. In summary, the soluble multicyclic polyesters obtained in this work are true polymers with molecular weights which are distinctly higher than those of the sol phase described by Flory for his "$a_2 + b_4$" polycondensations.[11]



5a,b : para n = 4, 6
6a-d : meta n = 5, 6, 8, 10

DSC Mesurements. The soluble multicyclic polyesters of structure **6** (Table 4) were subjected to DSC measurements with a heating rate of 20 °C/min. As expected, no melting endotherm was found, and WAXS measurements confirmed the absence of crystallinity. The broad glass-transition steps were found at relatively high temperatures compared to the flexibility of the aliphatic spacers, but the multicyclic architecture is a hindrance for high segmental mobilities.

Conclusion

The results of this work demonstrate that TTSBI is a useful tetrafunctional ("b_4-type") monomer for the preparation of multicyclic polyesters. It was found that the competition between cyclization (favoring multicycles) and chain growth (favoring gelation) depends very much on the concentration and on the structure of the dicarboxylic acid dichlorides used as comonomers of TTSBI. Aliphatic dichlorides such as sebacoyl chloride or HDBC yielded gels, even at the lowest concentration, presumably because the all-trans conformation of the aliphatic chain predominated under the given experimental conditions. Yet, dichlorides of aromatic ether dicarboxylic acids based on 3-hydroxy- and even 4-hydroxybenzoic acid proved to be useful for syntheses of multicyclic polyesters in high yields. Meta-functionalization and short aliphatic spacers favored cyclization more than para-functionalization and spacers with 10 methylene groups. These structure−property relationships of the dichlorides are of interest for the preparation of further multicyclic polyesters from various tri-, tetra-, or pentaphenols. Finally, the results of this work allow the conclusion that multicyclic polymers with relatively high molar masses (compared to the

sol phases in Flory's work[4,10,11]) may be prepared although the efficient cyclization reactions limit the chain growth.

References and Notes

(1) Kienle, R. H.; van der Meulen, F. A.; Petke, F. E. *J. Am. Chem. Soc.* **1939**, *61*, *2258.*
(2) Kienle, R. H.; Petke, F. E. *J. Am. Chem. Soc.* **1940**, *62*, 1053.
(3) Kienle, R. H.; Petke, F. E. *J. Am. Chem. Soc.* **1941**, *63*, 481.
(4) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(5) Kricheldorf, H. R.; Fechner, B. *Biomacromolecules* **2002**, *3*, 691.
(6) Kricheldorf, H. R.; Rost, S. *Macromolecules* **2004**, *37*, 7955.
(7) Kricheldorf, H. R.; Rost, S. *Polymer* **2004**, *45*, 3205.
(8) Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. *Macromolecules*, in press.
(9) Kricheldorf, H. R.; Schellenberg, J.; Schwarz, G. *Macromol. Chem. Phys.*, in press.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083.
(11) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3097.
(12) Jin, J.-I.; Oh, T.; Park, J.-H.; Huon, J. *J. Chem. Soc., Perkin. Trans. 2* **1986**, 343.
(13) Passmann, M.; Wilbert, G.; Cochin, D.; Zenthy, R. *Makromol. Chem. Phys.* **1998**, *199*, 179.
(14) Piatner, P.; Grizzati, N.; Seitz, N.; Schmidt, H.-W.; Heffner, G.; Ricker, M.; Rochefort, W. E.; Pearson, D. S. *Liq. Cryst.* **1994**, *17*, 811.
(15) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.

MA061675A