Multicyclic Poly(benzonitrile ether)s Based on 1,1,1-Tris(4-hydroxyphenyl)ethane and Isomeric Difluorobenzonitriles

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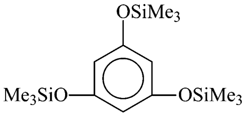
ABSTRACT: Silylated 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) was polycondensed in *N*-methylpyrrolidone with either 2,6-difluorobenzonitrile or 2,4-difluorobenzonitrile under conditions allowing for complete conversions of the C−F groups. With 1.0:1.0 stoichiometry, completely soluble polyethers were obtained from both isomeric difluorobenzonitriles. The MALDI−TOF mass spectra proved tree-shaped and cyclic polyethers to be the main products. With a molar excess of 10%, the 2,6-difluorobenzonitrile gave a cross-linked product at a concentration of 15 mmol/30 mL (THPE/NMP) or cross-linking occurred with 20 mol % excess at a concentration of 4 mmol/30 mL. However, the 2,4-difluoro isomer yielded soluble polyethers even in an excess of 50 mol %. Such an excess of the difluoro monomer had the consequence that linear and tree-shaped polyethers were never formed, and multicyclic oligomers or polymers became the predominant reaction products, so that even with ideal stoichiometry gelation did not occur. Multicycles free of functional (end) groups were the main reaction products under optimum conditions. The reason for the different cyclization tendencies of 2,6- and 2,4-difluorobenzonitrile were discussed on the basis of computer modeling of different conformations.

Introduction

Polycondensations of difunctional monomers with tri- or tetrafunctional ones ($a_2 + b_n$ polycondensations) have, in principle, a long tradition.[1−4] In Flory's work[4] emphasis was laid on the formation of networks from stoichiometric reaction mixtures (equal numbers of "a" and "b" functional groups). The dependence of the gelation point on the conversion or on other experimental parameters and the influence of a few large loops on the gelation point and on the structure of networks were studied.

In the past two decades "$a_2 + b_n$" polycondensations were studied from a different point of view.[5−20] Equimolar or nearly equimolar monomer mixtures were polycondensed with the purpose to avoid gelation even at conversions >99% and to isolate hyperbranched polymers. To the best of our knowledge, in all these studies the structure of the resulting hyperbranched polymers was discussed without consideration of cyclization reactions. However, recently we have demonstrated[21] that in kinetically controlled "linear polycondensations" (KCPs) cyclization competes with chain growth at any stage and at any concentration (even in bulk), so that at 100% conversion the polycondensate exclusively consists of cycles. Furthermore, when silylated phloroglucinol (**1**)[22] or silylated tris(4-hydroxyphenyl)ethane (THPE) (**2**)[21,23] were polycondensed with 4,4′-difluorosulfone (**3**), large amounts of cyclic oligoethers, bridged cycles (bicycles), and double, triple, and multiple bridged cycles were detected by means of MALDI−TOF mass spectrometry. These observations suggested that the hyperbranched poly(ether sulfone)s mainly consisted of cyclic building blocks when prepared by "$a_2 + b_3$" polycondensations. With the difluoroketone (**4**) as reaction partner[24] of **2**, simple cyclic oligomers were formed, but significant amounts of bridged cycles were not detected. Obviously, **4** is unfavorable for efficient bridging of cycles, and the lower signal-to-noise ratio of the MALDI−TOF mass spectra (MS) presented another hindrance for the observation of bridged cycles. The present work had the purpose to study polycondensations of **2** with 2,6-difluorobenzonitrile (**5**) or 2,4-difluorobenzonitrile (**6**) to shed more light on the role of cyclization in "$a_2 + b_3$" polycondensations. In this connection, it should be mentioned that polycondensations of silylated bisphenol A with **5** or **6** were recently studied in much detail.[25] Under optimized reaction conditions only cyclic oligo- and polyethers were found. These reaction conditions and results formed the basis of the present work.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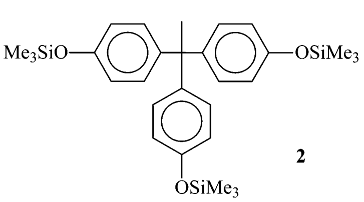
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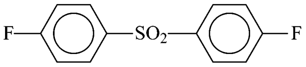
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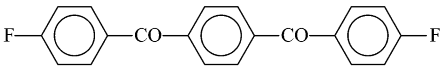
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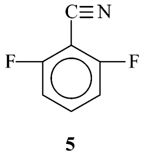
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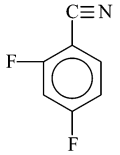
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Experimental Section

Materials. 2,4-Difluorobenzonitrile, 2,6-difluorobenzonitrile, and 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) were

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Table 1. Polycondensations of Silylated THPE (2) with 2,6-Difluorobenzonitrile in NMP

expt no.	THPE(mmol)[a]/ NMP(mL)	THPE[b]/ 2,6-DFBN	temp (°C)	time (h)	yield (%)	η_{inh}[c] (dL/g)
1	15/30	1.0/1.00	180−185	24	insol	
2	15/30	1.0/1.00	140−145	24	73	0.66
3	15/30	1.0/1.00	140−145	48	60	0.55
4	15/30	1.0/1.05	140−145	24	17[d]	0.19[d]
5	15/30	1.0/1.10	140−145	24	cross-linked	
6	4/30	1.0/1.10	140−145	48	95	0.40
7	4/30	1.0/1.20	140−145	48	68[d]	0.42[d]
8	4/30	1.0/1.30	140−145	48	cross-linked	

[a] Initial concentration. [b] Molar feed ratio of silylated THPE and 2,6-difluorobenzonitrile. [c] Measured at 20°C with c = 2 g/L in CH_2Cl_2/TFA (volume ratio 4:1). [d] After filtration.

purchased from Aldrich Co. (Milwaukee, WI) and used as received. The THPE was silylated by means of hexamethyldisilazane as described previously.[22] The *N*-methylpyrrolidone (kindly supplied by Bayer AG, Uerdingen, Germany) was twice distilled over P_4O_{10} in vacuo. The K_2CO_3 (purum analyticum) was purchased from E. Merck KG (Darmstadt, Germany) and used as received.

Polycondensations. (A) With 2,6-difluorobenzonitrile: No. 2, Table 1. 1,1,1-Tris(4-trimethylsiloxyphenyl)ethane (15 mmol), 2,4 (or 2,6)-difluorobenzonitrile (15 mmol) and K_2CO_3 (31 mmol) were weighed into a 100 mL three-necked flask under an atmosphere of dry nitrogen, and dry NMP (30 mL) was added. The reaction vessel was equipped with a mechanical stirrer and gas-inlet and gas-outlet tubes. The reaction mixture was stirred at 140−145 °C for a period of 24 or 48 h, and the liberated hexamethyldisiloxane was removed with a slow stream of dry nitrogen. Finally, the reaction mixture was poured into cold water, and the precipitated polyether was isolated by filtration.

(B) With 2,6-difluorobenzonitrile: No. 7, Table 1. 1,1,1-Tris-(4-trimethylsiloxyphenyl)ethane (4 mmol), 2,6-difluorobenzonitrile (4.8 mmol), and K_2CO_3 (5.5 mmol) were polycondensed in NMP (30 mL) for 48 h as described above.

(C) With 2,4-difluorobenzonitrile: No. 11, Table 3. 1,1,1-Tris(4-trimethylsiloxyphenyl)ethane (4 mmol), 2,4-difluorobenzonitrile (6.08 mmol), and K_2CO_3 (6.7 mmol) were polycondensed in NMP (30 mL) for 48 h as described above.

All yields were determined after reprecipitation from methanol an drying at 120 °C in a vacuum.

C−F Terminated Oligoethers of Bisphenol A. Silylated bisphenol A (4 mmol), 2,6-DFBN (4.8 mmol), and dry K_2CO_3 (5.2 mmol) were weighed into a cyclindrical glass reactor equipped with mechanical stirrer gas-inlet and gas-outlet tubes. NMP (30 mL) was added, and the reaction mixture was stirred for 48 h at 140−145 °C, whereby a slow stream of dry nitrogen was passed through the reaction vessel. After cooling, the reaction mixture was poured into water, and the precipitated oligoether was isolated by filtration. Yield 99%, η_{inh} = 0.26 dL/g in CH_2Cl_2/TFA (volume ratio 4:1).

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 were recorded with a Bruker Avance-400 NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$ (containing TMS) as solvent (and shift reference).

The MALDI−TOF mass spectra were recorded on a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All spectra were recorded in the reflectron mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions with dithranol as matrix and K-trifluoroacetate as dopant. The SEC measurements were performed on a PL-DG-802 apparatus equipped with a LC1120 HPLC pump and a Shodex RI 101 refractive detector. A combination of three PL mixed-bed columns was used with chloroform as eluent. Commercial polystyrene standards were used for calibration.

For conformational energy calculations the molecular modeling program "Spartan" of Wavefunction Inc. (based on a semiempirical approach) was used.

Results and Discussion

Polycondensations of 2,6-Difluorobenzonitrile. From polycondensations of silylated bisphenol A with isomeric difluorobenzonitriles it was learned that NMP is a suitable solvent quite analogous to syntheses of other aromatic polyethers.[25] The silylation of the diphenol had the purpose to avoid the formation of water and to avoid side reactions. This method proved to be particularly useful for polycondensations of phloroglucinol.[22] A temperature of 140−145 °C with reaction times of 48 h was found to allow for quantitative conversion when 2,6- or 2,4-difluorobenzonitrile was used as electrophilic monomer. Therefore, these reaction conditions were also used for all polycondensations of silylated THPE performed in this work (Table 1). However, before information about the optimum reaction conditions was available, one polycondensation of **2** and **5** was conducted with equimolar amounts at 180 °C and almost complete cross-linking was observed (No. 1, Table 1).

When the silylated THPE was polycondensed with an equimolar amount of the 2,6-monomer (**5**) at 140−145 °C, the isolated polyether was completely soluble in dichloromethane or chloroform (Nos. 2 and 3, Table 1), regardless of the reaction time. The inherent viscosity suggests a rather high molecular weight because the hydrodynamic volume of hyperbranched polymers is low. For aromatic hyperbranched polyesters having η_{inh} values <0.5 dL/g, weight-average molecular weights (M_w) above 5 × 10^5 Da were reported.[26,27] The polyethers derived from 2,6-difluorobenzonitrile proved to be in-

Table 2. Masses (in Da) of All K^+-Doped Reaction Products Observed in the MALDI−TOF Mass Spectra of the Reaction Products Isolated from Polycondensations of Silylated THPE and 2,4-Difluorobenzonitrile (6)

N	LbN	CN	B_1CN	B_2CN	B_3CN	B_4CN	B_5CN	B_6CN
2	1156	849						
3	1563	1256	1355					
4	1969	1662	1760	1859				
5	2374	2067	2166	2265				
6	2780	2473	2571	2670	2770			
7	3186	2879	2977	3076	3176			
8	3592	3285	3382	3481	3581	3680		
9	3998	3690	3788	3887	3987	4085		
10	4403	4096	4193	4292	4392	4491	4590	
11		4501	4599	4697	4798	4897	4995	
12			5005	5103	5203	5302	5401	(5500)
13				5509	5609	5707	5806	(5905)
14					6014	6112	6211	6310
15								6715

Table 3. Polycondensations of Silylated THPE (2) with 2,4-Difluorobenzonitrile in NMP[a] at 140−145 °C

expt no.	THPE[b]/2,4-DFBN	time (h)	yield (%)	η_{inh}[c] (dL/g)
1	1.0/1.00	24	65	0.07
2	1.0/1.05	24	71	0.07
3	1.0/1.10	24	81	0.08
4	1.0/1.15	24	79	0.09
5	1.0/1.20	24	77	0.09
6	1.0/1.10	48	87	0.08
7	1.0/1.20	48	85	0.08
8	1.0/1.30	48	77	0.08
9	1.0/1.40	48	89	0.07
10	1.0/1.50	48	91	0.12[d]
11	1.0/1.52	48	97	0.19[d]

[a] A concentration 4 mmol silylated THPE/30 mL NMP was used for all experiments. [b] Molar feed ratio of silylated THPE and 2,4-difluorobenzonitrile. [c] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 8:1). [d] After filtration from a few gel particles.

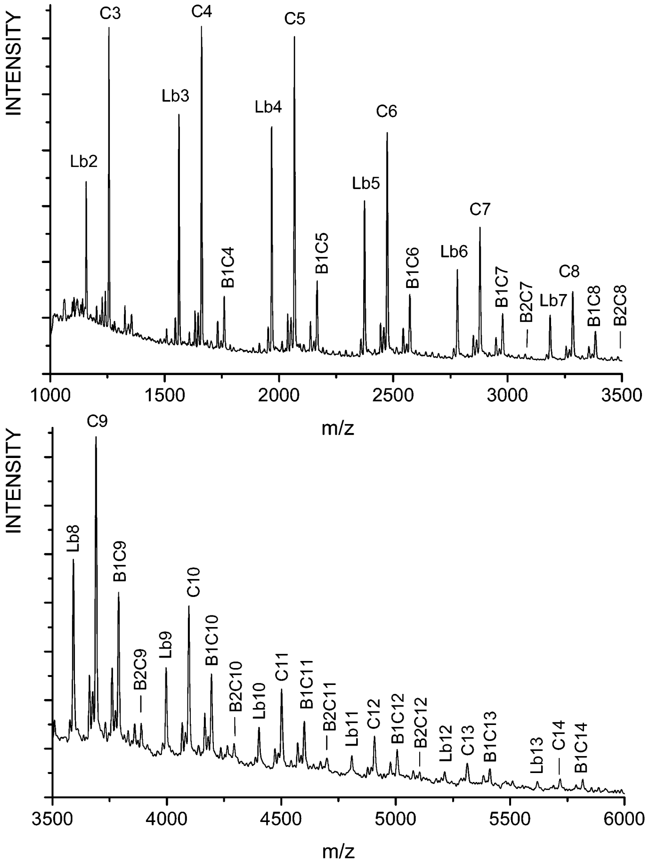


Figure 1. MALDI−TOF mass spectrum of the polyether prepared from 2,6-difluorobenzonitrile with a 1.0:1.0 feed ratio (No. 2, Table 1).

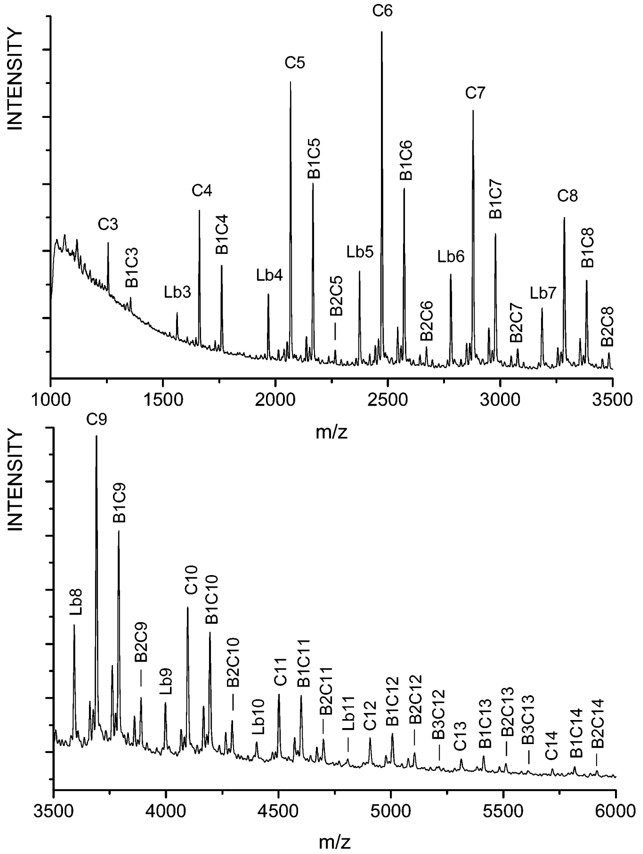
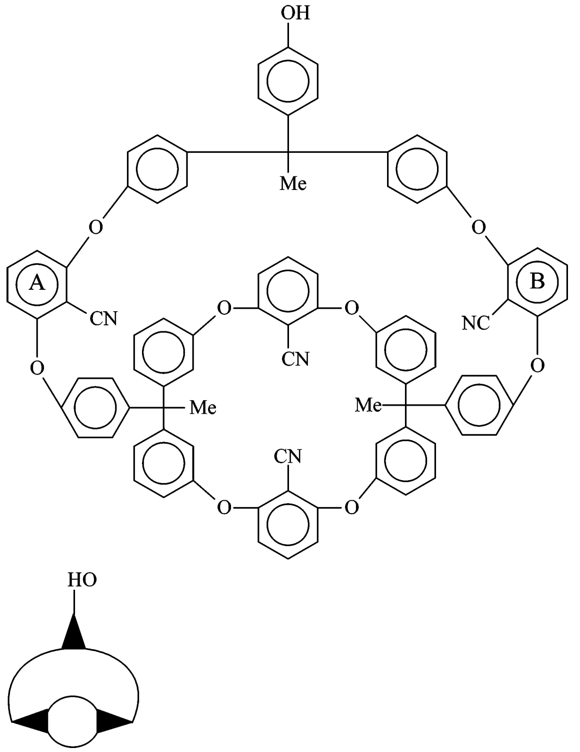


Figure 2. MALDI−TOF mass spectrum of the polyether prepared with a 5 mol % excess of 2,6-difluorobenzonitrile (No. 4, Table 1, soluble fraction).

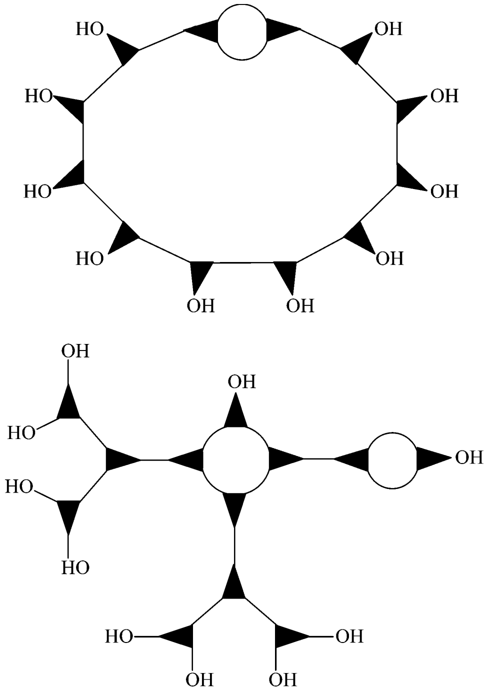
Scheme 1. B_1C3



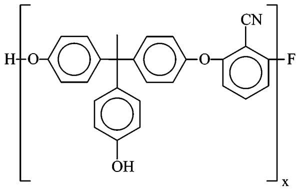
soluble in neat tetrahydrofuran, dichloromethane, or chloroform, so that we were not able to perform SEC measurements.

The MALDI−TOF mass spectrum presented in Figure 1 proved the existence of linear or branched chains (labeled **Lb** in Figures 1 and 2) and of cyclic oligomers (labeled **C**). These cycles may have the simple structure outlined in formulas **7C,** or they may have short side chains as illustrated in formula **7C′**. Furthermore, a low concentration of so-called "bridged cycles" (labeled **B**$_n$**CN** in the Figures) was detected. The index of **B** indicates the number of benzonitrile units bridging cycles or connecting cycles, and the number behind **C** indicates the total number of repeat units. This nomenclature and the three-dimensional nature of bridged cycles are illustrated in Schemes 1−4. In the formula of **B$_1$C3** (Scheme 1) either the benzonitrile units A or B may be understood as bridge units. In the case of **B$_1$C2** and **B$_1$C3** only one isomer can exist, whereas for all larger bridged cycles several isomers may be formed, as exemplarily illustrated for **B$_1$C12**, **B$_4$C12**, and **B$_6$C12**

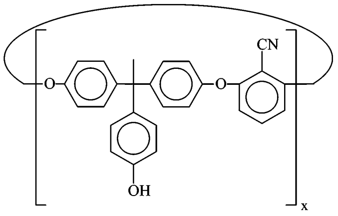
Scheme 2. Two Isomers of B$_1$C12



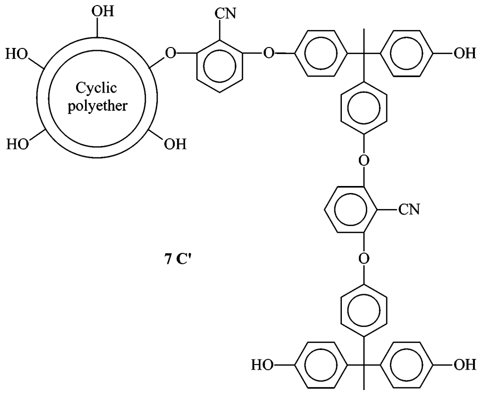
in Schemes 2–4, which cannot be distinguished by MALDI–TOF MS.



7 La

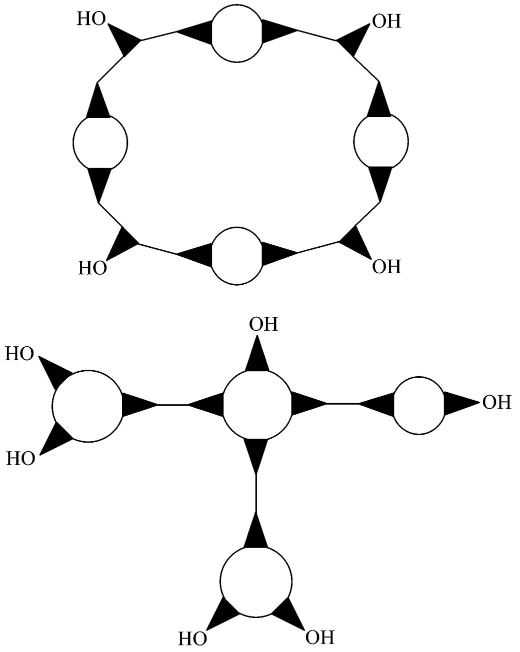


7 C

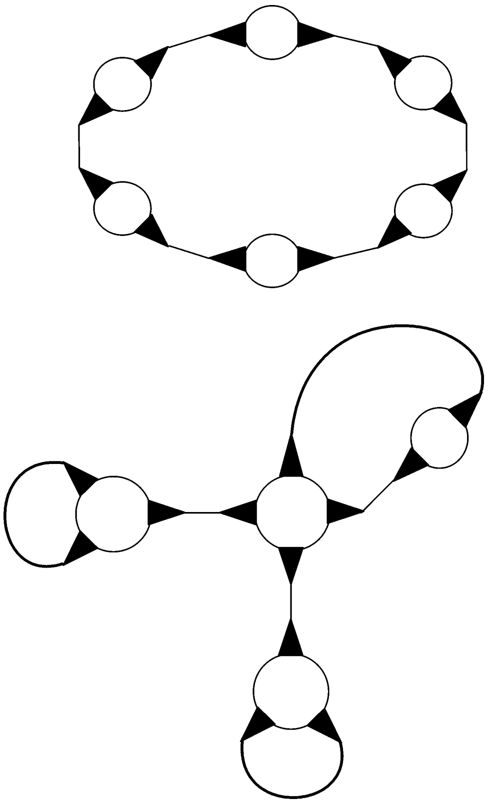


7 C'

Scheme 3. Two Isomers of B$_4$C12

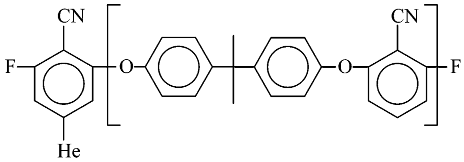


Scheme 4. Two Isomers of B$_6$C12



When the polycondensation of **2** with **5** was performed with a 5 molar excess of **5**, part of the reaction product was cross-linked (No. 4, Table 1). The soluble fraction was extracted with dichloromethane and characterized by MALDI–TOF MS (Figure 2). This mass spectrum proved that the excess of **5** had two interesting consequences in addition to cross-linking. First, the content of linear and branched polyethers was significantly reduced. Second, the content of "bridged cycles" was correspondingly enhanced. Cyclic systems containing up to three "bridge" units were detected (**7B$_3$C12**, **7B$_3$C13**, and **7B$_3$C14**). (The masses of the potassium-doped cycles, linear species, and multicycles as they were found in the isomeric polycondensation products of 2,4-difluorobenzonitrile are listed in Table 2.) Unfortunately, the moderate signal-to-noise ratio of these MALDI–TOF MS did not allow for the detection of more complex architectures. Concerning the structure of linear and branched polyethers, it should be mentioned that three types (labeled **La**, **Lb**, and **Lc**) may, in principle, be formed, corresponding to three different combinations of OH and C–F end groups. Yet, because of the excess of OSiMe$_3$ in all these polycondensations, polyethers possessing C–F end groups were never observed. The exclusive observation of **Lb** chains (linear or hyperbranched) indicates that the reaction conditions allowed for quantitative conversion of all C−F groups in the reaction mixture. A 10% molar excess of 2,6-difluorobenzonitrile caused almost complete cross-linking (No. 6, Table 1).

In this connection, it should be mentioned that attempts were made to confirm the end group analyses provided by the MALDI−TOF MS with NMR spectroscopy. For this purpose a linear "model compound" was synthesized (structure **8**) by polycondensation of silylated bisphenol A with a 20 mol % excess of 2,6-difluoronitrile. The ^{1}H NMR spectrum of this (polydisperse) "model compound" displayed an end group signal (a triplet) at 7.56 ppm (in $CDCl_3$/TFA 8:1), which by comparison with 2,6-DFBN was attributed to the proton para to the CN group (He in formula **8**). This signal was absent in the ^{1}H NMR spectra of the polyethers derived from THPE and 2,6-DFBN.



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Finally, three more polycondensations were performed at a 4 times lower concentration (Nos. 6−8, Table 1). This concentration was also used for all polycondensations of 2,4-DFBN (Table 3), and it is used for most current studies which will be presented in future publications. At this lower concentration, no gelation occurred at a feed ratio of 1.0/1.10, and only with a 20 mol % excess of 2,6-DFBN was partial cross-linking observed.

Polycondensation of 2,4-Difluorobenzonitrile. From "linear polycondensations" of **5** or **6** with silylated bisphenol A it was learned[25] that **6** involves a higher cyclization tendency than **5**, although both isomers have the fluoro atoms in the meta position. Therefore, it was an interesting question to find out to what extent the higher cyclization tendency of **6** is reflected in the polycondensations studied in this work. In a first series of polycondensations the reaction time was fixed at 24 h, and the molar excess of **6** was increased in steps of 5 mol % up to 20 mol % (Nos. 1−5, Table 3). All polycondensates proved to be completely soluble. To make sure that the conversions of the C−F groups were complete, a second series of polycondensations were performed with a total time of 48 h (Nos. 6−10, Table 3). In this series, the molar excess of **6** was increased in steps of 10% up to 50 mol %. No oligomers containing C−F groups were detected in the MALDI−TOF MS, evidencing their almost complete conversion.

The first surprising result was the complete solubility of most samples. Only when a 50 mol % excess of 2,4-difluorobenzonitrile was used (the optimum stoichiometry for cross-linking) a few gel particles were found (No. 10, Table 3). This observation indicates an extremely high cyclization tendency, taking into account the abovementioned complete conversion of C−F groups. Since cyclization competes with chain growth in an "a$_2$" + "b$_3$" polycondensation as well as in an "a$_2$" + "b$_2$" polycondensation, intensive cyclization limits the chain growth. In agreement with this interpretation, all samples derived from 2,4-difluorobenzonitrile gave low and similar viscosity values (Table 3). Furthermore, no high molar mass chains (M_n > 30 000 Da) were detectable in the elution curves, as exemplarily illustrated in Figure 3. However, the elution curve expanded to higher molar masses when the feed ratio was varied from 1.0:1.0 to 1.0:1.5 (Figure 3, curves A + B). The calibration with polystyrene yielded low number-average (M_n) and weight-average (M_w) data (see Figure 3) in agreement with the low viscosities. The calibration with polystyrene is perhaps not highly accurate but is justified by the fact that for low molar masses the hydrodynamic volumes of linear, branched, and cyclic species are not much different. Furthermore, a higher accuracy will not have any influence on the interpretation of our results and the message of this work.

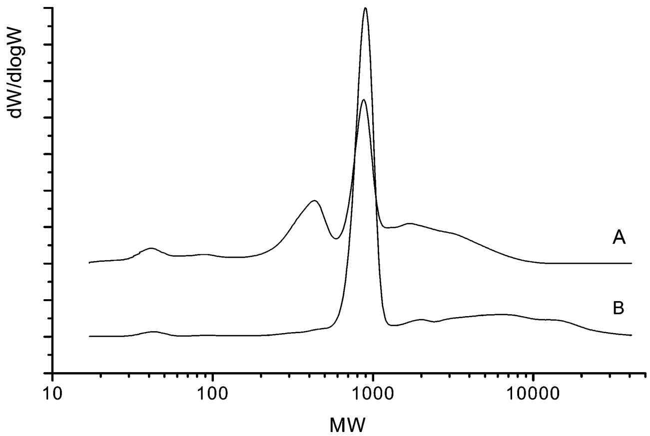
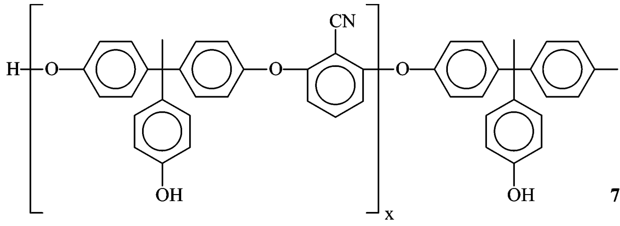
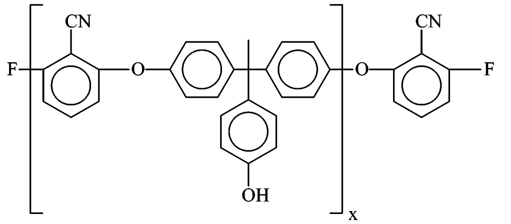


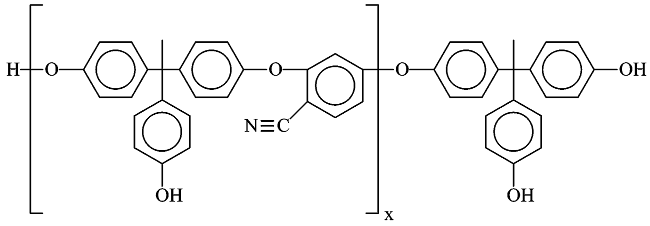
Figure 3. SEC elution curves of polyether derived from 2,4-difluorobenzonitrile: (A) feed ratio 1.0:1.0 (No. 2, Table 1), $M_n \approx 1300$ Da, $M_w \approx 2500$ Da; (B) feed ratio 1.0:1.5 (No. 10, Table 3), $M_n \approx 1400$ Da, $M_w \approx 4000$ Da.



7 Lb



7 Lc



9 Lb

The MALDI−TOF mass spectra of the samples prepared with an exact 1.0:1.0 feed ratio or with a 5 molar excess of 2,4-difluorobenzonitrile looked quite similar to those obtained from the 2,6-isomer (Figures 1 and 2). Linear or hyperbranched chains symbolized by

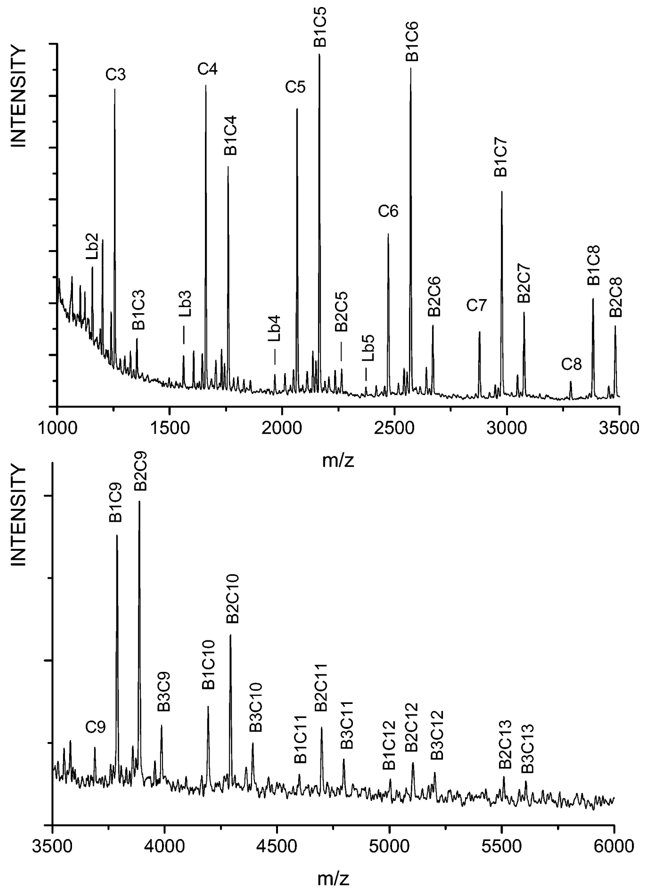


Figure 4. MALDI−TOF mass spectrum of the polyether prepared with a 20 mol % excess of 2,4-difluorobenzonitrile (No. 7, Table 3).

structure **9Lb** were observed up to a degree of polymerization (DP) of 10. Their masses and those of all cyclic species observed in the MS of polyethers derived from 2,4-difluorobenzonitrile are summarized in Table 2. The peaks of the "noncyclic species" (**Lb**) vanished when the excess of 2,4-difluorobenzonitrile increased, whereas the peaks of cycles and bridged cycles intensified. This trend is illustrated in Figures 4 and 5. Yet, at high feed ratios of 2,4-difluorobenzonitrile (>1.2) even the peaks of simple cycles began to fade away, and at a 50 mol % excess (No. 10, Table 1) the peaks of simple cycles had completely disappeared from the MS. On the other hand, multicycles containing up to six bridge units became detectable at an excess of 40 mol %. Particularly interesting is the appearance of multicycles such as $\mathbf{B_2C4}$, $\mathbf{B_3C6}$, $\mathbf{B_4C8}$, and $\mathbf{B_5C10}$ (i.e., $\mathbf{B}_{\boldsymbol{n}}\mathbf{C2}\boldsymbol{n}$) at a molar excess of 40% or higher. These multicycles do not possess free functional groups anymore and thus represent the low molar mass counterparts of infinite networks. Therefore, the multicycles $\mathbf{B}_{\boldsymbol{n}}\mathbf{C2}\boldsymbol{n}$ definitely prove that rapid cyclization and no other side reactions is the reason for the low molecular weights and for the low tendency of gelation. From the MS of polyether prepared with a feed ratio of 1.0/1.50 it was learned that the excess of 50 mol % had not sufficed yet to react all $OSiMe_3$ groups. Therefore, an additional polycondensation with an excess of 52 mol % was performed (No. 11, Table 3). The MALDI−TOF MS showed the expected simplification because the multicycles $\mathbf{B}_{\boldsymbol{n}}\mathbf{C2}\boldsymbol{n}$ were now the largely prevailing reaction products (Figure 6).

With the schematic formulas $\mathbf{B_1C12}$, $\mathbf{B_4C12}$, and $\mathbf{B_6C12}$ (Schemes 2−4), the following tendencies should be illustrated. The formation of large cycles competes with the formation of hyperbranched or star-shaped structures at any level of bridging. Increasing numbers of bridge units reduce and finally eliminate the possibility that hyperbranched structures can be formed. A higher content of bridge units favors the formation of compact globular molecules with low solution and melt viscosities as illustrated by the viscosity data listed in Tables 1 and 3. With ideal equivalent stoichiometry multicycles free of "end groups" ($\mathbf{B}_{\boldsymbol{n}}\mathbf{C2}\boldsymbol{n}$) are the only reaction products.

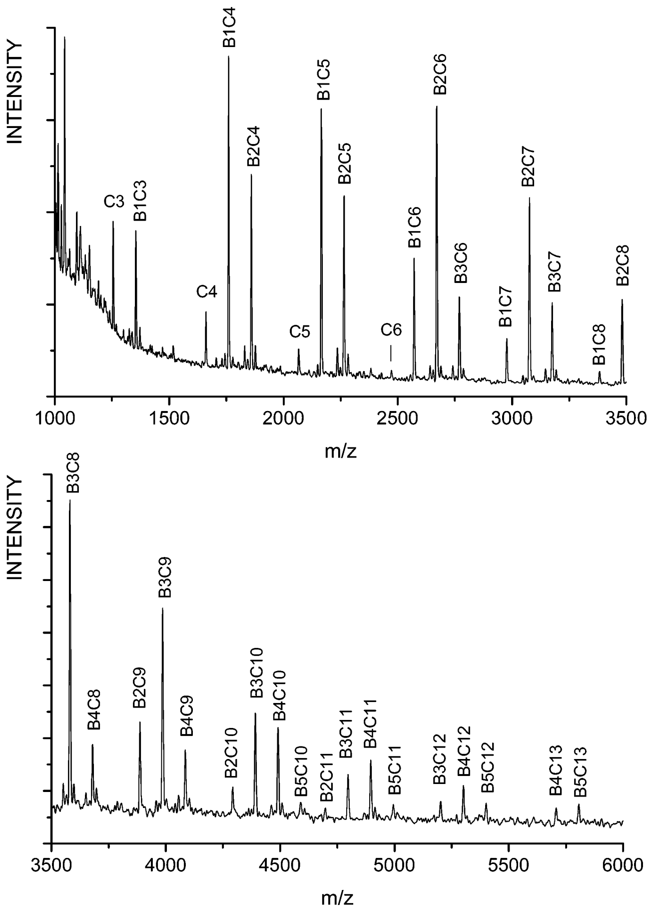


Figure 5. MALDI−TOF mass spectrum of the polyether prepared with a 40 mol % excess of 2,4-difluorobenzonitrile (No. 9, Table 3).

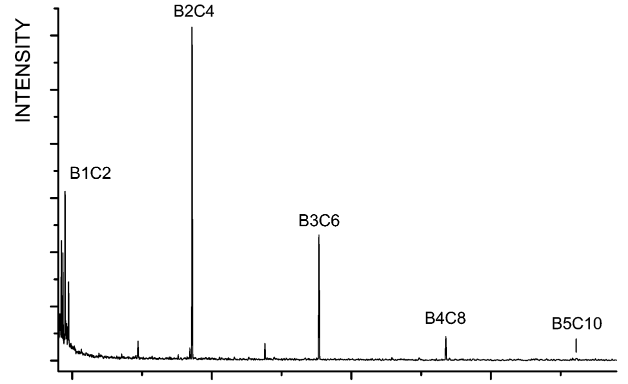
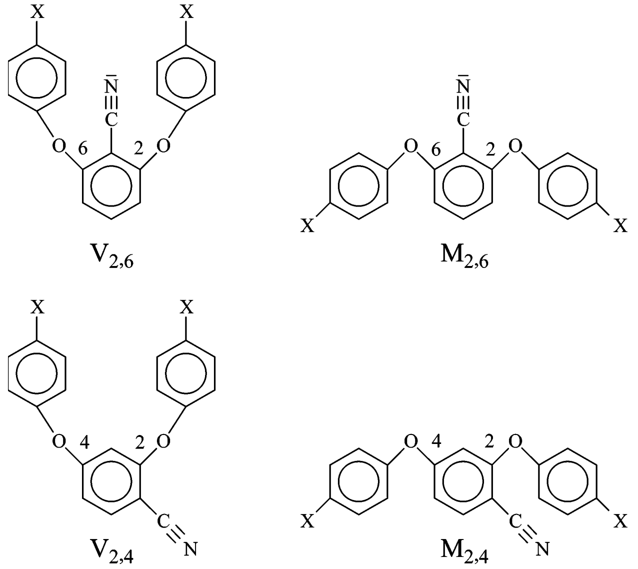


Figure 6. MALDI−TOF mass spectrum of the polyether prepared with a 52 mol % excess of 2,4-difluorobenzene (No. 11, Table 3).

Discussion. The results of this work clearly indicate that the cyclization tendency of 2,4- and 2,6-difluo-

Scheme 5



robenzonitrile in polycondensations with THPE are quite different. At first glance this difference is surprising because in both cases the F atoms are in the meta position. However, a satisfactory interpretation can be obtained by discussion of two types of conformations of the ether units labeled V and M in Scheme 5. These conformations result from rotation around the C_2–O and C_6–O bonds of the 2,6-isomer or around the C_2–O and C_4–O bonds of the 2,4-isomer. The relative energy minima depend on whether the electronic interactions between the nitrile group and neighboring phenoxy groups are attractive or repulsive in nature. Computer modeling of the isomeric model compounds presented in Scheme 5 indicates that repulsive electronic interactions are dominating. In consequence, M-like conformations are energetically more favorable in the case of the 2,6-isomer, whereas V-like conformations are more favorable for the 2,4-isomer. Furthermore, rotation around the $C_{1'}$–O bonds indicate that a coplanar position of both phenoxy groups is slightly more favorable than other positions. For V-like conformations the distance between the para positions of the phenoxy groups amounts to approximately 6.5 Å, while distances around 13.5 Å was found for the M-like conformations. Therefore, cyclization reactions of functional groups or chain segments in the para position of the phenoxy groups should be favored by V-like conformations. In summary, computer modeling of the conformational energies of the model compounds outlined in Scheme 4 provides a satisfactory explanation for the higher cyclization tendency in polycondensations of 2,4-difluorobenzonitrile.

Conclusion

The results of this work demonstrate again that syntheses of aromatic polyethers based on nucleophilic substitution of fluoraromatics with silylated di- or triphenols is a rather clean process which allows for almost complete conversion of the C–F groups under optimized conditions. Furthermore, the efficient formation of cycles and multicyclic compounds or building blocks first observed in syntheses of poly(ether sulfone)s from triphenols[21,23] is shown to be a general trend. At first glance quite surprising are the largely differing cyclization tendencies of 2,6- and 2,4-difluorobenzonitriles. Yet, a satisfactory explanation can be offered considering intramolecular electronic interactions and their consequences for different populations of V-like and M-like conformations (Scheme 5). The V-conformation favoring cyclizations should much more frequently occur in ether segments derived from 2,4-difluorobenzonitrile. The polycondensations of this work also demonstrate that “a_2“ + “b_3” polycondensations involving a high extent of cyclization strongly reduce the formation of hyperbranched structures and even prevent network formation when a nearly equifunctional stoichiometry is applied. It is obvious that dilution will favor cyclization at the expense of chain growth, so that gelation can be completely avoided despite optimum stoichiometry. In other words, “a_2 + b_3” polycondensations involving a high cyclization tendency will yield multicyclic oligomers and polymers at the expense of hyperbranched polymers or networks. To the best of our knowledge, this work presents for the first time direct spectroscopic evidence for the synthesis of $\mathbf{B}_n\mathbf{C}_{2n}$ multicycles via an “a_2 + b_3” polycondensation in concentrated solutions. The formation of bicyclic oligo(ether ketone)s under the conditions of the pseudo-high-dilution method has recently been reported by Colquhoun and co-workers.[28] Further studies of the influence of chain stiffness on the formation of hyperbranched and multicyclic aromatic polyethers will be presented in future publications.

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