Multicyclic Polyethers Derived from 1,4-Dicyanotetrafluorobenzene and Flexible Diphenols

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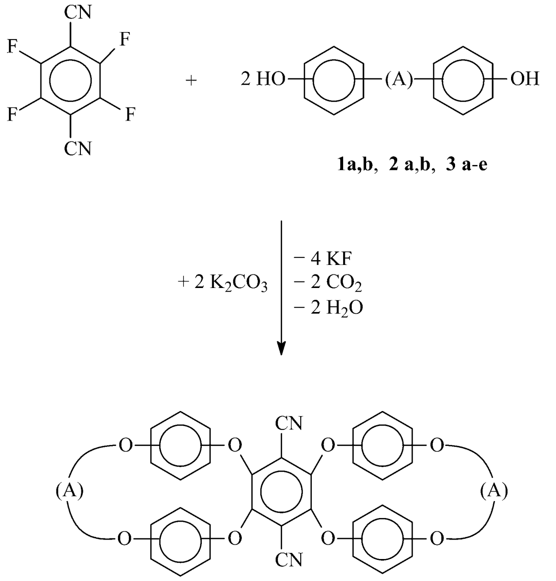
ABSTRACT: 1,4-Dicyanotetrafluorobenzene (DCTB) was polycondensed with various diphenols in DMF or DMSO using K_2CO_3 as catalyst and HF acceptor. At concentrations of 0.1 or 0.2 mol/L for DCTB, gels were obtained with 1,4-bis[2-(4-hydroxyphenyl)-2-propyl]benzene, with 1,3-bis[(4-hydroxyphenyl)-2-propyl]benzene and with α,ω-bis(4-hydroxyphenoxy) alkanes as comonomers. Yet soluble multicyclic polyethers were formed with α,ω-bis(3-hydroxyphenoxy) alkanes. The lengths of the alkane chains did not play any role for the successful syntheses of soluble multicycles. Furthermore, a model reaction with *p*-cresol was conducted, proving the feasibility of a quantitative tetrasubstitution of all four F-atoms in DCTB. The multicyclic polyethers were characterized by elemental analyses, ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, DSC, viscosity, and SEC measurements. As expected, high polydispersities (up to 8) were found. The DSC measurements indicated an amorphous character of all multicycles with glass-transition temperatures (T_gs) between 75 and 161 °C.

Introduction

Multicyclic polymers represent a new architecture which may be described as a three-dimensional arrangement of mutually connected smaller and larger cycles. Multicyclic polymers may also be considered as soluble nanogels. Multicyclic polymers may, in principle, be synthesized by $a_2 + b_n$ polycondensations, where a_2 means a bifunctional and b_n a multifunctional monomer. For a proper understanding of such "three-dimensional polycondensation" (a term coined by Flory),[1,2] it is useful to distinguish between polycondensations based on equimolar monomer mixtures and on equifunctional monomer mixtures. Using equimolar monomer mixtures, (hyper)branched polymers are the most likely reaction products (at least at high monomer concentrations). Equifunctional polycondensations meaning feed ratios of 1.5/1.0 for "$a_2 + b_3$" or 2.0/1.0 for "$a_2 + b_4$" systems will most likely result in insoluble gels when conducted in bulk. However, when conducted in moderately concentrated solutions (i.e., 0.02−0.2 mol/L) and when the structure of the monomers favors cyclization, gelation may be avoided and soluble multicyclic polymers will be the only reaction product. Whereas experimental and theoretical studies of $a_2 + b_2$ polycondensations have a long tradition,[2−5] little is known about "$a_2 + b_4$ polycondensations". Recently, we have published[6−8] a few examples of reversible, thermodynamically controlled polycondensations involving tetrafunctional monomers, which yielded soluble spirocycles and higher multicyclic oligomers. Furthermore, one example of an irreversible (kinetically controlled) $a_2 + b_n$ polycondensation was reported[9] using tetra(bromomethyl) methane as "b_4 monomer". In this context, the present work was aimed at studying an irreversible $a_2 + b_4$ polycondensation based on 1,4-DCTB as an electrophilic "b_4-monomer" and its reaction with diphenols. It should be elucidated how structure and flexibility of the diphenols influences the competition between cyclization and chain growth. Using an equifunctional stoichiometry (feed ratio 2:1), it should be found out if gelation can be avoided and soluble multicyclic polyethers can be isolated (eq 1). Polycondensations with equimolar stoichiometry yielding (hyper)branched polyethers will be described in a future publication. Finally, it should be mentioned that numerous syntheses of polyimides, poly(benzoxazole)s, poly(benzimidazole)s, poly(quindine)s, or poly(quinoxaline)s may also be considered as "$a_2 + b_4$" polycondensations. However, in those cases, a rapid and quantitative formation of five- or six-membered heterocycles is intended (and achieved) so that neither hyperbranched nor multicyclic polymers are formed.



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Experimental Section

Materials. 1,4-Dicyanotetrafluorobenzene (DCTB) was kindly supplied by Bayer AG (Leverkusen, Germany) and used after drying over P_4O_{10} in vacuo (mp 199−201 °C, Aldrich Catalog: mp 197−199 °C). Resorcinol, hydroquinone, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, and 1,10-dibromodecane were purchased from ACROS Chemicals (Geel, Belgium) and used as received. 4-Cyanotetrafluoropyridine (CTFP) and 1,3-bis[2-(4-hydroxy phenyl)-2-propylene]benzene (1,3-BHPPB, **1a**) and 1,4-bis[2-(4-hydroxy phenyl)-2-propylene]benzene (1,4-BHPPB, **1b**) were purchased from Aldrich Co. (Milwaukee, WI) and used as received.

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Table 1. Yields and Properties of α,ω-Bis(4-hydroxyphenyl) and α,ω-Bis(3-hydroxyphenyl) Alkanes

formula no.	yield (%)	mp (°C)	mass (Da)	elemental analyses			^{1}H NMR chemical shifts δ (ppm) (in $CDCl_3$/TMS)
					C	H	
2a	20	209−211	274.3	calcd	70.06	6.61	1.90 (m, 4H), 3.97 (m, 4H), 6.76 (m, 8H), 7.83 (s, 2H)
				found	69.66	6.50	
2b	18	187−189	302.4	calcd	70.06	6.61	1.42 (m, 4H), 1.66 (m, 4H), 3.83 (t, 4H), 6.53 (d, 4H), 6.72 (d, 4H), 8.85 (s, 2H)
				found	69.66	6.5	
3a	15	117−119[a]	260.3	calcd	69.22	6.20	1.91 (m, 2H), 3.98 (t, 4H), 6.28 (m, 6H), 6.92 (m, 2H, 6.11 (s, 2H)
				found	68.77	6.36	
3b	22	107−109	274.3	calcd	70.06	6.61	1.92 (m, 4H), 4.02 (m, 4H), 6.41 (m, 6H), 7.06 (m, 2H), 8.27 (s, 2H)
				found	69.57	6.89	
3c	17	104−106	288.3	calcd	70.81	6.99	164 (m, 4H), 1.82 (m, 4H), 3.97 (t, 4H), 6.40 (m, 6H), 7.05 (m, 2H), 8.23 (s, 2H)
				found	70.40	7.21	
3d	15	89−91	302.4	calcd	71.50	7.33	1.42 (m, 4H), 1.69 (m, 4H), 3.87 (t, 4H), 6.30 (m, 6H), 7.01 (m, 2H), 9.33 (s, 2H)
				found	71.40	7.34	
3e	15	80−82	358.5	calcd	73.71	8.44	1.41 (m, 12H), 1.75 (m, 4H), 3.93 (t, 4H), 6.40 (m, 6H), 7.05 (m, 2H), 8.23 (s, 2H)
				found	73.36	8.39	

Table 2. Yields and Properties of Multicyclic Polyethers Prepared from DCTB

exp no.	diphenol	yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	mass peaks (Da)[c] of multicyclic polyethers B_2C2, B_3C3, B_4C4, B_5C5, B_6C6, B_7C7, B_8C8, B_9C9, $B_{10}C10$, $B_{11}C11$, $B_{12}C12$, $B_{13}C13$, $B_{14}C14$
1	**3a**	95	0.18	161	1320, 1961, 2601, 3242, 3882, 4522, 5162, 5802, 6442, 7082, 7722, 8362,9002
2	**3b**	94	0.14	128	1376, 2044, 2713, 3381, 4049, 4717, 5386, 6053, 6721, 7389, 8057, 8724, 9392, 10059
3	**3c**	95	0.29	127	1432, 2188, 2825, 3521, 4218, 4914, 5482, 6306, 7002,7697, 8394, 9090, 9785
4	**3d**	97	0.36	120	1489, 2214, 2939, 3664, 4389, 5114, 5350, 6564, 7288, 8013, 8737, 9462, 10188, 10911
5	**3e**	90	0.41	75	1713, 2550, 3387, 4224, 5061, 5898, 6735, 7572, 8409, 9246

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [b] DSC measurements (2nd heating) conducted with a heating rate of 20 °C/min. [c] Incl. doping with a $K^{\oplus}$ ion.

1,4-Bis(4-hydroxyphenoxy)butane.[10] Hydroquinone (1.0 mol) and 1,4-dibromobutane (0.1 mol) were dissolved in ethanol (200 mL), and sodium dithionite (50 mg) was added. This mixture was heated to gentle reflux, and the solution of KOH (2.2 mol) in ethanol (100 mL) was added rapidly with stirring. After reflux for 3 h, the cold reaction mixture was acidified with 20% H_2SO_4. The ethanol was removed by means of a rotatory evaporator, and the residue was poured into water (2 L) with vigorous stirring. After 1 h, the crystallized crude product was isolated by filtration. The dry product was dissolved in acetone and stirred with charcoal for 2 h. The acetone was then evaporated and the residue twice extracted with a hot 3:1 mixture (by volume) of water and acetone. The pure monomer **2a** was crystallized by slow evaporation of the combined extracts. The diphenol **2b** was prepared analogously. The characterization of the biphenols **2a** and **b** is summarized in Table 1.

1,6-Bis(3-hydroxyphenoxy)hexane. Resorcinol (1.0 mol) and 1,6-dibromohexane (0.1 mol) were dissolved in ethanol (200 mL), and sodium dithionite (50 mg) was added. This solution was gently refluxed, and a solution of ROH (2.2 mol) in ethanol was rapidly added from a dropping funnel with stirring. This mixture was refluxed for 3 h, cooled, and acidified with 20% H_2SO_4 under cooling with ice. The ethanol was removed by means of a rotatory evaporator, and the residue was poured into water (2 L) with vigorous stirring. After storage for 20 h at 10−20 °C, the crystallized crude product was isolated by filtration and dried in vacuo at 20 °C. The dry product was dissolved in acetone and stirred with charcoal for 2 h. After filtration, the acetone was evaporated and the residue three times extracted with hot water. The combined extracts were concentrated in vacuo to approximately one-half of the original volume, and the pure monomer **3d** was isolated by filtration. The diphenols **3a**−**c** and **3d** were synthesized analogously. The diphenol **3a** has been mentioned in the literature.[11] The characterization of the diphenols is summarized in Table 1.

Model Reaction. *p*-Cresol (41 mmol), DCTB (10 mmol), and K_2CO_3 (22 mmol) were weighed into a 50 mL Erlenmeyer flask equipped with a magnetic stirring bar, and dry DMF (20 mL) was added. This mixture was stirred for 72 h at 75 °C and poured after cooling into water (200 mL). The precipitated product was isolated by filtration and recrystallized from dioxane. Yield 73%, mp 226−228 °C, FAB: $m/z = 553$ Da.

Elemental Analyses Calcd for $C_{36}H_{28}N_2O_4$ (552.64): C, 78.2 H; H, 5.11; N, 5.07. Found: C, 77.88; H, 5.04; N 5.08%.

^{13}C NMR ($CDCl_3$) δ: 20.60, 110.38, 110.62, 115.84, 130.00, 133.52, 147.15, 154.30 ppm.

Polycondensations of DCTB with α,ω-Bis(3-hydroxy phenoxy) Alkanes. DCTB (2.0 mmol) and a diphenol (4.0 mmol) were dissolved in dry DMF (23 mL), and K_2CO_3 (4.5 mmol) was added. The reaction mixture was magnetically stirred in a closed 50 mL Erlenmeyer flask for 72 h at 70 °C. Afterward, it was poured into water, and the precipitated polymer was isolated by filtration and dried at 60 °C in vacuo. Yields and properties of the polyethers are compiled in Table 2.

An analogous polycondensation was conducted with 4-cyanotetrafluoropyridine (2.0 mmol) and 1,3-bis(3-hydroxy phenoxy)-propane (4.0 mmol), and a soluble polyether was isolated in a yield of 97% with $\eta_{inh} = 0.15$ dL/g in CH_2Cl_2.

Analyses Calcd for $C_{36}H_{28}N_2O_4$ (616.6): C, 70.12; H, 4.58; N, 4.54%. Found: C, 69.51; H, 4.69; N 4.41%. Masses (Da) calcd for multicycles incl. $K^{\oplus}$: B_1C_1, 656; B_2C_2, 1272; B_3C_3, 1889; B_4C_4, 2503; B_5C_5, 3122; B_6C_6, 3739; B_7C_7, 4355; B_8C_8, 4972; B_9C_9, 5589; $B_{10}C_{10}$, 6205.

Measurements. The inherent viscosities were measured in CH_2Cl_2 using an automated Ubbelohde viscometer thermostated at 20 °C. 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 MALDI-TOF mass spectra were measured with a Bruker Biflex III spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All mass spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions using dithranol as matrix and K-trifluoroacetate as dopant. The fast atom bombardment (FAB) mass spectra were measured with a VG/70-205F spectrometer from VG Analytical using *m*-nitrobenzyl alcohol as matrix (Figure 1).

Results and Discussion

Syntheses of Flexible Diphenols. Commercial diphenols such as bisphenol A or bisphenol-*S*(4,4′-dihydroxy diphenyl sulfide) were assumed to be not flexible enough to favor cyclization to such an extent that gelation could be avoided in polycondensations with DCTB. 1,3-BHPPB (**1a**) and 1,4-BHPPB (**1b**) seemed to be more favorable due to two bond angles of 110° at the isopropyl groups and two bond angles of approximately

120° at the O atoms upon formation of ether groups. The 1,3 substitution at the central benzene ring seemed to be an additional advantage of **1a**. However, it was foreseeable that further more flexible diphenols were needed, and thus the diphenols of structure **2** and **3** should be synthesized. The preparation of such diphenols derived from hydroquinone (**2**) was described in the literature.[10,11] Two diphenols having four or six methylene groups (**2**, $n = 4$ or 6) were synthesized according to the published procedure. However, the diphenols mentioned in the literature were not characterized with respect to their purity. Neither measurements of melting points, chromatograms, nor mass spectra were reported. However, such a characterization is necessary because the syntheses are based on a condensation of α,ω-dibromoalkanes with a large excess of hydroquinone. Yet, even a 10-fold excess of hydroquinone does not completely prevent formation of oligomers (**5**), and their presence in small quantities is not detectable by elemental analyses, IR, ^{1}H NMR, or ^{13}C NMR spectra. Using FAB mass spectrometry, it was now detected that the diphenols **2a** and **b** indeed contained oligoethers when isolated as described in the literature. Extraction of the crude product by hot water proved to be an efficient purification method due to the low solubility of the oligoethers. In this way, pure monomers were obtained at the expense of high yields.

Two analogous diphenols derived from resorcinol (**3**, $n = 2$, 3) were mentioned in the literature as early as 1923.[11] As it was characteristic for that time, identity and purity of these diphenols were checked by elemental analyses and melting temperatures. The diphenols **3a**−**e** were synthesized in this work via the same procedure used for hydroquinone,[10] and the similar purification process was necessary to remove the oligoethers **6** (eq 2). The yields and properties of the purified diphenols **2a**,**b** and **3a**−**e** are summarized in Table 1.

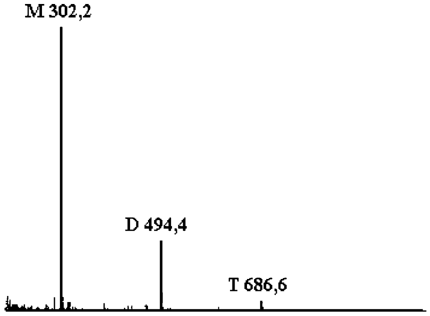
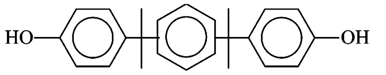
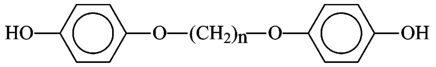


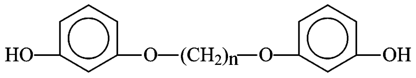
Figure 1. FAB mass spectrum of 1,6-bis(3-hydroxy phenoxy)hexane prior to the extraction of the monomer (M = monomer, D = dimer, T = trimer).



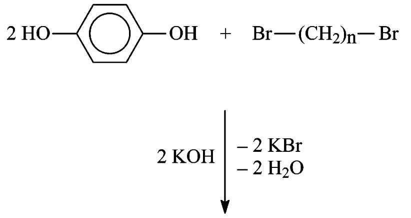
1 a : meta
1 b : para



2 a : n = 4
2 b : n = 6



3 a : n = 3
3 b : n = 4
3 c : n = 5
3 d : n = 6
3 e : n = 10



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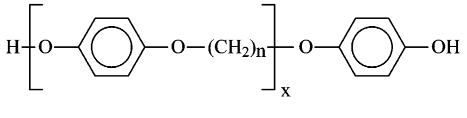

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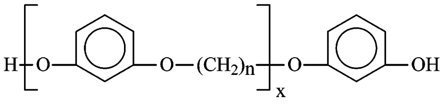

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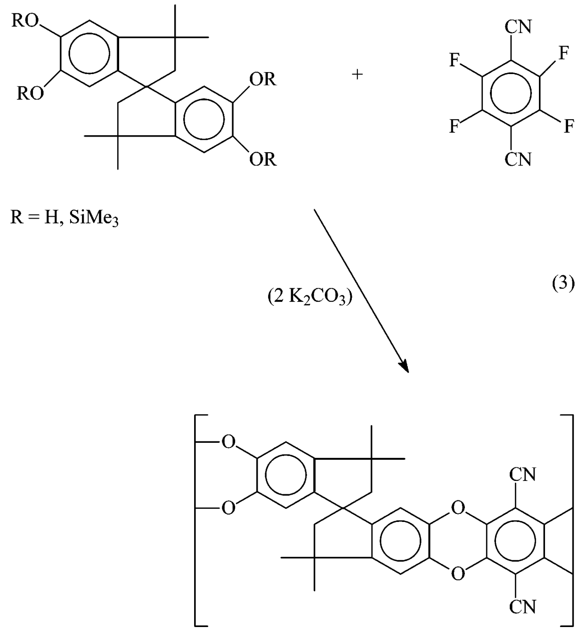
Model Reaction. The only kind of polycondensations DCTB has been used for as electrophilic monomer are syntheses of ladder polymers such as **7** (eq 3).[12−16] In this case, a complete substitution of all four atoms is favored due to the absence of any steric hindrance and because the ring closure is entropically favorable. To find out if a "tetrasubstitution" is also feasible under mild conditions with four phenols as reaction partners, a model reaction with *p*-cresol was performed. The reaction conditions which had been proven to allow for clean syntheses of ladder polymers (**7**) from tetrahydroxy tetramethyl spirobisindane were also used for the model reaction. This means that



(3)

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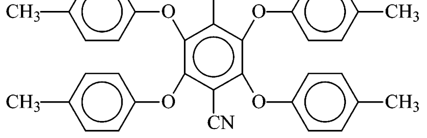


8

the condensation was conducted in DMF at 80 °C with K_2CO_3 as catalyst and HF acceptor. The model compound **8** was indeed isolated in high yield and characterized by elemental analyses, ^{13}C NMR spectroscopy, and FAB mass spectrometry. The elemental analyses agreed satisfactorily with the calculated values (see Experimental Section). The ^{13}C NMR spectrum proved the formation of a symmetrical substitution product, and the FAB mass spectrum exhibited one signal with the correct mass.

Polycondensations. On the basis of this successful model reaction, the polycondensations of DCTB with diphenols were conducted analogously in DMF at 80°C. Using a DCTB concentration of 0.08 mol/L and the diphenols **1a** or **1b** as comonomers, gelation occurred in both experiments. Lowering the monomer concentrations by a factor of 2 gave the same negative results. Therefore, the more flexible diphenols **2a** and **2b** were used as "a_2" monomers in subsequent experiments. A DCTB concentration of 0.08 mol/L was again used in the first two experiments, which resulted in gelation. Lowering the monomer concentration by a factor of **2** proved again unsuccessful. A further reduction of the concentration was not considered because it was learned from previous studies[12] that it is difficult to achieve high conversions (i.e., >99%) at concentrations ≤ 0.02 mol/L and because polycondensations with the diphenols **3a**−**3e** were successful at higher concentrations.

When the resorcinol-based diphenols **3a**−**3e** were polycondensed with DCTB at a concentration of 0.08 mol/L, all reaction products were completely soluble in CH_2Cl_2 or $CHCl_3$ containing 20 vol % of trifluoroacetic acid (TFA) regardless of the spacer length. In two initial experiments with **3b** as monomer, the reaction time was reduced from the standard value of 72 h to 48 h and 24 h. However, the MALDI-TOF evidenced that the conversions were not complete. Multicycles having C−F and/or C−OH (end)groups were detected in the mass spectra, as illustrated in Figure 2. For instance, the most intensive peak of byproducts (labeled X in Figure 2) corresponds to oligomers having two C−F groups, as exemplarily illustrated by formula **9**. However, a reaction time of 72 h sufficed for almost complete conversion, as demonstrated by the MS presented in Figures 3 and 4. These results show that polycondensations at low concentrations (≤ 0.02 mol/L), indeed, raise the problem of reaching high conversions. The MS presented in Figures 3 and 4 also confirm that the formation of multicyclic polyethers is not limited to low oligomers.

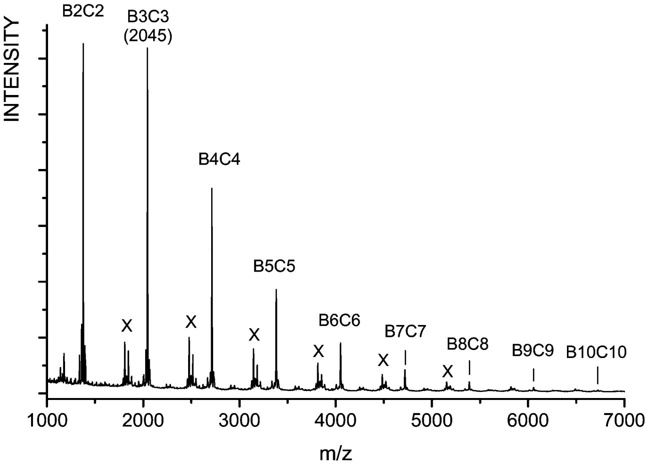


Figure 2. MALDI-TOF mass spectrum of the multicyclic polyether prepared from DCTB and 1,4-bis(3-hydroxy phenoxy)butane with a reaction time of 48 h.

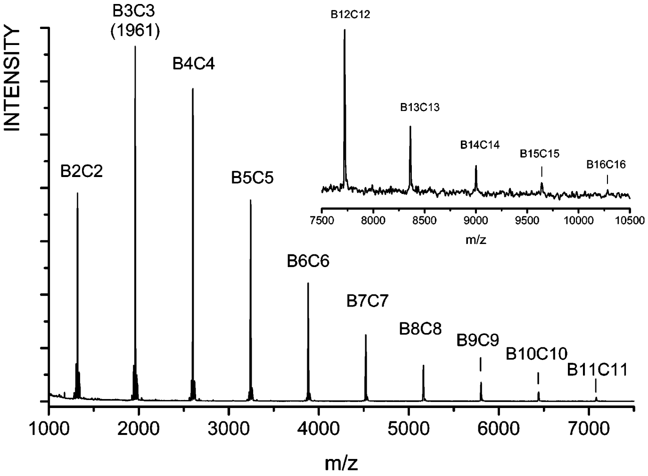


Figure 3. MALDI-TOF mass spectrum of the multicyclic polyether prepared from DCTB and 1,3-bis(3-hydroxy phenoxy)propane with a reaction time of 72 h (no. 1, Table 2).

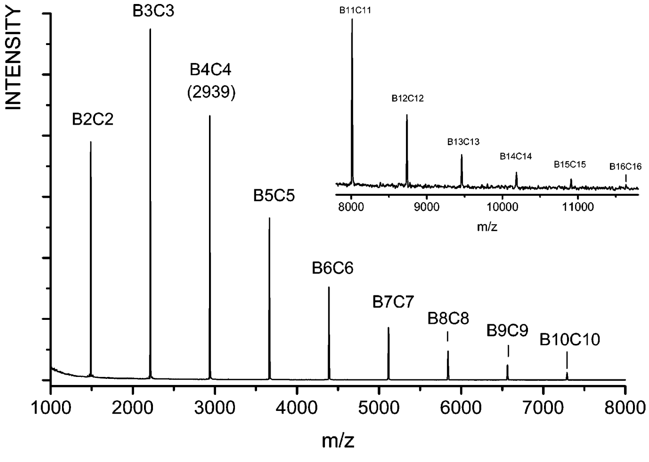
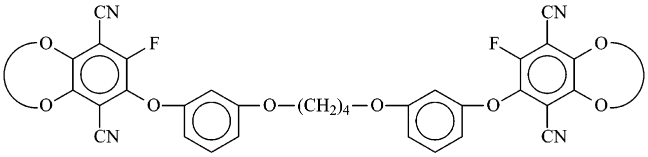


Figure 4. MALDI-TOF mass spectrum of the multicyclic polyether prepared from DCTB and 1,6-bis(3-hydroxy phenoxy)hexane with a reaction time of 72 h (no. 4, Table 2).



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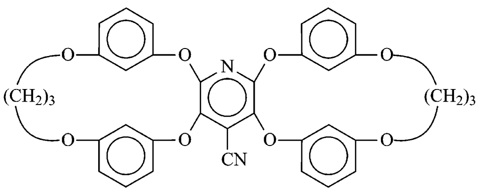

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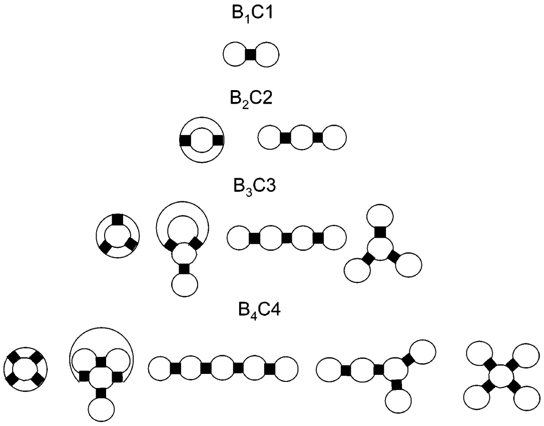
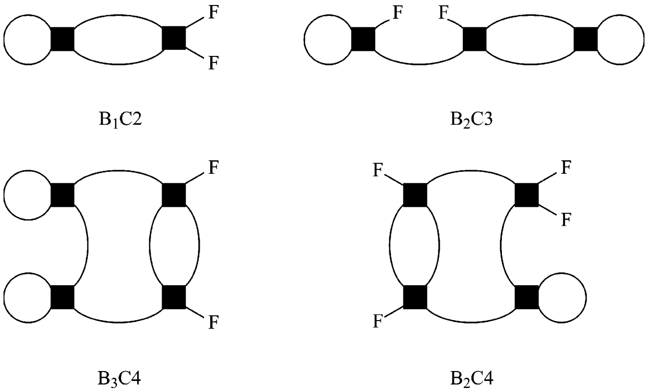
+ multicyclic oligoethers and polyethers

At this point, the terminology used for a simple denomination of these multicycles should be explained. In the term B_nCN, C means cycle and the figure behind C gives the total number of repeat units (i.e., the degree of polymerization calculated as combination of one a_2 and one b_4 unit). B means bridging unit resulting from incorporation of additional a_2 units. These B units either bridge a cycle or connect two cycles. The total number of cycles, which can be drawn in a two-dimensional formula, equals $B_n + 1$. If n equals N, the multicycles are free of

Scheme 1. Selected Isomers of B_nC_n (B_NC_N) Multicycles



Scheme 2. Selected examples of multicyclic oligomers B_nCN with $n < N$



"endgroups", and examples of their structure are outlined in Scheme 1. It is obvious that the number of potential isomers exponentially increases with *N*. For $n < N$, the multicycles contain "end groups" resulting from the functional groups of "b_4 monomers" (C−F in the present work). Scheme 2 presents four examples for such functional multicycles. Multicycles bearing functional groups may, of course, be of interest for further modifications, and they can be synthesized by using feed ratios of "a_2"/"b_4" below 2:1. However, the purpose of the present work is to find out if a perfect "tetrasubstitution" of DCTB is feasible so that B_nCn (or B_NCN) multicycles become the main products.

The characterization of the multicyclic polyethers by classical spectroscopic methods proved difficult. The multicyclic structures are, in principle, not questionable, and the presence or absence of small amounts of C + F or OH end groups can neither be checked by IR, ^{1}H, or ^{13}C NMR spectroscopy. The NMR signals are broad due to the presence of numerous isomers with slightly differing conformations. The signals of end groups are obscured by the feet of the broad main signals. Furthermore, reliable assignments of C−F groups are difficult to achieve without pertinent model compounds. Furthermore, SEC were not feasible because the multicyclic polyethers were neither completely soluble in neat THF, nor in neat chloroform, nor in neat DMAc. DSC measurements were, of course, feasible and confirmed the expected amorphous character of all multicyclic polyethers. The glass-transition temperatures (T_gs) displayed a strong dependence on the length of the aliphatic spacers (Table 2).

The successful polycondensation of DCTB with flexible diphenols suggested that soluble multicyclic polyethers may also be obtained from other activated tetrafluoroaromatics. To substantiate this suggestion, one polycondensation of the diphenol **3a** with 4-cyanotetrafluoropyridine was performed, and a soluble reaction product mainly consisting of the expected multicyclic polyethers (exemplarily illustrated by formula **10**) was indeed obtained. The MS presented in Figure 5 confirms the success of this polycondensation (the K-doped masses of the multicycles were listed in the Experimental Section).

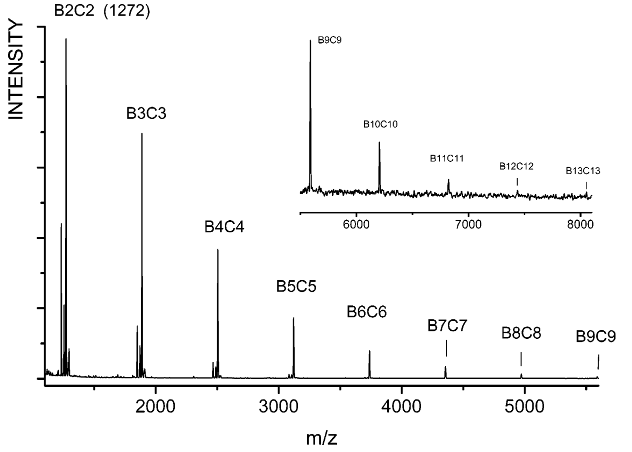


Figure 5. MALDI-TOF mass spectrum of the multicyclic polyether **10** prepared from 4-cyanotetrafluoropyridine and 1,3-bis(3-hydroxy phenoxy)propane with a reaction time of 72 h.

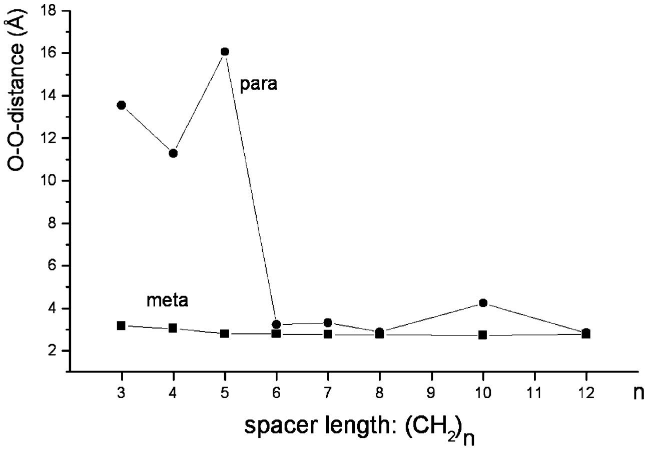


Figure 6. Distances of OH groups calculated for the energy minimum conformation of the diphenols **2** (curve A) and the diphenols **3** (curve B) plotted vs the number of CH_2 groups.

Computer Modeling. The enormous difference between the results obtained from the "hydroquinone diols" **2** on one hand, and the "resorcinol diols" **3**, on the other, prompted us to simulate and compare their low-energy conformations using the "Spartan 04" program of Wave Function, Inc.

The distances of the OH groups were calculated for the conformation of the lowest energy, expecting that this conformation possesses the highest frequency in the reaction mixture. The calculated OH distances were plotted against the number of CH_2 groups in the spacers of the diphenols **2** and **3**. The resulting diagram presented in Figure 6 allows two useful conclusions. First, the distances of the OH groups indicating the cyclization tendency is lower for the diphenols of structure **3**, regardless of "*n*". This trend corresponds to the higher cyclization tendency found for the polycondensations of these diphenols. Second, the distances of the OH groups in diphenols **2** and **3** are quite similar for six or more CH_2 groups. Therefore, these calculations would not allow for reliable prediction of the experimental results obtained in this work. This aspect is not surprising because this computer modeling of conformations was performed in a vacuum and does not consider the strong influence the solvation of OH groups and phenoxide ions may have. Nonetheless, the computer modeling of conformations is helpful for better understanding of given experimental data.

Conclusion

The model experiment and the polycondensation experiments of this work clearly demonstrate that a complete substitution of all four F atoms in DCTB by phenoxide ions can be achieved under the given reaction conditions. These results allowed for an evaluation of the structure of diphenols with regard to their cyclization tendency. Diphenols containing *para*-hydroxy phenyl groups favored chain growth to such an extent that cyclization was not efficient enough to prevent gelation. Even flexibilization of the diphenols with alkylene groups did not suffice to enhance the cyclization tendency sufficiently when the functional groups were in the para position. In contrast, *m*-hydrophenoxy groups attached to alkylene chains yielded soluble multicyclic polyethers, regardless of the length of the alkylene chains. In summary, slight changes in the structure of the diphenols may have a strong influence on the competition between cyclization and chain growth. The successful syntheses of soluble multicycles from the diphenols **3a**−**e** suggest that further classes of multicyclic polymers can be synthesized by variation of the electrophilic "b_4" monomer. A first confirmation for this suggestion comes from the polycondensation of 4-cyanotetrafluoropyridine with the diphenol **3a**. As illustrated by the MS of Figure 5, multicyclic polyethers of structure **10** were obtained. Further examples of similar "$a_2 + b_4$" polycondensations will be presented in a future publication.

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