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Cyclic Ladder Polymers Based on 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane and 2,3,5,6-Tetrafluoropyridines

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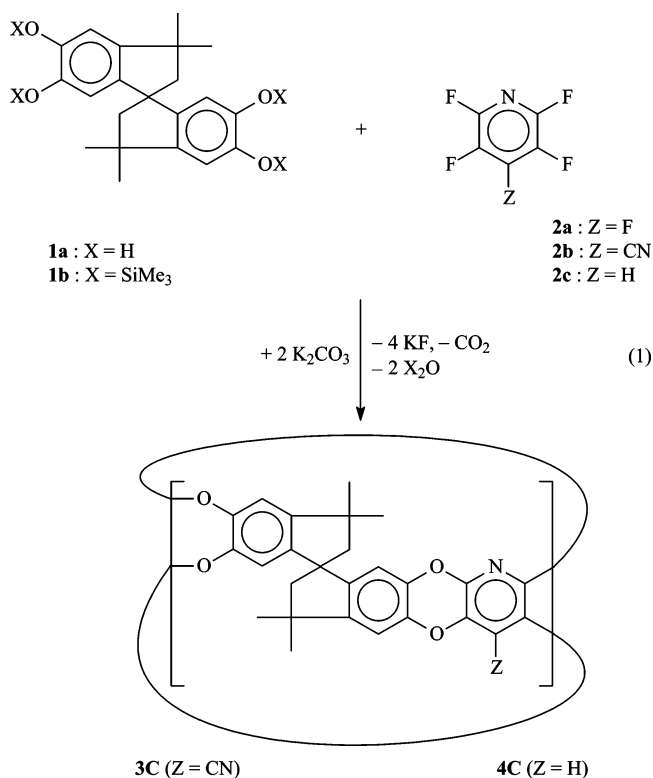
ABSTRACT: Silylated 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane, TTSBI, was polycondensed with 2,3,5,6-tetrafluoropyridine, 4-cyanotetrafluoropyridine (CTFP), or pentafluoropyridine. In the latter case, cross-linked products were obtained even under mild conditions. All other polycondensations yielded soluble ladder polymers. *N*-Methylpyrrolidine or sulfolane was used as reaction media, and both time and temperature were varied. In NMP, a nearly quantitative conversion was achieved even at 60 °C. With the exception of the predominantly formed cyclic tetramer, even- and odd-numbered cycles were formed with equal probabilities. The formation of the cyclic trimer indicates a considerable flexibility of the ladder structure. In sulfolane the conversion was incomplete even at 100 °C, but only even-numbered cycles were formed (detectable up to 10 000 Da). Analogous polycondensations of 2,3,5,6-tetrafluoropyridine (TFP) suffered from its lower reactivity and high volatility, resulting in a stoichiometric imbalance. TFP yielded odd- and even-numbered cycles in both solvents NMP and sulfolane, and even the strained cyclic dimer was formed, indicating a rather high flexibility of these ladder polymers. Linear oligomers having degrees of polymerization (DPs) around 10 or 15 were prepared from CTFP by means of substituted catechols as chain stoppers. Equimolar mixtures with cyclic ladder polymers did not indicate a selective detection of cycles by MALDI-TOF mass spectrometry.

Introduction

Recently, a British research group reported[1−5] on syntheses of ladder polymers from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane, TTSBI, by polycondensation with 1,4-dicyanotetrafluorobenzene or decafluorobenzophenone. Those studies were focused on the usefulness of these ladder polymers for gas separation membranes, for adsorption of small molecules, or for heterogeneous catalysts assuming an unusually high microporosity due to a high rigidity in combination with a loose chain packing generating a high free volume. For syntheses of normal aromatic polyethers, we have observed several times[6−8] that polycondensations involving silylated diphenols are cleaner and may yield higher conversions and molecular weights than analogous polycondensations of free diphenols. Similar observations were made for silylated triphenols.[9] Therefore, it was one purpose of this work to find out whether polycondensations of silylated TTSBI with the fluoropyridines **2a**, **2b**, or **2c** (eq 1, Scheme 1) take a clean course, allowing for high conversions and molecular weights. The second purpose was to check the formation of cyclic ladder polymers. We have recently presented a revised theory of step-growth polymerizations,[9] saying that cyclization competes with chain growth at all stages of the polymerization and at all concentrations, even in bulk. Therefore, this work should answer two more questions. First, is our theory of cyclization also valid for the seemingly rigid ladder polymers derived from TTSBI and tetra- or pentafluoropyridines **2a**−**2c**? Second, does the formation of cycles involve an odd−even effect?

In this context, it should be mentioned that cyclic ladder-type oligomers were obtained by several research groups[10−16]

Scheme 1. Synthetic Rout to the Cyclic Ladder Polymer Described in This Work

1a : X = H
1b : X = SiMe₃

2a : Z = F
2b : Z = CN
2c : Z = H

$$+ 2\ K_2CO_3 \quad \dfrac{-\ 4\ KF,\ -\ CO_2}{-\ 2\ X_2O} \quad (1)$$

3C (Z = CN)   **4C** (Z = H)

as a consequence of ring−chain equilibria when ladder polymers were prepared via Diels−Alder addition polymerization. In contrast to this thermodynamically controlled polyaddition, the synthetic approach presented in this work is a kinetically controlled polycondensation.

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Table 1. Polycondensations of Silylated TTSBI with 4-Cyanotetrafluoropyridine (CTFP)

expt no.	TTSBI/CTFP	solvent	temp (°C)	time (h)	yield (%)	$\eta_{inh}{}^a$ (dL/g)
1	1.0/1.0	NMP	20, 60, −, −	2, 20, −, −	99	0.21
2	1.0/1.0	NMP	20, 60, 100, −	2, 20, 6, −	97	0.29
3	1.0/1.0	NMP	20, 60, 100, 120	2, 20, 4, 4	98	0.28
4	1.0/1.0	NMP	20, 60, 100, 140	2, 20, 4, 4	99	0.25
5	1.0/1.0	sulfolane	20, 60, 100, −	2, 20, 6, −	100	0.58
6	1.0/1.2	sulfolane	20, 60, 100, −	2, 20, 6, −	99	0.18
7	1.0/1.0	sulfolane	20, 60, 100, 120	2, 20, 2, 6	99	slightly cross-linked

^{a} Measured at 20 °C with c = 2 g/L in dichloromethane + trifluoroacetic acid (volume ratio 8:1).

Table 2. Polycondensations of Silylated TTSBI with 2,3,5,6-Tetrafluoropyridine (TFP)

expt no.	TTSBI/CTFP	solvent	temp (°C)	time (h)	yield (%)	$\eta_{inh}{}^a$ (dL/g)
1	1.0/1.0	NMP	20, 60, 100, −	2, 20, 6, −	99	0.17
2	1.0/1.0	NMP	20, 60, 100, 140	2, 20, 2, 4	100	0.22
3	1.0/1.0	NMP	20, 60, 100, 160	2, 20, 4, 4	98	0.36
4	1.0/1.15	NMP	20, 60, 100, 160	2, 20, 4, 4	99	0.31
5	1.0/1.3	NMP	20, 60, 100, 160	2, 20, 4, 4	97	0.21
6	1.0/1.15	sulfolane	20, 60, 100, 160	2, 20, 4, 4	partially cross-linked	
7	1.0/1.3	sulfolane	20, 60, 100, 160	2, 20, 4, 4	partially cross-linked	

^{a} Measured at 20 °C with c = 2 g/L in dichloromethane + trifluoroacetic acid (volume ratio 8:1).

Experimental Section

Materials. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethylspirobis-indane (TTSBI) was purchased form ABCR Chemicals (76187 Karlsruhe, Germany) and used as received. Tetrafluoropyridine (TFP), pentafluoropyridine (PFP), and 4-cyanotetrafluoropyridine (CTFP) were purchased from Aldrich Co. (Milwaukee, WI) and also used as received. DMAA and *N*-methylpyrrolidone (NMP) were twice distilled over P_4O_{10} in vacuo. The potassium carbonate (p.a. quality) was purchased from E. Merck KG (Darmstadt, Germany). The sulfolane which was purchased from Clariant (Mülheim/Main, Germany) was azeotropically dried with toluene. Hexamethyldisilazane was kindly supplied by DEGUSSA AG (Hanau, Germany) and used as received.

Silylation of TTSBI. TTSBI (0.2 mol) and hexamethyldisilazane (0.3 mol) were stirred at a bath temperature of 140−145 °C for 24 h. The excess of hexamethyldisilazane was then removed in vacuo, and the product was distilled over a short-path apparatus in a vacuum of 10^{-2} mbar at a bath temperature of 200−210 °C. The yellowish syrup crystallized upon storage at 20 °C. Yield 94%, mp 73−75 °C. Analyses calcd for $C_{33}H_{56}O_4Si_4$ (623.17): C 63.09, H 8.97; found: C 63.38, H 9.17%.

^{1}H NMR (CDCl$_3$/TMS): δ = 0.14 (s, 18H), 0.25 (s, 18H), 1.28 (s, 6H), 1.32 (s, 6H), 2.03 (d, J = 13 Hz), 2.13 (d, J = 13 Hz), 6.06 (s, 2H), 6.44 ppm (s, 2H).

Polycondensations. *(A) With CTFP in Sulfolane* (No. 2, Table 1). In an atmosphere of dry nitrogen silylated TTSBI (7 mmol), CTFP (7 mmol), and K_2CO_3 (1.50 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer and gas-inlet and gas-outlet tubes. Dry sulfolane (30 mL) was added, and the reaction mixture was stirred for 2 h at 20 °C. The temperature was then raised to 60 °C for 20 h and finally to 100 °C for 6 h. Afterward, the reaction mixture was poured into water (500 mL); the precipitated polymer was isolated by filtration and dried at 80 °C in vacuo.

(B) With TFP in NMP (No. 3, Table 2). In an atmosphere of dry nitrogen, silylated TTSBI (7 mmol), TFP (7.0 mmol), and K_2CO_3 (20 mmol) were weighed into a cylindrical glass reactor equipped with mechanical stirrer and gas-inlet and gas-outlet tubes. Dry NMP (30 mL) was added, and the reaction mixture was stirred for 2 h at 20 °C, for 20 h at 80 °C, for 4 h at 120 °C, and for 4 h at 160 °C. The cold reaction mixture was poured into water; the precipitated polymer was isolated by filtration and dried in vacuo at 80 °C.

Measurements. The inherent viscosities were measured in a mixture of dichloromethane/trifluoroacetic acid (volume ratio 8:1) using an automated Ubbelohde viscometer thermostated at 20 °C.

The 400 MHz NMR spectra were recorded on a Bruker Avance 400 spectrometer in 5 mm o.d. sample tubes. A mixture of CDCl$_3$/trif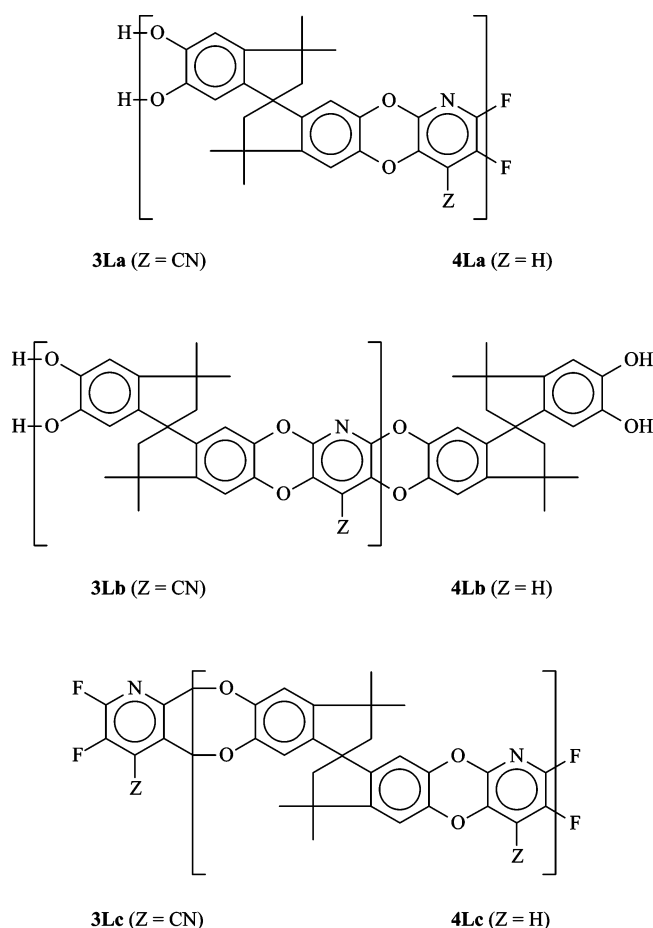luoroacetic acid (volume ratio 8:1) containing TMS served as solvent and shift reference. The 100.4 MHz ^{13}C NMR spectra were recorded with the same spectrometer in the same solvent using 10 mm o.d. sample tubes. The IR spectra were recorded from KBr pellets using a Nicolet "Impact 410". The MALDI-TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from hexafluoro-2-propanol solution using dithranol as matrix and K-trifluoroacetate as dopant. The SEC measurements were performed in a homemade apparatus equipped with a refractive index detector (JASCO, Japan) and a viscometer (WGE, Dr. Bures GmbH, Germany). Chloroform served as eluent and toluene as internal standard. Three SDV columns of PSS GmbH (Germany) were used at 30 °C. Commercial polystyrene standards were used for calibration in combination with the universal calibration method evaluated with WING PC 6.01 software of PSS GmbH.

Results and Discussion

Polycondensation of 4-Cyanotetrafluoropyridine (CTFP) in NMP. The first problem encountered in the course of this study was a clean and quantitative silylation of TTSBI. Diphenols such as bisphenol A usually allow an easy and quantitative silylation with hexamethyldisilazane in refluxing toluene or xylene and with chlortrimethylsilane + triethylamine in refluxing toluene. Surprisingly, all attempts to silylate TTSBI under these conditions did not result in a clean quantitatively silylated product. However, heating of TTSBI with neat hexamethyldisilazane proved successful, and the silylated tet-raphenol (**1b**) proved to be stable enough for distillation over a short-path apparatus in a high vacuum.

Syntheses of aromatic polyethers from silylated diphenols and difluoroaromats are usually conducted in NMP at 140−145 °C[6−8] when the fluoroaromat is highly reactive or at 160−165 °C when it is less reactive as it is true for 2,6-difluoropyri-dine.[17,18] Therefore, a first experiment with silylated TTSBI and CTFB was conducted in such a way that the reaction vessel containing the reaction mixture was placed into an oil bath preheated to 140 °C. Before the temperature of 140 °C was reached, an explosion-like polycondensation yielding a cross-linked product occurred. Therefore, all further polycondensations were started at 20 °C, and the next heating step was limited to 60 °C. At this temperature, the solution viscosity increased significantly, indicating a high conversion. Therefore, the first condensation listed in Table 1 was stopped after 20 h at 60 °C, and the precipitated polymer was characterized.

Scheme 2. Potential Reaction Products of Silylated TTSBI and CTFP or TFP

3La (Z = CN) **4La** (Z = H)

3Lb (Z = CN) **4Lb** (Z = H)

3Lc (Z = CN) **4Lc** (Z = H)

Figure 1. MALDI-TOF mass spectrum of the ladder polymer prepared with CTFP in NMP (no. 2, Table 1): (A) after precipitation into water; (B) after extraction with DMAA.

Despite the low reaction temperature, the MALDI-TOF mass spectrum (MS) indicated a high conversion. The cyclic ladder polymers were the main products (detectable up to 6000 Da). Only traces of **Lb** chains (defined in Scheme 2) having two TTSBI end groups were detectable. When the final temperature was raised to 100 °C (no. 2) and 120 °C (no. 3), the viscosity of the ladder polymers slightly increased, but the MALDI-TOF mass spectra were almost identical. Therefore, the MS presented in Figure 1 is representative for all three samples. The presence of small amounts of **Lb** chains and the absence of **La** and **Lc** chains suggest that the conversions of C−F groups were almost complete. Yet, the relatively high volatility of CTFP obviously caused a slight imbalance of the stoichiometry. Furthermore, traces of ladder polymers modified by reaction with water were found. Structure **5** provides a hypothetical illustration of such

5
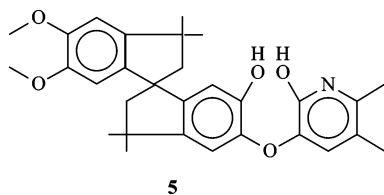
a structure. When the final reaction temperature was raised to 140 °C, the cycles remained the main products, but in addition to **Lb** chains and polymers of structure **5**, a new species having masses of 56 Da above those of the cycles appeared (together with other weak peaks). This surprising finding indicates that the cyclic ladder polymers are not stable at higher temperatures under the given conditions. To shed more light on this aspect,
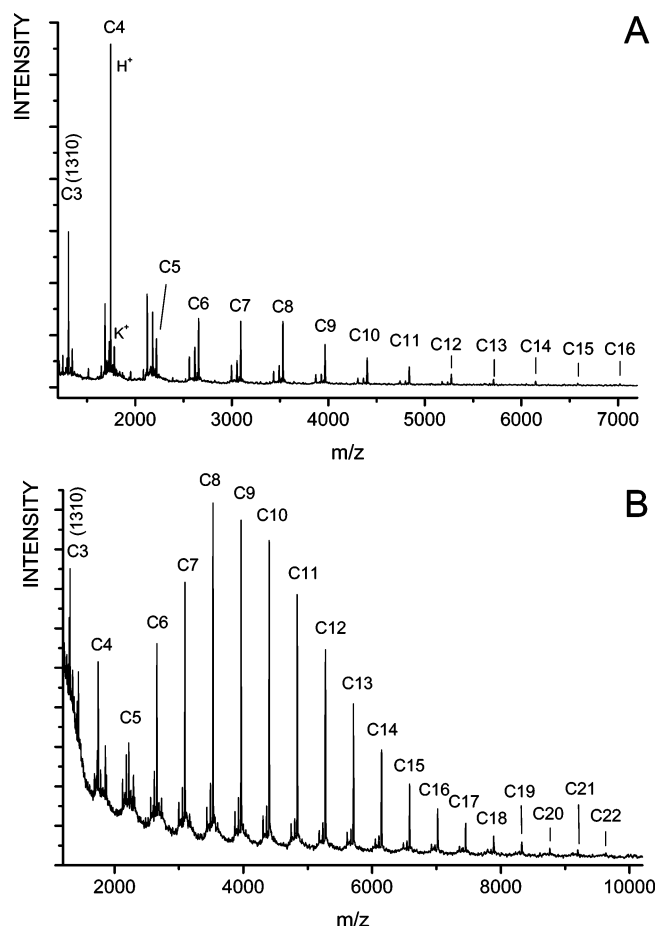
three portions of sample no. 1 (Table 1) were heated in DMF to 140 °C. In one experiment an equimolar amount (relative to the repeat unit) of K_2CO_3 was added, and in the second experiment KF was added, whereas in the third experiment the neat polymer was heated. Unchanged starting material was recovered from the second and third experiment, while modification of the chemical structure and partial degradation were found in the first experiment with K_2CO_3. However, a more detailed study of the K_2CO_3-promoted side reactions was not intended in this work.

An interesting result of all polycondensations performed in NMP is the nearly identical cyclization tendency of odd- and even-numbered chains above the hexamer (Figure 1). Below the hexamer the formation of the strain-free cyclic tetramer is strongly favored. After partial extraction of the low oligomers with DMAA, both odd- and even-numbered cycles were detectable up to a degree of polymerization (DP) of 22 corresponding to 9632 Da (Figure 1B). However, the most interesting result is the formation of the cyclic trimer. As illustrated in Scheme 3, **C3** may be formulated either with a dihedral angle of 60° at the spiro unit when the flanks are stiff or with an angle of 90° when the flanks are flexible and bent. A computer simulation with energy minimization based on the HyperChem software yielded the model presented in Figure 2. The dihedral angle is slightly lower but close to 90°, and the ladder structure shows a slight bending.

Scheme 3 was also presented to indicate that even in the case of small cycles isomers may exist due to different steric

Scheme 3. Alternative Connections and Conformations of the Cyclic Trimer (C3)

Scheme 4. Alternative Arrangements of TTSBI Groups in Repeat Units
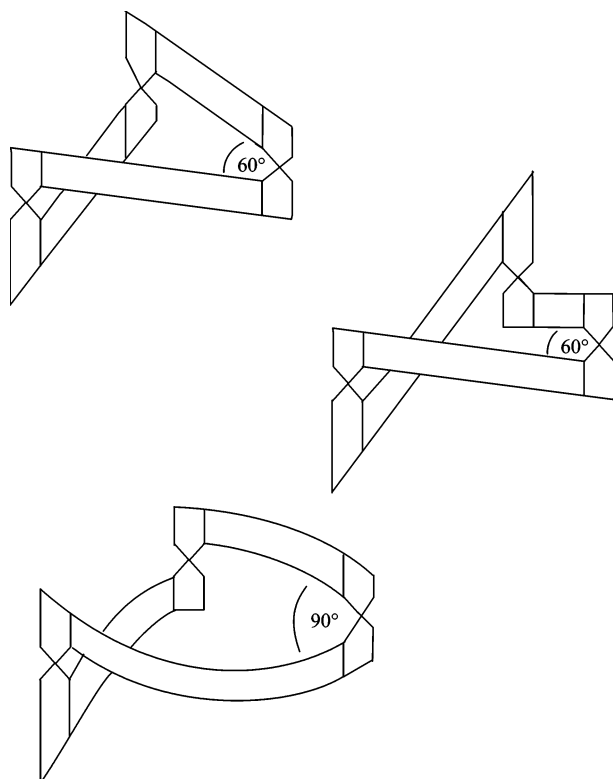
arrangements during chain growth and cyclization. A chain growth via fully solvated monomers and oligomers will also have the consequence that species with cisoid and transoid arrangement of TTSBI units are formed (Scheme 4). In principle, even two cisoid forms are possible by changing the position of the Py-N and −CN, respectively. The high content of cycles documented by the MS of Figure 1 and the equal probabilities of even- and odd-numbered cycles suggest that the ladder polymers are sufficiently flexible to allow for cyclization of all kinds of stereoisomers.

    Polycondensations of CTFP in Sulfolane. Three more polycondensations were conducted in sulfolane with a maximum reaction temperature of 100 °C (nos. 5−7, Table 1), whereby
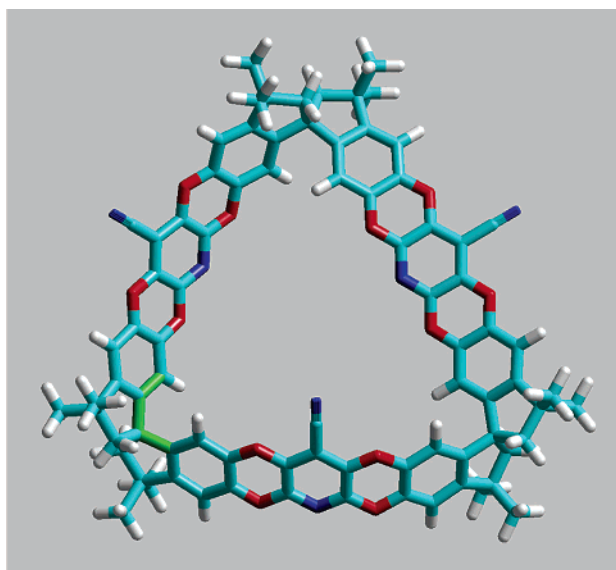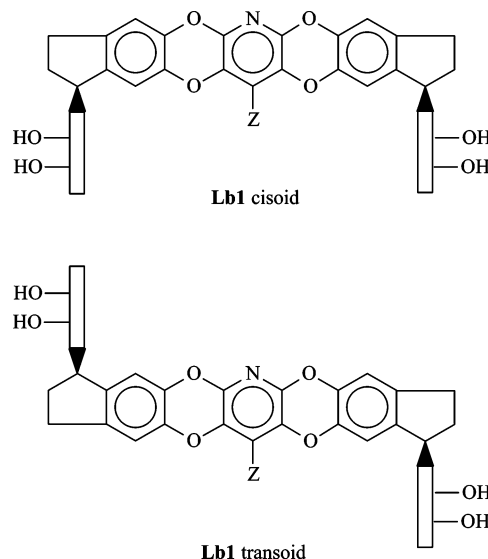
the feed ratio was varied. The highest molecular weight was obtained with a feed ratio of 1.0/1.0. The MALDI-TOF MS (presented in Figure 3) revealed that the cyclic ladder polymers were again the predominant reaction products. However, sizable amounts of **Lb** and (to a minor extent) **Lc** chains were also present, indicating incomplete conversion and slight imbalance of the stoichiometry due to a loss of CTFP. When an excess of CTFP was used, the content of **Lc** chains increased and that of **Lb** chains decreased. Yet, even with an excess of 20 mol %, the **Lb** chains did not completely disappear. The viscosity
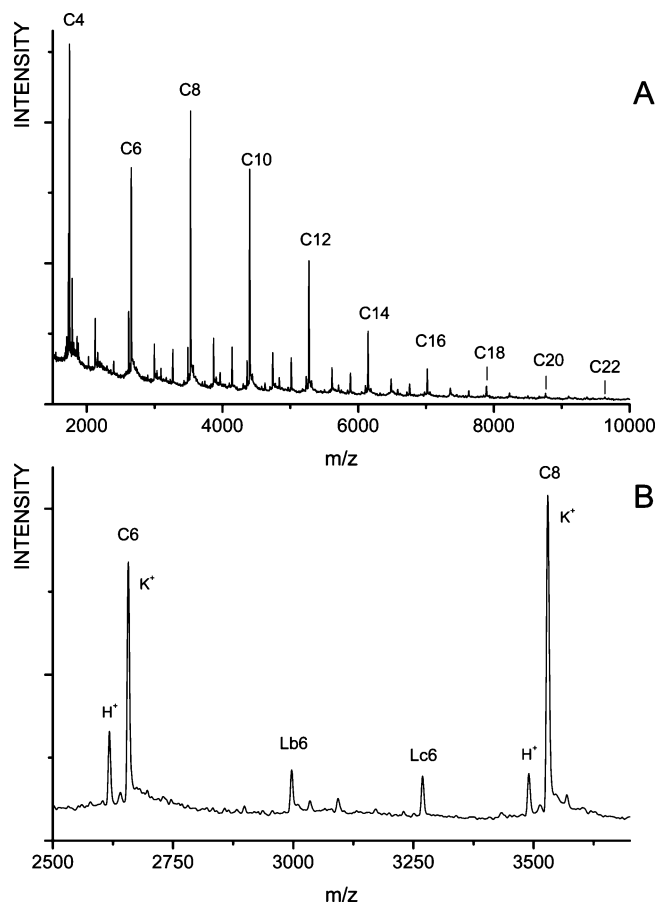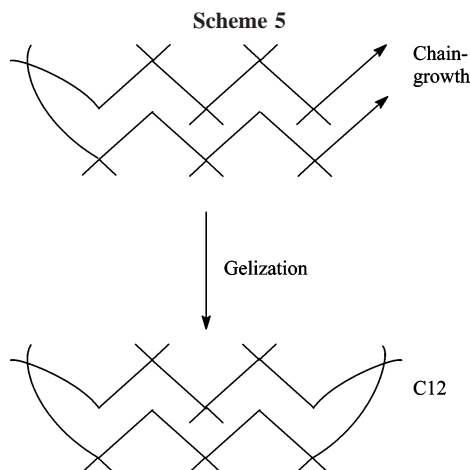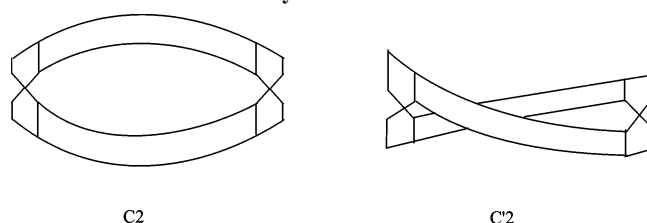

Figure 2. Model of the CTFP-based cyclic trimer **3C**3 as calculated with energy minimization by HyperChem software.

Figure 3. MALDI-TOF mass spectrum of the ladder polymer prepared with CTFP in sulfolane (no. 5, Table 1).

Scheme 5

Chain-growth

Gelization

C12

Scheme 6. Alternative Connection of the Repeat Units in the Cyclic Dimer

C2   C′2

A   **B**

Figure 4. Two models of the CTFP-based cyclic dimer **3C**2 as calculated with energy minimization via the MM + force-field method (A) or via the 99 force-field method of Hyper Chem software (B).

measurements also indicated that an excess of CTFP is unfavorable for high molecular weights. A higher reaction temperature (120 °C) also proved unfavorable because a small part of the reaction product was cross-linked (no. 7, Table 1). Therefore, the product obtained with a feed 1:1 ratio at 100 °C (no. 5) was the best product isolated from sulfolane.

The most amazing result of the polycondensations in sulfolane is the strong odd−even effect in the cyclization tendency because no odd-numbered cycles were detectable. In agreement with a relatively high cyclization tendency of the even-numbered chains, all linear chains (**Lb** and **Lc**) detectable in the MS were even-numbered species. Such an extreme favorization of even-numbered cycles was only observed for syntheses of semirigid liquid-crystalline polyesters in the nematic phase.[19] In this case, a hairpin conformation of the aliphatic spacer allows parallel-ization of the growing chains with an electronic interaction ($\pi-\pi$ charge transfer, DA, and dipole−dipole, DD) between the mesogen. A similar coplanar parallel chain growth is assumed for the ladder polymers, as illustrated in Scheme 5. Such a parallel chain growth necessarily results in the formation of even-numbered cycles, whereas the odd-numbered ones are excluded. Yet, this hypothesis has the problem that a highly strained "loop unit" is required. The most likely structure and conformation of such a "loop unit" is a TTSBI unit with a dihedral angle ≤80° and strong bending of the neighboring ladder units. Nonetheless, this hypothesis is supported by the following arguments. First, computer modeling with energy minimization yielded a cyclic dimer with the aforementioned characteristic of the "loop unit" provided that the "mirror-symmetrical" cycle C2 in Scheme 6 was taken into account. (The isomer involving crossing of the ladder units (C′2) is considerably more strained and far less likely.) Two different force-field methods yield the two slightly different models displayed in Figure 4. When open models of loop units were calculated, two different conformations were found. With *tert*-butyl end groups simulating a cleaved spiro unit of the cyclic dimer, the "ladder units" maintained a parallel array (Figure 5A) stabilized by CT and DD interactions. However, removal
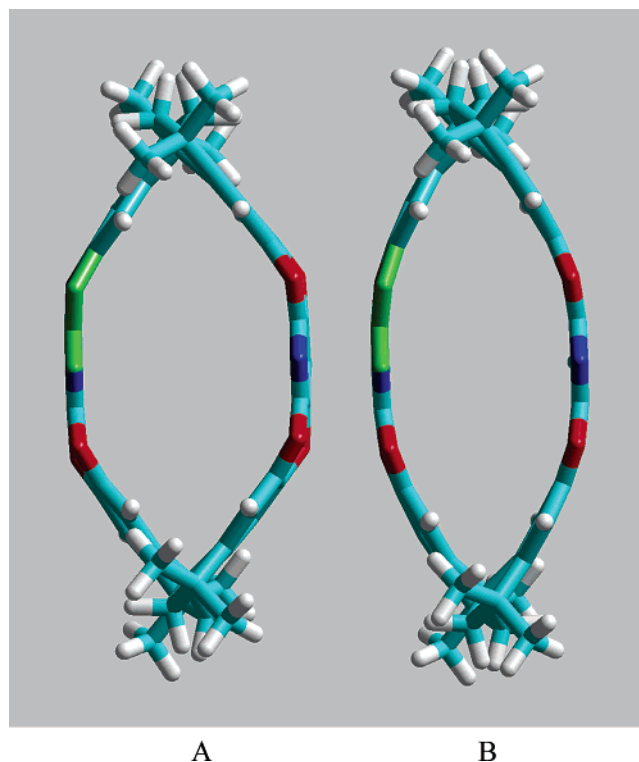
of the *tert*-butyl end groups led to an open conformation (Figure 5B). These energy minimum calculations were as usual con-ducted in vacuo. In reality, the solvation may play a key role for the stability of the "hairpin" conformation. At this point, the different properties of NMP and sulfolane come into play. Both solvents possess nearly the same dipole moments and dielectric constants, but the nucleophilicity, basicity, and donicity of NMP are far higher than those of sulfolane. This difference is, in principle, well-known, and a striking illustration has recently been published for the ring-opening polymerization of α-amino acid *N*-carboxyanhydrides.[20] Therefore, NMP can strongly solvate the acceptor site and positive ends of dipoles of the repeat units breaking up the parallel arrays, whereas sulfolane cannot. A further argument in favor of this hypothesis will be presented below.

Concerning the determination of molecular weights, SEC measurements of the sample no. 2 (Table 1) were conducted in chloroform using the universal calibration method. A number-average molecular weight (M_n) of 4300 Da was found together with a weight-average (M_w) of 39 000 Da, yielding a polydis-persity around 9. Such high polydispersities are characteristic for polycondensates (including aromatic polyethers) containing a high fraction of cycles.[9] Unfortunately, it was found that none of the samples prepared in sulfolane were completely soluble in tetrahydrofuran (THF), chloroform, or dimethylacetamide (DMAA), so that SEC measurements were not feasible. It was confirmed by MALDI-TOF MS that the insoluble fractions consisted of cycles. Originally, it was assumed that relatively low solubility of the cycles is a consequence of their crystal-linity, However, the WAXS powder patterns of sample nos. 2 and 5 did not provide clear-cut evidence for this assumption. Only two broad reflections were found at $2\vartheta = 14°$ and 18°. These broad reflections may result from an overlapping of the WAXS patterns of numerous slightly different crystallites of the individual ring sizes and isomers, or they indicate a moderate
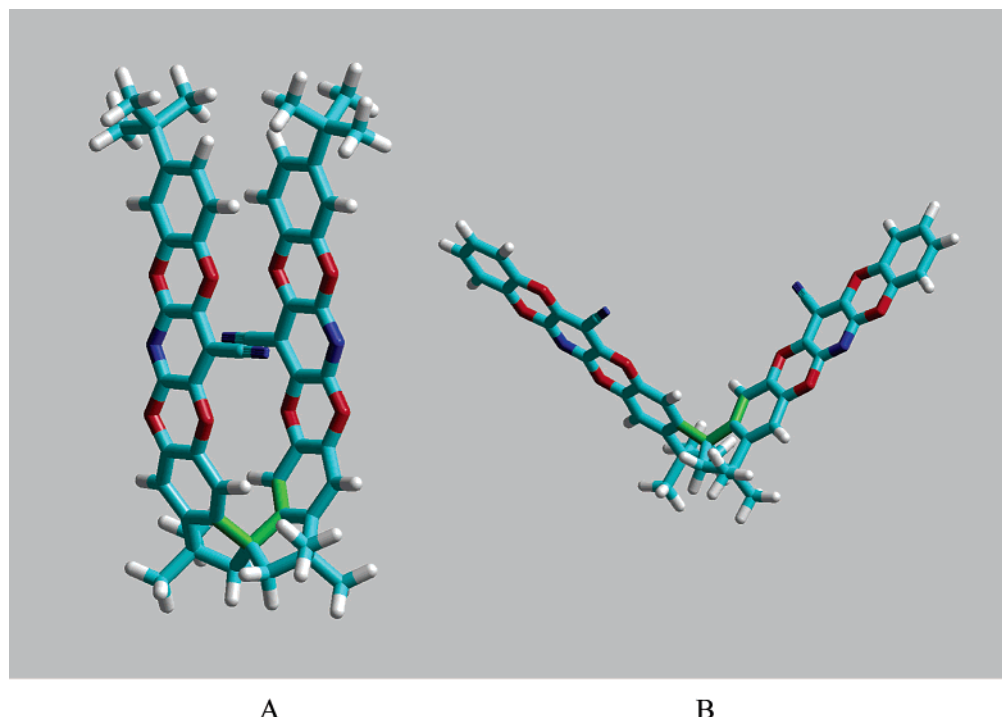
Figure 5. Noncyclic models of a loop unit calculated with energy minimization via the 99 force-field method of Hyper Chem software: (A) 4-*tert*-butyl end group; (B) C−H end groups.

degree of order of all species, an order which is somewhere in between that of an amorphous and a crystalline phase. Anyway, the WAXS patterns do not allow for a differentiation between samples of different composition such as nos. 2 and 5 and, thus, are useless for the characterization of these ladder polymers.

Polycondensations of Tetrafluoropyridines in NMP and Sulfolane. Polycondensations of silylated TTSBI with TFP were studied for two reasons. First, it should be found out whether TFP is reactive enough to yield ladder polymers of structure **4**. Second, it should be elucidated whether reaction temperatures above 120 °C favor side reactions (as observed for CTFP) or whether they favor high conversion and higher yields of cycles. Experiments 1−3 of Table 2 were conducted with a feed ratio of 1.0/1.0 and with variation of the temperature. The molecular weights increased indeed with the temperature. Furthermore, the MALDI-TOF MS evidenced that also the content of cycles increased with temperature. These findings suggest that temperatures above 120 °C are in fact needed to overcome the lower reactivity of TFP. However, the main products obtained in all three cases were **Lb** chains, indicating a considerable imbalance of the stoichiometry (Figure 6 and mass data in Table 4). This result was not unexpected because the boiling point of TFP (102 °C) is relatively low compared to the reaction temperatures. Because of the higher temperatures needed for rapid polycondensation, a considerable loss of TFP by evaporation is quite obvious. Therefore, two more polycondensations were conducted at the highest temperature with an excess of 15 or 30 mol % TFP (nos. 4 and 5). Because of this excess, the peaks of **Lb** chains vanished in the MS, and the peaks of cycles became predominant together with the peaks of **Lc** chains (Figure 7A). Yet, weak mass peaks of unidentified byproducts were also observable, and reaction conditions allowing for a rather clean polycondensation with high conversions were not found. Finally, two polycondensations were performed in sulfolane (nos. 6 and 7) to find out whether the formation of even-numbered cycles is also found when TFP is used as comonomer of TTSBI. Surprisingly, both products were partially cross-linked. None-
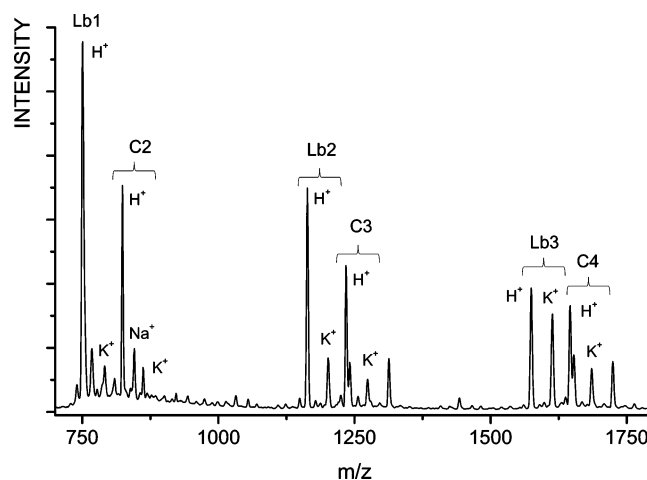

Figure 6. MALDI-TOF mass spectrum of the ladder polymer prepared with an equimolar amount of TFP in NMP (no. 3, Table 2).

theless, MALDI-TOF MS of the soluble fractions were obtained, which clearly indicated the formation of odd-numbered cycles (mainly **C3**), as demonstrated in Figure 7B. As expected, **Lc** chains were the main reaction product. Therefore, optimum reaction conditions allowing for a clean synthesis of ladder polymers from TFP were not found due to its lower reactivity.

Nonetheless, the polycondensations of TFP were particularly interesting because the formation of the cyclic dimer was detected, regardless if NMP or sulfolane was used as reaction medium (Figure 6). Traces of a cyclic dimer might also exist in the reaction products of CTFP, but a clear-cut identification in the MALDI-TOF MS was not feasible due to strong matrix signals. The most likely structure and conformation of a cyclic dimer have been illustrated in Figure 4 and Scheme 6 (C2) for the polycondensation of CTFP, but the computer yielded the analogous structure for the cyclic dimer of TFP. The formation of the cyclic dimer of TFP is one more finding supporting the chain-growth mechanism of even-numbered cycles formulated
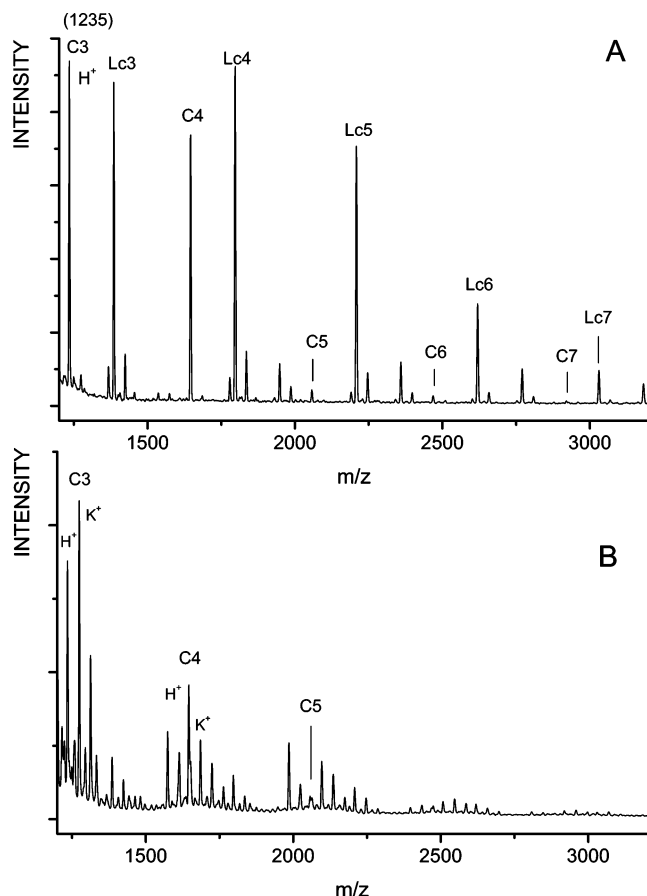
Figure 7. MALDI-TOF mass spectra of the ladder polymers prepared with an excess of TFP: (A) in NMP (no. 4, Table 2); (B) in sulfolane (no. 6, Table 2).

in Scheme 5. Another observation supporting this hypothesis is the formation of odd-numbered cycles in sulfolane when TFP is used. Strong CT and DD interactions are unlikely for a pyridine unit bare of nitrile groups, and thus, the stabilization required for a parallel coplanar chain growth is lacking, so that even in sulfolane a predominant formation of even-numbered cycles cannot be maintained.

Finally, it should be mentioned that MALDI-TOF mass spectrometry was preferentially used for the characterization of the ladder polymers because the classical spectroscopic were not much informative. IR spectra display a broad band at 3300−3500 cm^{-1} which may result from OH end groups, but traces of moisture may affect its intensity. A clear-cut correlation of this band with the content of OH end groups as evidenced by MALDI-TOF MS was, in fact, not found. All ^{1}H NMR signals are broad, featureless, and useless. The ^{13}C NMR signals were again broad due to the presence of numerous isomers and cycles with different ring size and slightly different conformations. Furthermore, a clear-cut assignment of individual signals requires cumbersome syntheses of model compounds what was not intended in this work.

Syntheses of Linear Oligomers. The finding that the main products of the polycondensations of CTFB (Table 1) are cyclic ladder polymers raised criticism of the reviewers of the first version of this paper and of a previous publication.[21] It was assumed that the ladder polymers are too rigid for cyclization and that the stereosequence is too unfavorable for the formation of all odd- and even-numbered cycles. It was suspected that the MALDI-TOF MS are highly selective for the detection of cycles and, thus, misinterpret the compositions

of the reaction products which were assumed to mainly consist of linear chains. Therefore, we intended to synthesize in this work linear oligomers and polymers and to study equimolar mixtures of linear and cyclic polymers by MALDI-TOF mass spectrometry.

Seven polycondensations were performed with the parameters listed in Table 3. In the first two experiments, free TTSBI **1a** was used under the reaction conditions recommended by Budd et al.[1−5] for polycondensations of DCTB (eq 2). The limitation
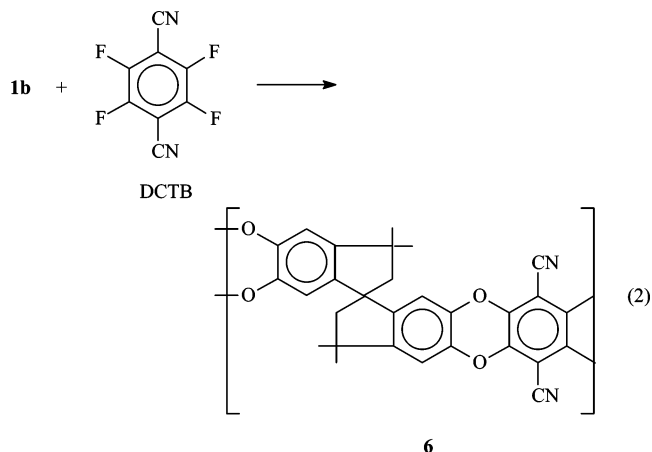
of the chain growth should be obtained by an imbalance of the stoichiometry so that telechelic polymers **3Lb** or **3Lc** should be formed. Yet, a complex mixture of products was obtained and not the desired clean linear polymers. As reported in a parallel publication,[22] analogous polycondensations of DCTB with **1a** also failed, even though high molar mass cycles were obtained when an ideal stoichiometry was used. Obviously, a perfect stoichiometry with a high extent of cyclization stabilizes the ladder polymers and minimizes side reactions. In an additional experiment, 4-*tert*-butylcatechol was added as chain terminator to prepare polymers of structure **8**. Again, a complex reaction product was obtained, although analogous polycondensations with DCTB were successful.[22]
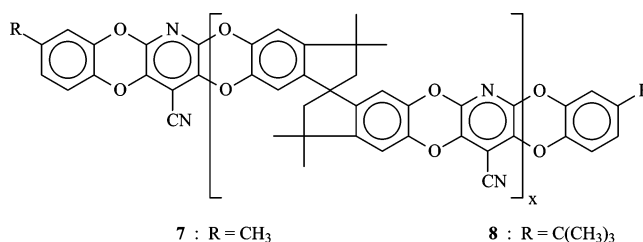
In two more experiments silylated TTSBI was used in combination with either free or silylated 4-*tert*-butylcatechol. Both polycondensations were successful, and the MALDI-TOF MS exclusively displayed mass peaks corresponding to structure **8**. Finally, two polycondensations were performed with silylated TTSBI and 4-methyl catechol with variation of the feed ratio. The resulting oligomers of structure **7** exhibited a singlet signal of the methyl end groups at 2.28 ppm (partially overlapping with the CH$_2$ signal of the repeat units), whereas the signal of the *tert*-butyl end groups was almost completely obscured by the broad CH$_3$ signals of the repeat units. The MALDI-TOF MS of sample no. 7 (Table 1) is displayed in Figure 8. Six equimolar mixtures of cyclic and linear ladder polymers were prepared by mixing the cyclic sample nos. 1 and 2 of Table 1 with the linear sample nos. 4, 6, and 7 of Table 3. Both mixtures of the linear polymer 4 (Table 3) did not exhibit any signal of

Table 3. Syntheses of Noncyclic (Linear) Oligomers

expt no.	derivative of TTSBI	TTSBI/CTFB	chain Terminator	solvent	temp (°C)	time (h)	yield (%)	η_{inh} (dL/g)
1	free TTSBI	10/19	−	DMF	70	72	64	0.08
2	free TTSBI	9/10	−	DMF	70	72	68	0.08
3	free TTSBI	9/10	4-TBC	DMF	70	72	62	0.06
4	silyl. TTSBI	9/10	4-TBC	NMP	60 + 100	20 + 8	63	0.10
5	silyl. TTSBI	9/10	silyl. 4-TBC	NMP	60 + 100	20 + 8	72	0.10
6	silyl. TTSBI	9/10	4-MeC	NMP	60 + 100	20 + 8	72	0.10
7	silyl. TTSBI	14/15	4-MeC	NMP	60 + 100	20 + 8	68	0.13

Table 4. Masses (Da, Including K$^+$) of Selected Cyclic and Linear Ladder Polymers

deg of polymer.	3 C	4 C	3 La	3 Lb	3 Lc	7 L	8 L
1	475.47	450.46	515.48	815.89	651.54	819.8	903.96
2	911.94	861.92	951.95	1252.36	1088.01	1256.27	1340.43
3	1348.41	1273.38	1388.42	1688.83	1524.48	1692.74	1776.9
4	1784.88	1684.84	1824.89	2125.3	1960.95	2129.21	2213.37
5	2221.35	2096.3	2261.36	2561.77	2397.42	2565.68	2649.84
6	2657.82	2507.76	2697.83	2998.24	2833.89	3002.15	3086.31
7	3094.29	2919.22	3134.3	3434.71	3270.36	3438.62	3522.78
8	3530.76	3330.68	3570.77	3871.18	3706.83	3875.09	3959.25
9	3967.23	3742.14	4007.24	4307.65	4143.3	4311.56	4395.72
10	4403.7	4153.6	4443.71	4744.12	4579.77	4748.03	4832.19

cyclic species, although the mass difference of 8 Da (see Table 4) suffices for their detection at intensity ratios ≤10:1. (The resolution of mass peaks was ≤2 Da depending on the mathematical treatment of the mass data.) In the MS of the four mixtures based on the linear polymer nos. 6 and 7 (Table 3) the peaks of linear chains were even predominant, but the peaks of the cycles were detectable. As illustrated by Figure 8 in mixtures containing the cyclic sample no. 1 (Table 1), only the mass peak of **C4** was strong, what is characteristic for this sample as documented by the MS of Figure 1. The relatively low intensities of the peaks of cycles may partially be attributed to the high average molecular weights. Yet, even the cyclic polymers have the maximum of their frequency distribution at masses below 3000 Da (like all polycondensates), and thus, their peaks should be particularly strong at low masses. In summary, our MALDI-TOF measurements did not provide any indication for a preferential detection of cyclic ladder polymers or for a suppression of linear chains in the presence of cycles. Analogous results were obtained from mixtures of cyclic and linear ladder polymers derived from DCTB (structure).[22]
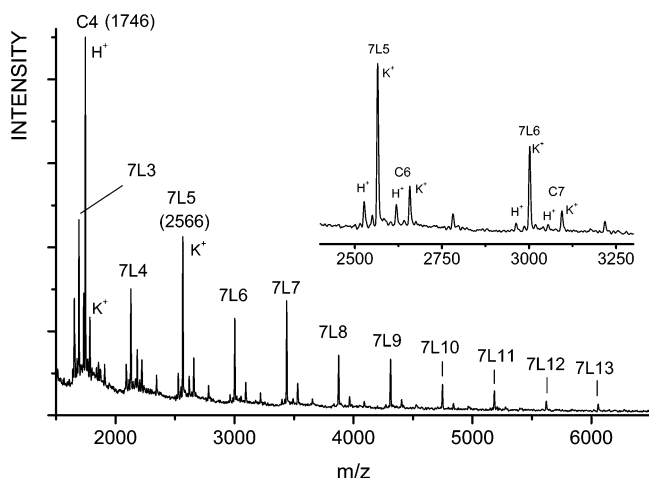

Figure 8. MALDI-TOF mass spectrum of an equimolar mixture of sample no. 1, Table 1 (labeled C), and linear sample of structure **7** (no. 7, Table 3) (labeled 7 L).

Conclusion

Silylated TTSBI proved to be a useful reaction partner of 2,3,5,6-tetrafluoropyridine or tetrafluoro-4-cyanopyridine, so that

ladder polymers of moderately high molecular weight were obtained, allowing for the casting of films. Reaction temperatures above 100 °C favored side reactions and degradation mainly catalyzed by potassium carbonate. In agreement with our theory of kinetically controlled polycondensations, cyclic oligomers and polymers were the predominant reaction products under optimized reaction conditions. However, unexpected and conspicuous is the strong solvent effect on the ring size. Whereas even- and odd-numbered chains had the same cyclization probability in NMP, the formation of even-numbered cycles was extremely favored in sulfolane. The lower reactivity of TFP and lower boiling point relative to CTFP had the consequence that it was difficult to obtain an optimum stoichiometry by conversions. Yet, interestingly odd-numbered cycles were found in addition to the even-numbered ones in both solvents NMP and sulfolane. In contrast, a particularly strong odd−even effect (detectable even in NMP) was found when silylated TTSBI (**1b**) was polycondensed with 1,4-dicyanotetrafluorobenzene (DCTB), yielding cyclic ladder polymers of structure **6**.[21] This means the strength of the odd−even effect decreases in the order

$$\text{DCTB} > \text{CTFB} > \text{TFB}$$

This order matches the decreasing acceptor strength of the electrophilic monomers and thus lends additional support to the hypothesis that the predominant formation of even-numbered cycles is due to a parallel growth of two chain segments associated via CT and DD interactions (Scheme 5). The existence of a strained "loop" unit is supported by the finding that polycondensations of TFP yielded a cyclic dimer.

The formation of a cyclic dimer of TFP together with the high cyclization tendency observed in all polycondensations of CTFP and DCTB[21,22] also demonstrates that these ladder polymers are pretty flexible. This conclusion is noteworthy because such ladder polymers were originally considered to be stiff[1−5] and unfavorable for dense chain packing, so that microporous membranes could be cast from their solution. However, the products prepared and studied by Budd et al.[1−5] were not characterized with respect to the content of cycles, but our recent studies[22] proved that the ladder polymers **6** prepared by Budd et al.[1−3] also consist of cycles. Therefore, it may finally be concluded that the cyclization tendencies of the ladder polymers **3** and **6** are quite similar to those of other aromatic polyethers.[7−9]

References and Notes

(1) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, *231*.

(2) Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D. *Adv. Mater.* **2004**, *16*, 456.

(3) Budd, P. M.; McKeown, N. B.; Fritsch, D. *J. Mater. Chem.* **2005**, *15*, 1977.

(4) Peter, M.; Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanema, E. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005**, *251*, 263.

(5) McKeown, N. B.; Budd, P. M.; Msayib, K. J.; Ghanem, B. S.; Kingston, H. J.; Tattershall, C. E.; Makhseed, S.; Reynolds, K. J.; Fritsch, D. *Chem.−Eur. J.* **2005**, *11*, 2610.

(6) Kricheldorf, H. R. *Silicon in Polymer Syntheses*; Kricheldorf, H. R., Ed.; Springer Publ.: Berlin, 1956; Chapter 5.

(7) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. *Macromolecules* **2003**, *36*, 4337.

(8) Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *36*, 4337.

(9) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 354.

(10) Godt, A.; Enkelmann, V.; Schluter, A. *Angew. Chem.* **1989**, *101*, 1704; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1680.

(11) Ashton, P. R.; Brown, G. R.; Isaacs, N. S.; Giuffrida, D.; Kohnke, F. H.; Matthias, J. P.; Slawin, A. M. Z.; Smith, D. R.; Stoddard, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 6330.

(12) Wegener, S.; Mullen, K. *Macromolecules* **1993**, *26*, 3037.

(13) Beukhoff, J.; Boese, R.; Klärner, F. G. *Tetrahedron Lett.* **1994**, *35*, 73.

(14) Cory, R. M.; McPhail, C. L.; Dikmans, A. J.; Vittal, J. J. *Tetrahedron Lett.* **1996**, *37*, 1983.

(15) Kintzel, O.; Schlüter, A.-D. *Acta Polym.* **1997**, *48*, 212.

(16) Kintzel, O.; Loger, P.; Weber, M.; Schlüter, A.-D. *Eur. J. Org. Chem.* **1998**, *99*, 105.

(17) Kricheldorf, H. R.; Jahnke, P. *Makromol. Chem.* **1990**, *191*, 2027.

(18) Kricheldorf, H. R.; Garaleh, M.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

(19) Kricheldorf, H. R.; Richter, M.; Schwarz, G. *Macromolecules* **2002**, *35*, 5449.

(20) Kricheldorf, H. R.; v. Lossow, C.; Schwarz, G. *Macromolecules* **2005**, *38*, 5513.

(21) Kricheldorf, H. R.; Fritsch, D.; Vakhtangishvili, L.; Schwarz, G. *Macromol. Chem. Phys.* **2005**, *206*, 2239.

(22) Kricheldorf, H. R.; Lomadze, N.; Fritsch, D.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.*, submitted for publication.