Macrocycles. 19. Cyclization in the Nematic Phase? Polyesters Derived from Hydroquinone 4-Hydroxybenzoate and Aliphatic Dicarboxylic Acids†

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ABSTRACT: Silylated hydroquinone 4-hydroxybenzoate (HHB) was polycondensed with aliphatic dicarboxylic acid dichlorides (ADADs) in bulk at temperature up to 240 °C. These polycondensations proceeded in the nematic phase, and both transesterification and "backbiting" degradation were avoided as evidenced by ^{1}H NMR spectroscopy. The nematic LC phases were characterized by optical microscopy and DSC measurements. The MALDI−TOF mass spectra revealed the formation of even-membered cycles (in addition to linear oligomers), whereas odd-membered cycles were almost absent. When the reaction mixture was slightly diluted with 1-chloronaphthalene, so that the polycondensation proceeded in the isotropic phase, odd-membered cycles with a predominance of the cyclic trimer were found. When free HHB was polycondensed with ADADs in 1-chloronaphthalene at 220 °C in 1,2-dichlorobenzene at 190 °C or in the presence of pyridine at 5−10 °C, again odd-membered cycles were found. Obviously, the nematic phase enforces a parallel alignment of polyester chains with strong electronic interaction of neighboring mesogens, so that cyclization can only occur in the case of even-membered chains via hairpin conformations of the aliphatic spacers.

Introduction

Numerous so-called LC-main chain polymers forming a nematic melt have been synthesized and studied over the past three decades.[1−3] More than 95% of these nematic LC-polymers contain ester bonds, because the ester linkage introduces flexibility and favors a linear conformation of the polymer backbones. The nematic LC-polyesters may be subdivided in two groups: first, fully aromatic polyesters, and second so-called semirigid polyesters containing flexible, aliphatic spacers. The fully aromatic LC-polyesters are typically random copolyesters such as the commercial products Vectra and "Sumicosuper" (Xydar). In the case of semirigid LC-polyesters, random copolymers, alternating copolymers, and homopolymers were synthesized. These structural differences are important, when a characterization by mass spectrometry is considered, because random copolymers are particularly unfavorable for MALDI−TOF mass spectrometry (complex peak pattern and low peak intensities).

The purpose of the present work was to find out if semirigid nematic polyesters can form cyclic oligo- and polyesters in the nematic phase, and such a study requires a MALDI−TOF mass spectrometric characterization of the reaction products. The scientific background of this study has two aspects. First, we have recently demonstrated[4−7] for various kinetically controlled syntheses of isotropic polyesters and other polycondensates that cyclization competes with propagation at any concentration and any conversion as expressed in eq 1. In contrast to the classical theory of Carothers[8] and Flory,[9] cyclization is an inherent property of all kinetically controlled polycondensations as predicted by Stepto et al.[10] and Gordon et al.[11] Second, it is well-known from theoretical calculations and experimental

$$\overline{DP} = \frac{1}{1-(p-\frac{1}{x^a})} \quad (1)$$

$\overline{DP}$ = average degree of polymerization; p = conversion of functional groups

a = V_{pr} / V_{cy} (rate of propagation / versus rate of cyclization)

X = variable factor (> 1.0) taking into account variations of the concentration

studies that polymer chains and chain segments have a high tendency to adopt a nearly parallel alignment inside a domain of a nematic phase. Upon shearing (stirring, extrusion) a parallelization of most domains will occur and many domains may even merge into a large (mono-) domain. A characteristic consequence of this particular supermolecular structure is a sharp drop of the melt viscosity upon shearing (e.g., upon stirring or extrusion), the so-called "shear thinning". From these properties of the nematic melt and from the highly anisotropic mechanical properties of LC-polymers, it has been concluded that entanglements are absent or at least extremely rare. In this connection, it was of particular interest to find out if the nematic phase allows cyclization in a kinetically controlled polycondensation process.

The polyesters suited for such a study should meet the following requirements. First, they should be homopolymers to simplify the mass spectroscopy. Second, a broad nematic phase should exist below 240 °C, because at higher temperatures transesterification and formation of cycles by backbiting are unavoidable. Third, these LC-polyesters should be soluble in volatile solvents to ease the preparation of irradiation targets for the MALDI−TOF mass spectroscopy. Only very few LC-polymers meet these requirements, and the polyesters of structure **1** were selected for the present study. An additional advantage of these polyesters is the regular sequence of three different monomer units, so that transesterification resulting in a scrambling of their

† Dedicated to Prof. R. W. Lenz on the occasion of his 75th birthday.

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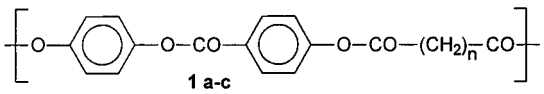
Table 1. Yields and Properties of Nematic Polyesters Prepared by Polycondensation of Bistrimethylsilyl Hydroquinone 4-Hydroxybenzoate with Various Aliphatic Dicarboxylic Acid Dichlorides in Bulk at 235−240 °C

dichlorides of	yield (%)	η_{inh}[a] (dL/g)	T_m[c] (°C)	T_i[c] (°C)	T_i[d] (°C)	lit. data T_m[e] (°C)	lit. data T_m[f] (°C)	elemental formula (fw)	elemental analyses	C	H
hexane-1,6-dicarboxylic acid	85.0	0.52	253	319	338−342	150−170	211	$C_{21}H_{20}O_6$ (368.38)	calcd	68.47	5.47
									found	68.41	5.48
octane-1,8-dicarboxylic acid	92.0	0.67	227	264	287−291	140−170	206	$C_{23}H_{24}O_6$ (396.43)	calcd	69.69	6.10
									found	69.24	6.10
decane-1,10-dicarboxylic acid	97.0	0.90	209	240	246−250	145−170	180	$C_{25}H_{28}O_6$ (424.49)	calcd	70.74	6.65
									found	70.21	6.66

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [b] From 100.4 MHz ^{13}C NMR spectra recorded in $CDCl_3$/TFA (volume ratio 4:1). [c] From DSC measurements with a heating rate of 20 °C/min. [d] Isotropization temperature as observed by optical microscopy. [e] From ref 13. [f] From ref 14.



1 a-c

a: n = 6 , **b**: n = 8 , **c**: n = 10

sequence should be detectable by ^1H NMR and ^{13}C NMR spectroscopy. These polyesters were previously synthesized and characterized by two different research groups.[12−14] Broad nematic phases were reported and melting temperatures below 212 °C.

Experimental Section

Monomers. Hydroquinone 4-hydroxybenzoate (HHB) was a gift of Bayer AG (Leverkusen, Germany). It had a gray color. The white product obtained after washing with methanol (and drying over P_4O_{10}) was used for all experiments (mp 241−243 °C; in ref 15, mp 242−245 °C). The dicarboxylic acid chlorides (ADADs) were purchased from Aldrich Co. (Milwaukee, WI) and used after distillation in vacuo. Pyridine was distilled over freshly powdered CaH_2. CH_2Cl_2 and toluene were distilled over P_4O_{10}. 1,2-Dichlorobenzene was distilled over P_4O_{10} in vacuo. 1-Chloronaphthalene was dried azeotropically and distilled in vacuo. All these solvents were purchased from Aldrich Co. Chlorotrimethylsilane and triethylamine were also gifts of Bayer AG and used as received.

Silylation of HHB. HHB (0.5 mol) and chlorotrimethylsilane (1.05 mol) were dissolved in dry toluene (1.2 L) and triethylamine (1.05 mol) was added dropwise with heating and stirring. Afterward, the reaction mixture was refluxed for 4 h, cooled with ice and filtered under exclusion of moisture. The filtrate was concentrated in vacuo and the product was distilled in portions of 50 g over a short-path apparatus in a vacuum of 10^{-3} mbar. Yield: 83%. Mp: 173−175 °C.

Anal. Calcd for $C_{19}H_{26}O_4Si_2$ (374.6): C, 60.92; H, 7.01. Found: C, 60.65; H, 6.87%.

Polycondensations. (A) Silyl Method in Bulk (Table 1). Silylated HHB (20 mmol), an ADAD (20 mmol), and benzyltriethylammonium (TEBA) chloride (10 mg) were weighed into a cylindrical glass reactor equipped with a mechanical stirrer and gas-inlet, and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 120 °C and the temperature was rapidly raised to 160 °C where the polycondensation started. The temperature was then raised in steps of 20 °C to 240 °C according to the progress of the polycondensation (monitored by the evolution of $ClSiMe_3$ and increasing viscosity of the melt). In the case of butane-1,4-dicarbonyl and hexane-1,6-dicarbonyl, solidification was unavoidable.

The experiments yielding samples nos. 1−5 of Table 2 were conducted with 50 mmol quantities of each monomer. The reaction vessel was opened after the mentioned time intervals, and 0.5 g samples were removed for characterization.

(B) Silyl Method in 1-Chloronaphthalene (Table 3). Silylated HHB (15 mmol), decane-1,10-dicarbonyl chloride (15 mmol), TEBA chloride (10 mg), and dry 1-chloronaphthalene (5 g) were weighed into a cylindrical glass reactor and polycondensed as described above.

Table 2. Polycondensation of Bistrimethylsilyl Hydroquinone 4-Hydroxybenzoate with Decane-1,10-dicarbonyl Chloride

expt no.	molar excess of the dichloride	temp (°C)	time (h)	yield (%)	DP[a]	η_{inh}[b] (dL/g)	comment
1A[c]	0	160[c]	0.5		6	0.39	LC, no cycles
1B[c]	0	180[c]	1.0		12	0.43	LC, no cycles
1C[c]	0	200[c]	1.5		60	0.70	LC, no cycles
1D[c]	0	220[c]	2.0		80	0.75	LC + cycles
1E[c]	0	235[c]	3.0		120	0.82	LC + cycles
2	0	235	4.0	96	135	0.86	LC + cycles
3	1	235	4.0	97	-	0.95	LC + cycles
4	2	235	4.0	99	-	1.20	LC + cycles
5	3	235	4.0	88	-	0.93	LC + cycles

[a] Average degree of polymerization as determined by ^1H NMR spectroscopy. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1). [c] Samples were taken from a larger batch.

Table 3. Polycondensations of Decane-1,10-dicarbonyl Chloride with Silylated HHB[a] or free HHB in Solution

expt no.	reaction medium	molar excess of the dichloride	temp (°C)	time (h)	yield (%)	η_{inh}[b] (dL/g)
1	1-chloronaphthaline	0	240			
2	1-chloronaphthaline	0	220	5	79	0.82
3	1-chloronaphthaline	1	220	5	82	0.61
4	1-chloronaphthaline	2	220	5	89	0.48
5	1,2-dichlorobenzene	0	180	24	84	0.57
6	1,2-dichlorobenzene	1	180	24	74	0.62
7	CH_2Cl_2 + pyridine	0	0−5/20	1/20	80	0.36
8	CH_2Cl_2 + pyridine	1	0−5/20	1/20	72	0.33
9	CH_2Cl_2 + pyridine	2	0−5/20	1/20	77	0.28

[a] Silalyted HHB was used in experiment no. 1 and free HHB in all other experiments. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/TFA (volume ratio 4:1).

(C) Method with Free HHB in 1-Chloronaphthalene (Table 3). HHB (15 mmol) and decane-1,10-dicarbonyl chloride were dissolved in dry 1-chloronaphthalene (50 mL) and heated to 220 °C for 5 h with stirring. The eliminated HCl was removed with a slow stream of nitrogen. The cold reaction mixture was poured into dry diethyl ether, and the precipitated polyester was twice washed with dry diethyl ether and dried at 80 °C in vacuo.

Analogous polycondensations were conducted in refluxing 1,2-dichlorobenzene.

(D) Pyridine Method. HHB (20 mmol) and decane-1,10-dicarbonyl chloride (20 mmol) were dissolved (or partially suspended) in dry dichloromethane (150 mL). After the reaction was cooled to approximately 1−2 °C, dry pyridine (80 mmol) was added dropwise with stirring. The reaction mixture was then stirred at room temperature for 4 d. The reaction mixture was concentrated to a volume around 100 mL and precipitated into diethyl ether. The isolated polyester was dried at 60 °C in vacuo whereby a remainder of pyridine hydrochloride sublimed.

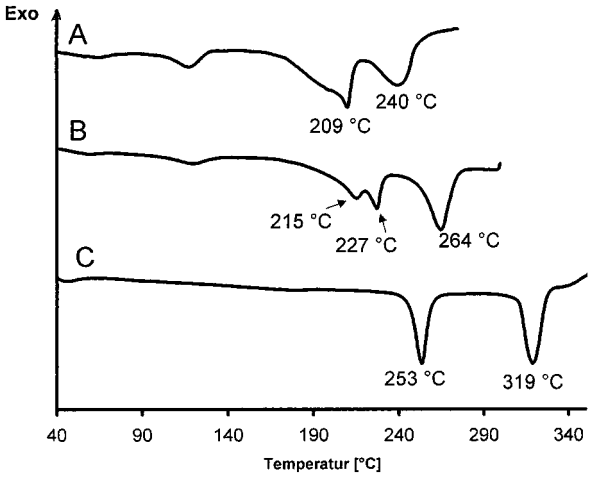


Figure 1. DSC measurements (1st heating, heating rate 20 °C/min): (A) polyester **1c**; (B) **1b**; (C) **1a**.

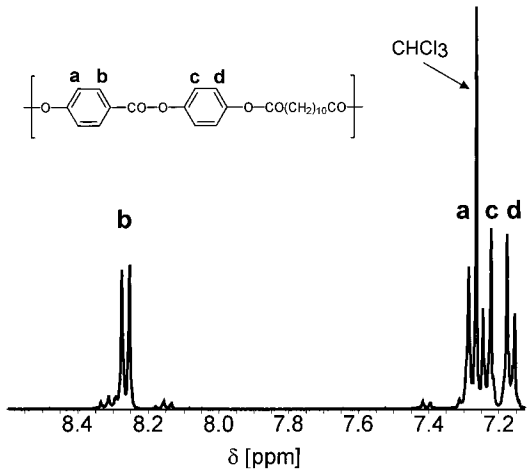


Figure 2. 400 MHz ^{1}H NMR spectrum of the aromatic protons of polyester **1c**.

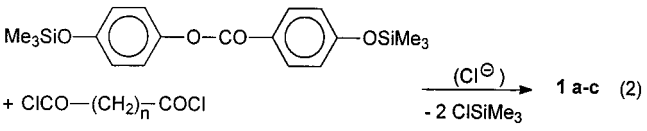
Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The DSC measurements were conducted with a PERKIN ELMER DSC-7 in aluminum pans under nitrogen at a heating rate of 20 °C/min.

The 400 MHz ^{1}H NMR spectra and the 100.4 MHz ^{13}C NMR spectra were obtained on a Bruker "Advance" FT spectrometer in 5 mm o.d. sample tubes. A 4:1 (by volume) mixture of $CDCl_3$ and trifluoroacetic acid (TFA) containing TMS was used as solvent and shift reference.

The MALDI−TOF mass spectra were recorded with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm) in the reflectron mode. An acceleration voltage of 20 kV and a cutoff range of 800 Da were used for all measurements. The irradiation targets were prepared from hexafluoro-2-propanol solution with dithranol as matrix and K−trifluoroacetate as dopant.

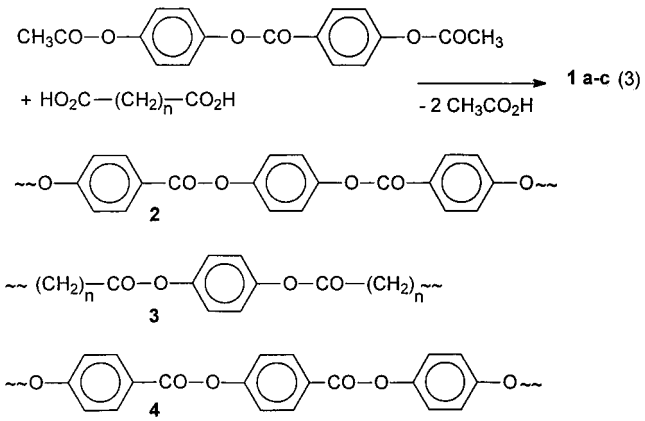
Results and Discussion

Polycondensation in Bulk. To study the possibility of kinetically controlled cyclizations in the nematic phase, polycondensations free of transesterifications had to be conducted in bulk. The only method meeting these requirements was the polycondensation of silylated HHB with ADADs catalyzed by chloride ions (eq 2).



From previous studies it was known[16,17] that this approach avoids transesterifications up to reaction temperatures around 240 °C. The ADADs were used in an excess of 1 mol % to compensate for the loss by distillation. In this way the three polyesters **1a**−**1c** were prepared, having the properties listed in Table 1.

The DSC revealed as expected two endotherms in the heating curve (Figure 1) and the corresponding two exotherms in the cooling trace. The optical microscopy revealed the characteristic mobile Schlieren texture of a nematic phase in the temperature range defined by both endotherms. As typical for most semirigid main chain LC-polymers increasing length of the spacer reduces both melting temperature (T_m) and isotropization temperature (T_i) with a narrowing of the LC phase. The phase transitions found in this work were considerably higher than those reported by other authors (Table 1). In the case of the Strzeleckis work[13] the low molecular weights (indicated by low viscosity data) may be responsible for part of this difference. The molecular weights reported by Krigbaum's group[14] were as high as those obtained in this work. However, both groups prepared their polyesters by transesterification of the diphenol bisacetate at temperatures up to 285 °C (eq 3). It is absolutely unlikely that a perfectly alternating

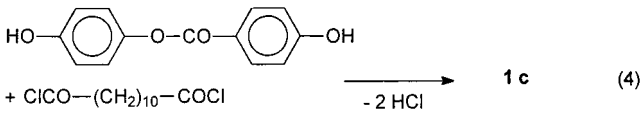


sequence was obtained under these conditions, and neither research group checked the structure of their polyesters. In a more or less randomized sequence, building blocks such as **2**, **3**, and **4** will be present. The building blocks **2** and **4** maintain the liquid crystalline character of these copolyesters, but the (partial) randomization of the sequence will lower the T_ms and broaden the temperature range of the isotropization (as reported[13,14]).

The synthetic approach used in this work was known to avoid transesterification below 250 °C. None the less, the structure of the isolated polyesters **1b** and **1c** was also checked by ^{1}H and ^{13}C NMR spectroscopy. As demonstrated in Figure 2 the ^{1}H NMR spectra of the aromatic protons revealed two doublets originating from the hydroquinone units. This signal pattern is characteristic for the alternating sequences of **1b** and **1c** where all hydroquinone units possess two different neighbors. In the case of symmetrical substitution (**2** and **3**) sharp singlet signals should appear. This assumption was proven by synthesis and ^{1}H NMR spectroscopy of hydroquinone bispropionate and hydroquinone bisbenzoate. The hydroquinone signal of the bisbenzoate appeared downfield of the propionate signal, and on the

basis of the observation the doublets "c" and "d" were assigned in Figure 2. Therefore, the ^{1}H NMR spectra of the polyesters **1b** and **1c** suggest that no significant transesterification has taken place. This suggestion was confirmed by the ^{13}C NMR which displayed the three CO signals expected for the alternating structure of **1a**−**1c** (176.7, 175.7, 167.0 ppm recorded in $CDCl_3$/TFA volume ratio 4:1) and only one signal for all four CH carbons of hydroquinone (130.0 ppm).

The unexpectedly high phase transitions (above all the high T_ms) prevented exhaustive polycondensations with high conversions in the nematic phase for the polyesters **1a**, because the maximum reaction temperature was limited to 240 °C, to avoid transesterification. Therefore, all further syntheses were focused on polyester **1c**. Two questions should be answered. First, at



(4)

which temperature and at which degree of polymerization (DP) does the LC phase appear, and does cyclization really occur in the nematic phase? Second, how does the molecular weight respond to variation of the feed ratio of both monomers? Experiments nos. 1A−1E of Table 2 were conducted in such a way that samples of approximately 0.5 g were taken from the reaction mixture after certain temperature and time intervals. These samples were characterized by inherent viscosities and by DP values which were determined from the ^{1}H NMR signals of the Me_3SiO end groups (assuming on the average one end group per chain). Optical microscopy revealed the typical mobile "Schlieren texture" of a nematic phase even for the sample obtained at the lowest reaction temperature (no. 1, Table 1). This means that the formation of low oligomers sufficed to stabilize a nematic phase. The characterization by MALDI−TOF mass spectroscopy revealed the presence of cycles only for samples polymerized at 220 or 235 °C. This observation is in perfect agreement with our concept of kinetically controlled polycondensations, where the cycles slowly pile up at low and moderate conversions (<95%) but dramatically increase at very high conversions. In contrast, the "backbiting degradation" of thermodynamically controlled polycondensations favors a rapid formation of cycles even at low to moderate conversions due to the large number of end groups.

For experiments nos. 2−5, heating from 160 to 240 °C was accelerated (3 h instead of 5 h), but the final temperature was maintained for 1 h more. Variation of the feed ratio revealed an optimum of the molecular weight for an 2 mol % excess of the dichloride. Obviously, selective distillation of the more volatile dichloride causes a slight imbalance of the stoichiometry, when a 1:1 feed ratio is used. A higher molecular weight means a higher and more perfect conversion of functional groups, and thus, on the basis of previous results[4−7] a higher fraction of cycles was expected.

The MALDI−TOF mass spectra revealed the presence of cyclic oligoesters in all samples of the polyesters **1a**−**1c** listed in Tables 1 and 2. Particularly interesting is the finding that almost exclusively even-membered cycles were formed as illustrated in Figures 3 and 4. This finding allows two important conclusions. First, it

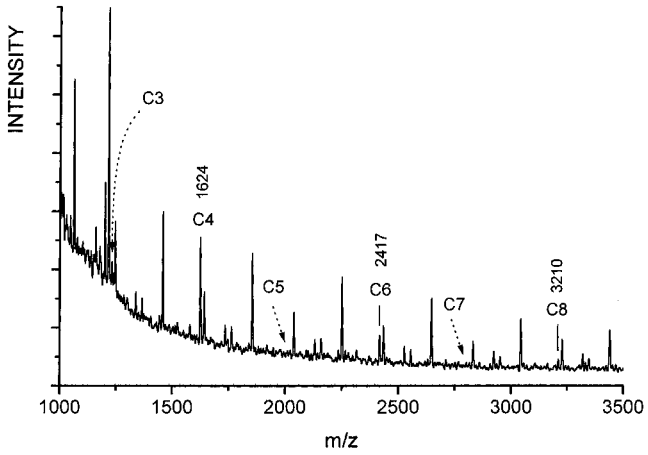


Figure 3. MALDI−TOF mass spectrum of polyester **1b** prepared by the "silyl method" in bulk.

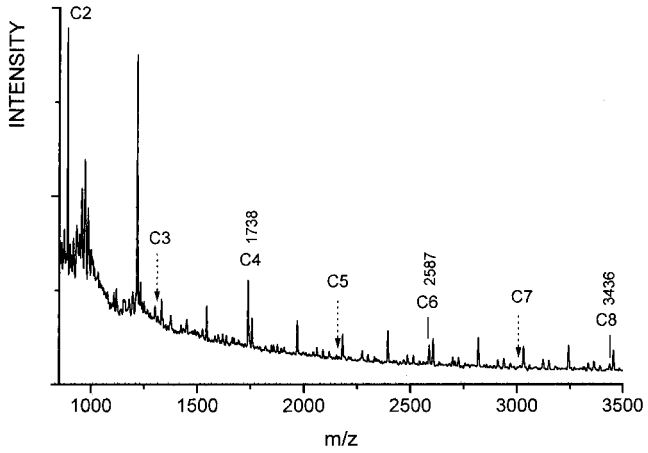
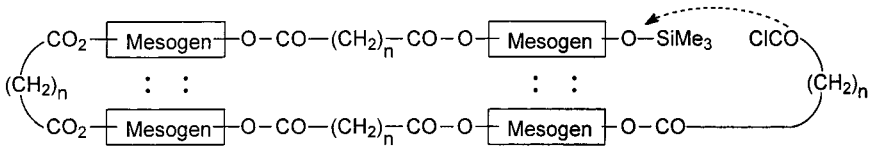


Figure 4. MALDI−TOF mass spectrum of the polyester **1c** prepared by the "silyl method" in bulk (no. 1, Table 2).

confirms the absence of backbiting, because this process should also yield odd-membered cycles. Second, the parallel chain packing in the nematic phase obviously favors a conformation, where the mesogens are in close contact (via dipole−dipole and dipole-π interactions) and the kinetically controlled cyclization proceeds via a hairpin conformation of the aliphatic space (Scheme 1). Such a conformation is clearly unfavorable for the formation of odd-membered cycles.

Polycondensations in Solution. To check the above formulated hypothesis of cyclization in the nematic phase (Scheme 1) several polycondensations yielding polyester **1c** were conducted in the isotropic phase. In the first experiments of this series (no. 1, Table 3), the mixture of the monomers was diluted with a small volume of 1-chloronaphthalene and the polycondensation was again performed at 240 °C (method B in the Experimental Section). The reaction mixture was transparent at any time indicating its isotropic character. The MALDI−TOF mass spectrum of the resulting polyester proved the formation of odd-membered cycles in quantities similar to those of the even-membered ones (Figure 5). Furthermore, free HHB was polycondensed with decane 1,10-dicarbonyl chloride in 1-chloronaphthalene at 220 °C with elimination of HCl (method C in the Experimental Section, nos. 2−4, Table 3). Analogous experiments were conducted in refluxing 1,2-dichlorobenzene (nos. 5 and 6, Table 3). All the polyester samples isolated from these five experiments have two characteristic properties in common. The ^{1}H NMR

Scheme 1



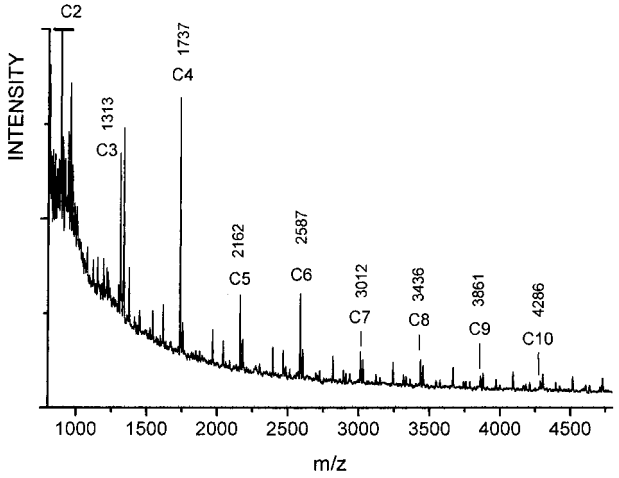


Figure 5. MALDI–TOF mass spectrum of the polyester **1c** prepared by the "silyl method" in concentrated 1-chloronaphthalene (no. 1, Table 3).

spectra proved the absence of transesterification and the mass spectra demonstrated the presence of odd-membered cycles (quite analogous to Figure 5).

Finally, three polycondensations of free HHB were conducted in CH_2Cl_2 at 5–10 °C. Pyridine served as HCl acceptor and the feed ratio of both monomers was slightly varied (nos. 7–9, Table 3). Regardless of the feed ratio, only rather low molecular weights were obtained. None the less, the mass spectra revealed the formation of odd-membered cycles and even-membered cycles. In summary, three different polycondensation methods were studied proceeding in an isotropic phase and all these "isotropic polycondensations" yielded odd-membered cycles in quantities comparable to those of the even-membered cycles. Therefore, these experiments clearly confirm that the exclusive formation of even-membered cycles in the nematic melt is the result of a chain packing and conformation that is characteristic for this LC phase.

Conclusion

The results of this work demonstrate that it is feasible to synthesize the polyesters of structure **1** in the nematic phase, so that the LC phase is formed in a very early stage of the polycondensation. The chemical structure of these polyesters has the advantage that the absence of transesterification and "backbiting" can be checked by NMR spectroscopy. The MALDI–TOF mass spectra revealed the formation of even-membered cyclic oligoesters in the nematic phase. The formation of odd-membered cycles was found, regardless of the synthetic method, whenever the polycondensation was conducted in an isotropic phase. These results allow the conclusion that kinetically controlled cyclizations may occur in the nematic phase based on a special type of supermolecular order involving parallelization and electronic contacts of the mesogens along with hairpin conformations of the aliphatic spacers. Further studies of this phenomenon are currently in progress.

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