ELSEVIER

Polymer 44 (2003) 2221–2230

polymer

www.elsevier.com/locate/polymer

Macrocycles 23. Odd–even effect in the cyclization of poly(ester imide)s derived from catechols

Abbas A. Shaikh, Gert Schwarz, Hans R. Kricheldorf*

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

Received 13 June 2002; received in revised form 22 November 2002; accepted 25 November 2002

Abstract

Various poly(ester imide)s, PEIs, were prepared from *N*-(4-carboxyphenyl) trimellitimide (4-CPTI) or from *N*-(3-carboxyphenyl) trimellitimide (3-CPTI). Various catechols or 5-methylresorcinol served as comonomers. MALDI-TOF mass spectrometry revealed that the PEIs derived from 4-CPTI and catechols contain significantly more even than odd cycles, whereas the PEIs derived from 3-CPTI and catechols contained almost equal amounts of odd and even-numbered cycles. The predominant formation of even-numbered cycles is explained by a 'hair pin' conformation of the growing oligomers based on strong donor–acceptor (DA) and dipole–dipole interactions. The resulting 'collapsed cycles' with parallel alignment of the 4-CPTI units have the consequence that most cyclic oligomers and polymers possess mesogenic properties and form a nematic melt. The temperature range of the nematic phase depends on the substituent of the catechol units.

Keywords: Poly(ester imide)s; Catechols; Nematic Phase

1. Introduction

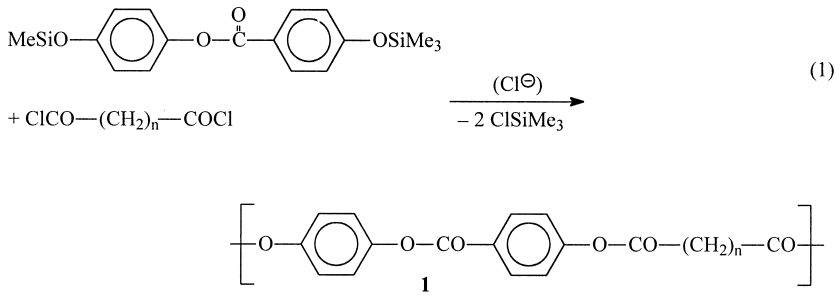
In the classical theory of polycondensation as developed by Carothers [1] and Flory [2,3] cyclization reactions do not play any role, and no differentiation between kinetically controlled and thermodynamically controlled polycondensations was made. Later Jacobson and Stockmayer proved [4] that in polymer syntheses involving equilibration reaction cyclic oligomers are formed by back-biting. When the equilibration reactions are rapid, the product mixtures represent at any stage of the polycondensation the thermodynamically most stable situation, and thus, such polymer syntheses are called thermodynamically controlled polycondensations (TCPs). In contrast, kinetically controlled polycondensations (KCPs) are characterized by absence of equilibration and back-biting reactions and the resulting reaction mixtures do not necessarily represent the thermodynamically most stable situation. Recently, Kricheldorf et al. [5,6] have demonstrated that cyclization competes with propagation at any stage of a KCP. The cycles formed in a KCP are stable over the whole course of the experiment and it has been predicted [4,7] for flexible aliphatic chains that their frequency decreases with the degree of polymerization according to $DP^{-3/2}$. For TCPs it has been predicted [4,8] and proven for numerous polymers [8,9] that the frequency of the cycles decreases with $DP^{-5/2}$. Regardless of the exact distribution function, the probability that even- or odd-numbered chains cyclize is, in principle, the same.

Quite recently a significant deviation from these distributions has been reported for the liquid crystalline polyesters of structure **1** [10]. When their syntheses were performed as KCP according to Eq. (1) in the nematic phase, almost exclusively even-numbered cycles were found. However, all syntheses conducted in the isotropic phase yield odd and even-numbered cycles in similar quantities decreasing with $DP^{-3/2}$ or $DP^{-5/2}$. These results suggest that the parallelization of chains and chain segments in the nematic phase generates conformations such as that of Scheme 1 stabilized by strong electronic interactions between the mesogens which, in turn, favor the formation of even-numbered

* Corresponding author. Tel.: +49-40-42838-3168; fax: +49-40-42838-6008.

E-mail address: kricheld@chemie.uni-hamburg.de (H.R. Kricheldorf).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00910-2



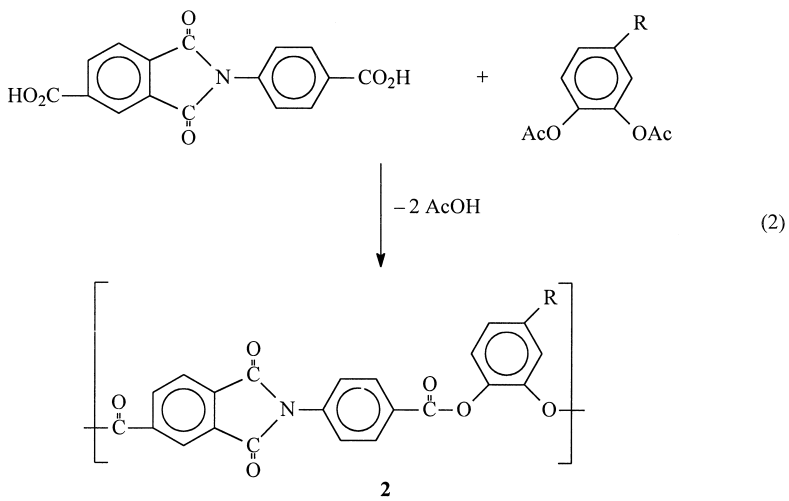
Scheme 1.

cycles. In a previous publication [11] it was reported that syntheses of poly(ester imide)s of structure **2** according to Eq. (2) give low molecular weights, and it was speculated that the chain growth was limited by intensive cyclization according to Eq. (3) (Schemes 2 and 3) [6]. In this context it was the purpose of the present work to reinvestigate the syntheses of the poly(ester imide)s, PEIs, **2** and to answer the following questions by means of MALDI-TOF mass spectrometry. Firstly, is cyclization indeed the main hindrance for the chain growth of the PEIs **2**? Secondly, does the existence of a liquid crystalline phase (reported for **2a**–**2c**) favor the formation of even-numbered cycles?

2. Experimental

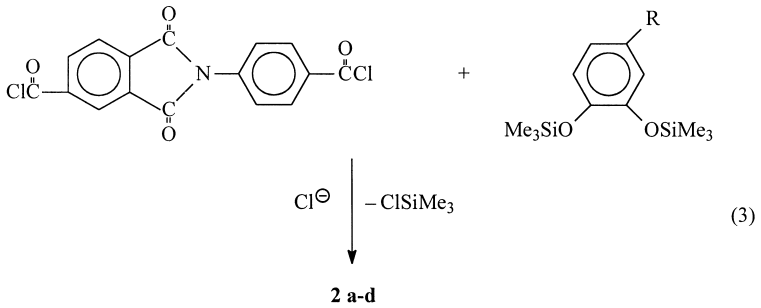
2.1. Materials

Trimellitic anhydride, 3-aminobenzoic acid, 4-aminobenzoic acid and thionyl chloride were gifts of Bayer AG (Leverkusen, Germany) and were used as received. Catechol, 4-methylcatechol, 4-*tert*-butylcatechol, 5-methylresorcinol, 2,3-dihydroxynaphthalene and 4-aminocinnamic acid were purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. Chloroform, toluene and dimethylformamide (DMF) were dried by distillation over P_4O_{10}.



a : R = H , **b** : R = CH_3 , **c** : 2,3-dihydroxy-naphthalene , **d** : R = $C(CH_3)_3$

Scheme 2.



Scheme 3.

2.2. Silylation of 4-tert-butylcatechol

4-*tert*-Butylcatechol (0.3 mol) and hexamethyldisilazane (0.2 mol) were refluxed in dry toluene (200 ml) until the evolution of NH_3 had almost ceased. The reaction mixture was concentrated in vacuo, and the product was distilled.

Yield: 95%, n_D^{25} 1.4665.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.26$ (s, 9H), 0.30 (s, 9H), 1.29 (s, 9H), 6.78–6.89 (m, 3H) ppm.

Catechol, 4-methylcatechol, 5-methylresorcinol and 2,3-dihydroxynaphthalen were silylated analogously and isolated in yields of 91–96%. Their syntheses and properties have been described before [11–13].

2.3. Acetylation of 4-tert-butylcatechol

4-*tert*-Butylcatechol (0.25 mol) and pyridin (5 ml) were dissolved in toluene (250 ml) and heated to 70 °C. Acetic anhydride (0.9 mol) was added dropwise with stirring and the reaction mixture was refluxed for 6 h. After cooling the reaction mixture was concentrated in vacuo and hot ligroin (200 ml) was added to the residue. After cooling in a refrigerator for 48 h, the crystallized product was isolated by filtration, washed with cold ligroin and dried in vacuo.

Yield: 74%, mp 51 − 52 °C.

^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.30$ (s, 9H), 2.26 (s, 3H), 2.28 (s, 3H), 7.12–7.31 (m, 3H) ppm.

2.4. N-(3-Chloroformylphenylene) 4-chloroformylphthalimide

2.4.1. N-(3-Carboxyphenylene)trimellitimide (3-CPTI)

Trimellitic anhydride (0.5 mol) and 3-aminobenzoic acid (0.5 mol) were heated in dry DMF (600 ml) to 120 °C for 2 h. Acetic anhydride (0.8 mol) and pyridine (5 ml) were added dropwise with stirring. The reaction mixture was then stirred at 120 °C for additional 4 h. The product which had precipitated after cooling was isolated by filtration, washed with water and dried in vacuo. The DMF filtrate was poured on crushed ice and water and a second crop of the product was isolated by filtration. Total yield: 50%.

2.4.2. Chlorination

The crude dicarboxylic acid (0.25 mol) was stirred in refluxing $SOCl_2$ (300 ml) and a solution of dry DMF (2 ml) in chloroform (20 ml) was added dropwise over a period of 2 h. The heating was continued until the evolution of HCl had almost ceased. The product which had crystallized after cooling with ice was filtered off under exclusion of moisture, intensively washed with warm ligroin and dried in vacuo. Yield: 87%, mp 201–203 °C.

Analyses calcd for C_{10} $H_7Cl_2NO_4$ (348.1); C 55.20, H 2.02, N 4.02, Cl 20.37%; found C 55.13, H 2.11, N 4.09, Cl 20.05%.

The dichlorides of *N*-(4-carboxyphenylene) trimellitimide, 4-CPTI, (mp 173–175 °C [14]) and of 4-aminocinnamic acid trimellitimide (mp 213–215 °C [15]) were prepared analogously as described previously.

2.5. Poplycondensations

2.5.1. Silyl method

N-(4-Chloroformylphenyl)-4-chloroformylphthalimide (20 mmol), a silylated diphenol (20 mmol) and 10 mg triethylbenzylammonium chloride (TEBA-Cl) were weighed into a cylindrical glass reactor equipped with a flat-blade stirrer and gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 160 °C. After 0.5 h the temperature was raised to 190 °C, after 0.5 h to 210 °C, after 0.5 h to 230 °C and after another 0.5 h to 250 °C. After 2 h at 250 °C the reaction mixture was cooled to 20 °C and the polymer was mechanically removed from the reactor.

In a second version (A′) 10 mg of TEBA-Cl was used, but the temperature was raised to 290 °C for 1.0 h.

In a third version (A″) 50 mg of TEBA-Cl was used as catalyst and the time at 250 °C was increased to 4 h. Afterwards, vacuum was applied for 6 min and the reaction mixture was cooled to 20 °C.

2.5.2. Acetate method

N-(4-Carboxyphenylene)trimellitimide (20 mmol), acetylated 4-*tert*-butylcatechol (21 mmol) and magnesium acetate (20 mg) were weighed into a cylindrical glass-reactor equipped with flat-blade stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 160 °C. The temperature was rapidly raised to 260 °C for 1.0 h. The temperature was then raised to 290 °C and maintained for 2 h. Afterwards vacuum was applied for

6 min. The reaction mixture was cooled to 20 °C and mechanically removed from the reactor.

2.6. Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. A 4:1 (by volume) mixture of CH_2Cl_2 and trifluoroacetic acid was used as solvent.

The 400 MHz ^{1}H NMR spectra were recorded with a Bruker 'Advance 400' FT NMR spectrometer in 5 mm o.d. sample tubes. A 4:1 (by volume) mixture of $CDCl_3$ and trifluoroacetic acid (containing TMS) served as solvent. The DSC measurements were conducted on a Perkin–Elmer DSC-7 at a heating rate of 20 °C/min in aluminum pans under nitrogen.

The MALDI-TOF mass spectra were recorded on a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were measured in the reflectron mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from trifluoroacetic acid solutions with dithranol as matrix and K-trifluoroacetate as dopant.

3. Results and discussion

3.1. Synthetic methods

For the present work the PEI **2d** was prepared from acetylated 4-*tert*-butylcatechol and 4-CPTI to complete the series of PEIs previously prepared by the same polycondensation method ('acetate method', Eq. (2), B in Table 1) [11]. Furthermore, the synthesis of **2a** was repeated via the acetate method (no. 3, Table 1). Moreover, all four PEIs **2a**–**d** were also prepared in a different way, namely by polycondensation of silylated catechols with the dichloride of 4-CPTI (Eq. (3), 'silyl method', A in Table 1). The silyl method was used to compare the influence of different synthetic methods on extent and selectivity of cyclization reactions. It was found in recent studies of copolyesters having alternating or blocky sequences [16,17] that the silyl method does not involve transesterification below 250 °C, and even at higher temperatures the occurrence of equilibration reactions is considerably lower than in the case of the acetate method. The relatively low inherent viscosities and the MALDI-TOF mass spectra (discussed below) indicated that the conversions were not satisfactory. Therefore, the syntheses of the PEIs **2a** and **2c** were repeated with a final reaction temperature of 290 °C (method A′), to achieve higher conversions and to find out if the structure of the reaction products is influenced by transesterification. Slightly higher solution viscosities were indeed found, but the conversions were again not satisfactory. These results suggested that temperature and time were sufficient even at 250 °C, whereas the catalyst was lost by decomposition and evaporation of the decomposition

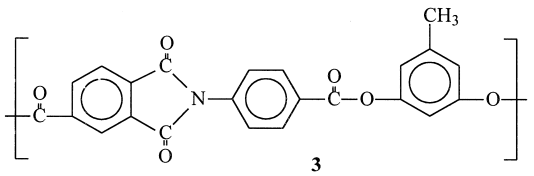
Table 1
Syntheses and properties of poly(ester imide)s derived from *N*-(4-carboxyphenyl) trimellitimide() and various catechols

Exp. no	Diphenol	Synth.method	Polymer no.	Temperature (°C)	Time (h)	η_{inh} [a] (dl/g)	T_g [b] (°C)	LC-phase (T_i (°C))	Cycles
1	Catechol	A	**2a**	160, 190, 210 230, 250	0.5, 0.5, 0.5 0.5, 2.0	0.09	142	Nematic (265–275)	Even
2	Catechol	A′	**2a**	160, 190, 210 230, 260, 290	0.5, 0.5, 0.50.5, 0.5, 1.0	0.10	145	Nematic (270–285)	Even
3	Catechol	B	**2a**	260, 290, 290	1.0, 2.0, 0.1V	0.08	158	Nematic (285–295)	Even
4	4-Methylcatechol	A	**2b**	160, 190, 210 230, 250	0.5, 0.5, 0.5 0.5, 2.0	0.08	154	Nematic (270–280)	Even
5	4-Methylcatechol	A′	**2b**	160, 190, 210 230, 260, 290	0.5, 0.5, 0.5 0.5, 0.5, 1.0	0.10	163	Nematic (275–285)	Even
6	4-Methylcatechol	A″	**2b**	160, 190, 210 230, 250, 250	0.5, 0.5, 0.5 0.5, 4.0, 0.1V	0.11	165	Nematic (275–285)	Even
7	2,3-Dihydroxy-naphthalene	A	**2c**	160, 190, 210 230, 250	0.5, 0.5, 0.5 0.5, 2.0	0.09	181	Nematic (415–425)	Even
8	4-*tert*-Butyl-catechol	A	**2d**	160, 190, 210 230, 250	0.5, 0.5, 0.5 0.5, 2.0	0.06	160	–	Even
9	4-*tert*-Butyl-catechol	A″	**2d**	160, 190, 210 230, 250, 250	0.5, 0.5, 0.5 0.5, 4.0, 0.1V	0.08	175	–	Even
10	4-*tert*-Butyl-catechol	B	**2d**	260, 290, 290	1.0, 2.0, 0.1V	0.07	178	–	Even

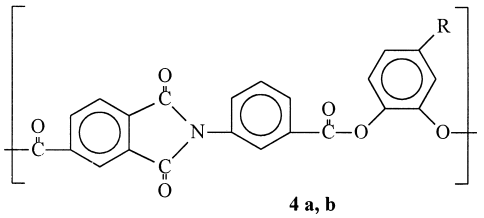
[a] Measured at 20 °C with $c = 2$ g/l in CH_2Cl_2/trifluoroacetic acid (4:1 by volume).
[b] DSC measurements with a heating rate of 20 °C/min.

products. Therefore, a third version of the silyl method (A″) was studied. The final temperature was again limited to 250 °C, but a five times larger quantity of the catalyst was added. Although the inherent viscosities did not significantly increase, the MALDI-TOF m.s. indicated the highest conversions for this third version of the silyl method.

Four more PEIs were prepared by the silyl method. The PEI **3** was obtained by polycondensation of a silylated 5-methylresorcinol as an isomer of PEI **2b** (Table 2). Furthermore, the dichloride of 3-CPTI was synthesized and polycondensed with silylated 4-methylcatechol or 4-*tert*-butylcatechol. In this way, the PEIs **4a** and **4b** were obtained which are isomers of the PEIs **2b** and **2d**. Finally, the PEI **5** was prepared from silylated 4-*tert*-butylcatechol by polycondensation with the chlorinated trimellitimide of 4-aminocinnamic acid (Table 2).

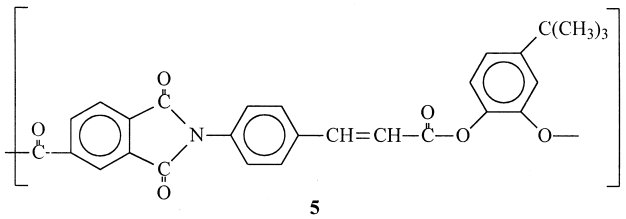


3



4 a, b

a : R = CH_3 **b** : R = $C(CH_3)_3$



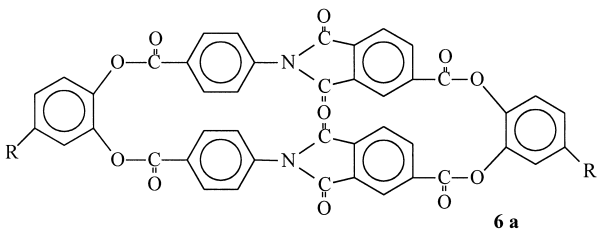
5

All reaction products were worked up in such a way that the crude polycondensates were mechanically removed from the reactor to avoid fractionation of oligomers by (re)precipitation from solvents into non-solvents. The yields of the crude PEIs were around 95%.

3.2. Chemical structure and phase transitions

The chemical structure of all PEIs was characterized by IR spectroscopy and ^{1}H NMR spectroscopy. As expected for the preparation of homopolymers, the spectroscopic data were in agreement with the desired structures and a detailed discussion is not necessary, in as much as numerous PEIs have been described over the past four decades [18]. Absolute molecular weights were not determined, because the PEIs of this work required acidic solvents so that the usual GPC eluents, THF and CH_2Cl_2, were not useful. A comparison of the inherent viscosities with those of aromatic poly(ether sulfone)s (characterized by SEC and light scattering) [19,20] suggest that the number average molecular weights of all PEIs listed in Table 1 fall into the range of 4000–8000 Da. Only one high molecular weight sample was obtained, namely **4b**.

Thermal properties and phase transitions were determined by optical polarizing microscopy and by DSC measurements. Glass-transition temperatures (T_gs) above 140 °C were found for all PEIs with the exception of **5**. Whereas the PEIs **3** and **4a**, **4b** were completely amorphous, the other PEIs were seemingly semicrystalline, but the melting endotherms in the DSC heating traces were flat and broad, presumably because individual components of the complex product mixtures (see below) crystallized separately (e.g. cyclic oligomers). Furthermore, it must be taken into account that cyclic oligomers may consist of several isomers. As illustrated by formulas **6a–d**, even the smallest cycle may form four isomers. In the case of cyclic tetramers up to 16 isomers may exist, when methyl- or *tert*-butylcatechol are used as comonomers.



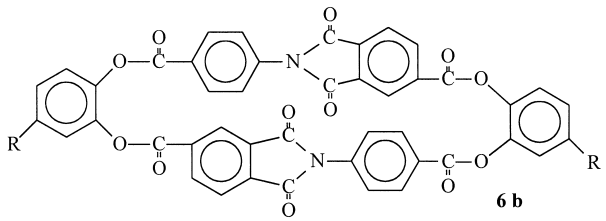
6 a

Table 2
Syntheses of various poly(ester-imide)s from silylated diphenols

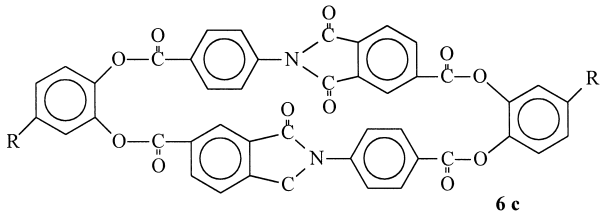
Exp. No.	Silylated diphenol	Polymer no.	η_{inh}[a] (dl/g)	T_g (°C)	Cycles
1	5-Methyl-resorcinol	**3**	0.18	178	Few odd + even
2	4-Methyl-catechol	**4a**	0.67	186	Odd + even
3	4-*tert*-Butyl-catechol	**4b**	0.17	182	Odd + even
4	4-*tert*-Butyl-catechol	**5**	0.05	130	Even

Reaction temperatures and times: 160 °C/0.5 h, 190 °C/0.5 h, 210 °C/0.5 h, 230 °C/0.5 h, 250 °C/4.0 h. DSC measurements with a heating rate of 20 °C/min.

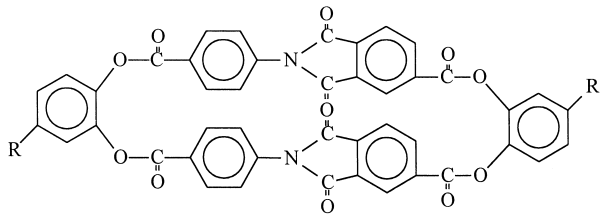
[a] Measured at 20 °C with c = 2 g/l in CH_2Cl_2/trifluoroacetic acid (4:1 by volume).



6 b



6 c



6 d

The optical microscopy (with crossed polarizers) revealed the formation of a nematic melt for the PEIs **2a–c** in agreement with a previous report [11]. The formation of this nematic phase was perfectly reversible upon repeated heating and cooling. The Schlieren texture, exemplarily shown in Fig. 1, did not perfectly agree with a classical threaded Schlieren texture, possibly because not all components of the reaction products had a liquid-crystalline character. On the other hand, it is obvious that the chemical structure of these PEIs does not allow for the formation of another type of liquid-crystalline phase, such as smectic-A or cholesteric, and thus, the assignment of a nematic phase is unambiguous. In this connection, it should be mentioned that crystallites melting above 320 °C were observable in the melts of **2a–c**. These crystallites most likely originate from cyclic dimers or tetramers which are present in relatively high quantities (see below). Furthermore, it is well known from several classes of oligomers and polymers that the cyclic dimers or tetramers possess the highest melting points of the system under consideration. Another interesting finding is the fact that the PEIs **2d** and **5** are isotropic. However, it is a quite normal structure-property relationship of liquid crystalline materials that space-demanding substituents attached to mesogens eliminate the mesogenic properties, and thus, the liquid-crystalline phase. Also all PEIs derived from m-functional building blocks (**3**, **4a** and **4b**) were isotropic. It is a well-known structure–property relationship [21,22] that the 120° angle incorporated by m-functional monomers into oligomers or polymers is highly unfavorable for the formation of a liquid-crystalline phase.

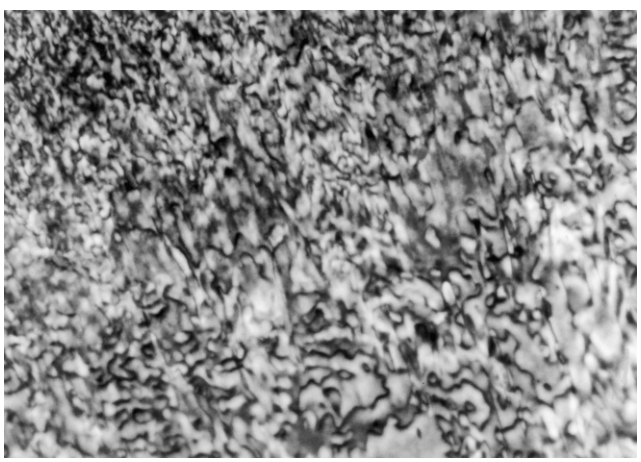


Fig. 1. Texture of the nematic melt of poly(ester imide) **2b** (prepared via the silyl method) after cooling from 300 to 270 °C.

3.3. MALDI-TOF mass spectrometry

The MALDI-TOF mass spectrometry provided the following information. In all mass spectra (m.s.) of the PEIs **2a–2d** prepared by the silyl method (A) or by the acetate method (B), strong peaks of even-numbered cyclic oligomers were detectable as shown in Figs. 2 and 3, whereas the mass peaks of odd-numbered cycles were very weak. The same trend was found for the PEI **5**. Only weak mass peaks of odd and even-numbered cycles were detectable in the m.s. of the PEI **3** derived from 5-methylresorcinol and 4-CPTI. In the m.s. of PEIs **4a** and **4b** derived from 3-CPTI both odd-numbered and even-numbered cycles were found in similar concentrations (Figs. 4 and 5).

In all m.s. of PEIs prepared by the silyl method mass peaks of four kinds of linear species were present. The most intensive peaks resulted from chains of the structures **2La**, **2Lb** and **2Lc** (Fig. 2). Their free OH-endgroups were formed by hydrolysis of the original $OSiMe_3$ and COCl groups during the preparation of the MALDI-TOF irradiation targets. The intensity ratio of the **2Lb/2Lc** chain varied with the excess of the silylated diphenol used in the feed. A slight excess of silylated catechols (or 5-methylresorcinol) was used to compensate for a loss by distillation, because these silalyted diphenols are more volatile than the dichlorides of 3-CPTI or 4-CPTI. The presence of these three kinds of linear chains indicates incomplete conversions despite the high reaction temperatures. Most likely the decomposition and sublimation of the catalyst (TEBA chloride) is responsible for these moderate conversions. When in an additional polycondensation a higher feed of the catalyst was used (method A″) the molecular weight of the PEI **2d** was slightly higher and the mass peaks of cycles relative to those of the linear species increased. These results were exemplarily illustrated for PEI

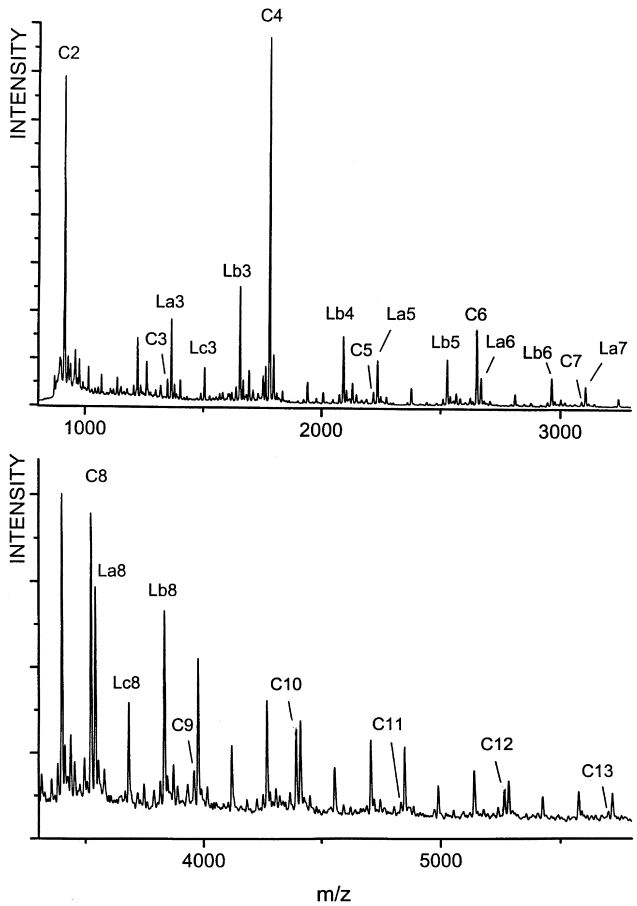


Fig. 2. MALDI-TOF mass spectrum of the poly(ester imide) **2c** prepared from silylated 2,3-dihydroxy naphthalene (no. 7, Table 1).

2d (no. 9, Table 1) in Fig. 3. Furthermore, extremely weak mass peaks of linear chains having the structure **2Ld** or **2Le** were observed. Their chain ends result from decarboxylation of **2Lc** chains. Either a few acid chloride groups were hydrolyzed during storage and handling of the imide monomer, or they were hydrolyzed during the polycondensation, because the nitrogen blown over the reaction mixture was not dry enough.

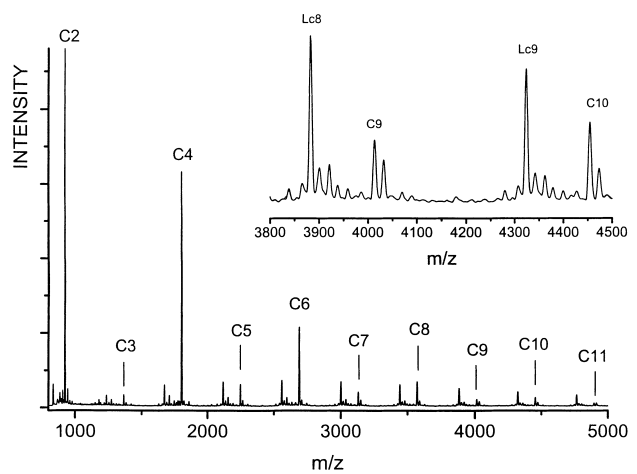


Fig. 3. MALDI-TOF mass spectrum of the poly(ester imide) **2d** prepared from silylated 4-*tert* butylcatechol (no. 9, Table 1).

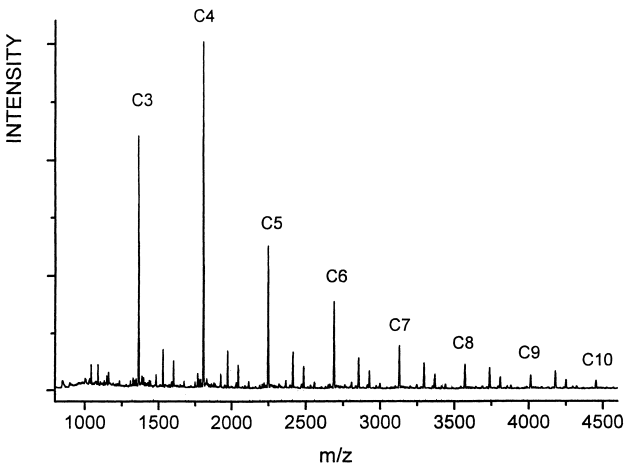
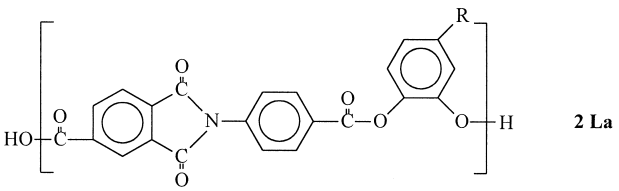
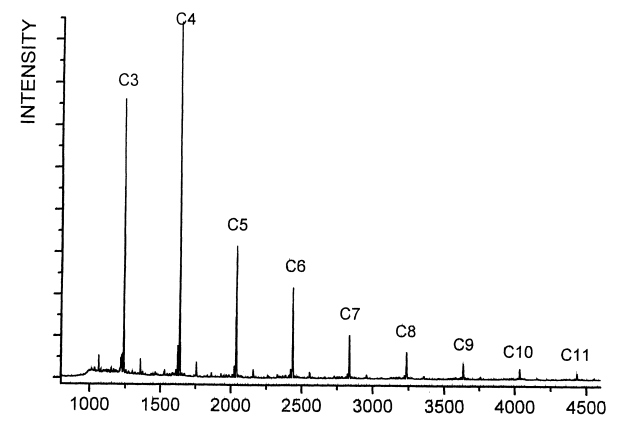


Fig. 4. MALDI-TOF mass spectrum of the poly(ester imide) **4a**.





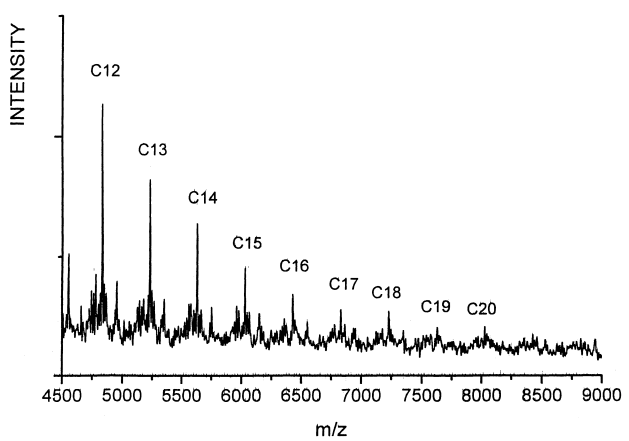
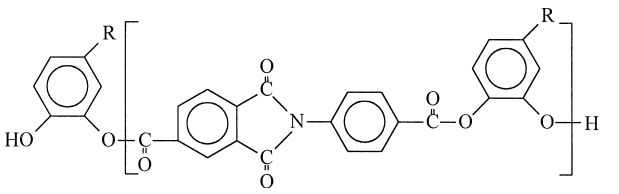
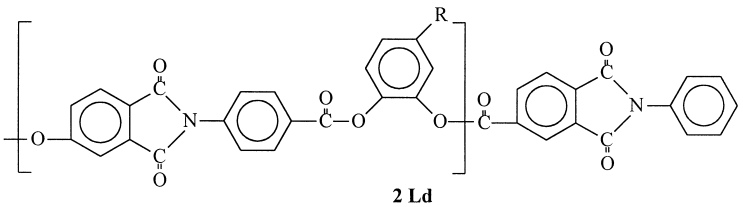


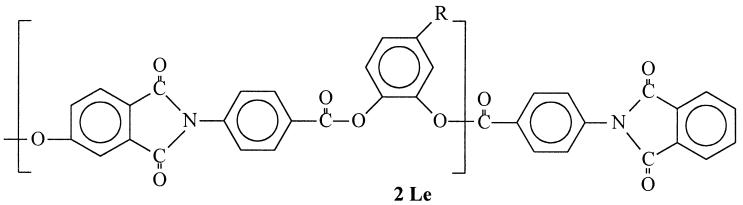
Fig. 5. MALDI-TOF mass spectrum of the poly(ester imide) **4b**.



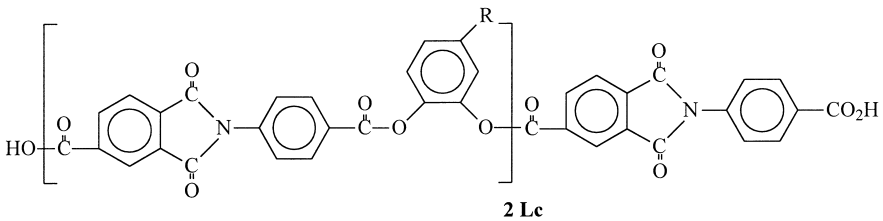
2 Lb



2 Ld



2 Le



2 Lc

The results discussed above demonstrate that the low molecular weights of most PEIs have a multiple origin: firstly, cyclization, secondly, incomplete conversion, thirdly imperfect stoichiometry, and fourthly (although to a negligible extent) hydrolysis and decarboxylation of acid chloride groups. The low concentration of cycles in PEI **3** and the high concentration of odd- and even-numbered cycles in **4a** and **4b** are expected for low conversions and different cyclization tendencies when the polycondensation is mainly or exclusively kinetically controlled [5,6]. As expressed by Eq. (4), cyclization competes with propagation at any concentration and at any stage of the polycondensation process. When the cyclization tendency is low (i.e. V_{pr}/V_{cy} is high in Eq. (4)), the fraction of cycles is necessarily low at low conversions. This is the situation of PEI **3**. For steric reasons the cyclization tendency is much higher when catechols are used as comonomers instead of resorcinols. Therefore, the fraction of cycles is relatively high at similar or higher conversions in the case of PEIs **4a** and **4b**.

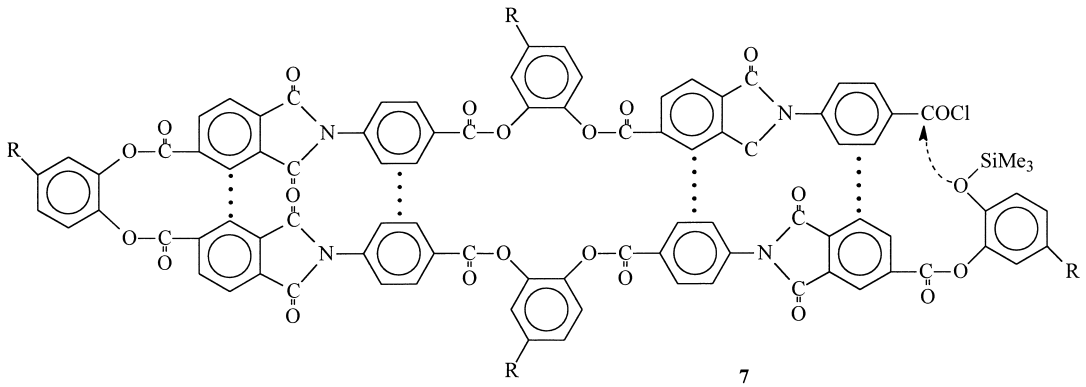
$$\overline{DP} = \frac{1}{1 - \left(p - \frac{1}{x^a}\right)} \tag{4}$$

where $\overline{DP}$ is the average degree of polymerization, p, the conversion of functional groups, $a = V_{pr}/V_{cy}$, the rate of propagation/versus rate of cyclization, and X is the variable factor (>1.0) taking into account variations of the concentration.

Particularly interesting is the predominance of the even-numbered cycles in the PEIs **2a–d** and **5**. Their formation may be explained by a cooperation between the steric effect of the catechols and strong electronic interactions ($\pi-\pi$-interaction, dipole–dipole and donor–acceptor interactions) between neighboring mesogenic imide building blocks. This kind of 'hair-pin' conformation is schematically illustrated in formula **7**. The pairwise and coplanar

alignment of the imide moieties clearly favors the formation of even-numbered rings. This interpretation is supported by a previously published [11] computer simulation of the energy minimum conformation of open-chain PEIs having the structure **2a**–**d**. This computer simulation favored the hair-pin conformation with pairs of coplanar imide moieties as shown in Fig. 6. In this connection, it should be mentioned that donor–acceptor interactions between coplanar aromatic imide units of neighboring chain segments have also been reported for other polyimides [23,24].

The MALDI-TOF m.s. also revealed that the odd–even effect of the cyclization gradually vanishes, when the chain length increases. For instance, in the original MALDI-TOF m.s. of **2d**, no. 9, (partially shown in Fig. 3), the mass peaks of cycles are detectable up to C16. The odd–even effect disappeared above C10. In the case of **2c** (Fig. 2) the odd–even effect is detectable up to the limit of the m.s. at C13. These observations indicate that for reasons of entropy the efficiency of parallel alignment and hair-pin conformation on the



7

cyclization reactions vanishes with increasing chain length. In this connection it should be mentioned that the odd–even effect was observed for all PEIs derived from catechols, regardless of the synthetic method. This means that for the PEIs of this work the presence or absence of transesterification reactions did not play a significant role with respect to the odd–even effect.

Finally, the question needs to be discussed, how the formation of even-numbered cycles is correlated with the existence of a nematic phase. The predominance of even-numbered cycles in the case of the isotropic PEIs **2d** and **5** proves that the nematic phase is not a prerequisite of the formation of a hair-pin conformation in contrast to the initially mentioned polyesters of structure **1**. Hair-pin conformation and even-numbered cycles are a direct consequence of the steric and electronic properties of the individual PEI chain. However, the 'collapsed' even-numbered cycles (Fig. 6) may play the role of calamitic mesogens stabilizing a nematic phase, when the substituents are not too bulky. In the case of **2d** and **5**, the steric demands of the *t*-butylgroups reduce the aspect (length/diameter) ratio of the collapsed cycles and suppress the mesogenic character. This is a quite normal consequence of Flory's theory of mesogenicity, which postulates a certain aspect ratio as a minimum for an efficient mesogenic character of a calamitic mesogen. Therefore, the assumption that the even-numbered cycles were formed via a hair-pin conformation and exist predominantly in this conformation (Fig. 6) explains all experimental findings of this work.

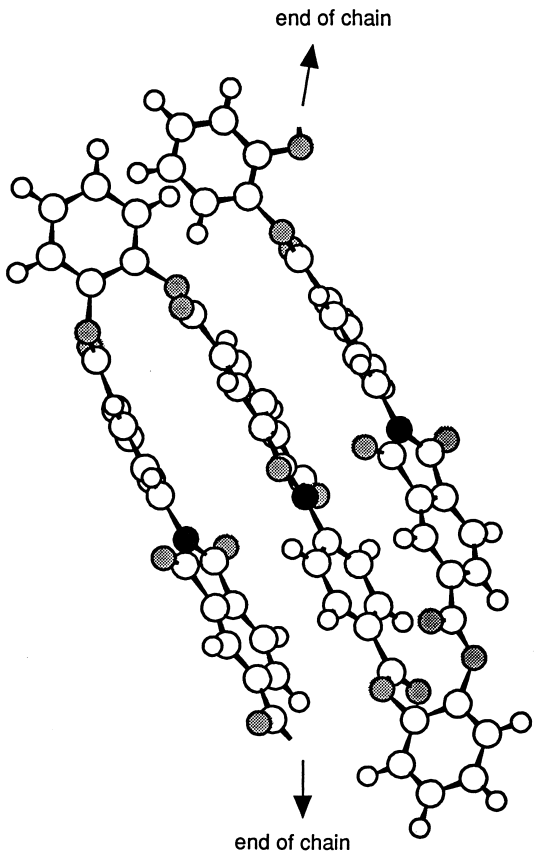


Fig. 6. Computer simulation of the energy minimum conformation of PEI **2a**.

4. Conclusion

The results of this work indicate that the low molecular weights obtained for all but one PEI are mainly a consequence of cyclization and partially a consequence of relatively low conversions. The low to moderate conversions might be a consequence of sublimation or decomposition of the benzyltriethylammonium chloride used as catalyst.

Particularly interesting is the predominant formation of even-numbered cyclic oligomers when catechol derivatives are polycondensed with 4-CPTI or with the dichloride of 4-aminocinnamic trimellitimide. It is concluded that the stereochemistry of the catechols in combination with strong electronic interaction between the *N*-phenylenetrimellitimide units favors the formation of hair-pin conformations which in turn favor the cyclization of even-numbered oligomers. The resulting 'collapsed cycles' may play the role of calamitic mesogens which enable the formation of a nematic melt. When compared to a recent study [10] dealing with cyclization in the nematic phase (Scheme 1), the results obtained in the present work differ in two significant aspects. Firstly, the synthetic method (including the presence or absence of transesterification) does not play a significant role. The structure of the monomers is decisive for selective cyclizations. Secondly, the formation of a nematic phase is not a prerequirement for the predominant formation of even-numbered cycles. Further studies concerning the preferential formation of even-numbered cycles in various polycondensation processes are currently in progress.

References

[1] Mark H, Whitby GS, editors. Collected papers of Wallace H. Carothers on polymerization. New York: Interscience; 1940.
[2] Flory PJ. Chem Rev 1946;39:137.
[3] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953. Chapter VIII.
[4] Jacobson H, Stockmayer WH. J Chem Phys 1950;18:1600.
[5] Kricheldorf HR, Rabenstein M, Maskos M, Schmidt M. Macromolecules 2001;34:713.
[6] Kricheldorf HR, Böhme S, Schwarz G. Macromolecules 2001;34:8879.
[7] Stepto RFT. In: Howard RN, editor. Developments in polymerization-3. Barhong: Applied Sci Publishers; 1982. Chapter 3.
[8] Semlyen JA. Adv Polym Sci 1976;21:42.
[9] Semlyen JA. In: Semlyen JA, editor. Large ring molecules. New York: Wiley; 1996. Chapter 1.
[10] Kricheldorf HR, Richter M, Schwarz G. Macromolecules 2002;35.
[11] Kricheldorf HR, Schwarz G, Domschke A, Linzer V. Macromolecules 1993;26:5161.
[12] Henglein FA, Krämer J. Chem Ber 1959;92:2585.
[13] Ho C-H. J Chin Chem Soc 1975;22:267.
[14] Kricheldorf HR, Bruhn C, Russanov A, Komarova L. J Polym Sci Part A Polym Chem 1993;31:282.
[15] Kricheldorf HR, Probst N, Gurau M, Berghahn M. Macromolecules 1995;28:6565.
[16] Kricheldorf HR, Eggerstedt S. Macromolecules 1998;31:6403.
[17] Shaik A, Richter M, Kricheldorf HR, Krüger RP. J Polym Sci: Part A: Polym Chem 2001;39:3371.
[18] Kricheldorf HR. Adv Polym Sci 1999;141:83.
[19] Kricheldorf HR, Böhme S, Schwarz G, Krüger RP, Schulz G. Macromolecules 2001;34:8886.
[20] Kricheldorf HR, Vakhtangishvili L, Schwarz G, Schulz G, Krüger RP. Polymer, Submitted for publication.
[21] Lenz, R.W., Jin J.I., Macromolecules, 1981, 14, 1405.
[22] Kricheldorf HR, Erxleben J. Polymer 1990;31:944.
[23] O'Mahoney CA, Williams DJ, Colquhoun HM, Mayo R, Young SM, Askari A, Kedrick J, Robson E. Macromolecules 1991;24:6527.
[24] Karcha RJ, Porter RS. J Polym Sci: Part B: Polym Phys 1993;31:821.