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# Liquid Crystalline Polyimides. 15. Role of Conformation and Donor–Acceptor Interactions for the Nematic Order of Poly(ester imide)s

**Hans R. Kricheldorf,* Gert Schwarz, Angelika Domschke, and Volker Linzer**

*Institut für Technische und Makromolekulare Chemie, Bundesstrasse 45,*
*W-2000 Hamburg 13, FRG*

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ABSTRACT: Three classes of poly(ester imide)s were synthesized: (I) polyesters of *N*-(4-carboxyphenyl)-trimellitimide and mono- or disubstituted hydroquinones, (II) polyesters of *N*-(4-hydroxyphenyl)-4-hydroxyphthalimide and mono- or disubstituted terephthalic acids, and (III) polyesters of *N*-(4-carboxyphenyl)-trimellitimide and various nonlinear diphenols. The characterization and comparison of these poly(ester imide)s revealed that two substituents per repeating unit significantly destabilize the nematic phase typical for the monosubstituted poly(ester imide)s. In contrast, poly(ester imide)s of *o*-diphenols form thermostable, enantiotropic nematic melts, although a linear conformation is energetically unfavorable.These results and literature data suggest that the interchain forces between temporarily coplanar chain segments play a significant role for the stabilization of the nematic phase, whereas geometrical factors such as chain stiffness, linear conformation, or length/diameter ratio play a minor role.

## Introduction

In a previous paper[1] dealing with poly(ester imide)s of benzophenone 3,3′,4,4′-tetracarboxylic anhydride the stabilization of the nematic melt by weak donor–acceptor interaction between the imide group and hydroquinone was discussed. However, clear evidence for the existence of such a donor–acceptor interaction was lacking at that time. Meanwhile, the existence of donor–acceptor complexes in various oligomers and polymers forming discotic mesophases has been demonstrated by Ringsdorf and coworkers.[2,3] Furthermore, an increasing number of poly(ester imide)s is found with structure–property relationships that are best explained by the existence of donor–acceptor interactions and not so much by a rigid-rod-like structure or conformation of the main chain.[4–6] The present work had the purpose to study the role of substitution patterns, chain stiffness, and donor–acceptor interactions for the stability of the nematic phases on a broader basis.

## Experimental Section

**Materials.** 4-Hydroxyphthalic acid, trimellitic anhydride, 4-aminobenzoic acid, and 4-aminophenol were gifts of Bayer AG (W-4150 Krefeld) and were used without further purification. Phenylhydroquinone, resorcinol, catechol, 4-methylcatechol, 4-nitrocatechol, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, and trimethylhydroquinone were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. 2,5-Di-*tert*-butylhydroquinone and 2,5-bis(hydroxyphenyl)-*p*-benzoquinone were purchased from Eastman Kodak (Rochester, NY). 2,5-Dimethoxyhydroquinone was prepared from benzoquinone according to ref 7. The diphenols were acetylated with an excess of acetic anhydride and a catalytic amount of pyridine in refluxing toluene and recrystallized from toluene/ligroin. In this way the bisacetates of 5-methylresorcinol,[8] 2,5-dimethoxyhydroquinone,[9] *tert*-butylhydroquinone,[10] and 2,5-di-*tert*-butylhydroquinone[11] were prepared. Reports on syntheses and properties of mono(alkylthio)[12] and 2,5-bis(alkylthio)-terephthalic acids[13] are in press. *N*-(4-Carboxyphenyl)trimellitimide[5,14] and acetylated *N*-(4-hydroxyphenyl)-4-hydroxyphthalimide[14,15] were synthesized as described previously.

***O,O′*-Bis(trimethylsilyl)-2,5-diphenylhydroquinone.** The commercial 2,5-diphenyl-*p*-benzoquinone was reduced to the corresponding hydroquinone by means of zinc powder in acetic acid according to the literature.[16] The melting point, 218–220 °C, agreed with the literature value.[16] The hydroquinone was silylated with an excess of hexamethyldisilazane in refluxing toluene (4 h). After concentration in vacuo the product was crystallized by portionwise addition of ligroin and cooling in a refrigerator.

**Table I. Yields and Properties of *O,O′*-Bissilylated Diphenols**

| *O,O′*-bistrimethylsilyl deriv of | yield (%) | mp (°C) or $n^{20}_{D}$ | elem anal. | | |
|---|---|---|---|---|---|
| | | | | % C | % H |
| 4-methylcatechol | 91 | 1.4719 | calcd | 58.15 | 9.01 |
| | | | found | 57.88 | 9.10 |
| trimethylhydroquinone | 72 | 1.4830 | calcd | 60.75 | 9.52 |
| | | | found | 60.36 | 9.77 |
| 2,5-diphenylhydroquinone | 66 | 148–150 | calcd | 70.88 | 7.44 |
| | | | found | 70.56 | 7.51 |
| 2,3-dihydroxynaphthalene | 95 | 54–55 | calcd | 63.11 | 7.94 |
| | | | found | 62.85 | 7.99 |

4-Methylcatechol and 2,3-dihydroxynaphthalene were silylated analogously. Trimethylhydroquinone was silylated with an equimolar mixture of hexamethyldisilazane and chlorotrimethylsilane in refluxing toluene. These three silylated monomers were purified by distillation in vacuo. For yields and properties, see Table I.

**Polycondensations. (A) Silyl Method.** The dichloride of *N*-(4-carboxyphenyl)trimellitimide (30 mmol), a bissilylated diphenol (30 mmol), and benzyltriethylammonium chloride (10 mg) were weighed into a cylindrical glass reactor equipped with a stirrer and gas inlet and outlet tubes. The reactor was placed into a metal bath preheated to 150 °C. The temperature was then raised in 20 °C steps to 290 °C over a period of 2.5 h. This temperature was maintained for 1 h under vacuum. The cold reaction product was dissolved in a mixture of $CH_2Cl_2$ and trifluoroacetic acid (volume ratio 4:1), precipitated into methanol, and dried at 120 °C in vacuo.

**(B) Acetate Method.** *N*-(4-Carboxyphenyl)trimellitimide (30 mmol), an acetylated diphenol (30 mmol), and MgO (10 mg) were weighed into a cylindrical glass reactor (equipped as described above) and placed into a metal bath preheated to 260 °C where the polycondensation slowly started. The temperature was raised to 290 °C over a period of 2.5 h, and then vacuum was applied for an additional hour. The cold polyester was worked up as described above.

**(C) Pyridine Method.** A diphenol (30 mmol) was dissolved in dry pyridine (100 mL) and cooled to 0 °C. A concentrated solution of the dichloride of *N*-(4-carboxyphenyl)trimellitimide (30 mmol) in 1,2-dichloroethane was added rapidly with stirring.

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1993.

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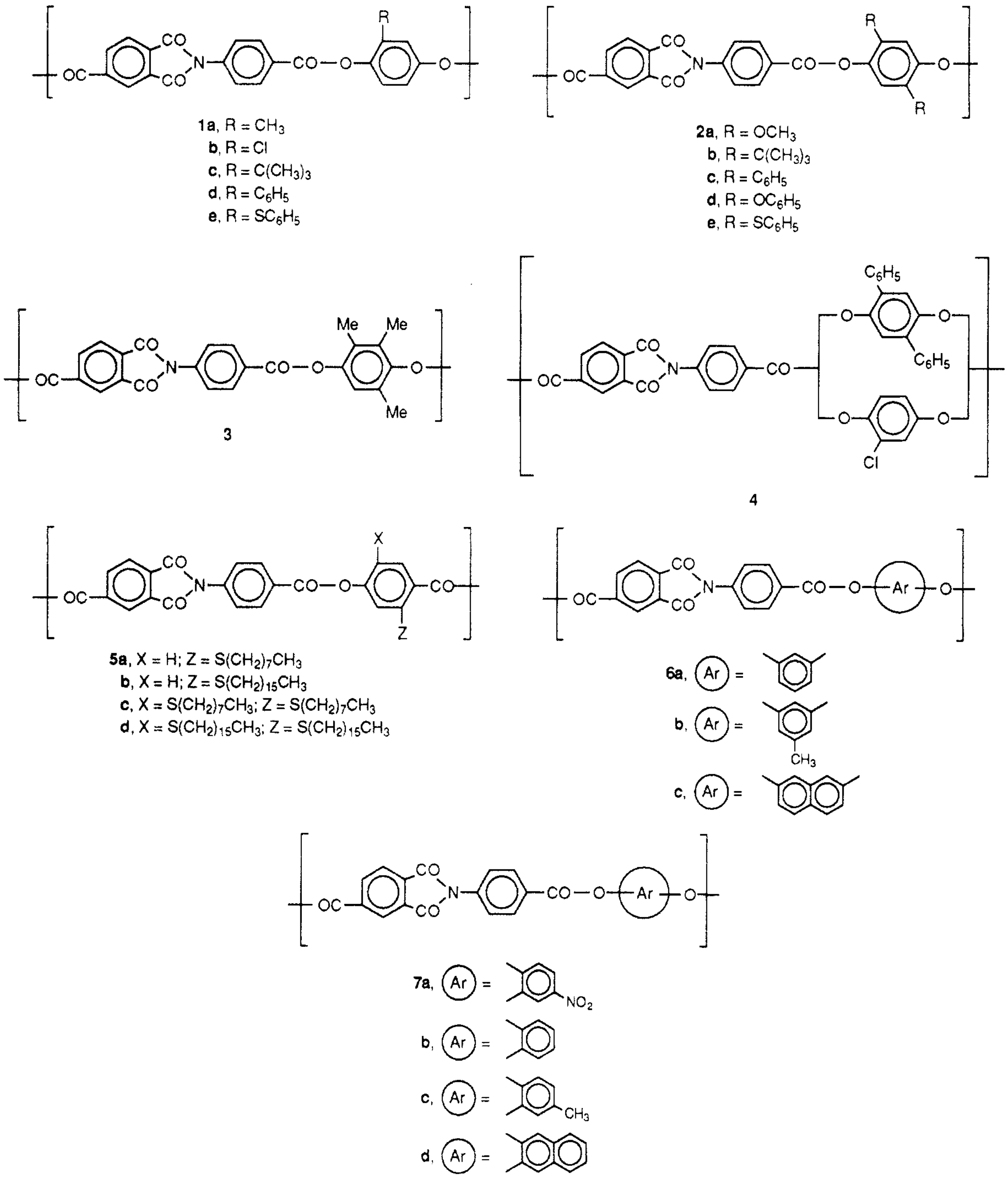
**Chart I**



Afterward, the reaction mixture was stirred for 30 min at 20 °C, then stirred for 2 h at 80 °C, and finally precipitated into methanol. The isolated polyester was dried, dissolved in a mixture of $CH_2Cl_2$ and trifluoroacetic acid (4:1 by volume), and precipitated again with methanol.

**Measurements.** Inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. DSC measurements were conducted with a Perkin-Elmer DSC-4 at a heating and cooling rate of 20 °C/min in aluminum pans under nitrogen. The 100-MHz $^1$H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5-mm-o.d. sample tubes. The WAXS powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Ca K$\alpha$ radiation. The 75.4-MHz $^{13}$C NMR CP/MAS spectra were measured on a Bruker MSL 300 in double-bearing $ZrO_2$ rotors at a spinning rate of 4000–4200 Hz.

## Results and Discussion

**Syntheses.** The structure–property relationships discussed in this work are mainly based on the following three groups of poly(ester imide)s: (A) polyesters derived from *N*-(4-carboxyphenyl)trimellitimide and substituted hydroquinones (**1a–e**, **2a–e**, **3**, and **4** (Chart I)), (B) polyesters derived from *N*-(4-hydroxyphenyl)-4-hydroxyphthalimide and substituted terephthalic acids (**5a–d**), and (C) polyesters of *N*-(4-carboxyphenyl)trimellitimide and *o*- or *m*-diphenols (**6a–d** and **7a–d**). Poly(ester imide)s **1a–d** and **2d,e** have been described previously.[4] Poly(ester imide) **2b** was prepared by polycondensation of bissilylated 2,5-diphenylhydroquinone with the dichloride of *N*-(4-carboxyphenyl)trimellitimide. This so-called "silyl method" (method A in Tables II–IV) was also used for the synthesis of polyesters **3**, **4**, **6a**, **6b**, and **7b–d**. The yields and properties of the silylated diphenols which have never been described before are summarized in Table I.

Poly(ester imide)s **5a–d** were obtained by polycondensation of the acetylated imide diphenol with the substituted terephthalic acids. This so-called "acetate method"

**Table II. Yields and Properties of Poly(ester imide)s Derived from Substituted Hydroquinones and *N*-(4-Carboxyphenyl)trimellitimide**

| polym formula | substituted hydroquinone | synth method | yield (%) | $\nu_{inh}$[a] (dL/g) | $T_g$[b] (°C) | $T_i$[c] (°C) | elem formula (form wt) | elem anal. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | % C | % H | % N |
| **1c** | *tert*-butylhydroquinone | B | 86 | 0.32 | 198[d] | >500 (dec) | $C_{26}H_{19}NO_6$ | calcd | 70.74 | 4.34 | 3.17 |
| | | | | | | | (441.4) | found | 68.05 | 4.64 | 3.44 |
| **2a** | 2,5-dimethoxyhydroquinone | C | 81 | 0.27 | 171 | 450 (dec) | $C_{24}H_{15}NO_6$ | calcd | 64.71 | 3.40 | 3.15 |
| | | | | | | | (445.4) | found | 63.54 | 3.59 | 3.40 |
| **2b** | 2,5-di-*tert*-butylhydroquinone | B | 92 | 0.56 | 234 | isotr | $C_{30}H_{27}NO_6$ | calcd | 72.42 | 5.47 | 2.82 |
| | | | | | | | (497.5) | found | 70.05 | 5.14 | 2.98 |
| **2c** | 2,5-diphenylhydroquinone | A | 42 | 0.60 | 216 | isotr | $C_{34}H_{19}NO_6$ | calcd | 75.97 | 3.56 | 2.61 |
| | | | | | | | (537.5) | found | 74.86 | 3.82 | 2.60 |
| **3** | trimethylhydroquinone | A | 90 | insol | | isotr | $C_{25}H_{17}NO_6$ | calcd | 70.25 | 4.01 | 3.70 |
| | | | | | | | (427.4) | found | 69.17 | 4.02 | 3.43 |
| **4** | chlorohydroquinone + phenylhydroquinone | A | 85 | insol | 200–205 | 345–365 | $C_{56}H_{29}ClN_2O_{12}$ | calcd | 70.26 | 3.05 | 3.48 |
| | | | | | | | (921.8) | found | 69.27 | 3.23 | 3.48 |

[a] Measured at 20 °C with $c = 2$ g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [b] From DSC measurements with a heating rate of 20 °C/min. [c] From optical microscopy with crossed polarizers and a heating rate of 10 °C/min. [d] $T_m = 276$ °C after annealing for 14 h at 230 °C.

**Table III. Yields and Properties of Poly(ester imide)s Prepared from (Alkylthio)terephthalic Acids and *N*-(4-Acetoxyphenyl)-4-acetoxyphthalimide (Method C)**

| polym formula | yield (%) | $\eta_{inh}$[a] (dL/g) | $T_g$[b] (°C) | $T_m$[b] (°C) | $T_i$[c] (°C) | elem formula (form wt) | elem anal. | | | | | layer dist (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | % C | % H | % N | % S | |
| **5a** | 76 | 0.39 | 130 | 225 | 390–400 | $C_{30}H_{27}NO_6S$ | calcd | 68.03 | 5.14 | 2.64 | 6.05 | 23.1 |
| | | | | | | (529.6) | found | 67.31 | 5.15 | 2.69 | 6.18 | |
| **5b** | 85 | 0.21 | 115 | | 190 | $C_{38}H_{43}NO_6S_2$ | calcd | 67.73 | 6.43 | 2.08 | 9.51 | 21.0 |
| | | | | | | (673.9) | found | 67.50 | 6.42 | 2.07 | 9.52 | |
| **5c** | 86 | 0.30 | 130 | 245 | 350–360 | $C_{38}H_{43}NO_6S$ | calcd | 71.11 | 6.75 | 2.18 | 5.00 | 33.9 |
| | | | | | | (641.8) | found | 69.50 | 6.61 | 2.39 | 5.08 | |
| **5d** | 85 | 0.16 | 85 | | 160 | $C_{54}H_{15}NO_6S_2$ | calcd | 72.20 | 8.41 | 1.56 | 7.14 | 35.3 |
| | | | | | | (898.3) | found | 70.61 | 7.77 | 1.68 | 7.24 | |

[a] Measured at 20 °C with $c = 2$ g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [b] DSC measurements with a heating rate of 20 °C/min. [c] From optical microscopy with a heating rate of 10 °C/min.

**Table IV. Yields and Properties of Poly(ester imide)s Derived from Resorcinols or Catechols and *N*-(4-Carboxyphenyl)trimellitimide**

| polym formula | substituent of resorcinol | synth method | yield (%) | $\eta_{inh}$[a] (dL/g) | $T_g$[b] (°C) | $T_i$[c] (°C) | elem formula (form wt) | elem anal. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | % C | % H | % N |
| **6a** | H | A | 96 | insol | 198–202 | *d* | $C_{22}H_{11}NO_6$ | calcd | 68.58 | 2.88 | 3.64 |
| | | | | | | | (385.3) | found | 67.91 | 3.09 | 3.38 |
| **6b** | 4-$CH_3$ | B | 83 | 0.20 | 186 | *e* | $C_{23}H_{13}NO_6$ | calcd | 69.17 | 3.28 | 3.51 |
| | | | | | | | (399.4) | found | 68.33 | 3.50 | 3.28 |
| **7a** | 4-$NO_4$ | C | 94 | insol | 98–100 | 260–270 | $C_{22}H_{10}N_2O_8$ | calcd | 61.40 | 2.34 | 6.51 |
| | | | | | | | (430.3) | found | 60.12 | 2.78 | 5.89 |
| **7b** | H | A | 96 | 0.10 | 150–155 | 260–270 | $C_{22}H_{11}NO_8$ | calcd | 68.58 | 2.88 | 3.64 |
| | | | | | | | (385.3) | found | 68.25 | 3.15 | 3.90 |
| **7c** | 4-$CH_3$ | A | 96 | 0.17 | 165–168 | 370–390 | $C_{23}H_{13}NO_6$ | calcd | 69.17 | 3.28 | 3.51 |
| | | | | | | | (398.4) | found | 68.56 | 3.17 | 3.58 |
| **7d** | naphthalene (condensed) | A | 97 | 0.10 | 178–181 | 420–430 | $C_{26}H_{13}NO_6$ | calcd | 71.73 | 3.01 | 3.22 |
| | | | | | | | (435.4) | found | 70.68 | 3.38 | 3.49 |

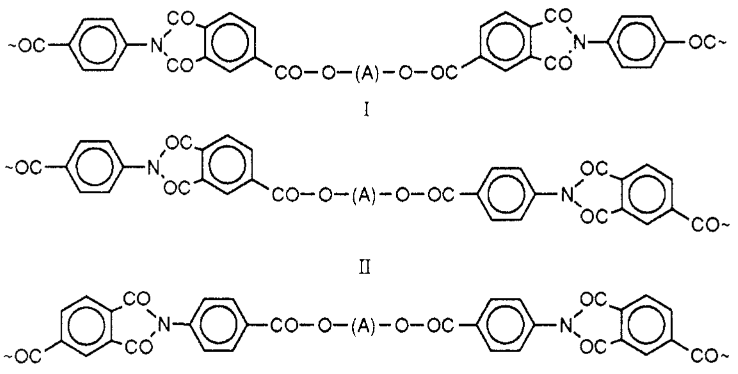
[a] Measured at 20 °C with $c = 2$ g/L in $CH_2Cl_2$/trifluoroacetic acid (volume ratio 4:1). [b] DSC measurements with a heating rate of 20 °C/min. [c] From optical microscopy with a heating rate of 10 °C/min. [d] Melting endotherm at 308 °C and isotropic melt. [e] Melting endotherm (weak) at 234 °C and isotropic melt.

(method B in Tables II–V) was also used for the synthesis of poly(ester imide) **9**. The imide diphenol which forms the basis of polyesters **5a–d** is difficult to obtain in the free or silylated form but easy to prepare as a bisacetate.[14,15] The same argumentation holds for **2b**. The bisacetate of 2,5-bis-*tert*-butylhydroquinone is easy to prepare, whereas the silylation is affected by steric hindrance. Thus the "acetate method" was the most convenient polycondensation method for these six poly(ester imide)s.

In the case of **2a** and **7a** the free diphenol was condensed with the acid dichloride of *N*-(4-carboxyphenyl)trimellitimide in pyridine. This so-called "pyridine method" (method C) was used for the preparation of **2a** and **7a**, because the methoxy and nitro groups are relatively unstable at the high temperatures required for the "silyl method" or "acetate method". The properties of poly(ester imide)s **2a–c**, **3**, **4**, and **5a–d** are summarized in Table II, and those of **6a,b**, and **7a–d** are listed in Table III.

**Properties of Poly(ester imide)s Derived from Substituted Hydroquinones.** Poly(ester imide)s **2a,b**, **3**, **4**, and **5a,b** were all characterized by DSC measurements, WAXS powder patterns, and optical microscopy. The glass transition temperatures are listed in Tables II and III. They are of no importance for the following discussion. All three aforementioned physical methods agree in that **2b** and **2e** are amorphous materials that form an isotropic melt above their glass transition temperatures ($T_g$'s). This result agrees with the previously reported properties of **2d,e** and stands in sharp contrast to the semicrystalline and liquid crystalline (LC) nature of **1a–d**. With the characterization of **2b** and **2c** this surprising structure–property relationship stands on a broader basis. Also, poly(ester imide) **2a** is noncrystalline, but it forms a nematic melt above the glass transition temperature. Obviously, decreasing steric demands of the substituents favors the formation of a nematic phase. This conclusion

**Chart II**



I

II

III

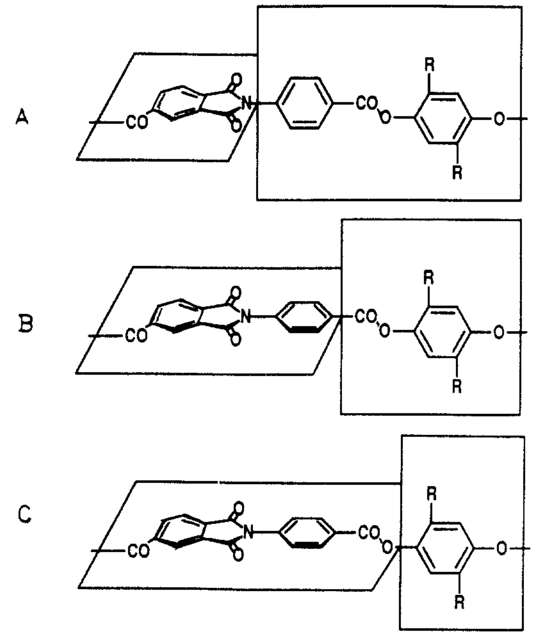
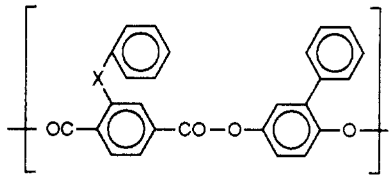


**Figure 1.** Formation of chiral repeating units by rotational isomerism of poly(ester imide)s **2a–e**.

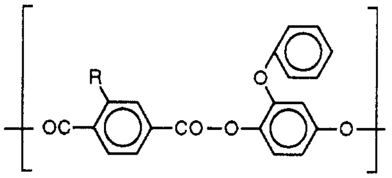
is supported by the properties of copolyester **4**. Here, the "dilution" of the two phenyl groups by the one small chloro substituent enables the existence of a nematic phase. Polyester **3** deviates from the properties of both series **1a–d** and **2a–e**, because it is highly crystalline with a melting point above 400 °C, where rapid thermal degradation prevents a reliable characterization of the melt.

The hypothetical explanation of these unexpected properties of **2a–e** forwarded in this work takes three parameters into account: sequence effects, conformation dependent chirality, and donor–acceptor interactions. Due to the lacking symmetry of trimellitimide, poly(ester imide)s of *N*-(4-carboxyphenyl)trimellitimide are copolymers of head-to-head and head-to-tail sequences (formulas I–III, Chart II). This lack of regularity is certainly unfavorable for the crystallization, but it doeos not suffice to explain the amorphous character of **2a–e**, because the poly(ester imide)s of hydroquinone,[4] chloro- and (phenylthio)hydroquinone,[4] and *tert*-butylhydroquinone (Table II) can crystallize. A second steric effect which causes at least a kinetic hindrance of crystallization is the conformation-dependent chirality of the repeating units of **2a–e**. As illustrated in Figure 1, rotation of the hydroquinone unit relative to the trimellitimide system leads to a time-dependent chirality which vanishes when all aromatic rings are coplanar.

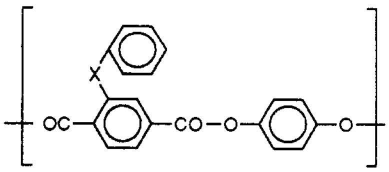
However, computer modeling with a force field program (Insight II of Biosym) indicates that a coplanar conformation of the entire repeating unit is not the energetically most favorable conformation. Also for reasons of entropy is it unlikely that all repeating units of a chain are permanently coplanar. Thus, poly(ester imide)s such as **2a–e** may tend to be amorphous like atactic poly($\alpha$-olefin)s, even if their chirality is not fixed by $\sigma$-bonds. However, the irregular sequences and conformations of poly(ester imide)s **2b–e** do not explain why they are not liquid crystalline, because the monosubstituted poly(ester imide)s show sequential and conformational isomerisms similar to those of the disubstituted ones. Therefore, the third parameter taken into account is a general steric hindrance of the LC character. Obviously, two substituents per repeating units efficiently destabilize the nematic order. This observation is not limited to poly(ester imide)s. For instance, the disubstituted poly(hydroquinone terephthalate)s **8** and **9** are exclusively isotropic or possess a low isotropization temperature (<200 °C, **8**, X = S).[17-19] In contrast, the monosubstituted analogs **10** and **11** are nematic with isotropization temperatures above 350 °C or even above 450 °C.[17-20]



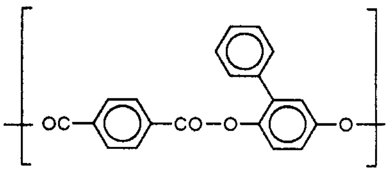
8, X = O, S



9, R = $CF_3$, $C_6H_5$



10, X = O, S



11

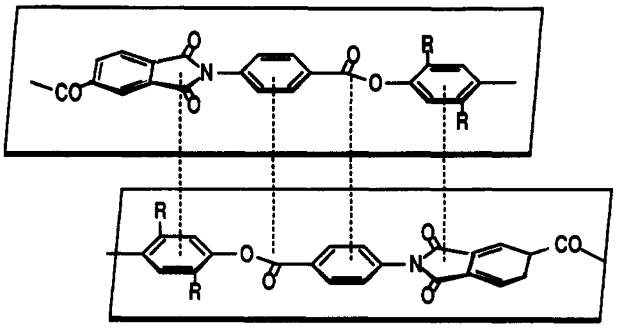


**Figure 2.** Donor–acceptor interactions in temporarily coplanar chain segments of poly(ester imide)s **1a–e** or **2a–e**.

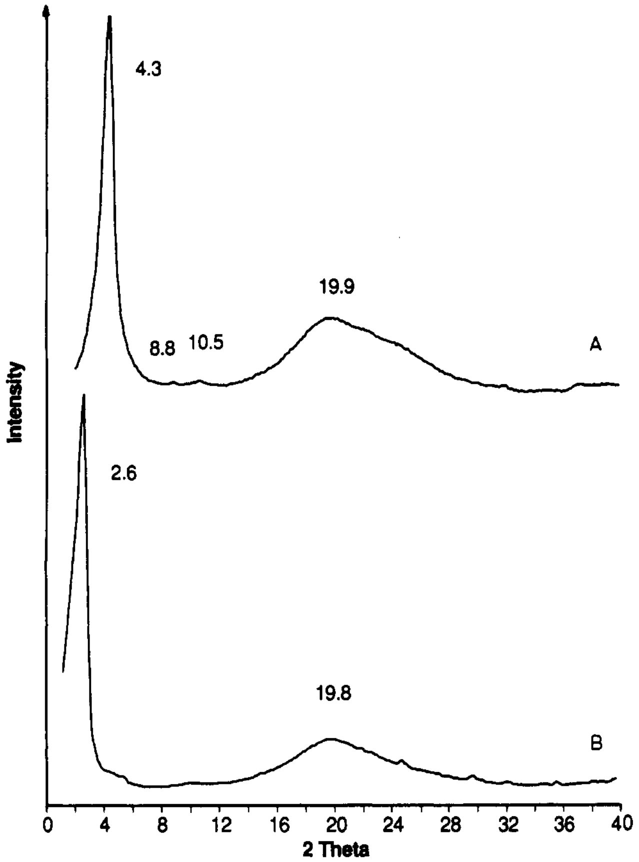


**Figure 3.** WAXS powder patterns of poly(ester imide)s **5c** (A) and **5b** (B).

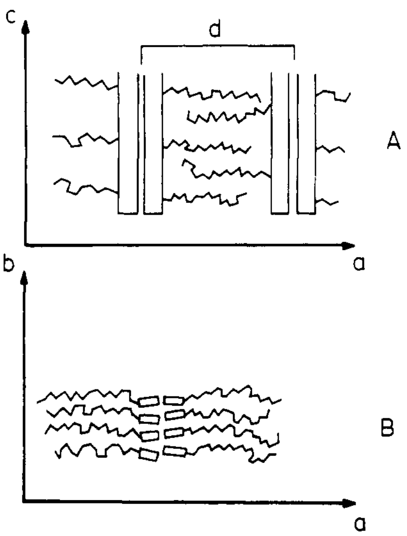


**Figure 4.** Scheme of the chain packing of the monosubstituted poly(ester imide)s **5a,b**.

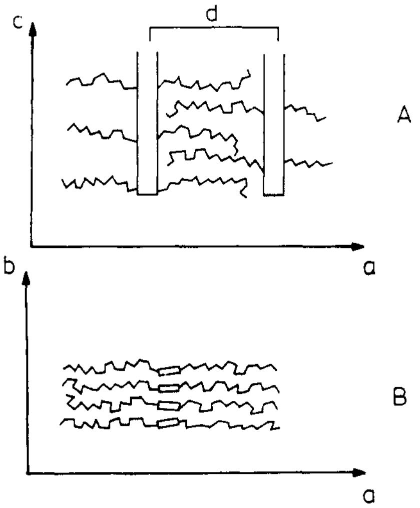


**Figure 5.** Schematic chain packing of the disubstituted poly(ester imide)s **5c,d**.

At this point the question arises if the second substituent substantially reduces the persistence length and thus eliminates the "rigid rod character" or if it hinders specific electronic interactions between neighboring coplanar chain segments. To elucidate the problem of reduced persistence length, space-filling models were constructed, and computer modeling with a force field program was conducted. Yet neither approach gave any indication that a second substituent reduces the persistence length. In contrast, a second *tert*-butyl group (**2b**) or phenyl group (**2c**) slightly enhances the chain stiffness because kinking and bending of the main chain may cause steric interactions between two substituents or one substituent and backbone. Consequently, the second hypothesis has to be examined. If the dipole–dipole and $\pi$–$\pi$ electron interactions of temporarily coplanar chain segments make a significant contribution to the nematic order (Figure 2), it is obvious that an increasing number and bulkiness of substituents destabilize this order, when the rotation of monomeric units according to Figure 1 is also taken into account. For the sake of brevity, all electronic interactions favoring the parallelization of chain segments will be summarized now under the term donor–acceptor interactions (DA).

**Poly(ester imide)s of Substituted Terephthalic Acids.** The WAXS powder patterns of the poly(ester imide)s **5a–d** (Figure 3) are characteristic for polymers with a sanidic layer structure. Polyesters and polyamides of 2,5-bis(dodecyloxy)terephthalic acid show similar WAXS patterns.[21-23] The layer distances calculated from the sharp, intense small-angle reflections (Table II) suggest that the sanidic chain packing involves a complete "interdigitating" of the side chains. The greater layer distances (*d*-spacings) of the monosubstituted polyesters also suggest that these polyesters form "double layers" by a back-to-back array of the backbones (Figure 4). A similar type of chain packing was reported for poly(3-*n*-alkyl-4-hydroxybenzoic acid)s.[24] The disubstituted poly(ester imide)s form "monolayers" analogous to those known for polyesters of 2,5-dialkoxyterephthalic acids (Figure 5). The WAXS powder patterns, $^{13}$C NMR CP/MAS spectra, and the DSC measurements (Figure 6) agree in that the alkyl side chains do not form crystalline paraffin domains between the stakes of the main chains. Yet a more detailed study of the solid state was beyond the scope of this work.

The DSC measurements revealed a characteristic difference between the mono- and disubstituted poly(ester imide)s because a melting endotherm is only detectable for **5a** and **5b** (Figure 6). Examination by optical microscopy confirmed that these endotherms are indeed

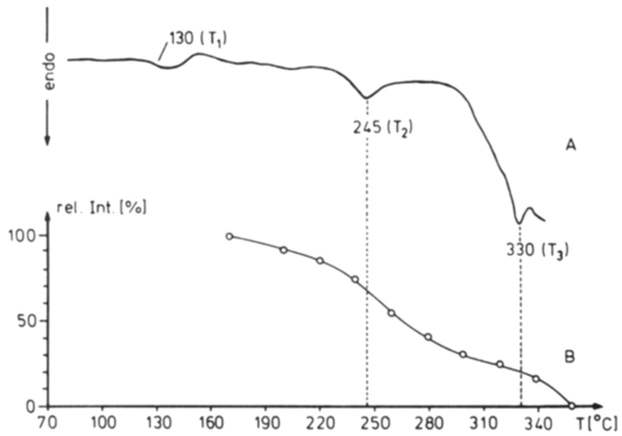


**Figure 6.** Thermal properties of poly(ester imide): (A) DSC heating curve (heating rate 20 °C/min); (B) intensity of the small-angle reflection.

transitions from a solid state to a mobile mesophase. In the case of **5c** and **5d**, mobile mesophases are formed immediately above the glass transition temperature (Table II). Another characteristic difference exists between the poly(ester imide) with short side chains (**5a,c**) and those with long side chains (**5b,d**). The schlieren texture of molten **5a** and **5c** indicates a normal nematic mesophase. This conclusion is confirmed by WAXS measurements of the melt which prove the absence of all reflections in the molten state. In contrast, a sharp small-angle reflection is detectable for the mobile mesophase of **5b** and **5d** (Figure 6B). Figure 6B illustrates for **5b** how the intensity of this small-angle reflection decreases with increasing temperature. Obviously, a kind of layer structure is maintained in the molten state. Such a mesophase may be called a liquid sanidic phase or a biaxially oriented nematic phase. Also, the texture of these mesophases is different from that of the nematic phase.

The most interesting aspect for the purpose of this work is the influence of the side chains on the stability of the mesophase regardless of its structure. The comparison of **5a,c** with **5b,d** reveals that doubling of the length of the side chains reduces the isotropization temperature by 30–40 °C. A similar side chain effect was also reported for the poly(3-*n*-alkyl-4-hydroxybenzoic acid)s **12**.[25] Taking into account the volume ratio of main chain and side chains and the persistence length, the dependence of the isotropization temperature on the length of the side chains was correctly calculated. This calculation exclusively based on entropy changes clearly does not explain the difference between the mono- and disubstituted poly(ester imide)s **5a,b** and **5c,d**. Here, the second substituent reduces the isotropization temperature by nearly 200 °C. Particularly informative is the comparison of **5b** with **5c**, because the volume ratio of the main chain and substituents is here nearly identical. Hence, the lower $T_i$ of **5c** (and **5d**) must be attributed either to a significantly shorter persistence length or to enthalpic interactions of **5a** and **5b** which are sterically hindered by the second substituent of **5c** and **5d**. Once again, no reason could be found for why and how the second substituent should reduce the persistence length. However, when higher temperatures enable the rotation of the aromatic rings around the para axes, two side chains prevent a direct interaction of neighboring main chains more efficiently. Thus, the structure–property relationships of **5a–d** agree well with those of poly(ester imide)s found for substituted hydroquinones.

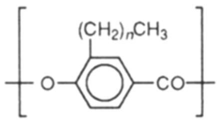


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**Figure 7.** Texture of poly(ester imide) **7c** at 310 °C.

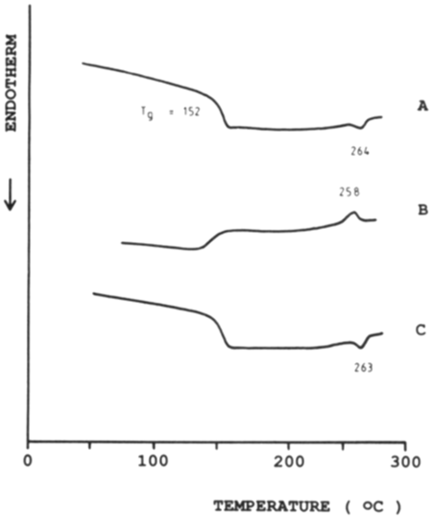
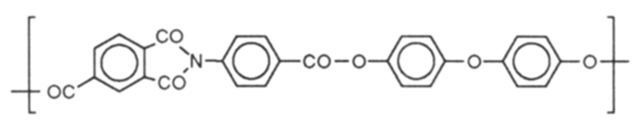


**Figure 8.** DSC measurements (heating and cooling rate 20 °C/min) of the catechol-based poly(ester imide) **7c**: (A) first heating; (B) first cooling; (C) second heating.

**Properties of Poly(ester imide)s Derived from Nonlinear Diphenols.** The carboxyl groups of *N*-(4-carboxyphenyl)phthalimide neither are arranged on a straight line nor is their arrangement strictly parallel. Hence, this dicarboxylic acid is a kind of kink unit. However, this kink effect is weak and a combination with a linear diphenol such as hydroquinones may induce a sufficiently effective rigid-rod overall structure of the main chain to allow for the formation of a nematic melt. This argumentation does not hold when nonlinear diphenols are used as comonomers, but optical microscopy unambiguously revealed that the poly(ester imide)s **6c** and **7a–d** form a nematic melt. This nematic phase shows a typical schlieren texture as illustrated by Figure 7 and is reversible upon cooling from the isotropic melt. The isotropization of **7a–c** is also detectable as a weak endotherm in the heating curves (Figure 8). In the case of **6a** the melting point is high (Table IV) and the melt is isotropic. Poly(ester imide) **6b** has a lower melting point, but its melt is again isotropic. Yet, the polyester of 2,7-dihydroxynaphthalene **6c** forms a nematic melt up to approx 420 °C, which is difficult to explain by a rigid-rod structure. However, the naphthalene ring is a better $\pi$-donor than

**Chart III**



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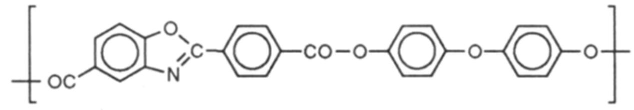

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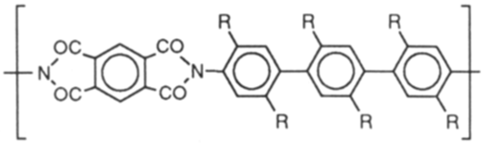
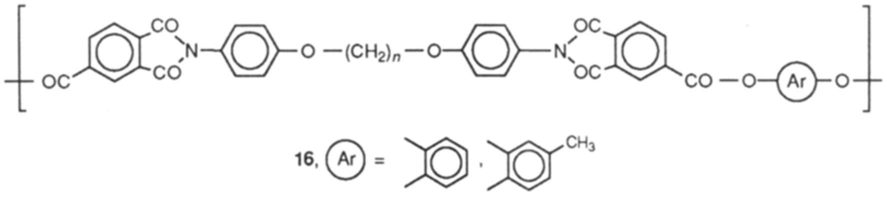


15, R = *n*-alkyl



16, Ar =

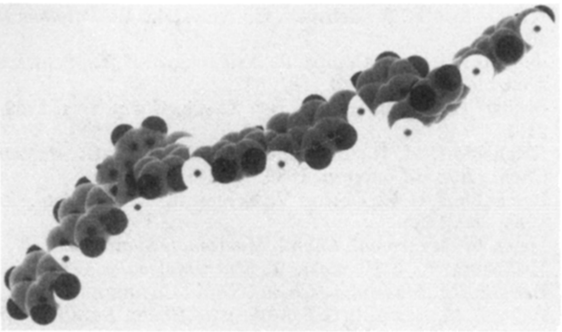


**Figure 9.** Most extended conformation of the catechol-based poly(ester imide) **7b** as obtained by molecular modeling with a force field program.

the benzene ring and, thus, can stabilize a DA interaction with a neighboring imide ring.

These poly(ester imide)s are again not able to adopt a linear conformation comparable with that of poly(hydroquinone terephthalate). Kinks or bends of the polyester backbone are unavoidable. One of the most extended conformations generated by computer modeling of **7b** with a force field program on the search for a relative energy minimum is displayed in Figure 9. The most interesting and informative result was obtained when the absolute energy minimum of all possible conformations was searched. Regardless of the conformation used as a starting point of the optimization process, a perfectly folded conformation with coplanar imide systems was obtained (Figure 10). The energy minimum of this folded conformation is 10–15% lower than all minima of more or less extended conformations and, thus, leaves little space for skepticism about the significance of the optimization processes. Computer modeling of poly(ester imide)s **7a**, **7d**, and **7d** gave analogous results. The chain folding is of course the typical result of the computer treatment of a single chain in vacuum. In a realistic nematic phase the electronic interactions will predominantly involve neighboring chains. However, the results of the computer modeling clearly indicate that the DA interactions of nearly coplanar imide systems dominate the overall conformational energy situation.

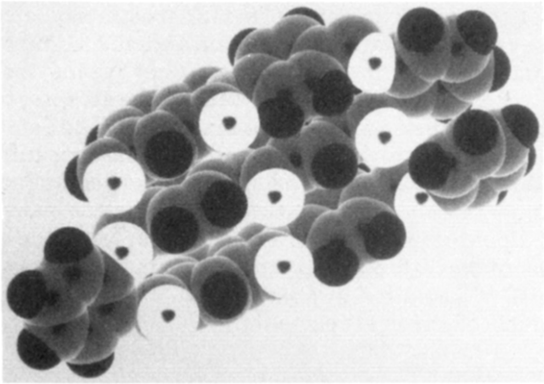


**Figure 10.** Energetically most favorable conformation of the catechol-based poly(ester imide) **7b** as obtained by computer modeling with a force field program.

Another interesting result emanating from the comparison of **7a–d** is the observation that the stability of the nematic phase strongly increases in the oder **7b** < **7c** < **7d** (see $T_i$ in Table IV). This trend cannot be explained by increasing linearity of conformation or chain stiffness. However, this order parallels an increase of electron density and polarizability of the $\pi$-electrons and suggests that the *o*-diphenols also participate in DA interactions with imide rings in the nematic phase. This observation also fits in with the nematic character of **6c** in contrast to **6a** or **6b**. The hypothesis of donor–acceptor interactions is further supported by the following observations. Poly(ester imide) **13** (Chart III) is thermotropic,[5] whereas polyester **14** is not despite a nearly identical stereochemistry.[26] Since the benzoxazole ring is an electron-rich $\pi$-system in contrast to the trimellitimide system, it cannot act as a $\pi$-acceptor for the electron-rich diphenyl ether unit, and this aspect seems to be decisive. Furthermore, a comparison of polyimide **15** and poly(ester imide)s **16** is of interest in this connection. Polyimide **15** is an ideal rigid-rod polymer and, thus, an optimum candidate for the formation of a LC phase from the stereochemical point of view. However, its melt is reported to be isotropic.[27] In contrast, poly(ester imide)s of structure **16** are highly flexible, and even the mesogenic group is neither linear nor stiff. Nonetheless, these poly(ester imide)s form nematic or smectic melts with isotropization temperatures >300 °C (described in a future part of this series[28]). This comparison suggests again that electronic interactions between coplanar $\pi$-systems may play a significant role for the formation of LC phases. If this interaction is hindered by substituents, even a perfect rigid-rod structure may not suffice to establish a mobile mesophase.

Furthermore, recent studies of three different research groups concerning the chain packing of oligo- and poly(ether imide)s revealed that the stacking of the aromatic rings occurs in such a way that imide groups are superimposed on electron-rich phenyl ether units and not on each other, as expected for an optimization of dipole–dipole interactions. Correspondingly, the authors[29–31] concluded that the chain packing in the solid state is governed by DA interactions.

To avoid misunderstanding, it should finally be emphasized that the DA interactions discussed in this work do not mean charge-transfer (CT) complex. CT complexes are an extreme case of DA interactions involving a true electron transfer which is spectroscopically detectable. To elucidate if the strongest imide acceptor used in polyimides and the best donors used in this work can form CT complexes, mixtures of $N,N'$-dihexylpyromellitimide and 2,7-diacetoxynaphthalene were examined in $10^{-4}$–$10^{-5}$ M $CHCl_3$ solution. No change of the UV spectra was detected. However, this negative result is no argument against the existence of DA interactions. It only means that an electron transfer from the "HOMO" of the acceptor to the "LUMO" of the donor does not take place. The detection of a normal DA interaction on dilute solution is difficult for three reasons: first, the spectroscopic consequences are poor, second, the polarization of electron pairs like any dipole–dipole interaction decreases with the sixth power of the distance, and third, any bimolecular reaction is in $10^{-4}$ M solution by a factor of $10^{10}$ less likely than in the melt of the neat reactants.

## Conclusion

The numerous observations discussed in this work suggest that, in addition to stereochemical factors such as rigidity, linearity, and symmetry, the strength and direction of interchain forces may play an important role for the stabilization of a nematic phase. Interactions between temporarily coplanar aromatic $\pi$-systems, particularly donor–acceptor interactions, can make an efficient contribution of this kind. This hypothesis, if correct, bears a couple of interesting consequences. For instance, a greater variety of nonlinear monomers may be considered as useful building blocks for LC polyesters. *o*-Diphenols and *m*-diphenols should not be called interrupting units.[32] Monosubstituted monomers (e.g., hydroquinones or terephthalic acids) are more useful for the synthesis of nematic polymers than di-, tri-, or tetrasubstituted monomers. Furthermore, a sharp borderline between nematic and mobile discotic phases should not exist.

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