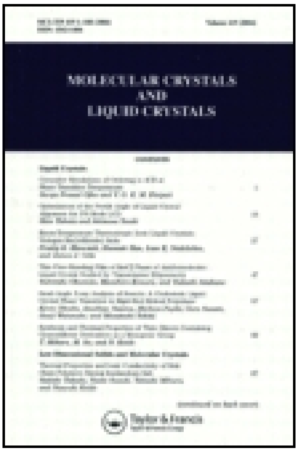

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Liquid-Crystalline Polyimides

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LIQUID-CRYSTALLINE POLYIMIDES

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Abstract: This paper presents a short review of liquid-crystalline (LC)polyimides. It is shown that it is difficult to obtain LC-polyimides free of ester groups. Only three examples of such polyimides have been found so far. LC-Poly(ester-imide)s may be subdivided into two groups. The first groups contains aliphatic spacers in the main chain and possesses a high tendency of forming layer structures in the solid state. The origin of the layer structures is discussed. The second group conprises poly(ester-imide)s with a fully aromatic main chain. The role of substituents, conformations and donor-acceptor interactions for the stabilization of nematic phases is discussed.

INTRODUCTION

Polyimides, including poly(amide-imide)s, poly(ester-imide)s and poly(ether-imide)s are known for several decades. Several members of this versatile group of polymers were commercialized by chemical companies in many countries. The high thermal stability and low sensitivity to oxydation of aromatic imide groups are the most useful and conspicious properties of polyimides. Polyimides were and are used as engineering plastics, thermosetting resins fibers, insulating laquers for electric wires and photoresists1-8). With exception of some copoly(ester-imide)s composed of three or more comonomers9,10) none of the numerous polyimides described before 1987 were reported to be thermotropic or lyotropic.

The research activities of the present author and other groups have meanwhile revealed that the best chance to obtain LC-polyimides consists of a combination of imide and ester groups in the main chain. The imide groups impart thermostability, stiffness polarity and sometimes linearity, the ester groups impart flexibility but also linearity. LC-Polyimides free of ester groups are rare and only three classes with this combination of properties were found by the present author so far[11-13]).

LC-POLYIMIDES FREE OF ESTER GROUPS

Starting from the "bisanilino spacer" 1 several classes of poly(ether-imide)s, 2, were prepared. Only the poly(ester-imide)s derived from 3,3',4,4'-biphenyl tetracarboxylic anhydride (X=σ-bond) form a LC-phase. The melting points display an odd-even effect upon variation of n. The melt exhibits a "batonet-texture" typical for a smectic A-phase. Detailed X-ray studies are in progress[11]).

Polycondensation of 1 with trimellitic anhydride yields the thermotropic poly(amide-imide)s 3. Again a layer structure in the solid state and a smectic melt with "batonet-texture" was observed[12]). Polycondensation of N-(4'-carboxyphenyl)trimellitimide (in the form of its acid chloride) with 1,4-diaminobenzene yielded the poly(amide-imide) 4. This polyaramide forms a lyotropic LC-phase in conc. H_2SO_4 above a concentration of 20% (w/v)[13]), despite its nonlinear backbone. Interestingly a more linear copolyamide containing terephthalic acid as comonomer was not lyotropic. This finding raises the questions, if a regular sequenz of amide groups is important for the formation of a lyotropic phase.

POLY(ESTER-IMIDE)S WITH ALIPHATIC SPACERS

Due to the stiff and planar structure of aromatic imide groups and owing to their high polarity the melting points of poly(ester-imide)s (PEI's) my be extremely high (e.g. > 500°C) particularly, when symmetrical imide units are present in the chain. In order to obtain meltable and soluble PEI's, incorporation of flexible spacers into the main chain is one (but not the only) successful strategy.

Interestingly, it was found that poly(ester-imide)s derived from highly symmetrical imide units, such as pyromellitic imide, naphthalene 1,4,5,8-tetracarboxylic imide etc. (5a-c,6,7) are not liquid crystalline. They are highly crystalline with degrees of crystallinity above 80%, and they form layer structures in the solid state but their melt is isotropic[14-17]. In this connection it should be noticed that preliminary publications of Aducci[18] and Sroog[19] suggest the existence of enantiopropic LC-phases in the case of poly(esterimide)s 5a. However detailed studies of the present author have shown[14] that these PEI's are indeed isotropic. Furthermore, the properties of the polycarbonates 8 confirm[20], that the pyromellitimide unit is a poor mesogen. However, a special class of PEI's based on N,N'-dihydroxypyromellitimide (9) was reported to possess broad nematic phases[21].

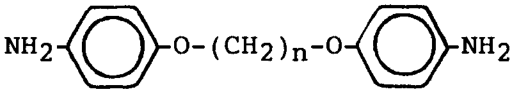
In contrast, thermotropic PEI's may be obtained by polycondensation of the dicarboxylic acids 10 with diphenols, such as hydroquinone, 2,6-naphthalene diol or 4,4'-dihydroxybiphenyl[22,23]. With other diphenols crystalline or amorphous isotropic PEI's were obtained. The thermotropic PEI's based on 10 form a smectic melt (smectic A according to texture) and they form layers in the solid state. According to X-ray data the layer distances of the solid state display a strong odd-even effect. Furthermore, the melting temperatures (T_m) show an odd-even effect, with the even spacers yielding the higher T_m's[23]. The ^{13}C NMR CP/MAS spectra indicate that the aliphatic spacers prefer gauche conformations. These results taken together suggest the layer-structures outlined in Figure 1. When 4-hydroxy benzoic acid is incorporated into a homopolyester of 10 and hydroquinone (copolymer 11) the following two changes take place. Firstly, the layer structure of the solid state is gradually transformed into a columnar mesophase with more or less perfect hexagonal chain packing (Fig. 2). Secondly, the LC-phase shows a gradual transition from smectic to nematic[24).

Another group of PEI's with interesting structure-property relationships are the two isomeric classes 12 and 13[25,26). For the PEI's 12, based on a imide diphenol, WAXD pattern and optical microscopy indicate a crystalline state with layer structure, but a nematic melt. The nematic melts of 12 show strong odd-even effect of the isotropization temperatures (T_i)[25). The properties of the isomeric PEI's 13 are completely different[26). In contrast to what Aducci and Sroog have claimed in a review[19), this class of PEI's does not form an enantiotropic LC-phase[26,27). However, short-living monotropic LC-phases may be observable upon rapid cooling from the isotropic melt[27). It is characteristic for the PEI's 13 that members with n ≥ 6 can form three different kinds of solid state as evidenced by DSC and X-ray measurements (Fig. 3).

When fibers of PEI's 13 (n ≥ 7) were spun from the isotropic melt, the X-ray fiber patterns indicate the formation of a highly perfect series of layers with the layer planes perpendicular to the fiber axis. Interestingly ^{13}C NMR CP/MAS spectroscopy and WAXD patterns indicate that there is no order inside the layers of spacers or mesogens. This means, the fibers exist (without annealing) in the form of a smectic glass, which may be considered as a frozen smectic-A structure. The formation of layers without any order inside the layers is thus best understood as phase separation on the nanometer scale. The difference between the non-polar alkane spacers and the highly polar imide groups is responsible for the high tendency of semi-rigid PEI's to form layer structures. This hypothesis is confirmed by the observation that PEI's containing polar poly(ethylene-glycol) spacers (e.g. 15) do not tend to form layers. These PEI's are amorphous and isotropic, obviously because polar spacer and imide unit are compatible with each other. Only long annealing (3 days) induces partial crystallization.

Whereas the PEI's derived from the dicarboxylic acid 14 and aliphatic spacers (13, 15, 16) do not form enantiotropic LC-phases, polycondensation of 14 with the semi-aliphatic spacers 17 yields nematic PEI's28). From the polycondensation of 14 with the chiral spacers 18a and b enantiomeric, cholesteric PEI's were obtained29).

Although the extension of the poor mesogen 14 by partially aromatic spacers (17,18) succeeded in the creation of LC-PEI's the extension with an aromatic ether group (structure 19) was not successful. The PEI's 19 are crystalline with layer structures in the solid state but form an isotropic melt30). In contrast, the crystalline PEI's 20 form enantiotropic LC-phases, despite a short imide unit. Obviously, the connection with 4,4'-dihydroxybiphenyl via an ester group generates the mesogenic character. It is of particular interest, that members with higher"n-values" (n= 10,11) are capable of forming both a smectic and a nematic phase31). Finally, PEI's derived from the dicarboxylic acids 21 should be mentioned32). With 4,4'-dihydroxybiphenyl again LC-phases were found, whereas with most other diphenols the melt is isotropic.



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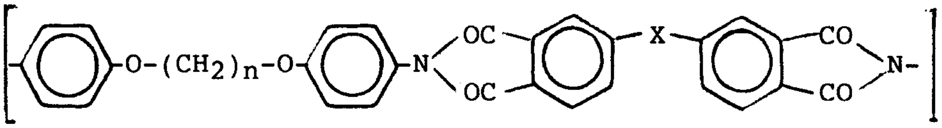
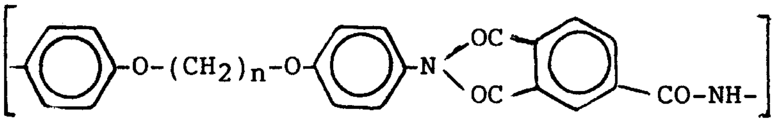


2

X = σ-bond
X = O, CO, SO_2, $C(CF_3)_2$



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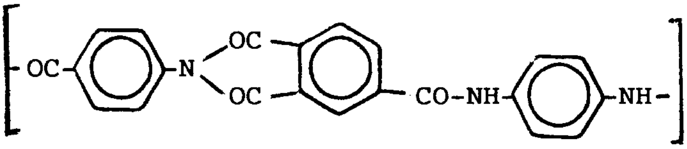

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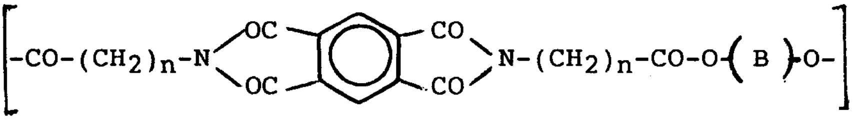
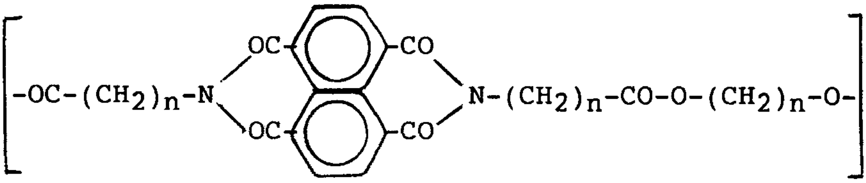


5

a: (B) = $-(CH_2)_n-$
b: (B) = $-(OCH_2CH_2)_m-$
c: (B) = various diphenols



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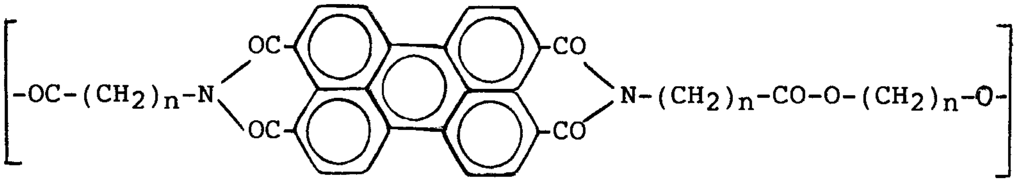

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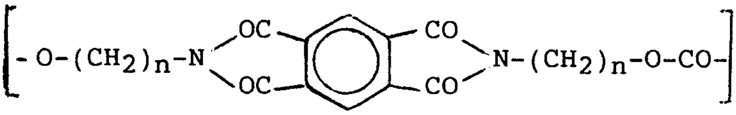

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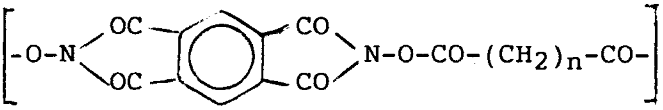

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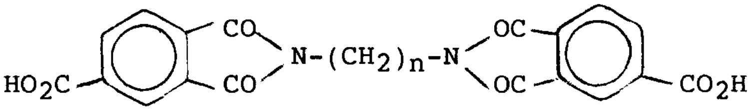

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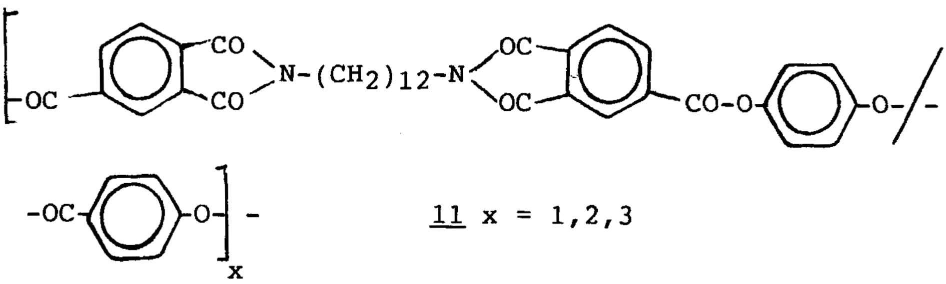
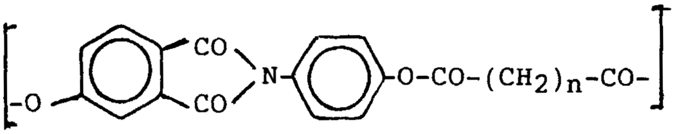
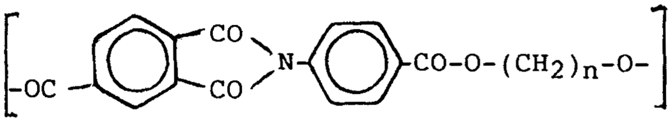


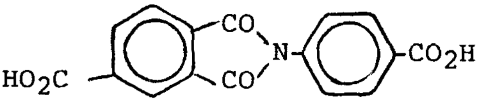
11 x = 1,2,3



12 n = 4 - 12



13 n = 4 - 12



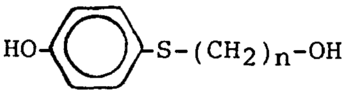
14

$HO-(CH_2-CH_2-O)_n-H$

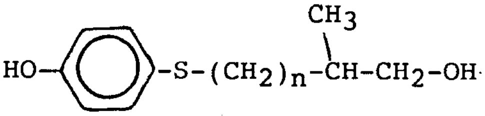
15 n = 2,3,4

$HO(CH_2)_3-S-(CH_2)_n-S-(CH_2)_3-OH$

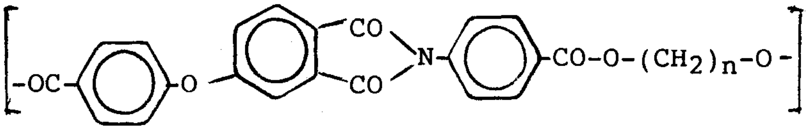
16 n = 4,6



17 n = 2 - 5



18 a: S
b: R



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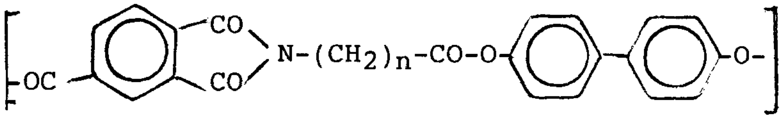

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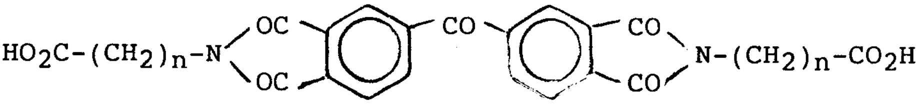

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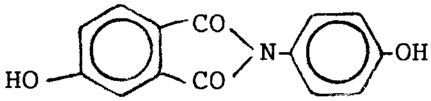

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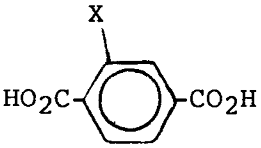


23 a: X = O

b: X = S

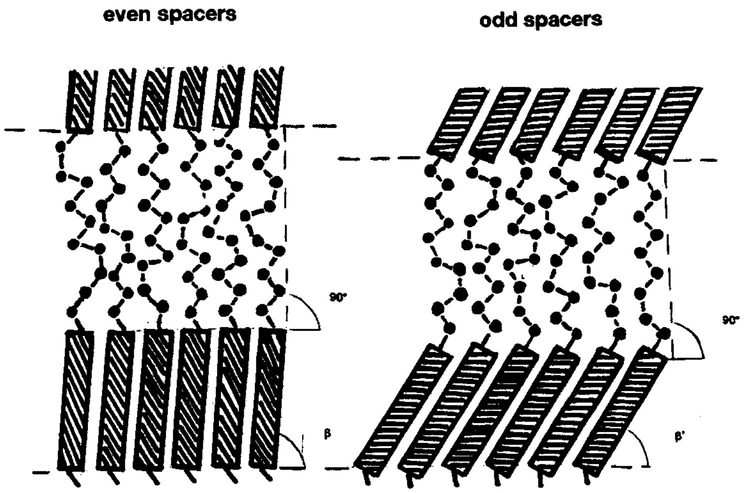


FIGURE 1: Schemes of the layer structures of PEI's derived from 10 and hydroquinone (or 4,4'-dihydroxybiphenyl) and of PEI 13.

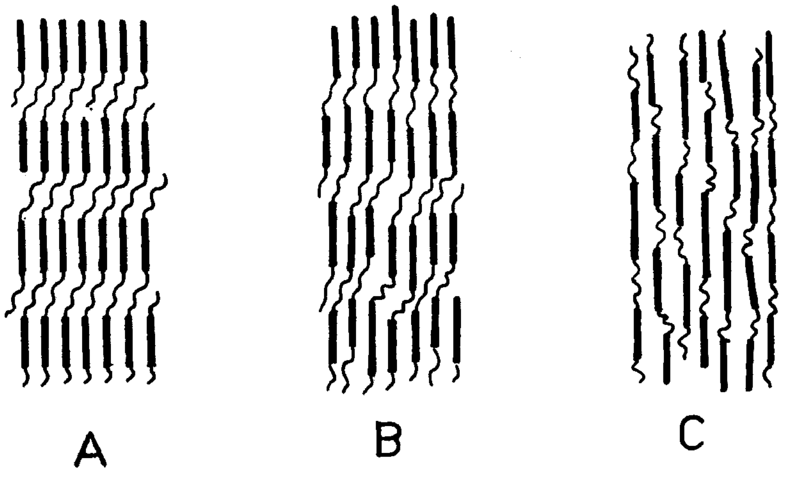


FIGURE 2: Schematic chain packing of the copoly(esterimide)s 11 with increasing molar fraction of 4-hydroxybenzoic acid (n = 1,2,3).

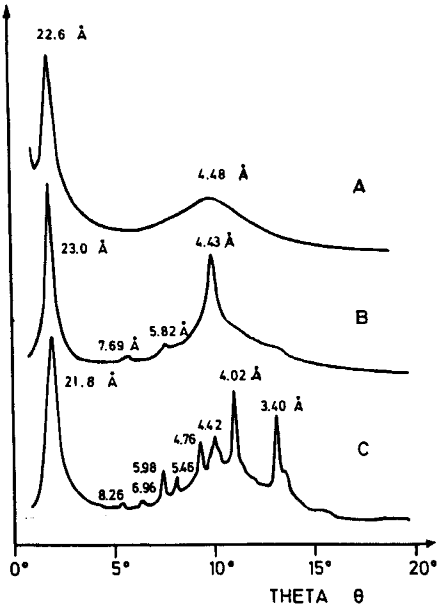


FIGURE 3: WAXD powder patterns of PEI 13 (n = 8): A) after quenching from the isotropic melt, B) after annealing at 160°C for 16 h; C) after annealing at 185°C for 16 h.

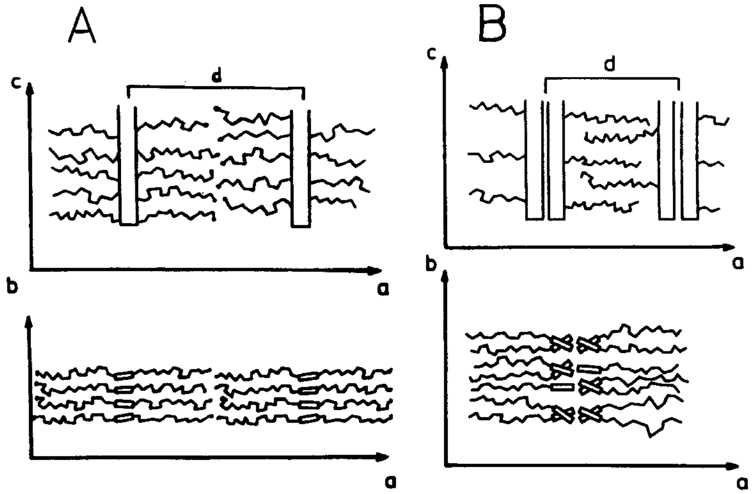


FIGURE 4: Schematic drawing of the layer structures formed by the PEI's derived: B) from 22 and mono(alkyl-thio)-terephthalic acids 24a, b; A) from 22 and bis-(alkyl-thio)terephthalic acids 25a, b.

PEI'S WITH FULLY AROMATIC MAIN CHAIN

Fully aromatic PEI's were first described in a patent of DuPont9) and later in a patent of Idemitsu Chem.10). However, these PEI's were all copolyesters of three or more monomers, and only one of them, namely the dicarboxylic acid 14, was an imide. Therefore, these copolyesters do not tell much about the properties of PEI's. When 14 is replaced by another dicarboxylic acid such as naphthalene-2,6-dicarboxylic acid, the properties of the copolyesters are esentially the same.

Thermotropic homopoly(ester-imide)s were obtained when the imide diphenol 22 was polycondensed with substituted terephthalic acids such as 23a or b33). These PEI's form a broad nematic melt. The PEI derived from 21 and unsubstituted terephthalic acid is neither meltable nor soluble in common inert solvents. Of particular interest are the PEI's derived from 22 and n-alkyl-substituted terephthalic acids 24a, b or 25a, b34). WAXD patterns suggest that these PEI's form a sanidic type of layer structures in the solid state (Figure 4). Upon melting the monosubstituted PEI's (24a, b) form a normal nematic phase, whereas the disubstituted ones (25a, b) presumably yield a biaxially oriented nematic melt.

The most interesting aspect of these PEI's consists of a comparison of 24a, b with 25a, b. In the latter case the isotropization temperatures (T_i) are 200°C below those of 24a, b. This difference cannot be attributed to entropic effects of the side chain, because the number of side chain carbons is identical for 24b and 25a. Since the second substituent does not reduce, but rather improve, the chain stiffness, it may be assumed that electronic interactions (e.g. dipole-dipole and donor-acceptor DA) between temporarily coplanar chain segments stabilize the nematic order of 24a and b. A second substituent in combination with rotation of the aromatic rings around their para-axis will certainly affect the efficiency of such electronic interactions. This new hypothesis of DA-interactions[32,34)] is supported by the following observations.

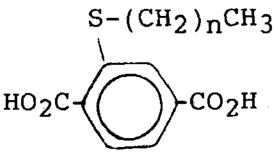
Polycondensation of the dicarboxylic acid 14 with hydroquinone yields a crystalline PEI which is neither meltable nor soluble. However, with monosubstituted hydroquinones such as 26a - e meltable or amorphous PEI's were obtained which form a nematic melt over a broad temperature range[33,35)]. An even higher tendency to crystallize and to form LC-phases was expected for the PEI's derived from 14 and the disubstituted hydroquinones 27a - e. Whereas 26a indeed obeys this expectation all PEI's with bulkier substituents show isotropic melts and are even amorphous in the case of 27c - e. Since again no reason is in sight, why a second bulky substituent reduces the chain stiffness, it is most likely that more and bulkier substituents hinder the electronic (DA) interaction between neighboring chain segments. In this connection a comparison of the polyesters 28 and 29 is of interest. PEI 28 is composed of the electron rich diphenylether unit and an electron deficient imide group. It forms a nematic melt obviously stabilized by DA-interactions[36)]. Incontrast, 29 exclusively contains electron rich rings, which can all serve as donors, but not as acceptors, and this polyester is isotropic[37)].

Another interesting comparison is that between PEI 30 and 31[34)]. The melt of 30 is isotropic, but that of 31 nematic. It is difficult see, why the chain stiffness of 31 should be higher. However, the naphthalene unit of 30 is a better π-donor than the resorcinol unit in 30. Even more conspicous are the properties of the PEI's 32 and 33[34)]. All four PEI's form a nematic melt, albeit they do not possess linear stiff structure. Furthermore, the stability of the LC-phase increases in the order 32a ~ 32b < 32c < 33 which is the order of increasing electron density of the catechol unit. Moreover, computer modelling with a force field program indicates that the conformation with the lowest energy is a perfectly folded chain (Fig. 5). This chain folding is, of course, typical for the "behavior" of one single chain in vacuum and does certainly not play an important role in a realistic nematic melt. However, the computer results prove that strong electronic interactions exist between the coplanar imide units. Such DA interactions were also reported by three different research groups38-40) for the solid state of several polyimides.

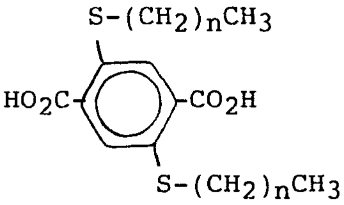
Another pair of polyimides which allows an interesting comparison has the structures 34 and 35. Polyimide 3441) may be called an intrinsically stiff polymer because no rotation around σ-bonds causes a deviation from its linear structure. However, this perfect rigid-rod is isotropic in the melt41). In contrast, the PEI's 35 are highly flexible and the mesogenic unit is neither symmetrical nor linear nor stiff. Yet, these PEI's form nematic or smectic melts depending on the length of the spacer42).

The structure property relationships discussed here and those of numerous other LC-polyesters reported polyesters can be summarized by the scheme of Figure 6. Most LC-polyesters exert relatively weak electronic interactions (mainly van der Vaals forces) and the formation of LC-phases is usually attributed to favorable steric factors such a high linearity, stiffness and/or symmetry. However, their is another diagonal relationship which indicates that LC-phases may exist, when less favorable steric factors are compensated by stronger electronic interactions with a directional sense, such as DA-interactions.

Finally aromatic PEI's of miscellaneous structures and properties should be mentioned. Thermostable, engineering plastics with high glass-transition temperature were obtained, when the diphenols 36 or 37 were polycondensed (in the form of bisacetates) with substituted terephthalic acids. However, thermotropic properties were only observed, when the OH-groups were attached in para positions[43,44]. Meltable PEI's (38 and 39) were also obtained by cocondensation of N-(3'-acetoxyphenyl)trimellitimide with 4-acetoxybenzoic acid or 6-acetoxy-2-naphthoic acid[45]. Nematic phases were only detectable, when the molar fractions of 4-hydroxybenzoic acid (4-HBA) or 6-hydroxy-2-naphthoic acid (2,6-HNA) were above 50%. The phase diagrams of both classes of copolyesters are outlined in Figures 7 and 8. In contrast, the copoly(ester-imide) obtained by cocondensation of the monomers 40 or 41 with 4-acetoxybenzoic acid proved to be highly crystalline, infusible and insoluble[46,47]. Nonetheles, the copoly(ester-imide)s of 40 are of interest, because they can be prepared in the form of needle-like crystals (whiskers) which may be useful as reinforcing components of composites. These results illustrate how broad the properties of PEI's may vary upon slight variation of their chemical structure.



24
a: n = 7
b: n = 15



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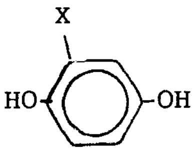
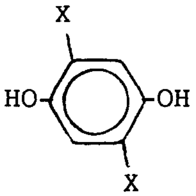
b: n = 15



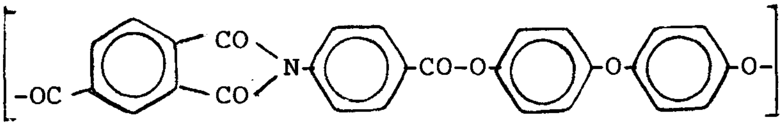
26

a: X = Cl
b: X = CMe_3
c: X = $-C_6H_5$
d: X = $-O-C_6H_5$
e: X = $S-C_6H_5$



27

a: X = OCH_3
b: X = CMe_3
c: X = C_6H_5
d: X = $O-C_6H_5$
e: X = $S-C_6H_5$



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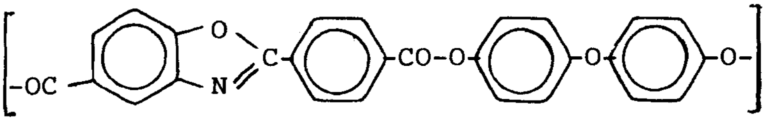

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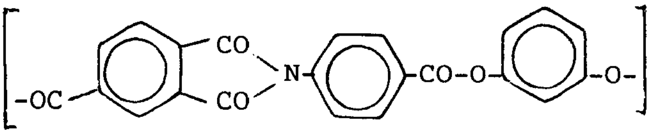
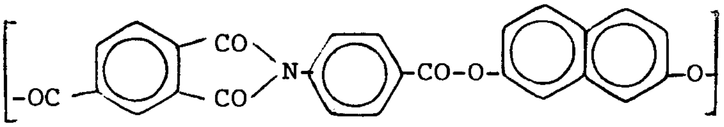


30



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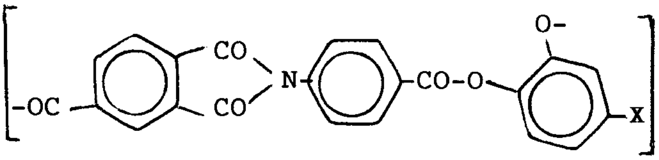
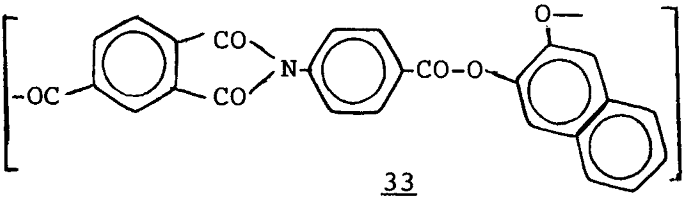


a: X = NO_2

b: X = H

c: X = CH_3

32



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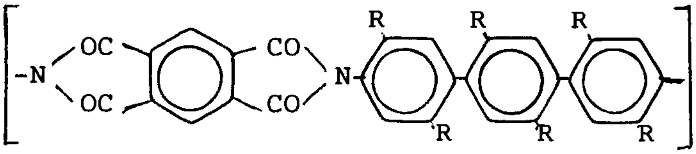
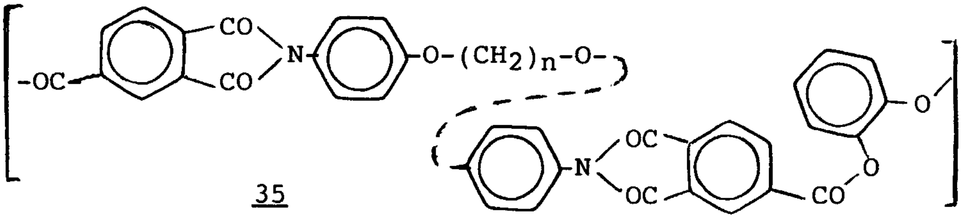


34

R = n-Alkyl



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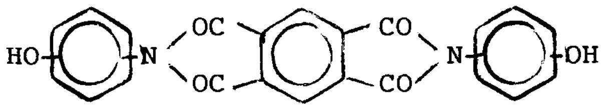
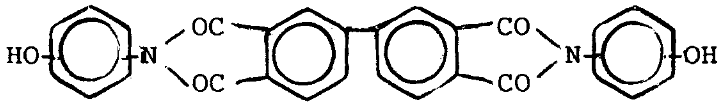


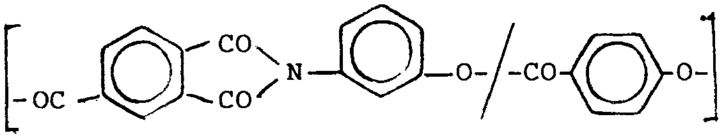
36

m or p



37

m or p



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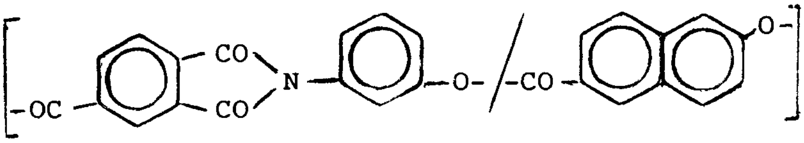

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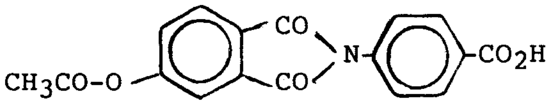

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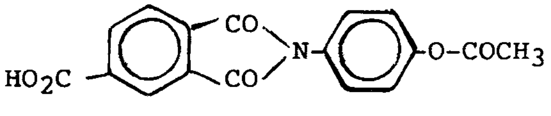

41

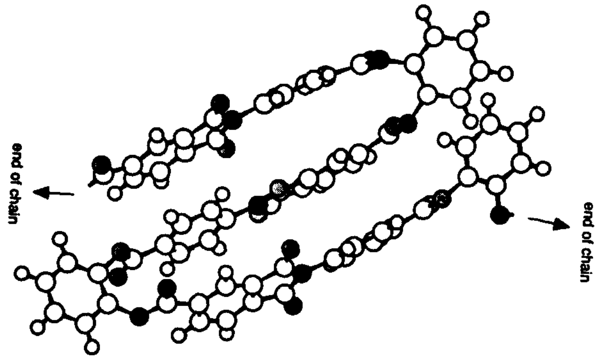

FIGURE 5: Folded conformation of PEI <u>32b</u> as obtained as absolute energy minimum by computer modelling.

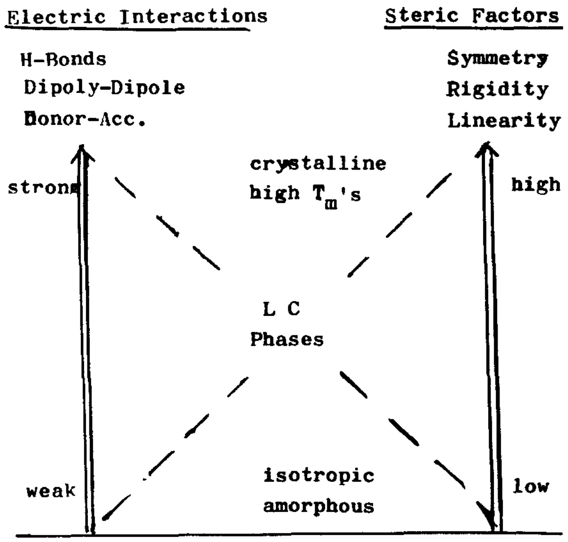

FIGURE 6: Scheme of polymer properties influencing the thermotropic character.

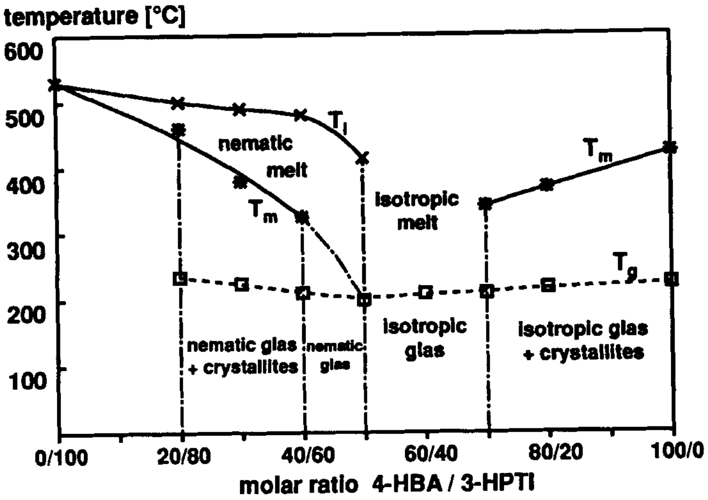

FIGURE 7: Phase diagram of copoly(ester-imide)s 38.

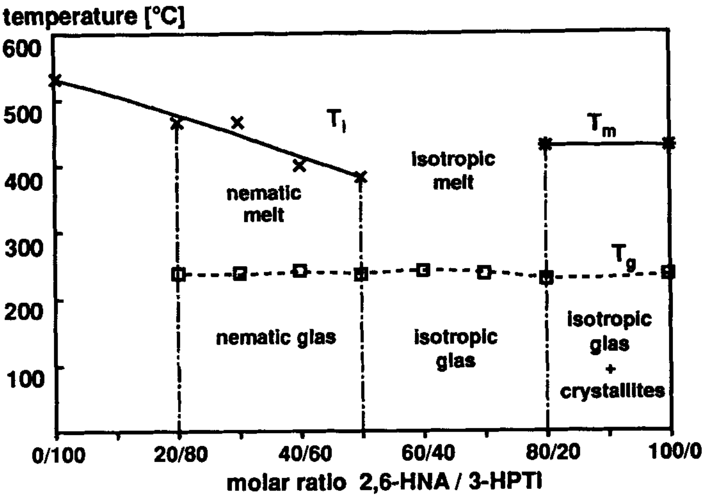

FIGURE 8: Phase diagram of copoly(ester-imide)s 39.

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