LC-Polyimides. 22. Thermotropic Poly(Amide-Imide)s Derived from New Bisimide Spacers and Biphenyl-4,4'-dicarboxylic Acids

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LC-POLYIMIDES. 22. THERMOTROPIC POLY(AMIDE-IMIDE)S DERIVED FROM NEW BISIMIDE SPACERS AND BIPHENYL-4,4'-DICARBOXYLIC ACIDS

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ABSTRACT

A new class of diamine spacers was synthesized from α,ω-diaminoalkanes and 4-nitrophthalic anhydride. The resulting α,ω-bis(4-aminophthalimido)alkanes were polycondensed with terephthaloylchloride, 2-phenylthioterephthaloylchloride, naphthalene-2,6-dicarboxylic acid dichloride, and 4,4'-biphenyl dicarboxylic acid dichloride. Most poly(amide-imide)s proved to be semicrystalline, forming a smectic layer structure in the solid state. Yet only the poly(amide-imide)s derived from 4,4'-biphenyl dicarboxylic acid are thermotropic and form a smectic and a nematic LC-phase. Due to the high temperatures employed, the reversibility of the phase transitions suffers from thermal degradation.

INTRODUCTION

Most liquid-crystalline (LC) polyimides reported so far are poly(ester-imide)s [1]. Four examples of LC-polyimides free of ester groups have recently been described: Poly(etherimide)s derived from pyromellitic imide [2] and from biphenyl-3,3',-4,4'-tetracarboxylic imide [3]; a lyotropic poly(amide-imide) 1 [4]; and a class of thermotropic poly(amide-imide)s 2 [5]. The present study was designed to elaborate another class of thermotropic poly(amide-imide)s, PAIs, based on a new type of spacer.

$$\left[-OC- \underset{CO}{\overset{CO}{\diagdown}} N- \bigcirc -CO-NH- \bigcirc -NH- \right]$$

1

$$\left[-NH- \bigcirc -O-(CH_2)_{\overline{n}}-O- \bigcirc -N \underset{OC}{\overset{OC}{\diagdown}} \underset{}{\diagup} CO- \right]$$
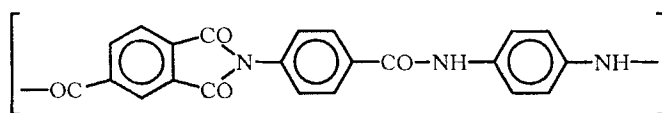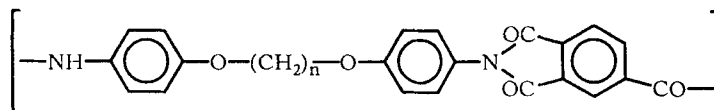
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EXPERIMENTAL

Materials

The α,ω-diaminoalkanes, 4-nitrophthalic acid, 2,6-naphthalene dicarboxylic acid, and 4,4′-biphenyldicarboxylic acid, were purchased from Aldrich Co. (Milwaukee, Wisconsin, USA) and used without purification. Hydrogenation catalyst Pt 5% on coal was purchased from Lancaster Co. (Karlsruhe, Germany). Dimethylformamide and N-methylpyrrolidone (gifts of BASF AG, Ludwigshafen, Germany) were distilled over P_4O_{10} in vacuo prior to use.

4-Nitrophthalic Anhydride

4-Nitrophthalic acid (0.5 mol) and acetic anhydride (2.0 mol) were refluxed for 4 hours and concentrated in vacuo. The product was isolated by distillation over a short-path apparatus in a vacuum of 10^{-3} bar. Yield 85%, mp 117–120°C (mp 120–121.5°C in Ref. 6).

α,ω-Bis(4′-nitrophthalimide)alkanes

4-Nitrophthalic anhydride (0.3 mol) and an α,ω-diaminoalkane (0.15 mol) were dissolved in dry dimethylformamide (350 mL) and stirred at 80°C for 1 hour. The temperature was then raised to 120°C for 4 hours, acetic anhydride (1 mol) was added, and the stirring was continued at 120°C for 4 hours. After cooling, water (100 mL) was added dropwise with stirring. The precipitated product was filtered off, washed with water, and dried in vacuo. Finally, the crude products were recrystallized from tetrahydrofuran.

Yields and properties are summarized in Table 1.

α,ω-Bis(4′-aminophthalimide)alkanes

An α,ω-bis(4′-aminophthalimide)alkane (30 mmol) was suspended or dissolved in tetrahydrofuran (400 mL) and hydrogenated with Pt 5% on charcoal. In contrast to the bisnitrophthalimidealkanes, the products were completely soluble in tetrahydrofuran. The catalyst was filtered off after complete hydrogenation, and the reaction mixture was concentrated in vacuo. The crystalline products with 10 or

TABLE 1.   Yields and Properties of α,ω-Bis(4-nitrophthalimide)alkanes

Formula	Yield, %	mp, °C	Elemental formula (formula weight)		Elemental analyses		
					C	H	N
3a	67	126–129	$C_{25}H_{24}N_4O_8$	Calcd	59.05	4.76	11.02
			(508.5)	Found	58.80	4.81	10.89
3b	30	173–176	$C_{26}H_{26}N_4O_8$	Calcd	59.77	5.02	10.72
			(525.5)	Found	59.68	4.97	10.39
3c	15	102–104	$C_{27}H_{28}N_4O_8$	Calcd	60.44	5.26	10.44
			(536.5)	Found	60.40	5.43	10.35
3d	29	161–164	$C_{28}H_{30}N_4O_8$	Calcd	61.08	5.49	10.18
			(550.6)	Found	60.78	5.58	10.05

12 CH_2 groups were recrystallized from toluene/tetrahydrofuran. The only products with 9 or 11 CH_2 groups were dissolved in a little CH_2Cl_2 and shaken with 200 mL of concentrated HCl. The precipitated hydrochlorides were isolated by filtration, washed with cold CH_2Cl_2, and dried over P_4O_{10} in vacuo. Yields and properties are summarized in Table 2.

Polycondensations

A) An α,ω-bis(4'-aminophthalimide)alkane (6 mmol) was dissolved in dry N-methylpyrrolidone (20 mL) and cooled to $-16/-20°C$. A dicarboxylic acid dichloride (6 mmol) was then added in an atmosphere of dry nitrogen, and the reaction mixture was stirred for 24 hours below 0°C and for 48 hours at 20–25°C. After dilution with 20 mL N-methylpyrrolidone, the product was precipitated into

TABLE 2.   Yields and Properties of α,ω-Bis(4-aminophthalimide)alkanes (**4b, d**) or Their Bishydrochlorides (**4a, c**)

Formula	Yield, %	mp, °C	Elemental formula (formula weight)		Elemental analyses		
					C	H	N
4a	45	224–227	$C_{25}H_{30}Cl_2N_4O_4$	Calcd	57.59	5.80	10.74
			(512.4)	Found	58.01	5.95	10.70[a]
4b	93	170–172	$C_{26}H_{30}N_4O_4$	Calcd	67.51	6.54	12.11
			(462.5)	Found	67.54	6.78	11.64
4c	75	204–207	$C_{27}H_{34}Cl_2N_4O_4$	Calcd	59.02	6.24	10.20
			(549.5)	Found	59.76	6.61	9.74[b]
4d	51	98–99	$C_{28}H_{34}N_4O_4$	Calcd	68.55	6.99	11.42
			(490.6)	Found	68.60	7.11	10.96

[a]Calculated for Cl, 13.93; found, 13.54%.
[b]Calculated for Cl, 12.99; found, 12.49%.

methanol, filtered off, and dried in vacuo. Finally, the polyamide was dissolved in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1), precipitated again into methanol, and dried at 80°C in vacuo.

B) The bishydrochlorides of **4a** or **4c** were used, and pyridine (25 mmol) was added to the N-methylpyrrolidone solution.

Measurements

The inherent viscosities were measured in an automated Ubbelohde viscometer thermostated at 20°C.

The IR spectra were recorded from KBr pellets with a Nicolet SXB-20 FT-IR spectrometer.

The 100 MHz ^{1}H-NMR spectra were obtained on a Bruker AC-100 FT spectrometer in 5 nm o.d. sample tubes. Internal TMS served for shift referencing in all cases.

The synchrotron radiation measurements were conducted at a wavelength of 1.50 Å at HASYLAB, DESY, Hamburg. A one-dimensional position sensitive detector and a vacuum oven with a heating rate of 10°C/min were used.

The WAXD powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered CuKα radiation.

The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The computer modeling of conformations and energy minima was conducted with the force field program CFF 91 Insight II/Discover of Biosym.

RESULTS AND DISCUSSION

Syntheses

It was the purpose of this study to synthesize new "bisimide spacers" of structure **4** and to determine if the polyamides derived from them possess a thermotropic character. Spacers **4a–d** were prepared by a two-step procedure. First, α,ω-diaminoalkanes were converted into bis(4-nitrophthalimide)s (Eq. 1), and these α,ω-bis(4-nitrophthalimide)alkanes **3a–d** (Table 1) were then hydrogenated with H_2/Pt. In order to avoid side reactions, these hydrogenations were conducted below 25°C. Whereas the diamines with an even number of CH_2 groups (**4b**, **d**) were crystalline and easy to recrystallize, those with an odd number of CH_2 groups (**4a**, **c**) were oily products. Therefore, these oils were transformed into crystalline bishydrochlorides for isolation and characterization (Table 2). The diamine spacers **4a–d** (or their hydrochlorides) and their precursors **3a–d** were characterized by elemental analyses as well as by IR and ^{1}H-NMR spectra. The IR spectra indicate complete imidization by the absence of amide groups. Examples of ^{1}H-NMR spectra are given in Fig. 1 (see also Fig. 2). As expected, the nitro group causes a significant downfield shift of the aromatic protons when compared with the aminophthalimide groups. Even the N—CH_2 protons of the "nitro spacers" **3a–d** experience a slight downfield shift (~ 0.1 ppm) relative to those of **4a–d**. Taken together, all spectra were in perfect agreement with the expected chemical structures.
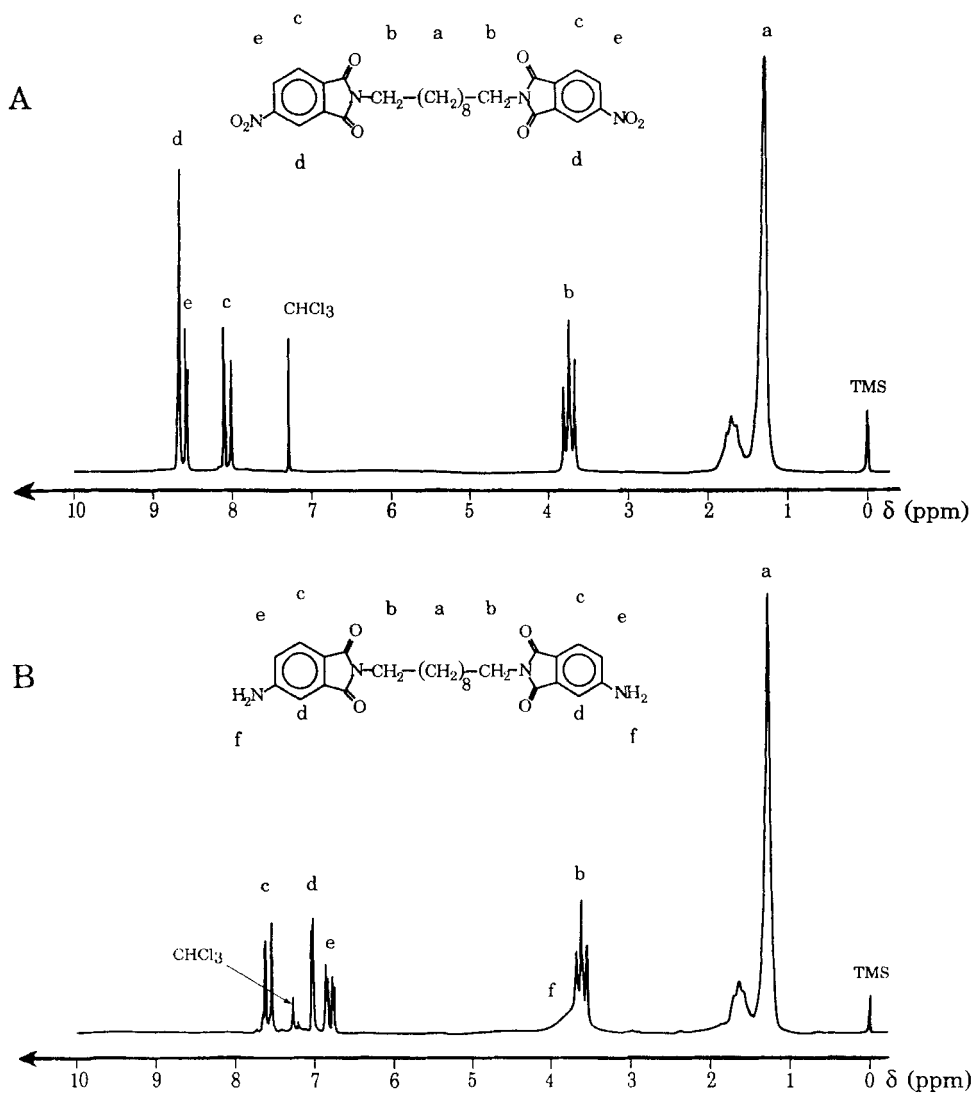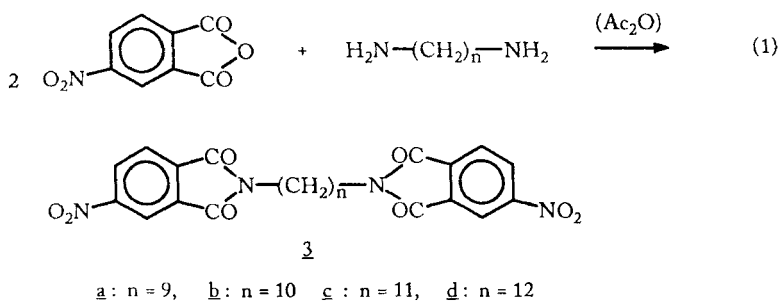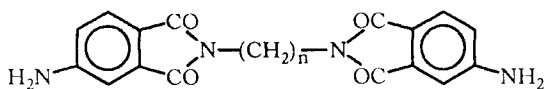
FIG. 1.   100 MHz ^{1}H-NMR spectra of **3b** and **4b** measured in CDCl$_3$.

$$\underline{3}$$

$\underline{a}$: n = 9, $\underline{b}$: n = 10 $\underline{c}$: n = 11, $\underline{d}$: n = 12

$\underline{4}$

$\underline{a}$: n = 9, $\underline{b}$: n = 10 $\underline{c}$: n = 11, $\underline{d}$: n = 12
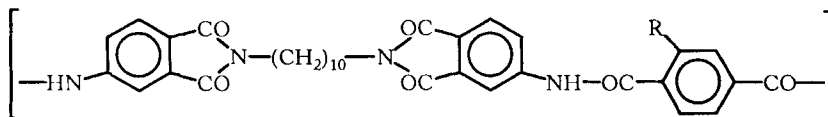
$\underline{5}$

$\underline{a}$: R = H $\underline{b}$: R = S-C$_6$H$_5$
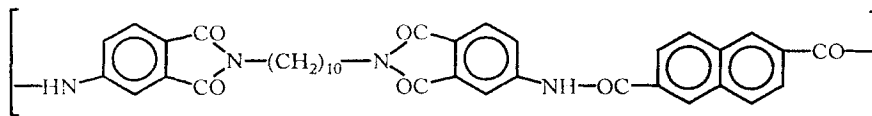
$\underline{6}$

$\underline{a}$: n = 9 $\underline{b}$: n = 10
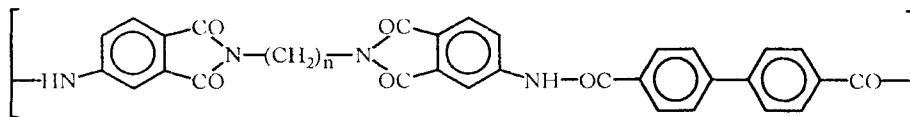
$\underline{7}$

$\underline{a}$: n = 9, $\underline{b}$: n = 10 $\underline{c}$: n = 11, $\underline{d}$: n = 12
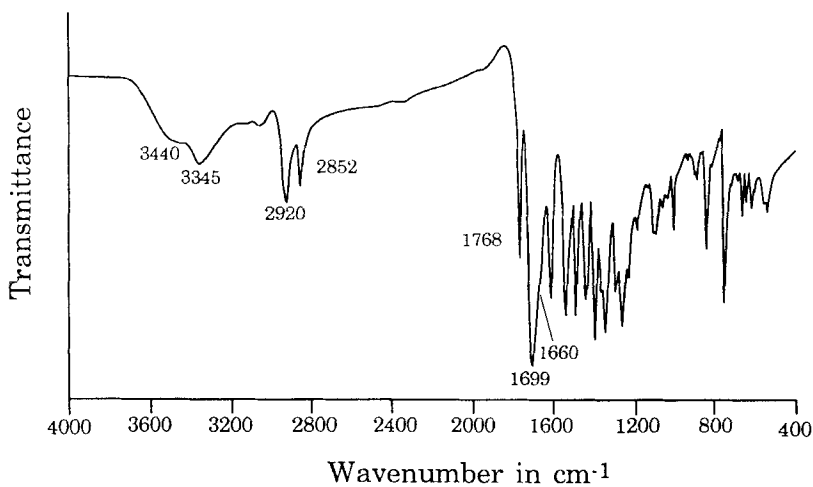
FIG. 2.   IR spectrum (KBr pellets) of poly(amide-imide) **7b**.

The polycondensations of the "diamine spacers" were conducted in neat N-methylpyrrolidone at temperatures below $0°C$ in the initial phase of the polycondensation (Method A). In the case of **4a** and **4c** the dihydrochlorides were used as starting materials in combination with pyridine as an HCl acceptor (Method B). In addition to terephthaloyl chloride, phenylthioterephthaloylchloride was used as a comonomer of the diamine **4b**. It was found in the case of aromatic polyesters derived from terephthalic acids that the phenylthio substituent significantly lowers the melting point and favors the formation of an LC-phase. A considerable reduction of the melting point was also observed for polyamide **5b** when compared to **5a** (Table 3).

In order to increase the dimensions of the mesogenic group, two more polycondensations were conducted with naphthalene 2,6-dicarboxylic acid dichloride. However, even the resulting PAIs **6a** and **6b** turned out to be isotropic. Therefore, 4,4′-biphenyldicarboxylic acid dichloride was used for further polycondensation, and the PAIs **7a–d** were isolated. All PAIs were characterized by elemental analyses, IR and ^{1}H-NMR spectroscopy, and DSC measurements. The yields and properties of the isotropic PAIs are summarized in Table 3; those of the thermotropic PAIs **7a–d** in Tables 4–6.

The IR spectra of all PAIs were quite similar. An example is given by the spectrum of **7b** in Fig. 3. The NH stretching band at 3345 cm^{-1} is characteristic for H-bonds of amide groups whereas the NH band at higher wavenumbers results from free NH groups or less perfect H-bonds. The shoulder at 1650–1680 cm^{-1} represents the CO stretch vibration of a *trans* amide group. The weak sharp band at 1768 cm^{-1} along with the intensive band at 1699 cm^{-1} are typical for the imide groups. The aliphatic signals in the ^{1}H-NMR spectrum of Fig. 4 agree well with those of the diamine spacer (Fig. 1). The acylation of the amino groups causes a slight downfield shift of the phthaloyl protons when compared to the diamines **4a–d**. In other words, all spectroscopic features agree well with the desired chemical structure.

## Characterization of the Thermotropic Poly(Amide-imide)s 7a–d

As evidenced by WAXD powder patterns (Fig. 4) and DSC measurements (Fig. 5), the PAIs **7a–d** (like **5b** and **6a, b**) are semicrystalline materials. Furthermore, the PAIs **7a–d** have in common that the melt formed immediately above the melting point has a liquid crystalline character. Interestingly, the liquid crystalline phases of the odd- and even-numbered PAIs exhibit slightly different textures. The texture of the PAIs with an odd-number of CH_2 groups may be described as marble-like (Fig. 6), whereas **7b** and **7d** display a "threaded schlieren texture" which is typical for most nematic LC-main chain polymers (Fig. 7).

In contrast to optical microscopy, both DSC measurements and WAXD powder patterns measured with synchrotron radiation at a variable temperature indicate that the thermotropic character of **7a–d** is more complex. The DSC heating curves of all four PAIs display two closely neighboring endotherms (Fig. 5). According to microscopic observations and synchrotron radion measurements (Fig. 8), the first endotherm (lower temperature) represents the true melting process, and is labeled T_{m_i} in Table 5. The synchrotron radiation measurements demonstrate that the middle-angle reflection indicating the existence of a smectic layer structure in the solid state survives the melting process and only vanishes at the temperature of the second

TABLE 3. Yields and Properties of the Isotropic Poly(Amide-imide)s **5a, b** and **6a, b**

Formula	Polycondensation[a] method	Yield, %	η_{inh},[b] dL/g	Elemental formula (formula weight)		Elemental analyses			T_g,[c] °C	T_m,[c] °C
						C	H	N		
5a	A	96	0.64	$C_{34}H_{32}N_4O_6$ (592.6)	Calcd	68.91	5.44	9.45	169	334
					Found	68.14	5.36	9.15		
5b	A	98	0.35	$C_{40}H_{36}N_4O_6S$ (700.8)	Calcd	68.36	5.45	7.97	158	Amorphous
					Found	68.63	4.72	7.32		
6a	B	87	0.32	$C_{37}H_{32}N_4O_6$ (628.7)	Calcd	70.69	5.13	8.91	181	335
					Found	69.71	5.14	8.80		
6b	A	95	0.41	$C_{38}H_{34}N_4O_6$ (642.7)	Calcd	71.01	5.33	8.72	178	369
					Found	70.39	5.61	8.63		

[a]A: Polycondensation of the free diamine. B: Polycondensation of the dihydrochloride.
[b]Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).
[c]From DSC measurements with a heating rate of 20°C/min.

TABLE 4.   Yields and Properties of the Thermotropic Poly(Amide-imide)s **7a–d**

Formula	Polycondensation[a] method	Yield, %	η_{inh},[b] dL/g	Elemental formula (formula weight)		Elemental analyses		
						C	H	N
7a	A	93	0.38	$C_{39}H_{34}N_4O_6$	Calcd	71.15	5.23	8.56
				(654.7)	Found	70.80	5.14	8.47
7b	B	95	0.45	$C_{40}H_{36}N_4O_6$	Calcd	71.84	5.42	8.38
				(668.7)	Found	70.98	5.33	7.99
7c	A	81	0.30	$C_{41}H_{38}N_4O_6$	Calcd	72.13	5.61	8.21
				(682.8)	Found	71.32	5.85	8.08
7d	B	90	0.53	$C_{42}H_{40}N_4O_6$	Calcd	72.40	5.79	8.04
				(696.8)	Found	71.38	5.74	7.79

[a]A: Polycondensation of the free diamine. B: Polycondensation of the dihydrochloride.
[b]Measured at 20°C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

endotherm (T_{m_2}). Therefore, it is obvious that PAIs **7a–d** form a smectic LC-phase between T_{m_1} and T_{m_2} and a nematic phase above T_{m_2}.

Unfortunately, a clear-cut identification of the smectic LC-phase was not feasible. Its narrow temperature range prevented an unambiguous identification of the texture because both the melting process and the formation of the nematic phase are gradual and overlapping with the temperature range of the smectic LC-phase. The layer distances (*d*-spacings) calculated from the middle angle reflections via the Bragg equation are again not unambiguous. These *d*-spacings are approximately 1 Å shorter than those measured at room temperature (Fig. 8 and Table 6). This small difference may be explained by stronger coiling (*trans* → *gauche* change) of the aliphatic spacer, and does not necessarily indicate a stronger tilting of the mesogens. However, as illustrated by Figs. 9 and 10, the mesogens may themselves adopt various conformations. Furthermore, three different spacial combinations of mesogen and spacers may exist, which can explain the measured *d*-spacings, even if a predominance of *gauche* conformations of the spacer is accepted (right half of

TABLE 5.   Phase Transitions of the Liquid-Crystalline Poly(Ester-imide)s **7a–d**

Formula	T_g,[a] °C	T_{m_1},[a] °C	T_{m_2},[a] °C	T_i,[b] °C
7a	156	325	351	435–445
7b	173	383	409	440–450
7c	148	322	342	380–390
7d	152	357	383	415–425

[a]From DSC measurements with a heating rate of 20°C/min.
[b]From optical microscopy (crossed polarizers) with a heating rate of 10°C/min.

TABLE 6. Experimental and Calculated Layer Distances of the Poly(Amide-imide)s **7a–d**

| | | d-Spacings calculated (Å) | | | | | |
| | | trans | | | gauche | | |
Polymer	d-Spacings measured (Å) at 25°C	$\alpha^a = 180°$	$\alpha_S{}^b = 123°$	$\alpha_M{}^c = 123°$	$\alpha^a = 180°$	$\alpha_S{}^b = 148°$	$\alpha_M{}^c = 148°$
7a	27.6	34.4	29.3	23.9	31.2	30.0	27.7
7b	27.6	35.5	29.9	25.1	32.3	30.7	28.6
7c	30.4	36.9	30.6	26.4	33.0	31.5	29.5
7d	30.4	38.0	31.3	27.6	34.8	32.3	30.5

[a]Mesogen upright and spacer upright (linear repeating unit).

[b]Mesogen upright forming an angle of 123° (all *trans*) and 148° (all *gauche*) with the tilted spacer.

[c]Mesogen tilted forming an angle of 123° (all *trans*) and 148° (all *gauche*) with the upright spacer.
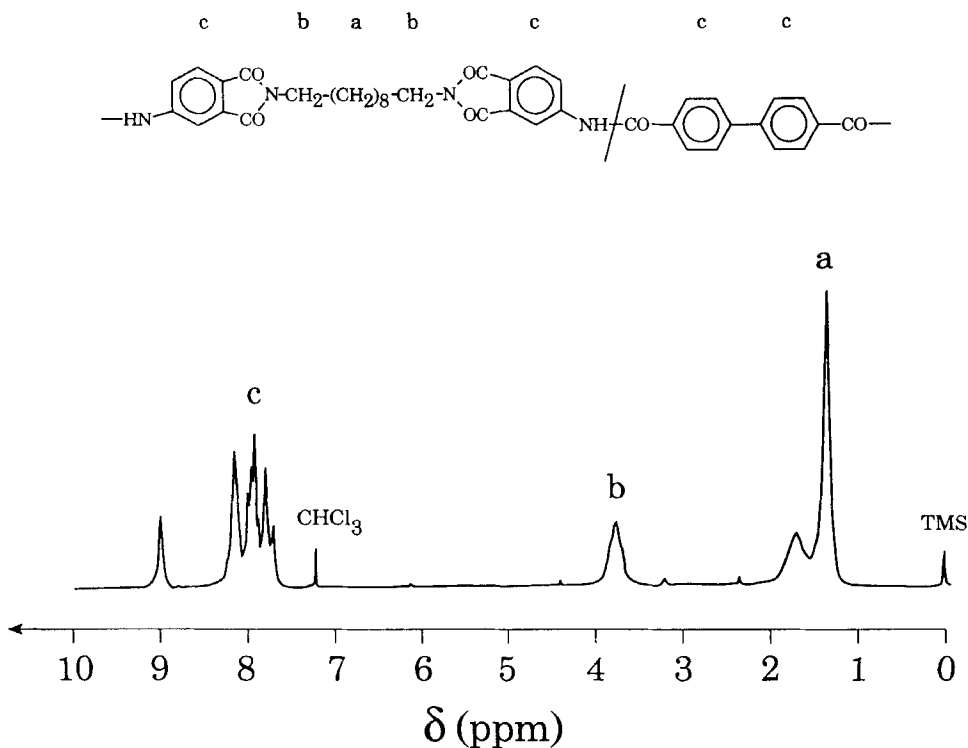

FIG. 3. ¹H-NMR spectrum of poly(amide-imide) **7b** measured in CDCl₃/trifluoro-acetic acid (volume ratio 4:1).
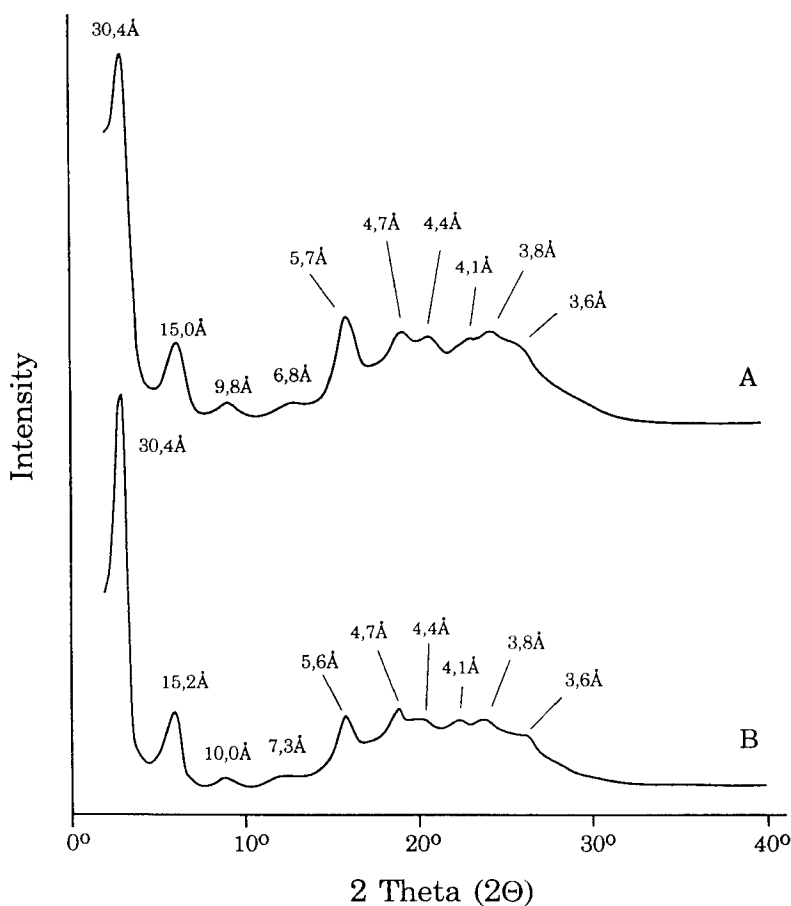
FIG. 4.   WAXD powder patterns of (A) poly(amide-imide) **7a**, (B) **7b**.

Table 6). First, the mesogen and the spacer form a straight line and are tilted relative to the layer plane. Second, the mesogen is in a rectangular position relative to the layer plane but the spacer is tilted. Third, the spacer is in a rectangular position but the mesogen is tilted.

Minimum energy calculations with a force-field program indicate for a single chain in vacuum that the mesogen and the spacer form an angle of 148° relative to each other when the spacer is in the all-*gauche* conformation. Whether this value is realistic for a melt at 250–300°C is an open question. Nonetheless, the *d*-spacings calculated with this angle and a tilted mesogen give the best fit with the measured *d*-spacings (last column of Table 6). However, this good fit of the WAXD data should not be considered as definite proof for a smectic LC-phase with tilted mesogens (smectic-C). In this connection, two comments are of interest. First, other thermotropic poly(amide-imide)s [5], poly(ether-imide)s [3], and poly(ester-imide)s [7–9] prefer a smectic-A phase with rectangular positions of the mesogens. Imide mesogens seemingly show no tendency to form tilted meso-phases. Second, the term smectic is not a synonym for liquid-crystalline. In contrast to low molar
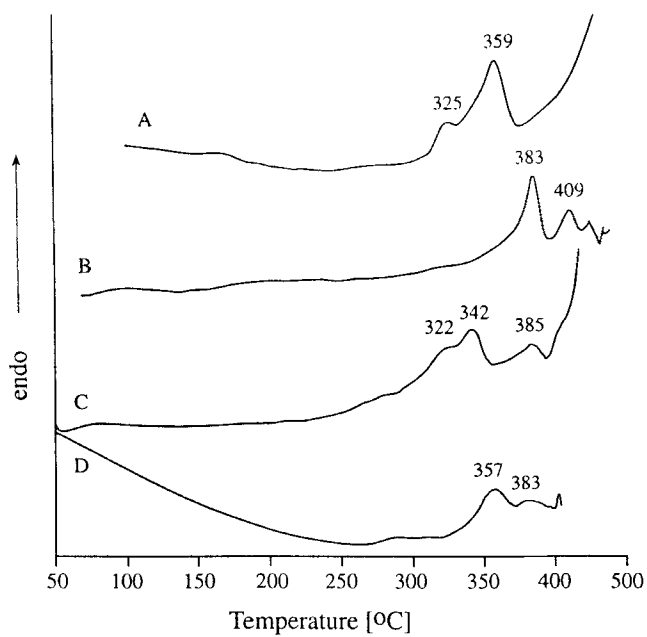
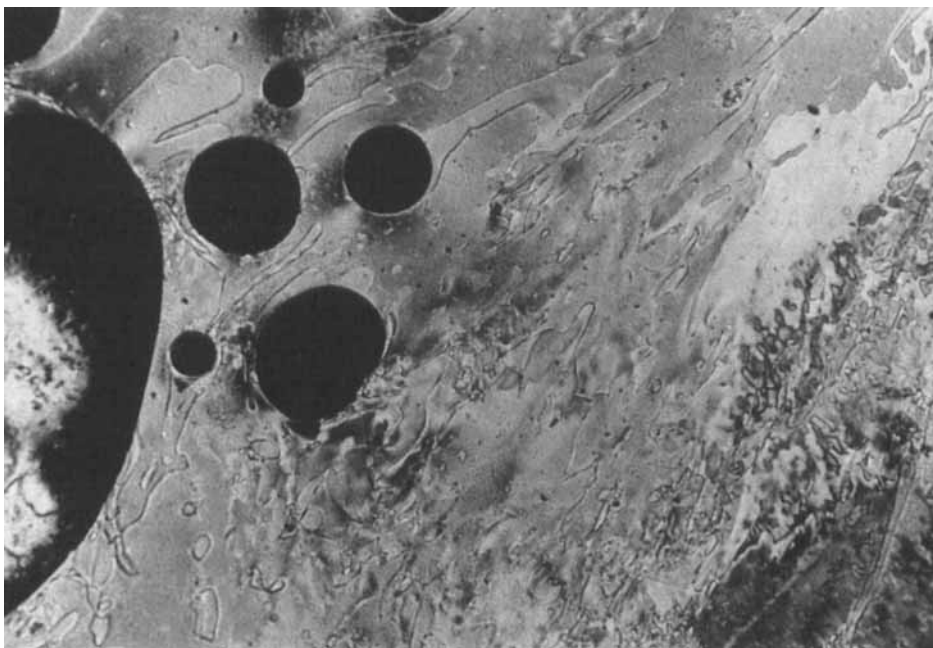FIG. 5.   DSC measurements (heating rate 20°C/min) of **7a–d**.

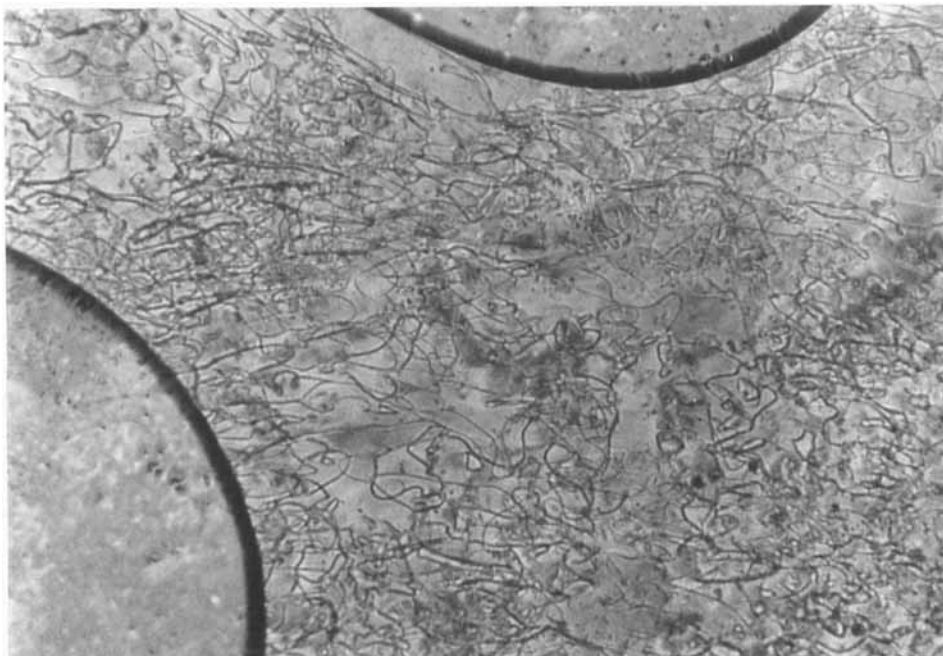FIG. 6.   Texture of poly(amide-imide) **7a** upon heating to 364°C.

FIG. 7.   Texture of poly(amide-imide) **7b** upon heating to 410°C.

mass-mesogens, LC-main chain polymers can only form two smectic LC-phases, namely A or C. All higher ordered smectic phases are solid meso-phases because the mesogens form "two-dimensional crystals" three-dimensionally "crosslinked" by the spacers.

The WAXD powder patterns of **7a–d** recorded at 25°C (e.g., Fig. 4) are almost identical for all four members of the series. The wide-angle reflections suggest the existence of an orthorhombic array of the mesogens (e.g., smectic-E or -H). Furthermore, a relatively sharp middle-angle reflection is present along with its higher order reflections. This middle-angle reflection indicates the existence of a rather perfect layer structure in the solid state. A layer structure was found for all polyimides built up by a regular sequence of aromatic imide groups and alkane spacers [1, 3, 5, 7–9]. Furthermore, ^{13}C-NMR CP/MAS spectroscopy and ^{2}H-NMR spectroscopy (of selectively deuterated spacers) have revealed that the alkane spacers are mobile even in the solid state of the polyimides. They adopt *gauche* and *trans* conformations with a clear predominance of *gauche* conformations. This general picture of the alkane spacers was confirmed in the present work by a ^{13}C-NMR CP/ MAS spectrum of **7d** which displays one broad signal of the central CH_2 groups ($\delta = 31$ ppm). This signal covers the chemical shifts of both *trans* and *gauche* confirmations.

Nonetheless, the middle-angle reflections do not allow a clear-cut differentiation between smectic-E (mesogens upright) and smectic-H (mesogens tilted) phases, because no reliable information on the angle between spacer and mesogen is available. When the computer data are taken into account (Table 6, last column), a
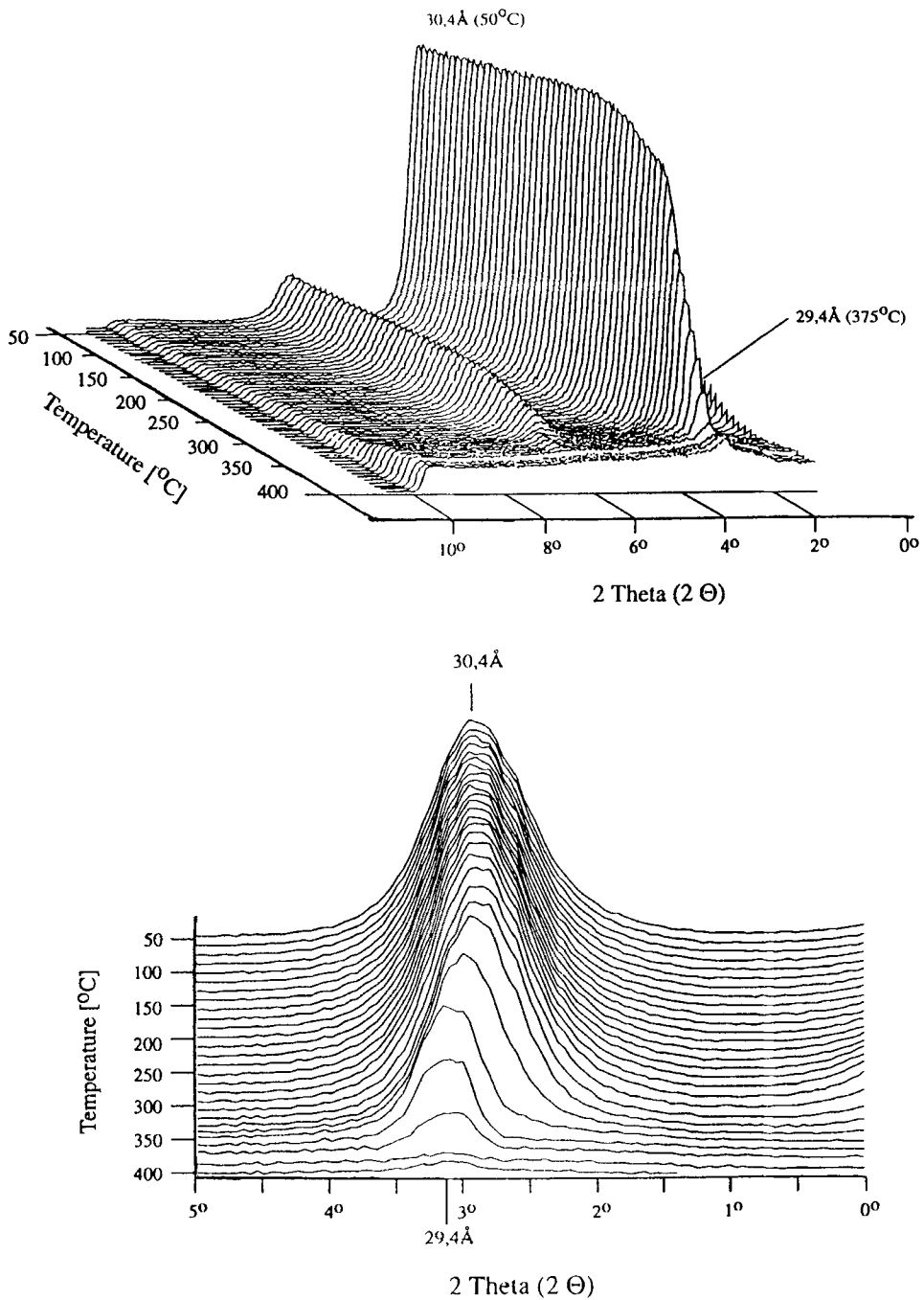
FIG. 8.   Synchrotron radiation measurements of **7d** with a heating rate of 20°C/min.
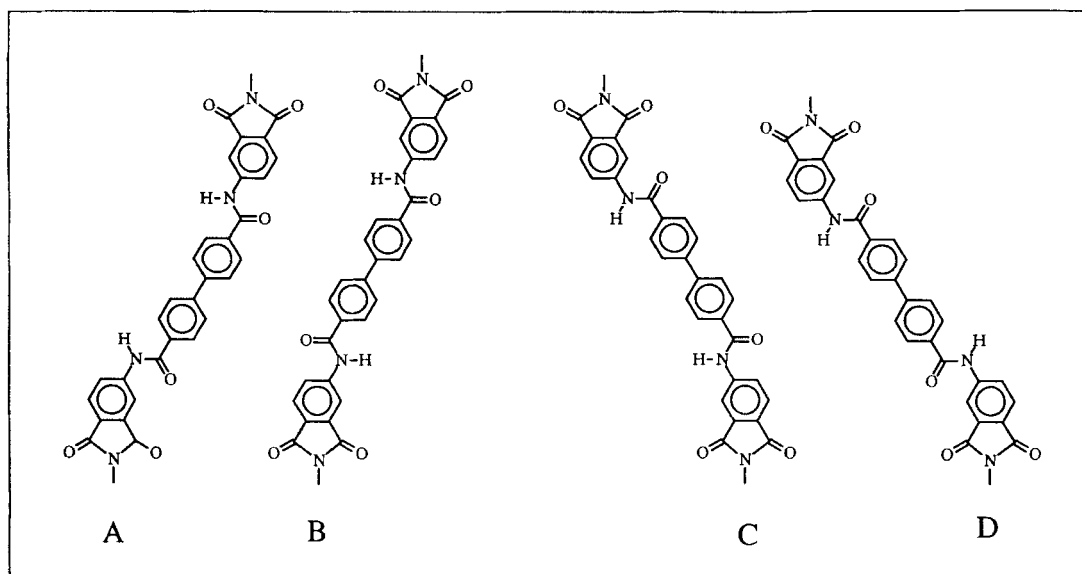
FIG. 9. Conformations of the mesogenic unit favoring a tilted position relative to the layer plane.
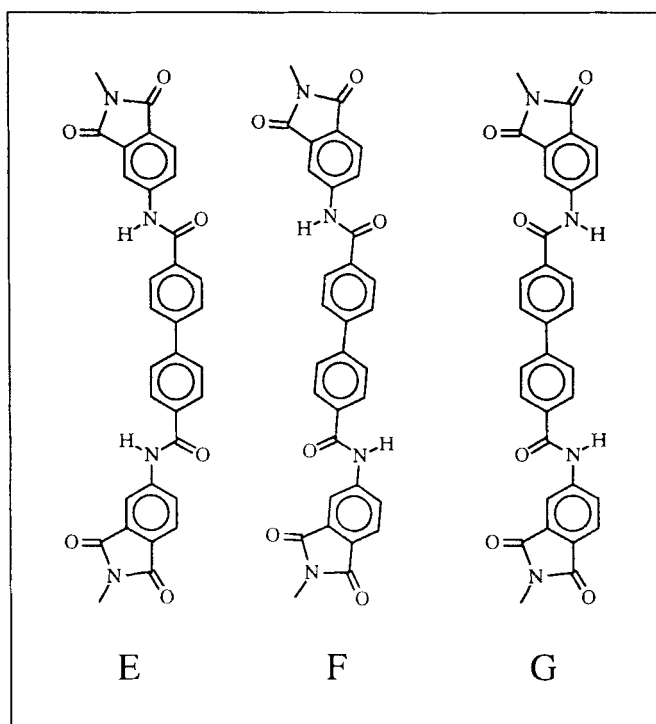

FIG. 10. Conformations of the mesogenic unit favoring an upright (perpendicular) position relative to the layer plane.

slight tilting of the mesogens in combination with upright spacers seems to give the best fit with the measured d-spacings. A more detailed study of the solid state was not conducted in the present work.

CONCLUSION

The new diamine spacers **4a–d** allowed the synthesis of thermotropic poly(amide-imide)s. However, only a few dicarboxylic acids will be suited for this purpose. The failure of terephthalic acid and naphthalene-2,6-dicarboxylic acid to yield LC-polyimides is paralleled by the properties of several poly(ester-imide)s, such as **8**. Also, in the case of **8** it is only the diphenyl derivative which yields a thermotropic polyimide. However, the PAIs **7a–d** differ from almost all LC-polyimides described thus far in that they can form two different kinds of LC-phases, a smectic and a nematic one.

8
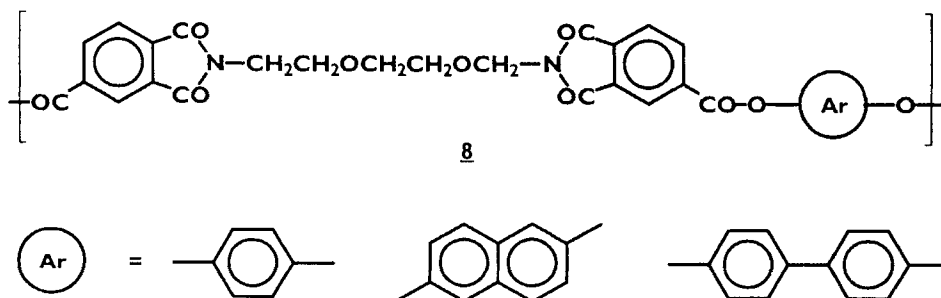
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