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Liquid-Crystalline Polyimides. 20. Photoreactive and Cholesteric Poly(ester−imide)s Based on 4-Aminocinnamic Acid Trimellitimide and Chiral Sulfide Spacers

Hans R. Kricheldorf,* Nicolas Probst, Mihai Gurau, and Matthias Berghahn

Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, FRG

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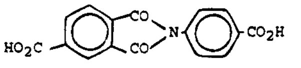
ABSTRACT: A dicarboxylic acid which served as a mesogen in all poly(ester−imide)s was prepared from 4-aminocinnamic acid and trimellitic anhydride. The acid chloride of this monomer was polycondensed with various chiral diols derived from (*S*)-3-bromo-2-methyl-1-propanol. Furthermore, copolymers containing various molar ratios of a chiral and a nonchiral spacer were studied. Most chiral poly(ester−imide)s form a cholesteric melt and a chiral smectic layer structure in the solid state. The cholesteric melt of three poly(ester−imide)s is capable of forming a Grandjean texture upon shearing. The color of this texture depends on the chemical structure, and it may vary with the temperature (thermochromy). Irradiation with UV light of a wavelength ≤360 nm allows rapid cross-linking and, thus, fixation of supramolecular order and color.

Introduction

This work is part of a broader study dealing with structure−property relationships of potentially liquid-crystalline (LC) polyimides.[1] Despite a relatively high degree of planarity, rigidity, and polarity, aromatic imide structures proved to be relatively poor mesogens. For instance, the dicarboxylic acid **1**, which is an inexpensive monomer based on trimellitic anhydride and 4-aminobenzoic acid, does not yield thermotropic poly(ester−imide)s with enantiotropic LC phases, when polycondensed with various types of aliphatic spacers.[2−5] Only a short-lived monotropic smectic A phase was detectable upon rapid cooling.[4,5] However, in combination with nonpolar aliphatic spacers, the polar imide mesogens (such as **1**)show a high tendency to form layer structures in the solid state. Such layer structures are interesting because they can adopt various levels of rotational and conformational order depending on the thermal history.[2,3,5]



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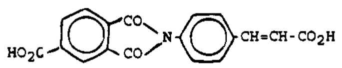

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In this connection poly(ester−imide)s based on the new dicarboxylic acid **2** should be studied. The extension of this monomer by a trans ethylene group should improve the mesogenic properties compared to **1**. Furthermore, the cinnamic group should be capable of photo-cross-linking. This property is particularly interesting in combination with a cholesteric phase, because layers or films with cholesteric order may reflect or transmit circularly polarized light of selected wavelength provided that they can form a Grandjean texture. Therefore, it was the aim of the present work to synthesize chiral poly(ester−imide)s of monomer **2** capable of forming a cholesteric melt. To the best of our knowledge LC polymers containing 4-aminocinnamic trimellitimide (**2**) have never been reported.

Experimental Section

Materials. Trimellitic anhydride was a gift of Bayer AG (Leverkusen, FRG) and used without further purification. 4-Aminocinnamic acid, (*S*)-3-bromo-2-methylpropanol, 3-bromo-propanol, 6-chlorohexanol, and 4-mercaptophenol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. *N*-Methylpyrrolidone (NMP; gift of BASF AG, Ludwigshafen, FRG) was purified by distillation over dry K_2CO_3 and P_4O_{10} in vacuo. Pyridine was distilled over freshly powdered calcium hydride. *N,N*-Dimethylformamide (DMF) was distilled over P_4O_{10} in vacuo. *o*-Dichlorobenzene was distilled without additive prior to use.

6-Hydroxy-1-mercaptohexane. A solution of 6-chloro-1-hexanol (0.2 mol) and thiourea (0.22 mol) in ethanol (30 mL) was refluxed for 6 h. After cooling in a refrigerator, the crystallized isothiouronium salt was filtered off, washed with diethyl ether, and dried at 50 °C in vacuo. The isothiouronium salt was refluxed in 4 N sodium hydroxide for 2 h (under nitrogen) and then acidified with 6 N hydrochloric acid. The resulting emulsion was extracted with diethyl ether (1 L) by means of a perforator for a period of 2 days. The ether extract was dried over Na_2SO_4, concentrated, and distilled in a vacuum of 10^{-1} mbar.

Yield: 88%. n^{20}_D: 1.4858. Elem anal. Calcd for $C_6H_{14}OS$ (134.3): C, 53.68; H, 10.51; S, 23.89. Found: C, 53.22; H, 10.47; S, 23.54.

(*S*)-(+)-1-(3-Hydroxy-2-methylpropyl) 1-(6-hydroxyhexyl) Sulfide (4b). 6-Hydroxy-1-mercaptohexane (0.1 mol) was added to a solution of sodium (0.105 mol) in deoxygenated ethanol (150 mL), and after 10 min a solution of (*S*)-(+)-3-bromo-2-methyl-1-propanol in ethanol (25 mL) was added dropwise with stirring in an atmosphere of nitrogen. The reaction mixture was refluxed for 2 h, diluted with water (200 mL), and concentrated (in vacuo) to a final volume of 200 mL. The resulting emulsion was extracted with diethyl ether in a perforator for a period of 2 days. The ether extract was dried over Na_2SO_4, concentrated, and distilled over

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Table 1. Synthetic Methods, Yields, and Properties of Poly(ester–imide)s Prepared from 4-Aminocinnamic Acid Trimellitimide

polym formula	synth[a] method	yield (%)	η_{inh}[b] (dL/g)	$[\alpha]^{20}_D$[c]	elem formula (formula wt)	elem anal.				
							C	H	N	S
5	A	76	0.27	−10.5	$C_{32}H_{37}NO_6S_2$ (595.8)	calcd	64.51	6.26	2.35	10.77
						found	63.30	6.21	2.33	10.63
6a	A	75	0.23	−5.2	$C_{24}H_{21}NO_6S$ (451.5)	calcd	63.85	4.69	3.10	7.10
						found	63.07	4.73	3.00	7.25
6b	A	86	0.20	−5.6	$C_{28}H_{29}NO_6S$ (507.6)	calcd	66.25	5.76	2.76	6.32
						found	64.29	5.47	2.87	6.13
6b′	B	87	0.56	−6.7	$C_{28}H_{29}NO_6S$ (507.6)	calcd	66.25	5.76	2.76	6.32
						found	65.22	5.60	2.87	6.20
7a	A	78	0.2	−27.3	$C_{28}H_{21}NO_6S$ (499.5)	calcd	67.32	4.24	2.80	6.42
						found	66.55	4.36	3.17	6.45
7a′	B	83	0.34	−26.4	$C_{28}H_{21}NO_6S$ (499.5)	calcd	67.32	4.24	2.80	6.42
						found	66.59	4.02	2.93	6.25
7b	A	87	0.23	−24.0	$C_{139}H_{103}N_5O_3S_5$ (2483.6)	calcd	67.22	4.18	2.81	6.45
						found	66.13	4.30	3.26	6.02
7c	A	86	0.25	−19.1	$C_{55}H_{40}N_2O_{12}S_2$ (985.1)	calcd	67.06	4.09	2.84	6.51
						found	66.01	4.25	3.07	6.02
7d	A	82	0.24	±0	$C_{27}H_{19}NO_6S$ (485.5)	calcd	66.80	3.94	2.89	6.60
						found	65.87	4.12	3.08	6.28

[a] (A) Polycondensation in pyridine/*N*-methylpyrrolidone. (B) Polycondensation in refluxing *o*-dichlorobenzene. [b] Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume at 4:1). [c] Measured at 20 °C with a concentration of $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume at 4:1).

a short-path apparatus in a vacuum of 10^{-3} mbar at a bath temperature of 170–180 °C.

Yield: 87%. n^{20}_D: 1.4966. $[\alpha]^{20}_D$ +4.2° ($c = 5$ g/L of $CHCl_3$). Anal. Calcd for $C_{10}H_{22}O_2S$ (206.3): C, 58.20; H, 10.75; S, 15.54. Found: C, 57.98; H, 10.73; S, 15.43. ^{1}H NMR ($CDCl_3$/TMS): δ 1.00 (d, 3H), 1.25–1.75 (m, 8H), 1.89 (m, 1H), 2.61 (m, 2H and t, 2H), 3.56 (d, 2H), 3.62 (t, 2H).

4-Aminocinnamic Acid Trimellitimide. A solution of trimellitic anhydride (0.26 mol) and *trans*-4-aminocinnamic acid hydrochloride (0.25 mol) in dry DMF was heated to 100 °C, and triethylamine (0.25 mol) was added dropwise with stirring. Afterward the reaction mixture was heated to 120 °C for 2 h, acetic anhydride (0.3 mol) was then added, and the heating was continued of an additional 1 h. After cooling, cold diethyl ether (500 mL) was added, and the yellow precipitate was isolated, washed with acetone and diethyl ether, and recrystallized from dioxane.

Yield: 55%. Mp: >300 °C (dec). Anal. Calcd for $C_{18}H_{11}NO_6$ (337.3): C, 64.10; H, 3.29; N, 4.15. Found: C, 63.95; H, 3.53; N, 4.38.

Acid Chloride of 4-Aminocinnamic Acid Trimellitimide. DMF (1 mL) was added to a suspension of 4-aminocinnamic acid trimellitimide (0.15 mol) in distilled thionyl chloride (250 mL), and the resulting mixture was refluxed with stirring until the evolution of HCl and SO_2 ceased. The clear solution was concentrated in vacuo until the product started to crystallize and was then rapidly poured with rigorous stirring into ligroin (1.5 L). The crystalline product was filtered off under exclusion of moisture and dried at 115 °C in vacuo.

Yield: 63%. Mp: 213–215 °C. Anal. Calcd for $C_{18}H_9NO_4Cl_2$: C, 57.78; H, 2.42; N, 3.74; Cl, 18.95. Found: C, 57.79; H, 2.56; N, 3.64; Cl, 19.01. ^{1}H NMR ($CDCl_3$/TMS): δ 6.70 (d, 2H), 7.68 (d, 2H), 7.95 (d, 1H), 8.14 (d, 1H), 8.58 (dd, 1H), 8.72 (d, 1H).

Polycondensation. (A) With Pyridine as HCl Acceptor. A spacer diol (20 mmol) was weighed into a cylindrical glass reactor equipped with a stirrer, gas inlet, and outlet tubes. Dry NMP (20 mL) and pyridine (5 mL) were added, and the resulting solution was cooled to 0 °C. The dichloride of 4-aminocinnamic acid trimellitimide (20 mmol) was added, and the reaction mixture was stirred for 8 h with cooling and for 40 h without cooling. Finally, the temperature was raised to 60 °C for 1 h, and after cooling the reaction mixture was poured into cold methanol. The precipitated polyester was filtered off, dried in vacuo, dissolved in CH_2Cl_2/trifluoroacetic acid (volume ratio 9:1), and precipitated again into methanol. Yields, inherent viscosities, and elemental analyses are summarized in Table 1.

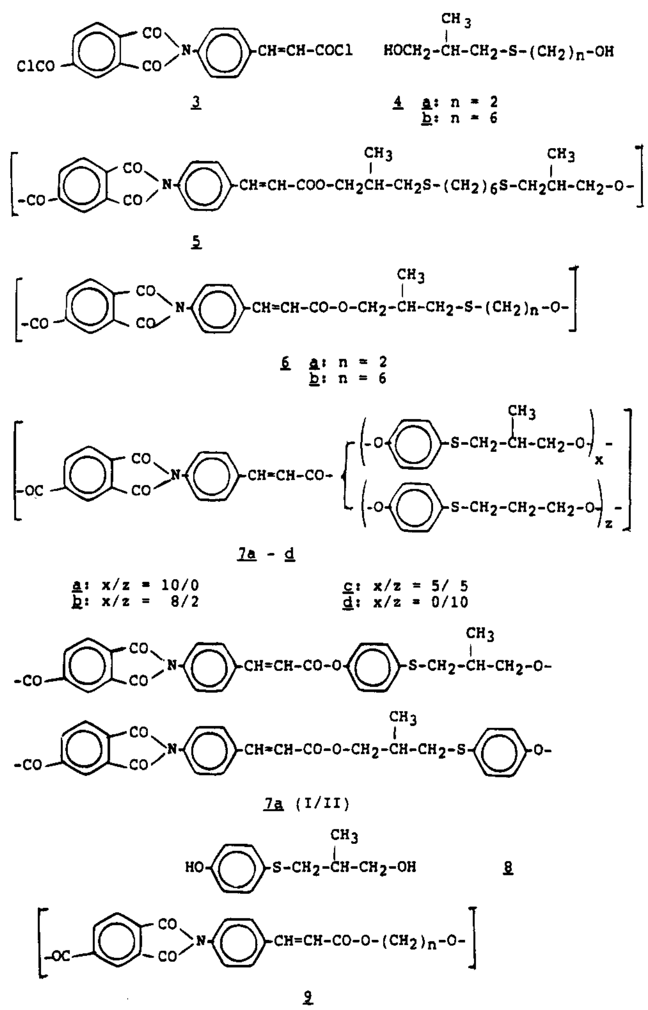
(B) Without HCl Acceptor. The dichloride of 4-aminocinnamic acid trimellitimide (10 mmol) and a spacer diol (10 mmol) were heated with stirring in dry *o*-dichlorobenzene (15 mL) for 2 h. HCl was removed with a slow stream of nitrogen. After cooling the reaction mixture was diluted with CH_2Cl_2 (10 mL) and trifluoroacetic acid (5 mL) and precipitated into methanol. The precipitated polyester was filtered off and dried 115 °C in vacuo.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C. The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen (standard heating and cooling rate: 20 °C/min). 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 WAXD powder patterns were recorded with a Siemens D-500 diffractometer using Ni-filtered Cu Kα radiation. The optical rotations were measured with a Perkin-Elmer Md 241 polarimeter at a wavelength of 589 nm using a cuvette of 10-cm path length. The UV spectra were recorded from films (thickness ≤0.1 mm) with a Cary 1115 spectrometer between 280 and 500 nm.

Results and Discussion

Syntheses. All poly(ester–imide)s, PEI's, of this work were prepared by polycondensation of the acid chloride **3** (Chart 1) with various chiral spacer diols. The dicarboxylic acid **2** was synthesized from trimellitic anhydride and 4-aminocinnamic acid hydrochlorides by two methods. In the case of method I, an amic acid was obtained in dimethylformamide and cyclized by addition of acetic anhydride. In the case of method II, 4-aminocinnamic acid hydrochloride and trimellitic anhydride were condensed in refluxing *m*-cresol. Both methods

Chart 1



gave similar yields (45–55%), but the purity of the product isolated from *m*-cresol was higher. The hitherto unknown acid chloride **3** was prepared from **2** in refluxing thionyl chloride.

Most of the aliphatic spacers used in this work were described in a previous part of this series.[6] However, the chiral spacer **4b** was synthesized for the first time in this work. Starting from 6-chlorohexanol and thiourea, 6-mercaptohexanol was prepared by a standard procedure. The 6-mercaptohexanol was in turn reacted with commercial (*S*)-3-bromo-2-methylpropanol, yielding the spacer **4b**.

All poly(ester–imide)s, **5**, **6a,b**, and **7a–d**, were synthesized by polycondensation of monomer **3** with the chiral diols at low or moderate temperature (0–60 °C) in the presence of pyridine as HCl acceptor. This method (A) did not yield high molecular weights, but it was known from a previous study[6] that it reliably avoids racemization. As exemplified by Figures 1–3 the IR and ^{1}H NMR spectra were in perfect agreement with the postulated structures.

An alternative approach is the polycondensation at high temperatures in the absence of an HCl acceptor. This method was reported by Lenz and co-workers,[7] but those authors never looked for HCl-catalyzed side reactions. It was shown previously[3] that polycondensations of the dichloride of **1** with aliphatic diols in bulk yield polyesters containing a significant amount of ether groups.

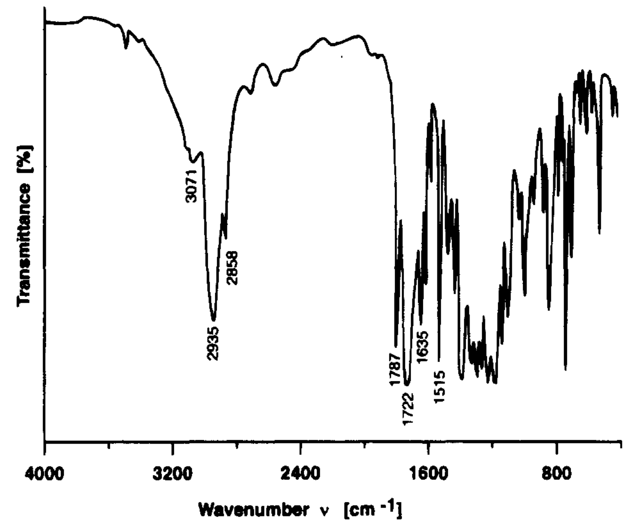


Figure 1. IR spectrum (KBr pellet) of poly(ester–imide) **6b**.

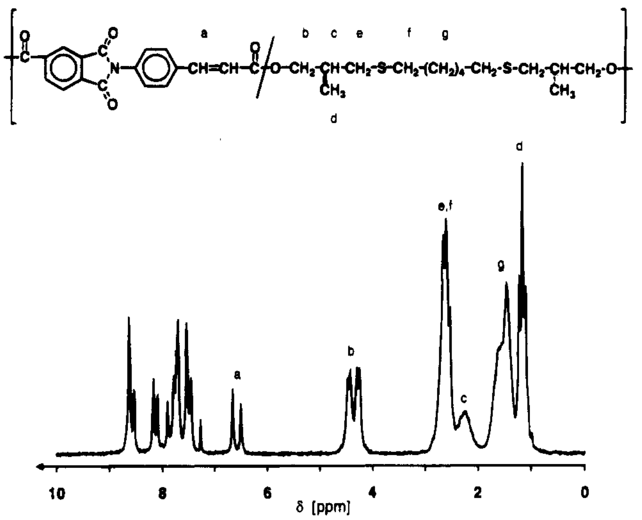


Figure 2. 100-MHz ^{1}H NMR spectrum of poly(ester–imide) **5** (measured in $CDCl_3$/trifluoroacetic acid, volume ratio 4:1).

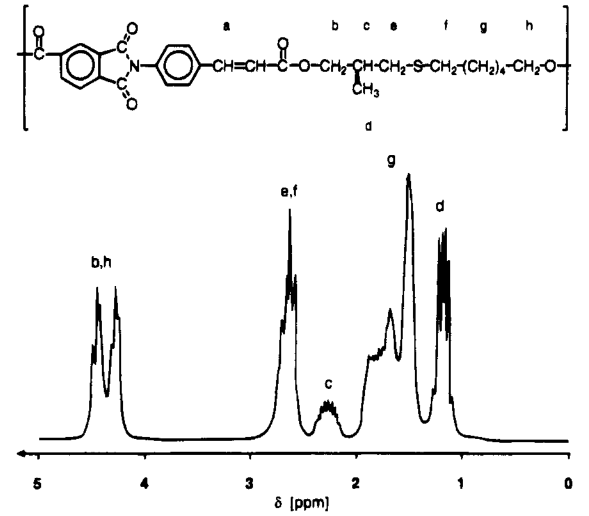


Figure 3. 200-MHz ^{1}H NMR spectrum of poly(ester–imide) **6b′** (measured in $CDCl_3$/trifluoroacetic acid, volume ratio 4:1).

In the present work the synthesis of **6b** and **7a** was repeated in refluxing *o*-dichlorobenzene without addition of an HCl acceptor. The ^{1}H NMR spectra (e.g., Figure 3) of the resulting PEI's **6b′** and **7a′** proved that ether groups were not formed above a level of 1 mol %. The presence of ether groups should be detectable by O–CH_2 signals in the range of 3.4–3.6 ppm, which were not present. Furthermore, no trans → cis isomerization

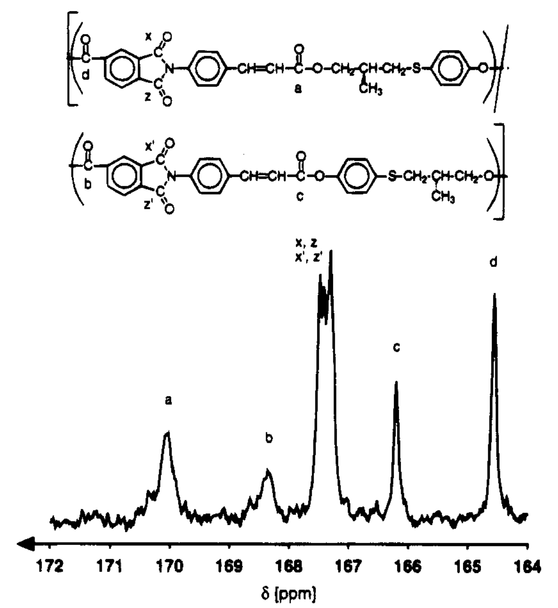


Figure 4. 25.3-MHz ^{13}C NMR spectrum (CO signals) of poly(ester–imide) **7a′** (measured in $CDCl_3$/trifluoroacetic acid, volume ratio 4:1).

of the cinnamic unit took place. Moreover, no racemization was observed, and the viscosities (molecular weights) were higher than those of **6b** and **7a** (Table 1). In other words, the polycondensation in *o*-dichlorobenzene proved to be an attractive alternative method in this case.

When the nonsymmetrical monomer **3** is polycondensed with a nonsymmetrical diol such as **4a,b** or **8**, copolyesters of two different repeating units will be formed as illustrated by **7a** (I/II). When the OH groups of the diol possess different reactivities as is true for spacer **8**, the isomeric repeating unit will be formed at different reaction rates and the resulting polyester does not necessarily contain a 1:1 ratio of both isomeric repeating units. In order to elucidate the sequence isomerism of **6a**, **6b**, **6b′**, **7a**, and **7d**, 200-MHz ^{1}H NMR or 25.4-MHz ^{13}C NMR spectra were recorded. As illustrated by Figure 2 for the PEI of the symmetrical spacer (5), the $O-CH_2$ protons feel the different anisotropics of the cinnamoyl and trimellitic residues and show two signals even at 100 MHz. An analogous splitting into two signals was observed in the case of **7a**, **7a′**, and **7d**. Their intensities proved that the isomeric sequences (e.g., **7a** (I/II)) were present in ratios around 8:10 when synthesized by method A. As illustrated by Figure 4, the ^{13}C NMR spectra of **7a–d** and **7a′** also indicate the presence of two isomeric repeating units. Whereas their ratio is 7:10 or 8:10 in the case of **7a** (Figure 4), a ratio close to 10:10 was obtained for **7a′**. Obviously, the higher reaction temperature reduced the selectivity. In the case of **6a**, **6b**, and **6b′** neither the 100-MHz ^{1}H NMR nor the 25.4-MHz ^{13}C NMR spectra gave a satisfactory resolution of all four possible ester groups. However, the 360-MHz ^{1}H-NMR spectra allowed a clearcut resolution of 4 $O-CH_2$ signals and proved that all three polyesters possess nearly random sequences.

Crystallinity and Phase Transitions of 5, 6a, and 6b. The thermal properties of PEI **5** were easy to characterize. Both DSC measurements and WAXD powder pattern agree in that this polymer does not crystallize despite annealing at 80 °C for 1 h. Furthermore, an isotropic character of the melt was found by optical microscopy. This result is remarkable, because all other PEI's of this work form a liquid-crystalline phase.

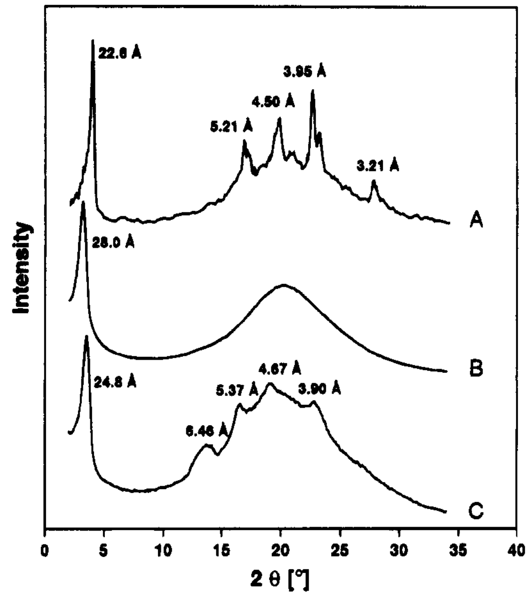


Figure 5. WAXD powder patterns of (A) PEI **6a**, (B) PEI **6b**, and (C) PEI **7a**.

The PEI's **6a** and **6b** (including **6b′**) have in common that the solid state has a smectic type of layer structure. The layer structure is evident from the middle angle reflections in their WAXD powder patterns corresponding to a *d*-spacing of 22.6 Å in the case of **6a** or 28.0 Å in the case of **6b** (Figure 5). Computer calculations with a force field program (DCFF 91, Insight II/Discover of Biosym) show that the measured *d*-spacings fit in with the existence of linear repeating units in rectangular position relative to the layer planes. The spacers may adopt gauche conformations stabilized by the influence of neighboring O or S atoms (oligo(ethylene oxides) are known to prefer gauche to trans conformations).

Interestingly, **6a** and **6b** (or **6b′**) differ in that **6a** is semicrystalline, whereas **6b** is not. The WAXD powder patterns exclude a hexagonal order of the mesogens and, thus, suggest that **6a** forms a chiral smectic E phase in the solid quasicrystalline state. The noncrystalline solid state of **6b** (and **6b′**) may be labeled "frozen chiral smectic A" because no WAXD reflections are detectable and because the mesogens are in an upright position. Nonetheless, both **6a** and **6b** (or **6b′**) form the same kind of liquid-crystalline phase. Optical microscopy revealed a cholesteric "schlieren texture" (similar to that of **7a** in Figure 8). Regardless of temperature, annealing, or mechanical treatment of the melt, a Grandjean texture was never obtained. The isotropization and anisotropization are easily detectable as endotherms and exotherms, respectively, in the DSC curves (Figure 6 and Table 2) in agreement with the microscopic observations.

The finding that **6a** and **6b** form an enantiotropic liquid-crystalline phase is not trivial. Poly(ester–imide)s based on the imide dicarboxylic acid **1** and aliphatic spacers never do form an enantiotropic LC phase, regardless if the spacer is chiral or not.[2-4] Thus, the LC character of molten **6a** or **6b** (and **6b′**) proves that the imide dicarboxylic acid **2** is the better mesogen. However, even in the case of **2** the PEI's derived from α,ω-alkanediols (**9**) form an isotropic melt above T_m and yield a monotropic LC phase only by supercooling

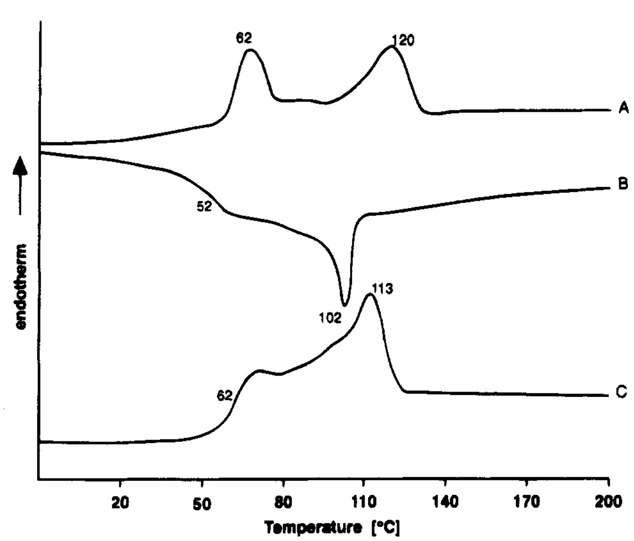


Figure 6. DSC measurements (heating and cooling rate 20 °C/min) of PEI **6b′**: A) first heating; B) first cooling, C) second heating.

Table 2. Thermal Properties of the Poly(ester–imide)s Prepared from 4-Aminocinnamic Acid Trimellitimide

polym formula	T_g[a] (°C)	T_m[a,b] (°C)	T_i[a] (°C)	T_i[b] (°C)	texture[b] (main color)[c]
5	33				isotropic melt
6a	69	157	173–176	173–177	schlieren texture
6b	53		108	108–118	schlieren texture
6b′	62		120	111–125	schlieren texture
7a	99	158	338	340–350	Grandjean texture (green)
7a′	113	225	352	350–360	Grandjean texture (green)
7b	100			350–360	Grandjean texture (red)
7c	100	190		370–380	Grandjean texture (orange)
7d	103	233–240		370–380	threaded (nematic) schlieren

[a] DSC measurements with a heating rate of 20 °C/min. [b] Optical microscopy with a heating rate of 10 °C/min. [c] As observed in the microscope by transmitted light.

(described in a future part of this series). When the phase transitions of **6a**, **6b**, and **6b′** were compared, lower T_g's and T_i's were found for **6b** and **6b′** due to the longer spacer. Remarkably, the higher molecular weight of **6b′** entails an increase of 10–12 °C for both T_g and T_i, when compared to **6b** (Table 2).

Crystallinity and Phase Transitions of 7a–d. The WAXD powder patterns of PEI's **7a–d** provided the following information. **7a** (and **7a′**) is semicrystalline and forms a layer structure (Figure 5C). The layer distance of 24.8 Å corresponds roughly to a linear repeating unit with a rectangular position relative to the layer planes. Since the WAXD reflection indicates an orthorhombic type of chain packing, this layer structure is obviously a (chiral) smectic E phase. Almost the same kinds of layer structures were found for PEI's derived from **1** and various aliphatic spacers.[2–5]

The PEI's **7b–d** have in common that they do not possess a well-defined layer structure. Furthermore, **7b** is completely noncrystalline. Its solid state is best described as a cholesteric glass. This description also holds for **7c**, but a low degree of crystallinity (<10%) is detectable here. As expected, the level of crystallinity of the homopolymers **7d** is distinctly higher. Yet despite annealing above the T_g, no layer structures were developed.

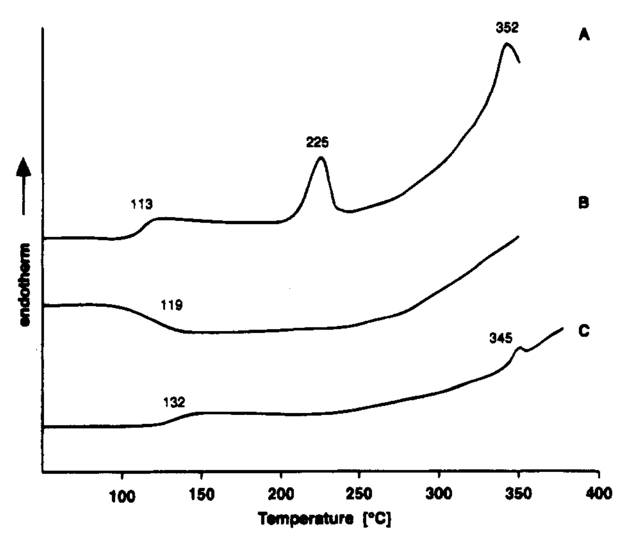


Figure 7. DSC measurements (heating and cooling rate 20 °C/min) of **7a**: (A) first heating after annealing at 200 °C (1 h), (B) first cooling, (C) second heating after annealing at 200 °C (1 h).

Examination of **7d** by optical microscopy revealed a nematic schlieren texture, which is a reasonable result considering the absence of a layer structure in the solid state. Nonetheless, the DSC measurements are somewhat more complex than expected, because two or even three weak endotherms are detectable regardless of which temperature was used for annealing. The endotherm at highest temperatures shows up between 233 and 240 °C and represents the transition to the nematic phase (T_m in Table 2). At least one additional endotherm appears in the temperature range of 192–212 °C depending on the annealing conditions. The meaning of this endotherm is not clear, but it has to be taken into account that this PEI has a low molecular weight. Also the DSC heating curve of annealed **7c** exhibits two weak endotherms. It is unclear why two endotherms are observable. The isotropization of both **7c** and **7d** occurs around 370–380 °C. It is accompanied by slow thermal degradation and is not clearly detectable in the DSC curves.

Also in the case of **7a** and **7b**, thermal degradation occurs above 360 °C, but the isotropization is detectable as an endotherm because it takes place at lower temperatures around 352 °C (Table 2 and Figure 7). Whereas the DSC curve of **7b** is bare of any melting endotherms, the heating curve of **7a** shows a melting endotherm at 158 °C and that of **7a′** a melting endotherm at 227 °C (Figure 7). Obviously, the higher molecular weight of **7a′** has a significant influence on the temperature of the phase transitions. However, all three PEI's **7a–c** have in common that their melt exhibits a cholesteric schlieren texture (Figure 8). Slight shearing between glass plates causes a macroscopic orientation of the domains, and a typical Grandjean texture (Figure 9) appears in contrast to the LC phase of **6a**, **6b**, or **6b′**. This Grandjean texture results from a macroscopic alignment of the helical domains and reflects and transmits circularly polarized light. In the case of **7a** and **7a′** the Grandjean texture is thermochromic, changing from red to green (as observed in the transmitted light) upon heating. This reversible change occurs at 180–190 °C in the case of **7a** and at 230–240 °C in the case of **7a′**. The copolyester **7b** looks mainly red in the transmitted light, whereas the Grandjean texture of **7c** changes gradually from orange to yellow upon heating. The homopolyester **7d** displays

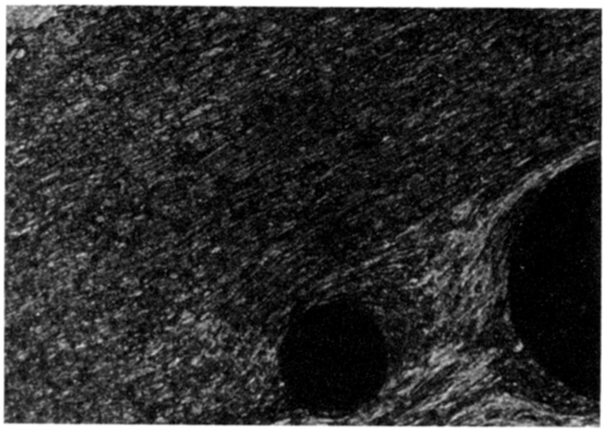


Figure 8. "Schlieren texture" of PEI **7a′** at 235 °C.

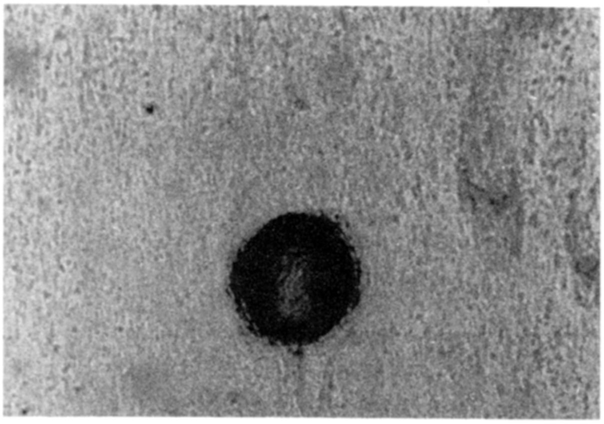


Figure 9. Grandjean texture of PEI **7a′** at 275 °C.

the typical threaded schlieren texture of a normal nematic phase.

Photo-cross-linking. UV spectra of the PEI's **6b** and **7a,b** revealed that the absorption rises sharply between 400 and 360 nm. Since it is well-known that cinnamic acid derivatives dimerize upon suitable irradiation, it is not surprising that films of **6a** and **6b** or **7a–d** rapidly cross-link upon irradiation with wavelengths ≤ 360 nm. Since the photo-cross-linking only requires seconds, whereas thermal degradation and thermal cross-linking are rather slow up to 350 °C, selective photo-cross-linking may be conducted over a broad temperature range. Hence, it is feasible in the case of **7a** (or **7a′**) to fix texture and color at selected temperatures. As described in a recent patent claim,[9] the resulting crosslinked surface possesses a scratch hardness which may be 50% higher than that of the best polyurethane laquers in the automotive industry.

Conclusion

The aforementioned results demonstrate that the imide dicarboxylic acid **2** is a better mesogen than **1** and allows the synthesis of LC poly(ester–imide)s, forming enantiotropic LC phases. PEI's consisting of **1** and chiral spacers form cholesteric phases which may show a thermochromic character. An additional advantage of monomer **1** is its sensitivity to photo-cross-linking. Therefore, photo-cross-linking of PEI's based in **1** may be used to produce multicolored films or laquered surfaces with high scratch hardness.

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