Photoreactive Cholesteric Polyesters Derived from 4-Carboxycinnamic Acid and Novel Chiral Spacers

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ABSTRACT: A homopolyester was prepared from 4-carboxycinnamic acid and a diol derived from 4-mercaptophenol and (*S*)-3-bromo-2-methyl-1-propanol. With this spacer and a 1:1 combination of 4-carboxycinnamic acid and naphthalene-2,6-dicarboxylic acid, copolyesters with random and with alternating sequences of the dicarboxylic acids were synthesized. The homopolyester and the random copolyester are noncrystalline materials with a broad cholesteric phase, whereas the alternating copolyester is semicrystalline. In contrast to the homopolyester, the copolyesters form a blue "Grandjean" texture over a broad temperature range. Upon irradiation in solution the cinnamoyl moiety undergoes trans–cis photoisomerization and (2 + 2) photocycloaddition. The cinnamic, benzoic, and naphthalene-2,6-dicarboxylic phenyl esters undergo photo-Fries rearrangements. The dominating reaction in spin-coated films is the photocycloaddition causing photocrosslinking. The efficiency of cycloaddition and their competition with the Fries reaction are dependent on the composition of the polymers and the conversion. The rearrangement is completely suppressed in films of the homopolyester **4**, and the photocycloaddition is more efficient than in the copolymers.

Introduction

Photoreactive chiral, thermotropic polymers are of interest for several reasons. Chiral, thermotropic polymers normally form at least cholesteric melts and glasses. In rare cases a chiral smectic liquid crystalline (LC) phase may be formed in addition to the cholesteric phase. The cholesteric phase is characterized by a helical array of molecules or chain segments with the consequence that cholesteric layers reflect and transmit circularly polarized light. The wavelength of this light depends on the temperature, because the helical pitch is dependent on the temperature.

Polymers with cinnamoyl moieties are photochemically reactive and may undergo efficient photocrosslinking via the (2 + 2)-photocycloaddition.[1,2] The photoreactivity of the cinnamoyl group in the solid state allows the modification of polymers at room temperature. In this way, the supramolecular structure can be frozen-in, the dynamics of relaxation processes can be restricted, and the optical properties as well as the solubility can be locally and irreversibly changed. Recently, the interest in photocrosslinking of LC polymers was stimulated by the light-induced stabilization of poled nonlinear optical (NLO) polymers[3] and the photochemical modification of liquid crystalline side-group polymers.[4–6] Photocrosslinking enables the microstructuration of films and the tailoring of surfaces or membranes with certain optical properties including the irreversibly optical storage of information.

The helical structure of a cholesteric mesophase is extremely sensitive to the variation of intermolecular interactions by factors such as temperature, impurities, and photoreactions.[7,8] Therefore, the photo-cross-linking itself can change the molecular order of its neighborhood. On the other hand, the molecular order surrounding a cinnamoyl unit influences its photoreactivity. For instance, the (2 + 2)-photocycloaddition is controlled by the nature of the crystal lattice (topochemical principle).[2] The photoreactive matrix of multiphasic cinnamoyl-containing polymers may be characterized as an ensemble of chromophore sites differing in geometry and mobility of the reactive sites and, thus, in their photoreactivity.[9] These reactive sites can be modified via the chemical structure of the neighborhood and via the order of the liquid crystalline[4] or crystalline phase.[10] In addition to the (2 + 2)-photocycloaddition, phenylcinnamate groups can undergo cis–trans photoisomerization and photo-Fries rearrangement in more mobile environments, such as solutions or melts. Systematic studies of these interesting structure–property relationships are scarce in the case of LC main-chain polymers.

Difunctional cinnamic acids such as 4-hydroxy- or 4-aminocinnamic acid are useful and interesting components of photoreactive polycondensates.[11–13] To the best of our knowledge, 4-carboxycinnamic acid has never been used as a monomer for thermotropic and, in particular, cholesteric main-chain LC polymers. The present work had the purpose to synthesize and characterize cholesteric polyesters containing 4-carboxycinnamic acid as a photoreactive building block. Further studies on cholesteric and photoreactive polyesters are in progress.

Experimental Section

Materials. 4-Carboxycinnamic acid was purchased from Lancaster Synthesis (Mülheim/Main, FRG) and used without purification. Naphthalene-2,6-dicarboxylic acid, 4-mercaptophenol, and (*R*)-3-bromo-2-methyl-1-propanol were purchased from Aldrich Chemical Co. (Milwaukee, WI) and also used without purification. The chiral spacer (*R*)-2-methyl-3-[(4-hydroxyphenyl)thio]-1-propanol (**2**) was prepared as described previously:[7] n^{20}_{D} 1.5887; $[\alpha]^{20}_{D}$ +3.5° (c = 2 g/100 mL in $CHCl_3$). Pyridine was distilled over freshly powdered CaH_2 and *N*-methylpyrrolidone (NMP) over P_4O_{10} in vacuo.

4-(Chloroformyl)cinnamoyl Chloride. Dimethylformamide (1 mL) was added to a suspension of 4-carboxycinnamic

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Table 1. Yields and Properties of Polyesters Derived from 4-Carboxycinnamic Acid

formula no.	yield (%)	η_{inh}[a] (dL/g)	$[\alpha]^{20}_{\text{D}}$ (deg)	elem form. (form. wt)		elem anal.		
						C	H	S
4	92	0.62	+46.4[b]	$C_{20}H_{18}O_4S$ (354.4)	calcd	67.78	5.12	9.04
					found	67.94	5.08	9.01
5	95	0.60	+49.0[c]	$C_{21}H_{18}O_4S$ (366.4)	calcd	68.83	4.95	8.75
					found	68.73	4.87	8.68
6a	82	0.56	+48.7[c]	$C_{21}H_{18}O_4S$ (366.4)	calcd	68.83	4.95	8.75
					found	69.04	4.87	8.83
6b	85	0.44	+51.0[c]	$C_{109}H_{90}O_{20}S_5$ (1880.2)	calcd	69.63	4.83	8.53
					found	69.01	4.67	8.46

[a] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1). [b] Measured at 20 °C with $c = 2$ g/100 mL in $CHCl_3$. [c] Measured at 20 °C with $c = 2$ g/100 mL in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1).

acid (0.1 mol) in freshly distilled thionyl chloride (125 mL), and the reaction mixture was refluxed until the evolution of SO_2 and HCl ceased. The excess of thionyl chloride was then removed in vacuo, and the residual product was recrystallized from chloroform/ligroin. Yield: 83%. Mp: 127−129 °C. Anal. Calcd for $C_{10}H_6CO_2O_2$ (229.06): C, 52.44; H, 2.64, Cl, 30.95. Found: C, 52.18; H, 2.56; Cl, 30.68. ^{1}H NMR ($CDCl_3$/TMS): δ 6.77 (d, 1H), 7.71 (d, 2H), 7.86 (d, 2H), 8.19 (d, 2H). Naphthalene-2,6-dicarbonyl dichloride was prepared analogously. Yield: 91%. Mp: 183−185 °C (lit.[14] mp 187 °C).

Ester Diol (3). A suspension of (*R*)-2-methyl-3-[(4-hydroxyphenyl)thio]-1-propanol[15] (**2**; 34 mmol) in water (30 mL) was purged from oxygen by a stream of nitrogen, NaOH (35 mmol) and benzyltriethylammonium chloride (20 mg) were added, and a clear solution was obtained by means of a high-speed stirrer. Afterward a solution of naphthalene-2,6-dicarbonyl chloride in 60 mL of dry CH_2Cl_2 was added, and the reaction mixture was stirred for 10 min. The precipitated product was finally filtered off, washed with acetone, and recrystallized from dioxane/water (volume ratio 3:2). Yield: 90%. Mp: 196−198°C. Isotropization: 206 °C. $[\alpha]^{20}_{\text{D}}$: 18.00° ($c = 2$ g/100 mL in dioxane). Anal. Calcd for $C_{32}H_{32}O_6S_2$ (576.7): C, 66.64; H, 5.59; S, 11.12. Found: C, 66.17; H, 5.51; S, 11.01. ^{1}H NMR ($CDCl_3$/trifluoroacetic acid (9:1 by volume)/TMS): δ 1.15 (d, 6H), 2.02−2.23 (m, 2H), 2.99 (m, 4H), 4.39 (d, 4H), 7.21 (d, 4H), 7.42 (d, 2H), 8.60 (d, 2H), 8.30 (d, 2H), 8.88 (s, 2H).

Polycondensations. A spacer diol (20 mmol) was dissolved in a mixture of dry pyridine (10 mL) and dry 1,2-dichloroethane (20 mL) and cooled under a slow stream of nitrogen to 0−2 °C. The 4-(chloroformyl)cinnamoyl chloride was then added at once, and the reaction mixture was stirred for 2 h at 0 °C and for 6 h at 60 °C. The cold reaction mixture was precipitated into methanol (600 mL); the precipitated product was isolated by filtration, washed with acetone, and dried in vacuo. The crude polyesters were finally dissolved in CH_2Cl_2 or a mixture (4:1 by volume) of CH_2Cl_2 and trifluoroacetic acid and precipitated again into cold methanol.

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

The DSC measurements were conducted with a Perkin-Elmer DSC-4 in aluminum pans under nitrogen.

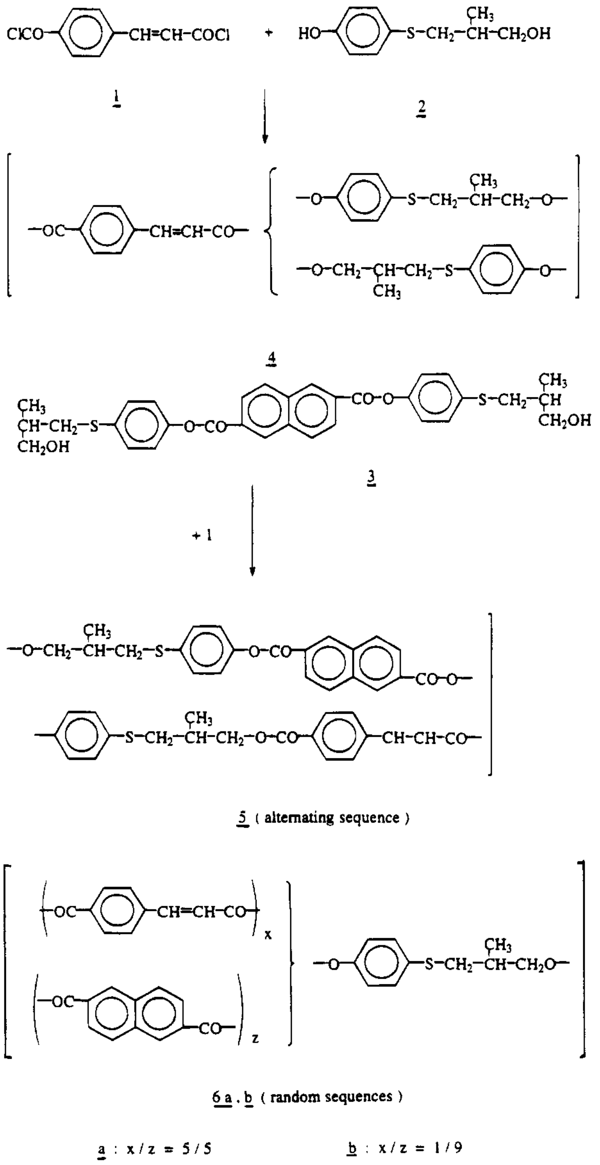
The 100-MHz ^{1}H NMR spectra were recorded on a Bruker AC-100 FT NMR spectrometer in 5-mm-o.d. sample tubes. The 25.3-MHz ^{13}C NMR spectra were recorded with the same instrument in 10-mm-o.d. sample tubes. Approximately 15 000 transients were accumulated for the spectra of Figure 2.

The IR spectra were obtained from KBr pellets on a Nicolet SXB-20 FT spectrometer.

The photochemical studies were conducted with a XBO lamp (150 W; Narva) as the radiation source. The light was collimated by a quartz lens and passed through a water filter and metal interference filter (313 nm; Zeiss). The films were spin-coated on quartz plates using $CHCl_3$ as the solvent. The amorphous films were annealed at 70 °C for 30 min. The UV−vis spectra were recorded as a function of irradiation time using the spectrophotometers "Lambda 2" and "Lambda 19" (Perkin-Elmer). Chloroform (Uvasol; Merck) was used as a solvent for the irradiation experiments in solution.

Results and Discussion

Syntheses. All polyesters of this work are based on the polycondensation of 4-carboxycinnamic acid in the form of its acid chloride (**1**) with chiral spacers in the presence of pyridine. The synthesis of the chiral spacer **2** from commercial (*R*)-3-bromo-2-methyl-1-propanol and 4-mercaptophenol was described previously.[15] A second reaction partner (**3**) was prepared from **2** by acylation with naphthalene-2,6-dicarbonyl chloride under the conditions of an interfacial condensation. The diluted sodium hydroxide almost exclusively deprotonates the



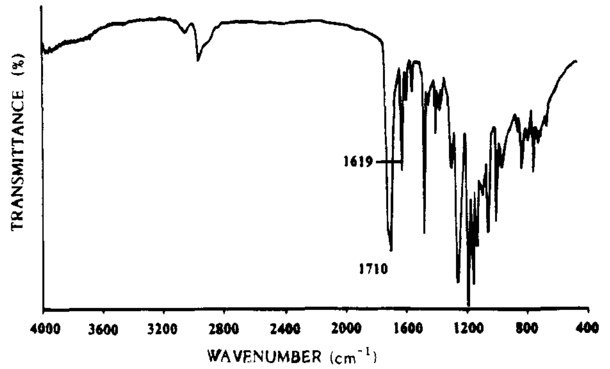


Figure 1. IR spectrum (KBr pellets) of the homopolyester.

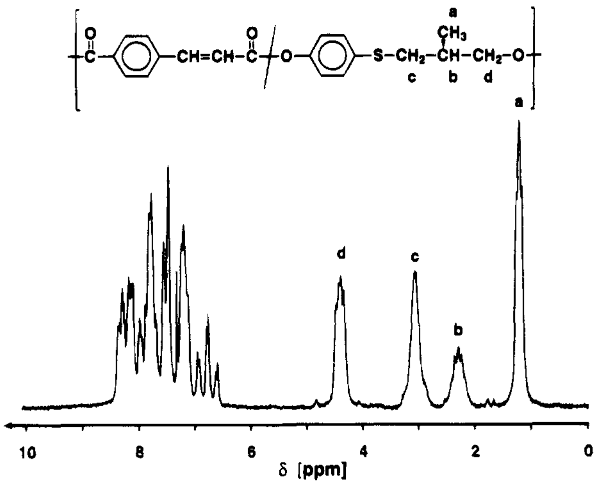


Figure 2. 100-MHz ^{1}H NMR spectrum of the homopolyester in $CDCl_3$.

phenolic OH which is 7–8 orders of magnitude more acidic than the CH_2OH group. The nucleophilicity of the resulting phenoxide anion is in turn several orders of magnitude higher than that of the CH_2OH group. The highly regioselective acylation expressed in formula **3** is confirmed by the ^{1}H NMR spectrum which shows that the chemical shift and coupling constants of the CH_2-OH groups of **3** are identical with those of **2**.

Monomer **3** is an interesting compound in itself, because DSC measurements and optical microscopy revealed that it forms a cholesteric phase between 196 and 206 °C. Furthermore, it forms a so-called "blue-phase" around 205 °C, which is characterized by its dark blue reflection and a mosaic-like texture.[16,17]

The polycondensation of spacer **2** with 4-(chlorocarbonyl)cinnamoyl chloride yielded the polyester **4**, which is a kind of copolymer of two isomeric repeating units. Analogously, the alternating copolyester **5** was obtained from **3** and 4-(chlorocarbonyl)cinnamoyl chloride. Furthermore, a random copolyester (**6a**) was prepared from spacer **2** and from an equimolar mixture of 4-(chlorocarbonyl)cinnamoyl chloride and naphthalene-2,6-dicarbonyl chloride. For the synthesis of **6b** both dicarboxylic acid chlorides were mixed in the molar ratio 1:9 prior to the polycondensation with **2**.

The chemical structure of polyester **4** is evidenced by the IR spectrum of Figure 1, which exhibits the "ester CO bond" at 1710 cm^{-1} and the sharp band of the trans ethylene group at 1619 cm^{-1}. The trans isomerism of the double bond was confirmed for all polyesters of this work by ^{1}H NMR spectra. As illustrated by Figure 2, doublet signals show up around δ 7 with a coupling constant of 16 Hz, characteristic for the trans cinnamoyl unit. The additional splitting of these signals reflects the different neighborhoods of aliphatic or aromatic ester groups.

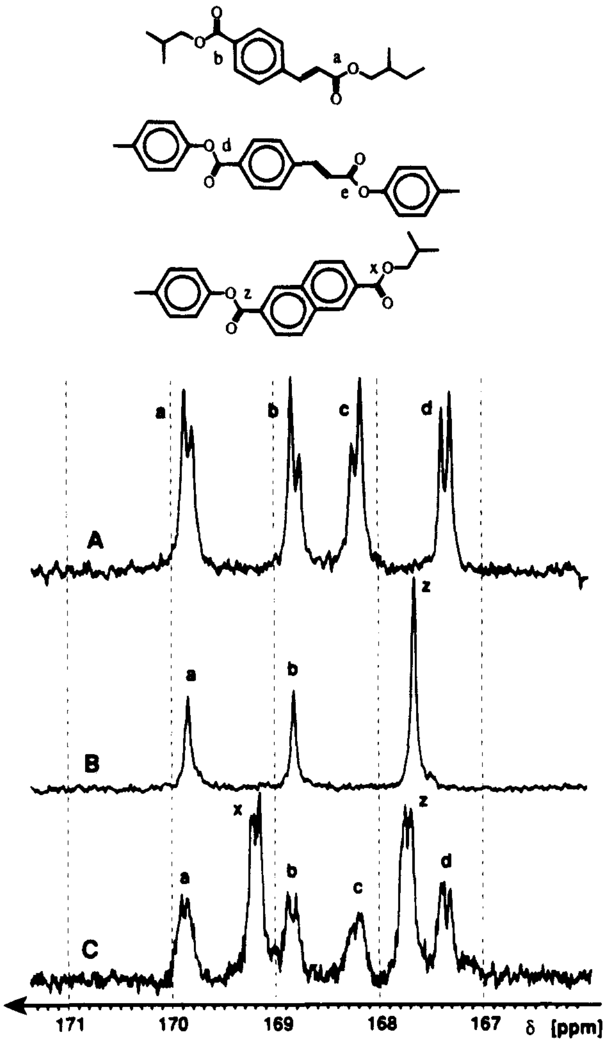


Figure 3. 25.3-MHz ^{13}C NMR spectra ($CDCl_3$/trifluoroacetic acid; volume ratio 4:1) of (A) homopolyester **4**, (B) alternating copolyester **5**, and (C) random copolyester **6a**.

The sequences of the polyesters **4**, **5**, and **6a** were characterized by ^{13}C NMR spectroscopy. As is typical for polyesters[18,19] and polyamides,[20,21] the carbonyl signals are most informative on sequence isomerism also in the case of **4a**–**6a**. In agreement with the structure given in formula **3** four CO signals (with fine structure) are observable in the spectrum of Figure 3A. The signal intensities suggest that the isomeric repeating units were formed at slightly different rates. Nonetheless, the overall sequence is close to randomness. The three CO signals expected for the alternating sequence of **5** are present in the spectrum of Figure 3B, and the six CO signals characteristic for the random sequence of **6a** (or **6b**) are observable in Figure 3C. The tentative assignments are based on comparisons of signal intensities and chemical shifts. Taken together, it may be said that all spectroscopic methods used in this work perfectly agree with the chemical structures depicted in formulas **4**–**6**.

The selection of naphthalene-2,6-dicarboxylic acid as the comonomer of 4-carboxycinnamic acid is based on the fact that the properties of the homopolyesters derived from spacer **2** and terephthalic acid or naphthalene-2,6-dicarboxylic acid were known in the beginning of this work.[22] It was found that the polyester of

Table 2. Thermal Properties of the Polyesters

formula no.	T_g[a] (°C)	T_m[a] (°C)	T_i[c] (°C)	T_i[b] (°C)	ΔH_i[a] (J/g)	texture[b]
4	60		337	335–340	5.0	colorful Schlieren, blue
5	69	170[c] 180[d]	314	315–320	4.0	Grandjean, blue
6a	62		315	320–330	5.0	Grandjean, blue
6b	68		335	330–340	4.0	Grandjean, blue

[a] From DSC measurements at a heating rate of 20 °C/min. [b] From optical microscopy with a heating rate of 10 °C/min. [c] Second heating without annealing. [d] Second heating after annealing at 160 °C for 1 h.

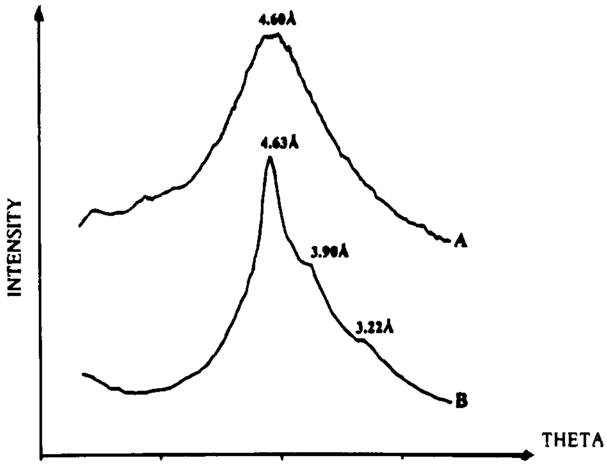


Figure 4. WAXD powder patterns of (A) the random copolyester **6a** and (B) the alternating copolyester **5**.

2 and terephthalic acid like polyester **4** does not form a Grandjean texture, whereas the polyester of **2** and naphthalene-2,6-dicarboxylic acid does. It was hoped that copolyesters of **1** and naphthalene-2,6-carboxylic acid combine two advantages: enough sensitivity to photocrosslinking and formation of a stable Grandjean texture.

Thermal Properties. After drying at 115 °C all polyesters were subjected to X-ray measurements. The WAXD powder patterns revealed that **4**, **6a**, and **6b** are amorphous materials in agreement with their random sequences. In contrast to that, a semicrystalline character was found for **5** (Figure 4). However, the degree of crystallinity was rather low (≤10%) even after annealing at 115 °C. For this reason and because the crystal lattice of **5** was not of particular importance for the purpose of this work, a detailed study of the solid state was not intended in this work, in as much as the WAXD pattern of **5** is not much informative.

Corresponding to the amorphous character of most polyesters, their DSC heating curves do not exhibit any melting endotherm. In addition to a glass transition step, only one weak endotherm is detectable, representing the transition from the liquid crystalline to the isotropic state. The DSC curves of polyester **5** are more complex and interesting (Figure 5). In addition to the glass transition step, three endotherms are detectable when this polymer is heated to 360 °C. Thermal degradation at such high temperatures prevents a good reproducibility of all three endotherms. However, when the heating is stopped at 260 °C, the first two endotherms are well reproducible (Figure 5C,D). According to optical microscopy, the endotherm at 170 °C represents the melting process. Both the intensity and temperature of both endotherms strongly depend on the thermal history of the sample.

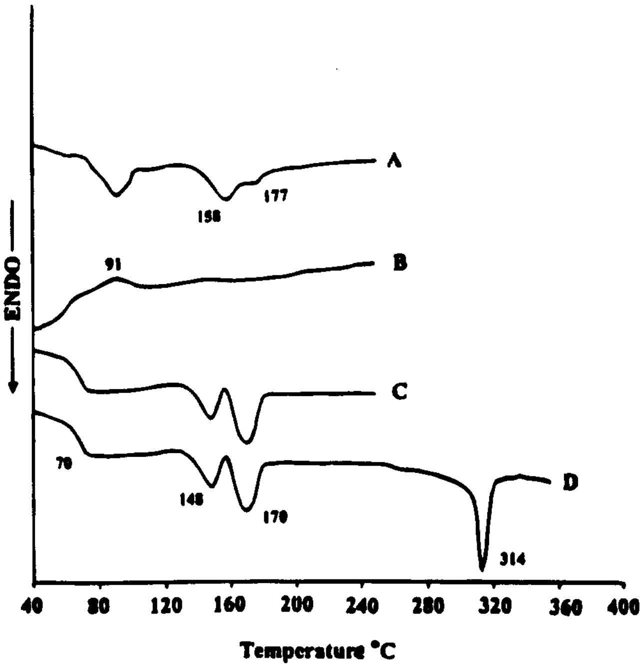


Figure 5. DSC measurements (heating/cooling rate, 20 °C/min) of the alternating copolyester **5**: (A) first heating; (B) first cooling; (C) second heating; (D) third heating.

Obviously the low-temperature endotherm (148 °C in Figure 5D) represents an early melting of less stable crystallites, as is quite often observed for semicrystalline polymers. Annealing at 150 °C eliminates this endotherm and yields a heating curve with two endotherms at 165 and 175 °C. Annealing at 160 °C for 1 h yields a weak endotherm at 145 °C and a strong melting endotherm at 180 °C. Cooling by −20 °C/min results in a broad crystallization exotherm around 90 °C (Figure 5B). Faster cooling prevents the crystallization and, thus, demonstrates that polyester **5** is a slowly crystallizing material.

Optical microscopy revealed that all four polyesters form a mobile cholesteric melt. In the case of **4**, a colorful "Schlieren texture" is observable which is somewhat different from the typical "threaded Schlieren texture" of a normal nematic phase. The same texture is formed by polyesters **5**, **6a**, and **6b**, but in these cases a slight shearing between glass plates produces a "Grandjean texture"[23,24] with a deep blue color in the reflecting light. This texture results from the macroscopic orientation of the helical domains. In the case of **5**, **6a**, and **6b** this texture is stable with almost the same color and, thus, helical pitch up to the isotropization temperature. Upon cooling from the isotropic melt, the Schlieren texture forms first, but shearing yields again the Grandjean texture. In other words, the optical effects were fully reversible despite the high isotropization temperatures, and thermal cross-linking was never observed. The stabilization of a Grandjean texture was strong reflection in the visible light was the reason why naphthalene-2,6-dicarboxylic acid was used as the comonomer of 4-carboxycinnamic acid.

Photochemical Aspects. The UV–vis spectrum of polymer **4** (Figure 6) is characterized by the absorbance maximum of the 4-carboxycinnamic moiety at 292 nm, whereas the spectra of the copolymers **5** and **6a** show a double transition at 290/298 nm and maxima of lower intensity at 340 and 360 nm caused by the naphthyl moiety. Upon irradiation of the polymers in chloroform

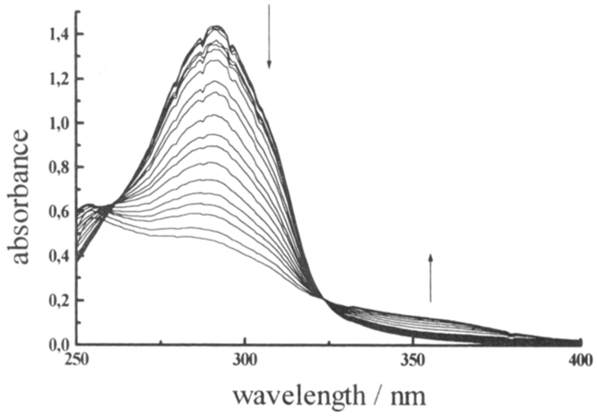


Figure 6. Change of the absorbance of polyester **4** (in chloroform) upon irradiation at $\lambda_{ex} = 313$ nm.

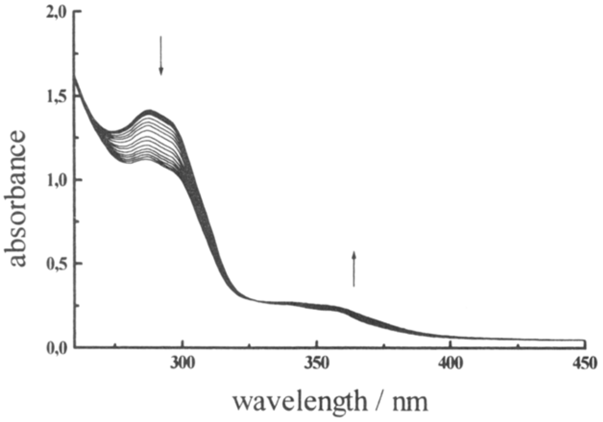


Figure 7. Change of the absorbance of copolyester **5** (in chloroform) upon irradiation at $\lambda_{ex} = 313$ nm.

using UV light the absorbance of the cinnamoyl unit at 290 nm is decreased, as shown in Figures 6–8. The change of the absorbance is caused by trans–cis photoisomerization and (2 + 2)-photocycloaddition. However, in contrast to the properties of the monomeric cinnamic ethyl ester, it was not feasible to distinguish between both reactions by kinetic measurement using UV–vis spectroscopy because of the high efficiency of the cycloaddition within the polymer coil. The spectral change of **4** is characterized by two isosbestic points at 324 and 261 nm up to 50% conversion, indicating the absence of postreactions. However, on continued irradiation the isosbestic points disappear. Simultaneously a smaller increase of absorbance is observed at 360 nm caused by the photo-Fries rearrangement of the different aromatic ester groups. These results suggest that in polyesters **4**, **5**, and **6a**,**b** all fully aromatic ester groups can undergo a photo-Fries rearrangement. The absorbance of the Fries photoproducts passes through a maximum and decreases upon continued irradiation.

Figure 9 shows that the kinetics of the photodegradation in solution are characterized by an efficient initial decrease of cinnamoyl absorbance and a much less efficient second part at higher conversion. The efficiency of the first range is higher in the case of polymer **4** in comparison to those of copolymer **5** and **6a**. The maximum of the conversion is also changed in the order of **4**, **6a**, to **5**. A more quantitative analysis of the photochemical properties is in progress in consideration of the spectral analysis of the copolymers and by means of IR measurements.

Spin-coated and, at 70 °C, annealed films of the liquid crystalline polymers were transparent and did not scatter light. In this paper the general photochemical properties of the polymers were studied in the glassy state at room temperature without anisotropic alignment. The irradiation of spin-coated films shows, in principle, a very similar spectral change (Figure 10). But in contrast to the solution the irradiation spectrum of **4** has only one isosbestic point, because the photo-Fries reaction is completely suppressed.

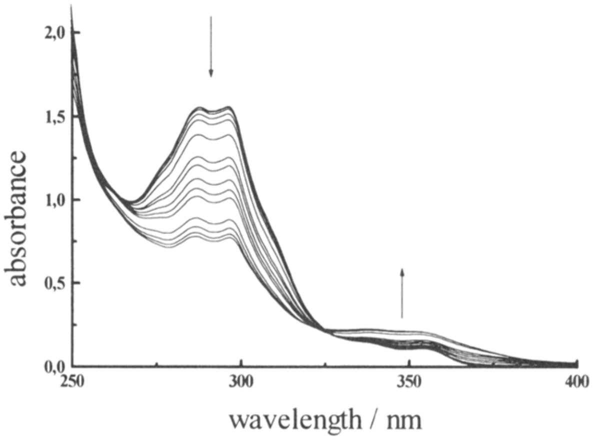


Figure 8. Change of the absorbance of copolyester **6a** (in chloroform) upon irradiation at $\lambda_{ex} = 313$ nm.

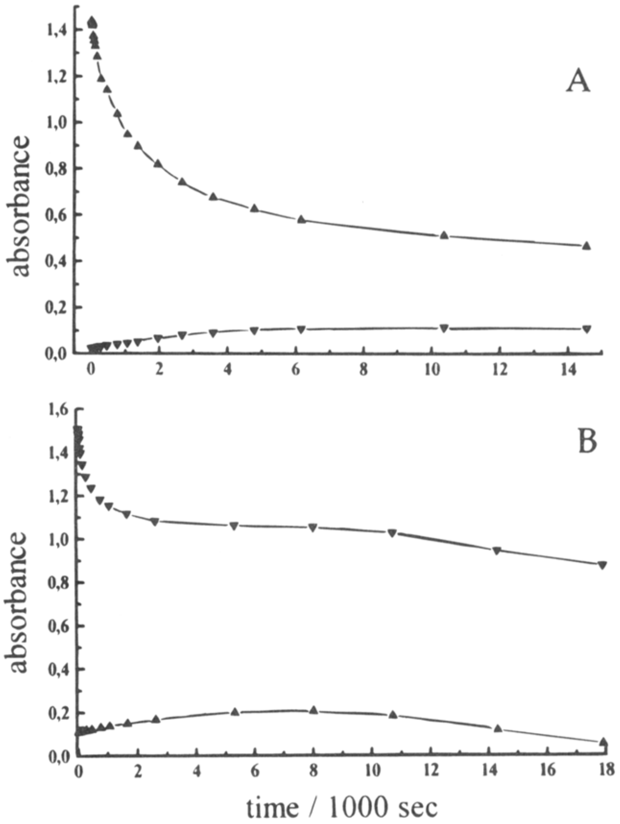


Figure 9. Change of the absorbance for the polymers (A) **4** and (B) **5** at 292 and 360 nm with variation of the irradiation time ($I_0 = 2.5$ mW/cm^2, $\lambda_{ex} = 313$ nm).

This result is in agreement with the matrix dependence of the photo-Fries reaction in ordered polymers as well as in mesophases of rod-like esters.[25]

In contrast to the aromatic ester units of 4-carboxycinnamic acid, the naphthalene-2,6-dicarboxylic acid ester moieties undergo photo-Fries rearrangements even in the solid state (i.e., in the spin-coated films) and not only in solution (Figure 10b).

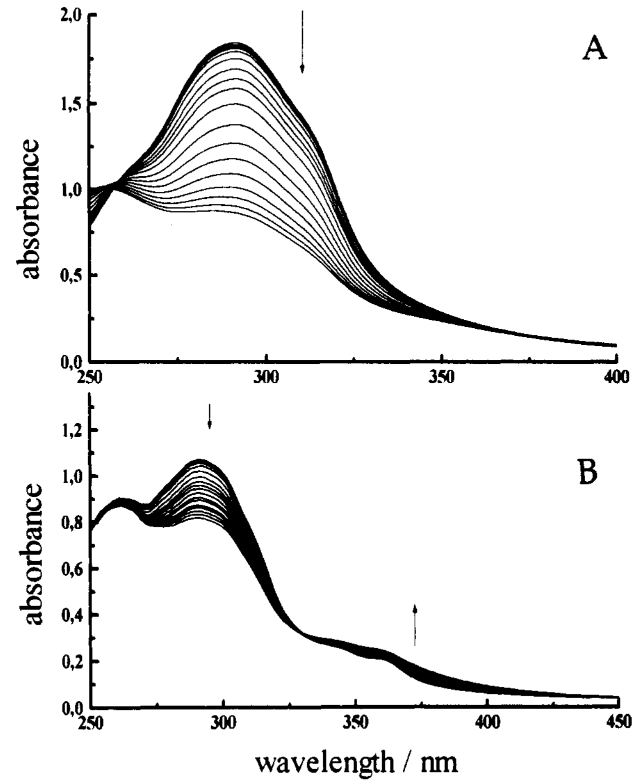


Figure 10. Change of the absorbance of spin-coated films of (A) polyester **4** and (B) copolyester **5** on irradiation at λ_{ex} = 313 nm.

The cross-linked films are characterized by a reduced solubility allowing microstructuration of films. Photochemical studies to freeze-in the helical structure of cholesteric ordered states of these polymers are in progress. In this connection it should be mentioned that the results of this work form part of a recent patent claim.

Conclusion

The chiral polyesters synthesized from the chiral spacer **2** and 4-carboxycinnamic acid all display a cholesteric phase. Interestingly, only the copolyesters containing 50 mol % of naphthalene-2,6-dicarboxylic acid are capable of forming a Grandjean texture which absorbs in the visible region. Upon UV irradiation the (2 + 2)-cycloaddition (photocrosslinking) is by far the predominant photoreaction in films of the polyesters **4**–**6**. The efficiency of this cycloaddition decreases in the order **4** > **5** > **6a** > **6b**. This result is of particular interest because the stability against thermal crosslinking and the sensitivity to UV-irradiation allows a controlled photocrosslinking and in this way a fixation of the cholesteric supramolecular order.

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