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New Polymer Syntheses. 95. Photosetting Cholesteric Polyesters Derived from 4-Hydroxycinnamic Acid and Isosorbide

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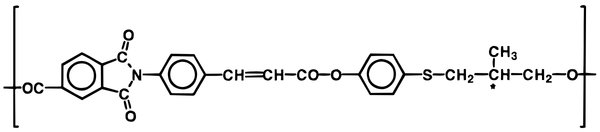
ABSTRACT: Two dicarboxylic acids were prepared by alkylation of 4-hydroxycinammic acid with 1,6-dibromohexane or 1,12-dibromododecane. The dichlorides of these dicarboxylic acids were polycondensed with mixtures of isosorbide and methylhydroquinone. All copolyesters then obtained showed nematic schlieren textures. Furthermore, three dicarboxylic acids were synthezised by alkylation of 4-hydroxycinammic acid with the ditosylates of di-, tri-, and tetraethylene glycol. Numerous copolyesters were prepared from the dicarboxylic acids and mixtures of isosorbide with methyl-, *tert*-butyl-, or phenylhydroquinone. Also 2,7-dihydroxynaphthalene was used as a comonomer. Almost all resulting copolyesters were cholesteric, and nearly 50% of them were capable of forming a Grandjean texture. The photochemical behavior of selected copolyesters was studied in solution in spin-coated films and in films with Grandjean texture. Depending on the reaction conditions, photo-cross-linking by 2 + 2 cycloaddition competed more or less successfully with the photo-Fries rearrangement and with the photoisomerization. UV irradiation (at 313 nm) of oriented films in the cholesteric melt caused disappearance of the Grandjean texture. However, irradiation below the glass-transition temperature caused stabilization of the Grandjean texture by photo-cross-linking.

Introduction

Polymers having a cholesteric character and containing photoreactive groups prone to photo-cross-linking are of interest as optically active films, coatings, or pigments for the following reason. Under the influence of shearing or of an electric field, it may be possible to align macroscopically the cholesteric domains, which contain helical supermolecular structures of mesogens. Such a macroscopic alignment of the helixes results in a selective interaction with incident white light. The wavelength matching the pitch of the helixes is selective reflected in the form of circularly polarized light (the so-called Grandjean (GJ) texture[1,2]). The transmitted light shows the complementary color. Any potential application requires a fixation of this Grandjean texture. Photo-cross-linking in the cholesteric melt is one promising approach in this direction.

Photochemical fixation of the Grandjean textures of liquid crystal (LC) main chain polymers has for the first time been reported for the poly(ester imide) **1**.[3] However, this poly(ester imide) and related cholesteric copolyesters have the shortcoming that the chiral building block is far too expensive for any potential application. Quite recently it was found that cholesteric polyesters capable of forming stable GJ textures can be prepared by incorporation of small amounts of the inexpensive commercial diol isosorbide into nematic polyesters.[4−8] In the case of copolyesters **2** it has been observed that the GJ texture is easily formed during their synthesis just by stirring of the reaction mixture. Therefore, it was the purpose of the present work to synthesize analogous photoreactive cholesteric copolyesters from 4-hydroxycinammic acid to combine their propensity to photo-cross-linking with an easy formation of Grandjean textures at moderate temperatures. In this connection it should be mentioned that syntheses and photochemical properties of polyesters derived from 4-hydroxycinammic acid (e.g., from monomers **3a** and **3b**) have been reported by Griffin, Hoyle, and coworkers.[9,10]



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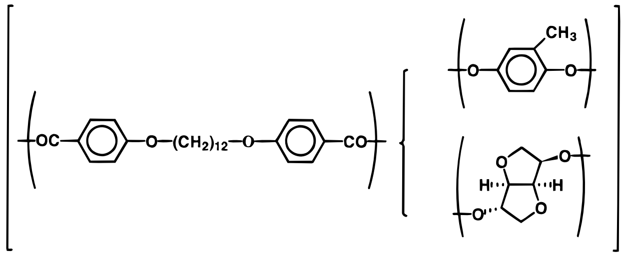

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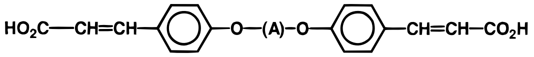
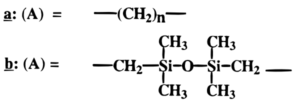


3a,b



a: (A) = $-(CH_2)_n-$

b: (A) = $-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-$

Experimental Section

Materials. 4-Hydroxycinnamic acid was a gift of BASF AG (Ludwigshaven, FRG). Tosyl chloride, 2,7-dihydroxynaphtha-

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lene, and thionyl chloride were gifts of Bayer AG (Leverkusen, FRG). 1,6-Dibromohexane, 1,12-dibromododecane, diethylene glycol, triethylene glycol, tetraethylene glycol, and methyl-, *tert*-butyl-, and phenylhydroquinone were purchased from Aldrich Co. (Milwaukee, WI). The ditosylates of the three ethylene glycols (also commercially available) were prepared according to the literature.[11] Isosorbide was dried over P_4O_{10} in vacuo prior to use.

Syntheses of the Dicarboxylic Acids. Hydroxycinnamic acid (0,5 mol) was dissolved in a solution of 2 mol of sodium hydroxide in 300 mL of water and 900 mL of dimethyl sulfoxide (DMSO). The solution was heated to 130 °C and the alkylene dibromide, respectively. The tosylate of the ethylene glycol was added slowly. After 3 h of stirring solid sodium hydroxide (0.5 mol) was added. The reaction mixture was stirred at 70 °C overnight and then diluted with water. After acidification with HCl and 2 h of stirring, the product was isolated and washed with much water. The crude products were recrystallized from dimethylformamide/water (yields 80−85%).

Polycondensations. Methylhydroquinone (9 mmol) and isosorbide (1 mmol) were weighed into a cylindrical glass reactor equipped with gas inlet and outlet tubes. 1-Chloronaphthalene (5 mL) and a dichloride of a dicarboxilic acid on the basis of hydroxycinnamic acid (10 mmol) were added. The reaction vessel was placed into an oil bath preheated to 150 °C, and the reaction mixture was homogenized with a mechanical stirrer. The temperature was then rapidly raised to 200 °C and maintained for 8 h. Finally, the PEI was dissolved in a mixture of CH_2Cl_2 and trifluoroacetic acid (4:1 by volume) and precipitated into methanol.

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

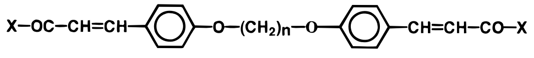
The DSC measurements were conducted with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen.

The 100 MHz ^1H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes.

Photochemical Studies. A HBO high-pressure mercury lamp was used for the irradiation experiments. The light was collimated by a quartz lens, passed through a water filter, a cutoff filter, and a metal interference filter (313 nm, Zeiss). A mixture of $CHCl_3$/trifluoroacetic acid (volume ratio 4:1) was used as solvent for the experiments in solution. The films were spin-coated on quartz plates using the same solvent mixture. The UV−visible absorbance spectra were recorded using a spectrometer "Lamda 2" (Perkin-Elmer).

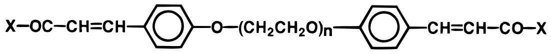
Results and Discussion

Syntheses. All copolyesters in this work were prepared by the same procedure. A dicarboxylic acid dichloride derived from 4-hydroxycinammic acid (e.g., **4c**, **4d**, or **5d−f**) was heated with a mixture of isosorbide and a suitable diphenol in 1-chloronaphthalene (eq 1). The liberated HCl was removed with a slow stream of nitrogen. The dicarboxylic acid dichlorides **4a** and **4b** were prepared by alkylation of 4-hydroxycinammic acid with 1,6-dibromohexane or 1,12-dibromododecane followed by chlorination with thionyl chloride. The dicarboxylic acids **4a**, **5b**, and **5c** have already been described by other authors.[12,13] In contrast, all the dichlorides **4c**, **4d**, and **5d−f** have never been described before. The dicarboxylic acids **5a−c** were prepared by alkylation of 4-hydroxycinammic acid with the ditosylates of di-, tri-, or tetraethylene glycol. The chlorination of **5a−c** was performed in refluxing thionyl chloride.



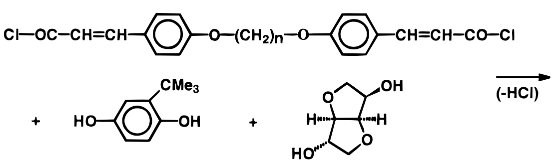
4a - d

a: n = 6, X = OH
b: n = 12, X = OH
c: n = 6, X = Cl
d: n = 12, X = Cl



5a - f

a: n = 2, X = OH
b: n = 3, X = OH
c: n = 4, X = OH
d: n = 2, X = Cl
e: n = 3, X = Cl
f: n = 4, X = Cl



6a - c and 7a - c (1)

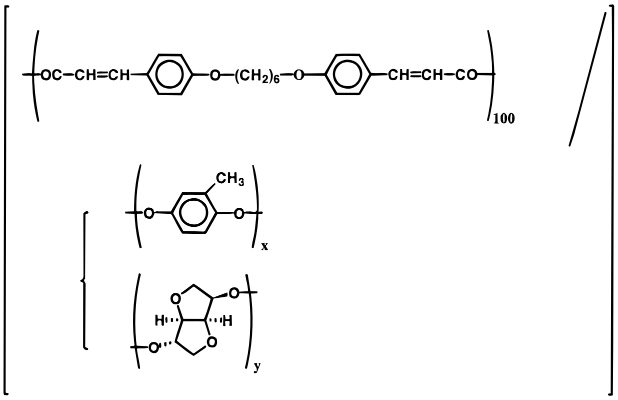
The yields and properties of the dicarboxylic acids **4a**, **4b**, and **5a−c** and their dichlorides are summarized in Table 1.

All copolyesters in this work were prepared with small quantities of isosorbide, because all previous studies of isosorbide containing copolyesters have demonstrated that a molar fraction above 15% (relative to the sum of the diols) is unfavorable for the formation of a Grandjean texture. Isosorbide is known[14] to possess a high twisting power and obviously a high molar fraction of isosorbide generated helixes with a pitch which is too small (or large) for an interaction with visible light. The substituted hydroquinones were selected as diphenols because the para position of the hydroxy groups favors the formation of a LC phase and because substituted hydroquinones have proven in previous studies[6−9] to be useful building blocks of noncrystalline cholesteric polyesters. 2,7-Dihydroxynaphthalene was used instead of the 1,4- or 2,6-monomer because crystallinity should be avoided and because the 2,7-isomer was found to be a useful component of noncrystalline nematic poly(ester imide)s.[10] The yields and properties of the copolyesters **6a−c** and **7a−c** containing alkane spacers are listed in Table 2. The yields and properties of **8a−c** and **9a−c** are compiled in Table 3, those of **10a−c** and **11a−c** in Table 4 and those of **12a−c** and **13a−c** in Table 5. The ^1H NMR spectrum displayed in Figure 1 is representative of the structure of all polyesters studied in this work.

Properties of the Polyesters 6a−c and 7a−c. The polyesters containing alkane spacers (**6a−c** and **7a−c**)

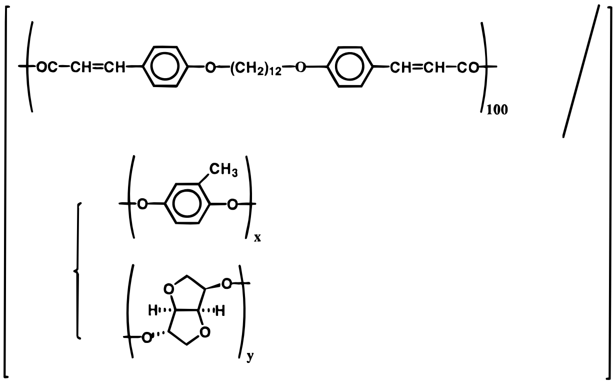
Table 1. Properties of the Acids and Acid Chlorids 4a−d and 5a−f

no.	melting temperature in °C	elem formula (formula wt)	elemental analyses	C	H	Cl
4a	208−210	$C_{24}H_{26}O_6$	calcd	70.23	6.38	
		(410 463)	found	69.39	5.98	
4b	182−183	$C_{30}H_{38}O_6$	calcd	72.85	7.74	
		(494 624)	found	71.98	7.45	
4c	101−103	$C_{24}H_{24}Cl_2O_4$	calcd	64.44	5.41	15.85
		(447 356)	found	63.12	4.81	16.15
4d	85−86	$C_{30}H_{36}Cl_2O_4$	calcd	67.79	6.83	13.34
		(531 516)	found	68.38	7.35	12.55
5a	290−292	$C_{22}H_{22}O_7$	calcd	66.32	5.57	
		(398 411)	found	66.07	5.42	
5b	227−224	$C_{24}H_{26}O_8$	calcd	65.15	5.92	
		(442 461)	found	64.51	5.94	
5c	186−187	$C_{26}H_{30}O_9$	calcd	64.19	6.22	
		(486 514)	found	63.64	6.21	
5d	128−130	$C_{22}H_{20}Cl_2O_5$	calcd	60.70	4.63	16.29
		(435 303)	found	60.24	4.55	15.89
5e	93−95	$C_{24}H_{24}Cl_2O_6$	calcd	60.14	5.05	14.79
		(479 354)	found	59.87	5.10	14.23
5f	64−66	$C_{26}H_{28}Cl_2O_7$	calcd	59.66	5.39	13.55
		(523 406)	found	59.28	5.46	13.25



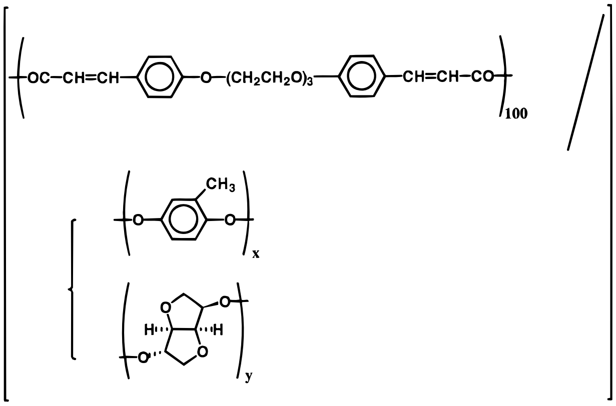
6a - c

a: x / y = 95 / 5
b: x / y = 90 / 10
c: x / y = 80 / 20



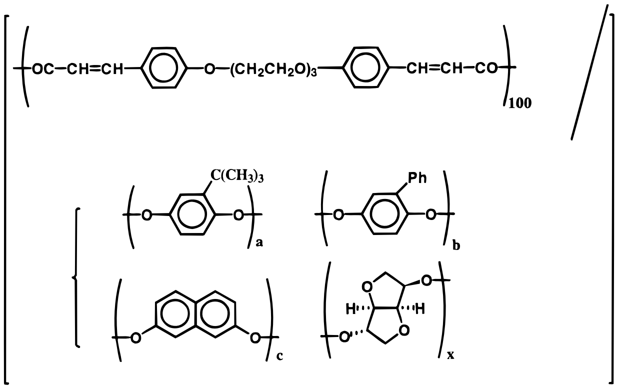
7a - c

a: x / y = 95 / 5
b: x / y = 90 / 10
c: x / y = 80 / 20



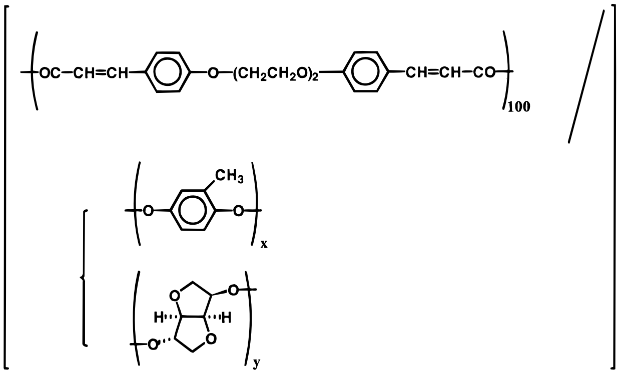
10a - c

a: x / y = 95 / 5
b: x / y = 90 / 10
c: x / y = 80 / 20



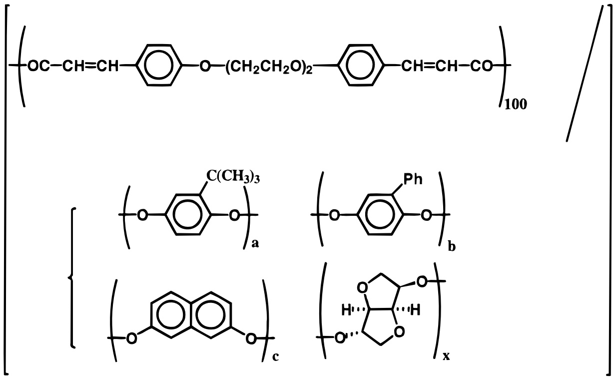
11a - c

a: a / x = 95 / 5
b: b / x = 95 / 5
c: c / x = 95 / 5



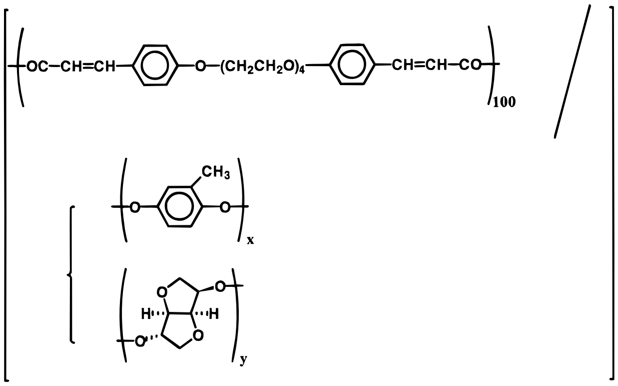
8a - c

a: x / y = 95 / 5
b: x / y = 90 / 10
c: x / y = 80 / 20



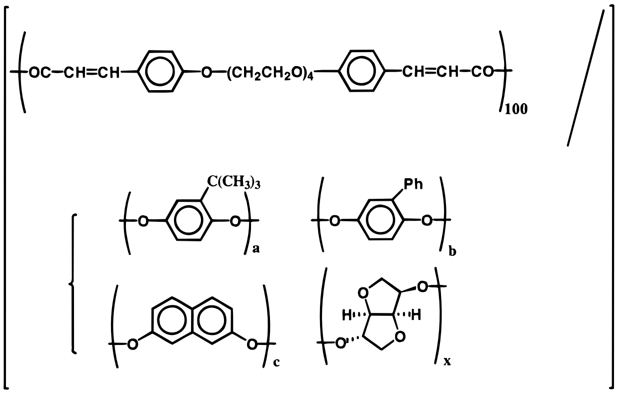
9a - c

a: a / x = 95 / 5
b: b / x = 95 / 5
c: c / x = 95 / 5



12a - c

a: x / y = 95 / 5
b: x / y = 90 / 10
c: x / y = 80 / 20



13a - c

a: a / x = 95 / 5
b: b / x = 95 / 5
c: c / x = 95 / 5

Table 2. Yields and Properties of the Copolyesters 6a−c and 7a−c Containing Alkane Spacers

no.	yield (%)	η_{inh}[a] (dL/g)	elem formula (formula wt)	elemental analyses			T_g[b] (°C)	T_i[c] (°C)	texture
					C	H			
6a	91	0.31	$C_{619}H_{602}O_{122}$	calcd	74.40	6.07	97	170−180	nematic schlieren texture
			(9 993 503)	found	73.89	6.11			
6b	93	0.26	$C_{309}H_{302}O_{62}$	calcd	74.11	6.08	96	160−170	nematic schlieren texture
			(5 007 765)	found	73.66	6.23			
6c	96	0.31	$C_{154}H_{152}O_{32}$	calcd	73.55	6.09	62	135−150	nematic schlieren texture
			(2 514 877)	found	73.10	6.18			
7a	94	0.28	$C_{739}H_{842}O_{122}$	calcd	76.02	7.27	9	75−85	nematic schlieren texture
			(11 676 743)	found	75.53	7.21			
7b	92	0.21	$C_{369}H_{422}O_{62}$	calcd	75.77	7.27	22	80−90	nematic schlieren texture
			(5 849 374)	found	75.22	7.35			
7c	82	0.23	$C_{184}H_{212}O_{32}$	calcd	75.28	7.28	−14	50−60	nematic schlieren texture
			(2 935 692)	found	74.87	7.39			

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

Table 3. Yields and Properties of the Copolyesters 8a−c and 9a−c Containing Diethylene Glycol Spacers

no.	yield (%)	η_{inh}[a] (dL/g)	elem formula (formula wt)	elemental analyses			T_g[b] (°C)	T_i[c] (°C)	texture
					C	H			
8a	98	0.29	$C_{579}H_{522}O_{142}$	calcd	71.31	5.40	74	250−260	cholesteric schlieren texture
			(9 752 403)	found	71.02	5.59			
8b	94	0.30	$C_{289}H_{262}O_{72}$	calcd	71.03	5.40	74	200−210	cholesteric schlieren texture
			(4 887 203)	found	70.69	5.52			
8c	95	0.25	$C_{144}H_{132}O_{37}$	calcd	70.46	5.42	75	180−190	nematic schlieren texture
			(2 454 603)	found	70.09	5.49			
9a	95	0.26	$C_{318}H_{299}O_{71}$	calcd	72.66	5.73	81	180−190	cholesteric schlieren texture
			(5 256 819)	found	72.30	5.70			
9b	94	0.25	$C_{337}H_{280}O_{71}$	calcd	74.05	5.16	68	170−180	cholesteric schlieren texture
			(5 465 876)	found	73.70	5.31			
9c	94	0.21	$C_{318}H_{261}O_{71}$	calcd	73.19	5.04	119		isotropic
			(5 218 515)	found	72.74	5.16			

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

Table 4. Yields and Properties of the Copolyesters 10a−c and 11a−c Containing Triethylene Glycol Spacers

no.	yield (%)	η_{inh}[a] (dL/g)	elem formula (formula wt)	elemental analyses			T_g[b] (°C)	T_i[c] (°C)	texture
					C	H			
10a	97	0.34	$C_{619}H_{602}O_{162}$	calcd	69.92	5.71	50	270−280	Grandjean texture green
			(1 0633 49)	found	69.67	5.78			
10b	99	0.40	$C_{309}H_{302}O_{82}$	calcd	69.66	5.71	52	200−210	Grandjean texture blue
			(5 327 75)	found	69.22	5.82			
10c	98	0.40	$C_{154}H_{152}O_{42}$	calcd	69.15	5.73	56	170−180	oily streaks
			(267 488)	found	68.78	5.82			
11a	96	0.29	$C_{338}H_{339}O_{81}$	calcd	71.26	6.00	61	185−195	Grandjean texture light blue
			(5 697 349)	found	70.88	5.98			
11b	95	0.29	$C_{357}H_{320}O_{81}$	calcd	72.60	5.46	59	190−200	Grandjean texture light blue
			(5 906 406)	found	72.37	5.62			
11c	97	0.30	$C_{338}H_{301}O_{81}$	calcd	71.74	5.36	87		isotropic
			(5 659 045)	found	71.41	5.44			

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

were characterized by optical microscopy, differential scanning calorimetry (DSC) measurements and wide-angle X-ray diffraction (WAXD) powder patterns. The WAXD measurements proved that these polyesters were noncrystalline. Furthermore, no middle angle reflection and, thus, no layer structure was detectable. Therefore, the glass-transition steps detectable in all DSC heating traces represent the transition from a frozen cholesteric phase to a liquid cholesteric phase. Surprisingly the DSC heating curves did not show well-defined endotherms of the isotropization process. Therefore, the isotropization temperatures were determined by optical microscopy with crossed polarizers (see Table 2). The LC phase of all these polyesters showed a kind of nematic schlieren texture, and shearing at various temperatures did never generate a GJ texture. Therefore, the properties of these polyesters were not studied in more detail.

Properties of the Polyesters 8a−c, 9a−c, 10a−c, 11a−c, 12a−c and 13a−c. The polyesters containing ethylene oxide spacers showed the following properties and tendencies. Most polyesters proved to be noncrystalline. Low degrees of crystallinity were typically observed for those polyesters having a low content of isosorbide (**8a**, **10a**, **12a**) because higher fractions of isosorbide are unfavorable for the crystallization. The WAXD powder patterns of Figure 3 are representative for the crystalline and noncrystalline members of these series. The polyesters derived from 2,7-dihydroxynaphthalene (**9c**, **11c**, **13c**) were isotropic, and thus, the solid state of these three polymers was a normal amorphous phase. All other polyesters formed a cholesteric melt,

Table 5. Yields and Properties of the Copolyesters 12a−c and 13a−c Containing Tetraethyleneglycol Spacers

no.	yield (%)	η_{inh}[a] (dL/g)	elem formula (formula wt)	elemental analyses	C	H	T_g[b] (°C)	T_i[c] (°C)	texture
12a	98	0.30	$C_{659}H_{682}O_{182}$	calcd	68.74	5.97	22	165−180	Grandjean texture
			(1 1514 55)	found	68.46	6.02			blue
12b	97	0.27	$C_{329}H_{342}O_{92}$	calcd	68.51	5.98	−2	90−100	oily streaks
			(576 828)	found	68.14	6.11			
12c	98	0.25	$C_{164}H_{172}O_{47}$	calcd	68.04	5.99	−32	70−80	nematic schlieren texture
			(289 514)	found	67.68	6.07			
13a	99	0.34	$C_{716}H_{796}O_{182}$	calcd	69.84	6.52	23	200−210	Grandjean texture
			(12 314 062)	found	69.23	6.59			blue
13b	97	0.29	$C_{754}H_{720}O_{182}$	calcd	71.34	5.72	22	100−110	oily streaks
			(12 693 872)	found	71.02	5.88			
13c	97	0.29	$C_{716}H_{682}O_{182}$	calcd	70.50	5.64	49		isotropic
			(12 199 150)	found	70.11	5.77			

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

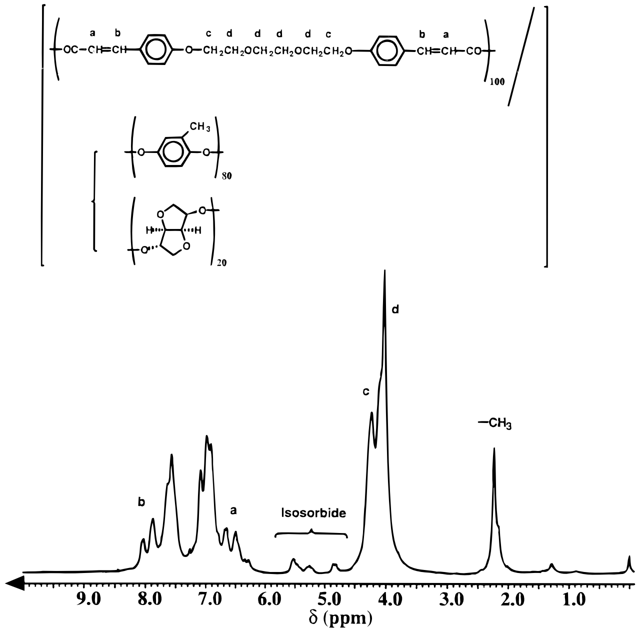


Figure 1. 100 MHz ^{1}H NMR spectrum of polyester **8c**.

so that their solid state was a frozen cholesteric phase (again no layer structure was detectable by X-ray measurements). The glass-transition temperatures (see T_gs in Tables 3−5) showed the following trends. Increasing length of the ethylene oxide spacers resulted, as expected, in lower T_gs. When the diphenols were varied, the highest T_gs were found for the polyesters of 2,7-dihydroxynaphthalene (**9c**, **11c**, **13c**). Variation of the molar fraction of isosorbide did not show influence in the case of **8a**−**c** or **10a**−**c** but had a strong effect in the series **12a**−**c**. Why this varies from the former series based on the shorter spacer is not clear at this time.

Quite analogous to the polyesters **6a**−**c** and **7a**−**c** the DSC curves of the ethylene oxide containing copolyesters did not show a distinct isotropization endotherm. Therefore the isotropization temperatures (T_i in Tables 3−5) were determined by optical microscopy. The increasing molar fraction of isosorbide caused a signifant lowering of the isotropization temperature (T_i) in all three series (**8a**−**c**, **10a**−**c**, **12a**−**c**). Surprisingly the change from the diethylene oxide to the triethylene oxide spacer did not reduce the T_is, whereas the tetraethylene oxide spacer generated lower T_is (Table 5). The cholesteric phases of the hydroquinone containing polyesters showed various types of schlieren textures including the typical "oily streaks" as examplified by Figure 2. GJ textures were obtained by shearing of the cholesteric melts of **10a,b** and **11a,b** or **12a** and **13a**. In agreement with previous studies the higher flexibility of the longer spacers and the lower concentrations of isosorbide favor the formation of a GJ texture.[5−8] All these GJ textures were greenish or bluish in the reflect light.

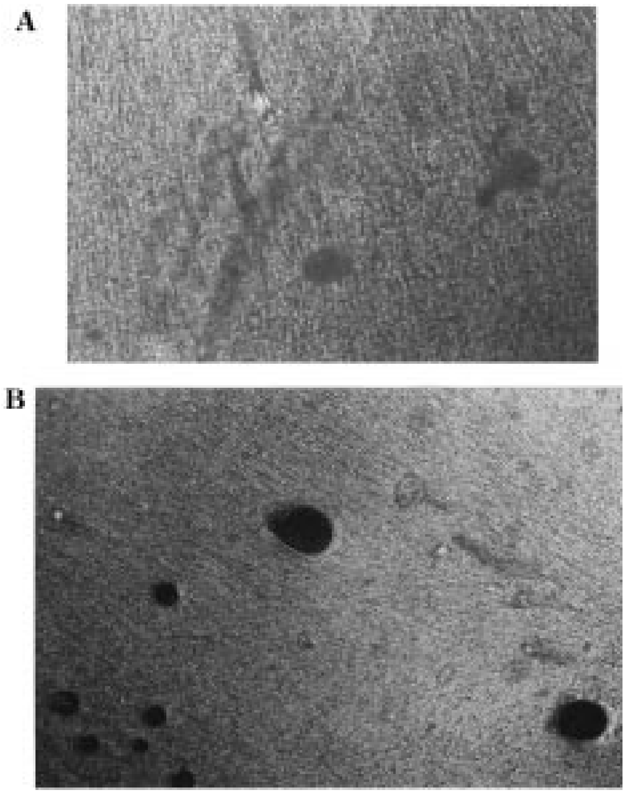


Figure 2. Schlieren texture of (A) polyester **8b** at 170 °C and (B) polyester **10a** at 175 °C.

Photochemical Studies of the Polyester 12a. The polyester **12a** is able to form a stable Grandjean texture down to room temperature. Therefore the relationship of its optical and photochemical properties has been studied in solution, in spin coated films, and in films having a GJ texture.

Figure 4 illustrates how the absorbance spectra of the polyester change with the conditions used for the preparation of the thin films (<1 μm). The absorption maximum of the $\pi \rightarrow \pi^*$ transition remains unchanged at 325 nm, but the profile of the band varies signifi-

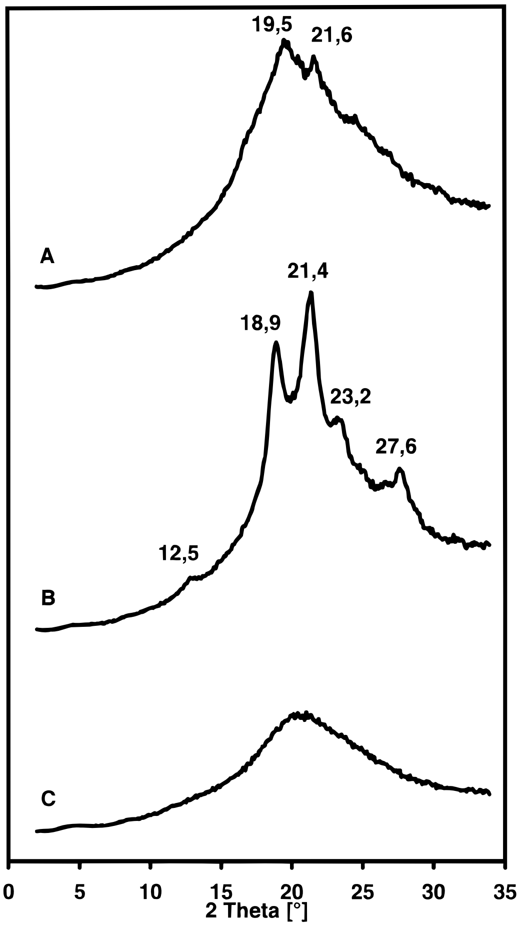


Figure 3. WAXD powder patterns of polyesters **8a**, **10a**, and **12a**.

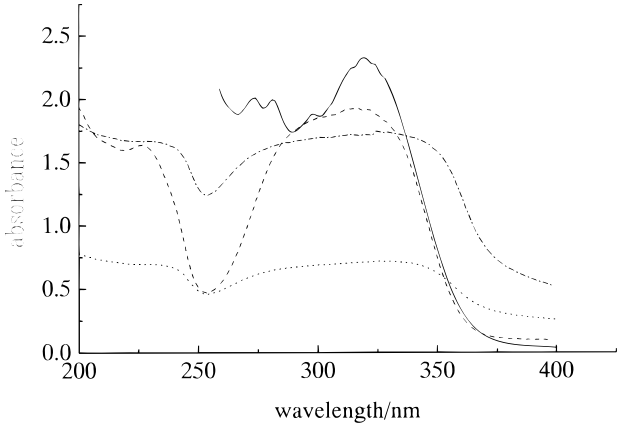


Figure 4. Absorbance spectra of polyester **12a** in solution (—), as freshly prepared film (— —) and annealed (···) film, and as GJ texture (-·-).

cantly with the "history" of the sample. The spectra of freshly spin-coated film is similar to that of the polymer in polar solvent, but the maximum becomes broader and the side maxima at 270 nm are shifted to longer wavelengths resulting in a minimum at 255 nm.

Figure 5 shows the UV–visible spectrum of polymer **12a** in solution and the change of absorbance on irradiating with UV light (313 nm). The spectrum is characterized by the absorbance of the different 4-alkoxy-cinnamic ester moieties with a maximum at 325 nm (in the case of **12a** diesters of methylhydroquinone (95 mol %) or isosorbide (5 mol %) exist). The irradiation with UV light leads to an approximately 80% decrease of the absorbance of the cinnamic ester bands. This effect is mainly caused by the (2 + 2) photocycloaddition but may include a minor contribution from the *E*/*Z* photoisomerization process. The presence and extent of this photoisomerization were not directly measurable from the UV–visible spectra. However, it was found from low molecular weight model compounds in high dilution (excluding the (2 + 2) cycloaddition) that the *E*/*Z* photoisomerization reaches an equilibrium at 15% conversion. Taking this value as the maximum contribution of the *E*/*Z* isomerization into account, the efficiency of the (2 + 2) cycloaddition of **12a** falls into the range of 65–80% conversion. Furthermore, it was found that the absorbance between 340 and 475 nm slightly increases (Figures 5 and 6). This change is caused by the photo-Fries reaction of the hydroquinone ester of the cinnamic acid. The rearrangement takes place via the homolytic cleavage of the ester bond between the hydroquinone and the cinnamic moiety, followed by the rearrangement of the radicals in the solvent cage forming *o*-hydroxylchalcone moieties. The increase of the absorbance at 400 nm and the discontinuous change of the spectra at 270 nm including the disappearance of isosbestic points indicate the existence of these side and postreactions.

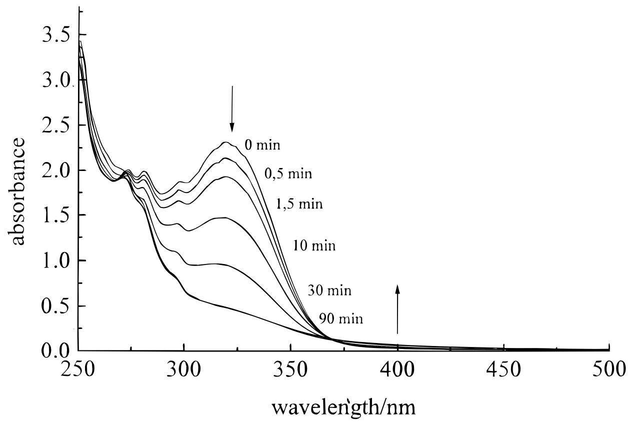


Figure 5. Absorbance spectra of polyester **12a** in solution upon UV irradiation ($\lambda_{ex} = 313$ nm).

The competition of the photocycloaddition and both side reactions has been discussed in more detail in other studies related to cinnamic acid esters.[16–18] They show that the ratio of the cycloaddition to both side reactions increases inside compact films. Obviously the nearly parallel alignment of chain segments in the LC phase favors the 2 + 2 cycloaddition at the expense of the Photo-Fries reaction and the *E*/*Z* isomerization. Furthermore, thin films have been prepared by spin coating or melting. The irradiation of freshly spin-coated films results in a change of the absorbance to that in solution. The photo-cross-linking is less rapid than in solution but the final conversion of nearly 82% is comparable. The annealing process of the spin-coated film at 60 °C causes a significant decrease of the absorbance at 325 and 240 nm going down to approximately 30% of the initial value with broadening of the spectrum (Figure 7). The simultanous decrease of the $\pi\pi^*$ transition polarized in direction toward the long axis and the $\Phi\Phi^*$ transition of the aromatic cores perpendicularly polarized to the long axis proves that this decrease is not effected by an out-off-plane orientation process. This observation is not understood up to now and under further investigation. The annealing process results in

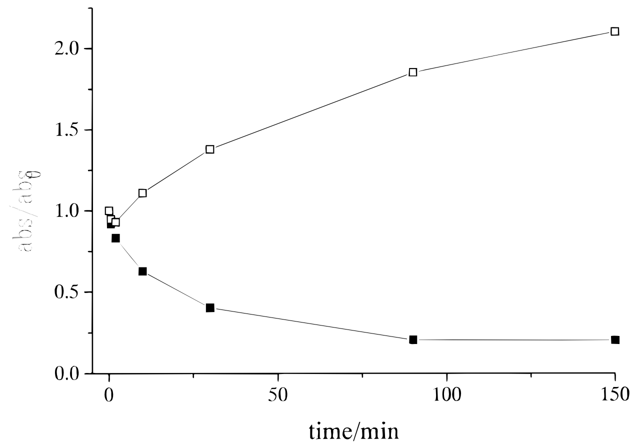


Figure 6. Normalized absorbance of polyester **12a** in solution at 320 (■) and 400 (□) nm versus the irradiation time (λ_{ex} = 313 nm).

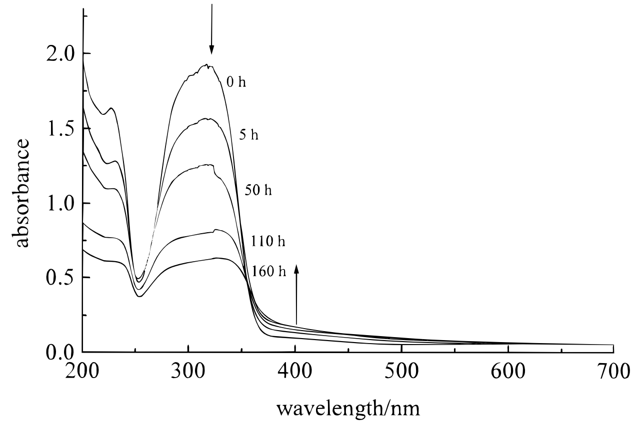


Figure 7. Absorbance spectra of polyester **12a** film upon annealing at 60 °C (160 h).

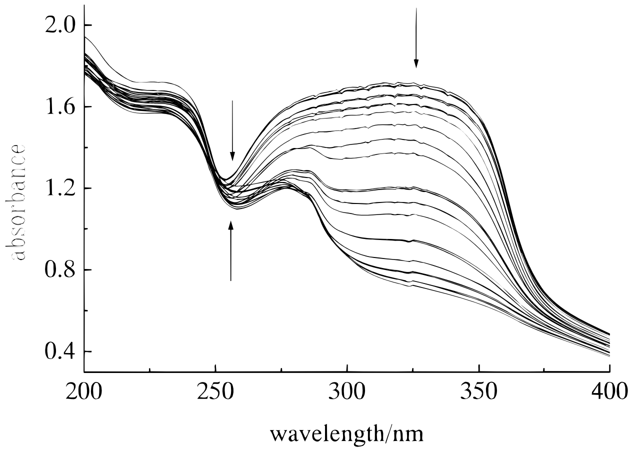


Figure 8. Change of absorbance of polyester **12a** as film with GJ texture at 20 °C upon UV irradiation (λ_{ex} = 313 nm) recorded over a period of 35 h of continuous irrradiation.

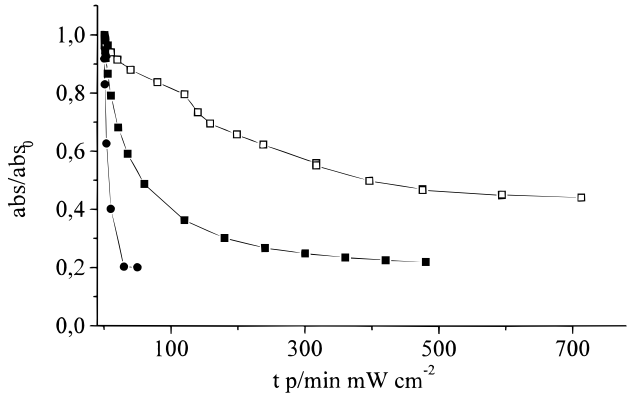


Figure 9. Normalized absorbance of **12a** in solution (●) at 320 nm, as freshly prepared film (■) and as GJ texture (□) upon irradiation at a wavelength of 330 nm.

establishing of the Grandjean texture. It is accompanied by the increase of light scattering caused by the formation of domains. The spectrum of this film agrees with that of the GJ texture obtained by slight dilution of the molten polymer with a minimum amount (1−3 drops) of solvent. The GJ texture is characterized by significant broadering of the cinnamoyl absorption band. Simultanously, an increase of absorbance in the range of 600−380 nm is observed.

The irradiation of these films at 60 °C in the mesophase results in the disappearance of the GJ texture at a conversion of approximately 25% of the cinnamic groups. The photoreactions forming truxillic and truxinic derivatives or *Z* isomers of the cinnamoyl moiety cause a change of the molecular structure which is unfavorable for their mesogenic character and, thus, for the stability of the GJ texture. On cooling to 20 °C the texture of the aligned film remains stable below the glass transition temperature. Figure 8 shows the change of the spectra upon irradiation. In this way 55−60% of the cinnamic moieties become cross-linked in the film (having a GJ texture). Figure 9 compares the photochemical behavior of the polymer in solution, of an annealed film with GJ texture and of a freshly prepared film. The highest conversion and efficiency of the photoreaction were observed in solution. Interestingly the photo-cross-linking of the freshly prepared film is more efficient (by a factor of 5) and yields a higher conversion than the annealed film. The main result is that the GJ texture remains stable while the photoreaction takes place. Hence, irradiation of the glassy aligned film stabilizes the supramolecular order or the GJ texture for a long time by photochemical cure. The color of the sample is not changed by this procedure. This is surprising because the photocycloaddition with a final conversion of approximately 55−60% means that the shapes of the rodlike ester moieties are changed forming products with cyclobutane rings. In some cases the procedure causes a decrease in the intensity of light scattering and in other cases an increase was observed. The cross-linking films turn insoluble and their GJ texture and shape remain unchanged upon heating to 200 °C.

Conclusions

The combination of flexible aliphatic spacers with 4-hydroxycinnamic acid, methylhydroquinone, and small amounts of isosorbide yielded the desired cholesteric polyesters. However, a quite unexpected result was the observation that only polyesters containing oligo(ethylene oxide) spacers were capable of forming a GJ texture, whereas all polyesters derived from alkane spacers did not. A few polyesters allowed a fixation of the GJ texture by cooling below T_g. A further stabilization (including higher temperatures) was possible by UV-induced photo-cross-linking of the cinnamoyl units in the cholesteric glassy state. The structure−property relationships between these functionalized main chain polymers with regard to their optical and photochemical properties are currently studied in more detail and will be described in a future publication.

References and Notes

(1) Boulignand, Y. *J. Phys.* **1973**, *34*, 603.
(2) de Jeu, A. W.; Verteugen, G. In *Thermotropic Liquid Crystals, Fundamentals*; Springer Verlag: Berlin, 1977.
(3) Kricheldorf, H. R.; Probst, N.; Gurau, M.; Berghahn, M. *Macromolecules* **1995**, *28*, 6565.
(4) Stumpe, J.; Ziegler, A.; Berghahn, M.; Kricheldorf, H. R. *Macromolecules* **1995**, *28*, 5306.
(5) Kricheldorf, H. R.; Probst, N. *Macromol. Chem. Phys.* **1995**, *196*, 3511.
(6) Kricheldorf, H. R.; Probst, N. *High Perform. Polym.* **1995**, *7*, 471.
(7) Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 603.
(8) Kricheldorf, H. R.; Krawinkel, T. *High Perform. Polym.*, in press.
(9) Haddleton, D. M.; Creed, D.; Griffin, A. C.; Hoyle, C. E.; Venkataram, K. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 391.
(10) Creed, D.; Griffin, A. C.; Gross, J. R. D.; Hoyle, C. E.; Venkataram, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 57.
(11) Bailey, D.; Tirrell, D.; Vogl, O. *J. Macromol. Sci.* **1978**, *A12*, 661.
(12) Li, C.-H.; Lai, W.-W.; Hsu, K.-Y.; Chang, T.-C. *J. Polym. Sci., Part A* **1993**, *31*, 27.
(13) Akabori, S.; Tsuchiya, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1623.
(14) Vill, V.; Fischer, F.; Thiem, J. *Z. Naturforsch.* **1988**, *43a*, 1119.
(15) de Abacho, J.; de la Campa, J.; Kricheldorf, H. R.; Schwarz, G. *Eur. Polym. J.* **1992**, *28*, 261.
(16) Stumpe, J.; Mertesdorf, C.; Ringsdorf, H. *Liq. Cryst.* **1991**, *9*, 337.
(17) Stumpe, J.; Selbmann, Chr.; Krysig, D. *J. Photochem. Photobiol., A Chem.* **1991**, *58*, 15.
(18) Stumpe, J.; Zaplo, O.; Kreysig, D.; Niemann, M.; Ritter, R. *Makromol.* **1992**, *193*, 1567.

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