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Liquid-Crystalline Main-Chain Polyesters with Lateral Aromatic Substituents

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Varying the structure of common main-chain polymers, a series of new mostly liquid-crystalline polyesters with y-shaped mesogens derived from hydroquinone diacetate with different lateral aromatic substituents (4-methoxyphenyl, 4-biphenyl) and 4,4′-alkylenedioxydibenzoic acids was synthesized. At given lateral group, the number of methylene units separating the aromatic ester triade mesogens ranges up to ten. First structure-property relationships could be determined using optical microscopy, differential scanning calorimetry and X-ray diffraction techniques. Corresponding to other types of liquid-crystalline polymers with laterally stressed mesogenic units, the anisotropic melts of our polyesters are nematic phases. Furthermore, X-ray investigations give hints to the existence of cybotactic groups. With increasing lateral substituents the lowering of the isotropization temperatures is accompanied by an enhanced tendency to form anisotropic glasses. Therefore, also polymers consisting of highly branched mesogenic building stones can form mesophases within a wide temperature interval.

INTRODUCTION

In the last years some efforts of creating new types of liquid-crystalline polymers with an unusual architecture, especially with respect to the molecular structure of the mesogenic building stones, have been undertaken.[1–3] One item of special interest in this field is the influence of an increasing lateral stress on the mesogenic molecular parts of common main-chain polymers. Nowadays, the properties of numerous low-molecular-weight liquid crystals and polyesters consisting of hydroquinone dibenzoate units with more or less flexible lateral groups are well known.[4,5] However, there are relatively few examples of liquid-crystalline materials possessing pendant aromatic substituents, e.g.[6,7] Corresponding polymers have received increased attention because of higher solubility without lowered thermal stability relative to the unsubstituted polyesters or polyamides.[8]

Recently we could report on a number of polyesters with mesogens carrying phenylazo side groups. Besides some peculiarities with respect to the phase structure,[9] they showed a strong tendency to form extended nematic phases.[10] In order to get more detailed information on these types of polymers and to improve their thermal stability, we synthesized main-chain polyesters with 4-methoxyphenyl or 4-biphenyl substituents and investigated their phase behaviour in dependence on the length of the flexible polymethylene spacers. An interesting aspect regarding

processing and application conditions of main-chain polymers should be whether rigid side groups can hinder crystallization or depress the melting temperatures while preserving the ability to form anisotropic melts.

EXPERIMENTAL

The preparation of the new polyesters with y-shaped mesogens is described in Scheme I.

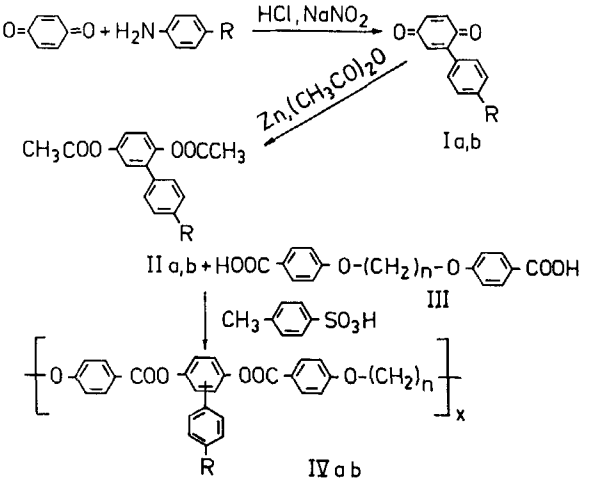
The appropriate amino compound was converted into the diazo salt and coupled with p-benzoquinone under emission of nitrogen. After reduction of the resulting quinones I and immediate esterification with acetic anhydride the hydroquinone derivatives II were obtained. Polyesters IV were prepared by melt polycondensation of the substituted hydroquinones II and dicarboxylic acids III.

The thermal behaviour of the polymers was investigated by means of polarizing microscopy and differential scanning calorimetry (DSC; heating/cooling rate 8 K/min). The number-average molecular weights of polymers soluble in chloroform were measured by analytical GPC in $CHCl_3$ calibrated with polystyrene standards. X-ray investigations of melt drawn fibres for phase identification were carried out using Ni-filtered CuK_α-radiation and a flat camera.

RESULTS AND DISCUSSION

The thermal properties and in case of sufficient solubility also the molecular weights of the synthesized polymers are summarized in Table I.

Polarizing microscopy as well as X-ray investigations give strong hints to the



a: R = $-OCH_3$; n = 4,5,6,8,10

b: R = ; n = 2,3,4,5,6,8,10

SCHEME I

TABLE I

Phase transition temperatures and molecular weights of the synthesized polymers (g: glassy, cr: crystalline, n: nematic, i: isotropic, P: polymeric)

Polymer	R	n	Phase transition temperatures (°C)	$\bar{M}_n$ (g·mol^{-1})
IV 1	-OCH$_3$	4	P_{cr} 250 P_i	
IV 2		5	P_g 90 P_i	
IV 3		6	P_{cr} (P_n 195 P_i) 199 P_i	
IV 4		8	P_{cr} (P_g 67 P_n 170 P_i) 184 P_i	19 800
IV 5		10	P_{cr} (P_g 60 P_n 149 P_i) 162 P_i	8 500
IV 6		2	P_g 122 P_n 202 P_i	
IV 7		3	P_g 128 P_i	
IV 8		4	P_{cr} (P_n 200 P_i) 220 P_i	
IV 9		5	P_g 108 P_i	
IV 10		6	P_g 100 P_n 177 P_i	
IV 11		8	P_g 84 P_n 152 P_i	17 300
IV 12		10	P_g 77 P_n 143 P_i	25 800

notion that all observed anisotropic melts are nematic phases. A representative X-ray fibre pattern of polymer IV 12 recorded at room temperature is given in Figure 1. Besides the outer diffuse scattering on the equator, the inner diffuse interference is splitted up indicating the structural feature of a nematic phase with cybotactic groups. This is in good agreement with investigations of other main-chain polymers possessing laterally stressed mesogenic units. Also polyesters with terminally and laterally linked mesogens,[3] cross-shaped mesogens[11] and rigid rod or semiflexible main-chain polymers with mesogenic side groups[12] exhibit predominantly nematic phases. On the other hand, polyesters derived from unsubstituted hydroquinone with main-chain spacers longer than five methylene groups can form also smectic phases.[13]

Generally, with increasing deviation from the rod-like shape of the mesogenic building stones, the thermal stability of the mesophases diminishes. This is demonstrated in Figure 2. With exception of polymer IV 6, the nematic-isotropic as well as the glass transition shift to lower temperatures with increasing length of the alkylene spacer in both homologous series. This is in accordance with observations at other thermotropic main-chain polyesters.[14] Polyesters IV 1–IV 5 with methoxyphenyl substituents show a strong crystallization tendency. Only polymers with long and even main-chain spacers (n = 6, 8, 10) are able to form metastable nematic phases by supercooling the isotropic liquids. As one example the thermal behaviour of polymer IV 5 investigated by DSC is shown in Figure 3.

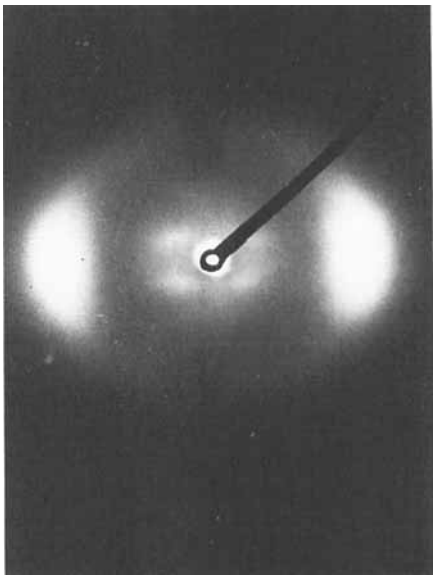


FIGURE 1 X-ray diagram of a melt drawn fibre of polymer IV 12 in the glassy nematic state at room temperature. The arrow indicates the drawing direction.

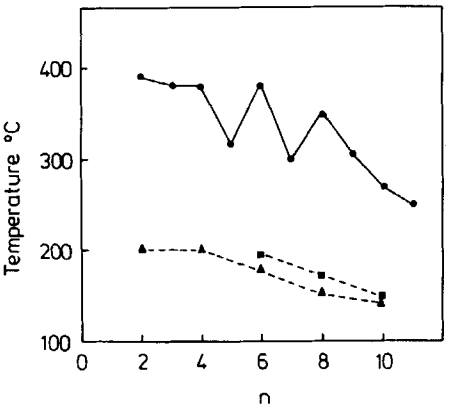


FIGURE 2 Comparison of the clearing temperatures for polyesters IV carrying different substituents in dependence on the number n of methylene units (● without lateral group,[13] ■ R = CH_3O—, ▲ R = C_6H_5—).

A shortening of the main-chain spacer leads either to a purely isotropic polyester even in the glassy state (n = 5, polymer IV 2) or to a relatively high melting material without any liquid-crystalline phase (n = 4, polymer IV 1).

The substitution of the methoxy group by a further phenyl ring yields polyesters IV 6–IV 12. The enhanced lateral part causes a considerable deviation of the mesogenic units from the rod-like shape. Nevertheless, all polymers of this series with an even number of methylene groups in the spacer units display nematic phases within a relatively wide temperature interval. The only occurrence of isotropic

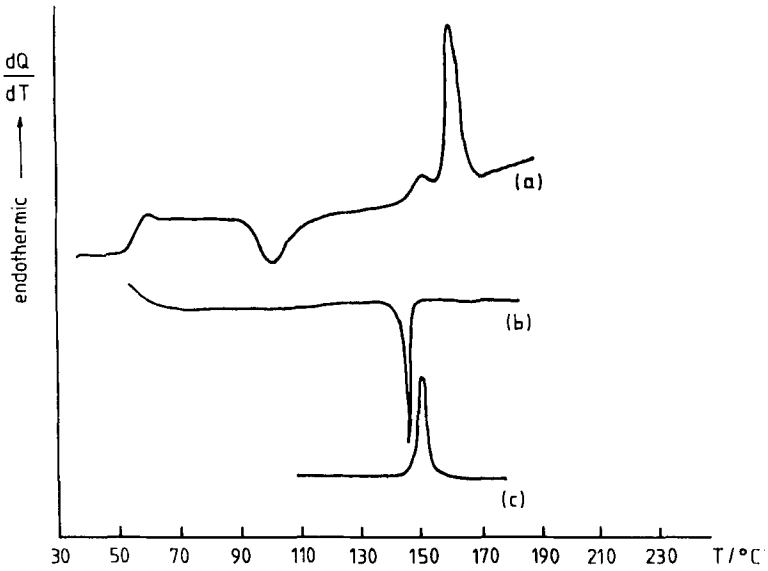


FIGURE 3 DSC curves of polyester IV 5. Heating/cooling rate 8 K/min. (a) Heating from the glassy nematic state; the exothermic peak at 100°C indicates the recrystallization, followed by a crystalline-crystalline transformation at 150°C and the melting point at 162°C. (b) Cooling from the isotropic melt; heating after cooling to 50°C reproduces curve (a). (c) Heating immediately after cooling to 110°C (about 40 K below the clearing point).

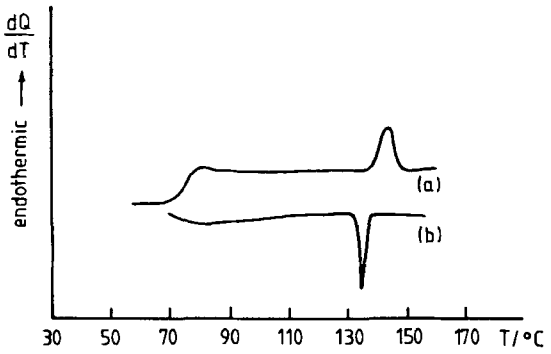


FIGURE 4 DSC curves of polyester IV 12. Heating/cooling rate 8 K/min. (a) Heating from the glassy state, (b) cooling from the isotrophic melt.

melts and glasses in case of polyesters with n = 3 (IV 7) and n = 5 (IV 9) reveals a distinct even-odd effect of the liquid-crystalline phase formation with respect to the spacer length. A general feature of the biphenyl substituted polymers is the freezing of the mesomorphic or isotropic order by cooling down into the glassy state. Apart from polymer IV 8, also long annealing times above the glass transition temperature did not result in any crystal growth. As a representative example the DSC curves of polyester IV 12 are given in Figure 4. Obviously, the formation of anisotropic melts with very low clearing temperatures in comparison with laterally

unsubstituted polyesters[14] should be due to the hindered crystallization of these macromolecules. This hindrance is a consequence of the branched molecular geometry. Therefore, in spite of a lower thermal stability the liquid-crystalline phases formed by the biphenyl substituted polyesters are more favoured than those of polymers having pendant methoxyphenyl substituents. So, the fixation of large rigid side groups to the mesogens of conventional main-chain polymers proved to be a reasonable way to gain noncrystallizing polyesters with liquid-crystalline phases in a suitable temperature range.

MATERIALS

2-4'-subst. Phenylbenzoquinones, I a,b

The preparation followed a procedure described by Reynolds and Van Allan[15] for the synthesis of 2-4'-acetylphenyl-benzoquinone.

To obtain the diazo salt solution of 4-aminobiphenyl DMF was used as solvent. The crude products were recrystallized from n-butanol.

R = —OCH_3: yield 90%, mp = 112°C;

R = —  : yield 85%, mp = 195°C (dec.).

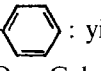
2-4'-subst. Phenylhydroquinone diacetates, II a,b

The compounds were synthesized using standard methods.[16] Recrystallization from alcohol yielded the pure products.

R = —OCH_3: yield 65%, mp = 78°C.

$C_{17}H_{16}O_5$	Calc.	C: 68.00% H: 5.33%
	Found	C: 67.46% H: 5.45%

IR: 3100–3000 cm^{-1} (=C—); 1760–1750, 1220–1180 cm^{-1} (—COO Phenyl); 2820, 1290 cm^{-1} (—OCH_3).

R = —  : yield 87%, mp = 120°C.

$C_{22}H_{18}O_4$	Calc.	C: 76.30% H: 5.20%
	Found:	C: 75.83% H: 5.28%

IR: 3100–3000 cm^{-1} (=CH—); 1760–1750, 1220–1180 cm^{-1} (—COO Phenyl).

4,4'-Alkylenedioxydibenzoic acids, III[17]

0.2 mol methylhydroxybenzoate, 0.1 mol α,ω-dibromoalkane, 0.6 mol K_2CO_3 and a catalytic amount of KI were refluxed in 250 ml of dry butanone for 40 hrs. After evaporation of the solvent and addition of 50 g KOH in 200 ml ethanol/water (vol. ratio 1:1) the ester groups were saponified by refluxing for 5 hrs. The resulting mixture is given into boiling water to get a clear solution and acidified with con-

centrated HCl. The precipitate was filtered, washed with water and recrystallized from DMF.

Yields: 60–90%; melting points: n = 2: 350°C (lit.: 352–355°C); n = 3: 334°C (lit.: 332–334°C; n = 4: 341°C (lit.: 338–341°C); n = 5: 286°C (lit.: 285–288°C); n = 6: 300°C (lit.: 290–292°C); n = 8: 289°C (lit.: 284–287°C); n = 10: 278°C (lit.: 273–274°C).

Polyesters

3 mmol of the hydroquinone diacetate derivative, an equimolar amount of the appropriate dicarboxylic acid and 4 mg p-toluenesulfonic acid monohydrate were heated from 150°C to 260°C during 1 h and then stirred at this temperature for 2 hrs. in a nitrogen atmosphere. After reducing the pressure slowly to about 0.5 Torr, the polycondensation was completed by stirring the melt for 4 hrs. at 250–260°C. The crude polyesters were dissolved in chloroform, 1,2-dichloreothane or 1,1,2,2,-tetrachloroethane, precipitated twice in acetone and dried in vacuum at 90°C for 20 hrs. Yields: 85–95%.

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