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SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALLINE POLYESTERS WITH Y-SHAPED MESOGENS

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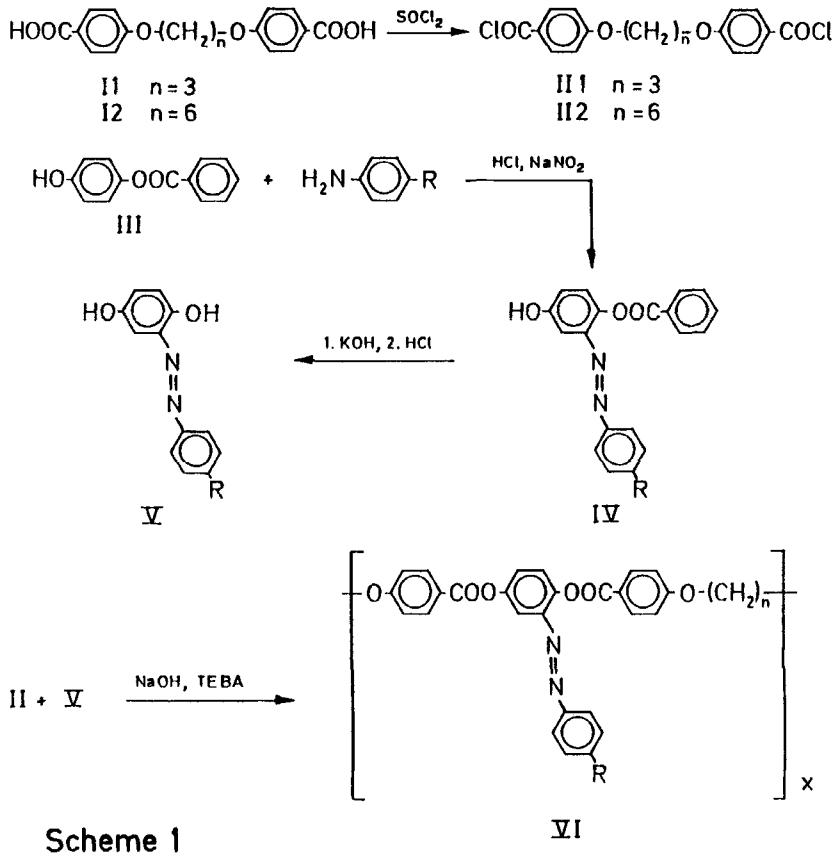
Abstract A number of new liquid crystalline polymers characterized by triad ester segments as mesogenic main chain units connected together by polymethylene spacers and endowed with lateral groups consisting of a rigid azobenzene part and different substituents were synthesized. These polyesters were subjected to polarizing microscopy, DSC and preliminary X-ray investigations. There are two opposing effects of lateral groups with respect to the mesophase stability.

INTRODUCTION

Classical main chain and comb-like liquid crystalline (LC) polymers with rod-like mesogens have been intensively studied resulting in a well understanding of structure-property relationships. In last years, the structural principles of both types have been combined in numerous chemical variations [1,2]. A special problem concerns the influence of lateral groups on the thermal mesophase behavior and the phase structure of LC main chain polymers. Based on extensive investigations in the field of low-molecular-weight liquid crystals [3], similar studies were undertaken with main chain polymers [4]. If the lateral group does act both as a structural disordering factor with respect to axial-ratio considerations and as a part of the mesogenic system,

the consequences on the mesophase properties should be of interest. Therefore, in our investigation we have varied the pendant substituents linked with the lateral mesogenic parts of Y-shaped LC-polyesters as well as the lengths of main chain polymethylene spacers.



Scheme 1

EXPERIMENTAL

The synthesis of this type of liquid crystal main

chain polymers is shown in Scheme 1.

In the first step the dicarboxylic acids I1 and I2 were converted into the corresponding acid dichlorides II1 and II2 by treatment with thionyl chloride.

In order to prepare the hydroquinone derivatives V hydroquinone was one-sided esterified with benzoylchloride for obtaining hydroquinone monobenzoate (compound III). Various aromatic amino compounds were converted into the diazo salts coupled with hydroquinone monobenzoate to form the compound IV. After saponification the hydroquinone derivatives V were obtained.

The polycondensation was carried out by action of the 4,4'-alkylenedioxydibenzoyl chlorides II1 or II2 on the hydroquinone derivatives V under liquid-liquid phase transfer conditions.

The liquid crystalline behavior of the polyesters was investigated by means of polarizing microscopy and differential scanning calorimetry (DSC). The DSC scan rate was 8 K/min. The number-average molecular weights were measured with an analytical GPC in THF calibrated against polystyrene standards. For preliminary identification of mesophases, X-ray experiments were performed using CuK_{α}-radiation monochromized by a graphite crystal with melt-drawn oriented fibres.

RESULTS AND DISCUSSION

The properties of the synthesized polyesters are summarized in Table I. Generally, the comparison of the clearing temperatures of these polymers with and without [6] lateral substituents on the middle p-phenylene ring demonstrates again that pendant groups reduce the thermal stability of the mesophases. But there are apparently two opposing effects: (i) the steric effect

TABLE I Polyesters and their characteristic data (P_g = glassy, P_{cr} = crystalline, P_n = nematic, P_{is} = isotropic) [5].

Polymer	n	R	Phase transition temperatures (°C)	$\bar{M}_n$
VI 1	3	OCH_3	P_g 96 LC 140 P_{is}	3700
VI 2	3	NO_2	P_g 124 LC 260 dec.	-
VI 3	6	OCH_3	P_g 74 LC 219 P_{is}	3500
VI 4	6	OC_6H_{13}	P_g 40 LC 173 P_{is}	4400
VI 5	6	C_6H_{13}	P_{cr} (P_g 44 LC) 103 LC 180 P_{is}	4100
VI 6	6	NO_2	P_g 100 LC 252 P_{is}	-
VI 7	6	CN	P_g 98 P_n 234 P_{is}	-

responsible for an impaired packing efficiency in the LC melt, (ii) a stabilization of the mesophases due to the interaction of polar substituents. Such an ambivalence has also been observed at similar polymers without rigid parts in the lateral units [7].

The X-ray fibre pattern measured at room temperature suggests a nematic structure of the polymer VI 7, but the patterns of the polymers VI 4 and VI 5 are different from that of VI 7. This can be seen in the case of VI 4 from Figure 1. The unusual feature is characterized by the occurrence of an inner and outer diffuse scattering on the equator. The outer reflexion corresponds to a mean lateral distance of about 4.5 Å whereas the diffuse scattering at $\Theta = 1.83^\circ$ implies the existence of a periodic spacing of about 24 Å. The figure shows further reflections of lower intensity positioned at the meridian of the pattern corresponding to a spacing of $d \simeq 12$ Å. More detailed X-ray investigations are in progress.

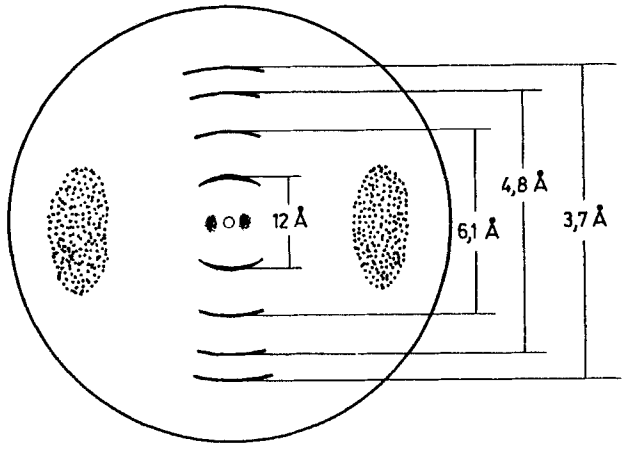


FIGURE 1 Schematic representation of the X-ray diagram of polymer VI4 (the fibre drawing direction is vertical).

MATERIALS

4,4'-Alkylenedioxydibenzoic acids (I)

The dicarboxylic acids were prepared from methyl 4-hydroxybenzoate [6]. I1 : m.p. 335 °C, yield: 85 %. I2 : m.p. 298 °C, yield: 85 %.

4,4'-Alkylenedioxydibenzoyl chlorides (II)

They are prepared from acids I with thionyl chloride and recrystallized from cyclohexane. II1 : m.p. 107-108 °C. II2 : m.p. 84 °C. Yield: 90 %.

Hydroquinone monobenzoate (III)

The preparation was carried out as described in reference 8 and recrystallized from ethanol/water (volume ratio 1:1); m.p. 163 °C, yield: 55 %.

2-Benzoyloxy-5-hydroxy-4'-subst. azobenzenes (IV)

The diazo salt of an appropriate 4-subst. aniline was

coupled with III as recommended in reference 8. R = NO_2, m.p. 198 °C; R = CN, m.p. 188 °C; R = C_6H_{13}, m.p. 77 °C; R = OC_6H_{13}, m.p. 85 °C; R = OCH_3, m.p. 149 °C; yield: 30-60 %.

2,5-Dihydroxy-4'-subst. azobenzenes (V) [8]

A suspension of IV in the 20-fold amount of ethanol/water (vol. ratio 1:1) was treated with a conc. aqueous solution of KOH till the colour changed from red to blue. The resulting solution was rapidly filtered and immediately acidified with conc. HCl. The precipitate was filtered, washed with water and recrystallized. R = NO_2, m.p. 195 °C (dec.); R = CN, m.p. 200 °C (dec.); R = C_6H_{13}, m.p. 125 °C; R = OC_6H_{13}, m.p. 121 °C; R = OCH_3, m.p. 180 °C (dec.); yield: 50-90 %.

Polyesters VI

All polyesters were prepared by catalyzed interfacial polycondensation [9]. The crude products were either redissolved in dichloroethane and reprecipitated into the 20-fold volume of methanol (R = OCH_3, OC_6H_{13}, C_6H_{13}) or extracted with methanol in a Soxhlet apparatus for 5 h (R = CN, NO_2). Afterwards, the polymers were dried in vacuum at 80 °C. Yield: 80-95 %.

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