

Synthesis and properties of dimesogenic liquid crystalline side group polymers

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SUMMARY

Liquid crystalline polymalonates with side groups consisting of two different mesogenic units separated by alkylene spacers from each other and from the polyester backbone have been prepared. According to microscopic observations, DSC measurements and X-ray studies, all polymers display smectic phases.

INTRODUCTION

Usually, side group liquid crystalline (LC) polymers are characterized by single mesogenic units attached to a main chain via flexible spacers. Depending on the type of the mesogenic unit, the thermal stability of LC phases formed by such polymers is more or less sensitive to the structure and extension of the non-mesogenic backbone segment between two neighbouring side groups. Indeed, the mesogenic properties of a polymer with a molar ratio of non-mesogenic to mesogenic structural units exceeding a relatively low critical value disappear. But with increasing anisometry of the mesogenic parts, a stabilization of the liquid crystalline behaviour can be observed (1,2). Another concept to achieve mesomorphic stabilization of LC polymers was the synthesis of combined systems with mesogens in the main chain and as side groups (A in Figure 1) (3) or polymers with crossing as well as terminally linked mesogenic units (B in Figure 1) (4). Furthermore, the same effect can be observed when one monomer unit contains two paired mesogenic side groups (C in Figure 1) (1). Due to the lateral interaction between mesogenic groups, the LC phases can be retained virtually unchanged up to a high dilution by non-mesogenic backbone links. In these cases, a microphase separation into coexisting isotropic and smectic A phases has been found (5).

Another route to realize dimesogenic polymers is to synthesize LC copolyethers with mixed mesogenic groups leading to a dual mesophase behaviour (6). The general disadvantage of such strategy is the uncertainty with respect to the distribution of different mesogenic units in the copolymer chain. Therefore, the goal of the research reported

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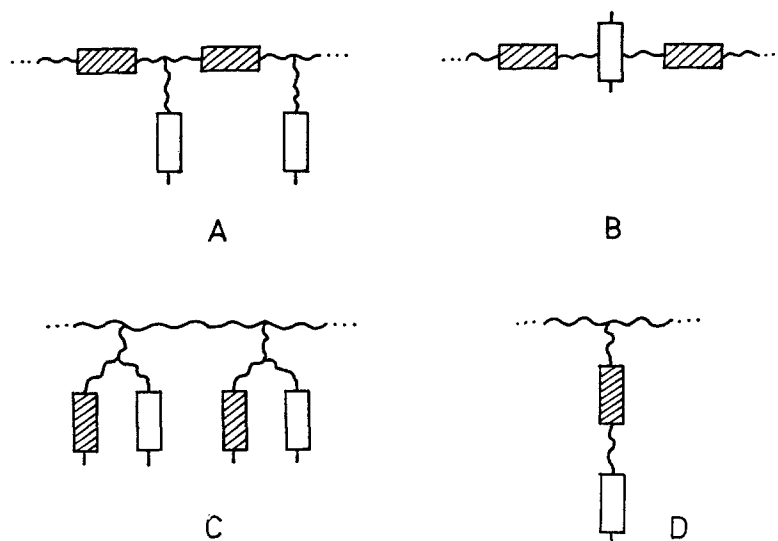


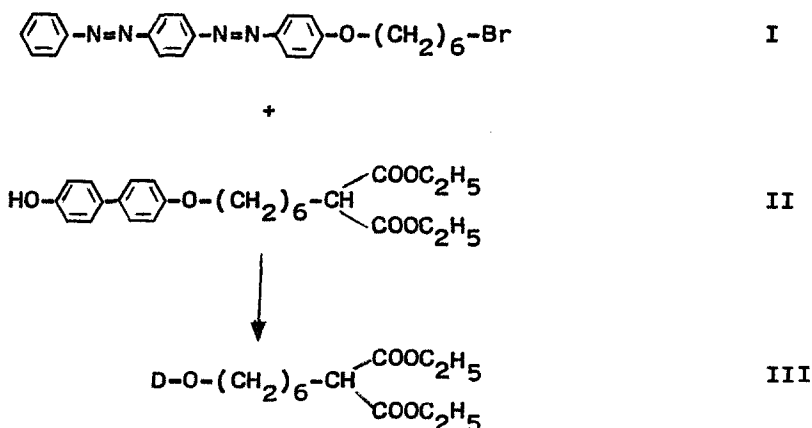
Figure 1: Schematic structure of different dimesogenic polymers

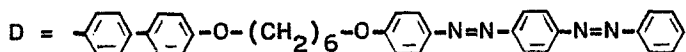
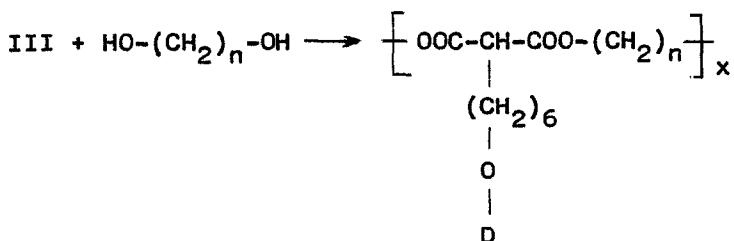
here was the synthesis of dimesogenic side group polymers with a definite structural arrangement of the different mesogenic building stones (D in Figure 1). Apart from our objective to study the polymorphy and phase structure of such unconventional LC polymers, the influence of a second mesogenic unit on the phase transitions of structurally related monomesogenic polymaltonates (7) roused our interest. Furthermore, such regular dimesogenic polymers should be candidates for the formation of separated microphases with coexistence of different liquid crystalline states.

EXPERIMENTAL

Materials

The polymaltonates were prepared according to the following scheme:





$n = 8, 12, 16$

4-[4-(6-bromohexyloxy)phenylazo]azobenzene (I)

7.3 g (24 mmol) of 4-(4-hydroxyphenylazo)azobenzene (isolated from a commercial azo dye paste, Farbwerk Wolfen) and 2.8 g (50 mmol) of KOH were dissolved in 75 ml of ethanol. This solution was added to a boiling mixture of 75 ml water, 24 g (98 mmol) dibromohexane and a catalytic amount of KI during 90 minutes. After refluxing for 10 hours and cooling down to room temperature the precipitate was filtered, washed with methanol and recrystallized first from n-butanol, then from n-nonane. Yield: 75 %. Transition temperatures: crystalline 128 °C smectic A 153 °C nematic 182 °C isotropic.

Diethyl-6-bromohexylmalonate

It was synthesized according to a literature procedure (8); b.p. (2 mm Hg): 160 °C; yield: 44 %.

Diethyl-6-[4-(4-hydroxyphenyl)phenoxy]hexylmalonate (II)

A solution of 11.9 g (64 mmol) 4,4'-dihydroxybiphenyl in 120 ml of dry butanone was added to a boiling mixture of 20.7 g (64 mmol) of diethyl-6-bromohexylmalonate, 21.5 g (154 mmol) K_2CO_3 , 180 ml butanone and a catalytic amount of KI during 4 hours. After refluxing for 40 hours the reaction mixture was poured into 300 ml of ethanol/water (vol. ratio 1:1). The precipitate was extracted with 500 ml of ethanol. After filtration the alcoholic solution was treated with 500 ml of water to precipitate the wished product. The crude material was purified by recrystallization from xylene/n-heptane (vol. ratio 3:2). m.p.: 92 °C, yield: 45 %.

Compound III

8.7 g (18.7 mmol) of I, 8 g (18.7 mmol) of II, 3.6 g (26.1 mmol) of K_2CO_3 , 150 ml of dry butanone, and a catalytic amount of KI were refluxed for 70 hours. After cooling down to room temperature the precipitate was filtered and washed first with ethanol, then with water to remove the inorganic salts. The crude product was recrystallized from 1,2-dichlorethane; yield: 60 %; transition temperatures: crystalline 147 °C unidentified smectic 160 °C smectic A 203 °C isotropic.

Diols

Commercial products ($n = 8$: Janssen, $n = 12$: Merck, $n = 16$: Aldrich) were used without further purification after drying in a vacuum exsiccator overnight.

Polyesters

The melt polycondensation was carried out as described previously (2).

Characterization

Thermal properties of the polyesters were studied using a polarizing microscope fitted with a hot stage. Additionally, their phase transitions were checked by DSC (Perkin-Elmer). The solubility at measuring temperatures was too small in order to determine molecular weights. X-ray diffraction patterns were taken with a flat film camera. Ni-filtered $\text{CuK}\alpha$ -radiation was used. Oriented samples were obtained by drawing fibres from the melt below the clearing points.

RESULTS AND DISCUSSION

Table I lists the properties of the LC polyesters and Figure 2 presents the DSC traces.

Table I: Phase behaviour of the synthesized dimesogenic polyesters

Code	Thermal Transitions ($^{\circ}\text{C}$) ^{a)}						
P8	P_c	165	(P_{s_1}	165)	P_{s_2}	237	P_i
P12	P_c	165	(P_{s_1}	150)	P_{s_2}	220	P_i
P16	P_c	165	P_{s_c}	181	P_{s_A}	203	P_i

a) c = crystalline; s_1 , s_2 = unidentified smectic phases; s_c = smectic C; s_A = smectic A; i = isotropic; P = polymeric.

Compared with the related monomesogenic side group polymers (7), the incorporation of the biphenyl unit into the side groups caused an increased width of the liquid crystalline phases due to higher clearing temperatures. Whereas the monomesogenic homologues with not more than 13 methylene groups in the backbone form also nematic phases, the dimesogenic ones exhibit only smectic phases. The increase in the length of the non-mesogenic main chain segment causes a decrease of the isotropization temperature.

With the exception of P16, the smectic phases exhibited unspecific optical textures.

The X-ray diffraction patterns of mechanically aligned specimens have some common features (Figure 3). They reveals relatively sharp outer reflections corresponding to

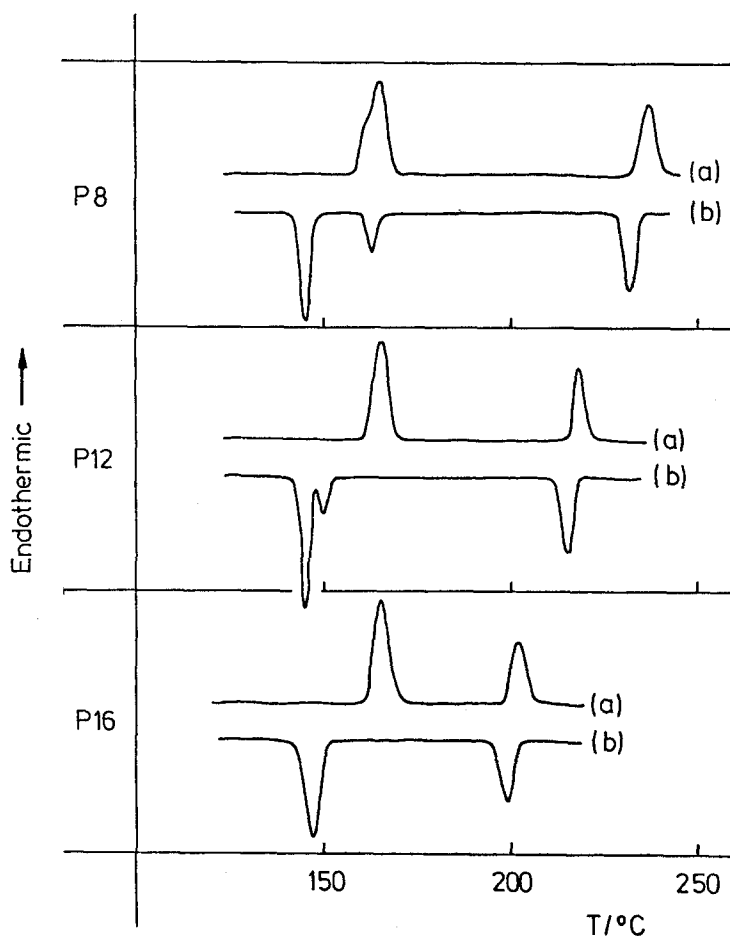


Figure 2: Heating (a) and cooling (b) DSC scans (8 K/min)

a well ordered lateral packing of the mesogens in the crystalline phase. The patterns of P12 and P16 (Figure 3b) show that the mesogenic side groups are preferentially oriented perpendicular to the fibre axis. Furthermore, the melt drawing orientation and the intensity of inner reflections increase with the extension of the non-mesogenic segments. It is remarkable that the periodic spacings perpendicular to the smectic layer planes are independent on the number of methylene groups in the backbone. Probably, the flexible main chains are not involved in the formation of the layers. More detailed X-ray studies are in progress.

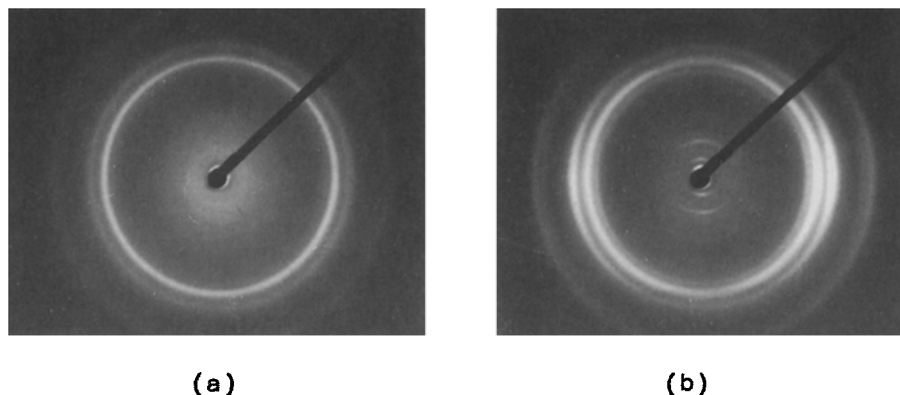


Figure 3: X-ray patterns of polymer PB (a) and P16 (b) at room temperature. Sample-film distance: 50 mm. Direction of the incident beam is perpendicular to the fibre axis

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