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Liquid crystalline polyesteramides containing crown ether units in the mesogenes

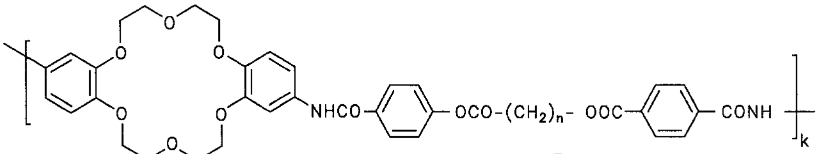
H. Fischer[1],* and V. V. Zuev[2]

[1]H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Royal Fort,
Bristol BS8 1TL, UK
[2]Academy of Sciences, Institute of Macromolecular Compounds, Bolshoi Pr. 31,
199004 St. Petersburg, Russia

Abstract Main chain liquid crystalline polyesteramides containing dibenzo-[18]-crown-6 moieties have been synthesized. Shown by polarisation microscopy and x-ray investigations, these polymers tend to form a mesophase with a layered structure, *e.g.* smectic A or smectic C type.

Introduction

In the past two decades a great variety of liquid crystalline (LC) main chain and side group polymers, as well as LC polymers with a more complex structure of the mesogenic fragment (crosses, discs, Y-shaped etc.), have been synthesized (1). Therefore, the molecular design in this field of polymer chemistry has been advanced considerably. Meanwhile, the search for various structural elements for improving polymer properties, *e.g.* the ability for complex formation, thermo- and photochromic properties etc., is continuing. One of the promising elements to incorporate into LC polymers is a crown ether moiety. LC side group polymers (2) and main chain polymers (3-5) have been already synthesized. However, the role of the crown fragment in the formation of mesophases has not yet been elucidated. One view is that this moiety can be inserted into the mesogen because of its rigidity and thus favour a mesophase formation (3). Other work has shown, that the crown ether group plays the role of a flexible spacer (4,5). The aim of this work was the synthesis of main chain polyesteramides **I**



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with dibenzo-[18]-crown-6 moieties in the main chain and the investigation of their mesophase behaviour.

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*Corresponding author

Experimental

All reagents were obtained from Soiuzreactiv (USSR) and purified before use by destillation (acid dichlorides, solvents) or recrystallisation (4-hydroxybenzoic acid (HBA) and 4.4'-diaminobenzo-[18]-crown-6 (DDAC)).

4.4'-(n-alkanoyldioxy)dibenzoic acids IIa-d: A solution of 0.04 mol of the n-alkane dicarboxic acid in 10 ml acetonitrile was added to a solution of 0.06 mol HBA in 70 ml acetonitrile and 7.5 ml (0.09 mol) pyridine while stirring. The reaction mixture was stirred at 25 °C for 2 hrs. The white precipitate was filtered, washed with water and 0.5N hydrochloric acid and with hot water and dried in vacuum. The yields were between 50 and 65 %.

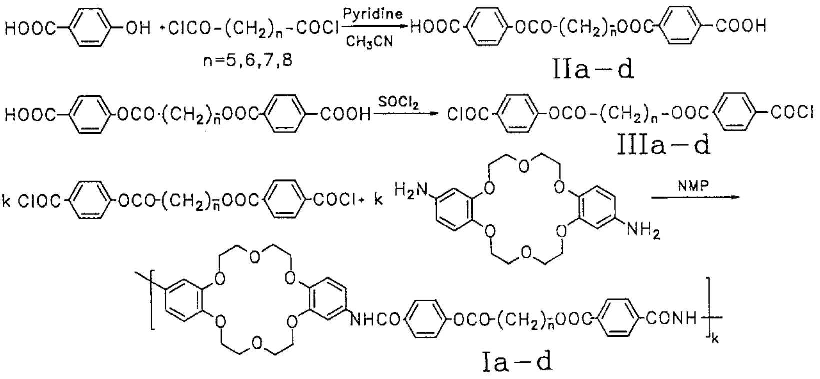
The dichlorides ***IIIa-d*** were prepared as described previously (6).

Polycondensation: A solution of 5 mmol of the dichloride **III** in 3 ml N-methyl-2-pyrrolidine (NMP) was added dropwise during stirring to a solution of 5 mmol of DDAC in 3 ml NMP at - 5 °C. The reaction mixture was stirred for another 2 hrs. allowing it to heat up to room temperature and subsequently poured into 100 ml methanol. The precipitate was filtered and dried. After reprecipitation from NMP into methanol, the polymers were filtered, washed with methanol and dried in vacuum. The yield was 90-95 %. The polyesteramides obtained were soluble in Dimethylformamide (DMF), NMP and trifluoroacetic acid (TFA).

The polymers were characterised by elemental analysis, IR spectroscopy (KBr, Bruker IFS 88) and ^{1}H and ^{13}C spectroscopy (solvent TFA, Bruker AC200). Polymer viscosities were measured in an Ubellohde viscosimeter, capillary no. 0 at 25 °C in TFA. DSC studies have been carried out using a Perkin-Elmer DSC 7 with a scanning rate of 20 K/min. POM studies have been performed with a Zeiss Ultraphot microscopy combined with a Linkam THM 600 hot stage and a SONY videorecorder for recording of unstable phase textures. X-ray experiments have been done at a GX 21 rotating anode with copper target, equipped with a graphite crystal monochromator and a 2-D GADDS detector X-1000 from Siemens. The usual time for collection of data for one frame was 20 seconds.

Results and discussion

The method of synthesis for the polyesteramides (scheme 1) made it possible to obtain polymers with a relatively high molecular weight.



Scheme 1

The inherent viscosities have been found to be $[\eta] > 0.4$ cm^3/g, a value which was for those type of polymers adopted with a molecular weight Mw higher than 10000 (7). This value of molecular weight exceeds the limit of molecular weight dependencies of phase transition temperatures (8). Thus reliability of conclusions about the relationship between structure and properties of these polymers was ensured.

The POM studies have shown that all polymers form an anisotropic melt, which is an initial identification of LC state formation. In general a fan shaped texture for the mesophases of the polyesteramides (see Figure 1) has been observed.

Figure 1: Optical micrograph of polyesteramide **Id**, 255 °C, 160 X

Since no fan shaped texture has ever been observed for nematic phases, that observation was a indication of the presence of a smectic phase . This result is supported by the x-ray investigations. Figure 2 shows a x-ray diffraction pattern of the polyesteramide with n = 7 at 250 °C.

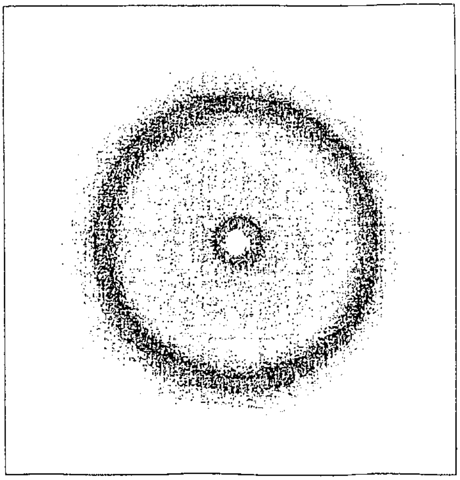


Figure 2: X-ray diffraction pattern of polyesteramide **Id**, 250 °C

A layer reflection at 26.5 Å is very clearly seen. Unfortunately, at these high temperatures, the polymer is quite unstable, and an oriented sample was not obtainable due to the high temperature and the low molecular weight. The pattern shows the existence of a smectic C or a smectic A phase; distinguishing between them is only possible by the observation of oriented samples. On the other hand, the texture is quite clearly a fan shaped texture and is closer to a smectic A phase. DSC studies have shown the following phase behaviour (see Table 1, Fig. 3).

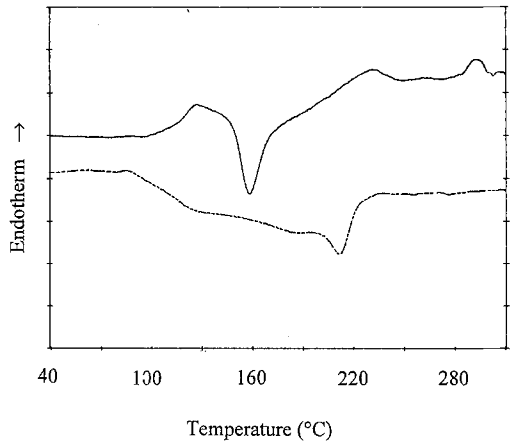


Figure 3: DSC traces of polyesteramide **Ia**, scan rate 10 K/min

Table 1: Properties of the synthesized Copolyesteramides Ia-d

Sample	[η] (cm³/g)	T cr->s (°C)	T s->is (°C)
Ia	0.45	242	294
Ib	0.45	223	286
Ic	0.44	230	297
Id	0.45	221	272

A glass transition at about 120 °C was observed for all polymers. After recrystallisation, the polyesteramides melt into a mesophase and finally pass into the isotropic phase between 270 and 300 °C.

The reason for mesophase formation of the polyesteramides **I** will be explained by the following. An incorporation of a crown ether unit into the stiff mesogen leads to a sufficient increase of the l/d ratio of the mesogen (see Fig. 4). The l/d ratio should favour a formation of a smectic phase. In fact, in the case of an insertion of the crown ether moiety into the mesogen, the length of the mesogen was estimated to be about 26 Å.

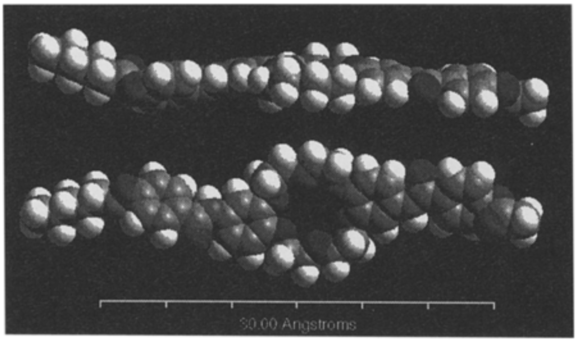


Figure 4: CPK-model of the mesogenic unit with the crown ether unit

This value is in good agreement with the layer spacing found by X-ray diffraction. This incorporation is particular effective due to the fact that the crown ether unit is not as flexible as it looks, molecular simulations have shown that the crown ether unit is a flat extended molecule. The appearance of a stable smectic phase is in contrary to the findings of Cowie and Fischer (4,5). In both studies, a diazo-[18]-crown-6 unit was used and only the appearance of nematic phases has been found. However, the crown ether unit used in those studies is quite different, the diazo-[18]-crown-6 cannot be as straight and flat incorporated into a mesogenic unit as the dibenzo-[18]-crown-6 derivatives used in this study. It is also known, that n-alkyl esters of 4.4-dibenzo-[18]-crown-6 dicarboxylic acid form smectic C phases in the melt (9). This indicates that the crown ether unit is rigid and an incorporation into a mesogen or an action as a mesogen is more likely. Moreover, the presence of interchain H-bonds favours the formation of a mesophase of the smectic type (10), as is observed in our case.

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