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Liquid crystal crown ether derived from cyclic tetramer of epichlorohydrin

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Summary

A liquid crystal crown ether is obtained by chemical modification of the cyclic tetramer derived from epichlorohydrin with sodium 4-cyano-4'-biphenoxide. The crown ether exhibits a nematic mesophase and a high glass transition temperature.

Introduction

A large number of side chain liquid crystal polymers have been synthesized in the last ten years. The influence of parameters such as the molecular weight of the polymer, the nature and the length of the spacer group and the nature of the mesogenic group and the polymer backbone has been studied (1). The large majority of the side chain liquid crystal polymers prepared up to now are derived from linear polymer backbones. Few examples of macrocyclic liquid crystal polymers (or oligomers) have been reported. Macrocyclic polyamides (2), polyamines (3) and polysiloxanes (4) presenting thermotropic mesophases have been prepared. Cyclotriphosphazenes containing mesogens in the side chains have been also described (5).

The synthesis of cyclic side chain liquid crystal oligomers appears interesting for two reasons :

The use of a cyclic backbone may lead to the formation of new types of mesophases (e.g. columnar). In the case of liquid crystal cyclic siloxanes, the theoretical calculations have predicted the formation of disc-like mesophases at low temperatures (6).

Moreover, cyclic oligoethers (such as crown ethers) and azamacrocycles readily complex metal ions. Crown ethers can incorporate alkali-metal ions with high complexation constants whereas the nitrogen analogues show affinity for transition metal ions (7). Thus, it appears possible to combine the complexing properties of these macrocyclic compounds and their self-assembly to liquid crystals. Complexation of metal cations may affect the mesomorphism and induce new liquid crystalline phases. Recently, the synthesis of liquid crystals bearing benzocrown ether ring has been reported and a study of the binding of alkali metal cations in the liquid crystal phase carried out (8).

The synthesis of liquid crystalline polymers containing crown ethers in the side chain and the study of the influence of complexation of alkali metal salts on the mesomorphism have been described by Percec et al. (9).

Very recently, we have reported the synthesis of side chain liquid crystalline polyethers obtained by chemical modification of polyepichlorohydrin with sodium 4-cyano-4'-biphenoxide (10). Nematic phases are observed when the amount of substitution is higher than 65 %.

The cationic oligomerization of epichlorohydrin leads mainly to the formation of cyclic oligomers among which the tetramer predominates (11).

In this communication, we present preliminary results on the synthesis and the characterization of a new liquid crystalline cyclic tetramer, having a crown ether structure, derived from epichlorohydrin.

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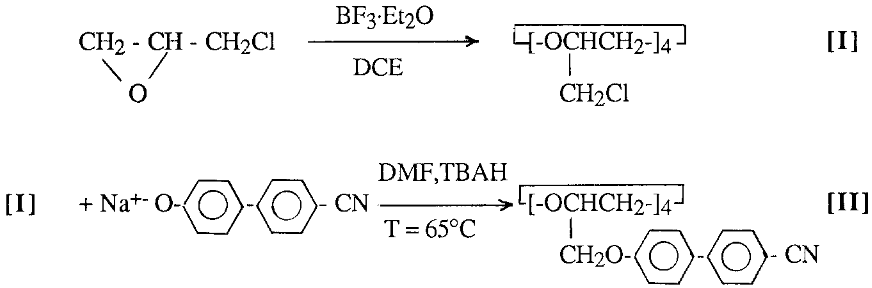
The synthesis of this tetramer is carried out in two steps :



Scheme 1 : Synthesis of LC cyclic tetramer

Experimental part

Reagents

Epichlorohydrin (ECH) and 1,2-dichloroethane (DCE) were distilled over CaH_2, N,N-dimethylformamide (DMF) was treated with potassium hydroxyde, then dried by azeotropic distillation with benzene and distilled under reduced pressure. Boron trifluoride diethyl etherate was distilled before use. Tetrabutylammonium hydrogen sulfate (TBAH) and 4-cyano-4'-hydroxybiphenyl (from Tokyo Kasei Kogyo Co, Ltd, Tokyo, Japan) were used without further purification. The sodium salt of 4-cyano-4'-hydroxybiphenyl was prepared by exchange reaction in dry ethanol containing sodium ethoxide. Ethanol was removed and the salt dried in vacuo.

Oligomerization

The oligomerization reaction was carried out by the dropwise addition of an epichlorohydrin solution in 1,2-dichloroethane (2,2 moles/l) to the 1,2-dichloroethane solution of the initiator (BF_3, Et_2O) (0.05 moles/l) with continuous stirring and maintaining the reaction temperature in the range 0 - 5°C during two hours. After raising at room temperature, the mixture was terminated with a 5 % NaOH aqueous solution and washed with water. After removing solvent and unreacted monomer under vacuum, the mixture of oligomers was allowed to stand at room temperature. After 7 days needle-like crystals formed were filtered and recrystallized two times in toluene.

Chemical modification

The chemical modification of cyclic ECH tetramer was carried out as previously described for the linear polymer (10). The evolution of the reaction was followed by ^1H NMR.

Measurements

IR spectra were recorded using a Bruker FT-IR IF S45 spectrometer. GPC analyses were carried out in THF on a Waters apparatus equipped with μ-styragel columns : 10^5, 10^4, 10^3, 500, 100 Å (refractive index and UV (254 nm) detections : flow rate 1 ml/min ; calibration vs polystyrene standards). ^1H and ^{13}C NMR spectra were recorded using a Bruker 200 MHz and a Bruker 50 MHz spectrometer, respectively ; $CDCl_3$ was used as solvent. The transition temperatures were measured using a differential thermal analyser (Perkin Elmer 7) operating at 20°C/min. Heptane and indium were used as the calibration standards. The thermal data were determined from the second heating scans. The glass transition temperature T_g was estimated from the point of intersection between the initial base line and the sloping portion of the line obtained as the base line shifts during the glass transition. Transition temperatures were taken as the maximum point of the endotherm. Optical observations were made using a polarizing microscope (Olympus BHA-P) equipped with a Mettler FP 52 hot-stage and FP 5 control unit. The mass spectrum (chemical ionization) was performed on a Nermag triple quadrupole R 3010 mass spectrometer.

Results and Discussion

Synthesis of ECH tetramer

The oligomerization of ECH with BF_3, Et_2O as initiator has been carried out according to the procedure described by Ito et al. (11). In the latter, a mixture of oligomers (tetramer, pentamer, hexamer, ...) is obtained. The tetramer is itself composed of several isomers due to the various possibilities of enchainments (head to tail, head to head, ...) and stereochemical combinations of enantiomeric units. One isomer can be obtained by allowing the mixture of oligomers to stand and by recrystallization of the obtained crystals. It has been established (12) that this isomer was the head to tail (RRSS) tetramer on the basis of X-ray crystallography. The four side groups ($-CH_2Cl$) are all in equatorial position.

The molecular weight of the crystalline material we have isolated was checked by **mass spectrometry** (negative mode - molecular ion : $[M - H]^-$, m/e = 367, 369, 371, 373, 375 corresponding to the tetramer with different combinations of isotopes of chlorine atom).

GPC shows the absence of higher oligomers (pentamer, hexamer, ...).

IR spectrum reveals the absence of any characteristic end-groups (carbonyl, hydroxyl, double bonds). The characteristic bands of CH_2Cl group are observed at 702 and 751 cm^{-1}.

Figure 1 shows the **^{13}C NMR spectrum** of the ECH tetramer. Three groups of signals are observed corresponding respectively to $\underline{C}H_2Cl$ (42.98 - 43.19 - 43.47 ppm), $O\underline{C}H_2$ (70.34 - 71.74 - 72.02 ppm) and $O\underline{C}H$ (79.98 - 80.32 - 80.57 ppm), carbon atoms. For each carbon, three signals are present, the low-field signal being largely predominant. This indicates that the tetramer is indeed highly enriched in one isomer.

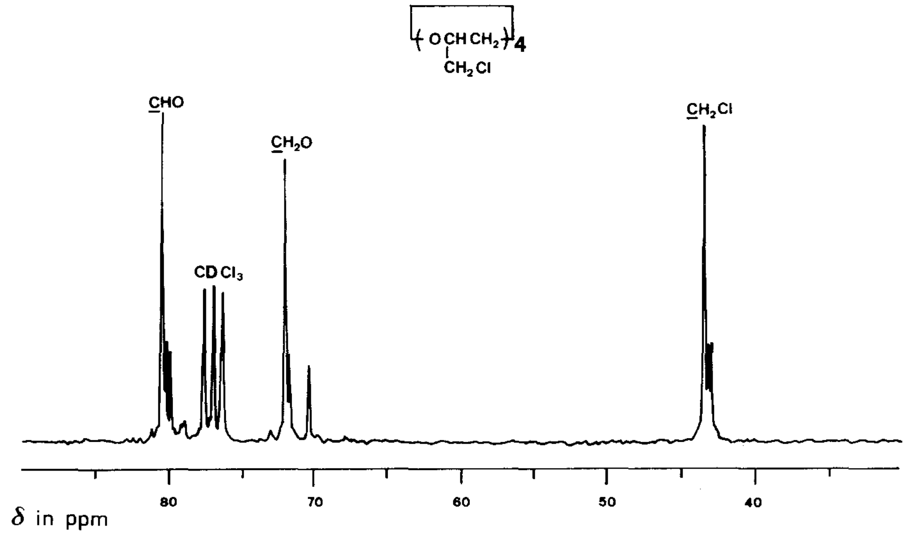


Fig. 1 : ^{13}C NMR spectrum of ECH cyclic tetramer [I] at 50 MHz in $CDCl_3$.

Chemical modification of ECH tetramer

The chemical modification of the tetramer was carried out in DMF using sodium 4-cyano-4'-biphenoxide at 65°C. The evolution of the reaction was followed by ^{1}H NMR using the intensities of the two aromatic peaks appearing at 6.95 ppm (2H) and 7.55 ppm (6H). The modification is quantitative after one week of reaction. IR spectrum shows the complete disappearance of CH_2Cl groups. The ^{13}C NMR spectrum of modified tetramer is shown in Figure 2. The assignment of different signals is reported below :
Chemical shifts (in ppm from TMS).

(a) 71.6 (b) 79.6 (c) 68.0 (1) 159.2 (2) 115.1 (3) 127.0
(4) 131.7 (5) 144.9 (6) 128.3 (7) 132.4 (8) 110.1 (9) 119.0

Each carbon atom presents only one signal. This simplicity of the spectrum confirms the symmetry of the macrocycle.

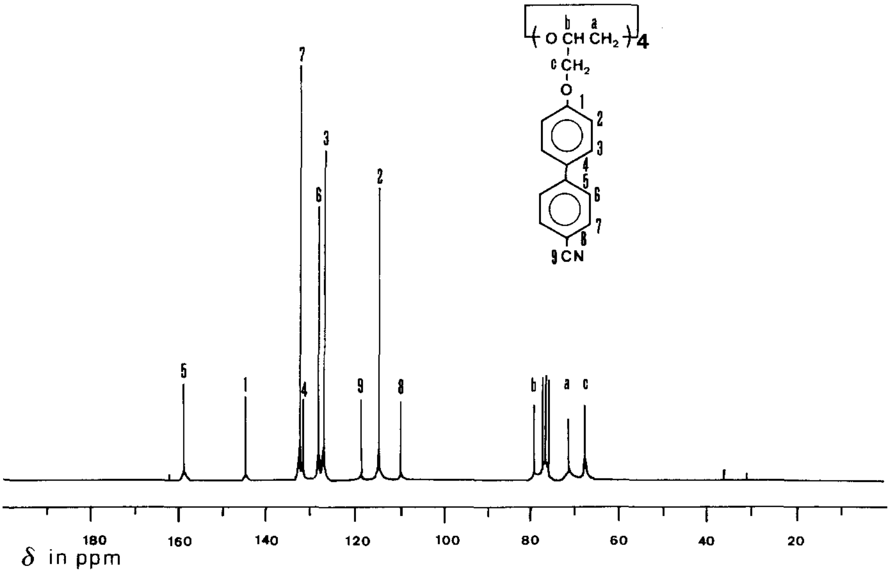


Fig. 2 : ^{13}C NMR spectrum of modified tetramer [II] at 50 MHz in $CDCl_3$.

Thermal properties of modified ECH tetramer

Thermal properties have been investigated by DSC and by optical microscopy using a polarizing microscope.

The **DSC** traces (Figure 3) are characterized by two transitions : a glass transition temperature at 83°C and a small endotherm at 130°C corresponding to the mesophase/isotropic transition.

Optical microscopy observations indicate that the macrocycle exhibit a nematic phase. The sample was heated above the isotropization temperature and then slowly cooled. On annealing for a long time (2 days) at 125°C, the formation of a stable schlieren texture, characteristic of a nematic phase is observed (Figure 4).

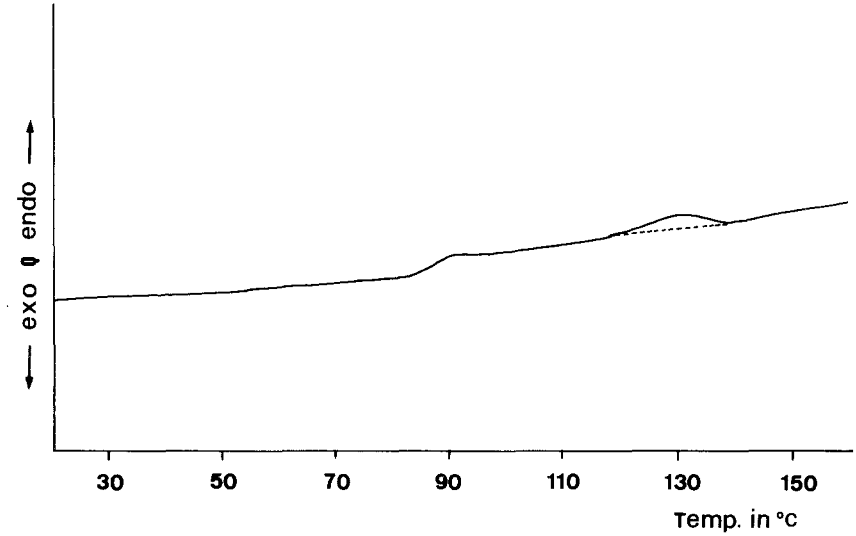


Fig. 3 : DSC trace of modified ECH tetramer.

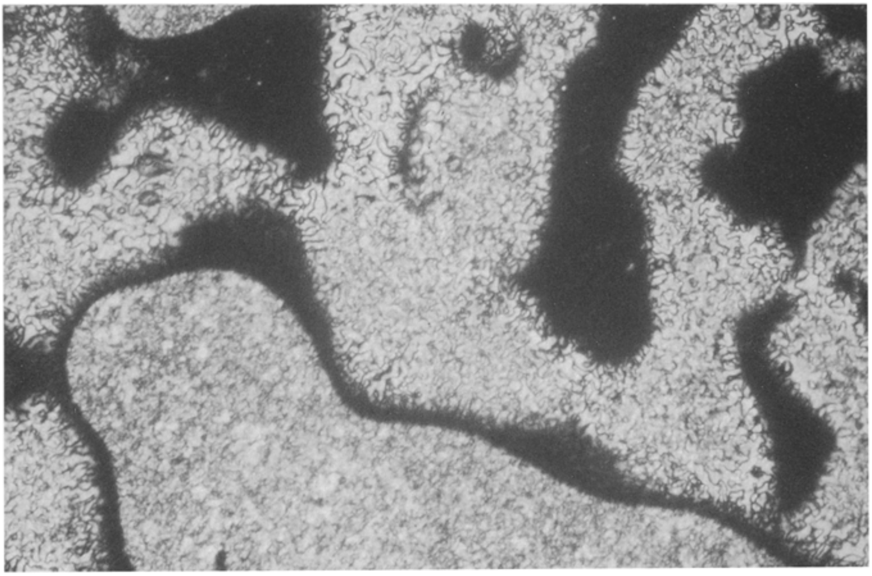


Fig. 4 : Texture of modified ECH tetramer at 125°C after annealing two days (crossed polarizers, magnification x 200).

The cyclic tetramer bearing pendant mesogenic groups presents liquid-crystalline behaviour. The occurrence of a nematic phase may be due to the non-flatness of the cyclic backbone. Rigid planar cores (phtalocyanines, porphyrins, ...) lead, generally, to the formation of columnar mesophases (13). Comparison with linear polymers derived from epichlorohydrin (a polymer with 91 % of mesogenic groups having a molecular weight of 11200 presents a glass transition temperature (T_g) of 86°C and an isotropization temperature (T_i) of 153,5°C (10)) indicates that the cyclic tetramer shows a rather high glass transition temperature (83°C). Therefore, the cyclic structure of the backbone increases hindrance to chain motions. The lower isotropization temperature (130°C) can arise from the increased coupling of the mesogenic group to the backbone leading to a decrease of the domain of mesomorphism ($\Delta T = 47$°C). Further studies include the synthesis and the characterization of macrocycles of various sizes and the influence of complexation of alkali metal cations on the mesomorphism.

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