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Synthesis and polymerization of liquid crystalline α-oxiranes containing 4-cyanobiphenyl and *p*-methoxyphenyl benzoate mesogenic groups

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SUMMARY

Synthesis of a new series of α-oxiranes having 4-cyanobiphenyl and p-methoxyphenyl benzoate mesogenic groups and phase behaviour of synthesized compounds are described. Polymerization of α-oxiranes with $BF_3.O(C_2H_5)_2$ and Et_3Al/H_2O/Acetyl acetone as initiators was carried out.The first initiator produced the olygomers displaying liquid crystalline properties while the second one gave the crystalline polymers with high degree of polymerization.

INTRODUCTION

In recent years increased works have been directed to the synthesis of new comb-like liquid crystalline polymers (LC) [1]. One of the goals of these investigations is devoted to the search of new polymeric chains which are able to influence on the properties of LC phase formed by mesogenic side groups. In the past few years it is found that polyvinyl ethers [2-4], polyphosphazenes [5] bearing mesogenic groups in the side chain belong also to the comb-like LC polymers which produce LC phase formation like polyacrylates,polymetacrylates and polysiloxanes [1,6,7]. Attempts to synthesize some LC polymers with the flexible main chain based on α-oxiranes have been done as well[8]. However the obtained compounds are charaterized by low molar mass. At the same time the polymerization of the simple oxiranes like ethylene oxide,propylene oxide and their aliphatic derivatives have been the subject of a lot of researches in nearly 30 years [9-11]. It was found that epoxides possessing polar groups (halogen,ester fragments,etc) can be polymerized either at the presence of some acids or of some bases. However products with high degree of polymerization (DP) have been obtained only by means of chelate catalysts on the base of aluminium and zinc [9].

In this paper the synthesis of two series of compounds containing α-oxirane rings and different mesogenic groups -4-cyanobiphenyl and p-methoxyphenyl benzoate,which are decoupled from α-oxirane rings by the methylenic groups of the different length (spacers) is described. These α-oxiranes bearing the above mentioned mesogenic groups were prepared for the first time by the epoxydation of the correspondent ethylene derivates,using the methods elaborated for epoxydation of the simple ethylene compounds [12-18].

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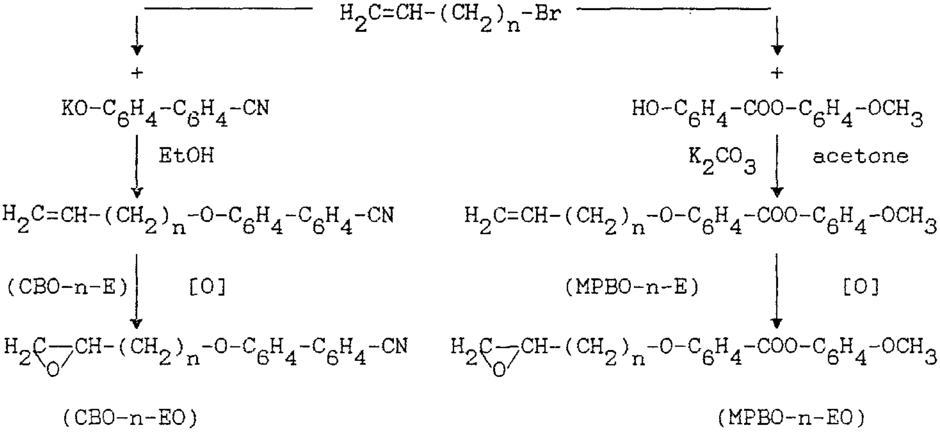
In order to prepare the olygomers as well as the polymers two different initiating systems based on $BF_3.O(C_2H_5)_2$ and Et_3Al/H_2O/Acetyl acetone were used.

EXPERIMENTAL

The synthesis of α-oxiranes was carried out according to the following scheme :



A. Synthesis of p-methoxyphenyl-p'-allyloxy benzoate (MPBO-1-E):

In a flat bottom flask that contained a magnetic stir bar 12.55 g (0.0514 mole) of p-methoxyphenyl-p'-hydroxybenzoate and 8.52g (0.0617 mole) of K_2CO_3 were dissolved in acetone (40ml). Afterwards 5.33ml (0.0617mole) of allyl bromide was added.The flask was equipped with a water-cooled condenser and the reaction was carried out with vigorous stirring at boiling point of acetone for one day. The precipitate (KBr) was filtered off and the filterate was added to water and extracted with chloroform.The organic layer was thoroughly washed by water several times and dried over magnesium sulfate for 12 hours. The solvent was removed by rotary evaporation.The solid white residue was recrystallized twice from methanol and purified by column chromatography (silicagel, chloroform). The chloroform was evaporated at reduced pressure and 11.5g of MPBO-1-E in form of white crystals was obtained (75%).

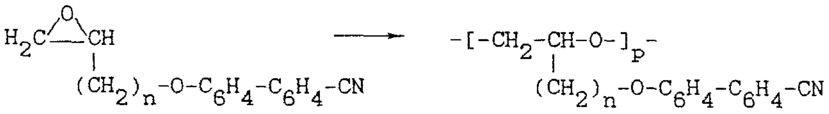
The other MPBO-n-E (n=2-4,9) were prepared by the same route. The yield is around 65-80% . In the synthesis of CBO-n-E (n=1-4,9) the phenolate obtained by the action of KOH on the 4-hydroxy-4'-cyanobiphenyl was used as the starting material, and the reaction was carried out in ethanol in similar conditions to give CBO-n-E in the yield of about 65-80% .

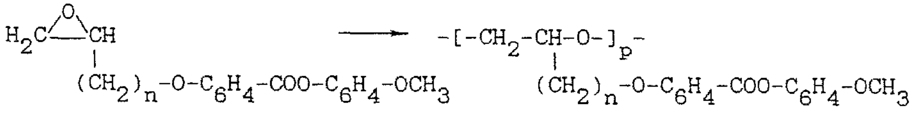
B. Epoxydation of MPBO-1-E

In a 3-neck round bottom flask, cooled in an ice bath and fitted with a thermometer, magnetic stirrer, drying tube and dropping funnel a solution of perbenzoic acid (8.46g, 0.0613mole) obtained as it was described by [19] in chloroform (60ml) was added. MPBO-1-E (11.5g, 0.0383mole) dissolved in $CHCl_3$(30ml) was added drop by drop to the flask such that the temperature did not rise above 3°C. After 2 hours the ice bath was removed and the reaction was allowed to continue at room temperature for 2 days. The reaction solution was washed with a solution of 5% of sodium bisulfite, 2% sodium carbonate and then with water until neutral. After drying the solution over magnesium sulfate the solvent was removed by rotary evaporation. The solid residue was recrystallized twice by treatment with methanol and purified thoroughly by column chromatography (silicagel, chloroform). After removing of chloroform at reduced pressure 7.86g (64.7 %) of p-methoxyphenyl-p'-(2-3-epoxy-propyloxy) benzoate (MPBO-1-EO) in form of white crystals was obtained.

The other MPBO-n-EO (n=2-4,9) and CBO-n-EO (n=1-4,9) were prepared by the same procedure. All α-oxiranes are white crystalline substances. Yield 60-80%.

C. Polymerization





The following general procedure was used to the polymerization experiments : A polymerization tube was charged with a solution of α-oxiranes in dichloroethane and degassed by three freeze-thaw cycles. A degassed by the same way solution of initiator was then added. The polymerization tube was sealed under strong Ar flow. After polymerization for the desired period at room temperature the tube was opened and the contents worked up as described for each of the following experiments.

C.1. Polymerization of MPBO-n-EO with $BF_3.O(C_2H_5)_2$ as initiator

A dichloroethane solution (5.6ml) of MPBO-1-EO (1.00g, 3.33mmole) and an etheral solution of $BF_3.O(C_2H_5)_2$ (0.25mmole in 2.74ml, 7.5% mole) were allowed to react for 10 days. The reaction mixture was diluted with $C_2H_4Cl_2$ and poured into methanol. The white product precipitated, was isolated and then washed several times in boiling methanol to give 0.04g (4%) of olygo (p-methoxyphenyl-p'-methoxy benzoate) oxirane (MPBO-1-OEO).

The other MPBO-n-EO (n=2-4,9) and CBO-n-EO (n=1-4,9) were allowed to polymerize in the same route.Yield :30-70%.

C.2.Polymerization of MPBO-1-EO with $Et_3Al/H_2O/AcAc$ as initiator

The initiator system $Et_3Al/H_2O/AcAc$(1.0/0.5/1.0) was prepared according to [20].MPBO-1-EO (1.00g,3.33mmole) in $C_2H_4Cl_2$ (8.03ml) was allowed to polymerize in the presence of $Et_3Al/H_2O/AcAc$ (0.16mmole,0.30ml,5 mole % Al with respect to monomer).After 10 days the polymerization tube was opened,the contents were diluted with $C_2H_4Cl_2$ and poured into methanol.The precipitated polymer was then dissolved in warm N-methyl pyrrolidone and reprecipitated from methanol.Afterwards the polymer was purified several time in boiling methanol.0.06g (6%)of poly(-p-methoxyphenyl-p'-methoxy benzoate) oxirane (MPBO-1-PEO) was obtained.Polymerization of the other MPBO-n-EO (n=2-4,9) and CBO-n-EO(n=1-4,9) was carried out in the same way. Yield :30-70%.

RESULTS and DISCUSSION

The analytical data of obtained α-oxiranes and polymerization products are summarized in Table 1.

The IR-spectra of synthesized compounds were recorded with the SPECORD M80 instrument using KBr pellets. For the α-oxiranes the absorption band at 915 cm^{-1} (epoxide) was observed. The absorption band at 1640(C=C),displayed in MPBO-n-E and CBO-n-E, had disappeared. In the IR-spectra of olygomers and polymers the absorption band at 915 cm^{-1} (asymetric oscillation of epoxide ring) was absent.

The ^1H NMR spectra (HMPA-d18)of some synthesized compounds were measured on a 300 MHz "Brucker" spectrometer . They were as as follow : MPBO-4-EO :δ= 1.48-1.73, ($-C_3H_6-$, multiplet), δ=2.38-2.62(epoxy protons,triplet), δ= 3.96-4.00 ($-CH_2O-$,triplet), δ=6.98-7.92 (protons of benzene ring,multiplet);MPBO-4-PEO : δ=1.26-1.52 ($-C_3H_6-$), δ=3.2-3.4 ($-CH_2-\underset{|}{C}H-O-$), δ=3.6-3.8 ($-CH_2O-$), δ=6.64-7.72 (protons of benzene ring),(Fig.1).

Considering the obtained results it was established that the olygomerization and polymerization were occured by the opening of the a-oxirane ring without any change of mesogenic side groups.

All prepared α-oxiranes are liquid crystals and their mesophase behaviours were investigated by a "POLAM" polarizing microscope equipped with a "Mettler FP-800" Thermosystem and a DSM-2 differential scanning microcalorimeter.The properties of synthesized α-oxiranes are listed in Table 2.

As one can see from Tab.2 the compounds MPBO-n-EO and CBO-n-EO (where n=1-4) are characterized by monotropic nematic phase,while MPBO-9-EO and CBO-9-EO form enantiotropic nematic one.

The transition from crystalline to nematic and to isotropic phases is accompanied by an enthalpy of transition of about 80-111 $J.g^{-1}$,while the enthalpy changes of transition from the nematic phase to the isotropic are very low (1.2-2.8 $J.g^{-1}$).

Table 1: The analytical data of α-oxiranes, their olygomers and polymers

α-OXIRANES	Calc.,% C	Calc.,% H	Calc.,% N	Found % C	Found % H	Found % N
MPBO-1-EO	68.00	5.33		68.32	5.26	
MPBO-2-EO	68.78	5.73		68.74	5.47	
MPBO-3-EO	69.51	6.10		69.76	6.28	
MPBO-4-EO	70.17	6.43		70.25	6.58	
MPBO-9-EO	72.81	7.76		73.11	7.76	
CBO-1-EO	76.49	5.18	5.57	76.18	5.10	5.32
CBO-2-EO	76.98	5.66	5.28	76.88	5.88	5.26
CBO-3-EO	77.42	6.09	5.01	77.21	6.13	5.04
CBO-4-EO	77.81	6.48	4.78	77.54	6.54	4.80
CBO-9-EO	79.34	7.99	3.85	78.98	8.08	3.87

OLYGOMERS	Found % C	Found % H	Found % N	POLYMERS	Found % C	Found % H	Found % N
MPBO-1-OEO	68.19	5.54		MPBO-1-PEO	68.15	5.43	
MPBO-2-OEO	68.58	5.66		MPBO-2-PEO	68.64	5.69	
MPBO-3-OEO	69.49	6.23		MPBO-3-PEO	69.91	6.31	
MPBO-4-OEO	70.37	6.51		MPBO-4-PEO	70.29	6.27	
MPBO-9-OEO	72.63	7.87		MPBO-9-PEO	72.40	7.96	
CBO-1-OEO	76.64	4.89	5.65	CBO-1-PEO	76.59	5.38	5.49
CBO-2-OEO	77.24	5.63	5.41	CBO-2-PEO	77.21	5.87	5.44
CBO-3-OEO	77.34	6.19	4.89	CBO-3-PEO	77.83	6.19	4.96
CBO-4-OEO	78.01	6.61	4.69	CBO-4-PEO	78.07	6.40	4.74
CBO-9-OEO	79.25	8.18	3.75	CBO-9-PEO	79.52	8.19	3.90

MPBO-n-OEO and CBO-n-OEO (n=1-4,9) denote the olygomers prepared by using $BF_3.O(C_2H_5)_2$ as initiator.

MPBO-n-PEO and CBO-n-PEO (n=1-4,9)-Polymers obtained by means of chelate catalyst ($Et_3Al/H_2O/AcAc$).

Table 2: Phase transition points and heats of transitions for compounds studied.

COMPOUND	Types of mesophase and phase transitions, °C	ΔH(K->I,K->N) $J.g^{-1}$	ΔH(N->I) $J.g^{-1}$
MPBO-1-EO	K 92.2 (N 91.8) I	93.9	1.5
MPBO-2-EO	K 102.2 (N 65.8) I	107.6	1.6
MPBO-3-EO	K 95.5 (N 72.4) I	97.9	1.8
MPBO-4-EO	K 78.6 (N 70.5) I	92.5	1.4
MPBO-9-EO	K 72.6 N 74.1 I	86.1	1.7
CBO-1-EO	K 113.5 (N 82.3) I	111.0	1.9
CBO-2-EO	K 67.2 (N 66.2) I	78.9	1.2
CBO-3-EO	K 85.4 (N 71.7) I	93.0	1.5
CBO-4-EO	K 70.3 (N 70.1) I	87.5	1.8
CBO-9-EO	K 67.3 N 70.3 I	96.0	2.8

K,N and I denote the crystalline, nematic and isotropic phases.

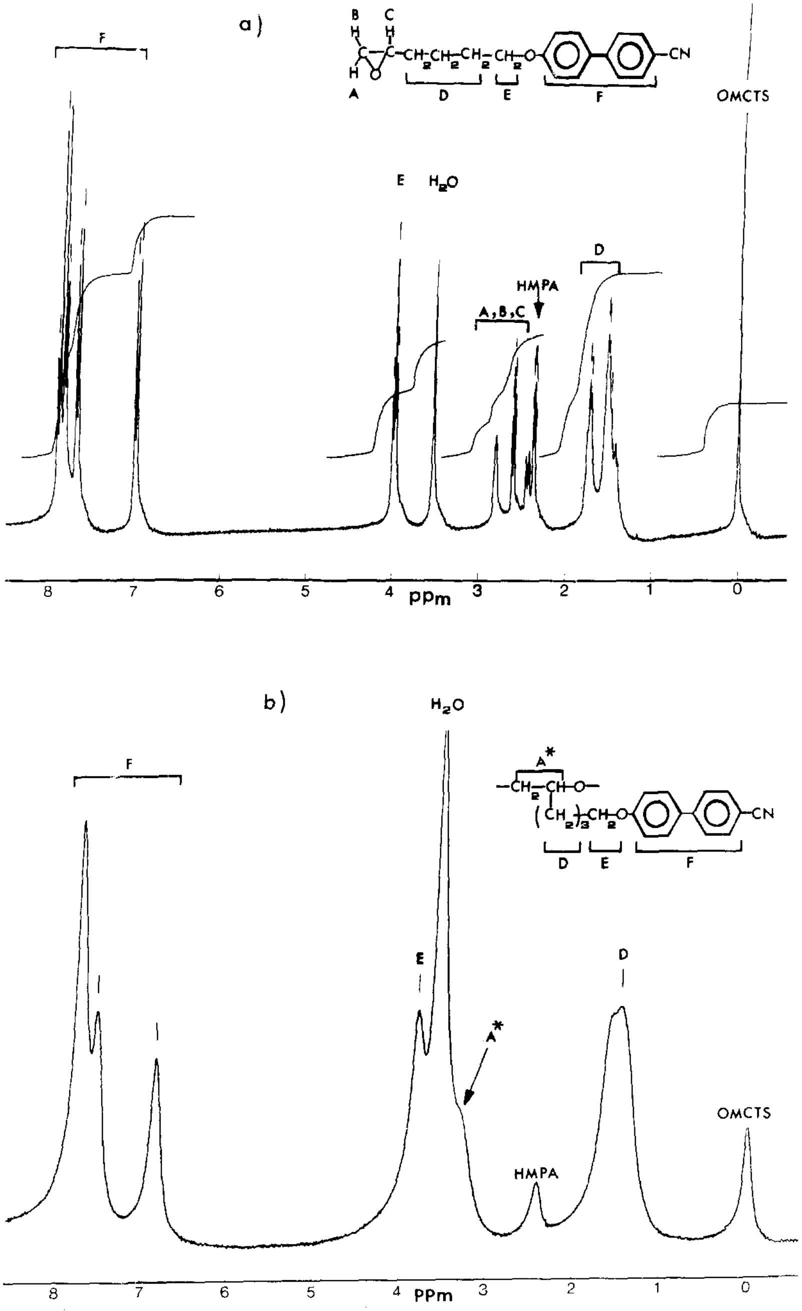


Fig.1: ^{1}H NMR spectra of MPBO-4-EO (a) and MPBO-4-PEO (b) (10% solution in Hexamethylphosphoramide -HMPA-d18, internal standard -0.5% Octamethylcyclotetrasiloxane-OMCTS)

Considering the data and the curves presented in Tab.2 and Fig.2 a dependence of phase transition temperatures (K->N,K->I and N->I) of CBO-n-EO on the odd and even number of methylenic groups was established, while this dependence for the MPBO-n-EO was observed only by transition from nematic to isotropic one.

Comparing the mesophase behaviours of synthesized by us α-oxiranes with those of some liquid crystals having the same mesogenic groups like :

I) - C_mH_{2m+1}-O-C_6H_4-COO-C_6H_4-OCH_3 (m=3-6,11) [21],and
II) - C_mH_{2m+1}-O-C_6H_4-C_6H_4-CN (m = 3-6,11) [22]

it was found that in comparision with the compounds I and II the incoporation of the oxirane ring in alyphatic substituents leads to a small decreasing of the thermostability of nematic mesophase and a remarkable increase of melting points of crystalline phase for a series of CBO-n-EO. All obtained by us α-oxiranes are liquid crystals , while the compounds I (m=3) , II (m=2-3) didn't form mesophase.

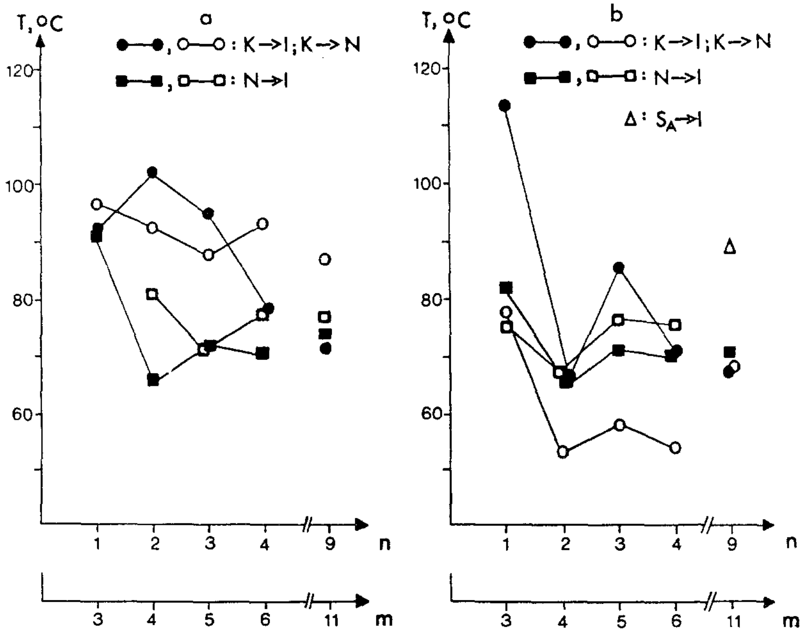


Fig.2 Phase transition points of homologous series:
a - MPBO-n-EO(●,■) and I (○,□),
b - CBO-n-EO(●,■) and II (○,□,Δ).

The polymerization of α-oxiranes with $BF_3.O(C_2H_5)_2$ as initiator produced olygomers (MPBO-n-OEO,CBO-n-OEO) of low molar mass. Their average degree of polymerization (DP) measured by GPC

[4,6] is at intervals of 4-30. Except MPBO-1-OEO and CBO-1-OEO the olygomers MPBO-n-OEO and CBO-n-OEO (n=2-4,9) are characterized by mesophase type S_A or N. The poly-α-oxiranes (MPBO-n-PEO,CBO-n-PEO) with high molar mass (for example MPBO-4-PEO,DP=220) were prepared only by means of chelate catalyst (Et_3Al/H_2O/AcAc). The inherent viscosity of these polymers in N-methyl pyrrolidone (60 °C) was about 0.1-0.7 dl/g.These polymers have a tendency to crystallize in contrast to analogous polyacrylates , polymetacrylates , polysiloxanes and polyvinyl ether bearing the same mesogenic side groups [4,6].The results of investigation on the mesophase state of obtained olygomers and polymers will be published later.

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