Polymer Bulletin 29, 49–56 (1992)

Polymer Bulletin

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

Pham Anh Tuan, S. G. Kostromin, and V. P. Shibaev*

Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119899, Russian Federation

Summary

The synthesis of a new series of α-oxiranes containing 4-cyanobiphenyl and *p*-methoxyphenyl benzoate mesogenic groups and the 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 oligomers displaying liquid crystalline properties while the second gave crystalline polymers with a high degree of polymerization.

Introduction

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

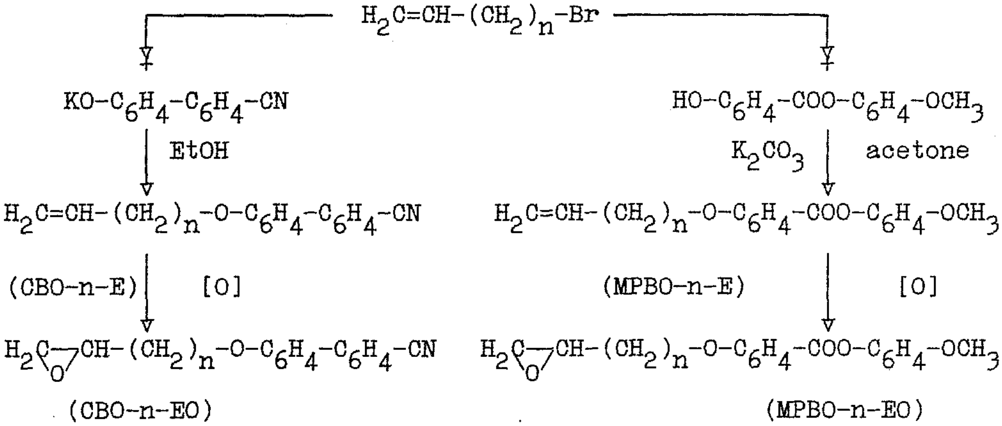
In this paper the synthesis of two series of compounds containing α-oxirane rings and various mesogenic groups -4-cyanobiphenyl and *p*-methoxyphenyl benzoate, which are decoupled from α-oxirane rings by methylenic groups of the varying length (spacers), is described. These α-oxiranes bearing the above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

*Corresponding author

In order to prepare the oligomers 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 containing a magnetic stirring bar 12.55 g (0.0514 mol) of *p*-methoxyphenyl-*p*'-hydroxybenzoate and 8.52 g (0.0617 mol) of K_2CO_3 were dissolved in acetone (40 ml). Afterwards,5.33 ml (0.0617 mol) of allyl bromide was added.The flask was equipped with a water-cooled condenser and the reaction was carried out with vigorous stirring at the boiling point of acetone for one day.The precipitate (KBr) was filtered off and the filtrate was added to water and extracted with chloroform.The organic layer was thoroughly washed with 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 (silica gel, chloroform).The chloroform was evaporated at reduced pressure and 11.5 g of MPBO-1-E in the form of white crystals was obtained (75%).

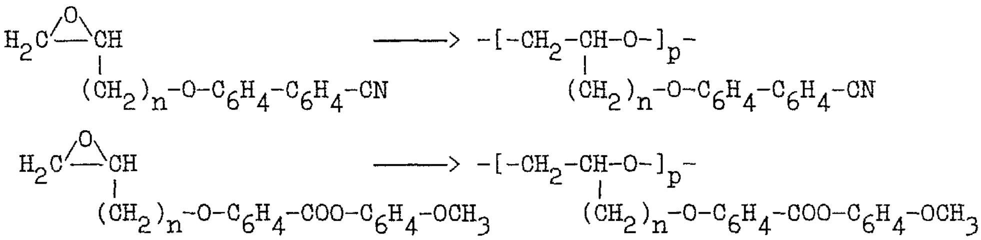
The other MPBO-n-E (n=2-4,9) were prepared by the same route. The yield is around 65-80% .In the synthesis of CBO-n-E (n=1-4,9), the phenolate obtained by the action of KOH on the 4-hydroxy-4'-cyanobiphenyl was used as the starting material, and the reaction was carried out in ethanol in similar conditions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

B.Epoxidation 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 (8.46 g,0.0613 mol) [19] in chloroform (60 ml) was added. MPBO-1-E (11.5 g,0.0383 mol) dissolved in $CHCl_3$(30 ml) was added drop by drop to the flask so that the temperature did not rise above 3^oC. 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% sodium bisulfite, 2% sodium carbonate and then with water until neutral. After removing the water from the solution over magnesium sulfate the solvent was removed by rotary evaporation.The solid residue was recrystallize twice by treatment with methanol and purified thoroughly by column chromatography (silica gel ,chloroform).After removing the chloroform at reduced pressure 7.86 g (64.7 %) of *p*-methoxyphenyl-*p*'-(2-3- epoxypropyloxy) benzoate (MPBO-1-EO) in form of the 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 followed for the polymerization experiments : A polymerization tube was charged with a solution of α-oxiranes in dichloroethane and degassed by three freeze-thaw cycles.A similary degassed solution of the 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 (5.6 ml) of MPBO-1-EO (1.00 g, 3.33 mmol) and an ethereal solution of $BF_3.O(C_2H_5)_2$ (0.25 mmol in 2.74 ml,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 precipitate was isolated and then washed several times in boiling methanol to give 0.04 g (4%) of oligo (-*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 by 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 (1.00 g,3.33,mmol) in $C_2H_4Cl_2$ (8.03 ml)was allowed to polymerize in the presence of $Et_3Al/H_2O/AcAc$ (0.16 mmol,0.30 ml,5 mol % 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 and 0.06 g (6%) of poly(-*p*-methoxyphenyl-*p*'-methoxybenzoate) 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 the α-oxiranes and polymerization products obtained 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 cm^{-1}(C=C), displayed in MPBO-n-E and CBO-n-E, had disappeared. In the IR-spectra of oligomers and polymers the absorption band at 915 cm^{-1} (asymmetric 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 follows : 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 ($-CH_2-CH-O-$), 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 oligomerization and polymerization occurred by the opening of the α-oxirane ring without any change of the mesogenic side groups.

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

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

α-Oxiranes	Calc.,% C	H	N	Found % C	H	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

Oligomers	Found,% C	H	N	Polymers	Found % C	H	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) - The oligomers were prepared by using $BF_3.O(C_2H_5)_2$ as initiator.

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

Table 2 Phase transition points and heats of transitions for the 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.

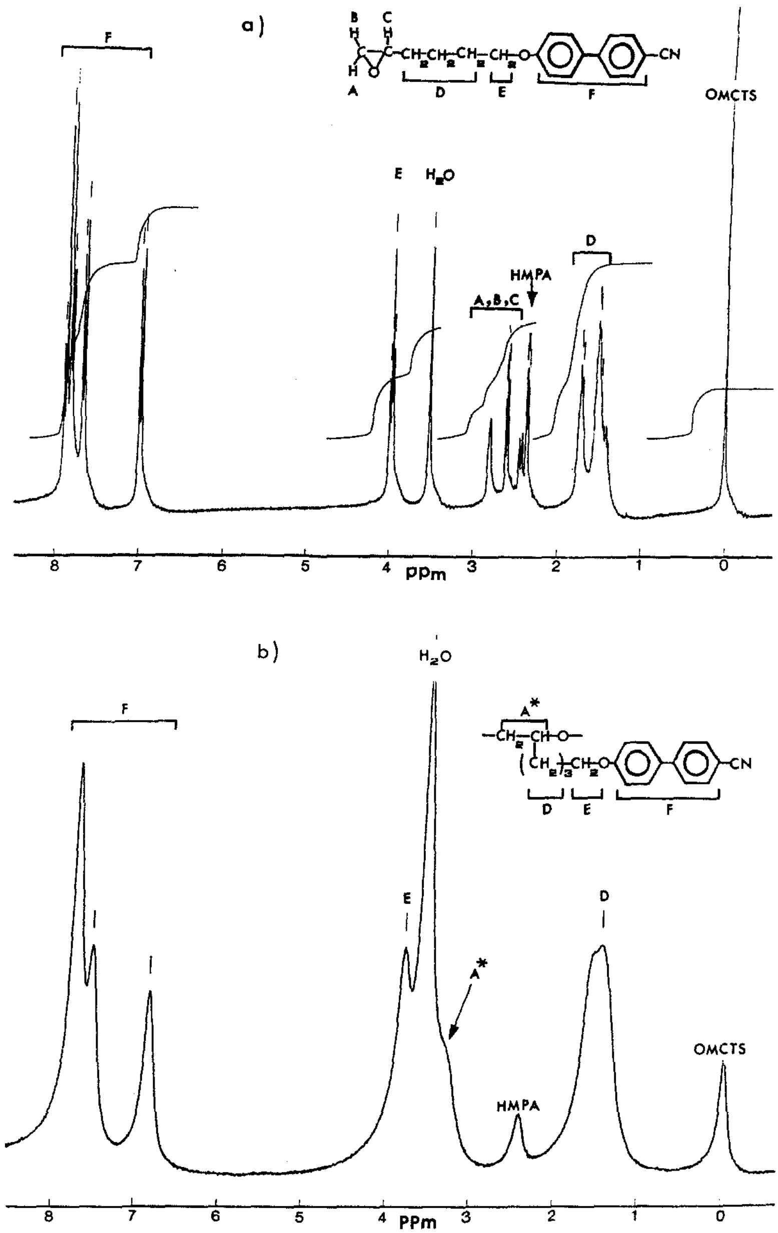


Fig.1 ^{1}H NMR spectra of MPBO-4-EO (*a*) and MPBO-4-PEO (*b*) (10% solution in Hexamethylphosphoramide -HMPA-d18, internal standard -0.5% Octamethylcyclotetrasiloxane-OMCTS)

Considering the data and the curves presented in Table 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 methylene groups was established, while this dependence for the MPBO-n-EO was observed only by transition from a nematic to an isotropic mesophase.

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

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 decrease in the thermostability of the nematic mesophase and a remarkable increase in the melting points of the crystalline phase for a series of CBO-n-EO. All the α-oxiranes obtained by us are liquid crystals, while the compounds I (m=3) , II (m=2-3) did not form a mesophase.

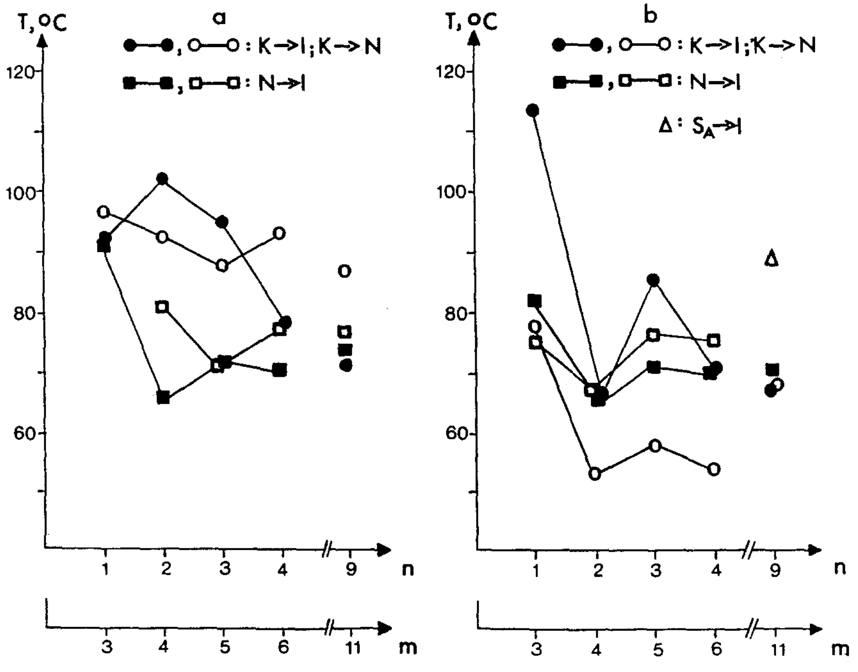


Fig.2. Phase transition points of homologous series:
a - MPBO-n-EO(●,■) and I (○,□),
b - CBO-n-EO(●,■) and II (○,□,Δ).

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

[4,6] is at interval of 4-30. With the exception of MPBO-1-OEO and CBO-1-OEO, the oligomers 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^{o}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 the investigation on the mesophase state of oligomers and polymers obtained will be published later.

REFERENCES

1. SHIBAEV V.P., in Liquid Crystalline Polymers (Ed.by PLATE N.), (in Russian), Chemia, Moscow, 190 (1988).
2. PERCEC V., TOMAZOS D., Polymer Bulletin, 18, 239 (1987).
3. SAGANE T., LENZ R.W., Polymer Journal, 20, 923 (1988).
4. KOSTROMIN S.G., NGO DUY CUONG, GARINA E.S., SHIBAEV V.P., Mol. Cryst.Liq.Cryst, 193, 177-184 (1990).
5. KIM C., ALLCOCK H.R., Macromolecules, 20, 1726-1727 (1987).
6. SHIBAEV V.P., KOSTROMIN S.G., PLATE N.A., Eur.Polym.J., 18, 651 (1982); Liquid Crystals, 2, 195 (1988).
7. GRAY G.W., LACEY D., NESTOR G., WHITE M.S., Makromol. Chem., Rapid Commun., 7, 71 (1986).
8. CZER F., NYITRAI K., HORVATH J., HARDY GY, Eur. Polym. J., 3, 259-264 (1985).
9. FURUKAWA J., SAEGUSA T., Polymerization of Aldehydes and Oxides, Wiley (Interscience), New York, N.Y. (1963).
10. VOGL O., MUGGEE J., BANSLEBEN D., Polym.J., 12, 667 (1980).
11. SHIH J.S., TIRREL D.A., Polymer Preprints, 24, N.2, 22-23 (1983).
12. KONDO T., SAEGUSA T., VOGL O., Polym.Bull.7, 513-520 (1982).
13. MATHIEU J., PANICO R., WEILL-RAYNAL J., L'amenagement fonctionel en synthese organic (in Russian, Moscow, 336 (1980)).
14. SWERN D., Organic reactions (in Russian, 7, 476-544 (1956)).
15. SWERN D, Chem.Rev., 45, 16-25 (1949).
16. MATSUMURA N., SONODA N., TSUTSUMI S., Tet.Let., N.23, 2029-2032 (1970).
17. PAYNE G., DEMING P., WILLIAMS P., J.of Org.Chem., 26, N.3, 659-663 (1961).
18. PAUL R., TCHELITCHEFF S., Bull.soc.chim.France, 898-899 (1948).
19. BRAUN G., Organic Syntheses (in Russian, 1, 337-340 (1949)).
20. VANDENBERG E.J., J.Polym.Sci. A-1, 75, 525-567 (1969).
21. DEMUS H, DEMUS D., ZASCHKE H., "Flüssige Kristalle in Tabellen", 66-69 (1974) (VEB Deutscher Verlag fur Grundstoffindustrie).
22. GRAY G.W., Liquid Crystal and Molecular Structure-Nematics. In: The Molecular Physics of Liquid crystals. Ed.by LUCKHURST G.R., GRAY G.W., London: Acad.Press., 23 (1979).

Accepted May 4, 1992 C