

Phase Transfer Catalysis in Polycondensation Processes (XX) Polyethers Containing an Oxetanic or Propylenic Spacer with Potential Liquid Crystalline Properties

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ABSTRACT

The present paper studies the influence of chains chemical structure on the ordering capacity of a series of copolyethers obtained from 3,3-bis(chloromethyl)oxetane or 1,3-dibromopropane and five types of bisphenols, as follows: 2,7-dihydroxynaphthalene, 4,4'-dihydroxyazobenzene, 4,4'-dihydroxydiphenyl, 1,1-bis(4'-hydroxyphenyl)cyclohexane and 2,2-bis(3'-methyl-4'-hydroxyphenyl)propane. The polymers are synthesized by phase transfer catalysis technique and characterized by ¹H NMR, DSC and optical microscopy in polarized light. Theoretical conformational analysis, using a computer MMX-88 programme, is performed, as well. The liquid crystalline polyethers behaviour is the most important property investigated. Only the polymers containing azobenzene and naphthalene units present a mesophase, but the transition temperatures are too high for a correct characterization.

Key Words: liquid crystalline polymers, polyethers, phase transfer catalysis, oxetane, theoretical conformational analysis

INTRODUCTION

In a series of previous published papers, the possible syntheses of some polyethers, starting from 3,3-bis(chloromethyl)oxetane, BCMO, and various bisphenols, by application of phase transfer catalysis as a working method, is discussed [1-5].

In the case of polyethers with liquid crystalline (LC) properties, the presence of the oxetanic ring on the chain raised some difficulties related to mesophase characterization, [2, 5, 6]. Such difficulties are

caused by the opening of the oxetanic cycles at temperatures over 250 °C which results in the polyethers cross-linking in isotropic phase (for this class of polymers, the isotropization temperatures ranged within 250-300 °C domain). As a result of cross-linking, the ordering process may be affected, or even completely destroyed, and the phase transitions corresponding to LC structures being not evidenced any more, either on cooling or during a second heating. Consequently, a correct characterization of the LC properties requires shifting of the isotropization temperatures below

220–230 °C.

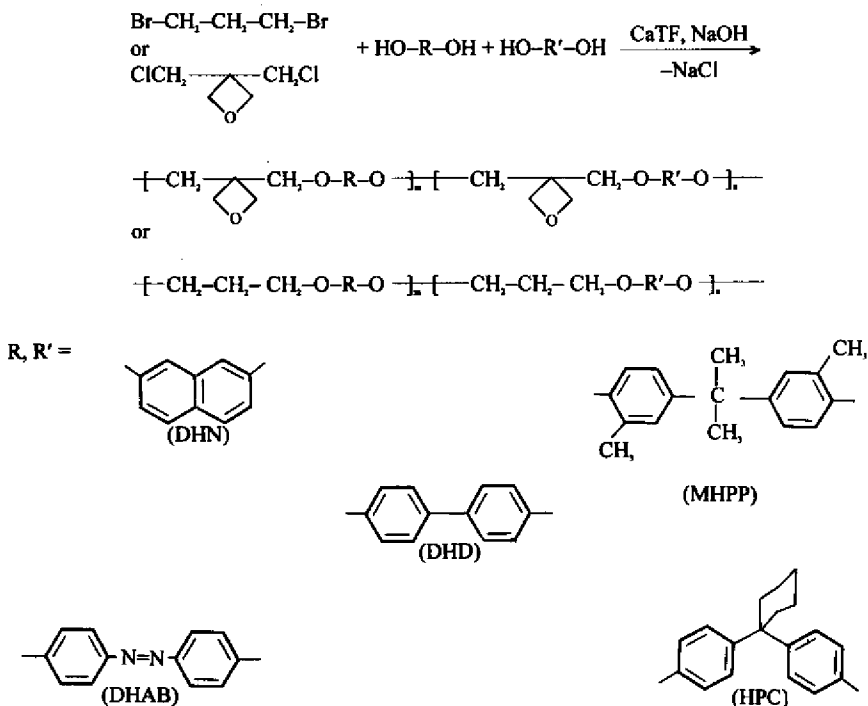
On the other hand, the presence of the oxetanic cycle on the chain evidences some advantages, as well. Thus, at a temperature of 160 °C, the oxetanic cycle may be opened under the action of an amine, which permits the chains chemical modification [7]. When diamines are employed, cross-linking materials, possessing non-linear optical properties, may be obtained [8].

The goal of the present study is the synthesis of some polymers with potentially liquid crystalline properties and presenting transition temperatures below 230 °C. It is known that one of the methods of reducing the transition temperatures involves utilization of copolymerization reactions. Nevertheless, the increase of the system disorder (as a result of copolymerization) may cause disappearance of the LC properties. The present study focuses on the influence of the

chains chemical structure on the ordering capacity of a series of copolyethers obtained from 3,3-bis-(chloromethyl)oxetane or 1,3-dibromopropane (DBP) and five types of bisphenols, as follows: 2,7-dihydroxynaphthalene (DHN), 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), 1,1-bis-(4'-hydroxyphenyl)cyclohexane (HPC) and 2,2-bis-(3'-methyl-4'-hydroxyphenyl) propane (MHPP).

EXPERIMENTAL

The copolyethers were synthesized by phase transfer catalysis using BCMO or DBP and various bisphenols (DHN, DHAB, DHD, HPC, MHPP). In a typical polycondensation reaction, 1 mmol bisphenols, 3g NaOH, and 5 mL H₂O were vigorously stirred into a 50 mL flask (for 10 min); after complete dissolution,



Scheme 1

1 mmol BCMO (or DBP) dissolved in 5 mL nitrobenzene was added and stirred for 5 min; 0.2 mmol tetrabutylammonium bromide was added to the flask and the temperature was raised to 85 °C. The mixture was maintained at this temperature for 5 h under stirring. Then the organic layer was washed with water, and the polymer was precipitated in methanol.

The solvents and phase transfer catalyst (tetrabutylammonium bromide) were supplied by Aldrich and were used without further purification.

The copolymers compositions were determined by ¹H NMR spectra, recorded on a Jeol-60 device (in CDCl₃ or DMSO).

The transition temperatures were determined by DSC analysis, on a Mettler 12 E device (the heating/cooling rate was 10 °C/min). The thermal behaviour was confirmed, additionally, by optical microscopy (OM) in polarized light, on a VEB Analytik microscope, equipped with a hot stage.

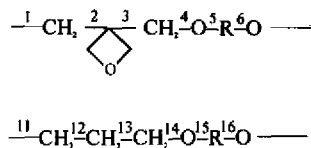
Theoretical conformational studies were performed on a Pentium-75 computer using MMX-88 programme [9].

RESULTS AND DISCUSSION

The copolymers were synthesized according to the reaction equations as in Scheme 1.

For a better understanding of the influence of the oxetanic cycle upon supramolecular structure and thermal properties of the synthesized polyethers, two types of spacers were used: BCMO and DBP. The DBP is a semi-flexible spacer, similar to BCMO, but it does not contain a rigid substituent at the central carbon; this permits a better chains arrangement and thus, an augmentation of interchain interactions. Theoretical conformational analyses effectuated permitted us to calculate the rotational barriers corresponding to both types of structural units (containing oxetanic or propylenic spacer) [10]. The code numbers of simple bonds corresponding to the structural units are presented as in Scheme II.

In the case of bonds 5, 6, 15 and 16, the rotational barriers depend strongly on bisphenols chemical structure, while bonds 1, 2, 3 and 4 (11, 12,



(Scheme II)

13 and 14, respectively) are less influenced by the chain structure. The conformational studies effectuated for a great number of polyethers evidenced that, from four simple bonds corresponding to the spacer, two are flexible (bonds 2, 3 and 12, 13, respectively) and two are rigid (1, 4 and 11, 14, respectively).

The rotational barriers corresponding to bonds 2, 3, 12 and 13 take values below 20 kJ/mol. In the case of bonds 1 and 4 the barriers have high values of above 2000 kJ/mol. Although the barriers corresponding to bonds 11 and 14 have only 500–700 kJ/mol (as a function of chains chemical structure), they can be considered as rigid bonds.

Therefore, one may appreciate that both spacers will have a similar behaviour, and are being semi-flexible. The differences that appear between these two types of copolyethers, will be determined by the intermolecular distances, are expected to have smaller values in the case of the propylenic spacer, due to the absence of the oxetanic cycle, asymmetric connected in the macromolecular chain.

Table 1 presents some characteristics of the polyethers containing the oxetanic spacer.

The first group of polymers taken into consideration, contains DHAB and DHN units (samples 1–3). The polymer that contains an excess of DHAB units (sample 1) presents an LC behaviour, but the temperatures of the thermal transitions are too high for a correct characterization. This polymer presents a mesophase around 240 °C, visible in polarized light. The endothermal crystalline transition/LC cannot be evidenced by the DSC technique, because cross-linking processes start at 245–250 °C, due to the opening of the oxetanic cycles. Isotropization of this sample takes place at 300 °C and it is accompanied by thermal decomposition.

Increasing the DHN units content (sample 2)

Table 1. Characteristics of the copolyethers containing an oxetanic spacer.

Sample no.	Copolymer composition	DP	\bar{M}_n
1	DHAB/DHN = 2.9/1	9	2500
2	DHAB/DHN = 1.1/1	12	3200
3	DHAB/DHN = 1/2.3	10	2500
4	DHD/DHN = 2.8/1	8	1800
5	DHD/DHN = 1.3/1	12	3000
6	DHD/DHN = 1/3.2	13	3100
7	HPC/DHN = 2.2/1	11	3500
8	HPC/DHN = 1.3/1	13	3800
9	HPC/DHN = 1/3.1	10	3250
10	MHPP/DHN = 2.4/1	14	4250
11	MHPP/DHN = 1.3/1	14	4000
12	MHPP/DHN = 1/2.6	12	3300

induces a diminution of the isotropization temperature, in spite of the fact that the molecular weight is higher. This behaviour is due to the asymmetrical linking of the naphthalene units in the chain, having as a result, a smaller ordering degree. This polyether does not present an LC behaviour, having only a semi-crystalline structure ($T_m=255-260$ °C, determined by OM). In this case the cross-linking processes that are superposed over the melting transition, hinder the DSC characterization, too. Because the cross-linking processes take place in the isotropic state, the chains ordering is impossible on cooling, therefore, an amorphous structure will result.

Sample 3 shows a melting temperature situated between 185–190 °C, however, the polymer is not an LC. On cooling, this polyether remains in an amorphous state. As the melting process takes place below 200 °C, one cannot take into consideration cross-linking reactions in the isotropic state. The conformational modifications occurring on first heating are probably responsible for this behaviour.

The next investigated polymer group contains DHD and DHN units (samples 4–6). Only the polymer, containing DHD units in excess (sample 4), presents a semi-crystalline structure; the other two are amorphous. The melting point of sample 4 is situated at high temperatures 260–265 °C, making impossible

a DSC analysis. No polymer from this group evidences LC properties. This behaviour is surprising because the DHD and DHN units are both a mesogen group. The explanation might involve conformational reasons. Additional studies are necessary to clarify this aspect.

In order to decrease the thermal transitions, we tried to introduce into the chains substituted bisphenols (HPC and MHPP) besides DHN units.

However, the presence of HPC units (samples 7–9), complicates too much the chains geometry. As the polymers presenting no ordering capacity have only amorphous structures.

The same behaviour is present when MHPP units are used (samples 10–12). The polyethers have amorphous structures.

The next spacer used was DBP. Table 2 lists some characteristics of these polyethers.

In the case of the propylenic spacer, the molecular weights are smaller than those corresponding to the oxetanic units. This is due to the dehydrobromination reactions that take place on the chain ends ($-\text{CH}_2-\text{Br}$), having as a result the formation of $-\text{CH}=\text{CH}_2$ end groups. Probably, these reactions take place at the interface between the organic and the aqueous phase, due to the high concentration of NaOH (40%).

The $-\text{CH}=\text{CH}_2$ end chains were evidenced in the ^1H NMR spectra at 4.5–4.7 and 5.0–5.5 ppm. The signal corresponding to $-\text{CH}_2-\text{Br}$ groups was

Table 2. Characteristics of the polyethers containing a propylenic spacer.

Sample no.	Copolymer composition	DP	\bar{M}_n
13	DHAB/DHN = 2.9/1	6	1600
14	DHAB/DHN = 1.1/1	8	1400
15	DHAB/DHN = 1/2.3	8	1750
16	DHD/DHN = 2.7/1	7	1600
17	DHD/DHN = 1.1/1	6	1300
18	DHD/DHN = 1/2.3	6	1250
19	MHPP/DHN = 3.5/1	8	2200
20	MHPP/DHN = 1.3/1	8	2000
21	MHPP/DHN = 1/2.6	8	2150

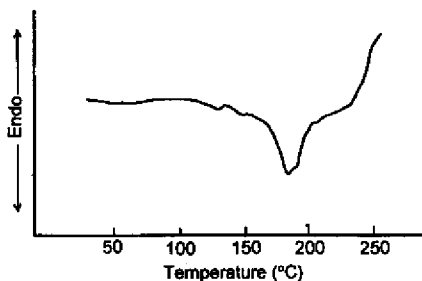


Figure 1. DSC thermogram of sample 13 at first heating.

completely disappeared.

As in the case of the oxetanic spacer, the polyether containing DHAB groups in excess (sample 13) presented LC properties. The mesophase was evidenced at 200 °C, the phase transition being present on the DSC thermogram (Figure 1).

Unfortunately the isotropization temperature exceeds the limit of thermal stability corresponding to this polymer. On the DSC curve (Figure 1) one can observe the degradation (exothermal) process that starts at 235–240 °C. Isotropization can be observed by OM and it takes place at 245–250 °C. Thermal degradation can be observed by OM too, through which a significant change of colour (from yellow to black) taking place.

Increase of the DHN units content (sample 14) results in the disappearance of the LC behaviour, and only a semi-crystalline polymer is being obtained ($T_m=218\text{--}220$ °C). This polyether keeps the ordering capacity after the first heating while, on cooling, a semi-crystalline structure is observed by OM.

Sample 15 has a similar behaviour as sample 14, presenting only a semi-crystalline structure on both heating and cooling ($T_m=175\text{--}180$ °C).

The next system subjected to investigation contains DHD and DHN units (samples 16–18). The first polymer (16) has a semi-crystalline structure with melting temperature situated between 245–250 °C. Simultaneously with melting, a degradation process, observed by OM, takes place. This thermal degradation does not permit DSC characterization.

Sample 17 shows an interesting behaviour. This

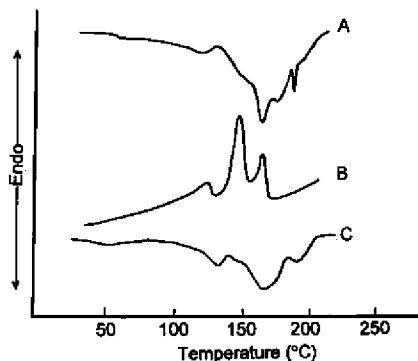


Figure 2. DSC thermograms of sample 17: (A) first heating; (B) first cooling; (C) second heating.

polymer presents three thermal transition on both heating and cooling (Figure 2).

On first heating, these transitions are studied at 165, 175 and 185 °C, respectively. On cooling, the exothermic transitions are shifted to 167, 155 and 130 °C, respectively. On second heating, they appear at 135, 165 and 192 °C. It is not certain that this polyether is an LC one. In our opinion, up to 140 °C, this sample is a mixture of crystalline and LC phases. OM cannot offer an answer to this problem. Solubility problems prevented fractionation of the sample in common solvents. Probably, two or several fractions with different molecular weights are present.

Additional studies are necessary to clarify this problem.

Sample 18 is a semi-crystalline polymer with a melting point situated between 145–150 °C.

Utilization of other bisphenols with complicated conformations (MHPP) results in amorphous structures (samples 19–21).

CONCLUSION

Only the DHAB and DHN- containing polymers may present a mesophase, but the thermal transitions are situated too high for a correct characterization.

In the case of polyethers with DHD and DHN units (in equimolecular ratio) additional studies are

necessary to clarify whether a mesophase, is present or not.

The oxetanic spacer induces higher thermal transitions (reported to the propylenic spacer).

In the case of the propylenic spacer the ordering process takes place more easily, however, due to the dehydrobromination reactions of chain ends, smaller molecular weights are obtained.

Decreasing of thermal transitions by means of substituted bisphenols, will result in the disappearance of the liquid crystalline properties, and only amorphous structures are being obtained.

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