Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Daoudi, A. , Buisine, J. M. , Hurduc, N. and Simionescu, C. I.(1998) 'Liquid Crystalline Polymers. VII. Polyethers Based on 3,3-Bis(Chloromethyl)Oxetane and Various Bisphenols with Potential Liquid Crystalline Behavior', Journal of Macromolecular Science, Part A, 35: 1, 151 — 160

To link to this Article: DOI: 10.1080/10601329808001967

URL: http://dx.doi.org/10.1080/10601329808001967

J.M.S.—PURE APPL. CHEM., A35(1), pp. 151–160 (1998)

LIQUID CRYSTALLINE POLYMERS. VII. POLYETHERS BASED ON 3,3-BIS(CHLOROMETHYL)OXETANE AND VARIOUS BISPHENOLS WITH POTENTIAL LIQUID CRYSTALLINE BEHAVIOR

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ABSTRACT

The present paper studies the influence of the chain's chemical structure on the thermal behavior of some polyethers. The investigated polymers were synthesised by phase transfer catalysis using 3,3-bis(chloromethyl)oxetane and various bisphenols as monomers. The polymers were characterized by ^{1}H-NMR spectroscopy, DSC technique and optical microscopy in polarized light. Theoretical conformational studies were also performed. Among the studied polymers, only those containing 4,4'-dihydroxyazobenzene and 4,4'-dihydroxybenzophenone can present liquid crystalline behavior. The copolyethers containing the 4,4'-dihydroxydiphenyl do not present liquid crystalline behavior.

INTRODUCTION

In a series of previous papers, the possible procurement of some polyethers was discussed, starting from 3,3-bis(chloromethyl)oxetane [BCMO] and various bisphenols, by the application of phase transfer catalysis as a working method [1-4].

In the case of polyethers with liquid crystalline [LC] properties, the presence of the oxetanic ring on the chain raised some problems related to mesophase characterization [2, 5]. Such problems are caused by the opening of the oxetanic cycles at temperatures over 250°C which results in the polyethers' crosslinking in the isotropic phase (for this class of polymers, the isotropization temperatures ranged within the 250-300°C interval). As a result of crosslinking, the ordering process may be affected, or even wholly destroyed, the phase transitions corresponding to LC structures not being 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 is evidence of 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 chain's chemical modification [6]. When diamines are employed, crosslinking materials, possessing non-linear optical properties, may be obtained [7].

The goal of the present study is the synthesis of some polymers containing the oxetanic cycleon the chain, with transition temperatures below 230°C, and possibly with liquid crystalline properties. It is known that one of the methods of reducing the transition temperatures involves the application of copolymerization reactions. Nevertheless, the increase of the system's disorder (as a result of copolymerization) may cause the disappearance of the LC properties.

The present study focuses on the influence of the chain's chemical structure on the ordering capacity of a series of copolyethers obtained from BCMO and five types of bisphenols, as follows: 4,4'-dihydroxyazobenzene (DHAB), bisphenol A (BPA), 4,4'-dihydroxydiphenyl (DHD), 4,4'-dihydroxybenzophenone (DHBP) and 4,4'-thiodiphenol (DHDS).

EXPERIMENTAL

The copolyethers were synthesized by phase transfer catalysis using BCMO and various bisphenols (DHAB, BPA, DHD, DHBP and DHDS). Details concerning the polymers' synthesis and characterization were previously reported [1, 2, 5].

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

The copolymer composition were determined by ^{1}-H-NMR spectra, recorded on a Bruker-300 MHz device (in $CDCl_3$ or DMSO).

The transition temperatures were determined by DSC analysis, on a SEIKO DSC 220 device (the heating/cooling rate was 10°C/min.). The thermal behavior was confirmed, too, by optical microscopy in polarized light, on a LEITZ DM RXP micro-scope.

Theoretical conformational studies were performed on a PC-486 computer using a MMX-88 program [8].

RESULTS AND DISCUSSION

The copolymers were synthesized according to the following reaction scheme:

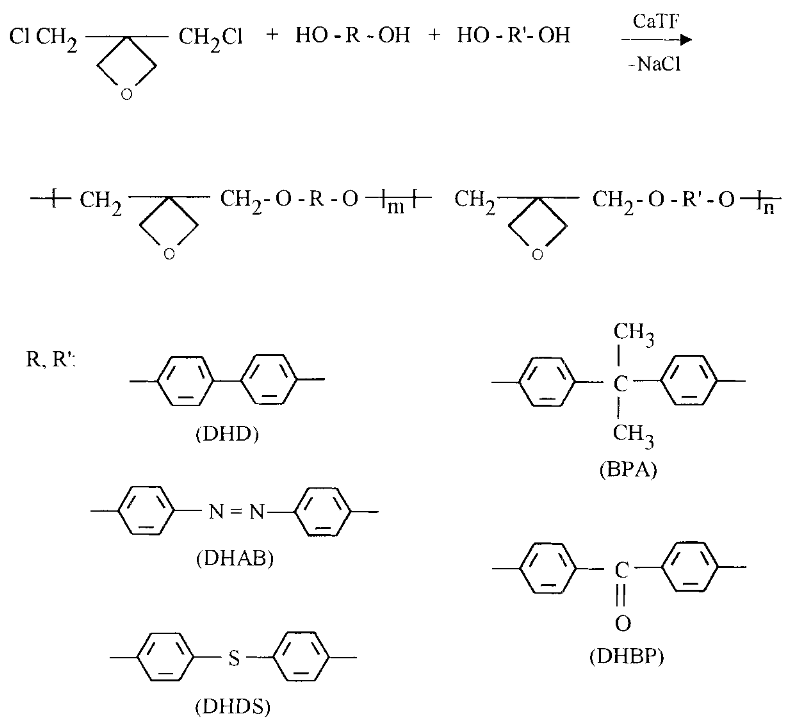

Table 1 presents the copolymer composition, the DP and T_g values, corresponding to the synthesized polymers.

TABLE 1. Some Characteristics of the Polymers Obtained

No.spl	Bisphenols used	Copolymer composition	DP	Tg (°C)
1	DHAB/DHBP	2.8/1.0	10	110
2	DHAB/DHBP	1.4/1.0	12	120
3	DHAB/DHBP	1.0/2.3	10	119
4	DHD/DHBP	2.3/1.0	11	126
5	DHD/DHBP	1.0/1.1	10	116
6	DHD/DHBP	1.0/3.1	10	105
7	BPA/DHBP	3.1/1.0	9	101
8	BPA/DHBP	1.0/1.0	10	101
9	BPA/DHBP	1.0/3.6	10	98
10	BPA/DHDS	4.0/1.0	21	107
11	BPA/DHDS	1.3/1.0	19	105
12	BPA/DHDS	1.0/2.1	20	96
13	DHD/DHDS	3.9/1.0	15	118
14	DHD/DHDS	1.2/1.0	13	110
15	DHD/DHDS	1.0/2.3	13	101
16	DHAB/DHDS	3.0/1.0	10	77
17	DHAB/DHDS	1.3/1.0	10	87
18	DHAB/DHDS	1.0/2.5	11	87

DP - degree of polymerization

Tg - glass transition

The DP were calculated for all polymers using ^{1}H-NMR spectra. T_g were taken at the temperature having 1/2 (ΔCp, and other transition temperatures at the top of the corresponding peak.

Concerning the LC behavior, only the first three samples could be considered. These samples presented high T_g values (between 110 and 120°C), which indicated the existence of a rigid chain. This rigidity was confirmed, too, by theoretical conformational studies (the rotational barriers between simple bonds of the basic chain were calculated). The presence of the oxetanic ring, asymmetrically connected to the chain, increases the rigidity of the spacer. The excess of azobenzene groups in Sample 1 generates isotropization temperatures up to 250°C. Under such conditions, a correct characterisation of the LC behavior is impossible, due to the crosslinking processes and to the thermal decomposition of the azobenzenic groups (at 280-300°C).

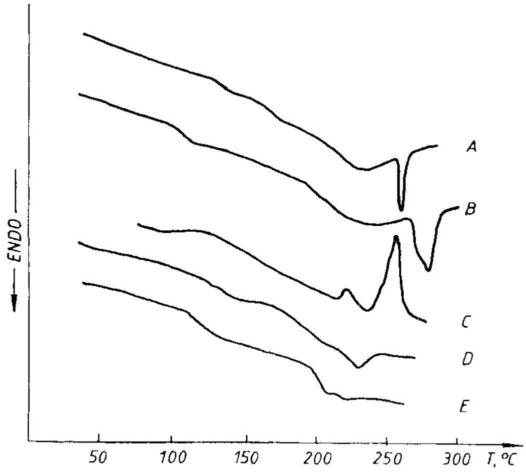

Figure 1. DSC thermogram of samples: **1** (A-first heating; B-second heating; C-first cooling); **2** (D first heating; E-second heating).

In spite of these difficulties, two endothermic signals, situated at 225°C and 250°C, respectively (Figure 1 curve A) could be observed on first heating. These signals were also present, on second heating, yet the first endotherm was diminished (Figure 1-curves A and B). The chemical modifications occurring on first heating, due to opening of the oxetanic rings are reflected by shifting of the T_g value from 139° to 110°C. On first heating, the polymer presented birefringence on shearing in polarized light between 225° and 250°C.

The same difficulties in the characterization process were met with Sample 2. On first heating, this sample presented two endothermic signals at 140 and 228° C, respectively (Figure 1-curve D). Although the maximum endothermic isotropization signal is present at 228°C, for a complete isotropization a heating process to 255°C is necessary. At this temperature, opening of a certain number of oxetanic rings probably takes place. Although, on cooling, we observed ordering of the system at 220°C in polarized light, the DSC curve does not reflect this phenomenon.

Increasing the DHBP units in the chain (sample 3) has as a result a change of thermal properties. On first heating, a strong endothermic signal appears (at 150(C) due to the melting process. However, on cooling, the sample presents only a poor orientation, probably due to some conformational modifications induced during heating (Figure 2-curve A and B). As the first heating continued up to

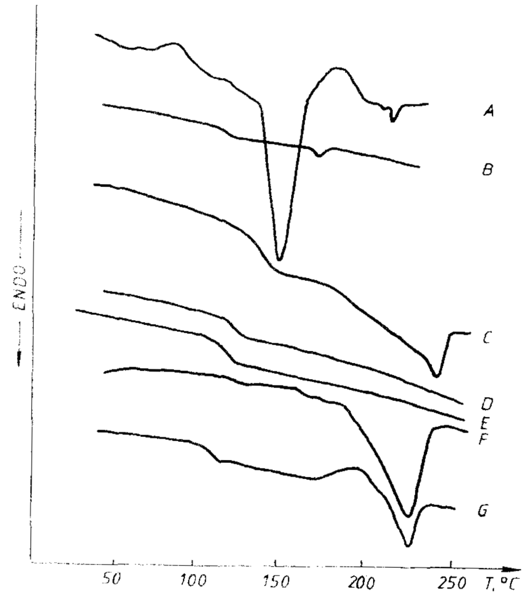

Figure 2. DSC thermogram of samples: **3** (A-first heating; B-second heating); **4** (C-first heating; D-second heating); **5** (E-second heating); **6** (F-first heating; G-second heating).

230°C, there are no important chemical modifications that could explain the disappearance of the endo thermic signal.

Conformational analysis studies may offer an answer to the above mentioned problem. The DHBP presents a semi-rigid behavior, the two simple bonds between the aromatic rings having rotational barriers of 80 kJ (first bond) and 160 kJ (second bond), respectively. At room temperature, these bonds are rigid and, as a consequence, after precipitation, the polymer can present ordering capacity due to the conformational stability. As a result, on first heating the polymer is semi-crystalline. On heating, the two bonds between the aromatic rings may become flexible (or semi-flexible) due to increased conformational polydispersity; such conformational modifications might explain the loss of ordering capacity, as well as the disappearance of exothermic signal (observed at 84°C).

The next system subjected to investigation contains DHD and DHBP groups (Samples 4-6); these polymers do not present LC behavior. If DHD exceeds DHBP (Sample 4), the melting point is situated at 245°C (Figure 2, curve C); however, for a complete isotropization, the polymer must be heated until 260°C.

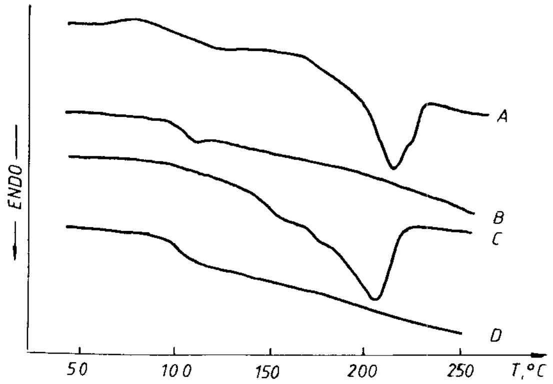

Figure 3. DSC thermogram of samples: **7** (A-first heating; B- second heating); **8** (C-first heating; D-second heating).

Under such conditions, weak crosslinking processes (equivalent to a branching process) take place, similarly with sample 1. Thus, the polymer loses its ordering ability, and only glass transition (126°C) is present on second heating (Figure 2, curve D).

Attention should be paid to the fact that, on shearing, Sample 4 presented a poor orientation, which was visible in polarized light at 210°C (on both heating and cooling). This behavior also appeared at Sample 5, (at 160°C), nevertheless this polymer was completely amorphous on both first and second heating (Figure 2, curve E).

As to Sample 6, the thermal behavior was similar with that recorded for sample 3 (Figure 2, curves F,G). In this case, the ordering capacity diminishes, but the polymer remains semi-crystalline (not completely amorphous). Intensity of the endothermic signals (225°C) reflects a clear reduction of the ordering degree after the first heating; the presence of glass transition only on second heating supports, too, this explanation. The differences appearing between Samples 3 and 6 may be due to the different geometry of DHAB reported to DHD. For Sample 6 too, exothermic signals appear, probably due to conformational modifications or ordering process (at 160°C on first heating and 190°C on second heating).

The next polymeric group contains BPA and DHBP (samples 7-9), characterized by lower glass transition values (98-105(C), compared with samples 1-6. We underline that none of these polymers presented an endothermic signal, corresponding to glass transition, on first heating (Figure 3, curves A,C).

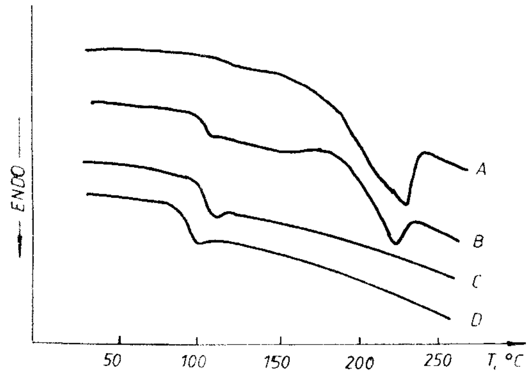

Figure 4. DSC thermogram of samples: **10** (A-first heating; B-second heating); **11** (C-second heating); **12** (D-second heating).

The differences observed with all polymers (Samples 7, 8 and 9) between the first and the second heating, reflect conformational modifications produced during the first thermal treatment (Figure 3), which can be due either to weak cross-linking reactions (as in the case of Samples 1 and 3), or to conformational modifications occurring after the first heating. Conformational analyses offer no answer to this question. The BPA is a rigid bisphenol, having two rotational barriers greater that 600 kJ between the aromatic rings [9].

On substituting DHBP by DHDS (Samples 10-12) no LC behavior can be obtained. The geometry of DHBP is similar to that of DHDS, however, DHDS's structural unit presents a lower polar surface area (13.5%), comparatively with DHBP (22.0%) [4].Further on, modification in chain polarity does not result in LC behavior.

If Samples 10 and 12 do not present conformational modifications after the first heating, Sample 11 evidences several changes (Figure 4).

For Sample 11, the crosslinking reactions should not be taken into consideration, as the polymer was heated (first heating) only up to 210°C. Optical microscopy reflects a very strong contraction process at 135°C, followed by a melting transition at 180°C.

The Samples (13-15) containing DHD and DHDS present a poor ordering capacity, which is not the case of Sample 13, with a melting point at 245°C, containing excess of DHD (Figure 5-curves A and B).

An explanation for the melting transition disappearance may be the same as in the case of Samples 1 and 4 (obtainment of branched polymers).

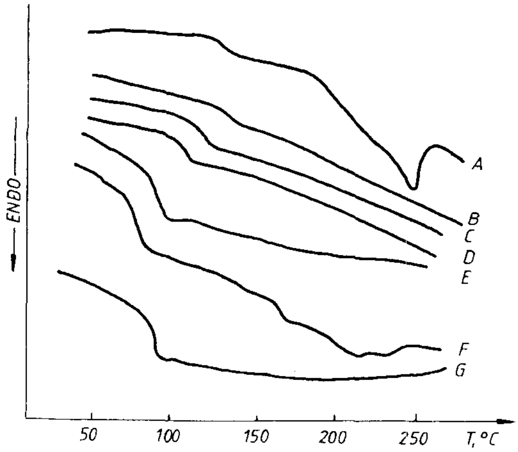

Figure 5. DSC thermogram of samples: **13** (A-first heating; B-second heating); **14** (C-second heating); **15** (D-second heating); **16** (E-second heating); **17** (F-second heating); **18** (G-second heating).

The last investigated system was that containing DHAB and DHDS groups (Samples 16-18). Quite surprising was the total disappearance of the ordering capacity, since only amorphous systems, with T_g values situated between 77° and 87°C resulted (Figure 5-curves E, F, and G). Not even Sample 16, containing an excess of DHAB groups, was a semi-crystalline polymer. The explanation for such a behavior may be the flexibility of the DHDS units, that can generate a too high conformational polydispersity to realize an ordered system.

CONCLUSIONS

Out of the polymers studied, only those containing DHAB and DHBP units present LC behavior. Unfortunately, the crosslinking processes that take place around 250°C make a correct characterization of the LC properties impossible . The attempts made at decreasing the transitions temperatures, by the increase of the disorder degree in the systems, resulted in the disappearance of the LC properties.

The copolymers containing DHD do not present LC behavior; however, on shearing, some of them give birefringence in polarized light,.

Theoretical conformational analyses reflected the possible occurrence of conformational modifications that can induce loss of the polymer's ordering capacity.

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Received February 21, 1997
Final revision received August 30, 1997