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LIQUID CRYSTALLINE POLYMERS: 10: SYNTHESIS AND THERMAL BEHAVIOR OF SOME POLYETHERS CONTAINING A HEXAMETHYLENIC SPACER

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LIQUID CRYSTALLINE POLYMERS: 10: SYNTHESIS AND THERMAL BEHAVIOR OF SOME POLYETHERS CONTAINING A HEXAMETHYLENIC SPACER

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The paper presents the synthesis and thermal behavior of some copolyethers containing a hexamethylene spacer. The polymers were obtained using a phase transfer catalysis technique, starting from 1,6-dichlorohexane and various bisphenols as follows: 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), bisphenol A (BPA), 2,7-dihydroxynaphtyl (DN) and 4-hydroxydiphenyl sulfide (BPS). The synthesized polyethers have low molecular weights, being situated in the oligomeric domain. The polymers were characterized by ¹H-NMR spectroscopy, DSC calorimetry and optical microscopy in polarized light. Only the polyethers containing DHAB, DHD and BPA units exhibited liquid crystalline phase. All liquid crystalline oligomers evidenced enantiotropic behavior.

Keywords: liquid crystals, phase transfer catalysis, oligomers, copolyethers, main chain polymer liquid crystals

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INTRODUCTION

Polymers with liquid crystalline (LC) properties represent an interesting research field, due to the unique behavior of these materials that combines two essential properties of the matter: order and mobility. Liquid crystals and their use in electronic displays and non-linear optical systems have become a problem of special importance in the last decade. The presence of the azobenzenic units in the chains confers the LC polymers the possibility of using them as optical memory systems.

Thermotropic LC polymers containing mesogenic groups in the main chain have been studied systematically by Sirigu, Lenz, Percec and others [1–7]. The phase transition temperatures corresponding to these polymers are often situated at high values, near the thermal stability limit. In order to decrease the transition temperature values, copolymerization processes or substituted mesogens can be used.

In a series of previous papers the possibility of obtaining polyethers and polyesters using phase transfer catalysis, some of which showing liquid crystalline properties [8–10], has been discussed. During these studies, which actually involved the synthesis of over, 1,400 homopolymers and copolymers, the influence of different parameters (chain conformation, chain flexibility, inter-chain interaction) over the capacity of mesophase generation was considered [8–12]. Attention was focused especially on the polyetheric structures obtained from bisphenols and dihalogenated compounds, the latter ones being chosen so that to permit a gradual modification of chains' flexibility. Our strategy of synthesis intended to separate as much as possible the influence of chain conformation, flexibility and inter-chain interaction over the LC behavior. Unfortunately, a complete separation of these factors is not possible.

The investigations started with 3,3-bis(chloromethyl)oxetane as a spacer, which proved to confer a semi-rigid character to the chains. Such rigidity led to high transition temperatures and caused many problems in evidencing the mesophase. Because many oxetanic homopolymers and copolymers presented isotropization temperatures around 300°C, the LC behavior could not be clearly evidenced (over 250°C, the oxetanic cycles are opening, generating three-dimensional structures). Consequently, the oxetanic spacer was replaced by a flexible one, the influence of the spacer length on the LC behavior being studied.

The goal of this paper was the synthesis and characterization of some copolyethers containing a hexamethylene spacer. The polymers were obtained using a phase transfer catalysis technique, starting

from 1,6-dichlorohexane (DCH) and various bisphenols as follows: 4,4'-dihydroxyazobenzene (DHAB), 4,4'-dihydroxydiphenyl (DHD), bisphenol A (BPA), 2,7-dihydroxynaphtyl (DN) and 4-hydroxydiphenyl sulfide (BPS).

METHODS

The polymers were synthesized by phase transfer catalysis in a liquid-liquid system. In a typical polycondensation reaction, 1.3 mmol mixture of bisphenols, 2.5 g NaOH and 5 ml H₂O were vigorously stirred in a 50 mL flask (for 10 minutes); 1.3 mmol DCH dissolved in 5 mL nitrobenzene were added and stirred for 5 minutes; 0.2 mmol tetrabutylammonium bromide were added to the flask and the temperature was raised to 85°C. The mixture was maintained at this temperature for 5 hours, under stirring. Then, the organic layer was washed with water and the polymer was precipitated in methanol. The precipitate was filtered, washed with methanol and water, and dried at 45°C under reduced pressure.

DHAB excepted, the other monomers, the phase transfer catalyst (tetrabutylammonium bromide) and the solvents were supplied by Aldrich and used without further purification. DHAB was obtained according to literature data [13] and purified by successive re-crystallization.

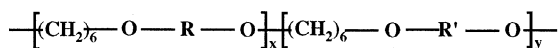
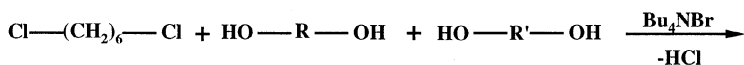
The copolymerization ratios and the numerical molecular weights were calculated using ¹H-NMR spectra recorded on a Bruker Avance 300 MHz device (with DMSO as a solvent). DSC thermograms were recorded on a Mettler 12E device, the heating/cooling rate being of 10°C/min. Optical microscopy studies in polarized light were made on a Olympus BH-2 device equipped with a Linkam TP 92 temperature controller.

RESULTS AND DISCUSSION

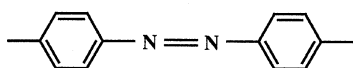
The polymers were obtained according to the following reaction Scheme 1.

Table 1 lists some characteristics of the synthesized polymers.

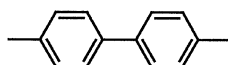
As one can see, the molecular weights, calculated using ¹H-NMR spectra, are relatively low, which means that the synthesized polyethers are situated within oligomers' domain. Due to the high values of the transition temperatures of the synthesized oligomers, we were not interested in performing reactions for obtaining high molecular weights. More over, we consider that the relationship between the chain conformation and the capacity to generate a mesophase can be



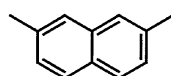
where R, R' are :



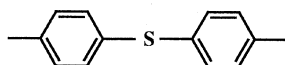
DHAB



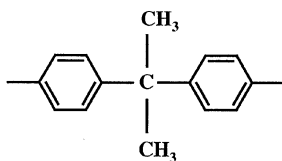
DHD



DN



BPS



BPA

SCHEME 1

better analyzed for lower molecular weights. For all copolymerization systems, three different molar feed ratios, i.e. 3/1, 1/1 and 1/3, respectively, were used. The differences between the feed and copolymerization ratios were caused by the differences in the transfer rates from the aqueous to the organic phase, corresponding to bisphenols.

The first analyzed group (Samples 1–3) contains DHAB and DHD units in the main chain. Sample 1 presents an enantiotropic behavior, with large mesophase stability. The crystalline melting transition is situated around 180°C, isotropisation taking place at 240°C (Figure 1). On second heating, the DSC curve suffers some modifications, which are probably due to the degradation processes that begin around 250–260°C for azobenzenic moieties [14]. On cooling, two endothermic signals are present at 230 and 175°C.

Figure 2 presents the optical micrograph corresponding to Sample 1, taken at 230°C.

With diminishing the azobenzenic units' content (Sample 2), the LC behavior is still present, but the transition temperature values

TABLE 1 Some Characteristics of the Synthesized Polymers

No.	Feed ratio	Copolymerization ratio	DP	Mn	
1	DHAB : DHD = 3 : 1	DHAB : DHD = 2.5 : 1	7	2030	LC
2	DHAB : DHD = 1 : 1	DHAB : DHD = 1 : 1.2	8	2290	LC
3	DHAB : DHD = 1 : 3	DHAB : DHD = 1 : 3.1	8	2250	LC
4	DHAB : BPA = 3 : 1	DHAB : BPA = 2.5 : 1	7	2150	SC
5	DHAB : BPA = 1 : 1	DHAB : BPA = 1 : 1.1	8	2450	LC
6	DHAB : BPA = 1 : 3	DHAB : BPA = 1 : 3.2	11	3400	SC
7	DHAB : DN = 3 : 1	DHAB : DN = 2.9 : 1	6	1690	SC
8	DHAB : DN = 1 : 1	DHAB : DN = 1.1 : 1	7	1910	SC
9	DHAB : DN = 1 : 3	DHAB : DN = 1 : 2.6	7	1800	SC
10	DHAB : TDP = 3 : 1	DHAB : TDP = 2.6 : 1	7	2090	SC
11	DHAB : TDP = 1 : 1	DHAB : TDP = 1 : 1.2	7	2100	SC
12	DHAB : TDP = 1 : 3	DHAB : TDP = 1 : 3.2	10	3000	SC
13	DHD : BPA = 3 : 1	DHD : BPA = 2.7 : 1	14	3970	SC
14	DHD : BPA = 1 : 1	DHD : BPA = 1 : 1.2	13	3900	SC
15	DHD : BPA = 1 : 3	DHD : BPA = 1 : 3.1	13	4000	SC

DP – degree of polymerization

Mn – molecular weight

LC – liquid crystalline phase

SC – semi-crystalline phase

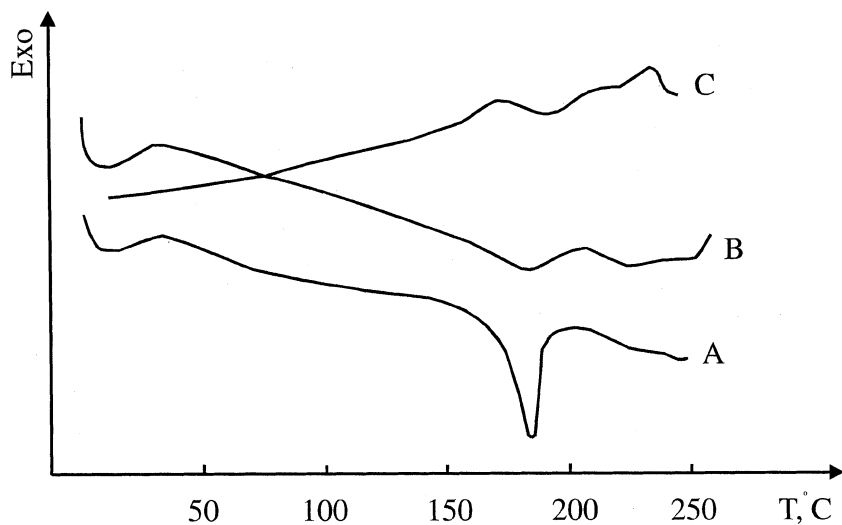


FIGURE 1 DSC thermograms corresponding to Sample 1: A-first heating; B-second heating; C-first cooling.

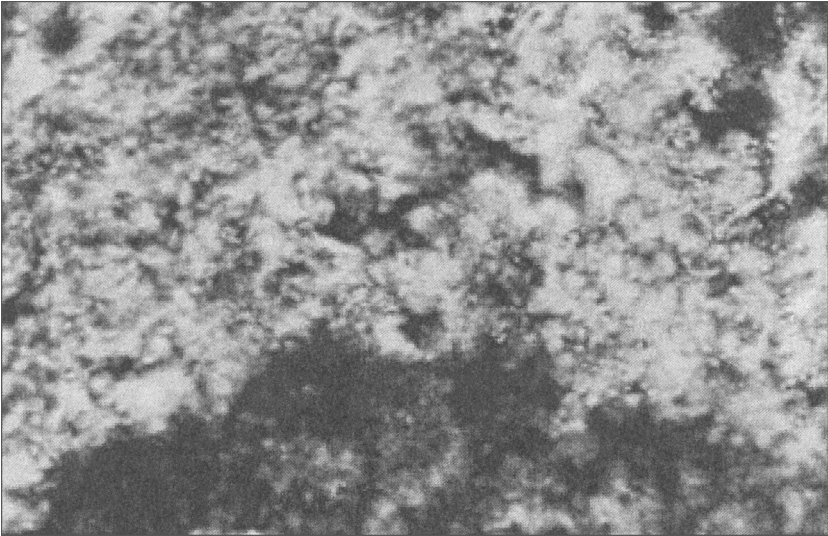


FIGURE 2 Optical micrograph of Sample 1 at 230°C ($\times 400$).

increase. As is shown in Figure 3, the crystalline melting point is situated at 185°C and the isotropisation above 260°C. Due to the degradation reactions that take place, the isotropisation process can not be evidenced. On the DSC thermogram, one can observe a strong

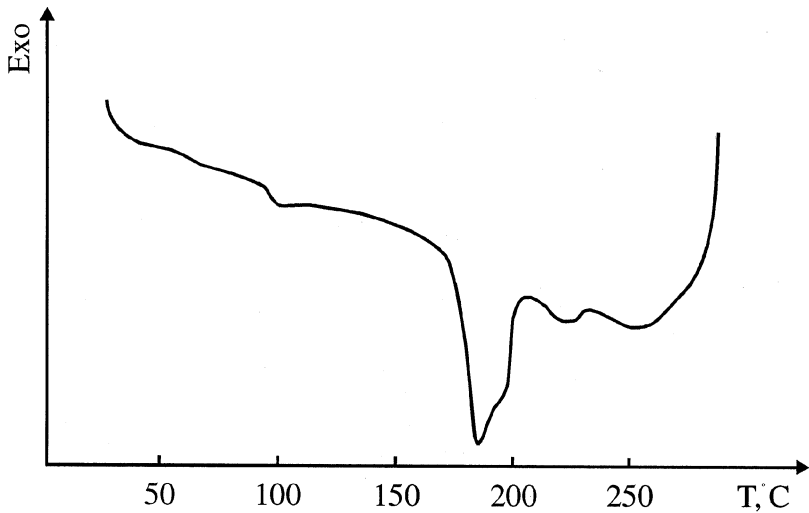


FIGURE 3 DSC thermogram corresponding to Sample 2 -first heating.

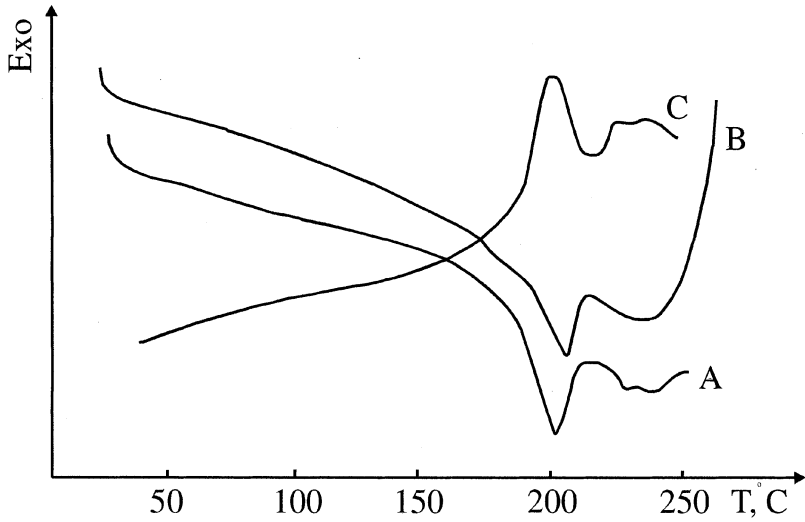


FIGURE 4 DSC thermograms corresponding to Sample 3: A-first heating; B-second heating; C-first cooling.

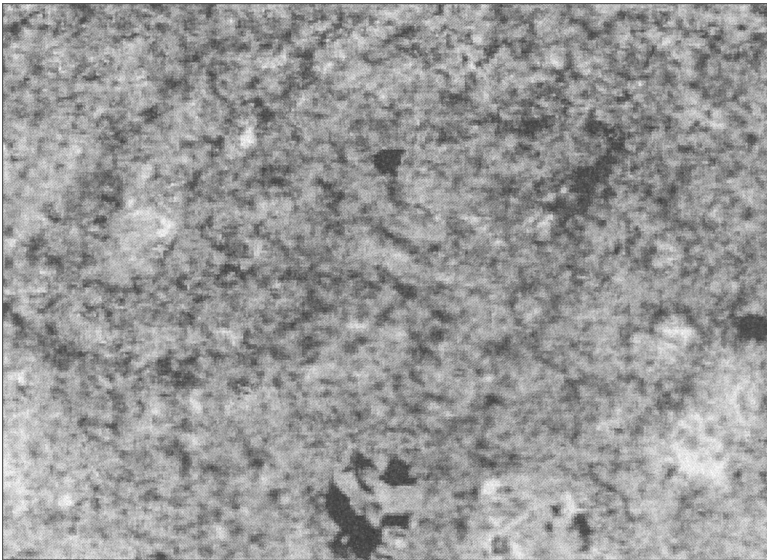


FIGURE 5 Optical micrograph of Sample 3 at 220°C ($\times 400$).

exothermal signal around 255°C. In these circumstances, the first cooling and second heating scans can not be registered. The mesophase was evidenced by optical microscopy in polarized light.

Sample 3 has a liquid crystalline behavior, too. DSC analysis (Figure 4) and optical microscopy (Figure 5) confirmed the mesophase presence. One should underline that the crystalline melting point is situated at 200°C, which is the highest value from this first group (Samples 1–3). This behavior is surprising, taking into consideration the polarity of the mesogenic units: a decrease in the azobenzene content should have led to lower transition temperatures. The thermal stability of Sample 3 is lower comparatively with Samples 1 and 2. The degradation process, accompanied by an exothermal signal, begins around 240°C (Figure 4-curve B), with 30°C lower than in the case of Samples 1 and 2. This is another unusual behavior, taking into consideration the higher thermal stability of DHD units in comparison with DHAB.

All these abnormal behaviors are probably induced by the structure of the flexible spacer and by the chain conformation. For similar polymer structures (polyethers containing DHAB and DHD mesogenic groups, linked with different spacers having an oxetanic, propylenic or diethyletheric structure) we have obtained only semi-crystalline products, if the DHD content exceeds the DHAB one [10, 15]. Our previous theoretical conformational studies have demonstrated that spacer's structure might play a very important role concerning the chain geometry and LC behavior [16, 17]. Additional conformational studies are still necessary to elucidate this behavior. The presence of the azobenzenic units in the chain is very important for technical applications, especially for optical storage materials. We have evidenced the *cis-trans* transition of the azobenzenic units, even if these are connected in the main chain [18].

The second group (Samples 4–6) contains DHAB and BPA as mesogenic groups. Only Sample 5 presents a LC behavior, the other two being semi-crystalline materials. Figure 6 present the DSC thermogram corresponding to Sample 4.

The thermogram evidenced a single endothermic signal corresponding to the melting point, situated at 200°C. The degradation process starts around 260°C.

Sample 5 presents a mesophase evidenced by DSC analysis and optical microscopy (Figure 7).

The presence of BPA moieties (that has a bent geometry) has as a result the decreasing of phase transition values. After a first heating/cooling cycle, the isotropization temperature decreases at 180°C, which is probably due to supra-molecular rearrangements. The signals

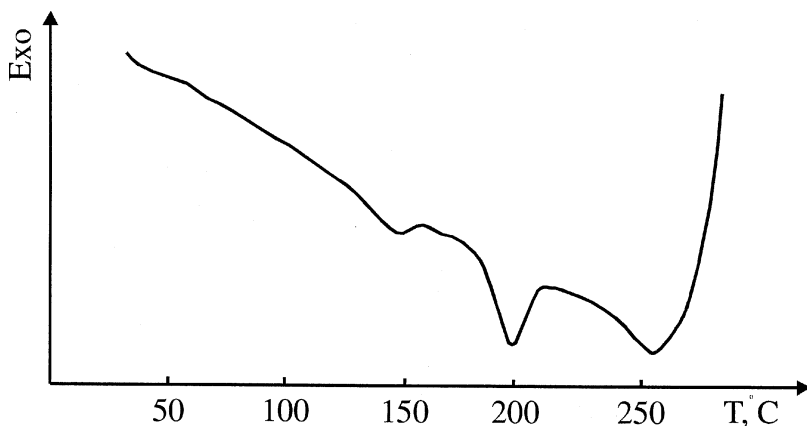


FIGURE 6 DSC thermogram corresponding to Sample 4-first heating.

corresponding to isotropic/LC and LC/crystalline transitions are present on the cooling curve at 170 and 110°C, respectively (Figure 7-curve C). With the increasing of the BPA content (Sample 6), the LC behavior disappears.

Replacement of BPA moieties with DN (Samples 7–9) results only in semi-crystalline materials, despite the fact that both bisphenols have a mesogenic character. These samples melt around 200°C.

The next investigated group contains DHAB and BPS moieties (Samples 10–12). As BPS has a similar geometry with BPA, a LC

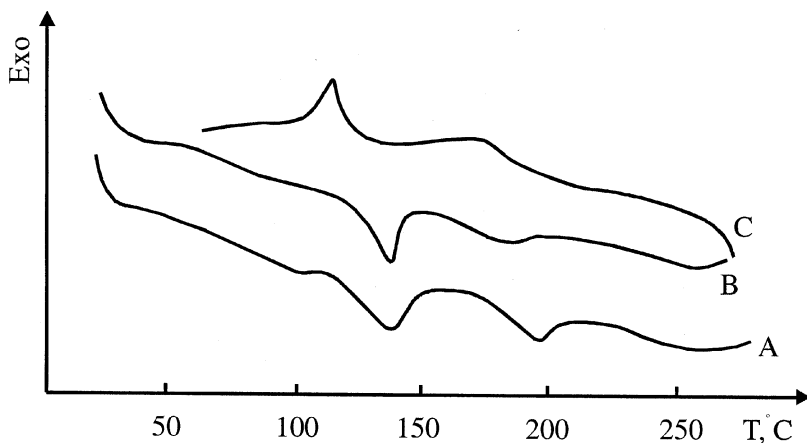


FIGURE 7 DSC thermograms corresponding to Sample 5: A-first heating; B-second heating; C-first cooling.

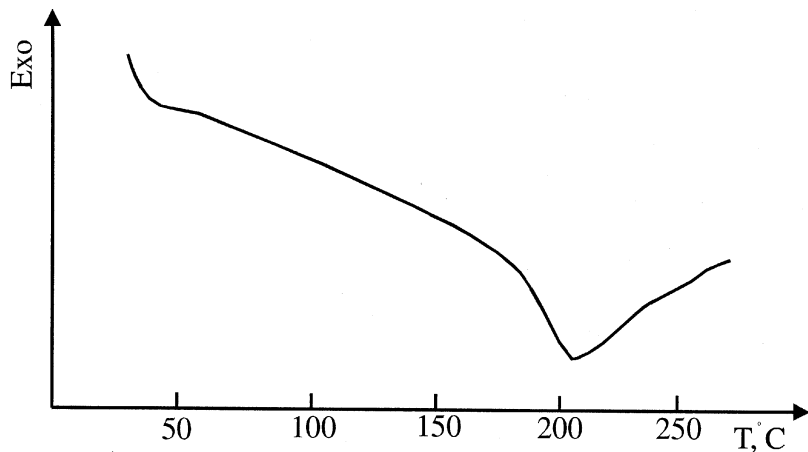


FIGURE 8 DSC thermogram corresponding to Sample 11-first heating.

behavior was expected. Yet, all products were semi-crystalline, probably due to the higher flexibility of the BPS units comparatively with BPA. Figure 8 presents a typical DSC thermogram for this group.

The last investigated group contains DHD and BPA units (Samples 13–15). No LC behavior was obtained. These products show higher melting point values, comparatively with Samples 7–12, situated around 225–230°C. Figure 9 plots a typical DSC thermogram for this group.

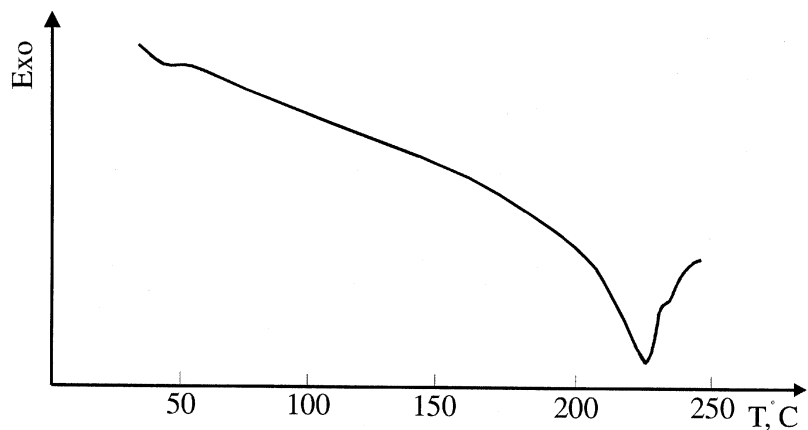


FIGURE 9 DSC thermogram corresponding to Sample 13-first heating.

CONCLUSIONS

From all investigated oligomers, only those containing DHAB, DHD and BPA units showed a LC behavior. Using two bisphenols with a linear geometry, we have obtained a LC behavior for all copolymerization ratios. The hexamethylene spacer has an important role both in the stabilization and inducement of the mesophase.

Replacement of DHD with a "bent" bisphenol has as a result only a single LC product.

All LC oligomers have an enantiotropic behavior, with a relatively large stability of the mesophase.

The investigated polyethers present high values of the transition temperatures, situated above 200°C. For the azobenzenic samples, above 250°C, the thermal degradation process starts, causing certain difficulties concerning LC characterization.

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