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PHASE-TRANSFER CATALYSIS IN POLYCONDENSATION PROCESSES. XIV. POLYETHERS WITH SEMIRIGID CHAIN

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ABSTRACT

This paper studies the main aspects of the ordering capacity of some polyethers as a function of their chemical structures. A polycondensation reaction, by phase-transfer catalysis, between 3,3-bis(chloromethyl)-oxetane and linear or “bent” bisphenols has been applied. In order to explain the thermal properties of the synthesized polymers, theoretical conformational studies were performed.

INTRODUCTION

Phase-transfer catalysis is a very convenient method for the synthesis of polymers [1–3], and is sometimes used to obtain compounds with liquid-crystalline (LC) properties [4, 5]. By the application of this method, polyethers and polyesters containing the oxetanic ring in the main chain, some of them with LC properties,

have been synthesized [6–8]. The geometry of the oxetanic ring is responsible for the special behavior of these polymers [9, 10].

The goal of this paper is to study the main aspects related to the supramolecular structure and the ordering capacity of some polyethers as a function of their chemical structure. To this end, 3,3-bis(chloromethyl)oxetane (BCMO) and linear or “bent” bisphenols were used for modify the chain’s geometry. Modifications of the atom groups between the aromatic rings also induced modifications in the flexibility and polarity of macromolecules.

EXPERIMENTAL

The polyethers were synthesized by polycondensation of BCMO with various bisphenols using phase-transfer catalysts. In a typical polycondensation reaction, 1 mmol bisphenol, 3 g NaOH, and 5 mL H₂O were vigorously stirred into a 50-mL flask (for 10 minutes); after complete dissolution, 1 mmol BCMO dissolved in 5 mL nitrobenzene was added and stirred for 5 minutes; 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 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.

BCMO synthesis was previously reported [11]. The following bisphenols were synthesized according to the literature indicated: 4,4'-dihydroxyazobenzene [12], 4,4'-dihydroxydiphenyl [13a], 4,4'-dihydroxydiphenylmethane [13b], 1,1-bis-(4-hydroxyphenyl)ethane [13c], 1,2-bis-(4-hydroxyphenyl)ethane [13d], 4,4'-dihydroxydiphenylether [13e], 1,1-bis-(4-hydroxyphenyl)cyclohexane [14], 2,2-bis-(3'-methyl-4'-hydroxyphenyl)propane [15], 2,2-bis-(3'-chloro-4'-hydroxyphenyl)propane [16]

Other bisphenols, solvents, and phase-transfer catalyst were supplied by Aldrich and were used without further purification. ¹H-NMR spectra were recorded on a Jeol-60 device. The transition temperatures were recorded by DSC (heating rate 10°C/min) on a Seiko DSC 220 device. In the case of semicrystalline polymers, the melting points were confirmed by optical microscopy in polarized light on a Leitz DM RXP microscope. Theoretical conformational studies were performed on a PC-486 using a MMX-88 program [17].

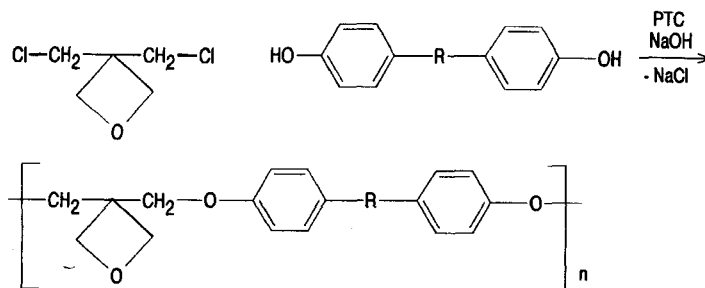
RESULTS AND DISCUSSION

The polymers were synthesized according to the reaction shown by Scheme 1.

Table 1 presents the chemical structures of the bisphenols and the main characteristics of the corresponding polymers.

The chemical structures were confirmed by ¹H NMR. For all polymers the signals of the oxetanic unit appeared at 4.25 and 4.75 ppm; the signal for the terminal —CH₂—Cl group was at 4.0 ppm. The signals of the bisphenolic protons are also presented in Table 1.

The data presented in Table 1 indicate that the molecular weights were relatively low ($M_n = 3000\text{--}7000$) (values determined by NMR spectroscopy). These



SCHEME 1.

values are probably the result of the low solubility of the polyethers obtained in organic solvents. As a consequence, the macromolecular chains leave the organic phase at a certain value of the molecular weight. The molecular weights can also be restrained by the process of transferring bisphenolates to the organic phase or by their reactivity.

The data presented in Table 1 reflect the differences between the ordering capacities of the polymers obtained. When linear bisphenols are used (Structures 1, 2, and 6), the ordering capacity is favored. In this situation the polymers result as semicrystalline structures directly from the synthesis, which is evidenced by the endothermic signal during the first heating. For structures 1 and 2, difficulties have been met in providing T_g by DSC measurement; rapid cooling ($50^\circ\text{C}/\text{min}$) is necessary to obtain the corresponding signals. This crystallization capacity can be explained by simple chain geometry, which determines its almost linear conformation (Fig. 1).

Some of the bent bisphenols present a semicrystalline morphology too, but the ordering capacity is smaller than in the case of linear bisphenols. This behavior is reflected by the ease of providing T_g , compared with Structures 1 and 2. The ordering capacity is influenced by both the geometry and the flexibility of the chain.

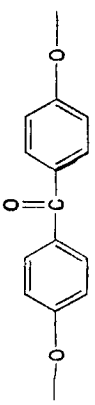
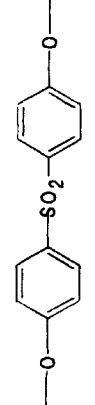
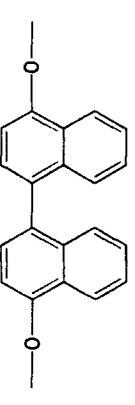
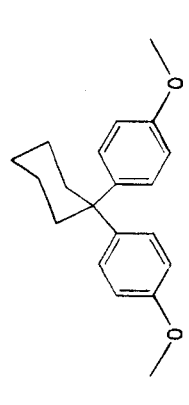
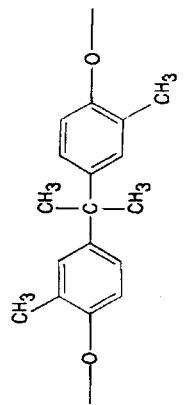
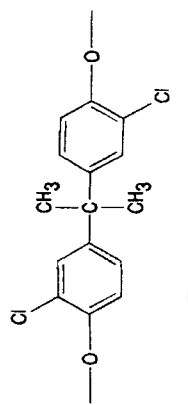
The influence of chain flexibility is evident by comparing Structures 3, 4, and 5. Figure 2 shows that the geometries of the structural units of these three polymers are similar.

However, there are differences between the flexibilities of the chains as determined by the rotational barriers around the inner bonds of the bisphenols (bonds a and b in Fig. 2). For Structure 3 these two bonds are flexible, while in the case of Structure 5 the bonds are rigid (Figs. 3 and 4). In the case of Structure 4, due to the presence of only one CH_3 group, one bond is rigid and the other one is flexible. Out of these three structures, only Structure 5, the most rigid one, shows semicrystalline behavior, with a melting point around 250°C . The loss of the ordering capacity when the chain's flexibility improves may be explained by the increase of the conformational polydispersities which will hinder the formation of crystalline structures.

For the polymer corresponding to Structure 6, due to the presence of the $-\text{CH}_2-\text{CH}_2-$ group between the aromatic rings, a greater flexibility may be expected compared with Structure 5. However, the rotational barrier around the central bond is higher than 4000 kJ/mol (Fig. 5). Rotation is permitted only within $\pm 110^\circ$; this value corresponding to the "gauche" conformation. One can expect

TABLE 1. Chemical Structures and Some Characteristics of the Polymers Obtained

No.	Structure of the bisphenolic unit	M_n	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$	$^1\text{H NMR, ppm}$
1		5000	126	250-255	7 and 8 (m, 8H, H_{aromatic})
2		5000	120	250-260	7 and 7.5 (m, 8H, H_{aromatic})
3		5200	87	Amorphous	3.8 (s, CH_2), 6.5-7 (m, 8H, H_{aromatic})
4		4500	83	Amorphous	1.75 (d, CH_3), 4.1 (m, CH), 6.5-7 (m, 8H, H_{aromatic})
5		5600	87	250-253	1.75 (s, CH_3), 6.5-7 (m, 8H, H_{aromatic})
6		7100	-	235-240	2.9 (s, $-\text{CH}_2-\text{CH}_2-$), 6.7-7.1 (m, 8H, H_{aromatic})
7		7000	87	162-175	6.8 (s, 8H, H_{aromatic})
8		7350	92	116	6.9-7.3 (m, 8H, H_{aromatic})

9		3000	103	230-235	6.9-7.1 and 7.8-8 (m, 8H, H _{aromatic})
10		3400	137	> 300	6.9-7.1 and 7.7-7.9 (m, 8H, H _{aromatic})
11		4200	—	230-235	6.7-8.2 (m, 12H, H _{aromatic})
12		4000	121	Amorphous	1.5 and 2.1 (m, 10H, C ₆ H ₁₀), 6.5-7.1 (m, 8H, H _{aromatic})
13		5700	95	Amorphous	1.7 (s, 6H, -CH ₃), 2.2 (s, 6H, -CH ₃), 6.6-7.1 (m, 6H, H _{aromatic})
14		4500	97	Amorphous	1.75 (s, 6H, -CH ₃), 7-7.5 (m, 6H, H _{aromatic})

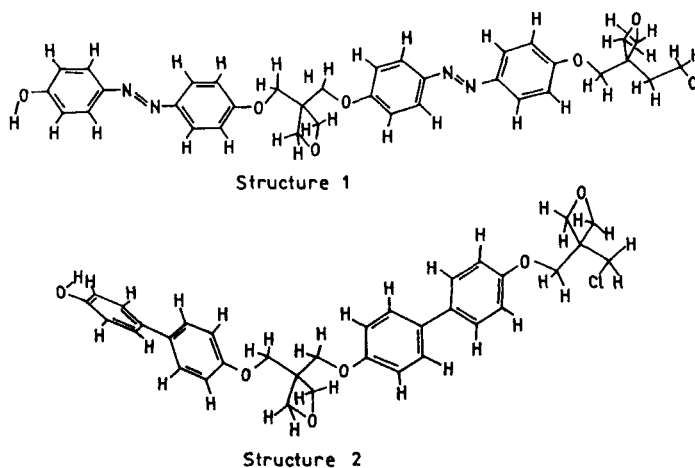


FIG. 1. Geometry of minimum energy corresponding to Structures 1 and 2.

that the *trans* (*anti*) conformation, favored energetically, will be preponderant in the polymeric chain. For these reasons the chain geometry seems to be similar to that of Structure 1. The melting point of Structure 4 is close to that of Structure 1.

The interchain interaction will also influence the ordering capacity. Theoretical conformational studies permitted the evaluation of the polar surface reported to the total surface area for each structural unit corresponding to the synthesized polymers (Table 2). The results can offer an image of the intensities of dipole-dipole interactions between the macromolecular chains (the polymers being presented in same sequence as in Table 1).

If Structures 3 and 7 are compared, it is observed that the first polymer is amorphous while the second one is semicrystalline. The geometries and flexibilities of both structures are similar, with only the polar surfaces being different. Structure

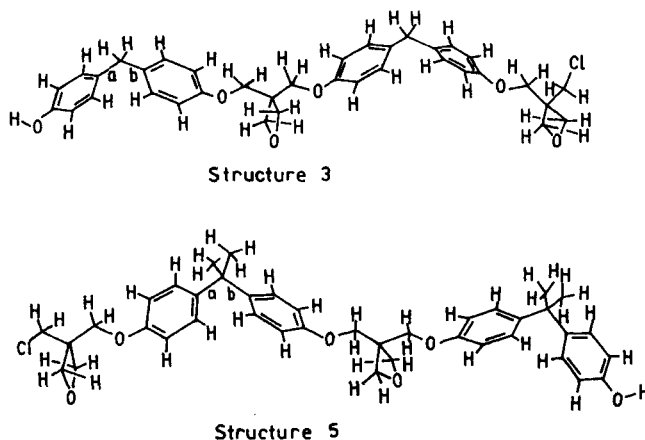


FIG. 2. Geometry of minimum energy corresponding to Structures 3 and 5.

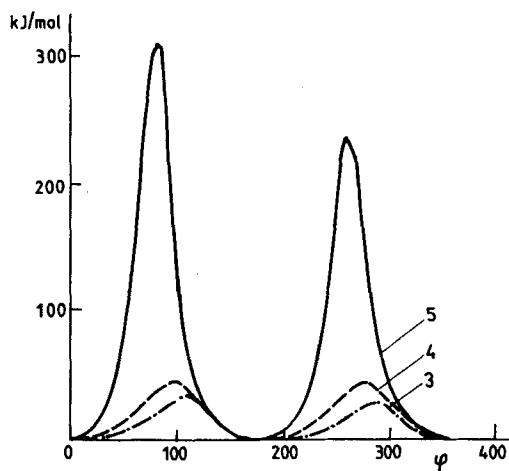


FIG. 3. Rotational barriers corresponding to Structures 3 (.....), 4 (---), and 5 (—): bond a.

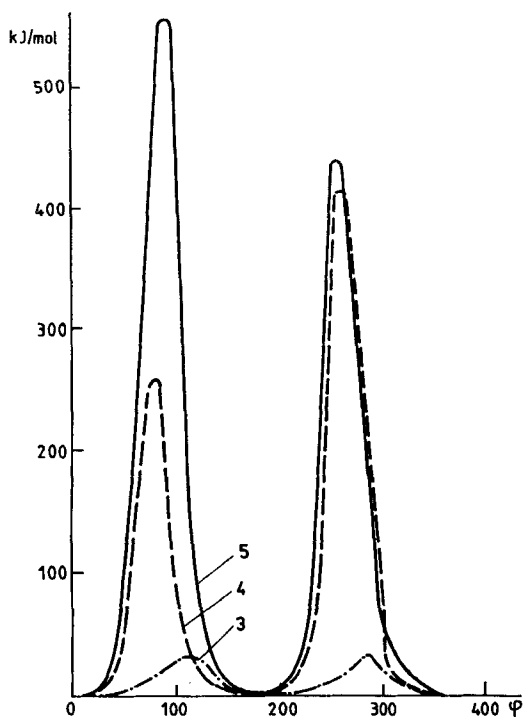


FIG. 4. Rotational barriers corresponding to Structures 3 (.....), 4 (---), and 5 (—): bond b.

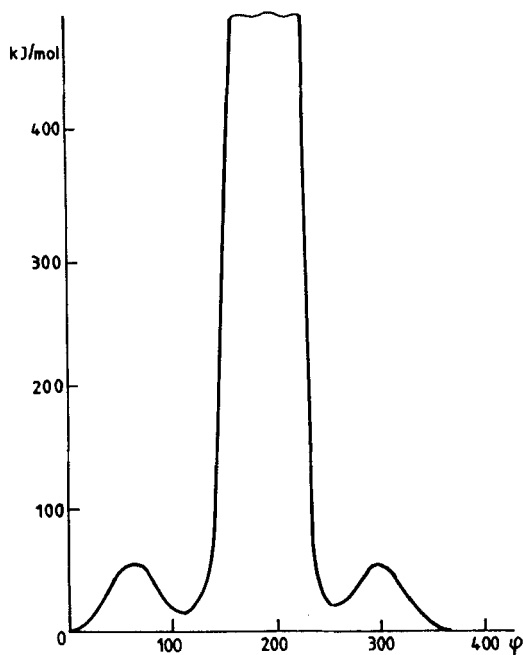


FIG. 5. Rotational barriers corresponding to the central bond of Structure 6.

TABLE 2. Polar Surface Area of Different Structural Units

Structure	Polar surface, %
1	17.4
2	12.6
3	11.8
4	12.0
5	11.2
6	11.4
7	15.3
8	13.5
9	17.8
10	22.0
11	9.5
12	9.5
13	9.2
14	10.5

7 is more polar than Structure **3**, and this aspect is probably responsible for its semicrystalline structure. This hypothesis may be taken into consideration for Structure **9**. Its polar surface represents 17.8% and the melting point increases to 235°C.

If the aromatic rings of bisphenols are substituted with $-\text{CH}_3$ or $-\text{Cl}$ groups (Structures **13** and **14**), the polymers obtained are amorphous. In this case, even if the chain's rigidity is higher compared with Structure **5**, the polymers are amorphous. This is a consequence of losing chain periodicity (in the absence of stereochemical control) of the aromatic ring substituents relative to the direction of the basic chain. These substituents cause removal of the chains, which will diminish the interchain interactions, as supported by the amorphous polymer with Structure **12** whose periodicity is higher if compared with Structures **13** and **14**.

The study permits several conclusions to be drawn on the LC properties of this type of polyethers.

If, in the case of classical mesogens (Structures **1** and **2**), it was possible to show the LC properties (for polymers having molecular weight lower than 5000 [8, 18]), for the other ones (Structures **3-14**) this was not possible. It must be underlined that the presence of the oxetanic ring in the main chain can produce crosslinking reactions at temperatures higher than 240°C due to ring-opening processes [19]. This behavior is undesirable for LC polymers because the tridimensional systems resulting in the isotropic phase do not permit ordering on cooling. Therefore, it is necessary to decrease the transition temperatures by increasing the degree of disorder of the system by using, for example, copolymerization reactions [7].

CONCLUSIONS

1. Utilization of BCMO as a flexible spacer confers on the polymers a semi-rigid character, inducing high values of the transition temperatures. Under such conditions, illustrating the LC properties, which requires lowering the transition temperatures, eventually through copolymerization reactions, may be difficult.
2. The capacity for ordering is influenced by the chain's rigidity and geometry. Improving the bisphenol flexibility will modify the chain flexibility, thus diminishing the capacity for ordering. This phenomenon is probably determined by an increase of the conformational polydispersities of this type of polyether with complex geometry.
3. Loss of the capacity for ordering caused by a too high flexibility may be counteracted by an increase of dipole-dipole interactions. Modification of these interactions may be achieved by changing the bisphenol's chemical structure.
4. Substituents on the aromatic rings or between the aromatic rings will decrease the ordering capacities of the polymer, caused either by an increase of the interchain distances or by a lack of chain periodicity.
5. The linear structure of the bisphenol used will aid the ordering capacities of the polymers by simplifying the geometry of the chains. For this type of polymers, LC properties may be shown.

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