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### Phase Transfer Catalysis in Polycondensation Processes. XXI. Molecular Modeling and Thermal Behaviour of Some Aromatic Polyethers Containing Oxetanic Rings in the Main Chain

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# Phase Transfer Catalysis in Polycondensation Processes. XXI. Molecular Modeling and Thermal Behaviour of Some Aromatic Polyethers Containing Oxetanic Rings in the Main Chain

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The paper studies the correlation between the structure and the thermal properties of some polyethers, using molecular simulation as a complementary method. The polymers were synthesized by phase transfer catalysis, starting from 3,3-bis(chloromethyl)oxetane and various bisphenols, as follows: 4,4'-dihydroxydiphenyl, bisphenol A, 4,4'-dihydroxydiphenylmethane, 1,1-bis-(4-hydroxyphenyl)ethane, 1,1-bis-(4-hydroxyphenyl)cyclohexane, 2,2-bis-(3'-methyl-4'-hydroxyphenyl)propane, 4,4'-dihydroxy-diphenylether, 4,4'-dihydroxydiphenyl-(1,2-ethane). The polyethers were characterized by thermogravimetric methods and different scanning calorimetry. Molecular simulations were performed using a force-field program HYPERCHEM (version 4.5). This study permitted to select the most recommended structures for a subsequent cross-linking process.

**Keywords:** Polycondensation; phase transfer; catalysis; molecular modeling

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## INTRODUCTION

Phase transfer catalysis has been frequently applied in the synthesis of polymers, due to its simplicity, and to the linearity of the resulting polymers. Previous works of ours we have discussed the possibility of obtaining polyethers and polyesters containing oxetanic rings in the main chain [1–6]. The presence of the oxetanic cycle induces a particular behavior, which is probably due to its specific geometry. Thus, on the DSC curves, the phase transitions present very large picks, although the polymers' polydispersity index is relatively low (1.5–1.7) for a polycondensation process. The presence of the oxetanic rings in the main chain is a great advantage, due to the possibility of chemical modification they offer. Thus, the oxetanic cycle may be opened, using an amine group [7]. When diamines or triflic acid [8] are used, three-dimensional structures, with non-linear optical properties or high mechanical resistance can be obtained. Taking into consideration these potential applications, is very important to know the thermal stability and chain conformation of these polyethers, in order to establish the optimal parameters for polymers' processing (if diamines are used as cross-linking reagents, temperatures up to 170°C are necessary).

The goal of this paper is to study the correlation between the structure and thermal properties of some polyethers, using molecular simulation as a complementary method. Molecular simulation is likely to benefit the study of polymers' properties by extending understanding of the chemical and physical processes occurring at molecular and atomic levels. By changing the chemical structure of the bisphenols used, the conformation and thermal behavior of the polymers was changed, too.

The polymers were synthesized by phase transfer catalysis, starting from 3,3-bis(chloromethyl)oxetane and various bisphenols, as follows: 4,4'-dihydroxydiphenyl (DHD), bisphenol A (BPA) 4,4'-dihydroxydiphenylmethane (DPM), 1,1-bis-(4-hydroxyphenyl)ethane (DPE), 1,1-bis-(4-hydroxyphenyl)cyclohexane (DPCH), 2,2-bis-(3'-methyl-4'-hydroxyphenyl)propane (MPP), 4,4'-dihydroxydiphenylether (DDE), 4,4'-dihydroxydiphenyl-(1,2-ethane) (DDPE).

## EXPERIMENTAL

The polymers were synthesized by phase transfer catalysis in liquid/liquid systems. Details concerning polymers' synthesis and characterization were previously reported [1–3]. The solvents and the phase transfer catalyst (tetrabutyl-ammonium bromide) were supplied by Aldrich, and were used without purification.

The thermal stability was studied in non-isothermal conditions, using a MOM Budapest device (heating rate 13.7°C/min). The kinetic taking over of data was performed using Freeman–Carroll [9] and Reich–Levi [10] methods.

The transition temperatures ( $T_g$  and  $T_m$ ) were determined by DSC analysis, on a SEIKO DSC 220 device (heating rate 10°C/min.).

The molecular simulations were performed using a force-field program HYPERCHEM (version 4.5) [11]. The initial macromolecular conformations of the simulated polyethers were optimized and the value of the total potential energy of the single chain was obtained. In order to search the real value for minimum energy (not a local minimum), the obtained conformation was followed by a molecular dynamic cycle and then re-minimized. The criterium of energy convergence was to obtain a residual root-mean-square force in the simulated system of less than 0.03 Kcal/mol · Å. Minimization was performed using a conjugate-gradient algorithm described by Fletcher and Reeves [12]. The degree of polymerization used in molecular simulations was  $DP = 8$ , the chain length being reasonable to our comments. The polar surfaces were obtained using the QSAR properties module.

## RESULTS AND DISCUSSION

The polymers were synthesized according to the following reaction scheme:

Table I presents some characteristics of the synthesized polymers.

One can observe that the molecular weights have relatively low values ( $M_n = 4000–7000$ ), due to poor solubility of the polyethers in the organic phase. As a consequence, the macromolecular chain leave

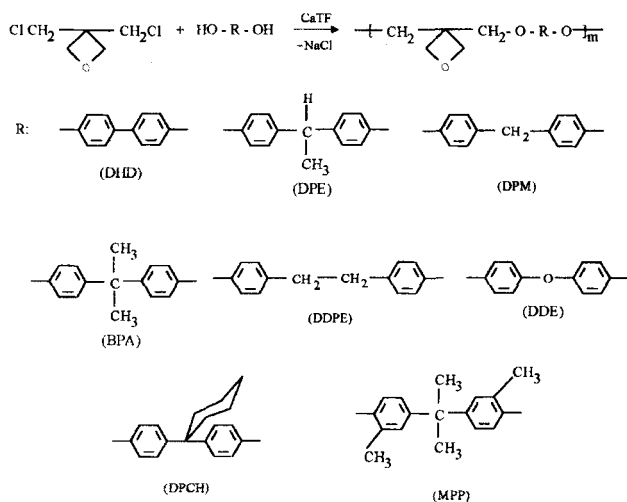


TABLE I Some characteristics of the synthesized polymers

Sample no.	Bisphenol code	$M_n$	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	Polar surface (%)
1	DHD	5000	120	255	6.3
2	DPM	5200	87	am.	4.2
3	DPE	4500	83	am.	5.4
4	BPA	5000	87	253	5.3
5	DDPE	7100	—	237	4.6
6	DDE	7000	87	170	6.5
7	DPCH	4000	121	am.	3.8
8	MPP	5700	95	am.	3.5

the solvent at a certain chain dimension. This behavior presents the advantage of a relatively low value of the polydispersity index, if taking into consideration that a polycondensation process was applied.

The bisphenols' structure was selected so that conformation, flexibility and inter-chain interactions should be modified gradually. Thus, the first bisphenol used (1) has a linear rigid geometry, followed by a flexible "bent" (2), a semi-flexible (3) and a rigid (4) one. Using polar atoms or various pendant groups (structures 6–8) one can modify the polar area, reported to the total surface, and thus, the intensity of the inter-chains' interactions.

The polymers present a degradation process in two or three steps. In Table II are given some thermo-gravimetric characteristics of the

TABLE II Thermogravimetric and kinetic characteristics of the synthesized polymers

Sample no.	$\Delta T_1$ ( $^{\circ}C$ )	$W_{\infty}^1$ (%)	$Ea_{\alpha = 10\%}$ (kJ/mol)
1	390–480	18.2	103
2	380–480	40.0	162
3	380–535	53.8	127
4	380–475	49.3	213
5	320–405	11.5	101
6	380–425	17.8	218
7	380–540	70.0	124
8	370–605	70.0	124

$\Delta T_1$  – first step of degradation;  $W^1$  – weight loss corresponding to the first step of degradation;  $Ea_{\alpha = 10\%}$  – activation energy corresponding to 10% weight loss.

synthesized polymers. We have reported only the characteristics corresponding to the first step of degradation, because we are interested especially in this stage of the process.

Sample 1 is a semi-crystalline polymer, having a good thermostability ( $T_i = 390^{\circ}C$ ). The bisphenol used in this case induced linear rigid chain geometry (Fig. 1). Rigidity is reflected by the  $T_g$  high value ( $120^{\circ}C$ ). The conformational analysis agrees with the experimental results, the polymer presenting ordering capacity (semi-crystalline structure).

This polymer can be used to obtain both non-linear optic, or high resistance materials, due to the chain linearity and rigidity, as well as to the presence of diphenyl groups. The processing of this structure can be effectuated up to  $250^{\circ}C$ . This is possible because the degradation process begins at  $390^{\circ}C$ .

If the diphenyl structure is substituted by a diphenylmethane one (Sample 2), an amorphous structure is obtained. In this case, the chain geometry is different, as reported to Sample 1 (Fig. 2) and more flexible ( $T_g = 85^{\circ}C$ ). Increase of chain flexibility due to the presence of  $—CH_2—$  groups between the aromatic rings, may generate

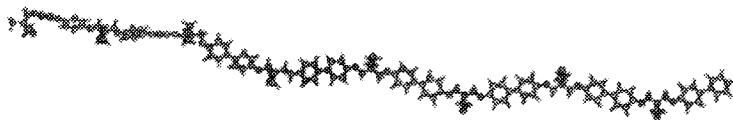


FIGURE 1 Chain conformation of Sample 1.

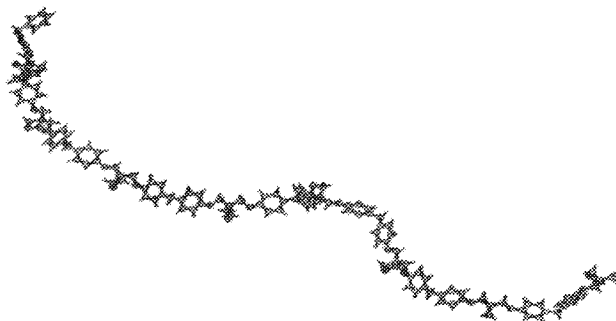


FIGURE 2 Chain conformation of Sample 2.

conformational polydispersity, which can explain the losses in the ordering capacity. Another explanation can be diminishing of the polar area, which is of only 4.2% (comparatively with 6.3% that corresponds to Structure 1). The thermal stability is similar to sample 1, the degradation processes beginning at 380°C.

The next structure investigated is Sample 3, that contains a semi-rigid bisphenol. The chain conformation of this polymer is similar to Structure 2 (Fig. 3).

This polymer presents an amorphous structure, in spite of its rigidity and of its higher polar surface (5.4%) comparatively with Structure 2. If considering the chemical structure of polymer 3, comparatively with polymer 2, increase of the polar surface is not justified (DPE contains one methyl group more than DPM). This behavior may be explained by the differences between the surfaces of phenolic oxygen atoms more shielded in polymer 2, with a diminished effective surface. Polymer 4, that presents a similar geometry of the bisphenolic groups, has the same polar surface. The thermal stability of polymer 3 is different comparatively with polymer 2. Decomposition begins at the same

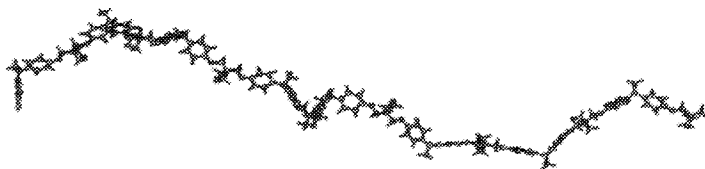


FIGURE 3 Chain conformation of Sample 3.

temperature, but the activation energy of the process is different. This low value of the activation energy may be explained by the presence of the hydrogen atom connected to a tertiary carbon atom.

In Table II are presented the activation energy corresponding to the first step of degradation (10% weight loss). We took into consideration this parameter because we are interested especially in the beginning of the degradation process.

Polymer 4 presents a more linear and rigid structure, this conformation being favorable to an ordering process (Fig. 4). It has a semi-crystalline structure with a melting point situated at 253°C.

Theoretically, this polymer presents a favorable structure and rigidity for the obtainment of highly resistant materials. The thermal stability is good, the degradation process beginning at 380°C.

Polymers 5 and 6 present a linear geometry (Figs. 5 and 6); they evidence also ordering capacity (semi-crystalline structures).

Polymer 6 has a polar surface area of 6.5%, that can explain the presence of a semi-crystalline structure in spite of the chain flexibility, which is similar to Sample 2.

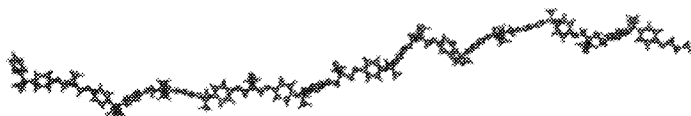


FIGURE 4 Chain conformation of polymer 4.

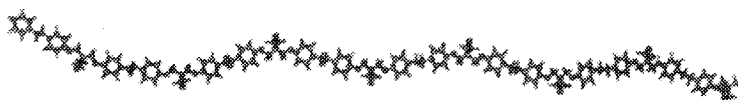


FIGURE 5 Chain conformation of Sample 5.

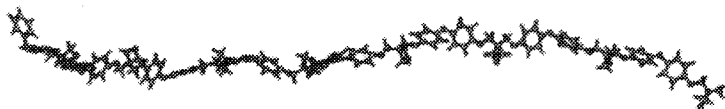


FIGURE 6 Chain conformation of Sample 6.



It is interesting to underline that the activation energies corresponding to 10% weight losses (Tab. II) are in direct correlation with the polar surfaces (PS means polar surface). For example:  $E_a(2)/E_a(6) = 0.74$  and  $PS(2)/PS(6) = 0.64$ ;  $E_a(7)/E_a(8) = 1$  and  $PS(7)/PS(8) = 1.1$ ;  $E_a(6)/E_a(7) = 1.76$  and  $PS(6)/PS(7) = 1.71$ .

## CONCLUSION

1. Molecular simulation can be a useful complementary method in polymers' characterization, offering explanations to certain behaviors and supporting the selection of the best polymer structure, for a determined practical application.
2. All polymers present good thermal stability, that permits cross-linking reactions at temperatures situated up to 170°C. The activation energy of the thermal degradation process is correlated with the polar surface of the polymer.
3. Conformational reasons recommended Structures 1,4 and 5 as the most suitable for non-linear optic or highly resistant materials.

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