

Phase transfer catalysis in the polycondensation processes

VIII. Internal rotational energies in polyesters obtained from 3,3-bis(chloromethyl) oxetane and dipotassium isophthalate

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SUMMARY

Rotation possibilities and rotational barriers in polyesters from 3,3-bis(chloromethyl)oxetane and dipotassium isophthalate were evidenced. Based on the obtained data it was presumed that every repeating unit behaves as a mesogenic, conferring liquid-crystalline properties to the polyester.

INTRODUCTION

The main chain liquid-crystalline polymers which do not contain rigid rod like mesogenic units, display usually virtual mesophases. Their behavior is tightly connected with the concept of flexible mesogenic units based on conformational isomerism (1-3).

In this paper we extend this concept to polyesters prepared from dipotassium isophthalate (DPI) and 3,3-bis(chloromethyl)oxetane (BCMO) under the phase transfer condition (4). These polymers have showed somewhat particular liquid-crystalline features. Thus, the phase transitions could be evidenced only on the first heating; after isotropization the sample remained amorphous. A 3 to 5 days annealing period was required to reorganize the macromolecular structure at a temperature higher than the glass transition point.

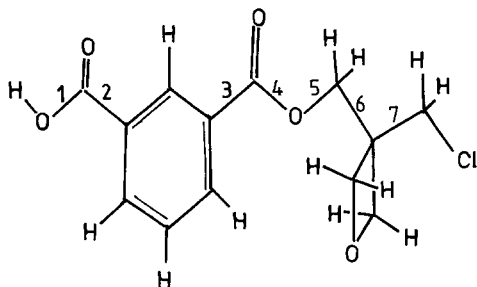
To define this aspect we have achieved conformational calculations by using a MMX program runned on a PC-386 computer (5,6).

RESULTS AND DISCUSSION

In order to establish the conformation of minimum energy, the calculations were undertaken upon the repeating unit of the polyester prepared from BCMO and DPI, corresponding to the Scheme I.

The link 1 in this structure appears to be a flexible one. The rotational barrier upon rotation about it reveals two maxima of 33.9 and 34.53 KJ/mol respectively (Fig.1).

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Scheme I. The arrangement of the isophthalate and oxetane units in the repeating sequence.

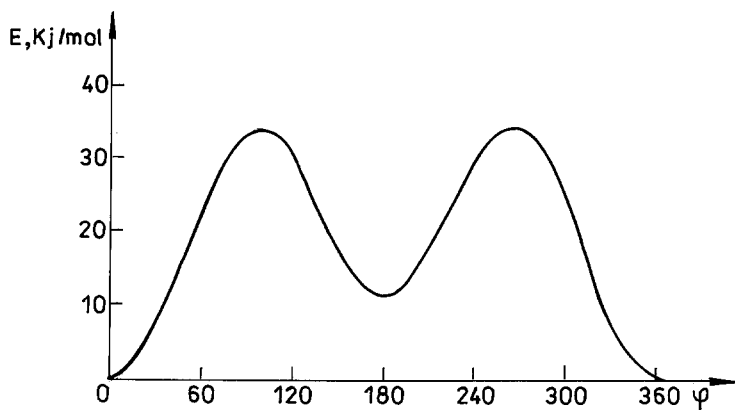


Figure 1. The potential energy of the polymeric chain vs. the angle of rotation upon the link 1 corresponding to **Scheme I**.

The assessment of these barriers was made by ignoring the fact that in the polymer chain the $>C=O$ group is linked to another BCMO unit, so that it becomes equivalent to link 4. In such conditions the rotation about it becomes very difficult, the rotational barrier reaching a maximum of 750 KJ/mol (see Fig.3).

Lower values were calculated for the corresponding maxima of potential energy upon rotation about links 2 and 3 (the rotational barrier is between 8.37 and 11.46 KJ/mol) (Fig.2). This means that aromatic rings are able to rotate in the polymer chain. In this point we must consider also the steric restrictions which appear due to interactions between

chains , also , the evidence that the aromatic ring is asymmetrically linked in the chain. It might be that under normal thermal conditions , the rotational possibilities of the aromatic units are limited.

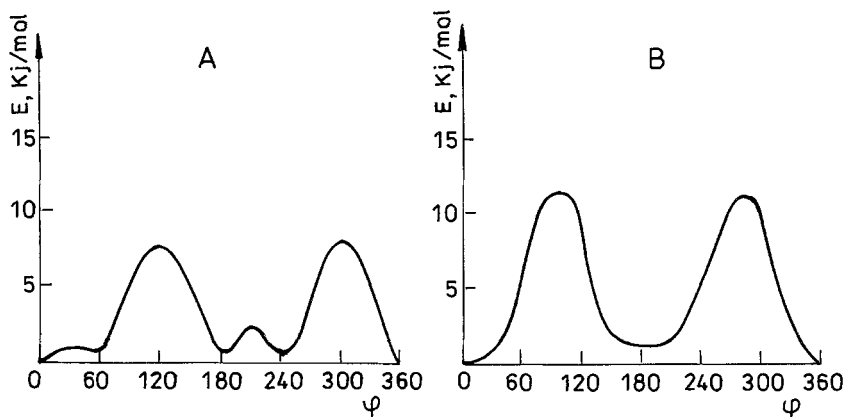


Figure 2. The potential energy of the polymeric chain vs. the angle of rotation upon the link 2 (A) and the link 3 (B) corresponding to **Scheme I**.

The potential energies upon rotation about links 4 and 5 (Fig.3) are very high (750 KJ/mol and 3153 KJ/mol , respectively) , so these links appear as very rigid.

A particular discussion require the links 6 and 7. The associated rotational barriers from the **Structure I** are 32 KJ/mol and 29 KJ/mol respectively (Fig.4) , which denote a rised flexibility in these points of the chain. One should consider, however, that in the polymer chain, the BCMO units are succesively incorporated between outstanding isophthalate units and the two bonds become equivalent. On the other hand , in spite of that the rotational barriers are not to high, rotation of the oxetane ring is not free. It is rather restricted because of interaction appearing between oxigens from oxetane ring and those in etheric bond.

Since the BCMO units are tightly bound in the polymer chain, one should consider that whole structural unit behaves as a mesogenic and the liquid-crystilline properties may be associated to these polyesters.

It is worth mentioning that as the chain length increased, the number of the phase transition was lower. This might be on account of high rotational barrier and on rigidity of the whole macromolecular chain. In its structure the mesogenics are directly bound one to another.

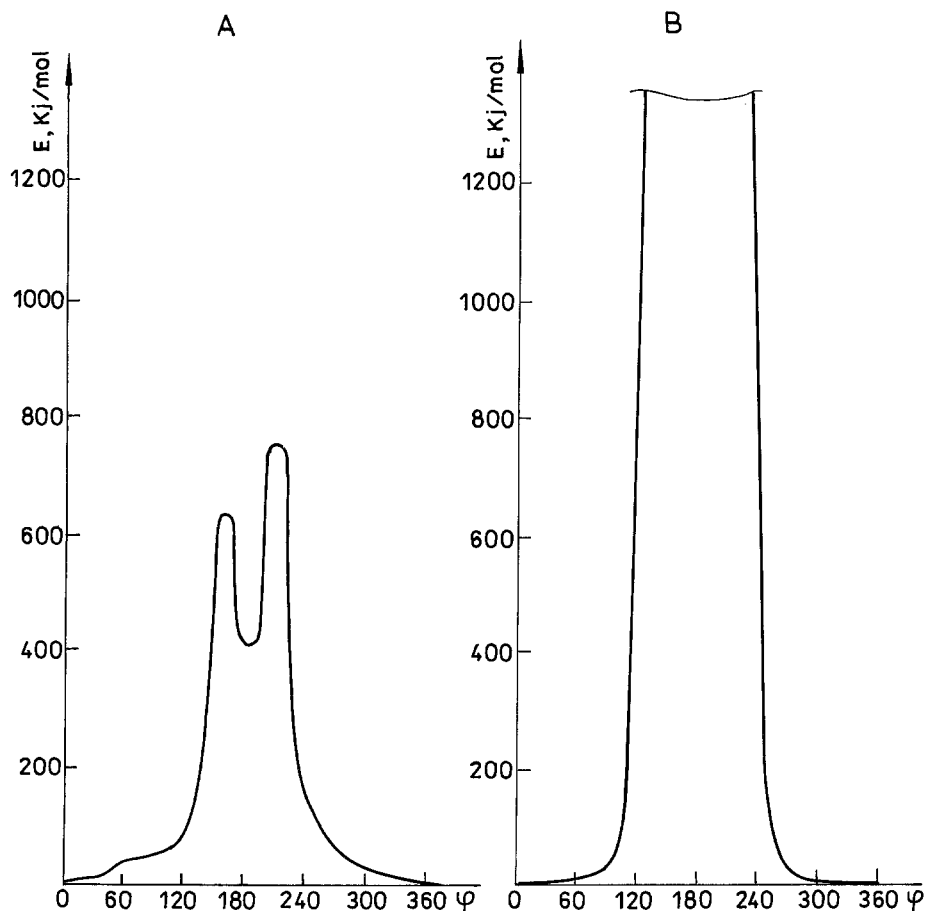


Figure 3. The potential energy of the polymeric chain vs. the angle of rotation upon the link 4 (A) and the link 5 (B) corresponding to Scheme I.

On isotropization, there are possible mutual rotations of the aromatic and oxetane units based on existing high kinetic energy. As a consequence, one may presume a change in geometry of mesogenics which may be different in every repeating unit.

The diversity in mesogenics geometry may explain difficulties in ordering of the polymer chains on cooling. And the annealing of the sample for a few days at a tem-

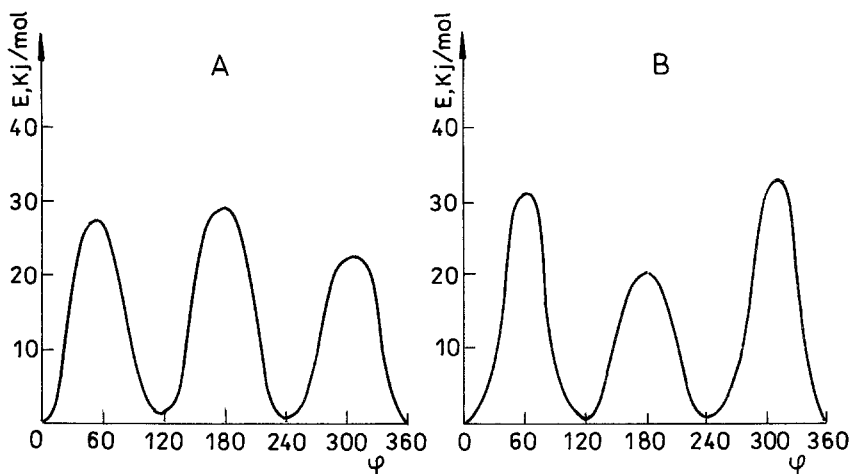


Figure 4. The potential energy of the polymeric chain vs. the angle of rotation upon the link 6 (A) and the link 7 (B) corresponding to Scheme I.

perature over the glass transition point is necessary, which allows to mesogenic units to reach a new equilibrium conformation and to build up a new order.

CONCLUSIONS

Based on the conformational calculations one may presume that polyesters synthesised from BCMO and DPI are rigid-chain polymers. The structural unit appears as a mesogenic and changes in its geometry are responsible for the ordering difficulties in the polymer on cooling.

Difference in geometry of mesogenic groups resulting in synthesis, may explain nonreproducibility of DSC analyses and of rheological data of liquid-crystalline polymers.

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