Conformational stability of poly(trimethylene oxide) by the CNDO/2 calculations

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The CNDO/2 calculations using the tight-binding approximation for polymers were carried out on poly(trimethylene oxide), $\{OCH_2CH_2CH_2\}_n$, assuming three crystal modifications, zigzag, orthorhombic, and trigonal forms. The relative stability among the three forms in the polymer was reasonably reproduced by the present calculations. The factors governing the conformational stability were demonstrated.

INTRODUCTION

There are three crystal modifications in poly(trimethylene oxide), (POM3); zigzag, $(TTTT)_2$, (ZPOM3), orthorhombic, $(TGGT)_2$, (OPOM3), and trigonal, TTTGTTTG', (TPOM3)[1,2]. From the experimental research[2] the following results were deduced: ZPOM3 is stable in the presence of water; trigonal one (TPOM3) is stable only as the stretched sample; and the OPOM3 is the most stable form in the ordinary solid state, although the energy difference among the three forms may be expected to be fairly small.

With the analogues, polyoxymethylene (POM), $\{OCH_2\}_n$, and polyoxyethylene (POE), $\{OCH_2CH_2\}_n$, the *trans* zigzag form is not the most stable form but they are stable in the helical form in the ordinary state[3,4], while the crystal structure of poly(tetramethylene oxide), $\{OCH_2CH_2CH_2CH_2\}_n$, is stable in the planar zigzag form[5]. In polyethylene, the *trans* zigzag form is the stable one[6]. Therefore, with increasing number of m in a monomer unit, $\{O-\{CH_2\}_m\}_n$, the *trans* zigzag form becomes more stable in these polymer analogues. POM3 has the possibility of both the helical and the planar zigzag polymers; this polymer is examined in this respect[7-11].

In the present work, the CNDO/2 calculations[12] were carried out on three modifications of POM3, i.e., ZPOM3, OPOM3, and TPOM3, assuming full crystal unit cell is the repetition unit and under tight-binding approximation[13].

The numerical calculations were made according to the procedure written in the previous papers[14,15]. Geometries used for the calculations are summarized in *Table 1*. The schematic structures and repetition unit used for calculations are shown in *Figure 1*.

RESULTS AND DISCUSSION

The total energies calculated are summarized in *Table 2*. From the calculated total energies it is found that OPOM3 is the most stable form, although the energy difference between OPOM3 and ZPOM3 is very small, and TPOM3 is the most unstable of the three. These correspond well with the experimental results[1,2]. We are not aware of the experimental energy difference among the crystal modifications up to the present time. However, the difference between ZPOM3 and OPOM3 is estimated to be $0.1 \sim 0.4$ kcal mol^{-1} (ZPOM3 − OPOM3) by using the semi-empirical potential function[7]. The present calculation agrees with this estimated value. In POM, the energy difference between the zigzag form and the helical form was calculated as ca. $0.05 \sim 0.07$ eV, and in POE the difference is estimated as 0.01 eV[15]. Therefore the energy difference between the helical form and the *trans* zigzag form becomes smaller with increasing m of the series $\{O\{CH_2\}_m\}_n$. When OPOM3 is stretched mechanically, it becomes TPOM3 (refs 1 and 2). By stretching, only two of the internal rotational angles in a unit segment in the skeleton of OPOM3 varied, i.e., from the $(TGGT)_2$ form to the TGTTTG'TT form. It is reasonable that the repetition unit is elongated by this mechanical stretching.

The results of the energy partitioning will be examined in more detail. As for the total intrasegment energy, TPOM3 is the smallest of the three while OPOM3 is the

Table 1 Geometries of POM3[a]

	ZPOM3	OPOM3	TPOM3
r(C–H), Å	1.09	1.09	1.09
r(C–O), Å	1.43	1.43	1.43
r(C–C), Å	1.54	1.54	1.54
ϕ(CCO)	110°	111°	110°
ϕ(CCC)	108°	112°	107°
ϕ(COC)	112°	112°	113°
ϕ(OCH)	109.332°	109.082°	109.332°
ϕ(CCH)	109.832°	109.832°	110.082°
τ(CCOC)	180°	180°	180°
τ(CCCO)	180°	63°	±67°

[a] From refs 1, 4 and 15. Angles in relation to hydrogens are adequately assumed

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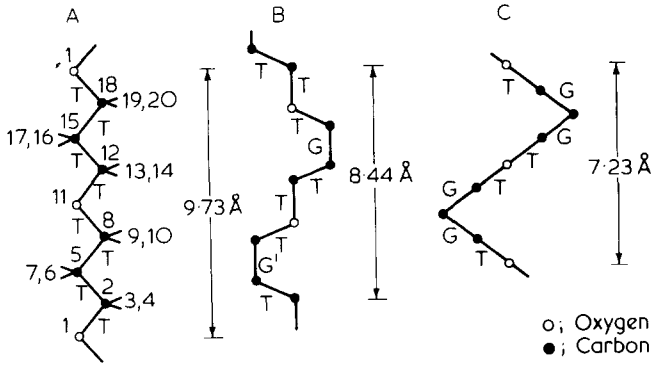

Figure 1 The schematic structures and repetition unit of the three modifications of poly(trimethylene oxide). A, ZPOM3; B, TPOM3; C, OPOM3

Table 2 Total energy (eV) of POM3

Energy[b]	OPOM3	ZPOM3	TPOM3
Total	-2421.99_2	-2421.99_0	-2421.93_0
Total intrasegment	−2394.62	−2394.70	−2394.74
Total one centre	−1955.48	−1955.66	−1955.54
Total two centre	−439.14	−439.05	−439.19
Resonance	−445.76	−445.72	−445.82
Exchange	−102.18	−102.18	−102.19
Electrostatic	108.80	108.85	108.82
Total intersegment	−27.37	−27.29	−27.19
0–1[a] Total	−13.67	−13.63	−13.59
Resonance	−14.39	−14.34	−14.30
Exchange	−2.53	−2.53	−2.52
Electrostatic	3.25	3.24	3.23
0–2 Total	−0.01	−0.01	−0.01

[a] For simplicity, 0–1 (segments) means the central and the first nearest neighbour segments, 0–2, 0–3, . . . refers to the central and the second, third, . . . nearest neighbour segments. In the present article, up to 0–4 segments were taken into consideration for all polymers under study. Energy terms: absolute values less than 0.01 eV are not listed.
[b] The meaning of the energy terms is shown in ref 15

largest. However, for the total intersegment energies, the energy order calculated is OPOM3 < ZPOM3 < TPOM3. From these results, it may be deduced that TPOM3 is stabilized largely by the intrasegment but the stabilizing energy does not compensate enough for the instability due to the intersegment interaction energy.

The one centre energy of the intrasegment is in the order: ZPOM3 < TPOM3 < OPOM3. The two centre energy is in the order: TPOM3 < OPOM3 < ZPOM3. The two centre energy in the intrasegment term is divided into three terms–resonance, exchange, and electrostatics. The equations to express these terms are shown in the previous paper[15]. To examine these terms in detail, the exchange terms of the three forms are almost the same. Therefore the resonance and the electrostatic terms should be responsible for the difference in the energy. The resonance term is the smallest in the TPOM3 while the electrostatic term is the smallest in OPOM3.

Firstly we analyse the contribution of each atom or bond to the energy difference among the different forms from the resonance term. The order of the resonance energy term is TPOM3 < OPOM3 < ZPOM3. As shown in *Table 3*, we can see that the elements (01,H6) and (O1,H7) contribute mainly to the energy difference. These are the same terms which are already explained in the case of POE[15] by '*trans* and *gauche* interactions'. Detailed description is found in the previous paper[15]. When the group O1–C2–C5–H6 or O1–C2–C5–H7 has the *gauche* conformation, either (O1,H6), or (O1,H7), destabilizes its molecular form. However, when this group has the *trans* conformation, the elements stabilize the form (see *Figure 1*). Therefore ZPOM3 is destabilized by these elements, whereas OPOM3 and TPOM3 are stabilized by this interaction. The elements (O1,H6) and (O1,H7) behave similarly to the elements (O11,H6) and (O11,H7) or (O11,H16) and (O11,H17). This *trans* interaction, therefore
TPOM3 forms in POM3. Mark *et al.* have also stated[7] that the $CH_2 \ldots CH_2$ and O...O interactions favour the $(TGGT)_2$ form (OPOM3) of POM3. The present calculation explains the concept of the interactions.

Secondly the electrostatic term will be discussed. In the cases of POM and POE, O...O electrostatic repulsion plays an important role in governing the electrostatic term in the two centre term in the intrasegment[15]. However, the O...O distances of ZPOM3, TPOM3, and OPOM3 are 4.86, 4.22, and 3.62 Å, respectively, and it would seem that the 0...0 repulsion does not take part in the elctrostatic term. This situation is reflected in the energy order of the electrostatic term in the intrasegment two centre terms, OPOM3 < TPOM3 < ZPOM3.

The contribution of the element to the electrostatic term is shown in *Table 3*. Fairly large energy differences appear in the elements (O1,C8), O1,O11), O1,C12), and (C2,O11).

As for the two centre terms in the 0-1 intersegments, the exchange and the electrostatic terms are almost the same in the three forms. Therefore, there is still a difference in the resonance term. Fairly large energy differences appeared in the elements summarized in *Table 3*. Here for example, (^{0}H16,^{1}O1) or (^{0}H17,^{1}O1) corresponds to the element (O1,H7) or (O1,H6) of the two centre term in the intrasegment, already described as the '*trans* and *gauche* interactions'. With the O-2 segments, there are no energy differences among the three forms.

Table 3 Large contribution elements on the energy difference among three forms of POM3[a]

	OPOM3	ZPOM3	TPOM3
Two centre term in the intrasegment			
Resonance			
(O1, H6)[a]	−0.03	0.04	0.04
(O1, H7)	0.04	0.04	−0.03
Electrostatic			
(O1, C8)	−0.18	−0.14	−0.18
(O1, O11)	0.21	0.16	0.19
(O1, C12)	−0.12	−0.09	−0.11
(C2, O11)	−0.18	−0.14	−0.15
Two centre term in the 0–1 segments			
(^{0}C12, ^{1}O1)	0.03	−0.01	−0.01
(^{0}C15, ^{1}O1)	0.11	0.13	0.13
(^{0}H16, ^{1}O1)	0.02	0.02	0.02
(^{0}H17, ^{1}O1)	−0.02	0.02	0.02
(^{0}C18, ^{1}O1)	−14.35	−14.33	−14.32
(^{0}C18, ^{1}C2)	−0.38	−0.39	−0.35

[a] Energy in eV
[b] Notations of the elements are the same as in ref 15

CONCLUSIONS

The conformational stability among the three forms of POM3, i.e. ZPOM3, OPOM3 and TPOM3, is governed by the balance of the total intrasegment and the intersegment energies. Therefore, it was concluded that the skeletal conformation of the polymer cannot be determined only from the stable conformation of its model molecule. In the intrasegment and the intersegment energies, the resonance and electrostatic terms, and the resonance term respectively, are mainly responsible for the energy difference among the three forms. The detailed contribution to the atoms or bonds is made in the present work (see *Table 3*).

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