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## A molecular mechanics and semiempirical molecular orbital study on the conformation of polynorbornene chains

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**Abstract** The conformational analysis of polynorbornene (PNB) chains was investigated with the AM1, MM2, AMBER and OPLS methods taking into consideration the possibility of binding of norbornene monomers to each other at various positions, i.e. *exo-exo*, *exo-endo*, *endo-endo*. The chain that is formed by connecting *exo-endo* positions of the monomers has lower torsional barrier energy than those formed with bonds at other positions and has more flexibility. It is determined that the thre-disyndiotactic chain formed by *exo-endo* addition adopts a helix structure and has a coil shape. The disyndiotactic chain formed by connecting norbornene monomers in mixed type has a linear structure. It is found that the repeat unit conformations of thre-disyndiotactic and disyndiotactic chains of PNB are TGTG<sup>-</sup> and (TGTG<sup>-</sup>)<sub>2</sub>, respectively.

**Keywords** PNB · Semiempirical and molecular mechanics methods · Conformational analysis

### Introduction

Norbornene is a prototypal strained, bicyclic olefin and as such a prominent model system in mechanistic organic chemistry. Since the double bond and the hydrogen atoms bound to the double bond in norbornene are not in the

same plane, the molecule is an *endo* pyramidized alkene [1]. Because the double bond in the *endo* pyramidized norbornene molecule does not have a planar structure, the faces of the double bond are also not equivalent. The electron density is greater on the *exo* side of the double bond. Numerous experimental and theoretical studies have shown that the reactivity of the double bond of norbornenes is characterized by a pronounced preference for *exo* attack [2, 3, 4, 5]. Related changes in hybridization and steric factors favor *exo* attack. However, it is possible to perform the addition to the norbornene molecule from the *endo* direction with various catalysts [6]. The polymerization reaction of norbornene by various catalyst systems and the properties of the polynorbornene polymers (PNB) formed have been described in detail in the literature [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. It is found that in polymerization reactions, polynorbornene (PNB) resulting from the addition of norbornene molecules to each other at various positions, i.e. *exo-exo*, *exo-endo* and *endo-endo* is formed [11]. Determination of the conformation, the structure and the stability of polymer chain are important. The conformation and the structure of the polymer chain are very important in determining the physicochemical and other properties. The aim of this work is to establish the detailed structure of PNB chains. The conformational analysis of the dimers (*n*=2) formed as a result of *exo-exo*, *exo-endo*, and *endo-endo* additions of norbornene molecules was performed by molecular mechanics MM2, [17] AMBER, [18] OPLS [19, 20] and semiempirical AM1 [21] methods and the stable conformations were determined in this study. The internal torsion barrier energies of different dimers were calculated. The conformational analysis of the polymer chain (*n*=8) was performed using molecular mechanics and AM1 methods taking into consideration the possibility of addition of norbornene molecules from various positions. The strain energies and the heats of formation of the polymer chains (*n*=8) having different steric regularity were calculated.

The repeating unit configuration was also determined for each PNB chain investigated. The conformational

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analysis of the polymer chain ( $n=32$ ) having different steric regularity was performed using molecular mechanics methods and the strain energies were calculated.

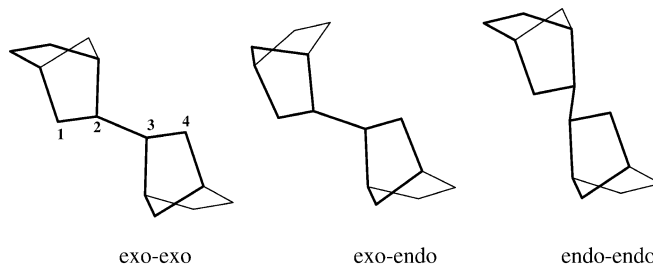
## Computational method

All calculations were performed using the HYPERCHEM 6.0 program [22] on an IBM PC Pentium-IV computer. The conformation analyses of norbornene dimers and polynorbornene chains ( $n=8, 32$ ) were performed using the HYPERCHEM 6.0 parameters for the MM2(MM+), AMBER and OPLS methods. Full geometry optimization was carried out employing the Polak–Ribiere conjugate-gradient method until an RMS gradient of  $0.0001 \text{ kcal } (\text{\AA} \text{ mol}^{-1})$  was reached. Force field options in the AMBER and OPLS methods are the HYPERCHEM 6.0 defaults. Therefore, for molecular mechanics calculations, the AMBER force field was utilized with a distance-dependent dielectric constant scaled by a factor of 1.1–4. Scale factors are the following: electrostatic 0.833, van der Waals 0.5. The OPLS force field was used with a dielectric constant scaled by a factor of 1 and 1–4 scale factors are the following: electrostatic 0.5 and van der Waals 0.125. Furthermore, all the calculations were also performed with the semiempirical method RHF/AM1 method with the Polak–Ribiere (conjugate gradient) algorithm (convergence limit of  $0.0001 \text{ kcal mol}^{-1}$ ) and an RMS gradient of  $0.001 \text{ kcal } (\text{\AA} \text{ mol}^{-1})$ . For the calculation of the potential curves of norbornene dimers of internal rotation around the central C–C single bond, the internal rotation angle ( $\phi$ ) was rotated in the range  $0$ – $360^\circ$  with a step of  $30^\circ$ , optimizing the geometry at each single step.

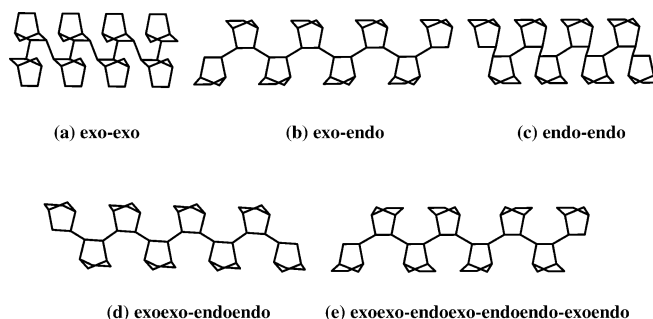
## Results and discussion

The full geometry optimizations of dimers (Scheme 1) formed with *exo–exo*, *exo–endo* and *endo–endo* bonding of norbornene molecules were carried out using the MM2, AMBER, OPLS and AM1 methods and the stable configurations were determined.

According to the results of the molecular mechanics and semiempirical AM1 methods, the 1–2–3–4 internal rotation angle (dihedral) ( $\phi$ ) for all three dimers in the stable conformations is almost equal to  $180^\circ$ . The internal rotation angle ( $\phi$ ), the strain energy ( $E_{\text{str}}$ ) and the heat of



**Scheme 1** The optimized geometries of dimers (AM1)



**Scheme 2** The structures of PNB chain ( $n=8$ )

formation ( $\Delta H_f^0$ ) of the stable conformations of the dimers are given in Table 1.

The internal rotation barrier energies ( $\Delta E$ ) were calculated (Table 1) and it was determined that the dimer formed by *exo–endo* addition had the lowest  $\Delta E$ . Thus, the dimer formed by *exo–endo* addition should be more flexible than the others (Scheme 1).

According to these data, the most stable of the dimers is the *exo–exo* dimer and the most unstable is the *endo–endo*. The internal rotation potential curve of each dimer was calculated by the molecular mechanics and AM1 methods and these curves are given in Fig. 1. According to the methods used, the least stable conformation of each dimer (the conformation having the maximum strain energy and heat of formation) is the conformation with an almost zero internal rotation angle ( $\phi$ ).

The structures of the PNB chain ( $n=8$ ) formed by addition of norbornene monomers from various positions are shown in Scheme 2. As seen from the scheme, norbornane molecules are in a regular sequence on both sides of the carbon–carbon chain plane. However, the positions of the repeating norbornane molecules in

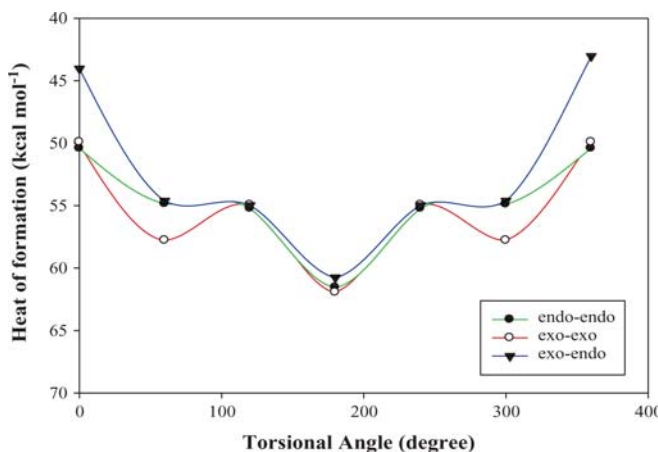
**Table 1** The calculated heat of formation ( $\Delta H_f^0$ ), strain energy ( $E_{\text{str}}$ ), internal rotational angle ( $\phi$ ) and internal barrier energy ( $\Delta E$ ) of the stable conformations of the dimers

The dimer	$\Delta H_f^0$		$E_{\text{str}}$ (kcal mol <sup>-1</sup> )				$\phi$ (°)				$\Delta E$ (kcal mol <sup>-1</sup> )		
	(kcal mol <sup>-1</sup> )	MM2	AMBER	OPLS	AM1	MM2	AMBER	OPLS	AM1	MM2	AMBER	OPLS	
<i>exo–exo</i>	-20.5	48.1	47.2	46.2	180	180	180	180	12.2	12.0	14.3	13.7	
<i>exo–endo</i>	-19.2	48.4	47.5	46.6	175.8	174.7	176.2	179.1	11.4	11.1	13.3	12.3	
<i>endo–endo</i>	-17.7	49.2	48.1	47.3	180	180	180	180	23.3	16.7	19.8	16.3	

**Table 2** The calculated heat of formation ( $\Delta H_f^0$ ) of different structures of PNB chain ( $n=8$ ), the strain energies ( $E_{str}$ ), the length ( $d$ ), and the conformation of repeating unit

Structure of the chain conformation <sup>a</sup> ( $n=8$ )		AM1		MM2		AMBER		OPLS	
		$\Delta H_f^0$ (kcal mol <sup>-1</sup> )	$d$ (Å)	$E_{str}$ (kcal mol <sup>-1</sup> )	$d$ (Å)	$E_{str}$ (kcal mol <sup>-1</sup> )	$d$ (Å)	$E_{str}$ (kcal mol <sup>-1</sup> )	$d$ (Å)
A	TCTC	49.19	4.98	262.27	5.19	258.43	5.0	263.65	5.11
B	TGTG <sup>-</sup>	1.49	5.18	223.63	4.98	218.38	4.97	214.71	4.85
C	TCTC	73.60	5.02	281.44	4.94	280.78	4.96	274.81	4.93
D	TGTG <sup>-</sup>	12.17	5.19	233.17	5.20	227.40	5.12	220.64	5.10
E	(TGTG <sup>-</sup> ) <sub>2</sub>	-19.29	9.98	220.93	10.15	215.41	10.30	211.15	10.11

<sup>a</sup>The values of dihedral angle in the repeating unit conformation are shown with 180°-T, ~0°-C, +120°-G and -120°-G<sup>-</sup> [23]

**Fig. 1** Internal rotational potential curves of norbornene dimers (AM1)

different configurational structures are different. The chain of the polymer is formed by connecting norbornene molecules in *exo-exo*, *endo-endo* and *exoexo-endoendo* formats (shown as a, c and d in Scheme 2, respectively). Norbornane molecules lying on different sides of this polymer chain are directed in opposite directions with respect to each other. When the methano-bridge positions of norbornane molecules are considered, it is possible to say that PNB molecules with a, c and d structures are erythrodiisotactic polymers. Norbornane molecules are regularly positioned on both sides of the polymer chain formed (Scheme 2b) by connection from *exo-endo* positions. The situation of norbornane molecules that lie on different sides of the backbone of the polymer chain in structure b are the same; i.e., the methano bridges of norbornane molecules in structure b reside on the same side. Thus, PNB in structure b is a threodiisotactic polymer. As shown in Scheme 2, the norbornane molecules following each other on both sides of PNB chains formed by bonding norbornene monomers in a mixed type (*exoexo-endoexo-endoendo-exoendo*) configuration are sequenced in the opposite configuration. The methano bridges in norbornane molecules following each other on both sides of the polymer chain are directed in different orientations. Thus, PNB in structure e (Scheme 2e) is a disyndiotactic polymer.

**Table 3** The calculated strain energies of different structures of the PNB chain ( $n=32$ )

Structure of the chain ( $n=32$ )	$E_{str}$ (kcal mol <sup>-1</sup> )		
	MM2	AMBER	OPLS
A	1,144.96	1,191.45	1,140.78
B	942.79	921.74	879.25
C	1,246.59	1,291.69	1,244.48
D	976.09	946.56	910.51
E	928.46	907.78	880.23

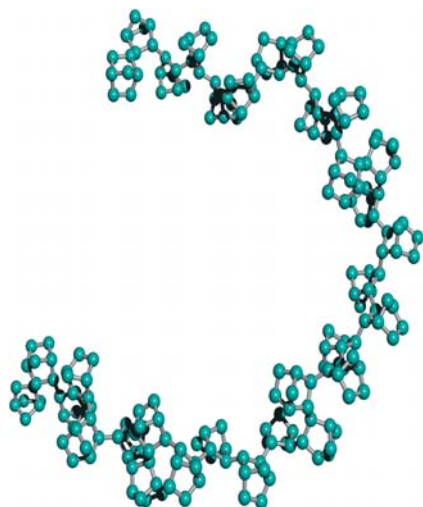
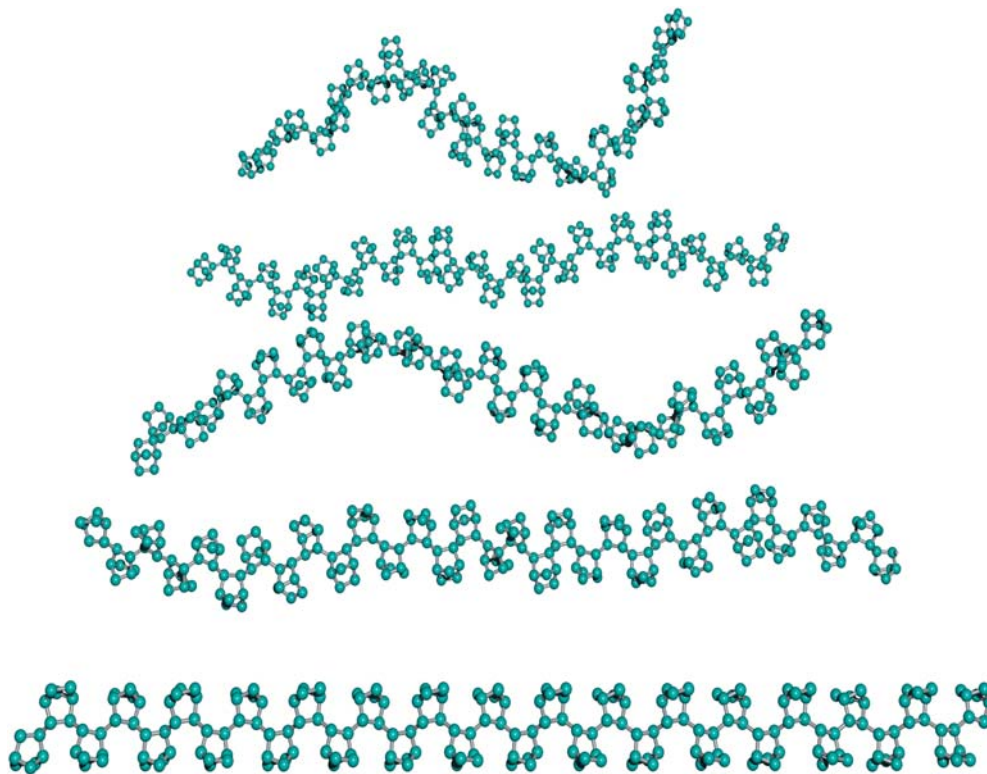
The full geometry optimizations of different conformations (Scheme 2) of the polybornene chain ( $n=8$ ) were performed with the AM1, MM2, AMBER and OPLS methods and the heat of formations and their strain energies were calculated. The results are shown in Table 2. The conformation of the repeating unit was determined and the length of polymer chain for each structure was calculated (Table 2).

As shown in Table 2, the PNB chain in structure e has the lowest heat of formation and strain energy. The second most stable PNB chain is structure b. Thus, the conformational analyses performed with semiempirical and molecular mechanics methods showed that the PNB polymer is essentially in either the e or b conformations. Because structures a and c have higher heats of formation and strain energies, they are unstable PNB chains. As a result, the lengths of the repeating unit found with various methods for every structure, are in quite good agreement.

For the sake of dependability of the results obtained, conformational analyses of structures with different steric regularity (Scheme 2) of the PNB polymer ( $n=32$ ) were performed by molecular mechanics and the strain energies were calculated (Table 3). The optimized geometries of structures a, b, c, d and e are given in Fig. 2.

According to MM2 and AMBER, the PNB chain ( $n=32$ ) has the lowest strain energy in structure e (Table 3). However, according to OPLS (optimized potential for liquid simulations), the PNB chain has the lowest strain energy in structure b (Fig. 3). On the other hand, the PNB (structure b) chain adopts a helix structure according to the OPLS results and the polymer has a coil shape (Fig. 3). Thus, the PNB polymer in structure b, which is formed by *exo-endo* addition of norbornene monomers, is more dominant in a liquid environment. It is clear that the experimental studies show formation

**Fig. 2** The optimized geometries (MM2) of structures a, b, c, d and e of the PNB chain ( $n=32$ )



**Fig. 3** The optimized geometry of structure b with the OPLS method

principally by *exo-endo* connection of norbornene molecules in a PNB chain. [11] Also, the experimental studies showed that the PNB polymer chain has a coil shape. [12, 14] Thus, the theoretical results are in agreement with experimental results.

Linear PNB polymer should have essentially structure e. The conformational analyses of the  $n=8$  and  $n=32$  chains of PNB are in agreement with each other and show that PNB has essentially structures e and b.

## Conclusions

In this study, computational techniques, i.e. molecular mechanics and semiempirical methods, were used to investigate the conformational analysis of the PNB chain. The conformational analysis of PNB chain ( $n=2, 8, 32$ ), which is formed by bonding norbornene molecules from various positions (*exo-exo*, *exo-endo*, *endo-endo*), was performed by semiempirical and molecular mechanic methods and gives the following results. The internal rotation angle is almost  $180^\circ$  in the stable conformations of dimers ( $n=2$ ). That is, norbornene molecules are in *trans* positions in the stable conformations of the dimers. The dimer formed with *exo-endo* bonding has a lower rotational barrier and is more flexible compared to others. The polymer chain has essentially e (disyndiotactic) and b (thredisyndiotactic) structures. Structure b is more dominant in a liquid environment. The possibility of a linear polymer chain in structure e is higher. The repeating unit conformation is found to be  $(TGTG^-)_2$  and  $TGTG^-$  in disyndiotactic and thredisyndiotactic structures of the PNB chain, respectively.

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