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## MNDO cluster model calculations on organic polymers

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**Abstract**—Heats of formation and unit cell translation vectors for several organic polymers are calculated using the MNDO method. The results compare favorably with experiment; the magnitude of the errors is comparable to those of the MNDO method when applied to molecules. *Keywords* (S)

*Keywords*: MNDO; polymers; heat of formation; heat of polymerization; clusters. *References* (75) (F)

### 1. INTRODUCTION

MNDO [1] has been applied with considerable success to molecules and ions, but to date only two reports of the application of MNDO to polymers have appeared [2, 3], and these were successful demonstrations that MNDO is a suitable tool for the study of polymers. No further publications have appeared; however, to a large extent this is due to the considerable time needed to calculate the self-consistent field in solids. Whereas in molecules the Fock matrix can be identified with the secular determinant, in solids separate secular determinants have to be constructed for each point sampled in the Brillouin Zone. In addition, the resulting secular determinants are complex, and as complex arithmetic is usually slower than the real analogue, solid state calculations are additionally lengthy.

In order to simplify the calculation of polymers, a "cluster" approach [4], previously developed for CNDO [5], has been adapted for use with the MNDO Hamiltonian. This relies on the fact that if the translation vectors are large enough, the nature of the bands in the Brillouin Zone will not change significantly on crossing the zone. Thus a sufficiently large unit cell would allow the use of only one point to represent the entire Brillouin Zone, one which can be positioned arbitrarily. For convenience the  $\Gamma$  point is obviously the most suitable. Clearly, if the fundamental unit cell is small, several may be needed in order that the translation vector be large enough to allow a single point to represent the entire Brillouin Zone.

The proposed method, then, uses a large unit cell and simply calculates the secular determinant corresponding to the gamma point. As this determinant is real, the associated eigenvectors are real, and real arithmetic can be used during the whole of the SCF calculation. Additional advantages of this approach include the use of single arrays to store the one electron, Fock and density matrices, as opposed to having one for each unit cell. On the other hand, the lack of separate density matrices for each unit cell makes the inclusion of the exchange interaction more difficult, and a modification to the basic MNDO expressions is required.

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## 2. COMPUTATIONAL METHOD

The basic equations used are those of MNDO [1], and the cluster model already described [4]. As both methods are quite straightforward, only a brief description need be given at this point.

If the unit cell is large enough, then a single point in  $k$ -space, the  $\Gamma$  point, is sufficient to specify the entire Brillouin Zone. The secular determinant for this point can be constructed by adding together the Fock matrices for the central unit cell with all unit cells. In turn, the Fock matrices are the sum of the one and two electron matrices, and as the cluster approach used here involves the direct construction of the secular determinant, our attention is first directed to the construction of these matrices. Given the central unit cell  $C(0, 0, 0)$  and surrounding unit cells  $C(i, j, k)$ , the contribution to the secular determinant due to the one electron matrix element  $H(\lambda, \sigma)$  is defined by

$$H(\lambda, \sigma) = \sum_i \sum_j \sum_k H(\lambda, \sigma)_{i,j,k}$$

where  $H(\lambda, \sigma)_{i,j,k}$  is the one electron matrix element between atomic orbital  $\varphi_\lambda$  in the central unit cell, and the atomic orbital  $\varphi_\sigma$  in unit cell  $C(i, j, k)$ .

In MNDO the two-electron coulomb and exchange integrals are equivalent. That is, an integral of type  $\langle \mu\nu(1/r_{12})\lambda\sigma \rangle$ , where atomic orbitals  $\varphi_\mu$  and  $\varphi_\nu$  are on atom A and atomic orbitals  $\varphi_\lambda$  and  $\varphi_\sigma$  are on atom B, can be either a coulomb or an exchange integral depending on the context. In solid-state work a distinction must be made between these two types of integrals; this distinction is made necessary by the different natures of the coulomb and exchange integrals. The solid-state coulomb integrals can be formed in the same way as the one-electron integrals, thus:

$$\langle \mu\nu(1/r_{12})\lambda\sigma \rangle = \sum_i \sum_j \sum_k \langle \mu\nu(1/r_{12})\lambda\sigma \rangle_{i,j,k}$$

The coulombic contribution to the secular determinant involves the repulsion between electrons in every unit cell with the electrons in the central unit cell, and therefore simple linear addition of the coulomb integrals is warranted.

On the other hand, the periodicity of the one electron and the coulomb terms is absent in the exchange interaction, and only the exchange terms arising from the atom in that unit cell which minimizes the interatomic distance can be used [4]. If the exchange integral between atoms A and B is to be calculated, and atom B is equidistant from atom A in two or more unit cells, then one orientation is arbitrarily chosen, and the exchange integrals calculated. The arbitrary choice of orientation can be justified as follows.

In the construction of the Fock matrix, the exchange integrals are multiplied by the density matrix element connecting the two atomic orbitals. If the situation exists where an atomic orbital is equidistant from another atomic orbital in two different unit cells, then the distance between the two atomic orbitals is necessarily large. Thus in Fig. 1, atom 4 in the cluster is equidistant from atom 1 in the cluster and 1' in the adjacent cluster. As atoms 1 and 1' are separated by the translation vector distance, the distance between atoms 1 and 4 is necessarily large. As density matrix elements are insignificant between atomic orbitals which are well separated, any errors introduced by an arbitrary choice of exchange integral are negligible. Only exchange terms between different atoms in the unit cell are calculated this way; the monocentric terms are calculated in precisely the same manner as for molecules.

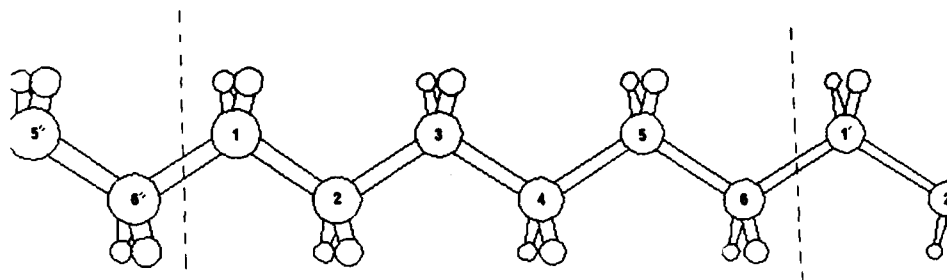


Figure 1. Model of cluster in polymer.

Every atom in the cluster appears to be in an environment in which it is in the center of the cluster. Thus atom 5 has as nearest neighbors atoms 4 and 6, and as second nearest neighbors atoms 3 and 1'. The covalent interaction between atoms 1 and 5 is very small, and by using the matrix elements for the 1-5 interaction to hold the 1'-5 interaction no increase in storage is required. While covalent interactions fall off rapidly with distance, ionic terms fall off only as  $1/r_{12}$ . As these terms are monocentric and are equivalent in all unit cells, they can be readily included without loss of generality.

While suitable for molecules, the Mataga-Nishimoto approximation [6] for the two-electron two-center integral is potentially unsuitable for solid-state application. At large values of  $r_{12}$  the integrals of type  $\langle \lambda\lambda(r_{12})\sigma\sigma \rangle$  can differ, depending on the nature of  $\varphi_\lambda$  and  $\varphi_\sigma$ . In order to correctly represent the potential arising from coulombic terms, all integrals of this type must have exactly the same value of  $14.397/r_{12}$ . Rather than attempt to change the MNDO formalism, a not inconsiderable task, the Mataga-Nishimoto approximation was retained. It was found the errors introduced by use of the Mataga-Nishimoto approximation were negligible when only the nearest few unit cells were used, and no large charge separation occurred within the unit cell.

It is necessary that the unit cell chosen should be large enough to ensure that any errors introduced due to a finite sampling of the Brillouin Zone or by neglecting non-zero interactions between atoms are insignificant. As there exists no simple *a priori* way of determining this size, a series of calculations were performed on polyacetylene and polyethylene, in which the number of fundamental unit cells was varied. The results are presented in Tables 1 and 2. Polyethylene is an example of a polymer in which all bonds

Table 1.  
Heat of formation of polyacetylene

No. of atoms in repeat unit	$\Delta H_f$ (kcal/mole)	$\Delta H_f$ per $C_2$ unit	Diff.	$R_{(C_1 C_2)}$ (Angstroms)	$R_{(C_2 C_3)}$
4	23.69	11.85	-1.74	1.459	1.359
6	25.25	8.41	-5.18	1.403	1.403
8	57.77	14.44	+0.85	1.472	1.355
10	65.18	13.04	-0.55	1.457	1.365
12	82.13	13.69	+0.10	1.464	1.358
14	94.40	13.49	-0.10	1.464	1.359
16	108.63	13.58	-0.01	1.463	1.358
18	121.90	13.54	-0.05	1.463	1.359
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**Table 2.**  
Heat of formation of polyethylene

No. of atoms in repeat unit	$\Delta H_f$ (kcal/mole)	$\Delta H_f$ per CH <sub>2</sub> Unit	Diff.	$R_{(C_1, C_2)}$ (Angstroms)
4	-17.60	-4.40	+0.31	1.5436
6	-27.00	-4.50	+0.21	1.5426
8	-37.46	-4.69	+0.02	1.5423
10	-47.04	-4.70	+0.01	1.5427
inf		-4.71		1.5426

are localized, and as expected the errors in the heat of formation decrease with increasing number of fundamental unit cells converging rapidly to a constant value of 4.71 kcal/CH<sub>2</sub> unit. On the other hand, polyacetylene has an extended  $\pi$  system; as a result, density matrix elements between relatively distant atoms are significant. As effects arising from truncating the exchange integrals are most evident in this type of system, convergence is markedly slower, seven unit cell being required in order to ensure that the heat of formation per monomer unit is acceptably close to the limiting value of 13.59 kcal/mole. The electronic structure of most organic polymers is likely to be intermediate between these two extreme structures, very few having either a more localized structure than polyethylene or a more delocalized structure than polyacetylene. According to Huckel theory,  $\pi$  systems with  $4n$   $\pi$  electrons are predicted to be less stable than analogous systems with  $4n + 2$   $\pi$  electrons. This results from the biradical nature of  $\pi$  systems with  $4n$   $\pi$  electrons. This effect is vividly demonstrated in the polyacetylene calculation. From Table 1 it is seen that those compound unit cells comprising an even number of monomers, the  $4n$   $\pi$  systems, are less stable than the adjacent compound unit cells. Even more dramatic is the variation in geometry of the compound unit cells with an increasing number of monomer units. Huckel theory predicts that  $4n + 2$  systems should have enhanced stability due to delocalization. This is seen in the trimer, where all C—C bond lengths are calculated to be equal. The trimer is isoelectronic with benzene and has a similar heat of formation—benzene: 21.21 kcal/mole vs. the trimer 25.3.

### 3. HEATS OF FORMATION

Values for the heats of formation for several polymers and their precursors were calculated; the results are presented here in Table 3 along with the values listed in the *Polymer Handbook* [7]. As the treatment described here is limited to isolated systems only, only those polymers for which gas-phase data are available are considered. The first set of polymers are those resulting from an olefin monomer polymerizing to form a saturated polymer. As MNDO reproduces the heats of formation of linear alkanes and olefins accurately, the error in the heat of formation of polyethylene is very low. Thus the experimental heat of formation [8] per CH<sub>2</sub> unit in a long-chain alkane converges asymptotically on -4.9 kcal/unit compared with the calculated value of -4.71. A one-dimensional nearest neighbor MNDO model [2] predicted the heat of formation per CH<sub>2</sub> unit as -4.624 kcal/unit, and with inclusion of second-nearest neighbor terms a value of -4.684 kcal/unit was obtained. This can be compared with the change in heat of formation per CH<sub>2</sub> unit calculated [2] using MNDO of -4.704 kcal/mole.

**Table 3.**  
Heats of formation  $\Delta H_f$  of polymers

Polymer	Chain configuration	$\Delta H_f$		Heat of polymerization		Diff.
		Monomer (kcal/mole)	Polymer	Calc.	Expt <sup>a</sup>	
Polyethylene	2*1/1	15.3	-9.4	24.7	22.3	+2.5
Isotactic polypropylene	2*3/1	4.9	-6.1	11.0	20.7	-9.9
Syndiotactic polypropylene <i>trgg</i>	4*2/1	4.9	-6.9	11.8	20.7	-9.1
Syndiotactic polypropylene <i>trgg</i>	4*4/1	4.9	-6.7	11.6	20.7	-9.3
Poly(1-butene)	2*3/1	0.3	-2.4	2.7	20.7	-18.0
<i>Trans</i> 1,4-poly(buta-1,3-diene)	4*1/1	28.9	6.0	22.9	18.6	+4.3
<i>Cis</i> 1,4-poly(buta-1,3-diene)	8*1/1	28.9	6.7	22.2	18.6	+3.6
Syndio 1,2-poly(buta-1,3-diene)	4*1/1	28.9	17.0	11.9		-5.5
Iso 1,2-poly(buta-1,3-diene)	2*3/1	28.9	17.0	11.7	17.4	-5.5
Poly( <i>cis</i> -1,4-isoprene)	4*2/1	18.8	9.6	9.2	16.8	-7.6
Poly( <i>trans</i> -1,4-isoprene)	4*1/1	18.8	7.1	11.7	16.8	-6.2
Poly(vinyl chloride)	4*1/1	4.9	-13.6	18.5	17.0	+1.3
Poly(tetrafluoroethylene)	2*4/1	-130.4	-169.2	38.8	37.0	+1.8
Isotactic polyacrylonitrile	2*1/1	44.1	33.0	11.1	18.3	-7.2
Syndiotactic polyacrylonitrile	4*1/1	44.1	30.7	13.4	18.3	-4.9
Nylon-6	7*2/1	-52.1	-50.4	-1.7	3.8	-5.5
Nylon-66	14*1/1	-86.7 <sup>b</sup>	-100.6	13.9		
Polyformaldehyde	2*1/1	-33.0	-40.3	7.3	7.4	+0.1
Poly(ethylene oxide)	2*1/1	-15.5	-41.7	25.2	24.9	+0.3
Poly(propylene oxide)	4*1/1	-37.1	-44.5	7.4	18.1	-10.7
Poly(tetramethylene oxide)	8*1/1	-59.3	-51.1	-8.2	5.0	-13.2
Poly(methyl methacrylate)	4*1/1	-77.9	-44.0	-33.9		
Poly(methacrylic acid)	4*1/1	-81.4	-57.5	-23.9		

<sup>a</sup>See ref. 6.

<sup>b</sup>See text.

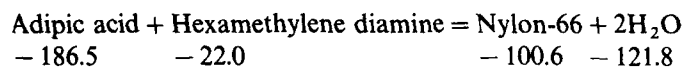
When the resulting polymer is sterically crowded, for example in poly(methyl methacrylate) the calculated heat of polymerization is markedly low, even to the point of predicting the polymer to be unstable with respect to the monomer. This is not altogether unexpected, being a consequence of a known defect in MNDO, namely the overestimation of the core-core repulsion energy [9]. On the other hand, the relative heats of polymers in different chain configurations are predicted accurately. Thus the calculated heats of formation of the two different forms of syndiotactic polypropylene, the all *trans* [10] form and the *trans-trans-gauche-gauche* [11] form, are predicted to have almost equal values, the all *trans* form being more stable by only 0.2 kcal/mole. Although the heat of polymerization,  $\Delta H_p$ , of polyformaldehyde and poly(ethylene oxide), are calculated accurately, the  $\Delta H_p$  of poly(propylene oxide) and poly(tetramethylene oxide) are severely in error. MNDO reproduces the heat of formation of ethers and polyethers accurately, but the  $\Delta H_f$  of small ring ethers are not well reproduced as shown in Table 4.

Only one condensation polymer is represented: nylon-66. In nylon-66 hexamethylene diamine and adipic acid condense to form poly(hexamethylene adipamide) with

**Table 4.**  
Heats of formation of Ethers

Molecule	Calculated	$\Delta H_f$ (kcal/mole)	
		Exp.	Diff.
Dimethyl ether	-51.2	-44.0	-7.2
Diethyl ether	-59.9	-60.3	+0.4
Di- <i>n</i> -propyl ether	-71.7	-75.7	+4.3
Di- <i>n</i> -butyl ether	-80.8	-79.8	-1.0
Formaldehyde	-32.9	-25.9	-7.0
Ethylene oxide	-15.5	-12.6	-2.9
Propylene oxide	-37.3	-22.6	-14.7
Tetrahydrofuran	-59.3	-44.0	-14.3
Tetrahydropyran	-62.0	-53.4	-8.6

the elimination of water. The MNDO heats of formation for this reaction are:



The  $\Delta H_p = 13.9$  kcal/mole is thus the heat of formation of nylon-66 plus two moles of water less the heat of formation of the precursors.

#### 4. UNIT CELL SIZES

Calculated and observed polymer repeat distances, usually a multiple of the monomeric unit, are presented in Table 5. In some polymers several chain configurations are observed, for these systems only the highest symmetry chain has been calculated.

In every case the calculated repeat distance is larger than that observed. MNDO predicts C—C bond lengths accurately with an average error of only 0.012 Å, but C—C—C bond angles are systematically too large by about 2 degrees. The net effect is that the  $C_1$ — $C_3$  distance is increased with the result that the calculated translation distances are uniformly too large.

#### 5. OTHER PROPERTIES

As the Hamiltonian used is that of MNDO, other properties such as interatomic distances and angles, charge separations, bond orders, vibrational frequencies, thermodynamic properties, etc, will be predicted with exactly the same accuracy as the molecular analogues. The eigenvalue spectrum as calculated consists of a set of discrete levels rather than bands. In order to obtain a band structure a full solid-state calculation involving sampling  $k$ -space at several points would be needed.

#### 6. COMPUTATIONAL ASPECTS

Computation times for one SCF calculation for various monomers and their polymers are shown in Table 6. Two factors contribute to the increase in time required to calculate polymer geometries. First of all, the unit cell may need to be a multiple of the fundamental unit cell in order to accurately represent the polymer chain. For large

**Table 5.**  
Polymer repeat distances

Polymer	No. of monomers in repeat distance	Repeat distance (Å)	
		Calc.	Expt.
Nylon-6	2	17.705	17.2
Nylon-66	1	17.712	17.2
Polyethylene	1	2.582	2.54
Poly( <i>trans</i> -1,4-isoprene)	1	5.133	4.75
Syndiotactic polyacetonitrile	2	5.190	5.1
Polytetrafluoroethylene	1	2.810	2.62
Polyacetylene	1	2.504	2.43
Syn 1,2-poly(buta-1,3-diene)	2	5.187	5.14
Iso 1,2-poly(buta-1,3-diene)	3	6.743	6.5
<i>Trans</i> 1,4-poly(buta-1,3-diene)	1	5.084	4.9
<i>Cis</i> 1,4-poly(buta-1,3-diene)	2	9.359	8.6
Syndiotactic polypropylene <i>tttt</i>	2	5.145	5.05
Syndiotactic polypropylene <i>ttgg</i>	4	7.965	7.40
Syndiotactic polyvinylchloride	2	5.181	5.1
Isotactic polypropylene	3	6.699	6.49
<i>Trans</i> -isoprene	1	5.133	4.7
<i>Cis</i> -isoprene	2	9.218	8.1
Poly(ethylene oxide)	2	7.170	7.1
Poly(propylene oxide)	1	4.895	4.8
Poly(tetramethylene oxide)	2	12.308	12.1
Poly(acrylic acid)	2	5.361	—
Poly(methyl acrylate)	2	5.351	—
Poly(methyl methacrylate)	2	5.399	—

**Table 6.**  
Computational times for one SCF

Molecule	CPU time(s)	Cluster	CPU time(s)
Ethylene	2.22	(CH <sub>2</sub> ) <sub>6</sub>	30.64
Caprolactam	54.85	((CH <sub>2</sub> ) <sub>5</sub> CONH) <sub>2</sub>	374.65
Butadiene	8.08	(CH <sub>2</sub> CHCHCH <sub>2</sub> ) <sub>2</sub>	52.37
Adipic acid	73.90		
Hexamethylene diamine	64.03	(CH <sub>2</sub> ) <sub>5</sub> CONH(CH <sub>2</sub> ) <sub>6</sub> NHCO	371.77
Water	1.08		
Tetrahydrofuran	16.53	((CH <sub>2</sub> ) <sub>4</sub> O) <sub>2</sub>	105.66
Propene	5.46	(CH <sub>2</sub> CHCH <sub>3</sub> ) <sub>3</sub> (Iso)	98.04
Formaldehyde	2.00	(CH <sub>2</sub> O) <sub>6</sub>	126.79

monomers, e.g. the precursors of nylon-66, one monomer may be sufficient. Secondly, the time taken to evaluate the overlap and two-center two-electron integrals is increased in proportion to the number of neighboring unit cells. For polymers this involves the central unit cell interacting with a total of three unit cells, itself and the two adjacent unit cells. As the secular determinant and two-electron integral strings are of the same size as the molecular analogue, the time required for iterating to self-consistency is not increased.

## 7. DISCUSSION

It is not necessary to perform a full solid-state calculation in order to accurately apply the MNDO technique to polymers; a considerably simplified cluster approach in which the Born-von Kärman [13] cyclic boundary conditions are applied to a large unit cell is quite adequate for most calculations of chemical interest. There are, however, various limitations of the cluster approach which must be recognized.

In order to use the cluster model, the translating unit cell must be large enough to ensure that atoms at one end of the cluster have a negligible density matrix element with atoms at the other end of the cluster. For small fundamental unit cells, this will necessitate the use of several unit cells in order to achieve a sufficiently large cluster. A simple test of the size of the cluster is to increase the cluster by one unit cell and recalculate the heat of formation. If the heat of formation per fundamental unit cell is unchanged, then the original cluster size was adequate.

This constraint on the size of the cluster is not as limiting as might appear at first sight. Most polymers of interest involve quite large fundamental translation vectors, either as a result of the constituent monomer units being large, such as those in nylon-66, or the presence of several monomers in the fundamental repeat unit, such as in isotactic polypropylene. In those few instances when the repeat unit is small, two or more repeat units will be required in order to obtain a sufficiently large cluster.

A more basic limitation to the method described here is inherent in the MNDO formalism. Both the precursors and the polymers are treated as if they were isolated, that is, no intermolecular forces are considered. In order to allow the computational study of polymers in the condensed phase, intermolecular forces must be included. A reparametrization of MNDO in which the core-core repulsion is modified by the inclusion of gaussian functions has been carried out. Using this new method, called AM1 [9], condensed states of polymers and precursors should be amenable to study.

A simple way to calculate polymer properties is to calculate the properties of the monomer and the first few oligomers, and by extrapolation estimate the properties of the high polymer. The main defect of such an approach is the large number of separate calculations necessary in order to determine precisely the effects of the end groups. For large systems the time required would be prohibitive. Thus, using MNDO the time required on a CRAY XMP computer to calculate the heat of formation of polydiacetylene was in excess of two hours [14]. This limitation is effectively removed by use of the cluster model allowing polymer calculations to be carried out with little more difficulty than encountered when similar molecules and ions are calculated at present.

The cluster model as a model for polymers can be regarded as intermediate between the oligomer approach and a full solid state treatment. Ideally properties of chemical interest would be calculated by the cluster model, and properties of primarily physical interest, such as conductivity and band structure, would be calculated using a full solid-state calculation involving sampling of the Brillouin Zone using a regular mesh.

The high speed of the method arises from the fact that the operations involved during the iterations required to achieve a self-consistent field are identical to those in the molecular analogue. Thus isotactic polypropylene, with nine heavy atoms in the repeat unit, requires little more time than adipic acid with ten heavy atoms. Any increase in speed arising as a result of symmetry factorizing the Fock matrix in more conventional solid-state methods is offset by the computational simplicity of the cluster model. For example, the number of one and two electron integrals that need to be stored is no

larger than that required for the molecular analogue. This model should therefore find particular application in *ab initio* work, where the two-electron integral lists required for solid-state work could be considerably reduced in length with concomitant saving in storage space.

The cluster method has been incorporated into the MOPAC program [15] available through the Quantum Chemistry Program Exchange, beginning with MOPAC Version 3.0. Derived polymer properties such as elastic moduli can be readily calculated using this program [16].

## 8. CONCLUSION

The frequently used MNDO technique combined with a simple cluster model provides a powerful tool for the study of organic polymers. Average errors in heats of polymerization are comparable with the average errors in heats of formation of molecules. Where polymerization reactions results in sterically crowded polymers, calculated  $\Delta H_p$  are systematically low, and allowance must be made for this. In extreme cases, for example poly(methyl methacrylate), the polymer is predicted to be unstable with respect to the monomer. As this is a defect in the MNDO method rather than in the cluster model, improvements in the Hamiltonian should alleviate this problem.

Lattice repeat distances are predicted accurately including those in cases where different chain conformations are possible.

A limitation of the cluster model—that the repeat unit must be large—is circumvented for systems with small repeat distances by use of a multiple unit cell. On the other hand, the method is ideally suited for polymers with intrinsically large monomeric units or polymers with several monomer units in the chain configuration.

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