

Notes

A Theoretical Synthesis of Poly(methyl methacrylate) (PMMA) by the Molecular Orbitals Calculation

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Abstract : The theoretical synthesis of the isotactic and syndiotactic poly(methyl methacrylate) were carried out as a model for real polymerization reactions following the normal chain reaction processes by repeating the uniform localization of wave functions with inclusion of the interaction between the end group of the cluster and an attaching molecule by the elongation method, and then, the calculated value was compared with the usual PM₃ calculation. The results revealed that a reaction of cluster with monomer molecules has made it possible to calculate the electronic structure and total energy of polymer with nearly infinite length and a matrix of constant dimension. The isotactic poly(methyl methacrylate) is more stable than syndiotactic one. The same tendency have been found between the experimentally measured pro-perties and a calculated total energy to explain the chain motion in isotatic and syndiotactic poly(methyl methacrylate).

Introduction

Quantum chemical calculations have been common and useful tools to investigate the electronic structures and geometries of small molecules,¹ but for large molecules or molecular clusters, such calculations have been difficult because their large sizes require enormous computational effort. Especially for polymer systems, it is impossible and unrealistic to treat a whole polymer chain, so it is inevitable to apply some kind of approximation to molecules themselves. For problems like these, several approaches have been presented to describe the effects of defects^{2,4} as well as end effects.⁵ Although there have been few investigations on systems with aperiodic arrangements of units, there have been some attempts for solving this type of problem with an averaging technique for the Hamiltonian.⁶

Recently Imamura proposed a new approach to this problem.⁷⁻¹¹ In this treatment the molecular

orbitals of an oligomer are first localized in a specified part of the molecule by uniform localization.¹² Next, the canonical molecular orbitals (**CMOs**) of an approaching monomer are added and the eigenvalue problem is solved after dropping some localized molecular orbitals (**LMOs**) which have no interaction with the monomer. By repeating this procedure, we can extend the chain length of polymer as long as we want.

In other words, this elongation method can be considered as a procedure for the theoretical synthesis of a polymer. We applied this theoretical synthesis method to calculate the electronic structure of poly(methyl methacrylate) (PMMA).

PMMA is an example of a disubstituted vinyl chain in which the substituents -COOCH₃ and -CH₃ differ in size and shape. The former is noncylindrical, and the latter resembles methylene(CH₂) in its effective size.

Method

This new approaching method for calculating

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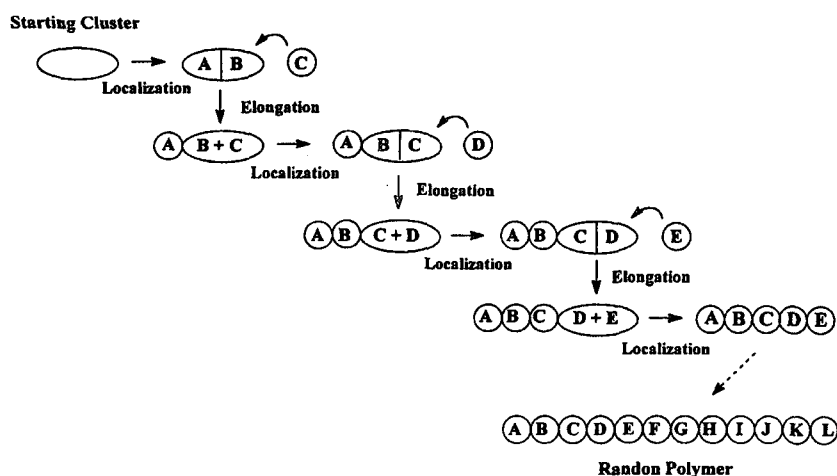


Figure 1. A schematic illustration for the procedure of the theoretical synthesis of a random polymer by the uniform localization molecular orbital method.

the electronic structure of polymers efficiently, is proposed as a model for real polymerization reactions following the normal chain reaction processes of initiation, propagation, and termination. The calculations are carried out by repeating the uniform localization²¹ of wave functions with inclusion of the interaction between the end group of the cluster and an attacking molecule as shown in Figure 1.

As a starting point, we choose a cluster which is an oligomer consisting of an appropriate number of n monomer units. The canonical molecular orbitals (CMOs) of this cluster $\{\psi_i\}$ are obtained as following:

$$\Psi_i = \sum_r^{all} C_{ir} \chi_r \quad (1)$$

where χ_r indicates the r th atomic orbital (AO) of the cluster. The cluster is then divided into two parts, A and B, with on the assumption that a new monomer is added to the end of B, as shown in Figure 2. Part A is the furthest in space from the attacking monomer and, in this study, usually consists of one unit. For the defined regions A and B, particular CMOs are localized in the region A and the others are in the region B among CMOs $\{\psi_i\}$ by using an appropriate unitary transformation, that is, the uniform transformation.

The details of this procedure were omitted here

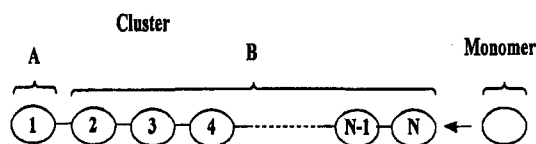


Figure 2. A schematic illustration of the region A and the region B defined in the cluster. The A part is represented by one unit.

and found in the relevant references.^{7, 12}

Next, the molecular orbital calculations are carried out for the system in which the cluster interact with a monomer approaching one end of the B part (see Figure 2). The eigenvalue problem for this system is represented with the occupied and the vacant LMOs as

$$\begin{vmatrix} H^{occ}(A,A)-\epsilon I & 0 & H^{occ}(A,B) & 0 & 0 \\ 0 & H^{occ}(A,A)-\epsilon I & 0 & H^{occ}(A,B) & 0 \\ H^{occ}(B,A) & 0 & H^{occ}(B,B)-\epsilon I & 0 & H^{occ}(B,M) \\ 0 & H^{occ}(B,A) & 0 & H^{occ}(B,B)-\epsilon I & H^{occ}(B,M) \\ 0 & 0 & H^{occ}(M,B) & H^{occ}(M,B) & H(M)-\epsilon I \\ -\epsilon S^{occ}(M,B) & -\epsilon S^{occ}(M,B) & & & \end{vmatrix} = 0 \quad (2)$$

where $H^{occ}(X,Y)$ indicates the matrix of Hamiltonian between the X part and the Y part of the cluster in the occupied space. The matrix element for

$H^{\text{occ}}(X, Y)$ is given as follows:

$$H_{ij}^{\text{occ}}(X, Y) = \int \phi_i^{\text{occ}}(X) H \phi_j^{\text{occ}}(Y) d\tau \quad (3)$$

where $\phi_i^{\text{occ}}(X)$ is the i th occupied orbital localized on the X part. The same notation is used for the vacant space. An M is used to denote the **CMOs** of the attacking monomer. I is a unit matrix and ϵ indicates eigenvalues. It should be pointed out that the matrices between the occupied space and the vacant space of the cluster vanish completely since all the matrix elements between the canonical occupied and the vacant orbitals are zero. This feature is retained throughout the unitary transformation among the occupied or the vacant orbitals. The notation ~ 0 denotes that the corresponding matrix elements have negligibly small values. The characteristic feature of this matrix is that the elements between the A part and the monomer are very small. This is a consequence of the fact that $\phi_i(A)$ is the i th orbital localized on the A part and $\phi_j(M)$ is the j th **CMO** of the monomer, and the distance between the A part and the monomer is large enough to be able to neglect the matrix elements

$$\begin{aligned} H_{ij}^{\text{occ}}(A, M), S_{ij}^{\text{occ}}(A, M) \\ \text{and } H_{ij}^{\text{vac}}(A, M), S_{ij}^{\text{vac}}(A, M) \end{aligned} \quad (4)$$

Thus when we solve Eq. (2), the matrix elements between the A part and the B part and also those between the A part and the monomer are deleted completely. In other words, we solve the eigenvalue problem including only the B part and the monomer which is shown by dotted line in Eq. (2).

The sequential procedure of localization with **CMOs** of the cluster, calculation of the interaction with an attacking monomer, followed by elongation of the cluster represent one cycle of this method. In the next cycle, the A part is lengthened by one unit (to the left in Figure 2). The same procedure is repeated, and the cluster is extended by one more unit.

The theoretical synthesis method was applied to isotactic and syndiotactic PMMA in order to discuss the total energies and electron density distribution in the frame work of the single chain itself. The bond lengths and bond angles of methylmetacrylate

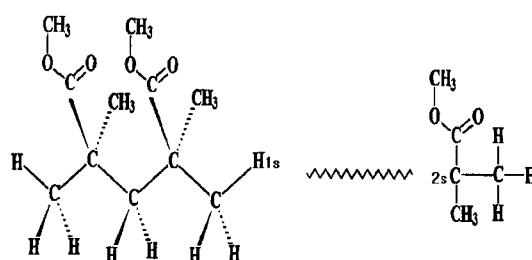


Figure 3. A schematic illustration of the procedure for the calculation.

monomer were taken from a general literature.¹⁷ The geometry optimization of all PMMA cluster are carried out by the PM₃ method.

Our calculations follow the procedure shown in Figure 3, although the polymerization process used in the scheme is hypothetical for convenience.

As the initiation step, we obtain the canonical MOs of the starting cluster, CH₃C(CH₃)(COOCH₃)CH₃. Then the cluster is elongated by adding the segment, CH₂C(CH₃)(COOCH₃)-H one after another, and these procedures simulate the experimental polymerization reaction.

In these calculations, we used a slightly tricky technique in order to keep the electronic structure of the oligomers to the singlet state as has been done in the previous paper.⁹ That is, the growing terminal is always capped by a hydrogen atom.

So the cluster remains to be closed shell throughout the elongation calculations, and the extension of cluster can be regarded as the "substitution" of a terminal hydrogen 1s orbital by the carbon 2s orbital of methylene group in the adding segment. In this procedure, MO coefficients of a terminal hydrogen atom in the original oligomer lose their basis functions, thus they must be regarded as the coefficients of the 2s orbital of the methylene carbon atom in the extended oligomer. This situation is schematically shown in Figure 3. Finally, the calculations of the required polymer is finished by adding the terminal group, CH₂C(CH₃)₂(COOCH₃).

Results and Discussion

PMMA is a disubstituted vinyl chain in which the substituents COOCH₃ and CH₃ differ in size and shape; the former is noncylindrical, and the latter

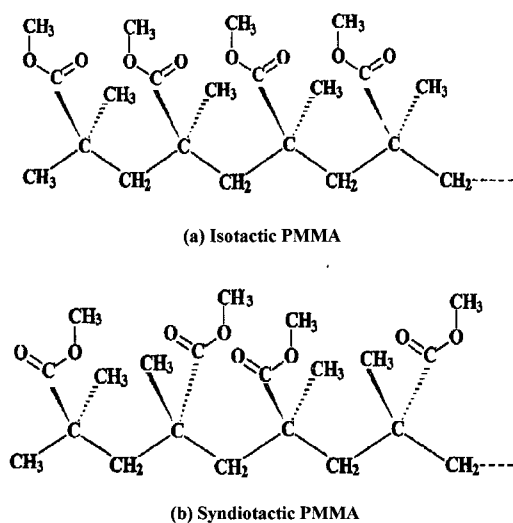


Figure 4. A isotactic and syndiotactic stereoregular chain of PMMA.

resembles the CH_2 skeletal group in its steric interactions. Owing to the planarity of the ester group, severe steric overlaps involving one or the other of its O atoms occur in conformation of a skeletal bond of irrespective of the rotational states of neighboring bonds.¹⁸ The difference between isotactic and syndiotactic stereoregular chains of PMMA is as shown Figure 4.

The physical properties of polymers are determined by the frequency spectra of their chain motions. The nuclear magnetic resonance (n.m.r) and spin-lattice relaxation experiments are the principal techniques used to investigate molecular motion of polymers in solution.

It is particularly interesting to note that n.m.r. studies on back bone chain motion of isotactic PMMA yield a lower value for activation energy (E_a). The value is $E_a = 15.5 \text{ kJ mol}^{-1}$ compared with $E_a = 23\text{-}25 \text{ kJ mol}^{-1}$ for the syndiotactic material¹⁹ and ^{13}C spin-lattice relaxation times (T_1) of the protons in isotactic PMMA were always longer than that of the comparable protons in the syndiotactic polymers.

The spin-lattice relaxation times (T_1) of carbon in isotactic PMMA was longer than that of the comparable carbon in syndiotactic polymer. These results are parallel to those for the proton's case.^{20, 21}

As another case,²² the incoherent inelastic neutron scattering spectroscopy which is particularly

well suited to the observation of torsional motion and vibration, because selection rules do not apply, was applied to study the torsional motions of side-groups in poly(propylene oxide), PMMA and poly (α -chloro methacrylate).

The potential function $V(\phi)$ for hindered internal rotation of a three-fold symmetric top about its axis of symmetry (in this case the bond joining the side group to the main chain) is assumed to be of the form:

$$V(\phi) = \frac{V_3}{2}(1 - \cos 3\phi) \quad (5)$$

$V_3 = 34.3 \text{ kJ mol}^{-1}$ found for the α -methyl group in syndiotactic PMMA is the most interesting feature. $V_3 = 13.8 \text{ kJ mol}^{-1}$ must be regarded as a normal value for a methyl group with an aliphatic main chain. V_3 for the $\alpha\text{-CH}_3$ group in isotactic and syndiotactic sequence of PMMA is the marked difference.

Such a large difference has never been reported for stereoisomer of small molecules and it have not observed same effects in other polymers arising from variations in stereoregular character.

In view of the tentative lower value of V_3 for $\alpha\text{-CH}_3$ groups in isotactic sequences than in syndiotactic sequences, it is particularly interesting to note that n.m.r studies on isotactic PMMA yield a lower value for activation energies too.

The result strongly indicates that the isotactic polymer chain has a greater mobility comparing with the syndiotactic one. The mobility appears to decrease with an increase in the bulkiness of the ester group in both isotactic and syndiotactic polymers.

The differences in infrared absorption characteristics between syndiotactic and isotactic PMMA were found over the entire spectral region of 2000 to 650 cm^{-1} .

The total energies for various length of cluster were calculated by both the present elongation method and the usual PM_3 method in Table I.

It is clear that the agreement between the two method is excellent and the elongation method is reliable enough for the PMMA containing polar group.

The atomic and bond population calculated by the elongation method are listed along with those

Table I. A Total Energies of the Syndiotactic and Isotactic PMMA

Cluster No*	Total Energy (eV)				ΔE (Iso-Syn)
	Syndiotactic Elongation	PM ₃	Isotactic Elongation	PM ₃	
1	-2936.1608	-2936.1608	-2935.6794	-2935.6794	0.4834
3	-5836.4855	-5836.4855	-5838.7627	-5838.7627	-2.2771
5	-8736.7980	-8736.7980	-8741.8487	-8741.8487	-5.0507
7	-11637.1115	-11637.1115	-11644.9364	-11644.9364	-7.8249
9	-14537.4259	-14537.4259	-14548.0244	-14548.0244	-10.5985

*The number of cluster is n of the $\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3)_n$ in PMMA.

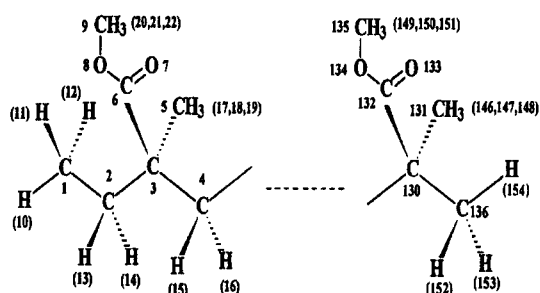


Figure 5. The numbering of atom in the theoretical synthesized PMMA consists of 10 cluster.

calculated by the usual PM₃ method. For simplicity, the populations of both end part are compared for the 10 cluster PMMA system in Figure 5 and Table II.

It is clear that the atomic and bond populations determined by the two methods are in excellent agreement for the end parts.

Moreover, the populations in one end part are also in excellent agreement with those in another end part, that is, the symmetry in the electron distributions is naturally conserved by the elongation method.

Conclusion

The syndiotactic and isotactic PMMA bears two different substituents which are hydrophobic and slightly hydrophilic group. The electronic structure and total energy of both stereoisomer were calculated by the elongation method. although the polymerization process used in the scheme is hypothetical for convenience. The calculations were carried out through a real polymerization reactions following the normal chain reactions process of initiation, propagation and termination, and compared with those obtained by usual method at

Table II. A Total Electron Density on Carbon and Hydrogen Atoms in the Chain of PMMA

	Syndiotactic		Isotactic	
	Elongation	PM ₃	Elongation	PM ₃
C ₁	4.0878	4.0870	4.1172	4.1173
C ₂	4.0525	4.0526	4.0237	4.0237
C ₃	4.1097	4.1097	4.1214	4.1215
C ₄	4.0544	4.0544	4.0574	4.0574
C ₅	4.1521	4.1521	4.1544	4.1544
C ₆	3.5932	3.5932	3.6487	3.6488
O ₇	6.3887	6.3888	6.3845	6.3846
O ₈	6.2723	6.2723	6.2731	6.2731
C ₉	3.9199	3.9199	3.9321	3.9321
C ₁₃₀	4.1710	4.1711	4.1155	4.1156
C ₁₃₁	4.4350	4.4350	4.1700	4.1701
C ₁₃₂	3.5902	3.5903	3.6403	3.6403
O ₁₃₃	6.3904	6.3904	6.3714	6.3714
O ₁₃₄	6.2691	6.2692	6.2759	6.2760
C ₁₃₅	3.9217	3.9216	3.9351	3.9351
H ₁₀	0.9534	0.9535	0.9503	0.9504
H ₁₁	0.9575	0.9575	0.9156	0.9157
H ₁₂	0.9393	0.9393	0.9590	0.9590
H ₁₃	0.9227	0.9227	0.9409	0.9410
H ₁₄	0.9278	0.9278	0.9102	0.9103
H ₁₅	0.9377	0.9378	0.9537	0.9538
H ₁₆	0.9450	0.9450	0.8937	0.8938
H ₁₇	0.9390	0.9390	0.9445	0.9446
H ₁₈	0.9495	0.9495	0.9403	0.9404
H ₁₉	0.9474	0.9474	0.9484	0.9484
H ₂₀	0.9493	0.9494	0.9586	0.9587
H ₂₁	0.9496	0.9496	0.9417	0.9417
H ₂₂	0.9537	0.9537	0.9549	0.9550
H ₁₄₆	0.9351	0.9352	0.9466	0.9466
H ₁₄₇	0.9019	0.9019	0.8617	0.8618
H ₁₄₈	0.9248	0.9249	0.9430	0.9430
H ₁₄₉	0.8935	0.8935	0.9114	0.9115
H ₁₅₀	0.9280	0.9280	0.9537	0.9537
H ₁₅₁	0.9205	0.9206	0.8925	0.8925
H ₁₅₂	0.9534	0.9535	0.9503	0.9504
H ₁₅₃	0.9575	0.9575	0.9156	0.9157
H ₁₅₄	0.9393	0.9393	0.9590	0.9580

PM₃ level.

It is clear that the agreement between the two methods is excellent in the electronic density distribution in both end part of polymer. A reaction of a cluster with monomer molecules has made it possible to calculate the electronic structure of polymers with nearly infinite length with a matrix constant dimension. The magnitudes of the activation energies suggest that the observed side-group motion is predominantly a torsional motion, and that the hindering barrier is largely intramolecular in character and all these experimental results indicate that the isotactic PMMA is more flexible than the syndiotactic one.¹⁹

From the calculated total energy of PMMA, the isotactic PMMA is more stable than syndiotactic one. An examination of these energies indicates that methyl side group and backbone motion in isotactic and syndiotactic PMMA are linked together. The reason that the isotactic PMMA is more stable than the syndiotactic one comes from the variations in stereoregular character such as α -methyl side group effect.

In other words, in the isotactic PMMA the intramolecular interaction make this system more stable. Accordingly, it should reasonably be expected that isotactic PMMA has a diversity of stable structures and thus is flexible in nature. The detailed study on the flexibility of isotactic PMMA is now in process.

The same tendency has been found between the experimentally measured activation energy, ¹³C spin lattice relaxation time and the calculated results.

The elongation method has been found to be reliable enough and widely applicable.¹⁻¹¹ In the present paper, the elongation method was proved to be also reliable and applicable for the nonperiodical and polar polymers with fairly long side chain. This results are encouraging for the theoretical study on the physicochemical properties of real polymers with long side chains.

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