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Electronic Structure and Ground State Properties of PMMA Polymer: I. Step-By-Step Formation and Stereo-Regularity of the Polymeric Chain—AM1-MO Treatment

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Electronic Structure and Ground State Properties of PMMA Polymer: I. Step-By-Step Formation and Stereo-Regularity of the Polymeric Chain—AM1-MO Treatment

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The equilibrium ground state geometric parameters of benzoyl peroxide (as free radical initiator), methylmethacrylate monomer (as a reference molecule), benzoyl-MMA radical (I), phenyl-MMA radical (II) and the three polymeric chain of PMMA (syndiotactic, isotactic, and atactic) are investigated theoretically using AM1-MO method. The stability of phenyl, benzoyl-MMA radicals, and the conformational properties of isotactic, syndiotactic, and atactic structures of PMMA polymers are discussed. The initiation and propagation steps of polymerization are investigated theoretically. The calculated geometric parameters are analyzed in terms of heat of formation, total energy, dipole moment, net charge, ionization potential, electron affinity, energy gap, and charge density maps (Total, HOMO, and LUMO).

Keywords: PMMA, benzoyl peroxide, molecular orbital calculations, geometry optimization, charge density

INTRODUCTION

The structures of simple carboxylic esters have received considerable elucidation from studies of dipole moments [1–4]. The conclusion from these studies is that simple aliphatic esters do not have free rotation

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about the carbonyl carbon ether oxygen bond but are planar with cis-configuration [5].

Poly(methyl methacrylate) is an example of a disubstituted vinyl chain in which the substituents COOCH_3 and CH_3 differ in size and shape: the former is noncylindrical and the latter resembles the CH_2 skeletal group in its steric interactions. Conformational energy calculations using conventional empirical methods was investigated in order to clarify the character of various interactions in the PMMA chain [6].

Oligomers of poly(methyl methacrylate) (PMMA) are interesting substances because of their stereochemistry in free radical oligomerization. The molecular structure of PMMA was the object of theoretical investigation in several chain sequences [6–12]. There is interesting research in C^{13} -NMR [13,14], X-ray crystal structure analysis, and ^1H -NMR spectroscopy [15]. Furthermore, there is previous molecular-orbital calculation of their interaction with Al-atom [16]. Also, an approach to the molecular structure of PMMA oligomers in case of anionic oligomerization by means of semi-empirical molecular-orbital calculations was carried out [17].

X-ray photoelectron spectroscopy (XPS) valence band spectra of PMMA was measured and simulated with the Dmol ab-initio molecular orbital program [18]. The authors performed the calculations with model compounds such as trimers, pentamers, or hexamers of the polymers and they found that the theoretical spectra of the oligomers show a good accordance with the experimental data.

Electron energy loss spectroscopy (EELS) analysis of PMMA was performed in combination with transmission electron microscopy (TEM) in order to evaluate the possibility to obtain chemical information on electron sensitive polymers. The authors found that the different chemical bondings are characterized by slight dependence on the molecular weight of the polymer before the degradation damage, which is in good agreement with molecular orbitals calculations [19].

In the absence of any systematic study of the electronic properties and bonding characteristics of these classes of polymers, most conclusions that relate the activities to structural factors are qualitative. The main objectives of the present article are to:

1. Explore the geometric features of benzoyl peroxide (as initiator) aiming to arrive at reliable ground state electronic structure parameters.
2. Investigate closely the ground state electronic structure parameters and stability of phenyl-and benzoyl-MMA radicals.

3. Theoretically explore the step-by-step formation of the polymeric chain from which the electronic and conformational properties of isotactic, syndiotactic, and atactic structures are discussed.

EXPERIMENTAL

Molecular Orbital Calculations

All molecular orbital calculations are carried out using the reliable semi-empirical AMI-MO method [20], because it takes very good account of the directional character of bonding and describes a polar bond more accurately than do any other method.

RESULTS AND DISCUSSION

This article attempts to present a quantitative interpretation of the electronic structure and ground state properties via total energy, heat of formation, ionization potential, electron affinity, net charge, energy gap and charge density distribution, highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) of (i) Benzoyl peroxide and benzoyl peroxide radical, (ii) Benzoyl-MMA radical and phenyl-MMA radical, (iii) Benzoyl-MMA dimer, Benzoyl-MMA trimer, and (iv) Different forms of the stereoregular structure of PMMA.

Benzoyl Peroxide (Initiator)

The equilibrium ground state geometric parameters of benzoyl peroxide as initiator are fully optimized. All the 3N-6 vibrational modes are considered in the optimization procedure. Full geometry optimization for such large molecule would involve at least 78° of freedom. This is computationally very expensive if one wants to utilize a reasonable basis set at the ab-initio level of theory. Thus the use of the reliable semi-empirical AMI-MO method becomes essential because it takes very good account of the directional character of bonding and describes a polar bond more accurately than do any other methods.

The numbering system, charge density maps (HOMO and LUMO), and final geometry of benzoyl peroxide are systematically presented in Figure 1. Ground state properties of benzoyl peroxide are presented in Table 1. Some general remarks on the obtained data are summarized as follows:

1. The dipole moment computed theoretically for benzoyl peroxide is 6.85 D. The σ -frame of the dipole moment was responsible for its high value.

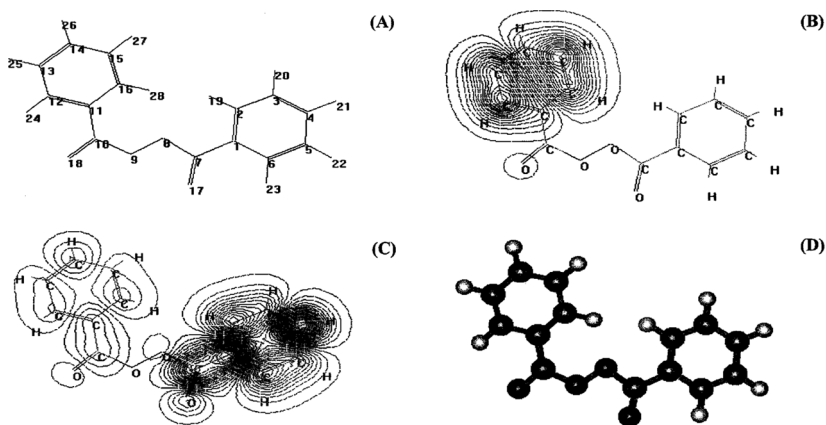


FIGURE 1 Numbering system (A), charge density maps (HOMO (B) and LUMO (C)), and final geometry of Benzoyl peroxide.

- The benzoyl peroxide is highly symmetric compound as indicated from the bond length C1–C7, C10–C11, C10–O9, and C7–O8.
- The π -bond order of C1–C7 and C10–C11 are very small (≈ 0.07) indicating no competitive interaction between subsystems (phenyl- and –CO–O–O–CO–). Also, the π -bond order of C7–O8 and C10–O9 are very small (≈ 0.13) which make the cleavage of O8–O9 bond very easy, which explains why benzoyl peroxide is used as initiator in the polymerization process.
- Another reason for the use of benzoyl peroxide as initiator is the symmetrical distribution of the charge densities on different moieties (C7, C10, O17, O18, O8, and O9 atoms) (c.f. Table 1).

TABLE 1 Ground State Properties, π -Bond Order, and Net Charge for Benzoyl Peroxide Initiator

| Ground state properties | Value | π -bond order | | Net charge | |
|---------------------------------|------------|-------------------|----------|------------|------------|
| | | Bond | P- π | Atom | Net charge |
| Heat of formation (Kcal) | -24.377 | C1–C7 | 0.066 | C7 | -0.3441 |
| Total energy (eV) | -3207.509 | C7–O8 | 0.138 | C10 | -0.3431 |
| Electronic energy (eV) | -18168.633 | C7–O17 | 0.902 | O8 | -0.1739 |
| Core-Core repulsion energy (eV) | 14961.124 | O8–O9 | 0.010 | O9 | -0.1106 |
| Ionization energy (eV) | 10.199 | O9–C10 | 0.158 | O17 | -0.2776 |
| Electron affinity (eV) | -0.718 | C10–O18 | 0.879 | O18 | -0.2885 |
| Energy gap (eV) | 9.481 | C10–C11 | 0.067 | | |
| Dipole moment (D) | 6.846 | | | | |

- The HOMO of benzoyl peroxide is of π -type and is 99.49% localized on phenyl. On the other hand, the LUMO is delocalized molecular orbital with considerable charge transfer (CT) from phenyl moiety to $-\text{CO}-\text{O}-\text{O}-\text{CO}-$ moiety.

In the next part of the calculations, the authors tried to find the ground state properties of the monomer MMA and MMA radical in the case of phenyl and benzoyl moiety. Also, the stability of the three structures of polymeric chain (syndiotactic, isotactic, and atactic forms) is discussed.

Methylmethacrylate Monomer

The ground state properties of the methylmethacrylate (MMA) monomer is taken as a reference molecule in the polymeric chain of poly(methylmethacrylate) (PMMA). Numbering system, charge density maps (HOMO and LUMO), and final geometry are represented in Figure 2. The ground state geometric parameters of MMA molecule are summarized in Table 2. Bond length, bond order, and net charge of MMA molecule are shown in Figure 3. Some general remarks can be considered:

- The active centers of MMA are C1, C2 and C3, O5 and O6, which are π -acceptor and σ -donor.
- The bond order of C1–C3 consists of s - σ (0.0968), p - σ (0.3769), and p - π (0.9325) (c.f. Figure 3).

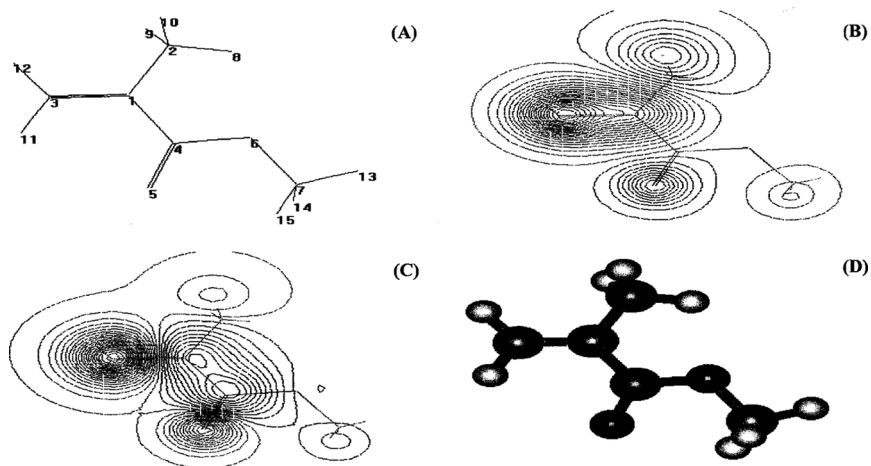


FIGURE 2 Numbering system (A), charge density maps (HOMO (B) and LUMO (C)), and final geometry of methylmethacrylate monomer.

TABLE 2 Ground State Properties for Methylmethacrylate Monomer

| Properties | Value |
|---------------------------------|-------------------------|
| Heat of formation (Kcal) | -75.909 |
| Total energy (eV) | -1391.032 |
| Electronic energy (eV) | -5309.688 |
| Core-Core repulsion energy (eV) | 3918.655 |
| Ionization energy (eV) | 10.467 |
| Electron affinity (eV) | 0.051 |
| Energy gap (eV) | 10.518 |
| Dipole moment (D) | 1.741 |
| Polarizability (EUS) | |
| α | 1.460×10^{-23} |
| β | 0.310×10^{-30} |
| γ | 0.293×10^{-36} |

- The HOMO of MMA is of π -type and is 77.5% localized on C1=C3 and LUMO is of π -type and is 66.8% localized on C1=C3. The moiety C1=C3 is the active part of MMA, especially C1, which is the active center for starting the propagation step.

Methylmethacrylate Radical

In the initiation process of the polymerization reaction of MMA, the initiator benzoyl peroxide decompose to form benzoyl radical or phenyl radical. At low temperature benzoyl peroxide radical is formed whereas at higher temperature CO_2 is evolved, forming phenyl radical. Therefore, phenyl and benzoyl radical may be formed and both could attack the MMA to give the initiator monomer radical. Two radicals may be formed (Scheme 1).

The formation of radical (I) or (II) in the reaction medium depends on the temperature used. From the theoretical calculations the authors tried to find which form (I) or (II) exists at room temperature via the stability, heat of formation, and dipole moment. The ground state properties of (I) and (II) are given in Table 3. The numbering system, charge density maps (HOMO and LUMO), and final geometry are represented in Figures 4 and 5. Some general remarks are given as follows:

- The formation of the radical (I) is more predominant in the reaction medium over (II) as indicated from the heat of formation. The heat of formation of radical (I) is greater than radical (II) by ≈ 80 Kcal/mol.

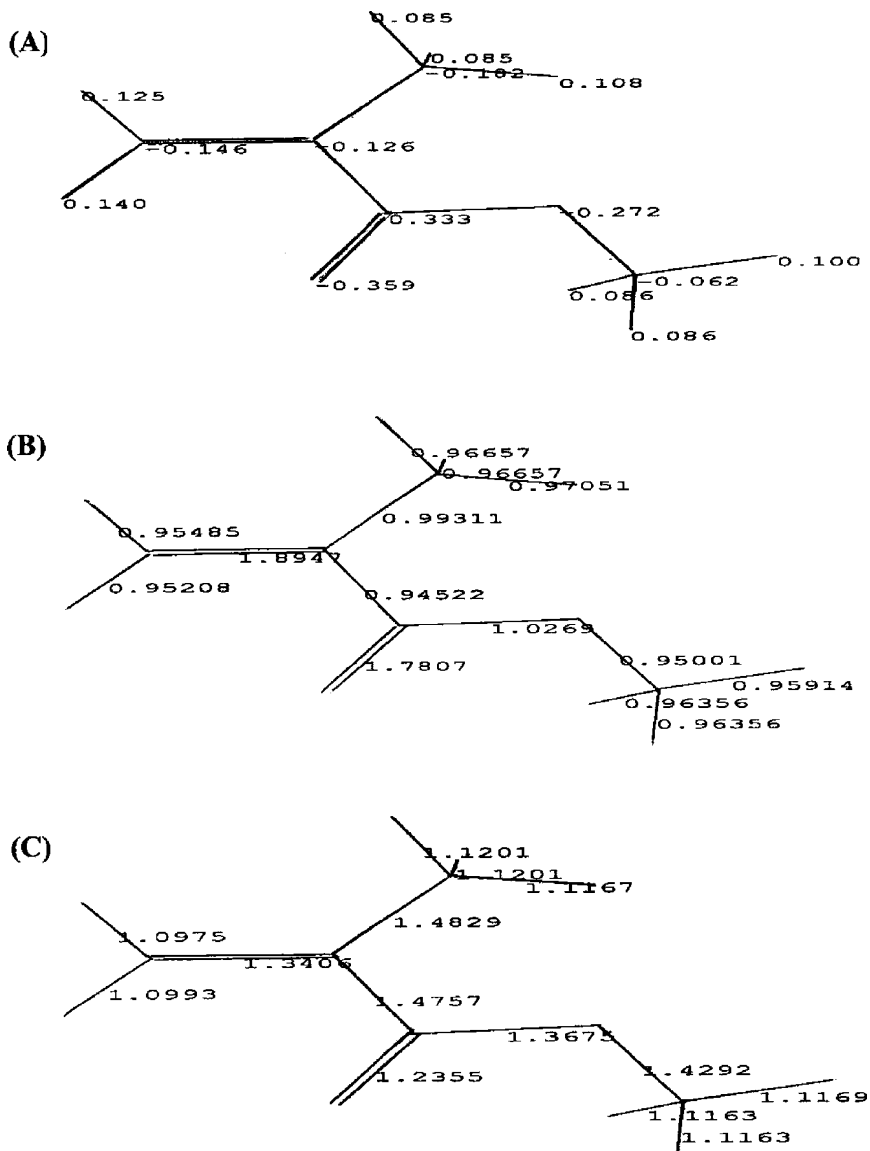
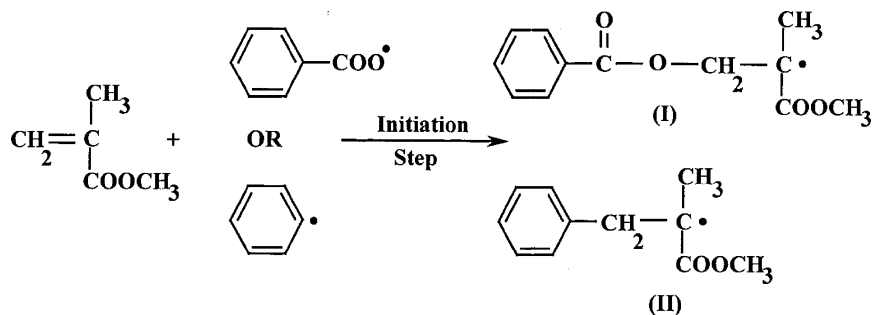


FIGURE 3 Net charge (A), bond order (B), and bond length (C) of MMA.

2. The stability of radical (I) at room temperature is greater than radical (II) as indicated from the total energy. Radical (I) is more stable by about ≈ 769 eV (17730 Kcal), that is, at room temperature there



SCHEME 1

is no probability for radical (II) to be formed and only radical (I) can exist. As the temperature raises over 60°C the probability of radical (II) formation gradually increases.

- The computed dipole moment, which measures the separation of charges, or the polarity, of radical (I) is greater than that of radical (II) by 3.78 D.

TABLE 3 Ground State Properties for Methylmethacrylate Radical

| Properties | Type | Value | |
|-------------------------|---------------------------------|-------------|--------------|
| | | Radical (I) | Radical (II) |
| Ground state properties | Heat of formation (Kcal) | -172.811 | -90.700 |
| | Total energy (eV) | -2998.461 | -2229.309 |
| | Electronic energy (eV) | -16492.947 | -11980.706 |
| | Core-Core repulsion energy (eV) | 13494.486 | 9751.396 |
| | Ionization energy (eV) | 3.155 | 2.662 |
| | Electron affinity (eV) | 2.430 | 3.809 |
| | Energy gap (eV) | 5.586 | 6.471 |
| | Dipole moment (D) | 11.048 | 7.268 |
| Charge density | HOMO | | |
| | IN | 6.325 | 8.354 |
| | R | 29.083 | 91.070 |
| | C* | 64.592 | 0.576 |
| | HUMO | | |
| | IN | 99.909 | 3.989 |
| | R | 0.090 | 95.976 |
| C* | 0.001 | 0.033 | |

IN = initiator; R = The rest of monomer molecules; C* = active center.

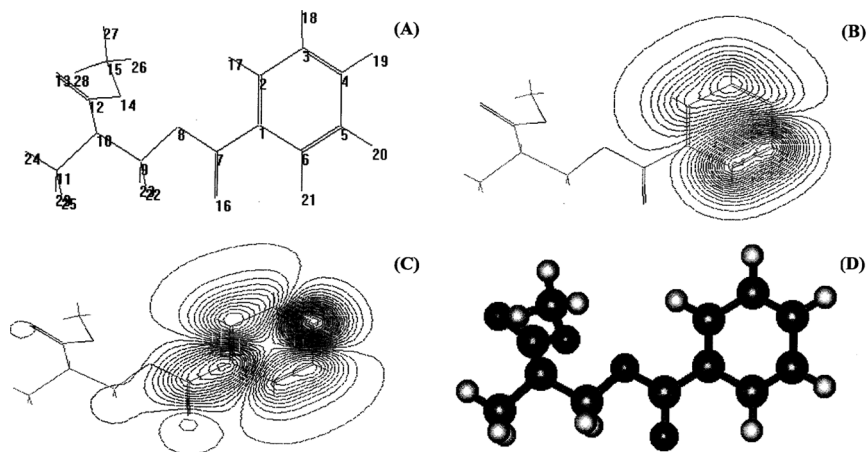


FIGURE 4 Numbering system (A), charge density maps (HOMO (B) and LUMO (C)), and final geometry of benzoyl-MMA radical (I).

4. Amount of charge located on C10, is the active center of radical (I), is 64.59%, whereas, the amount of charge on C13, which is the active center of radical (II), is 0.57%. Therefore, at room temperature radical (I) is the active radical to start the polymerization process.

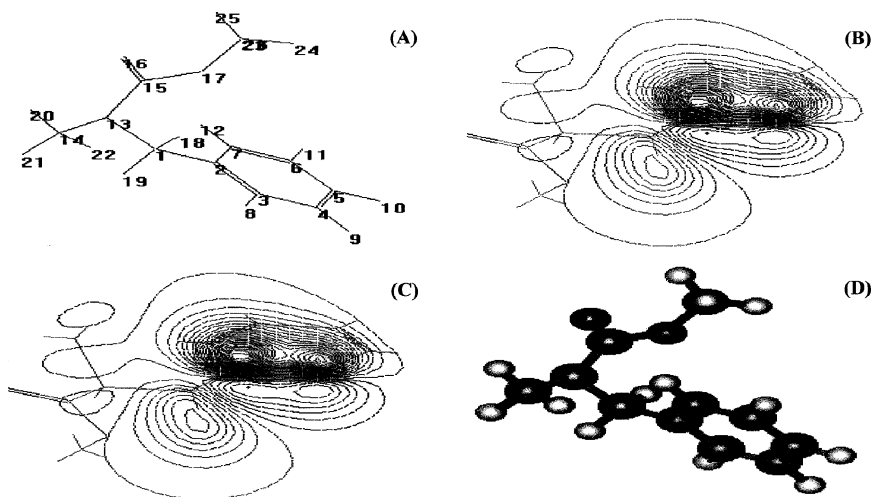


FIGURE 5 Numbering system (A), charge density maps (HOMO (B) and LUMO (C)), and final geometry of phenyl-MMA radical (II).

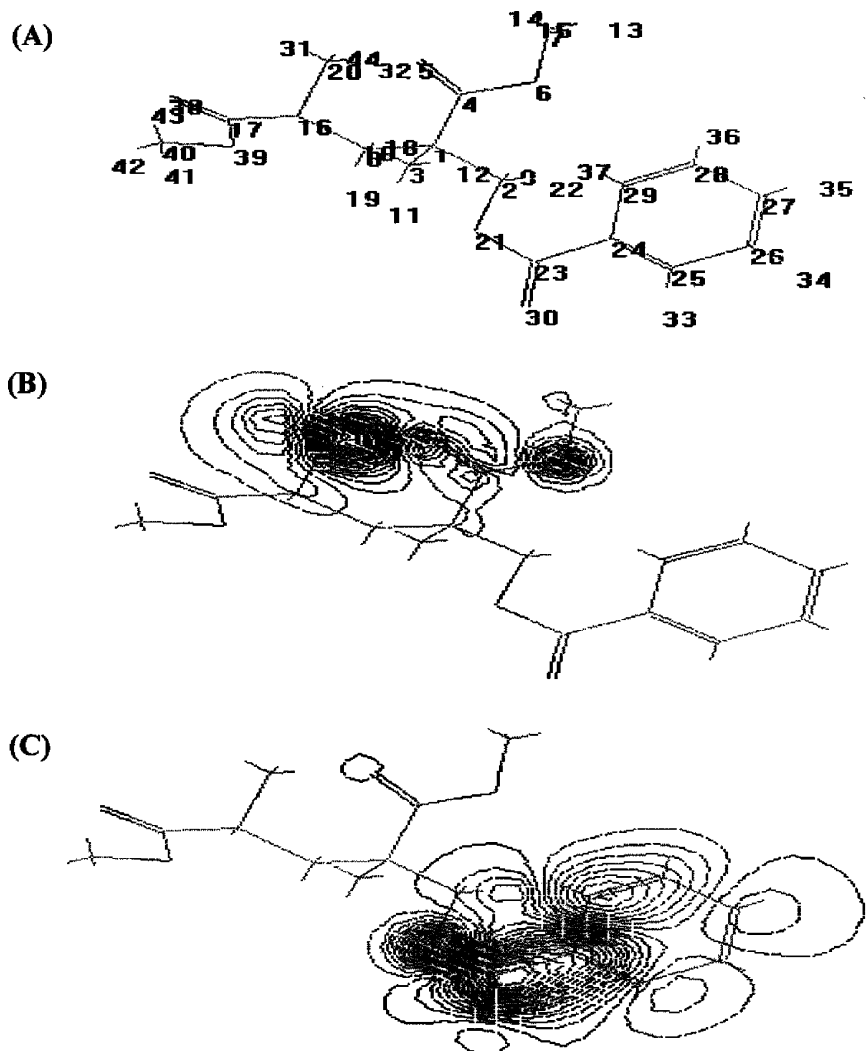


FIGURE 6 Numbering system (A), (B) HOMO and, (C) LUMO maps of benzoyl dimer MMA radical.

Therefore, at room temperature only radical (I) exists and as the temperature increases radical (II) may be formed as indicated from the heat of formation, total energy, and dipole moment. During the course of the calculations the authors considered only the benzoyl radical as initiator, because all polymerization conditions were carried out at 60°C.

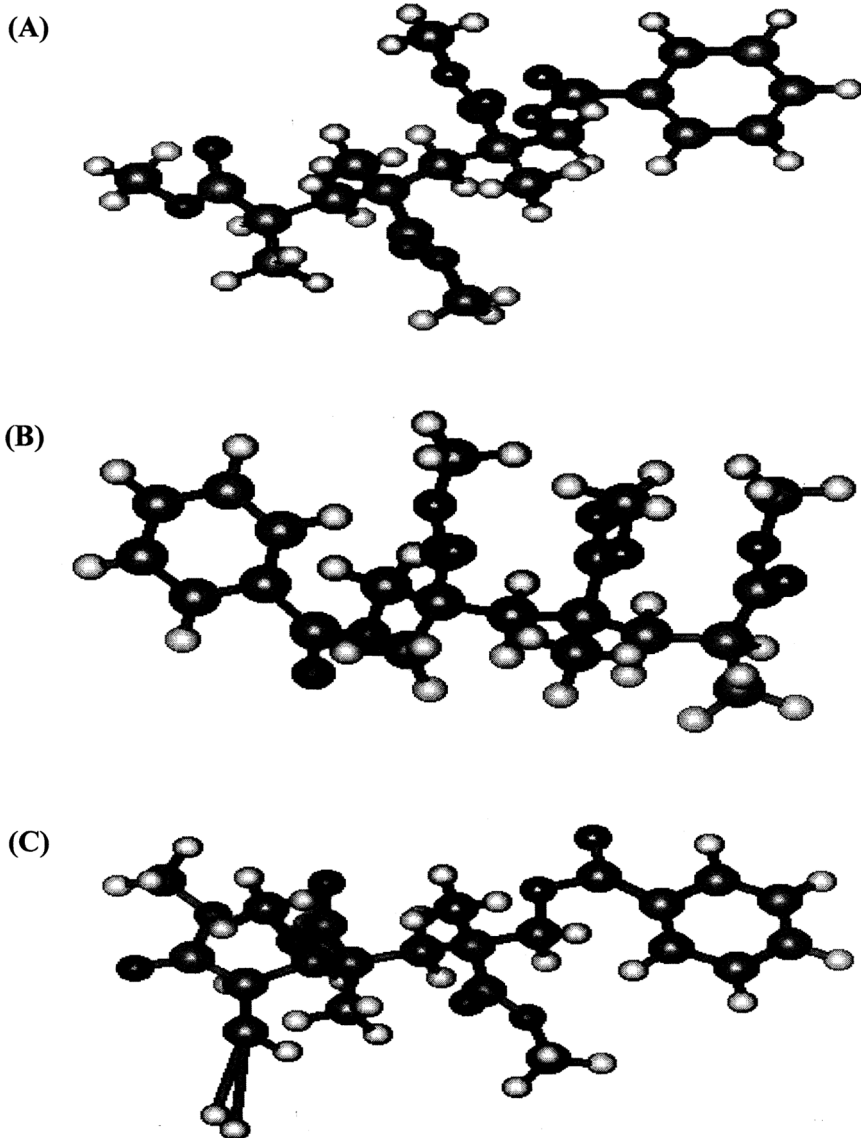


FIGURE 7 Final geometry of PMMA (A) syndiotactic, (B) isotactic, and (C) atactic.

Structure of Polymeric Chain

During the polymerization process (in the propagation step) the radical of benzoyl-MMA (I) attacks another monomer molecule to form

dimer radical. The dimer radical is fully optimized using AMI-MO method. The numbering system and charge density maps (HOMO and LUMO) are presented in Figure 6. The charge density migrated from C*10 in the benzoyl-MMA radical (c.f. Figure 4) to C*16 in the dimer radical. The migration of charge to C*16, indicate that C*16 is the active center of the dimer, which attacks another monomer molecule to form the trimer radical and so on to form the polymeric chain.

The polymeric chain of MMA may exist in three structures: syndiotactic (a), isotactic (b), and atactic (c). AMI-MO method was applied to find the most stable form of the structures a, b, and c. The three structures are represented in Figure 7. The ground state properties of structures a, b, and c are presented in Table 4.

Some general remarks are given as follows:

1. Thermodynamically, the syndiotactic form is the favorable structure in the reaction medium. The heat of formation of syndiotactic structure is greater than isotactic and atactic structure by 10 Kcal and 116 Kcal respectively.
2. The stability of any compound can be considered by total energy. The syndiotactic form is more stable than the isotactic form by about 0.5 eV (≈ 11.5 Kcal) and by 5.1 eV (≈ 117.5 Kcal) over the atactic form. Again, the syndiotactic form is the most stable structure in the reaction medium. This is in good agreement with the obtained data from J-value calculation from the IR-spectrum of the prepared PMMA samples, which indicate that they have syndiotactic structure [21,22].

TABLE 4 Heat of Formation, Total Energy, Electronic Energy, Nuclear Energy, Ionization Potential, Electron Affinity, Energy Gap, and Dipole Moment of the Three Structure of PMMA

| Ground state properties | Syndiotactic (a) | Isotactic (b) | Atactic (c) |
|---------------------------------|------------------|---------------|-------------|
| Heat of formation (Kcal) | -328.340 | -318.120 | -212.010 |
| Total energy (eV) | -5797.100 | -5796.600 | -5792.000 |
| Electronic energy (eV) | -48760.710 | -49475.770 | -48731.010 |
| Core-Core repulsion energy (eV) | 42963.613 | 43679.111 | 42938.950 |
| Ionization energy (eV) | 10.281 | 10.198 | 9.212 |
| Electron affinity (eV) | 0.421 | 0.521 | 0.651 |
| Energy gap (eV) | 9.859 | 9.677 | 8.562 |
| Dipole moment (D) | 4.133 | 3.695 | 6.260 |

CONCLUSION

Benzoyl peroxide molecule, as a free radical initiator, is a highly symmetric molecule as indicated from the calculated bond length, π -bond order and charge density maps. The σ -frame of the computed dipole moment is responsible for the high polarity of the molecule (≈ 6.85 D). The HOMO of MMA monomer (as a reference molecule) is of π -type and is 77.5% localized on the C1–C3 moiety, especially on C1, which is the active center for starting the propagation step. At room temperature the benzoyl radical (I) exits and as the temperature increases the phenyl radical (II) may be formed as indicted from the heat of formation the heat of formation of radical (I) is greater than radical (II) by ≈ 80 Kcal./mol. The amount of charge centered on the active center of radical (I) C10 is 64.5%, whereas, C13 of radical (II) is 0.5%. Therefore, at room temperature radical (I) is the predominant radical in the reaction medium. The results of MO calculations indicate that the syndiotactic form is the most stable structure in PMMA. The heat of formation of the syndiotactic structure is greater than isotactic and atactic structures by 10 and 116 Kcal./mol, respectively. Also, the total energy of the syndiotactic form is greater than isotactic and atactic form by 11.5 and 117.5 Kcal./mol, respectively.

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