

Experimental and Theoretical Evidences for Stability of Intermediates and Reaction Path during Pulsed Laser Photo-Polymerization of Acrylate Monomers

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Summary: Density Functional Theory (DFT) calculations at the B3LYP/3-21G basis set was carried out to determine the stability of intermediates during the pulsed laser polymerization (PLP) of acrylate monomers. The reaction path was determined successfully by calculating Electrostatic Potential Maps (ESP) for the selected systems. For this study, pulsed laser photo-initiated polymerization of methoxyacrylate monomers was carried out via a Q-switched Nd: YAG laser (2nd harmonic at 532nm). The monomers, n-butyl methoxyacrylate (B) and n-octadecyl methoxyacrylate (O) along with the activated initiator, benzoyl peroxide were dissolved in ethanol (EOH) and were exposed to the laser for 50 min. Reaction mixture, B: O in stoichiometry 1:1 for copolymerization and pure 'B' and 'O' solutions for homo-polymerization were treated with laser in order to study the reaction path based on transition state stabilities. Fourier Transform Infrared Spectroscopy (FTIR), Hydrogen Nuclear Magnetic Resonance (¹H-NMR) spectroscopy and elemental analysis were used for the structural elucidation of the products. The computed results were found in good agreement with the experimental findings and the comparisons revealed the effectiveness of the DFT-computed method for predicting mechanisms and path for new reactions.

Key Words: Laser induced photo polymerization, Methacrylates, Stimulated Raman emission, Characterization, DFT Studies.

Introduction

Discovery of living anionic polymerization has a great impact on the polymer science. It led to the key advances in synthetic polymer chemistry as well as physics by facilitating the production of well-defined material with precisely designed molecular architecture [1]. In addition, the quantitative descriptions of ion pairing phenomena, electron transfer processes as well as the details of radical processes are also studied. In addition, an ample theory of radical polymerization, characterization of the active species, a detailed mechanism of the reactions, kinetic and thermodynamic parameters for the relevant rate constants, and a structure–reactivity correlation, has been evaluated and explained mathematically [1, 2].

However, for the last few years density functional theory (DFT) has motivated many researchers from all over the world to explore the reaction path, to predict the transition states during the reaction and to check the feasibility of the reaction in physics and chemistry. In addition to the structural determinations, it has also been used for the interpretation and assignment of Infrared (IR), Ultraviolet (UV), Nuclear Magnetic Resonance (NMR) and Electron paramagnetic resonance (EPR) spectra [3]. The potential energy surfaces for the reactions have also been studied in detail by means of

various levels of quantum-mechanical methods and experimental data for the activation energies and to interpret the reaction sites, nucleophilic and electrophilic reactions. In view of the above, DFT methods is considered very useful in predicting the reaction barriers and could be used to determine transition states and path followed during the reaction [3, 4].

Acrylates are known to be polymerized by laser, a fast curing and energy efficient technique. The reaction mechanism usually involved free-radical polymerization reaction which largely depends upon the stability of the intermediate transition states, thus the reaction path can be determine by evaluating the stabilities of these states in the reaction mixture [1-4]. Also –OCH₃ group in methacrylate is known to exhibit stimulated Raman emission, which has also been used frequently for on-line monitoring of polymerization process [5-7]. However the reports on the experimental as well as theoretical studies of the stability of transition states and reaction path during pulsed laser polymerization of acrylate monomers are rare.

In this work, three reaction mixtures comprising pure n-butyl methoxy methacrylate (C₈H₁₄O₂), n-octadecyl methoxy methacrylate

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(C₂₀H₄₂O₂) and mixture of both aforementioned monomers in 1:1 ratio were prepared and then exposed to the laser light. The extent of polymerization was maximum for 1:1 ratio mixture. DFT calculations were employed to investigate the reaction path via calculating electrostatic potential maps and calculating the transition state stabilities in order to explain the feasibility of the reaction. FTIR and ¹H-NMR spectroscopic techniques and elemental analysis were used to characterize the material.

Experimental

Materials

All chemicals and reagents purchased were of high purity. Chemicals, *n*-butyl methoxymethacrylate (C₈H₁₄O₃) (Fluka, b.p = 160-163.5 °C), *n*-octadecyl methoxymethacrylate (C₂₀H₄₂O₃) (Fluka, b.p=101 °C), benzoyl peroxide (Sigma Aldrich, m.p = 103-105 °C) were used as received. Ethanol and methanol were used as solvents and were dried according to the reported method [8].

Equipment

Melting point was determined on a Mel-Temp. (mitamura Riken Rogyo, Inc.) by using open capillary tubes. FTIR spectra were recorded on Perkin Elmer 1600 series FTIR spectrophotometer. Nuclear magnetic resonance was carried out by using Bruker avance 300 digital NMR in DMSO-d₆ as solvent and tetramethylsilane as an internal standard. Elemental analyses were obtained on a Vaio-EL instrument. A commercial light-scattering spectrometer (BI-APD equipped with a BI9000AT digita Auto correlator) was used along with a He-Ne laser (output power ~ 400 mW at λ= 638 nm) as a light source. Relevant measurements were carried out at 25 ± 0.1 °C. Brookhaven BI 200S instrument fitted with a He- Ne Laser (Coherent Innova) with vertically-polarized incident light of wavelength λ = 632.8 nm and a BI 9000 AT digital correlator.

Methods

The apparatus was aligned carefully and the experiment was carried out in the dark to avoid noise (dark spectrum) owing to the tube lights and cosmic radiations, Fig. 1. Water supply, externally connected to a chillier, was turned on to stabilize the temperature of the instrument during the operation. The reaction mixtures were poured in a Pyrex conical flask having an optical window fused on its one side.

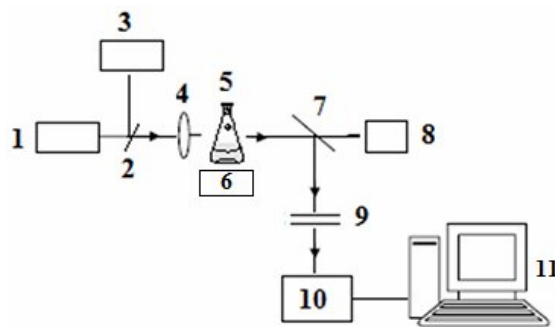
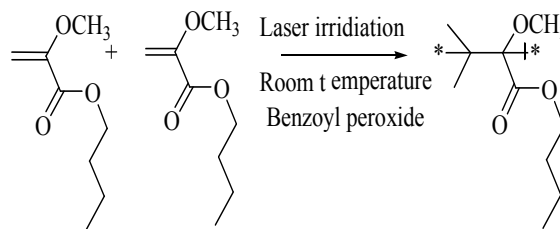


Fig. 1: Schematic representation of experimental setup for measuring Stimulated Raman Spectrum. (1) Nd YAG laser 532nm (2) Beam splitter (3) Energy meter (4) Lens (5) Flask containing reaction mixture (6) Stirrer (7) Beam splitter (8) Beam dump (9) Optical filter (10) Detector (11) Computer.

A Q-switched 2nd harmonic Nd-YAG (532nm) laser was focused on the reaction mixture through an optical window which was fused on one side of the flask. After 50 min, the reaction mixture was concentrated by using rotary evaporator. *n*-Hexane was added as a non-solvent to precipitate the product which was then filtered, dried and purified [9,10].

PMMA (B)

n-Butyl methoxyacrylate was dissolved in 200ml of ethanol. Initiator, benzoyl peroxide was added 5% by weight of the monomer, scheme 1.

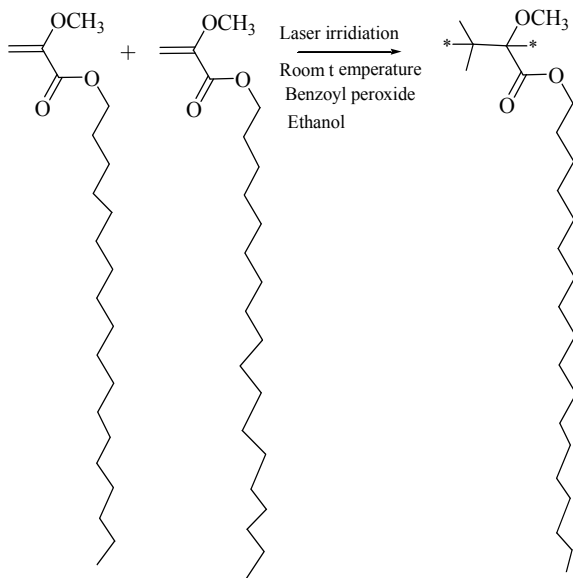


Scheme-1: PLP of *n*-butyl methoxyacrylate monomers (homopolymerization).

Yield 69%, White powder, FTIR (cm⁻¹, KBr): 2808 (aliphatic-CH), 1710 (C=O), 1011 (-O-), 1605. ¹H-NMR (300 MHz, CDCl₃): δ 1.06 (2H,d), 3.24 (3H,s), 4.08(2H,t), 0.9(7H,m) Elemental analysis, (C₈H₁₄O₃) calcd; (C 60.75, H 8.86), found; (C 60.01, H 7.99).

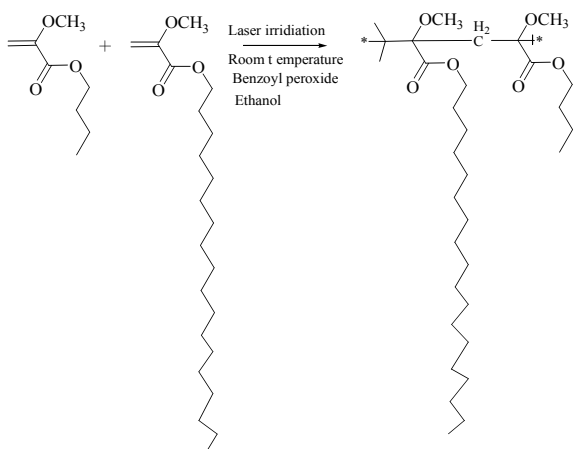
PMMA (O)

n-Dodecyl methoxyacrylate was dissolved in 200ml of ethanol. Benzoyl peroxide was added 5% by weight of the monomer, scheme-2.



Scheme-2: PLP of n-dodecyl methoxyacrylate monomers (homopolymerization).

Yield 61%, White powder, FTIR (cm^{-1} , KBr): 2808 (aliphatic-CH), 1723 (C=O), 1110 (-O-), 1605. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 1.71 (2H, d), 3.50 (3H,s), 4.15(2H,t), 1.57(5H, m), 1.29(m). Elemental analysis, ($\text{C}_{20}\text{H}_{42}\text{O}_3$) calcd; (C 72.72, H 12.73), found ; (C 71.84, H 11.97).



Scheme-3: PLP of n-butyl methoxyacrylate monomers and n-dodecyl methoxyacrylate monomers (1:1, copolymerization).

PMMA (B :O):

n-butyl methoxyacrylate and n-dodecyl methoxyacrylate were dissolved in 1:1 ratio in 200ml of ethanol along with the initiator which was added 5% by weight of the reactants, scheme-3.

Yield 96%, White powder, FTIR (cm^{-1} , KBr): 2998 (aliphatic-CH), 1750 (C=O), 1015 (-O-), 1625. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 3.24(3H,s), 4.08(m), 1.29 (14H, m), 1.0(m) Elemental analysis, ($\text{C}_{28}\text{H}_{56}\text{O}_6$) calcd; (C 68.85, H 11.47), found;(C 67.84, H 11.09).

Computational Methods

DFT calculations were carried out by Gaussian 03 following B3LYP method. The basis set used for the optimization of compounds was 3-21G .

The structure of the transition states were determined by DFT and by following B3LYP method using 3-21G basis set. The Synchronous Transit-Guided Quasi-Newton (STQN) use a linear synchronous transit or quadratic synchronous transit to get closer to the quadratic region of transition state and use the quasi-Newton or Eigen vector factor to perform the optimization. This method was employed with QST2 option to the opt keyword. QST2 require two molecules for specification, reactant and product. Gaussian 03 options of QST2 was used as it is very useful for automating the transition structure search for a given reactant and product.

Results and Discussion

Radical polymerization is among the most efficient methods initiated usually by radical formation of the initiator. The reaction mechanism largely depends upon the stability of the radical ions produced during the reaction. In order to have better understanding of reaction mechanism and path followed during pulsed laser polymerization, three reaction mixtures were prepared, scheme 1, 2 and 3. The monomers 'B' and 'O' were dissolved in ethanol along with the initiator in order to study homopolymerization reaction. For another experiment 1:1 ratio solution of B and O was prepared to study copolymerization under identical conditions. Benzoyl peroxide was activated by placing in oven for 24 hrs at 40 °C and was added at 5 % by weights of the reactants to the solution [11]. After the mixture was

irradiated by the laser for a particular duration, it was concentrated to 20 mL by rotary evaporator. n-Hexane was added to the concentrated mixture as a non-solvent to obtain white precipitates of the products. FTIR, $^1\text{H-NMR}$ spectroscopic techniques were used to confirm the functionalities in the products.

FTIR spectroscopic technique was used to confirm the functional groups present in the synthesized polymer Polymethylmethacrylate (PMMA). Significant changes were observed in the spectral properties of initial compounds and product as some of the signals disappeared and some new appeared. The structure of synthesized PMMA was confirmed by the presence of characteristic absorption peaks in their respective areas. Absorption peaks for (C=O) and (C-O) at $1750(\text{s})\text{ cm}^{-1}$ and $1115(\text{s})\text{ cm}^{-1}$ respectively confirmed the presence of ester linkage in the polymer, PMMA. Absence of a peak in the region 3982 cm^{-1} coincidence with the presence of peaks around 2900 cm^{-1} confirmed the presence of single bonds the macro-chains [12].

In order to support the FTIR results, $^1\text{H-NMR}$ spectroscopic analysis of PMMAs homopolymers and copolymers was carried out using TMS as an internal reference. Appropriate signals for PMMAs [13] were found in the spectrum and were consistent with the proposed structures.

The stoichiometry of PMMAs was confirmed by elemental (C, H, N) analysis. The calculations were made based on the structure of repeat unit present in the polymer chain. The results showed a good correlation between the proposed structures and the experimental results.

All polymers showed good solubility in common organic solvents like ethanol, methanol, acetone and chloroform etc. The copolymer polymer had hydrodynamic radius (R_h) of 16 nm whereas for O and B it was 10 and 8 nm respectively.

Pulsed Laser Polymerization (PLP)

Pulsed Laser polymerization of three aforementioned systems was carried out. Dark spectrum was saved as reference using computer aided Avasoft USB 2 software which was then subtracted from spectra to get noise free readings. The experiment was started from a very low power with oscillator at 8 and then increased to 9, 10, amplifier 1, 2, 3, and 4 respectively in order to record the threshold level and possible enhancements in the stimulated Raman scattering signal during polymerization. A speckle scattering was observed on screen using safety goggles. Free-radical photo

polymerization is known to be inhibited by molecular oxygen, which can scavenge the initiator resulting in the introduction of incubation period in the beginning of the reaction [13]. As the reaction was carried out under inert atmospheres, the exponential fit showed that was no incubation period in the beginning. Fig. 2.

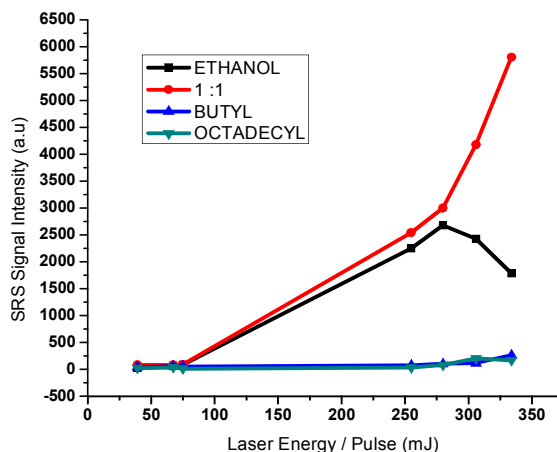


Fig. 2: Stimulated Raman Signals vs. Laser Energy during pulsed laser polymerization.

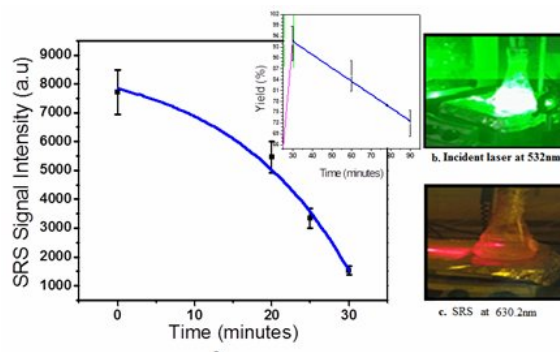


Fig. 3: (a) Stimulated Raman Signals vs Time. (b). Incident beam at 532nm.(c). Stimulated Raman Signal "SRS" at 630.2nm.

The system was found to emit stimulated Raman scattering (SRS) signals when irradiated by the laser light and which corresponded to 2957 cm^{-1} Raman mode of $\nu_s(\text{C-H})$ of O-CH_3 with $\nu_s(\text{C-H})$ of $\alpha\text{-CH}_3$ and $\nu_a(\text{CH}_2)$. It was observed that the SRS largely depend upon the extent of polymerization. [13, 14] To verify our finding, process was performed for different time spans (for 1B:1O composition) *i.e.*, 30, 60 and 90 min and the effect of exposure time on the yield during the polymerization was investigated. The results depicted that % yield of polymerization linearly reduced with time. [15, 16] It can also be seen in the Fig. 3 (a, b, c) that the SRS intensity decreased with the increase in exposure time. Fig. 3b and 3c showed that the incident beam was of green colour while the emitted was of red

colour. Consequently, SRS was used as a gauge to monitor polymerization and were plotted against laser energy, Fig. 2 [15-18]. It was found that the maximum signals were obtained during the copolymerization of 1B:1O mixture, whereas the emission during the homo polymerization of both monomers was less. However the behaviour of the three reaction mixtures can be explained based on the reaction mechanism involved.

Understanding relationships between structure and reactivity of material is important in order to investigate reaction mechanism involved. Radical polymerization mechanism usually involves the formation of radical which then attack on unsaturated monomers to initiate the reaction. Normally, Radical should be stable in order to efficiently fragment and initiate polymerization which depends upon both steric and electronic effects. Thus the reaction largely depends upon the stability of the radical ion formed during the reaction. Radical stability increases in the order methyl < primary < secondary < tertiary. Moreover any factor which can lead to the electron deficient site being delocalized

over a larger area will also stabilize electron poor species.

It is clear from the Fig. 4 that the much weaker SRS signals were observed from the reaction mixtures comprising 'B' and 'O' alone (for homo-polymerization). Based on the aforementioned discussion this might be due to the fact that the radical ion produced by the attack of the initiator on the 'O' monomer (R--O) was bulky and stable due to the presence of dodecyl group in its structure, however, it made it difficult for it to attack on another monomer comprising dodecyl due to the steric reason. In the case of the radical ion produced by the attack of the initiator on the 'B' resulted in the less stable structure (R--B) due to the presence of a small group as compare to the above discussed case and thus the polymerization was not feasible in this case as well. Whereas during the co-polymerization radical ion produced by the attack of initiator on 'O' resulted in a stable active specie (R--O) and that specie due to the steric factor, will prefer to attack on the relatively smaller monomer, *i.e.*, B.

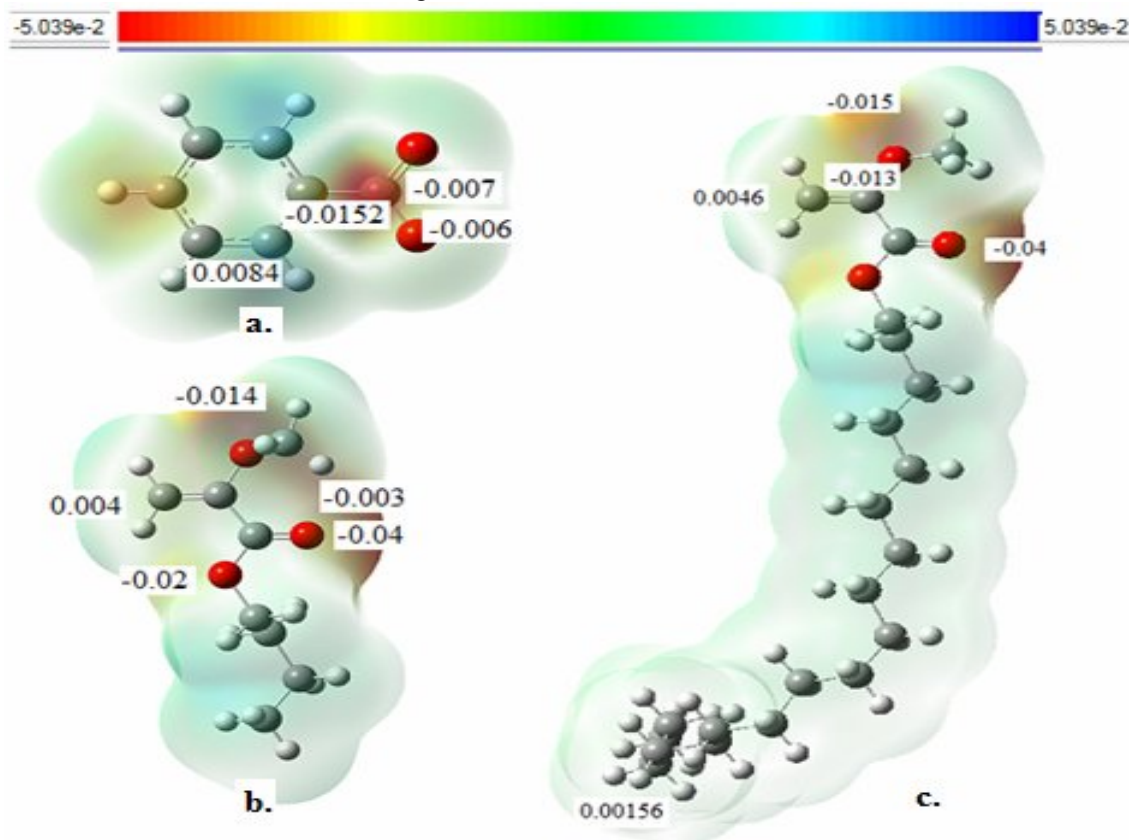


Fig. 4: Electrostatic potential maps of the initiator (a) and monomers, n-butyl methoxy acrylate (b) and n-dodecyl methoxy acrylate (c). Red shows negative charge whereas blue shows positive charge a. Initiator, b. n-Butyl methoxy acrylate, c. n-Dodecyl methoxy acrylate

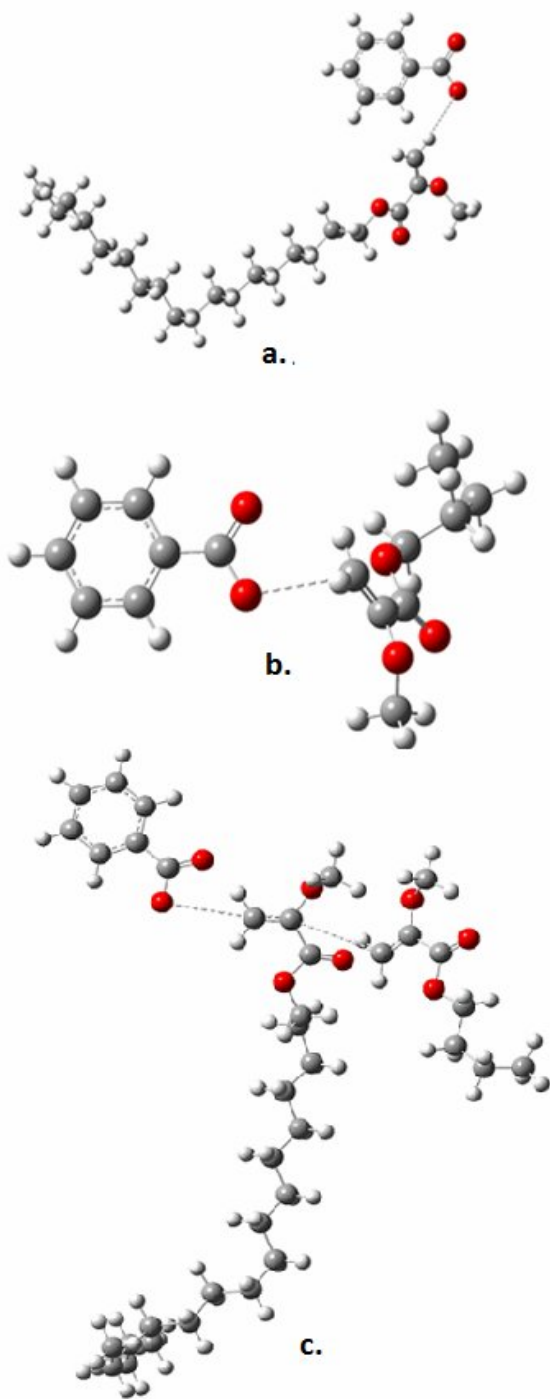


Fig. 5: Structures and energies of expected transition states during pulsed laser polymerization of acrylate monomers.

Theoretical Studies

The objective of this study is to complement our experimental findings and to investigate the

reaction path involved during the polymerization of methacrylate monomers.

DFT calculations can be used to study the electrostatic potential maps (ESP) around the molecules. These maps show the electronic distribution around the molecular surface and thus, can be used to predict reactive sites and relative reactivities towards electrophilic and nucleophilic attack. The charge distribution can also be used to study the interactions among the different species during the reactions, thus, can be used for the evaluation of reaction path and mechanism.

It is evident from the ESP, Fig. 4 that the negative area are around the 'O' atoms which are shown by red color whereas the blue color is representing the positive region in ESP. The 'O' atom in the radical has potential to attack on the positive side of the monomers *i.e.*, 'O' and 'B', thus the radical will attack the monomer from the side opposite to that of acrylate group. Moreover, the ESP map of 'O' is more positive as compare to that of 'B', therefore we can say that the radical will prefer to attack on 'O' in the reaction mixture comprising 'O' and 'B'. Consequently, R—O will be generated during the reaction which in turn will attack on 'B'. In order to support our findings from ESP maps, energies for all transition states *i.e.*, R-B-B', R-O-O', R-B-O and R-O-B were also calculated using the same basis set. Structures of the transition states and their energies are given in Fig. 5 and the data is tabulated in Table-1.

Table-1: Energy of transition states calculated by Gaussian 09 using basis set B3LYP/3-21G.

Radical ions	Stability of transition State (J)
R—O—O'	$4.29 \times 10^{-15} \text{J}$
R—B—B'	$6.60 \times 10^{-15} \text{J}$
R—O—B'	$8.9 \times 10^{-18} \text{J}$
R—B—O'	$8.9 \times 10^{-18} \text{J}$

It is evident from the values that R-O-B' and R-B-O have same stability and are more stable among the other two, thus indicating that under these conditions copolymerization is more feasible. However the reaction path seems to follow the transition state R-O-B based on ESP map as ,O, has more positive electrostatic potential map around it.

Conclusions

In the present work we have synthesized and characterized polymethacrylate homo and copolymers using pulsed laser polymerization technique. The experimental data showed that the copolymerization is more possible under the set conditions. DFT

calculation was used to investigate the reaction path by calculating transition states and electrostatic potential maps. The results obtained were in good agreement with the experimental data. It was found that the copolymerization was more feasible among selected system based on the stability of the transition states developed during the reaction. Also the reaction proceeded through the attack of the initiator on the 'O' followed by the formation of sterically stable and energetically favorable R—O—B' transition state. Thus mechanism involved during the pulsed laser polymerization can be evaluated employing computer aided programs.

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