

Computational studies of ultraviolet ablation of poly(methyl methacrylate)

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Abstract. The results from our recent molecular dynamics and electronic calculations studies of the interaction of ultraviolet light with poly(methyl methacrylate) are discussed. Molecular dynamics simulations in the photochemical and photothermal regimes demonstrate the delayed onset of ablation due to the slow pressure relaxation in the polymeric material. Electronic structure calculations show the possible wavelength-dependent pathways of exothermic and endothermic release of gaseous and small molecules which could induce the ablation process. The results from our studies are the centerpiece for the current development of the mesoscale model of the light irradiation of polymeric material.

1. Introduction

The overheating of a polymeric substrate by ultraviolet (UV) radiation leads to massive removal of material, or ablation. The technique of laser ablation is used in such industrial applications as fabricating ink jet printer nozzles [1], stripping polymer coating from glass cladding [2], patterning of circuit boards [3], and etching biopolymers in LASIK surgery [4]. Though numerous applications of laser ablation exist, the microscopic interactions which initiate and propel material from the substrate continue to be unclear.

When an energetic photon interacts with a substrate during laser processing, photothermal and photochemical reactions can occur [5]. In photothermal events, the energy of the photon generally cause heating of the absorbing material, while in photochemical events, the photon energy lead to direct covalent bond breaking. Both mechanisms along with photomechanical volume changes and stress-induced events can play a significant role in the ejection of material [6]. Computational modeling of such events can provide insights into the understanding of the complex nature of the ablation phenomenon.

Previously, molecular dynamics (MD) simulations were used to model the photothermal and photochemical interaction of UV light with an organic solid [7]. The resulting effects of the laser excitation showed the dependence of laser pulse width and laser fluence on the molecular yield [8, 9], energy and pressure distributions [10-12], and the phase of the target material in laser ablation [13]. The

simulations also observed an ablation threshold with a dependence on laser fluence [14, 15] and explained the presence of clusters in the ablation plume [16, 17]. The development of a coarse-grained chemical reaction model (CGCRM) allowed for reaction energetics to be incorporated into MD simulations via an algorithm similar to the kinetic Monte Carlo (KMC) method [18]. The photochemical processes and the various exothermic radical recombination reactions, which occurred due to photochemical scission of chlorobenzene molecules, resulted in a decrease of the ablation threshold.

In order to simulate the photochemical and photothermal effects of polymeric materials using the CGCR scheme, poly(methyl methacrylate) (PMMA) has been selected due to its known photochemistry, available experimental data, and use in applications such as pulsed laser deposition [19]. Several different bond cleavages can occur in PMMA after the absorption of a photon, as shown in figure 1. The main chain cleavage (Norrish type II) leads to the formation of MMA monomers and lower molecular weight PMMA chains. With the Norrish type I and ester elimination reactions, a side chain is cleaved, and the formation of small molecules including CO, CO₂, methane, methanol, and methyl formate. Moreover, cross-linking of polymers can be observed. Experimental studies have shown that the types of reactions occurring in PMMA vary with laser wavelength.

For example, at a wavelength of 157 nm, the Norrish type II reaction is dominant, showing the formation of mostly MMA monomers and smaller PMMA chains [20]. In contrast, for a longer wavelength of 248 nm, the Norrish type I reaction dominates, and CO, CO₂, C₂, methanol, methyl formate, and MMA monomers are detected in the ablation plume [21, 22]. With such a variety of possible reactive pathways for PMMA decomposition, the MD simulation must include the appropriate thermochemistry of the system following photon absorption.

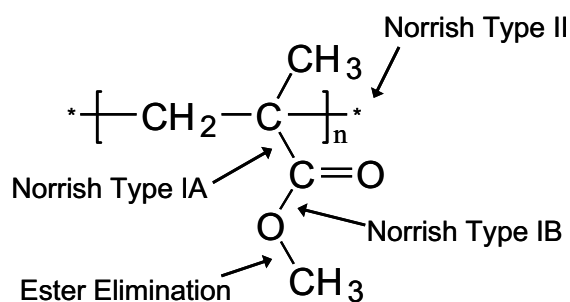


Figure 1: The photochemistry of PMMA.

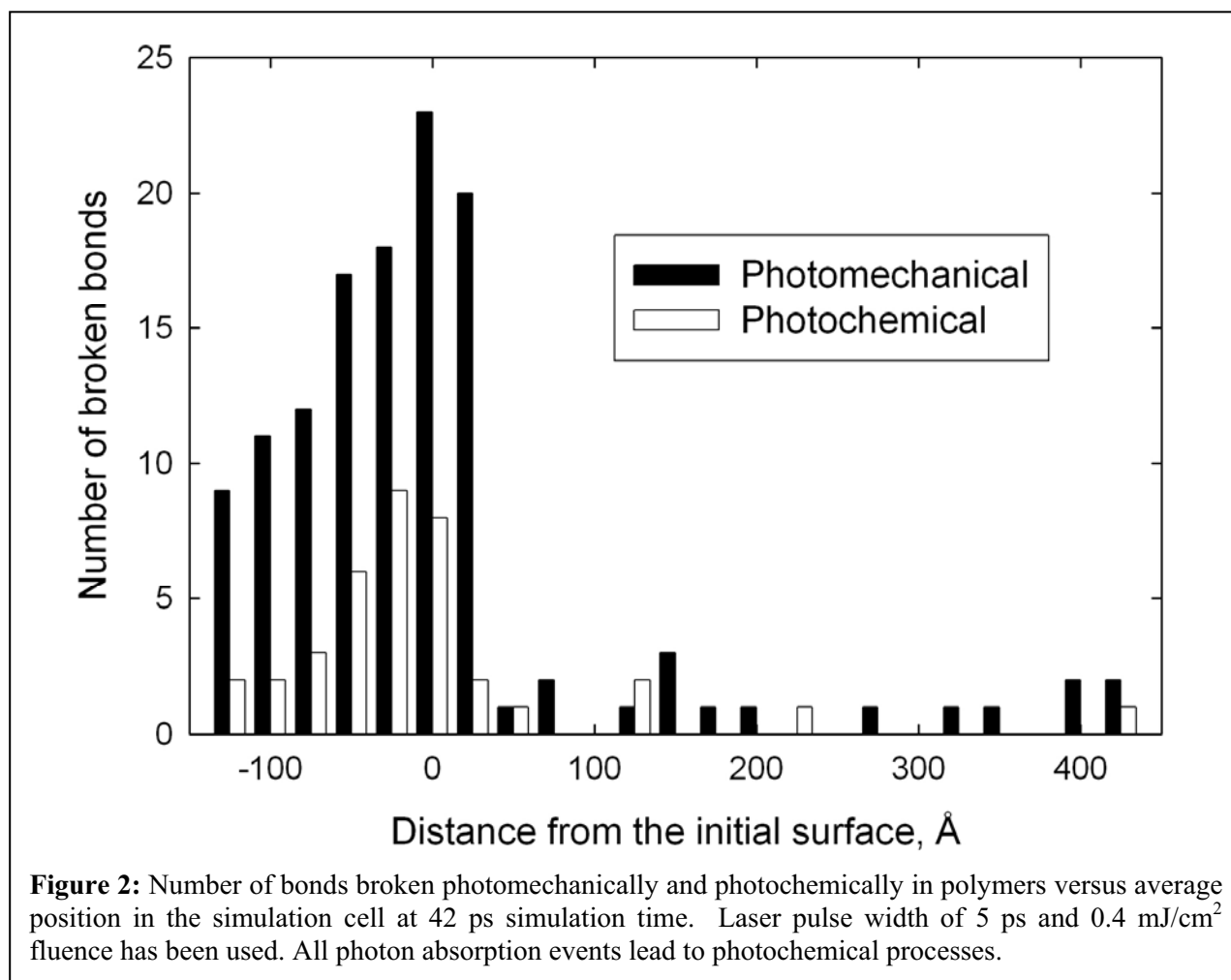
In efforts to create a comprehensive mesoscale model that will describe such complex phenomena, we have conducted thorough electronic structure calculations and coarse-grained molecular dynamics simulations. In this paper, we discuss the combined efforts of our two recent studies of PMMA. In the first study, the onset of laser ablation of PMMA has been simulated where both photochemical and photothermal reactions can occur as an outcome of photon absorption using the CGCRM [23]. Since 157 nm laser ablation was examined, the photochemical absorption caused Norrish type II scission of PMMA. In the second study, the results of electronic structure calculations of various possible activated pathways in PMMA that could occur as a result of photon absorption have been calculated [24]. Each study provides profound insights into the microscopic mechanisms of laser ablation.

2. MD simulations of laser ablation of PMMA

Photochemical and photothermal ablation of an amorphous PMMA solid was simulated using the CGCRM [23]. The details of the simulation are described elsewhere [23]. Briefly, a $5 \times 5 \times 13.6 \text{ nm}^3$ system consisted of 135 polymers; each contained 79 coarse-grained beads representing the C, O, CH₂, methyl, and carbonyl functional groups. Laser pulses widths of 5, 15, and 50 ps with a wavelength of 157 nm were used, and the absorption of photons was modulated by Beer's Law. The photochemical excitation led to the direct cleavage of the main chain bond (Norrish type II) and subsequent thermally activated unzipping of the polymer chain, formation of monomer species, as well as cross-linking of polymers. Photothermal excitation of PMMA was simulated by increase in the kinetic energy of a randomly chosen monomer by the amount equal to that of the photon.

Normally, the heating of a substrate would lead to thermal expansion of a material and an explosive phase transition [6]. However, the high viscosity and cohesive energy of polymers greatly delayed the thermal expansion and evaporation during the laser irradiation in both photochemical and photothermal processes. It has been shown that the ablation of polymers starts when the density of broken bonds in the surface layer reaches a certain critical value [25]. The direct scission events, as in photochemical processes, lead to modification of material and consequent reduction of molecular weight and cohesive energy of the polymer chain. However, the photochemical processes alone would require very high fluences to increase the energy density and number of broken bonds. Ablation, though, can be initiated at energies densities much lower than those required for vaporization due to the occurrence of photomechanical effects caused by laser-induced pressure build-up [6]. In the simulation, the heating was occurring at almost a constant volume, causing the pressure to build up.

The distribution of broken bonds in polymers due to photochemical bond cleavages and photomechanical stress immediately before the onset of ablation in the substrate is represented in figure 2. Each photon that is photochemically absorbed in the substrate breaks a main chain bond in a polymer, and the volume changes and stress defects associated with the bond break event and subsequent polymer unzipping generate a greater number of bond scissions. The number of broken bonds in polymers due to photomechanical effects increases 16% in the absorbing region which assists ablation. The eventual ejection of material occurred when the pressure forces exceeded the strength of PMMA substrate.



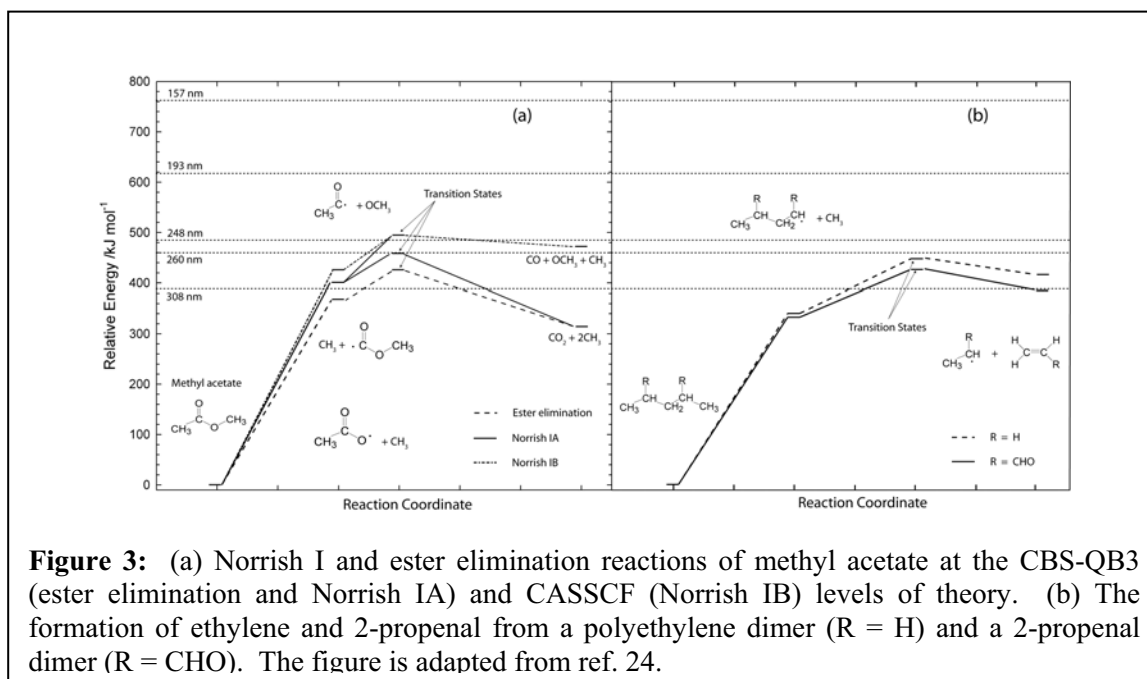
Ablation did not occur in PMMA until after the end of the laser pulse which agrees with experimental observations [26]. The intertwined structure of amorphous polymers does not allow fast thermal expansion and material relaxation. Therefore, in polymeric substrates, the initiation of ablation is tied to the strength of laser induced stresses which overcomes the strength of the intramolecular covalent bonds, the strength of the intermolecular interactions, and the interconnected nature of the polymer chains. In addition, lower fluences were required for ablation in the photochemical regime than in the photothermal regime.

3. Electronic structure calculations of activated pathways in PMMA

In order to implement the Norrish type I and ester elimination reactions into the CGCRM MD modeling effort, it is necessary to know the activation barriers of gaseous CO and CO₂ formation subsequent to the photon induced bond cleavage event. Electronic structure calculations were used to determine the energetics of various reaction pathways of radicals formed by UV radiation of PMMA [24]. CBS-QB3, density functional theory (DFT), and complete active space self-consistent field (CASSCF) levels of theory were used to compute reaction barriers and energies. Model compounds were methyl acetate, a polyethylene dimer, and a 2-propenal dimer which retain the essential bond functionality of PMMA. The stationary points and transition states were characterized by the presence of vibrational frequencies and performing intrinsic reaction coordinate (IRC) analyses.

The results of the Norrish type I and ester elimination reactions of methyl acetate calculated with CBS-QB3 and CASSCF are shown in figure 3a. Relative to the radical species, the release of CO₂ is exothermic, while the formation of CO is endothermic. In addition, the Norrish type II reactions and polymer unzipping reactions calculated with DFT are shown in figure 3b. From the radical species formed after the cleavage of the main chain bond, the reaction to produce ethylene and 2-propenal are endothermic reactions.

Figure 3 also displays the energies available at wavelengths commonly used in experimental investigations of PMMA ablation. The complete photochemical mechanism of molecular excitation and subsequent bond dissociation to form the radical species, however, is not known, and the discussion here is based only on energetics. At shorter wavelengths (157 nm and 193 nm), the amount of energy supplied by a photon is in excess of the reaction barriers and each of the products can, in principle, be formed. For 248 nm and 260 nm wavelengths, the photon energy can overcome the barrier to form CO₂ and can unzip the polymers but cannot overcome the barrier to form CO. However, during laser irradiation the necessary energy could be supplied by other photon absorption events, exothermic reactions, or by molecular collisions. For the longest wavelength of 308 nm, the energy of the photon is insufficient to form any of the products. Therefore, the ablation can occur predominantly by photothermal processes or by multiphoton absorption, followed by photomechanical processes.



In ablation of PMMA, each of the previously described reaction pathways is available, and the only limiting factor is the amount of energy that the photon deposits in the system. In addition, the exothermic release of CO_2 deposits more energy into the substrate which could fuel further chemical reactions or simply lead to heating of surrounding molecules. The possible formation of gaseous products and small molecules also could induce volume changes and stress in the substrate leading to more rapid material removal.

4. Conclusions

In this paper, two computational studies of UV ablation of PMMA were discussed. The MD simulations showed a delay in the onset of ablation at 157 nm. Due to high viscosity of polymers, minimal thermal expansion and evaporation were observed at low fluences or during laser irradiation. The primary mechanisms of the onset of polymer ablation at this wavelength and examined fluences are the photomechanical events and pressure relaxation. Also, activated reactions that could occur during laser excitation were determined using electronic structure calculations, and the possible laser wavelengths required to overcome the reaction barriers were discussed. The results from electronic structure calculations will be incorporated into the development of a comprehensive mesoscale model that will take into account the formation of small molecules on the conditions required for ablation, including volume changes, pressure relaxation, and deposition of energy.

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