Microscopic simulation of e-beam induced PMMA chain scissions with temperature effect

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Abstract. This study presents microscopic quantitative model of e-beam induced poly(methylmethacrylate) (PMMA) main-chain scissions. Scission processes are supposed to be caused by ester side group elimination, competing with hydrogen abstraction processes. Experimental values of PMMA radiation scission yield at different temperatures were obtained using direct Monte-Carlo algorithm for the simulation of e-beam scattering in PMMA/Si structure and detailed PMMA layer model for the simulation of exposed PMMA molecular weight distribution. The radiation scission yield increase at higher temperatures is associated by the increase of probability of remote PMMA main-chain scission, which follows the ester side group elimination. Temperature dependence of remote scission probability for the temperature range 20-180 °C is determined.

1. Introduction
Poly(methylmethacrylate) (PMMA) is widely used in advanced microlithography, with deep ultraviole as well as high energy radiation (γ-, electron beam, ion beam). The major chemical changes take place in PMMA during irradiation are main chain scissions, cleavage of pendent methyl ester groups, creation of new double bonds, and gas evolution (H₂, CO₂ etc.) (figure 1). PMMA main-chain scissions result in increased solubility of exposed areas, which causes great interest to them from the point of view of microlithography. Radiation scission yield \( G_s \), which represents mean number of chain scission per 100 eV energy deposition, is a key parameter for the scission rate determination. The conventional \( G_s \) value obtained for γ- and e-beam irradiation of poly(methyl methacrylate) at room temperature (PMMA) by gel permeation chromatography comprises 1.8-1.9 with 0.3 variance [1,2]. This value is proposed by different experiments showing dependence of \( G_s \) on exposure conditions. γ-irradiated PMMA samples provide mostly higher \( G_s \) value (1.23 for film, 1.85-2.15 for powder, 2.15 for commercial polymer, 3.6 for fractional polymer) than e-beam-irradiated ones (1.65 for film) [2]. The logarithm of \( G_s \) appears to vary linearly on \( 1/T \) with activation energy of approximately 1 kcal/mole for both γ- and e-beam-exposed PMMA samples [2] (figure 2). The extrapolated \( G_s \) values (T →∞) are 11.1 and 8.6 for γ- and e-beam irradiation, respectively. Qualitatively, the \( G_s \) value elevation at higher temperatures could be explained by cage effect. The excitation or ionization events in PMMA molecules caused by irradiation, give rise to reactive radical intermediates which result in main chain scission, detachment of side groups, and possibly depolymerization (near and above glass transition temperature). Being held in close proximity, the radicals may recombine, and the recombination rate seems to lower with increase of thermal motion. Thus, at higher temperatures the increased PMMA main-chain scission rate is caused by lower radical recombination rate.
Figure 1. Schematic diagrams of possible pathways of PMMA degradation under the high energy radiation [3]. Not all the possible intermediate radicals are shown.

Recent simulation studies of radiation-induced PMMA degradation consider PMMA main-chain scissions as a result of excitation or ionization of carbon atoms in PMMA backbone [4,5] (direct scission, Figure 1, process 3). However, according to various studies, the remote PMMA main-chain scission due to ester side group detachment (Figure 1, process 2) is also possible mechanism, which may dominate over direct scission [2,3]. Besides, the study of Choi shows that the number of generated C=C bonds is roughly equal to number of C=O bonds removed from the PMMA sample during irradiation and each PMMA main-chain scission is accompanied with removal of approximately five C=O bonds [6]. This emphasizes the importance of remote scission processes and requires the analysis of radiation-induced PMMA main-chain scission mechanisms in greater detail. In this study, the attempt to develop quantitative model of e-beam induced PMMA degradation at room and higher temperatures, based on the available experimental data on PMMA e-beam irradiation experiments, has been made. PMMA weigh distribution in e-beam lithography exposures is simulated to model the experimental $G_S$ value. The temperature effect on $G_S$ value is described in terms of remote scission probability temperature dependence. The temperatures of interest were between room temperature and 180 °C, because at lower temperatures PMMA main-chain scission rate is affected by the monomer existing in PMMA sample [7], whereas at higher temperatures thermal degradation processes contribution become significant.

2. Simulation of experimental radiation scission yield

2.1. e-beam scattering in PMMA/Si

The simulation of e-beam scattering in PMMA/Si structure was carried out by implementation of Direct Monte-Carlo algorithm with discrete energy loss model. ELSEPA software with Dirac–Hartree–Fock–Slater electron distribution model and muffin-tin model potential [8] was used for calculation of elastic scattering differential cross-sections for PMMA monomers (methyl methacrylate, MMA) and Si atoms. MMA elastic differential cross-sections were calculated as sum of H, C and O
Figure 2. Experimental values of PMMA radiation scission yield for γ- and e-beam-irradiated samples with theoretical linear dependence of log($G_S$) on 1/T.

Differential cross-sections multiplied by corresponding weights [9]. Inelastic e-beam scattering in PMMA layer was simulated using Dapor approach [10], considering electron-electron interactions, electron-phonon interactions and electron-polaron interactions, as well as electron reflection from the PMMA surface and electron free path correction in case of PMMA/Si interface crossing. E-beam interaction with PMMA valence electrons was simulated using Mermin energy loss function approach, while C and O inner-shell electronic excitation and ionization events were modelled in terms of generalized oscillator strength in hydrogenic approach (MEFL-GOS method [11]). For a simulation of secondary electron generation in ionization events, mean binding energy of PMMA valence electrons should be introduced. Various studies provide values from 4–15 eV range [12,13] as well as incident electron energy-dependent functions [5], and the exact value (or function) of mean PMMA valence electron binding energy is still tricky question. Following Dapor, in this study mean binding energy of PMMA valence electrons is assumed to be 15 eV, which is a value between the weighted average of the first ionization energies of the atomic constituents of PMMA and the weighted average of the lowest electronic energy levels of a model molecule for PMMA [14]. Electron-electron interactions with energy loss of primary electron higher than 15 eV were treated as ionization events, resulting in secondary electron generation, while the other were interpreted as excitations. Silicon energy loss function in form of extended-Drude expression with quadratic dispersion law (MuElec [15], extension of Geant4-DNA toolkit) was applied for the simulation of inelastic e-beam scattering in Si.

2.2. PMMA layer
Taking into account the molecular weight-based nature of $G_S$ obtained experimentally, to get a right estimation of e-beam induced PMMA main-chain scission rate one should simulate the exposed PMMA weight distribution. In this study the model of PMMA layer is employed for this purpose. Individual PMMA chains are simulated using ideal chain model with 109° cone and 0.28 nm pitch between successive monomers [4]. Simulated PMMA chains with required initial weight distribution are combined in predefined volume to achieve proper density (1.19 g/cc). Periodic boundary
conditions are assumed for the chains that go out of simulation volume. During the simulated chain combination, locations of empty areas in simulation volume are taking into account to avoid nonuniform monomer distribution.

2.3. PMMA main-chain scissions

Electron beam-induced PMMA main-chain scission are supposed to be a result of e-beam interaction with PMMA valence electrons [5,16,17]. The exact mechanism of PMMA main-chain scission under the effect of incident electron is not known, although some possible mechanisms are described in literature [6,18,19]. In recent simulation studies, the dominant approach considers direct scission due to the excitation or ionization of carbon atoms in PMMA main-chain, which leads to the rupture of C-C backbone bonds. However, according to Charlesby, Choi and other researchers (referred in introduction), the relative susceptibility of the ester side group to high energy radiation is much higher (the factor is ~40) than the relative susceptibility of the main chain to scission. Taking this fact into account, one could suggest strong suppression of direct scission (Figure 1, process 3) by the processes associated with ester group detachment (Figure 1, processes 1, 2). Thus, only remote PMMA main-chain scission mechanism (Figure 1, process 2) is taken into account in this study. Accordingly, the temperature effect on PMMA radiation scission yield is assumed to be caused by the higher probability of remote scission relatively to hydrogen abstraction at high temperatures.

The individual valence electron in MMA was associated with each simulated electron-electron interaction event (excitation and ionization) using standard Monte-Carlo technique [13]. According to Charlesby, each excitation or ionization event is potentially capable of causing one PMMA main-chain scission. However, there are oxygen valence electrons in PMMA that doesn’t form any intra- or intermonomer bonds. In this study, the electron-electron events associated with these electrons are not considered as potential source of scissions. The electron-electron events at incident electron energy lower than bond dissociation energy of the weakest bond in PMMA (C-C backbone bond [20]) are also excluded from consideration.

Simulated PMMA main-chain scission events and simulated PMMA chains are matched to each other in three-dimensional tables with 2 nm cell size. There is non-zero (~2%) part of cells with no monomers, thus in case of matching the electron-electron interaction event with one of such cells, events are moved to neighbour cell. This procedure allows to simulate exposed PMMA weight distribution for e-beam induced PMMA degradation model of any kind. The verification of degradation models was then carried out by the comparison of simulated $G_S$ values with ones obtained experimentally. Moreover, assuming linear dependence of log($G_S$) on 1/T one could obtain $G_S$.

3. Results and discussion

For the correct determination of PMMA scission mechanisms in temperature range of interest, $G_S$ value, obtained from exposed PMMA molecular weight distribution was simulated. The simulation followed the experiment of Harris [21] with typical exposure parameters – 10 keV primary electron energy and 100 μC/cm² frame exposure dose. The PMMA layer thickness was 500 nm, silicon was used as a substrate. The initial PMMA molecular weight distribution ($M_w = 5.63\times10^4$, $M_m = 2.26\times10^6$) was also reproduced Despite its minor influence on exposed PMMA molecular weight distribution [22]. Simulation volume was chosen as 100×100×500 nm³ to reach a tradeoff between the statistical significance of simulated scission data and computational time. For the simulation of experimental $G_S$ value, the theoretical relation between the number average weight of exposed PMMA ($M_f$) and number average of pristine PMMA ($M_m$) was used:

$$M_f = M_m [1 + G_S \epsilon M_m / \rho N_A]^{-1}$$

where $\epsilon$ is total energy deposition in PMMA layer, $\rho$ is PMMA density, $N_A$ is Avogadro number.

As it was mentioned above, direct scission processes are suppressed by remote scission and hydrogen abstraction processes. The experimental results provided by Charlesby and Choi could be explained if one assumes that each excitation or ionization events is followed by ester side group elimination. Then, in addition to ester group decomposition and subsequent gases evolution, two competing processes are possible – hydrogen abstraction (with probability $p_H$) and remote scission
(with probability \( p_S \)). Alongside, \( p_S \) increases with temperature and reaches the value of 1 at infinity temperature limit. The arguments in favor of this hypothesis are following. First, simulated \( G_S \) value for infinite temperature (when each excitation or ionization event is assumed as scission source) comprises 9.3, which is close theoretical value 8.6, proposed by Charlesby. Second, the calculated \( p_S \) value at room temperature (providing \( G_S = 1.65 \)), is roughly 0.22. According to Choi, the number of eliminated ester group is five times the number of scissions at room temperature, which leads to nearly unity probability of ester group elimination in each excitation or ionization event.

Using the approach described above, the temperature dependence of \( p_S \) was determined. 3D tables containing positions of scission events were obtained for \( p_S \) values in range 0.15-0.45 with 0.05 step. Then, molecular weight distribution-based \( G_S \) were determined for each value of \( p_S \). Finally, theoretical linear dependence of \( \log(G_S) \) on \( 1/T \) was used to obtain \( G_S \) values in range 20-180 °C with 15 °C step. The \( p_S \) value was determined to match to \( G_S \) at each temperature, which result in almost linear dependency of \( p_S \) on \( T \) in the temperature range of interest (figure 3).

![Figure 3](temperature-dependence-of-remote-scission-probability.jpg)

**Figure 3.** Temperature dependence of remote scission probability, obtained using simulated \( G_S \) values.

### 4. Conclusion

Presented algorithm of e-beam-induced PMMA main-chain scissions summarizes experimental data and provides quantitative microscopic explanation of temperature effect on PMMA radiation scission yield. The usage of recent models of e-beam interaction with PMMA and Si allows to expect high accuracy of the simulation of excitation and ionization events. Due to the domination of processes following ester side group elimination over direct scission processes, only remote scission and hydrogen abstraction are taken into account in this study. This simplifies the simulation algorithm significantly and allows to estimate the probability of remote scission (\( p_S \)) and hydrogen abstraction (\( p_H = 1 - p_S \)) at temperatures in range 20-180 °C. Outside this range the other processes may influence the radiation scission yield significantly – the interaction of PMMA monomer with PMMA radicals and thermal degradation processes at lower and higher temperatures, respectively.
Acknowledgments

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