Electron induced fragmentation of methyl acetate: side chain decomposition and decarboxylation as pathways to main chain scission of PMMA

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Main chain scission (MCS) resists are a prospective alternative to chemically amplified resist (CAR) in extreme ultraviolet lithography (EUVL), specifically as the solubility switching of these is based on direct chain scission and not acid formation and secondary, acid driven chain scission. Acid diffusion is thus not a concern with respect to LER and other stochastic effects. Poly methyl methacrilate (PMMA) is such a resist material which has shown good performance in electron-beam lithography (EBL)[1], and not unlike extreme ultraviolet lithography (EUVL), secondary low energy electrons are abundant in EBL, playing a determining role in the resist chemistry[2]. Correspondingly fragmentation of this material has been studied under direct electron exposure, and throughout the UV range from VUV and DUV to EUV and beyond[3,4].

Here we present dissociative ionization (DI) of methyl acetate as the chemically simplest proxy to study side chain induce fragmentation of PMMA[5]. We measured the AEs of all main fragments observed in electron ionization of this compound, and in conjunction with earlier DI and DEA measurements we used quantum chemical calculations to explore direct electron induced fragmentation of the side group and secondary (or concomitant) decarboxylation as pathways to MCS of PMMA.

Highest intensity fragment in DI of methyl acetate is CH_3CO^+, formed through loss of the methoxy radical. In analogy to PMMA this constitutes charge retention at the side group with decarboxylation leading to the stabilized tertiary carbocation, excluding MCS single electron ionization event. The lower intensity m/z 59, $CC(O)OCH_3^+$, on the hand, constitutes cleavage of the αC bond under formation with charge retention on the side group, which in analogy to PMMA constitutes direct formation of the main chain radical and thus provides a pathway to MCS. Differently, in DEA, no such direct pathway to the formation of the MC radical is observed. Fragmentation of the methyl ester bond with charge retention on the methyl group and a Norrish type II cleavage with charge retention on the methoxy group are however active channels both in DI and DEA, with decarboxylation threshold well below the AEs of these fragments.

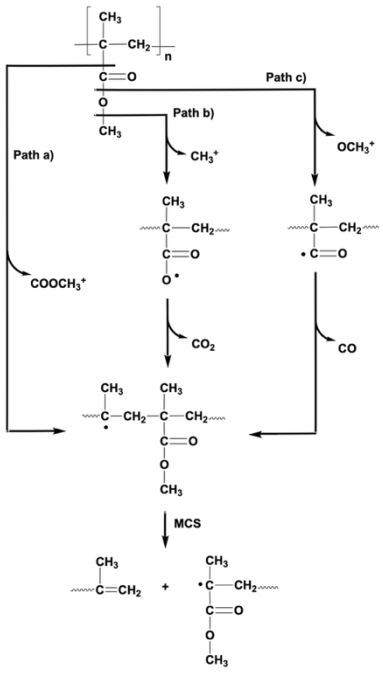


Figure 1. Side chain fragmentation and subsequent decarboxylation as paths to main chain scission of PMMA. Adapted from [1].

Hence, decarboxylation up on electron induced side chain fragmentation is an energetically viable path to MCS in PMMA and may play a significant role in the exposure chemistry of this resist material.

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References

[1] F. Rahman, et al. Microelectron Eng 224, 111238 (2020).
[2] J. Torok et al. . *Photopolym. Sci. Technol., 26(5), 625–634 (2013)*
[3] J.O. Choi, et al. **J. Vac. Sci. Technol., B:Microelectron. Process. Phenom.** 6(6), 2286–2289 (1988).
[4] G.H.-Y. et al. J. Photochem. Photobiol. A Chem 353, 306–315 (2018).
[5] R. Tafrishi, et al. J. Chem. Phys., 164, 104304 (2026)

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