

Study of the Interaction of Polymethylmethacrylate Fragments with Methyl Isobutyl Ketone

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Polymethylmethacrylate (PMMA) is the most widely used electron beam lithography resist. Upon exposure to electrons at appropriate doses, PMMA behaves as a positive-tone resist undergoing polymer chain scission. The resulting PMMA fragments of low molecular weight are soluble in suitable developers. Fig. 1(a) illustrates the dissolution of a PMMA sample after exposure to electrons with various doses. Numerical analysis of PMMA fragmentation at experimentally relevant conditions indicates that the presence of fragments containing less than approximately 10-20 MMA monomer units could be responsible for dissolution of exposed regions during development,¹ see also Fig. 1(b). However, the process of dissolution depends on the developer and development conditions. Furthermore, an investigation of the interaction of resist with developer at the molecular level is necessary for proper understanding and rational usage of the resist – developer chemistry, in addition to providing a useful analysis technique.

A popular developer for PMMA is a mixture of methyl isobutyl ketone (MIBK) with isopropanol (IPA). In this work, we investigate the interaction of short PMMA fragments (containing up to 10 MMA units) with one of these compounds, MIBK. For this purpose, we use molecular dynamics (MD) simulation with the Accelrys Materials Studio package, and employ the results to characterize the mixture in the spirit of the Flory-Huggins theory of polymers.² An outline of our MD simulation scheme and a visualization of a typical PMMA-MIBK mixture are shown in Fig. 2. Following the system construction and initial energy minimization, an NPT (isothermal-isobaric) ensemble simulation is performed for 750 ps to equilibrate volume and density. The results are shown in Fig. 3. Next, NVT simulations (1000 ps) are used for both mixtures and individual compounds to obtain the relevant energies. The potential energy of mixture (Fig. 4(a)) indicates a presence of attractive intermolecular forces as expected. Finally, the resulting enthalpy of mixing is used to calculate the Flory-Huggins parameters (χ) shown in Fig. 4(b). Unexpectedly, positive χ values have been found for MMA monomers ($n=1$) and dimers ($n=2$) indicating a limited miscibility of these small fragments with MIBK. We are continuing our MD simulations for IPA and water solvents as well as their mixtures, expecting that such studies will clarify the molecular mechanisms that determine dissolution of PMMA in popular MIBK:IPA and IPA:water developers.

¹ M. Aktary, M. Stepanova, and S.K. Dew, *J. Vac. Sci. Technol. B* **24**, 768 (2006)

² P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press: New York, 1995 (16th Ed.); Chapter 12.

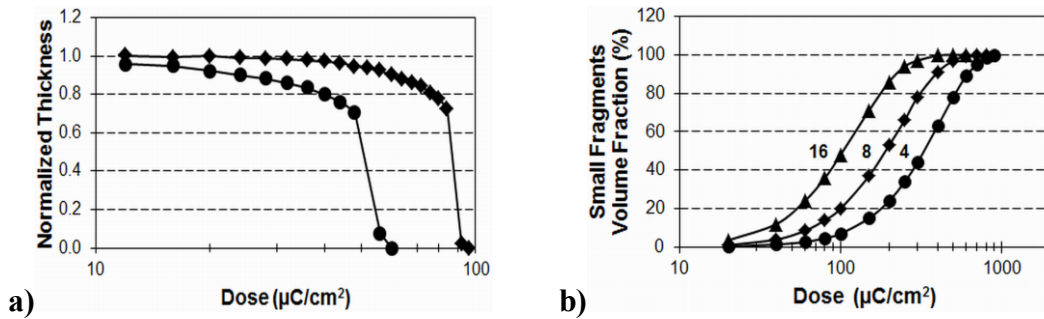


Figure 1: (a) Experimental contrast curves illustrating dissolution of PMMA 950k exposed with 10 keV electrons and developed for 5 sec in MIBK solvent (circles) and MIBK: IPA 1:3 mixture (diamonds), both at room temperature, and (b) simulated volume fraction of small PMMA fragments as a function of exposure dose in a grating structure. The three curves show the volume fractions of fragments containing less than 4, 8, and 16 monomers after 10 keV exposure.

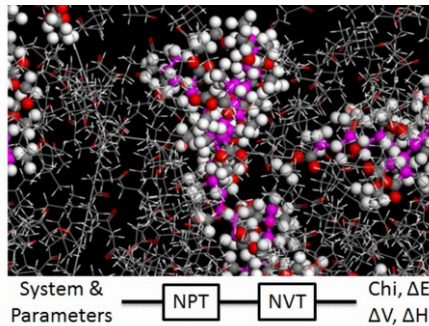


Figure 2: Molecular dynamics simulation scheme and visualization for a mixture of PMMA fragments (16.7% concentration in mixture by mass) with MIBK solvent.

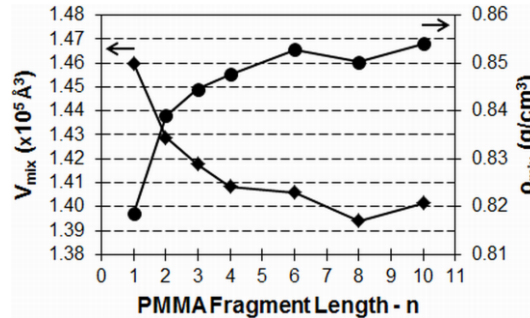


Figure 3: The simulation box volume and density for mixtures of PMMA fragments of various sizes with MIBK after NPT (isothermal-isobaric) equilibration (750 ps).

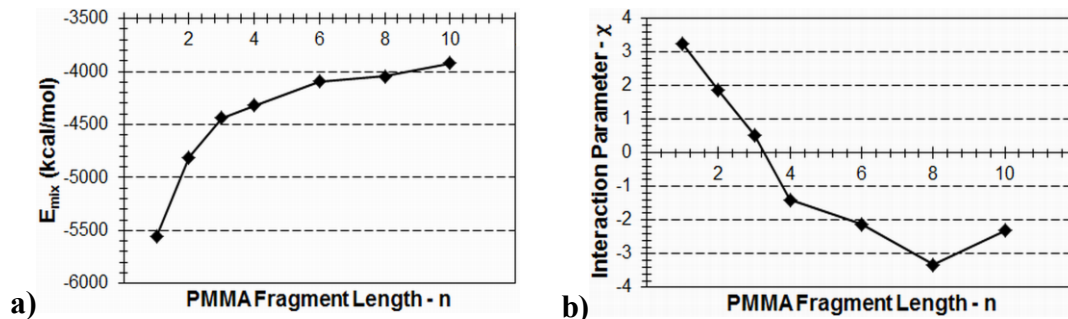


Figure 4: Potential Energy of mixture (a) and the Flory-Huggins interaction parameter χ (b) plots vs. PMMA fragment size in the PMMA-MIBK mixture after NVT (canonical ensemble) simulation (1000 ps). Large positive values of χ can be interpreted as a limited miscibility, whereas negative values correspond to well miscible mixtures.