Quantitative Structure-Property Relations for the Prediction of the Glass Transition Temperature of Molecular Resists

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There has been a large amount of interest recently on the use of molecular resists for use in next generation lithography, especially extreme ultraviolet (EUV) lithography. One of the main concerns about any photoresist, but especially molecular resists is their glass transition temperature (Tg). While most of the standard polymeric chemically amplified resist (CAR) platforms used have well known Tg's above 100^{o}C, a literature scan of molecular resists has shown a wide range of measured Tg's from near room temperature to greater than 160^{o}C. While there is some correlation between Tg and molecular weight for fully unprotected compounds, molecular weight is a very poor predictor of Tg for molecular resists as a whole due to the wide variety of structural moieties and protecting groups. This is well demonstrated in the fact that the Tg of molecular resists generally tends to decrease as protecting groups are added, despite the fact that the molecular weight increases. Figure 1 shows a plot of Tg vs. molecular weight for a large number of different molecular resists and number of protecting groups taken from literature.[1,2,3] There is poor correlation, if any, between Tg and molecular weight when molecular resists as a whole are considered. This result is to be expected since the Tg of materials is a function of the structural flexibility, molecular mobility, etc. We have developed several different quantitative structure-property relation models based on bond, group, and structural contribution along with other parameters that allow the prediction of the Tg of molecular resists based on their full chemical structure. It works well across multiple different levels of protection, different structure moieties, and different molecular sizes. Figure 2 shows a plot of predicted Tg vs. experimental Tg using one of the early models for the same set of compounds in Figure 1. This study will discuss that model and newer implementations of it that allow for more accurate prediction of Tg. A new larger set of molecular resists is also used to further validate the model.

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[1] De Silva, A., J. K. Lee, et al., *Chem. Mater.* **2008**, 20(4), 1606-1613.
[2] Hirayama, T., D. Shiono, et al., *Proc. SPIE,* **2005**, 5753, 738.
[3] De Silva, A., N. Felix, et al., *Proc. SPIE,* **2008**, 6923, 69231L.

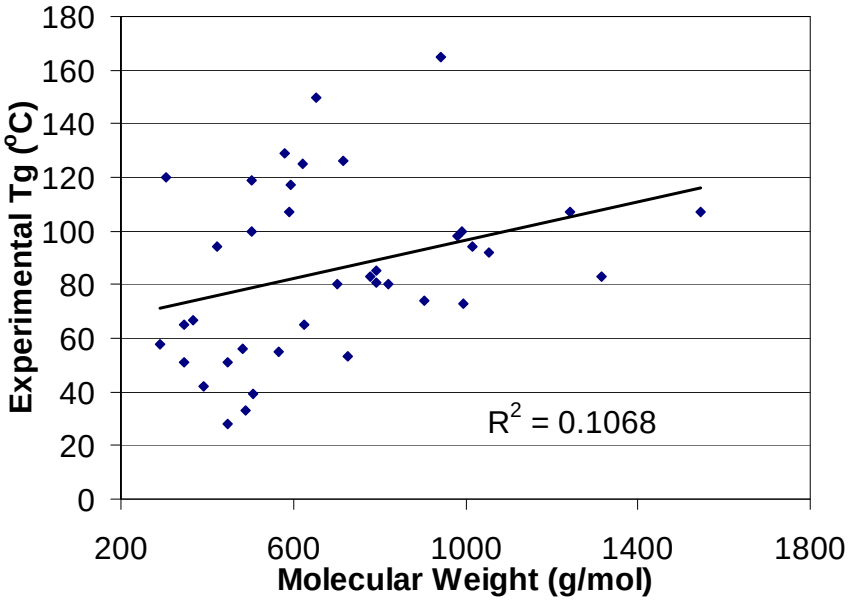

Figure 1. Tg vs. molecular weight for a large number of different molecular resists and number of protecting groups demonstrating the poor correlation between Tg and MW.

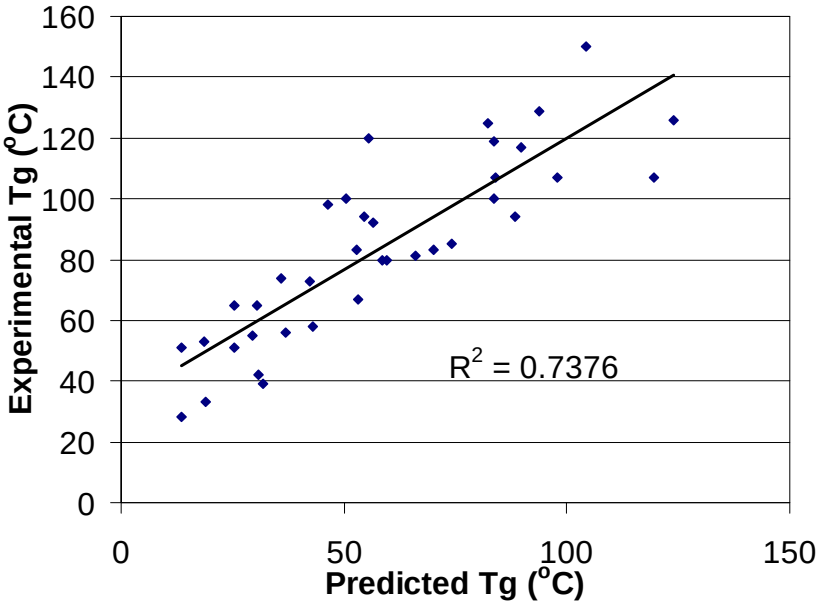

Figure 2. Experimental Tg vs. Tg predicted using the structure-property relationships such as bond and group contribution.