

The Effects of Solvent Choice on the Regioselectivity of Ketene Radical Polymerization

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Ketenes ($\text{H}_2\text{C}=\text{C}=\text{O}$) are versatile bifunctional molecules¹ that have been recently proposed as monomers for synthesizing conjugated polymers via radical polymerization. The radical chain propagation can in principle alternate between all three centers, C_α , C_β , and O, which may lead to very different polymer products. It is therefore important to understand the regioselectivity of ketene radical polymerization and to identify ways to control it. The purpose of this project is to determine the effect that solvents have on the regioselectivity of the radical system. This work studies the methyl silylacetate radical as a model of methyl trimethylsilyl-acetate, which has been shown to be promising in experiment. All data was obtained using the Q-Chem² program package and the $\omega\text{B97X-D}$ density functional³ in combination with the 6-311++G(3df, 3pd) basis set. Solvent effects were modeled by polarizable continuum models, which are dependent upon the dielectric constant (ϵ) of a solvent. A range of $0 \leq \epsilon \leq 80$ was sampled to approximate apolar solvents such as oxirane through polar solvents such as water. Frequency calculations and CHELPG charge analysis were performed to determine the effect that solvent has on vibrational frequency, dipole moment, spin density and atomic partial charge. These analyses were chosen to obtain an answer to the question “where is the radical?”: CHELPG charges and dipole moment provide direct information about the charge distribution, and vibrational frequencies are sensitive to bond strengths which is affected by the location of the radical electron. Importantly, these vibrational frequencies can be easily compared to experiment. Finally, the spin density yields a more qualitative picture of where there is unpaired electron density, or where the radical resides. Our results reveal a common pattern: the largest changes occurred for $\epsilon=1-10$, with very little change for $\epsilon=11-80$. Frequency was noted to have shifted by about 3 cm^{-1} within this range, and the partial charge on oxygen decreases by just under $-0.05e$, while only $0.02e$ of the extra negative charge are accounted for by the C_β the rest appears to be contributed by C_α . The magnitude of the dipole moment increases by about 0.5 Debye, which is quite significant. These findings indicate that choosing solvents in the $\epsilon=1-10$ range should allow one to significantly alter the regioselectivity, and these solvents should be explored experimentally for further study of the radical chain polymerization.

References:

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