Atomistic Simulations of Self-Organization in MDI Hard Domains

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Atomistic simulations have been performed under the auspices of an LDRD/DR* project on the Science of Polymer Aging to understand the competition between hydrogen bond registration and van der Waals packing among Bis-1,1'(methylphenyl-4-carbamate) molecules (MDI), which comprise the urethane "hard segment" in Estane, a segmented poly(ester urethane) copolymer used as a binder consitituent in certain plastic-bonded explosive formulations. Estane is thought to undergo microphase segregation into MDI-rich "hard domains" in a "soft" matrix of polyester, with the hard domains serving as thermally labile physical crosslinks that enhance the elastomeric properties of the polymer. The calculations provide insight into the physical driving forces that govern the extent of self-organized packing or crystallization of the chevron-shaped MDI units, which has been the subject of speculation in the literature [1]. Moreover, the simulations help define the minimum level of detail required to reproduce that structure in complementary coarse-grained simulations for Estane. The calculations were accomplished using software from Molecular Simulations, Incorporated (MSI) in conjunction with the Polymer Consistent Force Field (PCFF).

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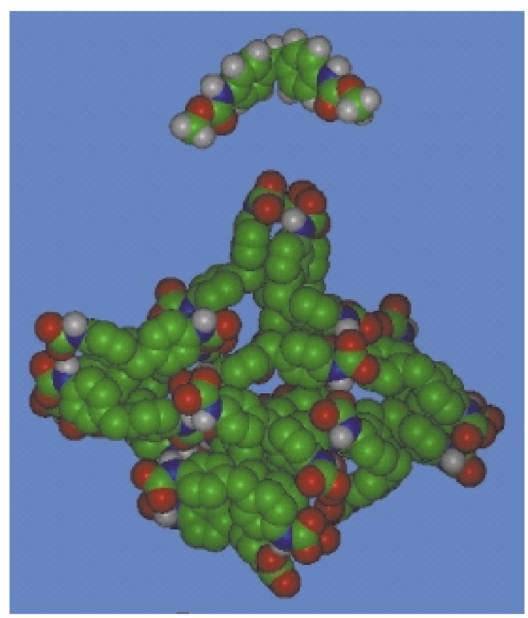
A "droplet" comprised of twenty methoxy-capped MDI units was constructed by positioning randomly oriented MDIs close to one another and then performing constant temperature molecular dynamics (300 K) for a period of 2 ns. A snapshot of the final configuration from the simulation is shown in the figure. All non-amine hydrogen atoms and terminal methyl carbons have been removed for clarity. From the figure, one can easily see that hydrophobic/hydrophilic interactions are important. There is a clear tendency to form hydrogen-bond chains between urethane groups on different molecules (strong hydrophilic interactions), while the hydrophobic regions of the molecules tend to align so as to maximize overlap between phenyl rings and/or the alignment of the central methyl carbon atoms. (We speculate that the hydrogen bond chains and phenyl ring stacking are the dominant drivers in this segregation.) Although the registration and stacking motif is imperfect, it is highly suggestive that these interactions lead to local ordering in an annealed material–although probably not crystallization–and provides important insight into the level of detail needed for our coarse-grained models of the hard segment in Estane. Planned extensions to this work include treatment of larger numbers of molecules and imposition of three-dimensional periodic boundaries.



**LDRD/DR (Laboratory Directed Research & Development/ Directed Research).*

[1] L. M. Leung and J. T. Koberstein, J. *Poly. Sci. B Poly. Phys.* **23**, 1883 (1985).