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Development of Model Systems for Computational Studies of MDI-Based Polyurethanes

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Abstract: Methylenediisocyanate-based (MDI) polyurethanes consist of two molecular moieties, namely, MDI hard segment and the polyol soft segments. The properties of these polymers are assumed to be highly connected to the packing of hard and soft segments. In this research, a computational model system was developed to represent the hard segments of a MDI-based polymeric system.

This model system is composed of two molecular moieties, namely, MDI and butane-diol (BDO). The hard segment is MDI and BDO is the chain extender. The initial molecular geometry was obtained by using AM1 method and it was further optimized to an equilibrium geometry using DFT/6-31G* level of theory with steepest decent algorithm. The model crystal system was built by using 64 of MDI-BDO molecules. The density of the model system was chosen to match the density of the actual MDI-based polyurethane with a high hard segment ratio. Density was calculated as 1.192 g/cm^3. Molecular Dynamics (MD) simulations were performed for this system for 200 ns at 300 K with the OPLS force field with periodic boundary conditions.

It is clearly seen in the optimized structure that the polymer molecule has a v-shaped (bent) hard segment owing to the sp^3 hybridization of the CH_2 carbon that connects the phenyl moieties. The distances of R(N–H), R(C=O) and R(C–O–) involved in hydrogen bonding are 20.1 Å and 39.0 Å, respectively. The H-bond distances obtained from the model system are in excellent agreement with the reported experimental values.

The model system was validated by calculating the glass transition temperature (Tg) of the system. Specific volume of the system was plotted against the temperature of the system. Specific volumes were obtained using 5ns MD simulations which were equilibrated at different temperatures. The calculated Tg was 105.00 °C and the reported value in the literature is 108.85 °C.

Based on the Tg values and the H-bonding patterns, it confirms that this novel MDI-BDO system is a valid model to represent the hard segments of the MDI-based polyurethanes. Further this model can be used in *in-silico* investigations of physiochemical properties of the hard segments of the MDI – based polymers.

Keywords: MDI, topology of MDI, dynamics of MDI, thermal transition, H-bonding

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