Karunarathna, B., Jayakody, R.S., Karunanayake, L. *et al.* Computational development and validation of a representative MDI-BDO–based polyurethane hard segment model. *J Mol Model* **27,** 37 (2021). https://doi.org/10.1007/s00894-020-04660-6

ABSTRACT:

Segmented polyurethanes show extraordinary physicochemical properties, mainly owing to the nature and the chemistry of the hard segment domains. There are yet many inexplicable physiochemical properties of MDI-BDO–based hard polyurethane segments such as the geometry, *cis–trans* isomerism, electronic structure, chemical reactivity, the inter-hard-segment interactions, and the photo-response. In the present study, it was attempted to develop and validate a model system that would facilitate further research on the structural and chemical properties of the MDI-BDO hard segments. It was found that the *trans* isomer of urethane bond is more stable than the *cis* isomer, and it is argued here that thermal transformation from *trans* to *cis* not possible due to the high rotational energy barrier. The differences between the calculated IR spectra of the *cis* and *trans* isomers are proposed as a powerful differentiation tool. The calculated Fukui indices show that *cis* and *trans* isomers are different in their chemical reactivity. The findings of the present study suggest intermolecular and intramolecular pi-stacking and highly plausible two significant types of hydrogen bond types between hard segments. In the present study, a model system for MDI-BDO hard segment was developed and successfully validated via computational experiments. Further calculations done with the new model provided an indispensable understanding of the structure, *cis–trans* isomerism, reactivity, and intermolecular interactions of the MDI-BDO hard segments. The proposed model can be further improved in the future by incorporating suitable soft segments. In summary, the model system developed and validated in the present study has provided new opportunities to understand and further study the structural and chemical features of the hard segments of the MDI-BDO–based polyurethane.