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| In-silico Studies of Complex Molecular Systems via Computational Modeling and Data-driven Atomistic Simulations: ‘Linear-to-Colloidal' Transition in Star Polymers  **Eirini Gkolfi** 1,2,#,\*, **Petra Bačová** 4 and **Vagelis Harmandaris** 1,2,3,\*  1 Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas (FORTH), GR-70013 Heraklion, Crete, Greece  2 Department of Mathematics and Applied Mathematics, University of Crete, GR-71409 Heraklion, Greece  3 Computation-based Science and Technology Research Center, The Cyprus Institute, Nicosia 2121, Cyprus  4 Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, IMEYMAT, Campus Universitario Río San Pedro s/n., Puerto Real, Cádiz 11510, Spain  # Presenting author: eirini.gkolfi@iacm..forth.gr  \* Corresponding authors: eirini.gkolfi@iacm..forth.gr and [vagelis@iacm.forth.gr](mailto:vagelis@iacm.forth.gr) |

abstract

Computer simulations of molecular systems complement experimental works due to their flexibility and lower cost. Polymers, which dominate material design, are at the forefront of industrial interest. Star-shaped polymers represent a promising macromolecular architecture in fields such as energy, biomaterials, and drug delivery, owing to their diverse behavior, ranging from linear-like to colloidal-like. The ‘linear-to-colloidal’ transition seems to be affected by the number and length of arms (linear chains) attached to the central branch point.[1,2] However, chemical effects remain unexplored, as most computational studies use simplified, generic models and experimental methods cannot capture easily the necessary intramolecular details.

In this work, we employ atomistic molecular dynamics (MD) simulations of star-shaped polymers and we use in-house data-driven algorithms to analyze the simulation results and predict the materials properties. Through the structural and dynamical behavior, we investigate how the number of arms (f) and arm length differently affect the behavior and molecular packing of polystyrene (PS) and poly(ethylene oxide) (PEO) stars in melts.[3] The results of these two chemistries are also discussed in terms of arms with an equal number of Kuhn segments – a statistical measure of chain length used in theoretical and coarse-grained (CG) models. Our computational analysis allows us to employ detailed intramolecular calculation such as the distribution of free volume around different parts of the molecule and segmental displacement. According to our results, the spherical shape, decreased intramolecular free space and increased intermolecular distances, along with a tendency toward convergence between center-of-mass and segmental displacements, which indicate colloidal-like behavior, are more pronounced in PS, particularly with shorter, more numerous arms.

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