# EFFECT OF MOLECULAR ARCHITECTURE ON THE LINEAR-TO-COLLOIDAL TRANSITION OF STAR POLYMERS THROUGH ATOMISTIC SIMULATIONS

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## ABSTRACT

Nowadays, there has been a growing interest in all-polymer nanocomposites as sustainable and versatile materials with a wide range of rheological behavior. Particularly star-shaped polymers which exhibit a unique soft and tunable character, transitioning from fully penetrable chain-like structures to particles resembling conventional solid additives, a phenomenon known as the linear-to-colloidal transition.[1,2] The dynamical behavior of these molecules seems to be tuned through the number of arms attached to the common branch point (functionality) and the arm length while recently the internal packing has been suggested as another tuning factor.[3]

This work aims to explore the molecular architecture dependence of the linear-to-colloidal transition in non-entangled stars within melts, using atomistic data from molecular dynamics (MD) simulations. We investigate two dissimilar polymer types, poly(ethylene oxide) (PEO) and polystyrene (PS) stars, differing in flexibility and glass transition. By varying functionality and arm length, we seek to modify mutual penetration and adjust local packing. In addition to our previous analysis,[4,5,6] a sophisticated grid-based algorithm is employed to estimate free volume in the systems, providing insights into dynamical properties and local packing of the stars. The flexibility of our computational

analysis allows for a detailed investigation, including heterogeneities in the distribution of unoccupied spaces around different molecular segments. This analysis reveals significant qualitative differences between the two monomeric types, highlighting distinctions in local packing and chain stiffness that cannot be examined through experimental studies or more generic (coarse-grained) models.

Our chemistry-specific results offer complementary knowledge on structural parameters influencing the unique behavior of stars, ranging from linear-like (random walk statistics) to colloidal-like. This research contributes to deeper understanding of materials composed of branch-like polymers, particularly in applications like all-polymer nanocomposites or nanostructured electrolytes.[7]

**KEYWORDS:** Star polymers, Free volume, Atomistic simulations, Molecular dynamics (MD) simulations

## REFERENCES

[1] Parisi D, Camargo M, Makri K, Gauthier M, Likos C, Vlassopoulos D. (2021). *J.Chem. Phys*. 155, 034901.
[2] Vlassopoulos D, Fytas G, Pakula T, Roovers J. (2001). *J.Phys.:Cond.Matter,* 13, R855.
[3] Johnson K, Glynos E, Sakellariou G, Green P. (2016). *Macromolecules*, 49, 15, 5669–5676.
[4] Gkolfi E, Bačová P, Harmandaris V. (2021). *Macromolecular Theory and Simulations,* 30, 2000067.
[5] Bačová P, Gkolfi E, Hawke L. D. G, Harmandaris V. (2020). *Physics of Fluids*, 32, 127117.
[6] Bačová P, Gkolfi E, Harmandaris V. (2023). *Nano Letter,* 23, 4, 1608–1614.
[7] Bačová P, Glynos E, Anastasiadis S. H, Harmandaris V. (2019). *ACS Nano,* 13, 2439.