The Link Between Star Polymer Structure and polymer/polymer-film dynamics

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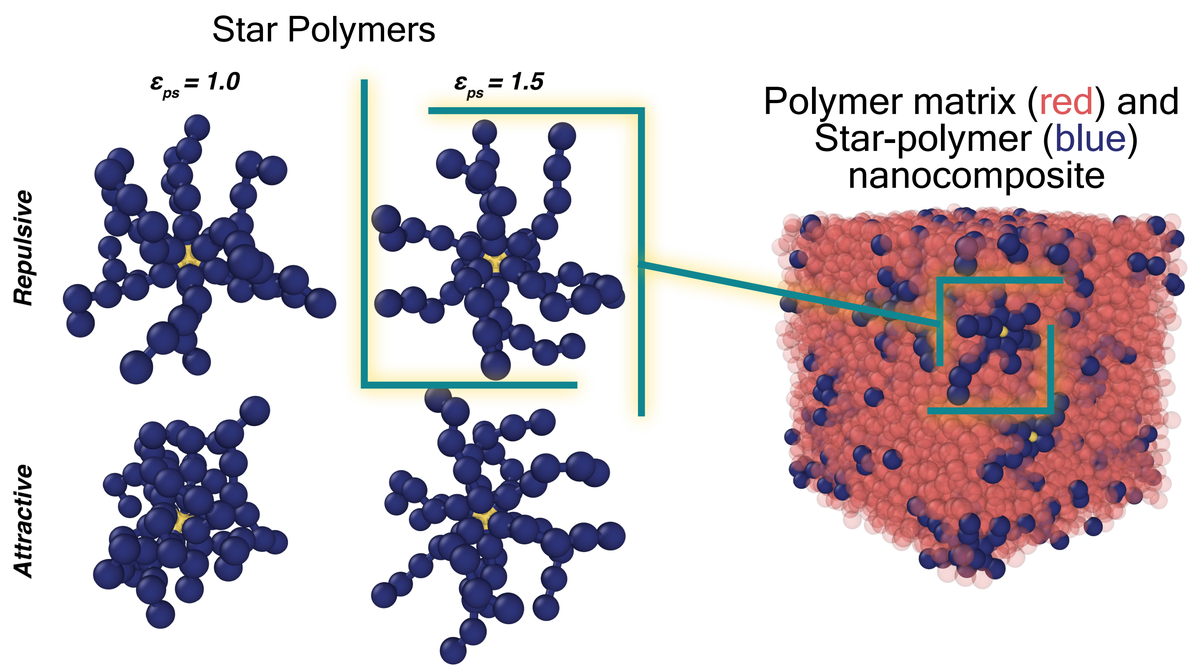
Introduction

Star polymers are an extension of traditional polymers consisting of many polymer "arms" linked to a central core. Previous work qualitatively characterized how the number and length of arms affected polymer matrix dynamics. It was shown that repulsive star arm interactions led to slower dynamics within bulk polymer matrices. We explicate this phenomenon by quantitively describing embedded star polymer conformations. We link the radius of gyration R_g to the relevant parameters (relaxation time and the breadth of the relaxation spectrum) which describe the polymer matrix dynamics. By tuning the interaction strength (ε_{ps}), we show that the resulting changes in dynamics are not solely due to the increased tendency for polymers to interact with stars. Rather, a change in conformation is what facilitates better interactions with stars and the polymer matrix.



These plots show the effect of attractive arm interactions at low interaction strengths. Larger interaction strengths push attractive stars towards fluffier conformations while repulsive stars remain relatively stable.

Methods

Simulations

- Simulations ran using LAMMPS
- XYZ periodic boundary conditions
- Harmonic spring and Lenard Jones potentials

Relevant Parameters

- R_g - Radius of gyration
- β - Stretching exponent
- τ - Characteristic relaxation time
- ε_{ps} - Polymer matrix and star bead interaction strength

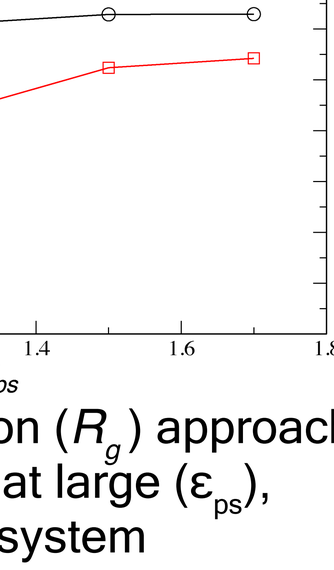
Conclusions

Main Findings

Flufflier star polymer conformations result in larger polymer matrix relaxation times as well as exhibit relaxation behavior only seen at larger interaction strengths. Fluffier star conformations allow for enhanced star-polymer & polymer-matrix interactions which alter polymer matrix dynamics by slowing relaxation time and raising the glass transition temperature of the materials.

Future Work

Work done with the bulk system helps identify the effects of star polymers near the middle of ultra-thin polymer films. Having identified how star confirmation affects the dynamics of the polymer matrix, we now have sufficient reference data to study the films.



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Results

- The radii of gyration (R_g) approach similar values, at large (ε_{ps}), for each system
- larger interaction strengths (ε_{ps}) produce similarly behaving relaxation profiles and larger (τ) differentials
- larger number of arms (f) promote non-monotonic behavior of (τ) and (β)