Coarse Graining Atactic Polystyrene and its Analogues

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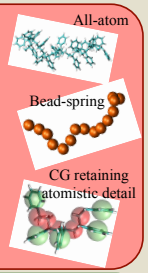
Abstract

Using a new set of coarse grain potentials for polystyrene, we provide new insight into interdiffusion. This potential incorporates 2 beads to represent one monomer. This 2:1 CG model presents an immense improvement over previous studies since it captures the stereochemistry of the polystyrene. These CG models can be back-mapped to the atomistic structure. With this successful model, we provide new insights into impacts of interfacial roughness on diffusion.



Interdiffusion

Adhesion, welding, self healing

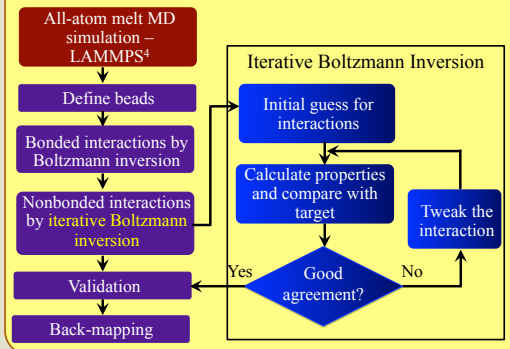
Manufacturing polymer based devices

- Neutron reflectometry experiments capture long time interdiffusion of polystyrene. At these time scales, the experiments capture overall diffusive motion. [1,2]
- Computational studies using bead-spring models were employed to study similar systems. These studies found that the onset of diffusion is dominated by chain ends.[3]
- Here we probe the onset of diffusion using a coarse grain model that carries some of the chemical information of the polymer.

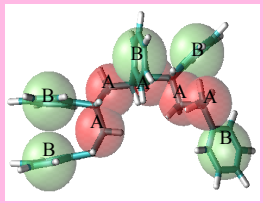
Goals

- Develop methodology for coarse graining of polystyrene and back-mapping the results to atomistic level
- Understand the mechanism of interdiffusion of polystyrene using this CG model

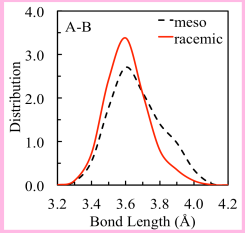
Methodology for Coarse Graining



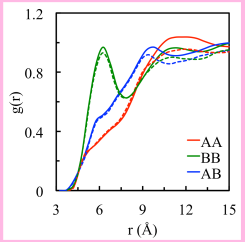
Coarse Graining Polystyrene



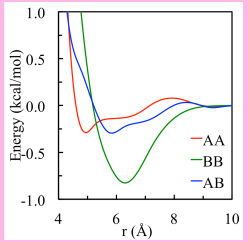
CG model of polystyrene - A bead represent the backbone and B bead represent the phenyl group[5,6]



Bonded distribution for meso and racemic pairs of atactic polystyrene

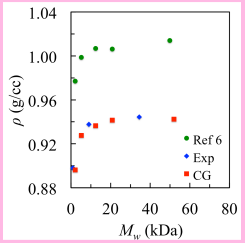


Radial distribution function from atomistic (solid lines) and CG model (dashed lines)[7]

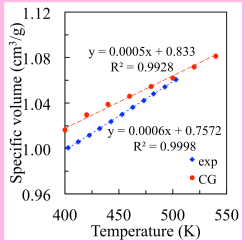


Non-bonded interaction energy between different type of beads obtained after fitting

Validation of CG model



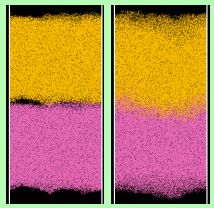
Density dependence of polystyrene on molecular weight. Experimental data is obtained from Ref 8.



Thermal expansion coefficient from CG model for M_w = 20 kDa and experiment[8] for M_w = 34.5 kDa

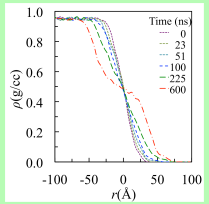
Interdiffusion of Polystyrene

Rough Interface



Starting state t = 200ns

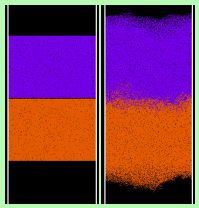
M_w = 50kDa, 139 chains in each block



Density profile

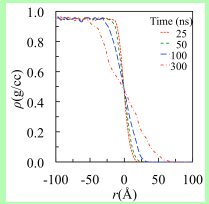
- Bulk diffusion coefficient decreases with increasing M_w.
- Time taken for interface to become homogeneous at 500K was ~50ns.
- At longer times (>200ns), interfacial profile does not remain smooth.

Smooth Interface

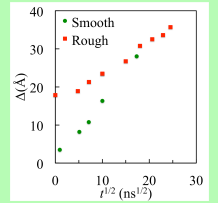


Starting state t = 200ns

M_w = 50kDa, 139 chains in each block



Density profile



Interpenetration width for the two cases

- It takes approximately 5ns to reach τ_d at 500K.
- At longer times (>200ns), interface profile does not remain smooth which was also observed in rough interface simulation.

Conclusions

- Potential for 2:1 coarse grain model of polystyrene is developed that capture the stereochemistry, using a single all-atom atactic polystyrene melt simulation.
  - An excellent match with the experimental result for the density dependence of M_w is obtained using our CG model.
  - Thermal expansion coefficient and compressibility calculated using our model match well with the experimental data.
  - Diffusion coefficient of atactic polystyrene decreases with increasing M_w. The scaling factor obtained from CG model increases with the M_w.
- Interdiffusion of polystyrene takes a different route for diffusion in rough and smooth interfaces.

References

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