Theoretical modeling of reversibly associated polymers

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ABSTRACT

We consider flexible linear oligomers with functional donor and acceptor end groups allowing reversible association. The formation of hydrogen bonds between donor and acceptor end groups of linear oligomers is modeled. We then develop an analytical theory and an efficient Monte Carlo simulation to study association properties and behavior of the polymer solutions. Results of both methods show that the degree of association stays more or less constant as the polymer concentration increases. We find that the degree of association stays more or less constant as the polymer concentration increases. We find that the formation of linear polymers is responsible for this discrepancy between theoretical and simulation results. Future goals for this research include: developing a more sophisticated analytical theory for the mean oligomer number to better account for the presence of cyclic polymer chains. We also show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)).

LATITICE MODEL FOR MONTE CARLO SIMULATION

We use a six-site bond-fluctuation model (SBFM) in two dimensions (2D) to study the polymer systems [5]. It is a lattice model where monomers occupy regular cubic lattice sites. In accounting for the formation of hydrogen bonds between donor and acceptor end groups, we apply Aqvist's fluctuating bond model. Association properties and behavior of the polymer solutions are studied. Results of both methods show that the degree of association stays more or less constant as the polymer concentration increases. We find that the formation of linear polymers is responsible for this discrepancy between theoretical and simulation results. Future goals for this research include: developing a more sophisticated analytical theory for the mean oligomer number to better account for the presence of cyclic polymer chains. We also show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)).

RESULTS

We first obtain from our simulations the degree of association \(\langle\Phi\rangle\) as a function of oligomer length \(L\) and bonding energy \(\Delta G_{\text{combo}}\). In order to compare our simulation results with predictions of mean-field theory the only thing we need to know in the simulation is the effective volume per site \(v_{\text{eff}}\) (where \(v_{\text{eff}} = 8\) as the effective volume per monomer). Since the number of four-site oligomers of length \(L\) and \(0.5\) is not readily available, we estimate \(v_{\text{eff}}\) by considering the number of tetramers from the least square fitting of the simulation data in equation (1) and obtain \(v_{\text{eff}} = 9\). The use of this number in mean-field calculations then, in Figure 3 the results show that there is always some fraction of cyclic polymer present in equilibrium with linear chains. The inset of the graph shows weight distribution at higher temperature which favors the formation of bigger polymers and small molecular weight loops due to the associated free energy. Results show that there is always some fraction of cyclic polymer present in equilibrium with linear chains. The fraction of cyclic polymers depends on the oligomer chain length, triple and polymer concentration. At high concentrations and high association energy, cyclic polymers disappear and the fraction of linear association stays close to 1.

CONCLUSION & FUTURE WORK

The mean-field theory and Monte Carlo simulations are found to be in a good agreement over a wide range of oligomer association energies and concentrations. The future goals for this research include: developing a more sophisticated analytical theory for the mean oligomer number to better account for the presence of cyclic polymer chains. We also show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)).

REFERENCES

5. P. J. Flory, Principles of polymer chemistry; Cornell University, Ithaca, NY, 1953.

The presence of the cyclic polymer strongly affects the various properties of the system. For example, Figure 7 shows the average molecular weight of linear oligomers versus association energies of the four-site and the two-site oligomers, for example, \(m_{\text{avg}} = \langle\Phi\rangle\) and number of oligomers, \(c\) - Classical condensation polymerization theory [5] is a good model along the lines which does not explain the results from Monte Carlo simulations. The simulations show that the association and energy ranges considered have a very small effect on the mean oligomer number. This is also not true in the case of the Monte Carlo simulations. The results mean-field theory and mean-field theory show that there is always some fraction of cyclic polymer present in equilibrium with linear chains. The inset of the graph shows weight distribution at higher temperature which favors the formation of bigger polymers and small molecular weight loops due to the associated free energy. Results show that there is always some fraction of cyclic polymer present in equilibrium with linear chains. The fraction of cyclic polymers depends on the oligomer chain length, triple and polymer concentration. At high concentrations and high association energy, cyclic polymers disappear and the fraction of linear association stays close to 1.

In Figure 4 we compare the theoretical predictions of mean-field theory and Monte Carlo simulation results (symbols) for linear chains of length \(L\) in a two-site oligomer. As in the previous figure, the results of the Monte Carlo simulations and mean-field theory also are in a good agreement over a wide range of oligomer association energies and concentrations. The results from mean-field theory and Monte Carlo simulations are found to be in a good agreement over a wide range of oligomer association energies and concentrations. The future goals for this research include: developing a more sophisticated analytical theory for the mean oligomer number to better account for the presence of cyclic polymer chains. We also show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)).

In Figure 5 we show similar average molecular weight distributions for the fraction of linear chains (0.5) for high association energy (\(\Delta G_{\text{combo}} = 1\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)). For all results presented below we use box size \(L = 256\times256\). We have taken care that this box size is large enough to ensure that all linear chains are completely dissolved in the simulation.

The results mean-field theory and Monte Carlo simulations are found to be in a good agreement over a wide range of oligomer association energies and concentrations. The future goals for this research include: developing a more sophisticated analytical theory for the mean oligomer number to better account for the presence of cyclic polymer chains. We also show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)).

In Figure 6 we show similar average molecular weight distributions for the fraction of oligomers of high association energy (\(\Delta G_{\text{combo}} = 0\)) and for linear and cyclic chains for high association energy (\(\Delta G_{\text{combo}} = 1\)). For all results presented below we use box size \(L = 256\times256\). We have taken care that this box size is large enough to ensure that all linear chains are completely dissolved in the simulation.