



Theoretical modeling of reversibly associated polymers

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ABSTRACT

We consider flexible linear oligomer chains with functionalized donor and acceptor end groups allowing reversible association (via hydrogen bonding). As a result of such association either linear or cyclic polymers are formed. These polymers exhibit a range of interesting properties including temperature dependent viscosity, phase behavior and rheological properties. We apply a mean field theory and Monte Carlo simulations to study association properties and behavior of the polymer solutions. Results of both methods show that the increase in polymer concentration or decrease in oligomer chain length results in the increase of the average degree of association. The increase in the energy of association has a similar effect. Monte Carlo simulation 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, rigidity and polymer concentration. At low concentration and high association energy, cyclic polymers dominate and the fraction of linear associated chains is always low.

INTRODUCTION

Oligomers functionalized by end groups capable of reversible association have attracted increasing interest during recent years [1-3]. Recent progress in synthesis has allowed the addition of functional groups to polymer ends that allows strong but reversible association. Among such functional groups are the complexes designed for simultaneous formation of multiple hydrogen bonds (Figure 1a reproduced from [1]) or DNA segments with complementary sequences at different ends (Figure 1b reproduced from [2]). These oligomers can effectively form long chain polymers through repeating the association of their functional end groups (Figure 1c). However, unlike the covalent bonding responsible for regular polymerization process, these bonds are reversible and temperature dependent. This allows one to control the extent of association and thus the average molecular weight of the polymers through the change in temperature or concentration of donor and acceptor groups in the solution. Viscosity, phase behavior and rheological properties of a polymer system are mostly determined by the distribution of molecular weights and therefore are also strongly influenced by these factors. This opens up possibilities to construct new materials with controllable properties taking advantage of this reversible bonding. In this research, we use a mean-field approach along with Monte Carlo simulations to study a system of oligomers with donor and acceptor end groups to understand the effects such as the energy of association, concentration, and oligomer length on the properties of the system.

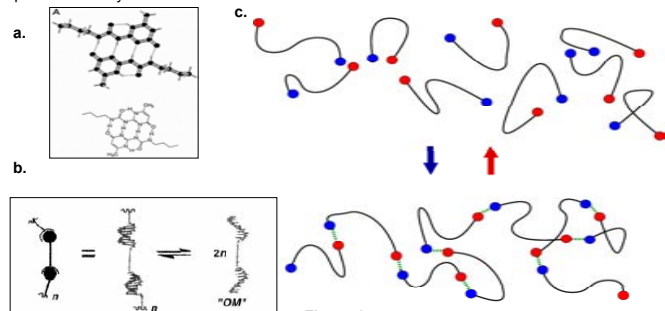


Figure 1

MEAN-FIELD APPROACH

Applying Flory-Huggins based theory we calculate the free energy of the polymer system as

$$F_{\text{total}} = F_{\text{ref}} + F_{\text{assoc}}.$$

The free energy of the reference system with noninteracting oligomers F_{ref} is given by

$$\frac{F_{\text{ref}}}{kT} = \frac{\Phi v}{N v_p} \ln \left(\frac{\Phi v}{N v_p e} \right) + (1 - \Phi) \ln \left(\frac{1 - \Phi}{e} \right)$$

where Φ is the volume fraction of oligomers in the solution, N is the oligomer chain length, while v and v_p are the characteristic volumes of solvent molecules and monomers. The contribution of the free energy from hydrogen bonding F_{assoc} can be written as

$$\frac{F_{\text{assoc}}}{kT} = -\frac{v}{V} \ln Z_{\text{assoc}}$$

where V is the volume of the system and the partition function of hydrogen bonding Z_{assoc} is given by

$$Z_{\text{assoc}} = P_{\text{comb}} W \exp \left(\frac{\Delta E_{\text{hb}}}{kT} n_{\text{hb}} \right)$$

where P_{comb} is the combinatorial factor for the number of ways that donors and acceptors of functionalized end groups can form n_{hb} hydrogen bonds, and $W = (v_{\text{hb}}/V)^{n_{\text{hb}}}$ is the probability that these donor and acceptor end groups are within the range and right orientations for formation of the corresponding hydrogen bonds, and ΔE_{hb} is the energy of the hydrogen bond. Minimizing F_{total} with respect to the degree of hydrogen bonding $p = n_{\text{hb}}/n$, where n is the number of oligomers in the system, we obtain

$$p = \exp \left(\frac{\Delta E_{\text{hb}}}{kT} \right) (1 - p)^2 \left(\frac{\Phi}{N} \right). \quad (1)$$

From the degree of association, we can derive various properties of the system, for example, the average molecular weight is given by $1/(1 - p)$ in number of oligomers each polymer contains.

LATTICE MODEL FOR MONTE CARLO SIMULATION

We use the so-called bond-fluctuation model (BFM) in 3 dimensions (3D) to study the polymer system [4]. It's a lattice model where monomers occupy regular cubic lattice sites. In accounting for the volume exclusion between monomers, the distance between monomers is required to be greater than $2a$, where a is the lattice spacing. For connected monomers in a chain, the bond length between them fluctuates between $2a$ and $\sqrt{10}a$, where the later is the maximum bond length ensuring that two chains will never cross each other without breaking a bond.

In our simulations, we place n monodisperse oligomers of the chain length N in a cubic box of lateral size L with periodic boundary condition in all three directions. The monomers at the two ends of an oligomer are selected as a donor and an acceptor. A hydrogen bond can form between a donor end and an acceptor end. This reduces the energy of the system by amount of the bonding energy ΔE_{hb} . This association is exclusive, so that no additional hydrogen bond can be formed with the same donor or acceptor.

In the Monte Carlo simulation, we perform random update to the system and average over the sequence of system configurations that are generated. In each Monte Carlo time step, we make nN moving attempts for the monomers, that is, in average each monomer will try to make a move once. In each moving attempt, we randomly choose one monomer and a direction from the 6 possibilities $\{\pm \hat{e}_x, \pm \hat{e}_y, \pm \hat{e}_z\}$ in 3D. The monomer is to move by one lattice unit a in the chosen direction. This move is rejected if the monomer is moving into a site of distance less than $2a$ from any other monomers. The move is also rejected if the monomer is moving into a site of distance greater than $\sqrt{10}a$ from any of the monomers that it is bound to covalently.

The subtle part of the simulation is the behavior of hydrogen bonds. Consider a move of a donor that is allowed after considering the volume exclusion and covalent bond length constraints. If the donor is associated with an acceptor through hydrogen bonding before the move, the bond is to be broken by move when the donor is moving to a distance greater than $\sqrt{10}a$ from the acceptor. Additionally, if after the move the donor is free, that is, it is not associated with any acceptors, it will randomly probe one of its neighboring sites within the distance $\sqrt{10}a$. If a free acceptor is present at the probed site, a hydrogen bond between them is to be formed after the move. Similar rules apply for moving an acceptor. The energy change of this move ΔE can be 0 or $\pm \Delta E_{\text{hb}}$ depending on the forming and/or breaking of the hydrogen bonds. Following Metropolis algorithm, the move is executed with probability $P = \min\{1, \exp[-\Delta E/(kT)]\}$ and rejected with probability $1 - P$.

For a given set of parameters $\{L, n, N, \Delta E_{\text{hb}}\}$, we measure the equilibrium molecular weight distributions of both linear and cyclic polymers formed by the reversible association of hydrogen bonding in the system. Various quantities can then be derived from these distributions.

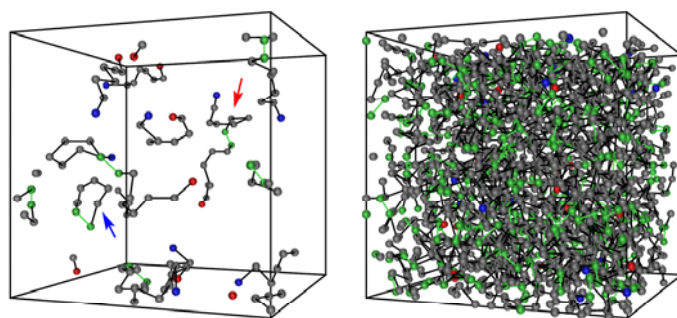


Figure 2

The snapshots of two typical configurations of the solutions of associated oligomers modeled by Monte Carlo simulations are shown in Figure 2. The dilute polymer solution (containing $n = 16$ oligomers) is shown on the left while the one to the right is for more concentrated solution (with $n = 256$ oligomers). These are typical concentrations considered in our simulations. In both cases the volume of the periodic box is $V = L^3 = 32^3$ and the bonding energy is $\Delta E_{\text{hb}}/(kT) = 8$. The free donor and acceptor end groups are colored in red and blue respectively while those forming hydrogen bonds are colored in green. The red arrow in the picture points to a linear polymer chain consisting of two oligomers while the blue arrow points to a cyclic polymer formed from a single oligomer. For all results presented below we use box size $V = 64^3$. We have taken care that this box size is sufficient for performing similar calculations with a smaller box size $V = 32^3$ without significant deviations in the simulation results.

RESULTS

We first obtain from our simulations the degree of association p as a function of oligomer chain length N and bonding energy $\Delta E_{\text{hb}}/(kT)$. In order to compare our simulation results with predictions of mean-field theory the only thing we need to know is the volume fraction of monomers in the solution $\Phi = nNv_{\text{monomer}}/L^3$ (where

v_{monomer} is the effective volume per monomer). Since the number of lattice sites occupied by each monomer in the Monte Carlo simulation is not readily available (in the method used) we estimate this number from the least square fitting of the simulation data to equation (1) and obtain $v_{\text{monomer}} \approx 2.545$. We use this number in mean field calculations thereafter. In Figure 3 the results of computer simulations (symbols) for the fixed number density of monomers ($nN = 8192$) and variable chain length are presented along with mean-field theory predictions (lines). The square boxes (simulations) in the graph

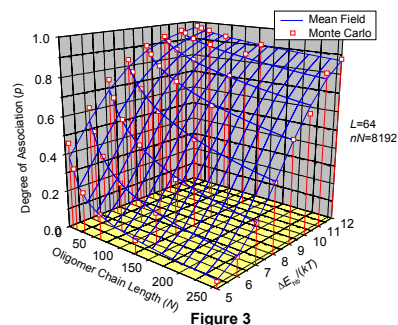


Figure 3

are very close to the mesh lines (theory) showing good agreement between mean-field theory and Monte Carlo simulations for the whole range of chain lengths and association energies considered.

In Figure 4 we compare the theoretical (lines) and Monte Carlo simulation results (symbols) for fixed oligomer chain length $N = 8$ and varying concentration. As in the previous figure, the increase in the energy of association is evidently increasing the degree of association. With increasing polymer concentration, number of donor/acceptor groups increases as does the degree of association. The results of Monte Carlo simulations and mean-field theory are also in a good agreement in the most of concentration and energy ranges considered, except for the dilute region of strongly associated polymers (high $\Delta E_{\text{hb}}/(kT)$). In this region the mean field theory predicts a decrease of degree of association but the Monte Carlo results show that the degree of association stays more or less constant.

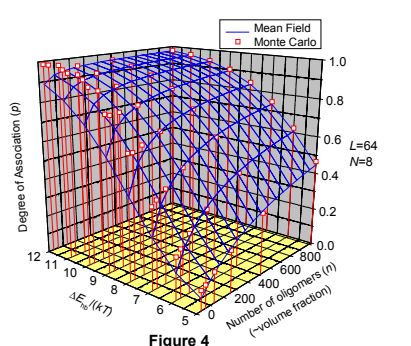


Figure 4

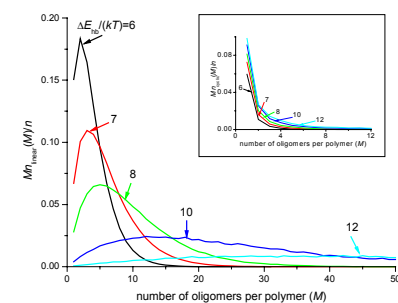


Figure 5

of the distribution shifts to the right (higher molecular weights) while becoming broader as the energy increases. The inset of the graph shows weight distribution of cyclic polymers. The fraction of cyclic polymers decreases rapidly as the overall molecular weight increases. Raising the bonding energy slows the rate of this decrease and increases the total number of cyclic polymers in the system. Considering the contribution of both linear and cyclic polymers we conclude that cyclic polymers are responsible for the initial decay in the molecular weight whereas linear ones define the molecular weight distribution at higher M .

In Figure 6, we show similar average molecular weight distributions for linear and cyclic chains for high association energy ($\Delta E_{\text{hb}}/(kT) = 12$) and fixed chain length while varying number of chains in the system (concentration) shown as numbers next to the lines. In this case the height of the peak for linear chains does not decrease as strongly as in Figure 5 whereas the width of the distribution considerably increases with an increase in concentration. For cyclic polymers the fraction of small molecular weight loops decreases at higher concentration which favors the formation of bigger loops.

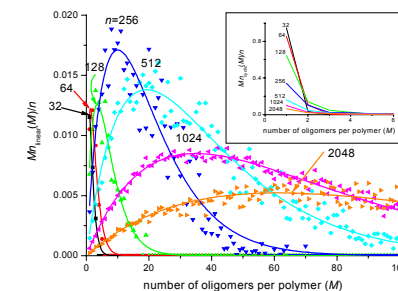


Figure 6

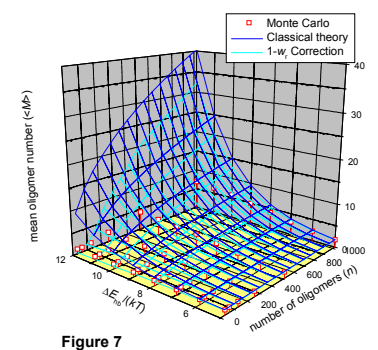


Figure 7

the simulation results. Apparently the average molecular weight of associated polymers formed in Monte Carlo simulations is smaller than that anticipated by classic polymerization theory. In other words the average number of chains formed in simulations is larger than expected in theory. This may be due to the formation of cyclic polymers or it may be connected with entropic effects which are not considered in classical polymerization theory [5].

CONCLUSION & FUTURE WORK

The results of mean-field theory and Monte Carlo simulations are found to be in a good agreement over most of the range of chain lengths, association energies and concentrations studied. Exceptions are the cases of low oligomer concentration and a high energy of hydrogen bonding. Analyzing the simulation data, we found that the formation of cyclic polymers is responsible for this discrepancy. The cyclic polymer chains maintain an equilibrium population that is always present in the system. This can dramatically change certain properties of the system. For example, in our study, we found the average molecular weight of the polymers is much reduced from what one would expect using classical expression for "condensation polymerization" [5]. While a simple correction to the effective degree of polymerization accounting for the weight fraction of cyclic polymers brings the estimate closer to the simulation results, there remains a significant deviation.

The future goals for this research include:

- Develop a more sophisticated analytical theory for the average molecular weight to better account for the presence of cyclic polymer chains.
- Study reversible association of different types of oligomers, for example, a mix of different oligomer chain lengths or functionalized end groups.
- Develop a computational model to study rheological properties of these systems, such as viscosity.
- Study the system under various boundary conditions, for example, the growth of reversibly associated polymers from a surface.

REFERENCES

1. E. Meijer, R. Sijbesma, F. Beijer, L. Brunsveld, B. Folmer, J. Hirschberg, R. Lange, and J. Lowe. *Science*, **1997**, 278, 1601-1604.
2. E. A. Fogleman, W. C. Yount, J. Xu, and S. L. Craig. *Angew. Chem. Int. Ed. Engl.* **2002**, 41(21), 4026-4028.
3. S. J. Rowan, P. Suwanmala, and S. Sivakova. *Polymer Preprints*, **2003**, 44(1), 616-617; S. J. Rowan and S. Sivakova. *Polymer Preprints*, **2003**, 44(1), 687-688.
4. K. Binder. *Monte Carlo and molecular dynamics simulations in polymer science*, Oxford University Press, New York, NY, **1995**.
5. P. J. Flory. *Principles of polymer chemistry*, Cornell University, Ithaca, NY, **1953**. (The equation for the number average molecular weight is $1/(1 - p)$. Accounting for cyclic polymers gives $(1 - w_c)/(1 - p)$ where w_c is weight fraction of cyclic polymers)