Monte Carlo Study of Reversibly Associated Polymers

Chun-Chung Chen\textsuperscript{a} and Elena E. Dormidontova\textsuperscript{b}

Department of Macromolecular Science and Engineering, Case Western Reserve University

REVERSIBLY ASSOCIATED POLYMERS

Reversibly associated polymers (RAPs) are macromolecules formed by reversible bonding such as donor-acceptor type hydrogen bonding arrays and complementary DNA sequences, shown below. In contrast to traditional covalent bonds, reversible bonds can be formed or broken depending on controllable parameters, such as temperature, concentration, and pH values. Thus, these polymers allow easier control of their properties and responsiveness to environmental changes. In our study, we employ analytical modeling and Monte Carlo simulations to study association properties of RAPs in good solvent conditions.

RING-CHAIN EQUILIBRIUM

At low oligomer concentration, the RAP consists of mostly rings while as concentration increases, chains take over. In the chain dominating region, the system is well described by a mean-field theory which depends only on the densities of donor and acceptor groups in the system.

METALLO-SUPRAMOLECULAR POLYMERS

Metallo-supramolecular polymers are formed through 1-to-2 coordination bonds between metal ligands and as shown in the extended model, flexibility of RAPs with increasing oligomer length have a smaller probability of forming small rings and the overall degree of association deviates from the mean-field prediction.

ROLE OF METALS

Non-cooperative bonding. With oligomer concentration fixed (c = 9.8 × 10^{-4} M), the degree of association increases with metal concentration until it reaches its maximum at the stoichiometric composition (1:1 metal:ligand ratio). Beyond the stoichiometric composition, the degree of association starts to decline as the metal concentration increases. A similar dependence is observed for the molecular weight, also reaching a maximum at a 1:1 metal-oligomer ratio. However, the decrease in the molecular weight is more considerable in the metal-rich region. By analyzing the distribution of metals among ligands, one can see that in the ligand-rich region, most of metals are bound to two ligands, while in metal-rich region, metal bonds are bound to no more than one ligand resulting in low molecular weight in this region.

COOPERATIVE BONDING

The rigidity of the donor-acceptor complex imparts an entropic penalty (ΔS) to the reversible bonding and decreases the overall degree of association. However, its impact on the crossover concentration of ring-to-chain transition is less significant comparing to the rigidity of the oligomer backbone. This can be seen from comparing the concentration c (shown in the Table) for flexible and semi-flexible RAPs (which differ in complex rigidity) and between semi-flexible and rigid RAPs (which differ in backbone rigidity). While the rigidity of oligomer backbone has a strong impact on the transition concentrations, it does not affect significantly the overall degree of association in the chain dominating region where the system is well described by the mean-field theory.

ANALYTICAL MEAN-FIELD THEORY

An analytical theory for the metal-ligand association can be derived from the consideration of “chemical scaling” between various metal and ligand species. Following results equations can be solved numerically and are in agreement with simulation results (lines in the Figures).

References


For supporting molecular weight in the metal-rich region, the fraction of single-bonded metals should be small and there should be little redistribution of metals from double- bonded to single-bonded ones. Using our analytical model, we have found the conditions when both of these conditions are satisfied (crossed-shaded area in the Figure). Thus to obtain high molecular weight polymers in metal-rich region the energy for the first (ΔS\textsubscript{1}) and the second (ΔS\textsubscript{2}) metal-ligand bonds should satisfy the following conditions:

ΔS\textsubscript{1} ≤ 3.775 kT and ΔS\textsubscript{2} ≥ 0.9 kT

FUTURE WORKS

Possible future directions of this project include studying the behavior of RAPs near surfaces or interfaces as well as predictions of rheological properties of the RAPs such as viscosity and diffusion coefficient which should allow more direct comparison with experimental results.

Emails:** chun-chung.chen@case.edu  **eed@case.edu

Monte Carlo Study of Reversibly Associated Polymers

Chun-Chung Chen\textsuperscript{a} and Elena E. Dormidontova\textsuperscript{b}

Department of Macromolecular Science and Engineering, Case Western Reserve University

REVERSIBLY ASSOCIATED POLYMERS

Reversibly associated polymers (RAPs) are macromolecules formed by reversible bonding such as donor-acceptor type hydrogen bonding arrays and complementary DNA sequences, shown below. In contrast to traditional covalent bonds, reversible bonds can be formed or broken depending on controllable parameters, such as temperature, concentration, and pH values. Thus, these polymers allow easier control of their properties and responsiveness to environmental changes. In our study, we employ analytical modeling and Monte Carlo simulations to study association properties of RAPs in good solvent conditions.

RING-CHAIN EQUILIBRIUM

At low oligomer concentration, the RAP consists of mostly rings while as concentration increases, chains take over. In the chain dominating region, the system is well described by a mean-field theory which depends only on the densities of donor and acceptor groups in the system.

METALLO-SUPRAMOLECULAR POLYMERS

Metallo-supramolecular polymers are formed through 1-to-2 coordination bonds between metal ligands and as shown in the extended model, flexibility of RAPs with increasing oligomer length have a smaller probability of forming small rings and the overall degree of association deviates from the mean-field prediction.

ROLE OF METALS

Non-cooperative bonding. With oligomer concentration fixed (c = 9.8 × 10^{-4} M), the degree of association increases with metal concentration until it reaches its maximum at the stoichiometric composition (1:1 metal:ligand ratio). Beyond the stoichiometric composition, the degree of association starts to decline as the metal concentration increases. A similar dependence is observed for the molecular weight, also reaching a maximum at a 1:1 metal-oligomer ratio. However, the decrease in the molecular weight is more considerable in the metal-rich region. By analyzing the distribution of metals among ligands, one can see that in the ligand-rich region, most of metals are bound to two ligands, while in metal-rich region, metal bonds are bound to no more than one ligand resulting in low molecular weight in this region.

COOPERATIVE BONDING

The rigidity of the donor-acceptor complex imparts an entropic penalty (ΔS) to the reversible bonding and decreases the overall degree of association. However, its impact on the crossover concentration of ring-to-chain transition is less significant comparing to the rigidity of the oligomer backbone. This can be seen from comparing the concentration c (shown in the Table) for flexible and semi-flexible RAPs (which differ in complex rigidity) and between semi-flexible and rigid RAPs (which differ in backbone rigidity). While the rigidity of oligomer backbone has a strong impact on the transition concentrations, it does not affect significantly the overall degree of association in the chain dominating region where the system is well described by the mean-field theory.

ANALYTICAL MEAN-FIELD THEORY

An analytical theory for the metal-ligand association can be derived from the consideration of “chemical scaling” between various metal and ligand species. Following results equations can be solved numerically and are in agreement with simulation results (lines in the Figures).

References


For supporting molecular weight in the metal-rich region, the fraction of single-bonded metals should be small and there should be little redistribution of metals from double-bonded to single-bonded ones. Using our analytical model, we have found the conditions when both of these conditions are satisfied (crossed-shaded area in the Figure). Thus to obtain high molecular weight polymers in metal-rich region the energy for the first (ΔS\textsubscript{1}) and the second (ΔS\textsubscript{2}) metal-ligand bonds should satisfy the following conditions:

ΔS\textsubscript{1} ≤ 3.775 kT and ΔS\textsubscript{2} ≥ 0.9 kT

FUTURE WORKS

Possible future directions of this project include studying the behavior of RAPs near surfaces or interfaces as well as predictions of rheological properties of the RAPs such as viscosity and diffusion coefficient which should allow more direct comparison with experimental results.

Emails:** chun-chung.chen@case.edu  **eed@case.edu