

# Theoretical and Computer Modeling of Supramolecular Polymers

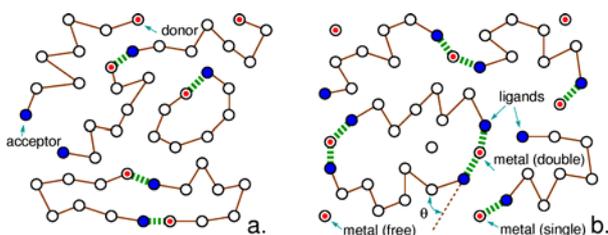
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## Introduction

Recent progress in supramolecular chemistry has made available a new class of polymers based on non-covalent interactions that combine the properties of traditional synthetic polymers with the versatility of biomolecules. [1] Various arrays for multiple hydrogen bonding have been developed that allow tuning the strength of association without losing its reversible character. These reversibly associating arrays can be used for the modification of traditional polymers to create materials with new properties. Such reversibly associating polymers are able to change their degree of polymerization in response to chemical parameters (solvent, pH) or physical parameters (temperature, flow fields). Their responsiveness means that they may find application in the general area of "smart materials" or in devices that effect energy, electron or ion exchange.

One of the recent developments in supramolecular chemistry is application of reversible metal-ligand complexes for creation of new materials with advanced properties. [2] Due to complexity of the synthetic procedures leading to the formation of high-molecular weight metal-supramolecular polymers, their physical characterization and analysis of properties is still in the early stage of development. [2]



**Figure 1.** Schematic representation of supramolecular assembly by donor-acceptor and metal-ligand interactions.

The present research aimed to obtain a theoretical insight of the basic principles of donor-acceptor (**Figure 1a**) and metal-ligand (**Figure 1b**) self-assembly achieved by analytical and computer modeling of the equilibrium supramolecular complexes leading to formation of linear chains (or rings). We will start by presenting the details of our analytical model and computer simulations followed by discussion of the results obtained for donor-acceptor associating polymers. Then we will consider metal-ligand complex formation and compare the results achieved for the both cases.

## Simulation

**Simulation model.** To study the supramolecular assembly we apply Monte Carlo simulations. We use bond fluctuation model (BFM) [3] to simulate oligomers (and metals) on a 3 dimensional (3D) cubic lattice with lateral size  $L = 64a$  (or larger) with periodic boundary conditions. In BFM model the distance between any monomers or metals can be no less than 2 cell sizes,  $2a$ . Furthermore, for any covalently or reversibly bonded pair of monomers or metals, the distance between the two must have one of the values  $2a$ ,  $5^{1/2}a$ ,  $6^{1/2}a$ ,  $3a$ , or  $10^{1/2}a$ . This model corresponds to the good solvent condition where the radius of gyration for the free oligomer scales as  $R_g \propto N^{0.55}$  with the number of monomers in an oligomer,  $N$ . Each oligomer carries at its ends two functional groups, which are identical (ligands) for metal-ligand interactions and complementary for donor-acceptor interactions. Each metal is assumed to form up to two reversible bonds with oligomer end-groups. Therefore, both cases exclude the possibility of branching. For donor-acceptor interactions there is only one enthalpic change  $\Delta E_{mi}$  per association, whereas in

metal-ligand interaction, cooperativity is allowed and the enthalpy (and entropy) change for the first and the second reversible bond of a metal may differ.

**Rigidity.** For an absolutely flexible bond there is no penalty for its bending. For a rigid chemical bond or a reversible bond (due to orientational specificity of donor-acceptor or metal-ligand interactions) there will be a penalty for bending,  $E_{st} = K(1 - \cos\theta)$ , where  $\theta$  is the angle characterizing deviation from linearity, as illustrated in **Figure 1**. In our simulations we choose the rigidity constant  $K = 5kT$ . This rigidity constant results in the same contribution to the partition function as restricting the bond angle to the range  $\theta \leq \theta_{cr} \approx 37^\circ$  corresponding to the entropy loss  $\Delta S \approx 2.3$ .

**Simulation procedure.** We perform Monte Carlo simulations with two types of updates: moving attempts of monomers or metals (using the Metropolis algorithm [4]) and bonding update for the ligands or acceptor. For the latter, after the moving attempt for an oligomer end-group, a reversible bond (if any) is assumed to be broken and a new bond is re-chosen from all possible ones with probabilities of their respective Boltzmann weights. For each system realization, we perform the series of moving attempts and bonding updates until the system reaches equilibrium, at which point the number of reversible bonds and molecular weight distribution are counted and averaged separately over subsequent MC steps.

## Analytical model.

To analyze the computer simulation results we apply the mean-field model [7] which accounts for the statistical probabilities of bond formation and translational entropy factors. For the case of **donor-acceptor interactions** this model predicts for the average degree of association:

$$p_a = \exp\left(\frac{\Delta F}{kT}\right) (1 - p_a)^2 \frac{2n_p v}{V} \quad (1)$$

where  $n_p$  is the number of oligomers,  $v$  is the reference volume and  $\Delta F/kT = \Delta E/kT - \Delta S$  is the free energy change per reversible association.

For **metal-ligand interactions** we obtain using our analytical model for the fraction of metals associated with two ligands:

$$2p_2 = \exp\left(\frac{\Delta F_2}{kT}\right) \left(2 \frac{n_p}{n_m} - p_1 - 2p_2\right) p_1 \frac{n_m v}{V} \quad (2)$$

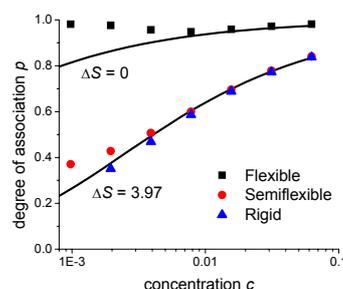
where  $p_1$  is the fraction of metal associated with oligomer only from one side:

$$p_1 = \exp\left(\frac{\Delta F_1}{kT}\right) \left(2 \frac{n_p}{n_m} - p_1 - 2p_2\right) (1 - p_1 - p_2) \frac{n_m v}{V} \quad (3)$$

where  $n_m$  is the number of metals and  $\Delta F_i/kT$  is the free energy change per first ( $i=1$ ) or second ( $i=2$ ) reversible association.

## Results and discussion

**Donor-acceptor interactions.** The Monte Carlo results for the overall degree of association in supramolecular polymers of different rigidity are presented in Figure 2 as a function of concentration. In all cases the oligomer length was  $N = 8$  and the association energy was  $\Delta E_{hb} = 8kT$ .

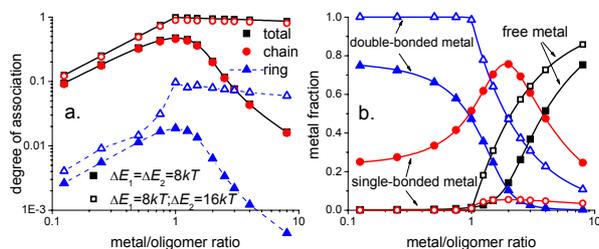


**Figure 2.** Monte Carlo simulation results (symbols) in comparison with the analytical model (lines) for the total degree of association,  $p$ , polymers of different rigidity as functions of concentration,  $c = n_p N/V$ .

We studied the following three cases: flexible polymers, semi-flexible and rigid polymers. Flexible polymers contain flexible oligomers and exhibit no entropic penalty for end-group association. Semi-flexible polymers are composed of flexible oligomers, but there is a rigidity (entropic penalty) enforced by the end group association. Finally, rigid polymers have both the intrinsic rigidity of oligomers and the rigidity enforced by end group association. Comparing flexible, semi-flexible and rigid polymers at not so small polymer concentration we found that the degree of association for semi-flexible polymers coincides with rigid ones and is smaller than for flexible polymers (Figure 2). Because the obtained results can be well-described by the simple analytical model (eq.1) we conclude that above certain concentration the degree of association depends mainly on the total number density of donor/acceptor groups as well as on energy/entropy of association and is not influenced by individual characteristic of spacers, such as their length or rigidity.

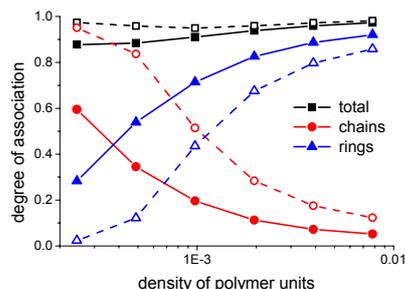
In contrast, the formation of rings and the crossover concentration signifying the boundary between ring-dominated and chain-dominated areas strongly depends on the individual characteristics of spacers and changes with spacer length or its rigidity. We found that this concentration for semi-flexible polymers is several times smaller than that for flexible polymers and it is nearly two orders of magnitude higher than that for rigid ones.

**Metal-ligand interactions.** Firstly we have kept the number of oligomers constant ( $n_p = 256$ ) and changed the number of metals from the metal-free to the metal excess case. The fraction of metals bonded to two oligomers ("double bonded metal") calculated with respect to the number of oligomers characterizes the average degree of association and is shown in Figure 3a. The average degree of association is well described by our analytical model (eqs.2,3). As is seen from Figure 3 most of the double bonded metals participate in chain formation and only a small fraction is forming rings. The average degree of association increases with an increase of overall metal fraction and reaches a maximum when the number of metals equals to the number of oligomers. At higher metal fraction the degree of association decreases if there is no cooperativity in the reversible association with the first and the second oligomer and it stays almost at the same level (or only slightly decreases) if the association with the second oligomer is strongly energetically preferable.



**Figure 3.** The average degree of association ( $2p_2n_m/n_p$ ) (a) and fraction of fraction single ( $p_1$ ), double-bonded ( $p_2$ ) and free ( $1-p_1-p_2$ ) metal (b.) as a function of metal content. Predictions of our analytical model are shown as solid lines.

To gain insight into the origin of this effect, we consider the distribution of reversible bonds between metals, i.e. the fraction of metals bonded with two, one or zero oligomers (Figure 3b). For the non-cooperative association the fraction of double-bonded metal is lower than in the cooperative case at any metal concentration. The main difference in cooperative and non-cooperative association becomes especially evident with an increase in the metal content beyond the stoichiometric concentration when the fraction of single-bonded and free metal increases (with subsequent decrease for the former). For the non-cooperative case formation of the second bond is disfavored since it enforces considerably stronger orientation limitations (involving 3 neighboring bonds) than the first one (involving only one bond). As a result the increase in single-bonded metal (at expense of double-bonded metal) occurs. For the cooperative case, the second bond is energetically preferable and this compensates for the entropy loss. Due to this the fraction of double-bonded metals decreases slower in this case and the average molecular weight of reversibly associated polymers remains high over a larger composition range.



**Figure 4.** Degree of association for flexible metal-ligand complexes of stoichiometric composition (solid symbols) compared with that for the donor-acceptor type association (open symbols).

At the stoichiometric composition the overall degree of association for metal-ligand complexes and relative fraction of chains decreases with decreasing concentration, whereas the fraction of rings increases. At some concentration a ring-to-chain transition occurs. This behavior is similar to that observed for reversibly associating oligomers carrying one donor and one acceptor group at each end. Results for the latter case are also shown in Figure 4 for comparison ( $\Delta E_{hb} = 8kT$ , open symbols, dashed lines). Although for the metal-ligand case the overall energy for association of two oligomer units is twice larger than for the donor-acceptor association case, the overall degree of association is lower. This is the result of considerably stronger entropic penalty for metal-mediated ligand association. Due to the same reason ring-formation is decreased in metal-ligand case and the ring-to-chain transition occurs at considerably lower concentration.

## Conclusion

For the donor-acceptor type of associations we found that above some crossover concentration formation of chains dominates ring formation. In this area the association behavior follows the same pattern, well-described by the analytical model and depends mainly on the number density of donor/acceptor groups. Below the crossover concentration the association is governed by the individual characteristics of oligomers and differs for chains of different rigidity and chain length. For metals-ligand complexes the maximum degree of polymerization is observed at the one-to-one ratio between metals and ligands. For the non-cooperative association the molecular weight of the complexes is noticeably smaller especially for metal-rich compositions than that for cooperative metal-ligand associations. Comparing to donor-acceptor-terminated associating polymers, metal-ligand complexes provide a considerably smaller degree of association. However, the chain fraction is noticeably enhanced in this case.

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