COMPUTER MODELING OF REVERSIBLE ASSOCIATION IN METALLO-SUPRAMOLECULAR POLYMERS

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Introduction

One of the recent developments in supramolecular chemistry is application of reversible metal-ligand complexes for creation of new materials with advanced properties.[1,2,3] Due to complexity of the synthetic procedures leading to formation of high-molecular weight metal-supramolecular polymers, their physical characterization and analysis of properties is still in the early stage of development.[1,2,3] The present research aimed to obtain a theoretical insight of the basic principles of metal-ligand self-assembly achieved by computer modeling of the equilibrium metal-ligand complexes leading to formation of linear chains (or rings).

Computational

Model. To study the reversible association between linear oligomers end-functionalized with acceptor sites for the ligand-metal complexation we apply Monte Carlo simulations. We use bond fluctuation model (BFM)[4,5] to simulate metals and oligomers of 8 monomers each (including end-groups) on a 3 dimensional (3D) cubic lattice with lateral size L = 64 with periodic boundary conditions. Each monomer or metal occupies one cell of the lattice of size a. In consideration of excluded volume, the distance between any two monomers (metals) or between a monomer and a metal can be no less than 2 cells size, $2a$. Furthermore, for any pair of monomers or metals that are bonded, covalently or by reversible association, the distance between the two must have one of the values $2a$, $5^{1/2}a$, $6^{1/2}a$, $7^{1/2}a$, or $10^{1/2}a$. This amounts to a total of 108 possible bond vectors in 3D. 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.

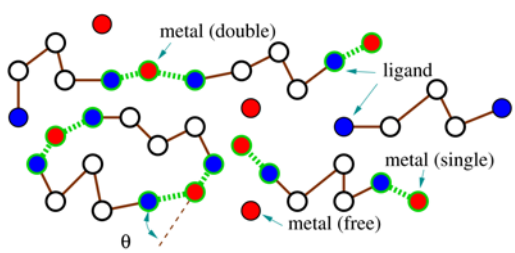

Figure 1. Schematic representation of the bond-fluctuation model for metal-ligand interaction.

Each oligomer carries two functional groups at its ends capable of forming one reversible bond with a metal. Similarly each metal can form up to two reversible bonds with oligomer end-groups. Therefore, the possibility of branching is excluded in this case. Here we will assume the same enthalpic gain ΔE_{ml} for the first and the second reversible bond of a metal. However, the entropic penalty for the first and the second reversible bonds of the metal will be different.

Rigidity. We assume the free oligomers to be absolutely flexible, so there is no penalty for bending any of the chemical bonds connecting the monomer units of an oligomer. Reversible interactions are orientationally specific, therefore there will be a penalty, $E_{st} = K(1-\cos\theta)$, for bending a reversible bond, where θ 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 $\theta \le \theta_{cr} \approx 37^\circ$ and amounts to a loss of entropy per reversible association of $\Delta S \approx 2.3$.

The rigidity imparted by a single bond formation between metal and oligomer is considerably smaller than that imparted by a double bonded metal. In the latter case even a small deviation from linearity in orientation of end-segments of oligomers participation in reversible associations with the same metal may result in the breakage of one of the bonds.

Simulation procedure. To calculate the properties of the model system defined above, we perform Monte Carlo simulations with two types of updates: moving attempts of monomers or metals (using the Metropolis algorithm[6]) and bonding update for the ligands. 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 the series of system configurations generated.

Results and Discussion

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 double bonded to oligomers (!) calculated with respect to the number of oligomers is shown in **Figure 2a**. As is seen, the fraction of double bonded metals increases with an increase of overall metal fraction and reaches a maximum when number of metals equals to the number of oligomers. At higher metal fraction the degree of association decreases due to the imbalance in the number of donor and acceptor groups.

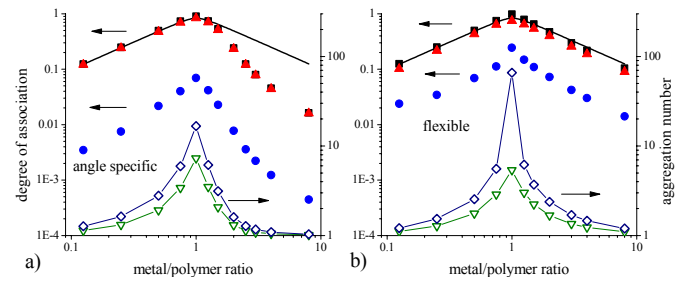

Figure 2. Fraction of double-bonded metal (also in chains and rings) and number- and weight average molecular weight of orientationally-specific (a) and non-specific (absolutely flexible) (b) metal-oligomer complexes.

The double-bonded metal participates in both chain (7) and ring (,) formation, whose fractions are also shown in **Figure 2a**. Due to high entropic penalty associated with bending of two reversible bonds formed with the same metal, participation of such metals in rings is considerably lower than in chains. As expected the largest contribution to the ring fraction is by rings formed by a single oligomer (with one mediated metal).

The overall number- (X) and weight-average (M) aggregation numbers strongly changes with metal fraction reaching a maximum at the balanced stoichiometric composition, as is seen from **Figure 2a**. Even at their maximum values the number and weight average remain relatively low, about 7 and 16 repeat units (oligomer + metal), respectively, despite of a strong enthalpic gain for association, $\Delta E_{ml} = 12kT$. For lower energy of association, e.g. $\Delta E_{ml} = 8kT$, the number and weight average degree of association decreases to 1.8 and 2.6 repeat units per chain at their maximum values, whereas the fraction of double bonded metals decreases to approximately 0.6 at its maximum. Therefore, it is required to have a rather high strength of metal-ligand interaction to get high-molecular weight assembly.

The degree of association (total, in rings and chains) as well as the number and weight average molecular weight decrease more rapidly in the metal-rich area compared to oligomer-rich area. To understand the origin of this effect we compared the results discussed above with the case of reversible, but orientationally nonspecific interactions (having no penalty for bending chemical or reversible bonds) shown in **Figure 2b**. In the latter case the curves for the double bonded metal fraction and number-/weight-average molecular weight become perfectly symmetric with respect to their maximum, which is naturally reached at the same stoichiometric composition. Therefore the reason for the asymmetry must be connected with the entropic penalties for reversible association in the former case (**Figure 2a**). We note that for orientationally-nonspecific case the overall degree of association and weight-average molecular weight are noticeably higher than for the orientationally-specific one.

We also compare the results for the overall fraction of double bonded metal, p_a, shown in **Figure 2** with predictions of a simple mean-field

approximation model which accounts for statistical probabilities of bonds formation and translational entropy factors:

$$p_a = \exp\left(\frac{\Delta E_{ml}}{kT}\right)(1-p_a)(r-p_a)\frac{2n_p v_{ml}}{V} \qquad (1)$$

where n_p is the number of oligomers, r is the ratio between number of metals and oligomers and v_{ml} is the volume of an associated metal-ligand pair. In our comparison with computer simulation results we use the complex entropic factor $\Delta s \equiv \ln(2n_p v_{ml}/V)$ as a fitting parameter. As is seen from **Figiure 2b**, there is a good agreement between theoretical predictions (for $\Delta s \approx 2.05$) and simulation results for the case of orientationally nonspecific interactions. For the angle specific case (**Figure 2a**) theoretical predictions (for $\Delta s \approx 7.26$) agree well with simulation results for bonding only for $r < 1$, whereas there are considerable deviations for $r > 1$.

To gain insight into the origin of this discrepancy, we consider the distribution of reversible bonds between metals, i.e. the fraction of metals with different numbers of reversible bonds formed with ligands. In **Figure 3**, we show the concentration dependence of the fraction of free metals (!), single-bonded metals (,), and double bonded metals (7) calculated with respect to metal fraction.

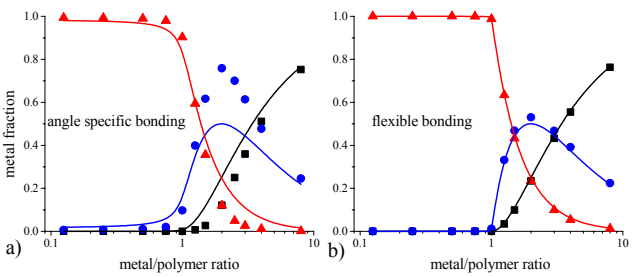

Figure 3. Fractions of free, single-bonded, and double-bonded metals as functions of metal/polymer ratio for orientationally-specific (a) and non-specific (absolutely flexible) (b) metal-oligomer complexes.

For both cases of angle-specific and angle non-specific interactions all metal atoms remain double-bonded at the metal concentration below stoichiometric composition. At higher metal concentration fraction of double-bonded metal considerably decreases, whereas the fraction of unbonded and single-bonded metal increases (with subsequent decrease for the latter). We compare in Figure 3 the results of simulations with theoretical predictions (solid curves):

$$\begin{cases} m_0 = \dfrac{(r-p_a)^2}{r^2}, & \text{fraction of free metals} \\ m_1 = \dfrac{2p_a(r-p_a)}{r^2}, & \text{fraction of single-bonded metals} \\ m_2 = \dfrac{p_a^{\,2}}{r^2}, & \text{fraction of double-bonded metals} \end{cases}$$

where p_a is defined by eq 1 and Δs are the same as for **Figure 2**. As before the model describes very well the behavior of flexible complexes (no angle – specificity for metal–ligand complexes). For angle-specific complexes there is quantitative agreement for $r < 1$, but at higher metal fraction the model overestimates the fraction of double-bonded and free metals and considerable underestimates that of single-bonded metals. The reason is that the model considers the orientational penalty for the first and the second bond formation to be the same, whereas in simulations (and in reality) formation of the second bond enforces considerably stronger orientation limitations (involving 3 neighboring bonds) than the first one (involving only one bond). To avoid these additional restrictions associated with the second bond formation, metals prefer to be involved in single-bonded complexes with ligands. As a result, the fraction of double-bonded metal considerably decreases for $r > 1$ and fraction of single-bonded metal increases. This explains the significant decrease in the degree of association and an average molecular weight in this region (**Figure 2**). Due to this asymmetry in the average molecular weight in the areas just above and just below the stoichiometric composition, it seems preferable to have less rather than more than the stoichiometric amount of metal to ensure higher overall molecular weight.

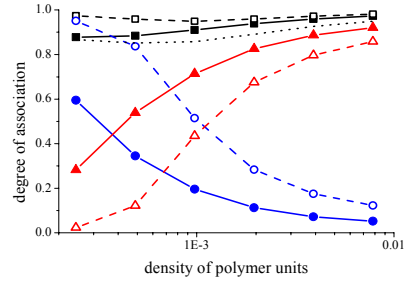

Figure 4. Degree of association for flexible 1:1 metal-ligand system compared with reversible end-associating polymers with donor-acceptor type association.

To study the effect of dilution on the metal-ligand system, we consider in **Figure 4** the degree of association for flexible (non-orientationally specific) complexes with $\Delta E_{ml} = 8kT$ at different polymer concentrations at a 1:1 metal-polymer ratio (filled symbols, solid lines). The black (!), blue (,), and red (7) symbols and lines are for the total degrees, ring fractions, and chain fractions of association, respectively. With decreasing concentration the overall degree of association and relative fraction of chains decreases, whereas that 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.[7] Results for the latter case are also shown in **Figure 4** for comparison ($\Delta E_{hb} = 8kT$ - open symbols, dashed lines; $6kT$ dotted line). Although for the metal-ligand case the energy for associating two polymer units is twice larger than for the donor-acceptor association case, the overall degree of association is lower (it is close to that for $\Delta E_{hb} = 6kT$ at low polymer density). 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.

Conclusions

For metals capable of bonding with up to two ligands, the maximum degree of polymerization is observed at the one-to-one ratio between metals and ligands. Accounting for the entropy loss associated with complex formation (rigidity), we find that for metal-rich compositions the molecular weight of the complexes is noticeably smaller than that in polymer-rich case. The reason for this asymmetry is the strong entropic penalty for formation of the second bond for the metal, leading to an increase in single-bonded metals for metal-rich compositions. 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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References

(1) Schubert U.S.; Eschbaumer C. *Angew. Chem. Int. Ed.* **2002**, *41*, 2892.
(2) Newkome G.R; Cho T.J.; Moorefield C.N.; Cush R.; Russo P.S.; GodÌnez L.A; Saunders M.J.; Mohapatra P. *Chem. Eur. J.* **2002,** *8*, 2946.
(3) Gohy, J-F.; Lohmeijer, B.G.; Varshney S.K; Schubert U.S. *Macromolecules* **2002,** *35,* 7427.
(4) Carmesin, I.; Kremer, K. *Macromolecules* **1988**, *21*, 2819.
(5) Deutsch, H.P.; Binder, K. *J. Chem. Phys.* **1991**, *94*, 2294.
(6) Metropolis, N.; Rosenbluth, A.W.; Rosenbluth, M.N.; Teller, A.H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(7) Chen, C.-C.; Dormidontova E.E. *submitted to Macromolecules.*