# Monte Carlo Study of Reversibly Associated Polymers

## Chun-Chung Chen[a] and Elena E. Dormidontova[b]

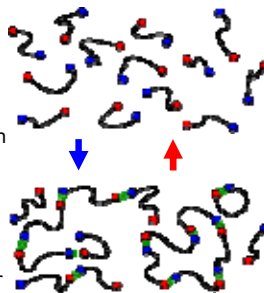### Department of Macromolecular Science and Engineering, Case Western Reserve University

## REVERSIBLY ASSOCIATED POLYMERS

Reversibly associated polymers (RAP) 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.

Sijbesma et al, 1997

Thus, these polymers allow easier control of their properties and are responsive to environmental changes. In our study, we employ analytical modeling and Monte Carlo simulations to study association properties of RAPs in good solvent conditions.

Fogleman et al, 2002

## MONTE CARLO SIMULATIONS

**Bond-fluctuation model**

Carmesin & Kremer 1988. Deutsch & Binder 1992.

We use the bond-fluctuation method to model oligomers end-functionalized by a donor and an acceptor group. The typical system size considered in our study is $L=64a$ where $a$ is the lattice spacing. Each oligomer consists of $N$ monomers including two end-functional groups. The energy change for forming a reversible bond is $E_{hb}=8kT$. Each monomer, on average, makes a moving attempt in each MC time step.

**Bonding update**

acceptor

donor

After a moving attempt of an acceptor, any existing reversible bond involving this acceptor is assumed to be broken. Boltzmann weights of all possible bonding configurations for the acceptor are calculated and one is chosen accordingly. The measurement of the associating properties starts after the system reaches equilibrium and is averaged over no less than $2^{22} \approx 4 \times 10^6$ configurations generated by subsequent MC time steps.

**Angle stiffness**

To consider the effect of angle stiffness and the rigidity of the donor-acceptor complex, for each stiff bond we apply the following bending energy

$$E_{st} = K_i(1-\cos\theta)$$

where $K_i$ is the stiffness parameter for monomer $i$, and $\theta$ is the bonding angle. Stiffness energy $E_{st}$ is connected with the entropic loss $\Delta S$ due to angle specificity of the association with $\Delta S=0$ for completely flexible complexes. Three types of RAP are considered in our study as shown in the Table above.

| Monomer type | Donor | Acceptor | Backbone | $c_x$ $(a^{-3})$ |
|---|---|---|---|---|
| Flexible | $K_i = 0$ | $K_i = 0$ | $K_i = 0$ | 8.9 10-3 |
| Semiflexible | $K_i = 5kT$ | $K_i = 5kT$ | $K_i = 0$ | 1.7 10-3 |
| Rigid | $K_i = 5kT$ | $K_i = 5kT$ | $K_i = 5kT$ | 3.9 10-6 |

Emails: a. chun-chung.chen@case.edu  b. eed@case.edu

## 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:

$$p=\exp[\Delta F_{hb}/(kT)](1-p)^2 n_{oligomer}$$

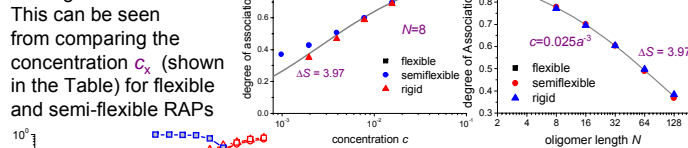where $p$ is the extent of association, $n_{oligomer}$ is the oligomer density and $\Delta F_{hb}/(kT) = \Delta E_{hb}/(kT) - \Delta S$ is the free energy change of the association. Flexible RAPs with increasing oligomer length have a smaller probability of forming small ring and the overall degree of association deviates from the mean-field behavior at different

**Extent of association $p$**

rings    chains

$N = 16$

mean-field prediction
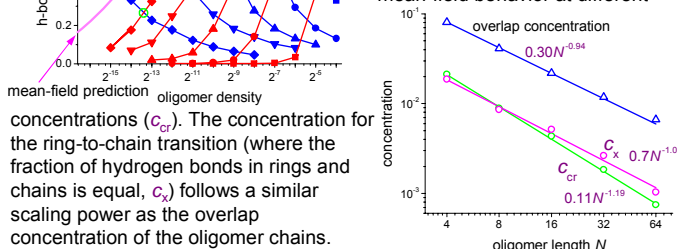
concentrations ($c_{cr}$). The concentration for the ring-to-chain transition (where the fraction of hydrogen bonds in rings and chains is equal, $c_x$) follows a similar scaling power as the overlap concentration of the oligomer chains.

overlap concentration  $0.30N^{-0.94}$

$c_x$  $0.7N^{-1.0}$

$c_{cr}$  $0.11N^{-1.19}$

## INFLUENCE OF RIGIDITY

The rigidity of the donor-acceptor complex imparts an entropic penalty ($\Delta S$) 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 $c_x$ (shown in the Table) for flexible and semi-flexible RAPs

$\Delta S = 0$

$\Delta S = 3.97$

$N=8$

- flexible
- semiflexible
- rigid

$c=0.025a^{-3}$

$\Delta S = 0$

$\Delta S = 3.97$

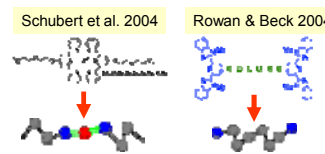- flexible
- semiflexible
- rigid

(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 significantly affect the overall degree of association in the chain dominating region where the system is well described by the mean-field theory.

$N=8$

flexible

semi-flexible

rigid

## METALLO-SUPRAMOLECULAR POLYMERS

Metallo-supramolecular polymers are formed through 1-to-2 coordination bonds between metal and ligands as shown in the examples below. Similar modeling technique as for the donor-acceptor-type RAPs can be applied to this case. We introduce metals in these systems as free monomers that can be bound with up to two ligands. Each oligomer carries two identical ligands at its ends. We have considered two types of metal-ligand association: 1) the energy change $\Delta E$ per each metal-ligand bond is the same (non-cooperative case) and 2) the energy for the first metal-ligand bond $\Delta E_1$ is different (smaller) than the energy for the second bond formed by the metal $\Delta E_2$ (cooperative case).

Schubert et al. 2004

Rowan & Beck 2004

| | | | |
|---|---|---|---|
| Non-cooperative | | $\Delta E$ | $2\Delta E$ |
| Cooperative | | $\Delta E_1$ | $\Delta E_1+\Delta E_2$ |

## ROLE OF METALS

**Non-cooperative binding**. With oligomer concentration fixed ($c = 9.8\times10^{-4}$ $a^{-3}$), the degree of association increases with metal concentration until it reaches its maximum at the stoichiometric composition (1-to-1 metal/oligomer 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 its maximum at the 1:1

$\Delta E = 8kT$

total

chain

ring
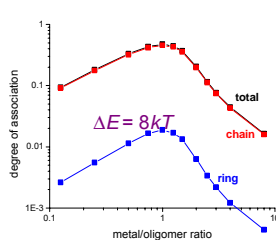
metal-oligomer ratio. However the decrease in the molecular weight is more considerable in the metal-rich region. By analyzing the distribution of metals among ligands, one can see that in the ligand-rich region, most of metals are bound to two ligands, while in metal-rich region metals are bound to no more than one ligand resulting in low molecular weight in this region.

$\Delta E_1 = \Delta E_2 = 8kT$

single-bond metal

$m_2$

double-bond metal

$m_1$

$m_s$ free metal

**Analytical mean-field theory**

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

$$K_1\times(2N_{oligomer} - M_1 - 2M_2)\times(M_{total} - M_1 - M_2) = M_1$$
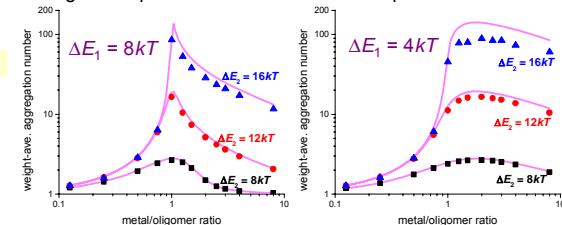
$K_1 = \exp[\Delta F_1/kT]$

$$K_2\times(2N_{oligomer} - M_1 - 2M_2)\times M_1 = M_2$$

$K_2 = \exp[\Delta F_2/kT]$

→ Solved for $m_1$ and $m_2$

## Cooperative bonding.

The effect of cooperativity (difference between $\Delta E_1$ and $\Delta E_2$) on the formation of metallo-ligand complexes are illustrated below. In general larger cooperativity results in higher molecular weight. The sharp decrease in the average molecular weight in metal-rich region changes into plateau-like behavior for complexes with smaller
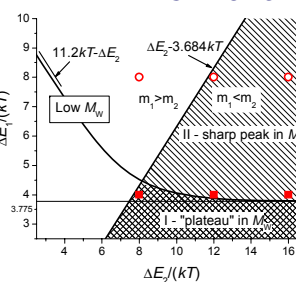
$\Delta E_1 = 8kT$

$\Delta E_2 = 16kT$

$\Delta E_2 = 12kT$

$\Delta E_2 = 8kT$

$\Delta E_1 = 4kT$

$\Delta E_2 = 16kT$

$\Delta E_2 = 12kT$

$\Delta E_2 = 8kT$

energy for the first metal-ligand bonding. The lines in the plot are estimated using condensation polymerization theory:

$$(1+p)/(1-p)$$

with $p$ being the degree of association.

## SELECTION CRITERIA

For sustaining 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 (cross-shaded area in the Figure). Thus to obtain high molecular weight polymers in metal-rich area the energy for the first ($\Delta E_1$) and the second ($\Delta E_2$) metal-ligand bonds should satisfy the following conditions:

$$\Delta E_1 \leq 3.775 \ kT \text{ and } (\Delta E_2-\Delta E_1)/kT \geq \Delta S_2 - \Delta S_1 \approx 3.684.$$

$11.2kT - \Delta E_2$   $\Delta E_2 - 3.684kT$

Low $M_w$

$m_1 > m_2$    $m_1 < m_2$

II - sharp peak in $M_w$

I - "plateau" in $M_w$

## 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.
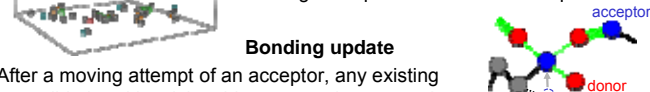
### References

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- C.-C. Chen & E. E. Dormidontova, *Supramolecular polymer formation by metal-ligand complexation: Monte Carlo simulations and analytical modeling*, J. Am. Chem. Soc. **126**, 14972 (2004)