

## Notes

## Linear Self-Assembled Systems and the Effect of Capping Defects

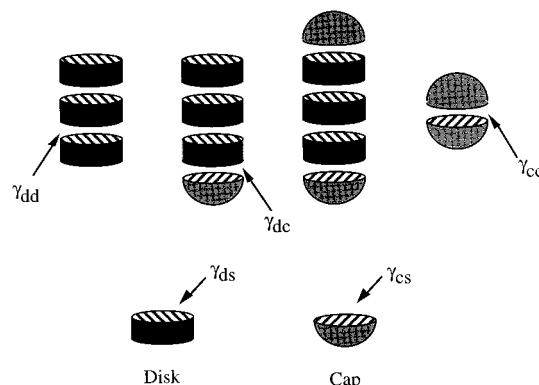
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Molecular self-assembly plays an important role in many systems, ranging from zeolites<sup>1</sup> to biological systems<sup>2–4</sup> and modified surfaces.<sup>5</sup> Of particular interest are systems that assemble into single-molecule thick fibers that may be millimetres in extent. Such linear self-assembled supramolecular structures have technological importance in the areas of molecular fibers,<sup>3,6–11</sup> wires,<sup>12,13</sup> and channels.<sup>13–15</sup> Systems that exhibit linear self-assembly are thought to associate through ionic interactions, hydrogen bonding, or aromatic  $\pi$ -stacking, which are facilitated by the molecule's shape, polarizability, or solubility. Molecules having electron rich components that are flat and stackable, such as polyaromatics or metalloporphyrins, self-assemble into linear structures that might serve as molecular wires. Molecules having a hollow interior, such as cyclodextrins and crown ethers, or the flexibility to assemble into open helices can serve as molecular channels.

In most of the literature systems, the formation of linear aggregates is reversible and the system exhibits an exceptionally low critical aggregation concentration (CAC). Below the CAC, molecules are largely unassociated; however, above the CAC, supramolecule self-assembly leads to a broad distribution in aggregate lengths. It would be a technological advantage to use the reversibility of the system to control the size or length of the aggregates and then to convert the reversible supramolecules into a permanent structure through polymerization. For example, a self-assembled channel needs to be tailored to the thickness of the membrane that it is to span, whereas a molecular wire should be long and defect free. This



- $N$  = Total number of disks  
 $N_c$  = Total number of caps  
 $n$  = number of aggregated disks (not counting caps)  
 $x_n^0$  = concentration of  $n$ -mers with 0 caps  
 $x_n'$  = concentration of  $n$ -mers with 1 cap  
 $x_n''$  = concentration of  $n$ -mers with 2 caps  
 $x_n = x_n^0 + x_n' + x_n''$   
 $y$  = concentration of unassociated caps  
 $y'$  = concentration of caps in double caps (hence there are  $y'/2$  double cap clusters)

**Figure 1.** Diagram of the possible disk–solvent, disk–disk, disk–cap, cap–cap, and cap–solvent aggregations and the associated interfacial energies ( $\gamma_{ds}$ ,  $\gamma_{dd}$ ,  $\gamma_{dc}$ ,  $\gamma_{cc}$ , and  $\gamma_{cs}$ , respectively).

note uses equilibrium concepts to demonstrate that the addition of defect molecules can shift the mean aggregation length, narrow the length distribution, and significantly raise the CAC.

## Theory

Consider a solution of molecules that aggregate reversibly into one-dimensional aggregates. We refer to these bicoordinate molecules as “disks”, as these may aggregate in a face-to-face manner forming a stack of  $n$  disks or an  $n$ -aggregate. Defect molecules, on the other hand, are single-coordinate and are represented as a hemisphere or “cap”. When incorporated within an  $n$ -aggregate, a cap becomes a reversible terminator, preventing further face-to-face stacking at the end of the  $n$ -aggregate, Figure 1. A cap that most effectively terminates one-dimensional aggregate growth would be one that provides significant steric hindrance. Examples of such caps for stackable metalloporphyrin systems include simple coordinating ligands, such as pyridine, and porphyrins having one face sterically hindered.

Let  $N$  and  $N_c$  be the concentration of disks and caps in solution, respectively.  $x_n^j$  is the concentration of disks associated into an  $n$ -aggregate with the superscript denoting the number of ends terminated by a cap:  $x_n^0$ ,  $x_n'$ , and  $x_n''$  being the concentration of disks in  $n$ -aggregates having none, one, or both ends terminated by a cap, respectively.  $y$  is the concentration of caps free or

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(1) Occelli, M. L.; Robson, H. E. *Synthesis of Microporous Materials*; Van Nostrand Reinhold: New York, 1992.

(2) Hill, T. L. *Linear Aggregation Theory in Cell Biology*; Springer-Verlag: New York, 1987.

(3) Hill, T. L.; Kirschner, M. W. *Int. Rev. Cyt.* **1982**, *84*, 185.

(4) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153.

(5) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.

(6) Fuhrhop, J.; Demoulin, C.; Boettcher, C.; Koning, J.; Siggel, U. *J. Am. Chem. Soc.* **1992**, *114*, 4159.

(7) Fuhrhop, J.; Bindig, U.; Siggel, U. *Chem. Commun.* **1994**, 1583.

(8) Fujiki, M.; Tabei, H.; Kurihara, T. *J. Phys. Chem.* **1988**, *92*, 1281.

(9) Sarson, L. D.; Ueda, K.; Takeuchi, M.; Shinkai, S. *Chem. Commun.* **1996**, 619.

(10) Terech, P.; Gebel, G.; Ramasseul, R. *Langmuir* **1996**, *12*, 4321.

(11) Tsuchida, E.; Komatsu, T.; Toyano, N.; Kumamoto, S.; Nishide, H. *Chem. Commun.* **1993**, 1731.

(12) Jorgensen, M.; Bechgaard, K. *J. Org. Chem.* **1994**, *59*, 5877.

(13) van Nostrum, C. F.; Picken, S. J.; Schouten, A.; Nolte, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957.

(14) Aida, T.; Takemura, A.; Fuse, M.; Inoue, S. *Chem. Commun.* **1988**, 391.

(15) Hartgering, J. D.; Granja, J. R.; Milligan, R. A.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 43.

unbound to any surface, and  $y$  is the concentration of caps that form cap–cap dimers. From the conservation of disks and caps, we formulate the following two constraints:

$$N = \int_1^{\infty} dn (x_n^0 + x_n' + x_n'') \quad (1)$$

$$N_c = \int_1^{\infty} dn \left( \frac{x_n'}{n} + 2 \frac{x_n''}{n} \right) + y + y' \quad (2)$$

The  $n$ -aggregate concentrations,  $x_n^i$ , are predicted as equilibrium concentrations, i.e., concentrations for which the enthalpic gain associated with face-face contacts balances the entropy loss of one-dimensional stacking. Each face-to-face contact between pairs of disks/caps is described by interfacial energy terms ( $\gamma_{dd}$ ,  $\gamma_{dc}$ ,  $\gamma_{cc}$ ) and the unbound disk and cap surfaces are assigned solution interfacial energies ( $\gamma_{ds}$ ,  $\gamma_{cs}$ ). As this study is limited to dilute concentrations, lateral interactions among  $n$ -aggregates that might lead to “bundles” of linear aggregates at moderate concentrations or liquid crystalline phases are not included. The free energy,  $F$ , in units of  $kT$ , of the system of  $N$  disks and  $N_c$  caps is cast as

$$\begin{aligned} F \approx & \int_1^{\infty} dn \left( \frac{x_n^0}{n} \right) (2\gamma_{ds} + (n-1)\gamma_{dd}) + \\ & \int_1^{\infty} dn \left( \frac{x_n^0}{n} \right) \ln \left( \frac{x_n^0}{n} \right) + \int_1^{\infty} dn \left( \frac{x_n'}{n} \right) (\gamma_{ds} + \gamma_{dc} + \\ & (n-1)\gamma_{dd}) + \int_1^{\infty} dn \left( \frac{x_n'}{n} \right) \ln \left( \frac{x_n'}{n} \right) + \int_1^{\infty} dn \left( \frac{x_n''}{n} \right) (2\gamma_{dc} + \\ & (n-1)\gamma_{dd}) + \int_1^{\infty} dn \left( \frac{x_n''}{n} \right) \ln \left( \frac{x_n''}{n} \right) + y \gamma_{cs} + y \ln y + \\ & \frac{y'}{2} \gamma_{cc} + \frac{y'}{2} \ln \frac{y'}{2} \quad (3) \end{aligned}$$

The first, third, and fifth terms on the right-hand side (RHS) of eq 3 represent the enthalpic contributions of the molecules, stacked into  $n$ -aggregates, and the second, fourth, and sixth terms are the loss of mixing entropy in forming these linear aggregates. The final three terms on the RHS represent the enthalpic gain and entropic losses for caps that are unassociated in solution or formed cap dimers. The sought values of  $x_n^0$ ,  $x_n'$ ,  $x_n''$ ,  $y$ , and  $y'$  are those that minimize the system's free energy, eq 3, subject to the conservation constraints, eqs 1 and 2. The distribution of  $n$ -aggregates  $x_n = x_n^0 + x_n' + x_n''$  follows the form

$$x_n \approx n[x_1 K]^n K^{-1} \quad (4)$$

where  $K = 1/(e^{-k^0} + e^{-k} + e^{-k'})$  is a function of the energetic parameters

$$k^0 = 2\gamma_{ds} - \gamma_{dd} + 1$$

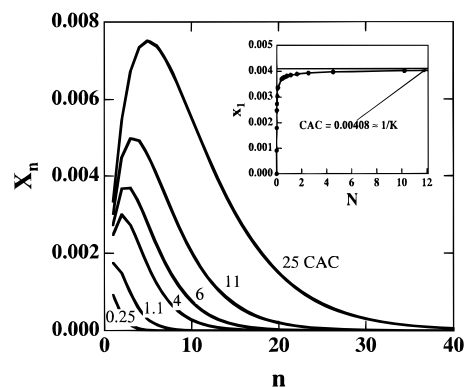
$$K = \gamma_{ds} + \gamma_{dc} - \gamma_{dd} + 1 + \lambda$$

$$K' = 2\gamma_{dc} - \gamma_{dd} + 1 + 2\lambda$$

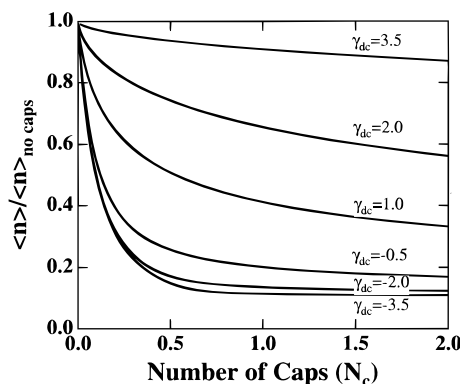
and  $\lambda$  is a constant that ensures the conservation of caps, eq 2.

## Results

Figure 2 shows the distribution of  $n$ -aggregates ( $x_n$



**Figure 2.** Size distributions for self-assembled disks at various concentrations ( $0.25\text{CAC} < N < 25\text{CAC}$ ) with fixed interfacial energies and cap concentration. Other parameters are  $\gamma_{dc} = -0.5$ ,  $\gamma_{ds} = 2.0$ ,  $\gamma_{dd} = -0.5$ ,  $\gamma_{cc} = -0.5$ ,  $\gamma_{cs} = 2.0$ , and  $N_c = 4 \times 10^{-7}$ .

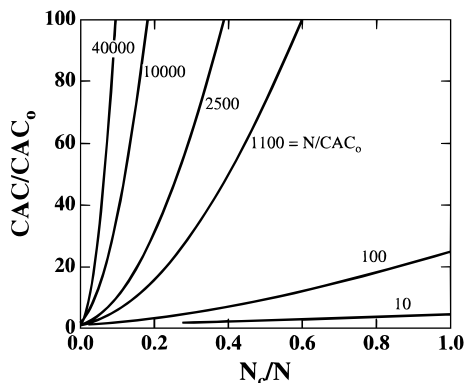


**Figure 3.** Plot of the reduced aggregation length vs the number of caps as a function of the disk–cap interaction energy ( $\gamma_{dc}$ ). Other parameters are  $\gamma_{ds} = 2.0$ ,  $\gamma_{dd} = -0.5$ ,  $\gamma_{cc} = -0.5$ ,  $\gamma_{cs} = 2.0$ ,  $l = 0.6$ , and  $N_0 = 0.406765$ .

versus  $n$ ) for a range of disk concentrations,  $N$ , keeping the concentration of caps,  $N_c$ , constant. Below the CAC ( $N < \text{CAC}$ ) the majority of molecules will be unassociated in solution and  $x_1 \approx N$ ; above the CAC, subsequent addition of molecules leads to an increase in the aggregation length with the concentration of unassociated molecules unchanged. The value of the CAC is defined as the limiting value of  $x_1$  at large concentration  $N \gg \text{CAC}$ , which corresponds to  $\text{CAC} \approx 1/K$ .  $\text{CAC}_0$  is defined as the critical aggregation concentration in the absence of caps  $\text{CAC}_0 = 1/K^0$ .

The CAC is fixed by the interfacial energies as shown in eq 4, so it is of interest to consider the factors that influence the CAC. Favorable (more negative) values of  $\gamma_{dd}$ ,  $\gamma_{cs}$ , and  $\gamma_{cc}$  decrease the CAC, as do unfavorable values of  $\gamma_{ds}$  and  $\gamma_{dc}$ . Thus, chemical modification of the disks and caps or changing the quality of the solvent will shift the CAC. This is shown in Figure 3 where the effect of the  $\gamma_{dc}$  interfacial energy on the mean aggregate size is plotted as a function of the cap concentration. In this case all of the curves asymptote to the same value of mean aggregate size, which is determined by  $\gamma_{dd}$  and  $N$ .

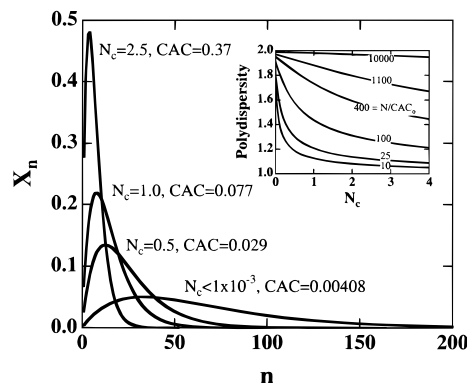
The CAC can be increased by the addition of caps. This is of particular importance for strongly associated systems (low CAC) where  $n$ -aggregates contribute to gelled solutions with high viscosity. By addition of caps to solution, the CAC can be increased beyond the concentration of disks such that the solution is composed mostly of unassociated molecules. Removal of the caps from the solution reduces the CAC such that aggregation proceeds. Figure 4 shows the relative increase in the CAC as a



**Figure 4.** Plot of the relative CAC as a function of the cap concentration for different disk concentrations. Numbers indicate the ratio of the disk concentration to the critical aggregation concentration in the absence of caps ( $CAC_0$ ). Interfacial energies as per Figure 2.

function of the ratio of caps to disks for a range of disk concentrations. It is evident that the CAC is most dramatically increased by the addition of caps to solutions that have large aggregates, i.e., solutions with disk concentration,  $N$ , far exceeding the critical aggregation concentration in the absence of defects,  $CAC_0$ . Solutions where assembly is limited to small  $n$ -aggregates,  $N < 25CAC$ , are comparatively unaffected by defect addition, as the disks are partitioned into free solution and cap-cap dimers rather than into a few small  $n$ -aggregates. Figure 5 shows the distribution of  $n$ -aggregates as the CAC is increased by an increase in the number of caps,  $N_c$ . Depending upon  $N$  and  $N_c$  and the interfacial energies, self-assembly results in a broad polydispersity in  $n$ -aggregates ( $\langle M \rangle_w / \langle M \rangle_n \leq 2.0$ ). Thus, addition of caps not only changes the expected length of the aggregate but also the breadth of the distribution.

In summary, a simple statistical theory has been developed for describing the molecular self-assembly of linear supramolecular structures such as molecular wires,



**Figure 5.** Graph showing the effect of increasing cap concentration (CAC) on the distribution of aggregate lengths ( $X_n$  versus  $n$ ), the disk concentration relative to the  $CAC_0$  is 1100. Inset shows the effect of cap concentration on the polydispersity (numbers indicate the relative disk concentration). Interfacial energies as per Figure 2.

channels, or fibers and the effect of capping species that terminate the growth of these chains. From this theory we obtain distributions of the aggregation length as a function of the interfacial energies and disk and cap concentrations. This gives insight into how the variables influence aggregation and provides a useful method for changing the CAC and hence the aggregation length.

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