Cooperative binding of polyethylene glycol to alkaline metal ions and the coil–helix phase transition

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Cooperative binding is often observed in biological systems, showing that a binding of the initial guest molecule changes structure of the host macromolecule to increase its binding affinity to another guest molecule. Cooperative binding is known to drastically enhance the catalytic or adsorption activity of the host macromolecule. On the other hand, very few example has been reported on synthetic polymers showing the cooperative host–guest binding, and their mechanistic study is scarcely carried out. Recently, we reported that polyethylene glycol (PEG) transforms into a helical structure and crystallizes upon coordination to alkaline metal cations in the presence of triiodide ion in water.[1] This crystallization is promoted with increasing length of PEG chain. However, the binding mechanism of PEG to those ions remained unknown.

Herein, we study the binding model of PEG to the alkaline metal cation by statistical mechanical approach and report that PEG shows cooperative binding to the alkaline metal cation in the presence of triiodide. The statistical model is built based on Zimm–Bragg model,[2] which was developed to model the coil–helix transition of protein alpha helix. The partition function Q of PEG is expressed in Equation (1):

$$Q = (1 \quad 1)\begin{pmatrix} 1 & 1 \\ n & w \end{pmatrix}^{N-1}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{(Eq. 1)}$$

N is the total number of ethylene oxide mer unit in the single PEG chain, and n and w are the statistical weight of nucleation and propagation of the helix, respectively (Figure 1). Typically, $n \ll 1$ and $w > 1$, so that the nucleation is more difficult than the propagation of the helix. The simulation curve calculated from this model agreed with the experimental result. This study shows that the coil–helix transition of PEG takes place in cooperative way and can be explained by Zimm–Bragg model.

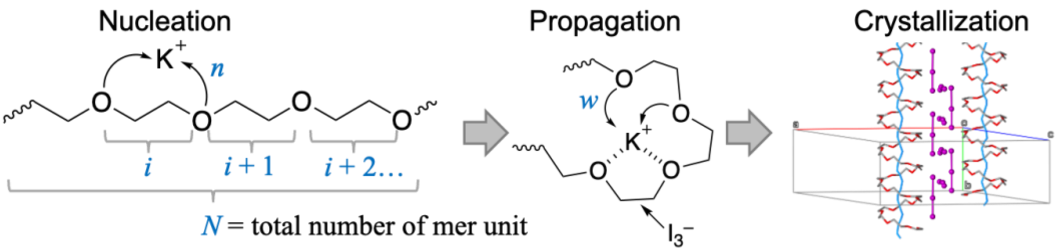

Figure 1. Zimm–Bragg model showing cooperative binding of PEG to potassium cation, starting from the nucleation to the propagation and finally the crystallization of the helix.

1) Patent pending to H. Zhou, R. Matsuno, T. Yamada, Japanese Patent Application No. 2022-004709, January 14, 2022. 2) B. Zimm and J. Bragg, *J. Chem. Phys.* 31, 526, 1959

