

2009年8月27日実施

2010年度立命館大学大学院理工学研究科
博士課程後期課程
入学試験問題（外国語科目）

応用化学型

【注意事項】

1. 解答は問題番号1、2、・・・ごとに解答用紙1枚を使用すること。
2. 解答用紙には専攻名、課程、受験番号、氏名、問題番号を解答用紙すべてに記入すること。
3. 無記名答案は無効、問題用紙および解答用紙は持ち帰らないこと。
4. 解答用紙はホッチキス止めしてあるので、はずさないこと。
5. 問題用紙が事前に届けでている型の問題であるか確認し、解答すること。
6. 外国語科目試験時間
10:00～11:30（90分）
試験時間中の途中退室は認めない。

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[外国語] 応用化学型

(以下の2問すべてに解答してください)

1. 次の英文を全文和訳せよ。

The concept of covalent polymerization of bifunctional monomeric units was pioneered by Staudinger in the early 1920s. He introduced the term “macromolecule” and proposed structural formulas for natural rubber, polystyrene, and polyoxymethylene that are still valid today. The invariance of the colloidal properties of these compounds in different solvents was one of the proofs adduced to support the concept of a linear sequence of covalent bonds exhibiting a large degree of polymerization (DP). The alternative model of a colloid-type aggregate stabilized by weaker secondary interaction was dismissed. Polymer science was then born, growing—distinct from colloid science—to produce the outstanding developments that have affected our lives.

Given the emphasis on the methods of synthesis and on the desirable properties of molecular polymers which continues to the present day, it is all too natural that the concept of a polymer composed by a long sequence of repeating units linked by noncovalent bonds received only limited attention. Thus, in spite of the fact that very long linear assemblies of globular proteins or micelles have been known for quite some time, the recognition of the potential of noncovalently bonded polymers had to wait until the early 1990s when significant developments in *supramolecular chemistry* occurred.

According to accepted current definitions, supramolecular chemistry is the chemistry of the intermolecular bond distinct from molecular chemistry, which is the chemistry of the covalent bond. Thus, it is now appropriate to regard a long sequence of units connected by secondary bonds as a supramolecular polymer, distinct from a molecular polymer when repeating units are linked by covalent bonds as originally shown by Staudinger.

(引用： *Supramolecular Polymers*, Ciferri, A. Ed., Marcel-Dekker, p.1-2)

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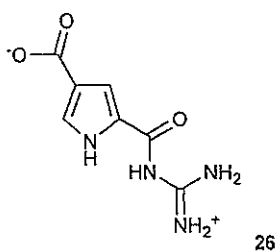
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2. 次の英文を全文和訳せよ。

In contrast with previous compound, the ^1H NMR spectrum of **26** does not show any signs of any intermolecular interactions at sub millimolar concentrations in $\text{DMSO-}d_6$, however there is indications of concentration dependent shifts that are consistent with the formation of linear aggregates in solution with interactions between the carboxylate and guanidinium moieties of neighbouring molecules.

The binding constant of this process was determined by analysis of the concentration dependence observed in the ^1H NMR spectrum in $\text{DMSO-}d_6$ through the concentration range of 1-100 mM with the guanidinium NH resonance followed. A plot of the observed chemical shift against concentration gives an isothermic binding curve that indicates a concentration dependent intermolecular association is occurring. As the pyrrole NH is not involved in the carboxylate binding mode due to geometric reasons this compound binds the carboxylate in a bidentate fashion, as opposed to the tridentate fashion seen previously and in this respect exhibits association constants that are constant to those displayed by simple guanidinium cation binding. The association constant of 22.2 M^{-1} is consistently smaller with the bidentate versus tridentate binding mode argument and is in agreement with similar values that are quoted in the literature.

Examination of the association process over a range of temperatures from 303 to 363 K using an NMR dilution experiment in which once again the guanidinium resonances were followed gave association constants that varied from 22.2 M^{-1} at 303 K to 70.5 M^{-1} at 363 K. Using a van't Hoff plot of the calculated binding constants, association in the temperature range studied was revealed to be endothermic and as a result the process driving oligomerization must therefore be entropic, the process presumably be driven by the release of solvent molecules from the binding site increasing the entropy of the system.



(引用 : *Macrocyclic Chemistry*, Gloe, K. Ed., Springer, p.167)