Academic Program [Oral A] | 19. Colloid and Interface Chemistry：Oral A

Wed. Mar 26, 2025 10:00 AM - 11:40 AM JST | Wed. Mar 26, 2025 1:00 AM - 2:40 AM UTC
[C]C506(C506, Bldg. 2, Area 2 [5F])

[[C]C506-1am] 19. Colloid and Interface Chemistry

Chair: Katsuaki Konishi, Kenichi Niikura

Japanese
10:00 AM - 10:10 AM JST | 1:00 AM - 1:10 AM UTC
[[C]C506-1am-01]
Glycosylated diarylmethyloxy-triazine library for fabricating a variety of supramolecular architectures via self-assembly in aqueous media

○Shuto Okuda[1], Shintaro Sugiura[2], Yuki Shintani[2], Natsuhisa Oka[1,3], Masato Ikeda[1,2,3,4] (1. Graduate School of Natural Science and Technology, Gifu University, 2. United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University, 3. Institute for Glyco-core Research (iGCORE), Gifu University, 4. Institute for Advanced Study, Center for One Medicine Innovative Translational Research (COMIT), Gifu University)

Japanese
10:10 AM - 10:20 AM JST | 1:10 AM - 1:20 AM UTC
[[C]C506-1am-02]
Formation of low-molecular-weight amine-tannic acid complexes and evaluation of their drug encapsulation function

○Chisaki Nakaji[1], Naoya Takei[1], Kenichi Niikura[1] (1. Nippon Inst. Tech)

Japanese
10:20 AM - 10:30 AM JST | 1:20 AM - 1:30 AM UTC
[[C]C506-1am-03]
Structure of coacervate from polycations and oppositely charged mixed micells

○Hikari Kamo[1], Katsunori Yoshida[1], Toshihiro Mori[2] (1. Kitasato University, 2. Mandom Corporation)

Japanese
10:30 AM - 10:40 AM JST | 1:30 AM - 1:40 AM UTC
[[C]C506-1am-04]
Molecular Dynamics Simulation of Biomolecular Adsorption on Alkyl β-Celluloside Assemblies.

○Kouichirou Ishibashi[1], Kai Sugiura[2], Takeshi Serizawa[2], Yoshiki Ishii[3], Go Watanabe[1,3,4] (1. Kitasato university Graduate School , 2. Sch. of Mater. and Chem. Tech., Inst. of Sci Tokyo., 3. Sch. of Front. Eng., Kitasato Univ., 4. KISTEC)

Japanese
10:40 AM - 10:50 AM JST | 1:40 AM - 1:50 AM UTC
[[C]C506-1am-05]
Formation of emulsions by amphiphilic molecules containing fluorinated aromatic units

○Misato Aoyagi[1], Kohei Sato[1] (1. Kwansei Gakuin University)

10:50 AM - 11:00 AM JST | 1:50 AM - 2:00 AM UTC
Break

Japanese

11:00 AM - 11:10 AM JST | 2:00 AM - 2:10 AM UTC

[[C]C506-1am-06]

Synthesis of Polymer-Based Tubular Micromotors Capturing Virus-Shaped Nanoparticles

○Yuki Kiuchi[1], Yuma Sakai[1], Teruyuki Komatsu[1] (1. Chuo university)

Japanese

11:10 AM - 11:20 AM JST | 2:10 AM - 2:20 AM UTC

[[C]C506-1am-07]

Synthesis of Copolymer-Based Tubular Micromotor

○Koki Ozawa[1], Saki Batori[1], Teruyuki Komatsu[1] (1. Chuo University)

Japanese

11:20 AM - 11:30 AM JST | 2:20 AM - 2:30 AM UTC

[[C]C506-1am-08]

Responsiveness of oleic acid vesicles in the reaction system where pH changes in the presence of oxygen

○Daichi Kushijima[1], Ryohei Tozaki[1], Shoi Sasaki[1], Kouichi Asakura[1], Taisuke Banno[1] (1. Keio University)

Japanese

11:30 AM - 11:40 AM JST | 2:30 AM - 2:40 AM UTC

[[C]C506-1am-09]

Synthesis of self-assembling block polymer composed of pH-responsive peptide and thermo-responsive amino acid-derived polymer.

○Taisei Kawai[1], Shin-nosuke Nishimura[1], Tomoyuki Koga[1] (1. Doshisha University)

日本化学会 第105春季年会 (2025)

糖とジアリールメチルオキシトリアジンを連結した自己集合性分子ライブラリーの構築

(岐阜大院自然科学[1]・岐阜大院連合創薬[2]・岐阜大 iGCORE[3]・岐阜大 COMIT[4])
○奥田 宗杜[1]・杉浦 進太郎[2]・新谷 勇喜[2]・岡 夏央[1,3,4]・池田 将[1,2,3,4]
Glycosylated diarylmethyloxy-triazine library for fabricating a variety of supramolecular architectures via self-assembly in aqueous media ([1]*Graduate School of Natural Science and Technology, Gifu University*, [2]*United Graduate School of Drug Discovery and Medical Information Sciences, Gifu University*, [3]*Institute for Glyco-core Research (iGCORE), Gifu University*, [4]*Institute for Advanced Study, Center for One Medicine Innovative Translational Research (COMIT), Gifu University*) ○Shuto Okuda[1], Shintaro Sugiura[2], Yuki Shintani[2], Natsuhisa Oka[1,3,4], Masato Ikeda[1,2,3,4]

Self-assembly of glycosylated molecules under aqueous conditions gives rise to a variety of supramolecular architectures with the surface of highly condensed saccharides, which allows us to emulate bio-interfaces. Thus, such soft materials have received significant attention as biocompatible matrices for cell culture and regenerative medicines. Nevertheless, it is still challenging to construct a library of glycosylated building blocks. To this end, 1,3,5-triazine (**Tz**) scaffold is useful to be introduced at the reducing end of saccharides without protecting groups[1], which could offer an opportunity to expand the repertoire of glycosylated self-assembling molecules. In this study, we constructed a library of glycosylated **Tz** for fabricating diverse supramolecular architectures via aqueous self-assembly. To investigate the influence of the saccharides on their self-assembly behavior, we introduced various monosaccharides and disaccharides into diarylmethyloxy-modified **Tz** as shown in **Figure 1**.

Keywords : supramolecular hydrogel; self-assembly; saccharides; triazine

水溶液条件下での糖修飾分子の自己集合は、糖鎖が高密度に提示された超分子構造を形成し、生体界面を模倣することを可能にする。そのようなソフトマテリアルは、細胞培養や再生医療用の生体適合性マトリックスへの応用が期待されている。しかしながら、多様な糖を修飾した自己集合性分子の合成は挑戦的な課題である。一方、1,3,5-トリアジン環 (**Tz**) が無保護の糖鎖の還元末端に選択的に導入できることが報告されている[1]。この反応を用いることで種々の糖鎖を導入した自己集合性分子の創製が可能になると着想した。本研究では、水中での自己集合により多様な超分子構造体を形成すると期待される糖鎖修飾 **Tz** (**Glyco-Tz(X)$_2$**) のライブラリーを構築した (**Figure 1**) 。自己集合挙動への糖鎖の影響を調べるため、ジアリールメチルオキシ基を修飾した様々な単糖と二糖を導入した。

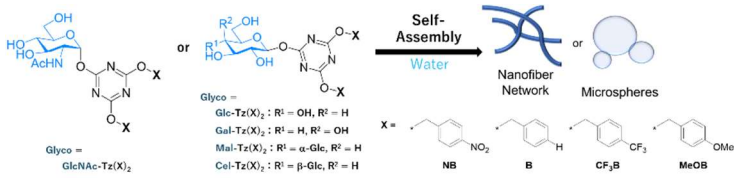


Figure 1 Chemical structures of diarylmethyloxy-modified **Tz** and schematic representation of their self-assembly.

[1] T. Tanaka, M. Noguchi, A. Kobayashi, S. Shoda, *Chem. Commun.,* **2008**, 2016.

日本化学会 第105春季年会 (2025)

低分子アミン-タンニン酸複合体の形成と薬剤内包機能評価

（日工大院工[1]・日工大応化[2]）○中路 千咲[1]・武井 直哉[2]・新倉 謙一[1,2]

Formation of low-molecular-weight amine-tannic acid complexes and evaluation of their drug encapsulation function ([1] *Environmental Symbiotic System Major, Nippon Institute of Technology* [2]*Department of Applied Chemistry, Faculty of Fundamental Engineering, Nippon Institute of Technology*) ○Chisaki Nakaji,[1] Naoya Takei,[2] Kenichi Niikura[1,2]

Various drug delivery systems (DDS), including polymeric micelles, have been developed for the delivery of antigenic proteins and nucleic acid. However, these carriers require complex preparation procedures and often have low biodegradability. Recently, polyphenols have attracted attention as a simple and effective approach for forming particles that encapsulate biological macromolecules. In this study, we demonstrate that tannic acid can efficiently and stably form complexes with drugs (including nucleic acids and proteins) in the presence of low-molecular-weight amines.

We investigated the effect of complexes formed between tannic acid and two low-molecular-weight amines: 1-Aza-18-crown 6-ether (Aza18C6) and 4,13-Diaza-18-crown 6-ether (Diaza18C6), on the loading of CpG nucleic acids and bovine serum albumin (BSA) proteins. The protein-loaded Aza18C6-TA and Diaza18C6-TA complexes were formed in a pH 7.4 phosphate buffer (10 mM). The Aza18C6-TA complex, which contains a single amino group, did not facilitate CpG loading, whereas the Diaza18C6-TA complex, which contains two amino groups, facilitated CpG loading. These results suggest that the presence of two amino groups in Diaza18C6 enhances the efficiency of nucleic acid uptakes. We also explored the impact of other low-molecular-weight amines on complexes formation and the stability of the resulting complexes.

Keywords : low-molecular-weight amine, tannic acid, nucleic acid

高分子ミセルなどを用いて、抗原タンパク質や核酸などを輸送するための輸送体は数多く開発されているが、調製の難しさや生分解性の低さが課題とされている。近年では、生体高分子を内包する簡便な粒子形成法として、ポリフェノールを用いる方法が注目されている。本研究では、低分子アミンを用いることでタンニン酸が薬剤(核酸やタンパク質)を効率的かつ安定に複合体を形成することを見出したので報告する。

私たちは、低分子アミンである 1-Aza-18-crown 6-ether (Aza18C6) および 4,13-Diaza-18-crown 6-ether (Diaza18C6)とタンニン酸との複合体が CpG 核酸および BSA タンパク質の取り込みに与える影響を検討した。pH7.4 リン酸緩衝液(10mM)中で、Aza18C6 及び Diaza18C6-TA-タンパク質複合体を形成した。アミノ基 1 つの Aza18C6-TA 複合体では CpG の取り込みが見られなかったが、アミノ基が 2 つある Diaza18C6-TA 複合体では CpG の取り込みが見られた。これより、2 つ以上のアミノ基が、核酸導入効率の向上に寄与したと考えられる。さらに、他の低分子アミンによる効果や、形成した複合体の安定についても検討を行った。

Structure of coacervate from polycations and oppositely charged mixed micelles

([1]*Skin Science Lab, School of Pharmacy, Kitasato University*, [2]*Skincare Lab, Mandom Corporation*) ○Hikari Kamo,[1] Katsunori Yoshida,[1] Toshihiro Mori[2]

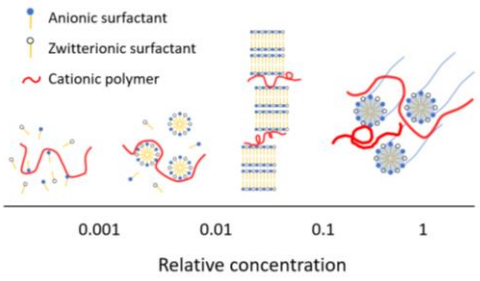
Keywords: Coacervate; Shampoo; Molecular assembly structure; Surfactant; Polycation

Polyelectrolytes and oppositely charged surfactant micelles interact strongly via electrostatic forces in aqueous solutions, leading to phase separation into either solid-liquid or liquid-liquid systems. The latter results in a concentrated phase (coacervate) and a dilute phase, a phenomenon known as coacervation.[1)] Coacervation has been applied in various technologies, including shampoos, food processing, water treatment, drug delivery for water-soluble anticancer agents, and DNA transfection into cells.[2)]

Typical shampoo formulations include cationic polymers as conditioning agents and anionic and amphoteric surfactants as cleansing agents. These components interact upon dilution during shampoo use, inducing phase separation and forming water-insoluble coacervates. This study investigated the physicochemical properties and structural changes of coacervates during the dilution process, using a commercially available non-sulfate shampoo as a representative example.

Turbidity measurements revealed a sharp increase in turbidity around a relative concentration of 0.4, indicating liquid-liquid phase separation and coacervation. Furthermore, the coacervates became increasingly elastic as dilution progressed, and SAXS measurements and polarized light microscopy confirmed the formation of a lamellar structure. Additionally, fluorescence probe measurements identified the critical aggregation concentration (CAC) of surfactants at a relative concentration of approximately 0.001. The results suggested that, with further dilution, the micelles disassemble, transitioning to a monodispersed state.

These findings demonstrated that the structural changes in coacervates are influenced by the interactions between polycations and micelles.



1) P. Ilekti, L. Piculell, F. Tournilhac, B. Cabane, *J. Phys. Chem. B* **1998**, 102, 344
2) Y. Wang, K. Kimura, Q. Huang, P. L. Dubin, *Macromolecules* **2000**, *33*, 3324.

アルキル化セルロース集合体に対する生体分子吸着現象の分子動力学シミュレーション

(北里大学大学院[1]・科学大物質理工[2]・北里大未来工[3]・神奈川県産総研[4])
○石橋　広一朗[1]・杉浦　開[2]・芹澤　武[2]・石井　良樹[3]・渡辺　豪[1,3,4]
Molecular Dynamics Simulation of Biomolecular Adsorption on Alkyl β-Celluloside Assemblies. ([1]*Graduate School of Science, Kitasato University*, [2]*School of Materials and Chemical Technology, Institute of Science Tokyo,* [3]*School of Frontier Engineering, Kitasato University,* [4] *Kanagawa Institute of Industrial Science and Technology*)
○Koichiro Ishibashi,[1] Kai Sugiura,[2] Takeshi Serizawa,[2] Yoshiki Ishii,[3] Go Watanabe[1,3,4]

Crystalline cellulose produced through enzymatic catalysis can be utilized in biological and environmental systems without altering its molecular structure. Furthermore, chemically modifying the molecular chain ends allows the cellulose interface to exhibit functional properties based on the functional groups. Previous experiments have demonstrated that the biomolecular adsorption of alkylated crystalline cellulose assemblies is influenced by the length of the alkyl side chain. However, the underlying mechanism of this phenomenon has not been fully elucidated through experimental results alone. To gain molecular insights into this mechanism, we performed all-atom molecular dynamics simulations of protein adsorption at the interface of various cellulose assemblies. By employing the umbrella sampling method, typically used in systems composed of small molecules, it was possible to compare and analyze the adsorption process of biomolecules on the cellulose assembly interface through free energy landscapes.
Keywords : Molecular Dynamics Simulation; Cellulose Assembly; Biomolecular Adsorption; Free Energy Calculation

酵素触媒の利用によって得られる結晶性セルロース集合体は、生体や環境系などにおいても集合構造を変質させずに利用可能である。また、分子鎖末端を化学修飾したセルロース集合体は、水界面においてその官能基に応じた特異的な機能を発現する。特に、セルロース集合体界面の生体分子吸着性が末端のアルキルの長さによって変化することが実験にて確認されている[1)]。しかし、この機能発現のメカニズムは実験事実に基づく経験的解釈にとどまっており、詳細を理解するためには分子レベルの解析が重要となる。本研究では、セルロース集合体に対する生体分子吸着現象を分子動力学(MD)シミュレーションで解析し、セルロースの界面構造の違いが生体分子との相互作用に及ぼす影響を考察した。一般的に低分子材料系にてよく用いられるアンブレラサンプリング法[2)]を利用することで、セルロース界面の吸着性や生体分子の微視的な吸着プロセスを自由エネルギー地形により比較解析が可能となった。

1) T. Serizawa *et al*., *Colloids Surf. B,* **220**, 112898 (2022).
2) K. Hiratsuka *et al*., *J. Mater. Chem. C,* **11**, 3949 (2023).

日本化学会 第105春季年会 (2025)

フッ素化芳香族性部位を有する両親媒性分子によるエマルジョンの形成

（関西学院大院理工）○青柳 美里・佐藤 浩平

Formation of emulsions by amphiphilic molecules containing fluorinated aromatic units

(*Graduate School of Science and Engineering, Kwansei Gakuin University*) ○Misato Aoyagi, Kohei Sato

Theranostics, the combination of therapeutics and diagnostics, has attracted considerable attention as a next-generation medical technology that improves patient quality of life while reducing side effects. In particular, microbubbles composed of perfluoroalkane surrounded by hydrophobic alkyl chains of phospholipids are expected to enable high-resolution imaging of organs through efficient reflection of ultrasound. In addition, the vibration of the microbubbles induced by ultrasound irradiation enables drug delivery to specific targets. However, the low stability of the microbubbles remains a major challenge.

Fig. Schematic illustration of a microbubble formed by phospholipid and perfluoroalkane.

In order to increase the affinity between lipids and perfluoroalkanes and to improve the stability of the microbubbles, synthetic lipids with fluorinated alkyl groups have been developed.[1] However, the toxicity of perfluoroalkyl compounds (PFAS) is a critical issue, requiring the development of new surfactants to replace conventional lipid analogues. In this study, we designed and synthesised novel amphiphiles without the introduction of perfluoroalkyl chains, yet capable of forming microbubbles, and evaluated their functions.

Keywords : Emulsions; Amphiphilic molecules; Fluorinated aromatic units

近年，患者の QOL 向上と副作用の軽減を同時に実現する次世代医療技術として，疾患の治療（therapeutics）と診断（diagnostics）を一体化させたセラノスティクス（theranostics）が大きな注目を集めている。特に，パーフルオロアルカンの周囲をリン脂質の疎水性アルキル鎖が取り囲んだ構造からなるマイクロバブルは，超音波を効率的に反射することで臓器の高解像度造影を可能にするほか，超音波照射に伴う振動誘起によって特定の病巣に薬剤を送達できると期待されている。一方，マイクロバブル自体の安定性が低いことが未解決の課題となっている。

そこで，脂質とパーフルオロアルカンとの親和性を高め，マイクロバブルの安定性を向上させるべく，アルキル鎖にフッ素原子を導入した脂質類縁体が開発されてきた[1]。しかし，近年パーフルオロアルキル化合物（PFAS）の毒性が問題視されており，従来の脂質類縁体に変わる新たな界面活性剤の開発が求められている。そこで本研究では，パーフルオロアルキル鎖を含まずともマイクロバブルを形成し得る新規分子を設計・合成し，その機能を評価した。

1) Y. Oda *et al*., *Int. J. Pharm.* **2015**, *487*, 64–71.

ウイルス形状ナノ粒子を捕集する高分子チューブマイクロモーターの合成

（中央大理工）○木内 勇希・坂井 悠真・小松 晃之

Synthesis of Polymer-Based Tubular Micromotors Capturing Virus-Shaped Nanoparticles

(*Faculty of Sci. and Eng., Chuo University*) ○Yuki Kiuchi, Yuma Sakai, Teruyuki Komatsu

We fabricated polymer-based tubular micromotors having Pt nanoparticles (PtNP) on the internal surface by photopolymerization and alternate layer-by-layer assembly technique using microporous polycarbonate (PC) membrane. These tubular micromotors were self-propelled in aqueous NH_3BH_3 solution by jetting H_2 bubbles.[1] The aim of this study is to synthesize polymer-based tubular micromotors having fetuin (Fet, sialoglycoprotein) on the exterior surface and to evaluate their ability of capturing influenza virus-shaped fluorescence nanoparticles (HA-FNP).[2] After photopolymerization of bis{2-(methacryloyloxy)ethyl}phosphate (BMP) in PC membrane (8.0 μm pore-diameter), Fe_3O_4 nanoparticles (MNP), poly-L-arginine (PLA), and PtNP solution were filtered through the membrane sequentially. The tubes obtained by dissolving PC template were soaked in aqueous avidin (Avi) and biotinylated Fet (bFet) solution, to yield bFet-Avi/PBMP/MNP/PLA/PtNP tubes (Fet/Pt tubes) (outer diameter: ca. 8.0 μm, tube length: ca. 18 μm). The Fet/Pt tubes were self-propelled in aqueous NH_3BH_3 solution by jetting H_2 bubbles and captured HA-FNP efficiently. The number of binding HA-FNP per single tube was determined by fluorescence spectroscopy.

Keywords : Micromotors; Anmonia Borane; Hydrogen Bubbles; Virus-Shaped Nanoparticles; Photopolymerization

我々は多孔性ポリカーボネイト(PC)膜をテンプレートとした独自の鋳型内光重合/交互積層法により、内孔表面に白金ナノ粒子(PtNP)を有する高分子チューブマイクロモーターを合成し、それがアンモニアボラン(NH_3BH_3)水溶液中で H_2 バブルを噴出しながら自走することを見出した [1]。本研究は、外表面にシアロ糖タンパク質であるフェチュイン(Fet)を配置した高分子チューブを合成し、そのインフルエンザウイルス形状蛍光ナノ粒子(HA-FNP)[2]捕集能を明らかにすることを目的とした。PC 膜(孔径 8.0 μm)の細孔内に bis{2-(methacryloyloxy)ethyl}phosphate(BMP)を光重合し、酸化鉄ナノ粒子(MNP)、ポリ-L-アルギニン(PLA)、PtNP の水溶液を順に通過させた。PC 膜を溶解・除去後、得られたチューブをアビジン(Avi)、ビオチン化 Fet(bFet)水溶液に順次浸漬させることで、目的の bFet-Avi/PBMP/MNP/PLA/PtNP チューブ(Fet/Pt チューブ)を得た(外径:約 8.0 μm、長さ:約 18 μm)。Fet/Pt チューブは NH_3BH_3 水溶液中で H_2 バブルを噴出しながら自走し、HA-FNP を効率よく捕集した。蛍光スペクトル測定からチューブ 1 本あたりの HA-FNP 結合数を算出した。

1) T. Komatsu *et al., ACS Appl. Bio Mater.* **2024**, *7*, 7740.
2) T. Komatsu *et al., Mater. Adv.* **2022**, *3*, 6988.

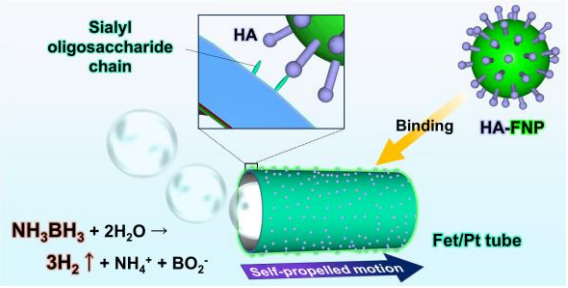


Fig. 1 Schematic illustration of capturing of HA-FNPs by Fet/Pt tube.

共重合体チューブマイクロモーターの合成

（中央大理工）○小澤 功輝・馬鳥 沙希・小松 晃之
Synthesis of Copolymer-Based Tubular Micromotor (*Faculty of Sci. and Eng., Chuo University*) ○Koki Ozawa, Saki Batori, Teruyuki Komatsu

Synthesis and application of self-propelled micromotors have attracted attention. We fabricated polymer-based tubular micromotors having Pt nanoparticles (PtNP) on the internal surface by photopolymerization and layer-by-layer assembly technique using a porous polycarbonate (PC) membrane. The tubular micromotors were self-propeled in aqueous H_2O_2 solution by jetting O_2 bubbles from the terminus.[1)] The aim of this study is to synthesize copolymer-based tubular micromotors composed of poly(bis{2-(methacryloyloxy)ethyl}phosphate-co-methacrylic acid) [P(BMP-co-MA)] for further functionarization of the polymer tubes. After photopolymerization of BMP and MA into the PC membrane (8.0 μm pore-diameter), magnetite nanoparticles (MNP), poly-L-arginine (PLA), and PtNP were filtered sequentially using layer-by-layer assembly technique. Dissolution of the PC membrane template yielded uniform hollow cylinder P(BMP-co-MA)/MNP/PLA/PtNP tubes (outer diameter ca. 8 μm, length ca. 18 μm). The tubes were self-propeled in aqueous H_2O_2 solution by jetting O_2 bubbles from the terminus. Activation of carboxyl groups on the tube wall allowed covalent binding of human serum albumin (HSA) to the outer surface.

Keywords : Copolymerization; Methacrylic Acid; Micromotors; Self-Propelling Ability; Pt Nanoparticles

水中で自走するマイクロモーターの合成と応用に注目が集まっている。我々は多孔性ポリカーボネイト（PC）膜を用いた鋳型内光重合/交互積層法により、内孔表面に白金ナノ粒子（PtNP）を有する高分子チューブマイクロモーターを合成し、それが H_2O_2 水溶液中で O_2 バブルを噴出しながら自走することを見出した[1)]。本研究は、高分子チューブのさらなる機能化を目指し、poly（bis{2-(methacryloyloxy)ethyl}phosphate-co-methacrylic acid）[P（BMP-co-MA）]共重合体チューブマイクロモーターを合成することを目的とした（**Fig. 1**）。PC 膜（孔径 8.0 μm）の内孔壁面で BMP と MA を光照射により共重合した後、酸化鉄ナノ粒子（MNP）、ポリ−L−アルギニン（PLA）、PtNP 水溶液を順次通過させた。PC 膜を溶解・除去することで、中空シリンダー構造の P(BMP-co-MA)/MNP/PLA/PtNP チューブを得た（外径：約 8.0 μm、長さ：約 18 μm）。このチューブは H_2O_2 水溶液中で O_2 バブルを噴出しながら自走した。また、管壁のカルボキシ基を活性化し、ヒト血清アルブミン（HSA）を外表面に共有結合した。

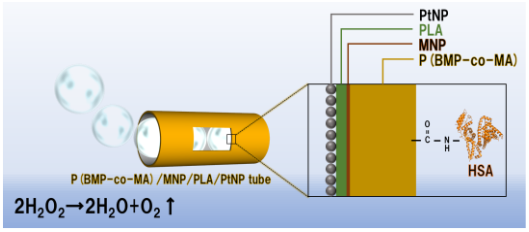


Fig. 1 Schematic illustration of HSA conjugated P(BMP-co-MA)/MNP/PLA/PtNP tubular micromotor in H_2O_2 solution.

1) T. Komatsu *et al. ACS Appl. Polym. Mater.* **2024**, *6*, 5822.

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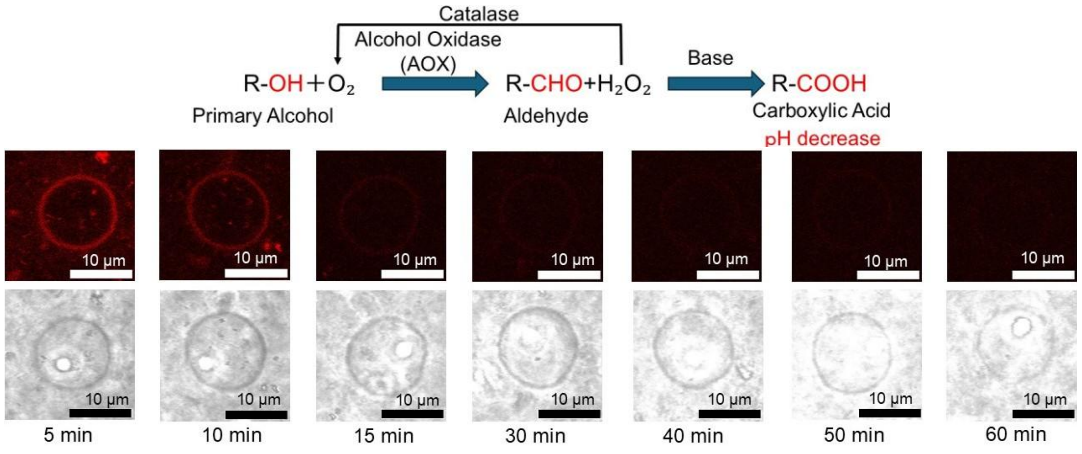
酸素存在下で pH が変化する反応系中でのオレイン酸ベシクルの応答性

（慶大理工）○串島 大智・涛崎 僚平・佐々木 翔生・朝倉 浩一・伴野 太祐
Responsiveness of Oleic Acid Vesicles in the Reaction System Where pH Changes in the Presence of Oxygen (*Keio University*) ○Daichi Kushijima, Ryohei Tozaki, Shoi Sasaki, Kouichi Asakura, Taisuke Banno

Vesicles, which can control the encapsulating and releasing behavior of substances by the slight changes in the external environment, have drawn considerable attention as functional materials. Here, we investigated the membrane permeability of oleic acid-vesicles in enzymatic reaction systems in which pH changes in the presence of oxygen. The fluorescent intensity of environmentally responsive Nile red in oleic acid-vesicles gradually decreased in Tris buffer at pH 8 containing alcohol oxidase and methanol. The decrease in pH over time was also confirmed in this observation system due to the generation of formic acid caused by methanol oxidation. We therefore deduce that the degree of neutralization of oleic acid changed with the pH decrease, leading to an increase in the membrane permeability of the vesicles.
Keywords : Oxygen; Enzymatic Reaction; Vesicles; pH Change; Oleic Acid

外部環境のわずかな変化により物質の取り込みおよび放出能を制御可能なベシクルは、機能性材料として注目されている。これまで光照射や pH 変化をトリガーとしたベシクルの膜透過性制御の事例は多数報告されているが、生命システムのように複数の化学反応が内在する化学反応系におけるものはほとんど報告例がない。本研究では、酸素存在下で pH が変化する酵素反応系におけるオレイン酸ベシクルの膜透過性を評価した。アルコールオキシダーゼとメタノールを添加した pH 8 の Tris 緩衝液中のオレイン酸ベシクルに、極性環境に応答する Nile red を加えて観察を行ったところ、膜内の蛍光強度が徐々に弱まった。この観察系においては時間とともに pH の低下が認められた。したがって、メタノールの酸化によるホルムアルデヒド、それに続くギ酸の生成にともなってオレイン酸の中和度が変化することで、ベシクルの膜透過性が上がったと考えられた。



pH 応答性ペプチドと温度応答性アミノ酸由来高分子からなるブロックポリマーの合成と自己集合特性

（同志社大理工 [1]）○河合 泰成 [1]・西村 慎之介 [1]・古賀 智之 [1]

Synthesis of self-assembling block polymer composed of pH-responsive peptide and thermo-responsive amino acid-derived polymer ([1]*Dept. of Molec. Chem. & Biochem., Doshisha University*) ○Taisei Kawai,[1] Shin-nosuke Nishimura,[1] Tomoyuki Koga[1]

Artificial peptides are known to form various nanostructures by self-assembly according to amino acid sequences, and have been applied as nanobiomaterials. Peptides with alternating arrangements of hydrophilic and hydrophobic amino acids form β-sheet structure and self-assembling in to nanofibers in water. Combining such self-assembling peptides with stimuli-responsive polymers is an attractive approach to functionalize the peptide nano-assemblies. In this study, we designed a thermo/pH-dual responsive hybrid polymer (PNAGAm-$(LE)_4$). This hybrid polymer contains UCST-type poly(*N*-acryloyl glycine amide) and amphipathic oligopeptide with leucine (L) / Glutamic acid (E) alternating sequence. Target block polymer was synthesized by combining solid phase peptide synthesis and atom transfer radical polymerization. The conformational and self-assembling properties of the polymer were investigated in aqueous solution.

Keywords : pH-responsive peptide; thermo-responsiveness; self-assembling; secondary structure; atom transfer radical polymerization (ATRP)

人工ペプチドはアミノ酸配列に従い、自己組織化によって様々なナノ構造体を形成することが知られており、ナノバイオ材料として応用が進んでいる。なかでも、親水性と疎水性のアミノ酸を交互に配列させたペプチドは、β-シート構造を基盤とするナノファイバーを形成する。こうした、自己組織化ペプチドと刺激応答性高分子を組み合わせた材料展開も進んでいる。本研究では、上部臨界溶液温度 (UCST) 型の温度応答性を示すポリ*N*-アクリロイルグリシンアミド (PNAGAm) と、pH 応答性のロイシン (L) /グルタミン酸 (E) 交互配列を有する自己組織性ペプチドからなるハイブリッドポリマー (PNAGAm-$(LE)_4$)を設計した (Fig.1)。自己組織性ペプチドには原子移動ラジカル重合 (ATRP) 開始部位を持つ$(LE(OtBu))_4$は Fmoc 固相合成法によって合成した。このペプチド担持樹脂を用いて触媒に$CuBr_2$/Me_6TREN、還元剤にアスコルビン酸を用いた ARGET ATRP により、NAGAm の重合を樹脂上で行った。得られた樹脂を TFA/DCM/TIS (v/v/v=98:1:1) で処理することで tBu 基の脱保護と樹脂からの切り出しを同時に行い目的のジブロックポリマーを得た。このポリマーの水溶液中での二次構造と自己組織化特性を検討した。

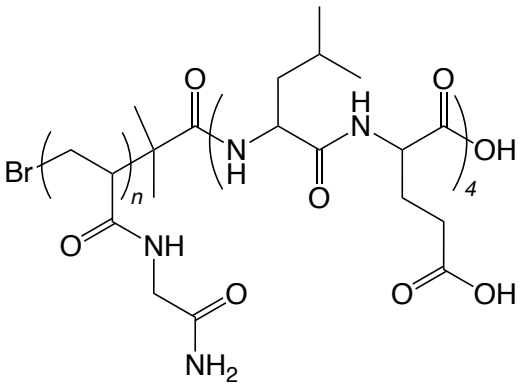


Fig. 1 Chemical structure of PNAGAm-$(LE)_4$