アカデミックプログラム［B講演］｜12. 有機化学—有機結晶・超分子化学：口頭B講演

2025年3月26日(水) 13:30 ~ 15:40 [F]2105(第4学舎 2号館 [1階] 2105)

[[F]2105-1pm] 12. 有機化学—有機結晶・超分子化学

座長：花山 博紀、大城 宗一郎

英語

13:30 ~ 13:50

[[F]2105-1pm-01]

異なる長さのアルキル鎖を持つモノマーが形成する超分子ロゼットの自己集合

○羅 雯雯[1]、花山 博紀[1]、矢貝 史樹[1] (1. 千葉大学)

英語

13:50 ~ 14:10

[[F]2105-1pm-02]

超分子ポリマーのダイナミクスを利用した高次構造選択的なモノマー変換反応

○板橋 裕毅[1]、花山 博紀[2]、矢貝 史樹[3] (1. 千葉大院融合理工、2. 千葉大工学研究院、3. 千葉大IAAR)

日本語

14:10 ~ 14:30

[[F]2105-1pm-03]

超分子ファイバーと界面活性剤の複合化による自律的なLiesegang-likeパターン形成

○窪田 亮[1]、生田 優力[1]、鳥越 祥吾[1]、浜地 格[1,2] (1. 京都大学、2. JST ERATO)

14:30 ~ 14:40

休憩

英語

14:40 ~ 15:00

[[F]2105-1pm-04]

コレステロール誘導体からなる階層性超分子プラスチック

○鄭 家昕[1]、渡邊 雄一郎[1]、室 和希[1]、梶谷 孝[2]、佐光 貞樹[3,4]、佐藤 久子[5]、杉安 和憲[1] (1. 京都大学、2. 東京科学大学、3. 物質・材料研究機構 、4. 早稲田大学、5. 愛媛大学)

英語

15:00 ~ 15:20

[[F]2105-1pm-05]

トリアシルグリセロール中での発光性超分子ブロックコポリマーの形成

○成瀬 美玖[1]、大城 宗一郎[2]、山口 茂弘[1,2,3] (1. 名大院理、2. 名大IRCCS、3. 名大ITbM)

英語

15:20 ~ 15:40

[[F]2105-1pm-06]

アミノ酸ジアミド置換アリーレンエチニレンの集合体特性に及ぼす対称性／非対称性の効果

○山田 沙絵子[1]、大城 宗一郎[2]、柳井 毅[1,3]、山口 茂弘[1,2,3] (1. 名大院理、2. 名大IRCCS、3. 名大ITbM)

Self-assembly of Heteromeric Supramolecular Rosettes formed from Monomers with Different Alkyl Chain Lengths

([1]Graduate School of Science and Engineering, Chiba University, [2]Graduate School of Engineering, Chiba University, [3]Institute for Advanced Academic Research, Chiba University)
○Luo Wenwen,[1] Hiroki Hanayama,[2] Shiki Yagai[3]

Keywords: Supramolecular Polymer; Self-Assembly; Barbituric Acid; Co-polymer; Side chains.

Supramolecular polymers (SPs) have attracted much attention as new polymer materials with reversible nature. One of the challenges to be addressed for the application of SPs is their bundling caused by interaction between sidechains, which can lead to phase-separation in solution. Randomizing alkyl sidechain lengths can prevent bundling[1], but this requires synthetic difficulties. We previously studied SPs of barbiturates with naphthalene and homogeneous side chains (-$C_{12}H_{25}$)[2]. These molecules hierarchically self-assemble into SPs by initially organizing into six-membered supermacrocycles (rosettes) and then stacking into fibers. However, the obtained SPs bundled each other, leading to precipitation. Here, we explored the possibility of preventing phase-separation through the formation of heteromeric rosettes from two molecules with different sidechain lengths.

We synthesized barbiturates **1**–**3**. Compounds **1** and **2** possess homogeneous side-chains -C_8H_{17} or -$C_{16}H_{33}$ respectively, while **3** possesses -C_8H_{17} and -$C_{16}H_{33}$ which are randomly distributed. All the molecules self-assembled to form SPs in non-polar solvent. AFM images revealed that bundling of SPs chains of **3** were suppressed while SPs of **1** and **2** were heavily bundled. Interestingly, SPs of the equimolar mixture of **1** and **2** afforded well-dispersed SPs like **3**. This result indicates that the hetero-rosette strategy to reduce phase separation of SPs.

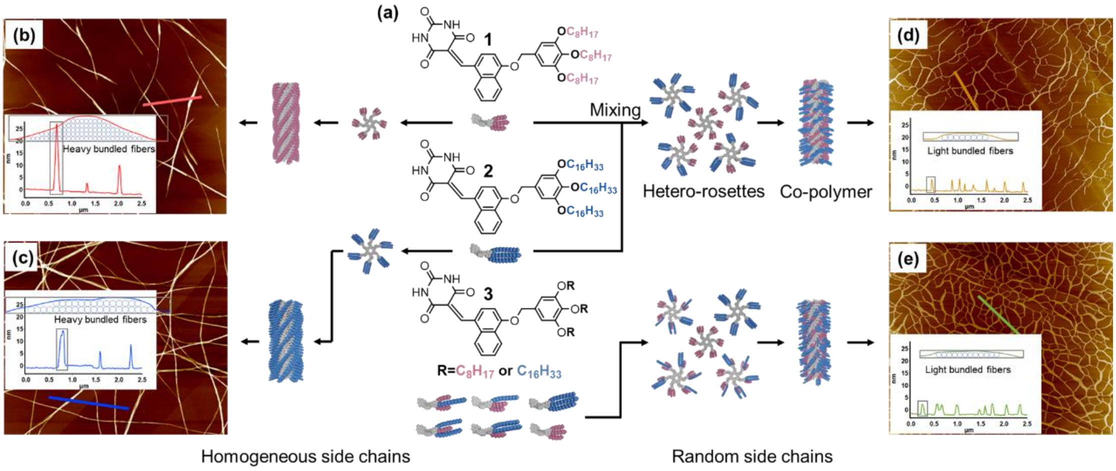

Figure 1. (a) Molecular structure of **1**, **2** and **3** and schematic representation of the supramolecular polymerization mechanism. (b-e) AFM images and height analysis of SPs composed of **1** (b), **2** (c), **3** (d) and the **equimolar mixture** (e).

1) T. Shimada, K. Sugiyasu, et al., *Chem. Sci.*, **2023**, *14*, 822.
2) S. Yagai, et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 6643.

Structure-Selective Monomer Conversion Reaction Depending on Dynamics of Supramolecular Polymers

([1]*Graduate School of Science and Engineering, Chiba University*, [2]*Graduate School of Engineering, Chiba University*, [3]*Institute for Advanced Academic Research, Chiba University*)
○Hiroki Itabashi,[1] Hiroki Hanayama,[2] Shiki Yagai[3]

Keywords: Supramolecular polymer; Dynamic covalent bond; Imine; Selective reaction; Nanoring

The exceptional hierarchical self-assembly systems in the biological realm are often driven by complex covalent reaction pathways and achieve outstanding functions by forming specific higher-order structures regulated by non-covalent interactions. Inspired by this dynamic system combining both covalent synthesis and non-covalent self-assembly, the field of supramolecular polymers (SPs) has recently focused on developing complex combination systems beyond self-assembly.[1] Although there are some reports on the bottom-up supramolecular polymerization from primordial building blocks through in situ monomer synthesis, the correlation between the higher-order structure of SPs and their chemical reactivity remains elusive.

Here, we demonstrate that C=C/C=N exchanging monomer conversion efficiency depends on the higher-order self-assembled structure, which allows us to in situ selectively transform specific SP structures (Fig. 1a). We previously reported that diphenylnaphthalene barbiturate derivative (**B-Nap**) afforded open/close-ended SPs with intrinsic curvature, and diphenylanthracene barbiturate derivative (**B-Ant**) afforded extended linear SPs.[2] Adding the imino diphenylanthracene derivative (**I-Ant**) to **B-Nap** curved SPs, they transformed into the linear SP of **B-Ant** through in situ C=C/C=N conversion. The fragmented helicoid SP of **B-Nap** had high reactivity, whereas the ring SP without termini and extended helicoid SP of **B-Nap** were inert due to the static nature (Fig. 1b).

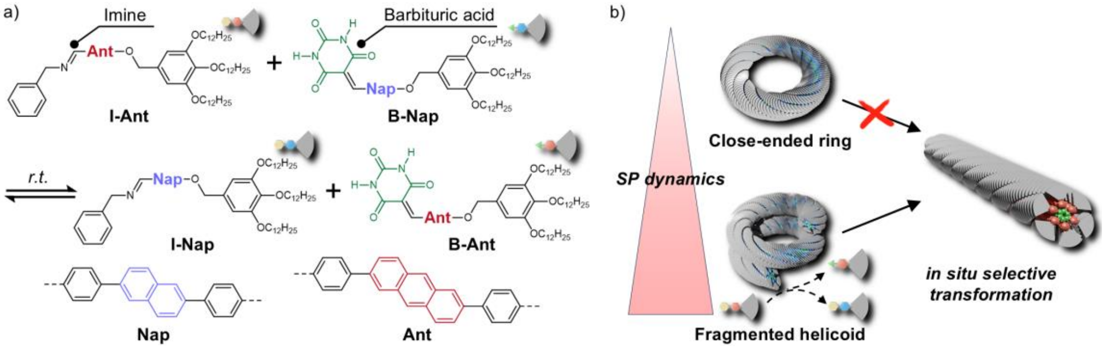

Figure 1. a) C=C/C=N exchanging reaction between **I-Ant** and **B-Nap**. b) Selective SP transformation depending on dynamics of SP.

1) E. Mattia, S. Otto, *Nat. Nanotechnol.* **2015**, *10*, 111; 2) S. Yagai et al., *Nat. Commun.* **2019**, *10*, 4578.

超分子ファイバーと界面活性剤の複合化による自律的な Liesegang-like パターン形成

（京大院工[1]・JST ERATO[2]）○窪田 亮[1]・生田 優力[1]・鳥越 祥吾[1]・浜地 格[1,2]

Autonomous Liesegang-like patterning by hybridizing supramolecular fibers with surfactant

([1]*Graduate School of Engineering, Kyoto University*, [2]*JST ERATO*) ○Ryou Kubota,[1] Yuriki Ikuta,[1] Shogo Torigoe,[1] Itaru Hamachi[1,2]

Spatial patterning of hydrogels hold promise for potential applications like cell culturing and regenerative medicine. The Liesegang phenomenon is a fascinating example of spatial pattern formation, where periodic precipitation patterns are generated by mixing oppositely-charged electrolytes in hydrogels. In this work, we discovered the autonomous formation of Liesegang-like spatial patterns in supramolecular hydrogels by hybridizing peptide-type hydrogelators and surfactants.

Keywords : Hydrogel; Supramolecule; Reaction-diffusion; Spatial patterning; Polymer

ヒドロゲルは高分子もしくは超分子の三次元網目構造からなる水を含んだ柔らかい材料である。その生体適合性の高さから、細胞培養や組織再生材料としての応用が期待され、様々なゲルパターニング技術が開発されてきた。ヒドロゲル内での自律的なパターニング現象の一例として、無機イオンの沈殿形成で観察される Liesegang 現象が知られている。Liesegang 現象では、ゲル内に溶解させた電解質に対し、その電解質と混合すると沈殿形成する電解質溶液を拡散させることで、周期的な沈殿パターンが自発的に形成される。このような Liesegang ring 現象は、ヒドロゲルのボトムアップによるパターン化に有用であると期待されるが、高分子・超分子ヒドロゲルにおける報告例は限られている。本研究では、ペプチド型ゲル化剤からなる超分子ヒドロゲルに対してカチオン性界面活性剤(DTAC)を添加することで、Liesegang リングに類似した周期的なパターンが形成することを発見した（Fig. 1）。共焦点顕微鏡による詳細な観察から、各バンドにおいて超分子ファイバーの密度や形態に違いがあることを明らかとした。本発表では詳細を報告する。

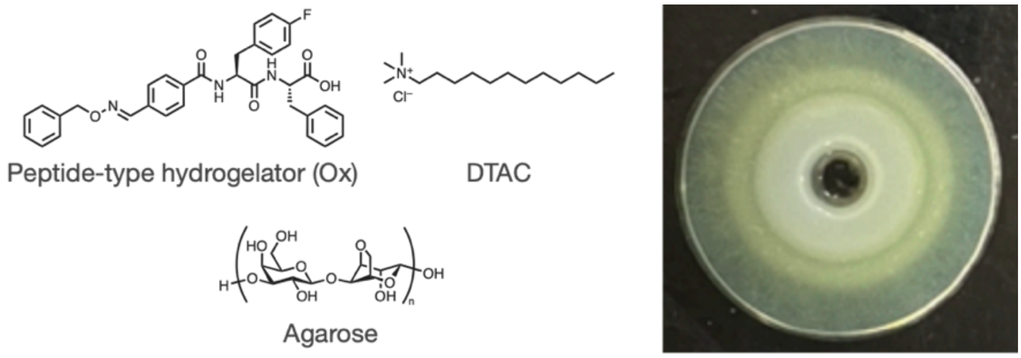

Fig. 1. Supramolecular Liesegang ring hydrogel comprising an anionic peptide-type hydrogelator and a cationic surfactant in an agarose.

Cholesterol-based supramolecular plastics with a hierarchical structure

([1]*Graduate School of Engineering, Kyoto University*, [2]*Core Facility Center, Science Tokyo,* [3]*Research Center for Macromolecules and Biomaterials, National Institute for Materials Science,* [4]*Graduate School of Advanced Science and Technology, Waseda University,* [5]*Graduate School of Science and Engineering, Ehime University*) ○Chia Hsin Cheng[1], Yuichiro Watanabe[1], Kazuki Muro[1], Takashi Kajitani[2], Sadaki Samitsu[3,4], Hisako Sato[5], and Kazunori Sugiyasu[1]*

Keywords: Cholesterol; Supramolecular Polymer; Sustainable Materials

In response to the pressing issue of plastic pollution, plastic reduction policies have been enacted globally. Despite these efforts, the annual production of plastic waste is still predicted to increase.[1] Supramolecular plastics, with their dynamic and reversible bonding natures, have emerged as a promising and sustainable solution to this problem.

In this study, we investigated the formation of free-standing supramolecular plastic films using naturally occurring cholesterol derivatives, which is well known to show one-dimensional self-assembling properties.[2-3] We designed and synthesized cholesterol-derived carbamates with three different alkyl chains to control their intermolecular interactions and hierarchical structures: Cholest-5-en-3β-yl *N*-hexyl carbamate (**C6**), Cholest-5-en-3β-yl *N*-dodecanoyl carbamate (**C12**), and Cholest-5-en-3β-yl *N*-octadecyl carbamate (**C18**). The process of the supramolecular plastic films is demonstrated in **Figure 1**. Each compound was melted at 100 °C and quenched into chunks at varying temperatures (room or cryogenic temperature). Subsequently, these chunks were pressed to form supramolecular plastic films using hydraulic pressing (0 to 98 kN) at room temperature. The length of the alkyl chains of the compounds significantly impacts the processability and mechanical properties of films.

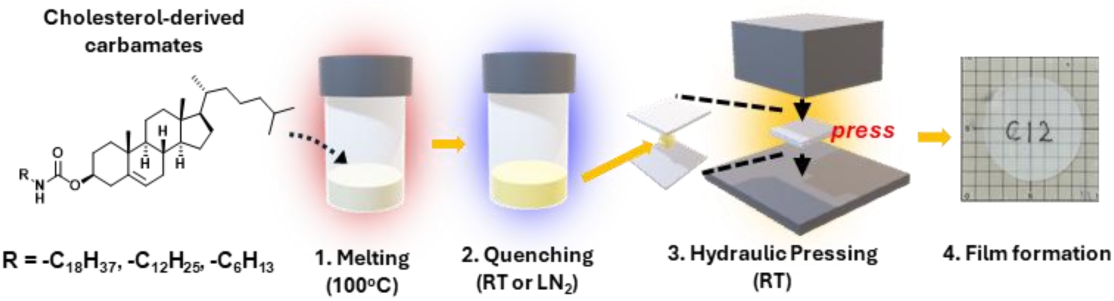

Figure 1. Chemical structures of cholesterol-derived carbamates (**C6**, **C12**, **C18**) and a schematic diagram of formation of a free-standing supramolecular plastic film

1) Borrelle, S. B., Rochman, C. M. *et al., Science.* **2020**, *369*, 1515. 2) Ishiwari, F., Fukushima, T. *et al.*, *Chem. Sci.* **2018**, *9*, 2028. 3) Weiss, R. G., *J. Am. Chem. Soc.*, **2014**, *136*, 7519.

Formation of Fluorescent Supramolecular Block Copolymers in Triacylglycerol

([1]*Graduate School of Science, Nagoya University,* [2]*Integrated Research Consortium on Chemical Sciences,* [3]*Institute of Transformative Bio-Molecules, Nagoya University*)
○Miku Naruse,[1] Soichiro Ogi,[2] Shigehiro Yamaguchi[1,2,3]

Keywords: Triacylglycerol; Fluorescent dye; Hydrogen bond; Supramolecular polymerization; Fluorescence imaging

Supramolecular assemblies of π-conjugated molecules exhibit characteristic photophysical properties, demonstrating their potential utility as tools for modulating cellular activities.[1] To harness functions provided by π-stacks in specific organelles, it is crucial to understand their self-assembly behavior in biological media. Recent studies have shown that commonly used organic solvents play a crucial role in pathway complexity of hydrogen-bond-directed supramolecular polymerization.[2] However, the impact of solute–solvent interactions on the kinetics of nucleated polymerization, especially in low-polarity biological media, such as lipid droplets, remains to be fully elucidated.

We herein investigate non-equilibrium supramolecular polymerization using triolein, a component of lipid droplets, as a model for biological media. For this purpose, supramolecular building blocks **1** and **2** were synthesized by combining a D-A-D-type fluorescent dye and an alanine-based diamide group bearing a chiral alkyl side chain (Fig. 1a). As previously shown, alanine-based diamide moiety is prone to the formation of an intramolecularly hydrogen-bonded pseudo cycle in the monomeric state.[3] The kinetic stability of **1** in the monomeric state was thus evaluated upon addition of triolein to a solution of **1** in 1-propanol with the triolein content of 97 vol%. Our detailed spectroscopic studies using additional two solvents having similar dielectric constants to triolein, ethyl oleate and dibutyl ether, revealed that the higher viscosity of triolein increases the lag time of the nucleation process. Furthermore, precipitation of fibrous aggregates was observed immediately in dibutyl ether (Fig 1b), while both triolein and ethyl oleate suppressed bundling of polymers. These results suggest that the long side chains, rather than the viscosity of the solvent, are effective in stabilizing the polymers. Using this understanding of the effects of triolein, we succeeded in formation of fluorescent supramolecular triblock copolymers composed of green-emissive **1** and blue-emissive **2** (Fig. 1c).

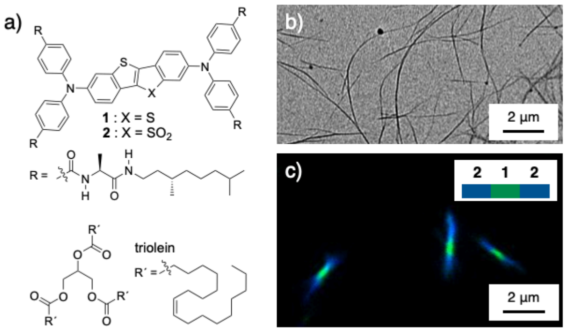

Figure 1. (a) Chemical structures of **1**, **2**, and triolein, (b) TEM image of **1** in the aggregated state obtained from a solution in dibutyl ether, and (c) fluorescence imaging of supramolecular triblock copolymers.

1) H.-B. Cheng, X.-J. Liang, J. Yoon *et al.*, Adv. Mater. **2023**, *35*, 2207546. 2) G. Vantomme, E. W. Meijer *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 17987. 3) S. Ogi, S. Yamaguchi *et al.*, *Angew. Chem. Int. Ed.* **2024**, *63*, e202416361.

Impact of Symmetry/Asymmetry on Aggregate Properties of Aryleneethynylenes having Amino-Acid-based Diamides

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○Saeko Yamada,[1] Soichiro Ogi,[2] Takeshi Yanai,[1,3] Shigehiro Yamaguchi[1,2,3]

Keywords: Self-assembly; Supramolecular polymers; π-Conjugated molecules; Molecular orientation; Photophysical properties

Supramolecular polymers composed of π-conjugated molecules exhibit diverse photophysical properties distinct from those of monomers. The establishment of molecular design strategies for controlling the packing structure of aromatic moieties is essential to realize supramolecular polymers with desired photophysical properties. In this context, seed-initiated supramolecular polymerization has received particular attention as it enables kinetic control over the structural parameters of π-stacked assemblies. We have reported that amino-acid-based diamide groups are useful for achieving seeded growth of various π-conjugated molecules.[1,2] However, the effect of symmetric/unsymmetric introduction of the diamide on aromatic interactions have not been fully elucidated.

Herein, we synthesized aryleneethynylenes **1** and **2** having leucine-based diamide groups on either one or both of the terminal phenyl moieties (Figure 1a). Microscopic studies revealed that both **1** and **2** form fibrous aggregates in low-polarity solvents (Figure 1b). While the UV-vis absorption spectra in their monomeric states were identical, the spectrum in the aggregated state of **1** exhibits a bathochromic shift, which is distinct from that of **2** showing a hypsochromic shift (Figure 1c). In addition, a circular dichroism (CD) spectrum with a bisignate Cotton effect was observed for the aggregates of **2**, while the aggregates of **1** showed a negative CD signal without a Cotton effect. We employed theoretical methodology to connect the results obtained from spectroscopic means to potential supramolecular packing models. Furthermore, we have demonstrated that the symmetrical/unsymmetrical introduction of leucine-based diamide influences not only the packing structure but also the self-assembly pathway, enabling elucidation of self-sorting behavior under non-equilibrium conditions.

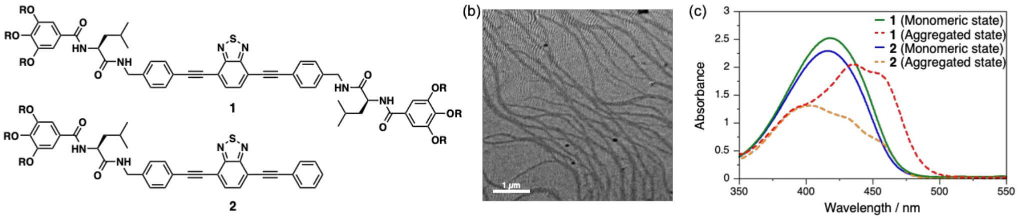

Figure 1. (a) Chemical structures of **1** and **2**, (b) TEM image of **1** in the aggregated state, and (c) UV-vis absorption spectra of **1** and **2** in the monomeric and aggregated states.

1) H. Choi, S. Ogi, N. Ando, S. Yamaguchi, *J. Am. Chem. Soc.* **2021**, *143*, 2953; 2) K. Matsumoto, N. Bäumer, S. Ogi, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2024**, *63*, e202416361.