アカデミックプログラム［Ｂ講演］｜18. 高分子：口頭Ｂ講演

2024年3月18日(月) 15:55 ~ 16:55 D342(3号館 [4階] 342)

[D342-1vn] 18. 高分子

座長：細野 暢彦、飯田 拡基

日本語

15:55 ~ 16:15

[D342-1vn-01]

多孔性金属錯体を用いたポリアルキルチオフェンの頭尾結合の識別と分離

〇高島 優[1]、澤山 拓[2]、細野 暢彦[1]、植村 卓史[1] (1. 東大院工、2. 東大院新領域)

英語

16:15 ~ 16:35

[D342-1vn-02]

ダブルネットワーク化と無機染色によるハイドロゲル中の荷電ポリマーネットワークの実空間可視化

〇野口 真司[1]、木山 竜二[1]、吉田 匡宏[1]、樫村 尚宏[1]、忠永 清治[1]、龔 剣萍[1]、野々山 貴行[1] (1. 北海道大学)

日本語

16:35 ~ 16:55

[D342-1vn-03]

超分子架橋による有機-無機高分子の複合化

山下 尚樹[1]、〇山岡 賢司[1]、以倉 峻平[1]、高島 義徳[1] (1. 大阪大学)

多孔性金属錯体を用いたポリアルキルチオフェンの頭尾結合の識別と分離

（東大院工[1]・東大院新領域[2]）○高島 優[1]・澤山 拓[2]・細野暢彦[1]・植村卓史[1]

Recognition and Separation of Head-to-Tail Polyalkylthiophenes by Metal–Organic Frameworks

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*Graduate School of Frontier Sciences, The University of Tokyo*) ○Yu Takashima,[1] Taku Sawayama,[2] Nobuhiko Hosono,[1] Takashi Uemura[1]

Poly(3-hexylthiophene) (P3HT) is a widely studied semiconductive polymer in the field of organic electronics. The electron conductivity of P3HT is known to be significantly influenced by the regioregularity (RR) of the main chain, making regioselective polymerization techniques crucial for achieving high-performance P3HT. However, conventional polymerization approaches face challenges related to catalyst design and technical complexity.[1,2] In this study, we developed a structure recognition and separation technique using nano-sized pores of metal-organic frameworks (MOFs) to give a new approach to obtain regioregular P3HT. We discovered that certain MOFs recognized regio-isomers of P3HT oligomers (dimer and tetramer) upon adsorption into the nanopores. Based on this finding, we successfully developed a column chromatography method using the MOFs as the stationary phase. This approach allows for RR-based separation of P3HT, enabling the extraction of highly regioregular P3HT from crude materials with lower RR.

Poly(3-hexylthiophene) (P3HT)は、有機エレクトロニクス分野において広く研究が行われている代表的な有機半導体高分子である。P3HTの導電性を向上させるためには高い頭尾結合割合（Regioregularity, RR）の実現が不可欠であるが、従来の合成方法では触媒設計や技術的煩雑さといった課題が残されていた[1,2]。そこで本研究では、高いRRのP3HTを得る全く新しいアプローチとして、多孔性金属錯体（MOF）が持つナノサイズの細孔を利用した精密な構造認識技術を開発した（Figure 1）。

数種のMOFを用いたオリゴチオフェン（二量体および四量体）の分離実験により、適切な細孔径の選択により結合位置異性を識別可能であることを発見した。また、MOFの細孔内にP3HTを直接導入する実験を試みたところ、RRが高いP3HTが選択的に吸着されることを見出した。さらに、同MOFを充填剤とした分取用カラムを作成し液体クロマトグラフィーを用いて分離することで、P3HTの粗重合生成物からRRが高いP3HTを選択的に抽出することに成功した。

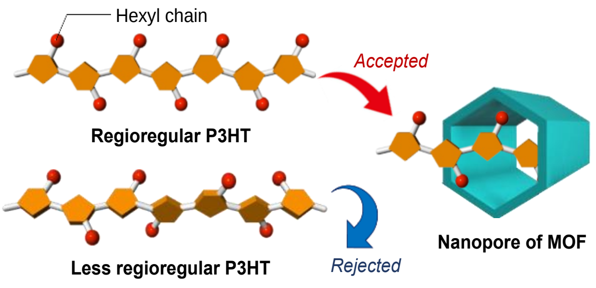

Figure 1. Schematic diagram of the regioselective adsorption of P3HT in the nanopores MOFs.

1) Y. Kim, et al., *Nat. Mater.* **2006**, *5*, 197-203.
2) P. Kohn, et al., *J. Am. Chem. Soc.* **2012**, 134, 4790-4805.

Real-Space Visualization of Charged Polymer Network of Hydrogel by Double Network Strategy and Mineral Staining

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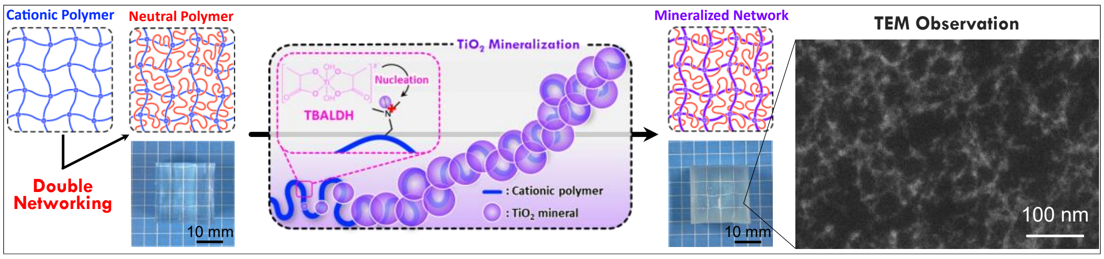
○ Shinji Noguchi,[1] Maradhana Agung Marsudi,[2] Ryuji Kiyama,[3] Naohiro Kashimura,[2] Masahiro Yoshida,[2] Kiyoharu Tadanaga,[4] Jian Ping Gong,[3,5] Takayuki Nonoyama[3]

Keywords: Mineral staining; Transmission Electron Microscopy; Hydrogels; Nanostructure

Hydrogels consist of three-dimensional polymer networks and water, and the network structure affects their physical properties. Synthetic hydrogels inevitably possess a hierarchical inhomogeneous network structure, and specific properties, such as fracture and subsequent crack propagation, strongly depend on the "local" structure. Thus, the local structure is essential for predicting such a phenomenon, and ideal techniques for analysis are required. Among the methods for structural analyses of hydrogels, the real-space imaging of a polymer network of hydrogel on a nanometer scale is one of the optimal ones; however, it is highly challenging. A well-known technique to enhance the electron density is electron staining with heavy element compounds such as uranyl acetate1) and phosphotungstic acid.2) However, synthetic polymer strands are thin, flexible, and susceptible to aggregation during staining or resinification. Then, the structural information at the mesh size scale is lost during sample preparation.

In this study, we propose a direct observation technique for cationic polymer networks using transmission electron microscopy (TEM). By combining the double network strategy and a TiO_2 mineral staining technique, we overcame the polymer aggregation and the low electron density of the polymer. An objective cationic network was incorporated into a neutral skeleton network to suppress shrinkage during subsequent staining. Titania mineralization using titanium bis (ammonium lactate) dihydroxide along the cationic polymer strands provided sufficient electron density for the objective polymer network for TEM observation.3) This observation technique enables the visualization of local structures in real space and is complementary to scattering methods for soft matter structure analysis.



Scheme 1. Strategy of the present study.

1) J. G. Stempak, R. T. Ward, *The Journal of Cell Biology* **1964**, *22*, 697–701. 2) W. F. Sheridan, R. J. Barrnett, *J Ultrastruct Res* **1969**, *27*, 216–229. 3) S. Noguchi, M.A. Marsudi, R. Kiyama, N. Kashimura, M. Yoshida, K. Tadanaga, J. Gong, T. Nonoyama, *submitted*.

超分子架橋による有機-無機高分子の複合化

（阪大院理）山下尚樹・○山岡賢司・以倉崚平・高島義徳

Organic-Inorganic Polymer Composites by Supramolecular Cross-linking Design

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Organic–inorganic materials have been widely utilized in various fields as multifunctional materials. Poly(dimethyl siloxane) (PDMS), a typical inorganic polymer, is blended with organic polymers for multifunctionality, but is immiscible with most polymers. We incorporated organic‐inorganic hybrid elastomers (PDMS-γCD-AAl⊃P(EA-HEMA) (x)) with movable and reversible crosslinks (**Fig. 1a**). Poly ethyl acrylate-r-hydroxy ethyl methacrylate (P(EA-HEMA)) penetrated the cavity of triacetylated γ-cyclodextrin (γCD), which was introduced into the side chains of PDMS-γCD-AAl. Allyl alcohol groups (AAl) of PDMS-γCD-AAl and HEMA in P(EA-HEMA) form hydrogen bonds between the polymers as reversible cross-links. x is molar ratio of HEMA in P(EA-HEMA). Introducing movable cross-links improved the compatibility of organic and inorganic polymers. The synergy of movable and reversible cross-links improved the toughness values (**Fig. 1b**). The design of PDMS-γCD-AAl⊃P(EA-HEMA) (x) incorporated cooperatively movable and reversible crosslinks to achieve high compatibility and mechanical properties[1].

Keywords : Movable cross-link, Hydrogen bond, Polymer blend, Mechanical properties, Structural analysis

有機高分子と無機高分子の複合化は、それぞれの特長を併せ持つ機能性材料を作製できるが、代表的な無機高分子であるポリジメチルシロキサン(PDMS)は、有機高分子と非相溶であるため、相分離し材料機能が失われる。本研究ではシクロデキストリン(CD)の空孔に高分子主鎖が貫通した可動性架橋と水素結合由来の可逆性架橋をPDMS とアクリレート系高分子(P(EA-HEMA) (x))間に導入し、混和性と靭性の向上に成功した[1]。

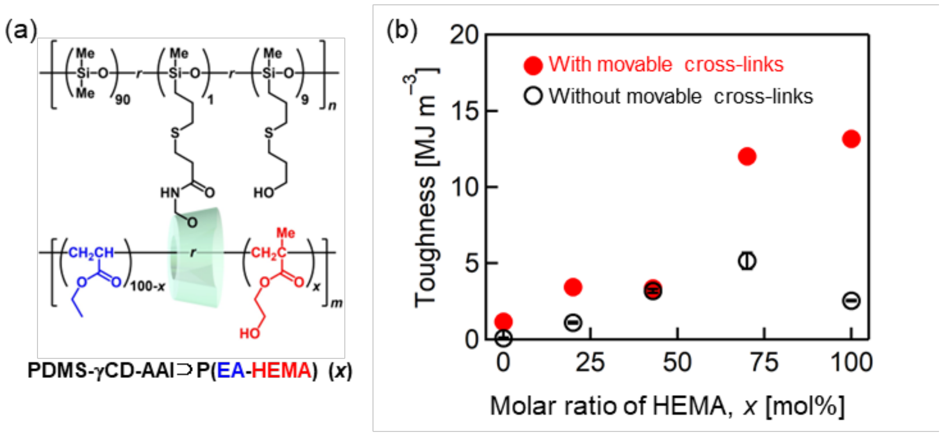

Figure 1. (a) Chemical structure and **(b)** toughness of PDMS-γCD-AAl⊃P(EA-HEMA) (x).

Ref. 1) N. Yamashita, K. Yamaoka, R. Ikura, Y. Takashima, et al., *Soft Matter* **2023**, *19*, 9074-9081.