Academic Program [Oral B] | 18. Polymer：Oral B

Wed. Mar 26, 2025 1:00 PM - 2:50 PM JST | Wed. Mar 26, 2025 4:00 AM - 5:50 AM UTC
[F]2404(2404, Bldg. 2, Area 4 [4F])

[[F]2404-1pm] 18. Polymer

Chair: Ryoyu Hifumi, Kazushi Fujimoto

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[F]2404-1pm-01]

Single-Chain Structure Analysis of Polymers by AFM Nanofishing from MOF Nanopores

○Yu Kono[1], Takashi Uemura[1], Nobuhiko Hosono[1] (1. Grad. Sch. of Eng., The Univ. of Tokyo)

Japanese
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[F]2404-1pm-02]

Aggregate structure and surface properties of thin films of polyethylene with terminal fluoroalkyl groups.

○Kaoru Tashiro[1], Satoru Honmura[2], Takashi Okazoe[2], Daisuke Kawaguchi[1] (1. The Univ. of Tokyo, 2. AGC Inc.)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[F]2404-1pm-03]

Composite Structure by Polyiodides,
I_n^{m-}, within Hydrophilic Polymer [IX];
"Dynamic Amphiphilicity" and Linkage as Pseudo-polymer Introduced by Polyiodide Ions. (1)

○Akio Kawaguchi[1] (1. Kyoto University)

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

Break

English
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[[F]2404-1pm-04]

Unraveling proton conductivity mechanism of alkyl sulfonated polyimides by molecular dynamics using neural network potential

○Attila Taborosi[1], Kentaro Aoki[2], Noboyuki Zettsu[1], Michihisa Koyama[1], Yuki Nagao[2] (1. Shinshu University, 2. Japan Advance Institute of Science and Technology)

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[[F]2404-1pm-05]

Compression-Induced Fracture and Region-Dependent Properties of Polymer Nanoparticles Revealed by All-Atom Molecular Dynamics Simulation

○Ikki Takahashi[1], Yoshiki Hieda[2], Yusuke Yasuda[3], Minoru Kato[1,4], Kazushi Fujimoto[5] (1. Grad. Sch. Life Sci., Ritsumeikan Univ., 2. Grad. Sch. Sci. & Eng., 3. Org. Res. Dev. Innov. Sci. & Tech., Kansai Univ., 4. Coll. Life Sci., Ritsumeikan Univ., 5. Fac. Chem., Mater. & Bioeng., Kansai Univ.)

Single-Chain Structure Analysis of Polymers by AFM Nanofishing from MOF Nanopores

(*Graduate School of Engineering, The University of Tokyo*) ○Yu Kono, Takashi Uemura, Nobuhiko Hosono

Keywords: *Metal-Organic Framework; Atomic Force Microscope; Single Molecule Force Spectroscopy; Nanopores; Sequencing*

The emergence of rapid DNA sequencing technologies, including nanopore sequencing, has dramatically accelerated progress in biological and medical research. In contrast, sequencing synthetic copolymers remains a formidable challenge due to the lack of fundamental techniques for accessing a single chain of polymers to identify the local monomer arrangement.[1] Recently, our research group discovered that polymer chains spontaneously adsorb into the nanopores of metal-organic frameworks (MOFs) from solution, where they become isolated as single chains within the pores.[2] In this study, we leveraged this unique feature of polymer adsorption into MOFs to develop a novel approach for single-chain structure analysis by combining it with single-molecule analysis using an atomic force microscope (AFM).

Single polymer chains with a thiol terminus encapsulated within the nanopores of a MOF single crystal were mechanically pulled out using a gold-coated AFM probe (**Figure 1a**). As model polymers, polyethylene glycols (PEGs) substituted with multiple phenyl rings or dimethylphenyl rings at regular intervals were examined to demonstrate the concept. The force on the probe was monitored during the pulling event, generating force curves with multiple peaks separated by regular intervals. The peak force values increased in correspondence with the size of the phenyl substitution group on the chain (**Figure 1b**). This result demonstrates that even subtle structural features of polymer chains, such as monomer mutations, substitutions, and their locations, can be identified with this method. This method enables direct reading of the structural information of synthetic polymers and is expected to pave the way for a new paradigm in polymer analysis technology.

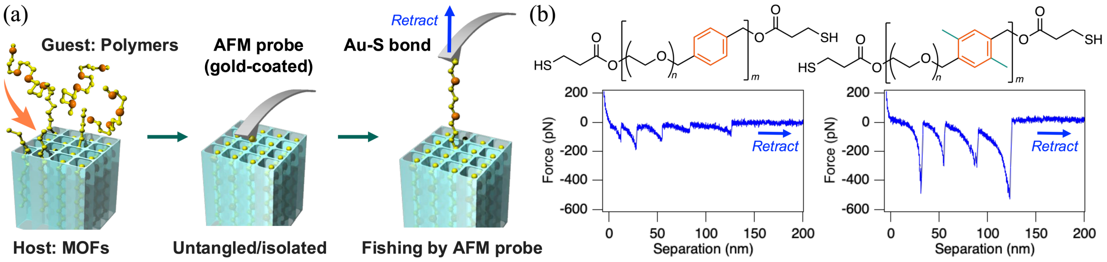


Figure 1. (a) Schematic of the nanofishing process. (b) Typical structures of the model analyte polymers (top) and representative force curves (bottom) for phenyl-substituted PEG (left) and dimethylphenyl-substituted PEG (right).

1) H. Multu, J.-F. Lutz, *Angew. Chem. Int. Ed.* **2014**, *53*, 13010.

2) N. Oe, N. Hosono, T. Uemura, *Chem. Sci.* **2021**, *12*, 12756.

末端にフルオロアルキル基を有するポリエチレン薄膜の凝集構造と表面特性

（東大院工 [1]・AGC [2]）○田代 薫 [1]・本村 了 [2]・岡添 隆 [2] ・川口 大輔 [1]

Aggregation structures and surface properties of thin films of polyethylene with terminal fluoroalkyl groups

([1]*Graduate School of Engineering, The University of Tokyo*, [2]*AGC Inc.*)
○Kaoru Tashiro,[1] Satoru Hommura,[2] Takashi Okazoe,[2] Daisuke Kawaguchi[1]

Chain-end-functionalization is an effective way to give additional properties to polymers. In our work, we envisioned that the fluorinated chain-ends of polyethylene (PE), which is a representative semicrystalline polymer, might segregate into amorphous phases at the surface, enabling control of surface wettability. PEs with terminal R_F groups ($R_F = C_2F_5, C_6F_{13}, C_8F_{17}$) were synthesized via ring-opening metathesis polymerization and subsequent hydrogenation. The surface free energy of the obtained PEs' films was lower than that of conventional PE, could be tuned by R_F groups and molecular weights.

Keywords : Polyethylene, End-functionalization, Fluorine

ポリエチレン(PE)に代表される結晶性高分子は、結晶と非晶が積層した高次構造を形成し、その末端は非晶部分に排斥される 1)。そのため、結晶性高分子の末端に官能基を導入することで非晶相選択的な機能化が期待される。これまでに、両末端にイオン性基を導入した PE の結晶構造とイオン伝導度に関する報告はあるが 2)、その他の機能化は十分に検討されていない。本研究では、最小限のフッ素使用量でフッ素由来の撥水撥油性表面を実現することを目指し、末端にフルオロアルキル(R_F)基を導入した PE を合成し、その膜表面の凝集構造とぬれ性について検討した。

R_F 基($R_F = C_2F_5, C_6F_{13}, C_8F_{17}$)を有する連鎖移動剤の存在下、シクロオクテンの開環メタセシス重合と続く二重結合の水素化により、両末端に R_F 基を有する PE を合成した(Scheme 1)。得られた PE の薄膜を調製し、広角 X 線回折測定に基づき結晶構造を明らかにし、X 線光電子分光法により R_F 末端が表面に偏析していることを確認した。水とジヨードメタンの接触角を測定し、表面自由エネルギー(γ)を算出した。その結果、いずれの PE も通常の HDPE に比べて低い γ を示し、その値は R_F 基の種類や分子量に依存した(Table 1)。以上より、末端に導入された R_F 基の偏析により表面の濡れ性を制御できると言える。R_F 末端基の空間分布については当日議論する。

Scheme 1. Synthesis of end-fluorinated polyethylene.

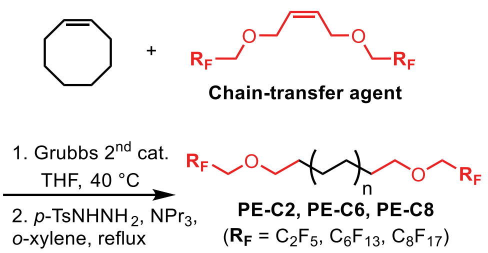


Table 1. Molecular weight, contact angle, and surface free energy for polymers used in this study.

Entry	M_n (kg/mol)	θ_{H2O} (°)	θ_{CH2I2} (°)	γ (mJ/m^2)
PE-C2-21k	21	103.7	58.9	29.5
PE-C2-5k	5.0	102.3	65.0	25.7
PE-C6-15k	15	109.8	68.6	24.0
PE-C6-6k	5.5	112.0	80.3	17.4
PE-C8-19k	19	109.8	75.8	19.7
PE-C8-7k	6.7	112.5	85.0	15.0
HDPE	12	105.4	57.0	30.9

1) Yuan S, and Schmidt-Rohr K. *Sci. Adv.* **2020**, *6*, eabc0059. 2) Mecking, S. Winey, K. I. *et al. Macromolecules* **2019**, *52*, 4949−4956.

日本化学会 第105春季年会 (2025)

親水性高分子をマトリクスとするポリヨウ素イオン I_n^{m-} と金属イオンとの塩形成 [IX]; ポリヨウ素イオンの「動的両親媒性」と連鎖構造 (1)

（京大複合研[1]）○川口 昭夫[1]

Composite Structure by Polyiodides, I_n^{m-}, within Hydrophilic Polymer [IX]; “Dynamic Amphiphilicity” and Linkage as Pseudo-polymer Introduced by Polyiodide Ions. (1)

([1]*Inst. Integrated Rad. And Nucl. Sci., Kyoto Univ.*) ○Akio Kawaguchi[1]

Interaction between hydrophilic polymers and polyiodide ions (PolyIod), I_n^{m-}, is well known as “iodine-starch complex”, for example. While such construction might be regarded as process in solution, diffusion of PolyIod’s advances rapidly in matrices system of hydrophilic polymers without their melting nor solving; occasionally, diffusion into crystallite region or modification of chain orientation are also observed for some polymers through diffusion of PolyIod’s, “iodine doping”. In addition, preceding existence of PolyIod’s activates interaction with other ions or moisture; inner precipitation of hardly solved salts prepared by “secondary doping” applied with preceding PolyIod’s can also introduce hybrid composite within various matrices including non-plasticized polymers . Furthermore, these actions are qualitatively expanded within hydrophobic matrices with aqueous solutions of PolyIod’s; diffusion with PolyIod’s is activated by aqueous solvents. These results can introduce a view of polymeric matrices applied with “PolyIod” as diffusion medium. And, such behaviors can be interpretated as “dynamic amphiphilicity” of PolyIod’s which is generalized by charge distribution and shearing among PolyIod’s linked by halogen bonds; hypothesized model is explained by modified charge distribution and by dynamic modulation in symmetricity of PolyIod molecules. It suggests charge propagation within ordered system constructed with polymer chains under hierarchic structure.

Keywords : Iodine; Hierarchic Structure; Amphiphilicity; Ionic Diffusion; Self-organization.

親水性高分子とヨウ素（ポリヨウ素イオン I_n^{m-}、PolyIod と略）との相互作用は「ヨウ素デンプン反応」として知られる水溶性高分子系に限らず、常温常圧下でも繊維・フィルムなどのバルク試料や分子鎖配向領域などにも容易に拡散する[1-3)]。時には結晶相での包接構造形成、拡散方向や延伸に依存した配向転換も認められることから、通常の無秩序な溶媒空間内での拡散ではなく、自己組織化も視野に入れた「構造化空間内での拡散・構造変調」として捉えるべき過程である[4)]。また調製溶液中のヨウ素種とは異なる構造の PolyIod が包接構造に関与するだけでなく、構造形成後にも環境中の湿度応答や事後的なイオン拡散（２次ドープ）が進行することから、動的な構造変調が示唆される[5)]。更に一連の反応は「疎水性マトリクスに対する PolyIod 水溶液処理」によっても定性的な拡張が認められることは、両親媒性を示している。その由来として PolyIod 間の連鎖（ハロゲン結合）と電荷移動（１分子上の分布対称性の揺らぎと分子間での交換）に伴って発現する「動的両親媒性（仮説）」が検討されている[6)]。これは直接的観測は容易ではないが、「ヨウ素デンプン反応」や PolyIod 水溶液の強力な殺菌力を説明すると同時に、構造化された空間内での電荷移動や領域選択的なイオン拡散を展望するものと考える。

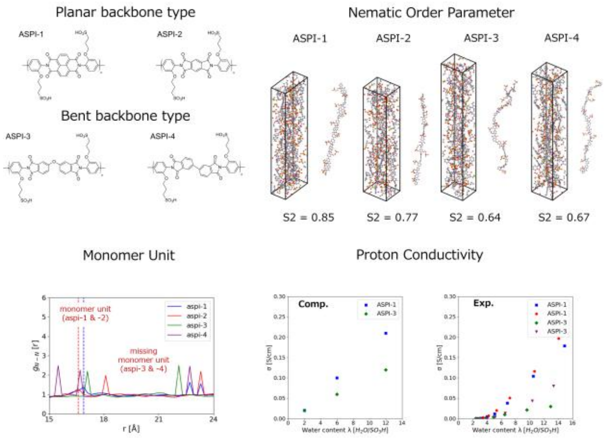
1) R.E. Rundle, et.al., *J. Am. Chem. Soc.* **1943**, *65*, 554.; 2) H. Arimoto, *J. Polym. Sci. ,Pt. A* **1964**, *2*, 2283.; 3) A. Kawaguchi, *Polymer.* **1994**, *35*, 2665.; 4) A. Kawaguchi, *ibid.* **1994**, *35*, 3797.; 5) A. Kawaguchi, et.al. *Polymer J.* **2011**, *43*, 385.; 6) 川口, *第20回ヨウ素学会シンポジウム.* **2017**, 104.

Unraveling proton conductivity mechanism of alkyl sulfonated polyimides by molecular dynamics using neural network potential

([1]*Research Initiative for Supra-Materials, Shinshu University*, [2]*School of Materials Science, Japan Advanced Institute of Science and Technology*) ○Attila Taborosi,[1] Kentaro Aoki,[2] Nobuyuki Zettsu,[1] Michihisa Koyama,[1] Yuki Nagao[2]

Keywords: alkyl sulfonated polyimides, molecular dynamics simulation, neural network potential, proton conductivity, structural analysis

Alkyl sulfonated polyimides[1] (ASPI) are promising polymer electrolyte membranes for fuel cells, with proton conductivity highly dependent on their molecular structure. Experimental findings[2] have shown distinct structural organizations and proton conductivity between planar (ASPI-1 & ASPI-2) and bent (ASPI-3 & ASPI-4) backbone types. To elucidate the difference at the molecular level, we employed molecular dynamics simulations with universal neural network potential (UNNP) called PreFerred Potential[3] (PFP) to explore the structural features, water uptake, and proton transport properties of these ASPIs. Planar ASPIs demonstrated the appearance of monomer units derived from the N-N radial distribution function, which reproduces the experimental observations.[2] Furthermore, planar ASPIs exhibited higher nematic order parameter values, indicating enhanced molecular order, and higher proton conductivity compared to bent ASPIs. Although both planar (ASPI-1) and bent (ASPI-3) backbone ASPIs exhibited similar volume expansion during water uptake, proton conductivity differences were not associated with sulfonic acid group solvation or deprotonation. However, the directional mean square displacement (MSD) analysis revealed that H and O atoms diffusion was greater along the polymer chain in planar than bent, explaining the difference in proton conductivity, which is related to the higher molecular order of planar types. These results provide valuable guidance for the design of ASPI materials with improved proton conductivity.



1) K. Krishnan *et al.*, *J. Mater. Chem. A* **2014**, *2*, 6895. 2) Y. Ono *et al.*, *Macromolecules* **2018**, *51*, 3351. 3) S. Takamoto *et al.*, *Nat. Commun.* **2022**, *13*, 2991.

This work was supported by JST, CREST Grant Number JPMJCR21B3, Japan.

全原子分子シミュレーションによる高分子微粒子の圧縮破壊と領域依存性の解明

（立命館大院生命[1]・関西大院理工[2]・関大 ORDIST[3]・立命館大生命[4]・関大化生[5]）○高橋 一輝[1]・稗田 吉希[2]・保田 侑亮[3]・加藤 稔[1,4]・藤本 和士[5]

Compression-Induced Fracture and Region-Dependent Properties of Polymer Nanoparticles Revealed by All-Atom Molecular Dynamics Simulation ([1]*Graduate School of Life Sciences*, *Ritsumeikan University*, [2]*Department of Chemistry and Materials Engineering*, *Graduate School of Science and Engineering*, *Kansai University*, [3]*Organization for Research and Development of Innovative Science and Technology* (*ORDIST*), *Kansai University*, [4]*Department of Applied Chemistry*, *College of Life Sciences*, *Ritsumeikan University*, [5]*Department of Chemistry and Materials Engineering*, *Faculty of Chemistry*, *Materials and Bioengineering*, *Kansai University*) ○Ikki Takahashi[1], Yoshiki Hieda[2], Yusuke Yasuda[3], Minoru Kato[1,4], Kazushi Fujimoto[5]

The elastic modulus and deformation behavior of polymer nanoparticles are crucial for their applications and have been studied through both experimental and molecular dynamics (MD) simulations. Nanoparticles made from brittle polymers reportedly do not exhibit stress yielding and instead display S-shaped stress–strain curves similar to those of rubber, yet the molecular mechanisms remain unclear. In this study, we prepared polymer nanoparticles that closely resemble real systems and conducted compression tests with all-atom MD simulations. True stress (σ_{true}) was calculated using the contact area between the compression plate and the nanoparticle (see Fig. 1). Contrary to previous assumptions, poly(methyl methacrylate) (PMMA), a brittle material, was found to yield at low strains as bulk PMMA. We further divided the nanoparticle interior into three radial regions to analyze the region-dependent internal fracture processes during compression. We will discuss the details on the day.

Keywords : Polymer Nanoparticle, *All-atom Molecular Dynamics Simulation*, *Compressive Fracture Mechanisms*, *Region Dependent Polymer Properties, Order Parameter Analysis*

高分子微粒子の弾性率や変形挙動は応用利用上重要なファクターであり、実験と分子動力学(MD)シミュレーションの両面から研究されてきた。脆性高分子材料による微粒子は応力降伏を示さず、ゴム材料に見られる S 字型の応力-ひずみ曲線を示すと報告されているが、その分子論的メカニズムは未だ明らかになっていない。

本研究では、現実の系を再現した高分子微粒子を作成し、全原子 MD 法による圧縮シミュレーションを行った。圧縮版と微粒子間の接触面積を用いて真応力(σ_{true})を算出し、Fig.1 に示した。脆性材料は微粒子化することでゴム状の応力応答を示すと考えられてきたが、脆性材料である Poly(methyl methacrylate) (PMMA)はバルク材料と同じく低ひずみ領域で降伏することが新たに明らかとなった。さらに微粒子内部を半径に応じて三つの領域に分割し、圧縮過程における内部破壊の領域依存性を解析した。詳細は当日議論する。

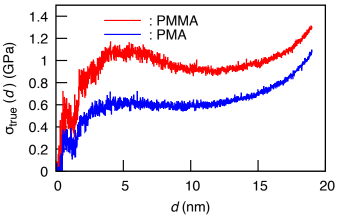


Fig.1 True stress-displacement curves of PMMA(red) and PMA(blue)