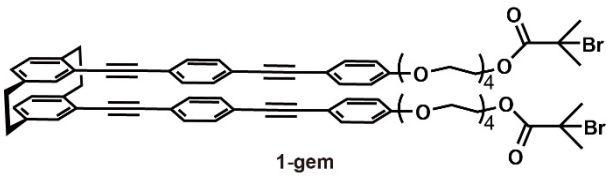
[2.2]パラシクロファンの置換位置選択的メカノケミカル反応

（東京科学大物質理工[1]）○清水翔平[1]・相良剛光[1]
Mechanochemical Reactions of [2.2]paracyclophane: Substitution-Dependent Structural Changes ([1]*Department of Materials Science and Engineering, Institute of Science Tokyo*)
○Shohei Shimizu,[1] Yoshimitsu Sagara[1]

Ultrasonication has been utilized to apply force near the center of polymer chains, enabling investigations on the mechanochemical responses of various molecular structures.[1–3] In this study, we report the mechanochemical reactivity of [2.2]paracyclophane consisting of two benzene rings bridged by two ethylene linkers. To investigate the regioselectivity, the mechanochemical responses were examined for [2.2]paracyclophane derivatives substituted at *pseudo*-meta, ortho, para, and gem positions upon ultrasonication. The sonication experiments were conducted after covalently incorporating the [2.2]paracyclophane derivatives into poly(methyl acrylate)s as initiators. The UV-vis absorption, photoluminescence, and ^{1}H NMR spectra were measured for the polymer solution before and after the sonication treatments. It was revealed that only the polymer covalently containing the *pseudo*-gem substituted [2.2]paracyclophane derivative **1-gem** gradually changes the spectra. These results mean that **1-gem** shows structural changes involving scission of covalent bonds in response to mechanical force. DFT calculations were performed to examine the reactivities depending on the substituted positions.
Keywords : Mechanochemistry; [2.2]paracyclophane; Ultrasonication

ポリマー溶液を超音波処理するとポリマー鎖の中心付近に大きな力が加わることを利用し、これまでに多くの分子骨格に対して力による構造変化が調べられてきた[1)–3)]。本研究では、歪んだ構造を持つ[2,2]パラシクロファン骨格のメカノケミカル反応を精査した。置換位置による応答性の差を明らかにするため、[2.2]パラシクロファン骨格の疑似メタ, 疑似オルト, 疑似パラ, 疑似ジェム位に置換基を導入し、超音波処理後の構造変化を比較した。超音波処理前後のポリマー溶液が示す紫外・可視吸収スペクトル、蛍光スペクトル、^{1}H NMR スペクトルを比較・精査すると、疑似ジェム位置換体 **1-gem** 骨格を含むポリマー溶液のスペクトルのみが超音波の照射時間が長くなるにつれて変化した。これは **1-gem** 骨格が機械的刺激を受けて共有結合の切断を伴う構造変化を示すことを意味する。また、置換位置選択性を DFT 計算によって精査した。



1-gem

1) M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755.
2) N. Willis-Fox, E. Rognin, T. A. Aljohani, R. Daly, *Chem* **2018**, *4*, 2499.
3) G. De Bo, *Macromolecules*, **2020**, *53*, 7615.