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Osaka University

## Abstract of Thesis

Name ( Yuyang Ding )

## Title

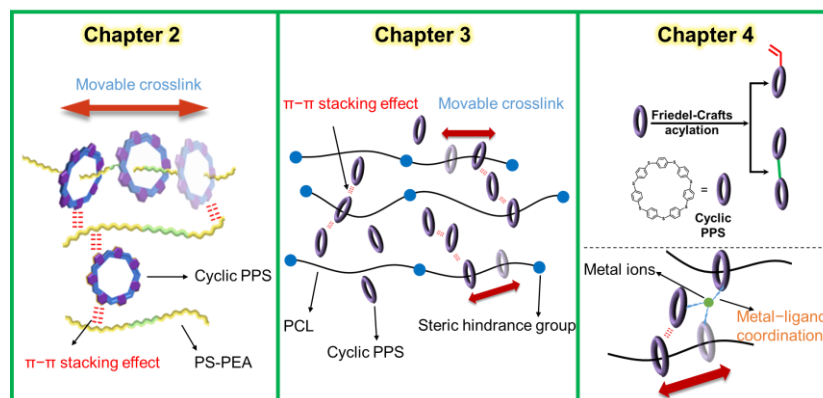
The application and modification of cyclic polyphenylene sulfide in supramolecular chemistry to reinforce polymers  
(ポリマーを強化するための超分子化学における環状ポリフェニレンスルフィドの応用と修飾)

## Abstract of Thesis

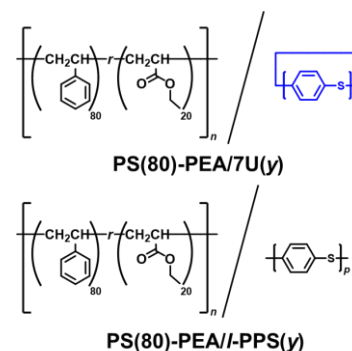
**[Introduction]** Crosslinks are crucial for the mechanical properties of polymers. The traditional covalent crosslink easily causes stress concentration and localized failure when the polymers are stretched. In supramolecular chemistry, reversible and movable crosslinks have been widely used to reinforce polymers by efficient energy dissipation. Cyclic polyphenylene sulfide (PPS) is the byproduct in the synthesis of linear PPS and has almost no application, leading to waste in resources and pollution on environment. Thus, by making use of macrocycle structure and benzene rings of cyclic PPS, movable and reversible crosslinks can be formed and used in the reinforcement of polymers, and make the application of cyclic PPS possible (**Figure 1**).

**[Chapter 2: Reinforcement of polystyrene-based materials by the addition of cyclic PPS]**<sup>1</sup> The used cyclic PPS is a mixture of oligomers ranging from 5 unit to 15 unit and mainly composed of 7-unit oligomer. In here, cyclic PPS is also named as 7U. Cyclic PPS and linear PPS with the same molecular distribution were mixed with styrene (St) and ethyl acrylate (EA) to obtain copolymers, respectively (**Figure 2**). After the introduction of EA and 7U, there are a four-fold increase in toughness and no change in Young's modulus compared with polystyrene. When the composition of copolymer was fixed, 7U led to a two-fold increase in toughness and linear PPS decreased the toughness significantly because of phase separation when the addition amount is same (**Figure 3**). 7U can form  $\pi$ - $\pi$  stacking effect with St units of the polymer chains and complex with the polymer chains to form rotaxane structures, generating reversible and movable crosslinks, respectively. And these interactions also made the polymers more homogeneous to prevent the stress concentration and localized failure when the addition amount of 7U is appropriate. Thus, 7U has the potential to reinforce polystyrene-based materials via supramolecular chemistry.

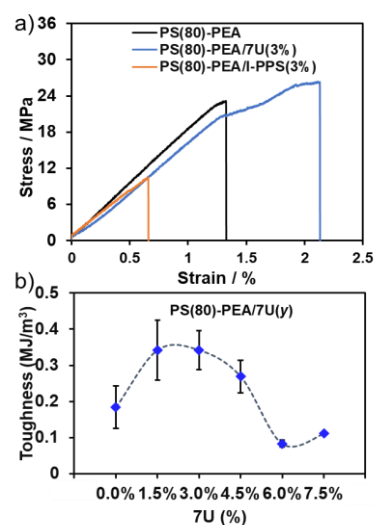
**[Chapter 3: Reinforcement of poly( $\epsilon$ -caprolactone) based materials by the addition of cyclic PPS]** Whether 7U is still able to reinforce polymers when there are no benzene rings in the polymer chains is



**Figure 1.** The research scheme of this thesis.



**Figure 2.** Chemical structures of PS(80)-PEA/7U(y) and PS(80)-PEA/l-PPS(y) where y refers to weight percents of PPS.



**Figure 3.** a) Stress-strain curves, b) toughness of PS(80)-PEA/7U(y).

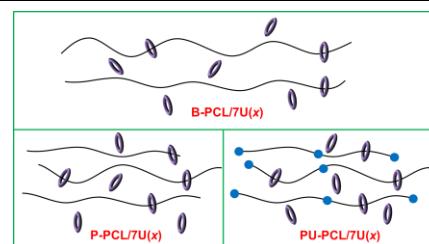
another problem to be considered and investigated. Poly( $\epsilon$ -caprolactone) (PCL) is a biodegradable aliphatic polyester without benzene rings. Three kinds of PCL-based materials were prepared to have different amount of rotaxane structures formed by 7U. B-PCL/7U(x) were obtained by blending 7U and PCL with high molecular weight ( $M_n=73$  kDa), P-PCL/7U(x) were prepared by the polymerization of  $\epsilon$ -caprolactone mixed with 7U, and PU-PCL/7U(x) were obtained by the reaction of PCL-diol and 4,4'-methylene diphenyl diisocyanate (MDI). The order of amount of formed rotaxane structures (less to more) is B-PCL/7U(x), P-PCL/7U(x) and PU-PCL/7U(x) (**Figure 4**). Because there is no interaction between PCL and 7U, the rotaxane structures are the key points to connect polymer chains by the movable and reversible crosslinks derived from the  $\pi$ - $\pi$  stacking effect between the 7U itself. When the dethreading of rotaxane structures was inhibited by the end-capped steric hindrance group, MDI units, in the case of PU-PCL/7U(x), there is a two-fold increase in toughness and no change in Young's modulus (**Figure 5**). Moreover, the introduction of 7U has almost no influence on the crystallinity of PCL, and the reorientation of crystals when the PCL-based materials were stretched. In the degradation experiments, the hydrophobicity of 7U and the crosslinks slowed down the enzymatic degradation when the dumbbell-sized samples were used. When the crosslinks based on the noncovalent interactions were broken by dissolution in the solvents, the degradation of PCL chains was almost not affected. Thus, even in the case when there are no benzene rings in the polymer chains, 7U can still be used to reinforce polymers by the reversible and movable crosslinks.

**[Chapter 4: Modification of cyclic PPS and investigation of metal-ligand coordination]** The modification of cyclic PPS is necessary to maintain the rotaxane structures as much as possible to have more efficient energy dissipation and have more application occasions. The acrylated cyclic PPS and cyclic PPS dimer were obtained by Friedel-Crafts acylation. Acrylated cyclic PPS has the potential to prepare other derivatives by the thiol-ene reaction, and cyclic PPS dimer maintains the applicability of cyclic PPS and can be used in each polymer system. Moreover, the metal-ligand coordination between metal ions and sulfur atoms of cyclic PPS was investigated by dissolving PCL polymers and mixing with zinc chloride solution, and subsequent casting. The PCL-based materials with zinc ion showed two-fold increase in the toughness and no change in Young's modulus (**Figure 6**). Probably, besides the  $\pi$ - $\pi$  stacking effect, cyclic PPS can also form metal-ligand coordination with metal ions, which is another noncovalent interaction that can form reversible crosslink to reinforce polymers further.

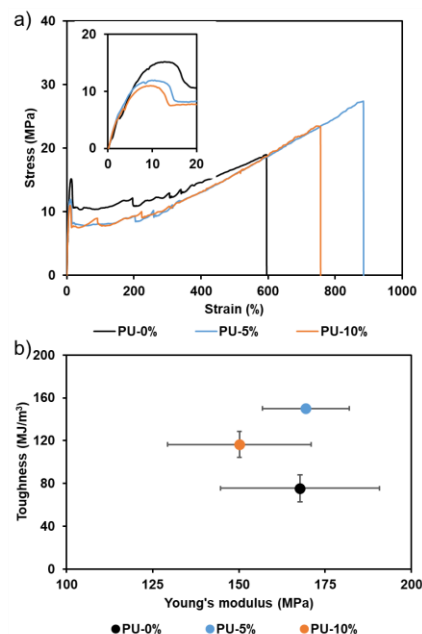
Thus, this research shows that cyclic PPS can reinforce polymers via supramolecular chemistry.

#### [Reference]

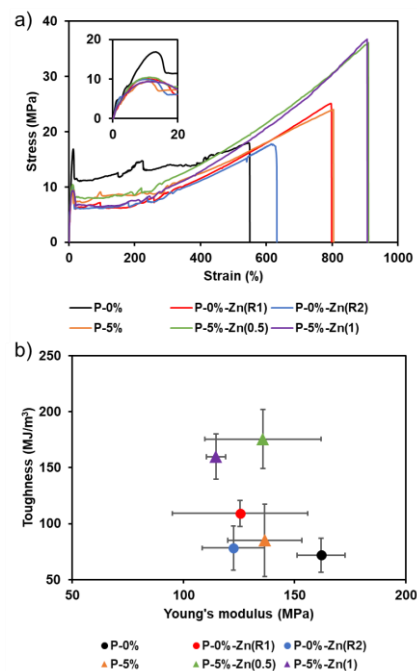
[1] Ding, Y.; Park, J.; Ikura, R.; Nara, S.; Toda, K.; Takashima, Y. *Macromolecules* **2023**, *56*, 3132–3140.



**Figure 4.** Schematics of B-PCL/7U(x), P-PCL/7U(x), and PU-PCL/7U(x), where x refers to the weight ratio of added 7U.



**Figure 5.** a) Stress-strain curves, b) toughness of PU-PCL/7U(x).



**Figure 6.** a) Stress-strain curves, b) toughness of P-0% and P-5% with different amount of  $Zn^{2+}$ .

## 論文審査の結果の要旨及び担当者

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## 論文審査の結果の要旨

学位申請者は、「The application and modification of cyclic polyphenylene sulfide in supramolecular chemistry to reinforce polymers(ポリマーを強化するための超分子化学における環状ポリフェニレンスルフィドの応用と修飾)」と題された博士論文を提出しました。この論文は、超分子化学による環状ポリフェニレンスルフィド (PPS) のポリマー材料の強化への応用に焦点を当てました。具体的には、環状 PPS がポリマー内で可動かつ可逆的な架橋を形成し、ポリマーの靱性向上への寄与について検討しました。

2章では、環状 PPS を用いたポリスチレン系材料の靱性向上について報告されました。一軸引張試験や分光分析・X線散乱解析を通じて、環状 PPS がポリマー鎖と可逆的かつ、可動性の架橋を形成することが明らかにしました。形成された可逆性架橋と可動性架橋が応力を均等に分散し、材料の靱性を向上させることが示されました。また、形成された架橋構造により、ポリマーの均一性が適度に向上し、材料の破損のリスクが低減されました。この結果、環状 PPS の応用研究に新たな可能性が示唆されました。

3章では、環状 PPS がベンゼンを含まないポリマー系であるポリカプロラク톤を強化できることが示されました。さまざまな分子構造設計を通じて、可動架橋の重要性がポリマーの靱性が向上しました。また、環状 PPS の導入がポリマーの結晶化特性や延伸時の結晶化に与える影響はほとんどありませんでした。これにより、環状 PPS を使用することで、あらゆる種類のポリマー系材料を強靱化の可能性が示されました。

4章では、環状 PPS の誘導体の合成に成功しました。これにより、環状 PPS のさらなる応用が可能となりました。そして、これらの誘導体はより高い可動性の架橋を形成でき、機械的特性の更なる向上に寄与しました。環状 PPS の硫黄原子は金属イオンとの配位を形成し、この可逆的な架橋結合を活用して機械的特性を改善することができました。これらの発見は、ポリマーの強靱化における環状 PPS の可能性を示唆しました。

この研究は、環状 PPS の応用に新たな道を開き、超分子化学の可能性を探求するだけでなく、実用的な意義を持ち、超分子化学の発展を促進するものでした。

よって、本論文は博士（理学）の学位論文として十分価値あるものと認めます。