Title	Design and Functional Exploration of Tough and Biodegradable Polymers with Movable Crosslinks for Enzymatic Degradation and Sustainable Use
Author(s)	Liu, Jiaxiong
Citation	大阪大学, 2025, 博士論文
Version Type	
URL	https://hdl.handle.net/11094/103245
rights	
Note	やむを得ない事由があると学位審査研究科が承認したため、全文に代えてその内容の要約を公開しています。全文のご利用をご希望の場合は、大阪大学の博士論文についてをご参照ください。

Form 3

Abstract of Thesis

Name	(Jiaxiong Liu)
Title	Design and Functional Exploration of Tough and Biodegradable Polymers with Movable Crosslinks for Enzymatic Degradation and Sustainable Use （可動性架橋を導入した高靭性・生分解性ポリマーの設計と持続可能性に向けた酵素分解性能の評価）

Abstract of Thesis

[Introduction] Plastics are everywhere and play a vital role in social development. However, because commercial plastics are hard to break down and are easily discarded as waste, plastic waste pollution has also become ubiquitous. In this context, developing tough and biodegradable next-generation polymers as substitutes for commercial persistent ones offers a sustainable solution. In this thesis (**Figure 1**), I introduced a small amount of cyclodextrin (CD)-based movable crosslinks to strengthen the polymers towards better performance. In addition, enzymes were employed as eco-friendly and efficient catalysts for polymer degradation and recycling. Finally, by tuning the chemical structures, versatile applications of polymers were developed.

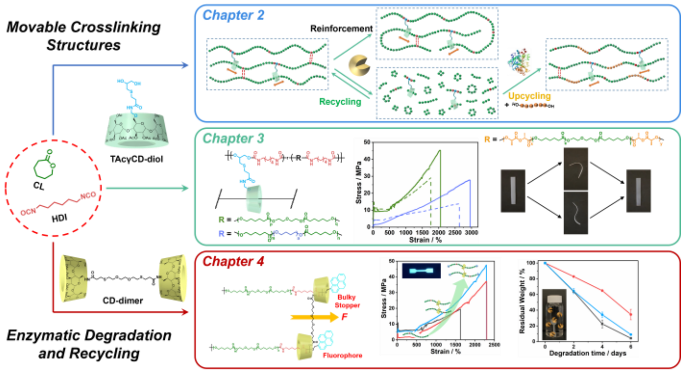

Figure 1. The conceptual figure of this thesis.

[Chapter 2: Exploring Enzymatic Degradation, Reinforcement, Recycling and Upcycling of Poly(ester)-Poly(urethane) with Movable Crosslinks][1] Poly(ε-caprolactone)-poly(urethane)s (PCL-PUs) with different polymer structures were prepared. Triacetylated γ-cyclodextrin (TAcγCD) diol was cooperated with PCL-diol (M_n = 3500) to form the host-guest complexes, which were then reacted with 1,6-diisocyanatohexane (HDI) catalyzed by dibutyltin diacetate (DBTDA) dissolved in dry *N*, *N*-dimethylformamide (DMF). The solution was stirred at 60 °C under N_2 for 24 h to achieve PCL-γCD(*x*)-PU (*x* = mol% of TAcγCD in PCL-PUs). For comparation, linear PCL-PU (*l*PCL-PU) and PCL-C(*y*)-PU with covalent crosslinks were prepared in the similar procedure (*y* = mol% of THEED in PCL-PUs; THEED: *N*, *N*, *N*′, *N*′-tetrakis(2-hydroxyethyl) ethylenediamine) (**Figure 2**). Tensile testing was applied to measure the mechanical properties of PCL-PUs. The stress-strain curves (**Figure 3a**) showed that PCL-γCD(*x*)-PU, including both stiffness and stretchability, were significantly improved compared with *l*PCL-PU and PCL-C(*y*)-PU, which was attributed to the sliding-ring effect as efficient energy dissipation. After that, PCL-PUs were catalyzed by Novozym 435 (immobilized lipase B from *Candida antarctica*) as the enzymes in organic solvent to measure the degradation efficiency (**Figure 3b**). *l*PCL-PU and PCL-C(y)-PU remained existed after 120 h, showing low degradation efficiency. On the contrary, the degradation efficiency of PCL-γCD(*x*)-PU was optimized for increases in TAcγCD content, indicting the positive role of TAcγCD in the enzymatic degradation.

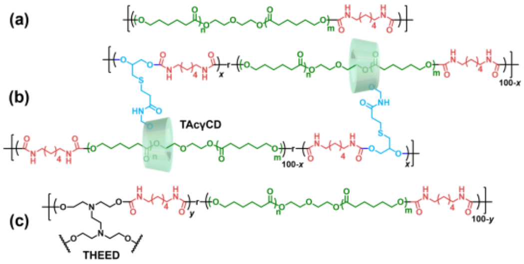

Figure 2. Chemical structures of **(a)** *l*PCL-PU, **(b)** PCL-γCD(*x*)-PU and **(c)** PCL-C(*y*)-PU.

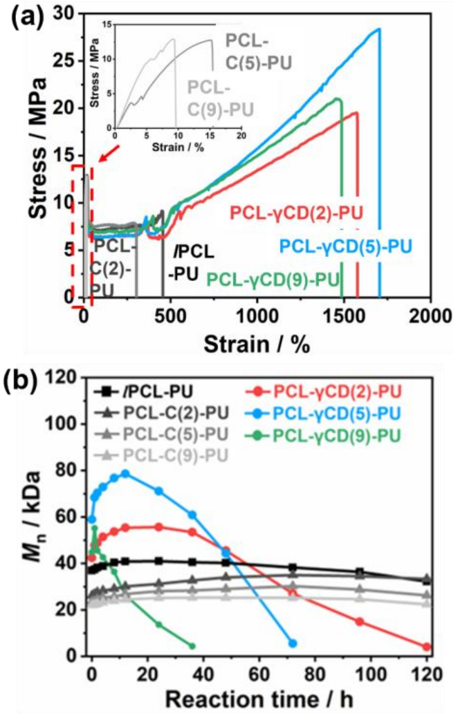

Figure 3. **(a)** Stress-strain curves and **(b)** Enzymatic degradation of PCL-PUs.

[Chapter 3: Tough, Multifunctional, and Biodegradable Poly(ester)-Poly(urethane) Enabled by Structure-Property Tuning for Versatile Applications] To broaden the applicability and practicability of the PUs, I further construct PUs with tailored property by tuning the chemical and polymer structures. At first, several polyols with different chemical structures were prepared as building blocks. After that, PUs with two kinds of polymer structures were prepared through convenient polyaddition between diols and HDI: γCD-PUs with TAcγCD-based movable crosslinks (5 mol%, 2.5 wt% TAcγCD-diol) and L-PUs with linear structures (**Figure 4**). Although PUs with different chemical structures performed different mechanical performances, γCD-PUs with movable crosslinks exhibited better performance than L-PUs(**Figure 5a**). This enhancement can be attributed to the incorporation of a low contents of movable TAcγCD-based crosslinks, which effectively dissipate energy and disperse stress from external forces. In addition, to evaluate the enzymatic degradation efficiency of the PUs, lipase PS (lipase PS Amano SD from Burkholderia cepacia LP-7) was used in phosphate buffer solution (0.1 mol/L, pH 7.0) at 37 °C (**Figure 5b**). By changing the chemical structures, PUs performed different enzymatic degradability. PCL-PUs and P(DMS-CL)-PUs showed the best and worst degradability due to the distinguished surface hydrophobicity. For P(CL-LLA)-PUs and P(TME-CL)-PUs, the introduction of bulky TAcγCD-based crosslinks reduced the chain interactions and thus facilitated the enzymatic degradation. Besides mechanical properties and enzymatic degradability, the functionality of polymers were also tuned for versatile applications, including biodegradable hydrophobic materials, thermosensitive shape-memory materials, adhesives, and strain sensor.

[Chapter 4: Ultratough and Biodegradable Fluorescent Poly(ester)-Poly(urethane) Enabled by Cyclodextrin Dimer-Based Movable Crosslinks and Terminal Bulky Fluorophore] To broaden the movable crosslinking structures of PUs, biodegradable PCL-PUs were also cooperated with TAcβCD dimer (diβCD) conveniently to prepare the highly movable crosslinking structures (PCL-PU/diβCD) (**Figure 6**). The introduction of diβCD highly improved the mechanical property of PCL-PU (**Figure 7**), because the CD-based sliding-ring effect can efficiently reduce the stress localization. Furthermore, the polymer chain-end was modified with pyrene (Py) as the terminal bulky group. As shown in **Figures 6** and **7**, the terminal Py group not only can serve as fluorophore to endow the polymers with fluorescence, but also can improve the mechanical performances due to its role as bulky stopper for movable diβCD (**Figure 7**). Moreover, the introduction of diβCD and terminal Py group can tune the enzymatic degradability of PCL segments, to achieve the ultratough and fluorescent biodegradable PU.

[Reference]

[1] Liu, J.; Takashima, Y. et al. *Chem* **2025**,*11*,102327.

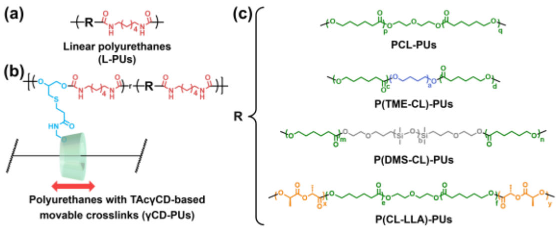

Figure 4. Polymer structures of **(a)** L-PUs and **(b)** γCD-PUs.**(c)** Chemical structures of PUs.

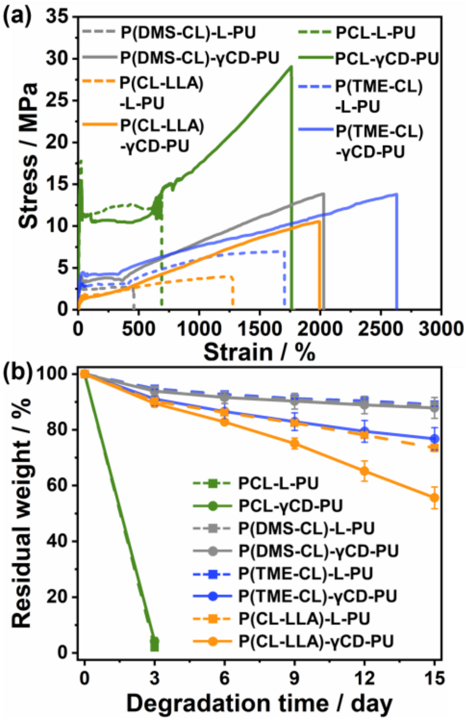

Figure 5. (a) Stress-strain curves and **(b)** Enzymatic degradation in buffer of PUs

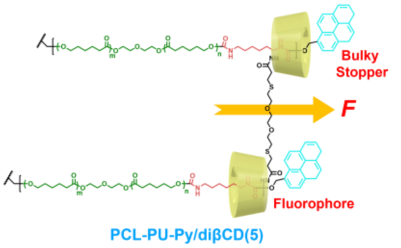

Figure 6. Chemical structure of PCL-PU-Py/diβCD(5).

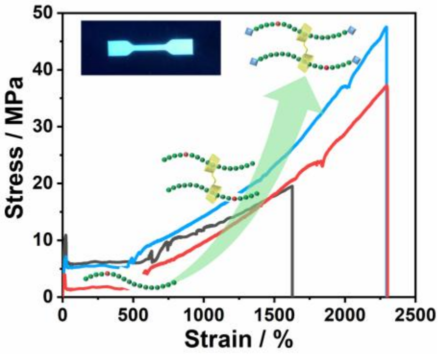

Figure 7. Stress-strain curves of PCL-PU (black), PCL-PU/diβCD(5) (red), and PCL-PU-Py/diβCD(5) (blue). Inset: PCL-PU-Py/diβCD(5) film under 354 nm UV light.

様式 7

論文審査の結果の要旨及び担当者

氏　名　（ Jiaxiong Liu ）			
論文審査担当者		（職）	氏　名
	主 査	教授	高島　義徳
	副 査	教授	寺尾　憲
	副 査	教授	山口　浩靖
	副 査	教授	橋爪　章仁

論文審査の結果の要旨

本論文は、**シクロデキストリン（CD）由来の可動性架橋構造**を利用して、高靭性かつ生分解性を併せ持つポリウレタン（PU）などの高分子材料を設計し、その**酵素分解挙動、リサイクル・アップサイクル、機能化**を総合的に検討した。目的は、材料強度と持続可能性を両立させ、酵素を利用した環境低負荷型リサイクル技術の開発に資する設計指針を提示した。

主な成果

1. **酵素分解性 PU の開発（第 2 章）**
   - ポリ(ε-カプロラクトン)骨格に TAcγCD を導入した可動性架橋 PU（PCL-γCD-PU）を合成。
   - 可動性架橋により高い靭性を維持しつつ、リパーゼ（Novozym 435）による酵素分解が促進されることを実証。
   - 酵素濃度、反応温度、基材構造を調整することで、**分解・強化・リサイクル・アップサイクル**の各プロセスを一種類の酵素で制御可能であることを示した。
2. **構造—物性相関の解明と多機能化（第 3 章）**
   - γCD ベース可動性架橋の含有量や化学構造を精密制御することで、機械特性・酵素分解性・機能（疎水性、形状記憶、接着、ひずみセンサー機能）を自在に調整可能であることを明らかにした。
   - 低含有量の CD 架橋でも高い機械強度と優れたリサイクル性を両立。
3. **高靭性蛍光性 PU の創製（第 4 章）**
   - TAcβCD 二量体（diβCD）を可動性架橋として導入し、末端にピレンを修飾した PU を合成。
   - 蛍光機能と機械強度の向上を同時に実現し、分子末端修飾が酵素分解挙動に大きく影響することを示した。

学術的貢献

- 可動性架橋構造が**酵素分解性高分子の分解効率を高める新たなメカニズム**を提示。
- 構造設計により**高靭性・機能性・環境適合性を同時に実現**する設計原理を確立。
- 一種類の酵素を用いた**分解／再構築プロセス制御**の実証は、サーキュラーエコノミー型高分子設計の新たな展開を示した。

以上のことから、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る。