論文 / 著書情報
Article / Book Information

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Title(English)	Reversible Crosslinking ? Decrosslinking Systems　Based on Reversible Addition ? Elimination between　Vicinal Tricarbonyl Compounds and Alcohols
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
学籍番号： Student ID Number		指導教員（主）： Academic Advisor(main)	高田 十志和
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis entitled "Reversible Crosslinking – Decrosslinking Systems Based on Reversible Addition – Elimination between Vicinal Tricarbonyl Compounds and Alcohols", the author described the reversible crosslinkable and decrosslinkable polymer systems utilizing reversible addition–elimination reactions between vicinal tricarbonyl compounds and alcohols, with the aim of fabrication of polymer materials which potentially possess chemically recyclable or self-healable properties.

Chapter 1, "Introduction", summarized the reversible crosslinking and decrosslinking systems utilizing the reversible covalent linkages, leading to polymer materials capable of chemical recycling and self-healing. The author emphasized that reversible addition–elimination of vicinal tricarbonyl moieties with alcohols is promising reaction for construction of networked polymer systems that can be reversibly crosslinked and decrosslinked under mild conditions.

In chapter 2, "Reversible Crosslinking and Decrosslinking System of Polystyrenes Bearing the Monohydrate Structure of Vicinal Tricarbonyl Group through Water–Alcohol Exchange", the author focuses on the direct water–alcohol exchange reaction on the pendant vicinal tricarbonyl moiety, which facilitated the crosslinking and decrosslinking procedure of polystyrene bearing vicinal tricarbonyl moieties in comparison with the addition–elimination method. By employing diphenylpropanetrione (DPPT) as a unit model compound for the polymer, the author demonstrated that the water–alcohol exchange reactions proceeded reversibly by changing solvents. Similarly to the model reactions, the polystyrene bearing monohydrate structure of vicinal tricarbonyl moiety was crosslinked with 1,6-hexanediol in acetone at ambient temperature in 5 days to afford the networked polymer in almost quantitative yield. On the other hand, the networked polymer was treated with an excess amount of water at an ambient temperature for 3 days to afford the original linear polymer in a high yield as a result of the decrosslinking through the water–alcohol exchange reaction.

In chapter 3, "Synthesis and X-ray Structural Analysis of an Acyclic Bifunctional Vicinal Triketone, Its Hydrate, and Its Ethanol-adduct", the author described the synthesis and characterization of an acyclic bifunctional vicinal tricarbonyl compound (bistriketone), its hydrate, and its ethanol-adduct. The bistriketone was synthesized by oxidation of the corresponding bis(1,3-diketone) with *N*-bromosuccinimide (NBS) in DMSO. The bistriketone was readily converted into its hydrate or its ethanol-adduct upon treatment with water-containing solvent or ethanol, respectively. Conversely, heating the hydrate or the ethanol-adduct *in vacuo* quantitatively regenerated the bistriketone. The X-ray crystallographic analysis indicated that the water and ethanol molecules added to the central carbonyl carbon atoms of the bistriketone. The cyclic voltammogram of the bistriketone indicated that the two vicinal tricarbonyl moieties acted as two-electron acceptor, though the generated dianion species was relatively labile.

In chapter 4, "Reversible Crosslinking and Decrosslinking of Polymers Containing Alcohol Moiety Utilizing an Acyclic Bifunctional Vicinal Triketone", the author employed the bistriketone as a reversible crosslinking–decrosslinking reagent or crosslinker for polymers containing hydroxyl groups. The network formation proceeded simply by adding a small amount of the bistriketone to a solution of poly(2-hydroxyethyl methacrylate) (PHEMA) in DMSO. Conversely, treatment of the crosslinked polymers with MeOH resulted in dissociation of the network to recover the original linear PHEMA in 94% yield along with the bistriketone in 54% yield. The network formation and dissociation behaviors were investigated in detail by ^{1}H NMR and SEC experiments. Similarly to PHEMA, reversible crosslinking and decrosslinking of poly(vinyl alcohol) (PVA) were achieved by using the bistriketone and by treatment of the resulting gel with H_2O/DMSO (1/9, v/v), respectively.

Chapter 5, "Conclusions", summarizes the results obtained in the work described in this thesis, and description for the perspectives of creation of functional polymer materials utilizing the vicinal tricarbonyl's function.

As stated above, the author has demonstrated that the addition–elimination equilibria between alcohols and vicinal tricarbonyl compounds could be controlled under mild conditions, and therefore, vicinal tricarbonyl–alcohol linkages are highly useful for the construction of reversible crosslinking and decrosslinking systems. The vicinal tricarbonyl–alcohol linkage that can be reversibly formed and dissociated under mild condition is of great interest from the viewpoint of supramolecular synthesis, chemical recycling, and self-healable polymeric materials. The author is convinced that this thesis offers fundamental knowledge to achieve such tasks.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 2 部提出してください。
Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 2 copies of 800 Words (English).