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学位の種類	博士(工学)
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学位論文題目	Synthesis of Polyesters Using an Organic Catalyst and Design of Polyester-based Double Network Gels (有機触媒を用いたポリエステル合成とポリエステルを基盤としたダブルネットワークゲルの設計)
論文審査委員	主査 准教授 高須 昭 則 教授 稲井 嘉 人 教授 鈴木 将 人 准教授 高木 幸 治 教授 楊 小平 (北京化工大学)

論文内容の要旨

Aliphatic polyesters, especially unsaturated polyesters, are now fascinating because of their biodegradability and biocompatibility. To synthesize aliphatic polyesters via an environment-friendly method, metal-free catalyst is essential. Moreover, how to enhance the mechanical strength of the polyesters in order to suit for further applications is also still remained subject. In this decade, for the continuous development of interpenetrating polymer networks (IPNs), double network (DN) concept was observed in some works.

Chapter 1: To synthesize polyesters and periodic copolymers catalyzed by nonafluorobutanesulfonimide (Nf_2NH), we performed ring-opening copolymerizations of cyclic anhydrides with tetrahydrofuran (THF). At high temperature (100-120 °C), the cyclic anhydrides copolymerized with THF via ring-opening to produce polyesters. At low temperature, ring-opening copolymerizations of the cyclic anhydrides with THF produced poly(ester-ether). When toluene (4 M) was used as a solvent, GAn reacted with THF (unit ratio: 1:2) to produce periodic copolymers.

Chapter 2: We report herein the polycondensations of unsaturated cyclic anhydrides with diols at moderate temperatures using the sublimating organic catalyst, Nf_2NH , to synthesize polyesters containing carbon-carbon double bonds. We initially synthesized isomerization-free unsaturated polyesters containing alternating maleate or itaconate and 3-methyl-1,5-pentanediol units. Additionally, using copolyesters containing maleate and itaconate units, we could selectively photo-crosslink the *exo*-type double bonds of the itaconate units to afford unsaturated polyester gels. Starting with these gels, we then isomerized the maleate unit *cis* double bonds to *trans* double bonds by a diethylamine-catalyzed *cis-trans* isomerization. The swelling properties of the gels were found to depend on the initial maleate to fumarate unit ratios (degree of isomerization) as well as the maleate to itaconate unit ratios.

Chapter 3: The Michael addition and UV-initiated radical polymerization were used to fabricate a one-pot method for synthesis of polyester-based DN gels. The unsaturated copolyesters containing itaconate and maleate units were prepared via polycondensation under mild conditions. Then a double-network (DN) gel was synthesized by two-steps. After dissolved polyester, methyl methacrylate (MMA) and UV-initiator in toluene, diamine was added into mixture. The first gel was prepared by the catalyst-free selective cross-linking of maleate double bonds with diamine at room temperature. Subsequently, the first gel was irradiated under UV-light for 3 h. The obtained hydrophobic polyester/poly(MMA) DN gel containing amino group with high mechanical strength showed shape recovery property. To expand the application of this method, a poly(ester-*co*-ether) / polyacrylamide DN hydrogel was also synthesized.

論文審査結果の要旨

Aliphatic polyesters, especially unsaturated polyesters, are now fascinating because of their biodegradability and biocompatibility. To synthesize aliphatic polyesters via an environment-friendly method, metal-free catalyst is essential. Moreover, how to enhance the mechanical strength of the polyesters in order to suit for further applications is also still remained subject. In this decade, for the continuous development of interpenetrating polymer networks (IPNs), double network (DN) concept was observed in some works.

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The results are summarized in three papers with peer review and are valuable for the Ph D. thesis.