

Title	-シクロデキストリンの包接錯体からなる分解性ポリ ロタキサンの分子設計
Author(s)	辛, 昊俊
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Description	Supervisor:金子 達雄, マテリアルサイエンス研究科 , 博士

ABSTRACT

Polyrotaxanes, demonstrated as a molecular necklace composed of a polymeric chain and cyclic compounds, are interesting in terms of their structural features. A mechanism of biodegradation based on the dissociation of supramolecular structure triggered by cleavage of end groups in a cleavable polyrotaxane can give various novel designs of biodegradable polymers. By utilizing these merits of supramolecular structure, we designed and prepared polyrotaxane hydrogel based on water-soluble hydrolyzable polyrotaxane and polyamide rotaxane composed of photo-cleavable 4,4'-diacetoamido- α -truxillic acid.

In chapter 2, a hydrolyzable polyrotaxane composed of an ester-containing poly(ethylene glycol) chain and α -cyclodextrins was prepared and showed gradual degradation into its water-soluble components in aqueous conditions, based on the dissociation of the polyrotaxane triggered by the hydrolysis of the ester groups.

In chapter 3, we designed and prepared various hydrolyzable polyrotaxane hydrogel composed of α -cyclodextrins, poly(ethylene glycol) with Mw 3K and 20K as back bone chain, and two types of crosslinker (linear and multi-arm PEG). One of the degradable polyrotaxanes was crosslinked between the internal rings with linear PEG chain and the other was crosslinked between the terminals with multi-arm PEG chain. Every hydrogels had good water content (>90%) and hydrophilic surface. The *internally*-crosslinked gels had higher compressive stress and initial modulus, while the *terminally*-crosslinked gels showed higher ultimate strain. These results imply that *terminally*-crosslinked gels were rigid and the *internally*-crosslinked gels were flexible. In stress relaxation test, the *internally*-crosslinked gels showed unique viscoelastic behavior, in which was similar to that of topological gel. We investigated the gradual degradation of the hydrogels in terms of changes in mass and storage modulus of the gels. The *internally*-crosslinked gels degraded and disappeared in a relatively shorter period than the *terminally*-crosslinked gels. The *terminally*-crosslinked gels survived for weeks with gradual degradation that allowed us to apply the degrading gels to a preliminary cell adhesion test. In the cell adhesion test, the number, size, and morphology of NIH 3T3 cells was changed by degradation of hydrogels and change of surface chemical characteristics due to cleavage of carboxyl residue introduced to hydroxyl group in CD at the same time.

In chapter 4, we introduced a unique chemical structure, polyrotaxane, to give structural rigidity to polymer back bones using a necklace-like structure and cinnamic acid as a photo-reactive monomer to prepare a new polyamide. By utilizing this unique concept, we designed aliphatic-aromatic polyamides containing the rotaxane structure composed of 4,4'-diacetoamido- α -truxillic acid, poly(ethylene glycol) bisamine (PEGBA) and methylated- α -cyclodextrin (Me- α -CD), and observed their thermo-mechanical performance and degradation behavior under UV-irradiation. The thermal degradation temperature of the polyamides was enhanced by inclusion complex formation with Me- α -CD, and the polyamide polyrotaxane was degraded by UV-irradiation via the photocleavage of the cyclobutane ring in 4,4'-diacetoamido- α -truxillic acid.

Keywords : hydrogel, supramolecular structure, hydrolyzable polyrotaxane, polyamide, photocleavage