論文 / 著書情報
Article / Book Information

題目(和文)	高分子ニトリルオキシド反応剤の創成及びそれを用いる精密分子集積法の開発
Title(English)	Synthesis of Polymer Nitrile N-Oxide Directed toward The Development of Precise Molecular Integration Method
著者(和文)	王晨綱
Author(English)	ChenGang Wang
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第9436号, 授与年月日:2014年3月26日, 学位の種別:課程博士, 審査員:高田　十志和,大塚　英幸,石曽根　隆,小西　玄一,早川　晃鏡
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第9436号, Conferred date:2014/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

論文の要約

所属：理工学研究科　有機・高分子物質専攻
氏名：王晨綱 (Wang, Chen-Gang)　学籍番号：11D07165

論文題目：高分子ニトリルオキシド反応剤の創成及びそれを用いる精密分子集積法の開発
Thesis Title: Synthesis of Polymer Nitrile *N*-oxide Directed toward the Development of Precise Molecular Integration Method

The title of this thesis is “Synthesis of Polymer Nitrile *N*-Oxide Directed toward the Development of Precise Molecular Integration Method” and is consist of 6 chapters. Based on the model studies of the synthesis and reactivity of the low molecular weight nitrile *N*-oxides, the author has described the synthesis of polymer nitrile *N*-oxides *via* living anionic polymerization and their application to the direct grafting reactions onto unsaturated bond-containing polymers under catalyst- and solvent-free conditions for the development of a novel molecular integration method for the first time.

In Chapter 1 “Introduction”, the general background of click chemistry including the reaction mechanism and the applications as a ligation tool for the construction of macromolecular architectures was described. As an important alternative to copper(I)-catalyzed azide-alkyne cycloaddition, the usefulness and molecular design of nitrile *N*-oxides are particularly emphasized to illustrate the potential utility on a novel click reaction for the connection of the research purpose and framework of this thesis.

In Chapter 2 “Synthesis and Characterization of Aliphatic Nitrile *N*-Oxide and Kinetic Study on Its Cycloaddition Reaction with Several Dipolarophiles”, the synthesis of 1,1-diphenylhexylnitrile *N*-oxide and its model cycloaddition reactions with a variety of dipolarophiles were described. A novel and effective one-pot synthesis of 1,1-diphenylhexylnitrile *N*-oxide from 1,1-diphenylnitroethene and *n*-butyl lithium as a carbon nucleophile *via* Michael addition and dehydration in one-pot was developed. It is also demonstrated that the 1,3-dipolar cycloadditions of the model nitrile *N*-oxide to several dipolarophiles proceeded smoothly to obtain the corresponding 1,4-disubstituted heterocycles, elucidating the versatile reactivity and high regioselectivity of the nitrile *N*-oxide.

In Chapter 3 “Synthesis of Polymer Nitrile *N*-Oxide and its Application to Catalyst-free and Solvent-free Click Grafting-onto Reaction”, polymer nitrile *N*-oxides were prepared from living polymer anion and 1,1-diphenylnitroethene, followed by treatment of conc. H_2SO_4 in one-pot in excellent yields. PMMA nitrile *N*-oxide, as an useful direct grafting agent, was reacted with poly(styrene-*co*-4-allyloxystyrene) to confirm its reactivity and to find the optimal grafting reaction condition. On the basis of the experimental results, it was found that the solvent-free condition accelerates the 1,3-dipolar cycloaddition to afford higher conversions. The PMMA nitrile *N*-oxide was further utilized to react with common polymers having unsaturated bonds to give various graft copolymers in a good conversion under catalyst- and solvent-free conditions, providing a grafting-onto protocol for facile synthesis of graft copolymers.

In Chapter 4 “Synthesis and Chemical Stability of Aliphatic Nitrile *N*-Oxides Derived from *trans*-β-Nitrostyrene”, the fundamental study of the substituent effects of nitrile *N*-oxide prepared from *trans*-β-nitrostyrene was described. A variety of nitrile *N*-oxides were prepared by using commercially available *trans*-β-nitrostyrene as a terminating agent to find a suitable structure and bulkiness of nucleophiles enough for isolation. It was indicated that the introduction of a tertiary carbon nucleophile to the position neighboring the nitrile *N*-oxide moiety could efficiently suppress the self-reaction of the nitrile *N*-oxides, while the existence of an ester group at the β-position of nitrile *N*-oxide moiety could provide further chemical stability for the isolation of nitrile *N*-oxide. It was found that the PMMA nitrile *N*-oxide derived from *trans*-β-nitrostyrene has excellent stability due to the presence of the β-ester group and bulky polymer chain. These successful results indicated that the chemical stability of nitrile *N*-oxides is controllable by manipulating the bulkiness of the substituents to provide a fundamental basis for the development of novel synthetic protocol of polymer nitrile *N*-oxides.

In Chapter 5 “Synthesis of Highly Reactive Polymer Nitrile *N*-Oxides for Effective Solvent-free Grafting Reaction”, the preparation of polymer nitrile *N*-oxides (including homopolymer and blockcopolymer nitrile *N*-oxides) from *trans*-β-nitrostyrene through a one-pot procedure was described. It is found that these polymer nitrile *N*-oxides exhibited high reactivity in grafting reactions onto polymers with unsaturated bonds because of the decrease of steric hindrance around the nitrile *N*-oxide moiety. The author also described the simple method to create functional glass surface using P*t*BMA-based nitrile *N*-oxide through the sequential click reaction and ester decomposition reaction without the use of solvent. The polymer nitrile *N*-oxide as a highly effective chemical ligation tool provides an important insight to a means for novel molecular integrations using highly processed materials made from common polymers as the scaffold.

In Chapter 6 “Conclusion”, the results from each chapter are summarized. Future prospect of use of polymer nitrile *N*-oxide and its applications is also stated toward the end of the presentation.