217
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With contributions by

N. Ajioka · K. Endo · H. Kaneko · N. Kashiwa · N. Kawahara
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Volume Editor

Prof. Shiro Kobayashi

R & D Center for Bio-based Materials
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku
Kyoto 606-8585, Japan
kobayash@kit.ac.jp

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Preface

It is generally accepted that a new material is often developed by finding a new synthesis method of reaction or a new reaction catalyst. Historically, a typical example may be referred to as a Ziegler–Natta catalyst, which has allowed large-scale production of petroleum-based polyolefins since the middle of the 20th century. New polymer synthesis, therefore, will hopefully lead to creation of new polymer materials in the 21st century. This special issue contributed by three groups focuses on recent advances in polymer synthesis methods, which handle the cutting-edge aspects of the advanced technology.

The first article by Yokozawa and coworkers contains an overview of the reaction control in various condensation polymerizations (polycondensations). Advanced technologies enabled the control of stereochemistry (regio-, geometrical-, and enantio-selections), chemoselectivity, chain topology, and stoichiometry of monomers, giving a high molecular weight polymer. It has been recognized for a long time, however, that polycondensation is a difficult process in controlling the reaction pathway, because the reaction is of step-growth and the reactivity of monomers, oligomers, and polymers are almost the same during the reaction and hence, the molecular weight of polymers and its distribution (M_w/M_n) are impossible to regulate. The authors' group developed a new reaction system (chain-growth condensation polymerization), changing the nature of polycondensation from step-growth to chain-growth; namely the propagating chain-end is active, allowing for control of the product molecular weight as well as the distribution. With a specific initiator and/or catalyst, the chain-growth condensation polymerization came close in behavior to that of an addition polymerization; a M_w/M_n value being even less than 1.2, like a living system, compared with that of a most probable value 2.0 for conventional polycondensations.

The second article by Kawahara and his coworkers focuses on polyolefin (PO)-based hybrid materials (POH), in view of their synthesis, structures, and properties. POs are currently the most widely and conveniently used polymeric materials as recognized by the production amount of over one hundred million tons annually in the world, due to the cheap price yet good properties. They are basically hydrocarbon polymers, and hence hydrophobic and less polar. These basic properties are to be modified by introducing a polar function for a wider use in practical applications. Preparation of POHs is one of the best ways to

provide a variety of desired properties with POs. There are three main synthetic routes to POHs; starting from PO macroinitiators, PO macromonomers, and reactive POs. Polymerization or copolymerization using these macroinitiators and macromonomers are carried out by recently developed methods (living polymerization, ATRP, RAFT, NMP, etc) to produce POHs of block, graft, or branched-type structures. Reactive POs can be coupled with other components to give POHs. In addition, living polymerization of olefins can also be a route for POH synthesis. A wide range of applications of these product POHs are exemplified.

The third article by Endo reviews synthesis and properties of cyclic polymers. Polymer structure is basically divided into two classes; linear and cyclic. Combinations of linear and/or cyclic structures yield a variety of architectures such as branched, graft, block, star, ladder, dendritic, catenane, rotaxane and other complicated structures through covalent and noncovalent bonds. A linear or cyclic structure has been an important, fundamental problem since the early stages of polymer science, and yet it is still new. Fortunately, recent developments of analytical methods enabled the structural elucidation of many of these architectures. The synthesis principle to lead to cyclic polymers can be cited as two main methods. One is the utilization of the ring-chain equilibrium, occurring in many polycondensations and ring-opening polymerizations. The other is the end-to-end cyclization (ring-closure reaction) method from α,ω-difunctional linear precursors, via bimolecular or unimolecular processes. Synthesis of a number of cyclic polymers has been achieved by addition, condensation, oxidation, metathesis, and ring-opening polymerizations as well as by polyaddition. A typical difference in physical property between cyclic polymers and linear polymers is also demonstrated.

We hope the readers will learn something new at the forefront of the polymer synthesis field from the above contributions.

May 2008, Kyoto Shiro Kobayashi

Contents