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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（総合化学）　氏名　高　添樂

学 位 論 文 題 名

Monomer Sequence Controllable Ring-opening Polymerization for Precise Synthesis of Polyester-based Copolymers
（ポリエステル系コポリマーの精密合成を指向した配列制御型開環重合に関する研究）

Synthetic polymer materials constitute a cornerstone in numerous sectors, encompassing food production, clothing, transportation, insulation, healthcare, and medicine. Despite their pivotal role in advancing human welfare, the disposal rate of polymeric materials annually falls significantly short in comparison to their generation. This disjunction has led to formidable environmental challenges, including air pollution emanating from open incineration, degradation of marine ecosystems, and the pervasive presence of microplastics resulting from plastic waste accumulation. There exists a pressing need to transition away from widely employed non-degradable petroleum-based polymers towards recyclable alternatives for fostering a sustainable plastics ecosystem. Over the past two decades, polyesters have emerged as prominent contenders among recyclable polymers due to their potential for hydrolytic cleavage of ester bonds, facilitating chemical recycling into smaller molecules, alongside the utilization of renewable monomer resources in their synthesis. Moreover, owing to their commendable mechanical properties and biocompatibility, polyesters have found extensive utility in packaging and biomedical applications. However, the imperative to displace petroleum-based polymers necessitates the development of economically viable polyester synthesis methodologies for large-scale production. Additionally, enhancing the functionality and performance of polyester materials is imperative to satisfy diverse application requirements. Addressing these challenges, this dissertation endeavors to advance a suite of ring-opening alternating copolymerization (ROAC) systems tailored for facile synthesis of well-defined polyesters featuring diverse structures. Through the establishment of self-switchable polymerization systems and monomer sequence fully controllable copolymerization systems, this work enables the synthesis of polyesters with precisely tunable repeating unit arrangements, thus advancing the frontier of polyester material design and application.

Chapter 2 elucidates the versatility of the alkali metal carboxylate (AMC) catalyst in ROAC for polyester synthesis and its potential as a switch catalyst for block copolymer production. Initially, the ROAC behavior of ethyl glycidyl ether with various cyclic anhydrides was investigated, validating this approach as an efficient route to synthesize polyesters with controllable structures. Subsequently, oxetane was successfully copolymerized with cyclic anhydrides, broadening the range of polyester structures achievable via ROAC. Furthermore, AMC was employed in epoxide ring-opening polymerization (ROP), confirming its ability to efficiently synthesize well-defined polyether. This underscores the potential of AMC as a switch catalyst capable of connecting two or more catalytic cycles for one-step synthesis of block copolymers. Building upon this, the author developed a one-pot, two-step method for synthesizing polyether-b-polyester.

Chapter 3 delves into the capability of AMC to connect two catalytic cycles for one-step synthesis of block polyester. The polymerization of epoxide with two cyclic anhydrides was explored to ascertain the reactivity trends among cyclic anhydrides with different structures. Based on the results, polyesters with desired structures and different tapered regions could be precisely synthesized. Similarly, the cyclic anhydride reactivity trend was confirmed in the polymerization of oxetane with two cyclic anhydrides. The incorporation of the oxetane monomer enriched the range of possible polyester structures and enhanced the adjustability of the system. Building upon the reactivity order of epoxides » oxetane, a polymerization scheme

involving one anhydride, epoxide, and oxetane was executed. Epoxide was first copolymerized with cyclic anhydride to form the first block, followed by copolymerization with oxetane/cyclic anhydride ROAC to form the second block. Furthermore, expanding the range of monomers, a quarterpolymerization involving two different cyclic anhydrides, epoxide, and oxetane was implemented for one-step synthesis of block polyester. This quarterpolymerization system offers a more flexible and adjustable main chain structure and monomer sequence, facilitating the design and synthesis of tailored block polyesters. Consequently, this self-switchable copolymerization platform holds promise and significance for both laboratory and industrial-scale production of block polymers with complex macromolecular architectures.

Chapter 4 introduces a self-switchable copolymerization system utilizing aziridine monomer, enabling the synthesis of various poly(amide ester)-based block copolymers with a phosphazene base catalyst. The physical properties of these copolymers were investigated. The terpolymerization of aziridine with two cyclic anhydrides was conducted, confirming the same reactivity trend of cyclic anhydrides observed in copolymerization with epoxide. In the conversational self-switchable copolymerization, the difference in chemical nature (or polarity) between the two blocks was not significant enough to induce phase separation. To achieve distinct chemical natures among different blocks in a one-step synthesized block copolymer, this research connected aziridine/cyclic anhydride ROAC with cyclic carbonate ROP under the same catalytic system, resulting in the synthesis of poly(amide ester)-b-polycarbonate. Additionally, aziridine/cyclic anhydride ROAC and epoxide/cyclic anhydride ROAC were connected in a quarterpolymerization system to one-step synthesize poly(amide ester)-b-polyester. The physical properties were investigated using differential scanning calorimetry and small-angle X-ray scattering measurements, confirming their phase separation behavior. This strategy allows for the flexible adjustment of each block's structure by selecting the appropriate combination of the four starting monomers, thereby laying the groundwork for synthesizing block copolymers with desired microphase-separated morphologies.

Chapter 5 explores a binary organocatalyzed copolymerization system capable of synthesizing poly(amide ester-ester) copolymers with various monomer sequences from the same monomer mixture. The copolymerization behavior of cyclohexene oxide (CHO)/phthalic anhydride (PA) ROAC and N-tosyl aziridine (TAz)/PA ROAC under a triethylborane (TEB)/t-Bu-P1-cocatalyzed system was investigated. Interestingly, an opposite effect of TEB on these two ROACs was observed. Building upon this observation, a TEB/t-Bu-P1-cocatalyzed terpolymerization system was devised. By varying the catalyst ratio, poly(TAz-alt-PA)-co-poly(CHO-alt-PA) copolymers with controllable monomer sequences were synthesized. To deepen the understanding of the monomer selectivity mechanism, energy calculations based on density functional theory were conducted. These calculations facilitated the design of other monomer sequence-controlled copolymerization systems, offering insights into the underlying mechanisms governing monomer selectivity in copolymerization reactions. This synthetic approach offers a straightforward method for producing copolymers with similar chemical compositions but varying monomer sequences, which can be valuable for exploring the relationship between monomer sequences and polymer properties.

Chapter 6 summarizes the results. In conclusion, this research has established a versatile platform for high-value added polyester production. The AMC-catalyzed ROAC systems outlined in Chapters 2 enable the efficient large-scale production of polyester homopolymers with diverse structures. Additionally, the self-switchable systems introduced in Chapters 3 and 4 offer a flexible approach for the one-step synthesis of polyester block copolymers. Furthermore, Chapter 5 presents a monomer sequence-controlled copolymerization system where the sequence of monomers in the synthesized polyester copolymers can be precisely manipulated by adjusting the cocatalyst ratio. These polymerization systems have significantly enhanced the synthesis of polyesters with tailored structures, laying the groundwork for future investigations into the correlation between comonomer sequences and polyester properties. This advancement contributes to the development of sustainable polymer material systems.