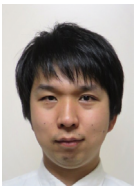
Polymer materials, Organic electronic materials

Construction of new π-stacked polymers based on precise polymerization reactions



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Abstract

We have successfully synthesized a novel π-stacked polymer based on poly(quinolylene-2,3-methylene) with amino acids derivatives as a side chain, obtained through our originally developed the living cyclocopolymerization, which can control the length of the π-stacked structure and terminal structures of the polymer. The shape of the amino acid substituents on the side chain is essential and greatly influences the formation process and stability of the π-stacked construction. When a bulky cyclohexyl alanine derivative was used as the side chain, the π-stacked helical structure was highly stable against high temperature and polar solvents.

Background & Results

The layered π-electron systems exhibit unique optoelectronic properties through the π-π interactions of aromatic compounds. However, it is still challenging to construct a stable π-stacked structure with a well-defined number of aromatic rings.

We report synthesizing a novel series of π-stacked poly(quinolylene-2,3-methylene)s (PQM) with amino acid derivatives bearing different substituents (Figure 1). In the resulting polymer, the neighboring quinoline rings of the main chain form a layered structure with π–π interactions, which is stabilized by intramolecular hydrogen bonds. Additionally, the thermal stability of π-stacked PQM is significantly improved by packing the substituents in the space between the side chains (Figure 2). When a bulky cyclohexyl alanine derivative was used as the side chain, the π-stacked helical structure maintained stability even in a polar solvent and high temperatures. Stabilizing the π-stacked system through the amino acid substituents resulted in a unique polymerization behavior. In the case of derivatives with leucine and cyclohexyl alanine, which form stable π-stacked helical structures, metastable structures with entangled main chains were formed in the initial polymerization stage. These structures underwent an irreversible structural change to achieve a thermodynamically stable helical π-stacked conformation as a nucleus for subsequent polymerization. After that, the polymerization reaction proceeded with the elongation of the π-stacked helical structure. Differences in the stability of these systems indicated that the amino acid substituents on the side chains determine the most thermodynamically stable π-stacked helical structure.

Significance of the research and Future perspective

π-Stacked polymers can stack aromatic rings via covalent bonds, which are attractive molecules for understanding physical properties and developing functions via π-π interactions. The π-stacked polymers produced in this study enable control of the long-range π-stack structure length and design of molecules utilizing the terminal structures and side chain, which are difficult to achieve with the general π-stacking construction method. Therefore, based on the synthesis of our π-stack polymers, we can expect to develop new molecular designs and functions that are not bound by conventional concepts in the development of materials for the realization of future society by understanding the physical properties via the π-stack structure and systematizing these properties.

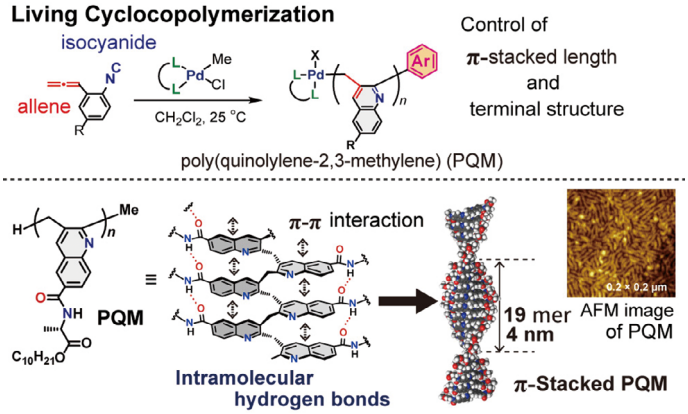

Figure 1 Precise Polymerization of π-staked Polymer Based on the Living Cyclocopolymerization.

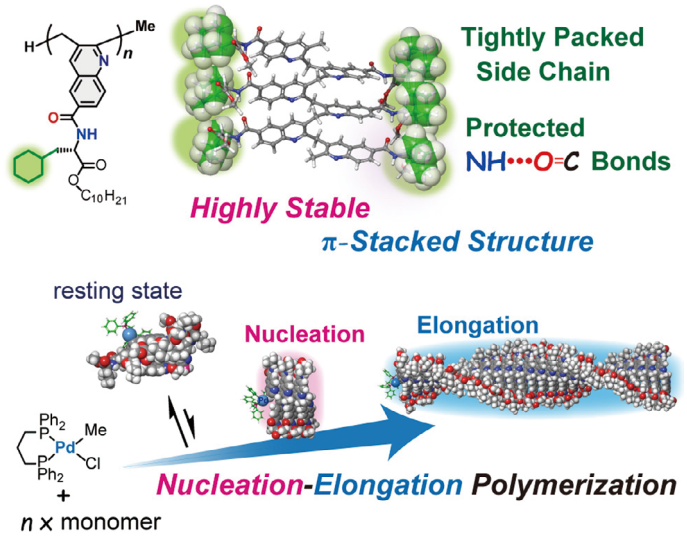

Figure 2 Elucidation of Structural Stabilization and Formation Mechanism of π-Stacked Polymers.

Patent
Treatise
Kanbayashi, Naoya; Kataoka, Yuki; Onitsuka, Kiyotaka et al. Journal of the American Chemical Society. 2022, 144 (13), p. 6080-6090, doi: 10.1021/jacs.2c01337
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