

論文の内容の要旨

論文題目

Study on the Quantitative Aminolysis Reaction of Poly(β -benzyl L-aspartate) (PBLA) as a Platform Polymer for Functionality Materials

(機能性材料のための基盤高分子Poly(β -benzyl L-aspartate) (PBLA)の定量的アミノリシス反応に関する研究)

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The author, throughout the present thesis, clarified the mechanism of the quantitative aminolysis reaction of poly(β -benzyl L-aspartate) (PBLA), focusing on the intermediate structure which enables this reaction to proceed quantitatively, the detailed structure of polypeptide backbone (namely, transition and chirality) (Chapter 2) and also clarified that the quantitative aminolysis reaction of PBLA with 0.5-fold amine compound proceeds alternately (Chapter 3). Especially, in Chapter 2, the author confirmed his suggestions described in Chapter 1 (General Introduction), was quite reasonable through ^1H NMR and infrared adsorption spectroscopy analyses.

In Chapter 2, the author identified the real identity which enabled this aminolysis reaction of PBLA to proceed promptly and quantitatively. It was the succinimide ring which was promptly formed by the activation of nitrogen atom by amine coordination which exists in the amide linkage of main chain, following the nucleophilic attack to the carbonyl group in the side chain of PBLA. The polarity of solvents and the secondary structure of the polymer strand were closely related to each other in terms of reactivity and stereoselectivity. The aminolysis reaction of PBLA treated with one equivalent amine against benzyl ester groups resulted in the complete conversion at 35 °C in random-coil solvents within 1 h. The racemization that accompanied this reaction was observed in random-coil solvents, but was efficiently suppressed in helicogenic solvents. This is worth mentioning that the optical purity of the L-isomers was maintained with the yield of 95 % in CH_2Cl_2 , which is unprecedentedly high. These data will apparently be a great advantage in its application as biomaterials.

In Chapter 3, the author developed the first example of versatile synthesis of alternating copolymers via the quantitative side chain reaction. It was verified that the aminolysis reaction of PBLA proceeds alternatively with 0.5-fold amine compounds, probably due to the resonance structures of succinimide intermediate. Thus it is possible to prepare the random and alternating copolypeptides respectively via the quantitative side-chain reaction of PBLA just by changing the addition procedure of amine compounds. This is the 1st report that the alternating copolypeptide was synthesized via the quantitative side chain reaction of polymer.

Throughout this thesis, the author obtained insight into the detailed structure of polyaspartamide prepared by the quantitative aminolysis reaction of PBLA and has shed light on the alternating polypeptide synthesis, which will be a novel methodology of various supramolecular materials and self-assembled materials. These insights should be used for developing a variety of advanced material and extended for more sophisticated polymer design.

* 論文提出者が提出したものを添附する。