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Organocatalytic Synthesis of End-functionalized Poly(methyl methacrylate)s Using Group Transfer Polymerization

(有機触媒を用いたグループトランスファー重合による末端官能基
化ポリ(メタクリル酸メチル)の合成)

End-functionalized polymers are receiving much attention in recent times, due to their wide applications in chemistry, medicine, and material science. In polymer chemistry, they are also very useful precursors for preparing polymers of interesting architectures like block, graft, and star-shaped copolymers and network structures. On the other hand, synthesis methods for quantitatively end-functionalized poly(methyl methacrylate)s (PMMA) have few reports and there is even no report of synthesis of hydroxyl functionalized star-shaped PMMA with well-defined arm number and uniform length to the best knowledge of the author, because precise synthesis of hydroxyl end-functionalized polymers is less-developed in comparison with other functionalized polymers due to the difficulty to achieve total functionalization and also to control the high reactivity of the hydroxyl end group. To overcome these problems, the author employed organocatalyzed group transfer polymerization (GTP) which has advantages as follow; (1) well-controlled PMMA is synthesized with minimum back-biting side reactions, (2) complete functionalization can be easily tailored by utilizing its livingness with an appropriate functionalized initiator or terminator, and (3) star-shaped polymer with defined arm number and uniform length can be synthesized using arm-first method by terminating living PMMA with appropriate multi-functional terminators as well as the core-first method by using multi-functional initiators to synthesize star polymers which can then be functionalized by terminating the living arm ends with appropriate terminators.

The following is the outline of this thesis;

Chapter 1 is a general introduction and describes the background and purpose of this research.

Chapter 2 describes the precise syntheses of α -end-functionalized PMMAs by organocatalyzed GTP using various functional trimethyl silyl ketal acetal (SKA) initiators and ω -end-functionalized PMMAs using functional α -phenylacrylate terminators. A detailed study of the termination reaction of the living chain ends of PMMA prepared by the *t*-BuP₄-catalyzed GTP method with benzaldehydes as terminators to synthesize

hydroxyl group ω -end-functionalized PMMAs is also described. $\text{Me}_3\text{SiNTf}_2$ and $t\text{-Bu-P}_4$ were effective organocatalysts for the α - and ω -end-functionalization of PMMA, and could easily produce PMMAs with predictable molecular weights and narrow polydispersities and quantitative functionalization efficiencies. The characterization of the obtained end-functionalized PMMA by size exclusion chromatography (SEC), ^1H NMR measurements, and MALDI-TOFMS measurements strongly suggested that the side reactions were avoided and defect-free α - and ω -end-functionalized PMMAs has been obtained.

Chapter 3 describes the core-first synthesis of well-defined star-shaped PMMAs functionalized with hydroxyl groups by the $t\text{-Bu-P}_4$ -catalyzed GTP for the first time. Based on the elementary study described in Chapter 2, $t\text{-Bu-P}_4$ was found to be a powerful catalyst for the hydroxyl end-functionalization of PMMA. For the core-first synthesis of the star-shaped PMMAs by GTP, the previously designed initiators possessing multiple numbers of silyl enolate groups $(\text{SKA})_3$, $(\text{SKA})_6$ and $(\text{SKA})_{12}$, were used as the cores respectively. The star-shaped PMMAs were then terminated by benzaldehydes terminators to synthesize three-, six- and twelve-armed PMMAs carrying three, six and 12 hydroxyl groups respectively at their chain ends. The arm-first synthesis of hydroxyl functionalized two-armed and three-armed star-shaped PMMAs is also described. As the name suggests, linear PMMAs were first synthesized as arms and then their reactive ends terminated electrophilically with multi- aldehydic terminators (terephthalaldehyde and benzene-1, 3, 5-tricarbaldehyde) to synthesize hydroxyl core-functionalized two-armed and three-armed star-shaped PMMAs.

Chapter 4 describes the organocatalytic synthesis of star block and miktoarm copolymers using the hydroxyl-functionalized precursors whose synthesis were reported in Chapter 3 as the macroinitiators. Star block copolymers were obtained when the hydroxyl-functionalized star-shaped PMMAs obtained by the core-first method was used as macroinitiators to initiate the ring-opening polymerization (ROP) of lactide. Miktoarm star polymers were obtained when the hydroxyl core functionalized star-shaped PMMAs were used as macroinitiators to initiate the ring opening polymerization ROP of lactide. The ^1H NMR measurements of the star block copolymers and miktoarm star polymers showed proton signals for the PMMA chain and PLLA chain simultaneously giving evidence that the star block and miktoarm copolymers containing two chemically different polymer arms in the same molecule was obtained. The thermal properties of the obtained star block and miktoarm copolymers were also investigated through their glass transition temperature (T_g).

Chapter 5 listed the overall conclusions of this thesis.