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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ブ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, since they are very useful precursors for preparing polymers of interesting architectures like block, graft, and star-shaped copolymers and network structures. Poly(methyl methacrylate) (PMMA) is very widely used polymer in industry, and its end-functionalization has been required. However, the synthesis methods for quantitatively end-functionalized PMMA has not yet been established. Especially there is no report of hydroxyl end-functionalization of PMMA although its usefulness as a precursor for synthesizing block copolymers. To achieve the quantitative end-functionalization of PMMA, the author employed organocatalyzed group transfer polymerization (GTP) which has advantages as follows; (1) well-controlled PMMA is synthesized with minimum back-biting side reactions, (2) complete functionalization can be tailored by utilizing its livingness by selecting an appropriate combination of organocatalysts and functionalized initiator or terminator, and (3) star-shaped polymers can be synthesized using arm-first method with multi-functional terminators (4) star-shaped polymers can be also synthesized by the core-first method with multi-functional initiators.

In chapter 2, the author investigated appropriate combinations of organocatalysts and initiators or terminators for the precise synthesis of α - and ω -end-functionalized PMMAs. The author found several trimethyl silyl ketene acetal (SKA) derivatives as effective initiators for α -end-functionalization in the presence of $\text{Me}_3\text{SiNTf}_2$ or $t\text{-Bu-P}_4$ catalysts. The author also found that α -phenylacrylate / $\text{Me}_3\text{SiNTf}_2$ and benzaldehyde / $t\text{-Bu-P}_4$ were effective terminators / organocatalyst combinations for the ω -end-functionalization. The characterization of the end-functionalized PMMAs by size exclusion

chromatography (SEC), ^1H NMR measurements, and MALDI-TOF MS measurements strongly suggested that the side reactions were avoided and defect-free synthesis of quantitatively α - and ω -end-functionalized PMMAs has been achieved.

In chapter 3, based on the findings obtained in chapter 2, the author describes the synthesis of star-shaped PMMAs functionalized with hydroxyl groups by using core- and arm-first methods. For the core-first synthesis, the previously designed initiators possessing multiple numbers of silyl enolate groups (SKA)₃, (SKA)₆ and (SKA)₁₂, were used as the cores respectively. The star-shaped PMMAs were then terminated by benzaldehydes terminators to ω -end-functionalize with hydroxyl groups at their chain ends. For the arm-first synthesis, multi-aldehydic terminators (terephthalaldehyde and benzene-1, 3, 5-tricarbaldehyde) were used to terminate the reactive ends of linear PMMAs. These star-shaped PMMAs synthesized with the arm-first method are expected to possess hydroxyl functionalized cores. The author showed that the aldehydic terminations is very effective for the preparation of hydroxyl functionalized star-shaped PMMAs.

In chapter 4, the author describes the organocatalytic synthesis of star block and miktoarm star polymers using the hydroxyl-functionalized precursors whose synthesis were reported in Chapter 3. The star block copolymers were obtained when the hydroxyl-functionalized star-shaped PMMAs prepared 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 prepared by the arm-first method were used as macroinitiators to initiate the ROP of lactide. The ^1H NMR and SEC measurements gave evidence that star block copolymers and miktoarm star polymers containing two chemically different polymer arms in the same molecule were obtained. The author showed that the hydroxyl-functionalized star-shaped PMMAs can be used as effective macroinitiators for the star block and miktoarm star PMMAs.

In conclusion, throughout the thesis the author focused on devoting his efforts to developing the synthesis method of the end-functionalized PMMA. The author established an efficient method for the synthesis of α - and ω -end-functionalized PMMA by organocatalyzed GTP. The quantitative synthesis of ω -end-functionalized PMMA with hydroxyl group is an especially great achievement in polymer chemistry. The usefulness of the hydroxyl ω -end-functionalized PMMA was demonstrated by successfully using them as precursors for the synthesis of star block copolymers and miktoarm star polymers. This thesis can be recognized to be awarded a PhD degree (engineering).