METHODS OF SYNTHESIZING STAR POLYMERS

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INTRODUCTION

Star polymers are defined as macromolecules that have linear polymeric arms extending radially from a central core, and are one of many structural classes of polymeric materials.[1] Due to their compact spherical structure, star polymers have lower intrinsic viscosities and melting points than linear polymers of similar composition and molecular weight.[2] The physical properties of star polymers and their ability to act as unimolecular micelles have drawn interest for a variety of applications, such as additives in motor oil, dispersants in the cosmetics industry, and potential drug delivery agents.[3-5] Star polymers with arms of two or more compositions (miktoarm star polymers) have garnered particular interest for their phase separation properties.[6] The synthesis of a star polymer is classified into one of three methods: arm-first, core-first, or coupling-onto synthesis.

ARM-FIRST SYNTHESIS

Arm-first synthesis of a star polymer involves the growth of the linear polymer arms and then cross-linking the ends of the arms together to create the core of the star structure. This is accomplished by creating the polymer arms through a living polymerization technique and then adding a cross-linking agent that has two vinyl groups, such as divinylbenzene. This simple, one-pot synthesis can create polymers with a large number of arms, but it results in a statistical distribution of the number of arms incorporated into each star.[1] Miktoarm star polymers can be synthesized easily using the arm-first method, but there is also a statistical distribution of the ratio of arm types in each molecule.[7]

CORE-FIRST SYNTHESIS

Using the core-first method of synthesizing star polymers involves growing the polymer arms starting from the core which contains multiple reactive sites.[1] This allows for the synthesis of star polymers with a very well-defined number of arms and core structure, but the number of arms on star polymers produced by this method is usually limited to numbers far smaller than possible with arm-first

synthesis. Through the use of reactive sites for orthogonal polymerization reactions, miktoarm star polymers can be synthesized with very high control over the product structure.[8]

COUPLING-ONTO SYNTHESIS

The coupling-onto method for star polymer synthesis can be viewed as a convergent synthesis with the growth of the polymer arms separate from the preparation of the core. The components are then assembled through a clean and efficient coupling reaction to complete the synthesis.[1] Due to its nearly quantitative yields and high functional group compatibility, an exemplary reaction used for this coupling is the copper-catalyzed Huisgen cycloaddition.[9] This method allows for very high control of the structure of both the arms and the core, but the attachment of the arms, in most cases, is random which decreases control of the overall product structure in miktoarm star polymer synthesis as compared to core-first synthesis.

SUMMARY

The synthesis of star polymers can be classified into one of three methods. Arm-first synthesis is a simple, one-pot method that involves cross-linking the ends of linear polymers which results in star polymers with a statistical distribution of arm numbers and an ill-defined core structure. Core-first synthesis involves growing the polymer arms from a core with multiple reactive sites. This increases the number of steps in the synthesis of the star polymer, but also greatly increases the amount of control on the product structure. The coupling-onto method is performed by attaching pre-synthesized linear polymers to a well-defined core through a highly efficient and clean coupling reaction. This convergent method allows for very high control over the entire product structure, but as more arms are attached to the core they can hinder further coupling reactions by blocking the reactive sites.

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