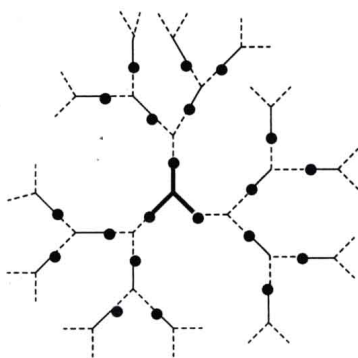
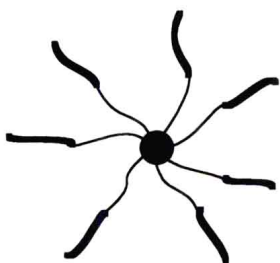


# STAR AND HYPERBRANCHED POLYMERS



edited by

**MUNMAYA K. MISHRA**  
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# Preface

The field of macromolecular engineering has grown very large indeed, too large to be covered in detail in a single book. This volume focuses on advances in one of the most important areas of polymer research today. The book is essentially divided into two parts that are interrelated in many respects, first examining star-branched polymers and then hyperbranched polymers. Information on new star polymers, hyperbranched polymers, dendritic polymers, and so on, is systematically provided. The strength of this book is in the design strategies that it offers for working with these important polymers, their characterization, properties, and application. The architecture and properties of dendrimers, starburst polymers, multi-arm star polymers, and comb polymers are discussed.

The book also covers the solution properties of the regular star polymers. This class of materials has been known for many years to polymer chemists; however, rapid development has occurred only since the proposal of the idea of dendritic polymers in the mid-1980s. The characteristics of the polymers discussed here include the size and shape of the molecules, their biological activities, their low viscosity in solution, their substrate-holding properties inside the molecule, etc. The unique properties of these polymers attract many chemists, not only in polymer chemistry but also in organic chemistry, biochemistry, medicine, organometallic chemistry, catalyst chemistry, and so on, for these new materials are expected to find applications in many areas.

We trust that this book will represent a vital source of information for researchers in macromolecular engineering. The book is directed to industrial

and academic scientists interested in designing new polymers, “polymers of geometrical beauty” and technological importance, as well as to students entering the wild world of contemporary polymer research and applications.

Certainly, future editions will include new developments as research continues. To our regret we could not include a chapter on star-branched polymers via radical polymerization since the research is still scanty and scattered, but we hope to include it in future editions.

It would not have been possible to complete a project like this without the help and participation of numerous individuals. We gratefully acknowledge all the contributors who made this book possible. Last, with love and appreciation MKM would like to acknowledge his wife and family for their support throughout the preparation of this book.

*Munmaya K. Mishra*  
*Shiro Kobayashi*



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# 1

## Synthesis of Branched Polymers: An Introduction

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### I. INTRODUCTION

Major developments in the science and technology of polymeric materials have resulted from the preparation and characterization of polymers with well-defined structures [1,2]. Well-defined polymers with low degrees of compositional heterogeneity can provide the information and insight necessary to understand and predict polymer structure–property relationships. Branching in polymers is a useful structural variable that can be used advantageously to modify the processing characteristics and properties of polymers. A branched polymer is comprised of molecules with more than one backbone chain; that is, it is a nonlinear polymer [3]. A branched polymer is characterized by the presence of branch points (junction points): (atoms or a small group from which more than two long chains emanate) and by the presence of more than two chain end groups.

Branching affects the crystallinity, crystalline melting point, physical properties, viscoelastic properties, solution viscosities, and melt viscosities of polymers [3–6]. However, it is difficult to predict the relationships between branching and properties based on the behavior of most branched polymers because the branching reaction generally occurs in a random fashion. As a con-

sequence, the number and types of branches per macromolecule are difficult to define except on an average basis.

Fundamental understanding of the effects of chain branching on polymer properties requires the availability of a variety of branched polymers with well-defined structures and low degrees of compositional heterogeneity [1,6]. Living chain reaction polymerizations are particularly suited for the preparation of these “model” polymers since it is possible to vary and control important structural parameters such as molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity, chain end functionality and the number of branches per molecule. Although a variety of mechanistic types of living chain reaction polymerization have been developed [6], living anionic polymerization, especially using alkylolithium initiators, is the paradigm [7] from which examples will be drawn for illustration of the general methods. This review will first consider the general polymerization methods that have been developed to synthesize regular star-branched polymers, heteroarm star-branched polymers, and other types of branched polymers, including graft copolymers [8]. Regular star-branched polymers have a single branch point and all arms exhibit low degrees of compositional heterogeneity with respect to composition, molecular weight, and molecular weight distribution. Heteroarm star-branched polymers [6,9], also described as mikto-arm star polymers [6], also have a single branch point, but the arms differ in either molecular weight or composition. When the arms differ in composition, heteroarm star-branched polymers can be considered as a special type of graft copolymer [8]. Finally, a brief review of dendrimers and hyperbranched polymers will be presented. Dendrimers are highly branched, three-dimensional macromolecules with a branch point at each monomer unit [10–14].

## II. SYNTHESIS OF BRANCHED POLYMERS

The methodology of living polymerization is ideally suited for the preparation of well-defined, star-branched polymers and copolymers with low degrees of compositional heterogeneity. Because termination and chain transfer reactions are absent and the chain ends may be stable for sufficient time periods (the laboratory time scale), these polymerizations have the following useful synthetic attributes for star polymer synthesis:

1. One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction stoichiometry. Multifunctional initiators with functionality  $n$  can form stars with  $n$  arms.

2. If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distributions ( $M_w/M_n \leq 1.1$ ) [15] are formed.
3. When all of the monomer has been consumed, the product is a polymer with reactive chain ends that can participate in a variety of post-polymerization reactions:
  - a. block copolymerization by addition of a second monomer, and/or
  - b. end-linking with multifunctional linking agents to form the corresponding star-branched polymers with uniform arm lengths.

In the following sections, the general methods for synthesis of regular star-branched polymers and heteroarm star-branched polymers will be described. Specific examples will be shown based on alkylolithium-initiated anionic polymerization.

## A. Postpolymerization, End Linking with Multifunctional Linking Agents

### 1. General Aspects

The products of living polymerizations are polymers that retain their active, propagating chain ends when all of the monomer has been consumed. Under appropriate conditions, these polymers exhibit well-defined, predictable number average molecular weights and narrow molecular weight distributions, i.e., low degrees of compositional heterogeneity. These living polymers can be reacted with multifunctional linking agents to form star-branched polymers in which the number of arms corresponds to the functionality of the linking agent, as shown in Eq. (1) where  $P^*$  is a living polymer chain,  $L(X)_n$  is a multifunctional linking agent of functionality  $n$ , and  $L(P)_n$  is a star-branched polymer containing  $n$  arms.



The main advantage of this methodology is that the arms of the resulting branched polymer are well defined because the precursor arms can be characterized independently from the star. Because of the well-defined arms, the number of arms can be readily determined by measuring the molecular weight of the star. In principle, a variety of well-defined, star-branched polymers with different numbers of arms can be prepared using this method by varying the functionality of the linking agents  $[L(X)_n]$ .



## 2. Anionic Polymerization

A wide variety of multifunctional linking agents have been investigated for preparation of star-branched polymers via anionic polymerization [7,16,17]. Arm functionalities range from 3 to very high values. However, many of the reported linking reactions, such as those involving polyfunctional alkyl halides, are complicated by side reactions such as elimination and metal-halogen exchange that lead to compositional heterogeneity. In contrast, linking reactions with polyfunctional silyl halides are very efficient and free of these complicating side reactions.

**a. Polyhalosilanes and Stannic Chloride.** One of the most general and useful methods for preparation of star-branched polymers is the reaction of polymeric organolithium compounds with multifunctional electrophilic species such as silicon tetrachloride, as shown in Eq. (2). A slight excess of living arm, PLi, is generally employed to drive the reaction to completion and to minimize the formation of stars with less than the stoichiometric number of arms. This in turn requires that the product be fractionated to obtain pure, star-branched polymer.



These linking reactions are not complicated by side reactions; however, they are sensitive to the steric requirements of the linking agents and the organolithium chain ends. For example, early work by Morton and co-workers [18] showed that the reaction of poly(styryl)lithium with a less than stoichiometric amount of silicon tetrachloride produced a polymer product composed of 26% of the four-armed star and 74% of the three-armed star polymers. More efficient linking can be effected using poly(butadienyl)lithium chain ends. This was illustrated by Zelinski and Wofford [19], who reacted poly(butadienyl)lithium with methyltrichlorosilane and silicon tetrachloride to efficiently form the corresponding three-armed and four-armed, star-branched polymers, respectively. Linking efficiency can also be improved by separating the Si-Cl groups with spacers such as methylene groups to reduce the steric repulsions in the linked product [20].

Linking with multifunctional silyl chlorides has been extended to stars with arm functionalities over one hundred by utilizing the linking reactions of poly(butadienyl)lithium with carbosilane dendrimers containing up to 128 Si-Cl bonds [21]. Star-branched polybutadienes with more than 250 arms were reported for the linking reactions of poly(butadienyl)lithium with the product from hydrosilation of 1,2-polybutadiene [22].

Fetters and co-workers [23,24] developed a general method for synthesis