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Synthesis of well-defined star-branched polymers by stepwise iterative methodology using living anionic polymerization

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ABSTRACT

This article reviews the synthesis of regular and asymmetric star-branched polymers with well-defined structures by methodologies using living anionic polymerization, especially focusing on the synthetic approaches accessible for precisely controlled architectures of star-branched polymers concerning molecular weight, molecular weight distribution, arm number, and composition. The reason for selecting living anionic polymerization from many living/controlled polymerization systems so far developed is that this living polymerization system is still the best to meet the strict requirements for the precise structures of star-branched polymers. Furthermore, we herein mainly introduce a novel and quite versatile stepwise iterative methodology recently developed by our group for the successive synthesis of many-armed and multi-compositional asymmetric star-branched polymers. The methodology basically involves only two sets of the reaction conditions for the entire iterative synthetic sequence. The reaction sequence can be, in principle, limitlessly iterated to introduce a definite number of the same or different polymer segments at each stage of the iteration. As a result, a wide variety of many-armed and multi-compositional asymmetric star-branched polymers can be synthesized.

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Abbreviations: NCA, *N*-Carboxyanhydrides; PA, Polyacetylene; DVB, Divinylbenzene; RLi, Alkyllithium; PS, Polystyrene; PI, Polyisoprene; PB, Polybutadiene; MMA, Methyl methacrylate; EO, Ethylene oxide; PMMA, Poly(methyl methacrylate); PEO, Poly(ethylene oxide); PSLi, Polystyryllithium; PS-SiCl$_2$, Chain-end-SiCl$_2$-functionalized PS; PBLi, Polybutadienyllithium; PILi, Polyisoprenyllithium; PI-SiCl$_2$, Chain-end-SiCl$_2$-functionalized PI; PI-SiCl-PS, In-chain-SiCl-functionalized diblock copolymer of PI and PS; DPE, 1,1-Diphenylethylene; PDMS, Poly(dimethylsiloxane); ^{t}BMA, *tert*-Butyl methacrylate; P^{t}BMA, Poly(*tert*-butyl methacrylate); PαMSLi, Poly(α-methylstyryl)lithium; 2VP, 2-Vinylpyridine; P2VP, Poly(2-vinylpyridine); PEE, Poly(ethylethylene); PFPO, Poly(perfluoropropylene oxide); PIB, Polyisobutylene; PMEVE, Poly(methyl vinyl ether); PIB-Fu, Chain-end-2-furan-functionalized PIB; BnX, Benzyl halide; BnBr, Benzyl bromide; BnCl, Benzyl chloride; ATRP, Atom transfer radical polymerization; NMP, Nitroxy-mediated polymerization; RAFT, Reversible addition-fragmentation chain transfer; PCL, Poly(ε-caprolactone); PTHF, Poly(tetrahydrofuran); SMP, 3-*tert*-Butyldimethylsilyloxymethylphenyl; PMSLi, Poly(4-methylstyryl)lithium; PMSiSLi, Poly(4-trimethylsilylstyryl)lithium; PMOSLi, Poly(4-methoxystyryl)lithium; PBMSiOSLi, Poly(3-*tert*-butyldimethylsilyloxystyryl)lithium; Bd, 1,3-Butadiene; PS-(Bd)$_n$, Chain-end-(Bd)$_n$-functionalized (PS)s; Anh, Anhydride; PS(BnBr)$_n$, Chain-end-(BnBr)$_n$-functionalized PS; PVS, Phenyl vinyl sulfoxide; MPVS, 4-Methylphenyl vinyl sulfoxide; PMPVS, Poly(4-methylphenyl vinyl sulfoxide).

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Contents

1. Introduction

Star-branched polymers are defined as polymers having more than three polymer segments (arm segments) radiating from a core. The exclusive hydrodynamic volumes of such polymers are highly restricted due to their topologically branched structures. Less entanglement of star-branched polymers is responsible for lower viscosity compared to linear analogs with the same molecular weights in solution and melt state [1–8]. A number of terminal groups may allow for low glass transition temperature, high solubility, and the possibility to introduce many useful functional groups into a polymer. There is a big difference in the segment densities between the core and outside shell. The star-branched polymer possessing many arms is known to behave like a monomeric rigid sphere, which is different from other branched polymers, such as comb-like polymers, graft copolymers, and hyperbranched polymers [9,10]. Because of such characteristics of star-branched polymers, clarification and quantification of the relationships among the architectures and physical properties in star-branched polymers are quite important and interesting from both a theoretical and practical viewpoint. It is therefore essential to synthesize model star-branched polymers with well-defined structures, in which all of the variables, including molecular weight, molecular weight distribution, arm number, and composition are precisely controlled.

Star-branched polymers are generally categorized into the following two types: regular star-branched polymers having the same arm segments and asymmetric (also called miktoarm or heteroarm) star-branched polymers having different arm segments, as shown in Fig. 1. The regular star includes star-branched polymers consisting of the same homopolymers or block copolymers. The asymmetric star-branched polymer further subdivides into four types according to the asymmetric architecture: (1) chemical structure asymmetry, (2) molecular weight asymmetry, (3) functional group asymmetry, and (4) topological asymmetry. Chemical structure asymmetry-based star-branched polymers have been the most frequently studied so far among them.

Similar to block copolymers, asymmetric star-branched polymers are expected to create novel morphological nanostructures and supramolecular assemblies, which are induced by phase-separation at the molecular level, followed by self-organizing thermodynamically immiscible different arm segments. Possible applications of such asymmetric structures include viscosity modifier, compatibilizer, templates for lithography, catalyst, and drug delivery system. Indeed, several recent publications demonstrated some advantages of using asymmetric star-branched polymers in gene and drug delivery, compared to the linear polymers. For instance, Rovers et al. reported that micelles self-assembled from poly(ε-caprolactone) and poly(ethylene glycol)-based asymmetric stars exhibited high drug loading capacity as well as facile release kinetics [11,12]. Zhu et al. also described high drug-loading efficiency and drug-encapsulation efficiency by using drug-conjugated asymmetric stars [13]. It has been, however, far more difficult to synthesize asymmetric star-branched polymers than regular ones because of the following reasons: (1) there are strict requirements for multistep quantitative-natured reactions corresponding to the introduction of different arms and (2) the isolation of intermediate polymers is often needed to obtain pure products. In order to overcome such difficulties and synthesize a variety of asymmetric star-branched polymers, we have proposed some novel synthetic methodologies based on a stepwise iterative approach which are introduced mainly in Section 5 and some additional syntheses in Section 6 [14–16].

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