

Precise synthesis of poly(methacrylate)-based miktoarm star polymers by a new stepwise iterative methodology using a formyl-functionalized 1,1-diphenylethylene derivative

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ABSTRACT

A new stepwise iterative methodology using living anionic polymers with a 1,1-diphenylethylene (DPE) derivative substituted with a protected formyl functionality bearing a 1,3-dioxolane (DOL) function, **2**, was developed in order to synthesize well-defined μ -star polymers composed of poly(methacrylate)-based arms. In this methodology, the following four reaction steps are involved in the reaction sequence and repeated in each process: (1) the reaction of formyl group with the functionalized DPE anion prepared from **2** and *sec*-BuLi to generate a hydroxyl group and reintroduce the DOL function at the same time, (2) conversion of the generated hydroxyl group to an α -phenylacrylate reaction site, (3) introduction of the arm segment via the reaction site, and (4) regeneration of the formyl group by deprotection of the DOL function. With the methodology, well-defined 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE μ -star polymers with nearly monodisperse distributions ($M_w/M_n \leq 1.05$) were successfully synthesized by repeating the above reaction sequence in each process. Typically, A, B, C, D, and E segments are poly(methyl methacrylate), poly(benzyl methacrylate), poly(allyl methacrylate), poly(6-(4-(4'-cyanophenyl)phenoxy)hexyl methacrylate), and poly(2-*tert*-butyldimethylsilyloxyethyl methacrylate), respectively.

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1. Introduction

Asymmetric star-branched polymers composed of chemically different arms, so-called mixed arm or miktoarm star-branched polymers abbreviated as μ -star polymers, have recently attracted much attention because their different arm segments are usually phase-separated at the molecular level, followed by self-organizing to form nano-ordered suprastructures and/or supramolecular assemblies in bulk as well as selected solvents [1–15]. Such morphological structures and assemblies are novel, characteristic, and, more importantly, quite different from those produced by linear block polymers due to their star-branched architectures. Accordingly, μ -star polymers are expected to play an important role as promising next-generation multiphase polymers with many potential applications in the fields of nanoscience.

Since the well-defined structure of a μ -star polymer is essential to elucidate the relationship between structure and morphological behavior, a variety of well-defined μ -star polymers have so far been

synthesized mainly by using living anionic polymerization systems [2,8,16–30]. However, a major problem is currently the lack of a general and established methodology to synthesize well-defined μ -star polymers composed of three or more different arm segments. In order to overcome this problem, we have, since 2001, developed a general and versatile methodology, based on a new conceptual “iterative approach” [31–35]. In this methodology, the reaction system is designed in such a way that the same reaction site is always regenerated after the introduction of an arm segment in each reaction sequence and this “arm introduction and regeneration of the same reaction site” sequence is repeatable. Therefore, arm segments can be successively and, in principle, limitlessly introduced by repeating the reaction sequence to afford a series of μ -star polymers with many arms. The first successful demonstration was a stepwise iterative methodology based on living anionic polymerization using a 1,1-diphenylethylene (DPE) function as a reaction site. By developing this methodology and further modified ones, we successfully synthesized a variety of well-defined μ -star polymers with many arms, such as 3-arm ABC, 4-arm ABCD, 5-arm ABCDE, 6-arm ABCDEF, 7-arm ABCDEFG, 6-arm A₂B₂C₂, 9-arm A₃B₃C₃, 4-arm ABC₂, 7-arm AB₂C₄, 15-arm AB₂C₄D₈, and 31-arm AB₂C₄D₈E₁₆ μ -star polymers [36–48].

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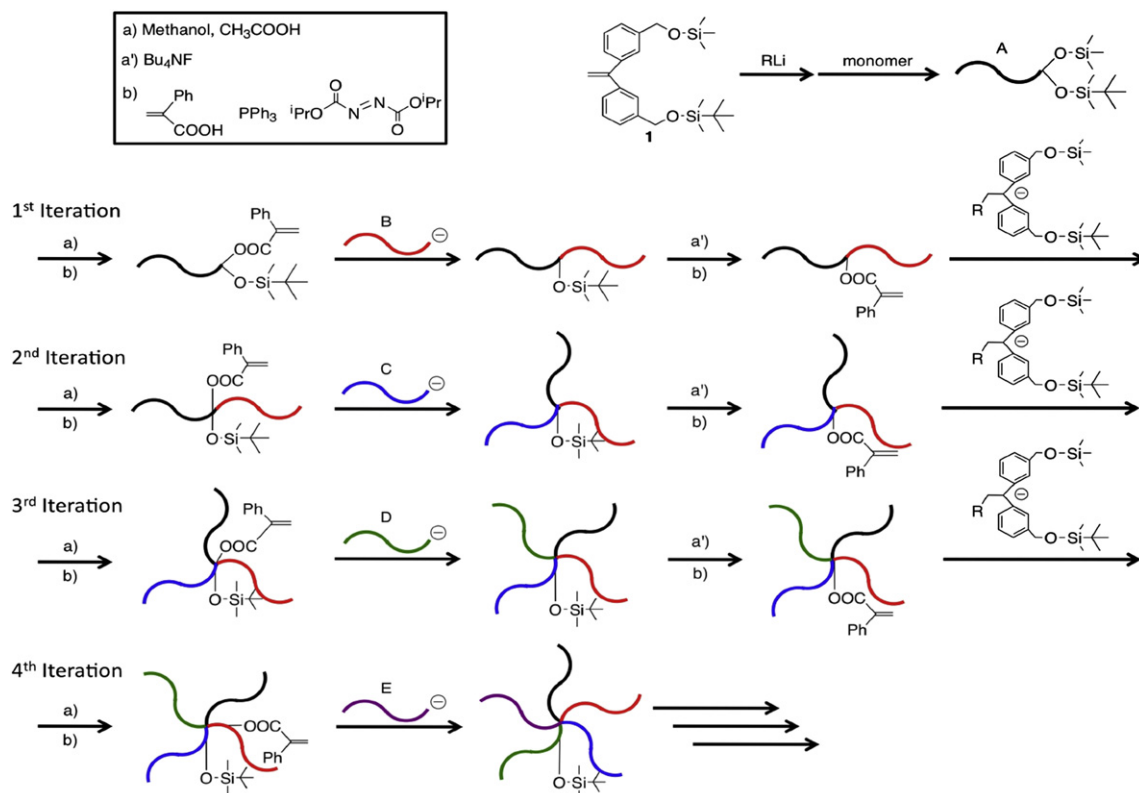
Since the living anionic polymers usable in these methodologies were required to react with the DPE reaction site, they were limited to only highly reactive living polymers of styrene, 1,3-butadiene, isoprene, and their derivatives. Very unfortunately, living polymers of methacrylate-type monomers cannot be applied to the above-mentioned methodologies because their chain-end enolate anions have no ability to react with the DPE function. Since a variety of methacrylate type monomers substituted with useful functional groups are now commercially available or readily prepared and many of such monomers undergo living anionic polymerization [49], the development of a new iterative methodology, capable of using living polymers of these functional methacrylate type monomers, is highly advantageous for the synthesis of many-armed μ -star polymers with functional groups. In particular, well-defined μ -star polymers composed of three or more different poly(methacrylate)-based arms ($M_n > 30$ kg/mol and $M_w/M_n \leq 1.1$) were not synthesized until 2011. Very recently, we demonstrated the successful synthesis of a series of such μ -star polymers by developing a specially designed stepwise iterative methodology using living anionic polymers with a DPE derivative substituted with two different silyl-protected hydroxyl functionalities, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-(3-trimethylsilyloxymethylphenyl)ethylene (**1**) [50].

The synthetic outline is shown in Scheme 1. At first, two silyl-protected functionalities, i.e., trimethylsilyl (TMS)- and *tert*-butyldimethylsilyl (TBDMS)-protected hydroxyl functionalities convertible to two reaction sites, are introduced at the chain-end of polymer (A). This was accomplished by the living anionic polymerization with the functionalized DPE anion derived from **1**. With the use of the TMS-protected functionality, the first reaction site was prepared via selective deprotection by treatment with K_2CO_3 in methanol, followed by conversion to an α -phenylacrylate (PA) function, and reacted with a living polymer (B) to link the B chain with the A

segment. Then, the second reaction site was similarly prepared from the TBDMS-protected functionality via deprotection by treatment with Bu_4NF , followed by conversion to the PA function, and subsequently reacted with the functionalized DPE anion to reintroduce both the TMS- and TBDMS-protected hydroxyl functionalities. Since they are the same as those introduced in the starting polymer (A), the above-mentioned reaction sequence can be repeated.

In the resulting in-chain-(TMS- and TBDMS-protected hydroxyl)-functionalized A-block-B, the first reaction site was again prepared from the TMS-protected functionality exactly in the same manner, and subsequently reacted with a living polymer (C). As a result, a core-(TBDMS-protected hydroxyl)-functionalized 3-arm ABC μ -star polymer was obtained. The second reaction site was prepared from the TBDMS-protected hydroxyl functionality and reacted with the functionalized DPE anion to introduce the TMS- and TBDMS-protected functionalities. By repeating the same reaction sequence two more times, a 4-arm ABCD, followed by a 5-arm ABCDE μ -star polymer could be successively synthesized. Typically, the A, B, C, D, and E segments used are PMMA, poly(ethyl methacrylate) (PEMA), poly(*tert*-butyl methacrylate) (P^t BMA), poly(benzyl methacrylate) (PBnMA), and poly(2-methoxyethyl methacrylate) (PMOEMA), respectively. These 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE polymers are the first successful well-defined μ -star polymers composed of all different poly(methacrylate)-based arms.

In this methodology, we designed the reaction system in such a way that two reaction sites are progressively prepared at different reaction stages, first used for the introduction of arm segment, second used for the regeneration of the same reaction site, and this “arm introduction-regeneration of the same reaction site” sequence is repeated for access to the next process. Therefore, the key of the methodology is the reaction of the second PA reaction site with the functionalized DPE anion to reintroduce two silyl-protected hydroxyl functionalities convertible to two reaction sites.



Scheme 1. Synthesis of μ -star polymers by a stepwise iterative methodology using **1**.

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