

Allyl functionalized telechelic linear polymer and star polymer via RAFT polymerization

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Abstract

Reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene using bisallyl trithiocarbonate as a chain transfer agent (CTA) was studied. The polymerization exhibited first-order kinetics and the molecular weight increased linearly with increase of monomer conversion. Well defined allyl-functionalized telechelic polystyrene (PS), poly(*tert*-butyl acrylate) (PtBA) and corresponding triblock copolymers, polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polystyrene (PS-*b*-PnBA-*b*-PS) and poly(*tert*-butyl acrylate)-*b*-polystyrene-*b*-poly(*tert*-butyl acrylate) (PtBA-*b*-PS-*b*-PtBA) were prepared as characterized with GPC and NMR analysis. The allyl-end groups of the telechelic PS have been switched to 1,2-dibromopropyl groups quantitatively by bromine addition reaction, further substitution of the bromide with azide was also made. Furthermore, star PS with allyl-end-functionalized arms was synthesized by RAFT polymerization of divinyl benzene using allyl-functionalized PS as a macro-CTA via arm-first approach. Star polymer with a thiol-functionalized core was generated by aminolysis reaction of the star polymer and ethylenediamine. As a result, difunctionalized star polymer with allyl and thiol groups was obtained and was used as a stabilizer for the formation of gold nanoparticles.

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1. Introduction

Telechelic polymers (α , ω -difunctional polymers) have been explored to a much extent in the past 20 years because they are precursors for preparing multi-block copolymers, grafted polymers, star polymers, and polymer networks [1–4]. A variety of telechelic polymers with terminals like hydroxy, carboxylic, epoxy groups and carbon–carbon double bond have been prepared by ionic polymerization, conventional radical polymerization, polycondensation and controlled radical polymerization (CRP) techniques [1–17]. Among these methods, CRP becomes an intriguing new technique that may generate polymers of controlled molecular weight and it may be carried out in the presence of many functional groups from monomers, initiators, or chain transfer agents (CTA) [4,9–17].

As early as CRP technique employed, nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) have been used for preparing telechelic

polymers [9–12]. However, it was generally done through two steps: polymer with one end being functionalized was synthesized firstly and then another end of polymer was functionalized by nucleophilic substitution, electrophilic addition, or radical addition. As an example of ATRP approach, hydroxyl telechelic polymers were prepared via ATRP of methyl methacrylate and butyl acrylate using 2-hydroxyethyl 2-bromoisobutyrate as initiator followed by nucleophilic substitution of the bromo-end group with 5-amino-1-pentanol [9]. As an example by NMP approach, α , ω -bisterpyridine-functionalized PS was prepared with a terpyridine initiator followed by a post-radical addition of terpyridinyl maleimide [13].

Furthermore, reversible addition-fragmentation chain transfer (RAFT) mediated radical polymerization, a typical type of CRP, has been used to prepare well-defined polymers with predetermined molecular weight and narrow polydispersity [14–19]. Trithiocarbonates, which can be synthesized with two good homolytic leaving groups, are effective RAFT agents to be applied to prepare telechelic polymers. In this case, the polymer chains grow in two directions and the leaving groups become the end groups inherently [14–17]. By this way, hydroxyl and carboxyl functionalized telechelic polymers have been

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synthesized by RAFT mediated polymerization in one step with the functional trithiocarbonate as a CTA [14–17]. For example, Pan et al. have synthesized hydroxyl telechelic polymers and triblock copolymers by RAFT polymerization using *N,N'*-azobis(isobutyronitrile) (AIBN) as an initiator and *S,S'*-bis(2-hydroxyethyl-2'-butyrate) trithiocarbonate as a CTA [14].

Star or star-shaped polymers have been prepared by various living polymerizations. The research motivation is the morphology, physical properties and functions of star polymer may considerably differ from those of the linear analogues [20–27]. The star polymers with functionalized peripheries or cores may have important applications as supramolecular hosts, catalyst scaffolds, or substrates for nanoparticle formation [18,22–26]. Synthesis of core functionalized star polymers has been made by arm-first approach with a functionalized divinyl chemical [22–26] or by core-first approach with a functional initiator or CTA [27,28].

Allyl group is a reactive functional group, which can be used for various addition reactions. Therefore, allyls in polymer may be transformed into many functional groups [29,30]. Furthermore, allyl-terminated polymer is a kind of macromonomer being applied to prepare grafted copolymer [31]. Such reactive polymers have been synthesized by polymerizations using allyl-functionalized initiator or monomer, or by modifications with allyl compound [29–36]. Bisallyl functionalized telechelic polymer may be applied to prepare the well-defined gels with uniform cross-linking network if the polymer can be generated by controlled polymerization.

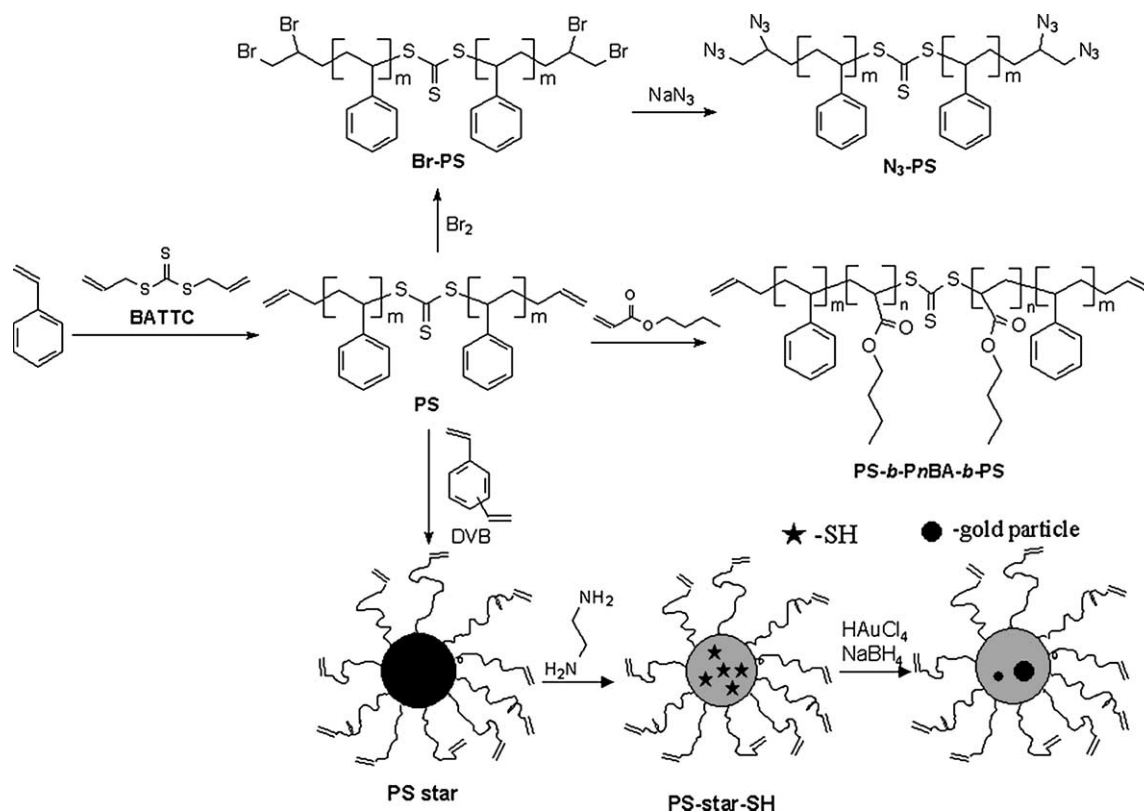
However, to the best of our knowledge, there is no report on preparing such novel allyl polymers by CRP.

In this paper, a bisallyl trithiocarbonate (BATTTC) was used as the CTA of a radical polymerization for synthesizing allyl-functionalized telechelic homopolymer and triblock copolymer. Allyl groups were also transformed into bromides, which further changed to azido groups by a reaction with NaN_3 . Furthermore, when radical polymerization of divinyl benzene using the allyl-functionalized telechelic polystyrene as a macro-CTA was carried out, star polystyrene with allyl-end-functionalized arms was synthesized. Followed by aminolysis with ethylenediamine, star polymers with allyl-end-functionalized arms and a thiol-functionalized core were obtained. The synthetic route is shown in Scheme 1.

2. Experimental

2.1. Materials

Styrene, *tert*-butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) were stirred with CaH_2 overnight and distilled under reduced pressure. Toluene was stirred with CaH_2 overnight and distilled. DVB (tech. $\geq 45\%$, Beijing Chemical Reagent) was passed through a basic alumina column before used. Allyl bromide was distilled before used. AIBN was recrystallized from ethanol. Other reagents were used as received.



Scheme 1. The synthesis route of bisallyl-functionalized telechelic polymers and star polymer and their properties thereof with BATTTC mediated RAFT polymerization.

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