



Feature Article

Cyclobutenyl macromonomers: Synthetic strategies and ring-opening metathesis polymerization

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ABSTRACT

In contrast to their (oxa)norbornenyl counterparts, cyclobutenyl derivatives have remained relatively unexplored in ring-opening metathesis polymerization (ROMP), despite ROMP of cyclobutene derivatives yields unsaturated polymers based on a strictly 1,4-polybutadiene backbone that is not easily attainable by other routes. This article summarizes work done in our group in the field of cyclobutenyl-capped macromonomers that are convenient building blocks for the synthesis of graft (bottle-brush) copolymers by ROMP via the so-called macromonomer (or grafting-through) route. Synthetic strategies employing orthogonal chemistries such as reversible deactivation radical polymerization techniques (atom transfer radical polymerization – ATRP, and reversible addition-fragmentation chain transfer (RAFT) polymerization) and recent developments using copper-catalyzed azide-alkyne cycloaddition click chemistry are highlighted. Furthermore, ROMP of the so-obtained macromonomers, including preliminary novel results regarding ROMP of cyclobutenyl-capped macromonomers prepared through RAFT polymerization and click chemistry are reported and discussed.

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1. Introduction

Ring-opening metathesis polymerization (ROMP) has been broadly applied for the synthesis of materials [1–5], including polymers with biological activities [6–9]. The development of well-defined, highly active and tolerant initiators (Fig. 1) based on ruthenium [10–13] and molybdenum [14–16] has opened new avenues to the synthesis of complex macromolecular architectures using ROMP [5,17]. Among the various strained cycloalkenes that can be used, norbornene and oxanorbornene derivatives are the most popular ROMP monomers because of their high ring strain, easy preparation, and the facility with which functional groups are attached [18–22].

Graft copolymers, also denoted as bottle-brush copolymers, are a unique class of polymers bearing densely grafted side chains that control the polymer conformation *via* steric repulsion [23,24]. Three main strategies can be used to prepare such graft copolymers: the grafting-from, the grafting-onto, and the grafting-through (or macromonomer) methods [25–28]. The grafting-through route has proven to be one of the most convenient methods for preparing well-defined graft copolymers, as it allows better control of grafts, backbone length, as well as the grafting density [29–31]. ROMP has emerged as a versatile methodology to generate graft copolymers by the grafting-through route and considerable work has been made using macromonomers having a norbornene [32–75] or an oxanorbornene [76–79] end-group as the “ROMP-able” entity. Compared to their (oxa)norbornene counterparts of similar ring strain (about 30 kcal/mol [80,81]), cyclobutene derivatives have been much less investigated in ROMP [82–96]. This can be ascribed to the difficulties associated with the synthesis of the corresponding monomers. Nonetheless, ROMP of cyclobutene derivatives yields unsaturated polymers based on a strictly 1,4-polybutadiene backbone that is not easily attainable by other synthetic processes such as anionic polymerization [97]. ROMP of cyclobutenyl macromonomers can thus afford 1,4-polybutadiene graft copolymers having a high density and an exact placement of the grafts. To make those graft copolymers with specific properties, the structures have to be controlled, thus well-defined side chains and backbone with pre-determined molecular weights and low polydispersity indices must be obtained using controlled/living polymerization processes.

In this paper, we summarize our work devoted to the synthesis and ROMP of cyclobutenyl macromonomers

prepared using various strategies including reversible deactivation radical polymerization (RDRP) processes: atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization, in the same way as click chemistry using copper-catalyzed azide-alkyne cycloaddition (CuAAC) [98].

2. Synthesis of cyclobutenyl precursors

A number of cyclobutene derivatives can be conveniently synthesized using *cis*-cyclobut-3-ene-1,2-dicarboxylic anhydride precursor (**1**, Scheme 1) [96]. Although anhydride **1** can be prepared by photochemical [2+2] cycloaddition between maleic anhydride and acetylene, this reaction is cumbersome and not totally safe. A new safe and original synthetic route to compound **1** was developed in our laboratory using (*Z*+*E*)- or (*E*)-dichloroethene as acetylene equivalents in the photochemical step [99]. Subsequent elimination in the presence of activated zinc provides anhydride **1** in good yield.

Reduction of **1** using lithium aluminum hydride affords *cis*-3,4-bis(hydroxymethyl)cyclobutene (**2**) in an almost quantitative yield (Scheme 2). Taking in account the known sensibility of ROMP to protic functionalities and to the stereochemistry of the monomer double bond [100–103], acetyl-protected derivatives **3** and **6** have been prepared (Scheme 2) according to literature procedures [104–106] to investigate their relative reactivity. Our initial work related to the ROMP of acetyloxymethyl cyclobutenes **3** and **6** (Scheme 2) had shown that monomer (**3**) with the *cis* stereochemistry is more reactive than its *trans* counterpart (**6**) owing to steric hindrance [94], we thus choose the *cis* stereochemistry as the starting point for subsequent works devoted to the synthesis of cyclobutenyl macromonomers.

3. Synthesis of ATRP inimers

ATRP was reported by Sawamoto et al. as ruthenium-mediated polymerization [107,108] and by Matyjaszewski et al. as copper-mediated polymerization [109–111]. A typical ATRP reaction requires an alkyl halide as the initiator. In order to prepare macromonomers bearing a cyclobutenyl group through ATRP, we choose to introduce a bromine initiating group in a series of cyclobutenyl-functionalized ATRP inimers (initiators-monomers) starting from diol **2**

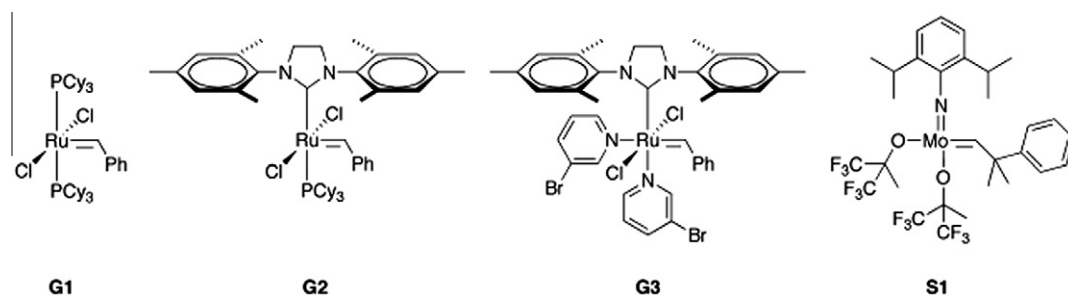


Fig. 1. Selected metathesis catalysts used as ROMP initiators (Cy = cyclohexyl).

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