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
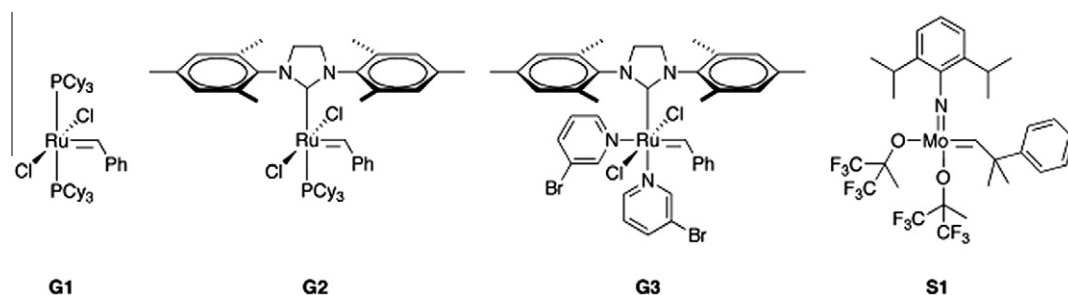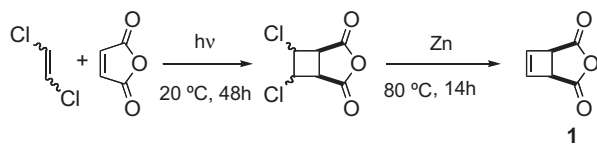

Fig. 1. Selected metathesis catalysts used as ROMP initiators (Cy = cyclohexyl).

Scheme 1. Synthesis of *cis*-cyclobut-3-ene-1,2-dicarboxylic anhydride (**1**).

(Scheme 3) [112–115]. Inimers **7** and **8** were prepared through esterification of 2-bromoisobutyryl bromide with **2** in the presence of triethylamine. Inimer **7** was obtained in 72% yield by reaction with an excess (2.5 equivalents) of 2-bromoisobutyryl bromide. Pure **8** was obtained in 76% yield by using a slight excess (1.1 equivalent) of 2-bromoisobutyryl bromide. The remaining hydroxyl group of **8** was then protected either by acetylation giving inimer **9** (94% yield) or by reaction with 1.2 equiv of *tert*-butyldiphenylchlorosilane (TBDMSCl) in the presence of imidazole, affording the corresponding silyl derivative **10** in 69% yield (Scheme 3). Inimer **10** affords a complete orthogonality between the silyl group and the ester group, allowing a selective regeneration of the hydroxyl functionality from the silyl moiety [116]. Such unsymmetrical inimers contain two initiating moieties that can initiate different polymerization mechanisms selectively and independently, giving rise to orthogonal (or dual) initiators [117].

4. Synthesis of clickable cyclobutenyl derivatives

Since its introduction by Sharpless et al. [98], the concept of click chemistry has received a considerable amount

of attention in polymers and materials science [118–125]. The Huisgen 1,3-dipolar cycloaddition reaction reported in 1965 [126] gained a considerable interest after the copper-catalyzed version was introduced in 2002 independently by Meldal et al. [127] and Sharpless et al. [128]. In our group, we have used the azide-alkyne 1,3-dipolar cycloaddition reaction in both copper-catalyzed (CuAAC) [79,129–131] and thermal Huisgen [132–139] versions.

In order to prepare complex architectures through the macromonomer route, we designed a series of clickable cyclobutenyl derivatives bearing either alkyne or azide groups, starting from anhydride **1** (Scheme 4) or diol **2** (Scheme 5) [129]. Dicarboximide **11** was obtained in overall 70% yield through reaction of *N*-propargylamine with anhydride **1** (Scheme 4).

Although bis-azide **12** (Scheme 5) is easily prepared by nucleophilic substitution after mesylate activation of the hydroxyl groups, this compound must be handled with care, considering the potential hazards associated with azides having a C/N ratio = 1 [98,129]. Alkynoate derivatives **14**–**16** were obtained in good (60%) to moderate (40%) yields by esterification of the corresponding alkynoic acids (Scheme 5) [129]. An additional spacing $(CH_2)_3$ chain was introduced in **15** and **16** in order to increase the accessibility during subsequent CuAAC reactions.

5. Synthesis of cyclobutenyl RAFT agents

Introduced by Rizzardo et al. in 1998 [140], the RAFT-mediated polymerization is nowadays one of the most versatile techniques of RDRP. RAFT polymerization is tolerant toward a wide variety of reaction conditions and
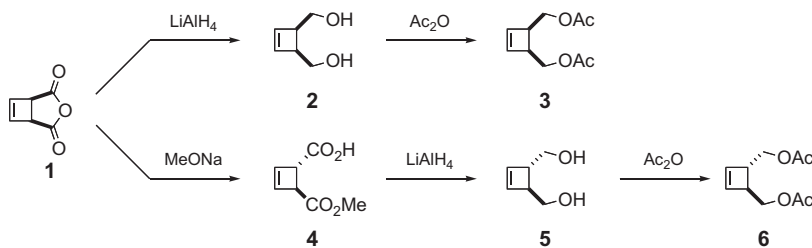
Scheme 2. Synthesis of stereoisomers of 3,4-disubstituted cyclobutenes **2**–**6**.
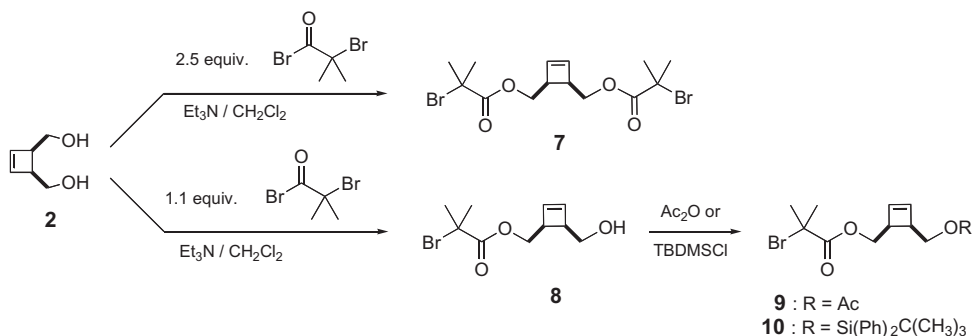
Scheme 3. Synthesis of ATRP inimers **7**–**10** (TBDMSCl = ClSi(Ph)$_2$C(CH$_3$)$_3$).

Scheme 4. Synthesis of clickable cyclobutenyl derivative **11**.

Scheme 5. Synthesis of clickable cyclobutenyl derivatives **12–16**.

functionalities, enabling control over the largest variety of monomers of all the RDRP techniques, including (meth)acrylamides [141–143]. RAFT polymerization uses thiocarbonylthio compounds as chain transfer agents (CTA) [144]. The thiocarbonylthio end-groups of the resulting polymers are easily remo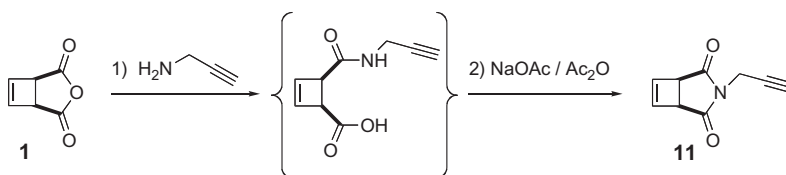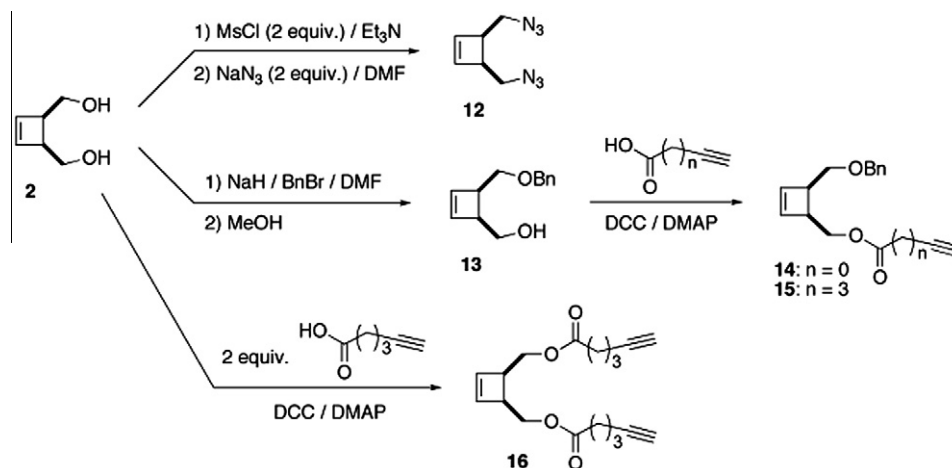ved or modified by a variety of methods [145–147]. Among the different thiocarbonylthio moieties that can be employed in RAFT polymerization, we choose the trithiocarbonate group [148] that can be easily incorporated into various CTA structures (including CTA for metathesis) as demonstrated in our previous works [149–152]. Cyclobutenyl RAFT agents **17** and **18** were prepared in good yield (80%) using the commercially available S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (Scheme 6) [129]. Such a modular strategy gives access to highly functionalized compounds like **18** which contains orthogonal functionalities: a "ROMP-able" cyclobutenyl moiety, a trithiocarbonate RAFT agent, and a clickable alkyne group that enables the anchorage of a wide variety of azido end-functionalized polymers.
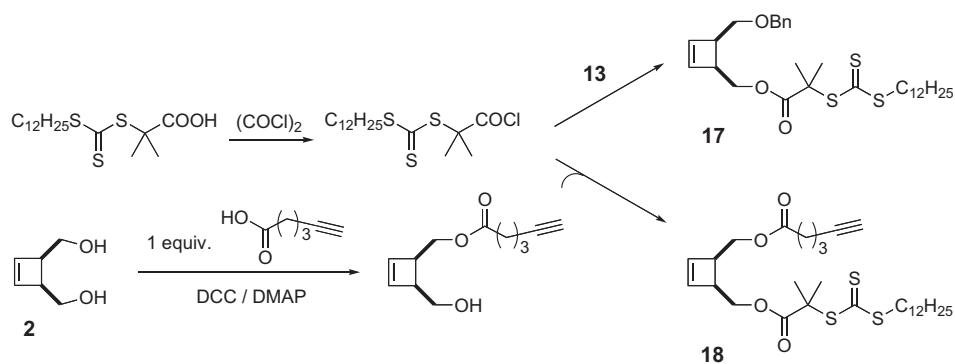
6. Synthesis of macromonomers by ATRP using cyclobutenyl inimers

Considering the reaction conditions required for the ATRP of most of the vinylic monomers (in toluene solution at temperature = 60–100 °C [153–155]) and the known ability of cyclobutenes to thermal ring-opening [105,106], we have investigated the thermal stability of the ATRP inimers under such conditions. It was found that compounds

2 and **7** are stable under ATRP conditions, i.e., up to 100 °C for 2 h [113].

ATRP of styrene, t-butyl acrylate (tBA), and methyl methacrylate (MMA) using N,N',N',N'',N''-pentamethyldiethylenetriamine (PMDETA) [112–114] or N-(pyridin-2-ylmethylene)octan-1-amine [156] as the ligand enabled the synthesis of well-defined macromonomers retaining the cyclobutenyl moiety with narrow polydispersities ($\overline{M}_{n,\text{SEC}} = 1600$–24, 500 g mol^{-1}; PDI = 1.06–1.24), including block copolymers, using both difunctional (Scheme 7) and monofunctional (Scheme 8) inimers. A series of amphiphilic macromonomers were obtained through subsequent acidolysis of the t-butyl ester groups using trifluoroacetic acid (Scheme 7) [114]. Importantly, ^{1}H NMR analysis revealed that acidolysis using trifluoroacetic acid occurs without alteration of the ester linkages between the cyclobutene moiety and the polymer chains [112,114].

In the case of difunctional inimer **7**, the similar efficiency of both initiator sites was demonstrated through hydrolysis of the ester linkage between the cyclobutenyl moiety and the polystyrene chain of a macromonomer. The so-obtained polystyrene showed a molecular weight of about half the value of the initial macromonomer while retaining a low polydispersity index [112]. All of the experimental criteria of a controlled polymerization were verified in these experiments, demonstrating the efficiency of the various inimers as ATRP initiators. More importantly, the cyclobutenyl insaturation survived intact the ATRP process as evidenced by ^{1}H NMR [112,113], in contrast with the norbornenyl moiety that was found to react competitively during ATRP of acrylates under similar

Scheme 6. Synthesis of cyclobutenyl RAFT agents **17** and **18**.
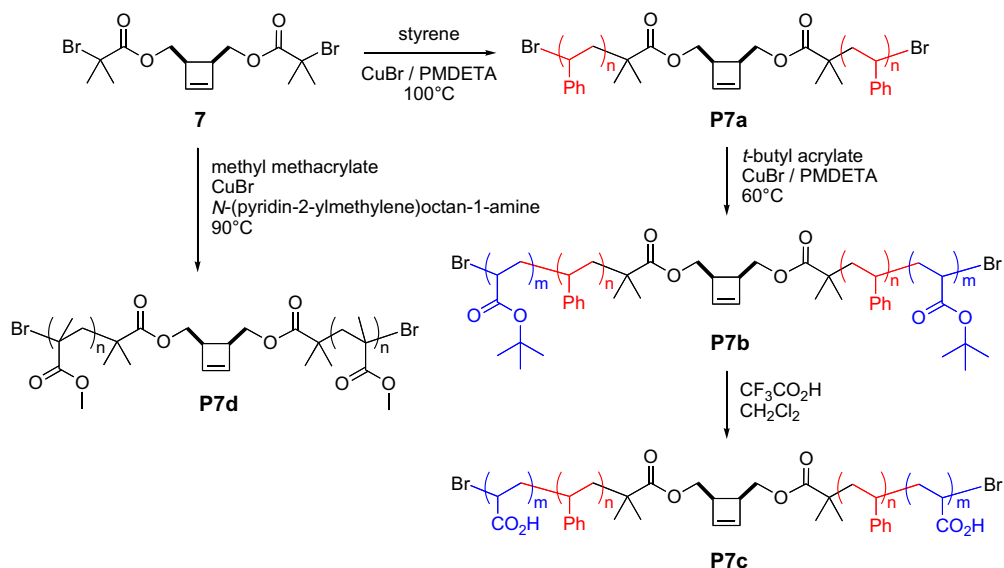
Scheme 7. Synthesis of cyclobutenyl-functionalized macromonomers using difunctional ATRP inimer **7**.

conditions [32]. Put all together, these results demonstrate that the prepared cyclobutenyl inimers act as efficient initiators for ATRP, affording well-defined cyclobutenyl-functionalized macromonomers.

7. Synthesis of macromonomers using CuAAC click chemistry

A variety of highly efficient click reactions have successfully been applied to prepare functional polymers via the post-polymerization modification route [79,118–125]. We exploited the commercial availability of ω-hydroxy-poly(ethylene oxide) monomethyl ether (PEO, molecular weight 2000 g mol^{-1}) and its easy transformation into azido- [157] and alkyne-terminated PEO [158] to prepare cyclobutene-based PEO macromonomers through CuAAC starting from clickable cyclobutenyl derivatives. Alkyne-functionalized cyclobutenes (**11**, **14–16** and **18**) and azido-functionalized cyclobutene **12** were reacted with azido-functionalized PEO (PEO-N$_3$) and alkyne-functionalized PEO, respectively, in the presence of copper bromide

and PMDETA (Schemes 9 and 10), affording the corresponding cyclobutene-based PEO macromonomers [129]. The competitive reaction that can take place between azido groups and strained cycloalkenes in a purely thermal cycloaddition process [159] was not observed under these conditions (room temperature), illustrating the orthogonality of the CuAAC reaction toward the cyclobutene group. The possibility of preparing polymer scaffolds having azide (or alkyne) termini via a post-polymerization route thus enables the synthesis of a wide range of cyclobutene end-capped macromonomers derived from virtually any polymer.

8. Synthesis of macromonomers using cyclobutenyl-functionalized RAFT agents

RAFT polymerization is known for its ability to mediate the RDRP of most vinylic monomers, including (meth)acrylamides that are known to be difficult to control with ATRP [140–142]. Moreover, the combination of RAFT polymerization with click chemistry has been reported to
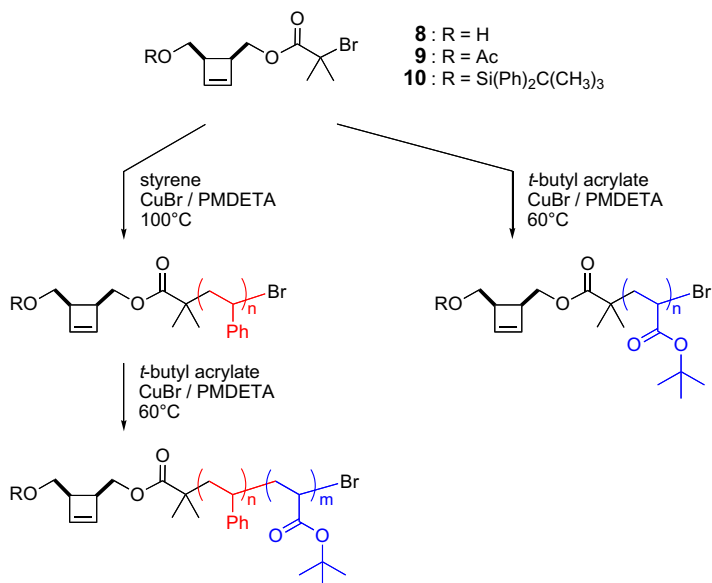
Scheme 8. Synthesis of cyclobutenyl-functionalized macromonomers using monofunctional ATRP inimers **8**–**10**.
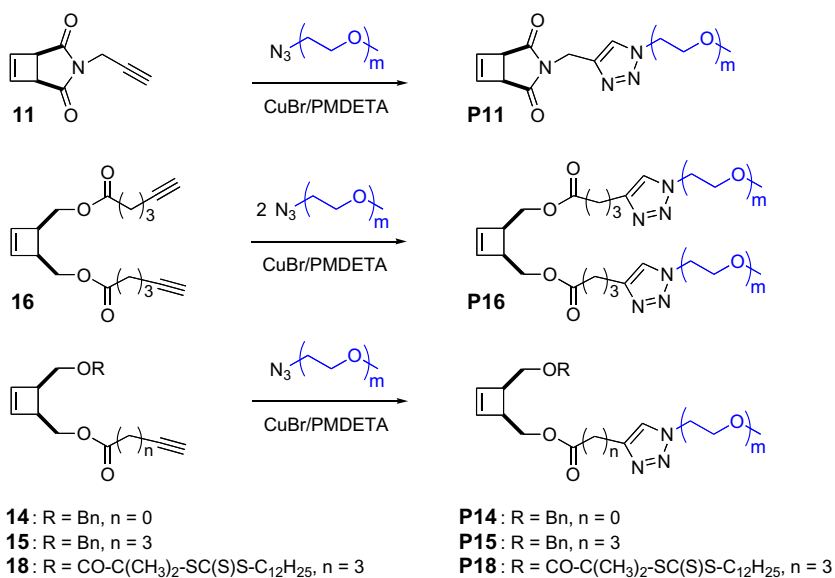
Scheme 9. Synthesis of cyclobutenyl-functionalized PEO macromonomers using CuAAC click chemistry between alkyne-functionalized cyclobutenyl derivatives and PEO-N$_3$.
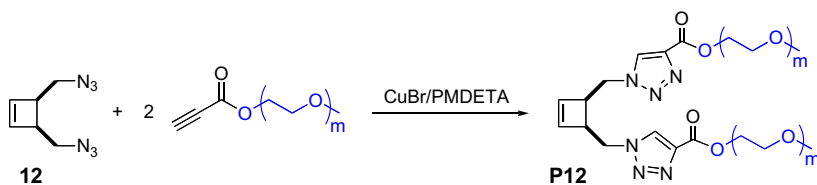
Scheme 10. Synthesis of cyclobutenyl-functionalized PEO macromonomers using CuAAC click chemistry between azido-functionalized cyclobutenyl derivatives and PEO-alkyne.

be highly efficient for the synthesis of complex macromolecular architectures [160–162]. To extend the variety of cyclobutenyl macromonomers, we investigated the RAFT polymerization of ethyl acrylate (EA) and N-isopropyl acrylamide (NIPAM) using azobisisobutyronitrile (AIBN) and 4,4′-azobis(4-cyanopentanoyl acid) (ACPA) as initiator, respectively, and CTAs **17** and **P18** (Scheme 11) [129].

Macromonomers **P17a**, **P17b**, and **P19** were obtained with molecular weights in the range 2800–11,400 g mol^{-1} having low polydispersity indices (PDI = 1.06–1.14). The orthogonality of the RAFT process toward the cyclobutene moiety was demonstrated by MALDI-TOF mass spectrometry that showed the presence of both the trithiocarbonate end-group and the cyclobutenyl insaturation at the chain-end or into the polymers chains [129]. The trithiocarbonate-derived cyclobutenyl CTAs can thus mediate efficiently the RAFT polymerization of various monomers, including acrylamides as demonstrated with NIPAM, extending the possibilities of preparing cyclobutenyl-capped macromonomers derived from monomers that are not easily polymerized using the ATRP process.

9. ROMP of cyclobutenyl macromonomers

The ROMP of polystyrene macromonomers **P7a** and polystyrene-b-poly(t-butyl acrylate) macromonomers **P7b** was first investigated using Grubbs' catalyst **G1** (Fig. 1) in toluene (Scheme 12) that showed only low conversion of the macromonomers [112]. Extended reaction times or higher temperature (50 °C) did not significantly diminish the amount of unreacted macromonomer. This result can be ascribed to the steric hindrance effect of the two polymer chains around the double bond, as previously observed in the case of norbornene-derived macromonomers with two polylactide arms [60].

Grubbs' second generation catalyst **G2** (Fig. 1) was then tested, as it is well known that **G2** is a more active catalyst than **G1** [10,163–165]. However, **G2** generally provides polymers with uncontrolled molecular weights and broad molecular weight distributions [4,165,166]. This has been attributed to relatively slow rates of initiation compared to propagation and to competitive chain transfer reactions along the backbone of the polymers [165,166]. As initially

suggested by Bowden et al. [60], we hypothesized that the steric crowding around the polymacromonomer active center will affect more the rate of propagation (k_p) than the rate of initiation (k_i) and will lower the ratio of k_p/k_i. Steric hindrance created by the high density of grafts is also expected to prevent the catalyst from reacting with the double bonds of the backbone, thus limiting chain transfer reactions ("backbiting") [60]. Polymerization of macromonomers **P7a** ($\overline{M}_{n,SEC} = 3500$ g mol^{-1}; PDI = 1.11) and **P7b** ($\overline{M}_{n,SEC} = 4300$ g mol^{-1}; PDI = 1.11) using **G2** ([macromonomer]$_0$/[**G2**]$_0$ = 10) as the initiator gave incomplete, although higher conversions as compared with **G1** under similar conditions. By increasing temperature (70 °C), concentration (0.01 up to 0.06 mol/L), and reaction time (up to 76 h), polymacromonomers having narrow and unimodal molecular weight distributions were obtained (PDI = 1.21–1.25) [112]. The absence of residual macromonomer as revealed by SEC analysis and the complete disappearance of the signal of the cyclobutenyl moiety in NMR spectra of the reaction mixtures demonstrated that the polymerizations went to completion. It can thus be concluded that the use of Grubbs' second generation catalyst **G2** for the ROMP of norbornenyl macromonomers [60] can be successfully extended to cyclobutenyl-capped macromonomers. Such an approach was subsequently used in the literature for the efficient ROMP of various norbornenyl macromonomers obtained via click chemistry [68].

Considering the reported compatibility of ruthenium catalysts with the triazole ring resulting from the click reaction [68,79,167], we began recently investigation of the ROMP of cyclobutenyl-capped PEO macromonomers obtained through CuAAC.

In contrast with the previously studied macromonomers, ruthenium catalysts **G2** and **G3** failed to initiate the polymerization of macromonomer **P11** [168]. Such a result can be ascribed to the coordination of the emerging ruthenium carbene metal center resulting in a stable chelation through a 5-membered ring between metal center and oxygen after the initiation step [85,169].

Macromonomers **P17a-b** and **P19** issued from RAFT polymerization have been tested using **G3** catalyst (Fig. 1). ROMP of macromonomers **P17a** and **P19** derived
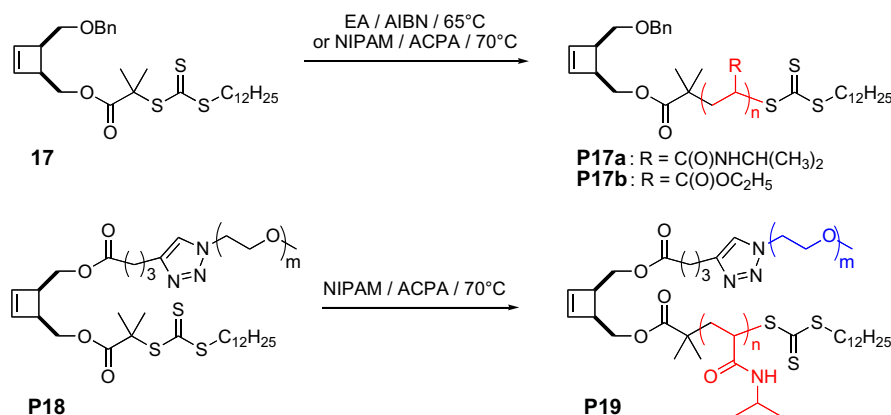
Scheme 11. Synthesis of cyclobutenyl-functionalized macromonomers using RAFT polymerization.
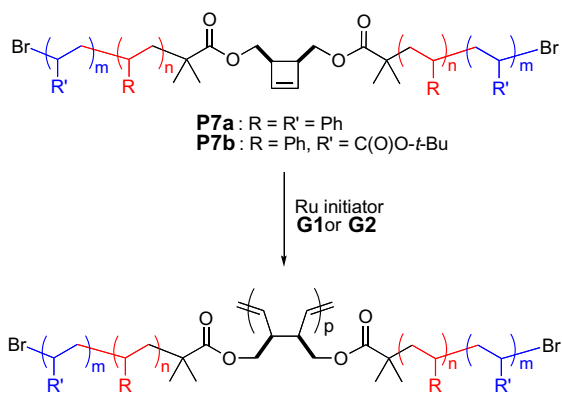
Scheme 12. ROMP of cyclobutenyl-functionalized macromonomers using ruthenium catalysts.

from NIPAM failed, probably due to the high concentration of amide groups that can deactivate the catalyst. In contrast, ROMP of macromonomer **P17b** derived from ethyl acrylate ([**P17b**]$_0$/[**G3**]$_0$ = 10), led to the expected polymacromonomer, although with a limited (70%) conversion [168]. Work is in progress in our group to test other ruthenium-based initiators with these macromonomers [170].

10. Conclusions and outlook

By exploiting the orthogonality of the cyclobutenyl functionality toward ATRP, RAFT polymerization, and click chemistry, modular strategies have been set up in order to prepare new cyclobutene-based molecules bearing orthogonal functionalities that enable the synthesis of well-defined cyclobutenyl-capped macromonomers. The resulting macromonomers show predictable molecular weights and narrow molecular weight distributions. The length of each block can be easily tuned thank to either RDRP techniques such as ATRP or RAFT polymerization or to highly efficient click reaction using easily available macromolecular precursors such as PEO.

The strategies summarized herein pave the way for the synthesis of well-defined macromonomers derived from a wide range of monomers and/or macromolecular precursors. Such cyclobutenyl-derived macromonomers can not only find applications in ROMP to synthesize heterografted molecular brushes with precisely controlled architecture, but also for other click reactions involving strained rings and other ligation strategies.

All the results gathered up to now collectively demonstrate that most of the cyclobutenyl-capped macromonomers obtained through RDRP techniques or click CuAAC reaction can be efficiently polymerized by ROMP, affording well-defined polymacromonomers. However, our results also show that, as already known in the literature [25,26,29], polymerization of macromonomers is still deficient in preparing high molecular weight graft copolymers. The ability to prepare amphiphilic macromonomers such as PEO-derived macromonomers of pre-determined molecular weights and controlled hydrophilic balance allows for the ROMP to be envisioned in aqueous dispersed media. It

is expected that such macromonomers will organize into micelles with the hydrophobic polymerizable end-groups concentrated in the cores. In ongoing studies we intend to employ this strategy for the preparation of 1,4-polybutadiene graft copolymers starting from cyclobutenyl-capped amphiphilic macromonomers.

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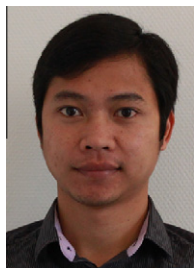[19] Feast WJ, Khosravi E. Synthesis of fluorinated polymers via ROMP: a review. J Fluorine Chem 1999;100:117–25.

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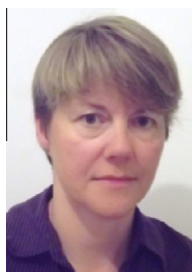
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