

RING-OPENING METATHESIS AND CONTROLLED RADICAL POLYMERIZATION: A TWO-STEP, ONE-POT ROUTE TO BLOCK AND GRAFT COPOLYMERS

Reported by Cyrus A. Anderson

October 1, 2007

INTRODUCTION

Block and graft copolymers have found use in many applications, including thermoplastic elastomers, compatibilizing agents for polymer blends, surfactants, and as templates for nanomaterial fabrication.^{1,2} As such, they are attractive for studying the various microstructures possible from judicious arrangement of polymer blocks.³ Control over copolymer microstructure and morphology, in turn, relies in part on the ability to combine diverse, well defined polymer segments into a common macromolecule.³ In recent years, ring-opening metathesis polymerization (ROMP)⁴ and controlled radical polymerizations (CRP) such as atom transfer radical polymerization (ATRP),^{5,6} reversible addition-fragmentation polymerization (RAFT),⁷ and nitroxide mediated polymerization (NMP)⁸ have matured and offer several advantages to well established ionic and free radical polymerizations for the production of block and graft copolymers. Most notable, however, are the functional group tolerance allowed by both ROMP and CRP relative to ionic polymerizations and the superior control over polymerization relative to free radical techniques. Thus, a broad set of monomers can be copolymerized and functional monomers can be incorporated directly into a given copolymer, thereby streamlining or eliminating post-functionalization.⁴⁻⁸

Additional compositional diversity can be imparted by using polymerization strategies that are tolerant of otherwise mechanistically incompatible monomers. Preparation of such polymers often requires post-functionalization of a polymer segment created from polymerization by one mechanism with a moiety capable of initiating polymerization proceeding by a different mechanism.⁹ The functional group tolerance observed among ROMP and CRP techniques offers the potential to achieve the copolymerization of “mechanistically incompatible” monomers through the use of heterofunctional initiators, difunctional chain transfer agents, and initiator-monomers. A survey of recent examples highlights how strategies involving tandem ROMP and CRP can efficiently generate topologies ranging from linear AB diblock copolymers to densely grafted core-shell bottle-brush polymers,¹⁰ often in one-pot from monomeric starting material.

BACKGROUND

A number of protocols allowing the combination of monomer segments created by distinct polymerization mechanisms have been investigated.¹¹ Indeed, some polymerizations can be performed in sequence without intermediate transformations, and examples of simultaneous ring-opening polymerization (ROP) and NMP have also been reported.^{12,13} The combination of ROMP and CRP techniques is interesting because the coupling of these two polymerizations allows the connection of non-polar segments (via ROMP) with polar segments (via CRP) and thus has the potential to generate unique microstructures and novel materials.

Control over polymer architecture and morphology relies on conducting a controlled polymerization. Living polymerization techniques, or polymerizations in which undesirable termination and chain-transfer reactions do not occur, give exceptional control.¹⁴ ROMP and CRP are not true living polymerizations, because of possible chain transfer or premature termination in the case of ROMP, and biradical coupling or disproportionation in the case of CRP. However, the state of the art in ROMP and CRP is such that the occurrence of these undesirable reactions is drastically reduced, thus both polymerization techniques exhibit the essential characteristics of living polymerizations: (1) fast and complete initiation, (2) linear relationship between monomer conversion and M_n , and (3) low PDIs (<1.5). Polymerizations possessing these characteristics can reliably produce low dispersity polymers of predetermined M_n .^{4,5} ROMP is proposed to occur by the mechanism outlined in Figure 1.⁴ CRPs are understood to take place according to the general mechanisms outlined in Figure 2.⁵

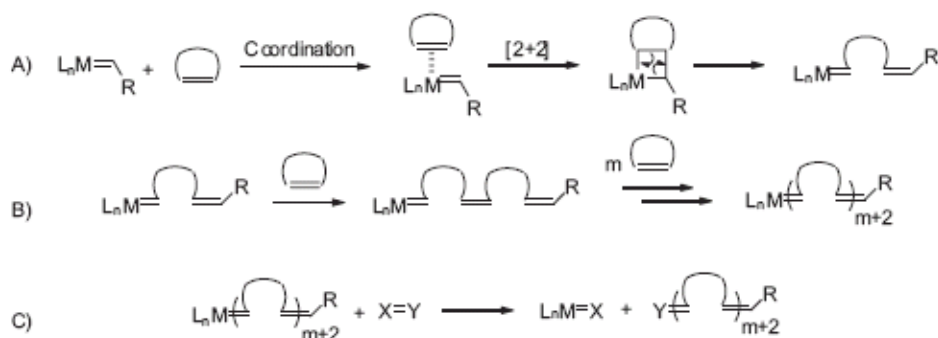


Figure 1. General mechanism for ROMP: A) initiation, B) propagation, C) termination.

The potential for ROMP and CRP to streamline the preparation of block and graft copolymers depends on the mutual tolerance of the ROMP system with CRP systems and vice-versa.¹⁵ Compatible systems thus allow polymerizations to be performed in tandem, which in this context refers to successive polymerizations conducted without intermediate synthetic transformations. Among the well defined

ROMP catalysts, Ru-alkylidene-based catalysts have demonstrated the widest functional group tolerance, and are compatible with the main families of initiators, vinyl monomers, and functionalized monomers used in CRPs.⁴⁻⁸ In addition, Ru metathesis catalysts have been shown to catalyze ATRP, an observation that has been used to further streamline tandem ROMP/CRP via auto-catalysis¹² also referred to as concurrent tandem catalysis (CTC).¹⁶ Similarly, the α -haloesters, alkyl-dithioesters, and nitroxides commonly employed as initiators in CRP do not interfere with the ROMP catalytic cycle. Furthermore, the active chain species in CRP react with neither strained olefin ROMP monomers, nor with the polyolefin-backbones resulting from ROMP.

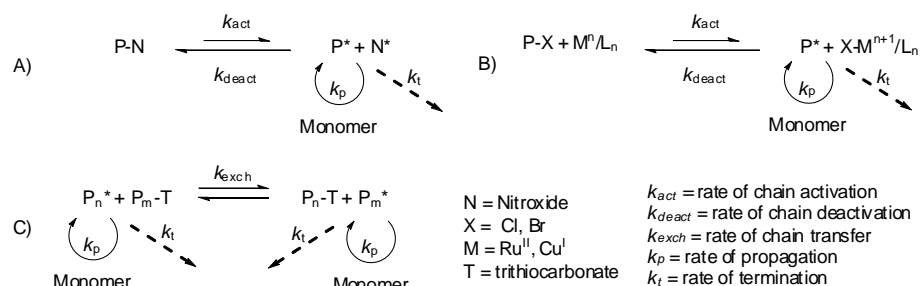


Figure 2. General mechanisms for CRP: A) NMP, B) ATRP, C) RAFT.

LINEAR BLOCK COPOLYMERS

Linear diblock copolymers feature two different segments (Figure 3-A) and have been used as thermoplastic elastomers, surfactants, and compatibilizing agents. Matyjaszewski and coworkers reported one of the earliest examples of an ROMP/CRP based process to prepare block copolymers.¹⁷ The synthetic approach towards an AB diblock copolymer relied on the ROMP of norbornene (NB) or dicyclopentadiene (DCPD) in the presence of Mo-alkylidene **1** (Figure 4) followed by termination with *p*-bromobenzaldehyde in a Wittig-type reaction. This, in effect, prepared a macromonomer for subsequent ATRP of styrene (St) or methyl acrylate (MA). Although not a tandem process, this example indicated that monomer segments from both polymerizations could be readily connected to produce diblock copolymers with high M_n (85,000-110000 g/mol) and low PDIs (1.06-1.07) for polynorbornene (PNB) containing polymers.



Figure 3. Linear block copolymer topologies via tandem ROMP/CRP: A) AB diblock, B) ABA triblock.

Motivated by the work of Matyjaszewski¹⁷ and reports of Ru-alkylidene complexes **2** catalyzing ATRP polymerizations,¹⁸ Grubbs and coworkers developed an alternate, streamlined strategy to ROMP/ATRP linear diblock copolymers.¹⁹ Ru-alkylidene **3** (Figure 4), bearing initiation sites for ROMP and ATRP was prepared. After confirming that **3** could mediate both ROMP and ATRP independently, it was shown that the complex could also facilitate both polymerizations simultaneously. ¹H NMR investigations of the copolymerization kinetics indicated sufficiently large differences between the rate of ROMP and ATRP ($k_{\text{obs}} = 3.5 \times 10^{-3} \text{ s}^{-1}$ and $1.2 \times 10^{-5} \text{ s}^{-1}$, respectively) to conclude the polymerizations occurred in tandem. Acting under the presumption that Ru catalyzed ROMP is dissociative with respect to the phosphine ligand,²⁰ it was found that the addition of excess tricyclohexylphosphine to the copolymerization mixture lead to nearly identical polymerization rates ($k_{\text{obs}} = 3.6 \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{obs}} = 3.7 \times 10^{-5} \text{ s}^{-1}$ for ROMP and ATRP, respectively) resulting in CTC. Simultaneous polymerization of cyclooctadiene and methyl methacrylate (MMA) in the presence of **3** gave the corresponding PB-PMMA (PB = poly-butadiene) diblock copolymer with monomodal distributions (PDI = 1.5-1.6) in 58-82% yield. Noteworthy is that upon completion of the simultaneous polymerization, the residual Ru species affected hydrogenation of the polymer backbone affording the corresponding poly(ethylene)-PMMA copolymer.

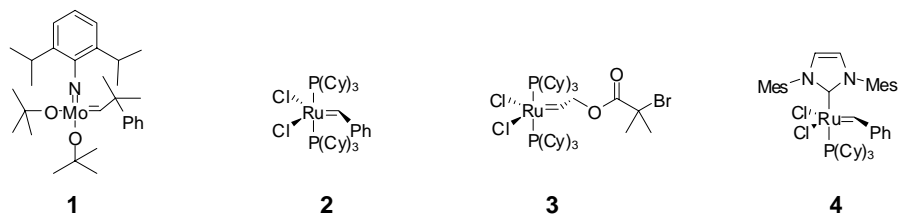


Figure 4. ROMP catalysts employed in ROMP/CRP change of mechanism polymerizations

ABA triblock copolymers feature a central segment flanked by two outer segments (Figure 3-B). ABA triblock copolymers have been studied as thermoplastic elastomers. Several examples of tandem ROMP/CRP to generate ABA triblock copolymers have been reported. Both examples make use of a difunctional chain-transfer agent (CTA) featuring an alkene that serves as an initiator for ROMP while the outer segments can grow by ATRP from α -bromoisobutyrate or chloroalkane initiators, or by RAFT via alkyl-trithiocarbonates. The ROMP/ATRP system investigated by Grubbs and coworkers²¹ resulted in low M_n (~8000 g/mol) PSt-poly(butadiene)-PSt with PDI = 1.63. This large PDI is possibly a result of chain-transfer reactions catalyzed by residual **2**. Better results were obtained when a two step protocol was employed. PSt-PB-PSt and PMMA-PB-PMMA triblock copolymers were obtained with PDIs ranging from 1.25-1.68. More recently, Hillmyer and coworkers have extended this approach to a

tandem ROMP/RAFT system using **4** and AIBN, respectively, to facilitate polymerization.²² A series of *Pt*BA-PB-*Pt*BA and PSt-PB-PSt triblock copolymers were prepared exhibiting PDIs ranging from 1.45-1.67.

NON-LINEAR BLOCK COPOLYMERS

A variety of non-linear block copolymers such as star-block polymers, multiarm star polymers, dendrimers, graft copolymers and cyclic block copolymers have been prepared. Practical applications include compatibilizers for polymer blends, impact modifiers, thermoplastic elastomers, and potential applications point towards templates for nanoscale fabrication and drug delivery.² Graft architectures such as random graft copolymers, brush copolymers, and core-shell brush copolymers¹⁰ have been realized via tandem ROMP/CRP (Figure 5). Graft copolymers are generally prepared from “grafting through,” “grafting to,” or “grafting from” (Figure 6).¹⁰ The most common approach via ROMP/CRP appears to be grafting from and has been demonstrated with all combinations of ROMP/CRP. This is typically achieved by utilizing an initiator-monomer capable of polymerizing by one mechanism and initiating polymerization by a second mechanism. Most initiator-monomers are derived from norbornene functionalized with a CRP initiator such as an α -haloester for ATRP, a dialkyl-trithiocarbonate for RAFT, or an alkoxyamine for NMP (Figure 7).

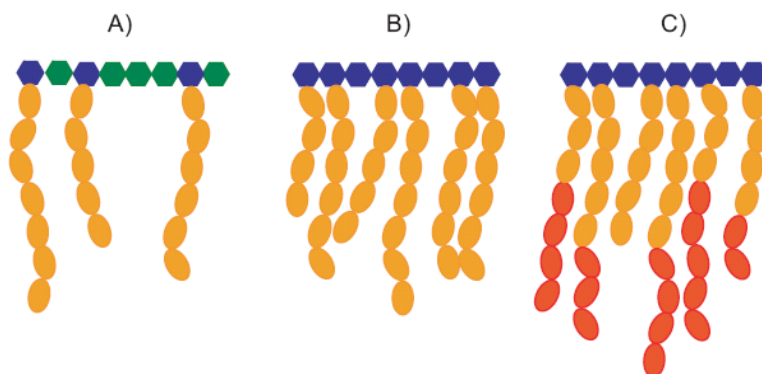


Figure 5. Non-linear block copolymer topologies accessible via tandem ROMP/CRP: A) random graft, B) bottle-brush, C) core-shell bottle brush.

Early demonstration of the applicability of tandem ROMP/CRP to branched architectures was reported by Weck and coworkers²³ in the preparation of randomly grafted PNB-g-P(*t*-butyl acrylate) (Figure 5-A). Copolymerization of initiator-monomer **5** and octanoyl-norbornene ester generated a PNB backbone featuring pendant initiation sites for ATRP. The pendant chains were grown from the resulting macroinitiator via copper mediated ATRP of *t*-butyl acrylate (*t*BA). The final polymer was collected in 50-57% yield and displayed a monomodal distribution with high M_w (162,000-173,000

g/mol) and PDI values ranging from 1.68-1.77. More recently, this strategy towards random graft copolymers has been streamlined by the use of CTC. Novak and coworkers report a one-pot, one-catalyst system in which **2** mediates ROMP and ATRP simultaneously.²⁴ Polymerization of initiator-monomer **6** and MMA in the presence of **2** led to P(**6**)-g-PMMA. Studies concerning the relative distance between initiator sites and the quality of polymer recovered indicated that when ROMP and ATRP initiation sites were separated by a long alkyl linker, polymers with lower PDI values (1.67) were obtained relative to monomers featuring initiation sites in close proximity (PDI >2.5). This distance dependence is believed to arise from unfavorable steric interactions at the initiation sites held close to the polymer backbone. It was also found that high monomer conversions and high MMA monomer concentrations led to poorly defined polymers, presumably as a result of inter-chain coupling.

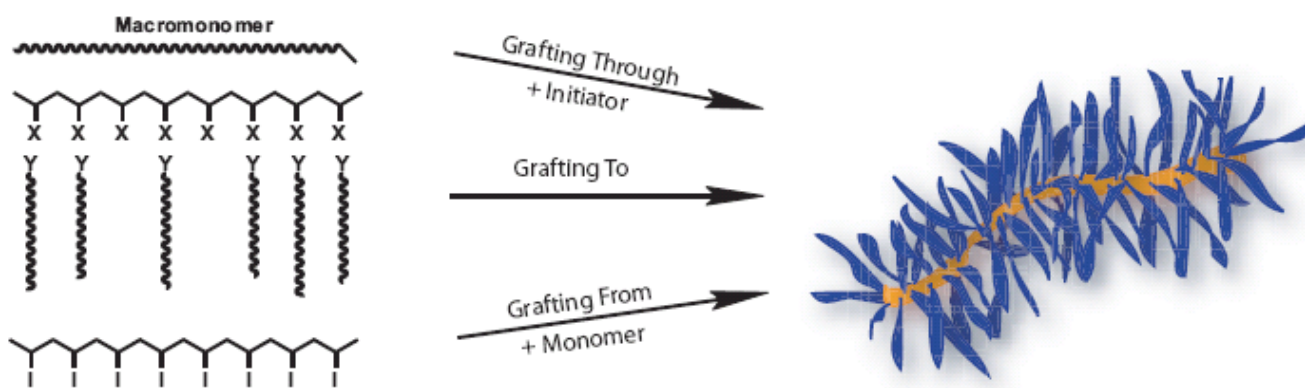


Figure 6. Synthetic approaches to graft copolymers.

Wooley and coworkers²⁵ attempted this same approach to prepare densely grafted bottle-brush copolymers (Figure 5-B) in one-step from monomeric starting material. It was anticipated that in the presence of **2**, **7** (Figure 7) would polymerize via ROMP to generate the polymer backbone, while pendant chains would simultaneously grow from the α -bromoisobutyrate moiety via ATRP of MMA to give a well defined bottle-brush copolymer. Polymerization kinetics experiments indicated that ROMP and ATRP occurred virtually in sequence due to differences in polymerization rates. However, this “one-feed” approach proved to be slow, exhibiting low conversions of MMA and large PDI values (>1.7) after prolonged reaction times. Control experiments indicated that the high concentrations of MMA necessary to prepare the pendant chains interfered with the ROMP. Presumably, chain-transfer to MMA via cross-metathesis is responsible for the undesirable PDIs. Furthermore, the small amount of **2** required for optimized ROMP, was insufficient for the amount of ATRP initiator present on the polymer

backbone and thus resulted in poor initiation efficiency, which is believed to contribute to the observed PDI and low MMA conversion. To overcome the problematic “one-feed” method, a “two-feed” procedure was adopted and produced better results. High M_n (521,000-1,000,000 g/mol) polymers with PDIs between 1.45-1.67 were recovered. Longer reaction times led to higher PDIs, most likely because of biradical coupling reactions occurring at high conversion.

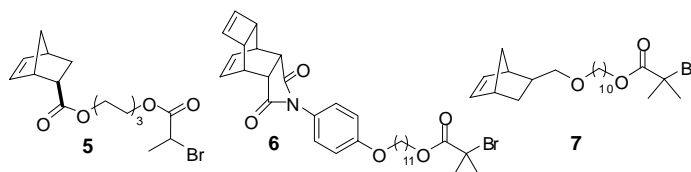
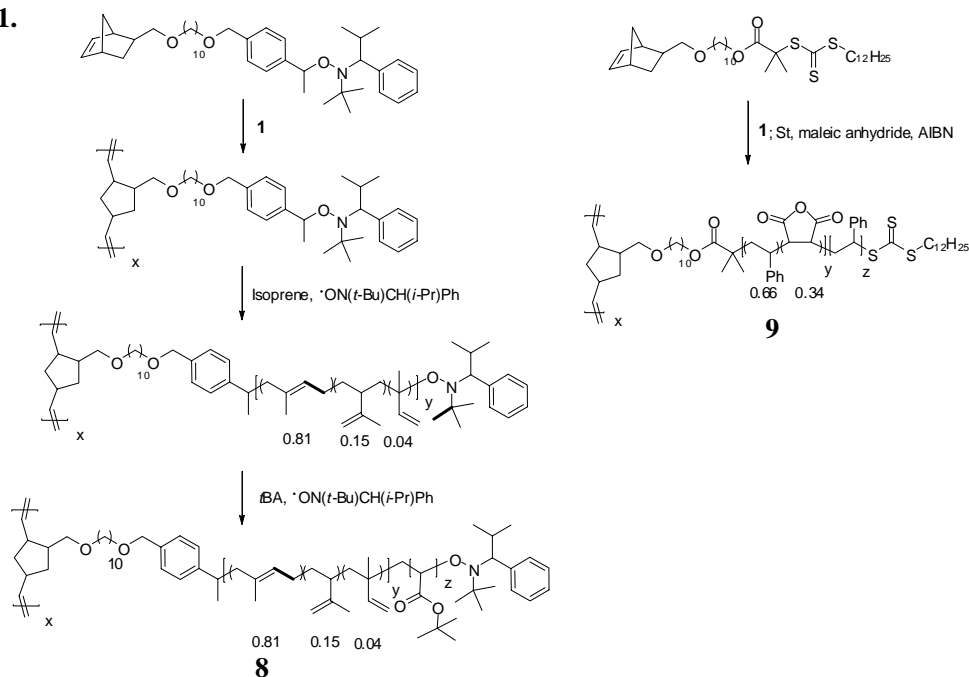


Figure 7. Initiator-monomers for tandem ROMP/CRP.

Recently, more complex architectures have been accessed via ROMP/NMP and ROMP/RAFT. Wooley and coworkers²⁶ report the synthesis of core-shell bottle brush copolymers (Figure 5-C) by extending the general approach to bottle brush polymer preparation. Through successive introduction of monomers for NMP core-shell bottle brush copolymers **8** were prepared (Scheme 1). This approach produced polymers with high M_n (1,410,000 g/mol) and low PDI values (1.23). These polymers were further elaborated through hydrolysis and cross-linking steps to prepare hollowed nanostructures. In follow-up work, Wooley and coworkers have accomplished the synthesis of similar core-shell brush copolymers **9** in one-pot via tandem ROMP/RAFT.²⁷ Core-shell brushes with high M_n (1,200,000 g/mol) and low PDIs (1.32) were obtained through this approach.

Scheme 1.



CONCLUSION

The application of tandem ROMP/CRP strategies towards the streamlined synthesis of complex architectures appears practical. Although ROMP/ATRP has been most widely applied and can be executed under CTC, most examples report PDIs larger than 1.5 as result of side reactions. Furthermore, finding optimized conditions for both polymerizations has proven difficult. Thus, multi-stage procedures appear to be necessary to achieve superior control over the tandem polymerizations. ROMP/NMP and ROMP/RAFT systems appear to be promising with respect to generating well defined graft copolymers. Routes to more complex architectures via CRP have been devised,²⁸ thus architectures more complex than those presented here are certainly possible by coupling ROMP to such methods, however this has yet to be demonstrated.

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