

Photo-Mediated Ring-Opening Metathesis Polymerization

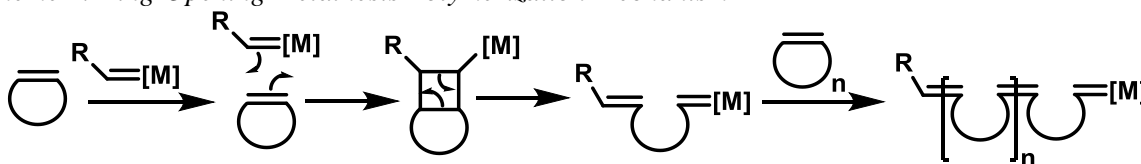
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Ring-opening metathesis polymerization (ROMP) is a widely-used technique to produce bulk amounts of polymer. In 1976, the first commercial use of ROMP was used to synthesize poly(norbornene) which was sold under the trade Norsorex (used in shoe-parts, bumpers and anti-vibration materials).¹ Since then, the industrial utility of ROMP has significantly increased, producing new polymers based on monomers such as dicyclopentadiene, cyclooctene and tetracyclododecene. ROMP is used to polymerize cyclic olefins via transition-metal alkylidene catalysts. The mechanism of ROMP begins with a [2+2] cycloaddition reaction between the cyclic olefin and alkylidene catalyst generating a cyclobutane intermediate. The intermediate then undergoes cycloreversion, rearranging π -bonds in the opposite fashion, producing a new alkylidene and olefin species. The reaction is driven forward by the relief of ring strain in the cyclic olefin, propagating until complete monomer consumption. Termination occurs via quenching with a vinyl ether, removing the alkylidene from the polymer backbone.²

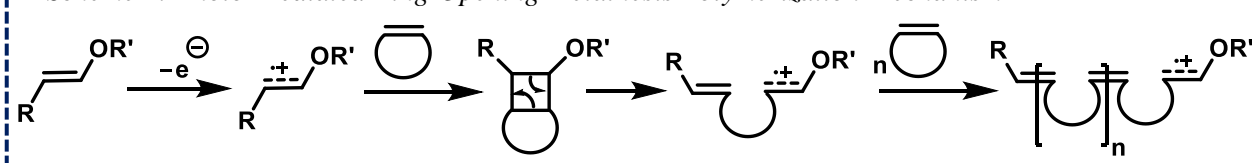
Scheme 1: Ring-Opening Metathesis Polymerization Mechanism



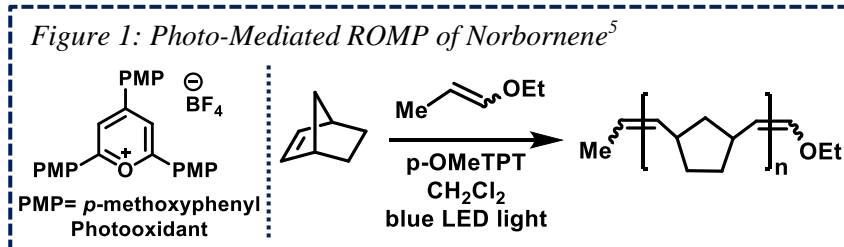
ROMP is a “living polymerization” which refers to a lack of chain transfer or termination events. “Living polymerization” reactions are characterized as having low molecular weight distributions (polydispersity index < 1.5), fast initiation rates compared to propagation rates, and a linear relationship between the number average molecular weight and monomer conversion.³ Thus, ROMP offers a route to synthesizing polymers with narrow molecular weight distributions and predictable molecular weights. These characteristics provide methods to generate more exquisite systems such as block-copolymers and end-functionalized polymers. Recent work focused on improving transition-metal alkylidene catalysts has led to catalysts that generate stereoregular, tactic polymers and catalysts that are tolerant of a wide-variety of functional groups (alcohols, amides, nitriles, etc.).³ Transition-metal catalysts (Ru, W, Mo and Re) are particularly expensive and are typically leftover as metallic byproducts in the polymer matrix. These byproducts preclude ROMP polymers from use in biological or electronic applications due to possible downstream oxidative reactions. Thus, efforts to utilize metal free variants of ROMP are particularly of interest.

In 2006, Chiba *et al.* demonstrated the first olefin cross metathesis using electrochemical techniques. Although this method was limited to few olefins, it presents a new metathetic mechanism occurring through electron transfer.⁴ The Boydston group utilized electron transfer to generate polymers via Photo-Mediated ROMP (PM-ROMP). This reaction is comprised of a

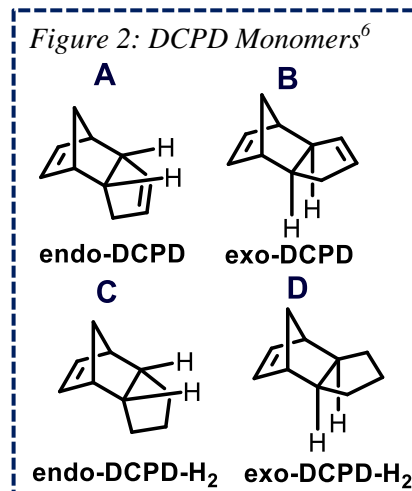
Scheme 2: Photo-Mediated Ring-Opening Metathesis Polymerization Mechanism⁵



photooxidant species, an enol ether initiator and a cyclic olefin. The proposed mechanism first involves the irradiation of photooxidant which then oxidizes an enol ether initiator to produce a radical cation (Scheme 2).⁵ This intermediate generates [2+2] complex with a cyclic olefin which then

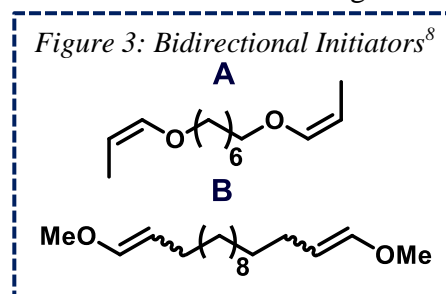


undergoes cycloreversion (similar to traditional ROMP, Scheme 1) The reaction continues to propagate, forming a polymer species. Initial reactions using a blue LED ($\lambda = 450\text{-}480\text{ nm}$) with a norbornene monomer, a pyrylium tetrafluoroborate (*p*-OMeTPT) photooxidant and a vinyl ethyl ether initiator (Figure 1) showed significant success in generating polymer with high monomer conversion (up to 80%). The polymerization was shown to have limited “living” characteristics”: high polydispersity (1.2 - 1.7) and a non-linear trend between monomer conversion and molecular weight. In the absence of light, the reaction terminated, but reinitiated when exposed to light. This property reveals the reversibility of this reaction and suggests that the photooxidant and the radical cation undergo reversible oxidation/reduction cycles.⁵ To test the utility of PM-ROMP other monomers were investigated. Endo-DCPD (a widely-used cyclic olefin) was subjected to polymerization which resulted in low conversions (10-20%) and low molecular weights. This phenomenon was attributed to either a steric clash between the cyclopentene ring and the incoming monomer or intermolecular reactions between neighboring olefins and the radical cation intermediate. Other DCPD monomers (Figure 2, A-D) were subjected to polymerization. Both exo- and endo-DCPD (Figure 2, A, B) failed to polymerize whereas hydrogenated monomers (Figure 2, C, D) successfully generated polymers. Thus, the major contribution was determined to be caused by intermolecular interactions with the olefin in the cyclopentene ring. Microstructural analysis using ^1H and ^{13}C nuclear magnetic resonance revealed that all polymers were largely atactic and mainly contained trans olefins.⁶ This property shows that PM-ROMP has some significant limitations in generating certain types of polymers and provides no stereochemical control.



Pascual *et al.* investigated the ability to synthesize block-copolymers using PM-ROMP.⁷ Norbornene and exo-DCPD- H_2 were subjected to polymerization conditions (polymerizing one monomer for a given time and subsequently adding the second monomer). Block copolymers were successfully synthesized which displayed the utility of PM-ROMP.⁷ Further investigations

focused on generating more diverse polymer architectures. Lu *et al.* developed a method to utilize bidirectional polymerization through difunctional enol ether initiators (Figure 3, A, B).⁸ Norbornene was subjected to polymerization conditions using these initiators. Both sets of initiators displayed high efficiencies leading to 80% monomer conversions with relatively low dispersities (1.2-1.3). Aside from the length of the alkyl chain, the marked difference



between these initiators is due to the position of the ether group within the polymer backbone. Polymerization using initiator 3A, places the vinyl ether within the polymer backbone, whereas polymerization with initiator B generates vinyl ethers as end groups. To that end, norbornene polymerized with initiator A can be degraded using hydrolysis. The polymer was subjected to acid hydrolysis using Amberlyst-15 ion-exchange resin. The polymer successfully broke down into chains with roughly half the molecular weight (24 kDa) of the original polymer chain (45 kDa).⁸ Further experiments utilized bidirectional growth to generate tri-block copolymers. To achieve this architecture, telechelic poly(ethylene glycol) (PEG) macroinitiators (end-functionalized with vinyl ethers) were utilized to generate ABA tri-block copolymers (A is norbornene and B is PEG). Gel-permeation chromatography (GPC) revealed that polymerization was successful. To elucidate the copolymer architecture the polymers were subjected to acid hydrolysis. A low and high molecular weight peak appeared on the gel-permeation chromatogram. The high molecular weight peak corresponded to poly(norbornene) fragments whereas the low molecular weight peak directly matched the molecular weight of the PEG macroinitiator.⁸

To assess the tolerance of PM-ROMP to functional groups, functionalized norbornene species were subjected to both homopolymerization and copolymerization with unfunctionalized norbornene. Homopolymerization proved to be largely unsuccessful with only 4D and 4G monomers generating polymeric species with high monomer conversions. On the other hand, a number of monomers (4 B, D, F, and H) were compatible with copolymerization. The chloro-substituted monomer 4G was found to successfully homopolymerize, but unsuccessfully copolymerize which was initially perplexing. ¹H NMR experiments were used to probe this effect, finding that norbornene incorporated into the polymer chain at a much higher rate than 4G.⁹ Thus, incorporation of 4G was inhibited. These results suggest that Photo-Mediated ROMP is tolerant to a limited number of functionalities.

Photo-Mediated ROMP is a promising synthetic technique which removes the need for costly and reactive transition metal catalysts. The current limitations to PM-ROMP highlight the need for further investigations to improve “livingness” of polymerization, to preclude intermolecular interactions and to increase functional group tolerance.

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