

Review

# Regio- and stereospecific cyclopolymerization of 1,6-heptadiynes

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## Abstract

The synthesis of poly(ene)s *exclusively* based on one single repetitive unit, i.e. 1,2-cyclopent-2-enylvinylene is described. Polymers containing >96% 1,2-cyclopent-2-enylvinylene units were obtained by low-temperature-initiated cyclopolymerization of diethyl dipropargylmalonate (DEDPM) by Mo(*N*-2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>. In the presence of quinuclidine, 100% five-membered ring structures were realized at room temperature, e.g. using Mo(*N*-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(OC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>. 4-(Ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthyl-1,6-heptadiyne was cyclopolymerized to determine the configuration of the double bond (i.e. the *cis/trans* ratio) and the tacticity of the poly(ene) backbone. Poly(4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthyl-1,6-heptadiyne) again consisted of >96% five-membered rings and possessed an all-*trans* tactic, presumably isotactic structure. A linear plot of number of monomers added (*N*) versus molecular weights suggested that the cyclopolymerization of DEDPM proceeded in a living manner. At least a class V living system was confirmed by the stepwise synthesis of poly(DEDPM). Molecular weight distributions (PDIs) of 1.16–1.37 result from ratios of the rate constants for polymerization (*k<sub>p</sub>*) to initiation (*k<sub>i</sub>*), *k<sub>p</sub>*/*k<sub>i</sub>* > 1. Influences of temperature, the base and steric and electronic effects of the arylimido and alkoxy ligand are presented. Complementary to the use of well-defined Schrock initiators, poly(DEDPM) containing exclusively five-membered rings was accessible by the use of the quaternary systems MoCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn-EtOH-quinuclidine and MoOCl<sub>4</sub>-*n*-Bu<sub>4</sub>Sn-EtOH-quinuclidine. Though virtually identical polymers were obtained, the polymerization systems themselves were controlled, yet *not* living as is the case with Schrock initiators. Selected polymer properties such as stability, degradation behavior, conductivity, and thermoresponsive behavior will be discussed. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Cyclopolymerization; Schrock initiators; Poly(ene)s; Conducting polymers

## 1. Introduction

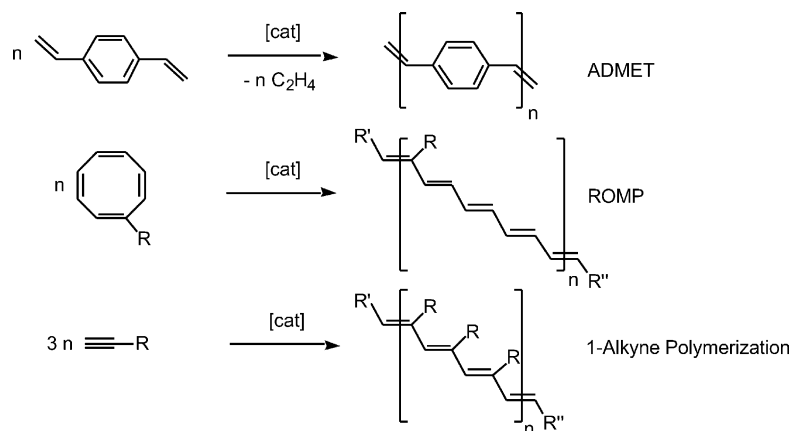
Soluble, conjugated organic polymers with a well-defined microstructure are of particular importance due to their optical and electronic properties [1–6]. Though poly(pyrrol)s are the most frequently used conducting polymers, poly(ene)s are still among the most investigated conjugated polymers. They are accessible via acyclic diene metathesis (ADMET) polymerization starting from  $\alpha,\omega$ -dienes [7–12], via ring-opening metathesis polymerization (ROMP) of poly(ene) precursors [13–23] or, preferably, via alkyne polymerization techniques (Scheme 1) [13–20].

While the ADMET route is preferably used in the synthesis of poly(*p*-phenylenevinylene)s (PPVs), the ROMP route is restricted to a few monomers and does not yet allow all the

structural variations that can be carried out using 1-alkyne polymerization. So far, the most straightforward access to such systems was the polymerization of 1-alkynes. Nevertheless, a general problem of poly(ene)s prepared therefrom are 1,3-interactions of the substituents in the final polymer, resulting in lower conjugation lengths compared to unsubstituted poly(ene) backbones [21,22]. Copolymerizations of 1-alkynes with suitable monomers that yield repetitive units consisting of monosubstituted trienes offer direct access to substituted yet highly conjugated and surprisingly stable poly(ene)s [23]. The cyclopolymerization of 1,6-heptadiynes containing appropriate substituents at the 4-position offers an attractive alternative to poly(1-alkynes)s resulting in poly(ene)s with cyclic recurring units along the backbone [24,25]. Usually these polymers display good solubility in common organic solvents such as C<sub>6</sub>H<sub>6</sub>, toluene, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, good long-term stability towards oxidation and high effective conjugation lengths (*N<sub>eff</sub>*) [20,24–26]. Poly(diethyl dipropargylmalonate) (poly(DEDPM)) itself has already

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Scheme 1. Various metathesis-based routes to conjugated polymers.

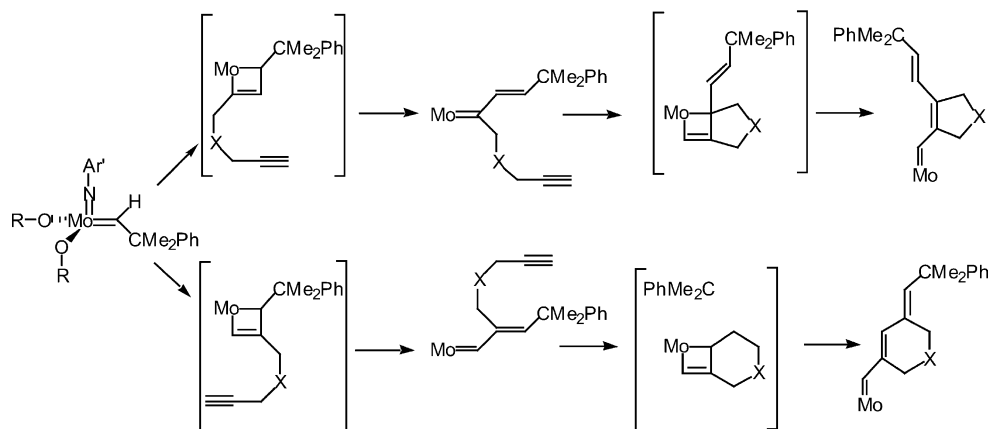
been prepared by Ziegler-type catalysts [27,28], Pd catalysts [29], anionic polymerization [30] and binary/ternary Mo- or W-based catalysts [31]. Unfortunately, these systems lead to mostly insoluble, ill-defined polymers with variable repetitive units and broad molecular weight distributions (polydispersity index (PDI)  $\gg 2$ ). However, well-defined high oxidation-state molybdenum carbenes cyclopolymerize 1,6-heptadiynes in a living manner to produce poly(ene)s that contain either a mixture of five- and six-membered rings [24,25] or exclusively six-membered rings [20,26]. Recently, we elaborated a synthetic route to poly(ene)s containing exclusively five-membered rings and a highly regular, tactic alternating *cis-trans* structure by cyclopolymerization of DEDPM with well-defined molybdenum-based initiators such as  $\text{Mo}(N\text{-}2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OC}(\text{CH}_3)_3)_2$  in the presence of quinuclidine [32,33]. In principle, cyclopolymerizations based on five-membered ring structures can also be realized with classical  $\text{MoCl}_5$ -based initiators. However, only oligomers with a  $\text{DP}_n < 6$  and broad polydispersities (PDIs  $< 4.2$ ) have been reported so far [34]. Alternatively, the synthesis of poly(DEDPM) exclusively consisting of five-membered rings has been accomplished using  $\text{Mo}(\text{CO})_6$  [35]. Acceptable  $\text{DP}_n$  ( $\leq 50$ ) and PDIs

( $\leq 2.2$ ) were obtained by this approach; however, reaction times of 48 h and reaction temperatures of  $100^\circ\text{C}$  appeared less attractive. In this contribution, the latest achievements in the stereo- and regioselective cyclopolymerization of various heptadiynes and hexadiynes are summarized.

## 2. Results and discussion

One of the most common working horses is diethyl dipropargylmalonate whose polymerization with a large variety of initiators has already been studied in detail [20,24,26]. Typically, both classical metathesis catalysts (e.g.  $\text{MoCl}_5/n\text{-Bu}_4\text{Sn}$ ) and well-defined Mo-based Schrock-type initiators yield poly(ene)s that contain a mixture of five- and six-membered rings (Scheme 2) [24,36]. The formation of one particular backbone structure solely depends on the mode of insertion of the monomer. If the first insertion steps proceed via  $\alpha$ -addition, five-membered rings are formed, if  $\beta$ -addition dominates, six-membered rings are formed.

So far, polymers exclusively consisting of six-membered rings have been prepared using the molybdenum imido alkylidene complex  $\text{Mo}(N\text{-}2\text{-}t\text{-Bu-C}_6\text{H}_4)(\text{CH-}t\text{-Bu})(\text{O}_2\text{CCPh}_3)_2$



Scheme 2. Possible structures in the cyclopolymerization of 1,6-heptadiynes.

[20,26]. These polymers were prepared in a living way and were therefore well defined in terms of microstructure, molecular weight and molecular weight distribution, yet displayed comparably low values for  $N_{\text{eff}}$ , typically  $\leq 20$  (in THF). This is believed to be a direct consequence of the six-membered ring-based cyclic recurring units, which can due to their chair conformation only account for a rather poor coplanarity. Our effort therefore focused on the development of suitable initiators that open access to five-membered ring-based microstructures (i.e. of poly(1,2-cyclopent-1-enylvinylene)s), since these should provide enhanced coplanarity and in due consequence highly conjugated materials.

### 2.1. Polymerization of diethyl dipropargylmalonate

The polymerization of DEDPM for the synthesis of poly(1,2-cyclopent-1-enylvinylene)s required some significant initiator tuning. While bulky ligands (e.g. carboxylates in the complex  $\text{Mo}(N\text{-}2\text{-}t\text{-Bu-C}_6\text{H}_4)(\text{CH-}t\text{-Bu})(\text{O}_2\text{CCPh}_3)_2$ ) force a monomer to undergo selective  $\beta$ -addition, small alkoxides do not necessarily favor  $\alpha$ -addition in a selective way. Nevertheless, a small ligand sphere around the molybdenum center was believed to be a necessary *yet not sufficient* requirement in order to favor selective  $\alpha$ -addition. In fact, molybdenum complexes of type  $\text{Mo}(N\text{-Ar})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$  exist in form of two rotamers [18,37]. Electronic and steric effects around the Mo center allow the tuning of their reactivity and selectivity. This has already been used for the synthesis of a large variety of stereoregular norborn-2-ene- and norbornadiene-based polymers [18,37–40]. Addition of a base such as quinuclidine has a strong impact on polymerization. Though a base is believed to be not coordinated to molybdenum during insertion [19], it strongly influences the reactivity of the entire system [14,41]. On one hand, the presence of a base particularly at low temperature favors the formation of (coordinated) *anti* isomer since it stabilizes this isomer [37]. On the other hand, it enhances the relative reactivity of the *syn* isomer. Fluoroalkoxide-based initiators such as  $\text{Mo}(N\text{-}2,6\text{-Me}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OCMe}(\text{CF}_3)_2)_2$  were not capable of forming poly(DEDPM) solely consisting of five-membered rings [24]. Neither addition of quinuclidine nor lower polymerization temperature significantly changed this situation. Since *syn-anti* interconversion is slow in these complexes, the final geometry of a cyclopolymerization-derived polymer must at least be influenced if not governed by both the relative reaction rates of the *syn* and *anti* isomers and the rate of interconversion. If this was true, initiators based on non-fluorinated alkoxides were expected to allow the preparation of the target polymer since they generally show fast *syn-anti* interconversion. As a matter of fact, Schrock initiators containing non-fluorinated alkoxides such as  $\text{Mo}(N\text{-}2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OCH}(\text{CH}_3)_2)_2$ ,  $\text{Mo}(N\text{-}2,6\text{-Me}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OC}(\text{CH}_3)_3)_2$ , and  $\text{Mo}(N\text{-}2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OC}(\text{CH}_3)_3)_2$  could be used for the living

polymerization of DEDPM to produce poly(ene)s solely based on five-membered rings [32,33]. Due to a significantly improved coplanarity, values for  $N_{\text{eff}}$  up to 52, corresponding to a  $\lambda_{\text{max}}$  of 592 nm (THF), were realized. These poly(ene)s exhibited a reversible thermochromic behavior and excellent film-building properties. Poly(DEDPM) $_{10 < n < 90}$  showed glass transition temperatures ( $T_g$ ) around 26 °C and was stable under air over months in the solid state as well as in solution (e.g.  $\text{CH}_2\text{Cl}_2$ ). In addition, poly(DEDPM) $_{10 \leq n \leq 90}$  was found to be thermally stable up to 185 °C under helium [32].

### 2.2. Polymerization of chiral monomers

In order to retrieve more accurate information about the actual configuration of the poly(ene) and the relative orientation of the repetitive units (i.e. tacticity), we performed a cyclopolymerization using the chiral monomer 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxy carbonyl-1,6-heptadiyne (**12**). The use of such a chiral monomer reduces the elements of symmetry one might detect during diade or triade interpretation (i.e. mirror plane, center of inversion, center of rotation) to one single element (i.e. center of rotation). Performing a standard triade interpretation with poly-**12**, an alternating *cis-trans* conformation was assigned to the polymer. Additionally, a highly tactic base was derived from the  $^{13}\text{C}$ -NMR spectrum. Unfortunately, due to the absence of coupling constants in a 500 MHz  $^1\text{H}$ - $^1\text{H}$ -correlated spectrum, we could not unambiguously distinguish between an iso- or syndiotactic structure. Nevertheless, these new poly(1,2-cyclopent-1-enylvinylene)s are the first poly(ene)s with such a highly ordered structure.

### 2.3. Other initiators

An important aspect in the large-scale synthesis of any material is costs. Despite their superiority, Schrock initiators are characterized by limited commercial availability and high sensitivity versus oxygen and moisture. Classical ternary systems have been investigated for this reason, yet were not able to compete with Schrock systems in terms of materials properties (i.e. definition, purity, etc.) so far. Nonetheless, we were still interested whether one might use classic systems in cyclopolymerization, and in particular for the synthesis of poly(ene)s solely consisting of five-membered rings. While standard ternary systems behaved as expected, yielding ill-defined polymers without any control over molecular weight, the addition of quinuclidine turned out to be a milestone in this area of research [33]. Thus, DEDPM was cyclopolymerized by  $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn-EtOH-quinuclidine}$  (1:1:5:1) and  $\text{MoOCl}_4\text{-}n\text{-Bu}_4\text{Sn-EtOH-quinuclidine}$  (1:1:2:1) to produce poly(DEDPM) exclusively based on 1,2-cyclopent-1-enylvinylene units. The initiator efficiency of  $\text{MoOCl}_4\text{-}n\text{-Bu}_4\text{Sn-EtOH-quinuclidine}$  (1:1:2:1) was as high as 91 %, the highest value ever reported for such systems, whereas the efficiency for the corresponding  $\text{MoCl}_5$ -based initiator was  $\leq 67\%$ . The absorption

maximum  $\lambda_{\max}$  for poly(DEDPM) was 587 nm, close to that one found for poly(DEDPM) prepared by a Schrock initiator (592 nm). A maximum effective conjugation length  $N_{\text{eff}}$  of 49 (THF) was calculated therefrom. A plot of number of monomers ( $N$ ) added versus molecular weights ( $M_n$ ) as determined by light scattering showed a linear dependence for both initiators. Multistage polymerizations of DEDPM indicated for both initiator systems that the catalytic species were active for at least 6 h in the presence of monomer yet did not fulfill the criteria of a living polymerization, i.e. stability of the active chain end in the absence of monomer. This must be regarded as one of the most significant disadvantages compared to well-defined Schrock initiators, which in most cases provide truly living polymerizations.

### 3. Summary

Cyclopolymerization offers access to conjugated polymers with cyclic recurring units. A large variety of monomers with different functionalities can be subject to this polymerization technique. The careful design of initiators allows the synthesis of stereoregular polymers, in addition the tuning of the initiator also allows sometimes dramatic changes in polymerization kinetics. In contrast to the parent poly(acetylene)s, poly(ene)s prepared by cyclopolymerization are remarkable stable and are therefore expected to play a more important part in those areas that are now dominated by poly(*p*-phenylenevinylene)s and poly(pyrrole)s, respectively.

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