

Polymerization of 1,6-diynes — Scope, structure and optical properties

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This minireview describes the recent advances in the field of 1,6-diyne polymerizations by olefin metathesis catalysts as well as the synthesis and characterization of related short-length oligoenes with respect to their structure and optical properties.

Keywords: Polyenes, polyacetylene, olefin metathesis, electron absorption, molybdenum, ruthenium, alkylidene complexes

Polymers with a fully conjugated backbone are of particular importance due to their semi-conductivity and their interesting optical properties¹. Such materials are of high interest due to their potential as organic conductors, in photonic switches, light-emitting devices, as well as in electronic devices. The structurally simplest polymer which a fully conjugated C=C double bond system is poly(acetylene)². It is prepared in a straight-forward fashion and shows high electrical conductivity upon doping. It exhibits a high third-order susceptibility, which renders it an interesting candidate for photonic devices. Nevertheless, this material has found only very limited application due to its poor solubility in common organic solvents and lack of stability under atmospheric conditions. Stability and solubility, in particular, are greatly improved in polyacetylenes bearing suitable substituents.

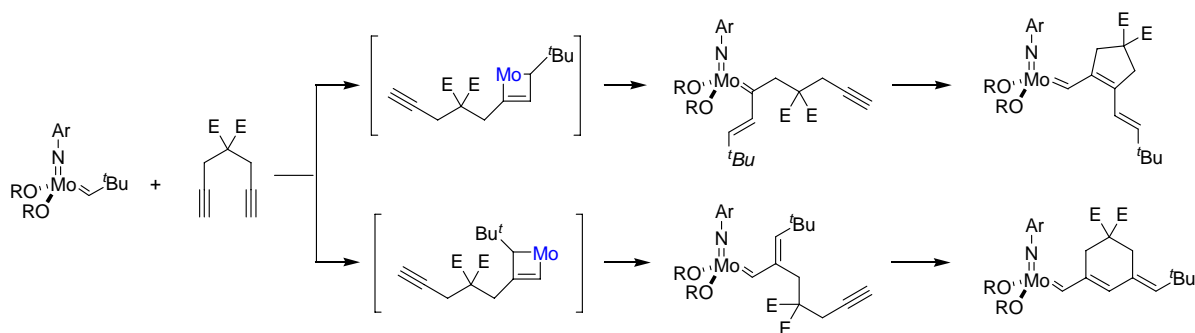
The extend of π -electron delocalization in one-dimensional polyacetylenes is directly reflected in the corresponding colour ranging from yellow over red and purple to a black, metallic appearance. Theoretical models correlating colour, fluorescence, and excited state description with the size of the conjugated system have been developed in the past and refined in recent years³. In order to validate such theoretical models a series of analogously substituted, homologous oligoenes must be available and their corresponding optical properties investigated in detail. A significant number of oligoenes with different length are found in nature playing a pivotal role for photosynthesis. Herein, carotenoids harvest light

energy and direct it towards the chlorophyll pigments in the reaction centres. Additionally, these compounds protect the reaction centres from oxidative damage by triplet quenching. Likewise, oligoenes are also essential for the process of vision and biological signalling colours. Despite this abundance of oligoenes in nature the compounds are not completely analogously substituted impeding proper theory validation. In order to prepare such a homologous series, new synthetic methodologies for the synthesis of soluble, defined short oligoenes and highly controlled polymerization with minimal regioerrors have been developed.

Polymerization of 1,6-diynes

In contrast to the low stability and solubility of poly(1-alkynes), polymers prepared from 1,6-diynes offer several advantages as they are readily soluble in common organic solvents and only slowly degrade upon exposure to oxygen⁴. The cyclopolymerization of 1,6-heptadiynes by olefin metathesis generates a polyacetylene backbone with annulated five- or six-membered rings (**Scheme I**). A polymer with exclusive incorporation of cyclopentene-rings is most desired since such materials show a higher degree of planarity and effective conjugation. In contrast, polymers with two adjacent cyclohexene moieties suffer from significant A^{1,3}-strain resulting in a twist of the polymer backbone.

In 1992, Schrock and Fox first prepared regular polymers from diethyl dipropargyl malonates (DEDPM) using catalysts like Mo(NAr)



Scheme I — Polymerization of 1,6-heptadiynes by olefin metathesis catalysts

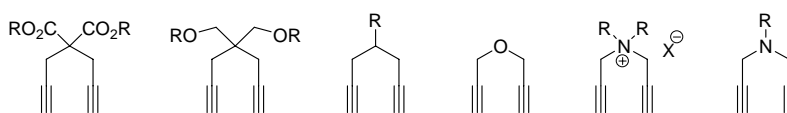


Figure 1 — Examples of diynes for polyacetylene formation

($\text{CHCR}^1\text{R}^2\text{R}^3$)(OR^4)₂ (Ref. 5). In particular, the use of catalysts like $\text{Mo}(\text{N}-2\text{-}t\text{-BuC}_6\text{H}_4)(\text{CHCMe}_3)(\text{O}_2\text{CCPh}_3)_2$ bearing very bulky carboxylate ligands resulted in DEDPM polymers with exclusive formation of six-membered rings⁶. Buchmeiser and co-workers later showed that molybdenum complexes like $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OCMe}_3)_2$ effectively polymerize DEDPM to give polymers incorporating > 95% cyclopentene units⁷. Such materials typically show a λ_{max} -value which is 20-30 nm higher compared to polymers consisting of cyclohexene substructure. Instead of using molybdenum neopentylidene or neophylidene complexes the employment of sterically less encumbered molybdenum alkylidene complexes allows for the preparation of materials with narrower polydispersities⁸. It was also demonstrated that suitably tuned ruthenium-based catalysts effectively promote the formation of polymers with predominant incorporation of cyclopentene units. In this respect, Grubbs-Hoveyda catalysts with trifluoroacetate ligands proved to be superior^{7g}. Recently, Buchmeiser and coworkers significantly extended the scope of diyne cyclopolymerization including *N,N*-dipropargylammonium salts and dipropargyl ethers using ruthenium-based metathesis catalysts giving polymeric materials with sole incorporation of five-membered rings (**Figure 1**) (Ref. 9). Noteworthy, polymerization of *N,N*-dipropargylamines turned out to be problematic under the reported reaction conditions as intramolecular stabilization of the intermediates and back-biting was observed. However, cyclopolymerization of dipro-

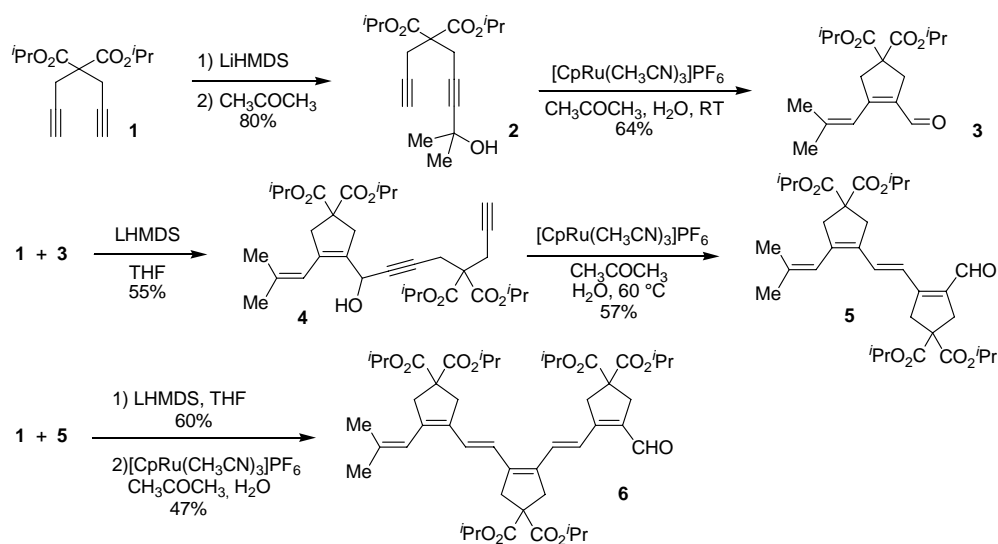
pargyl amines was reported to occur in moderate yields using catalysts like $\text{WCl}_6/\text{EtAlCl}_2$ or MoCl_5 (Ref. 10).

Synthesis of oligoenes

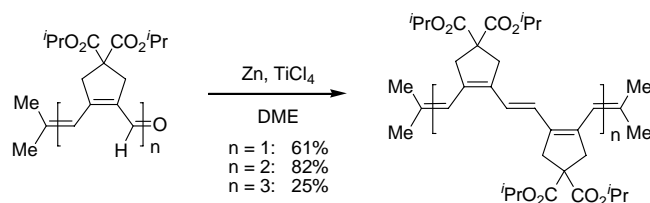
Despite the success in the field of diyne cyclopolymerization and the preparation of materials with long extended π -systems a direct correlation of the length of the conjugated system with the electron absorbance is hampered by the fact that even in well-controlled polymerization processes always a mixture of compounds with different chain length is obtained. Therefore, a new methodology for the direct synthesis of such compounds in pure form was developed^{11,12}. Although small oligoenes up to nine double bonds can be isolated in pure form from mixtures obtained by early-quenched polymerization reactions, longer oligoenes have to be prepared by a different, general protocol. Starting from the acetonide of di-2-propyl-dipropargyl malonate the corresponding dienal **3** was prepared using $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ as described by Trost and coworkers (**Scheme II**, Ref. 13).

By subsequent addition of di-2-propyl-dipropargyl malonate and Ru-catalyzed ring closure the corresponding homologous enals are accessible (referred to as dimeric **5**, and trimeric aldehyde **6**, respectively). By dimerization of these aldehydes under McMurry-conditions the corresponding dimeric, tetrameric, and hexameric oligoenes are prepared in a straightforward manner (**Scheme III**).

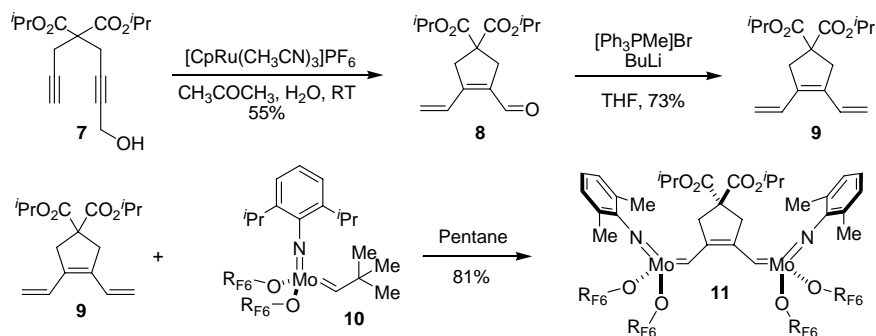
It was found that di-2-propyl malonates work very well since the corresponding products are more stable



Scheme II — Synthesis of oligoaldehydes



Scheme III — Synthesis of even-membered oligoenes by reductive homo-coupling

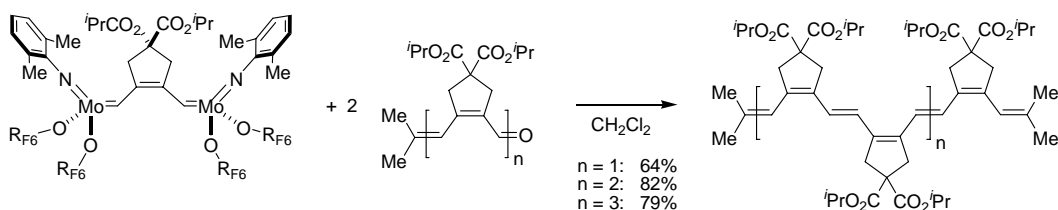


Scheme IV — Synthesis of bimetallic monomer complex

than the ethyl esters and highly crystalline facilitating purification. In principle, by repetition of this sequence even longer oligoenes are accessible. Nevertheless, for the synthesis of oligoenes with an odd number of monomeric units a different approach had to be developed. For this hydroxymethylene di-2-propyl diproparyl malonate **7** was cyclized using $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ to give dienal **8** with was

transformed to triene **9** in a Wittig reaction. From triene **9**, a bimetallic complex **11** was prepared by reaction with two equivalents of molybdenum alkylidene complex **10** ($\text{R}_{\text{F}_6} = \text{C}(\text{CF}_3)_2\text{Me}$, **Scheme IV**).

Complex **11** incorporating one monomeric moiety was then reacted with two equivalents of monomeric **10** to permit the isolation of trimeric, pentameric, and



Scheme V — Synthesis of odd-membered oligoenes

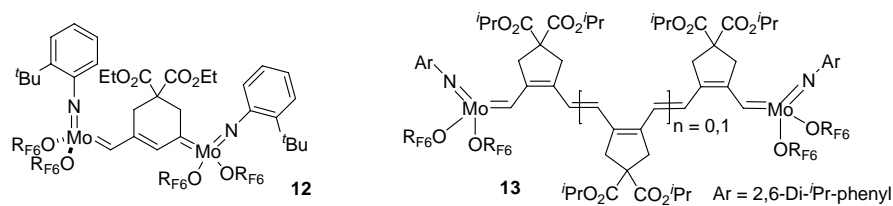


Figure 2 — Bimetallic molybdenum alkylidene complexes

heptameric oligoene, respectively (Scheme V). Thus, a homologically substituted sequence from dimeric to heptameric oligoene with a number of double bonds up to 15 was synthesized in pure form.

Since it was of interest whether the incorporation of a single cyclohexene ring into the conjugated system would result in a change in the electron absorption properties, a bimetallic complex **12** incorporating this ring size was prepared and transformed into the mixed trimeric oligoene by reaction with the monomer aldehyde **3** (Figure 2).

By a similar synthetic approach bimetallic complexes **13** incorporating dimeric and trimeric moieties were prepared (Figure 2, ref. 14). Herein, bimetallic complexes were treated with monomeric aldehyde **8** lacking methyl group protection at the terminal double bond. Repetition of this sequence of reactions with a molybdenum alkylidene and the aldehyde allowed the preparation of the corresponding pentamer. In order to suppress deleterious metathesis side reactions and to obtain materials with higher purity bimetallic molybdenum complex adducts with trimethylphosphine and quinuclidine were investigated. Although product formation was significantly slower the products were indeed formed in higher purity¹⁵. The crystal structures of the bimetallic complexes provided some insight into the planarity of conjugated systems along with the crystal structures of the dimeric and trimeric oligoenes lacking the two methyl groups on each terminal olefinic bond. In all cases, it was demonstrated that the olefinic double bonds have alternating *cis-trans*

geometry and that the conjugated system shows a high degree of planarity.

Optical properties

The synthesis of a completely homologically substituted series of oligoenes allowed the validation of quantum-mechanical models for the prediction of the electron absorption behaviour¹⁵. A simple approximation for the dependency of the strongly allowed $S_0 \rightarrow S_2$ transitions to the number N of double bonds of the conjugated system is given by the equation (refs. 16,17):

$$E(N) = A + B/N$$

Plots of the $E(0-0)$, $E(0-1)$, and $E(0-2)$ transition energies for the $S_0 \rightarrow S_2$ transition over $1/N$ are highly linear and allow extrapolation of N to infinity to give a limit of $\lambda_{\max} \approx 650$ nm in dichloromethane (Figure 3).

Conclusion

Using suitable transition metal catalysts 1,6-diynes can efficiently be polymerized to give well-defined polyacetylene polymers with high degree of planarity of the polymer backbone concomitant with high conductivity. By synthesizing pure homologically substituted oligoenes with increasing number of olefinic double bonds quantum-mechanical models for the explanation of electron absorption behaviour could be validated and applied to polyacetylenes. The deepened understanding of conjugated π -systems

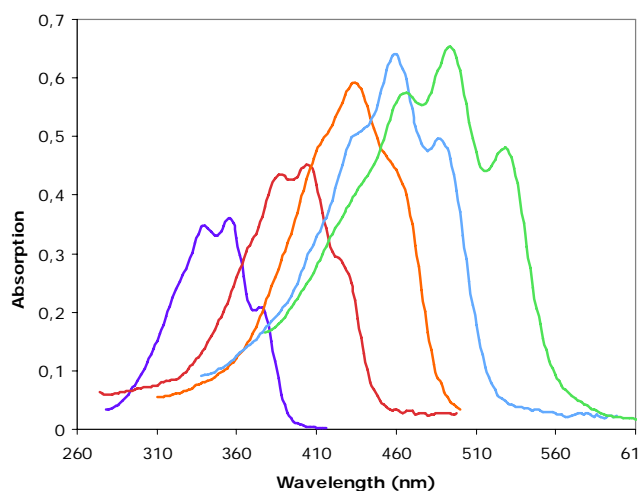


Figure 3 — Electron absorption spectra of oligoenes [dimer (purple), trimer (red), tetramer (orange), pentamer (blue), heptamer (green)]

should also provide more insight into the complex biologically important processes like vision and photosynthesis.

References

- (a) Friend R H, Gymer R W, Holmes A B, Burroughes J H, Marks R N, Taliani C, Bradley D D C, Dos Santos D A, Brédas J-L, Lögdlund M & Salaneck W R, *Nature (London)*, 397, **1999**, 121; (b) Coropceanu V, Cornil J, da Silva Filho D A, Olivier Y, Silbey R & Brédas J-L, *Chem Rev*, 107, **2007**, 926; (c) Shirota Y & Kageyama H, *Chem Rev*, 107, **2007**, 953; (d) Menard E, Meitl M A, Sun Y, Park J-U, Shir D J-L, Nam Y-S, Jeon S & Rogers J A, *Chem Rev*, 107, **2007**, 1117; (e) Günes S, Neugebauer H & Sariciftci N S, *Chem Rev*, 107, **2007**, 1324.
- (a) Lam J W Y & Tang B Z, *Acc Chem Res*, 38, **2005**, 491; (b) Masuda T, *J Polym Sci A*, 45, **2007**, 165; (c) Gal Y-S, Jin S-H & Park J-W, *J Polym Sci A*, 45, **2007**, 5679.
- Christensen R L, 'The Electronic States of Carotenoids', in *The Photochemistry of Carotenoids*, Vol 8, edited by H A Frank, A J Young, G Britton and R J Cogdell (Kluwer Academic Publishers, Dordrecht), p.137, **1999**.
- (a) Gibson H W, Bailey F C, Epstein A J, Rommelmann H, Kaplan S, Harbour J, Yang X-Q, Tanner D B & Pochan J M, *J Am Chem Soc*, 105, **1983**, 4417; (b) Choi S-K, Gal Y-S, Jin S-H & Kim H K, *Chem Rev*, 100, **2000**, 1645; (c) Buchmeiser M R, *Monatsh Chem*, 134, **2003**, 327; (d) Lam J W Y & Tang B Z, *J Polym Sci A*, 41, **2003**, 2607; (e) Krause J O, Wang D, Anders U, Weberskirch R, Zarka M T, Nuyken O, Jaeger C, Haarer D & Buchmeiser M R, *Macromol Symp*, 217, **2004**, 179; (f) Gal Y-S & Choi S K, *Polymer (Korea)*, 11, **1987**, 563; (g) Ryoo M-S, Lee W-C & Choi S-K, *Macromolecules*, 3, **1990**, 3029; (h) Jeon S-J, Cho D-J, Shim S-C, Kim T-J & Gal Y-S, *J Polym Sci A*, 7, **1999**, 877; (i) Naidu B V K, Oh B-H, Nam D-H, Hwang C-K, Jin S-H, Lim K-T, Wang H-S, Lee J W & Gal Y-S, *J Polym Sci*, 44, **2006**, 1555.
- (a) Fox H H & Schrock R R, *Organometallics*, 11, **1992**, 2763; (b) Fox H H, Wolf M O, O'Dell R, Lin B L, Schrock R R & Wrighton M S, *J Am Chem Soc*, 116, **1994**, 2827.
- (a) Schattenmann F J, Schrock R R & Davis W M, *J Am Chem Soc*, 118, **1996**, 3295; (b) Schrock R R, Tonzetich Z J, Lichtscheidl A G & Müller P, *Organometallics*, 27, **2008**, 3986.
- (a) Anders U, Nuyken O, Buchmeiser M R & Wurst K, *Angew Chem Int Ed (Engl)*, 41, **2002**, 4044; (b) Anders U, Nuyken O, Buchmeiser M R & Wurst K, *Macromolecules*, 35, **2002**, 9029; (c) Anders U, Nuyken O & Buchmeiser M R, *J Mol Catal A: Chem*, 213, **2004**, 89; (d) Krause J O, Zarka M T, Anders U, Weberskirch R, Nuyken O & Buchmeiser M R, *Angew Chem Int Ed (Engl)*, 42, **2003**, 5965; (e) Krause J O, Nuyken O & Buchmeiser M R, *Chem Eur J*, 10, **2004**, 2029; (f) Krause J O, Wang D, Anders U, Weberskirch R, Zarka M T, Nuyken O, Jäger C, Haarer D & Buchmeiser M R, *Macromol Symp*, 217, **2004**, 179; (g) Halbach T S, Krause J O, Nuyken O & Buchmeiser M R, *Macromol Rapid Commun*, 26, **2005**, 784; (h) Mayershofer M G, Nuyken O & Buchmeiser M R, *Macromolecules*, 39, **2006**, 3484.
- Adamchuk J, Schrock R R, Tonzetich, Z J & Müller P, *Organometallics*, 25, **2006**, 2364.
- (a) Vygodskii Y S, Shaplov A S, Lozinskaya E I, Vlasov P S, Malyschkina I A, Gavrilova N D, Kumar P S & Buchmeiser M R, *Macromolecules*, 41, **2008**, 1919; (b) Kumar P S, Wurst K & Buchmeiser M R, *J Am Chem Soc*, 131, **2009**, 387.
- Gal Y-S, Lee W-C, Jin S-H, Lim K T, Jang S-H, Lyoo W S, Han E & Kim S Y, *Macromol Res*, 15, **2007**, 267.
- Czekelius C, Hafer J, Tonzetich Z J, Schrock R R, Christensen R L & Müller P, *J Am Chem Soc*, 128, **2006**, 16664.
- Fox H H, Lee J-K, Park L Y & Schrock R R, *Organometallics*, 12, **1993**, 759.
- (a) Trost B M & Rudd M T, *J Am Chem Soc*, 127, **2005**, 4763; (b) Trost B M & Older C M, *Organometallics*, 21, **2002**, 2544.
- Scriban C, Schrock R R & Müller P, *Organometallics*, 27, **2008**, 6202.
- For a discussion on the electrochemical properties of poly(1,6-diynes), see Gal Y-S, Lee W-C, Lyoo W S, Jin S-H, Lim K W, Park Y-I & Park J-W, *Int J Photoenergy*, **2008**, 276027.
- Christensen R L, Fakash A, Meyers J A, Samuel I D W, Wood P, Schrock R R & Hultsch K C, *J Phys Chem*, 108, **2004**, 8229.
- Knoll K & Schrock R R, *J Am Chem Soc*, 111, **1989**, 7989.