Invited Review

Towards the Design of New Materials: Regio- and Stereoselective (Cyclo-) Polymerization of 1-Alkynes and 1,6-Heptadiynes

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Summary. The metathesis polymerization, respectively cyclopolymerization, of 1-alkynes and 1,6-heptadiynes using well-defined group VIA transition metal initiators is summarized. For purposes of comparison, selected quaternary catalytic systems used as alternatives as well as the properties of the resulting materials will be presented. Special consideration is given to the mechanistic advancements that have been made during the last decade, which allow the tailor-made synthesis of conjugated materials with interesting optical and electronic properties.

Keywords. Metathesis; Polymerizations; Metallocenes; Organometallics; Homogeneous catalysis.

Introduction

Fully conjugated polymers based on polyenes represent interesting materials for many applications in the fields of organic (semi-) conductors, optoelectronics, and photonics [1–6]. Unfortunately, polyacetylene as the simplest representative of this class of compounds suffers from insolubility, lack of processability, and insufficient stability versus oxygen. Nevertheless, substituted polyacetylenes overcome these problems. They are accessible *via* ADMET (acyclic diene metathesis) polymerization starting from α,ω-dienes [7–12], *via* ROMP (ring-opening metathesis polymerization) of polyene precursors [13–23] or, preferably, *via* alkyne polymerization techniques (Scheme 1) [24–31].

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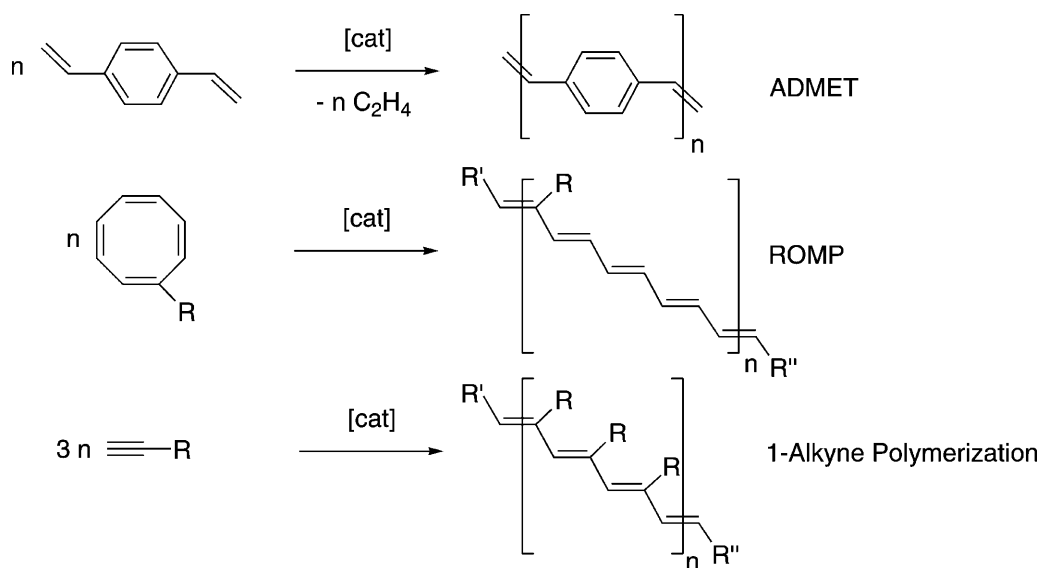
Scheme 1

While the ADMET route is preferably used nowadays 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. Though classic ternary systems can in principle be used for these purposes, terminal acetylenes are best polymerized by well-defined *Schrock*-type metathesis initiators to yield conjugated polyenes. In these materials, the degree of conjugation strongly depends on the electronic as well as steric nature of the substituents in the starting alkyne.

The desired coplanarity of the double bonds, a prerequisite for most applications, is described best by the effective conjugation length (N_{eff}). It is a measure for the number of coplanar double bonds in a conjugated system resulting from the overlap of the p_z-orbitals. Highly conjugated systems show narrow bandgaps between HOMO and LUMO, which result in low-energy charge-transfer (CT) bands. As a consequence, these materials exhibit strongly bathochromic shifts in absorption. In the following, a few recent 1-alkyne polymerization-based examples will be summarized and shall serve as illustrative examples for the tailor-made synthesis of conjugated polyenes.

Polymerization of Metallocene-Substituted 1-Alkynes

Besides of other intriguing properties, such as planar chirality, metallocenes are of interest because of their considerable *Lewis* basicity. Their direct or conjugative attachment to a polymer chain should in due consequence enhance the electron density along the main chain and therefore lower the HOMO–LUMO band gap. In addition, for nonlinear optical materials, *e.g.* used for frequency doubling, modulation, and switching, organometallic compounds,

metallocene based monomers, and polymers represent interesting materials for three reasons:
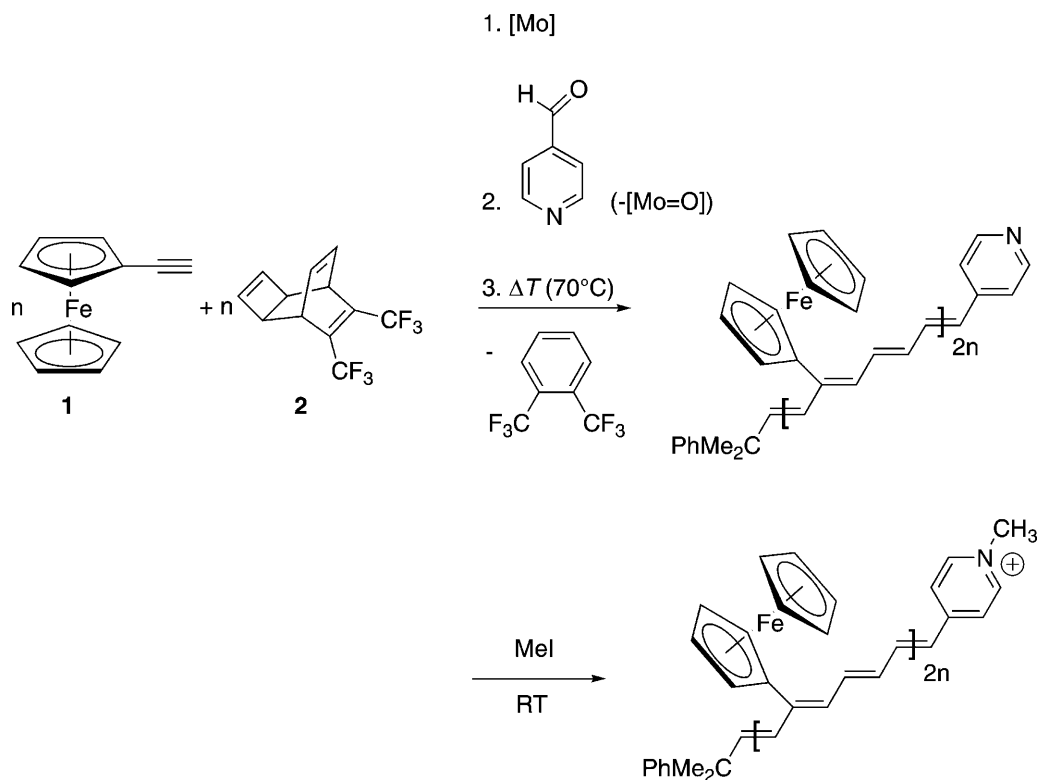
i) The compounds show metal-ligand (*M*–*L*) and *L*–*M* charge transfer (CT) bands in the UV-VIS region. These transitions are very often associated with large 2nd order nonlinearities.
ii) Intense color (and therefore high transition dipole moments) are responsible for high 2nd order nonlinearities.
iii) As metallocenes are stable in different oxidation states and β is expected to raise with $N^{3.05}$ ($N =$ number of carbons in the chain) for a charged species, cationic and anionic monomers and polymers seem to be promising compounds. Especially γ shows a high dependency on N ($\sim N^q$ with $5.0 < q < 5.25$) in charged systems.

Taking these features into consideration, the polymerization of the simplest metallocenyl alkynes, ferrocenyl- and ruthenocenylacetylene, was chosen as a starting point. A lot of attempts to polymerize ferrocenylacetylene (or better ethynylferrocene, (**1**)) in a controlled way have been reported [32, 33]. Nevertheless, none of the investigated systems allowed a high yield synthesis of poly(ethynylferrocene) with satisfying physical properties (especially with regard to polydispersity (PDI), solubility, and molecular weight). In all cases oligomers with low molecular weight and high PDIs (5–10) or insoluble, brown, probably partially oxidized, barely characterized polymers were obtained. No relevant information about the general polymer structure or possible cross-linkage was accessible at all. Based on the encouraging results in 1-alkyne polymerization obtained with well-defined Mo-based initiators [24, 25, 27, 28, 34], usually referred to as "*Schrock* initiators", we investigated to which extent these might be useful for the preparation of metallocenyl-substituted polyenes.

Ethynylferrocene and ethynylruthenocene itself are, due to the *Lewis* base character of the metallocene moiety, highly reactive terminal acetylenes. In contrast to the phenyl analogue they can in principle be polymerized with a large variety of classic *Schrock* initiators. Nevertheless, in order to obtain a well-defined polymerization system that offers in due consequence access to tailor-made polymers, one needs to keep in mind the two possible reaction pathways for 1-alkyne polymerization (Scheme 2).

Thus, the monomer can insert into the metal-carbene double bond via α- and via β-insertion. In principle, both insertion modes result in the formation of a conjugated polyene. Nevertheless, in particular with highly reactive monomers, β-insertion often results in the formation of ill-defined polymers because of the subtle differences in reactivity of the initiator and the first insertion products. If the rate constant for polymerization (k_p) is much larger than the rate constant for initiation (k_i) in these systems, only a low percentage of the initiator forms a propagating polymer chain, which directly results in a loss of control over molecular weight. One observes the precipitation of virtually insoluble polymer from the reaction mixture within a few seconds after initiation. At this point it should be mentioned that the ratios of k_i/k_p are conveniently determined *via* ^{1}H NMR [35] in case the polymerization system fulfills the criteria of a truly "living" system

Scheme 2

[36–38]. Based on the concept of "small alkoxides" developed by *Schrock* [28], where initiators that contain small alkoxide ligands should favor α-addition due to the absence of steric interaction between the monomer and these alkoxides, Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$ turned out to be the most satisfying initiator among many other investigated systems. It allowed the synthesis of homo- as well as of copolymers in high yield and with high selectivity in terms of inser-tion mode and consequently head to tail connectivity [39]. The polymerization systems are truly living, allowing the synthesis of the corresponding polyenes with designed molecular weight and PDIs typically <1.3. As a consequence of the living character, end-group functionalization was carried out with various alde-hydes including ferrocenealdehyde and pyridine-4-aldehyde (see also Scheme 3). Unfortunately, values for N_{eff} obtained with poly(ethynylferrocene) and poly(ethy-nylruthenocene) in *THF* were quite low (<10). This is a direct consequence of the presence of bulky groups in linear polyacetylenes, which often prevent high values for N_{eff} due to 1,3-steric interactions.

1-Alkyne-Ring-Opening Metathesis-Copolymerization

As an alternative, copolymers of alkynes bearing bulky substituents with *TCDTF6* (7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene, (**2**)) were synthe-sized. In the course of this copolymerization, usually referred to as the "*Durham Route*", the "Feast-momomer" is introduced into the polymer main chain and sub-sequently converted into three unsubstituted, conjugated double bonds via a thermally induced *retro-Diels Alder* reaction (Scheme 3) [39].

In the case of perfectly alternating copolymers, a sufficient separation of one substituent from the other is achieved. In the case of ferrocene-substituted alkynes, these copolymers exhibit a remarkable stability due to steric protection by the bulky substituent, despite the large number of unsubstituted double bonds. This directly translates into a significant bathochromic shift of the absorption, which can even be enhanced by endgroup functionalization, *i.e.* quaternization. Such a

Scheme 3

quaternization, simply carried out by treatment with methyl iodide, results in the formation of highly conjugated charged polyenes ($\lambda_{\max} = 595\,\text{nm}$, $N_{\text{eff}} = 54$, $CHCl_3$), which exhibit a strong solvochromic behavior. The preparation of such perfectly alternating copolymers using ROMP and 1-alkyne polymerization strongly depends on the ratios $k_{i(Ai)}/k_{i(Bi)}$ as well as $k_{p(Ai)}/k_{p(Bi)}$, where $k_{i(Ai)}$, $k_{i(Bi)}$, $k_{p(Ai)}$, and $k_{p(Bi)}$, *etc.*, represent the rates of insertion and the rates of propagation of the two monomers A (ethynylferrocene) and B (*TCDTF6*) at the corresponding insertion step i ($i = 1, 2, 3, \ldots$ DP = degree of polymerization) with the active carbene, respectively. Ideally, $k_{i(Ai)} \gg k_{i(Bi)}$ if the last monomer that was inserted was B and *vice versa*. These rate constants can be controlled rather by serendipity than on purpose, significantly limiting the applicability of this concept.

As a direct consequence, the synthesis of highly conjugated polyenes *via* the preparation of homopolymers from a single functional monomer still seems highly preferable. For that purpose, the substituted alkyne must fulfill at least two requirements in order to be suitable for the synthesis of polyenes with high values for N_{eff}. On one hand, the substituent should possess an electron-donating character in order to activate the carbon–carbon triple bond and make it more reactive towards a transition metal alkylidene, which usually speeds up initiation. In addition, a *Lewis*-base character provides an enhanced electron-density in the resulting polymer backbone. On the other hand, the substituent should be ideally designed such that the conjugated double bonds in the resulting polyene are as coplanar

as possible. In principle this may be achieved by reducing the steric interaction between the substitutents, *i.e.* by introducing spacers.

Spaced Metallocenylalkynes

4-(Ferrocenylethynyl)-4′-ethynyltolan: A Tailor-Made 1-Alkyne for Mechanistic Investigations

As already briefly mentioned, *Schrock et al.* proposed that the use of "small", electron-withdrawing alkoxides favors α-addition, whereas larger alkoxides should give raise to β-addition due to sterical hindrance. This concept proofed to be useful particularly in the polymerization of *o*-substituted phenylacetylenes, such as *o*-trimethylsilylphenylacetylene (*o-TMSPA*) and related compounds [28, 30], yet other terminal acetylenes (*e.g.* the above mentioned compounds ethynylferrocene and ethynylruthenocene) behaved in a different way, *i.e.* adding via α-insertion despite the use of large alkoxides in Mo(*N*-2,6-*Me*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*) (OC*Me*(CF$_3$)$_2$)$_2$, and *vice versa* with metal carbenes containing small alkoxides such as Mo(*N*-2,6-*Me*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*)(OC$_6$F$_5$)$_2$ · quinuclidine [39]. Evidently, not only the initiator, but also the monomer is part of the game. Thus, acetylenes containing electron withdrawing groups do not readily react even with one of the most reactive molybdenum based initiator, Mo(N-2,6-*i*-*Pr*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*) (OC*Me*(CF$_3$)$_2$)$_2$. Interestingly enough, neither do other either electron-rich, yet sterically hindered acetylenes, such as *t*-butylacetylene. As the ferrocene moiety obviously possesses some special properties with regard to the reactivity of the monomer itself, the polymerization of a tailor-made monomer, 4-(ferrocenylethy-nyl)-4′-ethynyltolan, a diethynyltolan-spaced homologue of ethynylferrocene, appeared promising for two reasons (Fig. 1).

First, this compound is sterically demanding and should therefore, if there is any reactivity at all, undergo β-addition. Second, it contains the ferrocene moiety, yet the reactivity of the terminal alkyne group is reduced because of the ethynyl-tolan spacer. Thus, the monomer is significantly less reactive than ethynylferro-cene, as the additional electron density is distributed over a larger π-system. As anticipated, this compound polymerized via β-addition using Mo(*N*-2,6-*i*-*Pr*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*)(OC*Me*(CF$_3$)$_2$)$_2$ as the initiator [40]. Evidence for this type of insertion was provided by ^{1}H NMR spectroscopy. Upon treatment of the initiator with 1 equiv. of the monomer, a sharp singlet for H$_\gamma$ appeared at 5.93 ppm. No coupling was observed. The signal for the terminal alkyne at 3.17 ppm disappeared and a new alkylidene resonance for H$_\alpha$ at 12.37 ppm appeared. Surprisingly, no signals for a second or third insertion product were observed, indicating a ratio of


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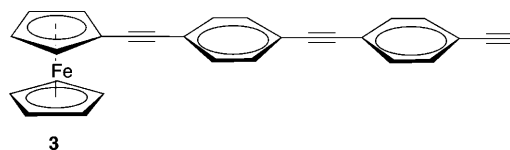
Fig. 1. 4-(Ferrocenylethynyl)-4′-ethynyltolan

$k_p/k_i \leq 1$. Beside the signals for H_α and H_γ, only one characteristic signal group for the ferrocene moiety of the first insertion product was observed. These NMR data were in accord with the living character of the polymerization, which was confirmed for the first time for a 1-alkyne polymerization that proceeded via β-addition, and indicated the importance of kinetic parameters (*i.e.* k_p/k_i) besides of insertion issues in order to maintain control over molecular weight. Consequently, and in contrast to other polymerizations proceeding *via* β-addition, the resulting materials containing up to 50 metallocene groups possessed excellent solubility and could be prepared with control over molecular weight and PDI (generally <1.3). For the first time there was access to the controlled synthesis of polyenes containing large side groups. Based on these encouraging results, we investigated whether this insertion and polymerization behavior was also true for other spaced 1-alkynes.

Tailor-Made Spaced Alkynes for Main Chain Tuning

In a further step, the conjugated ferrocenylacetylenes [2-(4-ethynylphenyl)vinyl] ferrocene (**4**), 1-(4-ethynylphenyl)-2-ferrocenyldiazene (**5**), and (2-ethynylphenyl) ferrocene (**6**) were synthesized (Fig. 2) [41].

The length and structure of these spacers had significant influence on the mode of insertion of the corresponding alkyne into the *Schrock*-carbene as well as on the structure of the resulting polyene. Compounds **4** and **5** underwent selective β-addition with both Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$ and Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$. This was not surprising, since their molecular structure was quite similar to that of **3** (Fig. 1). Interestingly, **6** turned out to be a sensitive probe for the steric (and electronic) situation of an initiator. Thus, polymerization proceeded via α-addition with Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$, while β-addition was observed with Mo(N-2,6-i-Pr_2-C_6H_3) (CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$. Since both initiators were based on identical alkoxides, an additional factor must be responsible for this observation. The transition state of both insertion modes provided some useful insight (Fig. 3).

As can be deduced therefrom, the 2-ferrocenylphenyl group gains maximum distance to the initiator end group (–CMe_2Ph) on the expense of steric interaction
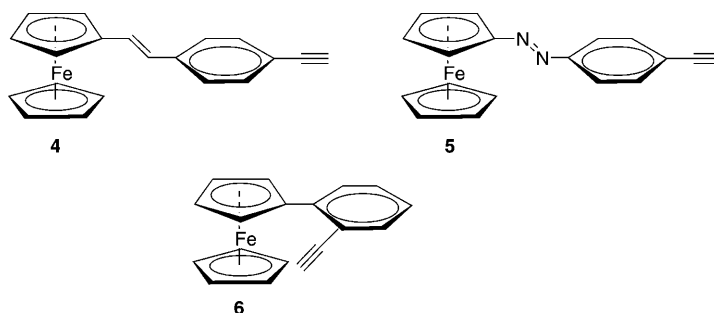
Fig. 2. Structures of [2-(4-ethynylphenyl)vinyl]ferrocene (**4**), 1-(4-ethynylphenyl-2-ferrocenyl-dia-zene (**5**), and (2-ethynylphenyl)ferrocene (**6**)
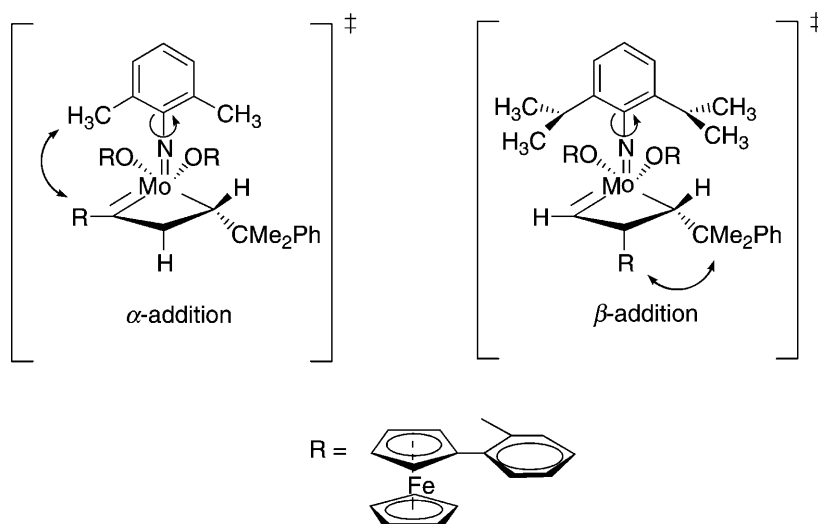
Fig. 3. Arylimido ligand-dependant insertion of **6**

with the comparable small methyl groups (chain end controlled, α-addition). In contrast, this is no longer possible in the case of the "large" isopropyl groups, the reaction is initiator controlled and proceeds via β-addition. This observation can only be made with o-substituted phenylalkynes with no steric interaction of the ferrocene substitutent with the hexafluoro-t-butoxide group.

For monomers (**4–6**) k_i was at least comparable to k_p, leading to truly living polymerization systems with good control over molecular weights. In terms of N_{eff}, polymers prepared from the linearly spaced monomers **4** and **5** possessed low effective conjugation ($N_{eff} < 10$, THF) while $poly$-**6** showed a significant bathochromic shift in absorption with a λ_{max} of 515 nm, corresponding to a N_{eff} of 17 (THF). π-stacking [42, 43] of the adjacent phenyl rings as proposed for (2-trimethylsilylphenyl)acetylene [28, 30] may serve as an explanation for the rather high value for N_{eff} compared to other metallocene-substituted polyenes, yet still lacks final proof.

In order to enhance effective conjugation lengths, a series of octamethyl-derivatized ferrocene-based 1-alkynes was synthesized (Fig. 4).

All monomers, [2-(4-ethynylphenyl)ethenyl]-1',2,2',3,3',4,4',5-octamethylferrocene (**7**), [2-(5-ethynylthien-2-ylethenyl]ferrocene (**8**), [2-(5-ethynylthien-2-yl)ethenyl]-1',2,2',3,3',4,4',5-octamethylferrocene (**9**), (E)-[2-(1'-ethynyl-2,2',3,3',4,4',5,5'-octamethylferrocenyl)ethenyl]-1',2,2',3,3',4,4',5-octamethylferrocene (**10**) and [2-(2-ethynylphenyl)ethenyl]-1',2,2',3,3',4,4',5-octamethylferrocene (**11**) polymerized via β-addition using Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OCMe(CF$_3$)$_2$)$_2$ as initiator. Nevertheless, again only the o-substituted analogue to **6**, [2-(2-ethynylphenyl)-ethenyl]-1',2,2',3,3',4,4',5-octamethylferrocene (**11**), allowed the synthesis of conjugated polyenes with values for N_{eff} of 20 (THF). In order to shed some light onto the principle question, whether the proposed *Lewis* base character of pendant or spaced ferrocenes really enhanced the electron density along the polyene backbone, ^{57}Fe *Mössbauer* experiments were carried out. Besides of the quadrupole splitting, in particular the isomer shift (IS) is a well-suited indicator for electron
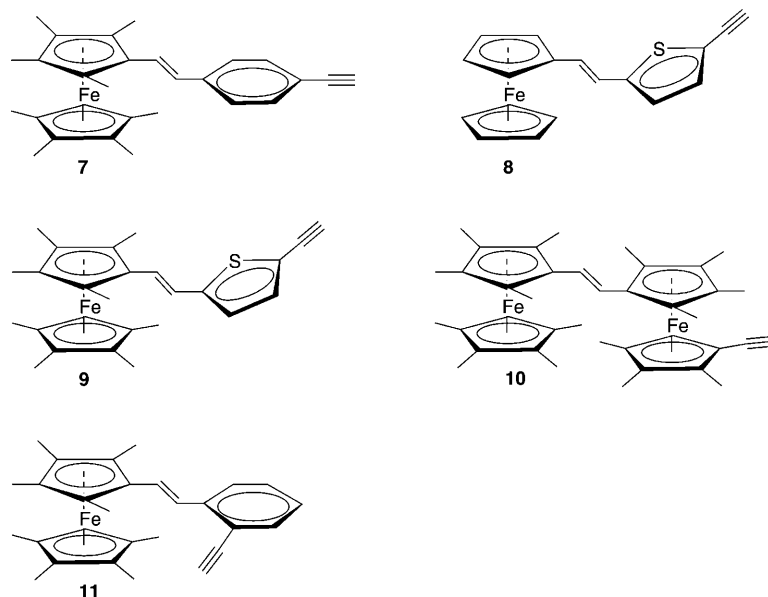
Fig. 4. Structures of [2-(4-ethynylphenyl)ethenyl]-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**7**), [2-(5-ethynylthien-2-yl)ethenyl]ferrocene (**8**), [2-(5-ethynylthien-2-yl)ethenyl]-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**9**), (E)-[2-(1′-ethynyl-2,2′,3,3′,4,4′,5,5′-octamethylferrocenyl)-ethenyl]-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**10**) and [2-(2-ethynylphenyl)ethenyl]-1′,2,2′,3,3′,4,4′,5-octamethylferrocene (**11**)

density around the metal core. If there was electron density transferred to the backbone, a positive deviation from the standard, in our case ferrocene and ethynylferrocene had to be observed. In fact, investigations revealed a significant positive deviation from the standard ISs, indicative for an electron transfer to the backbone [44]. It must be mentioned that cyclic voltammetry usually is the preferred method to answer such questions. Nevertheless, it was not applicable to ferrocene-containing polyenes since the pendant ferrocene units were addressed in a stepwise, yet non-reversible manner.

An application located in a completely different area of chemistry was accomplished taking advantage of the fact that per-alkylated ferrocenes form stable cations. Taking advantage of the ROMP-based grafting chemistry that was elaborated in our group [45–55], we constructed *poly*-**7** surface grafted silica for chromatographic purposes (Scheme 4) [56].

Briefly, living *poly*-**7** was surface grafted onto 2-norbornene-derivatized silica (Nucleosil 300-5). Finally, the pendant octamethylferrocene side group was oxidized with iodine to yield the corresponding poly(octamethylferricinium)-based support. It was successfully used in the separation of the oligonucleotides dT$_{12}$–dT$_{18}$ using anion chromatography.

In view of our initial goal, *i.e.* the synthesis of highly conjugated polyenes suitable for applications in photonics, electronics, and for sensors, we turned to an alternative polymerization technique that generally offers access to conjugated polyenes from a single monomer, yet prevents interaction of the side groups of adjacent repetitive units by a unique polymer construction.
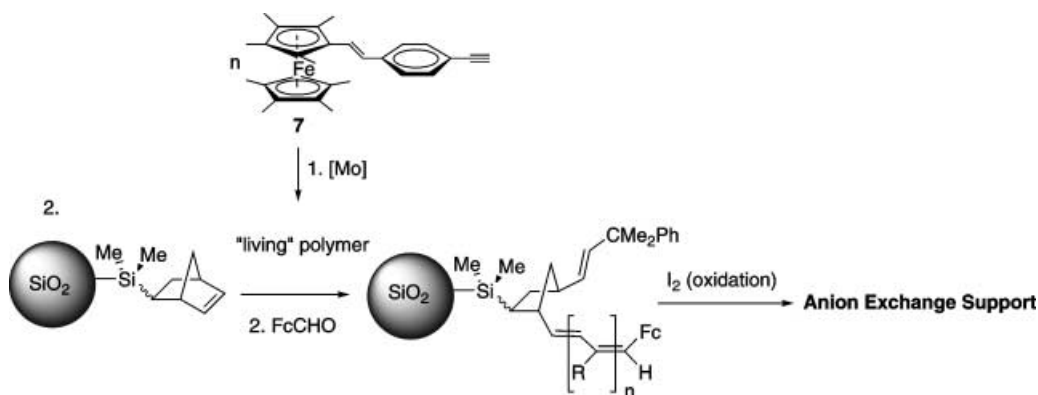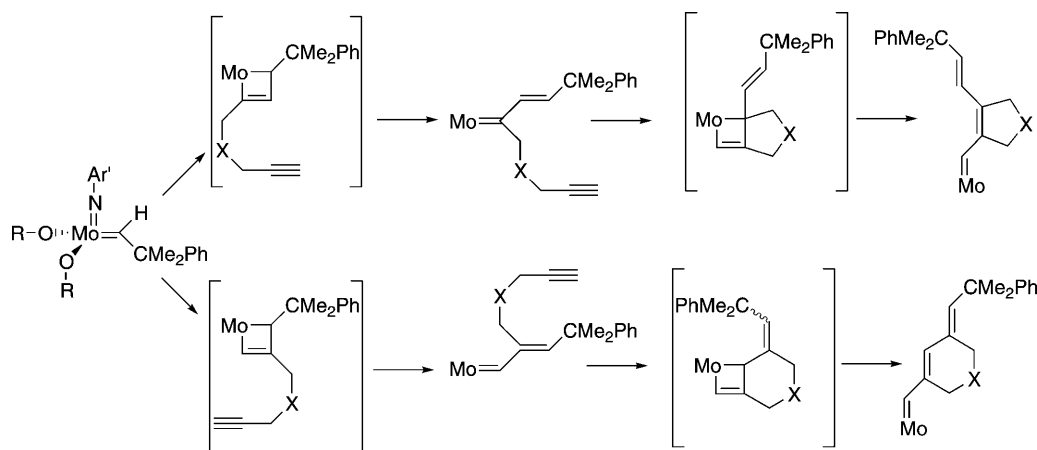
Scheme 4

Cyclopolymerization

The cyclopolymerization of 1,6-heptadiyne derivatives with substituents at the 4-position represents a powerful alternative to 1-alkyne polymerization [34, 57]. Polyenes with cyclic recurring units either based on five- or six-membered rings along the backbone are readily accessible by this approach. Usually this class of polymers displays [17, 19, 58–66] good solubility in common organic solvents (*e.g.* C_6H_6, toluene, CH_2Cl_2, $CHCl_3$), good long-term stability towards oxidation and high effective conjugation lengths [31, 34, 67]. They are accessible *via* the use of *Ziegler-Natta*-catalysts [68, 69], Pd-catalysts [70], anionic polymerization [71] as well as binary and ternary Mo- or W-based catalysts [72]. Unfortunately, many of these catalytic systems lead to mostly insoluble, ill-defined polymers with variable repetitive units and broad molecular weight distributions. However, well-defined *Schrock* initiators cyclopolymerize 1,6-heptadiynes in a living manner. One of the most common working horses is diethyl dipropargylmalonate (*DEDPM*) whose polymerization with a large variety of initiators has already been studied in detail [31, 34, 67]. Typically, both classical metathesis catalysts (*e.g.* $MoCl_5$/n-Bu_4Sn) and well-defined Mo-based *Schrock*-type catalysts yield polyenes that contain a mixture of five- and six-membered rings (Scheme 5) [34, 73]. The formation of one particular backbone structure solely depends on the mode of insertion of the monomer. If the first insertion steps proceed *via* α-addition, five-membered rings are formed, if β-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 Mo(N-2-t-Bu-C_6H_4)(CH-t-Bu)(O_2CCPh_3)$_2$ [31, 67]. 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_{eff}, typically ≤ 20 (*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

Scheme 5

(*i.e.* of poly(1,2-cyclopent-1-enylenevinylene)s), since these should provide enhanced coplanarity and in due consequence highly conjugated materials.

Polymerization of Diethyldipropargylmalonate (DEDPM)

The polymerization of *DEDPM* for the synthesis of poly(1,2-cyclopent-1-enylene-vinylene)s required some significant initiator tuning. While bulky ligands (*e.g.* carboxylates in the complex Mo(*N-2-t-Bu*C$_6$H$_4$)(CH-*t-Bu*)(O$_2$CCPh$_3$)$_2$) force a monomer to undergo selective β-addition, small alkoxides do not necessarily favor α-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 α-addition. In fact, molybdenum complexes of type Mo(*NAr'*)(CHC*Me$_2$Ph*)(O*R'*)$_2$ exist in form of two rotamers [29, 74]. 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 2-norbornene- and norbornadiene-based polymers [29, 41, 74–76]. 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 [30], it strongly influences the reactivity of the entire system [25, 77]. On one hand, the presence of a base particularly at low temperature favors the formation of (coordinated) *anti* isomer since it stabilizes this isomer [74]. On the other hand, it enhances the relative reactivity of the *syn* isomer. Fluoroalkoxide-based initiators such as Mo(*N-2,6-Me$_2$-*C$_6$H$_3$)(CHC*Me$_2$Ph*)(OC*Me*(CF$_3$)$_2$)$_2$ were not capable of forming poly(*DEDPM*) solely consisting of five-membered rings [34]. 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* isomer 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 Mo(*N*-2,6-*i*-*Pr*$_2$-C$_6$H$_3$)(CHC*Me*$_2$*Ph*)(OCH(CH$_3$)$_2$)$_2$, Mo(*N*-2,6-*Me*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*)(OC(CH$_3$)$_3$)$_2$, and Mo(*N*-2,6-*i*-*Pr*$_2$C$_6$H$_3$)(CHC*Me*$_2$*Ph*)(OC(CH$_3$)$_3$)$_2$ could be used for the living polymerization of *DEDPM* to produce polyenes solely based on five-membered rings [78, 79]. Due to a significantly improved coplanarity, values for N_{eff} up to 52 (!), corresponding to a λ_{max} of 592 nm (*THF*), were realized. These polyenes exhibited a reversible thermochromic behavior and excellent film-building properties. Poly(*DEDPM*)$_{10-90}$ 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.* CH$_2$Cl$_2$). In addition, poly(*DEDPM*)$_{10 \leq n \leq 90}$ was found to be thermally stable up to 185°C under helium [80].

Polymerization of Chiral Monomers

In order to retrieve more accurate information about the actual configuration of the polyene 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*)-(+)-menthoxycarbonyl-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}C NMR spectrum (Fig. 5).
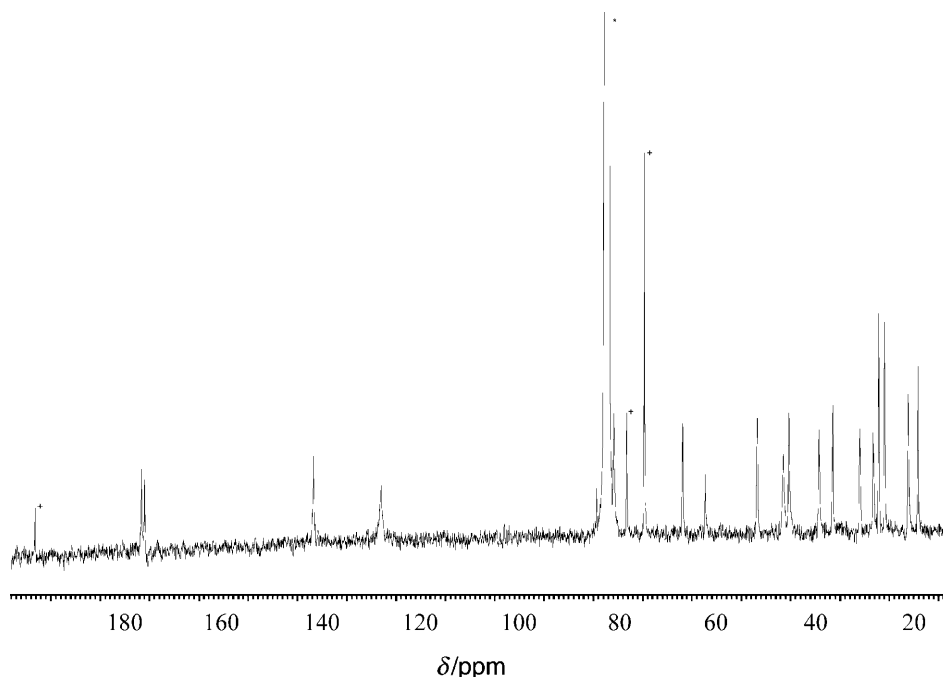

Fig. 5. ^{13}C-NMR spectrum of chiral poly-**12**; (+) denotes excess ferrocenealdehyde

Unfortunately, due to the absence of coupling constants in a 500 MHz ^{1}H, ^{1}H correlated spectrum, we could not unambiguously distinguish between an *iso-* or *syndiotactic* structure. Nevertheless, these new poly(1,2-cyclopent-1-enylenevinylene)s are the first polyenes with such a highly ordered structure.

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 polyenes 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 [81]. Thus, *DEDPM* was cyclopolymerized by MoCl$_5$:*n-Bu*$_4$Sn:EtOH:quinuclidine $= 1$:1:5:1 and MoOCl$_4$:*n*-Bu$_4$Sn:EtOH:quinuclidine $= 1$:1:2:1 to produce poly(*DEDPM*) exclusively based on 1,2-(cyclopent-1-enylene)-vinylene units. The initiator efficiency of MoOCl$_4$:*n*-Bu$_4$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 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_{eff} of 49 (*THF*) was calculated therefrom. A plot of number of monomers (*N*) added *vs* 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 hours 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.

Conclusion

1-Alkyne polymerizations and in particular cyclopolymerizations have left the area of basic research and are about to enter the field of application-oriented materials science. The knowledge about complex catalytic systems has reached a level that allows a straightforward tailor-made synthesis of materials with designed properties. The materials described here are currently under investigation for their peculiar physical properties such as conductivity, photoconductivity and applications in sensors. Despite these interesting and useful applications, which are certainly more located in the areas of physics or chemical engineering, one should not forget that any successful realization of "advanced materials" is dependant to a major part on synthetic chemistry. Furthermore, interdisciplinary research as the one described

here, crossing the borders between organic, organometallic, physical, and polymer chemistry, is required.

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