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Stereoselective Cyclopolymerization of 1,6-Heptadiynes: Access to Alternating *cis-trans*-1,2-(Cyclopent-1-enylene)vinylenes by Fine-Tuning of Molybdenum Imidoalkylidenes

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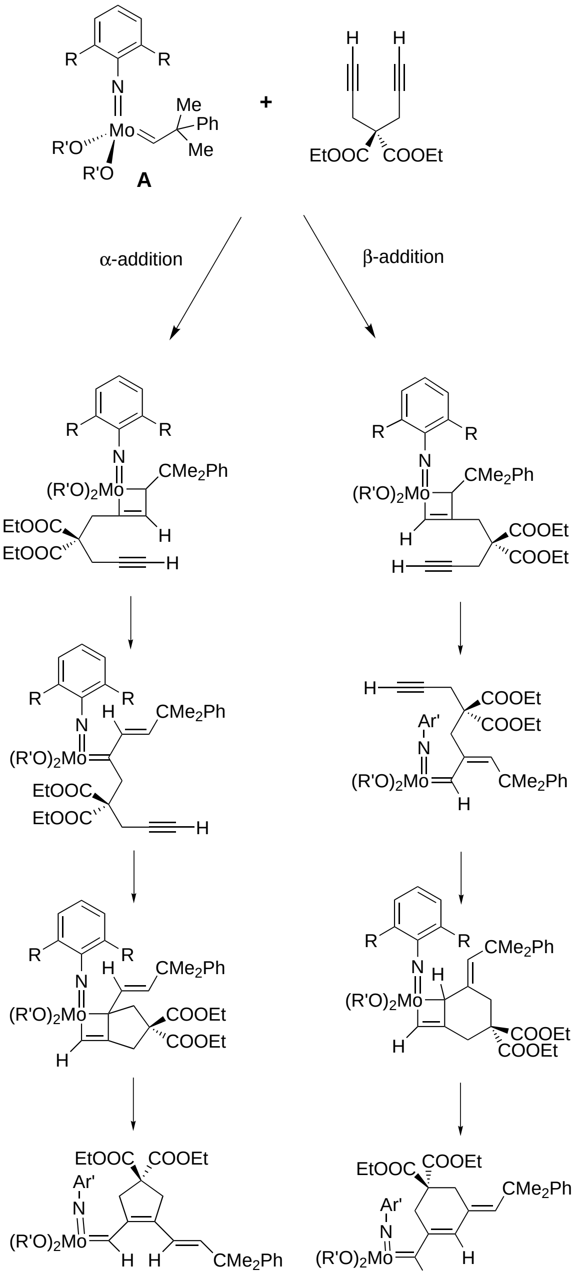
Soluble, conjugated organic polymers are of great potential because of their intriguing optical and electronic properties.[1] Areas of interest include their use as conducting or semiconducting polymers, organic light-emitting polymers, plastic solar cells, or more general, one or two-dimensional molecular wires. Any successful utilization depends on a high degree of definition as well as on the variability in the polymer structure. The cyclopolymerization of 1,6-heptadiynes containing suitable substituents at the 4-position offers an attractive access to polyenes with cyclic recurring units along the backbone.[2,3] The synthesis of such polymers requires the use of Ziegler-type catalysts,[4] Pd catalysts,[5] binary/ternary Mo- or W-based catalysts,[6] and anionic polymerization[7] Unfortunately, these methods lead to mostly insoluble, ill-defined polymers, variable repeating units (i.e. 1,2-(cyclopent-1-enylene)-vinylenes and 1,3-(cyclohex-1-enylene)-methylidene), and broad molecular-weight distributions (polydispersity index (PDI) ≥ 2). However, well-defined high-oxidation-state Schrock-type molybdenum carbenes cyclopolymerize 1,6-heptadiynes in a living manner, yet result in polyenes that contain a mixture of five- and six-membered rings.[2,3,8] Usually these polymers display 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 (N_{eff}).[2,3,9] The two different reaction pathways that are responsible for the formation of five- and six-membered ring structures are shown in Scheme 1.[2] The ring size of the polyene is influenced by steric and electronic effects of the ligands of the Schrock initiator **A**. Polymers



Scheme 1. Mechanisms for the cyclopolymerization of DEDPM with a Schrock-type initiator **A**.[2,3]

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exclusively consisting of six-membered rings can be prepared using the molybdenum complex $[\mathrm{Mo}(N\text{-}2\text{-}t\mathrm{Bu}\text{-}\mathrm{C_6H_4})(\mathrm{CH}\text{-}t\mathrm{Bu})(\mathrm{O_2CCPh_3})_2]$, where the bulky triphenylacetate ligands force the monomer to undergo selective β-addition.[9] While such selective β-additions are comparably easy to accomplish both in cyclopolymerization and 1-alkyne polymerization,[9,10] a Schrock-initiator-based synthesis of polyenes solely based on five-membered rings has not been accomplished to date, though diethyldipropargylmalonate (DEDPM) derived poly(1,2-(cyclopent-1-enylene)vinylene)s were formed with classical $\mathrm{MoCl_5}$-based initiators. However, only oligomers with a low degree of polymerization $(\mathrm{DP} < 6)$ and broad polydispersities $(\mathrm{PDI} \leq 4.2)$ were reported.[11]

To gain access to polymers containing exclusively five-membered rings, variations in both the imido and alkoxy ligand in complexes **A** were carried out. Based on the concept of small alkoxides developed by Schrock,[12] and on our results in 1-alkyne polymerization,[10,13] a small ligand sphere was believed to be necessary for, but not a guarantee of, selective α-addition. Additional information on the influence of the electronic nature of the alkoxide ligands as well as on steric effects of the aryl imido substituents was required.

We synthesized a variety of new Mo-based Schrock-type initiators based on fluorinated and non-fluorinated alkoxides (**A**), of which three were capable of selective α-addition (as indicated by ^{1}H NMR spectroscopic investigations of the first insertion products). Both **1** ($R = i\mathrm{Pr}_2$, $R' = t\mathrm{Bu}$) and **2** ($R = \mathrm{Me}$, $R' = t\mathrm{Bu}$) Figure 1[14]) cyclopolymerized DEDPM in the presence of additional base (quinuclidine) to give ferrocene (Fc) terminated poly-DEDPM with a five-membered-ring content of more than 95%. With **3** ($R = R' = i\mathrm{Pr}$), a starting temperature of −30 °C was sufficient for reaction. Polymer structures were identified according to standard procedures using 4,4-bis(ethoxycarbonyl)cyclopent-1-ene and 4,4-bis-(ethoxycarbonyl)cyclohex-1-ene as model compounds (the relative error in structure determination was < 3 %).[2] Thus, a typical ^{13}C NMR spectrum of a polymer containing both five- and six-membered ring structures shows at least two sets of carbonyl resonance signals that can be ascribed to carbons in different chemical environments within the polymer chain (Figure 2 top). The ^{13}C NMR spectra of polymers containing solely five-membered rings show one, sharp carbonyl resonance signal (Figure 2 bottom).

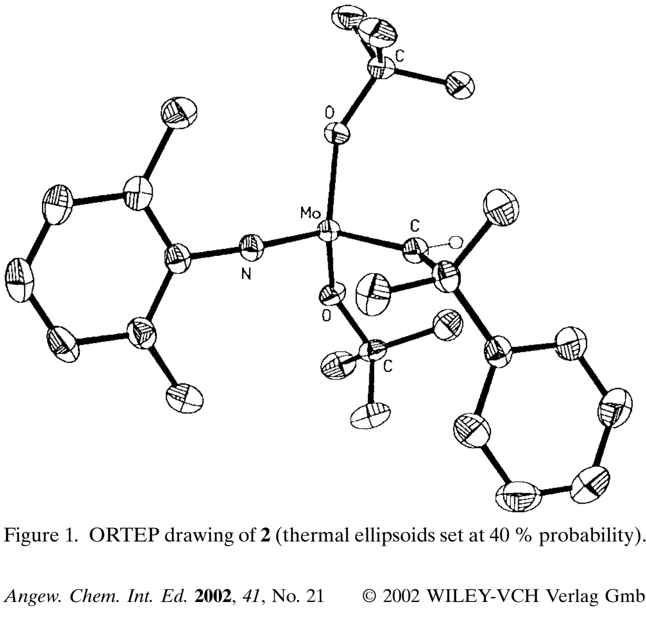

Figure 1. ORTEP drawing of **2** (thermal ellipsoids set at 40 % probability).

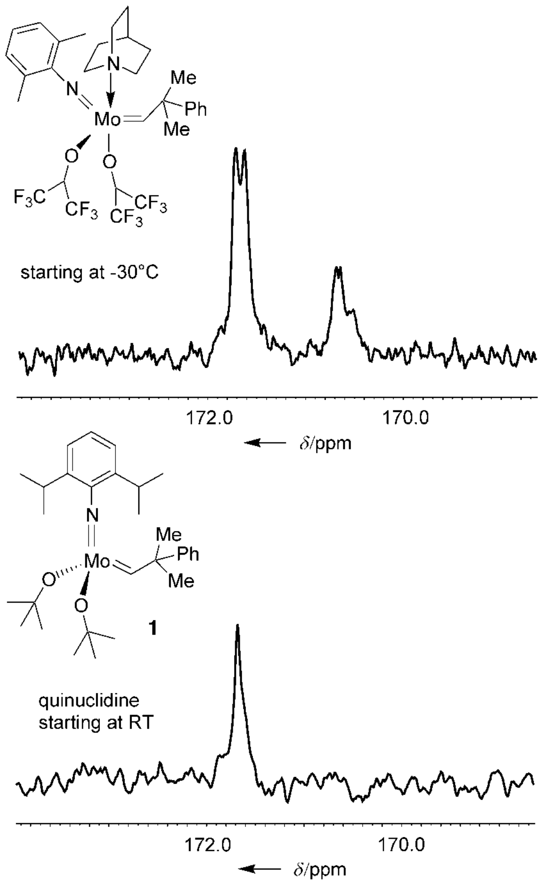

Figure 2. ^{13}C NMR spectra of poly-DEDPM$_{50}$ samples containing 70% five-membered rings (top) and > 95% five-membered rings (bottom).

A plot of the number-average molecular weight (M_n) versus the number of monomer equivalents of DEDPM (N) showed linear dependences for initiators **1**–**3**, that of initiator **1** is shown in Figure 3 and clearly underlines the necessity of an absolute method for molecular-weight determination such as light scattering. From this linear plot, the low PDIs (< 1.4) and

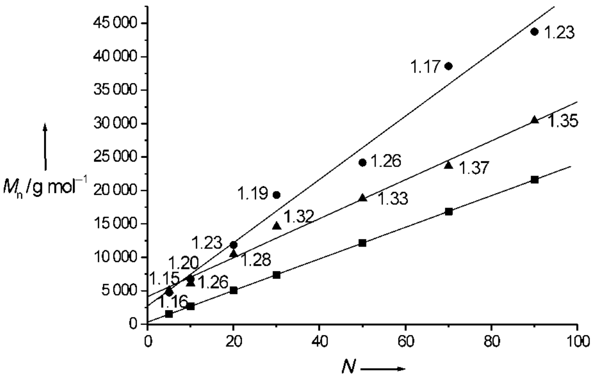

Figure 3. Plot of M_n versus number of monomer equivalents N for poly-DEDPM samples prepared using **1**-quinuclidine as initiator. The PDIs for the poly-DEDPM produced are given; ● gel permeation chromatography (polystyrene standard), ▲ light scattering, ■ calculated.

the complete consumption of monomer we conclude that chain transfer or termination are absent. The existence of at least a class V living system was confirmed by the stepwise synthesis of poly-DEDPM.[15] Furthermore, this plot perfectly fits the kinetic data obtained for initiators **1**–**3**. Thus, values for k_p/k_i were found to be 9, 14, and 114 for initiators **2**, **3**, and **1**, respectively, and serve as an excellent explanation for the small (positive) deviation of the light-scattering-derived values for M_n from theoretical values. We have demonstrated the broad applicability of the new initiators by the fact that other polyenes based on bulky monomers such as di-(1*S*, 2*R*, 5*S*)-(+)-menthyl dipropargylmalonate prepared by the action of **1** at −30 °C and terminated by ferrocene aldehyde also contain > 95 % five-membered rings.

While ring sizes and ratios of ring sizes may be determined conveniently by ^{13}C NMR spectroscopy, investigations on tacticity and *E*/*Z*-ratios of the vinylene units require some additional changes in the monomer. As has already been outlined for various norborn-2-ene and norbornadiene derivatives,[16,17] an additional element of chirality is required to break the symmetry between the repeating units. Therefore, 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (**4**) was synthesized and cyclopolymerized by **1** in the presence of quinuclidine. The ^{13}C NMR spectrum of poly-**4** (Figure 4) displays two sharp resonance signals around $\delta \approx 171$ ppm attributed to the two different ester carbonyl groups of a polymer that again contains > 95 % five-membered rings. The single, sharp resonance signal for the C-4 atoms at $\delta = 57$ ppm and the vinylene carbon at $\delta = 123$ ppm further support a highly regular five-membered-ring structure. For reasons of symmetry, one can distinguish between the few possible structures (*cis*, *trans*, *iso*-, or *syndiotactic*) by ^{1}H NMR spectroscopy.[16] An absolute assignment of tacticity would be possible if the resonance signal of the olefinic protons were sufficiently resolved. A ^{1}H,^{1}H COSY NMR spectrum was recorded for poly-$\mathbf{4}_{50}$ (500 MHz, [D$_8$]toluene, 85 °C). Two sets of *trans*-coupled protons were unambiguously identified by their resonance signals at $\delta = 6.19$, 6.83 ppm, $J = 16.5$ Hz and $\delta = 6.60$, 7.16 ppm, $J = 16.0$ Hz, respectively. These two sets were assigned to the end groups, FcCH=CH−P and P−HC=CHCMe$_2$Ph (P = polymer chain), respectively. A (broadened) signal at $\delta = 7.1$ ppm resulting from the overlap of the two resonance signals for the protons along the conjugated backbone did not show any observable coupling. Though this is indicative for a highly tactic structure, we cannot completely exclude that any existing coupling is not observable because of small chemical-shift differences, which thus, does not allow the unambiguous assignment of any tacticity.

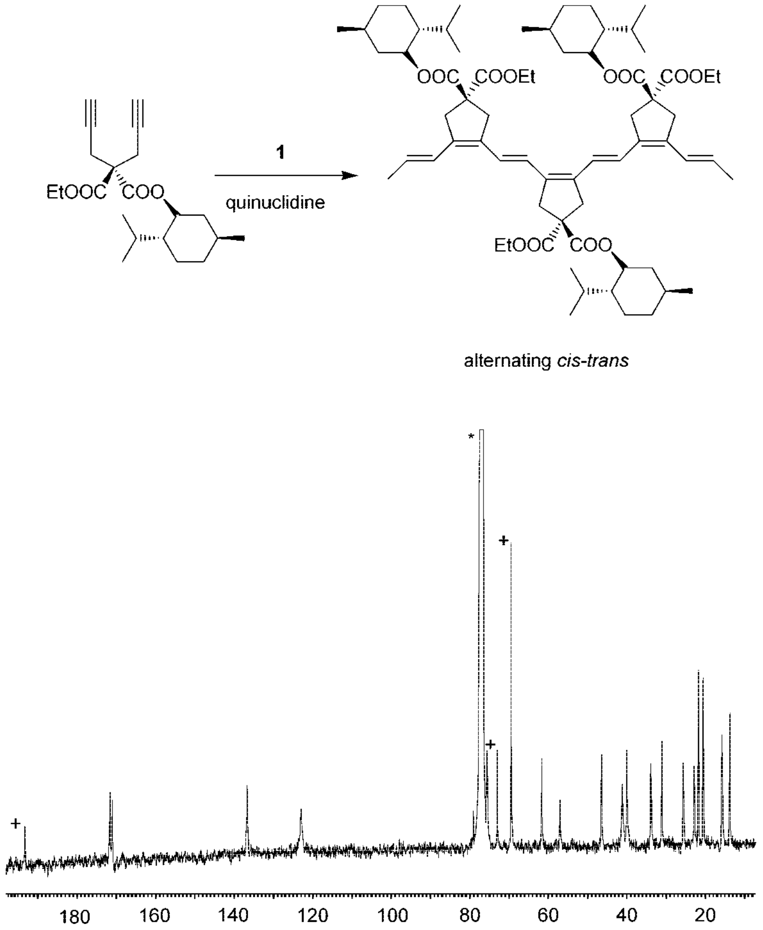

Figure 4. Synthesis and ^{13}C NMR spectrum of chiral, alternating *cis-trans* poly-**4** (DP = 50, $M_n = 18\,600$ g mol^{-1}, PDI = 1.26, * CDCl$_3$; + residual ferrocene aldehyde).

Despite the large set of data, mechanistic considerations, which would allow formulating a general rule for the synthesis of regular structures, are still speculative. The fact that non-fluorinated alkoxides are required for a selective backbone formation as well as the significant effects of additional base and temperature on the final polymer structure suggest that the rates of interconversion between the *syn* and *anti* forms of the initiators play an important role. Initiators based on non-fluorinated alkoxides show fast *syn*–*anti* interconversion[18] whereas a base favors the formation of the (base-coordinated) *anti* isomer.[19] Nevertheless, a quantitative description would necessitate kinetic data for the interconversion in non-fluorinated Mo-alkoxides. Unfortunately this interconversion is too fast for the reactivity differences between a *syn*- and *anti*-rotamer to be determined by current methods.

In summary, chiral polyenes with an alternating *cis-trans* structure containing solely five-membered rings and defined polymer end groups have been prepared. The physical properties of the new polyenes strongly differ from existing poly(heptadiyne) systems with a lower degree of definition in the polymer backbone. Thus, the new polyenes show significantly bathochromic shifts in the UV/Vis spectrum (591 nm versus 511 nm for six-membered ring structures, corresponding to $N_{\text{eff}} = 52$) as well as an entirely different solubility. They are stable under air over months in the solid state as well as in solution. Furthermore, no thermal decomposition is observed under He up to temperatures of 180 °C. They possess excellent film-forming properties with DP-dependant glass transitions around 25 °C.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a glove box (MBraun) or by using standard Schlenk techniques. [Mo(N-2,6-iPr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$·DME, [Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$]·DME, and [Mo(N-2,6-iPr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$] (**1**) as well as other compounds were prepared following literature procedures.[20] Experimental details can be found in the Supporting Information.

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Ambiphilicity: A Characteristic Reactivity Principle of π-Bound Phosphorus Heterocycles[**]

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*Dedicated to Professor Gottfried Huttner
on the occasion of his 65th birthday.*

Cyclooligomerization of phosphaalkynes, such as tBuC≡P (**1**), in the coordination sphere of reactive metal complexes predominantly leads to π complexes of the cyclodimer 1,3-diphosphete[1–4] or the cyclotrimer 1,3,5-triphosphabenzene.[5] However, pentaphosphametallocenes, such as the pentaphosphaferrocene derivative **2**, are obtained with reactive iron complexes[6,7] or free metal atoms.[8] Their formation requires that at least one P–C triple bond be broken (Scheme 1).

Oligophosphametallocenes are easily accessible substances with a series of interesting properties.[9] Thus, there is much interest in determining the mechanism of their formation. Because complete cleavage of **1** is very unlikely, even at a transition-metal center, we assume that initially formed cycloaddition products from **1** undergo intra- or intermolec-

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