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Living Cyclopolymerization of Diethyl Dipropargylmalonate by Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in Dimethoxyethane

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Summary: **Cyclopolymerization of diethyl dipropargylmalonate (1) by Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (2) in dimethoxyethane (DME) proceeds in a living manner to give a conjugated polyene that contains both five- and six-membered rings incorporated into the polyene backbone. Cyclization to give the five-membered ring is believed to prevent deactivation of the catalyst. GPC analysis shows that poly(1)$_n$ polymers have low polydispersities ($M_w/M_n \leq 1.25$) and values for M_n that increase linearly with the amount of monomer employed. The living nature of the polymerization was also demonstrated by synthesis of a block copolymer from 20 equiv of 1 followed by 200 equiv of 2,3-dicarbomethoxynorbornadiene (5).**

Unsaturated conjugated organic polymers are of great interest because of their potentially useful optical and electronic properties.[1] In order to exploit the fundamental properties of such materials fully, it is highly desirable to develop methods of preparing conjugated polymers by living polymerization methods.[2,3] For example, polyacetylenes have been prepared by living methods,[4] either indirectly by ring-opening metathesis methods[5-7] or, with some degree of success, directly from acetylene itself.[6,8] Potentially important candidates to polymerize in a living manner are dipropargyl derivatives (HC≡CCH$_2$XCH$_2$C≡CH; X = CH$_2$, C(CO$_2$R)$_2$, SiR$_2$, etc.), the polymerization of which by various classical catalysts yields substituted polyenes by as yet unknown mechanisms.[9-17] We report here the living cyclopolymerization of diethyl dipropargylmalonate[18] (1) by Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (2; Ar = 2,6-diisopropylphenyl)[19] in dimethoxyethane (DME).

Table I. GPC, UV/Vis, and Yield Data for poly(1)$_n$ Prepared Using 2 as the Initiator

polymer	M_n (g/mol)[a]	degree of polymerizn	M_w/M_n	λ_{max} (nm)[b]	yield (%)
poly(1)$_5$	3640	15	1.21	514 (504)	98
poly(1)$_{10}$	6110	26	1.24	534 (524)	93
poly(1)$_{15}$	7520[c]	32	1.18	548 (544)	99
poly(1)$_{20}$	8790	37	1.25	548 (544)	100
poly(1)$_{40}$	11600	49	1.16	552 (554)	96
poly(1)$_{80}$	23200	98	1.23[d]	556 (574)	97
poly(1)$_{20}$-(5)$_{200}$	48000[e]		1.09	548 (544)	98

[a] Determined by GPC on-line viscometry versus a polystyrene universal calibration curve (Viscotek). [b] In THF or (in parentheses) in acetonitrile. [c] M_n = 7550 (±1200) was obtained by vapor pressure osmometry. [d] A small amount of double-molecular-weight material was observed by GPC. [e] M_n vs polystyrene.

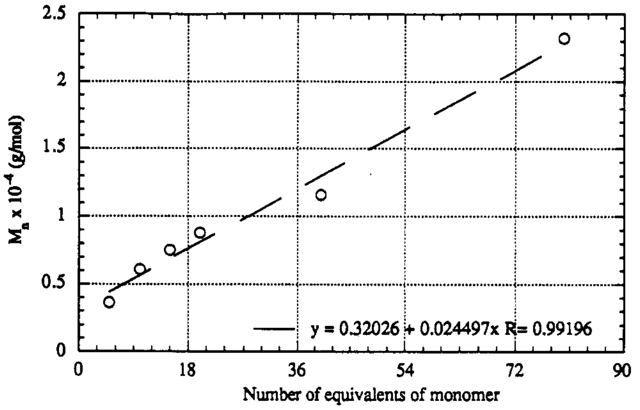

Figure 1. Dependence of the number average molecular weight (M_n) of poly(1)$_n$ on the number of equivalents of monomer added to the initiator.

We have not yet been able to polymerize monosubstituted alkynes[20,21] in a living manner, primarily, we believe, because addition of a monosubstituted alkyne to give an α-substituted metallacyclobutene leads to a relatively unreactive disubstituted alkylidene complex analogous to **3a** (Scheme I) when the intermediate metallacyclobutene ring opens.[22] However, in the case of a dipropargyl derivative (HC≡CCH$_2$XCH$_2$C≡CH) intramolecular formation of a five-membered ring in **3a** may be fast enough to yield another terminal alkylidene (**4a**) on the time scale of the polymerization reaction. Formation of a six-membered ring in a reaction involving a more reactive terminal alkylidene would transform **3b** into **4b**. An important side reaction that must be controlled is reaction of either **3a**

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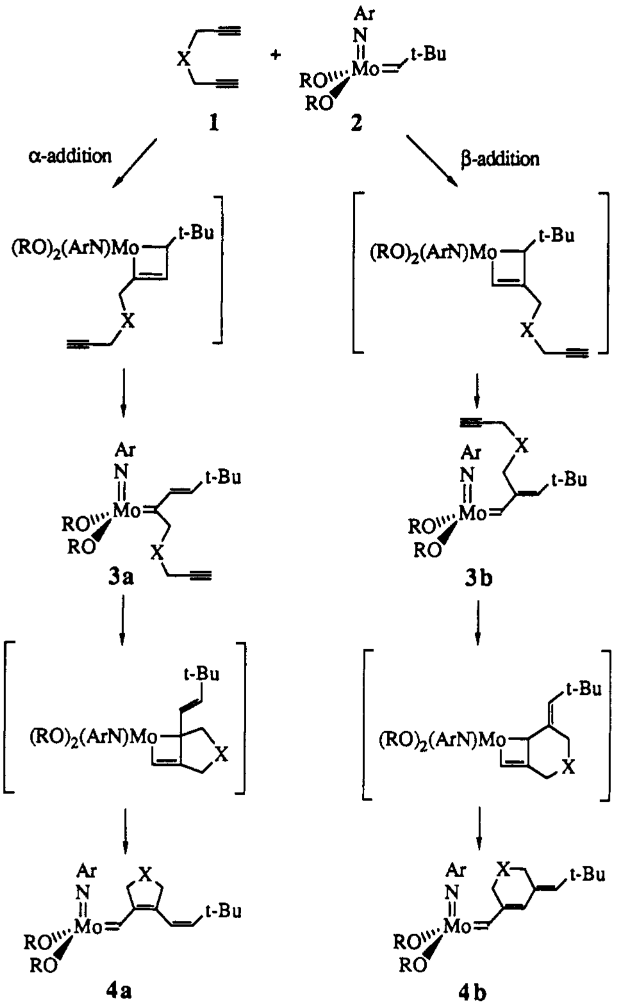
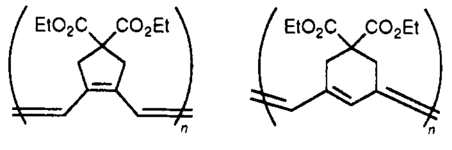
Scheme I



or (more likely) **3b** with additional monomer to give a chain having "dangling" triple bonds that eventually could lead to cross-linking.

A ^{1}H NMR spectrum of **2** (15 mg) in DME-d_{10} (800 μL) to which 2.5 equiv of **1** (13 mg) had been added showed that ca. 50% of **2** was consumed, no **1** remained, and two new H_α resonances with a total area of ca. 0.5 proton relative to initial **2** were observed at 13.03 and 12.41 ppm, positions that are characteristic of α-proton resonances in vinyl alkylidene complexes.[23] No resonances in the range of 7.5–8.5 ppm characteristic of β-protons in vinyl alkylidene complexes were observed, suggesting that no complexes of type **3a** were present.[23] We tentatively assign the new H_α resonances to complexes in which a five-membered (analogous to **4a**) or six-membered ring (analogous to **4b**) is attached to the alkylidene carbon atom.

Adding **1** to **2** in DME followed (after up to 2.5 h; see Table I) by cleaving off the polymer with benzaldehyde in a Wittig-like reaction yielded soluble poly$(\mathbf{1})_n$[16] (n = 5, 10, 15, 20, 40, 80) quantitatively.[24] GPC analysis coupled with viscometry in THF showed a single monomodal peak in each case with a polydispersity (M_w/M_n) of 1.25 or less and a degree of polymerization higher than expected, suggesting a faster rate of propagation relative to initiation. A plot of M_n for poly$(\mathbf{1})_n$ versus the number of equivalents of monomer employed is linear (Figure 1), consistent with the absence of secondary metathesis on the time scale of the experiment. A block copolymer also was prepared in high yield by adding 200 equiv of 2,3-dicarbomethoxynorbornadiene (**5**) to a solution of living poly$(\mathbf{1})_{20}$,[25] followed by cleavage with benzaldehyde (Table I). The quantitative yield and narrow polydispersity of the diblock are consistent with a living polymerization of both monomers. No acetylenic C–H bonds were detected in a solution IR spectrum of poly$(\mathbf{1})_{80}$. Approximately 5% of a polymer with double the expected molecular weight appears in poly$(\mathbf{1})_{80}$, which we ascribe to a small amount of chain linking through "dangling" terminal triple bonds. The ^{13}C NMR spectrum of poly$(\mathbf{1})_{80}$ reveals two carbonyl carbon resonances, while the ^{13}C NMR spectrum of poly(**1**) prepared using a $MoCl_5$ catalyst, which is proposed to contain six-membered rings, revealed only one carbonyl carbon resonance.[16] Therefore, we speculate that poly$(\mathbf{1})_n$ consists of a random distribution of five-membered and six-membered rings formed through what is nominally tail-to-tail and head-to-tail cyclopolymerization of the two acetylenic bonds in the monomer, viz.



The choice of solvent and catalyst is crucial to the successful synthesis of low-polydispersity poly(**1**). In THF, the poly$(\mathbf{1})_{20}$ obtained with **2** as the initiator showed a trimodal GPC peak pattern (polydispersity >2) that is consistent with cross-linking to give polymers that have double and several times the expected molecular weight. Other catalysts such as Mo(CH-t-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$[19] and W(CH-t-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$[26] in DME yielded similar results and, in the case of the latter, also low yields of polymer. Dimethoxyethane is likely to play a significant role in limiting secondary metathesis or termination reactions, as has been demonstrated for polymerizations by related catalysts in the presence of quinuclidine[6,8] or phosphine[27] and appears to encourage cyclization.

UV/vis data (λ_{max}) for poly(**1**) prepared here (Table I) suggest that poly(**1**) is indeed highly conjugated and reveal that λ_{max} continues to increase in a polymer containing approximately 200 double bonds. (In poly(**1**) prepared using classical catalysts $\lambda_{max} \approx$ 550 nm.[16]) It is important to note that molecular nonlinear optical (NLO) properties

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(24) In a representative polymerization, Mo(CH-t-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (28 mg, 0.04 mmol) was dissolved in 30 mL of DME that had been distilled twice from sodium–benzophenone ketyl under dinitrogen. Diethyl dipropargylmalonate (186 mg, 0.79 mmol) in 1 mL of DME was added all at once to the stirred solution. After 60 min, benzaldehyde (8 μL, 0.08 mmol) was added and the reaction mixture was stirred an additional 60 min. The mixture was concentrated to ~3 mL and the polymer was precipitated by dropwise addition to 80 mL of pentane. The polymer was collected by filtration and dried in vacuo overnight to yield a dark purple solid (192 mg, 100%). All manipulations were carried out under nitrogen in a drybox.

(25) Mo(CH-t-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (7 mg, 0.01 mmol) was dissolved in 8 mL of DME. Diethyl dipropargylmalonate (47 mg, 0.20 mmol) in 1 mL of DME was added all at once to the stirred solution. After 60 min, 2,3-dicarbomethoxynorbornadiene (417 mg, 2.0 mmol) in 1 mL of DME was added all at once. After 30 min, benzaldehyde (2 mL, 0.02 mmol) was added and the reaction mixture was stirred an additional 60 min. The mixture was concentrated to ~2 mL and was added dropwise to 80 mL of pentane to precipitate the polymer. The polymer was collected by filtration and dried in vacuo overnight to yield a dark purple solid (453 mg, 98%).

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(γ in this case) may depend much more strongly on chain length than does λ_{max}.[1]

The fact that a catalyst and conditions have been found to effect the living polymerization of 1 suggests that it may be possible to polymerize other $HC{\equiv}CCH_2XCH_2C{\equiv}CH$ derivatives. It is important to note that the initiator employed here is one of the members of a class of well-characterized initiators employed for ring opening of norbornenes and substituted norbornadienes[28] and therefore that it should be possible to synthesize other well-defined block copolymers relatively routinely and to prepare microphase-separated materials from them. Further studies in these directions are under way.

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The Ions MCp_2^+ (M = Sc, La): Significantly Bent Sandwich Species

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Summary: Ab initio calculations show that the hypothetical organometallic cations MCp_2^+ (M = Sc, La) have bent-metallocene structures. This is due to covalent σ-bonding contributions involving the totally symmetric metal d_σ orbitals, which favor bent geometries. While these orbitals contribute much less to covalent bonding in these systems than the d_π orbitals, their involvement is sufficient to result in bent structures.

Do heavy alkaline-earth-metal and lanthanide(II) metallocenes MCp_2 (M = Ca, Sr, Ba, Sm, Eu, Yb) prefer bent or linear sandwich structures?[2-5] While experimental structure determinations indicate bent geometries[2,3] (cf. Figure 1 for the definition of the bending angle), these refer either to gas-phase thermal average structures at elevated temperatures[2] or to solid-state structures where nonnegligible intermolecular interactions are present.[3] Our recent ab initio pseudopotential calculations show that all of these species have very shallow bending potentials.[5] While the calculated equilibrium structures for M = Ba, Sm, Eu deviate slightly from linearity, $CaCp_2$ and $YbCp_2$ probably are linear.[5] These results for the metallocenes contrast sharply with those for simpler MX_2 species (e.g., X = halogen, H, CH_3, NH_2, OH). The latter show significantly bent structures (except for the lighter metal Ca).[6a-e] Covalent σ-MX-bonding contributions (involving metal d orbitals) favor bent structures,[6] but π-bonding contributions favor linear MX_2 geometries.[6d] Since the Cp^- ligand functions mainly as a π donor, the reduced preference for bent structures in the MCp_2 compounds becomes clear.[5]

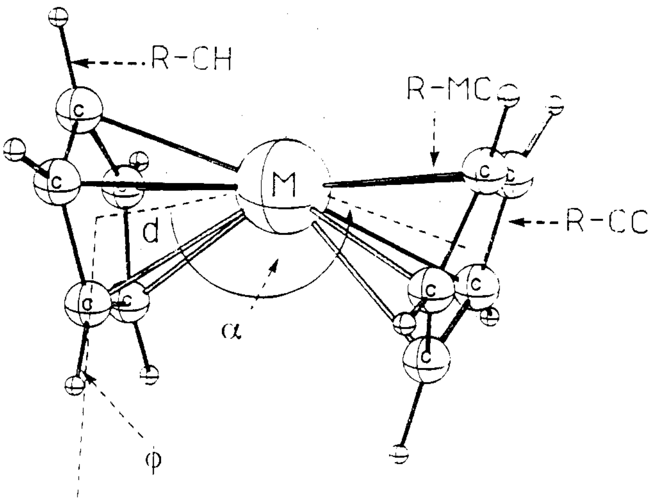

Figure 1. Definition of internal coordinates for MCp_2 and MCp_2^+.

In addition to these covalent bonding contributions, the polarization of the cation by the anions favors bent structures, whereas the repulsion and polarization of the anions favors linear geometries.[6a,c] Thus, two explanations for the at least slightly bent equilibrium geometries of the heavier MCp_2 species (e.g. M = Ba, Sm) may be envisaged: (a) the polarization of the metal cation by the ligands[2d,5] or (b) the presence of small σ-bonding contributions

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