Fine-Tuning of Molybdenum Imido Alkylidene Complexes for the Cyclopolymerization of 1,6-Heptadiynes To Give Polyenes Containing Exclusively Five-Membered Rings

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ABSTRACT: Diethyl dipropargylmalonate (**1**) was cyclopolymerized by various well-defined molybdenum-based Schrock initiators to produce polymers exclusively based on 1,2-cyclopent-1-enylenvinylene units. For this purpose, variations in both the imido and alkoxy ligand in molybdenum alkylidene complexes of type Mo(NAr′)(CHCMe$_2$Ph)(OR)$_2$ (Ar′ = 2,6-*i*-Pr$_2$C$_6$H$_3$; 2,6-Me$_2$C$_6$H$_3$; OR = OCH(CF$_3$)$_2$, OCH(CH$_3$)$_2$, OC(CH$_3$)$_3$) were carried out. Polymers containing >95% 1,2-cyclopent-1-enylenvinylene units were obtained by low-temperature-initiated cyclopolymerization of **1** by Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCH(CH$_3$)$_2$)$_2$ (**2**). In the presence of quinuclidine, >95% five-membered ring structures were realized at room temperature using Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$ (**3**) and Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$ (**4**). In contrast, molybdenum initiators containing electron-withdrawing alkoxides such as Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCH(CF$_3$)$_2$)$_2$(quinuclidine) (**5**) or the nonfluorinated analogue Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCH(CH$_3$)$_2$)$_2$(quinuclidine) (**6**) do not exclusively generate five-membered ring structures, either in the presence of quinuclidine or at low temperatures. Molecular structures of **3** and **5** were determined by X-ray crystallography. The exact ratio of five- to six-membered rings was based on ^{13}C NMR data of 4,4-bis(ethoxycarbonyl)cyclopent-1-ene (**7**) and 4,4-bis(ethoxycarbonyl)cyclohex-1-ene (**8**), which served as model compounds. 4-(Ethoxycarbonyl)-1,6-heptadiyne (**9**) and di(1*S*,2*R*,5*S*)-(+)-menthyl dipropargylmalonate (**10**) were cyclopolymerized by **4** in the presence of quinuclidine to investigate the influence of bulky 4-substituents on the polymerization. 4-(Ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (**12**) was synthesized from ethyl-(1*S*,2*R*,5*S*)-(+)-menthyl malonate (**11**)- and cyclopolymerized by **4** in the presence of quinuclidine to determine the configuration of the double bond (i.e., the cis/trans ratio) and the tacticity of the polyene backbone. Poly-**12** consists of >95% five-membered rings and possesses an alternating cis−trans structure. In contrast to cyclopolymers of **1** containing both ring sizes, poly-**1**, consisting solely of five-membered rings, is virtually insoluble in THF. A degree of polymerization (DP) dependent UV−vis absorption is found. The absorption maximum λ_{max} for poly-**1** with DP ≥ 50 is 591 nm, and the value for the maximum effective conjugation length (N_{eff}) that can be calculated therefrom is 52. Molecular weights and polydispersity indices (PDIs) of the polymers were determined in CHCl$_3$ by GPC vs PS. Complementary, light-scattering (LS) data were collected at λ = 690 nm and MALDI−TOF mass spectroscopy was applied in order to calculate absolute molecular weights. A linear plot of number of monomers added (n) vs molecular weights as determined by LS suggests that the cyclopolymerization of **1** proceeds in a living manner. At least a class V living system was confirmed by the stepwise synthesis of poly-**1**. Molecular weight distributions (PDIs) of 1.16−1.37 result from ratios of the rate constants for polymerization (k_p) to initiation (k_i), k_p/k_i, > 1. These values were determined by NMR for the reaction of **1** with all relevant initiators and were 9, 14, 114, and 347, respectively, for initiators **3**, **2**, **4**, and **5**. Influences of temperature, the base and steric and electronic effects of the arylimido and alkoxy ligands on polymer structure were investigated.

Introduction

Soluble, conjugated organic polymers are of great interest because of their optical and electronic properties.[1−6] Poly(acetylene) itself as the simplest representative of this polymer class has been intensively studied, but suffers from its lack of processability, solubility in common organic solvents, and insufficient stability toward oxygen. To overcome the problems, mono- and disubstituted alkynes have been polymerized.[7] In a first approach, classical metathesis catalysts based on MoCl$_5$ or WCl$_6$ and alkylating cocatalysts such as *n*-Bu$_4$Sn or EtAlCl$_2$ were used. Unfortunately, many of the resulting polymers possessed broad molecular weight distributions, and significant amounts of byproducts were observed.[8−10] Complementary, catalytic systems based on MoOCl$_4$, WOCl$_4$, and various rhodium complexes have been used in living polymerizations of substituted acetylenes.[11−23] Nevertheless, in these systems little is known about both the active species and polymer structures. The synthesis of poly(acetylene)s may also be accomplished by use of substituted poly(cyclooctatetraene)s via ring-opening metathesis polymerization (ROMP).[44−54] In alkyne polymerization, the living polymerization of 2-butyne,[24] ortho-substituted phenylacetylenes,[25,26] ethynyl-substituted metallocenes,[27−31]

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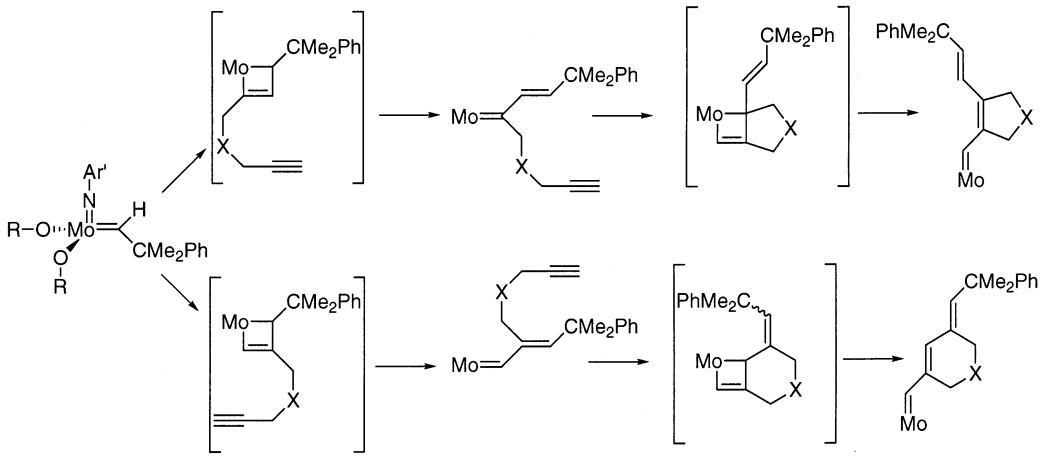
Scheme 1. Two Possible Pathways that Give Access to Five- and Six-Membered Ring Structures



and α,ω-diynes[32−34] was achieved by the use of well-defined Schrock carbenes.

A general problem of polyenes prepared from 1- or 2-alkynes are 1,3-interactions of the substituents, resulting in lower conjugation lengths compared to unsubstituted polyene backbones.[9,10] 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 polyenes.[27] Alternatively, similar to the cyclopolymerization of 1,5-hexadienes[35−39] and aza- and oxaheptadienes,[40−42] the cyclopolymerization of 1,6-heptadiyne derivatives with substituents at the 4-position can be carried out.[32,43] Polyenes with cyclic recurring units along the backbone are readily accessible by this approach. Usually this class of polymers displays good solubility in common organic solvents (e.g., C_6H_6, toluene, CH_2Cl_2, $CHCl_3$), good long-term stability toward oxidation, and high effective conjugation lengths (N_{eff}).[32−34] They have been prepared using Ziegler−Natta catalysts,[55,56] Pd catalysts,[57] anionic polymerization[58] and binary and ternary Mo- or W-based catalysts.[59] 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 high oxidation state molybdenum carbenes cyclopolymerize 1,6-heptadiynes in a living manner. One of the most common monomers is diethyl dipropargylmalonate (**1**) whose polymerization with a large variety of initiators has already been studied in detail.[32−34] 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.[32,60] Nevertheless, polymers exclusively consisting of six-membered rings have been prepared using the molybdenum imido alkylidene complex Mo(N-2-*tert*-Bu-C_6H_4)(CH-*tert*-Bu)(O_2CCPh_3)$_2$.[33,34] These polymers not only were well-defined in terms of microstructure, molecular weight, and molecular weight distribution but also represented interesting materials with third-order nonlinear behavior.[61] In principle, cyclopolymers based on five-membered ring structures can also be realized with classical $MoCl_5$-based initiators. However, only oligomers with a DP < 6 and broad polydispersities (PDIs ≤ 4.2) have been reported so far.[62] Alternatively, the synthesis of poly-**1** exclusively consisting of five-membered rings has been accomplished using Mo-$(CO)_6$.[63] Acceptable DPs (≤50) and PDIs (≤2.2) are obtained, however, reaction times of 48 h appear less attractive. To the best of our knowledge, poly-**1** prepared by well-defined Mo-based catalysts consisting of 1,2-cyclopent-1-enylenvinylene units have not been reported so far. Therefore, our effort has been directed toward the development of suitable initiators that open access to such microstructures.

Results and Discussion

Dipropargylmalonate esters are widely used 1,6-heptadiyne derivatives producing soluble polymers. The two different reaction pathways that give access to polymers containing either five- or six-membered rings are shown in Scheme 1.[32] It has been proposed that cyclopolymerization of 1,6-heptadiyne derivatives proceeds via an "alkylidene mechanism", in which the triple bond of the monomer reacts with a Mo=C bond to give either an α-substituted or *β*-substituted metallacyclobutene intermediate, which then opens to give an alkylidene complex. Subsequent reaction of the remaining triple bond of the monomer in an intramolecular cyclization step successively leads to a five- or six-membered ring predetermined by the initial α- or *β*-addition step. Intramolecular addition must be fast relative to intermolecular addition of the second triple bond to a Mo=C bond in order to avoid cross-linking. In accordance with the proposed mechanism, the ring size is influenced by both the substitution pattern of the monomer as demonstrated by Choi et al.[62] and the steric and electronic effects of the ligand sphere around the Mo center of a Schrock-type catalyst. As can be deduced from Scheme 1, the use of bulky ligands (e.g., carboxylates) in the complex Mo(N-2-*tert*-BuC_6H_4)(CH-*tert*-Bu)(O_2CCPh_3)$_2$ forces the monomer to undergo selective *β*-addition in the first addition step. The following reaction steps result in the formation of a polyene that contains exclusively six-membered rings along the polymer backbone.[33,34]

To produce polyenes exclusively consisting of five-membered rings, we carried out variations in both the imido and alkoxy ligand in molybdenum alkylidene complexes of type Mo(NAr′)(CHCMe$_2$Ph)(OR)$_2$ (Ar′ = 2,6-*i*-$Pr_2C_6H_3$; 2,6-$Me_2C_6H_3$; OR = $OCH(CF_3)_2$, $OCH(CH_3)_2$, $OC(CH_3)_3$). Figure 1 summarizes the initiators prepared for this study.

Ligand Variation in Molybdenum-Based Catalysts. On the basis of the concept of small and large alkoxides developed by Schrock,[25,26] a small ligand

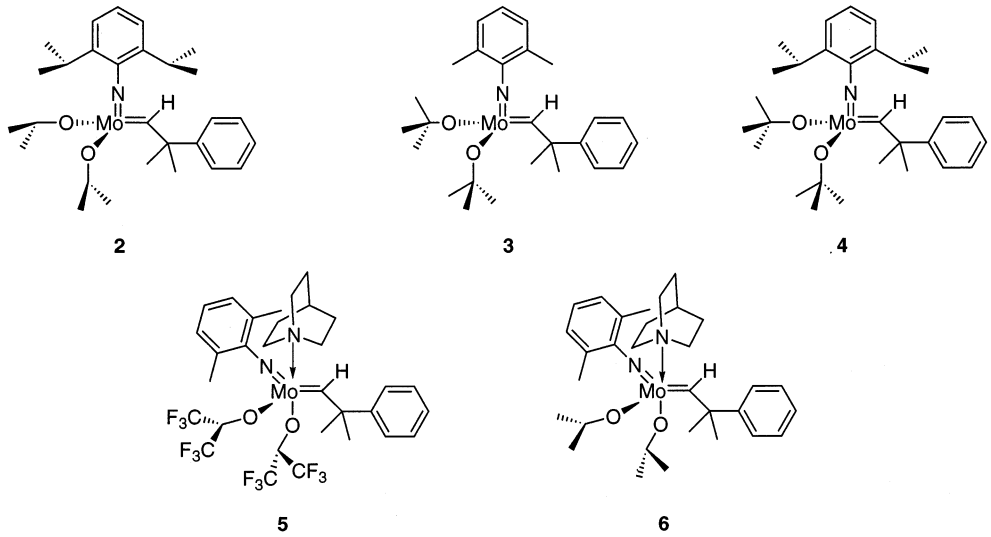


Figure 1. Structure of Mo-based initiators used in this study.

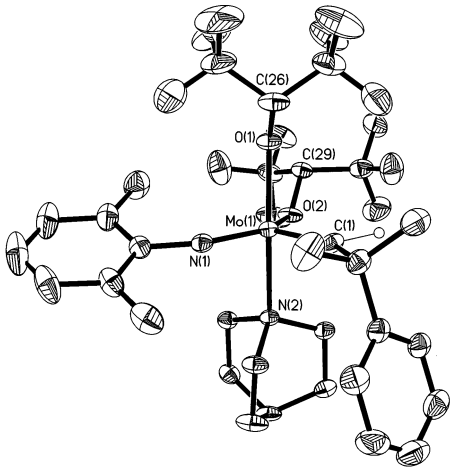


Figure 2. ORTEP drawing of **5**.

sphere around the molybdenum center was believed to be a necessary requirement to favor selective α-addition. We started our investigations with initiator **5** bearing methyl groups at the 2,6-position of the imido ligand and electron-withdrawing hexafluoroisopropoxide ligands. **5** as well as all other initiators was synthesized according to the standard route described for Mo-based initiators from the corresponding molybdenum bis(triflates).[60,64,65] For steric and electronic reasons, quinuclidine is required to stabilize the catalyst. The X-ray structure of **5** is shown in Figure 2 and relevant data are summarized in Tables 1 and 2.

Quinuclidine leads to a conformational change of the complex. The coordination sphere around Mo can be described either as a distorted trigonal bipyramid or a square pyramid. In the trigonal bipyramidal description, the quinuclidine ligand (N(2)) and one hexafluoroisopropoxide ligand (O(1)) occupy the two axial positions. The Mo(VI) atom is displaced 0.09 Å out of the C(1)−N(1)−O(2) plane, whereas the axial bond angle O(1)−Mo(1)−N(2) is 159.6(1)° and the three equatorial angles are 108.7(2)° for N(1)−Mo(1)−C(1), 135.1(2)° for N(1)−Mo(1)−O(2), and 115.5(2)° for C(1)−Mo(1)−O(2). This structure is similar to that of *syn*-Mo(CHCMe$_2$Ph)(NAd)(OCH(CF$_3$)$_2$)$_2$(2,4-lutidine) (Ad = 1-adamantyl).[26]

In the polymerization of **1**, **5** yields only 61% five-membered rings corresponding to 61% α-addition. Starting the polymerization at −30 °C increased α-selectivity up to 70%. On one hand, this was quite surprising since a similar system, Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCH(CF$_3$)$_2$)$_2$(2,4-lutidine), polymerizes *o*-trimethylsilylphenylacetylene (*o*-TMSPA) *exclusively* via α-addition.[25,26] On the other hand, this result is in accordance with other

Table 1. X-ray Crystal Data Collection and Refinement Parameters for 3 and 5

	3	**5**
mol formula	$C_{26}H_{39}MoNO_2$	$C_{31}H_{36}F_{12}MoN_2O_2$
fw	493.52	792.56
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (No.2)	*Pbca* (No. 61)
a (pm)	1025.99(4)	1895.87(6)
b (pm)	1031.93(6)	1756.55(4)
c (pm)	1273.37(9)	2093.55(6)
α (deg)	86.885(3)	90
β (deg)	89.483(3)	90
γ (deg)	81.720(4)	90
vol (nm^3)	1.33216(13)	6.9719(3)
Z	2	8
temp (K)	233(2)	223(2)
calcd density (Mg/m^3)	1.230	1.510
abs coeff (mm^{-1})	0.512	0.471
color, habit	yellow plate	colorless plate
no. of reflcns with $I > 2\sigma(I)$	3294	3395
goodness-of-fit on F^2	1.060	1.064
R indices $I > 2\sigma(I)$	R1 = 0.0290	R1 = 0.0387
	wR2 = 0.0675	wR2 = 0.0742

Table 2. Selected Bond Lengths (pm) and Bond Angles (deg) for 5[a]

	Distances (pm)		
Mo(1)−N(1)	173.9(3)	Mo(1)−C(1)	188.5(4)
Mo(1)−O(2)	198.2(2)	Mo(1)−O(1)	203.0(2)
Mo(1)−N(2)	227.2(3)	N(1)−C(11)	140.7(5)
C(1)−C(2)	150.8(6)	C(1)−H(1)	127(5)
	Angles (deg)		
N(1)−Mo(1)−C(1)	108.71(18)	N(1)−Mo(1)−O(2)	135.14(14)
C(1)−Mo(1)−O(2)	115.50(17)	N(1)−Mo(1)−O(1)	99.73(13)
C(1)−Mo(1)−O(1)	98.14(15)	O(2)−Mo(1)−O(1)	81.66(10)
N(1)−Mo(1)−N(2)	91.24(12)	C(1)−Mo(1)−N(2)	94.44(14)
O(2)−Mo(1)−N(2)	78.49(10)	O(1)−Mo(1)−N(2)	159.64(10)
C(26)−O(1)−Mo(1)	128.9(2)	C(29)−O(2)−Mo(1)	135.1(2)
C(11)−N(1)−Mo(1)	157.0(3)	C(23)−N(2)−C(21)	107.7(3)
C(23)−N(2)−C(19)	107.1(3)	C(21)−N(2)−C(19)	108.0(3)
C(23)−N(2)−Mo(1)	110.1(2)	C(21)−N(2)−Mo(1)	112.1(2)
C(19)−N(2)−Mo(1)	111.7(2)	H(1)−C(1)−C(2)	99(2)
H(1)−C(1)−Mo(1)	109(2)	C(2)−C(1)−Mo(1)	151.4(4)

[a] Estimated standard deviations are given in parentheses.

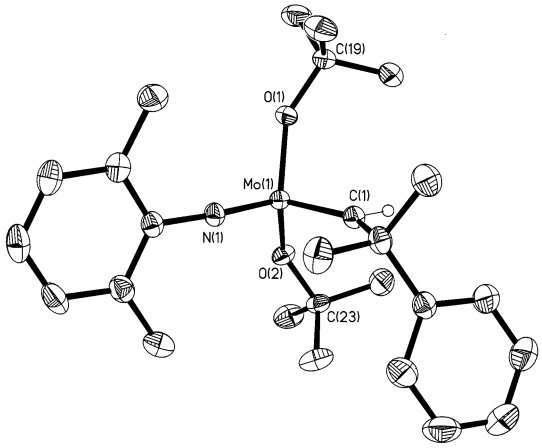


Figure 3. ORTEP drawing of **3**.

Table 3. Selected Bond Lengths (pm) and Bond Angles (deg) for 3[a]

	Distances (pm)		
Mo(1)−N(1)	172.9(2)	Mo(1)−C(1)	188.5(3)
Mo(1)−O(2)	188.9(2)	Mo(1)−O(1)	189.4(2)
O(1)−C(19)	144.1(3)	O(2)−C(23)	144.4(3)
N(1)−C(11)	139.2(4)	C(1)−H(1)	92(3)
	Angles (deg)		
N(1)−Mo(1)−C(1)	101.68(12)	C(1)−Mo(1)−O(2)	106.96(10)
N(1)−Mo(1)−O(2)	113.96(10)	C(1)−Mo(1)−O(1)	107.43(11)
N(1)−Mo(1)−O(1)	114.87(9)	O(2)−Mo(1)−O(1)	110.99(8)
C(19)−O(1)−Mo(1)	142.2(2)	C(23)−O(2)−Mo(1)	142.0(2)
C(11)−N(1)−Mo(1)	170.8(2)	H(1)−C(1)−C(2)	111(2)
H(1)−C(1)−Mo(1)	105(2)	C(2)−C(1)−Mo(1)	144.2(2)

[a] Estimated standard deviations are given in parentheses.

polymerization data for **1** with Mo-based catalysts containing fluorinated alkoxy ligands, which typically produce 2:1 mixtures of five- and six-membered rings.[32,43]

In molecular catalysis, as a general rule, a decrease in activity of a catalyst often results in an increase of selectivity. Consequently, we decided to move from fluorinated alkoxy ligands to nonfluorinated analogues. Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OCH$(CH_3)_2)_2$·quinuclidine (**6**) as the nonfluorinated analogue was prepared next. The base adduct **6** cannot be isolated and is generated in situ. Compared to **5**, initiator **6** displayed an increased α-selectivity. Polymers containing 68% five-memebered rings can be prepared with this initiator. This percentage can even be enhanced to 85% starting polymerization at low temperatures. Not unexpected, the significant effects of additional base and temperature on the final polymer structure already suggested that the rates of interconversion between the *syn* and *anti* forms of the initiators might play an important role. Since *tert*-butoxide-based initiators are known to possess the fastest rates of interconversion,[66,67] Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OC$(CH_3)_3)_2$ (**3**) was prepared and isolated in its base-free form. The X-ray structure of **3** is shown in Figure 3, and relevant structural data are summarized in Tables 1 and 3. Compound **3** crystallizes as a pseudotetrahedral complex in the *syn* form.

In contrast to **5**, the Mo atom in the solid-state structure of **3** adopts an approximate tetrahedral environment with bond angles between the ligands in the range of 101.7(1)° and 114.9(1)°. The bond lengths to the imido and alkylidene groups are almost identical to **5**. Thus, Mo(1)−N(1) is 1.739(3) Å and Mo(1)−C(1) is 1.885(4) Å in **5**; in **3** values of 1.729(2) and 1.885(3) Å, respectively, are found. The main difference between the two structures are the bond distances to the alkoxy groups, which is driven by the different nucleophilicity of these ligands. In **5**, the presence of electron-withdrawing CF_3 groups leads to values for Mo(1)−O(1) and Mo−O(2) of 2.030(2) and 1.982(2) Å, respectively. The C−O distance of the alkoxy group C(26)−O(1) and C(29)−O(2) is shortened to 1.361(5) and 1.378(4) Å, respectively. The slightly longer bond Mo(1)−O(1) in **5** is a result of the trans effect of the weakly coordinated quinuclidine group, with a Mo−N(2) distance of 2.272-(3) Å. Vice versa, the bond distances to the Mo atom are shorter in **3**, Mo(1)−O(1) and Mo(1)−O(2) are 1.894-(2) and 1.899(2) Å, respectively, the C−O distance is elongated to 1.441(3) Å for C(19)−O(1) and to 1.444(3) Å for C23−O(2).

Table 4. Polymerization Results[a] and UV/Vis Data[b] for Poly-1_{50}

catalyst	base	T_0 (°C)	five-membered rings (%)	λ_{max}[b] (nm)
5		25	61	545
5		−30	70	550
6		25	68	554
6		−30	85	592
3		25	88	591
3		−30	84	591
3	quinuclidine	25	>95	591
2		25	68	551
2		−30	>95	589
2	quinuclidine	25	76	554
4		25	91	591
4		−30	91	592
4	quinuclidine	25	>95	592
4	quinuclidine	40	90	592

[a] Spectra were obtained at 25 °C in a 0.05 M solution of $Cr(acac)_3$ in $CDCl_3$ at 300 MHz. [b] In $CHCl_3$.

While the use of **3** in its base-free form results in about 88% α-selectivity, addition of 1.1 equiv of quinuclidine *increased α-selectivity to > 95%*. To determine the steric influence of the substitutents at the 2,6-position of the arylimido ligand, we exchanged the methyl groups with isopropyl groups. The resulting initiator Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(OCH$(CH_3)_2)_2$ (**2**) offered access to polymers *based exclusively on five-membered ring structures* if the polymerization was started at −30 °C. Changing from isopropoxide to the sterically more demanding *tert*-butoxide group, the use of quinuclidine resulted in the *formation of > 95% five-membered rings at room temperature*. A summary of these data is given in Table 4.

Cyclopolymerizations. Polymerization of **1** was carried out in CH_2Cl_2 as a noncoordinating solvent by catalysts **2**−**6** and was terminated in a Wittig-like reaction by adding ferrocene aldehyde as a capping reagent. After precipitation in pentane, a dark colored powder with a metal luster was obtained which was soluble in $CHCl_3$, CH_2Cl_2, toluene, or DME with a deep purple color. Molar masses were determined by GPC vs PS (in $CHCl_3$) as well as by light scattering using $CHCl_3$ as solvent (Table 5). A plot of the number-average molecular weight (M_n) vs the number of monomer equivalents of **1** showed a linear dependence (Figure 4).

From this linear plot together with relatively low PDI's (<1.4) and the complete consumption of the monomer, we conclude that chain transfer or termination are absent and polymerizations therefore fulfill the

Table 5. GPC and UV/Vis Data for Poly-1_n Prepared Using the Catalyst 4-Quinuclidine as the Initiator in CH_2Cl_2[a]

poly-$\mathbf{1}_n$	M_n(calcd)[b]	M_n[c]	M_w/M_n[c]	M_n [d]	M_w/M_n [d]	M_n [e]	M_w/M_n [e]	λ_{max}[f] (nm)	ϵ[f] (10^6 cm^2 mmol^{-1})
$n = 5$	1512	4759	1.15	5028	1.16	2458	1.08	538	0.28
$n = 10$	2693	6758	1.20	6110	1.26	2223	1.15	578	0.31
$n = 20$	5056	11 851	1.23	10 470	1.28	3163	1.10	586	0.67
$n = 30$	7418	19 334	1.19	14 600	1.32	n.a.	n.a.	588	1.22
$n = 50$	12 144	24 179	1.26	18 800	1.33	n.a.	n.a.	590	0.70
$n = 70$	16 869	38 591	1.17	23 640	1.37	n.a.	n.a.	590	1.70
$n = 90$	21 595	43 761	1.20	30 420	1.35	n.a.	n.a.	591	1.96

[a] Details of the procedure are described in the Experimental Section. [b] Including end groups. [c] Determined by GPC vs PS with the RI detector. [d] Determined by light scattering at 690 nm. [e] Determined by MALDI−TOF mass spectroscopy. [f] In $CHCl_3$.

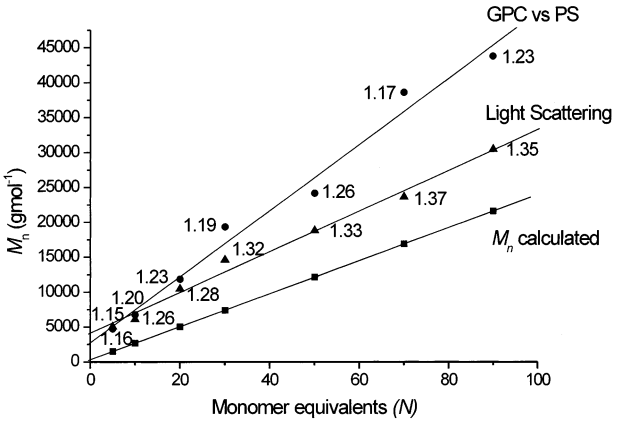


Figure 4. Plot of M_n vs number of monomer equivalents (N) and PDIs for initiator **4** in the presence of quinuclidine (compare Table 5).

Table 6. Determination of k_p/k_i for Cyclopolymerization of 1 with Catalysts 2−5[a]

catalyst	5 rings (%)	H_α of catalyst (ppm)	H_α of insertion products (ppm)	k_p/k_i
5	70	13.99, 13.41, 12.61, 12.37	13.32, 12.47	347
4	>95	11.42	12.51, 12.65, 13.42, 13.45	114
2	>95	11.35	11.25	14
3	>95	11.39	12.27, 12.31	9

[a] For reaction conditions, see Table 4 and the Experimental Section.

necessary requirements to be regarded as "living". For a more accurate description, Matyjaszewski[68] suggested a useful ranking for living systems based on the ratios of the rate constants of chain transfer, propagation, and chain termination. According to our findings, the present polymerization system is still active after at least 4 h. Thus, polymerizations resumed upon addition of **1** to a living system after this time. GPC measurements revealed no significant changes in the polydispersities of the resulting polymers compared to those prepared in a one-step procedure. On the basis of these reaction times, the present system satisfies at least a class V living system. Another important aspect in any polymerization system is the ratio of the rate constants for propagation and initiation, k_p/k_i, which can be determined by ^{1}H NMR.[69] Data are summarized in Table 6. Not unexpectedly, initiator **5** containing fluorinated ligands shows the highest value for k_p/k_i (347). Unfortunately, k_p/k_i is still high (9, 14, 114) for initiators **3**, **2**, and **4**. Nevertheless, this explains the small (positive) deviation of the LS-derived values for M_n from theoretical values (Figure 4).

Microstructure. The ratio of five- to six-membered rings along the polyene backbone can be determined by

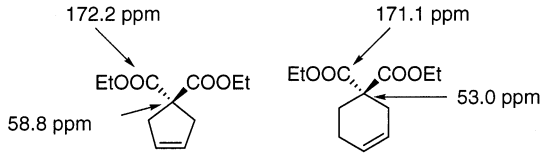


Figure 5. Structure and NMR shifts of relevant signals of 4,4-bis(ethoxycarbonyl)cyclopent-1-ene (**7**) and 4,4-bis(ethoxycarbonyl)cyclohex-1-ene (**8**).

^{13}C NMR. Both the signals of the quaternary carbon atoms of five- and six-membered rings occurring at 57−58 and 54−55 ppm, respectively, and of the carbonyl groups were used.[32] A general problem in quantitative NMR analysis is accuracy of the relative signal intensity. Relaxation phenomena caused by different molecule sizes and molecule dynamics as well as NOE effects caused by ^{1}H broadband decoupling may lead to falsification of signal intensities of ^{13}C NMR resonances. In an effort to avoid these experimental difficulties, we synthesized two model compounds, 4,4-bis(ethoxycarbonyl)cyclopent-1-ene (**7**) and 4,4-bis(ethoxycarbonyl)-cyclohex-1-ene (**8**) (Figure 5).[79] These molecules contain a cyclohexene or a cyclopentene unit, respectively, and a quaternary carbon atom with a chemical environment identical to the one in the polymer and are therefore appropriate cutouts of the polymer structure.

Quantitative ^{13}C NMR measurements of mixtures of the model compounds showed that the exact ring ratio can be determined with an error <3% by addition of Cr(acac)$_3$ as a relaxation agent.[70] Lack of Cr(acac)$_3$ leads to errors ≤30% in quantification. A typical ^{13}C NMR spectrum of a polymer containing both five- and six-membered ring structures is shown in Figure 6a. Resonances for the carbonyl atoms at 171.6 and 170.5 ppm are observed. While polymers containing both ring sizes show at least two sets of carbonyl (and quaternary carbon) resonances that can be ascribed to carbons in different chemical environments within the polymer chain (Figure 6a), ^{13}C NMR spectra of polymers containing solely five-membered rings show single, sharp signals (Figure 6b).

Cyclopolymerization of Other 1,6-Heptadiyne Derivatives. To investigate the steric influence of substituents at position 4 of the 1,6-heptadiyne system and the compatibility of other monomers than **1** with Mo-based catalysts, we cyclopolymerized 4-(ethoxycarbonyl)-1,6-heptadiyne (**9**) and di(1*S*,2*R*,5*S*)-(+)-menthyl dipropargylmalonate (**10**) using **4** in the presence of quinuclidine. In the case of **9** we achieved only 77% five-membered rings, even if the polymerization was started at − 30 °C. The relatively low α-selectivity of **4** for **9** compared to **1** can be explained by the low steric demands of the substituents at position 4. It was surprising that **10** cannot be cyclopolymerized at all by **4** in the presence of quinuclidine. The bulky menthyl groups apparently prevent any monomer approach to

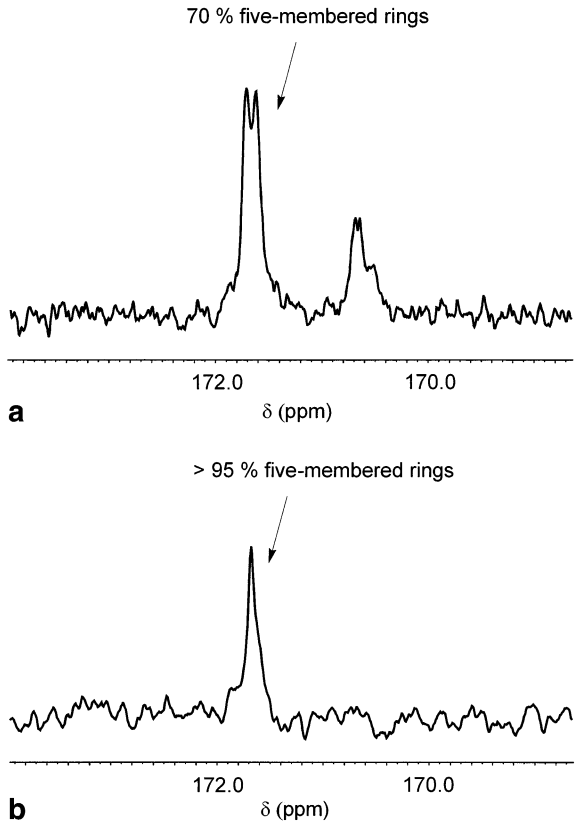


Figure 6. (a) ^{13}C NMR spectrum of the carbonyl region of poly-**1**$_{50}$ synthesized by low-temperatureinitiated cyclopolymerization using catalyst **5**. (b) ^{13}C NMR spectrum of the carbonyl region of poly-**1**$_{50}$ synthesized by catalyst **4** in the presence of quinuclidine.

the molybdenum center. Nevertheless, poly-**10** containing >95% five-membered rings was realized by low-temperature (−30 °C) initiated cyclopolymerization by **4** in the *absence* of quinuclidine. This provides further evidence that quinuclidine (and presumably any base) needs to dissociate prior to monomer insertion.[26]

While ring sizes and ratios thereof may be determined conveniently by ^{13}C NMR, 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,[71,72] an additional element of chirality is required in order to break the symmetry between single repetitive units. Therefore, 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (**12**) was synthesized and cyclopolymerized by catalyst **4** in the presence of quinuclidine. The ^{13}C NMR-spectrum of poly-**12** (Figure 7) displays two sharp carbonyl resonances around $\delta = 171$ ppm that can be attributed to the two different ester carbonyl groups of a polymer that contains only one ring size. The single, sharp signal at $\delta = 57$ ppm provides unambiguous evidence that the polymer consists >95% of five-membered rings.

To determine both tacticity and cis/trans configuration of the vinylene moiety, a 500 MHz ^{1}H,^{1}H COSY spectrum was recorded for poly-**12**$_{10}$ at 85 °C (toluene-d_8). Two sets of trans-coupled protons were unambiguously identified 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, Fc = ferrocenyl), respectively. A (broadened) signal at $\delta = 7.1$ ppm resulting from the overlap of the two resonances for the

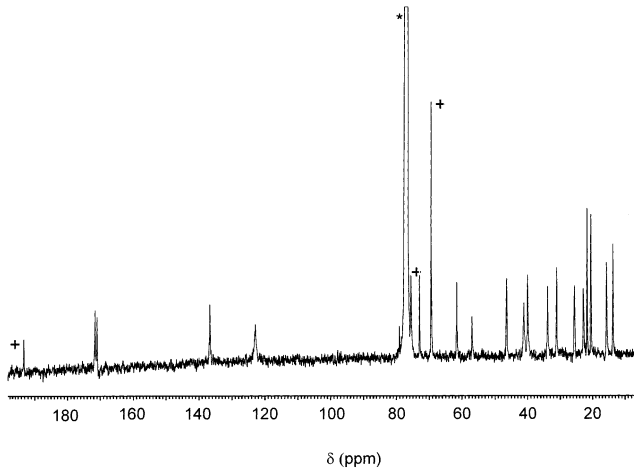


Figure 7. ^{13}C NMR spectrum of poly-**12**$_{50}$ synthesized by catalyst **4** in the presence of quinuclidine (∗ denotes $CDCl_3$; + denotes excess ferrocene aldehyde).

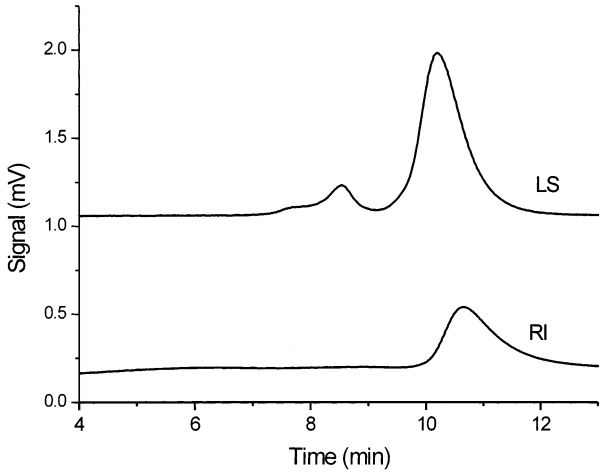


Figure 8. LS and RI signals of the SEC of poly-**1**$_{70}$.

protons along the conjugated backbone did not show any observable coupling. Unfortunately, we cannot completely exclude the possibility that any existing coupling is not observable due to small shift differences. We therefore cannot unambiguously assign any tacticity. Nevertheless, in summary, both ^{1}H and, in particular, ^{13}C NMR data, which reveal only one sharp signal for the vinylene carbon, strongly suggest that poly-**12** possesses a highly regular, alternating cis-(cyclopent-1-enylene-derived) and trans-(vinylene-derived) structure.

Polymer Properties. Values for M_n deduced from GPC vs PS are higher than those detected by light scattering (LS), which is an absolute method. This is in accordance with the assumption that poly-**1** possesses a comparably rigid backbone and therefore the mass concentration within a defined volume is not as high as in PS. Important enough, a linear relationship between n and M_n is obtained with both methods. Figure 4 summarizes these data. Additional information that is obtained by LS shall be discussed in more detail. The LS trace of the size-exclusion chromatograms of polymers prepared from a [M]:[I] ratio of 70:1 (Figure 8) is characterized by one main and another additional (high molecular weight) signal.

Since the high molecular weight signal does not show any concentration-dependent behavior and increases with time, it cannot be ascribed to a simple aggregate.

Table 7. UV/Vis Data and Values for N_{Eff} of Poly-1_n

polymer	λ_{max} (nm)[a]	E (eV)	DP[b]	N_{eff}[c]	N[d]
poly-$\mathbf{1}_5$	538	2.30	20	23	41
poly-$\mathbf{1}_{10}$	578	2.14	24	42	49
poly-$\mathbf{1}_{20}$	586	2.12	43	46	87
poly-$\mathbf{1}_{30}$	588	2.11	60	49	121
poly-$\mathbf{1}_{50}$	590	2.10	78	51	157
poly-$\mathbf{1}_{70}$	590	2.10	99	51	199
poly-$\mathbf{1}_{90}$	591	2.10	127	52	255

[a] In $CHCl_3$. [b] Calculated from M_n in column 5 of Table 5. [c] Average conjugation length calculated from the relationship $E = 1.9368 + 8.4391/N_{eff}^{0.75}$ where E is the energy of the transition. [d] Number of double bonds in conjugation.

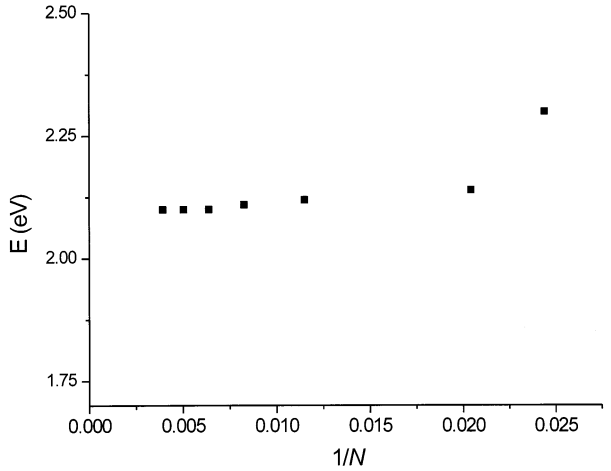


Figure 9. Plot of E vs $1/N$ for poly-**1**.

Thus, this observation is tentatively attributed to a intermolecular reaction of the double bonds along the polymer backbone, a process that takes place during storage and not during synthesis, indicating that cyclopolymerization is much faster than cross-linking. Detailed investigations on the polymer stability using GPC, UV, and DSC-TGA, respectively, are under way. Molecular weights of poly-$\mathbf{1}_5$, poly-$\mathbf{1}_{10}$, and poly-$\mathbf{1}_{20}$ as determined by MALDI−TOF mass spectroscopy are 2458, 2223, and 3163, respectively, corresponding to DPs of 9, 8, and 12. Apparently, high molecular weight fractions, though visible up to a DP of 30, do not desorb as well as the low molecular ones, thus preventing quantification. In view of these data, MALDI−TOF cannot be used to confirm molecular weights derived from LS.

Values for λ_{max} range from 538 to 591 nm, indicating a comparable strong coplanarity of the polymer backbone. Interestingly, these values are significantly higher than those for poly-**1** consisting of six-membered rings (λ_{max} < 511 nm in THF). A plot of the transition energy (in eV) vs $1/N$ (where N is the nominal average number of double bonds) for the series of poly-$\mathbf{1}_n$ samples in Table 7 is shown in Figure 9.

The finding that λ_{max} does not change significantly within $50 < N < 90$ suggests a maximum effective conjugation length (N_{eff}) ≤ 50. Values for N_{eff} were calculated on the base of poly(acetylene) model compounds (Table 7). In principle, the possibility that absorption spectra are a result of the linear superposition of the absorptions of shorter conjugated segments as found for polyenes consisting of solely six-membered rings,[73] still remains. Nevertheless, in view of the comparably high values for λ_{max} this appears less likely.

Mechanism and Propagating Species. Reaction of **1** with molybdenum alkylidenes that form exclusively five-membered rings proceeds via α-addition. This model was again confirmed by investigations concerning the first insertion product. In all cases, the original α-H signal disappeared and a set of two trans-coupled alkene protons, e.g., at $\delta = 5.94$ and 5.72 ppm, respectively, $J = 16.0$ Hz for **4**-quinuclidine, was observed. This is in accordance with the "small alkoxide" model developed by Schrock et al.[25] Nevertheless, the use of a comparably small alkoxide is a necessary yet insufficient requirement. Molybdenum complexes of type Mo(NAr′)(CHCMe$_2$Ph)(OR′)$_2$ exist in form of two rotamers.[72,74] 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 norborn-2-ene- and norbornadiene-based polymers.[29,30,72,74,75]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,[26] it strongly influences the reactivity of the entire system.[76,77] 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 **5** are not capable of forming poly-**1** solely consisting of five-membered rings.[32] As can be deduced from the data summarized in Table 4, neither addition of quinuclidine nor lower polymerization temperature significantly changes this situation. Since *syn*−*anti* interconversion is slow in these complexes, we propose *that the final geometry of a cyclopolymerization-derived polymer is at least influenced if not governed by both the relative reaction rates of the syn and anti isomer and the rate of interconversion*. If this were true, initiators based on nonfluorinated alkoxides should in fact allow the preparation of the target polymer since they show a fast *syn*−*anti* interconversion. The use of the nonfluorinated analogue **6** already allows the synthesis of poly-**1** at −30 °C that contains 85% five-memebered rings. Addition of quinuclidine to initiators **3** and **4** leads to the formation of poly-**1** containing solely five-membered rings.

To retrieve more information about the actual propagation species, initiators **2**, **3**, and **4** were characterized by low temperature ^{1}H NMR. Even at −60 °C, only signals for the *syn* form of the alkylidene species were observed. Similarly, upon addition of 1 equiv of **1**, only *syn* insertion products were observed. Nonetheless, this does not mean that small amounts (≤1%) of the by far more reactive *anti* rotamer are still present yet not visible. A profound discussion of reactivity and selectivity in the presence of quinuclidine, which influences *syn*−*anti* interconversion, would certainly necessitate absolute values for this process.

Conclusions

Catalyst tuning of well-defined Mo-based Schrock-carbenes for cyclopolymerization of 1,6-heptadiyne derivatives allows for the first time the synthesis of high molecular weight polyenes consisting virtually *exclusively* of five-membered rings. Beside a comparably small ligand sphere around the Mo center, polymerizations require special conditions such as low starting temperatures or the presence of quinuclidine. Polymerizations are living and presumable proceed via the more reactive *anti* isomer and require *syn*−*anti* isomerization to be faster than polymerization. The characterization of this class of polymers by light-scattering (LS) GPC

was carried out. Absolute molar masses determined by this method lie far below those values determined by GPC vs PS and underline the necessity of LS-detection for rigid polymers. Polymers prepared from 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (**12**) and Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$(quinuclidine) (**4**-quinuclidine) possess a highly regular, alternating cis−trans structure.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a MBraun glovebox or by using standard Schlenk techniques. Reagent grade dimethoxyethane (DME), diethyl ether, tetrahydrofuran, toluene, and pentane were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and $CDCl_3$ were distilled from calcium hydride under nitrogen. Ethylchloromalonate was distilled before use. Benzene-d_6 was distilled in vacuo from Na/benzophenone. Dichloromethane as polymerization solvent, benzene-d_6, and $CDCl_3$ were passed through a column of activated alumina prior to use. All other reagents were reagent grade (Aldrich, Fluka, Merck, STREM) and used as received without further purification.

Diethyl dipropargylmalonate (**1**),[78] 4-(ethoxycarbonyl)-1,6-heptadiyne (**9**),[43] di(1*S*,2*R*,5*S*)-(+)-menthyl dipropargylmalonate (**10**),[43] 4,4-bis(ethoxycarbonyl)cyclopent-1-ene (**7**),[79] 4,4-bis(ethoxycarbonyl)cyclohex-1-ene (**8**),[79] Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$DME,[80] Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$DME,[80] and Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$ (**2**)[80] were prepared as described in the literature.

Gel permeation chromatography (GPC) vs poly(styrene) (PS) was carried out using Shodex K-802.5, K-804, and K-805 columns, a 410 differential refractometer, and a 486 UV-detector for measurements in $CHCl_3$ (all from Waters). Samples were filtered through a 0.22 μm Teflon filter (Millipore) in order to remove particles. GPC columns were calibrated vs polystyrene standards (Polymer Standards Service (PSS), molecular weights 347 to 2.7 × 10^6 Da). Gel permeation chromatography (GPC) with light-scattering detection was carried out using a Waters Styragel HR 4E column, a Waters 2414 differential refractometer, a Waters 484 UV detector, and a Wyatt mini-dawn light-scattering detector (λ = 690 nm) on samples in $CHCl_3$. UV/vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range 300−800 nm. Elemental analyses (C, H, N) were performed on a Elementar Vario EL analyzer. MALDI−TOF spectra were recorded on a Bruker Biflex III spectrometer using dithranol (1,8,9-trihydroxyanthracene) as a matrix. NMR data were obtained at 300.13 MHz (^{1}H) and 75.48 MHz (^{13}C) and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are given in hertz. FT-IR spectra were recorded on a Bruker Vector 22 (ATR spectra) specrometer and a Bruker IFS 55 spectrophotometer (KBr spectra), respectively.

Mo(N-2,6-*i*-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OCH(CH$_3$)$_2$)$_2$ (2).[80] A cold (−30 °C) solution of LiOCH(CH$_3$)$_2$ (42 mg, 0.636 mmol) in diethyl ether (5 mL) was added dropwise to a prechilled solution (− 30 °C) of Mo(N-2,6-*i*-Pr_2-C_6H_3)(CHCMe$_2$Ph)(OTf)$_2$DME (250 mg, 0.316 mmol) in 12 mL of diethyl ether. Under stirring, the reaction mixture was allowed to warm to room temperature. After 1 h, the solvent was removed in vacuo, and the resulting solids were extracted with pentane. The filtered pentane extracts were concentrated to approximately 1 mL and stored at −30 °C. Yellow-orange crystals (112 mg, 68%) were isolated in two crops. This compound slowly decomposes in substance under Ar at ambient temperature. ^{1}H NMR (C_6D_6): δ 11.35 (s, 1 H, *syn*-C*H*CMe$_2$Ph), 7.50 (d, 2 H, $^3J_{HH}$ = 6.86, H_{ar}), 7.30−7.25 (m, 5 H, H_{ar}), 7.14 (m, 1 H, H_{ar}), 4.60 (sept, 2 H, $^3J_{HH}$ = 5.94, C*H*Me$_2$), 4.09 (sept, 2 H, $^3J_{HH}$ = 6.85, C*H*Me$_2$), 1.76 (s, 6 H, CHC*Me*$_2$Ph), 1.40−1.28 (m, 24 H, CH*Me*$_2$ and OCH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 265.7 (*syn*-*C*HCMe$_2$Ph), 153.7, 150.7, 146.5, 129.2, 127.8, 126.5, 126.4, 123.5, 79.6 (s, O*C*HMe$_2$), 53.2 (s, CH*C*Me$_2$Ph), 32.1 (s, CHC*Me*$_2$-Ph), 28.9 (s, *C*HMe$_2$), 24.3 (s, CH*Me*$_2$), 14.6 (s, OCH*Me*$_2$). Anal. Calcd for $C_{28}H_{43}MoNO_2$: C, 64.48; H, 8.31; N, 2.69. Found: C, 63.66; H, 8.26; N, 2.56.

Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OC(CH$_3$)$_3$)$_2$ (3). A solution of lithium *tert*-butoxide (56 mg, 0.699 mmol) in diethyl ether (2.5 mL) was prechilled to −30 °C and added dropwise to a cold (−30 °C) suspension of Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$-Ph)(OTf)$_2$·DME (250 mg, 0.340 mmol) in 5 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature while it was stirred. After 1 h, the solvent was removed in vacuo and the residue was extracted with pentane. The extracts were filtered through Celite, and the filtrate was evaporated to dryness in vacuo. Recrystallization from a minimum amount of pentane at −30 °C gave yellow-orange crystals in two crops (124 mg, 74%). ^{1}H NMR (C_6D_6): δ 11.39 (s, 1 H, *syn*-C*H*CMe$_2$Ph), 7.43 (d, 2 H, $^3J_{HH}$ = 7.91, H_o Ph), 7.16 (dxd, 2 H, $^3J_{HH}$ = 8.29, 6.78, H_m Ph), 7.00 (t, 1 H, $^3J_{HH}$ = 7.16, H_p Ph), 6.93−6.83 (m, 3 H, N*Ar*′), 2.43 (s, 6 H, *Me*NAr′), 1.67 (s, 6 H, CHC*Me*$_2$Ph), 1.28 (s, 18 H, OC(C*H*$_3$)$_3$). ^{13}C NMR: δ 264.1 (*syn*-*C*HCMe$_2$Ph), 156.2, 150.7, 136.2, 128.6, 128.3, 126.7, 126.5, 126.3, 77.6 (O*C*Me$_3$), 52.4 (s, CH*C*Me$_2$Ph), 32.3 (s, OC*Me*$_3$), 31.9 (s, CHC*Me*$_2$Ph), 20.1 (s, *Me*NAr′). Anal. Calcd for $C_{26}H_{39}MoNO_2$: C, 63.27; H, 7.96; N, 2.84. Found: C, 62.94; H, 7.86; N, 2.83.

Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OCH(CF$_3$)$_2$)$_2$·quinuclidine (5). A cold (−30 °C) solution of potassium hexafluoro *tert*-butoxide (200 mg, 0.970 mmol) in Et$_2$O (4 mL) was added dropwise to a prechilled suspension (−30 °C) of Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$·DME (350 mg, 0.476 mmol) in 7 mL of diethyl ether. The mixture was stirred for 30 min. Quinuclidine (65 mg, 0.585 mmol) was added in one portion, and the solution was stirred for another 30 min. The solvent was removed in vacuo, and the resulting solids were extracted with pentane. The combined pentane extracts were filtered and concentrated to approximately 1 mL and stored at −30 °C. Yellow needles (302 mg, 79%) were isolated in three crops. ^{1}H NMR (C_6D_6): δ 13.99, 13.41 (s, *anti*-C*H*CMe$_2$Ph), 12.61, 12.37 (s, *syn*-C*H*CMe$_2$Ph), 7.13−6.70 (m, 8 H, H_{ar}), 6.20 (sept, $^3J_{HH}$ = 6.85, 1 H, C*H*(CF$_3$)$_2$), 4.37 (sept, $^3J_{HH}$ = 6.40, 1 H, C*H*(CF$_3$)$_2$), 3.10−2.69 (m, 6 H, NC*H*$_2$), 2.62 (s, 6 H, *Me*NAr′), 1.91 (s, 6 H, CHC*Me*$_2$Ph), 1.06−0.78 (m, 7 H, NCH$_2$C*H*$_2$, C*H*$_{quinuclidine}$). ^{13}C{^{1}H} NMR: δ 308.4 (s, *anti*-*C*HCMe$_2$Ph), 294.7 (s, *syn*-*C*HCMe$_2$Ph), 153.9, 147.8, 134.9, 129.3, 129.1, 128.9, 127.2, 126.8, 126.4, 126.3 (*C*$_{ar}$, *C*F$_3$), 83.9 and 75 (q, $^2J_{CF}$ = 31.6, 30.8, *C*H(CF$_3$)$_2$)), 53.3 (s, NC*H*$_2$), 52.9 (s, CH*C*Me$_2$Ph), 32.3 (s, CHC*Me*$_2$Ph), 26.1 (s, NCH$_2$*C*H$_2$), 21.0 (s, *C*H$_{quinuclidine}$), 19.8 (s, *Me*NAr′). Anal. Calcd for $C_{31}H_{36}F_{12}MoN_2O_2$: C, 46.98; H, 4.58; N, 3.53. Found: C, 47.08; H, 4.70; N, 3.22.

Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OCH(CH$_3$)$_2$)$_2$·quinuclidine (6). A solution of lithium isopropoxide (7.8 mg, 0.118 mmol) in diethyl ether (0.7 mL) prechilled to −30 °C was added dropwise to a cold (−30 °C) suspension of Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$·DME (43.6 mg, 0.059 mmol) in 2.1 mL of diethyl ether. After the mixture was stirred for 5 min, quinuclidine (8 mg, 0.072 mmol) was added, and the mixture was stirred for another 5 min. The solvent was removed in vacuo, and the resulting solids were extracted with pentane. The combined pentane extracts were filtered and evaporated to dryness. The remaining solid was dissolved in CH_2Cl_2 and directly used for polymerization. All attempts to isolate the compound in a pure form failed. ^{1}H NMR (C_6D_6): δ 11.68 (s, 1H, *syn*-C*H*CMe$_2$Ph), 7.46 (d, 2 H, $^3J_{HH}$ = 7.77, H_o Ph), 7.05−6.67 (m, 6 H, H_{ar}), 4.35 (sept, $^3J_{HH}$ = 6.40, 2 H, OC*H*Me$_2$), 2.83 (t, $^3J_{HH}$ = 7.77, 6 H, NC*H*$_2$), 2.56 (s, 6 H, *Me*NAr′), 1.88−0.96 (m, 25 H, CHC*Me*$_2$Ph, OCH*Me*$_2$, NCH$_2$C*H*$_2$, and C*H*$_{quinuclidine}$). ^{13}C{^{1}H} NMR (C_6D_6): δ 270.0 (*syn*-*C*HCMe$_2$-Ph), 150.0, 136.9, 136.8, 132.3, 129.2, 128.9, 126.8, 126.4, 59.2 (s, O*C*H(CH$_3$)$_2$), 57.3 (s, CH*C*Me$_2$Ph), 47.8 (s, N*C*H$_2$), 32.2 (s, CHC*Me*$_2$Ph), 27.8 (s, NCH$_2$*C*H$_2$), 23.1 (s, NCH$_2$CH$_2$*C*H), 19.4 (s, *Me*NAr′), 14.6 (s, OCH*Me*$_2$).

Ethyl-(1*S*,2*R*,5*S*)-(+)-menthyl Malonate (11). Ethylchloromalonate (10 g, 66.4 mmol) was dissolved in 150 mL of diethyl ether. (1*S*,2*R*,5*S*)-(+)-Menthol (10.38 g, 66.4 mmol**)** was dissolved in 20 mL of diethyl ether. The solution containing the alcohol was added to the acid chloride solution at 0 °C over a period of 2 h. The solution was stirred for 12 h at room

temperature. Saturated aqueous $NaHCO_3$ was added to the diethyl ether solution until bubbling ceased. The organic layer was extracted with water (3 × 20 mL) and washed once with brine (10 mL). The organic fraction was dried over $MgSO_4$. The solution was filtered, and the diethyl ether was removed in vacuo. The solid product was crystallized from pentane at −80 °C to give a colorless oil (16.3 g, 91%). ^{1}H NMR ($CDCl_3$): δ 4.70 (dt, $^3J_{HH}$ = 10.9, 4.4, 1 H, C*H*O$_2$C), 4.17 (m, 2 H, CO$_2$C*H*$_2$CH$_3$), 3.31 (s, 2 H, C*H*$_2$(CO$_2$)$_2$), 2.00 (m, 1 H, $H_{menthyl}$), 1.87 (dxsept, $^3J_{HH}$ = 2.7, 6.7, 1 H, C*H*Me$_2$), 1.65 (m, 2 H, COOCHC*H*$_2$), 1.50−1.30 (m, 2 H, $H_{menthyl}$), 1.25 (t, $^3J_{HH}$ = 7.25, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.20−0.70 (m, 12 H, $H_{menthyl}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.6 (s, *C*OOEt), 166.1 (s, *C*OO$_{menthyl}$), 75.6 (s, COO*C*H$_{menthyl}$), 61.4 (s, COO*C*H$_2$CH$_3$), 46.9, 42.1, 40.6, 34.2, 31.4, 26.0, 23.3, 21.9, 20.7, 16.2, 14.0 (s, COOCH$_2$*C*H$_3$). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.68; H, 9.67.

4-(Ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (12). Ethyl-(1*S*,2*R*,5*S*)-(+)-menthyl malonate (7.5 g, 27.7 mmol) was dissolved in 20 mL of dry THF. The solution was added over 30 min to a suspension of NaH (1.33 g, 55.5 mmol) in 150 mL of THF. After the evolution of H_2 had ceased, propargyl bromide (6.6 g, 55.5 mmol) was added. Gas evolution resumed. The solution was stirred for 12 h. Water was added (30 mL), and the organic layer was separated. The organic layer was washed with water and was dried over $MgSO_4$. The solvents were removed to afford a yellow oil. The crude product however contained ethyl-(1*S*,2*R*,5*S*)-(+)-menthyl malonate, 2-propargylethyl-(1*S*,2*R*,5*S*)-(+)-menthyl malonate, and 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne. Unfortunately, all attempts failed to separate the dialkylated product by standard chromatographic techniques. Therefore, the alkylation procedure was repeated as described above with the crude product to yield a second crude product, which obtained only 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne. The product was distilled using a bulb tube to yield a crystalline colorless solid (5.24 g, 54%). ^{1}H NMR ($CDCl_3$): δ 4.70 (dxt, $^3J_{HH}$ = 10.9, 4.4, 1 H, C*H*O$_2$C), 4.23 (dxq, $^1J_{HH}$ = 31.9, $^3J_{HH}$ = 7.1, 1H, CO$_2$C*H*HCH$_3$), 4.13 (dxq, $^1J_{HH}$ = 31.9, $^3J_{HH}$ = 7.3, 1 H, CO$_2$CH*H*CH$_3$), 2.97 (m, 4 H, C*H*$_2$C≡CH), 2.00 (m, 2 H, CH$_2$C≡C*H*), 1.86 (dxsept, $^3J_{HH}$ = 2.7, 7.1, 1 H, C*H*Me$_2$), 1.65 (m, 2 H, $H_{menthyl}$), 1.60−1.30 (m, 3 H, $H_{menthyl}$), 1.24 (t, $^3J_{HH}$ = 7.1, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.08−0.71 (m, 12 H, $H_{menthyl}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.7 (s, *C*OOEt), 168.1 (s, *C*OO$_{menthyl}$), 78.52 (s, C_{alkin}), 78.50 (s, C_{alkin}) 76.2 (s, COO*C*H$_{menthyl}$), 71.63 (s, C_{alkin}), 71.62 (s, C_{alkin}), 62.0 (s, COO*C*H$_2$CH$_3$), 56.3 (s, C_{ipso}), 46.8, 40.3, 34.1, 31.3, 25.8, 23.0, 22.43 (s, *C*H$_2$C≡CH), 22.41 (s, *C*H$_2$C≡CH), 21.9, 20.7, 15.9, 13.9 (s, COOCH$_2$*C*H$_3$). Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.82; H, 8.66.

Synthesis of Poly(1,6-heptadiyne)s. The procedure described for poly-**1**$_{50}$ is generally applicable to all other polymerizations. **4** (6.98 mg, 0.013 mmol) was dissolved in 3 mL of CH_2Cl_2. Quinuclidine (1.55 mg, 0.014 mmol) was added to the catalyst solution and stirred for 20 min. A solution of **1** (150 mg, 0.635 mmol) in 0.5 mL of CH_2Cl_2 was added all at once to the vigorous stirring solution. After 2 h, ferrocene aldehyde (27.2 mg, 0.127 mmol) was added, and the reaction mixture was stirred for 60 min. The mixture was concentrated to ∼ 1 mL, and the polymer was precipitated by dropwise addition of the solution to 50 mL of pentane. The polymer was collected by filtration and dried in vacuo to yield a dark purple solid (121 mg, 78%). Quantitative conversion of **1** was observed by TLC (thin-layer chromatography). Poly-**10**$_{50}$ and poly-**12**$_{50}$ were soluble in all common organic solvents and were purified by passing a CH_2Cl_2 solution through a short column of Al_2O_3.

Poly-1$_{50}$. IR (KBr, cm^{-1}): 3390 m, 2977 m, 1725 s, 1465 m, 1444 m, 1385 m, 1366 m, 1249 s, 1182 s, 1156 s, 1094 m, 1069 m, 1047 m, 1007 m, 946 m, 896 m, 859 m, 777 m, 627 m. ^{1}H NMR ($CDCl_3$): δ 6.70 (br m, 2 H, $H_{olefinic}$), 4.23 (br m, 4 H, OC*H*$_2$Me), 3.41 (br m, 4 H, C*H*$_{2allylic}$), 1.30 (br m, 6 H, OCH$_2$*Me*). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 171.6 (*C*OO), 136.6 and 122.8 ($C_{olefinic}$), 61.6 (OCH$_2$Me), 56.9 (C_{ipso}), 41.1 ($C_{allylic}$), 13.8 (OCH$_2$*Me*).

Poly-9$_{50}$. ^{1}H NMR ($CDCl_3$): δ 7.10−6.70 (br m, 2 H, $H_{olefinic}$), 4.26 (br m, 4 H, OC*H*$_2$Me), 3.40−2.20 (br m, 5 H, C*H*$_{2allylic}$, C*H*COOEt), 1.28 (br m, 6 H, OCH$_2$*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.3 and 174.6 (*C*OOEt), 138.9, 137.8, 137.3, 136.9, 136.1, 135.3, 134.9, 132.4, 125.8, 122.8, 120.8 ($C_{olefinic}$), 60.4 (O*C*H$_2$Me), 41.0, 40.6, 39.8 36.8, 35.6, 33.7, 29.3, 29.1, 28.4, 27.0, 26.4, 23.4, 21.9 ($C_{allylic}$, *C*HCOOEt), 14.0 (OCH$_2$*Me*).

Poly-10$_{50}$. ^{1}H NMR ($CDCl_3$): δ 7.10−6.30 (br m, 2 H, $H_{olefinic}$), 5.00−4.50 (m, 2 H, COOC*H*$_{menthyl}$), 3.60−2.80 (br m, 4 H, C*H*$_{2allylic}$), 2.20−0.50 (br m, 36 H, $H_{menthyl}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 170.8 (*C*OO$_{menthyl}$), 136.8 and 122.6 ($C_{olefinic}$) 75.5 (COO*C*H$_{menthyl}$), 57.7 (C_{ipso}), 46.6, 40.3, 33.8, 31.0, 23.1, 22.4, 22.1, 21.7, 20.6, 15.8 (OCH$_2$*Me*).

Poly-12$_{50}$. IR (film, cm^{-1}): 2955 m, 2869 m, 1726 s, 1682 s, 1455 m, 1426 s, 1183 m, 1070 bs, 957 m, 820 s, 743 m, 700 m. ^{1}H NMR ($CDCl_3$): δ 6.90−6.30 (br m, 2 H, $H_{olefinic}$), 4.75−4.60 (m, 1 H, $H_{menthyl}$), 4.35−4.05 (br m, 2 H, OC*H*$_2$Me), 3.70−3.00 (br m, 4 H, C*H*$_{2allylic}$), 2.20−0.50 (br m, 21 H, $H_{menthyl}$, OCH$_2$*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.6 (COOEt), 171.0 (*C*OO$_{menthyl}$), 136.7 and 122.8 ($C_{olefinic}$), 75.5 (COO*C*H$_{menthyl}$), 61.6 (O*C*H$_2$Me), 57.0 (C_{ipso}), 46.4, 41.1, 40.0, 33.8, 31.1, 25.6, 22.8, 21.7, 20.6, 15.8, 13.8 (OCH$_2$*Me*).

Determination of the Microstructure. In a typical experiment, 4,4-bis(ethoxycarbonyl)cyclopent-1-ene (**7**) (10.0 mg, 0.047 mmol) and 4,4-bis(ethoxycarbonyl)cyclohex-1-ene (**8**) (10.7 mg, 0.047 mmol) were dissolved in a 5 mol % solution of Cr(acac)$_3$ in $CDCl_3$. Integration of the carbonyl resonances after ^{13}C NMR experiment related to the weighted samples displayed a error smaller than 3% in quantification of the compounds.

COSY NMR Spectra. Spectra were obtained on a Varian Unity plus 500 using a standard software package. Spectra were acquired in toluene-d_8 at 26 and 85°C, respectively.

Determination of the Ratio of k_p to k_i. Experiments were carried out at 25 °C in $CDCl_3$ according to procedures described in the literature.[69] Values for k_p/k_i are listed in Table 6.

X-ray Data. Data collection was performed on a Nonius Kappa CCD with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[81] Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. Structures were solved with direct methods and refined against F^2 using the SHELX program suite.[82,83] Hydrogen atoms were added geometrically and refined using a riding model except at the carbene atom C(1), for which they were refined as regular atoms with an isotropic displacement parameter. All nonhydrogen atoms were refined with anisotropic displacement parameters.

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Supporting Information Available: Tables giving details about the crystallographic data of compounds **3** and **5** (structures of which are given in Figures 3 and 2, respectively), including crystal and refinement data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters. This material is available free of charge via the Internet at

http://pubs.acs.org. X-ray crystallographic data in CIF format are available from the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, U.K.) on quoting the depository numbers CCDC-179436 (**3**) and 179437 (**5**), the names of the authors, and the journal citations.

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