2668 *Macromolecules* **2003,** *36,* 2668−2673

First Controlled Cyclopolymerization of Diethyl Dipropargylmalonate by $MoCl_5-n\text{-}Bu_4Sn-EtOH-$Quinuclidine and $MoOCl_4-n\text{-}Bu_4Sn-EtOH-$Quinuclidine To Give Highly Regular Polyenes Consisting Exclusively of 1,2-(Cyclopent-1-enylene)−Vinylene Units

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Received October 21, 2002; Revised Manuscript Received February 12, 2003

ABSTRACT: Diethyl dipropargylmalonate (DEDPM) was cyclopolymerized by $MoCl_5-n\text{-}Bu_4Sn-EtOH-$quinuclidine (1:1:5:1) and $MoOCl_4-n\text{-}Bu_4Sn-EtOH-$quinuclidine (1:1:2:1), respectively, to produce poly(DEDPM) exclusively based on 1,2-(cyclopent-1-enylene)vinylene units (EtOH = ethanol). The exact ratio of five- to six-membered rings was determined by quantitative ^{13}C NMR measurements. The initiator efficiency of $MoOCl_4-n\text{-}Bu_4Sn-EtOH-$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 ≤67%. The absorption maximum λ_{max} for poly(DEDPM) was 587 nm. A maximum effective conjugation length (N_{eff}) of 49 was estimated therefrom. Molecular weights and polydispersity indices (PDIs) of the polymers were determined in $CHCl_3$ by size exclusion chromatography (SEC) vs polystyrene (PS). Additionally, light-scattering (LS) data were collected at $\lambda = 690$ nm in order to calculate absolute molecular weights. Polydispersities ≤1.9 were obtained. A plot of number of monomers (N) added vs molecular weights as determined by LS shows 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 h in the presence of monomer yet do not fulfill the criteria of a truly living polymerization. The ^1H NMR spectrum of the in situ prepared $MoCl_5$-based initiator showed two triplet carbene resonances at $\delta = 11.27$ and 11.02 ppm, indicating the presence of more than one butylidene species. Accordingly, the ^{13}C NMR spectrum of the $MoCl_5$-based initiator showed carbene resonances at $\delta = 276.0$, 275.9, 272.4, 271.3, 262.7, and 261.6 ppm. Identical triplet resonances were observed for the $MoOCl_4$-based initiator at $\delta = 11.27$ and 11.07. The corresponding ^{13}C NMR spectrum revealed carbene resonances at $\delta = 276.1$, 262.7, and 261.6 ppm.

Introduction

Soluble, conjugated organic polymers with a well-defined microstructure are of particular importance due to their optical and electronic properties.[1−6] The cyclopolymerization of 1,6-heptadiynes containing appropriate substituents at the 4-position offers an attractive access to polyenes with cyclic recurring units along the backbone.[7,8] Usually these polymers display good solubility in common organic solvents such as C_6H_6, toluene, CH_2Cl_2, $CHCl_3$, good long-term stability toward oxidation and high effective conjugation lengths (N_{eff}).[7−10] Poly(diethyl dipropargylmalonate) (poly(DEDPM)) has been prepared by Ziegler-type catalysts,[11,12] Pd catalysts,[13] anionic polymerization,[14] and binary/ternary Mo- or W-based catalysts.[15] Unfortunately, these systems lead to mostly insoluble, ill-defined polymers with variable repetitive units and broad molecular weight distributions (polydispersity index (PDI) ≫ 2). However, well-defined high oxidation-state molybdenum carbenes cyclopolymerize 1,6-heptadiynes in a living manner to produce polyenes that contain either a mixture of five- and six-membered rings[7,8] or exclusively six-membered rings.[9,10] Recently, we elaborated a synthetic route to polyenes containing exclusively five-membered rings and a highly regular, tactic alternating cis−trans structure by cyclopolymerization of DEDPM with well-defined molybdenum-based initiators such as $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OC(CH_3)_3)_2$ in the presence of quinuclidine.[16,17] In principle, cyclopolymers based on five-membered ring structures can also be realized with classical $MoCl_5$-based initiators. However, only oligomers with a $DP_n < 6$ and broad polydispersities (PDIs < 4.2) have been reported so far.[18] Alternatively, the synthesis of poly(DEDPM) exclusively consisting of five-membered rings has been accomplished using $Mo(CO)_6$.[19] Acceptable DP_ns (≤50) and PDIs (≤2.2) were obtained by this approach; however, reaction times of 48 h and reaction temperatures of 100 °C appeared less attractive. Despite the superiority of Schrock initiators, we were interested in the principle question whether $MoCl_5$- and $MoOCl_4$-based initiators as cheap alternatives for larger-scale industrial manufacture were capable of generating poly(DEDPM) containing only five-membered rings. In addition, we investigated whether this could be accomplished under mild and straightforward reaction conditions and, important enough, whether the properties of the polymers were similar to those prepared by Schrock initiators. We now report for the first time the cyclopolymerization of 1,6-heptadiynes by

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10.1021/ma021604l CCC: $25.00

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

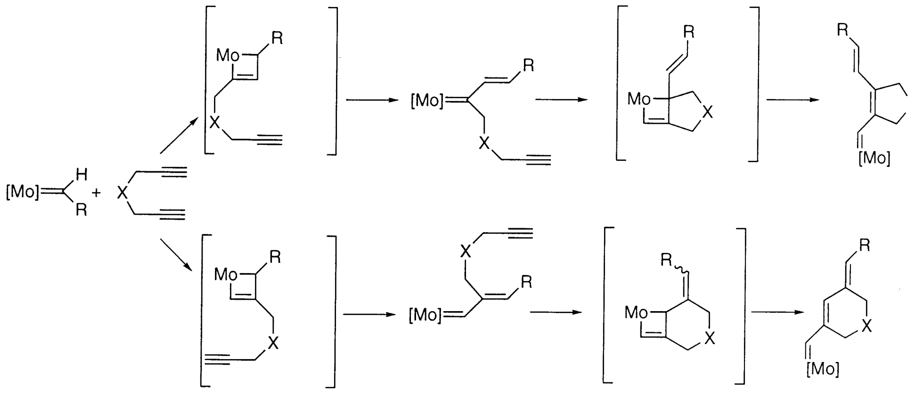

Table 1. GPC and UV−Vis Data and Initiator Efficiencies for Poly(DEDPM)$_{50}$[a] Prepared Using MoCl$_5$−*n*-Bu$_4$Sn−EtOH−Quinuclidine−DEDPM as Initiator in CH$_2$Cl$_2$[g]

MoCl$_5$−*n*-Bu$_4$Sn−EtOH−Q[b]−DEDPM	5-rings[c] (%)	M_n[d]	M_w/M_n[d]	M_n[e]	M_w/M_n[e]	yield (%)	λ_{max}[f] (nm)	[P*]/[Cat] (%)
1:1:0:0:50	90	62 700	3.68	45 400	3.67	57	586	26
1:1:1:0:50	83	133 000	3.38	132 000	3.50	70	587	9
1:1:2:0:50	88	98 600	2.78	87 000	2.41	74	585	14
1:1:3:0:50	89	112 000	2.61	93 200	2.33	79	584	8
1:1:4:0:50	86	133 000	1.88	99 600	2.08	77	586	12
1:1:5:0:50	88	117 000	1.79	94 500	1.80	70	585	13
1:1:6:0:50	85	120 000	1.96	96 000	1.98	68	583	12
1:1:5:1:50	> 95	20 300	1.68	17 700	1.23	64	587	67

[a] M_n(calculated) = 12 069 g/mol. [b] Q = quinuclidine. [c] Spectra were obtained at 25 °C in a 0.05 M solution of Cr(acac)$_3$ in CDCl$_3$ at 300 MHz. [d] Determined by GPC vs PS with the RI detector. [e] Determined by light scattering at λ = 690 nm. [f] In CHCl$_3$. [g] Polymerizations were carried out at room temperature.

a MoOCl$_4$-based initiator and two quaternary catalytic systems (i.e. 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)) that can cyclopolymerize DEDPM in a controlled way to yield conjugated polyene backbones containing exclusively five-membered rings (EtOH = ethanol). In addition to standard polymer properties, we investigate the nature of the polymerization active carbene species by ^{1}H and ^{13}C NMR spectroscopy and the lifetime of the initiators by time dependent multistage polymerizations.

Results and Discussion

MoCl$_5$-Based Initiators. Dipropargylmalonate esters are attractive monomers to produce soluble polyenes. The two different reaction pathways that produce polymers containing either five- or six-membered rings are shown in Scheme 1.[7] It has been proposed that metathesis-based 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.[18] as well as by steric and electronic effects of the ligand sphere around the Mo center as demonstrated for Schrock-type initiators.[9,10,16,17,20−22]

In the first step, MoCl$_5$-based systems were used to cyclopolymerize DEDPM. The resulting polymers with five- and six-membered rings showed relatively high molecular weights with broad polydispersities. Unfortunately, cyclopolymers based on five-membered ring structures were only accessible with DP$_n$s < 6 and PDIs ≤ 4.2 with these classical MoCl$_5$-based initiators.[18] To tune this initiator system for a controlled cyclopolymerization of DEDPM, we varied the stoichiometry of the initiator components (Table 1).

A 1:1 mixture of MoCl$_5$/*n*-Bu$_4$Sn in CH$_2$Cl$_2$ as a noncoordinating solvent generated poly(DEDPM) with a M_n of 45 400 g/mol (PDI = 3.67). Upon addition of ethanol, PDIs decreased with increasing amounts of ethanol while the molar masses remained virtually unchanged in the range of 100 000 g/mol. Initiation efficiencies were in the “classical” range of 9−14%. The effect of ethanol in the case of MoOCl$_4$-based initiators has already been intensively discussed in the literature. Other groups have proposed that ethanol coordinates with the active species and thus stabilizes the initiator.[23,24] A 5-fold excess of ethanol appeared to be the optimum amount for this system, yielding poly(DEDPM) with a PDI of 1.80 containing ≤ 90% five-membered rings (Figure 1A). In the third step we extended the MoCl$_5$-based initiator system by adding 1 equiv of quinuclidine. As previously observed for Schrock initiator-based polymerization systems,[16,17] this had a tremendous effect on polymerization behavior. The value for M_n with 17 700 g/mol decreased by a factor of 5 in comparison to an initiator system free of quinuclidine. Cyclopolymerizations proceeded with an initiation efficiency of 67% and poly(DEDPM) prepared by this novel MoCl$_5$-based initiator consisted of >95% five-membered rings. A representative ^{13}C NMR spectrum is shown in Figure 1B.

Table 2. GPC and UV−Vis Data and Initiator Efficiencies for Poly(DEDPM)$_{50}$[a] Prepared Using MoOCl$_4$−*n*-Bu$_4$Sn−EtOH−Quinuclidine−DEDPM as Initiator in CH$_2$Cl$_2$[g]

MoOCl$_4$−*n*-Bu$_4$Sn−EtOH−Q[b]−DEDPM	5-rings[c] (%)	M_n[d]	M_w/M_n[d]	M_n[e]	M_w/M_n[e]	yield (%)	λ_{max}[f] (nm)	[P*]/[Cat]
1:1:2:0:50	89	134 000	3.05	131 000	3.18	76	587	9
1:1:2:0[b]:50	81	141 000	2.69	92 400	3.72	79	550	13
1:1:2:1:50	>95	19 600	1.75	13 000	1.94	73	587	91

[a] M_n(calculated) = 12 069 g/mol. [b] Q = quinuclidine. [c] Spectra were obtained at 25 °C in a 0.05 M solution of Cr(acac)$_3$ in CDCl$_3$ at 300 MHz. [d] Determined by GPC vs PS with the RI detector. [e] Determined by light scattering at λ = 690 nm. [f] In CHCl$_3$. [g] Polymerizations were carried out at room temperature.

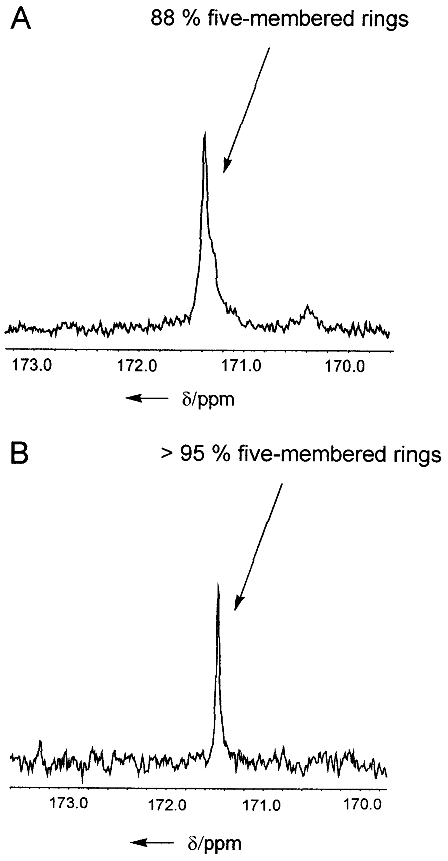

Figure 1. ^{13}C NMR spectra of the carbonyl region of poly(DEDEPM)$_{50}$ synthesized using (A) MoCl$_5$−*n*-Bu$_4$Sn−EtOH (1:1:5) and (B) MoCl$_5$−*n*-Bu$_4$Sn−EtOH−quinuclidine (1:1:5:1) as the initiator in CH$_2$Cl$_2$ at room temperature.

The microstructure was determined by quantitative ^{13}C NMR spectroscopy based on the different chemical shifts characteristic for five- and six-memebered ring systems.[17] Thus, poly(DEDPM) containing both ring sizes generally has resonances at 171.5 and 170.5 ppm for the carbonyl carbons and at 57.0 and 54.3 ppm for the quaternary aliphatic ring carbons of the five and six-membered rings, respectively. The single resonances at δ = 171.5 ppm and at δ = 56.9 ppm, confirmed that the microstructure of poly(DEDPM) prepared by MoCl$_5$−*n*-Bu$_4$Sn−EtOH−quinuclidine (1:1:5:1) contained virtually solely (>95%) five-membered rings.

MoOCl$_4$-Based Initiators. As an alternative to MoCl$_5$-derived initiators, we investigated the use of MoOCl$_4$-based systems. With such systems, living polymerizations of various 1-alkynes have already been reported,[23−27] nevertheless, the use of a MoOCl$_4$-based initiator for the cyclopolymerization of DEDPM only resulted in gel-type polymers so far.[28] Our investigations started with MoOCl$_4$−*n*-Bu$_4$Sn-EtOH (1:1:2). Cyclopolymerization of DEDPM yielded poly(DEDPM) with an M_n of 130 000 g/mol and a PDI of 3.18 that contained approximately 90% five-membered rings (Table 2).

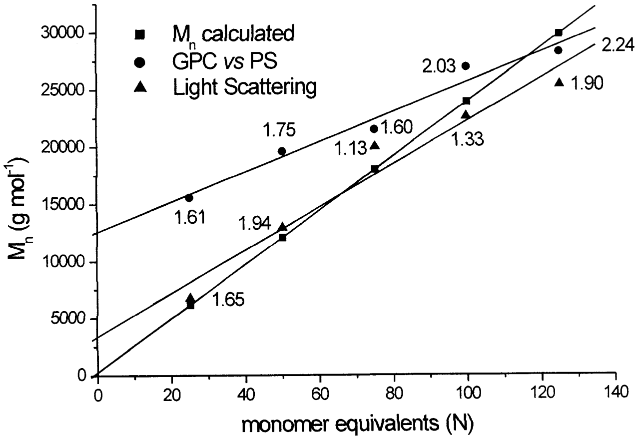

Figure 2. Plot of M_n vs number of monomer equivalents (N) and polydispersity indices for MoCl$_5$−*n*-Bu$_4$Sn−EtOH−quinuclidine (1:1:5:1).

Surprisingly, substituting CH$_2$Cl$_2$ by anisole, which has been reported to be the preferred solvent in 1-alkyne polymerization using MoOCl$_4$-based initiators due to its coordinating abilities,[23,24] did not positively affect the PDI or five-membered-ring content in the cyclopolymerization of DEDPM. As an alternative, encouraged by the results obtained with the MoCl$_5$−*n*-Bu$_4$Sn-EtOH system, we added 1 equiv of quinuclidine as the fourth initiator component. As observed for the MoCl$_5$−*n*-Bu$_4$Sn−EtOH−quinuclidine system, the selectivity for the formation of five-membered rings increased up to >95% and the values for M_n (13 000 g/mol) and PDI (1.94) indicated a more controlled polymerization system than obtained in the absence of quinuclidine. From these parameters, we calculated an initiation efficiency of about 91%, the highest value ever reported so far for these systems. The data provided here clearly underline the necessity of fine-tuning of standard systems in order to achieve a more well-behaved polymerization system.

Polymer Properties. The absorption maximum λ_{max} for poly(DEDPM) prepared from both initiators was 587 nm. This directly translates into a maximum effective conjugation length N_{eff} of 49,[29] numbers that are at least comparable to those of poly(1,2-(cyclopent-1-enylene)−vinylene)-based poly(DEDPM) obtained with Schrock initiators (λ_{max} = 591 nm, N_{eff} = 52).[16,17] To retrieve more information about the effectiveness of our Mo-based quaternary initiators, we carried out additional experiments. A plot of molecular weights vs number of monomer equivalents (N) is linear (Figures 2 and 3; Tables 3 and 4). As observed for poly(1,2-(cyclopent-1-enylene)−vinylene)-based poly(DEDPM) obtained with Schrock initiators, molar masses determined by light scattering (LS), which is an absolute method, were lower than those determined by size exclusion chromatography (SEC) vs polystyrene (PS). In contrast to Schrock initiator derived systems, where the content of high molecular weight components was ≪1%, LS data of the

Table 3. GPC and UV/Vis Data for Poly(DEDPM)$_n$ Prepared Using $MoCl_5$−n-Bu_4Sn−EtOH−Quinuclidine (1:1:5:1) as Initiator in CH_2Cl_2[a]

poly(DEDPM)$_n$	M_n(calcd)[b]	M_n[c]	M_w/M_n[c]	M_n[d]	M_w/M_n[d]	yield (%)	λ_{max}[e] (nm)	ϵ[e] (10^6 cm^2 mmol^{-1})
$n = 25$	6162	13 700	1.46	8200	1.25	61	583	0.79
$n = 50$	12 069	20 300	1.68	17 700	1.23	64	587	1.75
$n = 75$	17 975	22 800	1.88	21 400	1.75	65	587	1.93
$n = 100$	23 882	26 000	1.72	25 000	1.58	72	587	2.24
$n = 125$	29 789	28 200	1.96	29 000	1.95	76	587	2.57

[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] In $CHCl_3$.

Table 4. GPC and UV/vis Data for Poly(DEDPM)$_n$ Prepared Using $MoOCl_4$−n-Bu_4Sn−EtOH−Quinuclidine (1:1:2:1) as Initiator in CH_2Cl_2[a]

poly(DEDPM)$_n$	M_n(calcd)[b]	M_n[c]	M_w/M_n[c]	M_n[d]	M_w/M_n[d]	yield (%)	λ_{max}[e] (nm)	ϵ[e] (10^6 cm^2 mmol^{-1})
$n = 25$	6162	15 600	1.61	6770	1.65	72	585	0.98
$n = 50$	12 069	19 600	1.75	13 000	1.94	73	587	1.67
$n = 75$	17 975	21 500	1.60	20 000	1.13	84	585	1.99
$n = 100$	23 882	26 900	2.03	22 600	1.33	88	586	2.47
$n = 125$	29 789	28 200	2.24	25 300	1.90	86	586	2.93

[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] In $CHCl_3$.

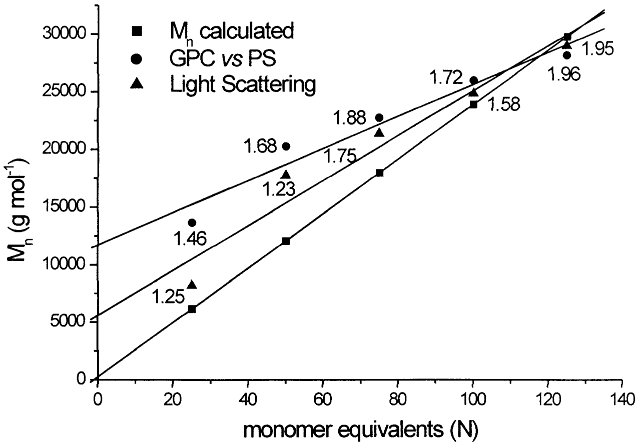

Figure 3. Plot of M_n vs number of monomer equivalents (N) and polydispersity indices for $MoOCl_4$−n-Bu_4Sn−EtOH−quinuclidine (1:1:2:1).

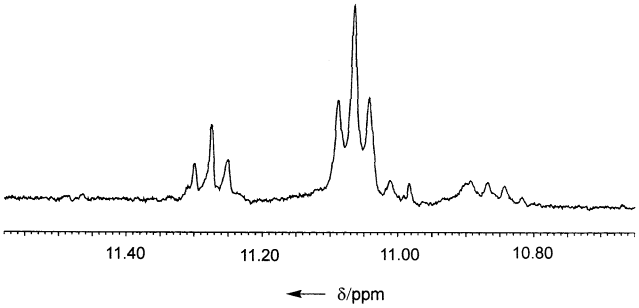

Figure 4. ^{1}H NMR spectrum of the carbene region of $MoOCl_4$−n-Bu_4Sn−EtOH−quinuclidine (1:1:2:1).

quaternary systems revealed significant amounts (5%) of additional high molecular weight signals. Since these showed no concentration-dependent behavior, these must be attributed to an intermolecular reaction of the double bonds along the polymer backbone.[16,17]

In a multistage polymerization setup with a defined stoichiometry (DEDPM:Mo:Sn:EtOH:quinuclidine = 50:1:1:5:1 for $MoCl_5$ and 50:1:1:2:1 for $MoOCl_4$), we added further monomer to both initiator systems within 1, 3, and 6 h after the polymerization had been started. Using the same amounts of monomer, polymerizations proceeded up to basically identical values for M_n (approximately 24000 g/mol) with both initiators. Furthermore, SEC signals remained unimodal up to 6 h *in which case unreacted monomer was present throughout.* Nevertheless, once all monomer was consumed, the active initiator decomposed rapidly. We therefore conclude that all polymerization active carbene species generated at the beginning were still active after at least 6 h and that all polymerization-active molybdenum compounds formed prior to or at the beginning of the polymerization. Nevertheless, though the initiator systems presented here offer access to a controlled polymerization setup in terms of molecular weight, polymer backbone and PDI, they do not allow *living* polymerizations within the original limits of this definition.[30] Interestingly, ^{13}C NMR data of the polyenes prepared with the present systems are identical to those obtained with Schrock initiators, indicating a highly regular alternating cis−trans structure.[16,17] Unfortunately, this point cannot be investigated further at the present stage, since adequate knowledge about the actual catalytic species is not yet available (vide infra). Another interesting aspect in view of future applications is the residual metal content of the polyenes. Since metals can promote polymer degradation, they must be removed. Polyenes prepared from $MoCl_5$, $MoOCl_4$ and Schrock initiators were precipitated once in pentane, dissolved in aqua regia, and subjected to inductively coupled plasma-optical emission spectroscopy (ICP−OES). These measurements revealed a Sn content ≤230 ppm for the first two types of initiators. The Mo content was 0.4, 0.4 and 0.2%, respectively.

Catalytic Species. To retrieve information about the actual catalytic species, a ^{1}H NMR spectrum of a $MoOCl_4$-based initiator prepared in situ was recorded. It revealed triplets at $\delta = 11.27$ and 11.07 ppm, respectively, which were attributed to the corresponding carbene species (Figure 4). The fact that triplets ($J \approx 7.3$ Hz) were observed suggested the formation of molybdenum butylidenes; nevertheless, the actual composition of the initiator still remains purely speculative. Unfortunately, we could not determine values for k_p/k_i as is usually possible with well-defined Schrock carbenes. In accordance with the ^{1}H NMR spectrum, the ^{13}C NMR spectrum of the in situ prepared $MoOCl_4$-based initiator revealed signals at $\delta = 276.1$, 262.7, and 261.6 ppm, indicating the presence of more than one carbene species. Whether all of them are polymerization active could not be clarified. Interestingly, identical triplet resonances were observed for the $MoCl_5$-based initiator at $\delta = 11.27, 11.02$. The corresponding ^{13}C NMR again revealed basically identical carbene resonances at $\delta = 276.0, 275.9, 272.4, 271.3, 262.7$, and 261.6 ppm. This suggests that at least similar initiators form from different Mo species at different oxidation states.

Nonetheless, since the exact nature of the active catalytical species remains unknown, we can only speculate that quinuclidine coordinates to a Mo-based carbene complex, presumably a Mo−butylidene and favors selective α-addition in the first step to yield poly(DEDPM) selectively based on five-membered rings.

Summary and Conclusion

The controlled cyclopolymerization of DEDPM by $MoCl_5$−*n*-Bu_4Sn−EtOH−quinuclidine (1:1:5:1) and $MoOCl_4$−*n*-Bu_4Sn−EtOH−quinuclidine (1:1:2:1) has been described. Poly(DEDPM) exclusively based on 1,2-(cyclopent-1-enylene)vinylenes was prepared. The $MoCl_5$- and $MoOCl_4$-based initiators described here are easy to prepare and cheap, yet they suffer from a lack of knowledge about their molecular structures. Nevertheless, the high initiation efficiencies of 67% for $MoCl_5$-based initiators and 91% for $MoOCl_4$-based initiators, which have never been reported before, the mild reaction conditions and the ease of preparation are certainly a major improvement in the development of these multicomponent initiators.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a MBraun LabMaster 130 glovebox or by using standard Schlenk techniques. Reagent grade anisole, ethanol and pentane were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane (p.a.) and $CDCl_3$ (p.a.) were distilled from calcium hydride under nitrogen. Dichloromethane-d_2, benzene-d_6, chloroform-d_1, and ethanol were passed through a column of activated alumina prior to use. $Cr(acac)_3$ (>97%, Fluka) $MoCl_5$ (99.6%, Strem), $MoOCl_4$ (>97%, Strem), and tetrabutyltin (98%, Aldrich) were used as received without further purification. Quinuclidine (>95%, Fluka) was recrystallized from pentane. Diethyl dipropargylmalonate (DEDPM) was prepared as described in the literature and checked for purity by NMR and elemental analysis.[31] Samples for SEC were filtered through a 0.22 μm Teflon filter (Millipore) in order to remove particles. Size exclusion chromatography vs PS was carried out using Shodex K-802.5 (6 μm, 80 Å), K-804 (7 μm, 200 Å), K-805 (10 μm, 500 Å) columns (Polymer Laboratories, all 300 × 8 mm i.d.), a Waters 410 differential refractometer, and a Waters 486 UV detector for measurements in $CHCl_3$. The flow rate was 1.0 mL/min. SEC columns were calibrated vs polystyrene standards (Polymer Standards Service (PSS), molecular weights 347 to 2.7×10^6 Da). SEC with light-scattering detection was carried out using a Waters Styragel HR 4E column (300 mm × 7.8 mm i.d., PS, bead size 5 μm, pore size 10^4 Å, effective molecular weight range 5000−600 000), a Waters 2414 differential refractometer, a Waters 484 UV detector, and a Wyatt mini-dawn light-scattering detector ($\lambda = 690$ nm) on samples in $CHCl_3$. Measurements were carried out at 25 °C, flow rate was 0.7 mL/min. A dn/dc value of 0.465 mL/g was determined from measurements in $CHCl_3$ using a RI-LS viscosity detector (Viscothek). UV/vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range 300−800 nm. NMR data were obtained at 300.13 MHz (^1H) and 75.48 MHz (^{13}C) on a Bruker ARX 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are given in Hz. FT-IR spectra were recorded on a Bruker Vector 22 (ATR spectra) and a Bruker IFS 55 spectrophotometer, respectively. A Jobin Yvon JY 38 plus was used for ICP−OES measurements and a MLS 1200 *mega* for microwave experiments.

Synthesis of Poly(DEDPM)$_{50}$ by $MoCl_5$—*n*-Bu_4Sn—EtOH—Quinuclidine. $MoCl_5$ (3.47 mg, 0.013 mmol) was suspended in 0.5 mL of CH_2Cl_2, a solution of *n*-Bu_4Sn (4.41 mg, 0.013 mmol) in 0.5 mL of CH_2Cl_2 was added and stirred for 20 min. Addition of ethanol (3.7 μL, 2.92 mg, 0.063 mmol) results in a clear red solution, which was stirred for another 20 min. Quinuclidine (1.55 mg, 0.014 mmol) was added and stirred for further 20 min. A solution of DEDPM (150 mg, 0.635 mmol) in 0.5 mL of CH_2Cl_2 was added all at once to the vigorous stirring solution. After 12 h, ferrocene aldehyde (27.18 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 (98 mg, 64%). Quantitative conversion of DEDPM was observed by TLC (thin-layer chromatography).

Poly(DEDPM)$_{50}$. $M_n = 17\,700$; PDI = 1.23. IR (ATR, cm^{-1}): 3383, 3003, 2881, 1728, 1629, 1468, 1441, 1366, 1343, 1300, 1247, 1186, 1156, 1094, 1070, 1048, 1013, 978, 949, 934, 902, 861, 838, 811, 778 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.70 (br m, 2H, $H_{olefinic}$), 4.22 (br m, 4H, OCH_2Me), 3.30 (br m, 4, $CH_{2allylic}$), 1.30 (br m, 6H, OCH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.5 (COO), 136.5 and 122.7 ($C_{olefinic}$), 61.5 (OCH_2Me), 56.8 (C_{ipso}), 41.0 ($C_{allylic}$), 13.7 (OCH_2Me).

Synthesis of Poly(DEDPM)$_{50}$ by $MoOCl_4$—*n*-Bu_4Sn—EtOH—Quinuclidine. $MoOCl_4$ (3.22 mg, 0.013 mmol) was dissolved in 0.5 mL of CH_2Cl_2 to give a yellow solution. A solution of *n*-Bu_4Sn (4.41 mg, 0.013 mmol) in 0.5 mL of CH_2Cl_2 was added and stirred for 20 min. EtOH (1.5 μL, 1.17 mg, 0.025 mmol) was added, and the solution was stirred for another 20 min. Quinuclidine (1.55 mg, 0.014 mmol) was added and stirred for further 20 min. A solution of DEDPM (150 mg, 0.635 mmol) in 0.5 mL of CH_2Cl_2 was added all at once to the vigorous stirring solution. After 12 h, ferrocene aldehyde (27.18 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 (112 mg, 73%). Quantitative conversion of DEDPM was observed by TLC (thin-layer chromatography).

Poly(DEDPM)$_{50}$. $M_n = 13\,000$; PDI = 1.94. IR (ATR, cm^{-1}): 3384, 2977, 2161, 1978, 1721, 1444, 1366, 1246, 1157, 1094, 1069, 1049, 1009, 947, 902, 861, 778, 650, 603 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.90 (br m, 2H, $H_{olefinic}$), 4.23 (br m, 4H, OCH_2Me), 3.32 (br m, 4, $CH_{2allylic}$), 1.30 (br m, 6H, OCH_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.7 (COO), 136.7 and 122.9 ($C_{olefinic}$), 61.7 (OCH_2Me), 57.0 (C_{ipso}), 41.2 ($C_{allylic}$), 13.8 (OCH_2Me).

Preparation of in Situ Catalysts. $MoCl_5$ and $MoOCl_4$-based initiators were prepared for in-situ-NMR measurements as described above in benzene-d_6. The initiation efficiencies ([P*]/[Cat], where P* is the propagating species and Cat is $MoCl_5$ or $MoOCl_4$) were calculated from the monomer conversion and the degree of polymerization of the polymers (based on LS).

Selected NMR Data for $MoCl_5$—*n*-Bu_4Sn—EtOH—Quinuclidine. ^1H NMR (C_6D_6): δ 11.27 (t, $^3J_{HH} = 7.23$ $CH_{carbene}$), 11.02 (t, $^3J_{HH} = 6.66$, $CH_{carbene}$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 276.0, 275.9, 272.4, 271.3, 262.7, 261.6 ($C_{carbene}$).

Selected NMR Data for $MoOCl_4$—*n*-Bu_4Sn—EtOH—Quinuclidine. ^1H NMR (C_6D_6): δ 11.27 (t, $^3J_{HH} = 7.25$ $CH_{carbene}$), 11.07 (t, $^3J_{HH} = 7.25$, $CH_{carbene}$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 276.1, 262.7, 261.6 ($C_{carbene}$).

Dissolution of Polymers. Aqua regia (3.0 mL) was added to the polymer (20 mg). The mixture was placed inside high-pressure Teflon tubes, and leaching was carried out under Microwave conditions (50, 600, and 450 W pulses, respectively; $t = 32$ min). After cooling to room temperature, the mixture was filtered and measured by ICP−OES ($\lambda = 202.030$ nm, ion line, for Mo; $\lambda_1 = 224.605$ nm, $\lambda_2 = 189.926$ ion lines, for Sn).

The background was measured at $\lambda = 224.589$ and 189.913 nm, respectively.

Acknowledgment. Financial support provided by the Austrian Science Fund (FWF, Vienna, START project Y-158), the Deutsche Forschungsgemeinschaft, and Freistaat Bayern is gratefully acknowledged. We thank L. Friebe, D. Schönfelder, and M. Mayershofer for SEC measurements vs polystyrene (PS) standards. Special thanks are expressed to T. Kotre for NMR spectroscopic measurements.

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MA021604L