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Mechanism of the Regio- and Stereoselective Cyclopolymerization of 1,6-Hepta- and 1,7-Octadiynes by High Oxidation State Molybdenum−Imidoalkylidene *N*-Heterocyclic Carbene Initiators

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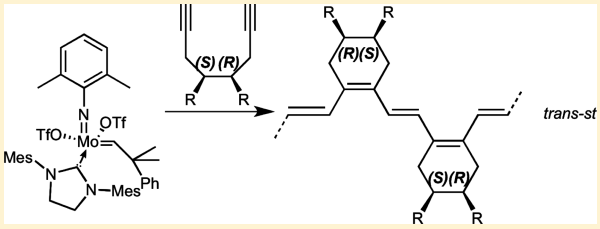
Supporting Information

ABSTRACT: The regio- and stereoselective cyclopolymerization of a series of 1,6-heptadiynes and 1,7-octadiynes, i.e., of 4,4-bis(ethoxycarbonyl)-1,7-heptadiyne (**M1**), 4-ethoxycarbonyl-4-(1*R*,2*S*,5*R*)-(−)-menthyloxycarbonyl-1,6-heptadiyne (**M2**), (*R*,*S*)-4,5-bis((1*R*,2*S*,5*R*)-(−)-menthyloxymethylcarboxymethyl)-1,7-octadiyne (**M3**), and (*S*,*S*/*R*,*R*)-4,5-bis((1*R*,2*S*,5*R*)-(−)-menthyloxymethylcarboxymethyl)-1,7-octadiyne (**M4**), by the action of the molybdenum−imidoalkylidene N-heterocyclic carbene (NHC) complexes (Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(OTf)$_2$(IMesH$_2$) (**I1**), Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_3)(OTf)$_2$(IMesH$_2$) (**I2**), (Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OTf)(OCH(CF_3)$_2$)-(IMesH$_2$) (**I3**), Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(OTf)$_2$(IMes) (**I4**, IMesH$_2$ = 1,3-dimesitylimidazolidin-2-ylidene, IMes = 1,3-dimesitylimidazolin-2-ylidene) and by the molybdenum−imidoalkylidene monoaryloxide monopyrrolide (MAP) complexes Mo(N-2,6-*i*Pr_2-C_6H_3)(CHCMe_2Ph)(2,5-Me_2-pyrrolide)(O-2,6-Me_2-C_6H_3) (**MAP1**), Mo(N-2,6-*i*Pr_2-C_6H_3)(CHCMe_2Ph)(2,5-Me_2-pyrrolide)(O-2,6-Mes_2-C_6H_3) (**MAP2**), and Mo(N-2-*t*Bu-C_6H_4)(CHCMe_2Ph)(2,5-Me_2-pyrrolide)(O-2,6-Mes_2-C_6H_3) (**MAP3**) is described. With initiators **I1**−**I4**, high regioselectivity >96% was observed in the polymerization of **M1**−**M4**, allowing for virtually selective *α*-insertion. These initiators displayed also high stereoselectivity, allowing for *all-trans* polyenes with up to 96% syndioselectivity. By contrast, the MAP initiators **MAP1**−**MAP3** showed poor regioselectivity (26−62% *α*-selectivity). A polymerization mechanism is proposed that explains for the high stereo- and regioselectivity of the Mo−imidoalkylidene NHC complexes.



INTRODUCTION

The cyclopolymerization of 1,6-hepta- and 1,7-octadiynes has been widely used for the syntheses of soluble, conjugated polymers possessing a rigid backbone.[1−29] Equally important, it can also be used as a probe to determine both the regio- and stereoselectivity of insertion and to come up with a polymerization mechanism for a specific initiator system. Two different pathways for the cyclopolymerization of *α*,*ω*-diynes with Schrock-type molybdenum carbenes exist (Scheme 1).[3,4]

Thus, the monomer can undergo either *α*- or *β*-addition. The first addition step of the monomer to the metal alkylidene is decisive for the structure of the resulting repeat unit. In the absence of any backbiting, the polymer structure is a concise record of all previous insertion steps. For first-generation Schrock initiators, the concept of large and small alkoxides was developed by the Schrock group and allowed for the selective *β*-addition of monomer.[1,2] Our group was capable of extending this concept to selective *α*-addition by using first-generation Schrock initiators bearing small alkoxides, an additional coordinating base, and low temperatures.[18,20−24,30,31] In that context not only the alkoxide but also the imido ligands played a predominant role in the control of the regioselectivity.[32,33] Recently, molybdenum−imidoalkylidene NHC bis(triflate)[34] and cationic tungsten−oxoalkylidene NHC complexes[35] have been developed in our group. Particularly molybdenum−imidoalkylidene NHC bistriflates display high reactivity for various norborn-2-enes, 7-oxanorborn-2-enes, and diynes and are also tolerant toward nitrile, amino, hydroxyl, and carboxylic acid groups.[34] We were interested in the polymerization mechanism that applies in the polymerization of *α*,*ω*-diynes with these novel initiators. Equally important, we wished to find out about the stereo- and regioselectivity of these novel complexes and therefore addressed the issues of tacticity and *cis*/*trans* selectivity in cyclopolymerization. Since the cationic species derived from Mo−imidoalkylidene NHC bis(triflate) complexes resemble to some extent molybdenum−imidoalkylidene monoalkoxide monopyrrolide (MAP) catalysts developed by the Schrock group,[36,37] and since these systems have

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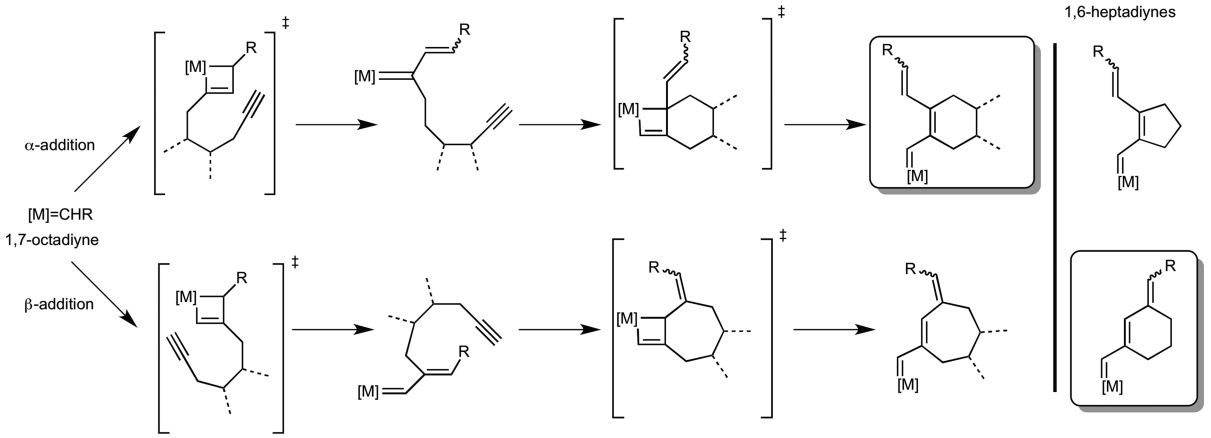
Scheme 1. Pathways for the Cyclopolymerization of α,ω-Diynes with a Metal Alkylidene[3,9]



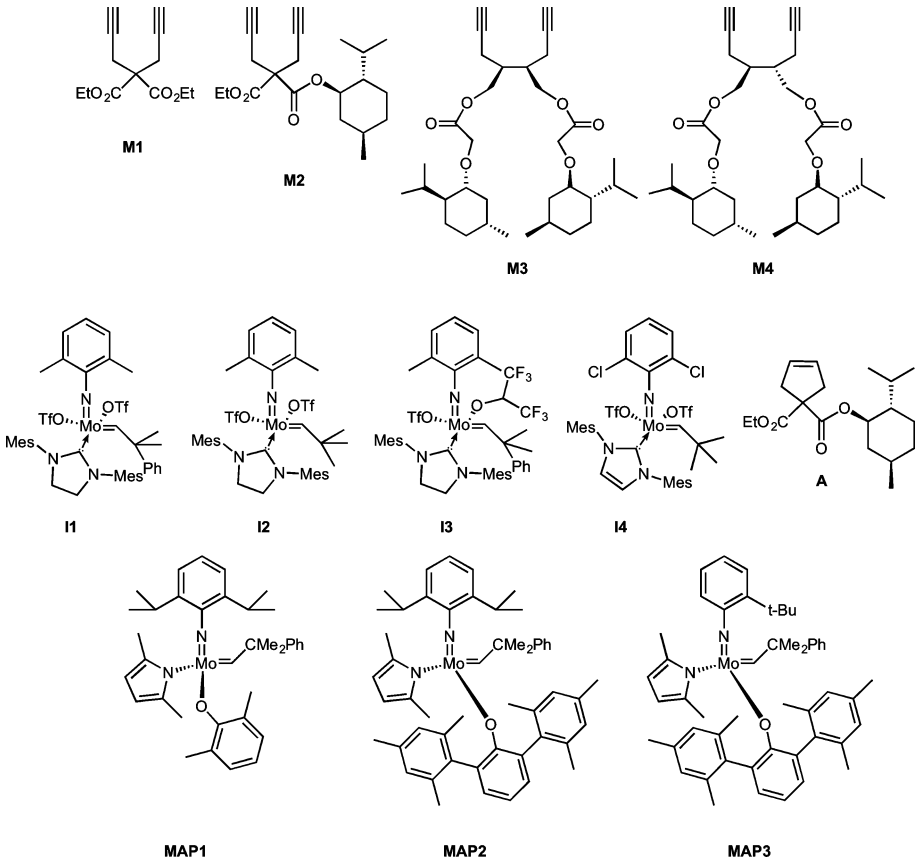


Figure 1. Structure of model compound **A** and of initiators **I1**−**I4** and **MAP1**−**MAP3** used for the cyclopolymerization of monomers **M1**−**M4**.

also been reported to display a high degree of regio- and stereospecifity both in olefin metathesis[38−42] and in ring-opening metathesis polymerization,[43−45] we also extended our investigations onto this class of initiators. Here we report our results.

RESULTS AND DISCUSSION

Synthesis of Initiators, Monomers, and Model Compound A. $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(OTf)_2(IMesH_2)$ (**I1**),[34] $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_3)(OTf)_2(IMesH_2)$ (**I2**),[34] $(Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OTf)(OCH(CF_3)_2)(IMesH_2)$ (**I3**),[46] and $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_3)(OTf)_2(IMes)$ (**I4**)[46] as well as the monoalkoxide monopyrrolide (MAP) initiators **MAP1** and **MAP2**[36,43,47,48] (Figure 1) were prepared according to the literature. Starting from $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OTf)_2(DME)$ (**1**), the bispyrrolide (**2**) could be prepared by adding 2 equiv of lithium 2,5-dimethylpyrrolide. Conversion of **2** with 1 equiv of 2,2″,4,4″,6,6″-hexamethyl-*m*-terphenol led to the formation of **MAP3** (Scheme 2).

MAP1, **MAP2**, and **2** were characterized by single-crystal X-ray structure. **MAP1** (Figure 2) crystallizes in the triclinic space group *P*1, a = 936.88(4) pm, b = 960.41(4) pm, c = 1894.22(9) pm, α = 86.863(3)°, β = 85.260(2)°, γ = 70.338(2)°, and Z = 2. **MAP2** (Figure 3) also crystallizes in the triclinic space group, *P*1, a = 1039.30(7) pm, b = 1191.83(7) pm, c = 3756.2(2) pm, α = 92.528(3)°, β = 93.652(4)°, γ = 107.923(3)°, and Z = 4.

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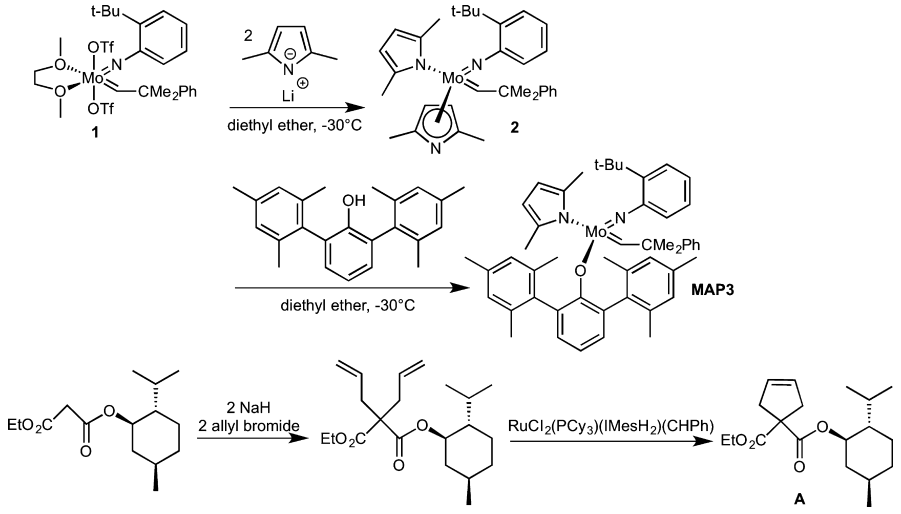
Scheme 2. Synthesis of MAP3 and of Model Compound A



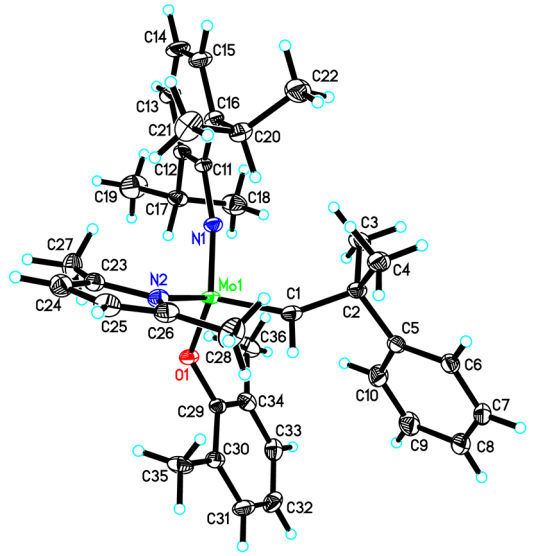


Figure 2. Single-crystal X-ray structure of **MAP1**. Selected bond lengths (pm) and angles (deg): Mo(1)−N(1) 173.53(16), Mo(1)−C(1) 187.4(2), Mo(1)−O(1) 192.75(14), Mo(1)−N(2) 203.07(17); N(1)−Mo(1)−C(1) 103.70(8, N(1)−Mo(1)−O(1) 115.19(7), C(1)−Mo(1)−O(1) 106.70(7), N(1)−Mo(1)−N(2) 108.93(7), C(1)−Mo(1)−N(2) 106.63(8), O(1)−Mo(1)−N(2) 114.72(7).

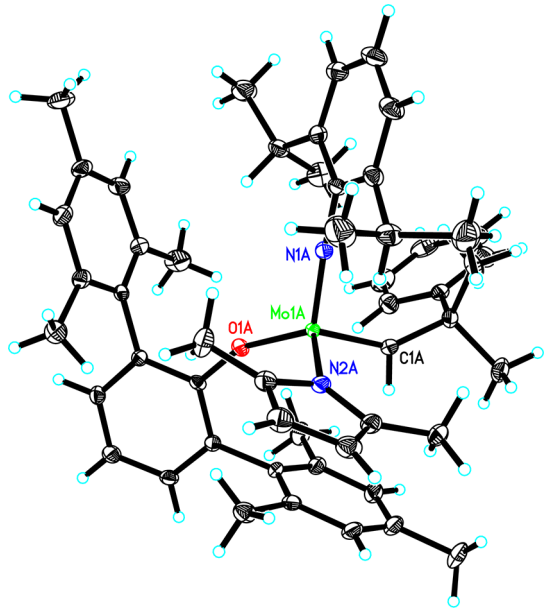


Figure 3. Single-crystal X-ray structure of **MAP2**. Selected bond lengths (pm) and angles (deg): Mo(1A)−N(1A) 173.2(3), Mo(1A)−C(1A) 188.8(4), Mo(1A)−O(1A) 192.8(3), Mo(1A)−N(2A) 202.6(3), O(1A)−C(29A) 135.4(5); N(1A)−Mo(1A)−C(1A) 101.88(16), N(1A)−Mo(1A)−O(1A) 117.37(14), C(1A)−Mo-(1A)−O(1A) 112.92(15), N(1A)−Mo(1A)−N(2A) 103.39(15), C-(1A)−Mo(1A)−N(2A) 103.16(16), O(1A)−Mo(1A)−N(2A) 116.17(13).

Compound **2** (Figure 4) again crystallizes in the triclinic space group, *P*1, a = 867.15(7) pm, b = 1132.46(10) pm, c = 1519.45(13) pm, α = 92.600(5)°, β = 99.484(4)°, γ = 104.196(4)°, and Z = 2. In all three complexes, the ligands adopt a tetrahedral configuration. Relevant bond lengths and angles for **MAP1**, **MAP2**, and **2** are summarized in Figures 2−4. Both in **MAP1**/**MAP2** and in **2** the length of the metal alkylidene as well as the metal−nitrogen distances are inconspicuous and comparable to related compounds.[36,37]

4-(Ethoxycarbonyl)-4-(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl-1,6-heptadiyne (**M2**)[49] and 4,4-bis(ethoxycarbonyl)-1,6-heptadiyne (**M1**)[23,24] were synthesized according to the literature. Model compound **A** was synthesized by alkylation of ethyl-(1*R*,2*S*,5*R*)-(−)-menthylmalonate with NaH/allyl bromide followed by ring-closing metathesis (RCM) using the second-generation Grubbs initiator (Scheme 2).[23]

Regio- and Stereoselective Cyclopolymerization with Mo−Imidoalkylidene−Bistriflate NHC Initiators. Cyclopolymerization of **M1**−**M4** (Figure 1) was accomplished by the action of initiators **I1**−**I4**, respectively. Cyclopolymerization of **M1** by the action of **I1** yielded poly-**M1** with ≥99% α-insertion selectivity (Figure S26, Supporting Information). This high α-insertion selectivity is in line with previous reports on the cyclopolymerization of other 1,6-heptadiynes such as 4,4-bis[(3,5-diethoxybenzoyloxy)methyl]-1,6-heptadiyne by the action of **I2**.[34]

Generally, cyclopolymerization-derived polyenes can exist in their *cis* or *trans* form and be either isotactic (*it*), syndiotactic (*st*), or atactic (*at*). If initiation and propagation proceed in a

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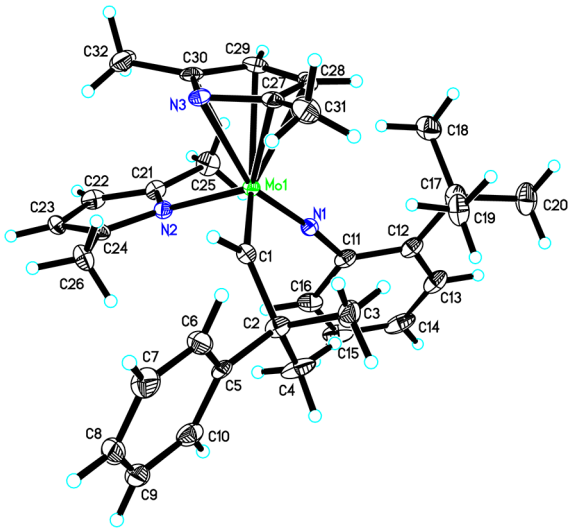

Figure 4. Single-crystal X-ray structure of **2**. Selected bond lengths (pm) and angles (deg): Mo(1)−N(1) 173.3(2), Mo(1)−C(1) 192.5(2), Mo(1)−N(2) 209.5(2), Mo(1)−C(28) 236.0(2), Mo(1)−C(27) 240.0(2), Mo(1)−C(29) 243.4(2), Mo(1)−N(3) 245.5(2), Mo(1)−C(30) 247.9(3); N(1)−Mo(1)−C(1) 101.25(10), N(1)−Mo(1)−N(2) 100.27(9), C(1)−Mo(1)−N(2) 101.95(9), N(1)−Mo(1)−N(3) 159.00(8), C(1)−Mo(1)−N(3) 86.94(9).

controlled and defined manner, then the resulting polymers should either display a *cis*- or *trans*-syndiotactic (*st*) or isotactic (*it*) structure. While any predominant *cis*- or *trans*-configuration in the polymer chain can easily be determined by IR spectroscopy, the tacticity of poly(α,ω-diyne)s cannot be determined unless the monomer contains at least one chiral center, usually in the side chain. In this case, and only in this case, one can together with IR data and with the aid of correlated ^{1}H NMR spectroscopy distinguish between *cis*-/*trans*-*st*/*it* structures.[3−5,9,20−24,31,50,51] The cyclopolymerization of 4-ethoxycarbonyl-4-(1*R*,2*S*,5*R*)-(−)-menthyloxycarbonyl-1,6-heptadiyne (**M2**) was accomplished by the action of **I2**, **I3**, and **I4**. The ^{13}C NMR spectra of the corresponding polymers were virtually identical, which suggests that neither the nature of the NHC (IMes vs IMesH$_2$) nor of the imido-ligand (2,6-Me$_2$-C$_6$H$_4$ vs 2,6-Cl$_2$-C$_6$H$_4$) has a strong influence on regio- and stereoselectivity. The ^{13}C NMR spectrum of poly-**M2** prepared by the action of **I2**, representative for the polymers obtained with all other initiators, is shown in Figure 5.

Signals at δ = 172.0 and 171.4 ppm can be assigned to the two carbonyls. Their chemical shifts are in full agreement with those in model compound **A** (δ = 172.4 and 171.8 ppm). The *ipso*-carbon at δ = 57.5 ppm is typical for α-insertion-derived polyenes, and its chemical shift fits again to the one in model compound **A** (δ = 59.1 ppm). No additional signals for β-insertion-derived structures are visible. The IR spectrum of this polymer shows only *trans*-configured double bonds at 955 cm^{-1}. Consequently, either *trans-it* or *trans-st* diads must be present. As outlined in Figure 6, a *trans-st* structure would have uncoupled olefinic protons, while a *trans-it* structure would show coupled protons.

Based on the ^{1}H,^{1}H−COSY spectrum of poly-**M2** prepared by the action of **I2** (Figure S29, Supporting Information), which shows no coupling of the main signal at δ = 6.68 ppm, a

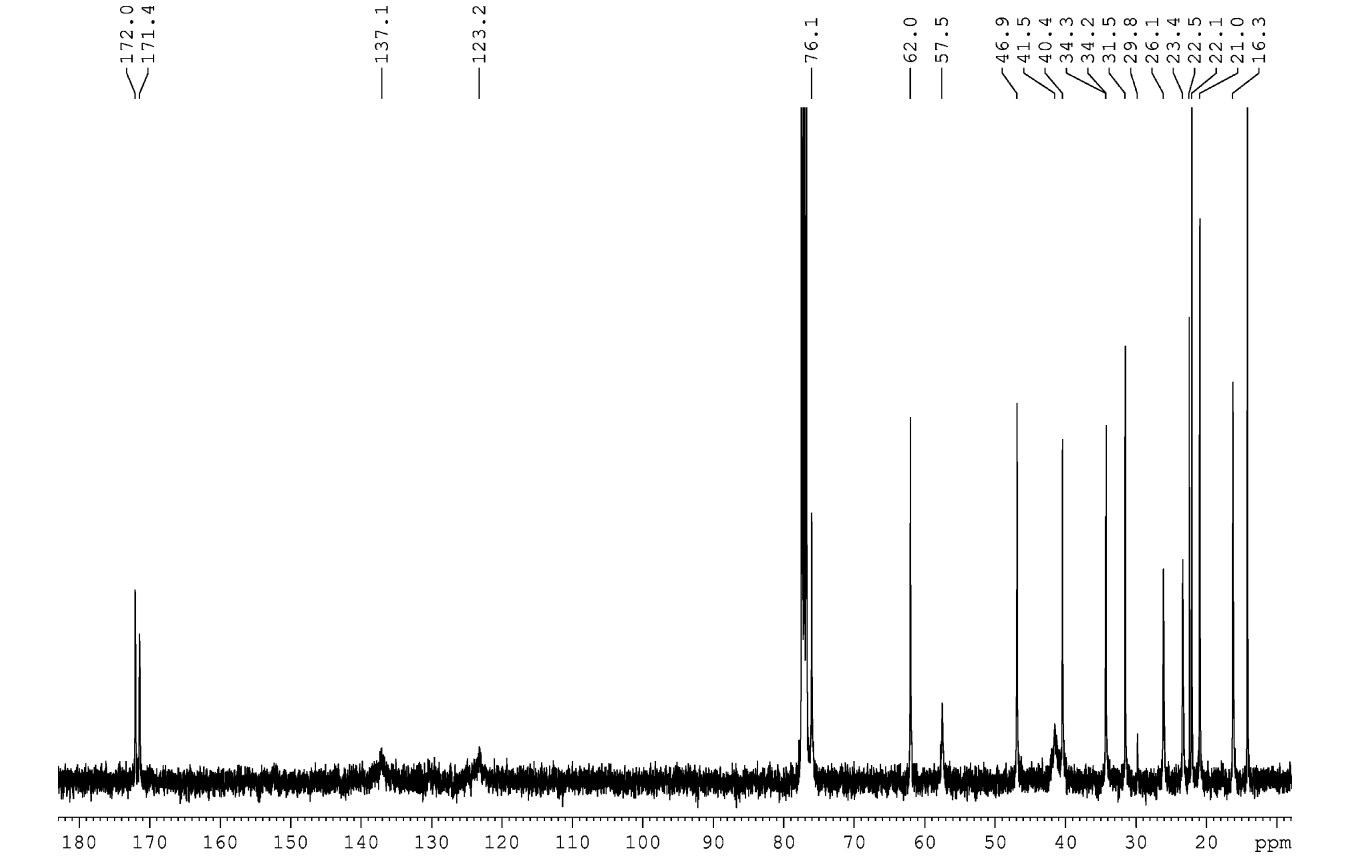

Figure 5. ^{13}C NMR spectrum ($CDCl_3$) of poly-**M2** prepared by the action of **I2**.

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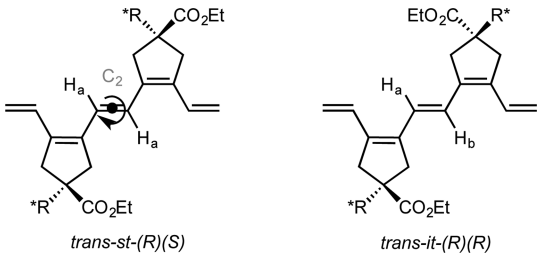

Figure 6. Structure of *trans-it* and *trans-st* diads of poly-**M2** (R = chiral group).

>96% α-insertion derived, *all-trans*, >96% *st* structure is assigned to this polymer. Notably, because of the rigid character of the backbone, the ^{1}H NMR spectra of poly(ene)s show a by far lower resolution than the ^{1}H NMR spectra of tactic poly(cyclopropene)s, poly(norbornene)s, or poly(norbornadiene)s.[52−56] Nonetheless, the ^{1}H,^{1}H−COSY spectra still allow for concluding on tacticity.[5]

The polymerization of **M3** by the action of **I1** yielded poly-**M3**. The ^{13}C NMR spectrum of poly-**M3** prepared by the action of **I1** is shown in Figure 7.

Signals at δ = 132.0 (*C*H═), 125.1 (*C*═C), and 28.5 ppm (CH_2) can be clearly assigned to an α-insertion-derived, i.e., 6-membered repeat unit.[5] The absence of any additional signals for β-insertion-derived repeat units and the number of carbons visible in the ^{13}C NMR clearly point toward selective α-insertion (>99%). The IR spectrum of poly-**M3** (Figure S42, Supporting Information) shows *trans*-configured double bonds ($\nu_{C=C}$ = 951 cm^{-1}). According to Figure 8a, a *trans-it* structure should show two coupled olefinic protons, while the olefinic protons in a *trans-st* structure should be uncoupled. The ^{1}H,^{1}H−COSY spectrum of poly-**M3** prepared by the action of **I1** (Figure S41, Supporting Information) shows one large olefinic peak at δ = 6.96 ppm and no cross-coupling signals. Olefinic signals in the range of δ = 5.4−6.6 ppm are assigned to the end groups. Therefore, even when taking the end groups into account, poly-**M3** prepared by the action of **I1** is formed via >99% α-addition and exist as >99% *trans*, >72% *st* polymer.

The polymerization of (racemic) (*S*,*S*/*R*,*R*)-4,5-bis-((1*R*,2*S*,5*R*)-(−)-menthyloxymethylcarboxymethyl)-1,7-octadiyne (**M4**) by the action of **I1** yielded poly-**M4**. Its ^{13}C NMR spectrum is shown in Figure 9.

Signals at δ = 170.9 (C═O), 131.8 (*C*H═), 125.2 (*C*═C), and 28.4 ppm (CH_2) can again be clearly assigned to an α-insertion-derived, i.e., 6-membered, repeat unit.[5] As for poly-**M3**, no signals for β-insertion-derived repeat units are observed. The IR spectrum of poly-**M4** shows both *trans*- and *cis*-configured double bonds (950 and 700 cm^{-1}, Figure S46, Supporting Information). The ^{1}H,^{1}H−COSY spectrum of poly-**M4** prepared by the action of **I1** (Figure S45, Supporting Information) shows one large uncoupled signal at δ = 6.97 ppm. Again, the coupled signals at 5.8 < δ < 6.8 ppm are assigned to end groups. According to the possible regular structures shown in Figure 8b, either *cis-it* or *trans-it* structures must be expected. Accordingly, poly-**M4** forms by the action of **I1** via selective α-addition and exists as *cis/trans-it* polymer (>66% *it*).

Polymerization Mechanism. Polymerization of **M2** and **M3** by the action of **I1**−**I4** yields predominantly *trans-st*-

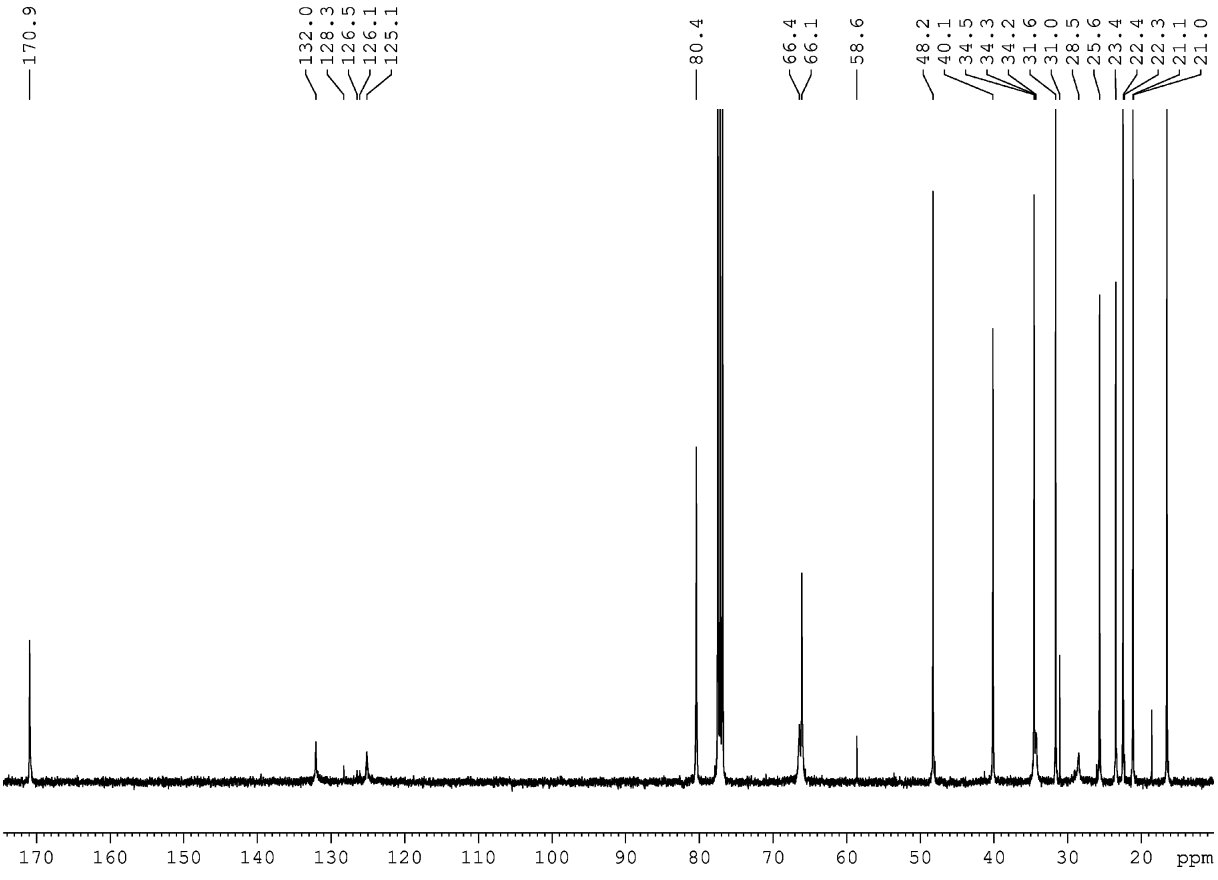

Figure 7. ^{13}C NMR spectrum ($CDCl_3$) of poly-**M3** prepared by the action of **I1**.

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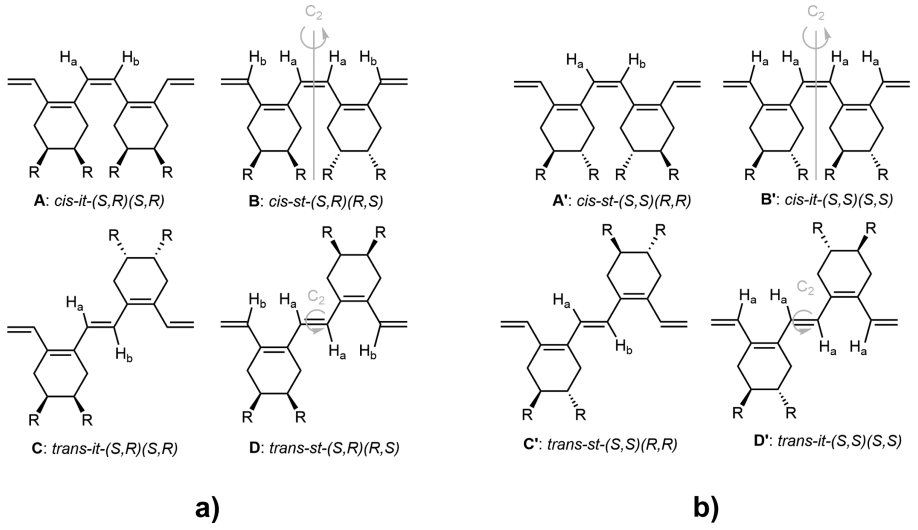

Figure 8. Possible microstructures of cyclopolymerization-derived chiral poly(1,7-octadiyne)s. R = chiral group; (a) poly-**M3**; (b) poly-**M4**.

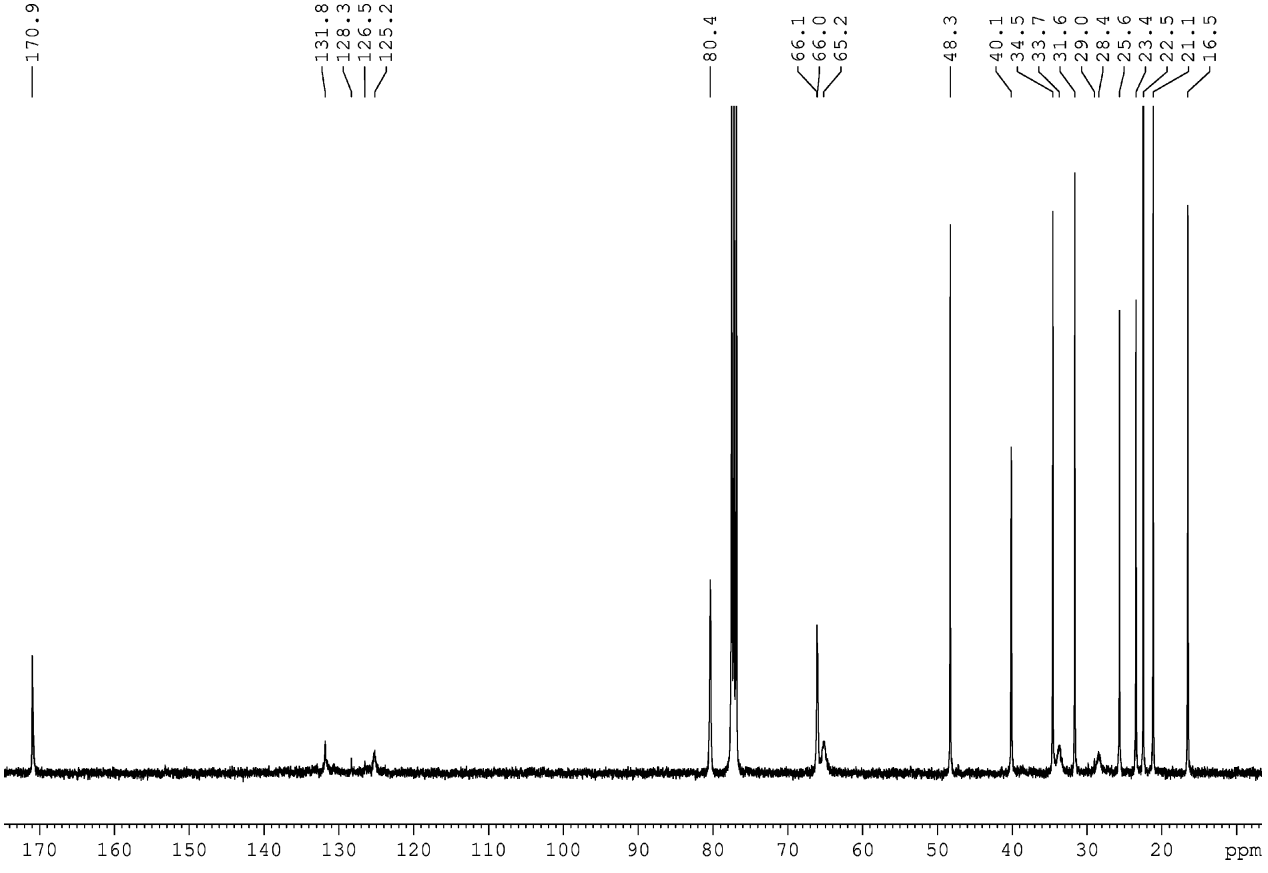

Figure 9. ^{13}C NMR spectrum ($CDCl_3$) of poly-**M4** prepared by the action of **I1**.

polymers. According to calculations carried out on other group 6 and 7 metathesis catalysts,[57−59] as well as in view of results published by the Schrock group on 2,5-dimethylpyrrolide complexes,[60] which propose attack of monomer *trans* to the strongest σ-donor, i.e., *trans* to the NHC, we suggest the mechanism shown in Scheme 3.

^{19}F NMR measurements (Figures S47−S49) suggest that one OTf^- group in **I1** and in **I3** is only weakly bound to Mo (δ = −76.6 and −78.1 ppm), forming a (weak) contact ion pair (Figures S47−S49). Upon addition of monomer, signals for weakly bound OTf^- groups are found at $77.2 < \delta < 79$ ppm. Consequently, both the initiators and propagating species are drawn in their cationic form. Starting from a cationic *syn*-isomer, **M3** approaches the metal α-selectively and *trans* to the NHC. The two chiral R-groups point away from the R-groups at the growing polymer chain (chain end control). An α-addition-derived transition state forms, resulting in the formation of a disubstituted alkylidene. Formation of a *trans*-double bond must be a result of the relatively large substituents at the molybdacyclobutene. Notably, the configuration at

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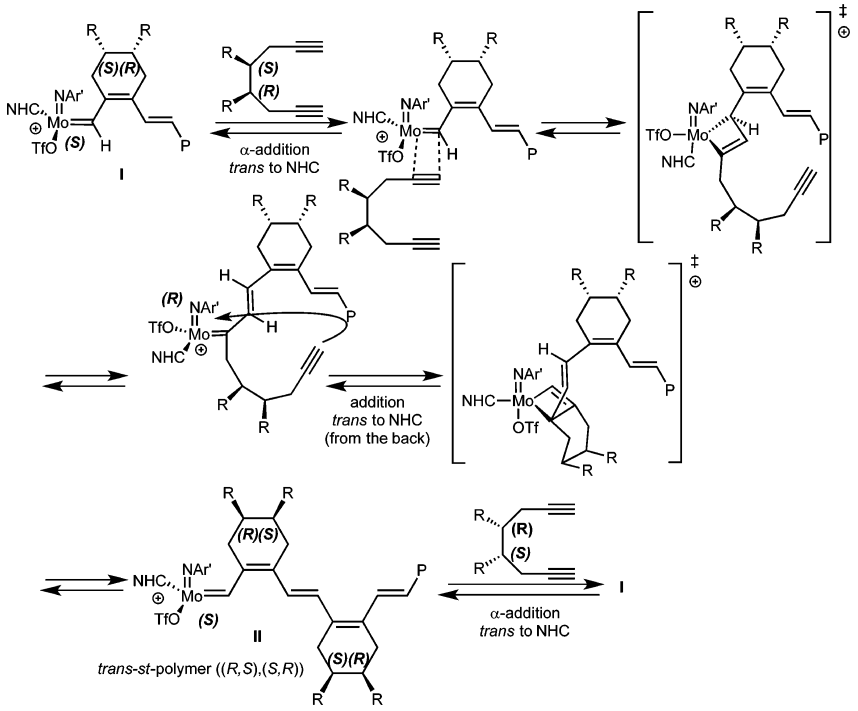
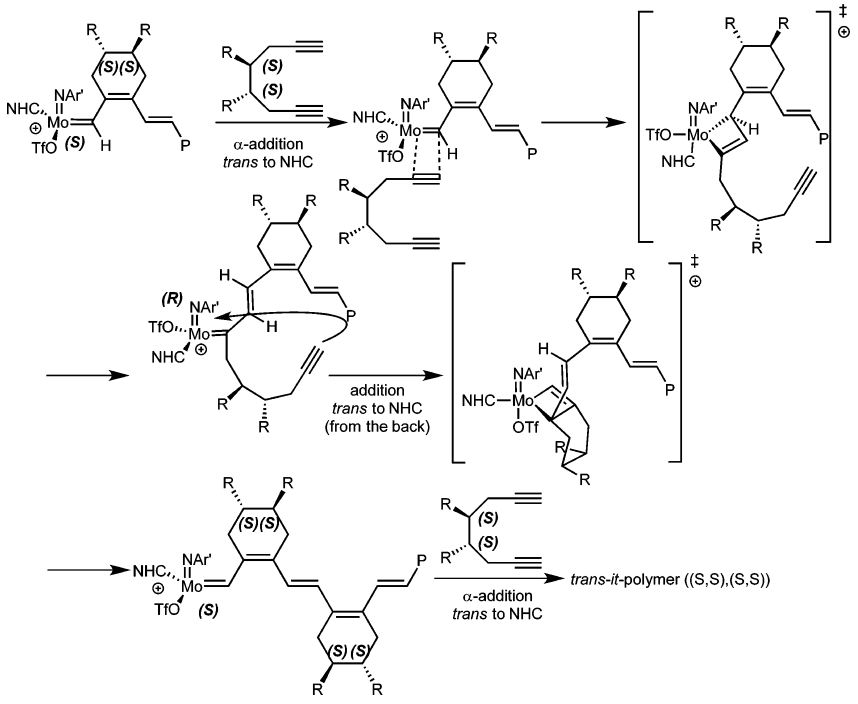
Scheme 3. Formation of α-Insertion-Derived *trans-st*-Poly-M3 (R = (-)-Menthyl-O-CH_2-$COOCH_2$−)



Scheme 4. Formation of α-Insertion-Derived *trans-it*-Poly-M4 (R = (-)-Menthyl-O-CH_2-$COOCH_2$−)



molybdenum has changed at that point from S to R (or *vice versa*). Now, the second alkyne group present in the monomer again approaches the metal intramolecularly *trans* to the NHC. Metallacyclobutene formation followed by cycloreversion results in an α-addition-derived, *trans-st*-polymer. Provided the fact that the bulky menthyl groups in the monomer point away from those in the growing polymer chain (*anti*-approach), the consecutive insertion of two monomers again leads to the propagating species **I**. The same sequence is also possible for **M2** (not shown), and consequently poly-**M2** has a >96% α-insertion derived, *all-trans*, >96% *st* structure. The situation with **M4** seems to be different. There, one might speculate whether the *trans*-configuration of the two chiral groups always leads to some steric interaction between the growing polymer chain and the monomer, irrespective of the initial approach of the monomer to the initiator. However, as outlined in Scheme 4, in case **M4** follows the same reaction pathway as **M2** and **M3**, an α-insertion-derived, *it* polymer is formed. The situation where an S-configured initiator reacts with the S,S-enantiomer has been chosen arbitrarily; however, the arguments apply for

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Table 1. Results of the Cyclopolymerization of M1 by the Action of MAP1−MAP3[a]

initiator	additive	solvent, T [°C]	M_n (found) [g mol^{-1}]	PDI	λ_{max} [nm]	yield[b] [%]	χ_5[c] [%]	χ_6[d] [%]
MAP1	–	CH_2Cl_2, rt	20500	1.4	–	93	57	43
MAP2	–	CH_2Cl_2, rt	27000	8	542	91	29	71
MAP2	–	toluene, rt	52700	10	542	84	26	74
MAP3	–	toluene, rt	53500	11	548, 585	95	62	38

[a]Poly-**M1**: M_n(theor) = 12126 g/mol; monomer:initiator = 50:1, Q = quinuclidine. [b]Isolated yields. [c]Fraction of α-insertion-derived repeat units. [d]Fraction of β-insertion-derived repeat units; rt = room temperature.

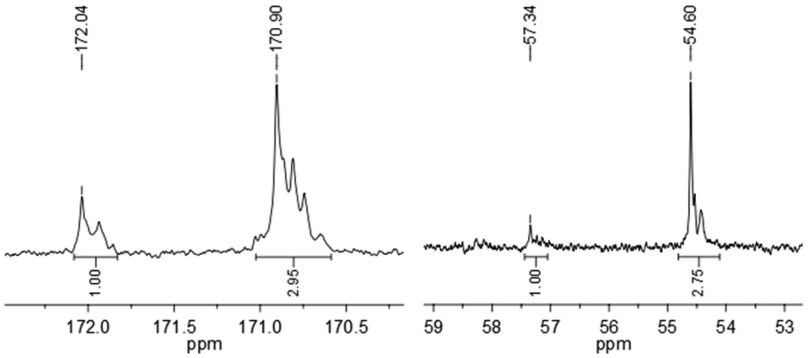

Figure 10. Integration of carbonyl signals (left) and aliphatic, *ipso*-carbons (right) of poly-**M1** prepared by the action of **MAP2**.

any combination provided the fact that the corresponding initiator−monomer couples form selectively, i.e., *S*/*S*,*S* and *R*/*R*,*R* or *S*/*R*,*R* and *R*/*S*,*S*.

Finally, a few additional issues have to be kept in mind. First, initiators **I1**−**I4** exist in their racemic forms. Despite the fact that release of triflate can well be expected to occur selectively for the triflate that experiences the strongest *trans*-effect,[34] the resulting cationic species must therefore exist in form of their racemates, too. Now, what is the consequence? For both **M2** and **M3**, enantiomeric polymer chains can form, no matter which enantiomer of the initiator forms the propagating species. With **M4**, which exists in form of a racemate, the situation must be somewhat different. There, two enantiomeric polymer chains can only form if the (*S*)-enantiomer of the initiator selectively reacts with the (*S*,*S*) enantiomer and the (*R*)-enantiomer of the initiator selectively reacts with the (*R*,*R*)-enantiomer of the monomer. This implies that consecutive insertion of two enantiomeric monomers into the metal alkylidene, i.e., (*S*,*S*) followed by (*R*,*R*), does not occur. In fact, this makes sense. A situation in which one enantiomer could either be followed by the same or by the other enantiomer would imply negligible differences between the corresponding diastereotopic transitions states ($\Delta\Delta G^{\ddagger} < 2$ kcal) and would therefore probably lead to mostly atactic structures.

Cyclopolymerization with Mo-MAP Initiators. In terms of structure, **I1**−**I4** are at least to some extent comparable to MAP initiators. Since no data on the cyclopolymerization propensity of MAP initiators existed, we prepared **MAP1**−**MAP3** for these purposes. **MAP1** is based on a small alkoxide; **MAP2** and **MAP3** contain a large alkoxide. An additional feature of **MAP3** is the "small" arylimido group. The cyclopolymerization of **M1** by the action of **MAP1**−**MAP3** in toluene or CH_2Cl_2 led to purple polymers with complete monomer conversion. Polymerization results are summarized in Table 1. Analysis of the ^{13}C NMR spectra revealed poor α-insertion selectivity in the range of 26−62%. A typical ^{13}C NMR spectrum is shown in Figure 10.

In line with Schrock's concept of small and large alkoxides, the use of the sterically demanding terphenoxide in **MAP2** allowed for a β-insertion selectivity of 74%, which is however still lower than the ones reported earlier for the bis(triphenylacetate) complexes (100% β-insertion).[1,2] However, we obviously cannot rule out that a careful ligand tuning in MAP-type complexes would also provide improved regioselectivity in the cyclopolymerization of diynes. Obviously, the novel Mo−imidoalkylidene NHC complexes closely follow the polymerization mechanism proposed for MAP-type catalysts.[51,61] The reason for their substantially better regioselectivity might be related to a lower propensity to undergo Berry rotation; however, this is purely speculative at this stage.

We finally wish to address the issue of whether the proposed tacticities could be confirmed by an alternative, independent method. The Schrock group very recently proposed low degree epoxidation or bromination of poly(norbornene)s as a viable method.[62] Unfortunately, despite its beauty, this method cannot be applied to polymers with conjugated double bonds for obvious reasons.

■ SUMMARY

The regio- and stereoselective cyclopolymerization of 1,6-hepta- and 1,7-octadiynes by Mo−imidoalkylidene NHC-based initiators has been carried out and a viable mechanism has been developed. According to the proposed mechanism, initiators **I1**−**I4** behave quite similarly to the known MAP initiators; however, at least based on the results obtained with **MAP1**−**MAP3**, they display higher regioselectivity. Current work focuses on tuning the activity and selectivity of these initiators, e.g., by replacing one triflate by fluorinated alkoxides or by using NHCs with a second, chelating group. Results will be reported in due course.

■ EXPERIMENTAL SECTION

General. All experiments were carried out in a N_2-filled glovebox (Lab Master 130, MBraun, Garching, Germany) or by standard Schlenk techniques. All chemicals used were purchased from Sigma-

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Aldrich (Munich, Germany), Alfa Aesar (Karlsruhe, Germany), ABCR (Karlsruhe, Germany), or Merck (Darmstadt, Germany) and were dried and distilled prior to use. All other chemicals were dried and degassed by well-established techniques. Dichloromethane, diethyl ether, toluene, pentane, and tetrahydrofuran (THF) were dried using a solvent purification system (SPS, MBraun) and stored over molecular sieves. Polymer solutions were filtered through a 0.2 μm filter (Sartorius, Germany) prior to GPC measurements to remove any insoluble particles. GPC measurements were carried out on a system consisting of a Waters 515 HPLC system with a Waters autosampler, PolyPore columns (300 × 7.5 mm, Agilent Technologies, Böblingen, Germany), and a Waters 2489 UV/vis and a Waters 2414 refractive index detector. For thin layer chromatography a coated aluminum foil with silica gel endowed with a fluorescence indicator (Merck, silica gel 60 F254) was used. UV-active substances were detected at 254 and 366 nm; for coloring $KMnO_4$ was used. For column chromatography, silica gel (Fluka, 60M: 0.040−0.063 mm grain size, 230−400 mesh ASTM) was used as stationary phase. For the different mobile phases used *vide infra*. NMR spectra were recorded on a Bruker Avance III 400 at 400 MHz for proton and 101 MHz for carbon. All spectra were recorded at room temperature and calibrated to characteristic solvent signals. Analysis of the NMR data was accomplished with the aid of the Topspin 3.0 program package. Chemical shifts (δ) are reported in ppm relative to the solvent signal, coupling constants (J) in hertz (Hz). The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and b = broad. The pulse sequences cosyqf90 (Bruker) and zgpg30 were used for 2D COSY and 13C NMR measurements. IR spectra were carried out on an IFS 28 (Bruker) using NaCl cuvettes. UV/vis values were measured in $CHCl_3$ using a PerkinElmer Lambda 2 or a UV-1800 Shimadzu UV spectrometer. GC-MS data were recorded on an Agilent Technologies device consisting of a 7693 autosampler, a 7890A GC, and a 5975C quadrupole MS equipped with an SPB-5 fused silica column (34.13 m × 0.25 mm × 0.25 μm film thickness). Dodecane was used as internal standard. The injection temperature was set to 150 °C. The column temperature ramped from 45 to 250 °C within 8 min and was then held for further 5 min. The column flow was 1.05 mL/min. IR spectra were measured on an ATR/FT-IR spectrometer Bruker IFS 128 in the area 4000 to 400 cm^{-1} and analyzed by the OPUS software (Version 7.2). Wavenumbers are reported in cm^{-1}. Mass spectra were measured at the Institute of Organic Chemistry of the University of Stuttgart on a Bruker Daltonics Microtof Q mass spectrometer. Initiators **I1**,[34] **I2**,[34] **I3**,[42] and **I4**[46] and the MAP initiators **MAP1**−**MAP2**[36,43,47,48] were prepared as described in the literature. 4,4-Bis(ethoxycarbonyl)-1,7-heptadiyne (**M1**),[4] 4-(ethoxycarbonyl)-4-(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl-1,6-heptadiyne (**M2**),[23,24] (*R*,*S*)-1,7-octadiyne-4,5-dimethyl dimenthylate (**M3**),[5] and (*R*,*R*/*S*,*S*)-1,7-octadiyne-4,5-dimethyl dimenthylate (**M4**)[5] were prepared according to the literature.

Ethyl ((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)malonate. The compound was prepared according to ref 23. Ethyl chloromalonate (5.00 g, 33.2 mmol, 1 equiv) was dissolved in 100 mL of dry diethyl ether. (−)-Menthol (5.19 g, 33.2 mmol, 1 equiv) was dried *in vacuo* and dissolved in 10 mL of Et_2O and added at 0 °C to the reaction mixture over a period of 45 min. The solution was stirred for 20 h at room temperature. Then a saturated solution of aqueous $NaHCO_3$ was added until the formation of gas had ceased. The aqueous fraction was extracted three times with water and once with brine. The combined organic fractions were dried over Na_2SO_4 and filtered, and the solvent was removed *in vacuo*. The resulting oil was precipitated from *n*-pentane at −80 °C. A colorless oil could be obtained (7.58 g, 28.1 mmol, 84%). ^{1}H NMR ($CDCl_3$): δ = 4.73 (t × d, 1H, $^3J_1$ = 10.8 Hz, $^3J_2$ = 4.4 Hz, OCH), 4.26−4.12 (m, 2H, CH_2), 3.34 (s, 2H, CH_2), 2.08−1.98 (m, 1H, CH), 1.89 (d × sept, 1H, $^3J_1$ = 7.0 Hz, $^3J_2$ = 2.7 Hz, CH), 1.74−1.62 (m, 2H, CH), 1.56−1.32 (m, 2H, CH_2), 1.27 (t, 3H, $^3J_1$ = 7.2 Hz, CH_3), 1.15−0.71 (m, 12H, CH, CH_3). IR (cm^{-1}): 2954 (m), 2928 (m), 2869 (m), 1729 (s), 1456 (m), 1411 (w), 1387 (m), 1368 (m), 1265 (s), 1180 (s), 1145 (w), 1096 (m), 1080 (w), 1035 (m), 1011 (w), 989 (m), 904 (w), 842 (m), 685 (w), 598 (w).

4-(Ethoxycarbonyl)-4-(1R,2S,5R)-(−)-menthoxycarbonyl-1,6-heptadiene. Ethyl-(1*R*,2*S*,5*R*)-(−)-menthylmalonate (6.00 g, 22.2 mmol) was dissolved in 10 mL of dry THF and added slowly to a stirred suspension of NaH (3.55 g, 60 wt %, 88.8 mmol) in 100 mL of THF. Once the formation of gas had ceased, allyl bromide (7.6 mL, 88.8 mmol) was added, and the mixture was stirred for another 6 h. Then, the mixture was chilled to 0 °C, and a saturated aqueous NH_4Cl solution (40 mL) was added. A white solid precipitated. The organic layer was separated, washed with water (2 × 20 mL) and brine (2 × 20 mL), and dried over $MgSO_4$. Finally, the solvent was purified by bulb distillation. A colorless oil (6.23 g, 81%) was isolated after freeze-drying. ^{1}H NMR ($CDCl_3$): δ = 5.69−5.56 (m, 2H, C*H*=CH_2), 5.16−5.06 (m, 4H, CH=CH_2), 4.69 (t × d, $^3J_1$ = 10.9 Hz, $^3J_2$ = 4.4 Hz, 1H, CO_2CH), 4.20 (d × q, $^2J_1$ = 10.8 Hz, $^3J_2$ = 7.1 Hz, 1H, CO_2CHH), 4.07 (d × q, $^2J_1$ = 10.8 Hz, $^3J_2$ = 7.1 Hz, 1H, CO_2CHH), 2.71−2.57 (m, 4H, CH_2CH=CH_2), 2.01−1.94 (m, 1H, $H_{menthyl}$), 1.86 (d × sept, $^3J_1$ = 7.0 Hz, $^3J_2$ = 2.8 Hz, 1H, $CH(Me)_2$), 1.71−1.62 (m, 2H, CO_2CHCH_2), 1.54−1.31 (m, 2H, $H_{menthyl}$), 1.24 (t, $^3J_1$ = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.09−0.70 (m, 12H, $H_{menthyl}$).^{13}C{^{1}H}NMR ($CDCl_3$): δ = 171.0 (s, CO_2Et), 170.4 (s, $CO_{2menthyl}$), 132.4 (s, CH=CH_2), 119.3 (s, CH=CH_2), 75.6 (s, $CO_2CH_{menthyl}$), 61.4 (s, CO_2CH_2), 57.1 (s, C_{ipso}), 47.0, 40.7, 36.6, 34.3, 31.5, 25.7, 22.9, 22.1, 21.0, 15.9, 14.2. IR (cm^{-1}): 3078 (w), 2954 (m), 2924 (m), 2869 (m), 1729 (s), 1641 (w), 1455 (m), 1417 (w), 1387 (m), 1366 (m), 1323 (w), 1285 (s), 1215 (s), 1194 (s), 1141 (m), 1096 (m), 1038 (m), 991 (m), 961 (m), 917 (m), 845 (w), 637 (w).

*Ethyl ((1R,2S,5S)-2-Isopropyl-5-methylcyclohexyl)cyclopent-3-ene-1,1-dicarboxylate (**A**).* 4-(Ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(−)-menthoxycarbonyl-1,6-heptadiene (110 mg, 323.8 μmol) was dissolved in 5 mL of CH_2Cl_2. Then a solution of $RuCl_2(PCy_3)$-$(IMesH_2)$(CHPh) (14,4 mg, 17.5 μmol) in 2 mL of CH_2Cl_2 was added slowly, and the mixture was stirred for 4 h. After adding ethyl vinyl ether and 10 mL of water, the organic layer was separated, the aqueous fraction was extracted with CH_2Cl_2, and the solvent was removed *in vacuo* to yield a colorless oil, which was further purified by column chromatography. A colorless oil (97.8 mg, 97%) was obtained. ^{1}H NMR ($CDCl_3$): δ = 5.64−5.57 (m, 2H, C*H*=C*H*), 4.69 (t × d, $^3J_1$ = 10.9 Hz, $^3J_2$ = 4.4 Hz, 1H, CO_2CH), 4.22 (d × q, $^2J_1$ = 10.8 Hz, $^3J_2$ = 7.1 Hz, 1H, CO_2CHH), 4.10 (d × q, $^2J_1$ = 10.8 Hz, $^3J_2$ = 7.1 Hz, 1H, CO_2CHH), 3.07−2.91 (m, 4H $(O_2C)_2C(CH_2)_2$), 2.02−1.94 (m, 1H, $H_{menthyl}$), 1.84 (d × sept, $^3J_1$ = 7.0 Hz, $^3J_2$ = 2.8 Hz, 1H, $CH(Me)_2$), 1.73−1.60 (m, 2H, CO_2CHCH_2), 1.55−1.32 (m, 2H, $H_{menthyl}$), 1.25 (t, $^3J_1$ = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.10−0.71 (m, 12H, $H_{menthyl}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 172.4 (s, CO_2Et), 171.8 (s, $CO_{2menthyl}$), 127.7 (s, CH=CH), 127.9 (s, CH=CH), 75.5 (s, $CO_2CH_{menthyl}$), 61.7 (s, CO_2CH_2), 59.1 (s, C_{ipso}), 47.0, 41.0, 40.9, 40.5, 34.3, 31.5, 26.0, 23.2, 22.1, 20.9, 16.1, 14.1. IR (cm^{-1}): 3063 (w), 2953 (m), 2924 (m), 2869 (m), 1728 (s), 1455 (m), 1387 (m), 1367 (m), 1339 (w), 1252 (s), 1178 (s), 1097 (m), 1067 (m), 1038 (m), 1010 (w), 961 (m), 915 (m), 697 (w).

*Mo(N-2-t-BuC$_6$H$_4$)(CHCMe$_2$Ph)(2,5-dimethylpyrrolide)$_2$ (**2**).* A solution of Mo(N-2-*t*-BuC_6H_4)$(CHCMe_2Ph)(OTf)_2$(DME) (280 mg, 0.389 mmol) in 50 mL of diethyl ether was chilled to −30 °C, and lithium-2,5-dimethylpyrrolide (80.6 mg, 0.798 mmol) was added slowly. The mixture was stirred for 3 h, yielding a red solution. The solvent was removed *in vacuo*; then the residue was dissolved in CH_2Cl_2 and filtered through Celite. The solution was concentrated and pentane was added. An orange solid was obtained by fractionated crystallization. ^{1}H NMR (C_6D_6): δ = 13.41 (s, 1H, MoC*H*), 7.55 (d × d, $^3J_1$ = 7.8 Hz, $^2J_2$ = 1.5 Hz, 1H), 7.45−7.39 (m, 2H), 7.24−7.18 (m, 2H), 7.15 (d × d, $^3J_1$ = 7.9 Hz, $^2J_2$ = 1.4 Hz, 1H), 7.13−7.09 (m, 1H), 6.90 (t × d, $^3J_1$ = 7.6 Hz, $^4J_2$ = 1.6 Hz, 1H), 6.85−6.80 (m, 1H), 6.59 (br s, 2H, 2xNC(Me)C*H*), 5.89 (br s, 2H, 2 × NC(Me)C*H*), 2.49−1.87 (br s, 12H, 4 × NCCH_3), 1.77 (s, 6H, MoCH=C$(CH_3)_2$), 1.42 (s, 9H, C$(CH_3)_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ = 153.5 (s, NCCtBu), 147.6 $(CH_3)_2CC(C_5H_5)$, 140.6 $(C(CH_3)_3)$, 133.6, 127.1, 125.8, 125.6, 125.2, 124.8, 124.4, 109.0 (br s, NCMeC), 101.5 (br s, NCMeC), 57.9, 34.4, 30.3, 28.5, 15.87 (br s, NCCH_3).

*Mo(N-2-t-BuC$_6$H$_4$)(CHCMe$_2$Ph)(2,2″,4,4″,6,6″-hexamethyl-m-terphenyl)(2,5-dimethylpyrrolide) (**MAP3**).* A chilled solution of 2,2″,4,4″,6,6″-hexamethyl-*m*-terphenol (148.5 mg, 449.4 μmol) in 5 mL of diethyl ether was added over a period of 10 min to a chilled

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solution of **2** (252 mg, 447.5 μmol) in 50 mL of diethyl ether and stirred for 5 h. All volatiles were removed, and the residue was washed once with diethyl ether and twice with pentane to obtain a yellow solid. ^{1}H NMR (C_6D_6): δ = 11.28 (s, 1H), 7.26−7.22 (m, 2H), 7.14−7.07 (m, 3H), 7.03−6.88 (m, 6H), 6.84 (s, 2H), 6.78 (s, 2H), 6.68 (d × d, $^3J_1$ = 7.7 Hz, $^4J_2$ = 1.6 Hz, 1H), 6.07 (s, 5H), 2.37 (s, 3H), 2.20 (s, 6H), 2.14 (s, 6H), 2.04 (s, 6H), 1.78 (s, 3H), 1.62 (s, 3H), 1.48 (s, 3H). Anal. Calcd for $C_{50}H_{58}MoN_2O$: C, 75.16; H, 7.32; N, 3.51. Found: C, 75.09; H, 7.37; N, 3.49.

Cyclopolymerizations. Cyclopolymerization of α,ω-diynes was carried out in dry dichloromethane or chloroform at the indicated temperature inside a nitrogen-filled glovebox using the indicated initiators. All monomers and solvents were dried and filtered through neutral Al_2O_3 prior to use. Polymerizations were started by the addition of a solution of the initiator in 1 mL of the indicated solvent to the monomer dissolved in the same solvent. In case quinuclidine was used, it was added to the solution of the initiator. Polymerizations with MAP catalysts were terminated by addition of ferrocenylaldehyde (10 mol equiv with respect to the initiator). All other polymers were collected by precipitation from methanol or *n*-pentane containing 1 vol % of CF_3COOH, followed by centrifugation and drying *in vacuo*. All polymers were stored under a N_2 atmosphere.

*Representative Polymer Data. Poly-**M1**.* The polymer was prepared from **I1** (0.004 g, 0.0042 mmol) and the monomer **M1** (0.05 g, 0.213 mmol) in CH_2Cl_2 in 84% isolated yield. Polymerization was started at −30 °C and allowed to run for 1 h. ^{1}H NMR ($CDCl_3$): δ = 6.68 (br, m, 2H), 4.27 (br, m, 4H), 3.43 (br, m, 4H), 1.30 (br, m, 6H). ^{13}C NMR ($CDCl_3$): δ = 172.1, 137.1, 128.4, 126.3, 123.4, 62.1, 57.0, 41.6, 14.2. IR (cm^{-1}): 2977 (m), 1720 (s), 1444 (w), 1367 (s), 1245 (s), 1157 (w), 1065 (s), 946 (s), 629 (m). UV/vis ($CHCl_3$): λ_{max} = 592, 547 nm; M_n = 8500 g/mol, PDI = 2.1; α-insertion: ≥99%.

*Poly-**M2**-(**I2**).* ^{1}H NMR ($CDCl_3$): δ = 6.68 (bs, 2H, CH), 4.74 (bs, 1H, OCH), 4.50−2.59 (m, 6H, CH_2), 2.58−0.42 (m, 22H, CH, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ = 172.0, 171.4 137.1, 123.2, 76.1, 62.0, 57.5, 46.9, 41.5, 40.4, 34.3, 34.2, 31.5, 26.1, 23.4, 22.1, 21.0, 16.3, 14.2. IR (cm^{-1}): 2953 (m), 2925 (m), 2868 (m), 1727 (s), 1455 (m), 1387 (m), 1367 (m), 1247 (s), 1176 (s), 1097 (m), 1048 (m), 1008 (m), 981 (m), 913 (m), 862 (m), 845 (m), 802 (w) 634 (m), 598 (w), 576 (w). UV/vis ($CHCl_3$): λ_{max} = 550 nm, 591 nm; M_n = 32 300 g/mol, PDI = 2.1; α-insertion: ≥96%; isolated yield: 83%.

*Poly-**M2**-(**I3**).* ^{1}H NMR ($CDCl_3$): δ = 6.69 (bs, 2H, CH), 4.74 (bs, 1H, OCH), 4.35−3.0 (m, 6H, CH_2), 2.20−0.42 (m, 22H, CH, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ = 172.0, 171.4 137.1, 123.1, 76.1, 62.0, 57.5, 46.9, 41.6, 40.4, 34.2, 31.7, 31.5, 26.1, 23.4, 22.5, 22.3, 22.1, 21.0, 16.3, 14.2. IR (cm^{-1}): 2953 (m), 2926 (m), 2868 (m), 1725 (s), 1454 (m), 1387 (m), 1366 (m), 1245 (s), 1160 (s), 1096 (m), 1066 (w), 1048 (m), 1009 (m), 981 (m), 947 (s), 912 (m), 862 (m), 845 (m), 700 (w) 630 (m), 597 (w). UV/vis ($CHCl_3$): λ_{max} = 552 nm, 588.5 nm; M_n = 27 500 g/mol, PDI = 1.8; α-insertion: ≥90%; isolated yield: 77%.

*Poly-**M2**-(**I4**).* ^{1}H NMR ($CDCl_3$): δ = 6.63 (bs, 2H, CH), 4.67 (bs, 1H, OCH), 4.41−2.59 (m, 6H, CH_2), 2.19−0.38 (m, 22H, CH, CH_2, CH_3). ^{13}C NMR ($CDCl_3$): δ = 172.0, 171.5, 137.4, 123.4, 76.1, 62.0, 57.7, 46.9, 41.6, 40.5, 36.1, 34.3, 34.3, 31.6, 26.2, 23.4, 22.5, 22.1, 20.9, 16.3, 14.2. IR (cm^{-1}): 2953 (m), 2925 (m), 2868 (m), 1724 (s), 1450 (m), 1386 (m), 1367 (m), 1245 (s), 1167 (s), 1096 (m), 1027 (s), 980 (m), 952 (m), 911 (m), 861 (m), 844 (m), 797 (w), 720 (w), 635 (m), 576 (m), 515 (m). UV/vis ($CHCl_3$): λ_{max} = 547 nm, 585 nm; M_n = 47 500 g/mol, PDI = 4.0; α-insertion: ≥93%; isolated yield: 60%.

*Poly-**M3**-(**I1**).* ^{1}H NMR ($CDCl_3$): δ = 7.0 (bs, 1H, CH), 6.72−5.66 (m, 1H, CH), 4.60−3.84 (m, 8H, OCH_2), 3.25−2.99 (m, 2H, CH), 2.88−1.85 (m, 10H, CH, CH_2), 1.75−1.13 (m, 8H, CH_2), 1.0−0.55 (m, 24H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ = 170.9, 132.0, 128.3, 126.5, 126.1, 125.1, 80.4, 66.4, 66.1, 48.2, 40.1, 34.5, 34.2, 31.6, 25.6, 23.4, 22.4, 22.3, 21.1, 16.5. IR (cm^{-1}): 2951 (m), 2918 (m), 2867 (m), 1757 (s), 1732 (m), 1454 (m), 1384 (m), 1367 (m), 1277 (m), 1187 (m), 1118 (s), 951 (m), 909 (m), 843 (m), 700 (w), 573 (w). UV/vis ($CHCl_3$): λ_{max} = 469 nm; M_n = 25 300 g/mol, PDI = 1.3; α-insertion: ≥99%; isolated yield: 47%.

*Poly-**M4**-(**I1**).* ^{1}H NMR ($CDCl_3$): δ = 7.0 (bs, 1H, CH), 6.75−5.71 (m, 1H, CH), 4.60−3.77 (m, 8H, OCH_2), 3.32−3.03 (m, 2H, CH), 2.83−1.89 (m, 10H, CH, CH_2), 1.87−1.13 (m, 8H, CH_2), 1.1−0.55 (m, 24H, CH, CH_3). ^{13}C NMR ($CDCl_3$): δ = 170.9, 131.8, 128.3, 126.5, 125.2, 80.4, 66.1, 66.0, 65.2, 48.3, 40.1, 34.5, 33.7, 31.6, 29.0, 28.4, 25.6, 23.4, 22.5, 21.1, 16.5. IR (cm^{-1}): 2951 (m), 2918 (m), 2867 (m), 1756 (s), 1732 (s), 1454 (m), 1368 (m), 1276 (m), 1236 (w), 1179 (m), 1118 (s), 1027 (w), 950 (m), 909 (m), 873 (m), 843 (m), 700 (m), 575 (w). UV/vis ($CHCl_3$): λ_{max} = 463 nm; M_n = 24 200 g/mol, PDI = 1.5; α-insertion: ≥99%; isolated yield: 24%.

■ ASSOCIATED CONTENT

Supporting Information

Selected ^{1}H, ^{13}C, ^{19}F, COSY NMR, and GC-MS spectra of monomers, intermediates, and polymers; crystallographic details on **MAP1**, **MAP2**, and **2**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01185.

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Notes

The authors declare no competing financial interest.

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