

Factors Relevant for the Regioselective Cyclopolymerization of 1,6-Heptadiynes, *N,N*-Dipropargylamines, *N,N*-Dipropargylammonium Salts, and Dipropargyl Ethers by Ru^{IV}-Alkyldiene-Based Metathesis Initiators

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Abstract: The factors relevant for the regioselectivity of insertion of various 1,6-heptadiynes, *N,N*-dipropargylamines, *N,N*-dipropargylammonium salts and dipropargyl ethers into different Ru^{IV}-alkyldienes, i.e., [Ru(CF₃COO)₂(IMesH₂)(=CHR)], (R = 2,4,5-(MeO)₃-C₆H₂ (**11**), 2-(2-PrO)-5-NO₂-C₆H₃ (**13**), 2-(2-PrO)-C₆H₄ (**14**)), [Ru(CF₃COO)₂(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-5-NO₂-C₆H₃)] (**12**), [Ru(CF₃COO)₂(3-mesityl-1-((1′*R*)-1′-phenylethyl)-imidazolin-2-ylidene)(=CH-2-(2-PrO)-C₆H₄)] (**15**) and [Ru(C₆F₅COO)₂(IMesH₂)(=CH-2-(2-PrO)-C₆H₄)] (**16**), (IMesH₂ = 1,3-dimesitylimidazolin-2-ylidene), is described. ¹³C NMR experiments revealed that all polymers synthesized by the action of **11–16** consisted virtually solely (>95%) of five-membered repeat units, i.e., (cyclopent-1-enylene)-1,2-vinylenes, 3,4-(1*H*-2,5-dihydropyrylenium)-3,4-vinylenes, and (2-pentyl-2,5-dihydrofurylene)-3,4-vinylenes, respectively. The ¹³C NMR-based assignments were supported by the synthesis of model compounds, i.e., (cyclopent-3-ene-1,1-diyl)dimethylbis(tris(3,5-dimethoxyphenyl)carboxylate) (**MC1**) and *N*-propyl-*N*-ethyl-2,5-dihydro-pyrrolium tetrafluoroborate (**MC2**), as well as by ene–yne cross metathesis reactions of 3-(propargyloxy)-1-octyne (**M6**) with trimethylallylsilane. In the polymerization of *N*-ethyl-*N,N*-dipropargylamine (**M9**), an intermediate was isolated that sheds light onto the role of heteroatoms in the 4-position of 1,6-heptadiynes in cyclopolymerization. In addition, in the cyclopolymerization of **M9** by **14** the product resulting from back-biting has been isolated and explains for the low polymerization propensity of Ru-alkyldienes for *N*-alkyl-*N,N*-dipropargylamines.

Introduction

Conjugated polymers play an important role in various electronic applications.^{1,2} Apart from their conductivity, their photo- and electroluminescence properties are attracting great interest. Owing to their luminescence properties, they are also used in several electronic applications, such as organic light-emitting diodes (OLEDs), solar cells, photovoltaic devices, lasers, all-plastic full-color image sensors, and field effect transistors.^{3–7} In addition, they possess interesting third-order

nonlinear properties.⁸ Poly(acetylene) is the simplest representative of an organic conjugated polymer and has been studied intensively.⁹ However, because of the poor solubility and stability, poly(1-alkyne)s including poly(acetylene) have never found their way into any application. Instead, other, more stable conjugated materials are used.^{3–6,10} Poly(acetylene)s derived from the cyclopolymerization of (substituted) 1,6-heptadiynes with the help of metathesis catalysts^{11,12} possess cyclic structures recurring along the conjugated backbone, thus providing enhanced stability and excellent processability.¹⁰ The repeat units of such cyclopolymerization-derived polymers may consist of either five- or six-membered rings, depending on the insertion mode of the monomer into the initiator (Scheme 1). Usually, one refers to these two different insertion modes as α - and β -insertion (addition), respectively.¹³ While both polymers are conjugated, it has been shown that particularly those based on

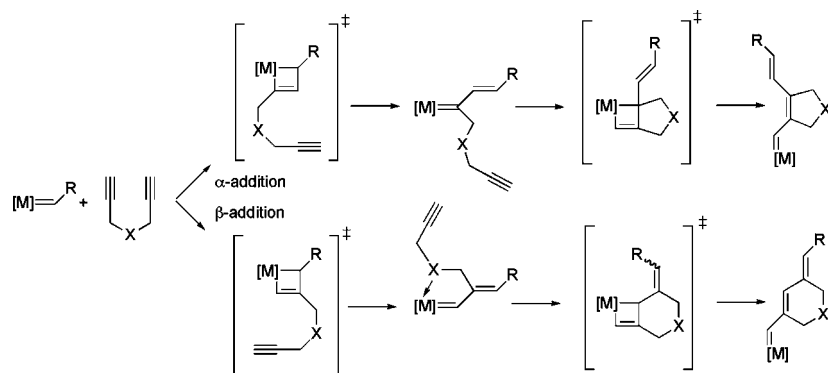
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Scheme 1. Formation of Poly(ene)s Based on Five- and Six-Membered Repeat Units^a

^a For X = N, O coordination to the metal is proposed.

five-membered repeat units possess higher effective conjugation lengths and higher conductivity.¹⁴

In principle, ternary systems,¹⁵ well-defined Mo-based Schrock-type catalysts^{13,16–25} and fluorocarboxylate-modified Grubbs-type metathesis catalysts^{14,26–31} may be used for cyclopolymerization. Here, particularly Schrock and in selected cases also the modified Grubbs-type initiators allow for controlled or even living^{32,33} polymerizations. Important enough, Schrock-type initiators allow for accomplishing cyclopolymerizations in a both stereo- and regioselective manner, offering access to both five- and six-membered repeat units. In contrast to that, cyclopolymerizations triggered by Ru^{IV}-based metathesis initiators based on the Ru(CF₃COO)₂(IMesH₂)(CHR) motif so far produced poly(ene)s that were *exclusively* (>95%) based on five-membered ring units, i.e., 1,2-(cyclopent-1-enylene)-

vinylenes.^{14,26–30,34} We were interested in the questions, which factors actually determine the ring size of the repeat unit in the final Ru-alkylidene triggered, cyclopolymerization-derived polymer, whether the formation of five-membered repeat units was a general principle, and if yes, why? For that purpose, we performed variations in the initiators' structure, i.e., in the nature of the *N*-heterocyclic carbene, the fluorocarboxylate ligand, as well as in the benzylidene moiety. Complementary, we synthesized sterically demanding, aromatic or alkoxyarylester-derived 1,6-heptadiynes. In addition, we investigated the cyclopolymerization of 4-aza-1,6-heptadiynes, quaternary dialkylammonium salts, as well as of the ether-derived monomer 3-(propargyloxy)-1-octyne (**M6**) by initiators **I1–I6**. A summary of the monomers and initiators that have been used is given in Figure 1. The ring-sizes of the polymers' repeat units were determined by ¹³C NMR and confirmed with the aid of model compounds that were prepared via ring-closing metathesis (RCM) of the corresponding diallyl progenitors by the action of the second-generation Grubbs catalyst RuCl₂(IMesH₂)(PCy₃)(CHPh). Since poly-**M6**, whether based on five- or six-membered repeat units would be characterized by the same number of signals in the ¹³C NMR, ene-yne cross metathesis reactions of **M6** with trimethylallylsilane were carried out to trap the "first-insertion" product of the polymerization and determine its ring size.

Results and Discussion

Synthesis of Monomers and Initiators. The synthetic route for the preparation of monomers **M1–M3** entailed the reduction of diethyl dipropargylmalonate with LiAlH₄ to form the corresponding dialcohol,^{20,21} which was then subject to esterification reactions using various arylcarboxylic chlorides. Yields were ≥90% throughout. Monomers **M4** and **M5**, which are based on *N,N*-dialkyl-*N,N*-dipropargylammonium salts, were prepared via quaternization of the parent dipropargylamines with triethyloxonium tetrafluoroborate in 77% and 91% yield, respectively (Scheme 2).

The structures of all monomers are summarized in Figure 1. Initiators **I1–I4** were prepared according to published procedures.^{14,26,27,35,36} **I5** was accessible via reaction of [RuCl₂(3-mesityl-1-((1'*R*)-1'-phenylethyl)-imidazolin-2-ylidene)(=CH-2-(2-PrO)C₆H₄)]³⁷ with CF₃COOAg. **I5** crystallizes in the orthor-

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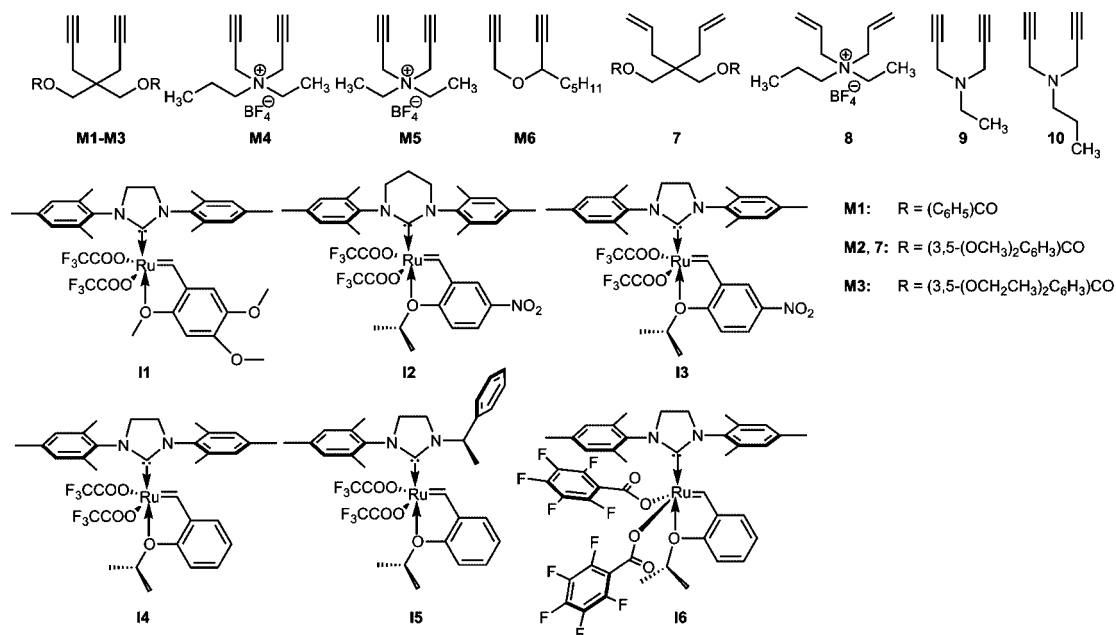
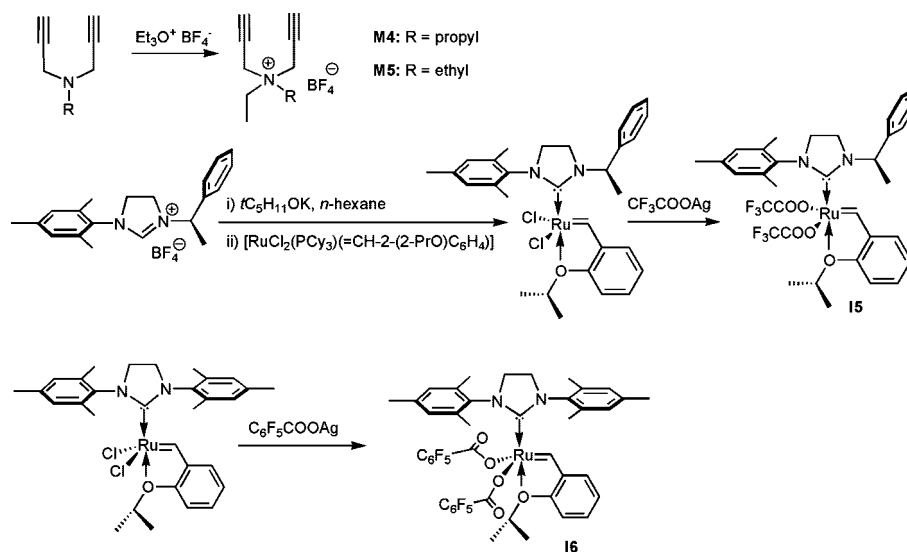


Figure 1. Structure of compounds M1- M6, 7, 8, M9, M10, and initiators I1-I6.

Scheme 2. Synthesis of M4 and M5, as well as of I5 and I6



hombic space group $P2_12_12_1$, $a = 989.76(2)$ pm, $b = 1122.53(2)$ pm, $c = 3099.91(6)$ pm; $\alpha = \beta = \gamma = 90^\circ$, $Z = 4$. Its structure is shown in Figure 2; relevant bond lengths and angles are also summarized in Figure 2. Compared to other bis(trifluoroacetate) derivatives of the second-generation Grubbs-Hoveyda catalyst, changes in the ligand sphere hardly affect the Ru-alkylidene. Thus, the bond length of the Ru-alkylidene (182.7(3) pm) is identical to the one found in **I2**³⁶ and **I4**,³⁵ respectively. The same accounts for the distance Ru(1)–O(1) (227.77(18) pm). Furthermore, the angle between the two trifluoroacetate ligands is $\sim 160^\circ$ as found in **I2** and **I4**. Finally, **I6** was prepared from $[\text{RuCl}_2(\text{IMesH}_2)(=\text{CH}-2-(2\text{-PrO})-\text{C}_6\text{H}_4)]$ via reaction with $\text{C}_6\text{F}_5\text{COOAg}$ (Figure 1, Scheme 2).

Insertion Mode, Polymer Structure, and Mechanistic Investigations. Polymerization of 1,6-Heptadiynes Containing a Carbon at the 4-Position. The cyclopolymerization of 1,6-

heptadiynes by well-defined metal alkylidenes proceeds either via α - or β -addition of one triple bond to the metal alkylidene, followed by cyclization, thus resulting in the formation of five- and six-membered repeat units along the polymer backbone (Scheme 1).^{13,16,38}

Polymerization of **M1**, **M2**, and **M3** by the action of **I1**, **I2**, or **I3** proceeded smoothly and produced the corresponding polymers poly-**M1**, poly-**M2**, and poly-**M3** in 71–83% isolated yield. Monomer conversion was $>99\%$ in all cases. Polydispersity indexes (PDIs) were in the range of 1.4–2.5. Though monomer conversion was $>99\%$, a comparison of the theoretical values for M_n with those determined by GPC (Table 1) revealed that none of these polymerizations was living or even controlled.

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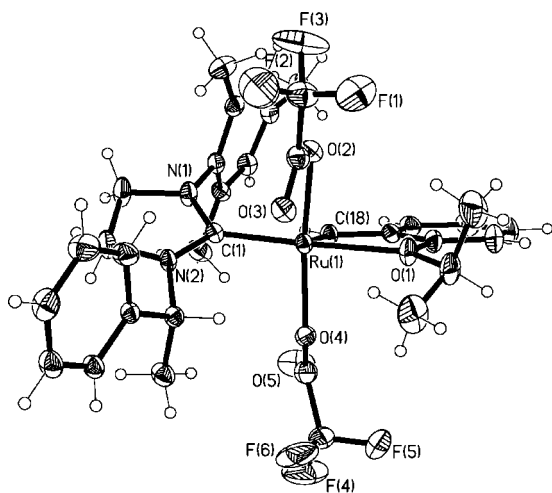


Figure 2. Single-crystal X-ray structure of **15**. Ru(1)–C(18): 182.7(3) pm; Ru(1)–C(1): 199.9(3) pm; Ru(1)–O(1): 227.8(2) pm; O(4)–Ru(1)–O(2): 158.79(8)°; C(1)–Ru(1)–O(1): 176.57(9)°.

^1H and ^{13}C NMR spectra revealed that upon initiation with **I1–I6**, poly-**M1**, poly-**M2**, and poly-**M3**, were formed via selective α -addition, thus resulting in polymers based on >95% five-membered ring units. A representative ^{13}C NMR spectrum is shown in Figure 3; for the ^{13}C NMR of the poly-**M2** and poly-**M3** prepared by the action of **I1–I6**, kindly refer to the Supporting Information.

The carbon signals around 123–137 ppm (poly-**M1**, poly-**M2**, and poly-**M3**) represent the olefinic carbons of the polymers. The number of the carbon signals exactly fits a five-membered ring-based repeat unit (a six-membered ring-based repeat unit would result in three additional signals). In addition, a model compound, i.e., (cyclopent-3-ene-1,1-diyl)dimethyl bis(tris(3,5-dimethoxyphenyl)carboxylate) (**MC1**) was synthesized via ring-closing metathesis (RCM) from the progenitor **7** using the second-generation Grubbs catalyst $\text{RuCl}_2(\text{IMesH}_2)(\text{PCy}_3)(\text{CHPh})$ (Scheme 3).

MC1 is a mimic of the repeat unit of poly-**M2**. As a matter of fact, the ^{13}C NMR chemical shifts of **MC1** (39.4 ppm (C_{quat}), 166.3 ppm (CO)) fitted those of poly-**M2** (39.8 ppm (C_{quat}), 166.2 ppm (CO)) very well, thus further supporting the five-membered ring structure. From the signal/noise ratio of the ^{13}C NMR spectra of the polymers, a five-membered ring content of at least 95% was assigned. It is noteworthy that the cyclopolymerization of 1,6-heptadiynes that contain both small (e.g., bis(methoxycarbonyl))^{14,26–28,35} and large, bulky groups as realized in **M1–M3** by Ru-alkylidenes resulted in polymers virtually solely based on five-membered repeat units. Apparently, there is no influence of the size of the substituents in the 4-position of the monomer on the mode of insertion. This is in sharp contrast to Schrock-catalyst-triggered cyclopolymerizations.³⁹ There, the ring size of the repeat unit is strongly affected by the size of the substituent in the 4-position of the heptadiyne. Thus, the cyclopolymerization of 4-ethoxycarbonyl-1,6-heptadiyne, e.g., by the binuclear initiator 1,4-{Mo(N-2,6-(2-Pr)₂C₆H₃)[OCMe(CF₃)₂]₂-CH)₂C₆H₄ results in polymers with a five-membered ring content of only 32%, while the cyclopolymerization of 4,4-bis(*tert*-butoxycarbonyl)-1,6-heptadiyne by the same catalyst gives rise to polymers with a five-membered

ring content of 58%. This low or negligible influence of the monomer's size on the mode of insertion into Ru-alkylidenes may be explained by the reaction cascades shown for both α - and β -insertion (Scheme 4).

Thus, monomers have been proposed to preferably coordinate *trans* to the N-heterocyclic carbene (NHC), though more recently also a side-on coordination was proposed and found.^{37,40,41} α -Addition, finally resulting in five-membered repeat units, apparently can proceed without any significant steric interaction between any of the initiator's ligands and the growing polymer chain. In contrast to that, the formation of the *second* ruthenacyclobutene in course β -addition results in a strong interaction of the NHC and the growing polymer chain, which apparently impedes this reaction pathway. Since all metathesis reactions are considered reversibly,⁴² the initiator is not blocked and may, after cycloreversion, proceed via α -addition.

If all that was true, then neither the size of the NHC nor the size of the fluorocarboxylates should have a significant influence on the mode of insertion. As a matter of fact, this was found true at least for initiators **I1–I6**. The same regioselectivity of insertion of monomers **M1–M3**, i.e., α -addition, was observed, irrespective of the fact that both the NHC ligand in **15** and the pentafluorobenzoate ligand in **16** may well be regarded as sterically demanding. So far, the results obtained perfectly fit the ones reported earlier for comparatively "small" monomers such as dimethyldipropargyl malonate and diethyldipropargyl malonate polymerized by pentafluoropropionate and heptafluorobutyrate derivatives of the second-generation Grubbs–Hoveyda catalyst²⁷ and suggest that Ru-alkylidenes in fact selectively form poly(enes) based on five-membered repeat units, irrespective of the initiator used.

1,6-Heptadiynes Containing Amines at the 4-Position. Next, we were interested whether *N*-alkyl-*N,N*-dipropargylamines could be polymerized by Ru-alkylidenes and what the mode of insertion would be. As mentioned earlier,³⁰ neither *N*-ethyl-*N,N*-dipropargylamine (**M9**) nor *N*-propyl-*N,N*-dipropargylamine (**M10**) could be polymerized by any of the initiators to a significant extent. Thus, upon mixing **14** and **M9** in a 1:3 ratio inside an NMR tube, we could still observe significant amounts of both the monomer and **14** after 1 h. A weak new Ru-alkylidene signal at 17.07 ppm indicated that initiation had occurred. We assign these findings to a strong coordination of the amine-nitrogen to the metal. After capping the reaction of **M9** with **14** after 1 h with ethyl vinyl ether, we were still able to detect significant amounts of a compound with $m/z = 245$ g/mol⁻¹ by GC-MS. This m/z value can be attributed to the capped intermediates **IM1** or **IM2** (Scheme 5). Such an intermediate has to the best of our knowledge never been observed before. It provides not only unambiguous proof for the polymerization mechanism proposed by Schrock et al.,^{13,16} but is also indicative for the strong *intramolecular* coordination of the amine moiety to the metal center, which strongly stabilizes this intermediate, irrespective of the mode of insertion (Scheme 1). In contrast to *N*-aryl-*N,N*-dipropargylamines,³¹ coordination apparently becomes very strong in "small" and basic *N*-alkyl-*N,N*-dipropargylamines (alkyl = ethyl, propyl), which ultimately leads to the total shut down of polymerization after two monomer insertions. Thus, prolonged reaction of **M9** with **14**

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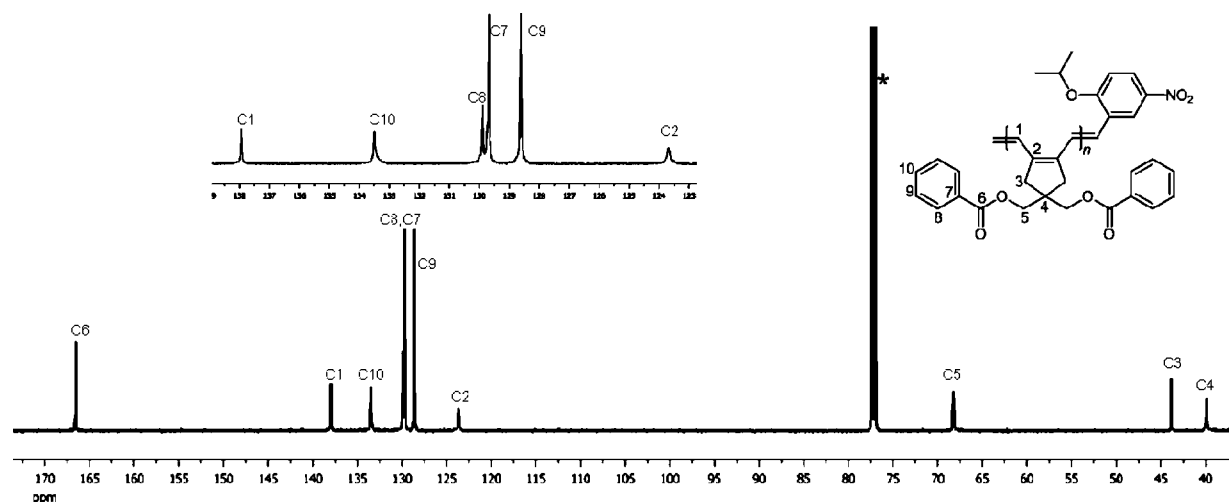
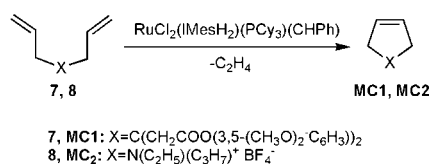
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Table 1. Selected GPC and UV–Vis Data (All in CHCl₃) of Polymers Synthesized by the Action of Initiators **I1–I3**, Respectively^a

M	[M]/[I]	I	M _n (theor.) [g/mol] ^b	M _n (found) [g/mol]	M _w (found) [g/mol]	PDI	λ _{max} [nm]	yield [%] ^c
M1	1:100	I1	36 200	17 900	31 000	1.72	588	76
M1	1:50	I1	18 200	23 500	46 900	1.91	588	79
M1	1:30	I1	11 000	18 600	32 700	1.75	589	76
M2	1:100	I1	45 400	27 400	43 600	1.52	586	80
M2	1:50	I1	22 800	30 800	58 100	1.86	591	81
M2	1:30	I1	13 700	22 000	38 300	1.73	590	75
M3	1:100	I1	53 800	16 800	28 800	1.71	584	73
M3	1:50	I1	27 000	14 200	21 300	1.45	583	75
M3	1:30	I1	16 200	15 000	23 900	1.51	583	71
M1	1:100	I2	36 200	13 000	19 900	1.53	588	76
M1	1:50	I2	18 200	9800	16 100	1.64	581	78
M1	1:30	I2	11 000	21 600	39 900	1.84	588	72
M2	1:100	I2	45 400	16 800	28 800	1.73	586	80
M2	1:50	I2	22 800	12 400	24 400	1.96	586	79
M2	1:30	I2	13 700	19 600	35 000	1.78	588	83
M3	1:100	I2	53 800	21 400	35 300	1.67	588	75
M3	1:50	I2	27 000	14 200	21 300	1.49	583	75
M3	1:30	I2	16 200	18 400	28 900	1.52	582	78
M1	1:100	I3	36 200	13 000	24 600	1.88	583	70
M1	1:50	I3	18 200	12 000	22 500	1.87	583	75
M1	1:30	I3	11 000	12 100	29 600	2.45	588	79
M2	1:100	I3	45 400	30 500	54 000	1.77	591	82
M2	1:50	I3	22 800	37 700	17 900	2.10	589	74
M2	1:30	I3	13 700	18 000	30 400	1.68	587	80
M3	1:100	I3	53 800	21 500	55 600	2.58	593	72
M3	1:50	I3	27 000	24 200	60 600	2.49	592	71
M3	1:30	I3	16 200	18 800	33 100	1.75	589	80

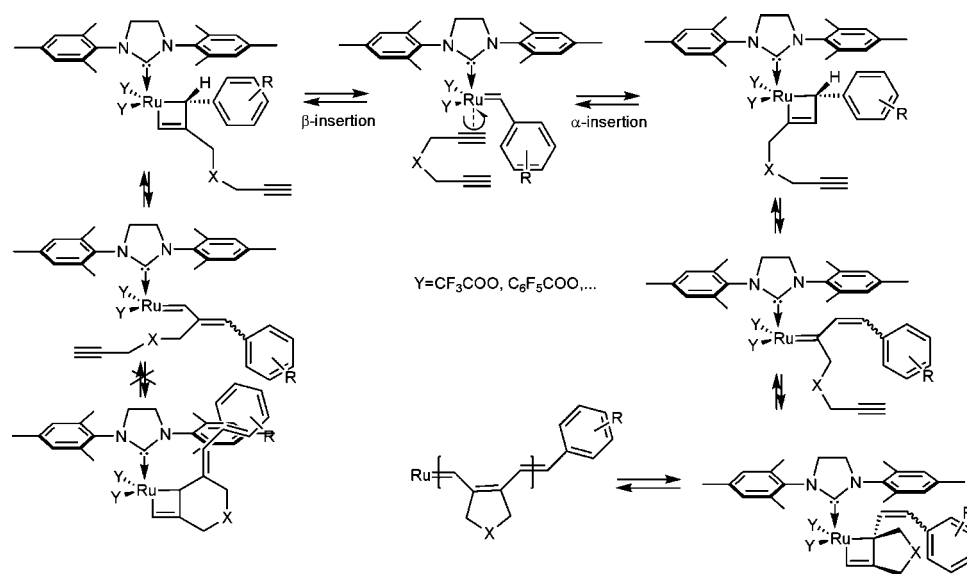
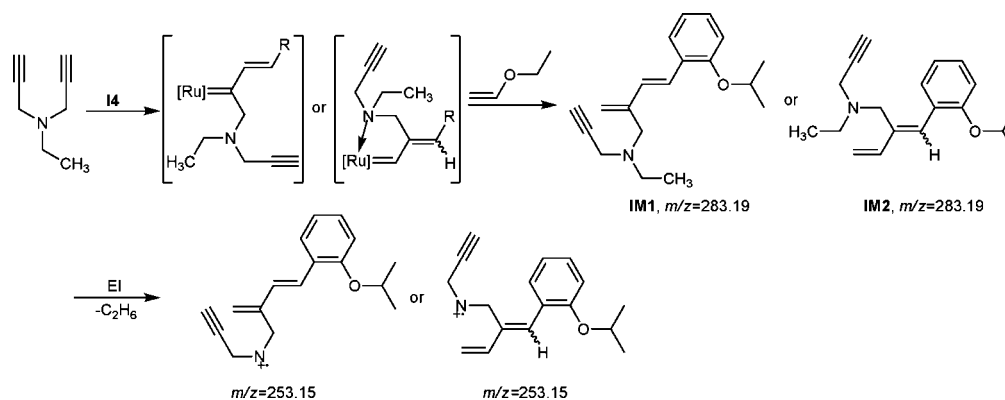
^a Polymerization conditions: CHCl₃, 55 °C, 24 h. ^b Including end groups. ^c Isolated yields.

**Figure 3.** ¹³C NMR spectrum of poly-**M1** in CDCl₃ synthesized by the action of **I2** (the asterisk denotes CDCl₃).**Scheme 3.** Synthesis of Model Compounds **MC1** and **MC2** via RCM

allowed for the isolation of compound **11** in 32% yield. It apparently forms via insertion of **M9** into **I4**, consecutive insertion of one further propargyl moiety of **M4** into the Ru-alkylidene followed by back-biting (Scheme 6). The signals of the pending propargyl group in **11** have been clearly identified by IR (3294 cm⁻¹) and by ¹H NMR (3.3 (CH₂, d, J = 2.4 Hz) and 2.2 ppm (CH, t, J = 2.4 Hz), Supporting Information). Both the ¹H and ¹³C NMR data fit the proposed structure **11** which

forms either via consecutive α,α or α,β insertion. Structures **11a** and **11b** would be formed via consecutive β,α and β,β insertion, respectively, and would, at least in theory, give similar NMR spectra. Nevertheless, because of the high ring strain of the bicyclic structures, they may well be ruled out. (Structure **11a** may additionally be ruled out by NMR for symmetry reasons). The result of this reaction is thus formation of **11** under regeneration of the initiator **I4**. This initiator regeneration may also be followed by ¹H NMR. Thus, after ~18 min, the intensity of the starting alkylidene signal at 17.45 ppm becomes weaker on the expense of the signal of the first insertion product at 17.07 ppm. Toward the end of the reaction, however, the ratio of the propagating over the starting alkylidene strongly decreased again (Supporting Information).

At this point it is worth emphasizing that, e.g., norborn-2-ene-based monomers bearing tertiary amine moieties may well

Scheme 4. Reaction Cascade for Ru-Alkylidene-Triggered Cyclopolymerization Proceeding via α - or β -Addition**Scheme 5.** Proposed Structures of **IM1** and **IM2** Formed via the Reaction of **M9** with **I4**

be polymerized by a series of Grubbs-type initiators,⁴³ further supporting the idea that rather the formation of the cyclic intermediates than a simple coordination of the amine to the ruthenium is responsible for the low polymerization propensity of 4-aza-1,6-heptadiynes. Similar coordination of heteroatoms to a Ru center as described here has been reported by Grubbs et al., however, for Ru-alkylidenes with the heteroatom directly attached to the carbene.⁴⁴ There, the corresponding intermediates resulting from coordination of the heteroatom to the metal are based on three-membered rings. In due consequence, stabilization is comparably poor, and the corresponding metal complexes are in fact active in various olefin metathesis reactions.

1,6-Heptadiynes Containing Quaternary Ammonium Moieties at the 4-Position. From Scheme 1 it becomes apparent that the stabilization of the intermediate is only possible in case X is a coordinating moiety, e.g., N or O (as in **M6**). If all that was true, *quaternary dipropargylammonium salts* such as **M4** or **M5** should *not* be capable of forming such an intermediate and should therefore behave similar to **M1–M3** and other monomers.²⁸ In due consequence, poly(ene)s virtually solely based on five-membered ring-based repeat units might be expected.

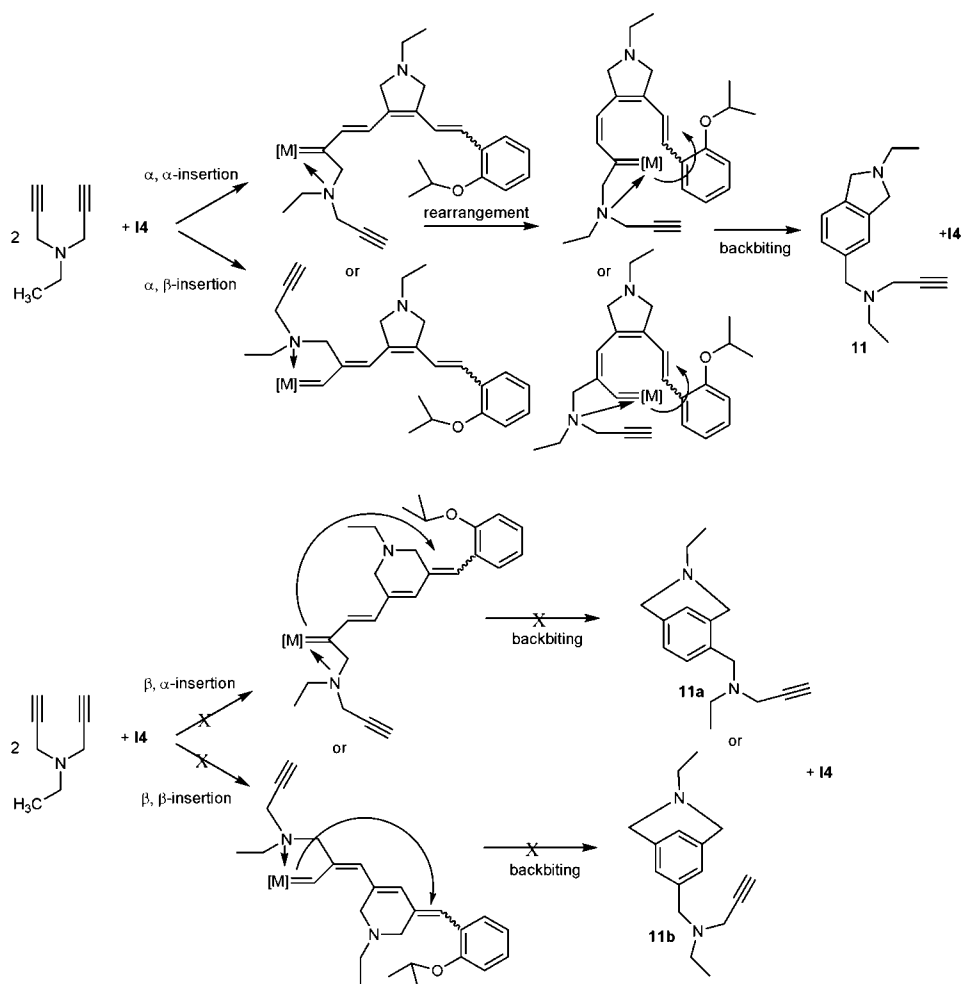
In fact, both **M4** and **M5** can be polymerized by **I1–I6**. The corresponding polymers were obtained in 28–98% isolated

yield. Generally, monomer conversion was >99%, lower yields were a result of the good solubility of the polymers, particularly of the low-molecular-weight ones. PDIs were in the range of 1.01–1.9 (Table 2). Again, none of these polymerizations was living or controlled. It must be emphasized that all molecular weights were determined by calibration vs poly(styrene).

Poly-**M4** and poly-**M5** prepared by any of the initiators **I1–I6** again consisted virtually solely (>95%) of five-membered repeat units. The two carbon signals around 125–135 ppm again represent the olefinic carbons of the polymers (Figure 4). The number of the carbon signals again exactly fits a five-membered ring-based repeat unit and the chemical shifts (124.6 ppm (C=C), 68.9 ppm (N⁺CH₂C=C)) of the model compound *N*-propyl-*N*-ethyl-2,5-dihydropyrrolium tetrafluoroborate (**MC2**, Scheme 3), prepared via RCM from **8**, fit the ones of poly-**M4** (123.9 (C=C), 68.05 ppm (N⁺CH₂C=C)) very well.

Polymerization of 1,6-Heptadiynes Containing an Ether Moiety at the 4-Position. We finally turned to the polymerization of 3-(propargyloxy)-1-octyne (**M6**). To our delight, poly-**M6** could be prepared by the action of all initiators **I1–I6**. Interestingly, the polymerization of **M6** by the action of **I2** proceeded in a controlled manner (Table 2). Thus, molecular weights (M_n) increased linearly with the number of monomer equivalents added. A graph of number of monomer equivalents (N) vs M_n is shown in Figure 5. Equally important, the number average molecular weight, M_n , of poly-**M6**₅₀ prepared by the action of

(43) Bandari, R.; Knolle, W.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2007**, *28*, 2090.

Scheme 6. Reaction of **M9** with **I4** and Formation of **11** via Back-BitingTable 2. Selected GPC and UV–Vis Data of Poly-**M4** and Poly-**M5** (All in DMF) and of Poly-**M6** (All in CHCl_3) Synthesized by the Action of **I2**, **I3**, and **I4**, Respectively

M	[M]/[I]	I	M_n (theor.) [g/mol] ^a	M_n (found) [g/mol]	M_w (found) [g/mol]	PDI	λ_{max} [nm]	yield [%] ^b
M4	1:200	I2	50 400	10 900	11 000	1.01	523	38 ^c
M4	1:100	I2	25 300	10 000	10 700	1.06	536	40 ^c
M4	1:50	I2	12 700	8800	9100	1.03	537	31 ^c
M4	1:30	I2	7700	7000	7100	1.02	538	30 ^c
M4	1:200	I4	50 300	39 400	45 000	1.14	523	96 ^c
M4	1:100	I4	25 200	35 300	55 200	1.56	541	98 ^c
M4	1:50	I4	12 700	7200	7400	1.03	535	97 ^c
M4	1:30	I4	7700	7000	7200	1.02	537	98 ^c
M5	1:200	I2	47 600	10 900	11 300	1.03	490	35 ^d
M5	1:100	I2	23 900	10 700	11 500	1.07	480	28 ^d
M6^e	1:200	I2	33 000	12 700	19 000	1.40	510	90
M6^e	1:100	I2	16 600	6100	12 100	1.97	485	88
M6^e	1:50	I2	8400	4000	7300	1.78	451	85
M6^e	1:30	I2	5100	3600	7100	1.96	467	92
M6^e	1:50 + 50	I2	16 800	11 200	19 400	1.70	491	-
M6^e	1:200	I3	33 000	4700	9000	1.96	524	85
M6^e	1:100	I3	16 600	4400	8600	1.95	522	88
M6^e	1:50	I3	8400	4300	8599	1.91	525	84
M6^e	1:30	I3	5100	3900	6900	1.75	469	90

^a Including end groups. ^b Isolated yields. ^c CH_2Cl_2 , 40 °C, 24 h. ^d $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 50 °C. ^e CHCl_3 , 50 °C, 24 h.

I2 doubled upon addition of another 50 monomer equivalents after 24 h (Figure 6). On the basis of the ranking of living systems suggested by Matyjaszewski,³² this polymerization would fulfill a class VI living system. The comparably low

values for M_n and the PDIs in the range of 1.40–1.97 (Table 2), however, do not support such a living system and ask for further investigations on the polymers' end groups, e.g., by MALDI-TOF.

This raises the question why **M6** can be polymerized in such a controlled manner by **I2** while the other monomers **M1**–**M5**

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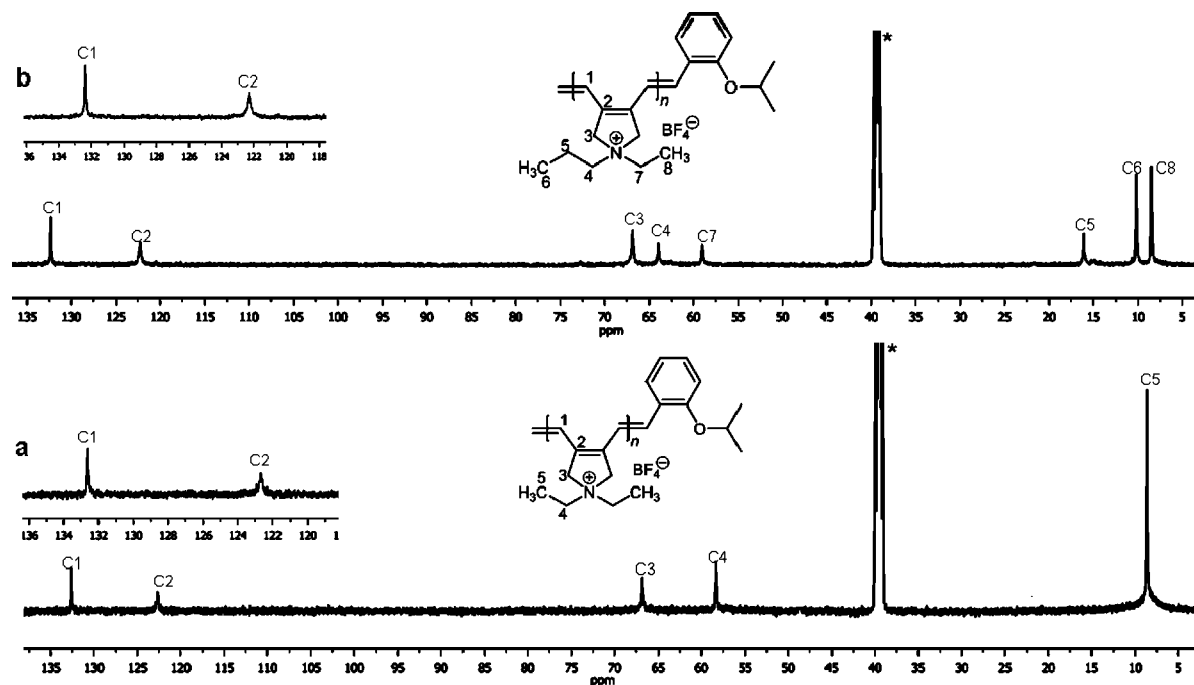


Figure 4. ^{13}C NMR spectra of poly-M5 (a) and poly-M4 (b) in $\text{DMSO-}d_6$ synthesized by the action of **I4** (the asterisk denotes $\text{DMSO-}d_6$).

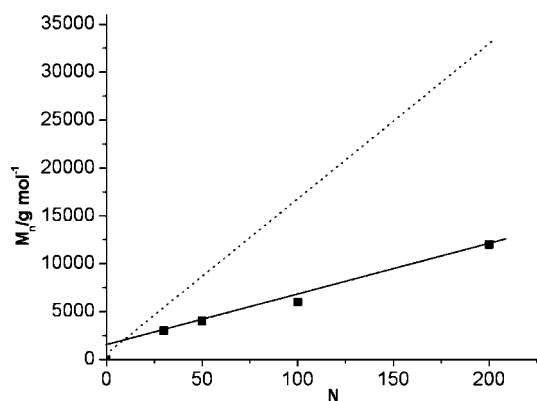


Figure 5. Correlation of M_n with the number of monomer equivalents (N) for the polymerization of **M6** by the action of **I2**. Dotted line: $M_{n(\text{theor.})}$, solid line $M_{n(\text{found})}$.

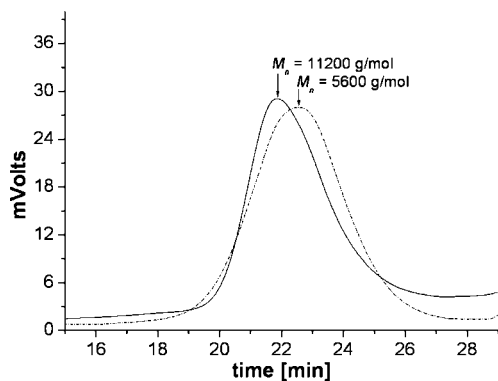


Figure 6. GPC trace of poly-M6 prepared by the action of **I2**. Dashed line, 50 equiv of **M6**; full line, another 50 equiv of **M6** added to the living polymer.

cannot. In order to gain control over molecular weights, the rate constant of initiation, k_i , should be larger than the rate constant of polymerization, k_p , i.e., $k_i/k_p > 1$. All initiators **I1–I6**

are stabilized by a chelating ether group which is removed from the initiator upon initiation, i.e., is moved to the polymer end. Due to the lack of any additional stabilization, k_i/k_p for **M1–M5** may well be expected to be low. The ratio of k_i/k_p may be determined by ^1H NMR provided the fact that all monomer has been consumed and no chain transfer or termination occurs.⁴⁵ As a consequence of the sensitivity of ^1H NMR, insertion products are usually visible down to values for $k_i/k_p > 0.002$. As a matter of fact, though polymer formed, no insertion products could be detected in the polymerization of **M4** by **I2**, **I4–I6** at all, supporting values for $k_i/k_p \leq 0.002$. However, as proposed above, the polymerization of **M6** is characterized by an intermediary, intramolecular chelation by the monomer's ether group. This should reduce k_p and thus enlarge k_i/k_p . Though again no insertion products could be detected for **M6** polymerized by the action of **I2**, **I5**, and **I6**, its polymerization by the action of **I4** in fact resulted in a series of signals corresponding to different insertion products at $\delta = 17.60$, 17.31 , and 17.22 ppm. Due to the overlap with the parent initiator signal, the values for k_i/k_p could not be calculated accurately, however, a rough estimation was made. Thus, for the polymerization systems **M6/I4**, a value for k_i/k_p of roughly 0.05 ± 0.02 was found. This increase in k_i/k_p is in fact believed to be responsible for the control in polymerization of **M6** by **I4**.

In contrast to the polymers discussed above, the polymer structure of poly-M6 (Figure 7) cannot be clarified by ^{13}C NMR since both five- and six-membered repeat units result in the same number of carbon atoms. Instead, we carried out an ene-yne cross metathesis reaction between **M6** and allyltrimethylsilane (Scheme 7). This allowed for isolating the “capped first insertion product” **12**, which was based on a five-membered ring, too.

Physico-chemical Properties of Polymers. The phenylester-derived polymers poly-M1, poly-M2, and poly-M3 were isolated as silky dark violet powders. They showed excellent solubility

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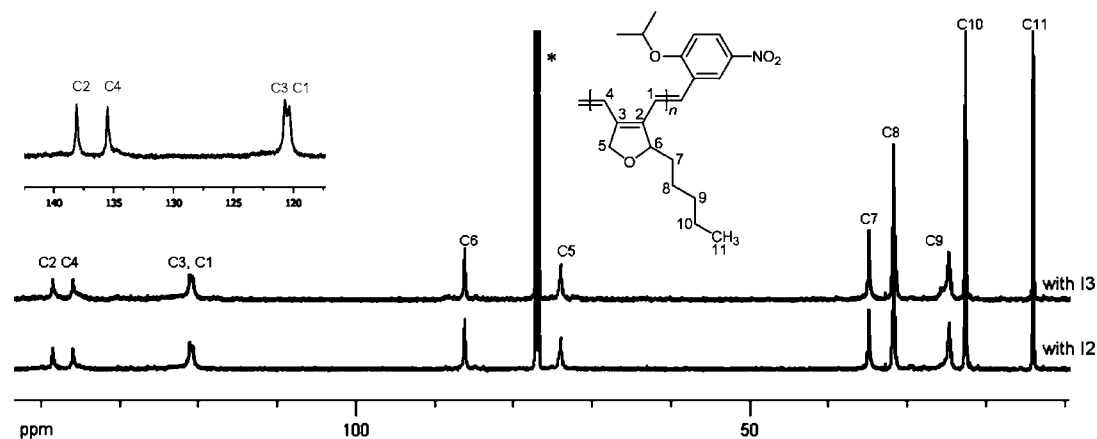
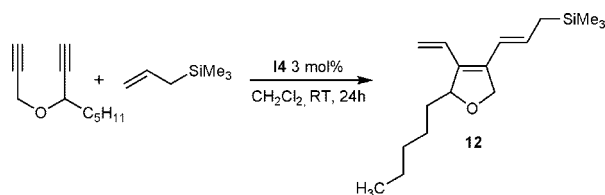


Figure 7. ^{13}C NMR spectra of poly-**M6** in CDCl_3 synthesized by the action of **I2** (bottom) and **I3** (top), respectively (the asterisk denotes CDCl_3).

Scheme 7. Ene–Yne Cross Metathesis Reaction between **M6** and Allyltrimethylsilane



in common organic solvents such as CHCl_3 , CH_2Cl_2 , and THF. UV–vis spectra of the polymers measured in chloroform revealed absorption maxima in the range from 581 to 593 nm (Tables 1 and 2). Similar absorption maxima (592 nm) have been observed for cyclopolymerization-derived poly(ene)s based on 1,6-heptadiynes with comparably small substituents at the 4-position.^{20–24} The fact that poly-**M1**, poly-**M2**, and poly-**M3** bearing large substituents at the 4-position possess similar absorption maxima suggests that the effective conjugation length in such poly(ene)s is rather dependent on the ring size of the repeat unit than on the substituents in the 4-position.

Poly-**M1**, poly-**M2**, and poly-**M3** showed excellent long-term stability toward air and moisture; thus, there was no observable change in the UV–vis spectra of the polymers upon exposure to air and moisture for several days. Poly-**M4** and poly-**M5** were isolated as dark red powders. They showed instant solubility in CH_3COOH , DMSO, DMF, and water. The UV–vis spectra of poly-**M4** and poly-**M5** in DMF revealed absorption maxima in the range from 480 to 538 nm.

Finally, poly-**M6** was isolated as a dark-red polymer. It possessed excellent solubility in organic solvents and displayed a significant hypsochromic shift in absorption, resulting in absorption maxima in the range of 451–525 nm (Table 2).

Conclusions

A series of trifluoroacetate- and pentafluorobenzoate-modified Grubbs–Hoveyda-type metathesis initiators have been investigated for their capability of polymerizing sterically demanding, ester-derived 1,6-heptadiynes, dipropargylamines, dipropargylammonium salts, and an alkyl-substituted dipropargyl ether. The

most relevant findings were (i) all polymers were virtually solely (>95%) based on five-membered repeat units, i.e., 1,2-(cyclopent-1-enylene)vinylenes for poly-**M1**, poly-**M2**, and poly-**M3**, 3,4-(1*H*-2,5-dihydropyrrolium)vinylenes for poly-**M4** and poly-**M5** and 3,4-(2-pentyl-2,5-dihydrofurylenevinylene) for poly-**M6**; (ii) the ether-derived poly-**M6** could be prepared in a controlled manner by the action of **I2**; and (iii) the amine-based monomers **M9** and **M10** cannot be cyclopolymerized to a significant extent due to the intramolecular stabilization of the intermediates and significant back-biting. The results presented here clearly indicate that neither the size of the initiator's substituents nor the nature and size of the substituents at the 4-position of 1,6-heptadiynes determine the size of the cyclic rings along the polymer main chain. Instead, the formation of the second ruthenacyclobutene during β -addition is strongly disfavored while the one in course of α -addition is not. Therefore, so far, the synthesis of cyclopolymerization-derived polyenes with six-membered repeat units remains the sole domain of Schrock catalysts.^{8,17,18,46} Present investigations focus on quantum chemical calculations that provide detailed insights into this particular matter as well as on the synthesis of cyclopolymerization-derived poly(ene)s with improved conductivity. These results will be reported in due course.

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Supporting Information Available: Information on general experimental details, details on **M1–3**, **M5–M10**, **7**, **8**, **I5**, **I6**, **MC 1–2**, ene–yne metathesis product of **M6** and allyltrimethylsilane, X-ray details of **I5**, and structure of the compound formed via the reaction of **M10** with **I4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA804563T

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