Factors Relevant for the Ruthenium–Benzylidene-Catalyzed Cyclopolymerization of 1,6-Heptadyines

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Abstract: Fourteen metathesis initiators that had been designed for use in the living polymerization of diethyl dipropargylmalonate (DEDPM), including the Hoveyda catalyst $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1a**), as well as $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1b**), $[Ru(CF_3CF_2COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1c**), $[Ru(CF_3CF_2CF_2COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1d**), $[RuCl_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(MeO)_3{-}C_6H_2)]$ (**2a**), $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(MeO)_3{-}C_6H_2)]$ (**2b**), $[Ru(CF_3CF_2COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(MeO)_3{-}C_6H_2)]$ (**2c**), $[Ru(CF_3CF_2CF_2COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(MeO)_3{-}C_6H_2)]$ (**2d**), $[RuCl_2(IMes)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**3a**), $[Ru(CF_3COO)_2(IMes)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**3b**), $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)]$ (**4a**), $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)]$ (**4b**), $[Ru(CF_3CF_2COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)]$ (**4c**), and $[Ru(CF_3CF_2CF_2COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)]$ (**4d**) (IMes = 1,3-dimesitylimidazol-2-ylidene; $IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) were prepared. Living polymerization systems could be generated with DEDPM by careful tuning of the electronic nature and steric placement of the ligands. Although **1a**, **2a**, **3a**, **3b**, and **4a** were inactive in the cyclopolymerization of DEDPM, and initiators **1b–d** did not allow any control over molecular weight, initiators **2b–d** and **4b–d** offered access to class VI living polymerization systems. In particular, compounds **2b** and **4d** were superior. The livingness of the systems was demonstrated by linear plots of M_n versus the number of equivalents of monomer added (N). For initiators **2b–d** and **4b–d**, values for k_p/k_i were in the range of 3–7, while **1b**, **1c,** and **1d** showed a k_p/k_i ratio of >1000, 80, and 40, respectively. The use of non-degassed solvents did not affect these measurements and underlined the high stability of these initiators. The effective conjugation length (N_{eff}) was calculated from the UV/Vis absorption maximum (λ_{max}). The final ruthenium content in the polymers was determined to be 3 ppm.

Keywords: carbenes · metathesis · poly(acetylene) · polymerization · ruthenium

Introduction

Conjugated soluble polymers are of significant interest because of their optical and electrical properties.[1–6] Poly(acetylene), which has been extensively studied, is highly conductive after doping, yet is insoluble and extremely sensitive to air. Therefore, it is hard to process, and for this reason, alternative materials such as poly(phenylenes) (PPs), poly(*p*-phenylenevinylenes) (PPVs), poly(thiophenes), and poly(pyrrols) are currently under investigation. Despite the significant progress that has been made with these types of materials, the development of stereo- and regioselective cyclopolymerization of 1,6-heptadiynes has revitalized the area of poly(acetylene)-type materials because it offers access to both highly conjugated and soluble poly(acetylenes).[7,8] In particular, the use of well-defined Schrock-type catalysts offers access to soluble poly(acetylenes) that contain only one type of repetitive unit. These are either based on five-membered (cyclopent-1-enylenevinylenes)[9,10] or six-membered rings (cyclohex-1-enylene-3-methylidenes),[11,12] although fine-tuned quaternary systems may also be used for these purposes.[13] In addition, the poly(acetylenes) can be prepared at least in a class V, and in most cases a class-VI[14] living manner; this means that the initiator attached to the polymer remains active for at least 24 h. Despite these advancements, a major drawback of molybdenum-based chemistry is the extreme sensitivity of these systems towards oxygen and moisture. In an effort to accomplish such cyclo-

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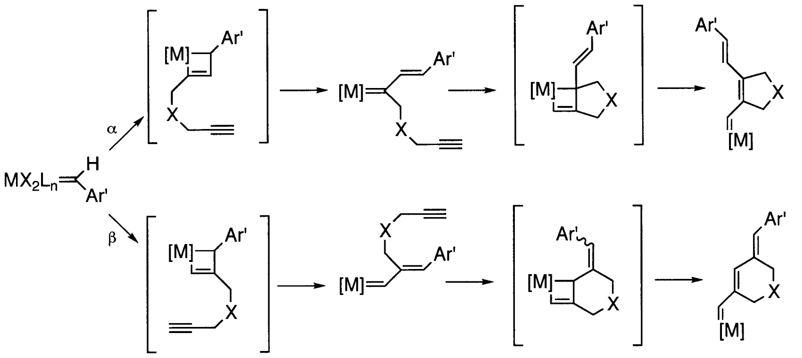
polymerizations with less sensitive initiators, we recently reported on the first ruthenium-based metathesis initiators, $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$[15] and $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(OMe)_3{-}C_6H_2)]$.[16] These were used to polymerize diethyl dipropargylmalonate (DEDPM) to give virtually only five-membered ring structures, that is, the repetitive units were based on cyclopent-1-enylenevinylenes.[16] In this paper, we report in detail the design of living polymerization systems, and describe how variations in the N-heterocyclic carbene (NHC) ligand (either electron-rich or electron-poor) affect the activity of an initiator. In addition, the effect that substitution of the chlorine ligand by electron-withdrawing, fluorinated carboxylates has will be reported. Even more importantly, we will show how the electronic and steric character of the benzylidene moiety directly translates into an initiator's ability to form a class VI living system, in which full control over molecular weight is gained.

Results and Discussion

There are two possible pathways, usually referred to as α- and β-insertion (Scheme 1), by which well-defined metathesis initiators give access to five- or six-membered ring structures.



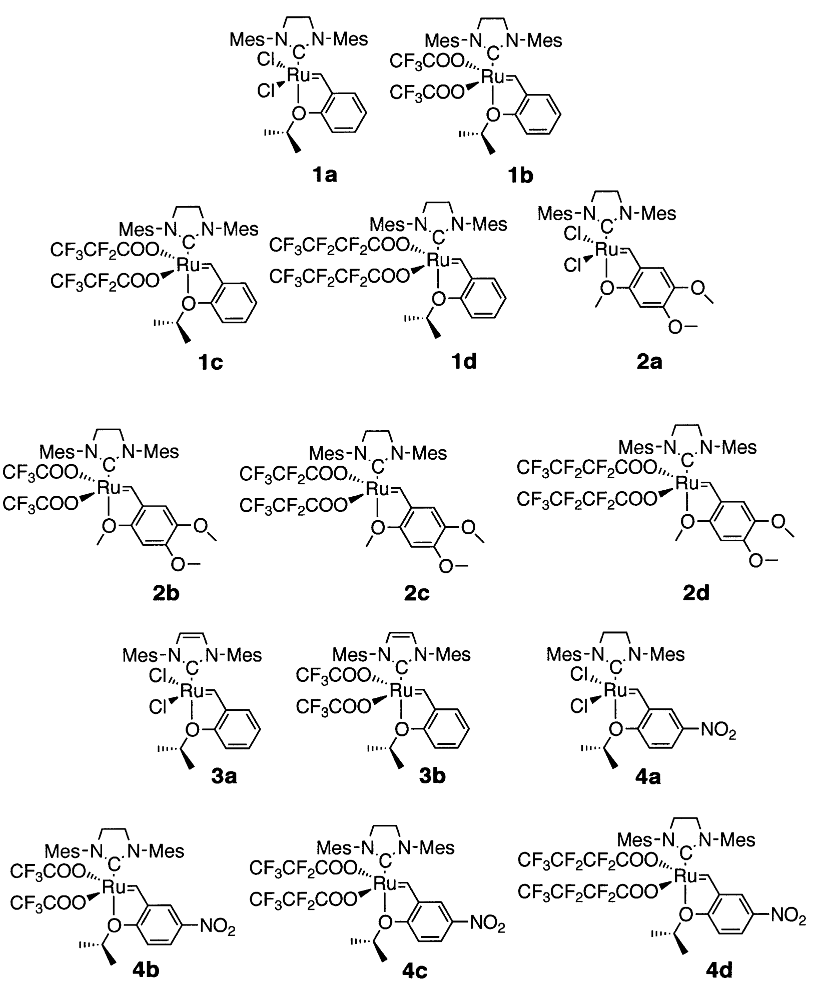
Scheme 1. The two different reaction pathways for cyclopolymerization of 1,6-heptadiynes.

For Schrock-type catalysts, access to six-membered rings can occur by the introduction of bulky, electron-poor ligands such as triphenylacetates, whereas sterically less demanding groups and the addition of a base such as quinuclidine leads to the formation of poly(acetylenes) that are virtually solely based on five-membered rings. In any case, the reactivity of the molybdenum initiator has to be decreased in order to gain regiocontrol. This implies that although Schrock catalysts that contain the $(CF_3)_2MeCO$ group are highly active, they cannot be used for stereoselective cyclopolymerizations. There is strong evidence that cyclopolymerizations catalyzed by ruthenium-based metathesis initiators undergo reaction by the same mechanism as Schrock-type catalysts. In particular, addition of DEDPM to a solution of the former initiator gives rise to new alkylidene signals in the ^1H NMR spectrum.[16] As is the case in cyclopolymerizations catalyzed by a Schrock catalyst in the presence of a base such as quinuclidine, dissociation of the benzylidene ligand *o*-alkoxy group in ruthenium-based initiators must be fast. Only then can a well-behaved system, in which the rate constant of initiation (k_i) is comparable to the rate constant of propagation (k_p) (i.e. $k_p/k_i < 10$), be established. Below are presented the systematic variations that have been carried out in the ligand sphere of a ruthenium-based metathesis initiator.

Substitution of the chlorine ligands by fluorinated carboxylates: Recently, we have shown that exchange of chlorine by electron-withdrawing carboxylic silver salts can be achieved in phosphane-free ruthenium-based metathesis initiators such as the Grubbs–Hoveyda catalyst **1a**.[17] When strongly electron-withdrawing ligands are used, the resultant ruthenium complexes are monomeric rather than dimeric.[18] The use of a phosphane-free initiator was found to be imperative because substitution of the chlorines by CF_3COOAg, for example in $[RuCl_2(IMesH_2)(CHPh)(PCy)_3]$, resulted in the precipitation of $AgCl{\cdot}PCy_3$ (Cy = cyclohexyl) and the formation of the unstable 14-electron species $[Ru(CF_3COO)_2(IMesH_2)(CHPh)]$. Thus, initiators **1b–d** (Scheme 2) were prepared by reaction of $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1a**) with CF_3COOAg, CF_3CF_2COOAg, and $CF_3CF_2CF_2COOAg$, respectively.

While **1a** did not polymerize DEDPM, initiators **1b–d** were found to be active in the cyclopolymerization of this monomer. This indicates that electron-withdrawing carboxylates are important for such polymerizations. Interestingly, the values for k_p/k_i[19] decreased from >1000 (**1b**) to 80 (**1c**) to 40 (**1d**). Unfortunately, none of these initiators allowed the molecular weight of the resultant polymers to be controlled. Only polymers with low polydispersity indices (PDIs) (1.25–1.55) and identical molecular weights (ca. 11000 $g\,mol^{-1}$), irrespective of the stoichiometry of polymerization, were obtained. Nevertheless, these polymers were virtually made up of only five-membered rings; this indicates that initiators **1b–d** undergo selective α-addition (Scheme 1), and that irrespective of the size of the carboxylate groups used, DEDPM can undergo selective α-insertion.

Variations in the NHC ligand: Encouraged by the finding that it was possible to reduce the k_p/k_i ratio in initiators **1b–d** simply by changing the carboxylates, we decided to synthesize an analogue of **1b**, in which the more electron-poor unsaturated IMes moiety was used instead of the electron-rich $IMesH_2$ group. This change was of particular interest since it is well known from the literature that both ligands give rise to quite a distinct reactivity in metathesis reactions,



Scheme 2. Structures of initiators **1a–d**, **2a–d**, **3a**, and **3b**, and **4a–d**.

although in most cases this is not able to be predicted for a particular substrate.[20] Interestingly, the resultant initiator **3b** was found to be completely inactive in the cyclopolymerization of DEDPM; this indicates that the NHC portion of the catalyst has to be electron rich in order to be suitable for cyclopolymerization of DEDPM.

Variations in the benzylidene group: After having determined that initiators of the general formula $[Ru(CF_3(CF_2)_n\text{-}COO)_2(IMesH_2)({=}CH\text{-}2\text{-}RO{-}Ar)]$ are in principle capable of cyclopolymerizing DEDPM, it was our aim to design initiators that would give rise to living polymerizations.[14,21] It is generally accepted that if the nucleophilic character of the 2-alkoxy oxygen atom in $[RuX_2(IMesH_2)({=}CH\text{-}2\text{-}RO{-}Ar)]$ is decreased, a dramatic increase in the catalytic activity is observed for ring-closing metathesis (RCM) and other related reactions.[22,23] The decrease in nucleophilicity reduces the chelating character of the oxygen group, and thus, facilitates formation of the catalytically active 14-electron ruthenium species. Moreover, quite impressive turnover numbers (TONs) in comparison to the parent Grubbs–Herrmann[24–32] or Grubbs–Hoveyda catalyst[17] can be achieved with such systems in RCM and related reactions under mild conditions (0 °C to room temperature). Unfortunately, these systems decompose more easily, particularly at higher temperatures, and must be stored at 4 °C. In view of this information, we attempted to design initiators for cyclopolymerizations that would show increased insertion rates (i.e. $k_p/k_i < 10$). One can easily imagine that the insertion step is the key to reducing the k_p/k_i ratio, as the benzylidene moiety becomes the polymer end group and is transported away from the ruthenium core once a monomer has undergone insertion. Therefore, in order to increase initiation rates while leaving propagation rates unaffected, any reversible coordination of the 2-alkoxy group in the benzylidene moiety must be kept to a minimum, or better still must be suppressed. To improve insertion efficiency, we independently pursued two pathways. We aimed to decrease the nucleophilic character of the alkoxy oxygen in the benzylidene moiety, as well as reduce its steric hindrance. Apparently, such incremental changes are not at all trivial. For example, when the $({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)$ group in $[RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ was replaced by a $({=}CH\text{-}2\text{-}MeO{-}C_6H_4)$ group, the resultant initiator was unstable and completely unsuitable for use in any metathesis reaction.[17] However, it was later shown by Grela et al. that introduction of two additional electron-donating methoxy groups can in fact stabilize this system[33] to yield the stable Grubbs–Hoveyda-type catalyst **2a**. Therefore, initiators **2b–d** were prepared by using the same α-asarone-derived ligand. The k_p/k_i values (2–6) obtained for subsequent DEDPM cyclopolymerizations were in fact found to be lower than those obtained with Schrock catalysts,[9,10] and from the graphs obtained by plotting the number of equivalents of DEDPM (N) versus M_n (Figure 1, 2), they could be considered to have occurred in a class VI[14] living manner.

The degree of livingness was determined by adding DEDPM to a living polymer after 48 h. However, bimodal GPC traces or peak broadening, which are indicative of termination reactions, were not observed with respect to a reference sample. In an additional experiment, 2–3 molar equivalents of DEDPM were added to initiators **2b–d** in $CDCl_3$, but changes in the NMR spectra were not observed even after more than 48 h. Interestingly, significant differences were found in the PDIs of the resultant polymers. In particular, poly(DEDPM) prepared in the presence of **2b** showed PDIs < 1.8, while poly(DEDPM) prepared from **2c** and **2d** showed PDIs up to 2.11. Therefore, in view of the

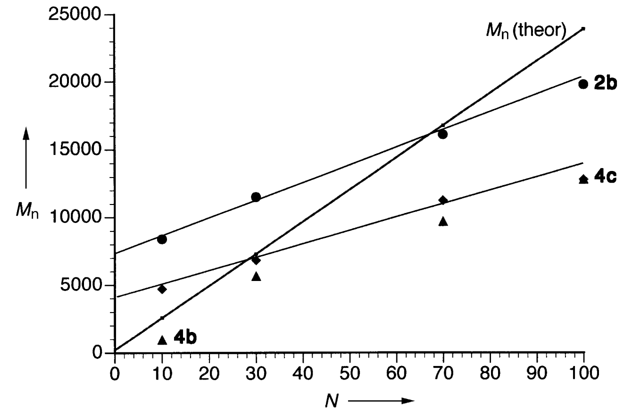


Figure 1. Plot of the number of equivalents of DEDPM (N) versus M_n for **2b** (●), **4b** (▲), and **4c** (◆).

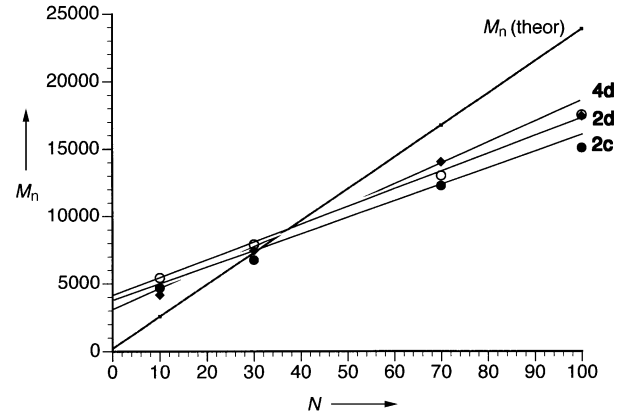


Figure 2. Plot of the number of equivalents of DEDPM (N) versus M_n for **2c** (●), **2d** (○), and **4d** (◆).

stability of the living polymer, the chain-transfer reactions must occur without initiator deterioration. The same high stability of living polymer chains was also found for initiators **1b**–**d**. In terms of polymer structure, >96% of the resultant poly(acetylenes) consisted of five-membered rings. Interestingly, polymerization of chiral 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (ECMCH) with **2b** provided a tactic polymer, >96% of which contained five-memebered rings in an alternating *cis/trans* structure that was first observed with Schrock-type catalysts (Figure 3).[9,10]

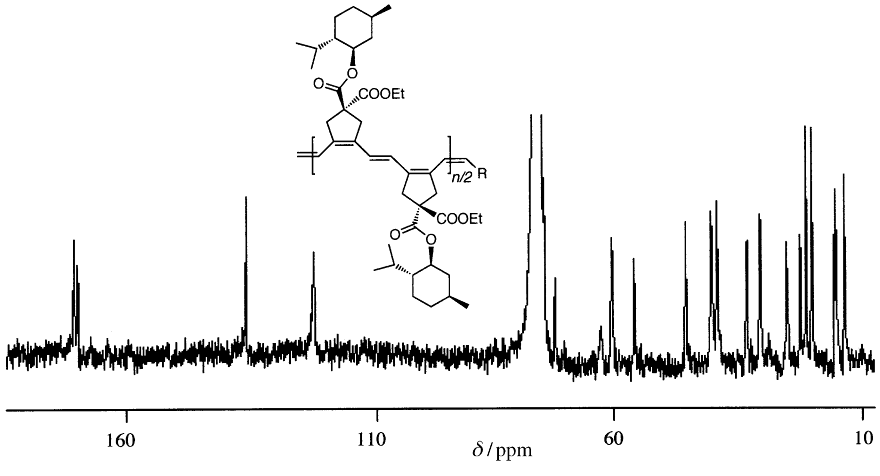


Figure 3. ^{13}C NMR spectrum of chiral, tactic poly(ECMCH), which was prepared with the use of **2b** and consists of >96% five-membered ring structures.

In an extension of these investigations, we were interested to determine whether the steric conditions provided by the methoxy group were the only factors responsible for insertion efficiency and the degree of livingness. Furthermore, we wanted to determine whether a decrease in the nucleophilic character of the 2-alkoxide could generate a truly living system. Grela et al. reported a dramatic increase in reactivity in RCM reactions upon introduction of a nitro group into the 5-position of the (=CH-2-(2-PrO)$-C_6H_4$) moiety.[34] To determine whether this correlation was also true for cyclopolymerizations, initiators **4a**–**d** were prepared. As all other initiators that bear chlorine, **4a** was totally inactive. Nevertheless, substitution of the chlorines by fluorinated carboxylates generated active catalysts. As a matter of fact, initiators **4b**–**d** cyclopolymerized DEDPM in a class VI living manner with k_p/k_i ratio values of 4–7. While the cyclopolymerization of DEDPM with **4b** and **4c** gave rise to PDIs of 2.31 and 1.88, respectively, the PDI calculated for **4d** was only 1.6. From these results it can be proposed that large alkoxides successfully suppress chain-transfer reactions. Once again, all the polymers obtained with these initiators virtually (>96%) contained only cyclopent-1-enylenevinylenes.

It is worth mentioning that, as determined by ^{1}H NMR spectroscopy, initiators **2b**–**d**, **3b**, and **4b**–**d** were obtained in quantitative yield, and could be used without further purification. However, column chromatography could be used to remove any remaining silver chloride impurities (e.g. for elemental analysis), in which case the isolated yields were reduced to about 65%. The chemical shifts of the alkylidene protons for initiators **2a**–**d**, **3a** and **3b**, and **4a**–**d** were in the range of $\delta = 17.14$–17.59 ppm. Contradictory to previous reports,[35] a correlation between the pK_a of the carboxylic acid and either the chemical shift of the alkylidene protons or the tertiary proton in the 2-PrO group could not be found. Since the synthesis of metal-free products is an important issue for electronic and optical applications, all polymers were dissolved in aqua regia and were subjected to inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements. This study found that the final ruthenium content was 3 ppm.

A comparison of all the polymerization data (Table 1), especially for initiators **2b**–**d** and **4b**–**d**, indicated that the best initiators were **2b** and **4d**. First, they showed the best linear

Table 1. Summary of polymerization results for initiators **1a–d**, **2a–d**, **3a** and **3b**, and **4a–d**.

Initiator	n	M_n(theor)	M_n(RI)	PDI(RI)	λ_{max}	E [eV]	N_{eff}	k_p/k_i
1a	10–100	no reaction	–	–	–	–	–	–
1b	10–100	–	13200	1.51	584	2.123	45	> 1000
1c	10–100	–	9900	1.25	584	2.123	45	80
1d	10–100	–	10200	1.25	584	2.123	45	40
2a	10–100	no reaction	–	–	–	–	–	–
2b	10	2600	8400	1.79	576	2.153	39	3
2b	30	7300	11500	1.26	578	2.145	41	–
2b	70	16700	16100	1.46	583	2.127	44	–
2b	100	23800	19700	1.48	584	2.123	45	–
2c	10	2600	4700	1.70	577	2.149	40	6
2c	30	7300	6700	1.84	583	2.127	44	–
2c	70	16700	12200	1.65	584	2.123	45	–
2c	100	23800	15100	1.94	584	2.123	45	–
2d	10	2600	5400	1.61	576	2.153	39	2
2d	30	7300	7900	1.65	581	2.134	43	–
2d	70	16700	13000	1.99	585	2.119	46	–
2d	100	23800	17500	2.11	585	2.119	46	–
3a	10–100	no reaction	–	–	–	–	–	–
3b	10–100	no reaction	–	–	–	–	–	–
4a	10–100	no reaction	–	–	–	–	–	–
4b	10	2600	1000	1.11	570	2.175	35	4
4b	30	7300	5700	1.27	573	2.164	37	–
4b	70	16700	9700	1.76	581	2.134	43	–
4b	100	23800	12000	2.31	582	2.130	44	–
4c	10	2600	4700	1.54	571	2.171	36	7.3
4c	30	7300	6800	1.55	582	2.130	44	–
4c	70	16700	11300	1.32	583	2.127	44	–
4c	100	23800	12800	1.88	586	2.116	47	–
4d	10	2600	4200	1.59	571	2.171	36	4.8
4d	30	7300	7500	1.50	579	2.141	41	–
4d	70	16700	14000	1.29	585	2.119	46	–
4d	100	23800	17400	1.34	586	2.116	47	–

correlations between M_n and N, which is in fact a result of the low k_p/k_i values, and second, both initiators produced polymers that had comparably low PDIs, and whose molecular weights were able to be highly controlled. In particular, **4d** gave the lowest PDI values. Nevertheless, from a synthetic point of view, it needs to be mentioned that initiator **4d** was prepared by a two step process, while **2b** is conveniently accessible from commercially available α-asarone.

Conclusion

We have presented a new class of ruthenium-based metathesis initiators that allow the cyclopolymerization of DEDPM to yield polyenes that are exclusively based on cyclopent-1-enylenevinylenes. From a systematic variation of all the ligands, the following requirements for cyclopolymerization-active systems were found: 1) both the chlorine ligands must be replaced with strongly electron-withdrawing carboxylic salts such as $CF_3(CF_2)_xCOOAg$ ($x=0$–2) the NHC ligand has to be electron rich; and 3) the steric hindrance and electronic nature of the benzylidene ligand has a strong influence on the living character of the DEDPM polymerization. Therefore, increased insertion efficiencies will be obtained the more weakly the oxygen fragment is coordinated to the ruthenium core, as this will lead to lower k_p/k_i values. Two new types of initiators (**2b–d** and **4b–d**) that fulfil these criteria were prepared and these were found to be suitable for use in class VI living polymerizations of DEDPM. All the initiators studied brought about 100 % α-insertion of the monomer, and as a result, the poly(acetylenes) formed virtually contained (>96 %) five-membered ring structures. In addition, the use of larger fluorinated carboxylates further reduced chain-transfer reactions and resulted in polyenes with low PDIs. Current efforts in our laboratories focus on further systematic variations of these new initiators in order to extend their applicability to other 1,6-heptadyines.

Experimental Section

General remarks: NMR data were obtained at 300.13 MHz for proton and 75.47 MHz for carbon in the solvents indicated at 25 °C on a Bruker Spectrospin 300 spectrophotometer, and are listed in parts per million downfield from tetramethylsilane. IR spectra were recorded on a Bruker Vector 22 using ATR technology. Elemental analyses were carried out at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany, while mass spectra were recorded at the Anorganisch-Chemisches Institut, TU München, Germany. A Jobin Yvon JY 38 plus instrument was used for inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements, while an MLS 1200 mega instrument was used for microwave experiments. Gel-permeation chromatography (GPC) using UV/RI detection was carried out in $CHCl_3$ using PLgel 5 μm MIXED-C columns (PLgel 5 μm Guard, 50 × 7.5 mm, PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 5 μm MIXED-C, 600 × 7.5 mm) and a 410 differential refractometer detector (all from Waters). Samples were filtered through 0.2 μm Teflon filters (Millipore) in order to remove any particles. GPC columns were calibrated against polystyrene standards (Polymer Standards Service (PSS), molecular weights 580 to 1.57×10^6 g mol^{-1}). UV/Vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range 300–800 nm. Unless stated otherwise, synthesis of the ligands and initiators was performed under an argon atmosphere according to standard Schlenk techniques, or in an Ar-mediated dry-box (MBraun, Germany). Reactions with silver salts were done in the absence of light. Reagent grade tetrahydrofuran (THF) and methanol (MeOH) were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane and chloroform were distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Ethyl vinyl ether (EVE), $[RuCl_2(IMesH_2)(PCy_3)(=CHPh)]$, ($IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene), CF_3COOAg, CF_3CF_2COOAg, $CF_3CF_2CF_2COOAg$, α-asarone, and 2-iodopropane were purchased from Fluka (Buchs, Switzerland). $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{–}C_6H_4)]$,[17] $[RuCl_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(OMe)_3\text{–}C_6H_2)]$,[33] and $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{–}C_6H_3)]$[34] were prepared according to literature procedure. The synthesis of $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(OMe)_3\text{–}C_6H_2)]$,[15] $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{–}C_6H_4)]$,[15] $[RuCl_2(IMes)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{–}C_6H_4)]$,[16] and $[Ru(CF_3COO)_2(IMes)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{–}C_6H_4)]$[16] is described elsewhere. A ruthenium standard that contained 1000 ppm ruthenium was purchased from Alfa Aesar/Johnson Matthey (Karlsruhe, Germany).

$[\mathrm{Ru(CF_3CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)}]$ (1c): A solution of $\mathrm{CF_3CF_2CO_2Ag}$ (259.4 mg, 0.958 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)}]$ (300 mg, 0.479 mmol) in THF (10 mL). While stirring was continued for 30 min, the colour of the reaction mixture changed from green to lilac and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the filtrate was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in $\mathrm{CH_2Cl_2}$ and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a lilac powder (317 mg, 0.36 mmol, 75 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.59$ (s, 1H; Ru=CHAr), 7.55 (dd, 1H; aromatic CH), 7.34–7.12 (m, 5H; aromatic CH), 6.94 (dd, 1H; aromatic CH), 6.63 (d, 1H; aromatic CH), 4.57 (septet, 1H; $\mathrm{(CH_3)_2C}H\mathrm{OAr}$), 4.15 (s, 4H; $\mathrm{N(CH_2)_2N}$), 2.47 (s, 12H; mesityl *o*-$\mathrm{CH_3}$), 2.30 (s, 6H; mesityl *p*-$\mathrm{CH_3}$), 1.10 ppm (d, 6H; $(\mathrm{C}H_3)_2\mathrm{CHOAr}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 316.3$, 209.2, 159.4, 152.2, 142.2, 138.4, 137.8, 133.4, 129.3, 128.7, 122.9, 121.8, 107.9, 73.4, 50.3, 20.1, 19.0, 16.8 ppm. FTIR (ATR-mode): $\tilde{\nu} = 2978$ (br), 2922 (br), 2366 (w), 2108 (w), 1699 (s), 1586 (w), 1481 (m), 1433 (m), 1375 (m), 1311 (s), 1267 (s), 1210 (vs), 1154 (vs), 1021 (s), 938 (m), 847 (m), 809 (m), 726 cm^{-1} (m); MS (CI): *m/z*: 883.2 $[\mathrm{M{+}H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{37}H_{38}F_{10}N_2O_5Ru}$ (881.76): C 50.40, H 4.34, N 3.18; found: C 50.49, H 4.28, N 3.07.

$[\mathrm{Ru(CF_3CF_2CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)}]$ (1d): A solution of $\mathrm{CF_3CF_2CF_2CO_2Ag}$ (307 mg, 0.958 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)}]$ (300 mg, 0.479 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to lilac and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the filtrate was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in $\mathrm{CH_2Cl_2}$ and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a lilac powder (343 mg, 0.35 mmol, 73 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.51$ (s, 1H; Ru=CHAr), 7.44 (dd, 1H; aromatic CH), 7.26–7.03 (m, 5H; aromatic CH), 6.88 (dd, 1H; aromatic CH), 6.53 (d, 1H; aromatic CH), 4.46 (septet, 1H; $\mathrm{(CH_3)_2C}H\mathrm{OAr}$), 4.05 (s, 4H; $\mathrm{N(CH_2)_2N}$), 2.37 (s, 12H; mesityl *o*-$\mathrm{CH_3}$), 2.20 (s, 6H; mesityl *p*-$\mathrm{CH_3}$), 0.91 ppm (d, 6H; $(\mathrm{C}H_3)_2\mathrm{CHOAr}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 326.3$, 219.0, 168.9, 162.0, 151.9, 148.2, 147.6, 139.0, 137.4, 132.7, 131.6, 119.7, 76.7, 60.1, 34.3, 29.9, 28.8, 26.5 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2978$ (br), 2922 (br), 2366 (w), 2330 (w), 2114 (w), 1698 (s), 1589 (w), 1481 (m), 1446 (m), 1378 (m), 1320 (s), 1265 (s), 1208 (vs), 1153 (s), 1112 (s), 1084 (s), 1033 (m), 959 (m), 928 (s), 848 (m), 802 (m), 719 cm^{-1} (m); MS (CI): *m/z* 983.4 $[\mathrm{M{+}H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{39}H_{38}F_{14}N_2O_5Ru}$ (981.78): C 47.71, H 3.90, N 2.85; found: C 47.51, H 3.90, N 2.71.

$[\mathrm{Ru(CF_3CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2,4,5\text{-}(OMe)_3{-}C_6H_2)}]$ (2c): A solution of $\mathrm{CF_3CF_2CO_2Ag}$ (115 mg, 0.425 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2,4,5\text{-}(OMe)_3{-}C_6H_2)}]$ (140 mg, 0.213 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to yellow-green and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the filtrate was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in ethyl acetate and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a yellow-green powder (131 mg, 0.143 mmol, 67 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.19$ (s, 1H; Ru=CHAr), 7.26–6.74 (m, 4H), 6.42 (s, 1H), 6.26 (s, 1H), 4.02 (s, 4H), 3.90 (s, 3H), 3.75 (s, 3H), 3.49 (s, 3H), 2.32 (s, 6H), 2.22 ppm (s, 12H; mesityl *o*-$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 311.1$, 207.6, 187.1, 162.1, 150.1, 143.5, 137.9, 136.9, 135.9, 134.9, 128.7, 108.0, 104.6, 95.0, 58.2, 55.2, 50.7, 29.8, 20.1, 16.7 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2924$ (br), 2856 (br), 2364 (w), 1955 (w), 1670 (m), 1599 (m), 1483 (m), 1458 (m), 1437 (m), 1409 (m), 1320 (m), 1255 (s), 1205 (vs), 1151 (s), 1024 (m), 915 (w), 852 (w), 813 (m), 751 cm^{-1} (m); elemental analysis calcd (%) for $\mathrm{C_{37}H_{38}F_{10}N_2O_7Ru}$ (913.76): C 48.63, H 4.19, N 3.07; found: C 48.37, H 4.42, N 3.45.

$[\mathrm{Ru(CF_3CF_2CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2,4,5\text{-}(OMe)_3{-}C_6H_2)}]$ (2d): A solution of $\mathrm{CF_3CF_2CF_2CO_2Ag}$ (136 mg, 0.425 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2,4,5\text{-}(OMe)_3{-}C_6H_2)}]$ (140 mg, 0.213 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to yellow-green and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the solvent was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in ethyl acetate and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a yellow-green powder (136 mg, 0.134 mmol, 63 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.14$ (s, 1H; Ru=CHAr), 7.26–6.78 (m, 4H), 6.40 (s, 1H), 6.26 (s, 1H), 4.02 (s, 4H), 3.90 (s, 3H), 3.76 (s, 3H), 3.50 (s, 3H), 2.34 (s, 6H), 2.22 ppm (s, 12H; mesityl *o*-$\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 311.6$, 208.0, 161.8, 143.4, 137.9, 137.0, 136.0, 135.0, 128.3, 108.0, 104.5, 95.0, 58.2, 55.2, 50.7, 28.2, 20.1, 16.7 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2922$ (br), 2361 (w), 1671 (m), 1599 (m), 1458 (m), 1407 (m), 1331 (m), 1266 (s), 1205 (vs), 1116 (s), 1079 (m), 1033 (m), 1014 (m), 964 (m), 928 (m), 852 (m), 811 cm^{-1} (w); elemental analysis calcd (%) for $\mathrm{C_{39}H_{38}F_{14}N_2O_7Ru}$ (1013.78): C 46.21, H 3.78, N 2.76; found: C 45.91, H 4.12, N 2.55.

$[\mathrm{Ru(CF_3CO_2)_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (4b): A solution of $\mathrm{CF_3CO_2Ag}$ (94.8 mg, 0.429 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (144 mg, 0.214 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to brown and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the solvent was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in ethyl acetate and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a brown powder (120 mg, 0.145 mmol, 68 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.28$ (s, 1H; Ru=CHAr), 8.42 (d, 1H), 8.03 (dd, 1H), 7.46 (d, 1H), 7.31 (t, 1H), 7.18 (t, 1H), 7.11 (s, 1H), 6.65 (d, 1H), 4.64 (septet, 1H), 4.09 (s, 4H), 2.40 (s, 6H), 2.20 (s, 12H), 0.90 ppm (d, 6H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 301.2$, 206.2, 176.3, 156.2, 142.3, 137.9, 133.3, 132.3, 128.9, 127.7, 126.6, 124.2, 117.4, 109.8, 50.4, 31.0, 20.8, 19.1, 16.7 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2928$ (br), 2855 (br), 2362 (w), 1959 (br), 1680 (m), 1482 (m), 1437 (m), 1336 (m), 1263 (s), 1189 (vs), 1138 (s), 1021 (m), 954 (m), 844 (m), 797 (m), 723 cm^{-1} (w); MS (CI): *m/z*: 826.3; elemental analysis calcd (%) for $\mathrm{C_{35}H_{37}F_6N_3O_7Ru}$ (826.74): C 50.85, H 4.51, N 5.08; found: C 51.18, H 4.31, N 5.21.

$[\mathrm{Ru(CF_3CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (4c): A solution of $\mathrm{CF_3CF_2CO_2Ag}$ (116 mg, 0.428 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (144 mg, 0.214 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to brown and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the filtrate was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in ethyl acetate and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a brown powder (119 mg, 0.128 mmol, 60 %). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 17.38$ (s, 1H; Ru=CHAr), 8.42 (d, 1H), 7.88 (d, 1H), 7.44 (d, 1H), 7.30 (t, 1H), 7.19 (t, 1H), 7.11 (s, 1H), 6.64 (d, 1H), 4.56 (septet, 1H), 4.09 (s, 4H), 2.40 (s, 6H), 2.19 (s, 12H), 0.91 ppm (d, 6H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 310.3$, 214.8, 168.4, 164.7, 150.9, 150.6, 147.6, 146.4, 144.9, 140.9, 137.5, 136.3, 134.1, 132.9, 126.4, 118.4, 59.0, 46.4, 33.4, 28.7, 21.6, 18.5 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2929$ (br), 2856 (br), 2361 (w), 2124 (br), 1959 (br), 1690 (m), 1600 (w), 1484 (w), 1413 (m), 1328 (m), 1264 (s), 1213 (vs), 1162 (s), 1097 (m), 1025 (vs), 956 (m), 853 (w), 813 (m), 730 cm^{-1} (w); elemental analysis calcd (%) for $\mathrm{C_{37}H_{37}F_{10}N_3O_7Ru}$ (926.76): C 47.95, H 4.02, N 4.53; found: C 48.23, H 4.38, N 4.74.

$[\mathrm{Ru(CF_3CF_2CF_2CO_2)_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (4d): A solution of $\mathrm{CF_3CF_2CF_2CO_2Ag}$ (105 mg, 0.327 mmol, 2 equiv) in THF (2 mL) was slowly added to a stirred solution of $[\mathrm{RuCl_2(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2{-}C_6H_3)}]$ (110 mg, 0.163 mmol) in THF (10 mL). While stirring was continued for 30 min, the color of the reaction mixture changed from green to brown and a precipitate formed. The precipitate was centrifuged, the solution was filtered through a 0.2 µm Teflon filter, and the filtrate was evaporated to dryness. The following manipulations were then done under air. The solid was redissolved in ethyl acetate and passed over a short pad of silica, the solvent was evaporated, and the resultant solid was dried under vacuum to give a brown powder (104 mg, 0.101 mmol, 62 %). ^{1}H NMR ($CDCl_3$): $\delta = 17.40$ (s, 1 H; Ru=CHAr), 8.42 (d, 1 H), 7.88 (d, 1 H), 7.44 (d, 1 H), 7.29 (t, 1 H), 7.19 (t, 1 H), 7.12 (s, 1 H), 6.64 (d, 1 H), 4.55 (septet, 1 H), 4.09 (s, 4 H), 2.41 (s, 6 H), 2.19 (s, 12 H), 0.90 ppm (d, 6 H); ^{13}C NMR ($CDCl_3$): $\delta = 301.7$, 206.2, 156.2, 142.3, 142.0, 139.0, 137.9, 136.3, 134.5, 132.3, 128.9, 127.7, 127.1, 125.5, 124.2, 117.8, 109.8, 50.4, 31.0, 25.2, 24.8, 20.8, 19.0, 16.8 ppm; FTIR (ATR-mode): $\tilde{\nu} = 2929$ (br), 2857 (br), 2358 (w), 2121 (br), 1959 (br), 1681 (br), 1483 (w), 1404 (m), 1334 (m), 1262 (s), 1212 (vs), 1081 (m), 1023 (vs), 963 (m), 931 (m), 853 (w), 804 (m), 752 cm^{-1} (w); elemental analysis calcd (%) for $C_{39}H_{37}F_{14}N_3O_7Ru$ (1026.77): C 45.62, H 3.63, N 4.09; found: C 45.99, H 4.01, N 4.39.

Typical polymerization procedure: Polymerizations were performed under argon. A solution of $[Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO){-}C_6H_4)]$ (**1b**) (1 equiv, 3.13 mg, 0.004 mmol) in CH_2Cl_2 (0.3 mL) was added to a solution of DEDPM (74 equiv., 3.0 mL, 70 mg, 0.30 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 4 h, then EVE (0.5 mL) was added and the mixture was stirred for a further 30 min. The solvent was removed under vacuum and then MeOH (10 mL) was added to the residue. After sonification, stirring was continued for another 30 min. The product was then centrifuged and dried under vacuum to give a lilac-gold powder (64 mg, 91 %).

Livingness: All manipulations were carried out under Ar-mediated drybox conditions. A solution of DEDPM (70 mg, 0.296 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of **2b** (48.2 mg for degree of polymerization (DP) = 5, 24.1 mg for DP = 10, 8.0 mg for DP = 30, 4.8 mg for DP = 50, 3.4 mg for DP = 70, 2.4 mg for DP = 100) in CH_2Cl_2 (3 mL), and the mixture was stirred for 4 h. EVE (0.5 mL) was then added and stirring was continued for a further 30 min. The solvent was removed under vacuum, MeOH (10 mL) was added, and stirring was continued for another 30 min. The product was then centrifuged and dried under vacuum to yield a lilac-gold powder (54.6–64.6 mg, 78–92 %).

To determine the class of livingness, a sample with a DP of 50 was prepared as described above. A small aliquot was terminated with EVE and the sample was then precipitated from MeOH and subjected to GPC. The remainder of the reaction mixture was stirred for 48 h, at which time DEDPM was added to give a theoretical degree of polymerization of 100. After termination with EVE and precipitation from MeOH, the sample was subjected to GPC. Bimodal GPC traces or band broadening, which are indicative of termination reactions, were not observed. $M_n(\text{theor}) = 23\,835$, $M_w = 43\,700$, $M_n = 25\,400$, PDI = 1.72.

ICP-OES measurements: Aqua regia (3.0 mL) was added to a sample of poly(DEDPM) (10.0 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 ICP-OES measurements for ruthenium were taken ($\lambda = 240.272$ nm, ion line; $\lambda = 240.287$ and 240.257 nm, background). A content of 3 ppm ruthenium was determined.

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