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Peculiarities of the Ru^{IV}-Alkylidene Triggered Cyclopolymerization of *N*-(bis(alkyloxy)aryl)-Containing 1,6-Heptadiynes

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Summary: Some peculiarities in the cyclopolymerization of 1,6-heptadiynes containing an amine-nitrogen at the 4-position are presented and discussed within the context of cyclopolymerization of N-free 1,6-heptadiynes.

Keywords: conjugated polymers; cyclopolymerization; metathesis

Introduction

The cyclopolymerization of 1,6-heptadiynes represents a powerful alternative to 1-alkyne polymerization.[1–5] Heptadiynes with substituents at the 4-position generally possess good solubility in common organic solvents (e.g. C_6H_6, toluene, CH_2Cl_2, $CHCl_3$), good long-term stability towards oxidation and high effective conjugation lengths.[1,3,6,7] During the last five years, we and others[7–13] were interested in the controlled, stereo- and regioselective, living cyclopolymerization of 1,6-heptadiynes as well as in structure-property relationships of these materials.[14–25] In this context, one aim is to produce soluble polymers with highly regular repeat units. This allows on the one hand for retrieving fundamental information on the insertion mechanism and on the catalyst's requirements. On the other hand it allows for the correlation of materials properties such as absorption spectra, conductivity and non-linear optical behavior with the polymer structure. So far, the living cyclopolymerization of 1,6-heptadiynes may be accomplished by a series of Schrock and modified Grubbs type initiators. In addition, the careful choice of a catalyst allows for establishing a stereo- and regioselective insertion mode, offering access to polymers based on one single repeat unit. In this context, Schrock-type initiators[14–16,18,19] such as $Mo(N\text{-}2,6\text{-}(2\text{-}Pr)_2\text{–}C_6H_3)(OC(CH_3)_3)_2\text{-}(CHCMe_2Ph).quinuclidine$, $Mo(N\text{-}2,6\text{-}(CH_3)_2\text{–}C_6H_3)(OC(CH_3)_3)_2(CHCMe_2Ph).quinuclidine$ as well as modified Grubbs type initiators[20–22] such as $Ru(CF_3COO)(IMesH_2)(CH\text{-}2,4,5\text{-}(OCH_3)_3C_6H_2)$ (**2**) or $Ru(CF_3COO)(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{–}C_6H_3)$ (**3**) have to be mentioned. All these initiators allow for the formation of poly(1,6-heptadiynes) with repeat units based on 5-membered rings, i.e. cyclopent-1-enylene-1,2-vinylenes. In contrast, the polymerization of N-(bis(alkyloxy)aryl)-containing 1,6-heptadiynes, e.g. 3,4-bis(octyloxy)-N,N-dipropargylaniline (**1**) by various Ru-based catalysts, e.g. by **2**, **3** and $Ru(CF_3COO)_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=$CH\text{-}2\text{-}(2\text{-}PrO\text{-}5\text{-}NO_2\text{–}C_6H_3)$ (**4**) ($IMesH_2 = $ 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) is characterized by some peculiarities that shall be presented in the following.

Experimental Part

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further

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purification. Tetrahydrofurane (THF), pentane, diethyl ether, toluene and methylene chloride were dried by an MBraun solvent purification system (SPS). NMR data were obtained on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by GPC at 40 °C on an LC-10AD liquid chromatograph equipped with an SIL-10 ADVP auto injector, a CTO-10AC column oven, an SCL-10AVP system controller and an RID-10A refractive index detector (all Shimadzu). A precolumn and three consecutive Plgel 5 μm MiniMIX-c columns (7.5 x 300 mm, Polymer Laboratories) were operated in $CHCl_3$ applying a flow of 0.3 ml/min. The initiators $Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2,4,5\text{-}(OCH_3)_3–C_6H_2)$,[21] $Ru(CF_3COO)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}5\text{-}NO_2–C_6H_3)$,[21] $Ru(CF_3COO)_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}5\text{-}NO_2–C_6H_3)$,[23] ($IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene) were prepared according to the literature. ^{13}C-NMR spectra of polymers were recorded in 0.5 M solution of $Cr(acac)_3$ in $CDCl_3$.

Polymerization Reactions

All polymerizations were carried out in oven-dried glass-ware with dry solvents under a nitrogen atmosphere or inside a glove box. In two separate vials the exact amount of monomer and catalyst, respectively, were weight in and dissolved in dichloromethane. The monomer-solution was added to the catalyst-solution under vigorous stirring. After that, the polymerization mixture was stirred for 12 hours at the indicated temperature and then terminated by adding an excess of ethyl vinyl ether. The solvent was evaporated almost to dryness and the polymer was precipitated by adding an excess of pentane. The precipitate was collected and dried *in vacuo* over night.

Results and Discussion

The cyclopolymerization of 3,4-bis(octyloxy)-N,N-dipropargylaniline (**1**) was accomplished by the action of various Ru-based catalysts,

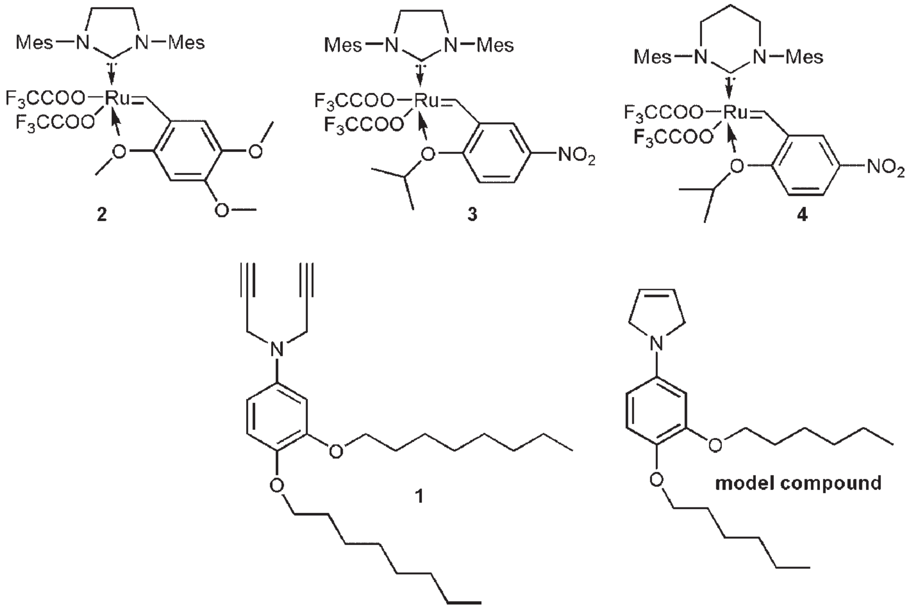


Figure 1.
Structure of monomer **1** the Ru-based catalysts **2–4**.

Table 1.
Summary of polymerization results for monomer **1** using initiators **2**–**4**.

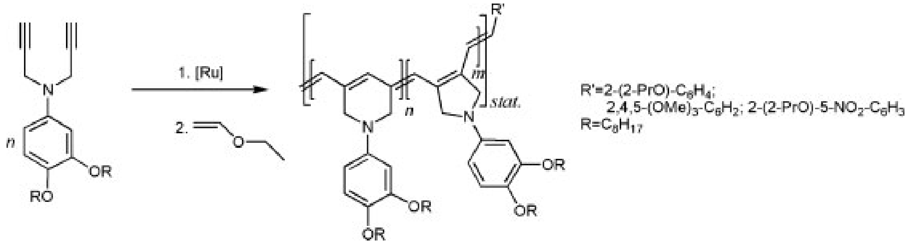
monomer/initiator	T	N	M_n (theor.)[a]	M_n (found)	M_w/M_n	yield (isol.)
	(°C)		(g/mol)	(g/mol)		(%)
1/2	20	100	42790	5200	1.42	16
1/2	40	100	42790	4700	1.32	29
1/2	50	100	42790	4100	1.59	7
1/2	60	100	42790	25800	1.37	9
1/3	20	100	42803	5100	1.42	15
1/3	40	100	42803	5300	1.25	10
1/3	50	100	42803	3900	1.54	10
1/4	20	100	42803	12400	2.13	33
1/4	40	100	42803	–	–	0
1/4	50	100	42803	–	–	0

[a] Including end groups. N = number of monomer equivalents added to the initiator.

i.e. $Ru(CF_3COO)_2(IMesH_2)(=CH$-2,4,5-$(OCH_3)_3-C_6H_2)$ (**2**), $Ru(CF_3COO)_2$-$(IMesH_2)(=CH$-2-(2-PrO-5-NO_2–$C_6H_3)$ (**3**), $Ru(CF_3COO)_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (=CH-2-(2-PrO-5-NO_2–C_6H_3) (**4**) ($IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene, Figure 1)). Reactions were carried out at different temperatures and were terminated with ethyl vinyl ether. Polymerization results are summarized in Table 1. As can be deduced there from, polydispersities were fairly low, however, polymerization yields were modest ($\leq$33%). In no case, the theoretical degree of polymerization (100) was achieved.

However, the most striking and most important feature of poly-**1** is that it consists of a mixture of 5- and 6-membered ring-based repeat units, i.e. (3,4-(1*H*-2,5-dihydropyrrylidene)vinylene)s and (3,5-(1,2,5,6-tetrahydropyridinylidene) methylidene)s (Scheme 1). Figure 2 shows a ^{13}C-NMR of poly-**1** prepared by the action of **1**. NMR spectra were recorded in the presence of a relaxation reagent, i.e. $Cr^{III}(acac)_3$ in order to ensure correct integration. Peak assignment was accomplished with the aid of the model compound, i.e. N-(3,4-bis(hexyloxy)phenyl)-1*H*-2,5-dihydropyrrol (Figure 1), which is mimicking the repeat unit of cyclopolymers based on 5-membered ring structures. Particularly the quaternary aryl-carbons in *m*-position to the amine moiety were found to allow for distinguishing between 5- and 6-membered ring structures.

A typical ratio of 5- over 6-membered rings found for poly-**1** made by the action of **4** was 70:30. This finding, i.e. the fact that poly(ene)s derived from N-(bis(alkyloxy)-aryl)-containing 1,6-heptadiynes contain a *substantial percentage, i.e. 30% of 6-membered rings*, i.e. 3,5-(1,2,5,6-tetrahydropyridinylidene) methylidene)s, is highly unusual. As a matter of fact, *all* poly(ene)s prepared from N-free 1,6-heptadiynes so far were *solely* based on 5-membered ring structures, i.e.



Scheme 1.
Cyclopolymerization of **1** and structure of the polymers obtained.

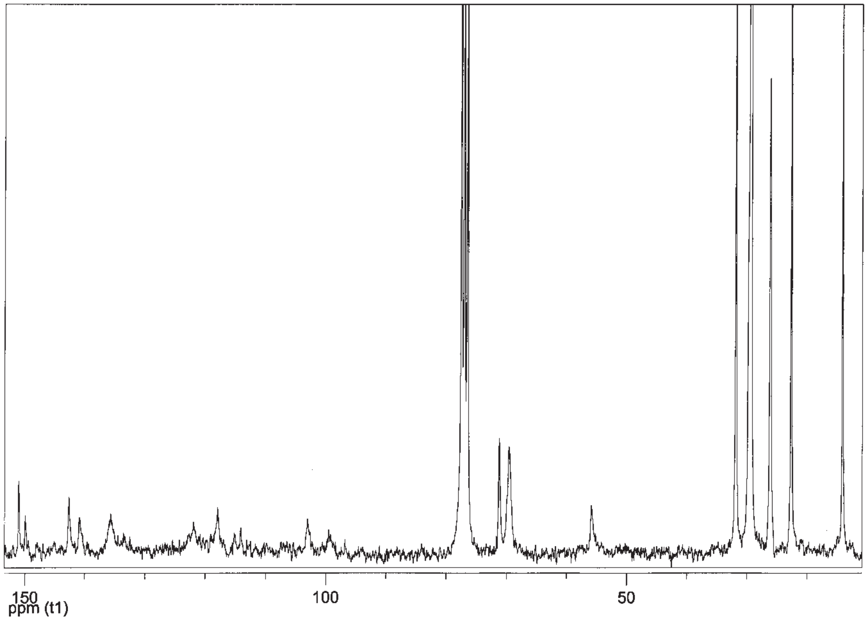
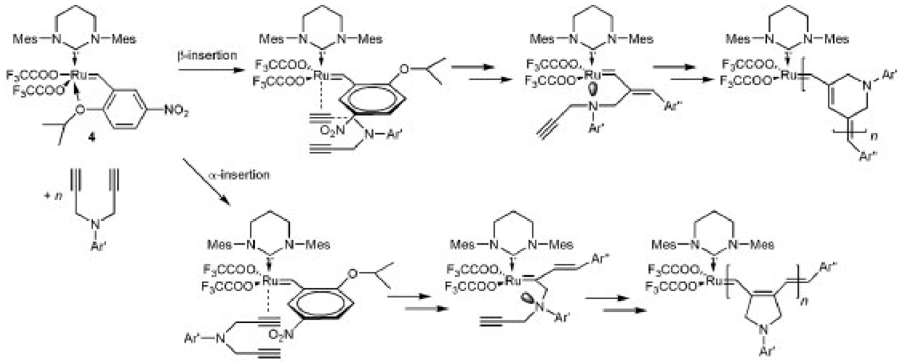


Figure 2.
^{13}C-NMR of poly-**1** prepared by the action of **4**. Peak assignment: 150.0 ($C_{\text{m-ar-O-5-membered ring structure}}$), 149.9 ($C_{\text{m-ar-O-6-membered ring structure}}$), 142.6 ($C_{\text{p-ar}}$), 140.9 ($R_2\underline{C}{=}CHR_{\text{6-membered ring}}$), 135.7, 121.9, 117.9 ($C_{ar}$), 115.2 ($C_{ar}$), 114.1 ($C_{ar}$), 103.0, 99.5, 71.2 ($OCH_2$), 69.6 ($CH_2{-}N_{\text{6-membered ring}}$ and $O\underline{C}H_2$), 55.9 ($\underline{C}H_2{-}N_{\text{5-membered ring}}$), 31.9 ($CH_2$), 29.4 ($CH_2$), 26.2 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$).

(3,4-(1*H*-2,5-dihydropyrrylidene)vinylene)s. Until now, there exists only one report by our group on *one* single exception, where a content of roughly 5% of six-membered ring structures obtained in a Ru^{IV}-alkylidene triggered cyclopolymerization has been observed. In this particular case, N,N-dipropargyl diethylmalonate and the same initiator, i.e. $Ru(CF_3COO)_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (=CH-2-(2-PrO-5-NO_2–C_6H_3) (**4**), were used.[23] Both the finding that a comparably large percentage of mixed repeat units has been observed and the low polymerization yields are strongly indicative for the direct involvement of the nitrogen in course of



Scheme 2.
Reaction pathway for the formation of 5- and 6-membered rings in the Ru^{IV}-alkylidene-mediated cyclopolymerization of N-(bis(alkyloxy)aryl)-containing 1,6-heptadiynes.

the catalytic cycle, which is shown in Scheme 2.

As can be seen, the reaction pathway characterized by a β-insertion, which ultimately leads to 6-membered ring structures, entails an intermediate, where the nitrogen is in the δ-position to the Ru-center, thus allowing for the formation of a stable N → Ru chelate. In addition, this N → Ru chelation further aggravates the subsequent reaction of the second alkyne moiety, thus slowing down propagation rates. In contrast, this is by far less favorable in the case of α-insertion, where the N is in γ-position to the Ru. This would only allow for an N → Ru chelate within a four-membered ring structure and may well be expected less favorable.

Conclusion

The cyclopolymerization of N-(bis(alkyloxy) aryl)-containing 1,6-heptadiynes can be accomplished with various bis(trifluoroacetate)-modified Ru^{IV}- alkylidenes. An unprecedented high contents of repeat units based on 6-membered rings, i.e. 3,5-(1,2,5,6-tetrahydropyridinylidene)methylidene)s, has been found. A simple explanation for the experimental finding has been proposed. Theoretical considerations, which back up the proposed involvement of the N-lone pair within the catalytic cycle, are under way.

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