Macromolecules **1999,** *32,* 21−26

Influence of Initiator and Monomer Structure on the Polymerization of Acetylene Monomers Using Schrock-Type Molybdenum Carbenes

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Received June 18, 1998; Revised Manuscript Received October 22, 1998

ABSTRACT: The polymerization of acetylene monomers using homogeneous Schrock-type initiators of the general formula Mo(CHR′)(NAr)(OR)$_2$ with different substitution patterns was investigated. The influence of the ligands at the molybdenum center and of donor functions at the β-position with respect to the monomer's triple bond on the polymerization was studied by means of NMR spectroscopy and size exclusion chromatography. The results clearly indicate that kinetics and mechanism of the metathesis reaction strongly depend on the structures of monomer and initiator. The use of partially fluorinated alkoxy ligands instead of aliphatic alkoxides leads to a change of the regiochemistry of the insertion. Ether functions in the monomer tend to slow the reaction, giving rise to polymers with a narrow molecular weight distribution probably due to coordination of the oxygen atom to the metal center.

1. Introduction

Olefin metathesis and the mechanistically related ring-opening metathesis polymerization of cyclic olefins have gained enormous interest in both industrial and academic fields.[1−8] After the first publications on norbornene polymerization catalyzed by titanium compounds, Chauvin postulated a model for the reaction mechanism that remained valid.[9−12] The metathesis polymerization of acetylenes proceeds in an analogous way via a metallacyclobutene intermediate,[13] leading to conjugated polymers. These polymers are of interest for their interesting electrical, optical, and optoelectronic properties.[14−19] Polymerizations of acetylene monomers described in the literature are mostly initiated by classical metathesis catalysts such as molybdenum or tungsten halides and an organometallic cocatalyst such as tetrabutyltin.[20] Though sometimes effective, these catalyst systems are rather ill-defined, thus making an exact study of the metathesis reaction difficult.

In this contribution we present our research on the oligomerization of 1-octyne and 4-oxa-1-octyne using the homogeneous initiator Mo(CHR′)(NAr)(OR)$_2$. The objective of our research was to gain a deeper understanding of the parameters controlling the insertion of the acetylene monomer into the metal−carbon double bond and the dependence of both reaction rates and reaction mechanism upon the ligands at the catalytic site and the structure of the monomer. Special attention will be paid to the regiochemistry of the insertion and the molecular weights of the resulting polymers.

2. Experimental Part

Substances. Propargyl alcohol (Aldrich, 99%) was distilled prior to use. 1-Bromobutane-d_9 (Deutero GmbH) and 1-octyne (Lancaster, 98+%) were used without further purification. Dimethylformamide (Fluka, 99%) was dried by distillation from CaH$_2$. Benzene-d_6 was distilled under nitrogen.

5,5,6,6,7,7,8,8,8-Nonadeuterio-4-oxa-1-octyne was prepared as follows: A 2 g (13.7 mmol) sample of 1-bromobutane-d_9 in 4 mL of dimethylformamide was stirred with 1.54 g (27.4 mmol) of propargyl alcohol and 1.2 g (21.4 mmol) of KOH at room temperature. Effective stirring is essential under these reaction conditions. The mixture soon became turbid due to precipitation of KBr. After 2 h, 10 mL of aqueous HCl (5 wt %) was added. The mixture was extracted with 20 mL of pentane. The organic layer was washed with another 10 mL of aqueous HCl. The phases were separated, and the organic phase was distilled. The product should be stored in a refrigerator. Yield: 1013 mg of $C_7H_3D_9O$ (121.08 g/mol, 8.37 mmol, 61.1%). Boiling point: 132 °C. ^{1}H NMR: $\delta = 2.41$ (t, $J = 2.3$ Hz, 1H, CH), 4.13 (d, $J = 2.3$ Hz, 2H, CH$_2$). ^{13}C NMR: $\delta = 14.06$ (CD$_3$), 22.35 (CD$_2$), 30.55 (CD$_2$), 69.09 (CD$_2$O), 57.97 (CDCl$_3$)(CH$_2$CCH), 73.97 (CH$_2$$C$CH), 80.15 (CH$_2CC$H). Due to C−D coupling, the signals of the deuterium-substituted carbon atoms are split and of low intensity. FT-IR: 3303 (s, ν(CH)$_{\text{alkyne}}$), 2945 (w, ν(CH)$_{\text{alkane}}$), 2891 (w, ν(CH)$_{\text{alkane}}$), 2847 (m, ν(CH)$_{\text{alkane}}$), 2217 (s, ν(cd$_{\text{alkane}}$)), 2111 (m, ν(CH)$_{\text{alkyne}}$), 2075 (m, ν(CD)$_{\text{alkane}}$), 1443 (m, ν(CH)$_{\text{alkane}}$), 1361 (m, ν(CC)$_{\text{alkane}}$), 1243 (m, ν(CO)), 1174 (m, ν(CO)), 1115 (s, ν(CO)), 1086 (s, ν(CD)$_{\text{alkane}}$), 1034 (s, (CD)$_{\text{alkane}}$), 918 (m, (CC)$_{\text{alkane}}$), 664 (s, ν(CC)$_{\text{alkane}}$). GC: $t_r = 2.14$ min. MS: $m/z = 16$, 18, 30, 34, 39, 43, 55, 57, 64, 71, 87, 103, 119, 120, **121**.

Polymerizations. Polymerization was carried out in a glovebox filled with nitrogen at an oxygen content of <5 ppm and a water content of <1 ppm. The initiators Mo(CHR′)(NAr)(OR)$_2$ were prepared according to a literature procedure[21] and stored at −24 °C in the glovebox. All monomers were dried by distillation from CaH$_2$ prior to the transfer into the glovebox. For the polymerizations, 15 mg of the initiator was reacted with a 5-fold excess of the monomer in 0.8 mL of C$_6$D$_6$ at room temperature. Immediately after mixing the reactants, the solution was transferred into an NMR tube, and the tube was taken out of the glovebox for the NMR measurements. The spectra were recorded about 15 min after the reaction was started. After the NMR measurement, the reaction was quenched by the addition of a large excess of benzaldehyde. The mixture was allowed to react overnight at room temperature to ensure complete termination. The next day, molecular weights of the sample were determined directly from the solution without isolating or precipitating the polymer before.

Measurements. FT-IR spectra were recorded for films using a BRUKER IFS 55 spectrometer using the film method. IR data are given as ν/c in cm^{-1}. NMR spectra of oxaoctyne were recorded using a BRUKER ARX 300 spectrometer in CDCl$_3$ as solvent at room temperature. For the in-situ NMR measurements, a BRUKER WH-52 was used. Chemical shifts

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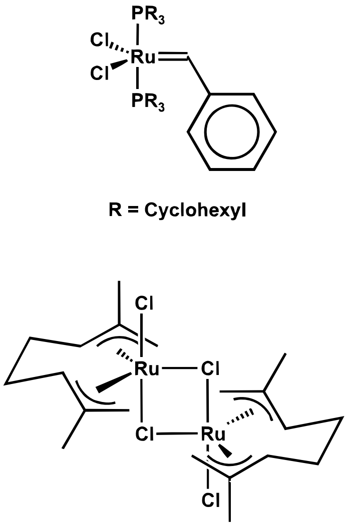
10.1021/ma980964z CCC: $18.00

are given in ppm relative to TMS. GC/MS spectra were measured with a Hewlett-Packard HP 5890 series II equipped with a mass selective detector HP 5971 A (EI-MS, 70 eV) using the temperature program AS100OK. As columns, fused silica capillary columns HP-1 (length 50 m, diameter 0.2 mm, film thickness 0.33 μm) were used. MS data are given in atomic mass units. Molecular weights were determined by size exclusion chromatography (SEC) using chloroform as solvent, a Merck-Hitachi L 6200 intelligent pump, SDV-gel separation columns of Polymer Standard Service (10^6, 10^4, and 10^2 Å, 5 μm particle size), and detection at 254 nm with a UV spectrometer LC-55 S (Perkin-Elmer). Polystyrene standards ($M_n = 685-1.8 \times 10^6$ g/mol, PDI < 1.1, Polymer Standard Service) were used for calibration.

3. Results and Discussion

In recent years research in the field of olefin and acetylene metathesis has focused on metathesis catalysts based upon tungsten,[4,20−22] molybdenum,[23−27] and ruthenium.[28−33] Therefore, we first investigated the polymerization of alkynes with ruthenium carbenes using the carbene systems described by Grubbs[31] and Herrmann[32] (formula 1) under reaction conditions that had proved to be suitable for the metathesis of cyclic olefins.



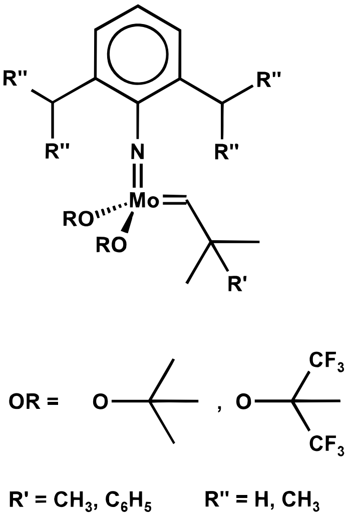
(1)

All attempts to initiate the polymerization of various acetylenes with these catalyst systems failed so far. This result is in good agreement with the fact that, to our knowledge, the metathesis polymerization of triple bonds with ruthenium systems has never been described. Ruthenium carbene systemes are generally considered less reactive than their W and Mo analogues.[1] However, the reason for this difference is not clear. This might be due to steric or electronic aspects. Thus, σ-coordination of the terminal alkyne to the metal center leading to a ruthenium acetylide might occur. This arrangement is not possible with cyclic olefins which do not have acidic hydrogen atoms and can exclusively coordinate to the metal via their π-electron system. Alternatively, the differing steric demands for coordination of these systems to the metal center of a catalytically active complex might influence the outcome. Especially for the Grubbs-type ruthenium complexes surrounded by bulky phosphine ligands, it appears plausible that coordination of the linear alkyne moiety to the ruthenium atom is sterically much more demanding than the coordination of an olefin.

Table 1. Ligands and Codes for the Molybdenum Initiators Mo(CHR′)(NAr)(OR)$_2$ (Scheme 2)

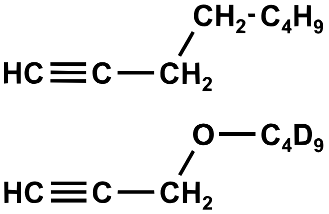
code	tBu	HF	DMtBu	DMHF
R	$OC(CH_3)_3$	$OC(CH_3)(CF_3)_2$	$OC(CH_3)_3$	$OC(CH_3)(CF_3)_2$
R′	CH_3	CH_3	C_6H_5	C_6H_5
R″	CH_3	CH_3	H	H

In contrast to the ruthenium systems, polymerization of acetylenes with catalysts based upon tungsten and molybdenum has been known for years.[34−49] To get access to a detailed study on the reaction mechanism, we decided to use well-defined Schrock-type initiators of the general formula Mo(CHR′)(NAr)(OR)$_2$ (formula 2). These types of carbenes have already been shown to initiate the polymerization of acetylene monomers.[44−49] Ligands and abbreviations of the respective derivatives are listed in Table 1.



(2)

In our experiments, a 5-fold excess of the monomers 1-octyne and 4-oxa-1-octyne-d_9 (formula 3) was reacted



$$HC{\equiv}C{-}CH_2{-}CH_2{-}C_4H_9 \qquad HC{\equiv}C{-}CH_2{-}O{-}C_4D_9 \qquad (3)$$

with 15 mg of catalyst in 0.8 mL of C_6D_6 in an NMR tube. For the oxa-functionalized monomer, we decided to use a partially deuterated monomer to reduce the number of hydrogen atoms in order to enhance the resolution of the NMR spectra. In the following, the monomers will be referred to as octyne and oxaoctyne only. After recording the proton spectrum and terminating the reaction by the addition of benzaldehyde, we determined the molecular weights of the oligomers formed by means of size exclusion chromatography. In all cases except one, conversions of the monomer were 100% after 15 min. Only in one case (see below) ca. 25 min was necessary for complete conversion.

The System tBu Catalyst/Oxaoctyne. Figure 1 shows the in-situ NMR spectrum of the reaction of the tBu catalyst with a 5-fold excess of oxaoctyne.

This spectrum shows several significant differences from the spectrum of the pure catalyst.[21] First, one recognizes the signals of poly(oxaoctyne). The broad

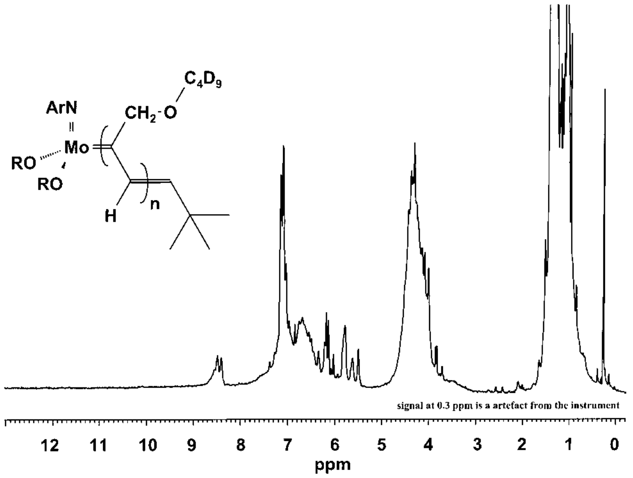


Figure 1. In-situ NMR spectrum of the reaction of tBu catalyst (OR = $OC(CH_3)_3$) and 4-oxa-1-octyne-d_9 in benzene-d_6.

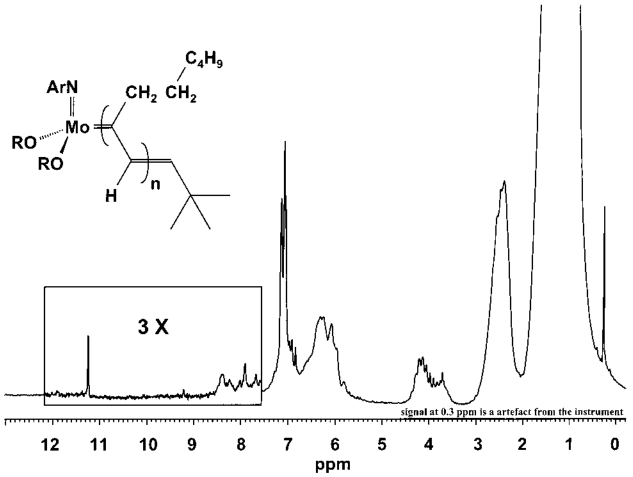


Figure 2. In-situ NMR spectrum of the reaction of tBu catalyst (OR = $OC(CH_3)_3$) and 1-octyne in benzene-d_6.

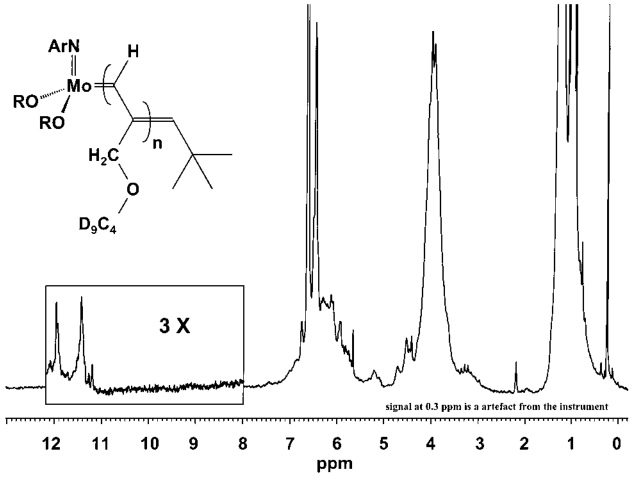


Figure 3. In-situ NMR spectrum of the reaction of HF catalyst (OR = $OC(CH_3)(CF_3)_2$) and 4-oxa-1-octyne-d_9 in benzene-d_6.

signals at about 1 ppm arise from the aliphatic methyl and methylene groups, whereas those at about 4.3 ppm can be assigned to the methylene groups next to the ether bridge. The peaks between 5.5 and 7 ppm can be assigned to the hydrogen atoms connected directly to the polymer main chain. The multitude of the signals can be due to several reasons: (i) Cis–trans isomers in the conjugated polymer backbone give rise to a large number of magnetically inequivalent protons that can undergo long-range coupling. This leads to an relatively complex coupling pattern. (ii) In the relatively short chains (monomer/catalyst = 5:1) the varying distance of the respective monomer moieties to the metal center causes differing chemical shifts. Nevertheless, the large number of signals is indicative of a low degree of stereoregularity in the polyinsertion product.

The monomer's proton resonance can still be detected in the spectrum 15 min after starting the reaction. Another 10 min later these peaks have disappeared, as shown in Figure 2. So, at this stage, conversion is complete. Thus, it can be shown that these β-functionalized alkyne ethers can be polymerized with Schrock-type molybdenum carbene initiators. The ether function in the β-position to the triple bond does not prevent polymerization. This is an essential aspect as the introduction of a triple bond in the course of monomer synthesis via the propargyl alcohol route[45] is much easier than the use of acetylide anions.

Another crucial aspect of the spectrum shown in Figure 2 is the disappearance of the catalyst's original carbene signal at 11.3 ppm. Instead of that, two signals at about 8.5 ppm are observed which can be assigned to hydrogen atoms in the β-position to molybdenum.[44,46–48] From that observation, three very important conclusions can be drawn: (i) Initiation of the polymerization is complete; i.e., chain propagation is not faster or maybe even slower than the initiation step. (ii) In the course of the insertion step, the substituent at the monomer's triple bond is arranged in the α-position to molybdenum. The hydrogen atom at the triple bond becomes a H atom in the β-position to the metal. This mode of insertion is commonly referred to as α-insertion. (iii) The presence of two signals at about 8.5 ppm might be indicative of different configurations at the metal–carbon double bond or at the next following C–C double bond.

The System tBu Catalyst/Octyne. Figure 2 shows the in-situ NMR spectrum of the reaction of the tBu catalyst with a 5-fold excess of octyne.

As in the case of oxaoctyne, this spectrum shows the signals of the polymer. Due to the absence of the electron-withdrawing ether group, the peaks of the methylene group in the α-position to the main chain are shifted about 2 ppm upfield and show a resonance at about 2.5 ppm relative to TMS. Considering the signals of the hydrogen atoms connected to the main chain, it becomes obvious that in the case of octyne instead of oxaoctyne there are considerably fewer peaks. From this, it might be concluded that the stereochemistry of the insertion step is essentially more regular with respect to cis–trans isomers in the backbone.

An important difference of the spectra recorded using octyne and oxaoctyne can be seen in the carbene regions at 11 and 8.5 ppm, respectively. Figure 3 still shows the signals of the original carbene. The distinct signals of the new β-carbene with oxaoctyne (Figure 2) possess a markedly decreased intensity when octyne is used. Furthermore, they show a more complicated splitting pattern. The signal at about 4 ppm can be interpreted as a result of two superimposing heptets indicative of the presence of more than one carbene species in the reaction medium.

In contrast to the ether-functionalized monomer, the chain propagation step in this system seems to be substantially faster than initiation. Even with a 5-fold excess of monomer there still remains a considerable amount of the original catalyst. This is indicative of the fact that coordination of the ether function to the metal center exerts a more pronounced influence of the initiation than on the propagation step. Thus, the use of octyne instead of the ether analogue seems to increase the rate of the propagation step relative to the initiation.

In both cases, polyinsertion proceeds via α-insertion. Signals in the region at about 11 ppm indicative of the formation of new α-carbenes via β-insertion are not observed.

The System HF Catalyst/Oxaoctyne. Figure 3 shows the in-situ NMR spectrum of the reaction of the HF catalyst with a 5-fold excess of oxaoctyne.

Like in the cases discussed above, one clearly can identify the signals of the resulting polymer at about 4 and 6 ppm. Conversion of the monomer is complete after 15 min already, which indicates the higher reactivity of fluorinated catalysts systems relative to their aliphatic analogues. This behavior is also known from the formally analogous ring-opening metathesis polymerization of norbornene and its derivatives.[1]

The peaks in the region around 6 ppm representing the olefinic hydrogen atoms show a relatively complex coupling pattern. Obviously, the use of the ether-functionalized monomer leads to polymers with low stereoregularity with respect to cis−trans configurations in the polymer main chain with both aliphatic and fluorinated initiators. One striking feature of this spectrum is the presence of two sharp signals around 12 ppm. The signal at 12.1 ppm can be assigned to the original carbene, whereas the signal at 11.4 ppm indicates the formation of a second, new α-carbene. Resonances around 8.5 ppm indicative of hydrogen atoms in the β-position are not observed. Compared to the results obtained above with the tBu catalyst, the use of fluorinated molybdenum carbenes brings about the following effects: (i) The ratio of the rates of chain propagation to initiation is markedly enhanced. Consequently, even with a 5-fold excess of monomer initiation is not quantitative with respect to the initiator. About half of the original carbene remains unreacted. (ii) The direction of the insertion steps is reversed. Instead of the α-insertion proved for the tBu-system, the insertion of the monomer moieties proceeds via β-insertion.

The System HF Catalyst/Octyne. Figure 4 shows the in-situ NMR spectrum of the reaction of the HF catalyst with a 5-fold excess of octyne.

This spectrum shows essentially the signals of the original catalyst and the resulting poly(1-octyne). The insertion product from alkyne and molybdenum carbene is not observed. The sharp and intense peak at about 12.1 ppm is assigned to the original carbene, as is the heptet at about 4 ppm. Nevertheless, conversion of the monomer is quantitative. Evidently, only a very small part of the Schrock system reacts with octyne and converts the residual monomer extraordinarily fast. Like in the case discussed above, the use of fluorinated carbene systems leads to a very fast chain propagation relative to the initiation, bringing about rather high molecular weights (M_n = 9600 g/mol) and a high polydispersity of 1.62. These values are distinctly higher than those observed for the other systems discussed so far. A comparative survey of the molecular weights will be given below. In analogy to the results discussed so far, one should suppose that polymerization proceeds via β-insertion.

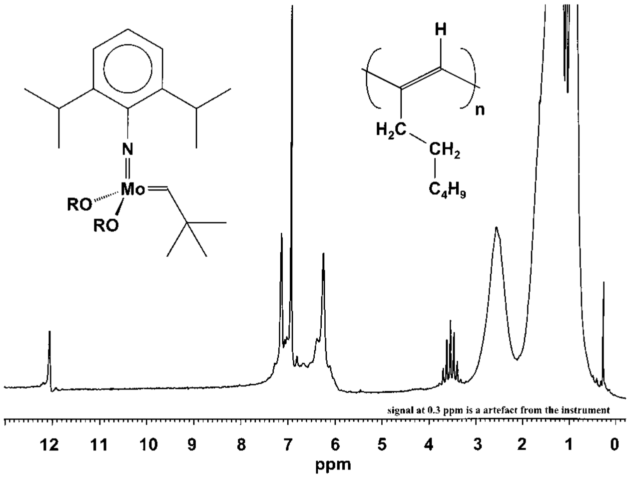


Figure 4. In-situ NMR spectrum of the reaction of HF catalyst (OR = $OC(CH_3)(CF_3)_2$) and 1-octyne in benzene-d_6.

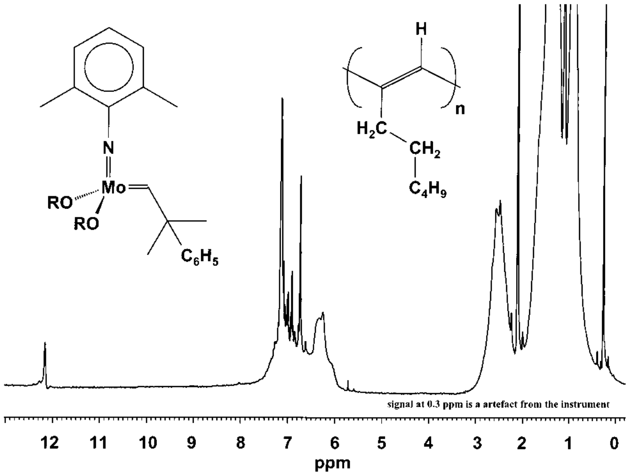


Figure 5. In-situ NMR spectrum of the reaction of DMHF catalyst (OR = $OC(CH_3)(CF_3)_2$) and 1-octyne in benzene-d_6.

The resonance signal of the hydrogen atoms connected to the polymer main chain is relatively sharp. This is indicative of a highly stereoregular polyinsertion product formed with the use of octyne instead of propargyl ethers. This observation is in good agreement with the results mentioned above.

Catalysts with Methyl Substituents. The behavior of carbenes with methyl substituents at the aromatic ring (DMtBu and DMHF, cf. Table 1) will be demonstrated by the example of the combination DMHF catalyst/octyne. Figure 5 shows the in-situ NMR spectrum of this system.

From this spectrum, almost the same conclusions can be drawn as in the case of the HF catalyst/octyne system (Figure 4). As in that spectrum, one observes exclusively the signals of the original carbene and the resulting poly(1-octyne). The region of the aromatic protons of the ligand system shows a more complicated coupling pattern, but these effects are also observed in the spectrum of the pure catalyst. Instead of the heptet of the isopropyl group there is just the singlet of the methyl group at about 2 ppm.

The stereochemistry of the polymer is comparatively well-defined. The formation of new carbene species is

Table 2. Molecular Weights and Polydispersities of the Polymers Formed in the NMR Experiments[a]

initiator	monomer	M_n[b]	M_w/M_n[b]
tBu	4-oxa-1-octyne-d_9	900	1.08
HF	4-oxa-1-octyne-d_9	1100	1.15
tBu	1-octyne	1400	1.23
HF	1-octyne	9600	1.62
DMtBu	4-oxa-1-octyne-d_9	1000	1.16
DMHF	4-oxa-1-octyne-d_9	1300	1.28
DMtBu	1-octyne	1800	1.36
DMHF	1-octyne	8500	1.60

[a] Polymerized in 0.8 mL of benzene-d_6 with 15 mg of initiator and a 5-fold excess of monomer. [b] Detected by means of SEC.

not observed. Thus, the ratio of the rate constants for chain propagation vs initiation seems to be very big. Molecular weights ($M_n = 8500$ g/mol) and polydispersity (1.60) are also very high for this system (see Table 2). Nevertheless, an influence of the substituents at the aromatic ring upon the insertion is not observed. The same refers to the other three combinations (DMHF/oxaoctyne, DMtBu/oxaoctyne, DMtBu/octyne). Therefore, these systems will not be discussed in detail.

Summarizing Discussion. Table 2 gives a survey of the experimentally determined molecular weights and polydispersities of the macromolecules formed in the NMR experiments.

The SEC results confirm the conclusions that were already drawn from the NMR spectra: The nature of the substituents at the aromatic ring does not exert a remarkable influence on the resulting polymer molecular weight. All experimentally determined molecular weights are above the theoretical values (710 g/mol for poly(1-octyne) and 765 g/mol for poly(4-oxa-1-octyne-d_9)). This is probably due to the calibration of the SEC apparatus by means of polystyrene. Owing to the stiff, conjugated backbone, the hydrodynamic volume of a polyacetylene is distinctly larger than that of a polymer with comparable side groups but with a saturated main chain. Thus, retention times in the SEC measurement are shorter, which leads to the assignment to higher molecular weights when leaving the chromatography column.

The SEC results also reflect the result from the NMR studies concerning the ratios of the rate constants for the propagation and the initiation step which are very high when either octyne as monomer or initiators with fluorinated alkoxy ligands—or a combination of both—are used. For these combinations, especially high molecular weights are obtained. This can be directly related to the NMR observation that only very little of the initiator reacts with the alkyne and that the resulting conjugated carbene converts the residual monomer very fast. Therefore, part of the initiator remains unreacted though the monomer has been completely consumed. Notwithstanding, the high concentration of unreacted initiator enhances the probability for the initiation of new chains while others are already growing. Thus, such systems produce polymers with a comparatively broad molecular weight distribution.

Another feature of the data in Table 2 is the observation that polydispersities increase with increasing molecular weights. This relation is shown in Figure 6. The catalysts with methyl groups at the aromatic ligand system seem to yield higher polydispersities at comparable molecular weights than the isopropyl analogues. One reason might be that the less bulky methyl groups favor chain propagation more than initiation, thus even more enhancing the ratio of the respective rates. This, again, suggests that the transition state of chain propagation is sterically more demanding than that of the initiation step.

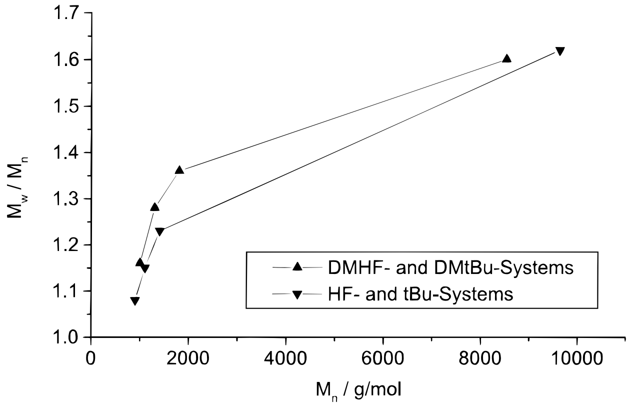


Figure 6. Polydispersities of the polymers as a function of their molecular weights.

An important aspect of the use of these Schrock-type initiator systems is the fact that no considerable amount of trimerization has been observed in these and previous studies.[45] This seems to be an important advantage of these systems. On using classical metathesis catalysts based upon $MoCl_5$ and WCl_6, up to 88% trimerization was reported.[50] As acetylene trimerization is favored thermodynamically due to the formation of aromatic benzene derivatives, a catalyst system suitable for alkyne polymerization must be able to suppress this tendency.

4. Conclusions

In this study, we investigated the influence of ligands and monomer structure on the polymerization of acetylene monomers using Schrock-type molybdenum carbenes in order to provide a better understanding of the factors controlling polymerization mechanisms and kinetics. All systems investigated have the ability to convert both 1-octyne and 4-oxa-1-octyne rapidly and quantitatively without a significant amount of trimerization. The influence of catalyst and substrate structure can be summarized as follows:

Regiochemistry of the Initiation Step. Irrespective of the presence of an ether function in the monomer, fluorinated initiator systems insert the monomers via β-insertion. This regiochemical preference is reversed for nonfluorinated initiators. This behavior might be related to the tendency of the fluorinated system to adopt a syn form at the metal—carbon double bond, whereas the tBu analogue prefers to adopt the anti configuration.[51]

Sterochemistry of the Double Bonds. From the NMR experiments, it can be concluded that monomers with an ether function adopt a less regular configuration at the double bonds in the polyacetylene main chain.

Reactivity of the Initiator. From a comparison of the catalyst systems for oxaoctyne, it follows that fluorinated systems reach complete monomer conversion faster than nonfluorinated ones, as is also known from the ring-opening metathesis polymerization with these systems.[1] Only in one case (tBu catalyst/oxyoctyne) conversion was not complete after 15 min.

Reactivity of the Monomer. From an analogous comparison, it follows that ether functions in the β-position to the triple bond of the monomer decrease its reactivity with respect to the overall rate, probably due to coordination of the oxygen atom to the metal center.

Kinetics of Chain Initiation and Propagation. With increasing reactivity of the monomer/initiator system the ratio of the rates of chain propagation to initiation increases markedly, leading to exceptionally high molecular weights and narrow polydispersities.

Substitution at the Aromatic Ring of the Carbene. This structural parameter does not exert a strong influence on the polymerization. For methyl substituents, chain propagation seems to be accelerated relative to the initiation reaction, leading to slightly higher molecular weights and polydispersities.

The reasons for these differences still have to be elucidated in detail. Further research on this field is necessary for a better understanding of the way these fascinating metalorganic systems behave.

Acknowledgment. The authors thank Dr. B. Winkler for his kind collaboration and Dr. M. R. Buchweiser and J. W. Feast for the careful revision of this manuscript. This work was supported by the Stiftung Stipendienfonds des Verbandes der Chemischen Industrie.

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MA980964Z