Living Metathesis Polymerization of [*o*-(Trifluoromethyl)phenyl]acetylene by Molybdenum-Based Three-Component Catalysts

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ABSTRACT: Living metathesis polymerization of [*o*-(trifluoromethyl)phenyl]acetylene, a phenylacetylene with an electron-withdrawing group, has been achieved by using molybdenum-based three-component catalysts. Thus polymerization by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5 mole ratio) catalyst in toluene at 30 °C produced a polymer having a narrow molecular weight distribution; $\bar{M}_w/\bar{M}_n = 1.06$. Upon three consecutive additions of fresh monomer feeds to completely polymerized systems, the $\bar{M}_n$ of the polymer increased in direct proportion to monomer conversion, while the $\bar{M}_w/\bar{M}_n$ remained < 1.1. The initiator efficiency was ca. 0.10. The $MoCl_5$–*n*-Bu_4Sn–EtOH (1:1:0.5) catalyst also induced living polymerization, though the $\bar{M}_w/\bar{M}_n$ (ca. 1.20) was somewhat larger. Effects of catalyst components and polymerization conditions have been studied.

Introduction

The synthesis and properties of substituted polyacetylenes have recently been under intensive research.[1,2] Among various acetylenes, ortho-substituted phenylacetylenes such as [*o*-(trifluoromethyl)phenyl]acetylene[3] (*o*-CF_3PA) and [*o*-(trimethylsilyl)phenyl]acetylene[4] (*o*-Me_3SiPA) polymerize with W and Mo catalysts to provide high molecular weight polymers. Control of the molecular weight distribution (MWD) of these polymers, however, has been impossible. Living polymerization is useful for that purpose and further is helpful for the elucidation of the polymerization mechanism.

Recently, we and Schrock's group have found a few living systems for substituted acetylenes: (i) $MoOCl_4$(or $MoCl_5$)–*n*-Bu_4Sn–EtOH for 1-chloro-1-alkynes and *o*-Me_3SiPA;[5] (ii) Ta carbene for 2-butyne;[6] and (iii) $NbCl_5$ (in cyclohexane) for 1-(trimethylsilyl)-1-propyne.[7] Among these catalysts, the first type is composed of a molybdenum chloride ($MoOCl_4$ or $MoCl_5$), *n*-Bu_4Sn (cocatalyst; an organometallic), and ethanol (third component; an oxygen-containing compound). Many molybdenum chloride/cocatalyst systems were known earlier, and the use of the third component was examined on the analogy with olefin metathesis catalysts,[8] which led to the Mo-based three-component catalysts. While a drawback of these catalysts is that the propagating species is not quantitatively formed, an advantage is their easy preparation. Regarding the kind of monomer, it was unknown whether phenylacetylenes with electron-withdrawing groups would undergo living polymerization.

In the present study, we sought catalyst systems that would effect living polymerization of *o*-CF_3PA, a phenylacetylene with an electron-withdrawing group. Effects of $MoOCl_4$- and $MoCl_5$-based catalysts and polymerization conditions on the MWD of the polymer were studied in detail. Consequently, the living nature of the polymerization by $MoOCl_4$(or $MoCl_5$)–*n*-Bu_4Sn–EtOH catalyst has been proved by a narrow MWD and a progressive increase of polymer molecular weight proportional to monomer consumption.

Experimental Section

The monomer, *o*-CF_3PA, was prepared by Okuhara's method.[9] $MoOCl_4$, $MoCl_5$ (both from Strem Chemicals; purities >99%), and organometallic cocatalysts were commercially obtained and used without further purification. Polymerization solvents were purified by the standard methods,[5] care being taken to remove traces of moisture and oxygen.

Preparation of catalyst solutions and polymerizations were carried out under dry nitrogen in prebaked flasks with use of three-way stopcocks and syringes. Two-component catalysts (e.g., $MoOCl_4$–*n*-Bu_4Sn) were prepared by mixing the components in a solution followed by aging at 30 °C for 15 min. Three-component catalysts (e.g., $MoOCl_4$–*n*-Bu_4Sn–EtOH) were obtained by further adding a third component (an oxygen-containing compound) to the molybdenum chloride/cocatalyst mixture thus obtained and aging at 30 °C for an additional 15 min.

Polymerizations were initiated by adding a monomer solution to a catalyst solution and quenched by adding a small amount of methanol to the polymerizing system. Monomer conversions were measured by gas chromatography (silicone DC550 3 m, 100 °C). The formed polymers were isolated by precipitation into methanol, and their yields were determined by gravimetry.

The MWD curves of the polymers were observed by gel permeation chromatography using a Jasco Trirotar liquid chromatograph [eluent $CHCl_3$; Shodex A803, A804, and A805 polystyrene gel columns (8.0 i.d. × 500 mm each)]. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) of the polymers were calculated from the chromatograms on the basis of a polystyrene calibration (ten monodisperse polystyrene standards from $\bar{M}_n = 2 \times 10^3$ to 1×10^6 were used, and the calibration curve was applicable over that molecular weight range). Mole ratios of the propagating species (i.e., polymer chain) to the molybdenum chloride employed ($[P^*]/[Cat]$, initiator efficiencies) were calculated.

Results

Polymerization by $MoOCl_4$- and $MoCl_5$-Based Catalysts. Figure 1 illustrates the MWD curves of poly(*o*-CF_3PA)s obtained with various types of Mo catalysts. The monomer conversions were all ≥95% irrespective of the number of catalyst components and the kind of molybdenum chlorides.

As seen in Figure 1, the MWD for $MoOCl_4$ alone is broad with a polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of ca. 2. In contrast, a two-component catalyst consisting of $MoOCl_4$ and *n*-Bu_4Sn (cocatalyst) appreciably narrows the MWD of polymer ($\bar{M}_w/\bar{M}_n$ 1.15). Further, a three-component

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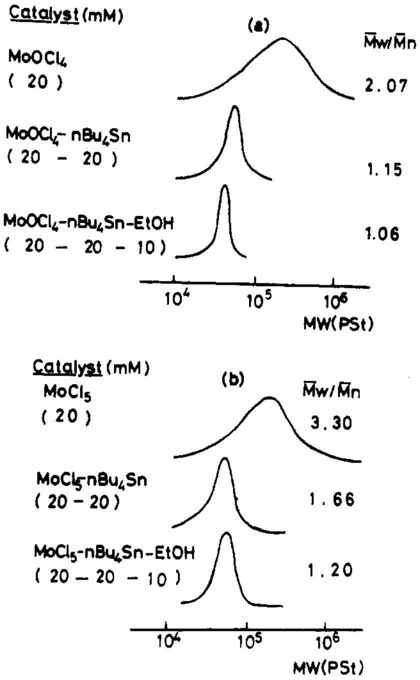


Figure 1. MWD curves of poly(o-CF_3PA) obtained with Mo catalysts (polymerized in toluene at 30 °C for 3 h; $[M]_0 = 0.50$ M, conversion ≥95%).

catalyst containing ethanol (third component) produced a polymer whose $\bar{M}_w/\bar{M}_n$ is as low as 1.06.

When $MoCl_5$-based catalysts were employed, the $\bar{M}_w/\bar{M}_n$ ratios were larger than those with the corresponding $MoOCl_4$-based catalysts (Figure 1). n-Bu_4Sn and ethanol, however, had similar influences on MWD, and the $\bar{M}_w/\bar{M}_n$ became fairly small (1.20) with $MoCl_5$–n-Bu_4Sn–EtOH catalyst.

Thus, the $MoOCl_4$- and $MoCl_5$-based three-component catalysts proved to yield poly(o-CF_3PA)s with narrow MWDs. Hence, the polymerization with these types of catalysts were studied in more detail.

Polymerization by $MoOCl_4$-Based Catalysts. In the following, the effects of catalyst components and polymerization conditions on the MWD were examined, and then the livingness of the polymerization by $MoOCl_4$–n-Bu_4Sn–EtOH was confirmed by means of a "monomer addition experiment".

At first, what kind of organometallic cocatalysts would be effective in decreasing the $\bar{M}_w/\bar{M}_n$ ratio was examined (Table I). A mixture of $MoOCl_4$ and ethanol, i.e., a catalyst system without a cocatalyst, provided only a polymer whose MWD was broad, and the initiator efficiency was as low as ca. 0.01. Interestingly, tetraalkyltins such as n-Bu_4Sn and Me_4Sn as cocatalysts made the $\bar{M}_w/\bar{M}_n$ 1.1 or even smaller and raised the initiator efficiency up to 0.06–0.11. Other cocatalysts, in contrast, did not change $\bar{M}_w/\bar{M}_n$ substantially.

Figure 2 shows the effect of n-Bu_4Sn (a cocatalyst) concentration. The $\bar{M}_w/\bar{M}_n$ sharply decreased to below 1.1 with increasing n-Bu_4Sn concentration and then leveled off when [n-Bu_4Sn] ≥ [$MoOCl_4$]. The initiator efficiency increased with n-Bu_4Sn concentration to become virtually constant (ca. 0.10) when [n-Bu_4Sn] ≥ [$MoOCl_4$]. Thus, the amount of n-Bu_4Sn should be equal to or slightly higher than that of $MoOCl_4$ to attain narrow MWDs and high initiator efficiencies.

Effects of various oxygen-containing compounds (third components) are shown in Table II. The $\bar{M}_w/\bar{M}_n$ (=1.15) is fairly small even with $MoOCl_4$–n-Bu_4Sn, that is, without use of any oxygen-containing compound. However, ethanol as a third component made the value (=1.06) clearly smaller and closer to unity. Acetic acid and acetone were similarly effective, whereas phenol appears ineffective. These findings suggest that not the presence of a labile proton but rather the steric crowding around the oxygen atom of the third component is important.

Table I
Effects of Cocatalysts on the Polymerization of o-CF_3PA by $MoOCl_4$(or $MoCl_5$)–Cocatalyst–EtOH (1:1:0.5)[a]

cocatalyst	polymer $\bar{M}_n/10^3$	$\bar{M}_w/\bar{M}_n$	[P*]/[Cat]
	$MoOCl_4$–Cocatalyst–EtOH		
none	312	2.07	0.014
n-Bu_4Sn	39.1	1.06	0.11
Me_4Sn	75.7	1.10	0.056
Ph_4Sn	346	1.96	0.012
n-Bu_3SnH	290	2.61	0.015
Et_3SiH	258	1.75	0.017
Et_3Al	294	1.94	0.014
	$MoCl_5$–Cocatalyst–EtOH		
none	449	4.35	0.009
n-Bu_4Sn	100	1.20	0.043
Me_4Sn	71	1.26	0.060
Ph_4Sn	333	2.52	0.013
n-Bu_3SnH	575	3.96	0.074
Et_3SiH	329	3.11	0.013
Et_3Al[b]	268	3.46	0.016

[a] Polymerized in toluene at 30 °C for 3 h; $[M]_0 = 0.50$ M, [Cat] = 20 mM; conversion = 100%. [b] Conversion = 53% in this run.

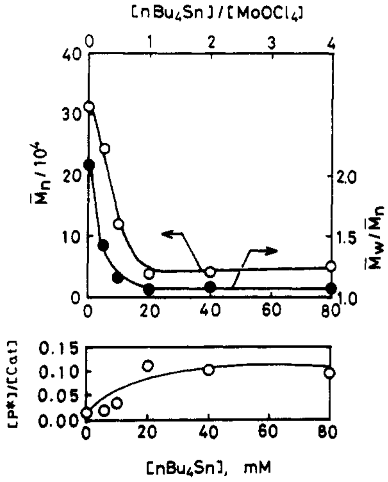


Figure 2. Effects of n-Bu_4Sn concentration on the polymerization of o-CF_3PA by $MoOCl_4$–n-Bu_4Sn–EtOH (polymerized in toluene at 30 °C for 3 h; $[M]_0 = 0.50$ M, [$MoOCl_4$] = 20 mM, [EtOH] = 10 mM; conversion ~100%).

Figure 3 depicts the effect of ethanol (a third component) concentration. The narrowest MWDs ($\bar{M}_w/\bar{M}_n$ = 1.04–1.05) were achieved at the ratio [EtOH]/[$MoOCl_4$] from 0.5 to 1.5. Hence [EtOH] should be at least half as much as [$MoOCl_4$]. The initiator efficiency is roughly 0.10 irrespective of ethanol concentration.

The polymerization with $MoOCl_4$–n-Bu_4Sn–EtOH proceeded quantitatively not only in toluene but also in several other solvents, as seen in Table III. The $\bar{M}_w/\bar{M}_n$ of polymer was below 1.1 in toluene and anisole but was larger in chlorobenzene and carbon tetrachloride. Judged from the $\bar{M}_w/\bar{M}_n$ values, toluene is most suitable for the present living polymerization.

The effect of temperature was examined (Figure 4). The $\bar{M}_w/\bar{M}_n$ was smaller than 1.1 in the range from −30 to +30 °C, whereas the ratio became as large as 1.6 at 60 °C. The $\bar{M}_n$ slightly increased with decreasing temperature. Thus, temperature should be +30 °C or below to maintain the small $\bar{M}_w/\bar{M}_n$.

Since the catalyst components and polymerization conditions narrowing the MWD had been made clear, the

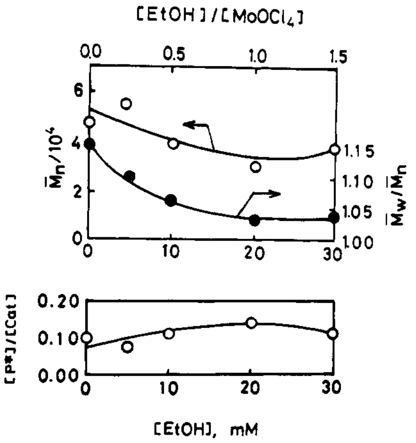


Figure 3. Effects of ethanol concentration on the polymerization of o-CF$_3$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH (polymerized in toluene at 30 °C for 3 h; $[M]_0$ = 0.50 M, [MoOCl$_4$] = [n-Bu$_4$Sn] = 20 mM; conversion ~100%).

Table II
Effects of Oxygen-Containing Compounds on the Polymerization of o-CF$_3$PA by MoOCl$_4$(or MoCl$_5$)–n-Bu$_4$Sn–O-compd (1:1:0.5)[a]

O-compd	polymer $\bar{M}_n/10^3$	polymer $\bar{M}_w/\bar{M}_n$	polymer [P*]/[Cat]
	MoOCl$_4$–n-Bu$_4$Sn–O-compd		
none	42.6	1.15	0.10
EtOH	39.1	1.06	0.11
PhOH	136	1.20	0.031
CH$_3$CO$_2$H	25.0	1.07	0.17
CH$_3$CO$_2$-n-Bu	28.6	1.10	0.15
CH$_3$CO$_2$-t-Bu	25.4	1.10	0.17
acetone	36.2	1.05	0.12
	MoCl$_5$–n-Bu$_4$Sn–O-compd		
none	142	1.66	0.030
EtOH	100	1.20	0.043
PhOH	161	2.74	0.026
CH$_3$CO$_2$H	55	1.32	0.077
CH$_3$CO$_2$-n-Bu	58	1.23	0.073
CH$_3$CO$_2$-t-Bu	81	1.48	0.053
acetone	64	1.24	0.067

[a] Polymerized in toluene at 30 °C for 3 h; $[M]_0$ = 0.50 M, [Cat] = 20 mM; conversion = 100% in all runs.

Table III
Solvent Effects on the Polymerization of o-CF$_3$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH (1:1:0.5)[a]

solvent	polymer $\bar{M}_n/10^3$	polymer $\bar{M}_w/\bar{M}_n$	polymer [P*]/[Cat]
toluene	39.1	1.06	0.11
anisole	47.8	1.09	0.089
PhCl	21.3	1.23	0.19
CCl$_4$	37.3	1.27	0.11
(CH$_2$OCH$_3$)$_2$[b]			

[a] Polymerized at 30 °C for 3 h; $[M]_0$ = 0.50 M, [MoOCl$_4$] = 20 mM; conversion = 100%. [b] Conversion = 7% in this run.

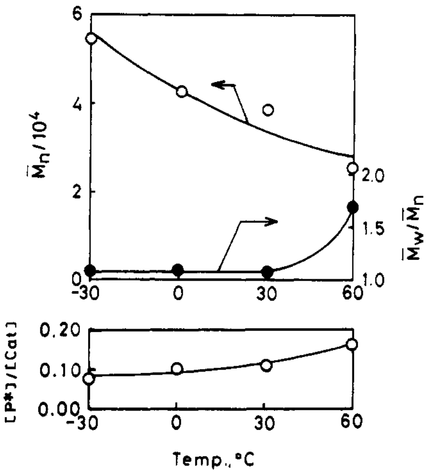


Figure 4. Effects of temperature on the polymerization of o-CF$_3$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH (1:1:0.5) (polymerized in toluene for 3 h; $[M]_0$ = 0.50 M, [MoOCl$_4$] = 20 mM; conversion ~100%).

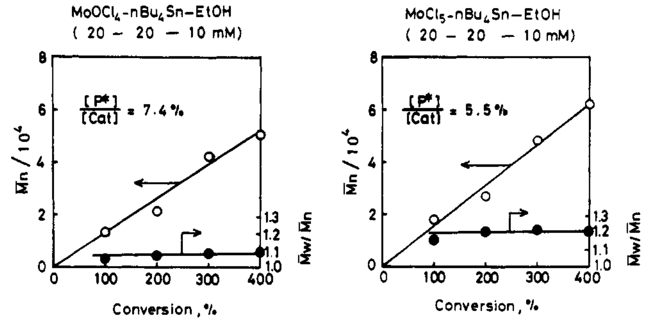


Figure 5. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(o-CF$_3$PA) as functions of monomer conversion in the "monomer addition experiment" (polymerized in toluene at 30 °C for 5 min each; $[M]_0 = [M]_{added}$ = 0.10 M; monomer readdition repeated three times).

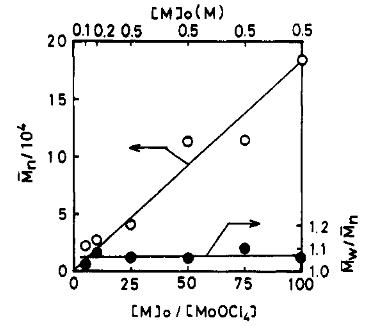


Figure 6. Effects of $[M]_0$/[MoOCl$_4$] on the polymerization of o-CF$_3$PA by MoOCl$_4$–n-Bu$_4$Sn–EtOH (1:1:0.5) (polymerized in toluene at 30 °C for 3 h; conversion ~100%).

living nature of the polymerization was examined: The polymerization by MoOCl$_4$–n-Bu$_4$Sn–EtOH at 30 °C turned out to be too fast (completed within a few minutes) to study the relationship between conversion and $\bar{M}_n$. Therefore, changes in $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were followed by supplying new monomer feeds (up to three times; each $[M]_0$ restrained to 0.10 M) to the completely polymerized system (such a procedure is usually called a "monomer addition experiment"). As seen in Figure 5, the $\bar{M}_n$ of the formed polymer continued to increase in direct proportion to monomer consumption (number of monomer additions). Meanwhile, the $\bar{M}_w/\bar{M}_n$ remained below 1.1. These data verify that this polymerization is living. The initiator efficiency ([P*]/[Cat]), however, is no more than 0.07.

Figure 6 shows the dependences of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ on the monomer-to-catalyst ratio ($[M]_0$/[MoOCl$_4$]). The $\bar{M}_w/\bar{M}_n$ is smaller than 1.1 over a wide range (5–100) of the ratio. The $\bar{M}_n$, which should be given by $[M]_0$/[P*] at 100% conversion in living polymerization, is proportional to $[M]_0$/[MoOCl$_4$] in the present system. This indicates that the propagating species (P*) is formed at a constant proportion against MoOCl$_4$.

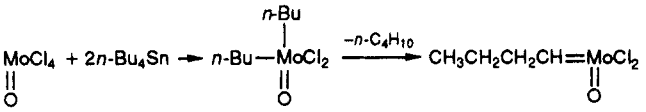
Polymerization by MoCl$_5$-Based Catalysts. Effects of cocatalysts on the polymerization by the MoCl$_5$-based three-component catalyst resemble those with the MoOCl$_4$-based counterpart (Table I). Thus, alkyltins such as n-Bu$_4$Sn and Me$_4$Sn exclusively produce polymers with narrow MWDs. As seen in Table II, many oxygen-containing compounds more or less decrease the $\bar{M}_w/\bar{M}_n$, among which ethanol leads to the smallest ratio.

The results of the monomer addition experiment using $MoCl_5$–n-Bu_4Sn–EtOH catalyst are shown in Figure 5. The $\bar{M}_w/\bar{M}_n$ is about 1.2 irrespective of monomer conversion, being somewhat larger than that for the $MoOCl_4$–n-Bu_4Sn–EtOH system. The $\bar{M}_n$, however, increases in direct proportion to monomer conversion even after the fourth supply of monomer feed. This means that living polymerization has occurred also in this system.

Discussion

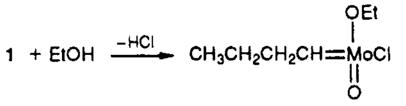
The above-described results manifest that $MoOCl_4$–n-Bu_4Sn–EtOH and $MoCl_5$–n-Bu_4Sn–EtOH catalysts effect living polymerization of o-CF_3PA. As living polymerization catalysts, the former surpasses the latter on the basis of their $\bar{M}_w/\bar{M}_n$ ratios (ca. 1.05 vs ca. 1.20) and initiator efficiencies ($[P^*]/[Cat]$ = 0.11 vs 0.04). Further, concerning the kind of monomer, the present study has revealed that o-CF_3PA, which is a phenylacetylene with an electron-withdrawing group, also undergoes living polymerization.

In the following, we discuss each elementary process related to the findings in this study. In the first place, the initiation reaction is formation of a metal carbene, because it is now accepted generally that the propagating species are metal carbenes.[1,6] The formation of metal carbenes has been confirmed or suggested in reactions of W and Mo chlorides with either acetylenes or organometallics, e.g., $WCl_6/HC{\equiv}CPh$,[10] WCl_6/Me_4Sn,[11] and $MoCl_5/MeLi$.[12] Therefore, it seems reasonable to assume that metal carbene 1 is formed at first in the present system.



$$\underset{\underset{O}{\|}}{MoCl_4} + 2n\text{-}Bu_4Sn \rightarrow n\text{-}Bu{-}\overset{n\text{-}Bu}{\underset{\underset{O}{\|}}{MoCl_2}} \xrightarrow{-n\text{-}C_4H_{10}} CH_3CH_2CH_2CH{=}\underset{\underset{O}{\|}}{MoCl_2}$$

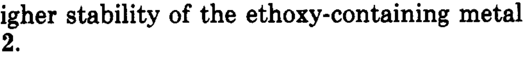
1



$$1 + EtOH \xrightarrow{-HCl} CH_3CH_2CH_2CH{=}\overset{OEt}{\underset{\underset{O}{\|}}{MoCl}}$$

2

The function of ethanol is considered to replace a chlorine ligand of metal carbene 1 by an ethoxy ligand to form metal carbene 2. Since the ethoxy ligand is less electron-withdrawing than the chlorine ligand, metal carbene 2 should be less active but more stable than 1. This is one reason that Mo-based three-component catalysts work as living polymerization catalysts. The initiator efficiency for the $MoOCl_4$–n-Bu_4Sn–EtOH system is ca. 0.10. Though far from being quantitative, this value is significantly larger than 0.007 for WCl_6–Me_4Sn, which does not involve an ethoxy ligand.[11] This fact also supports the higher stability of the ethoxy-containing metal carbene 2.

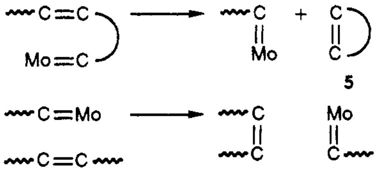


3

4

The propagation reaction consists of two steps; i.e., reaction of a metal carbene, 3, with an acetylene to form a metallacyclobutene, 4, and the subsequent ring scission of 4 to regenerate a metal carbene. The result that $MoOCl_4$ is superior to $MoCl_5$ for living polymerization should be associated with the relative stabilities of the propagating species 3 and 4. In this connection, it has been shown by molecular orbital calculations that, when a Mo=O bond is present, the stabilities of metal carbene and metallacyclobutane approach each other and hence metathesis reactions proceed smoothly.[13]

Possible termination reactions include a spontaneous decomposition of the metal carbene intermediates and/or their reactions with impurities present in the system.[14] The ethoxy-containing metal carbenes will be stable enough to elude these terminations.



5

Chain transfer to a double bond of the polymer chain may occur either intramolecularly or intermolecularly. The intramolecular reaction is a back-biting reaction, which produces cyclic olefins 5, resulting in a decrease of polymer molecular weight. The intermolecular reaction may change the MWD of the polymer but does not decrease the polymer molecular weight. These chain transfer processes seem less likely for acetylenes having bulky groups. This idea is consistent with the fact that sterically crowded acetylenes often yield high molecular weight polymers.[1]

The above considerations lead to the conclusion that, to achieve living polymerization of substituted acetylenes, the following requirements should be satisfied: (i) addition of a third, oxygen-containing catalyst component (to stabilize the propagating species); (ii) use of a sterically crowded monomer (to repress chain transfer). These are, however, not the sufficient conditions. Further study is underway to improve living polymerization catalysts and to elucidate what type of monomers are suited for living metathesis polymerization.

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