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On the role of catalyst components in the living metathesis polymerization of substituted acetylenes by $MoOCl_4$-based systems

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Summary

The role of components in $MoOCl_4$-based living polymerization catalysts was studied. The MALDI TOF MS spectra of the poly(*o*-[(trifluoromethyl)phenyl]acetylene)s prepared with *n*-Bu_4Sn and Et_3Al as cocatalysts suggested a difference of 28(C_2H_4) in polymer molecular weight. This indicates that the formed polymer possesses an alkyl group of cocatalyst in the initiating chain end, which implies the transalkylation between $MoOCl_4$ and a cocatalyst and the subsequent formation of a Mo carbene. Sterically uncrowded aliphatic alcohols were useful as the third catalyst components. Addition of EtOH to the catalyst system led to the increase of activation enthalpy and the change of activation entropy from a negative to positive value in the propagation reaction, which suggests that EtOH coordinates to the propagating end competitively with the monomer.

Introduction

Living metathesis polymerization of substituted acetylenes has been accomplished with two types of catalysts, i.e., molybdenum imido alkylidene complexes (Schrock carbenes) and $MoOCl_4$- and $WOCl_4$-based systems. Schrock carbenes induce the excellent living polymerization of α,ω-diynes, ethynylferrocene and ortho-substituted phenylacetylenes [1]. Thus far, we have found that the $MoOCl_4$-cocatalyst-EtOH systems (cocatalysts: *n*-Bu_4Sn, Et_3Al, Et_2Zn, and *n*-BuLi) [2a-d] and $WOCl_4$-cocatalyst-*t*-BuOH systems (cocatalysts: *n*-Bu_4Sn, EtMgBr, and *n*-BuLi) [2e,f] effect living polymerization of various substituted acetylenes such as ortho-substituted phenylacetylenes, 1-chloro-1-*n*-alkynes, *tert*-butylacetylene, 1-chloro-2-phenylacetylene and internal aliphatic acetylenes [3]. The polymerization induced by $MoOCl_4$- and $WOCl_4$-based catalysts shows different features from those with Schrock carbenes. For instance, the initiation efficiencies of $MoOCl_4$- and $WOCl_4$-based systems are rather low (2-50%), whereas those of Schrock carbenes are quantitative. Further, $MoOCl_4$- and $WOCl_4$-based catalysts are useful for both mono- and disubstituted acetylenes, while Schrock carbenes have been known to be effective only for monosubstituted acetylenes [4].

There are still many unsolved problems with the $MoOCl_4$- and $WOCl_4$-based catalysts such as the role of catalyst components, the structure of initiating and terminating chain ends, and the initiation and termination reactions. In the metathesis polymerizations with well-defined catalysts such as Schrock carbenes [5] and Ru carbenes [6], the polymerization mechanism is clear in many cases. On the other hand, the elucidation of the reaction mechanism is difficult in the systems using classical metathesis catalysts and few studies have been reported [7]. Here, we examined the living polymerization of *o*-[(trifluoromethyl)phenyl]acetylene (*o*-CF_3-phenylacetylene) by $MoOCl_4$-based catalysts in detail by means of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI TOF MS) and kinetic analyses, and clarified the roles of cocatalysts and third catalyst components.

Experimental part

o-CF_3-Phenylacetylene and *o*-[(trimethylsilyl)phenyl]acetylene (*o*-Me_3Si-phenylacetylene) were prepared with reference to the literature methods and distilled twice from CaH_2 at reduced pressure before use [purity >99.9% by gas chromatography (GC)] [8]. $MoOCl_4$ (Strem) and solutions of *n*-BuLi and Et_3Al (Kanto Chemical) were used without further purification. *n*-Bu_4Sn was distilled twice from CaH_2 at reduced pressure before use. Anisole as the polymerization solvent was washed with aqueous sodium hydroxide solution (5%) and water successively, dried over anhydrous calcium chloride, and distilled twice from sodium metal (purity >99.9% by GC). Ethanol (EtOH) was distilled twice from $Mg(OEt)_2$ (purity >99.9% by GC). Other alcohols were purified by the conventional methods.

All the procedures of catalyst preparation and polymerization were carried out under dry nitrogen. Unless otherwise stated, catalyst solutions were prepared as follows: At first, $MoOCl_4$ was dissolved in anisole. This anisole solution of $MoOCl_4$ was mixed with an anisole solution of cocatalyst, and the mixture was aged at room temperature for a suitable time (15 min for *n*-Bu_4Sn, 5 min for Et_3Al, and 20 min for *n*-BuLi) as in previous studies. Then, an anisole solution of third catalyst component was further added to the $MoOCl_4$-cocatalyst solution. The mixture was aged at room temperature for an additional 15 min. Polymerizations were carried out in a pre-baked Schlenk tube equipped with a three-way stopcock usually at 30 °C. Polymerizations were quenched with a large amount of methanol. The monomer conversions were measured by GC (Shimadzu GC-14B; CBP10-M25-025), and the polymer yields were determined by gravimetry.

The molecular weight distributions (MWD) of polymers were recorded on a gel-permeation chromatograph (GPC) (Jasco PU930; eluent chloroform; Shodex K805, 804, 803 and 802.5 polystyrene gel columns; RI and UV detectors). The number- and weight-average molecular weights (M_n and M_w, respectively) of the polymers were determined by using polystyrene calibration. The initiation efficiencies ($[P^*]/[Mo]$; $[P^*]$ and [Mo] are the concentrations of the propagating species and $MoOCl_4$, respectively) were calculated from the monomer conversion and the degree of polymerization (based on GPC) of the polymers.

MALDI TOF MS spectra were measured on a Voyager Elite mass spectrometer [PerSeptive Biosystems (MA, USA)]. A program called Grams (Galactic Industries, Salem, New Hampshire) was used for the display, reduction, and analysis of MALDI data. The calculation of polydispersity ratios was performed using a program supplied by Kieth Waddell of PerSpective Biosystem. An accelerating voltage of 25,000V was employed. The laser intensity, grid voltage, guide wire voltage and the delay time were chosen in each spectrum so as to increase the signal-to-noise ratio to a value of at least 2000. All spectra were accumulations of at least 128 scans. The polymer samples were purified beforehand by fractional collection with GPC. The samples for MALDI-TOF MS analyses were prepared as follows: A THF solution of trans, trans-1,4-diphenyl-1,3-butadiene matrix (20 mg/mL) and a THF solution of a polymer (5 mg/mL) were prepared. A volume of 10 µL of the matrix solution was mixed with 2 µL of the polymer solution. Aliquots of 0.5 µL of this mixture were then spotted on a MALDI sample plate and air-dried before analysis. All samples were run in the positive ion mode.

Results and Discussion

Identification of the initiating chain end by MALDI TOF MS

Previous studies have revealed the following points regarding cocatalysts [2]: (i) *n*-alkylmetal compounds that possess enough alkylating ability for $MoOCl_4$ are effective as cocatalysts in the $MoOCl_4$-based living systems; and (ii) the organometallics having only aromatic or branched alkyl groups do not work as cocatalysts. However, it has not been clarified how the cocatalysts function. We prepared poly(*o*-CF_3-phenylacetylene) with a low molecular weight and a narrow MWD with $MoOCl_4$-*n*-Bu_4Sn-EtOH(1:1:2) and $MoOCl_4$-Et_3Al-EtOH(1:1:4), and measured the MALDI TOF MS spectra of both polymers in order to obtain information about the initiating chain end (Figure 1).

Each peak of the MALDI TOF MS spectra of the polymers is very clear and sharp, and weaker peaks due to by-products are not observed. The difference of molecular weight (MW) of each peak is constant and close to the MW of *o*-CF_3-phenylacetylene (170.13). This implies that the polymers are so stable that no reactions such as degradation of the main chain, substituents, and end groups proceed during polymerization, isolation and measurement. Further, this suggests that both initiating and terminating chain ends possess uniform structures.

Interestingly, the MW of each peak of the polymer formed with $MoOCl_4$-*n*-Bu_4Sn-EtOH is larger than that with $MoOCl_4$-Et_3Al-EtOH, where the difference is constant and 28.8 g/mol. This value is close to the difference (28.0 g/mol) of MW between the *n*-butyl group in *n*-Bu_4Sn and the ethyl group in Et_3Al. This result manifests that the polymers possess an alkyl group from the cocatalyst at the initiating chain end, in other words, an alkyl group of the

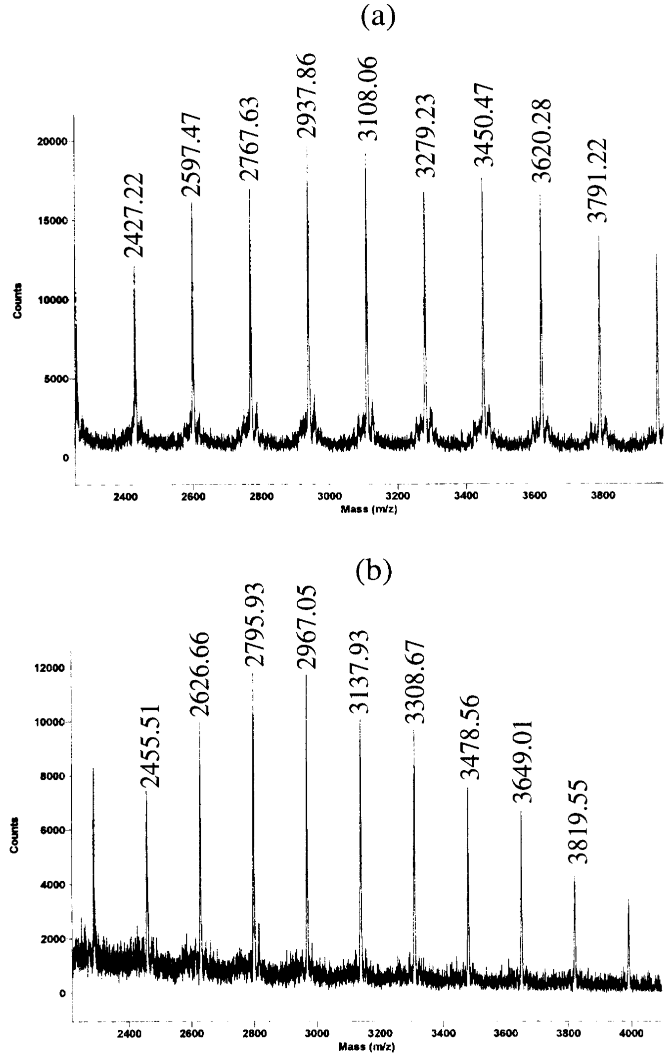


Figure 1. MALDI TOF MS spectra of poly(*o*-CF_3-phenylacetylene)s prepared with (a) $MoOCl_4$–Et_3Al–EtOH(1:1:4) and (b) $MoOCl_4$–*n*-Bu_4Sn–EtOH(1:1:2) [polymer (a) M_n 3040, M_w/M_n 1.09 by MALDI-TOF MS; M_n 1780, M_w/M_n 1.14 by GPC (PSt calibration in $CHCl_3$), polymer (b) M_n 2780, M_w/M_n 1.06 by MALDI-TOF MS; M_n 1620, M_w/M_n 1.09 by GPC (PSt calibration in $CHCl_3$) (polymerized in anisole at 30 °C for 30 min; $[MoOCl_4]$ = 20 mM, $[M]_o$ = 0.10–0.20 M)].

cocatalyst becomes part of the initiating species. Hence one can speculate the reaction between $MoOCl_4$ and a cocatalyst in the period of catalyst aging, as follows: transalkylation takes place between $MoOCl_4$ and a cocatalyst, and then the alkyl group on the Mo becomes an alkylidene by α-H elimination. These result and speculation correspond with Ivin's finding that a $L_nW{=}CH_2$ species is formed from a mixture of WCl_6 and Me_4Sn. In previous studies, we have found that the initiation efficiency varies in a wide range with the kind of cocatalysts; i.e., 40% (n-Bu_4Sn), 20% (Et_3Al), 8% (Et_2Zn), and 2% (n-BuLi) [2]. It is assumed that the initiation efficiency depends on the yield of the above-stated reaction between $MoOCl_4$ and cocatalysts.

In order to obtain information about the terminating chain end, the MW of the end was calculated from the following equation.

MW = (repeat unit x N) + (initiating chain end) + (terminating chain end)

= (170.13 x N) + (28.032 + 14.016 x n) + X

where N is the degree of polymerization and n is the number of methylene spacer (n = 0 for Et_3Al and = 2 for n-Bu_4Sn). The molecular weights of the terminating chain end are calculated to be 19.25 for the n-Bu_4Sn-based polymer and 18.45 for the Et_3Al-based polymer. The polymerization reactions were quenched by adding a large amount of methanol. However, as described below, alcohols do not decompose the propagating species but only decelerate the polymerization extremely. Since the MW of the terminating chain end equals 19, it is likely that the oxygen molecule reacts with the propagating species, $L_nMO{=}CR'P$ (P: polymer chain), to form $L_nMo{=}O$ and O=CR'P. The same reaction has been observed in the polymerization of norbornene with a Schrock carbene [9]. However, a problem remains in that the observed MW of ca. 19 do not agree with the value of oxygen, 16.0 g/mol.

Effect of third catalyst components

In order to clarify the effect of third catalyst components, we investigated the polymerization of o-CF_3-phenylacetylene by use of $MoOCl_4$-n-Bu_4Sn-ROH(1:1:2) (Table 1). The polydispersity ratios (M_w/M_n) were usually around 1.05 irrespective of the kind of alcohols. Among the alcohols, those which are sterically uncrowded in the vicinity of the hydroxyl group (e. g., MeOH, EtOH, i-PrOH and t-$BuCH_2OH$) provided high initiation efficiencies ($[P^*]/[Mo]$) up to ca. 45%. This suggests that these alcohols are useful to stabilize the initiating species by coordination to the vacant site and, in turn, to generate the propagating species in large amounts. In contrast, the alcohols having either acidity (CF_3CH_2OH and PhOH) or large steric hindrance (t-BuOH) hardly affected the initiation efficiency. This shows that these alcohols do not coordinate to the initiating species.

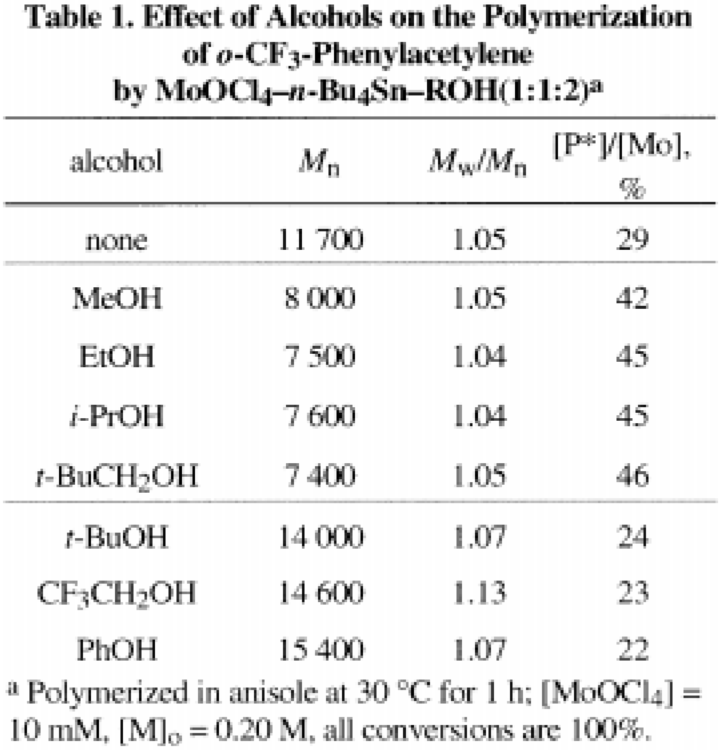


Table 1. Effect of Alcohols on the Polymerization of o-CF_3-Phenylacetylene by $MoOCl_4$–n-Bu_4Sn–ROH(1:1:2)[a]

alcohol	M_n	M_w/M_n	$[P^*]/[Mo]$, %
none	11 700	1.05	29
MeOH	8 000	1.05	42
EtOH	7 500	1.04	45
i-PrOH	7 600	1.04	45
t-$BuCH_2OH$	7 400	1.05	46
t-BuOH	14 000	1.07	24
CF_3CH_2OH	14 600	1.13	23
PhOH	15 400	1.07	22

[a] Polymerized in anisole at 30 °C for 1 h; $[MoOCl_4]$ = 10 mM, $[M]_o$ = 0.20 M, all conversions are 100%.

Next we examined the effect of larger amounts of EtOH on the polymerization of *o*-CF_3-phenylacetylene catalyzed by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:x) under the same conditions as in Table 1. The amount of EtOH was varied from none to 6.0 vol% (1.02 M) of the total volume. Large amounts of EtOH remarkably decelerated the polymerization; i.e., the polymerization was finished instantaneously at 0 °C without EtOH, while it needed 3 days for completion at 50 °C with 6.0 vol% of EtOH. The initiation efficiency varied with the amount of EtOH as follows: initiation efficiency 29% (no EtOH), 38% (10 mM), 45% (20 mM), 42% (2.0 vol% (0.34 M)), 47% (4.0 vol% (0.68 M)), and 46% (6.0 vol% (1.02 M)). These results mean two things; i.e., (1) a two-fold excess of EtOH is enough to increase the initiation efficiency, in other words, the nature of the propagating species changes with a catalytic amount of EtOH, and (2) a large excess of EtOH neither decomposes the propagating species nor changes its amount. A previous study [2a] has revealed that the character of $MoOCl_4$-*n*-Bu_4Sn-EtOH catalyst drastically changes on addition of a two-fold excess of EtOH.

Activation parameters for the propagation reaction

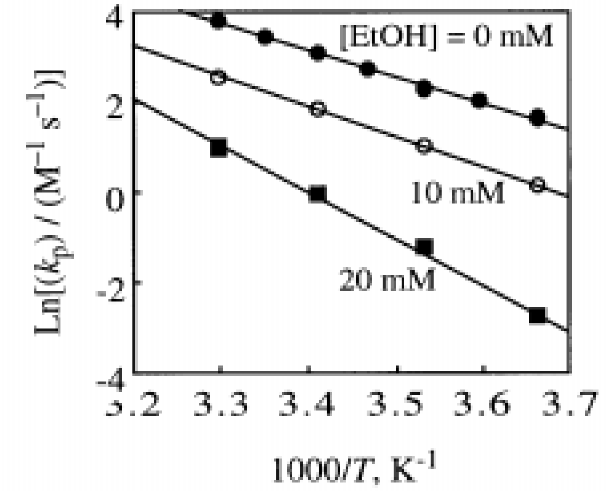


Figure 2. Arrhenius plots of the propagation rate constant in the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-BuLi–EtOH (1:1:x) (polymerized in anisole; [$MoOCl_4$] = 10 mM, $[M]_0$ = 0.10 M).

In the polymerization of *o*-CF_3-phenylacetylene, propagation rate constants and their activation parameters were determined for several $MoOCl_4$-based catalyst systems to gain insight into the role of the third catalyst components. The catalytic systems of $MoOCl_4$-*n*-BuLi-EtOH (1:1:0-2) and $MoOCl_4$-*n*-BuLi-CF_3CH_2OH (1:1:0-4), which are characterized by the constant initiation efficiency irrespective of the presence or absence of the third component, were employed for the living polymerization of *o*-CF_3-phenylacetylene [10]. The polymerizations were first order with respect to monomer, indicating that the concentration of the propagating species remained constant throughout the

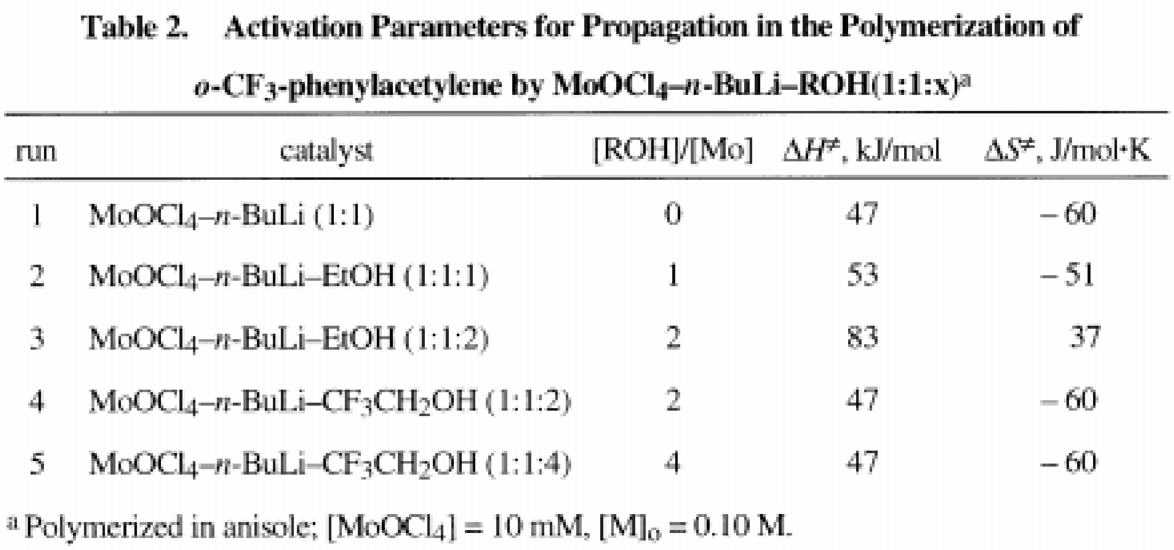


Table 2. Activation Parameters for Propagation in the Polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-BuLi–ROH(1:1:x)[a]

run	catalyst	[ROH]/[Mo]	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J/mol·K
1	$MoOCl_4$–*n*-BuLi (1:1)	0	47	– 60
2	$MoOCl_4$–*n*-BuLi–EtOH (1:1:1)	1	53	– 51
3	$MoOCl_4$–*n*-BuLi–EtOH (1:1:2)	2	83	37
4	$MoOCl_4$–*n*-BuLi–CF_3CH_2OH (1:1:2)	2	47	– 60
5	$MoOCl_4$–*n*-BuLi–CF_3CH_2OH (1:1:4)	4	47	– 60

[a] Polymerized in anisole; [$MoOCl_4$] = 10 mM, $[M]_0$ = 0.10 M.

polymerizations regardless of temperature and the kind and concentration of alcohols. Propagation rate constants (k_p) were calculated using the absolute molecular weight determined with a relationship of M_n(VPO) = 1.47 x M_n(GPC). Figure 2 illustrates Arrhenius plots of the propagation rate constant for the polymerization by $MoOCl_4$-*n*-BuLi-EtOH (1:1:0-2). The activation parameters of the propagation reaction are given in Table 2.

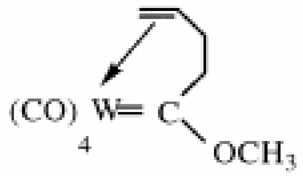
The activation entropy of the polymerization using $MoOCl_4$-*n*-BuLi (1:1) possesses a large negative value (Table 2, run 1). This suggests that the degree of freedom of the propagating chain end decreases upon the coordination of monomer to the vacant site of a Mo carbene in the propagation reaction. The activation parameters for the polymerization of *o*-Me_3Si-phenylacetylene are similar to that of *o*-CF_3-phenylacetylene (Table 3, run 1). These negative values of activation entropy probably mean that anisole as solvent does not coordinate to the vacant site of Mo carbene. These activation parameters of the polymerization of both monomers are comparable with those for the conventional polymerizations using the Rudler carbene (Table 3, run 5-7).

When a two-fold excess of EtOH was added to the $MoOCl_4$-*n*-BuLi system, the activation enthalpy appreciably increased (Table 2, run 3). This implies that the coordination of monomer to the Mo carbene needs more energy because EtOH interacts with Mo carbene and stabilizes it. Further, the activation entropy assumes a positive value as in the case of other EtOH-containing systems (Table 3, run 2-4). These data means that the degree of freedom of the propagating chain end increase when acetylene coordinates to it. The following mechanism appears probable based on the above-stated results: EtOH coordinates to the vacant site of Mo carbene in the systems where EtOH is present, and hence EtOH must be removed for monomer coordination and the subsequent propagation. The removal of EtOH

Table 3. Activation Parameters for Propagation in the Polymerization of Various Acetylenes by Mo- and W-Based Catalysts

run	catalyst	monomer	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J/mol·K	reference
1	$MoOCl_4$–*n*-BuLi (1:1)	*o*-Me_3Si-phenylacetylene	43	–85	This work
2	$MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)	*o*-CF_3-phenylacetylene	87	58	This work
3	$MoOCl_4$–Et_3Al–EtOH (1:1:4)	*o*-CF_3-phenylacetylene	78	17	3b
4	$MoOCl_4$–Et_2Zn–EtOH (1:1:3)	*o*-CF_3-phenylacetylene	79	25	3c
5	Rudler carbene[a, b]	1-heptyne	70	–67	11a
6	Rudler carbene[a, b]	phenylacetylene	43	–147	11b
7	Rudler carbene[a, b]	*o*-Me_3Si-phenylacetylene	70	–66	11c

[a]



[b] Non-living system.

gives rise to both a large activation energy and a positive activation entropy. In other words, EtOH coordinates to the propagating end competitively with the monomer, and a two-fold excess of EtOH appears necessary to form a stabilized Mo species. As a similar examples, it has been reported that 2,4-lutidine, a Lewis base, and the monomer coordinate to the Mo carbene competitively in the polymerization of *o*-Me_3Si-phenylacetylene by a Schrock carbene [ld].

On the other hand, the activation parameters of the propagation reaction with $MoOCl_4$-*n*-BuLi-CF_3CH_2OH (1:1:0-4) were constant no matter whether CF_3CH_2OH was present or absent. Thus, it is concluded that CF_3CH_2OH in catalytic amounts does not interact with the Mo carbene.

Conclusion

In the present study, the role of catalyst components in $MoOCl_4$-cocatalyst-EtOH ternary living polymerization systems was investigated. On the basis of the results obtained, the roles of cocatalyst and EtOH are inferred as follows: The reaction of $MoOCl_4$ with a cocatalyst (e.g., *n*-Bu_4Sn) gives rise to transalkylation on the Mo atom and the subsequent α-H elimination of the alkyl group to form a carbene. EtOH as a third catalyst component seems to work so as to generate a certain amount of stabilized Mo carbene during catalyst aging. Further, EtOH coordinates to the propagating end competitively with the monomer in the propagation reaction.

Acknowledgment

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4. Schrock carbenes can polymerize 1-chloro-1-octyne and *t*-butylacetylene. However, the polymerizations are sluggish and non-living. This also means that Schrock carbenes are not useful for sterically crowded acetylenes. On the other hand, the polymerization of α,ω-diynes and ethynylferrocene by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:2) was too fast to control. This also supports that moderate steric hindrance of monomer is necessary to achieve living polymerization with

MoOCl$_4$-based catalysts.

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10. The major reason why the MoOCl$_4$-*n*-BuLi-ROH system instead of MoOCl$_4$-*n*-Bu$_4$Sn-ROH was chosen for kinetic study is that, whereas the polymerization by latter catalyst system is too fast to estimate k_p correctly in the temperature range of 0-30 °C, one can monitor the polymerization by the former catalyst accurately.
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