Polymerization of Aliphatic Disubstituted Acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH Catalyst: Formation of Polymers with Narrow MWDs and Confirmation of the Living Character

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ABSTRACT: The polymerization of aliphatic disubstituted acetylenes was examined with $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2) ternary catalyst in anisole at 0 °C. Various linear aliphatic disubstituted acetylenes such as 2-nonyne provided polymers with narrow molecular weight distributions (weight-average molecular weight/number-average molecular weight = 1.05–1.20). The living character of the polymerization was proven by both the time profile of the polymerization and the multistage polymerization of 2-nonyne. The initiation efficiency was about 3%, which is rather low. Although 5-dodecyne, which has a triple bond in a more inner part, polymerized more slowly than 2-nonyne, their living characters were hardly different. Diblock copolymers were synthesized by the sequential living polymerization of internal linear alkynes. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2697–2701, 2000

Keywords: living polymerization; metathesis polymerization; substituted acetylene; internal alkyne; molybdenum catalyst; block copolymer

INTRODUCTION

A variety of living polymerization systems using transition metal catalysts have been developed recently. Substituted acetylenes polymerize by metathesis and insertion mechanisms. The living polymerization of substituted acetylenes has been achieved with Schrock carbenes,[1–5] $MoOCl_4$-based ternary catalysts,[6–8] and Rh catalysts.[9,10]

We have found that fairly many substituted acetylenes (e.g., 1-chloro-1-alkynes,[11] *tert*-butylacetylene,[12] and various ortho-substituted phenylacetylenes[13]) polymerize in a living fashion in the presence of the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst in a toluene solution. Except for 1-chloro-1-alkynes, however, there have been no examples of disubstituted acetylenes that polymerize in a living fashion with $MoOCl_4$-based catalysts. Schrock et al.[14] achieved the living polymerization of 2-butyne by using a Ta carbene. This polymerization provides a polymer with low polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.05] at a quantitative initiation efficiency. However, no other monomers were found to undergo living polymerization with this catalyst. Schrock et al.'s Mo carbenes are also capable of the living polymerization of several monosubstituted acetylenes but no disubstituted ones.

Recently, it was found that the $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2) catalyst in conjunction with an anisole solvent accomplishes a very narrow molecular weight distribution (MWD; M_w/M_n = 1.02) and a fairly high initiation efficiency ([P*]/[Cat] ~ 40%) in the polymerization of [*o*-(trifluoromethyl)phenyl]acetylene.[15] Thus, anisole is

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Table I. Polymerization of Various Internal Alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2)[a]

Monomer	Conversion (%)	M_n[b]	M_w/M_n[b]	[P*]/[Cat] (%)
CH_3—C≡C—*n*-C_7H_{15}	100	38,000	1.15	3.6
CH_3—C≡C—*n*-C_6H_{13}	100	40,000	1.05	3.1
CH_3—C≡C—*n*-C_5H_{11}	100	36,000	1.08	3.1
CH_3—C≡C—*n*-C_3H_7	100	21,000	1.20	3.9
C_2H_5—C≡C—*n*-C_6H_{13}	100	36,000	1.08	3.1
n-C_3H_7—C≡C—*n*-C_6H_{13}	100	45,000	1.16	3.4
n-C_4H_9—C≡C—*n*-C_6H_{13}	100	50,000	1.18	3.4
CH_3—C≡C—$CH(CH_3)C_2H_5$	17	—	—	—
CH_3—C≡C—$C(CH_3)_3$	3	—	—	—

[a] Polymerized in anisole at 0 °C for 24 h. $[M]_0$ = 100 mM; $[MoOCl_4]$ = 10 mM.
[b] Determined by GPC with polystyrene calibration.

clearly preferable as a solvent to toluene, which was frequently used previously. Consequently, the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system may be able to increase the kinds of monomers polymerizable in a living fashion.

In this study, we investigated the polymerization of various internal alkynes with the $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole system. Eventually, it was found that 2-alkynes (e.g., 2-nonyne, 2-hexyne, 2-octyne, and 2-decyne) and other internal alkynes (e.g., 3-decyne, 4-undecyne, and 5-dodecyne) undergo living polymerization. Furthermore, diblock copolymers were synthesized by the sequential living polymerization of internal alkynes.

EXPERIMENTAL

Internal alkynes (Lancaster) such as 2-nonyne were distilled twice from CaH_2 before use. $MoOCl_4$ was used as received (Strem; purity > 99%). Et_3Al and *n*-BuLi were commercially obtained as solutions. *n*-Bu_4Sn and EtOH were distilled twice before use. Anisole as the polymerization solvent was washed twice with an aqueous NaOH solution, dried over $CaCl_2$, and distilled twice from Na under a nitrogen atmosphere.

The catalyst solution was prepared as follows: An anisole solution of $MoOCl_4$ was mixed with an anisole solution of *n*-Bu_4Sn, and the mixture was aged at room temperature for 15 min. An anisole solution of EtOH was further added to this $MoOCl_4$–*n*-Bu_4Sn solution, and the mixture was aged at room temperature for an additional 15 min. Polymerizations were initiated by the addition of a monomer solution to the catalyst solution. All the procedures were carried out under dry nitrogen. Unless otherwise specified, polymerizations were carried out in anisole at 0 °C, $[M]_0$ = 0.10 M, and $[MoOCl_4]$ = 10 mM. Polymerizations were quenched with a toluene/methanol mixture (volume ratio = 1/1). Polymer yields were determined by gravimetry.

The MWDs of the polymers were recorded on a gel permeation chromatograph (GPC; Jasco PU930; eluent = chloroform; Shodex K805, 804, and 803 polystyrene gel columns; refractive index detector). The M_n's and M_w's of the polymers were determined with polystyrene calibration. Initiation efficiencies ([P*]/[Cat]) were calculated from the yield and the degree of polymerization of the polymers.

RESULTS AND DISCUSSION

Polymerization of Various Internal Alkynes

The polymerizations of various aliphatic disubstituted acetylenes catalyzed by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2) were examined (Table I). All the linear alkynes were completely consumed under the conditions of Table I. The formed polymers possessed fairly narrow MWDs, suggesting living polymerization. However, the initiation efficiencies were about 3–4%, which is rather low. In contrast, 4-methyl-2-pentyne and 4,4-dimethyl-2-pentyne, which are branched internal alkynes, hardly polymerized, probably because of steric hindrance.

To clarify whether the polymerization of linear internal alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH is a living polymerization or not, the time profile of

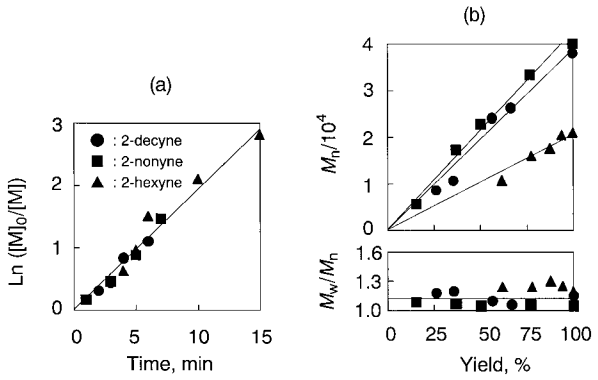

Figure 1. (a) First-order plots and (b) yield–M_n and yield–M_w/M_n plots for the polymerization of various 2-alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2; polymerized in anisole at 0 °C; $[M]_0$ = 100 mM, $[MoOCl_4]$ = 10 mM).

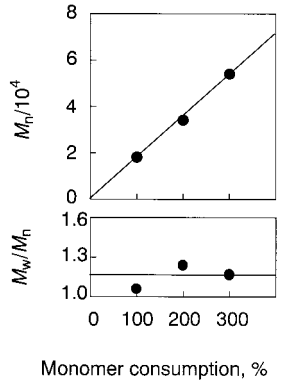

Figure 3. Multistage polymerization of 2-nonyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2; polymerized in anisole at 0 °C for 15 min each; $[M]_0$ = $[M]_{add}$ = 50 mM, $[MoOCl_4]$ = 10 mM).

the polymerization was examined. As seen in Figure 1(a), 2-alkynes such as 2-decyne, 2-nonyne, and 2-hexyne polymerized practically at the same rate regardless of the alkyl chain length (k_p = 9.21 $M^{-1}s^{-1}$). The monomers were completely consumed in 1 h. The first-order plots show good linear relationships. This indicates that the polymerization proceeds in the first order with respect to the monomer, whereas the concentration of the propagating species remains constant throughout the polymerization. Figure 1(b) plots M_n and M_w/M_n against the polymer yield. The M_n increases in direct proportion to the polymer yield with every monomer, whereas the polydispersity ratio remains as low as 1.05–1.25. Thus, one can conclude that 2-alkynes polymerize in a living fashion and behave similarly despite the alkyl chain length.

Figure 2 shows the results for the polymerizations of 3-decyne, 4-undecyne, and 5-dodecyne, in which one substituent is invariably an *n*-hexyl group and the other is ethyl, *n*-propyl, and *n*-butyl, respectively. As the smaller alkyl group in these monomers becomes longer, the rate of polymerization decreases [Fig. 2(a)]. This tendency holds even though 2-nonyne is included. This means that this catalyst exhibits high activity for internal alkynes that have a short alkyl group and a long one, which appears to be a common trend with Mo catalysts.[16,17] The rates of polymerization were as follows: k_p(3-decyne) = 21.0 × 10^{-2} $M^{-1}s^{-1}$, k_p(4-undecyne) = 6.94 × 10^{-2} $M^{-1}s^{-1}$, and k_p(5-dodecyne) = 5.59 × 10^{-2}

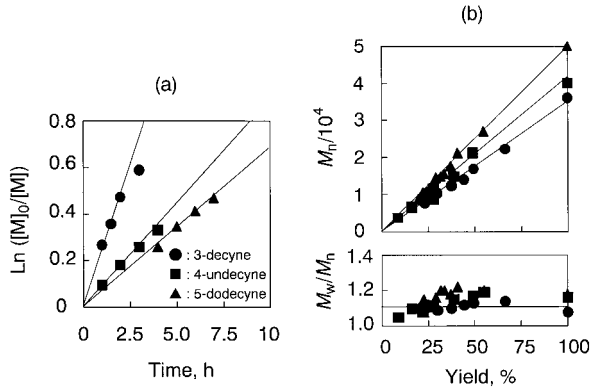

Figure 2. (a) First-order plots and (b) yield–M_n and yield–M_w/M_n plots for the polymerization of various internal alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2; polymerized in anisole at 0 °C; $[M]_0$ = 100 mM, $[MoOCl_4]$ = 10 mM).

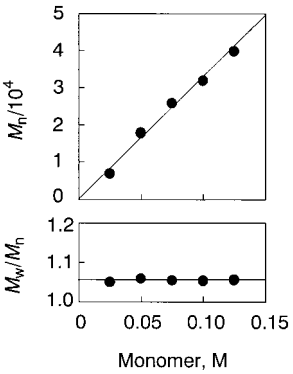

Figure 4. Effect of the initial monomer concentration on the polymerization of 2-nonyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2; polymerized in anisole at 0 °C for 1 h; $[MoOCl_4]$ = 10 mM; all the conversions were ~100%).

Table II. Polymerization of 2-Nonyne by $MoOCl_4$–cocatalyst-EtOH (1/1/x)[a]

Catalyst	Mole Ratio	M_n (10^4)[b]	M_w/M_n[b]	[P*]/[Cat] (%)
$MoOCl_4$–n-Bu_4Sn–EtOH	1/1/2	4.0	1.05	3.1
$MoOCl_4$–Et_3Al–EtOH	1/1/4	3.5	1.16	3.6
$MoOCl_4$–Et_2Zn–EtOH	1/1/3	13.0	1.10	1.0
$MoOCl_4$–n-BuLi	1/1	30.1	2.06	—

[a] Polymerized in anisole at 0 °C for 24 h. $[M]_0$ = 100 mM; $[MoOCl_4]$ = 10 mM. All the conversions were ~ 100%.
[b] Determined by GPC with polystyrene calibration.

$M^{-1}s^{-1}$. Figure 2(b) indicates the increase of the M_n proportional to the polymer yield as well as small dispersity ratios around 1.1–1.2. Thus, one can see that 3-, 4-, and 5-alkynes also polymerize in a living manner, although their polymerization rates are fairly different.

Detailed Examination of 2-Nonyne Polymerization

To further confirm the living character of 2-nonyne polymerization, a multistage polymerization was carried out by monomer feeds being supplied three times repeatedly (Fig. 3). Consequently, the M_n of the polymer increased in direct proportion to the polymer yield, whereas the polydispersity remained low. No dead polymer was formed at all, even after the third stage, indicating that this system involves a sufficiently stable living species.

Figure 4 shows the effect of the initial monomer concentration. In the range 0.025–0.125 M, 2-nonyne quantitatively produced polymers with a narrow MWD (M_w/M_n = 1.05), and the M_n increased in direct proportion to the initial monomer concentration. The narrow MWD supports a living character, and the relationship between the M_n and the initial monomer concentration indicates the constancy of the initiation efficiency.

To learn what $MoOCl_4$-based catalysts are effective, several alkylating agents were examined as cocatalysts (Table II). 2-Nonyne was completely consumed with n-Bu_4Sn, Et_3Al, Et_2Zn, and n-BuLi as cocatalysts. The former three cocatalysts provided polymers with low polydispersities (M_w/M_n 1.05–1.10), suggesting that living polymerizations proceeded. The initiation efficiencies with these cocatalysts were about 1–4%, which is rather small.

The effect of the EtOH concentration was investigated in the polymerization by $MoOCl_4$–n-Bu_4Sn–EtOH (1/1/0–3). Under the conditions in Figure 5, 2-nonyne was completely consumed in the entire range examined. In the absence of EtOH, the polymerization was finished within 1 h to provide a polymer with a high molecular weight ($M_n = 20 \times 10^4$) and a fairly narrow MWD (M_w/M_n =1.08). This means that this polymerization is probably a living system, but the initiation

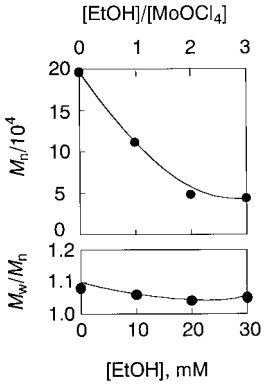

Figure 5. Effect of the EtOH concentration on the polymerization of 2-nonyne by $MoOCl_4$–n-Bu_4Sn–EtOH (1/1/2; polymerized in anisole at 0 °C for 1 h; $[M]_0$ = 100 mM, $[MoOCl_4]$ = 10 mM; all the conversions were ~100%).

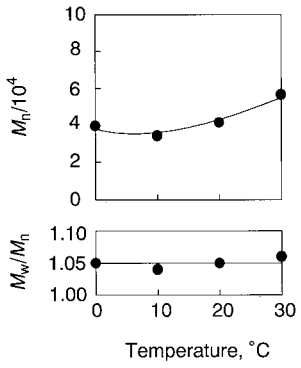

Figure 6. Effect of the temperature on the polymerization of 2-nonyne by $MoOCl_4$–n-Bu_4Sn–EtOH (1/1/2; polymerized in anisole for 1 h; $[M]_0$ = 100 mM, $[MoOCl_4]$ = 10 mM; all the conversions were ~100%).

Table III. Block Copolymerization of Various Internal Alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1/1/2)[a]

Monomer **1**[a]	Monomer **2**[a]	Temperature (°C)	Time (h)	M_n (10^4)[d]	M_w/M_n[d]
2-Nonyne	3-Decyne	0	0.25[b]/72[c]	3.3	1.31
2-Nonyne	4-Undecyne	0	0.25/72	3.2	1.13
2-Nonyne	5-Dodecyne	0	0.25/72	3.2	1.13
3-Decyne	2-Nonyne	30	6/0.25	Bimodal	—
4-Undecyne	2-Nonyne	30	6/0.25	Bimodal	—
5-Dodecyne	2-Nonyne	30	6/0.25	Bimodal	—

[a] Polymerized in anisole at 0 °C. $[M]_0$ = 50 mM, $[M]_{add}$ = 50 mM; $[MoOCl_4]$ = 10 mM. All the conversions were ~ 100%.
[b] The first-stage polymerization.
[c] The second-stage polymerization.
[d] Determined by GPC with polystyrene calibration.

efficiency is as low as 0.6%. With increasing EtOH concentration, the M_n of the polymer decreased progressively to approach 5×10^4 at [EtOH] = 20 mM, and the M_w/M_n also decreased slightly to become 1.05 at the same concentration. Thus, a catalyst composition of $MoOCl_4$/*n*-Bu_4Sn/EtOH = 1/1/2 (molar ratio) is favorable to achieve both high initiation efficiency and low polydispersity.

This polymerization proceeded quantitatively in the temperature range 0–30 °C under the standard conditions. As seen in Figure 6, the polydispersity ratio remained constant at 1.05 in the range 0–30 °C. However, the M_n somewhat decreased at 0 and 10 °C. Thus, 0 and 10 °C seem preferable as polymerization temperatures.

Block Copolymerization between Internal Alkynes

Block copolymerization between internal alkynes was examined (Table III). When 2-nonyne was polymerized in a living fashion and, subsequently, an internal alkyne (3-decyne, 4-undecyne, or 5-dodecyne) was added, diblock copolymers with relatively narrow MWDs (M_w/M_n ~ 1.1–1.3) were selectively obtained. In contrast, when the order of monomer addition was reversed, the final products showed bimodal GPC curves. Thus, it seems necessary to polymerize 2-nonyne, which is more reactive, at first and then a 3-, 4-, or 5-alkyne for the selective synthesis of block copolymers.

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