Living Polymerization of Substituted Acetylenes by a Novel Binary Catalyst, $MoOCl_4$−*n*-BuLi

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ABSTRACT: A novel $MoOCl_4$-based binary catalyst, $MoOCl_4$−*n*-BuLi, induced the living polymerization of *o*-CF_3-phenylacetylene. A catalyst composition of $MoOCl_4$:*n*-BuLi = 1:1 and anisole as polymerization solvent were favorable. The polydispersity ratio of the polymer was as small as 1.02; the initiator efficiency was no more than 1.5−2.5%. The living nature was confirmed by both multistage polymerization and time dependence of the polymerization. Ethanol in catalytic amounts decelerated the polymerization but hardly affected its living nature. *n*-Alkyllithiums were generally useful as second catalyst components. The polymerization proceeded in a living manner in the temperature range 0−30 °C. *o*-Me_3Si-phenylacetylene, *o*-*i*-Pr-phenylacetylene, and 1-chloro-1-octyne also polymerized in a living fashion; their polydispersity ratios were 1.03, 1.08, and 1.08, respectively.

Introduction

Recently, living polymerization is under intensive research in various polymerization processes. Living metathesis polymerization of cycloolefins has made great progress in the past decade, based on the development of novel well-defined catalysts such as titanacyclobutanes,[1] Schrock carbenes,[2] and ruthenium carbenes.[3] Substituted acetylenes polymerize by either metathesis or insertion mechanism. Living polymerizations of substituted acetylenes have also been achieved by using Schrock carbenes,[4−7] $MoOCl_4$-based ternary catalysts,[8−11] and rhodium complexes.[12]

We have found that the $MoOCl_4$−*n*-Bu_4Sn−EtOH catalyst effects living polymerization of a variety of substituted acetylenes; e.g., ortho-substituted phenylacetylenes (ortho substituent = Cl, Me, *i*-Pr, CF_3, Me_3Si, Me_3Ge, etc.), 1-chloro-1-alkynes, and *tert*-butylacetylene. The polydispersity ratio of the poly(1-chloro-1-octyne) formed is about 1.1−1.2.[8] *tert*-Butylacetylene affords a stereoregular living polymer.[9,10] Further, phenylacetylenes with *o*-CF_3 and *o*-Me_3Si groups give polymers having $M_w/M_n < 1.1$.[11] Recently, excellent living polymerization catalyst systems have been developed, which employ Et_3Al[13] and Et_2Zn[14] as second catalyst components (cocatalysts) and anisole as the polymerization solvent.

In the present study, we examined *n*-BuLi as cocatalyst to develop a new $MoOCl_4$-based living polymerization catalyst and studied in detail the polymerization using this catalyst. [(*o*-Trifluoromethyl)phenyl]acetylene (*o*-CF_3-phenylacetylene) and [(*o*-trimethylsilyl)phenyl]acetylene (*o*-Me_3Si-phenylacetylene) were mainly used as monomers. Anisole, which dissolves $MoOCl_4$ completely, was employed as a polymerization solvent.

Experimental Section

o-CF_3-phenylacetylene[15,16] and *o*-Me_3Si-phenylacetylene[17] were prepared with reference to the literature methods. $MoOCl_4$ (Strem), *n*-BuLi (Kanto Chemical; hexane solution, 1.60 M), and other alkyllithiums (Kanto Chemical or Aldrich) were commercially obtained and used without further purification. Anisole as 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). Toluene, another polymerization solvent, was washed with sulfuric acid (5%), aqueous sodium hydroxide solution (5%) and water, dried over anhydrous calcium chloride, and distilled twice from CaH_2 (purity >99.9% by GC). Other solvents were purified by the standard methods. Ethanol was distilled twice from $Mg(OEt)_2$ (purity >99.9% by GC) and stored as anisole solution.

All the procedures were carried out under dry nitrogen. Unless otherwise stated, catalyst solutions were prepared as follows: An anisole solution of $MoOCl_4$ and an anisole solution of *n*-BuLi were mixed, and the mixture was aged at room temperature for 20 min. If necessary, an anisole solution of ethanol was further added to the $MoOCl_4$−*n*-BuLi solution, and the mixture was aged at room temperature for an additional 15 min. Polymerizations were initiated by addition of monomer solution to the catalyst solution. Polymerizations were carried out at 30 °C in a prebaked Schlenk tube equipped with a three-way stopcock; the concentrations of $MoOCl_4$ and monomer were 10 mM and 0.10 M, respectively. Polymerizations were quenched with an anisole/methanol mixture (volume ratio 1:1). 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 polystyrene gel columns; RI detector). The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were determined by using a polystyrene calibration. The initiator efficiency ([P*]/[Cat]) was calculated from the yield and the degree of polymerization of a polymer.

Results and Discussion

Effects of Solvents and Ethanol. The effect of solvents on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi−EtOH (1:1:*x*) was examined (Figure 1). The polymerizations in anisole proceeded smoothly irrespective of ethanol concentration to yield polymers with very narrow MWD (M_w/M_n 1.02), which suggests living polymerization. It is especially worth noting that even the binary $MoOCl_4$−*n*-BuLi (1:1) catalyst accomplishes narrow MWD, if it is taken into account that all the prevous $MoOCl_4$-based catalysts required ethanol as the third component. The initiator efficiencies, i.e., the [P*]/[Cat] ratios, were 2−2.5% and were rather small.

When toluene was used as solvent, the polymerization by $MoOCl_4$−*n*-BuLi (1:1) proceeded rapidly, but the

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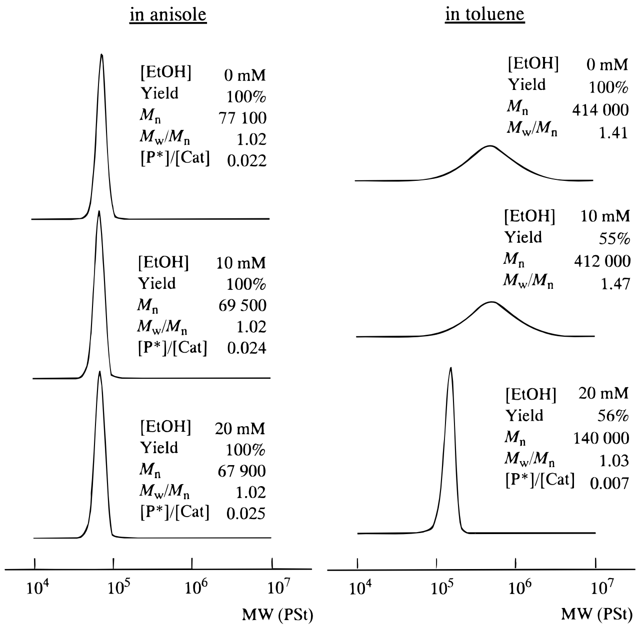

Figure 1. Effects of solvents and ethanol (third catalyst component) on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-BuLi–EtOH (1:1:*x*) (polymerized at 30 °C for 2 h; [$MoOCl_4$] = 10 mM; $[M]_0$ = 0.10 M).

MWD of the formed polymer was not narrow (Figure 1). Use of $MoOCl_4$–*n*-BuLi–EtOH (1:1:1) as catalyst remarkably reduced the polymerization rate and hardly changed the MWD. In contrast, the $MoOCl_4$–*n*-BuLi–EtOH (1:1:2) catalyst produced a polymer of fairly narrow MWD (M_w/M_n 1.03), though the MWD was rather irreproducible and the initiator efficiency was very low. In tetrahydrofuran as polymerization solvent, no polymer was obtained. The data using chlorobenzene as solvent were as follows: polymer yield 100%, M_n 17.3 × 10^4, M_w/M_n 1.41 with $MoOCl_4$–*n*-BuLi (1:1); polymer yield 100%, M_n 21.7 × 10^4, M_w/M_n 1.15 with $MoOCl_4$–*n*-BuLi–EtOH (1:1:2).

Thus it was proven that the binary system, $MoOCl_4$–*n*-BuLi (1:1), provides poly(*o*-CF_3-phenylacetylene) with a narrow MWD in anisole solution. Clearly, anisole is preferable to other solvents in the present polymerization. One of the reasons for this is that a catalytic amount of $MoOCl_4$ dissolves in anisole completely. Another reason is the weak basicity of the anisole. The catalyst systems, $MoOCl_4$–Et_3Al–EtOH[13] and $MoOCl_4$–Et_2Zn–EtOH,[14] required ethanol as the third catalyst component to achieve narrow MWD in anisole, whereas the present catalyst system did not. This is probably because Et_2AlCl and EtZnCl, which may react with molybdenum carbenes but will be decomposed in the presence of ethanol, are formed in the former systems while just a salt, LiCl, is formed in the latter system. In the ternary systems, another function of ethanol is to stabilize the propagating ends by coordination in the form of ethoxy group or ethanol itself. However, ethanol does not seem very necessary for this purpose in anisole solvent owing to its moderate basicity and, in turn, its solvation to and stabilization of the propagating end.

Effects of Organolithium Cocatalysts. The effect of *n*-BuLi concentration was examined in the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–*n*-BuLi (1:*x*) in anisole solution (Table 1). With $MoOCl_4$ alone, i.e., without *n*-BuLi, the polymerization was finished instantaneously to quantitatively give a polymer of M_n 9.06 × 10^4 and M_w/M_n 1.15. In contrast, as described above, $MoOCl_4$–*n*-BuLi (1:1) induced smooth polymerization to yield a polymer whose polydispersity ratio was very narrow (M_w/M_n 1.02). The $MoOCl_4$–*n*-BuLi (1:2) catalyst, however, broadened the MWD. Further, no polymer was formed in the presence of a 3-fold excess of *n*-BuLi. These results indicate that a mole ratio of $MoOCl_4$:*n*-BuLi = 1:1 is optimal.

Table 1. Effect of *n*-BuLi Concentration on the Polymerization of *o*-CF_3-Phenylacetylene by $MoOCl_4$–*n*-BuLi[a]

[*n*-BuLi], mM	[*n*-BuLi]/[$MoOCl_4$]	polymer yield, %	$M_n/10^4$	M_w/M_n
0	0	100	9.06	1.15
10	1	100	7.71	1.02
20	2	100	10.03	1.21
30	3	0		

[a] Polymerized in anisole at 30 °C for 1 h; [$MoOCl_4$] = 10 mM; $[M]_0$ = 0.10 M.

Table 2. Effect of Alkyllithiums on the Polymerization of *o*-CF_3-Phenylacetylene by $MoOCl_4$–Alkyllithium (1:1)[a]

alkyllithium	yield, %	$M_n/10^4$	M_w/M_n
none	100	9.06	1.15
MeLi	100	3.05	1.06
n-BuLi	100	7.17	1.02
n-HexLi	100	9.41	1.02
s-BuLi	70	28.4	~1.6
t-BuLi[b]	15	28.8	~1.6
PhLi	45	32.1	~1.6

[a] Polymerized in anisole at 30 °C for 1 h; [$MoOCl_4$] = 10 mM; $[M]_0$ = 0.10 M. [b] Polymerized for 5 h.

The reaction of $MoOCl_4$ with *n*-BuLi should produce LiCl. Hence the possibility was examined that lithium chloride might coordinate to the propagating end and stabilize it. The polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$–LiCl (1:1) was completed immediately to provide a polymer of M_n 19.6 × 10^4 and M_w/M_n 1.07; thus this polymerization is practically the same as that by $MoOCl_4$ alone. No monomer was consumed in the presence of a 20-fold excess of LiCl over $MoOCl_4$. The $MoOCl_4$–*n*-BuLi–LiCl (1:1:1) system yielded a living polymer of M_n 7.89 × 10^4 and M_w/M_n 1.03. These results indicate that LiCl hardly affects the present catalyst system.

Various alkyllithiums were examined as second catalyst components in the polymerizations of *o*-CF_3-phenylacetylene (Table 2). *o*-CF_3-Phenylacetylene was consumed in 20 min with $MoOCl_4$–MeLi (1:1). As compared with the $MoOCl_4$–*n*-BuLi (1:1) system, the initiator efficiency increased but the MWD broadened slightly. *n*-Hexyllithium gave essentially the same result as that of *n*-butyllithium. In contrast, *s*-BuLi, *t*-BuLi, and PhLi made the polymerization sluggish and the MWD rather broad. These results suggest only that *n*-alkyllithiums are useful as cocatalysts of the $MoOCl_4$-based binary systems.

Proof of Living Polymerization. Figure 2 shows the result of so-called multistage polymerization. Monomer feeds were supplied twice repeatedly. The M_n of the polymer increased in direct proportion to the polymer yield no matter whether ethanol was present or not. Meanwhile, the polydispersity ratios remained 1.05 or smaller. This clearly indicates that these polymerizations using $MoOCl_4$–*n*-BuLi (1:1) and $MoOCl_4$–*n*-BuLi–EtOH (1:1:2) are both living polymerizations.

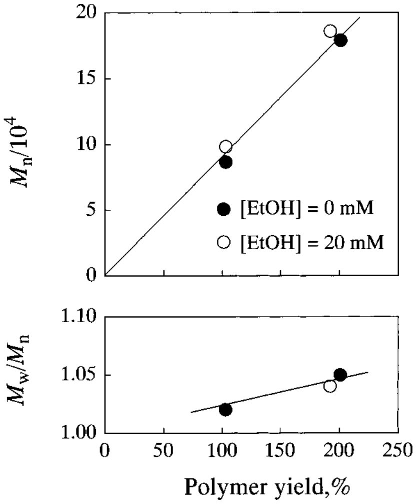

Figure 2. Multistage polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi (1:1) (polymerized in anisole at 30 °C; $[MoOCl_4]$ = 10 mM; $[M]_0 = [M]_{added}$ = 0.10 M).

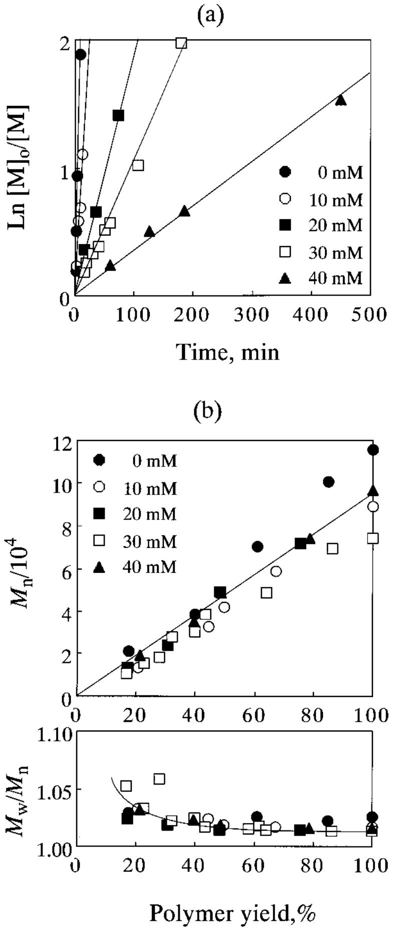

Figure 3. Effect of ethanol concentration on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi−EtOH (1:1:*x*); (a) first-order plots, (b) yield vs M_n and vs M_w/M_n plots (polymerized in anisole at 30 °C; $[MoOCl_4]$ = 10 mM, $[M]_0$ = 0.10 M).

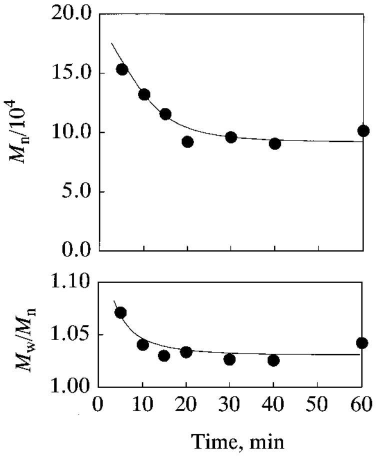

Figure 4. Effect of catalyst aging time on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi (1:1) (polymerized in anisole at 30 °C for 30 min; $[MoOCl_4]$ = 10 mM; $[M]_0$ = 0.10 M; all yields are ~100%).

Figure 3a shows first-order plots with respect to monomer concentration in a range of ethanol concentration, 0−40 mM. While the polymerization rate sharply decreases with increasing ethanol concentration, logarithmic $[M]_0/[M]$ increases in direct proportion to the polymerization time irrespective of ethanol concentration. This indicates that the polymerization is first order with respect to monomer, while the concentration of the propagating species remains constant throughout the polymerizations. As seen in Figure 3b, the plots of M_n vs polymer yield give a single straight line passing through the origin. This also confirms that the present system is a living polymerization system irrespective of the presence and absence of ethanol. The initiator efficiency determined from the slope of this line was 1.5%. The M_w/M_n diminishes to 1.02 at high polymer yields. Thus, it turns out that ethanol hardly affects the living nature of polymerization but just deceleretes the polymerization.

The initiator efficiencies for other polymerization systems of *o*-CF_3-phenylacetylene by $MoOCl_4$-based catalysts in anisole are as follows: $MoOCl_4$−*n*-Bu_4Sn−EtOH (1:1:2), ~40%;[18] $MoOCl_4$−Et_3Al−EtOH (1:1:4), ~20%;[13] $MoOCl_4$−Et_2Zn−EtOH (1:1:3) ~8%.[14] Thus, the initiator efficiency of $MoOCl_4$−*n*-BuLi (1:1) (1.5−2.5%) is apparently smaller than those of other systems. The reason for this is not evident at the moment, because the mechanism of the initiation reaction has not completely been elucidated. It can be said that the initiator efficiency depends on several factors such as the facility of the Mo carbene formation from $MoOCl_4$ and cocatalyst, and the stability and reactivity of the generated Mo carbene.

Effects of Reaction Conditions. The effect of catalyst aging time was examined in the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi (1:1) (Figure 4). Catalyst aging was carried out at room temperature. The initiator efficiency increased and the polydispersity ratio approached unity when the aging time was 20 min or longer. The aging at 0 °C resulted in smaller initiator efficiencies. Thus the aging of catalyst was usually carried out for 20 min at room temperature. In the case of $MoOCl_4$−*n*-BuLi−EtOH (1:1:2), a most favorable result was obtained when the catalyst solution was aged for 15 min at room temperature after addition of ethanol to the above-stated $MoOCl_4$−*n*-BuLi solution.

Figure 5 shows the effect of initial monomer concentration on the polymerization of *o*-CF_3-phenylacetylene by $MoOCl_4$−*n*-BuLi (1:1). In the range 0.01−0.20 M, *o*-CF_3-phenylacetylene quantitatively produced polymers with narrow MWD and the M_n increased in direct proportion to the initial monomer concentration. The

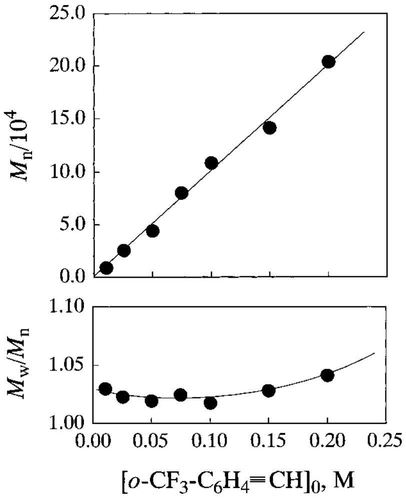

Figure 5. Effect of initial monomer concentration on the polymerization of o-CF$_3$-phenylacetylene by MoOCl$_4$−n-BuLi (1:1) (polymerized in anisole at 30 °C for 1 h; [MoOCl$_4$] = 10 mM; all yields are ~100%).

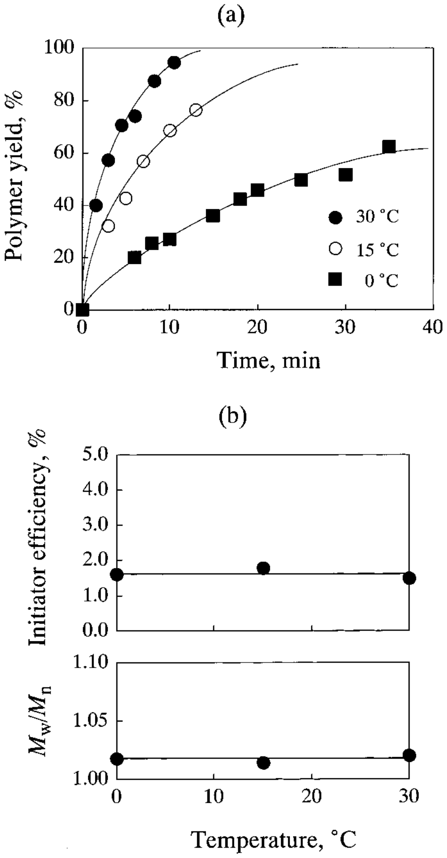

Figure 6. Effects of temperature on the polymerization of o-CF$_3$-phenylacetylene by MoOCl$_4$−n-BuLi (1:1): (a) time vs polymer yield curves; (b) temperature vs initiator efficiency and vs M_w/M_n plots (polymerized in anisole; [MoOCl$_4$] = 10 mM; [M]$_0$ = 0.10 M; all yields are ~100% in part b).

initiator efficiency obtained from the plot is 1.5%. These results also support the conclusion that this polymerization is a living polymerization.

Figure 6a shows the effect of polymerization temperature on the rate of polymerization of o-CF$_3$-phenylacetylene by MoOCl$_4$−n-BuLi (1:1). The polymerization was finished within 20 min at 30 °C, while it took about 90 min at 0 °C to complete the polymerization. The effects of temperature on the initiator efficiency and M_w/M_n are shown in Figure 6b. The initiator efficiency was 1.5% and the M_w/M_n of the formed polymer was 1.02 independent of polymerization temperature. Thus, the livingness was preserved in the temperature range 0−30 °C.

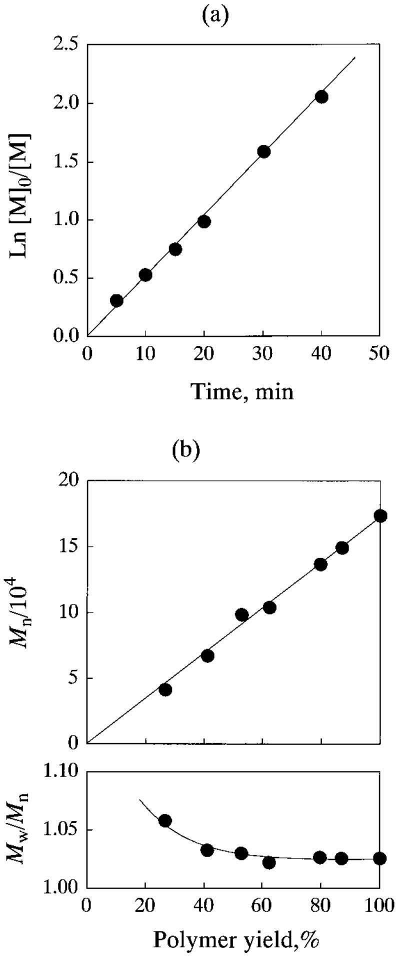

Figure 7. Polymerization of o-Me$_3$Si-phenylacetylene by MoOCl$_4$−n-BuLi (1:1): (a) first-order plot; (b) yield vs M_n and vs M_w/M_n plots (polymerized in anisole at 30 °C; [MoOCl$_4$] = 10 mM; [M]$_0$ = 0.10 M).

Polymerization of Other Monomers. Polymerizations of other acetylene monomers by MoOCl$_4$−n-BuLi (1:1) were examined. o-Me$_3$Si-phenylacetylene polymerized in a living fashion, a time profile which is depicted in Figure 7. The first-order plot with respect to monomer concentration is just linear. The plot of M_n vs polymer yield gives a straight line passing through the origin, from which the initiator efficiency is determined to be 1.0%. The M_w/M_n is as small as 1.03 at high polymer yields.

o-i-Pr-Phenylacetylene, which has a medium-sized ortho-substituent, also gave a living polymer; i.e., when it was polymerized for 1 h under the standard conditions, monomer conversion 100%, M_n 11.4 × 10^4, and M_w/M_n 1.08. In contrast, o-F-phenylacetylene, whose ortho-substituent is sterically less demanding, did not polymerize in a living fashion: polymerized for 4 h, monomer conversion 25%, M_n 4.0 × 10^3, and M_w/M_n 1.34. The data for phenylacetylene are as follows: polymerized for 4 h, monomer conversion 40%, M_n 3.6 × 10^3, and M_w/M_n 1.38. 1-Chloro-1-octyne, a disubstituted acetylene, polymerized smoothly with this catalyst to give a living polymer: polymerized for 5 min, monomer conversion 100%, M_n 14.6 × 10^4, and M_w/M_n 1.08. Such a tendency regarding the monomers that undergo living polymerization with $MoOCl_4$–n-BuLi (1:1) is similar to those for previous systems such as $MoOCl_4$–n-Bu_4Sn–EtOH, $MoOCl_4$–Et_3Al–EtOH, and $MoOCl_4$–Et_2Zn–EtOH.

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