Living Polymerization of [*o*-(Trifluoromethyl)phenyl]acetylene by $WOCl_4$-Based Catalysts Such as $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1)

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ABSTRACT: A novel $WOCl_4$-based ternary catalyst, $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH, induced the living polymerization of [*o*-(trifluoromethyl)phenyl]acetylene. A catalyst composition of $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH = 1:1:1 was suitable, and sterically crowded alcohols such as *t*-BuOH were favorable as the third catalyst components. The polydispersity ratio of the polymer formed in anisole at 30 °C was as small as 1.04, and the initiation efficiency was no more than about 2%. The living nature of the polymerization was confirmed by the dependence of polymer molecular weight on conversion. Further, two $WOCl_4$-based binary systems, $WOCl_4$−*n*-BuLi (1:1−2) and $WOCl_4$−EtMgBr (1:1), were also useful as living polymerization catalysts. The polydispersity ratio and the initiation efficiency for the former system (W:Li = 1:1) were 1.08 and 0.9%, respectively, and those for the latter were 1.11 and 5%. These are the first examples of W-based catalysts effective for the living polymerization of substituted acetylenes.

Introduction

In recent years, there has been significant progress in the development of transition-metal catalysts with well-defined structures, such as metallocene catalysts, nonmetallocene catalysts, and metal carbenes, which has enabled achievement of living polymerization of various monomers. Thus, the following examples are known in the polymerization of ethylene and α-olefins by early-transition-metal catalysts: the formation of polyethylene with very low polydispersity by use of diene complexes of Nb and Ta,[1] living polymerization of 1-alkenes by chelating diamide complexes of Ti,[2] and living polymerization of 1-hexene by a Zr complex containing a tridentate diamido ligand.[3] Recently, polymerization of olefins by late-transition-metal catalysts (Ni,[4,5] Pd,[4] Fe,[6] and Co[6]) has gathered much attention, and reportedly, Ni−diimine complexes induce the living polymerization of propylene.[4] Further, Ni and Pd complexes work as effective catalysts for the living polymerization of 1,3-butadiene, allenes, and isonitriles,[7] and certain Pd complexes accomplish the addition-type living polymerization of cycloolefins.[8] Living metathesis polymerization of various cycloolefins by Schrock carbenes[9] and Ru carbenes[10] is now well-known.

Living polymerization of substituted acetylenes has been accomplished by the use of Schrock carbenes, $MoOCl_4$-based catalysts, and Rh complexes. Schrock and co-workers have achieved excellent living polymerization of ethynylferrocene, α,ω-diynes, and ortho-substituted phenylacetylenes by using imido alkylidene complexes, which are typical Schrock carbenes.[11] Further, polymerization of phenylacetylenes with a mesogenic group[12] and terminal aliphatic acetylenes[13] was investigated by use of Mo imido alkylidene complexes; the former monomer undergoes living polymerization. A Ta carbene, another Schrock carbene, polymerizes 2-butyne in a living manner.[14] Several Rh catalysts polymerize phenylacetylene in a living manner to give stereoregular (cis−transoidal) living polymers.[15] Thus far, we have found that the $MoOCl_4$-cocatalyst-EtOH systems[16] (cocatalysts: *n*-Bu_4Sn, Et_3Al, Et_2Zn, and *n*-BuLi) effect living polymerization of various substituted acetylenes such as ortho-substituted phenylacetylenes, 1-chloro-1-alkynes, *tert*-butylacetylene, internal aliphatic acetylenes, and internal diacetylenes.[17] The propagating species in these systems are assumed to be Mo carbenes formed from $MoOCl_4$ and cocatalysts, and propagation proceeds by a metathesis mechanism.

Among group 6 transition-metal catalysts, both Mo[9a−d] and W[9c,e] carbenes of the Schrock type are known to induce the living ring-opening metathesis polymerization of cycloolefins. On the other hand, living metathesis polymerization of substituted acetylenes has been accomplished only by Mo-based systems, i.e., Schrock-type Mo carbenes[11,12] and $MoOCl_4$-based catalysts.[16] Thus, the aim of the present study is to develop W catalysts that enable the living polymerization of substituted acetylenes. We examined living polymerization of [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3-phenylacetylene) by using various $WOCl_4$-based systems. Eventually, novel W-based living polymerization catalysts, such as $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH, $WOCl_4$−*n*-BuLi, and $WOCl_4$−EtMgBr, were developed, and the features of the living polymerization systems thereby were revealed.

Experimental Section

o-CF_3−Phenylacetylene was prepared from 2-iodobenzotrifluoride and 2-methyl-3-butyn-2-ol with reference to the literature[18] and distilled twice from CaH_2 at reduced pressure [purity >99.9% by gas chromatography (GC)]. $WOCl_4$ (Fluka) and several organometallic reagents (*n*-BuLi, *s*-BuLi, EtMgBr, Et_3Al, Et_2Zn, and Et_3B) (Kanto Chemical) were used without further purification. *n*-Bu_4Sn and *n*-Bu_4Ge were distilled twice from CaH_2 at reduced pressure before use. Ph_4Sn was purified by recrystallization from methanol. 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). *tert*-Butyl alcohol (*t*-BuOH) was distilled twice from sodium *tert*-butoxide (purity >99.9% by GC) and stored as an anisole solution. Other alcohols were purified by the conventional methods.

All of the procedures of catalyst preparation and polymerization were carried out under dry nitrogen. Unless otherwise stated, catalyst solutions were prepared as follows: First,

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$WOCl_4$ (orange powder) was dissolved in anisole to give a black solution. This anisole solution of $WOCl_4$ was mixed with an anisole solution of *n*-Bu_4Sn, and the mixture (black solution) was aged at room temperature for 15 min. Then, an anisole solution of *t*-BuOH was further added to the $WOCl_4$−*n*-Bu_4-Sn solution, which turned dark-green. The mixture was aged at room temperature for an additional 15 min to eventually become a bluish-purple solution. Polymerizations were carried out in a prebaked Schlenk tube equipped with a three-way stopcock usually at 30 °C; the concentrations of $WOCl_4$ and monomer were 10 mM and 0.10 M, respectively. 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 the 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*]/[W]; P* is the propagating species; W is $WOCl_4$ or WCl_6) were calculated from the monomer conversion and the degree of polymerization (based on GPC) of the polymers.

Results and Discussion

Development of the $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH System. In the conventional Mo-based ternary systems, $MoOCl_4$ is preferable to $MoCl_5$ as the main catalyst from the viewpoint of living polymerization.[19] The reason for this preference might be the low acidity and better solubility of $MoOCl_4$ due to the oxo ligand. We employed both $WOCl_4$ and WCl_6 as the main catalysts at first and examined the polymerization of *o*-CF_3-phenylacetylene in an anisole solution (Figure 1). The MWD curves of the poly(*o*-CF_3-phenylacetylene)s formed with $WOCl_4$-based catalysts are shown in Figure 1a. The monomer was not consumed at all with $WOCl_4$ alone. In the presence of an *n*-Bu_4Sn cocatalyst equivalent to $WOCl_4$, polymerization proceeded virtually instantaneously to give a polymer having a relatively narrow MWD (M_w/M_n ∼1.3). When an equivalent amount of *t*-BuOH was further added to the $WOCl_4$−*n*-Bu_4Sn (1:1) system, polymerization proceeded slower, and quite interestingly, the polydispersity ratio (M_w/M_n) of this polymer became as small as 1.04. This suggests living polymerization. Neither $WOCl_4$−*t*-BuOH (1:1) nor $WOCl_4$−*t*-BuOH−*n*-Bu_4Sn (1:1:1; the order of addition is opposite to the above system) was effective, suggesting that *t*-BuOH reacts with $WOCl_4$ to deactivate it. When WCl_6, which possesses stronger Lewis acidity, was used as the main catalyst, the polymers obtained did not show narrow MWDs (Figure 1b). Thus, it is concluded that only the $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH system accomplishes narrow MWD, among these six W-based catalysts.

Several solvents were examined in an attempt to enhance the living nature of the $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH system. In toluene and chlorobenzene, which are often used in the metathesis polymerization by Mo and W catalysts, polymerization proceeded very slowly with long induction periods to end up with the formation of polymers possessing high molecular weights and broad MWDs (M_n ∼1 000 000, M_w/M_n ∼ 2.0). In contrast, when anisole was employed, the resulting polymer exhibited a quite narrow MWD (M_w/M_n ∼ 1.04). No monomer was consumed in diethyl ether, *tert*-butyl methyl ether, or 1,2-dimethoxyethane. Thus, one can see that anisole is the most favorable solvent for the present living polymerization. Probably anisole plays two roles to achieve excellent polymerization; one is that it dissolves $WOCl_4$ completely, and the other is that it weakens Lewis acidity of $WOCl_4$ by coordination or solvation to stabilize it.

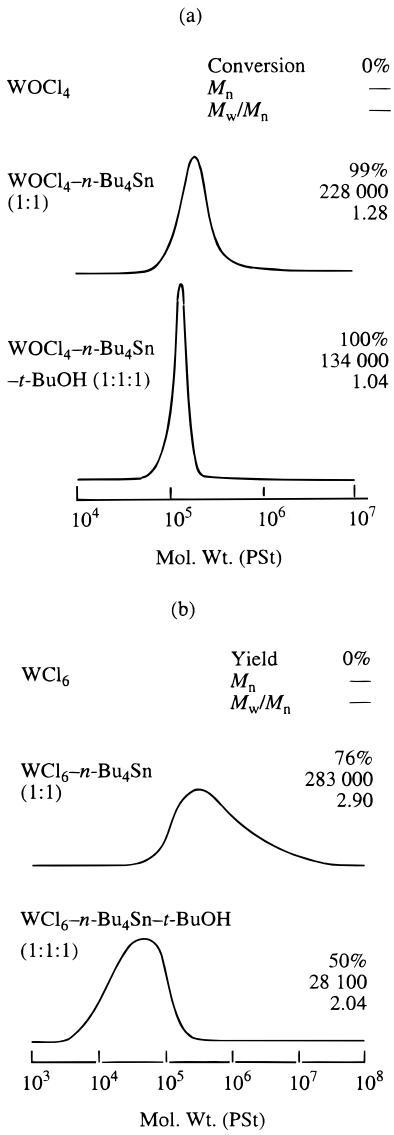

Figure 1. MWD curves of poly(*o*-CF_3-phenylacetylene)s formed with (a) $WOCl_4$- and (b) WCl_6-based catalysts (polymerized in anisole at 30 °C for 5 h; [Cat] = 10 mM, $[M]_0$ = 0.10 M).

Table 1. Effect of Alcohols as Third Catalyst Component on the Polymerization of *o*-CF_3-Phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−alcohol (1:1:1)[a]

alcohol	M_n	M_w/M_n	[P*]/[W], %
MeOH	101 000	1.21	1.7
EtOH	101 000	1.17	1.7
i-PrOH	136 000	1.06	1.3
t-BuOH	134 000	1.04	1.3
PhOH	103 000	1.23	1.7
CF_3CH_2OH	105 000	1.33	1.6

[a] Polymerized in anisole at 30 °C for 1 h; [$WOCl_4$] = 10 mM, and $[M]_0$ = 0.10 M; all monomer conversions were ∼100%.

Table 1 shows the effects of alcohols as the third catalyst components. In the case of $MoOCl_4$-based ternary systems, sterically uncrowded, relatively basic alcohols such as MeOH and EtOH are useful as the third catalyst components, whereas other types of alcohols such as *t*-BuOH, PhOH, and CF_3CH_2OH are

Table 2. Effect of Catalyst Composition on the Polymerization of *o*-CF_3-Phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:*x*:*y*)[a]

W:Sn:ROH	polym. time h	conversion %	M_n	M_w/M_n	[P*]/[W] %
1:1:1	2	100	105 000	1.05	1.6
1:2:1	2	100	104 000	1.06	1.6
1:3:1	2	99	98 300	1.09	1.7
1:4:1	2	92	95 700	1.11	1.6
1:1:2	24	91	145 000	1.16	1.1
1:1:3	24	17[b]	40 000	1.56	

[a] Polymerized in anisole at 30 °C; $[WOCl_4] = 10$ mM, and $[M]_0 = 0.10$ M. [b] The major product was cyclotrimer.

not.[19,20] In contrast, the $WOCl_4$−*n*-Bu_4Sn−alcohol system gave different results; i.e., MeOH and EtOH yielded polymers with rather broad MWDs ($M_w/M_n \sim 1.2$), whereas bulkier alcohols such as *t*-BuOH and *i*-PrOH achieved much narrower MWDs where $M_w/M_n = 1.04$−1.06. On the other hand, PhOH and CF_3CH_2OH, slightly acidic alcohols, were hardly effective. The following speculation is possible: Although relatively basic alcohols, both unbulky and bulky ones, can coordinate to the W species, only the W complexes formed with bulky alcohols might be both stable and active simultaneously. This is not the case with the Mo systems, where bulky alcohols cannot easily form complexes with Mo whose atomic radius is smaller than that of W.

The composition of the $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH catalyst was examined (Table 2). To 4-fold excess amounts of *n*-Bu_4Sn, 1 equiv showed virtually the same catalytic function to yield polymers with very narrow MWDs ($M_w/M_n \sim 1.05$−1.11). This suggests that 1 equiv of *n*-Bu_4Sn is sufficient for the alkylation and carbene formation of $WOCl_4$. On the other hand, excessive *t*-BuOH exhibited adverse effects. For example, the polymerization by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:3) was very sluggish and yielded not only a polymer with broad MWD but also a large amount of cyclotrimers. Thus, it was concluded that a composition of $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH = 1:1:1 is preferable, and hence, this system was examined in more detail below.

On the Living Nature of the Polymerization by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH. To confirm the livingness of the polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1), its time profile was examined (Figure 2). The polymerization was too fast at 30 °C for the monomer consumption to be monitored, and so it was carried out at 0 °C. Figure 2a shows the first-order plot with respect to monomer concentration. Here, logarithmic $[M]_0/[M]$ increases in direct proportion to the polymerization time, indicating that the polymerization is first-order with respect to the monomer, whereas the concentration of the propagating species remains constant throughout the polymerization. As seen in Figure 2b, the plot of M_n versus monomer conversion gives a straight line passing through the origin, and the M_w/M_n remains as small as around 1.04. This proves that the present polymerization is a living system.

The initiation efficiency determined from the slope of Figure 2b was 2.4%, and the values determined independently and shown in Tables 1 and 2 are 1.1−1.7%. These initiation efficiencies of around 2% are much smaller than the value of 40% for the $MoOCl_4$−*n*-Bu_4-Sn-EtOH (1:1:1) system.[20] The low initiation efficiency is probably attributable to both difficulty in the formation of the initiating metal carbene species and their

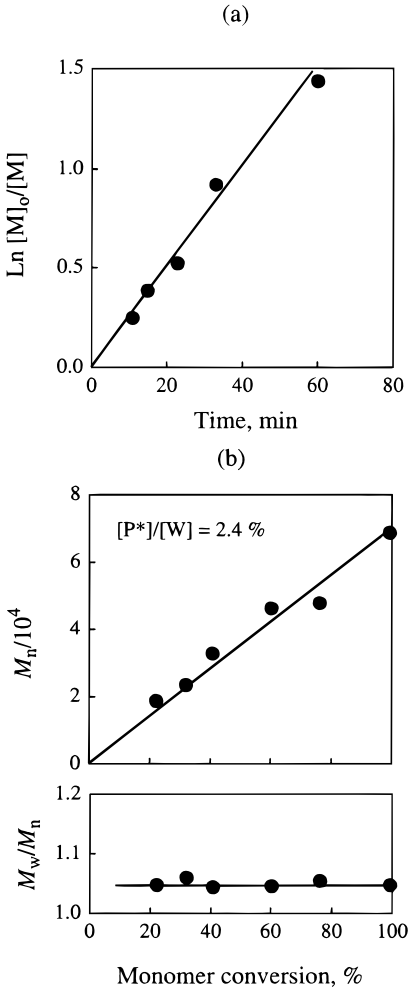

Figure 2. Polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1) (a) first-order plot and (b) monomer conversion vs M_n and M_w/M_n plots (polymerized in anisole at 0 °C; $[WOCl_4] = 10$ mM, $[M]_0 = 0.10$ M).

instability. However, it is rather useful to prepare high-molecular-weight living polymers and block copolymers from the synthetic viewpoint. The propagation rate constant (k_p) determined using the initiation efficiency was 1.9 M^{-1} s^{-1} at 0 °C. This k_p value is similar to 1.4 M^{-1} s^{-1} for $MoOCl_4$−*n*-Bu_4Sn−EtOH (1:1:1).[20]

To know the stability of the propagating species, the so-called multistage polymerization was carried out. That is, the supply of the *o*-CF_3-phenylacetylene monomer was repeated three times to the completely polymerized system at intervals of 2 h. When the second and third monomer feeds were consumed, the polydispersity ratios of the polymers remained below 1.10, and the polymer molecular weight increased progressively. The plot of monomer conversion vs M_n, however, gave a straight line which did not pass the origin but which possessed a positive intercept; this suggests that the living polymer is gradually deactivated during the multistage polymerization. This result contrasts with the $MoOCl_4$-based systems where multistage living polymerization of *o*-CF_3-phenylacetylene perfectly holds and where the lifetime of the living polymer is about 1 day or longer.[20]

The mechanism of the formation of the initiating species and the structure of the propagating species are speculated to be as follows: Reaction of $WOCl_4$ with *n*-Bu_4Sn will generate a very active metal carbene,

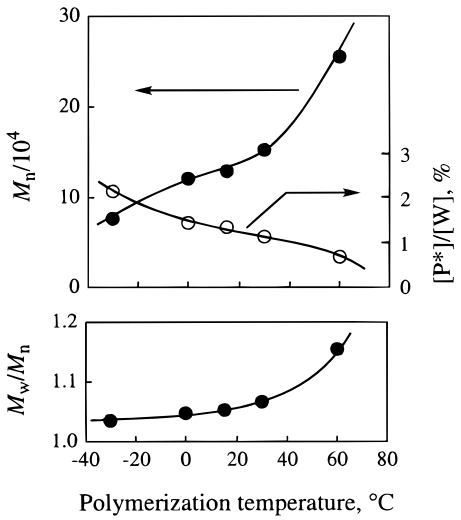

Figure 3. Effect of polymerization temperature on the polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1) (polymerized in anisole for 18 h (for 7 days at −30 °C; $[WOCl_4]$ = 10 mM, and $[M]_0$ = 0.10 M; all monomer conversions were 100%).

n-$C_3H_7CH{=}WOCl_2$, according to the literature.[21] This metal carbene should be stabilized by *t*-BuOH through either exchange of Cl with O-*t*-Bu or weak coordination of *t*-BuOH itself; it is not clear at the moment which structure is correct. This stabilized metal carbene appears to induce the present living polymerization. No information about the geometric structure of the polymer has been obtained by NMR spectroscopies.

Effects of Reaction Conditions. The effect of polymerization temperature was studied in the polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1) (Figure 3). The polymerization was finished instantaneously at 60 °C, whereas it required about 7 days at −30 °C to complete the polymerization. With lowering in the polymerization temperature, the polymer molecular weight decreased; i.e., the initiation efficiency increased, and the MWD narrowed. This suggests that the initiating and propagating species are more stable at low temperatures.

The effect of initial monomer concentration ($[M]_0$) was examined (Figure 4). As seen in Figure 4, the M_n did not increase in proportion to $[M]_0$, but the initiation efficiency increased with increasing amount of monomer feed. It is hence assumed that the initiation reaction in this system is an equilibrium reaction depending on the concentrations of both the initiating species and the monomer. In the $MoOCl_4$-based systems, on the other hand, the M_n increases in direct proportion to $[M]_0$, indicating that a certain amount of the Mo-based initiating species forms during the catalyst aging time and then it reacts with the monomer quantitatively.[20]

Effects of Other Organometallic Cocatalysts. In the case of the $MoOCl_4$-based living polymerization catalysts, not only *n*-Bu_4Sn but also Et_3Al,[16b] Et_2Zn,[16c] and *n*-BuLi[16d] work as effective cocatalysts, whereas Ph_4Sn, Et_3B, EtMgBr, and *n*-Bu_4Ge are ineffective.[16a] This suggests that the effective cocatalysts must possess strong alkylating ability. Further, the initiation efficiency in the Mo systems varies in a wide range of 2−40%, depending on the kind of cocatalyst. Thus, these organometallics were examined as cocatalysts in an attempt to develop other $WOCl_4$-based catalysts. Unless otherwise stated, polymerizations were carried out

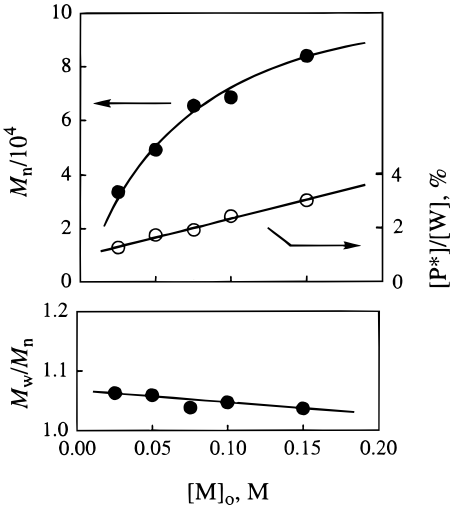

Figure 4. Effect of initial monomer concentration on the polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-Bu_4Sn−*t*-BuOH (1:1:1) (polymerized in anisole at 30 °C for 1 h; $[WOCl_4]$ = 10 mM; all monomer conversions were 100%).

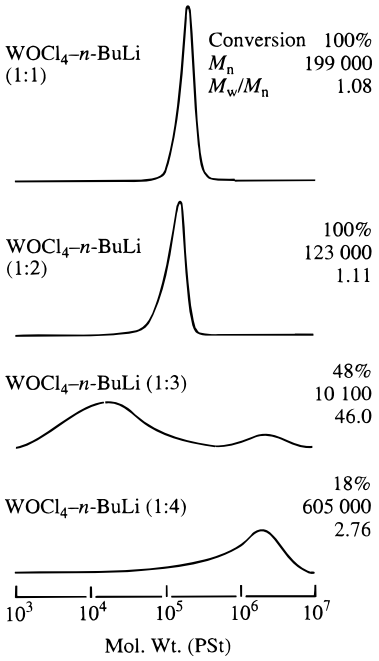

Figure 5. Effect of *n*-BuLi concentration on the polymerization of *o*-CF_3-phenylacetylene by $WOCl_4$−*n*-BuLi (1:*x*) (polymerized in anisole at 30 °C for 48 h; $[WOCl_4]$ = 10 mM, and $[M]_0$ = 0.10 M).

under the following conditions: in anisole, 30 °C, 24 h, $[WOCl_4]$ = 10 mM, and $[M]_0$ = 0.10 M. Consequently, use of *n*-BuLi and EtMgBr as cocatalysts in addition to *n*-Bu_4Sn provided narrow MWD, whereas none of Et_3Al, Et_2Zn, Ph_4Sn, Et_3B, and *n*-Bu_4Ge was useful. Successful examples are detailed below.

n-BuLi provides a Mo-based binary living polymerization catalyst, $MoOCl_4$−*n*-BuLi (1:1).[16d] Figure 5 shows the MWD curves of the polymers obtained with the $WOCl_4$−*n*-BuLi systems. The polymerization by $WOCl_4$−*n*-BuLi (1:1) proceeded smoothly to yield a polymer with low polydispersity. The living nature of this system was verified by monitoring the time profile of the polymerization. The initiation efficiency was 0.9% and very low. A 1:2 mixture of $WOCl_4$ and *n*-BuLi formed a polymer having somewhat broader MWD. In contrast, when a 3-fold excess of *n*-BuLi or more was employed, the

Table 3. Effect of Catalyst Composition on the Polymerization of *o*-CF_3-Phenylacetylene by $WOCl_4$−*n*-BuLi−*t*-BuOH (1:*x*:*y*)[a]

W:Li:ROH	M_n	M_w/M_n	[P*]/[W], %
1:1:0	199 000	1.08	0.9
1:1:1	200 000	1.13	0.9
1:1:2	236 000	1.14	0.7
1:2:0	124 000	1.11	1.4
1:2:1	209 000	1.14	0.8
1:2:2	250 000	1.12	0.7

[a] Polymerized in anisole at 30 °C for 24 h; $[WOCl_4] = 10$ mM, $[M]_0 = 0.10$ M; all conversions were 100%.

Table 4. Effect of Catalyst Composition on the Polymerization of *o*-CF_3-Phenylacetylene by $WOCl_4$−EtMgBr−*t*-BuOH (1:*x*:*y*)[a]

W:Mg:ROH	conversion, %	M_n	M_w/M_n	[P*]/[W], %
1:1:0	17	8 100	1.11	3.6
1:1:0[b]	56	23 300	1.13	4.1
1:1:0[c]	100	30 300	1.22	5.6
1:2:0	71	21 300	4.56	
1:3:0	56	23 700	2.00	
1:1:1	21	10 400	1.58	
1:2:1	59	27 600	1.76	

[a] Polymerized in anisole at 30 °C for 48 h; $[WOCl_4] = 10$ mM, and $[M]_0 = 0.10$ M. [b] Polymerized for 14 days. [c] Polymerized at 50 °C for 14 days.

polymerization was extremely decelerated and the MWD of the polymer broadened. It is very interesting that binary systems, $WOCl_4$−*n*-BuLi (1:1−2), form polymers with narrow MWDs, like the Mo case.

The effect of *t*-BuOH in the $WOCl_4$−*n*-BuLi (1:1−2) systems was examined (Table 3). The formed polymer possessed narrow MWDs irrespective of *t*-BuOH concentration (0−2 equiv). However, the polymerization appreciably slowed with increasing amounts of *t*-BuOH; e.g., the polymerization was finished within 20 min with $WOCl_4$−*n*-BuLi (1:1), whereas it took 24 h with $WOCl_4$−*n*-BuLi−*t*-BuOH (1:1:2). This is the same tendency as in the $MoOCl_4$−*n*-BuLi−EtOH (1:1:*x*) system.[16d]

Table 4 shows results for the polymerization using EtMgBr as a cocatalyst. The polymerization by $WOCl_4$−EtMgBr (1:1) proceeded very slowly to form a polymer with narrow MWD, suggesting the livingness of this system. It is noteworthy that the initiation efficiency of $WOCl_4$−EtMgBr (1:1) was about 5% and the largest among all $WOCl_4$-based systems. When larger amounts of EtMgBr were used, the MWDs of polymers were not narrow. Addition of *t*-BuOH resulted in the disappearance of the livingness of the $WOCl_4$−EtMgBr system. It is worth noting that a novel binary system, $WOCl_4$−EtMgBr (1:1) effects living polymerization, whereas $MoOCl_4$−EtMgBr (1:1) does not.[16a]

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