

Living Metathesis Polymerization of Several Substituted Acetylenes by MoOCl₄-Et₃Al-EtOH

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ABSTRACT: Living polymerization of several substituted acetylenes such as [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me₃Si-phenylacetylene), 1-chloro-1-octyne, (*o*-methylphenyl)acetylene (*o*-Me-phenylacetylene) was investigated by using a MoOCl₄-based catalyst, MoOCl₄-Et₃Al-EtOH (1:1:3–4). It was proved that *o*-Me₃Si-phenylacetylene polymerizes in a living fashion with the MoOCl₄-Et₃Al-EtOH catalyst in the temperature range 0–30°C. The M_w/M_n was as small as 1.05. The absolute M_n values of poly(*o*-Me₃Si-phenylacetylene) were determined by vapor pressure osmometry (VPO), and the following relationship was obtained; M_n (VPO) = 1.28 × M_n (GPC; polystyrene calibration). The activation parameters for the polymerization of *o*-Me₃Si-phenylacetylene were determined as $\Delta H^\ddagger = 73 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -13 \text{ J mol}^{-1} \text{ K}^{-1}$. MoOCl₄-Et₃Al-EtOH induced the living polymerization of 1-chloro-1-octyne as well to give a polymer with small polydispersity. Polymerization of *o*-Me-phenylacetylene formed a stereoregular living polymer having an M_w/M_n of 1.2 and 90% *cis* structure. Polymerizations of a few other phenylacetylenes having bulky *ortho* substituents also yielded living polymers, which is a tendency similar to those with previous MoOCl₄-based catalysts.

KEY WORDS Living Metathesis Polymerization / Molybdenum Catalyst / Substituted Acetylene / Ternary Catalyst / Stereoregularity /

Use of transition metal catalysts enables the synthesis of polymers from various monomers such as α -olefins, cycloolefins and acetylenes, which hardly polymerize in other polymerization processes.¹ In recent years, a variety of living polymerizations have been achieved by using transition-metal catalysts, typical examples of which are living polymerization of α -olefins^{2–5} and living ring-opening metathesis polymerization (ROMP) of cycloolefins.^{6–8} Living polymerization of substituted acetylenes has also been accomplished by use of several transition-metal catalysts including Schrock carbenes,^{9–13} MoOCl₄-based catalysts,^{14–16} and rhodium complexes.^{17,18} Schrock carbenes induce the living polymerization of α,ω -diynes,^{9,10} ethynylferrocene,¹¹ and *ortho*-substituted phenylacetylenes.^{12,13} Certain rhodium-based catalysts polymerize phenylacetylene in a living manner to give a stereoregular living polymer.^{17,18}

Previously, we found that the MoOCl₄-*n*-Bu₄Sn-EtOH/toluene (catalyst/solvent) system effects the living polymerization of various substituted acetylenes such as *ortho*-substituted phenylacetylenes, 1-chloro-1-alkynes and *t*-butylacetylene.^{14,15} Our recent studies on the MoOCl₄-based catalysts have focused on the availability of cocatalysts.^{19–22} It was consequently found that Et₂Zn¹⁹ and *n*-BuLi²⁰ work as effective cocatalysts in the MoOCl₄-cocatalyst-EtOH system to achieve excellent living polymerization of [*o*-(trifluoromethyl)phenyl]-acetylene (*o*-CF₃-phenylacetylene). In both cases, poly(*o*-CF₃-phenylacetylene) with quite narrow molecular weight distribution (MWD) ($M_w/M_n < 1.03$) is attainable in quantitative yield. Interestingly, the living polymerization of substituted acetylenes is accomplished without ethanol as the third component when *n*-BuLi is employed as a cocatalyst.

As a part of our studies on the development of novel MoOCl₄-based catalysts, we recently reported that a new

catalyst/solvent system, MoOCl₄-Et₃Al-EtOH/anisole, polymerizes *o*-CF₃-phenylacetylene in a living fashion.²¹ Poly(*o*-CF₃-phenylacetylene) with very narrow MWD was obtained in quantitative yield. In the present study, we applied this catalyst system to various substituted acetylenes aiming at clarifying the features of the polymerization catalyzed by the MoOCl₄-Et₃Al-EtOH/anisole system.

EXPERIMENTAL

The monomers such as *o*-Me₃Si-phenylacetylene, 1-chloro-1-octyne, *o*-Me-phenylacetylene were prepared with reference to the literature methods.^{23–25} The crude products were distilled twice from CaH₂ before use. MoOCl₄ was used as received (Strem, purity >99%). Et₃Al was commercially obtained as 1.0 M toluene solution and diluted with anisole to a 0.10 M solution. *n*-Bu₄Sn and EtOH were distilled before use. After removal of benzaldehyde by using (2,4-dinitrophenyl)hydrazine, anisole was washed twice with aqueous NaOH solution, followed by distilling twice from Na under a nitrogen atmosphere.

Catalyst solution was prepared as follows: MoOCl₄ (50 μmol) was weighed under nitrogen and placed in a Schlenk tube, and anisole (2.0 mL) was added. An anisole solution (0.50 mL) of Et₃Al (50 μmol) and an anisole solution (0.5 mL) of EtOH (200 μmol) were successively added to the MoOCl₄ solution at 1 min interval, and the catalyst solution was aged for 15 min with stirring. Then polymerization was initiated by adding an anisole solution (2.0 mL) of monomer (1.0 mmol) to the catalyst solution. The polymerization was quenched with a methanol/acetic acid/anisole mixture (volume ratio 1:1:1). The polymerization mixture was washed with 5% hydrochloric acid and then water, and subsequent evaporation of the volatile materials afforded polymer. In the case of *o*-Me-phenylacetylene, the polymerization

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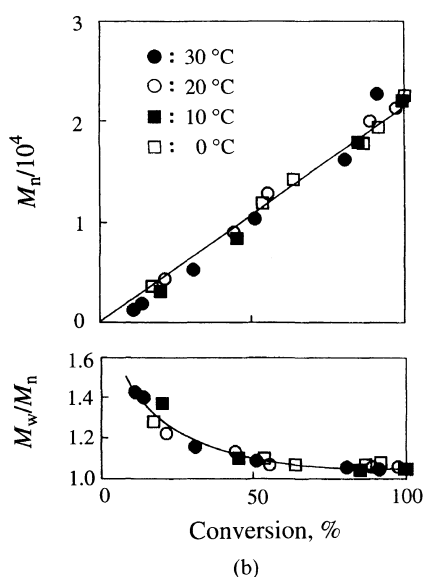
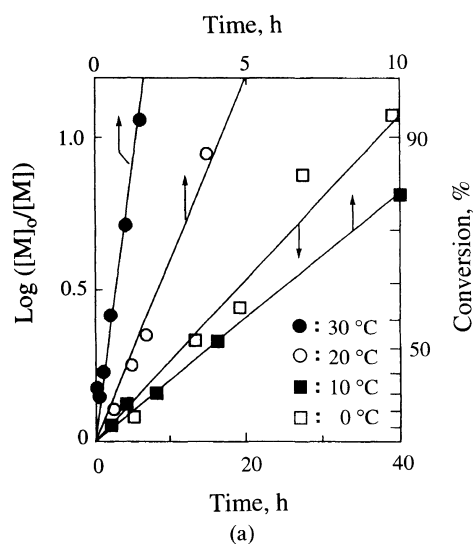


Figure 1. Temperature dependence of the polymerization of *o*-Me₃Si-phenylacetylene by $\text{MoOCl}_4\text{-Et}_3\text{Al-EtOH}$ (1:1:4); (a) first-order plots, (b) plots of monomer conversion vs. M_n and vs. M_w/M_n (polymerized in anisole; $[\text{MoOCl}_4]=10\text{ mM}$, $[\text{M}]_0=0.20\text{ M}$).

mixture was diluted with toluene and reprecipitated into methanol. The monomer conversions were determined by gas chromatography. The polymer yields were determined by gravimetry.

The MWD's of polymers were recorded on a gel-permeation chromatograph (GPC) (JASCO PU930; eluent chloroform; Shodex K805, 804, 803, and K802 polystyrene gel columns; RI detector). The relative number- and weight-average molecular weights (M_n and M_w , respectively) were calculated by use of a polystyrene calibration. The absolute M_n values were determined by vapor pressure osmometry (VPO) with a Knauer vapor pressure osmometer (solvent: CCl_4 ; standard: dibenzyl). The polymer samples used were purified by fractionation using a preparative GPC (JASCO PU930; eluent chloroform; Shodex H2001 column; RI detector) followed by freeze-drying of benzene solution at 0°C . ^{13}C NMR spectra of polymers were measured in CDCl_3 at room temperature on a JEOL GSX-270 spectrometer (67.5 MHz for ^{13}C).

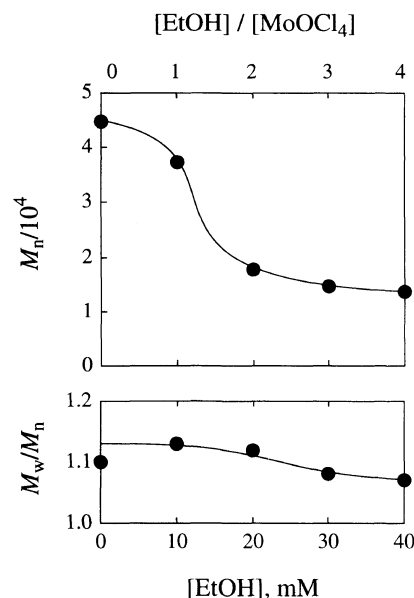


Figure 2. Effect of ethanol concentration on the polymerization of *o*-Me₃Si-phenylacetylene by $\text{MoOCl}_4\text{-Et}_3\text{Al-EtOH}$ (1:1:*x*) (polymerized in anisole at 30°C ; $[\text{MoOCl}_4]=10\text{ mM}$, $[\text{M}]_0=0.10\text{ M}$, all the conversions were 100%).

RESULTS AND DISCUSSION

Living Polymerization of *o*-Me₃Si-Phenylacetylene

Figure 1 shows the time dependence of the polymerization of *o*-Me₃Si-phenylacetylene using $\text{MoOCl}_4\text{-Et}_3\text{Al-EtOH}$ (1:1:4). The polymerization was finished within 2 h at 30°C , while it took 50 h at 0°C for the completion of the polymerization. The first-order plots gave a single straight line passing through the origin, indicating that the concentration of propagating species is constant throughout the polymerization and independent of temperature in the range $0\text{--}30^\circ\text{C}$. The M_n increased in direct proportion to the monomer conversion, and the MWD narrowed with increasing conversion to become as small as 1.05 at high conversions. Thus, one can conclude that this polymerization is a living system.

The effect of ethanol concentration was examined in the range of $[\text{EtOH}]=0\text{--}40\text{ mM}$, *i.e.*, $[\text{EtOH}]/[\text{MoOCl}_4]=1\text{--}4$ (Figure 2). Though a narrow MWD was attained without the addition of ethanol to the catalyst ($M_w/M_n \sim 1.1$), the M_n was rather large, meaning that the initiator efficiency was rather low ($\sim 4\%$). The M_n decreased with increasing amount of ethanol, and the initiator efficiency became 13% at $[\text{EtOH}]=40\text{ mM}$. Meanwhile, the M_w/M_n diminished to 1.08. These results reveal that addition of a four-fold excess of ethanol is preferable to achieve excellent living polymerization of *o*-Me₃Si-phenylacetylene.

In order to estimate the absolute values of initiator efficiency and propagation rate constant (k_p), absolute M_n values were determined by VPO. Figure 3 depicts the plot of M_n (VPO) vs. M_n (GPC), which gave the following relationship: M_n (VPO) = $1.28 \times M_n$ (GPC; polystyrene calibration). The absolute initiator efficiency was calculated from this relationship and the results of Figure 1(b) was 11%; *cf.* the value based on GPC 14%. The propagation rate constants were: $0.37\text{ M}^{-1}\text{ s}^{-1}$ (30°C), 0.13 (20°C), 0.039 (10°C), 0.014 (0°C).

Ahrrhenius plot of the k_p values (Figure 4) provided

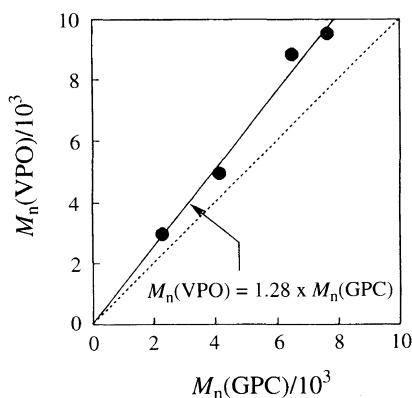


Figure 3. Relationship between M_n (GPC) and M_n (VPO) of poly(*o*-Me₃Si-phenylacetylene)s obtained with MoOCl₄-Et₃Al-EtOH (1 : 1 : 4).

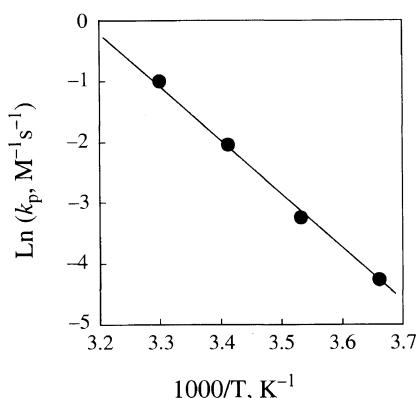


Figure 4. Arrhenius plot of the propagation rate constant in the polymerization of *o*-Me₃Si-phenylacetylene by MoOCl₄-Et₃Al-EtOH (1 : 1 : 4) (polymerized in anisole; [MoOCl₄] = 10 mM, [M]₀ = 0.20 M).

the activation parameters for the polymerization of *o*-Me₃Si-phenylacetylene by MoOCl₄-Et₃Al-EtOH (1 : 1 : 4): $\Delta H^\ddagger = 73 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -13 \text{ J mol}^{-1} \text{ K}^{-1}$. The activation parameters for *o*-CF₃-phenylacetylene are $\Delta H^\ddagger = 78 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 17 \text{ J mol}^{-1} \text{ K}^{-1}$.²¹ Since the polymerization is the first order with respect to the monomer concentration, it seems that the rate-determining step is the coordination of a monomer to the propagating species irrespective of the monomer structure. The activation enthalpies hardly depend on the monomer structure and are much larger than the entropy terms. On the other hand, the activation entropy varies considerably depending on the monomers, which might be due to the difference in the bulkiness of *ortho*-substituents.

Living Polymerization of 1-Chloro-1-octyne

Figure 5 illustrates the effect of ethanol concentration on the polymerization of 1-chloro-1-octyne by MoOCl₄-Et₃Al-EtOH/anisole. With increasing ethanol concentration to 20 and 30 mM, the MWD narrowed and simultaneously the M_n decreased, *i.e.*, the initiator efficiency increased. This is the same tendency as the cases of *o*-CF₃- and *o*-Me₃Si-phenylacetylenes. However, when a four-fold excess of ethanol was added, polymerization was not finished in 1 h and further the polymer had a rather broad MWD.

The time profile of the polymerization of 1-chloro-1-

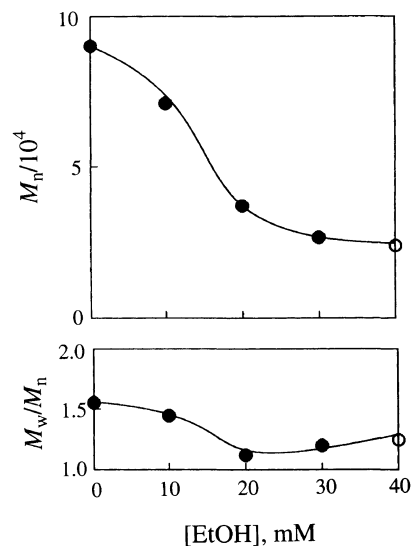


Figure 5. Effect of ethanol concentration on the polymerization of 1-chloro-1-octyne by MoOCl₄-Et₃Al-EtOH (1 : 1 : *x*); (polymerized in anisole at 30°C; [MoOCl₄] = 10 mM, [M]₀ = 0.10 M, all the conversions were 100%).

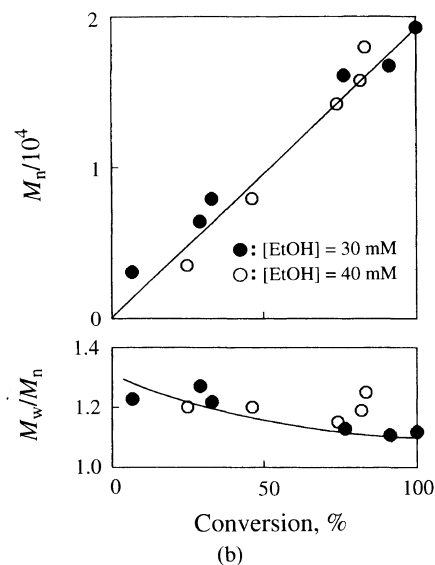
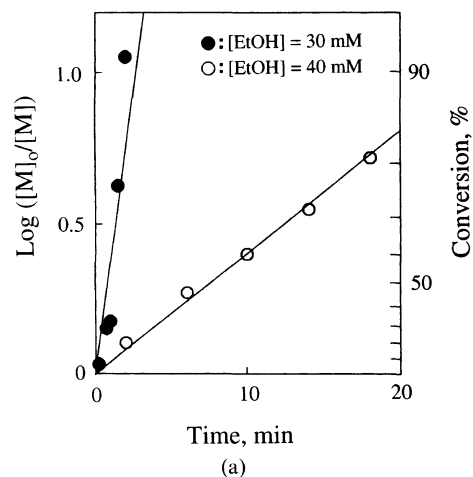


Figure 6. Polymerization of 1-chloro-1-octyne by MoOCl₄-Et₃Al-EtOH (1 : 1 : 3–4); (a) first-order plots, (b) plots of monomer conversion vs. M_n and vs. M_w/M_n (polymerized in anisole at 30°C; [MoOCl₄] = 10 mM, [M]₀ = 0.10 M).

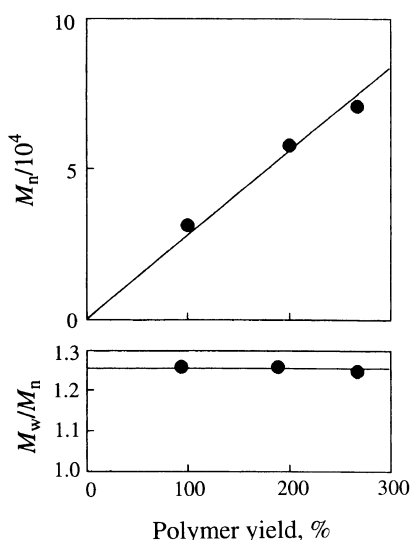


Figure 7. Multistage polymerization of *o*-Me-phenylacetylene by MoOCl₄-Et₃Al-EtOH (1:1:4) (polymerized in anisole at 0°C; [MoOCl₄] = 10 mM, [M]₀ = [M]_{added} = 0.10 M).

octyne was examined at [EtOH] = 30 and 40 mM (Figure 6). When MoOCl₄-Et₃Al-EtOH (1:1:3) was employed, both the first-order plot and the conversion- M_n plot showed straight lines passing through the origin, and the MWD stayed narrow. These results manifest that this polymerization is a living system. On the other hand, in the case of [EtOH] = 40 mM, the MWD broadened at a late stage, and the polymerization leveled off at ca. 80% conversion.

Stereospecific Living Polymerization of *o*-Me-Phenylacetylene

o-Me-Phenylacetylene polymerized in a living fashion with MoOCl₄-Et₃Al-EtOH/anisole similarly to *o*-CF₃- and *o*-Me₃Si-phenylacetylenes, though the polymerization was faster and the MWD was somewhat broader. Thus, in the multistage polymerization of *o*-Me-phenylacetylene, the M_n increased in proportion to polymer yield, while the M_w/M_n remained below 1.3²⁶ (Figure 7).

The *cis* content of poly(*o*-Me-phenylacetylene) can be evaluated by ¹³C NMR. The living polymer (M_w/M_n 1.2) obtained with MoOCl₄-*n*-Bu₄Sn-EtOH/toluene at -30°C possesses a relatively high *cis* content (77%).²⁷ It is noteworthy that the MoOCl₄-Et₃Al-EtOH (1:1:4) forms a living poly(*o*-Me-phenylacetylene) with high stereoregularity (M_w/M_n ~ 1.2, *cis* 90%) (Table I). This polymer can be called a stereoregular living polymer. In contrast, the *cis* content of the polymer formed without ethanol was no more than 61%. A similar but more remarkable tendency has been observed with *t*-butylacetylene.²⁸ That is, the polymerization of *t*-butylacetylene with MoOCl₄-*n*-Bu₄Sn-EtOH/toluene leads to a stereoregular living polymer (M_w/M_n ~ 1.12, *cis* 97%), whereas the polymerization with MoOCl₄ provides a polymer with only 57% *cis*. These phenomena can be explained in terms that the geometric isomerization undergoes under more acidic conditions like the MoOCl₄ alone or MoOCl₄-cocatalyst systems.

Polymerization of Other Acetylenes

The effect of bulkiness of *ortho*-substituents was

Table I. Effect of ethanol concentration on the polymerization of *o*-Me-phenylacetylene by MoOCl₄-Et₃Al-EtOH^a

[EtOH]/mM	Polymer yield/% ^b	M_n ^c	M_w/M_n ^c	<i>cis</i> / % ^d
0	21	39600	3.52	61
10	97	148500	4.05	70
20	97	57000	1.17	76
30	96	38800	1.19	88
40	90	40900	1.24	90
50	83	51300	1.16	80
60	61	41700	1.18	82

^a Polymerized in anisole at 0°C for 15 min; [MoOCl₄] = 10 mM. ^b Methanol-insoluble part. ^c Determined by GPC. ^d Determined by ¹³C NMR.

Table II. Polymerization of various *ortho*-substituted phenylacetylenes by MoOCl₄-Et₃Al-EtOH^a

Monomer	Polymn. time	Polymer yield/%	M_n	M_w/M_n
	min			
HC≡CC ₆ H ₅	120	40	3200	2.62
HC≡CC ₆ H ₄ - <i>o</i> -F	120	46	4800	2.10
HC≡CC ₆ H ₄ - <i>o</i> -Cl	1	100	23500	1.30
HC≡CC ₆ H ₄ - <i>o</i> - <i>i</i> -Pr	1	100	37200	1.14

^a Polymerized in anisole at 30°C; [MoOCl₄] = 10 mM, [M]₀ = 0.10 M.

examined in the polymerization of phenylacetylenes by MoOCl₄-Et₃Al-EtOH/anisole (Table II). Phenylacetylene itself and *o*-F-phenylacetylene, whose *ortho*-substituent is sterically hardly demanding, produced polymers having broad MWD's. On the other hand, *o*-Cl-phenylacetylene and *o*-*i*-Pr-phenylacetylene, which possess medium-sized *ortho*-substituents, gave polymers with narrow MWD's. Thus one can see that the MWD narrows with increase in the bulkiness of *ortho*-substituent. This tendency is the same as in previously developed systems such as MoOCl₄-*n*-Bu₄Sn-EtOH/toluene,²⁹ MoOCl₄-Et₂Zn-EtOH/anisole,¹⁹ and MoOCl₄-*n*-BuLi/anisole.²⁰ This means that steric effect of *ortho*-substituents in phenylacetylene plays a vital role in achieving living polymerization by using MoOCl₄-based catalysts.

CONCLUSIONS

In the present and preceding²¹ studies, we applied MoOCl₄-Et₃Al-EtOH/anisole system to various substituted acetylenes aiming at clarifying the features of polymerizations induced by this system. Eventually, the present study revealed the following: (i) *o*-Me₃Si-phenylacetylene gave a living polymer which has a very narrow MWD; (ii) 1-chloro-1-octyne also polymerized in a living fashion; and (iii) *o*-Me-phenylacetylene yielded a stereoregular living polymer. The following points can be referred to as features of the present MoOCl₄-Et₃Al-EtOH/anisole system as compared with MoOCl₄-*n*-Bu₄Sn-EtOH/toluene: (1) higher initiator efficiencies for various monomers; e.g., [P*]/[Cat] 20% vs. 10% for *o*-CF₃-phenylacetylene, 14% vs. 13% for *o*-Me₃Si-phenylacetylene, 14% vs. 3% for 1-chloro-1-octyne; (2) low polydispersity ratios for various polymers; e.g.,

M_w/M_n 1.02 vs. 1.10 for poly(*o*-CF₃-phenylacetylene), 1.03 vs. 1.07 for poly(*o*-Me₃Si-phenylacetylene), 1.10 vs. 1.20 for poly(1-chloro-1-octyne); (3) high reproducibility in catalyst preparation and polymerization, which enables detailed studies on the polymerization kinetics.

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