Living metathesis polymerization of substituted acetylenes by MoOCl$_4$–Et$_2$Zn–EtOH and MoOCl$_4$–n-BuLi systems

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Abstract

Several organometallic compounds were examined as second catalyst components (cocatalysts) of the MoOCl$_4$-cocatalyst(–EtOH) system with the motivation of development of novel catalysts for the living polymerization of substituted acetylenes. Catalyst systems such as MoOCl$_4$–Et$_2$Zn–EtOH and MoOCl$_4$–n-BuLi have proven to be very effective for the living polymerization of substituted acetylenes. Suitable mole ratios of the catalyst components (MoOCl$_4$:Et$_2$Zn:EtOH = 1:1:3 and MoOCl$_4$:n-BuLi = 1:1) made it possible to achieve living polymerization of substituted acetylenes including (*o*-trifluoromethyl)phenylacetylene, (*o*-trimethylsilyl)phenylacetylene, *o*-isopropylphenylacetylene, and 1-chloro-1-octyne. Use of anisole instead of toluene as solvent remarkably improved the living nature of polymerization to provide polymers with extremely narrow molecular weight distributions (1.03–1.14) in quantitative yields. Sequential living polymerization of two monomers by these catalyst systems produced block copolymers with low polydispersities without the formation of homopolymers. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Metathesis polymerization; Living polymerization; Molybdenum catalyst; Organometallic cocatalyst; Substituted acetylene; Block copolymerization

1. Introduction

In recent years, living polymerization is under intensive research in the field of polymer science. Especially, energetic study on the transition metal-catalyzed polymerization has provided diverse living polymerization systems of a wide variety of monomers including olefins [1–4], 1,3-butadiene [5], allenes [6], and carbodiimide [7], and so on. One of the recent remarkable progresses in the living polymeriza-

tion by transition metal catalysts is seen in the ring-opening metathesis polymerization of cycloolefins. Several well-defined catalysts such as titanacyclobutanes [8,9], Schrock carbenes [10,11], and ruthenium carbenes [12] are quite effective for the living polymerization of cycloolefins.

Substituted acetylenes are known to undergo living polymerization by so-called metathesis catalysts such as Schrock carbenes [13–18] and MoOCl$_4$-based ternary catalysts [19–23] as well as rhodium catalysts [24] (Table 1). It was revealed in authors' laboratory during the last decade that the MoOCl$_4$–n-Bu$_4$Sn–EtOH cata-

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Table 1
Living polymerizations of substituted acetylenes by various transition metal catalysts

Catalyst	Monomer	M_w/M_n	Reference
$MoCl_5$–n-Bu_4Sn–EtOH	$ClC{\equiv}C$–n-C_6H_{13}	1.27	[19,20]
$MoOCl_4$–n-Bu_4Sn–EtOH	$ClC{\equiv}C$–n-C_6H_{13}	1.13	[21]
$NbCl_5$/cyclohexane	$MeC{\equiv}CSiMe_3$	1.17	[25]
$(ArO)_3pyTa{=}CMe$	$MeC{\equiv}CMe$	1.03	[13]
$(R_3CO)_2(ArN{=})Mo{=}CHR$	$(HC{\equiv}CCH_2)_2C(CO_2Et)_2$	1.20	[15]
$(R_3CO)_2(ArN{=})Mo{=}CHR$	$HC{\equiv}C$–ferrocenyl	1.06	[17]
$(R_2HCO)_2(AdN{=})(lutidine)Mo{=}CHR$	$HC{\equiv}CC_6H_4$–o-$SiMe_3$	1.04	[18]
$(Ph_3P)_2(nbd)Rh$–$C{\equiv}CPh$	$HC{\equiv}CPh$	1.17	[24]

lyst induces living polymerization of a variety of substituted acetylenes in toluene solution (Scheme 1) [26]. For example, quantitative formation of high molecular weight poly(1-chloro-1-octyne) with low polydispersity is feasible by use of this catalyst [21]. One of the interesting features of this catalyst is that a stereoregular living polymer is formed from *tert*-butylacetylene [22]. Further, the polymerization of phenylacetylenes having o-CF_3, o-Me_3Si, and o-Me_3Ge groups catalyzed by $MoOCl_4$–n-Bu_4Sn–EtOH produces living polymers with quite narrow molecular weight distributions ($M_w/M_n < 1.05$) [23].
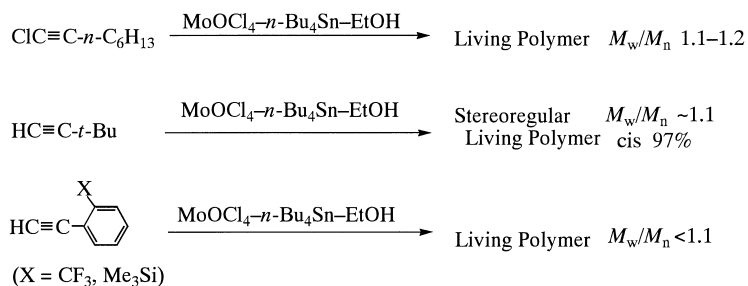
In the living polymerization of substituted acetylenes with $MoOCl_4$-based catalysts, previous research mainly focused on the availability of monomers, and attempts have scarcely been made to expand the range of second catalyst components (organometallic cocatalysts). The present article intends to overview our recent developments of novel $MoOCl_4$-based living

polymerization catalysts. The efficacy of Et_2Zn and n-BuLi as second catalyst components is demonstrated. Mostly, (o-Trifluoromethyl)phenylacetylene (o-CF_3PA) has been employed as monomer. Further, application of the present catalysts to the synthesis of block copolymers is described.

2. Results and discussion

2.1. $MoOCl_4$–Et_2Zn–EtOH system

As mentioned above, the $MoOCl_4$–n-Bu_4Sn–EtOH catalyst in toluene accomplishes living polymerization of substituted acetylenes. In a similar way, Et_2Zn as an organometallic cocatalyst has recently proven to be effective for the living polymerization of acetylenes [27]. In the Et_2Zn system, use of anisole instead of toluene as solvent greatly improves the living nature of the polymerization. Fig. 1 illustrates

Scheme 1. Living polymerization of substituted acetylenes with $MoOCl_4$–n-Mu_4Sn–EtOH (1:1:1) in toluene.
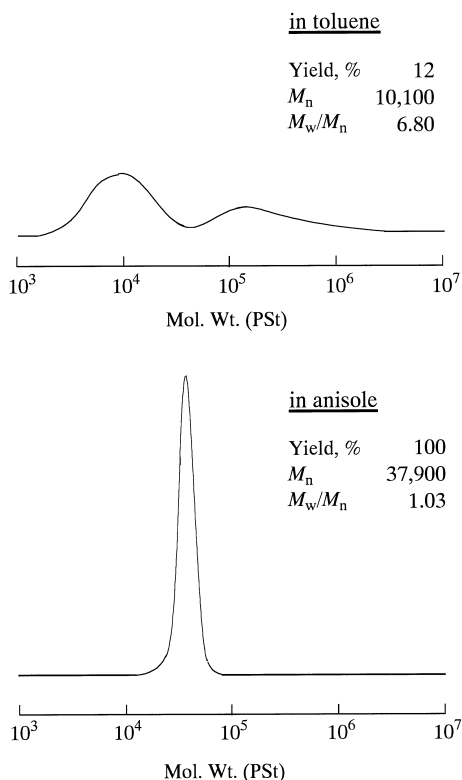
in toluene

Yield, %	12
M_n	10,100
M_w/M_n	6.80

in anisole

Yield, %	100
M_n	37,900
M_w/M_n	1.03

Fig. 1. Solvent effect on the polymerization of o-CF$_3$PA with MoOCl$_4$–Et$_2$Zn–EtOH (1:1:3) (polymerized at 30°C for 24 h (in toluene) or 30 min (in anisole); [MoOCl$_4$] = 10 mmol dm^{-3}, [M]$_0$ = 200 mmol dm^{-3}).

the GPC profiles of poly(o-CF$_3$PA)s prepared with MoOCl$_4$–Et$_2$Zn–EtOH (1:1:3) in toluene and anisole. The polymerization in toluene gives a bimodal polymer with broad molecular weight distribution (M_w/M_n = 6.80), which is indicative of the presence of plural propagating species. In addition, the conversion of o-CF$_3$PA is not completed even if the polymerization time is prolonged to 24 h. On the contrary, use of anisole solvent leads the polymerization to completion within 30 min to quantitatively form a polymer with extremely narrow molecular weight distribution. Higher ability of anisole to dissolve the catalyst than toluene makes the polymerization system homogeneous, which seems to contribute to the excellent living nature of the polymerization.

A previous work demonstrated that addition of ethanol as a third catalyst component is

indispensable to achieve the living polymerization of substituted acetylenes by MoOCl$_4$–n-Bu$_4$Sn [19]. A similar tendency is observed with the MoOCl$_4$–Et$_2$Zn–EtOH catalyst regarding the effect of ethanol concentration. Fig. 2 shows GPC curves of poly(o-CF$_3$PA) produced at ethanol concentrations in the range 0–30 mmol/dm^{-3}. Though the monomer is completely consumed within 1 h irrespective of ethanol concentration, the molecular weight and its distribution appreciably depend on the ethanol concentration. The molecular weight distribution is somewhat broad without ethanol but progressively narrows with increasing ethanol concentration. Eventually, the polydispersity ratio becomes as small as 1.03 at [EtOH]/[MoOCl$_4$] = 3. The molecular weight decreases with increasing ethanol concentration.
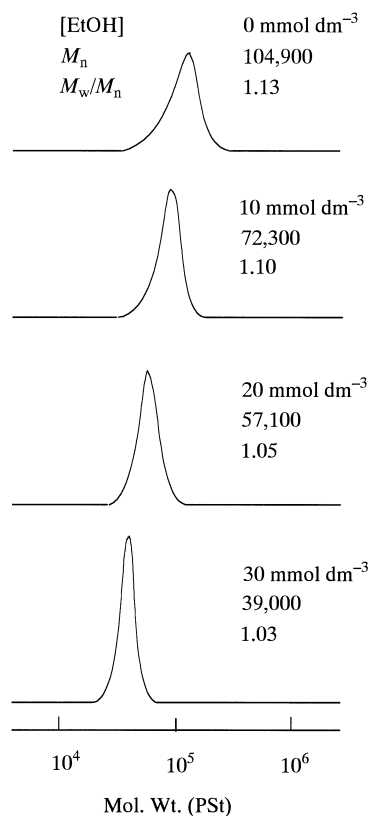

[EtOH]	0 mmol dm^{-3}
M_n	104,900
M_w/M_n	1.13

	10 mmol dm^{-3}
	72,300
	1.10

	20 mmol dm^{-3}
	57,100
	1.05

	30 mmol dm^{-3}
	39,000
	1.03

Fig. 2. Effect of ethanol (third catalyst component) concentration on the polymerization of o-CF$_3$PA with MoOCl$_4$–Et$_2$Zn–EtOH (1:1:x) (polymerized in anisole at 30°C for 1 h; [MoOCl$_4$] = 10 mmol dm^{-3}, [M]$_0$ = 200 mmol dm^{-3}).

Thus, the addition of ethanol evidently improves the living nature and initiator efficiency of the polymerization.

Fig. 3 plots the molecular weight and polydispersity ratio against the polymer yield in the temperature range of 0–30°C. A single linear relationship holds between the polymer yield and molecular weight for all the temperatures. Poly(o-CF$_3$PA)s with extremely narrow molecular weight distributions ($M_w/M_n \sim 1.03$) are quantitatively produced in all cases. These results reveal that the termination and chain transfer reactions are negligible in the present polymerization. Fig. 4 illustrates the result of a multistage polymerization experiment, from which one can recognize that the molecular weight of polymer increases in proportion to the polymer yield, maintaining its low polydispersity even after the third charge of the monomer has been consumed. All these data demonstrate that the polymerization of o-CF$_3$PA with MoOCl$_4$–Et$_2$Zn–EtOH proceeds in a living fashion.

Several other acetylenes also undergo living polymerization with the present catalyst system, MoOCl$_4$–Et$_2$Zn–EtOH (1:1:3) (Table 2). For
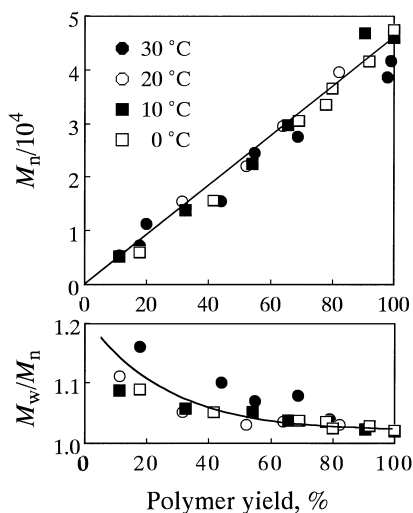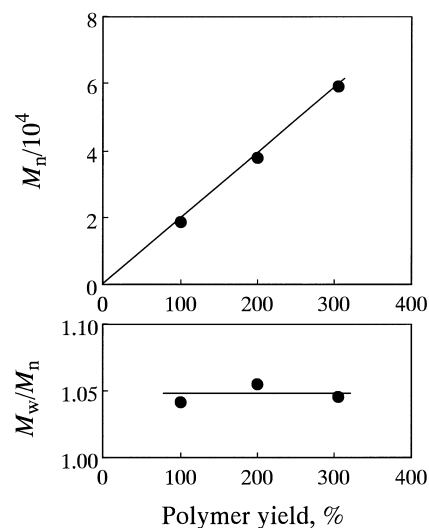

Fig. 4. Multistage polymerization of o-CF$_3$PA with MoOCl$_4$–Et$_2$Zn–EtOH (1:1:3) (polymerized each time for 45 min in anisole at 30°C; [MoOCl$_4$] = 10 mmol dm^{-3}, [M]$_0$ = [M]$_{add}$ = 100 mmol dm^{-3}).

instance, the polymerization of (o-trimethylsilyl)phenylacetylene (o-Me$_3$SiPA) with this catalyst results in the quantitative formation of a polymer with extremely narrow molecular weight distribution. Phenylacetylenes with relatively small ortho-substituents such as o-isopropylphenylacetylene (o-i-PrPA) and o-methylphenylacetylene (o-MePA) also polymerize in a living fashion, but slight broadening of the molecular weight distribution is observed in each case. No living characters are found in the polymerizations of phenylacetylene (PA) and o-fluorophenylacetylene (o-FPA) which are sterically less crowded. 1-Chloro-1-octyne, a disubstituted acetylene, offers a polymer with low polydispersity but in moderate yield.

2.2. MoOCl$_4$–n-BuLi–EtOH and MoOCl$_4$–n-BuLi systems

Similarly to the MoOCl$_4$–Et$_2$Zn–EtOH system, a combination of MoOCl$_4$, n-BuLi and EtOH has proven to induce living polymerization of acetylenes. Fig. 5 presents GPC profiles of the poly(o-CF$_3$PA)s obtained with MoOCl$_4$–

Fig. 3. Plots of M_n and M_w/M_n vs. yield of poly(o-CF$_3$PA) produced with MoOCl$_4$–Et$_2$Zn–EtOH (1:1:3) at various temperatures (polymerized in anisole; [MoOCl$_4$] = 10 mmol dm^{-3}, [M]$_0$ = 200 mmol dm^{-3}).

Table 2
Polymerization of various substituted acetylenes by $MoOCl_4$–Et_2Zn–EtOH (1:1:3)[a]

Monomer	Polymerization time (h)	Yield (%)	$M_n/10^3$	M_w/M_n
$HC\equiv CC_6H_4$–o-$SiMe_3$	5	100	37.5	1.04
$HC\equiv CC_6H_4$–o-i-Pr	0.5	100	79.9	1.14
$HC\equiv CC_6H_4$–o-Me[b]	0.5	100	77.2	1.23
$HC\equiv CC_6H_4$–o-F	2	69	6.1	1.74
$HC\equiv CC_6H_5$	2	52	5.0	1.61
$ClC\equiv C$-n-C_6H_{13}	1	52	120.7	1.13
$ClC\equiv CPh$	4	69	82.7	1.39

[a] In anisole, 30°C; $[M]_0 = 200$ mmol dm^{-3}, $[MoOCl_4] = 10$ mmol dm^{-3}.
[b] $[M]_0 = 0.05$ mmol dm^{-3}.

n-BuLi–EtOH in toluene and anisole at various mole ratios of ethanol to $MoOCl_4$. Polymerizations in toluene solution either without ethanol or with 1 equivalent of ethanol provide the polymers with broad molecular weight distributions and inflate the molecular weights of the polymers. The formation of polymer with low polydispersity entails the addition of 2 equivalent of ethanol to $MoOCl_4$ in toluene solution.

On the contrary, the living polymerization of o-CF_3PA is readily achieved in anisole regardless of the ethanol concentration. Namely, the polymerization in anisole results in the quantitative formation of the polymer with extremely narrow molecular weight distribution even in the absence of ethanol. There is no significant difference in the molecular weight of polymer by changing ethanol concentrations. It should be
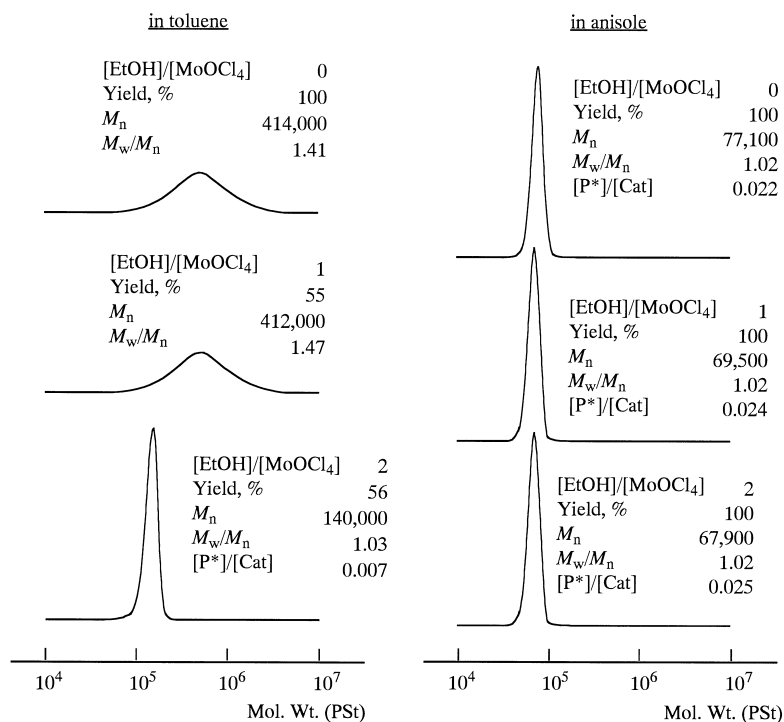

Fig. 5. Effects of solvents and ethanol (third catalyst component) on the polymerization of o-CF_3PA with $MoOCl_4$–n-BuLi–EtOH (1:1:x) (polymerized at 30°C for 2 h; $[MoOCl_4] = 10$ mmol dm^{-3}, $[M]_0 = 100$ mmol dm^{-3}).

emphasized that the addition of ethanol only causes a decrease in the rate of polymerization in anisole, but does not affect the living nature of the polymerization (see text). These results are obviously different from those of the $MoOCl_4$–Et_2Zn–EtOH catalyzed polymerization.

Fig. 6 shows the plots of polymer molecular weight and polydispersity ratio vs. polymer yield at various ethanol concentrations. All of the plots of molecular weight against yield provide a straight line passing through the origin, while the polydispersity is quite low at medium to high polymer yields irrespective of ethanol concentration. These results lead to the conclusion that termination and chain transfer are negligible during the polymerization. The multistage polymerization experiment (Fig. 7) demonstrates that the molecular weight of polymer increases in direct proportion to the polymer yield while its narrow molecular weight distribution is maintained regardless of the presence and absence of ethanol. In other words, the propagating center stays active even after the
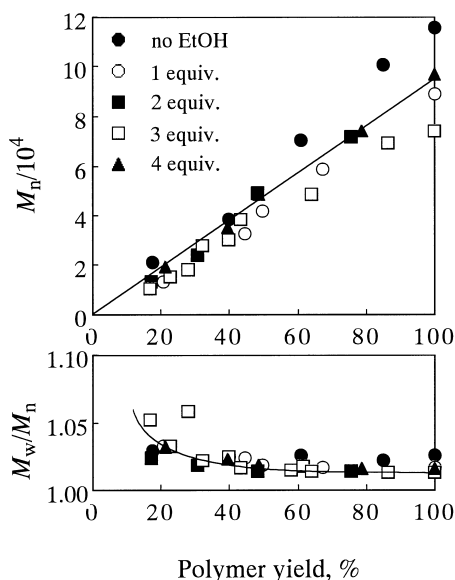
Fig. 7. Multistage polymerization of o-CF_3PA with $MoOCl_4$–n-BuLi (1:1) (polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mmol dm^{-3}, $[M]_0 = [M]_{added} = 100$ mmol dm^{-3}, $[EtOH] = 0$ or 20 mmol dm^{-3}).

monomer has been completely consumed in the presence or absence of ethanol. All these data strongly evidence that the present polymerization proceeds in a living fashion.

The first-order plots of the polymerization at various ethanol concentrations are illustrated in Fig. 8. Logarithmic $[M]_0/[M]$ increases proportionally to the polymerization time irrespective of ethanol concentration, which reveals that the polymerization rate obeys the first order kinetics. The slope of the first-order plot decreases

Fig. 6. Plots of M_n and M_w/M_n vs. yield of the poly(o-CF_3PA)s produced by $MoOCl_4$–n-BuLi–EtOH (1:1:x) at various ethanol concentrations (polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mmol dm^{-3}, $[M]_0 = 100$ mmol dm^{-3}).
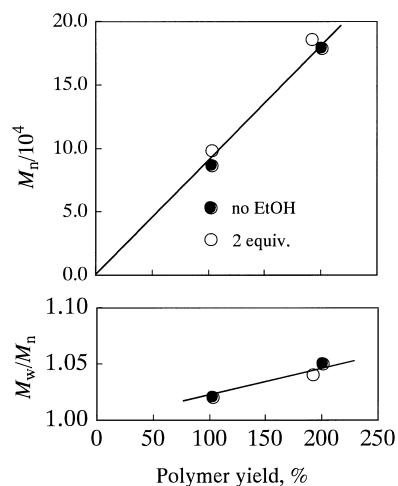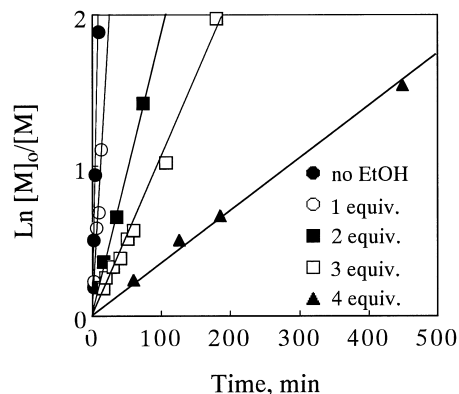
Fig. 8. First-order plots for the polymerizations of o-CF_3PA with $MoOCl_4$–n-BuLi–EtOH (1:1:x) at various ethanol concentrations (polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mmol dm^{-3}, $[M]_0 = 100$ mmol dm^{-3}).

Table 3
Polymerization of various substituted acetylenes by $MoOCl_4$–n-BuLi (1:1)[a]

Monomer	Polymerization time (h)	Yield (%)	$M_n/10^3$	M_w/M_n
$HC \equiv CC_6H_4$–o-$SiMe_3$	2	100	170	1.03
$HC \equiv CC_6H_4$–o-i-Pr	1	100	114	1.08
$HC \equiv CC_6H_4$–o-F	4	25	4.0	1.34
$HC \equiv CC_6H_5$	4	40	3.6	1.38
$ClC \equiv C$–n-C_6H_{13}	5 min	100	146	1.08

[a] In anisole, 30°C; $[M]_0 = 200$ mmol dm^{-3}, $[MoOCl_4] = 10$ mmol dm^{-3}.

with increasing ethanol concentration. In the range of the mole ratio of ethanol to $MoOCl_4$ from 0 to 4, there is no significant difference in the molecular weight of the formed polymer (Fig. 6). It is, therefore, concluded that ethanol only gives rise to the deceleration of the polymerization.

The tendency concerning the availability of the monomers that undergo living polymerization with $MoOCl_4$–n-BuLi is similar to that for the previous $MoOCl_4$-based systems (Table 3). For example, o-Me_3SiPA and o-i-PrPA polymerize in a living fashion with $MoOCl_4$–n-BuLi to give the polymers with quite narrow molecular weight distributions in quantitative yields. In contrast, o-FPA and PA, which bear no or small ortho-substituents exhibit no living nature in their polymerizations. It should be noted that 1-chloro-1-octyne polymerizes smoothly with $MoOCl_4$–n-BuLi leading to the formation of a living polymer in quantitative yield, whereas the $MoOCl_4$–Et_2Zn–EtOH catalyst results in low yield of poly(1-chloro-1-octyne).

2.3. Block copolymerizations

The ability of these polymerization systems to provide living polymers makes it possible to supply well-defined block copolymers consisting of plural substituted acetylenes [28]. As an example, Fig. 9 illustrates GPC curves for the block copolymerization of o-Me_3SiPA with o-CF_3PA catalyzed by $MoOCl_4$–n-BuLi. The formation of the living polymer of o-Me_3SiPA with low polydispersity is in consistence with the results shown in Table 3. After the addition

of o-CF_3PA to the polymerization solution, the GPC peak of the polymer shifts towards a high molecular weight region while its molecular weight distribution remains narrow. No GPC trace attributed to the prepolymer of o-Me_3SiPA is observed in the block copolymer, which means that the initiation efficiency of the second-stage polymerization is quantitative. A similar block copolymer of o-CF_3PA with o-Me_3SiPA can be obtained by using $MoOCl_4$–Et_3Al–EtOH as well [29]. However, owing to the difference in the initiator efficiency (~ 0.02 with $MoOCl_4$-n-BuLi vs. ~ 0.16 with $MoOCl_4$–Et_3Al–EtOH), the sequence lengths of the blocks become much shorter under the same conditions; e.g., M_n 2.1×10^4, M_w/M_n 1.04, $m = 60$, $n = 60$ with $MoOCl_4$–Et_3Al–EtOH). A block copolymer of 1-chloro-1-octyne with o-CF_3PA
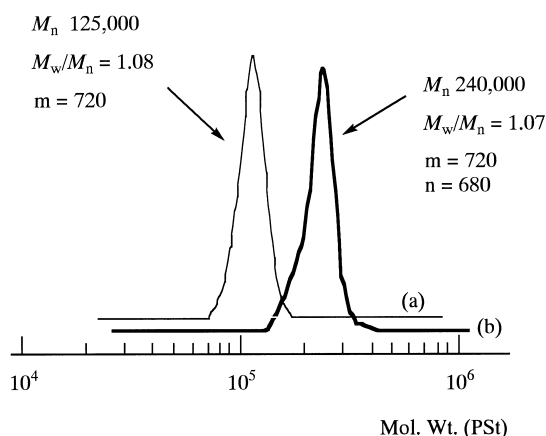
Fig. 9. GPC curves of (a) poly(o-Me_3SiPA) and (b) block copolymer of o-Me_3SiPA with o-CF_3SiPA produced by $MoOCl_4$–n-BuLi (polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mmol dm^{-3}, $[M]_0 = [M]_{added} = 100$ mmol dm^{-3}).

is also selectively formed with $MoOCl_4$–*n*-BuLi. Namely, the polymerization of *o*-CF_3PA with living poly(1-chloro-1-octyne) ($M_n = 1.5 \times 10^4$, $M_w/M_n = 1.05$) leads to the selective formation of a block copolymer of 1-chloro-1-octyne with *o*-CF_3PA having M_n and M_w/M_n values of 2.4×10^4 and 1.21, respectively.

3. Summary

In the present article, we have surveyed our recent studies on new living polymerization systems of substituted acetylenes. Suitable combinations of $MoOCl_4$ with alkylmetals enable to supply well-defined polyacetylenes with living chain ends. Polymers with high molecular weights and extremely narrow molecular weight distributions are attainable with $MoOCl_4$–Et_2Zn–EtOH and $MoOCl_4$–*n*-BuLi catalysts. The stability of living chain end also makes it possible to offer the well-controlled block copolymers of substituted acetylenes.

Acknowledgements

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