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Selective synthesis of various di- and triblock copolymers from substituted acetylenes through sequential living polymerization by $MoOCl_4$-based catalysts in anisole

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Abstract

Block copolymerization of substituted acetylenes through the sequential addition process was studied by use of three $MoOCl_4$-based living polymerization catalysts in anisole solvent. In the case of the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst system, diblock copolymers with very narrow molecular weight distributions were selectively formed from any combinations of two monomers among 1-chloro-1-octyne (ClOc), [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA), and [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) irrespective of the order of monomer addition. When the $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–*n*-BuLi catalysts were employed, several diblock copolymers with higher molecular weights were obtained owing to lower initiation efficiencies. With these catalysts, however, the order of monomer addition affected the block copolymerization, and reversing the orders that selectively gave block copolymers resulted in contamination by the homopolymers from the first monomers. The use of $MoOCl_4$–*n*-Bu_4Sn–EtOH enabled to produce ABC- and ABA-type triblock copolymers composed of ClOc, *o*-Me_3SiPA, and *o*-CF_3PA regardless of the order of monomer addition. ABC-type triblock copolymers with very high molecular weights could be synthesized using $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–*n*-BuLi, when the monomers were successively polymerized in the order of ClOc, *o*-Me_3SiPA, and *o*-CF_3PA. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the most convenient methods for preparing block copolymers is multistage polymerization of plural monomers using living polymerization systems. To date, a great number of block copolymers have been synthesized by living anionic polymerization. On the contrary, examples for the syntheses of block copolymers by means of living polymerizations with transition metal catalysts have been rapidly increasing in recent years. Block copolymerizations of the same kinds of monomers have been demonstrated for olefins [1–3], cycloolefins [4–10], allenes [11], acrylates [12,13], isocyanates [14], isocyanides [15,16], and so forth. Block copolymers comprising different kinds of monomers have also been reported; examples include block copolymers from the combinations of cycloolefins and acetylene derivatives [17–21], 1,6-heptadiyne derivatives and norbornene derivatives [22], substituted allenes and isocyanides [23], 1,3-butadiene and isocyanides [24,25], and ϵ-caprolactone and lactides [26].

Regarding substituted acetylenes, block copolymerization of phenylacetylene with (*p*-methoxyphenyl)acetylene by a Rh catalyst has been reported [27]. We studied the living polymerization of substituted acetylenes with Mo catalysts to find that $MoOCl_4$-based catalysts induce the living polymerization of a variety of substituted acetylenes such as 1-chloro-1-octyne (ClOc), [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA), and [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) [28,29]. Further, a few block copolymers of substituted acetylenes were prepared by means of living polymerization catalyzed by $MoOCl_4$–*n*-Bu_4Sn–EtOH (mole ratio 1:1:1) in toluene [30]. However, this living polymerization was rather unsatisfactory from the viewpoint of selective synthesis of the block copolymers. For instance, the molecular weight distributions (MWD) of the formed block copolymers were somewhat broad [e.g. M_w/M_n 1.24, 1.31 for poly(ClOc)-*block*-poly(*o*-CF_3PA)], and the combination of monomers that could produce block copolymers was quite limited.

Recently, we have found that the use of anisole instead of

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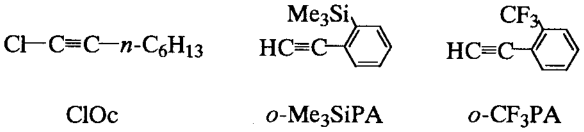

Scheme 1. The monomers used.

toluene as a solvent in the living polymerization with $MoOCl_4$–n-Bu_4Sn–EtOH brings about both the improvement of initiation efficiency and the narrowing of MWD [31]. In other words, the living nature is greatly enhanced by conducting the polymerization in anisole. Hence, it is expected that the polymerization in anisole enables the selective synthesis of block copolymers with very narrow MWDs. It has also been revealed that not only n-Bu_4Sn but also Et_3Al [32,33] and n-BuLi [34] serve as effective second catalyst components (cocatalysts) in the $MoOCl_4$-catalyzed living polymerization in anisole. Since block copolymerizations using Et_3Al and n-BuLi cocatalysts have not been studied, it is of interest to examine the efficacy of these cocatalysts in block copolymerization.

In this paper we report the selective synthesis of various diblock, and ABC- and ABA-type triblock copolymers of substituted acetylenes by applying the sequential addition technique to the living polymerization system by $MoOCl_4$-based catalysts. ClOc, o-Me_3SiPA, and o-CF_3PA were used as monomers (Scheme 1). The $MoOCl_4$–n-Bu_4Sn–EtOH (1:1:2), $MoOCl_4$–Et_3Al–EtOH (1:1:3), and $MoOCl_4$–n-BuLi (1:1) systems were employed as polymerization catalysts, and anisole as solvent. In consequence, selective synthesis of various diblock, and ABC- and ABA-type triblock copolymers was achieved irrespective of the order of monomer addition, when $MoOCl_4$–n-Bu_4Sn–EtOH was employed. Further, several block copolymers with extremely high molecular weights were obtained by using $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–n-BuLi.

2. Experimental

2.1. Materials and measurements

The three monomers used, i.e. ClOc [35,36], o-Me_3SiPA [37,38] and o-CF_3PA [39–41], were prepared according to the literature methods. $MoOCl_4$ (Strem), Et_3Al (Kanto Chemical; toluene solution) and n-BuLi (Kanto Chemical; hexane solution) were commercially obtained and used without further purification. n-Bu_4Sn (Wako Chemical) was distilled twice and stored as anisole solution (0.10 M). Anisole as polymerization solvent was washed with aqueous sodium hydroxide (5%) and water successively, dried over anhydrous calcium chloride, and distilled twice from sodium metal. Ethanol (Wako Chemical) was distilled twice from $Mg(OEt)_2$ and stored as anisole solution (0.20 or 0.30 M). All the polymerization procedures were carried out under dry nitrogen.

The MWDs of the formed polymers were observed by gel-permeation chromatography (GPC) [Jasco PU930; eluent chloroform; Shodex K805, 804, 803 columns (Showa Denko, Co); RI and UV detectors). The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were determined by using a polystyrene calibration. The initiation efficiencies ($[P^*]/[Cat]$) were calculated from the polymer yields and the degrees of polymerization. Gas chromatographic analyses were performed on a Shimadzu GC-8A instrument (silicone DC-550, 3 m).

2.2. Polymerization procedures

Catalyst solutions were prepared as follows: $MoOCl_4$ and a cocatalyst (n-Bu_4Sn, Et_3Al or n-BuLi) were mixed in anisole, and the solution was aged at room temperature for 5 min. Then an anisole solution of ethanol was added to the $MoOCl_4$–cocatalyst solution, and the mixture was aged at room temperature for an additional 15 min. Polymerizations were carried out at 30°C in a pre-baked Schlenk tube equipped with a three-way stopcock. The concentrations of both initial and added monomers ($[M]_0$ and $[M]_{added}$) were 0.10 M, and the concentration of $MoOCl_4$ was 10 mM. Polymerizations were quenched with an anisole/methanol mixture (volume ratio 1:1). The formed polymers were precipitated in methanol, filtered, and dried under vacuum. The monomer conversions and the polymer yields were determined by gas chromatography and gravimetry, respectively.

The first-stage polymerizations were initiated by the addition of a monomer solution (2 ml, $[M] = 0.25\ M$) to the catalyst solution (3 ml, $[MoOCl_4] = 16.7$ mM). When $MoOCl_4$–n-Bu_4Sn–EtOH was used, ClOc, o-Me_3SiPA, and o-CF_3PA were polymerized for 15, 40, and 25 min, respectively. In the case of $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–n-BuLi catalysts, the polymerizations of ClOc, o-Me_3SiPA and o-CF_3PA were continued for 5, 25 and 15 min, respectively. It was confirmed beforehand that the monomer conversion reached 100% within these periods of time.

Block copolymerizations were carried out by the addition of a second monomer solution (2 ml, $[M] = 0.25$ M) to the solution of living polymer formed by the first-stage polymerization. When $MoOCl_4$–n-Bu_4Sn–EtOH was used, the polymerizations of ClOc, o-Me_3SiPA, and o-CF_3PA, were carried out for 15, 60, and 40 min, respectively. In the case of $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–n-BuLi, the polymerization time of ClOc, o-Me_3SiPA and o-CF_3PA were set to be 5, 40 and 30 min, respectively. For preparing triblock copolymers, a third monomer solution (2 ml, $[M] = 0.25$ M) was added to the solution of the living polymer formed by the second-stage polymerization. The third monomer was polymerized for another 60 min. The monomers were completely consumed in all cases after polymerization for these periods of time.

Table 1
Block copolymerization of substituted acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH(1:1:2). (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomer conversions were quantitative)

Run	1st monomer[a]	2nd monomer[b]	M_n[c]	M_w/M_n[c]	$[P^*]/[Cat]$, %[d]
1	ClOc	*o*-Me_3SiPA	15 200	1.10	23.6
2	ClOc	*o*-CF_3PA	11 900	1.09	23.6
3	*o*-Me_3SiPA	*o*-CF_3PA	9280	1.06	37.3 (28.9)
4	*o*-Me_3SiPA	ClOc	11 000	1.12	37.3 (28.9)
5	*o*-CF_3PA	ClOc	9210	1.12	41.5 (28.2)
6	*o*-CF_3PA	*o*-Me_3SiPA	9410	1.08	41.5 (28.2)

[a] $[M]_0 = 0.10$ M.
[b] $[M]_{added} = 0.10$ M.
[c] Determined by GPC using a polystyrene calibration.
[d] Estimated from the first-stage polymerization. The values without parentheses were calculated on the basis of the relative M_n values by GPC, while those in parentheses were based on the absolute M_n values by VPO [32,33].

3. Results and discussion

3.1. Block copolymerization of ClOc, o-Me_3SiPA and o-CF_3PA with $MoOCl_4$–n-Bu_4Sn–EtOH

The block copolymerizations between two monomers among ClOc, *o*-Me_3SiPA, and *o*-CF_3PA (6 combinations in total) were examined with use of $MoOCl_4$–*n*-Bu_4Sn–EtOH (mole ratio 1:1:2) in anisole, the results of which are summarized in Table 1. Quite interestingly, block copolymers selectively formed irrespective of the order of monomer addition in every combination. That is, all of the produced polymers exhibited unimodal GPC profiles (M_n ca. 9000–15 000), and no peak attributable to the homopolymer from the first monomer was detected. The MWDs of the produced block copolymers were quite narrow (M_w/M_n 1.06–1.12). It is especially worth noting that the polydispersities are low (M_w/M_n 1.06–1.08) in the block copolymers from *o*-Me_3SiPA and *o*-CF_3PA (runs 3 and 6). The initiation efficiencies of the first-stage polymerizations were in a range of ca. 24–42% according to GPC (probably, 20–30% according to VPO), while those of the second-stage polymerization were quantitative.

The block copolymerization of ClOc with *o*-CF_3PA was next examined by changing the feed ratio of two monomers. The concentration of the first monomer was fixed at 0.10 M, and that of second monomer was varied in the range 0.050–0.50 M (Table 2). When ClOc was the first monomer, both monomers were consumed quantitatively and block copolymers with low polydispersities were formed irrespective of the feed ratios. Reversing the addition order of the two monomers also gave the corresponding block copolymers in the same way. These results indicate that the length of both units in the block copolymer can be controlled simply by changing the amount of the feed monomers.

Under the previously reported $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:1)/toluene catalyst/solvent system, only a combination of ClOc and *o*-CF_3PA selectively forms block copolymers in both orders of monomer addition, and the MWDs of the block copolymers are relatively broad (M_w/M_n 1.24, 1.31) [30]. Thus the present $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:2)/anisole system is far superior as evidenced by the selective synthesis of all of six kinds of diblock copolymers from ClOc, *o*-Me_3SiPA, and *o*-CF_3PA.

3.2. Comparison of $MoOCl_4$–n-Bu_4Sn–EtOH, $MoOCl_4$–Et_3Al–EtOH, and $MoOCl_4$-n-BuLi

So far, it has proven that, in addition to *n*-Bu_4Sn, alkylating agents such as Et_3Al and *n*-BuLi are effective as cocatalysts for the $MoOCl_4$-catalyzed living polymerization of substituted acetylenes and that the most characteristic difference between these cocatalysts is observed in the initiation efficiency [32–34]. Here, a comparison was made with respect to the behavior of block copolymerizations by $MoOCl_4$–*n*-Bu_4Sn–EtOH, $MoOCl_4$–Et_3Al–EtOH, and $MoOCl_4$–*n*-BuLi.

Table 3 summarizes the results for the block copolymerization of all the combinations of two monomers among ClOc, *o*-Me_3SiPA, and *o*-CF_3PA with $MoOCl_4$–Et_3Al–EtOH (mole ratio 1:1:3). In all combinations, the order of monomer addition drastically influenced the block copolymerization. For example, when *o*-Me_3SiPA or *o*-CF_3PA was added to the solution of living poly(ClOc), the corresponding block copolymers were selectively obtained (runs 1 and

Table 2
Block copolymerization of ClOc with *o*-CF_3PA by $MoOCl_4$–*n*-Bu_4Sn–EtOH(1:1:2). (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomer conversions were quantitative)

Run	1st monomer ($[M]_0$, M)	2nd monomer ($[M]_{added}$, M)	M_n[a]	M_w, M_n[a]
1	ClOc (0.10)	*o*-CF_3PA (0.050)	9230	1.09
2	ClOc (0.10)	*o*-CF_3PA (0.10)	11 900	1.09
3	ClOc (0.10)	*o*-CF_3PA (0.20)	20 400	1.06
4	ClOc (0.10)	*o*-CF_3PA (0.50)	40 700	1.04
5	*o*-CF_3PA (0.10)	ClOc (0.050)	7070	1.12
6	*o*-CF_3PA (0.10)	ClOc (0.10)	9210	1.12
7	*o*-CF_3PA (0.10)	ClOc (0.20)	14 200	1.13
8	*o*-CF_3PA (0.10)	ClOc (0.50)	29 400	1.13

[a] Determined by GPC using a polystyrene calibration.

Table 3
Block copolymerization of substituted acetylenes by $MoOCl_4$–Et_3Al-EtOH(1:1:3). (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomer conversions were quantitative)

Run	1st monomer[a]	2nd monomer[b]	M_n[c]	M_w/M_n[c]	$[P^*]/[Cat]$, %[d]
1	ClOc	*o*-Me_3SiPA	36 900	1.11	8.0
2	ClOc	*o*-CF_3PA	37 600	1.11	8.0
3	*o*-Me_3SiPA	*o*-CF_3PA	21 100	1.09	15.7 (12.2)
4	*o*-Me_3SiPA	ClOc	27 300	1.25 (bimodal)[e]	–
5	*o*-CF_3PA	ClOc	23 000	1.18 (bimodal)[e]	–
6	*o*-CF_3PA	*o*-Me_3SiPA	23 100	1.18 (bimodal)[e]	–

[a] $[M]_0 = 0.10$ M.
[b] $[M]_{added} = 0.10$ M.
[c] Determined by GPC using a polystyrene calibration.
[d] Estimated from the first-stage polymerization. The values without parentheses were calculated on the basis of the relative M_n values by GPC, while those in parentheses were based on the absolute M_n values by VPO [32,33].
[e] Two peaks at 11 000 and 30 000 in a ratio of ca. 1:6 (run 4), at 11 000 and 25 000 in ca. 1:6 (run 5), and at 11 000 and 23 000 in ca.1:30 (run 6).

2). In a similar way, living poly(*o*-Me_3SiPA) is possible to quantitatively initiate the polymerization of *o*-CF_3PA, leading to the selective formation of the block copolymer (run 3). In these cases, no homopolymer formed. In contrast, when the order of monomer addition was reversed (runs 4–6), the resulting products showed bimodal elution curves in the GPC measurement due to the formation of block copolymer and a byproduct; the ratio of the two peaks were ca. 6:1 (runs 4 and 5) and 30:1 (run 6). The byproducts in the block copolymerizations are attributable to the homopolymers from the first monomers, since those of runs 4 and 5 exhibited UV absorptions due to poly(phenylacetylene)s at 350 nm.[1] This result implies that, in the cases of runs 4–6, the homopolymerization of the second monomer is not induced and that the cross propagation from the propagating end to the second monomer does not proceed perfectly.

A similar phenomenon was also observed in the block copolymerization by $MoOCl_4$–*n*-BuLi (Table 4). Namely, selective block copolymerizations occurred when *o*-Me_3SiPA or *o*-CF_3PA was polymerized with the living chain end of poly(ClOc), or when *o*-CF_3PA was polymerized after *o*-Me_3SiPA (runs 1–3), while small amounts of homopolymers (ca. 1/10–1/4 to the block copolymers) formed when the order of monomer addition was reversed (runs 4–6). The MWDs of poly(ClOc)-*block*-poly(*o*-Me_3SiPA) and poly(ClOc)-*block*-poly(*o*-CF_3PA) were somewhat broad ($M_w/M_n > 1.2$) compared with those produced by other catalysts.

When two monomers were selected and polymerized successively keeping the order of (1) ClOc, (2) *o*-Me_3SiPA, (3) *o*-CF_3PA with $MoOCl_4$–Et_3Al–EtOH or $MoOCl_4$–*n*-BuLi, the corresponding block copolymers were selectively formed. However, unless this order is followed, the selective block copolymerization is not accomplished, because of the contamination by the homopolymer from the first monomer. In general, contamination by the homopolymer from the first monomer may take place when the reactivities of the first and second monomer are very different, or when one employs a second monomer with lower initiation efficiency than that of the first one, or when the stability of the propagating end is unsatisfactory. However, none of these seems to apply to the unsuccessful results observed with $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–*n*-BuLi. For example, the rate of homopolymerization increases in the order of *o*-Me_3SiPA <

Table 4
Block copolymerization of substituted acetylenes by $MoOCl_4$–*n*-BuLi(1:1). (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomer conversions were quantitative)

Run	1st monomer[a]	2nd monomer[b]	M_n[c]	M_w/M_n[c]	$[P^*]/[Cat]$, %[d]
1	ClOc	*o*-Me_3SiPA	267 000	1.26	1.2
2	ClOc	*o*-CF_3PA	242 000	1.21	1.2
3	*o*-Me_3SiPA	*o*-CF_3PA	239 000	1.07	1.4 (1.1)
4	*o*-Me_3SiPA	ClOc	230 000	1.30 (bimodal)[e]	–
5	*o*-CF_3PA	ClOc	154 000	1.29 (bimodal)[e]	–
6	*o*-CF_3PA	*o*-Me_3SiPA	181 000	1.18 (bimodal)[e]	–

[a] $[M]_0 = 0.10$ M.
[b] $[M]_{added} = 0.10$ M.
[c] Determined by GPC using a polystyrene calibration.
[d] Estimated from the first-stage polymerization. The values without parentheses were calculated on the basis of the relative M_n values by GPC, while those in parentheses were based on the absolute M_n values by VPO [32,33].
[e] Two peaks at 120 000 and 260 000 in a ratio of ca. 1:4 (run 4), at 80 000 and 170 000 in ca. 1:6 (run 5), and at 80 000 and 190 000 in ca.1:10 (run 6).

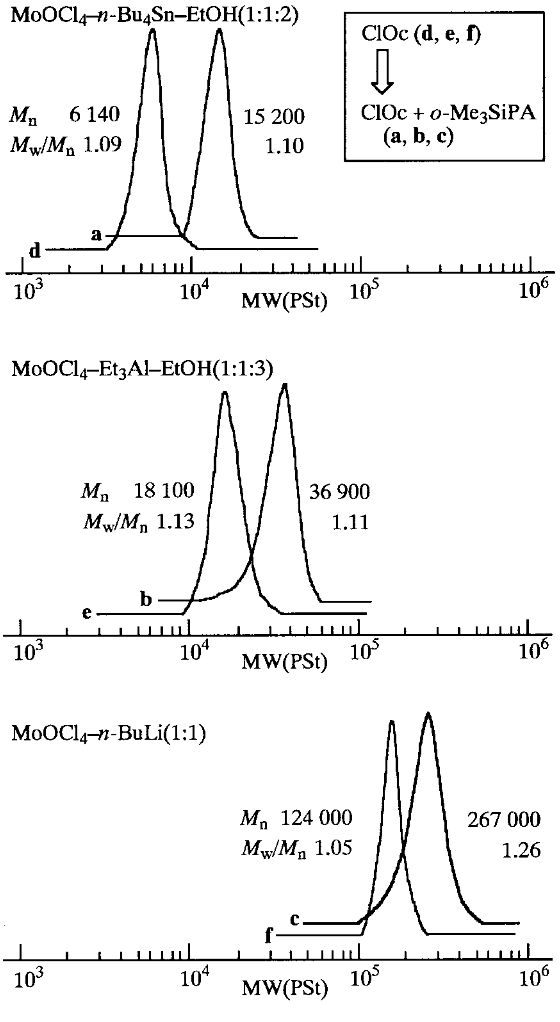

Fig. 1. GPC curves of poly(ClOc)-*block*-poly(*o*-Me_3SiPA)s (curves a, b, and c). The samples are from run 1 of Tables 1, 3, and 4. Curves d, e, and f are for the corresponding poly(ClOc)s formed in the first stage.

o-CF_3PA < ClOc regardless of cocatalyst, which does not agree with the effective order to give the block copolymers selectively. There is no significant difference between *o*-Me_3SiPA and *o*-CF_3PA with respect to the initiation efficiency. Further, we have demonstrated that the living ends of all the monomers employed here exhibit sufficient life time under the present conditions [28,29,31–34]. Thus, the exact reason for the imperfect block efficiencies is not clear at present. Now we are studying block copolymerizations by expanding the kind monomers to clarify what governs the block efficiency, in other words, the cross propagation efficiency, and will publish in the future.

As described in previous papers [28,29], the kind of cocatalyst greatly influences the initiation efficiency of the $MoOCl_4$-catalyzed living polymerization of substituted acetylenes. Therefore, the change of cocatalyst may give an alternative method to control the M_n of the block copolymer. As an example, the GPC profiles for the block copolymerization of ClOc with *o*-Me_3SiPA with the three $MoOCl_4$-based catalysts are illustrated in Fig. 1, where *o*-Me_3SiPA was polymerized sequentially after ClOc. When the second monomer had been completely consumed in the $MoOCl_4$–*n*-Bu_4Sn–EtOH system, the GPC elution peak shifted towards the high molecular weight side maintaining its narrow MWD, indicating the selective formation of a block copolymer (curve a). Similarly, $MoOCl_4$–Et_3Al–EtOH achieved the selective block copolymerization (curve b), and the M_n of the resulting block copolymer was 36 900 which was more than two times as large as that obtained with $MoOCl_4$–*n*-Bu_4Sn–EtOH. Emphasis should be placed on the fact that the selective production of a block copolymer with extremely high molecular weight (M_n 267 000) is possible by use of $MoOCl_4$–*n*-BuLi (curve c) without a serious broadening of the MWD.

The effect of cocatalyst was further examined for the block copolymerization of ClOc with *o*-CF_3PA (Fig. 2). Successive polymerization of *o*-CF_3PA after ClOc gave block copolymers selectively regardless of the kind of catalyst. The M_n values of the block copolymers depended on the cocatalyst and increased in the order of *n*-Bu_4Sn < Et_3Al < *n*-BuLi. As illustrated in Fig. 3, a similar tendency was recognized with the M_n of the block copolymers in the combination of *o*-Me_3SiPA and *o*-CF_3PA as well; i.e. the magnitude of M_n lies in the order of *n*-Bu_4Sn < Et_3Al < *n*-BuLi.

Thus it turned out that the M_n of the block copolymer could be roughly controlled by the change of cocatalyst, which would facilitate to investigate the polymer properties in detail. An example was given by the fact that the block copolymers obtained with $MoOCl_4$–*n*-BuLi show excellent film-forming ability, which permits the research for their microdomain structure [42].

3.3. Synthesis of ABC- and ABA-type triblock copolymers

As mentioned above, the conventional catalyst/solvent system, $MoOCl_4$–*n*-Bu_4Sn–EtOH/toluene, lacks in the ability to provide block copolymers from a wide range of substituted acetylenes. Therefore, both the combination of monomers and the order of monomer addition are strictly limited, and consequently only ABA-type triblock copolymers from 1-chloro-1-hexyne and 1-chloro-1-hexadecyne have been demonstrated as the example of the synthesis of the triblock copolymer composed of substituted acetylenes [43]. There has been no attempt to synthesize ABC-type triblock copolymers from substituted acetylenes.

In contrast, as described above, the use of $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole allows the formation of diblock copolymers from ClOc, *o*-Me_3SiPA, and *o*-CF_3PA irrespective of the combination and the addition order. Based on this result, we examined the preparation of ABC-type triblock copolymers with $MoOCl_4$–*n*-Bu_4Sn–EtOH (Table 5). Regardless of the order of monomer addition, the GPC traces of the formed block copolymers were unimodal, and their polydispersities were as low as 1.04–1.17. Thus it was possible

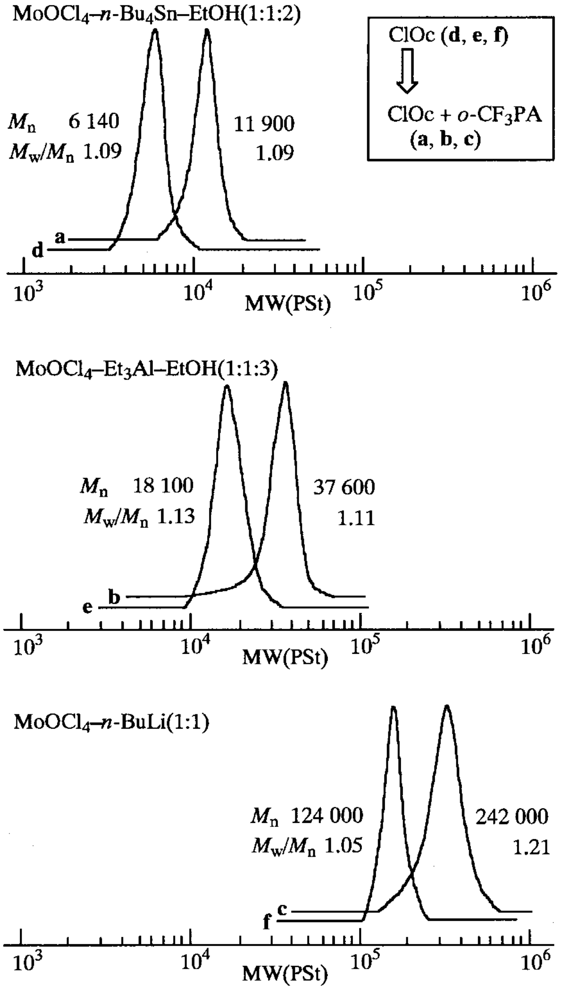

Fig. 2. GPC curves of poly(ClOc)-*block*-poly(*o*-CF_3PA)s (curves a, b, and c). The samples are from run 2 of Tables 1, 3, and 4. Curves d, e, and f are for the corresponding poly(ClOc)s formed in the first stage.

to selectively synthesize all of the six possible ABC-type triblock copolymers under this system. The M_n values of the block copolymers were between 16 000–22 000, which depended on the initiation efficiency of the first-stage polymerization.

In the case of $MoOCl_4$–Et_3Al–EtOH and $MoOCl_4$–*n*-BuLi, diblock copolymers were exclusively formed when the monomer addition followed the order of ClOc, *o*-Me_3SiPA, and then *o*-CF_3PA. On the basis of this finding, an attempt was made to synthesize triblock copolymer by employing the three $MoOCl_4$-based catalysts and keeping this order of addition. It is concluded from Fig. 4 that ABC-type triblock copolymers were selectively obtained with any of the three $MoOCl_4$-based catalysts. Similarly to the diblock copolymerization, the M_n values of the copolymers can be roughly controlled by varying the cocatalyst.

The diblock copolymers from the two monomers among ClOc, *o*-Me_3SiPA, and *o*-CF_3PA were obtained irrespective of the order of the monomer addition in $MoOCl_4$–*n*-Bu_4Sn–EtOH. Therefore it is expected that ABA-type triblock copolymers containing these monomers can be prepared in various combinations.

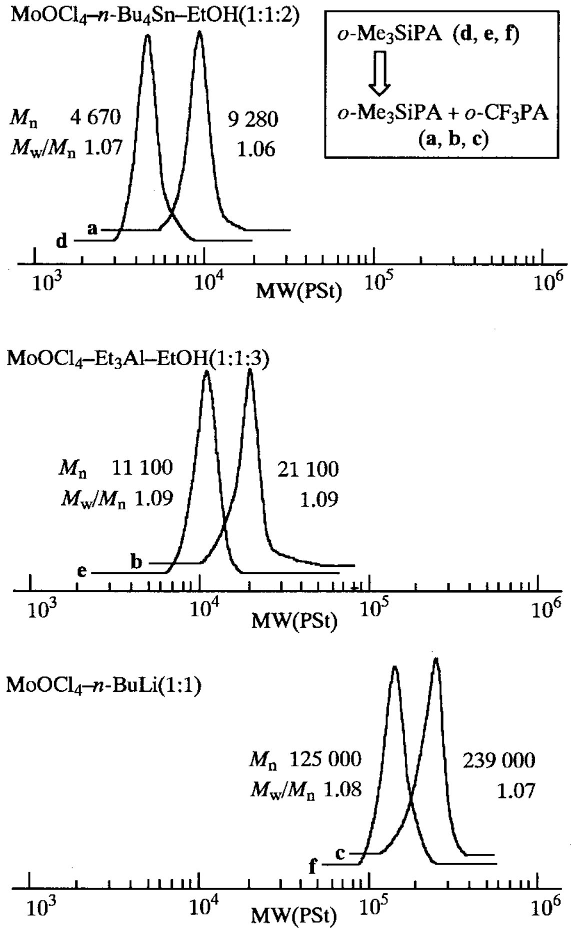

Fig. 3. GPC curves of poly(*o*-Me_3SiPA)-*block*-poly(*o*-CF_3PA)s (curves a, b, and c). The samples are from run 3 of Tables 1, 3, and 4. Curves d, e, and f are for the corresponding poly(*o*-Me_3SiPA)s formed in the first stage.

Preparation of ABA-type triblock copolymer was feasible with use of $MoOCl_4$–*n*-Bu_4Sn–EtOH as expected (Table 6). In all of the six cases, the GPC traces were unimodal and their polydispersities were as low as 1.06–1.18. This manifests that the selective ABA-type triblock copolymerization

Table 5
ABC-type ternary block copolymerization of substituted acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH(1:1:2). (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomers were converted quantitatively)

Run	1st monomer[a]	2nd monomer[b]	3rd monomer[b]	M_n[c]	M_w/M_n[c]
1	ClOc	*o*-Me_3SiPA	*o*-CF_3PA	20 900	1.09
2	ClOc	*o*-CF_3PA	*o*-Me_3SiPA	22 300	1.08
3	*o*-Me_3SiPA	*o*-CF_3PA	ClOc	15 500	1.12
4	*o*-Me_3SiPA	ClOc	*o*-CF_3PA	17 800	1.18
5	*o*-CF_3PA	ClOc	*o*-Me_3SiPA	16 800	1.16
6	*o*-CF_3PA	*o*-Me_3SiPA	ClOc	16 200	1.17

[a] $[M]_0 = 0.10$ M.
[b] $[M]_{added} = 0.10$ M.
[c] Determined by GPC using a polystyrene calibration.

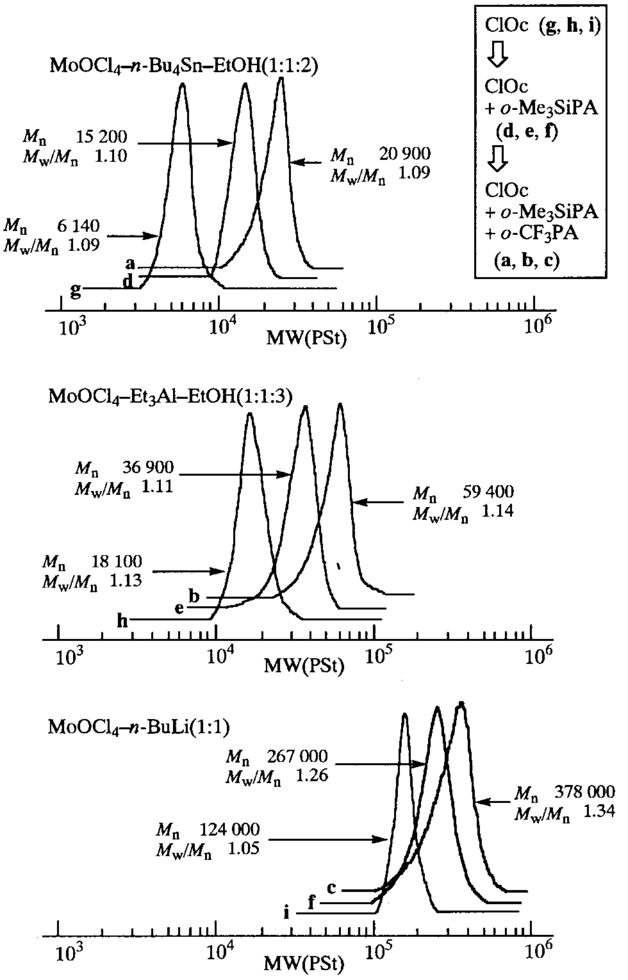

Fig. 4. GPC curves of poly(ClOc)-*block*-poly(*o*-Me_3SiPA)-*block*-poly(*o*-CF_3PA)s (curves a, b, and c). The sample for a is from run 1 of Table 5. Curves d, e, and f and curves g, h, and i are for the first- and second-stage polymers, respectively.

took place in all cases. The ABA- and BAB-type triblock copolymers with very narrow MWD were obtained particularly from *o*-Me_3SiPA and *o*-CF_3PA (runs 3 and 6). The M_n of the formed copolymers were about 14 000 to 21 000 within a relatively narrow range. On the other hand, the selective synthesis of the ABA-type triblock copolymer by using $MoOCl_4$–Et_3Al–EtOH or $MoOCl_4$–*n*-BuLi should be impossible on the basis of the tendency in the diblock copolymerization.

Table 6
ABA-type ternary block copolymerization of substituted acetylenes by $MoOCl_4$–*n*-Bu_4Sn–EtOH(1:1:2) (Polymerized in anisole at 30°C; $[MoOCl_4] = 10$ mM; all the monomers were converted quantitatively)

Run	1st monomer[a]	2nd monomer[b]	3rd monomer[b]	M_n[c]	M_w/M_n[c]
1	ClOc	*o*-Me_3SiPA	ClOc	20 900	1.14
2	ClOc	*o*-CF_3PA	ClOc	20 400	1.12
3	*o*-Me_3SiPA	*o*-CF_3PA	*o*-Me_3SiPA	14 100	1.06
4	*o*-Me_3SiPA	ClOc	*o*-Me_3SiPA	16 600	1.14
5	*o*-CF_3PA	ClOc	*o*-CF_3PA	13 900	1.18
6	*o*-CF_3PA	*o*-Me_3SiPA	*o*-CF_3PA	15 000	1.08

[a] $[M]_0 = 0.10$ M.
[b] $[M]_{added} = 0.10$ M.
[c] Determined by GPC using a polystyrene calibration.

In summary, we have demonstrated the synthesis of block copolymers from substituted acetylenes by use of $MoOCl_4$-based living polymerization catalysts. Thus, $MoOCl_4$–*n*-Bu_4Sn–EtOH/anisole has proven to be the most effective for the production of block copolymers and a wide range of polymer architecture, which are inaccessible with other catalysts. Control of the ratio of block lengths is readily achieved by the ratio of feed monomers, and appropriate selection of a cocatalyst can roughly steer the M_n of the block copolymer. It should be noted that block copolymers with extremely high molecular weight above 1×10^5 and desired block lengths are also obtainable with the *n*-BuLi-containing catalyst. The facility of the preparation of the present catalysts, in conjunction with the availability of various substituted acetylenes, will provide an excellent route to new advanced functional materials based on π-conjugated polymers.

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