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Synthesis of block copolymers containing 1-chloro-2-phenylacetylene, 2-nonyne, and (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene through sequential living polymerization by $MoOCl_4$-based catalysts

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Abstract

Block copolymerization of 1-chloro-2-phenylacetylene (ClPA), 2-nonyne, and (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene (*p*-BuF_4PA) as novel comonomers through the sequential addition process was studied by use of $MoOCl_4$-based living polymerization catalysts. The acetylenes that are known to undergo living polymerization and block copolymerization, i.e. 1-chloro-1-octyne (ClOc), [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA), and [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) were employed as conventional comonomers. When ClPA was used in combinations with these conventional comonomers, diblock copolymers with narrow molecular weight distribution were selectively formed in the presence of $MoOCl_4$-*n*-Bu_4Sn-EtOH irrespective of the order of monomer addition. On the other hand, 2-nonyne and *p*-BuF_4PA selectively produced block copolymers with the conventional comonomers only when the comonomers were supplied in suitable addition orders. Several diblock copolymers with higher molecular weight were obtained by using either $MoOCl_4$-Et_3Al-EtOH or $MoOCl_4$-*n*-BuLi catalyst, which is due to their lower initiation efficiencies. Use of $MoOCl_4$-*n*-Bu_4Sn-EtOH enabled the preparation of ABA-type triblock copolymers composed of ClPA and ClOc. ABC-type triblock copolymers were produced using $MoOCl_4$-*n*-Bu_4Sn-EtOH from *o*-Me_3SiPA, *o*-CF_3PA, and *p*-BuF_4PA.

Keywords: Block copolymerization; Substituted acetylene; Living metathesis polymerization

1. Introduction

One of the most useful methods to synthesize block copolymers is multistage polymerization of plural monomers using living polymerization systems. In metathesis polymerization, syntheses of block copolymers have been achieved by means of sequential living polymerization of two cycloolefins [1,2], 2-butyne and norbornene [3], acetylene and norbornene [4], and 1,6-heptadiyne and a cycloolefin [5]. Further, block copolymer of substituted phenylacetylenes was prepared by Rh-catalyzed living polymerization [6].

We have been studying the living polymerization of substituted acetylenes with Mo and W catalysts to find that $MoOCl_4$- and $WOCl_4$-based catalysts induce the living polymerization of a variety of substituted acetylenes; among those monomers, typical ones include 1-chloro-1-octyne (ClOc), [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA), and [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) [7–10]. In the preceding paper, we reported the synthesis of several block copolymers from these monomers by means of their sequential living polymerization catalyzed by $MoOCl_4$-*n*-Bu_4Sn-EtOH [11]. Apart from these findings, the living polymerization of 1-chloro-2-phenylacetylene (ClPA), 2-nonyne, and (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene (*p*-BuF_4PA) was accomplished with $MoOCl_4$-*n*-Bu_4Sn-EtOH more recently [12–14]; the living character of these monomers, however, is more or less inferior to that of the above-stated monomers. Thus it seemed very interesting to examine whether these monomers can be used for the synthesis of various novel block copolymers.

This paper reports on the synthesis of various diblock and ABC- and ABA-type triblock copolymers from combinations of ClPA, *p*-BuF_4PA, and 2-nonyne with other substituted acetylenes by $MoOCl_4$-based catalysts. As shown in Scheme 1, the monomers employed are classified into two groups; i.e. group A comonomers (novel comonomers; ClPA, 2-nonyne, and *p*-BuF_4PA) and group B comonomers (conventional comonomers; ClOc, *o*-Me_3SiPA, and *o*-CF_3PA). The $MoOCl_4$-*n*-Bu_4Sn-EtOH

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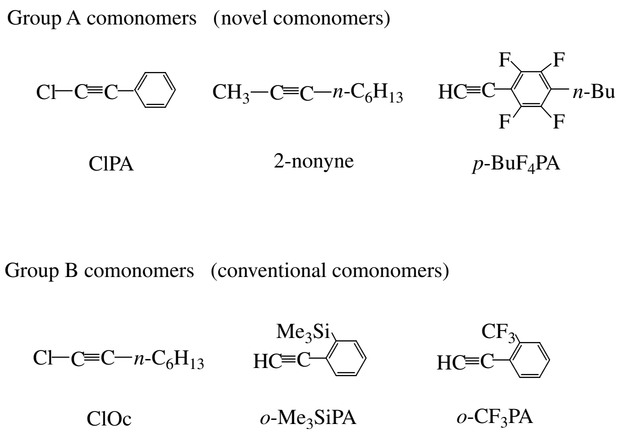


Scheme 1.

(1:1:2), $MoOCl_4$-Et_3Al-EtOH (1:1:3), and $MoOCl_4$-*n*-BuLi (1:1) systems were used as polymerization catalysts. Consequently, selective synthesis of novel diblock and ABC- and ABA-type triblock copolymers was achieved with $MoOCl_4$-*n*-Bu_4Sn-EtOH. Further, several block copolymers featuring high molecular weights were obtained by use of the $MoOCl_4$-Et_3Al-EtOH and $MoOCl_4$-*n*-BuLi systems.

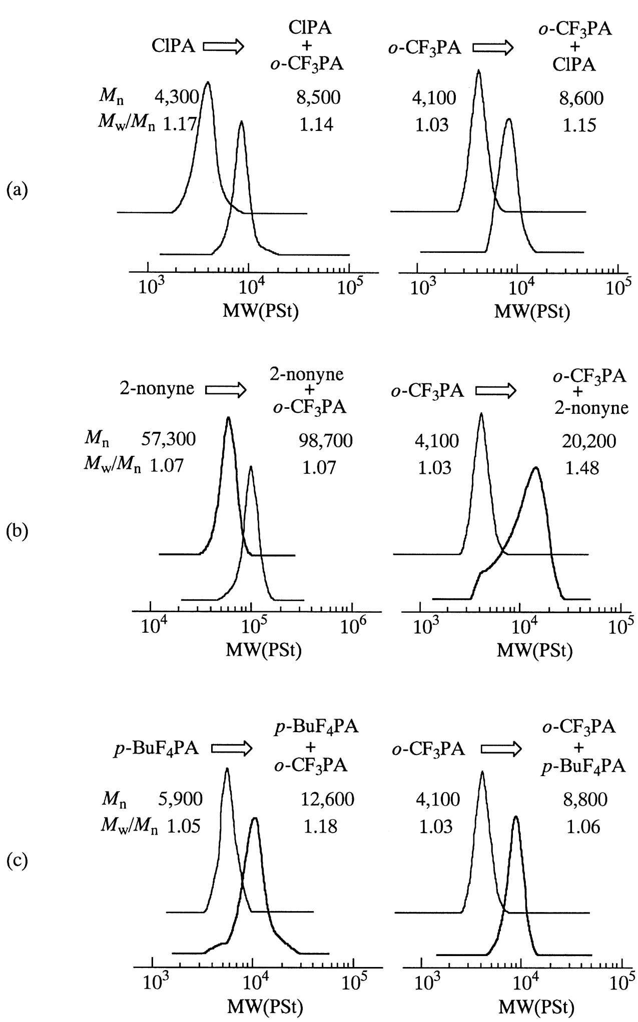


Fig. 1. Block copolymerization of *o*-CF_3PA with the novel comonomers catalyzed by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:2).

2. Experimental

2.1. Materials and measurements

ClPA [15], ClOc [15], *p*-BuF_4PA [16,17], *o*-Me_3SiPA [18,19], and *o*-CF_3PA [16,17] were prepared according to the literature methods. 2-Nonyne (Lancaster) was distilled twice under reduced pressure before use. $MoOCl_4$ (Strem), Et_3Al (Kanto Chemical), and *n*-BuLi (Kanto Chemical) 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 molecular weight distributions (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. Initiation efficiencies ($[P^*]/[Cat]$) were calculated from the polymer yields and the degrees of polymerization. Monomer conversions were measured by GC (Shimadzu GC-14B equipped with a CBP10-M25-025 capillary column or Shimadzu GC-8A equipped with a silicone DC-550 (3 m) column), and polymer yields were determined by gravimetry.

2.2. Polymerization procedures

Solution of the $MoOCl_4$-*n*-Bu_4Sn-EtOH catalyst, as an example, was prepared as follows: $MoOCl_4$ and *n*-Bu_4Sn were mixed in anisole, and the solution was aged at room temperature for 5–15 min. Then an anisole solution of ethanol was added to the $MoOCl_4$-*n*-Bu_4Sn solution, and the mixture was aged at room temperature for an additional 15 min. Polymerizations were carried out at 30°C in a prebaked 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 first-stage polymerizations were initiated by the addition of a monomer solution to a catalyst solution. When

Table 1
Block copolymerization of ClPA with the conventional comonomers catalyzed 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]
1	ClPA	ClOc	11 400	1.18
2	ClPA	o-Me_3SiPA	10 200	1.23
3	ClPA	o-CF_3PA	8 480	1.14
4	ClOc	ClPA	14 100	1.21
5	o-Me_3SiPA	ClPA	9 420	1.21
6	o-CF_3PA	ClPA	8 600	1.15

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

$MoOCl_4$-n-Bu_4Sn-EtOH was used, 2-nonyne, ClPA, ClOc, o-Me_3SiPA, o-CF_3PA, and p-BuF_4PA were polymerized for 1, 12, 15, 40, 25 min, and 9 h, respectively. In the case of $MoOCl_4$-Et_3Al-EtOH and $MoOCl_4$-n-BuLi catalysts, the polymerizations of 2-nonyne, ClPA, ClOc, o-Me_3SiPA, o-CF_3PA, and p-BuF_4PA were performed for 1, 3, 5, 25, 15 min, and 15 h, 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 to the solution of living polymer formed by the first-stage polymerization. When $MoOCl_4$-n-Bu_4Sn-EtOH was used, the polymerizations of 2-nonyne, ClPA, ClOc, o-Me_3SiPA, o-CF_3PA, and p-BuF_4PA were carried out for 10, 15, 15, 60, 40 min, and 15 h, respectively. In the case of $MoOCl_4$-Et_3Al-EtOH and $MoOCl_4$-n-BuLi, the polymerization time of 2-nonyne, ClPA, ClOc, o-Me_3SiPA, o-CF_3PA, and p-BuF_4PA were set to be 10, 15, 5, 40, 30 min, and 24 h, respectively. For the preparation of triblock copolymers, a third monomer solution was added to the solution of the living polymer formed by the second-stage polymerization. The monomers were completely consumed in all cases after polymerization.

Table 2
Block copolymerization of 2-nonyne with the conventional comonomers catalyzed 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]
1	2-nonyne	ClOc	87 700	1.13
2	2-nonyne	o-Me_3SiPA	101 000	1.07
3	2-nonyne	o-CF_3PA	98 700	1.07
5	ClOc	2-nonyne	20 200	1.68 (trimodal)
6	o-Me_3SiPA	2-nonyne	12 200	1.30
7	o-CF_3PA	2-nonyne	20 200	1.48 (bimodal)

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

3. Results and discussion

3.1. Block copolymerization catalyzed by $MoOCl_4$-n-Bu_4Sn-EtOH

The diblock copolymerizations of o-CF_3PA with group A comonomers (ClPA, 2-nonyne, and p-BuF_4PA) were examined with use of $MoOCl_4$-n-Bu_4Sn-EtOH; the chromatograms of the formed polymers are shown in Fig. 1. When ClPA was employed as comonomer, block copolymers were selectively formed irrespective of the order of monomer addition (Fig. 1(a)). Thus, each of the produced polymers exhibited a unimodal and narrow MWD, and no peak attributable to the homopolymer from the first monomer was detected. In the case of 2-nonyne, a diblock copolymer was selectively obtained when the monomers were supplied in the order of 2-nonyne and then o-CF_3PA (Fig. 1(b)). In contrast, the formed diblock copolymer showed a broad MWD in the case of the opposite order of monomer addition. When p-BuF_4PA was added to a solution of living poly(o-CF_3PA), only the corresponding diblock copolymer was produced (Fig. 1(c)). When the order of addition was reversed, the GPC profile of the polymer exhibited a shoulder due to poly(p-BuF_4PA).

Table 1 summarizes the results for the block copolymerization of all the combinations of ClPA with the group B comonomers, (ClOc, o-Me_3SiPA, and o-CF_3PA) catalyzed by $MoOCl_4$-n-Bu_4Sn-EtOH. The produced block copolymers are characterized by narrow MWD ($M_w/M_n \sim 1.2$) irrespective of the order of monomer addition, which indicates the selective formation of block copolymers. Living poly(ClPA) is stable enough to continue to grow perfectly in the monomer addition experiment, and its reactivity in polymerization is close to those of the group B comonomers. These factors seem to be responsible for the successful block copolymerization using ClPA.

Next, block copolymerizations of 2-nonyne with the group B comonomers were examined (Table 2). Living poly(2-nonyne) quantitatively initiated the polymerization of the group B comonomers to form the corresponding block copolymers in all the monomer combinations (Table 2, runs 1–3). When 2-nonyne was used as the second-stage monomer, the GPC profiles of the products showed broader MWDs due to the formation of a block copolymer and a dead polymer (Table 2, runs 4–6). Formation of the homopolymer from the first monomer is attributable to the incomplete cross propagation from the living polymers of the conventional monomers to 2-nonyne. Thus, 2-nonyne should be employed as the first monomer in the block copolymerizations using 2-nonyne.

Table 3 shows the results of block copolymerization between p-BuF_4PA and one of the group B comonomers. When these conventional monomers were added as second monomers to living poly(p-BuF_4PA), the MWD curves of the formed polymers were bimodal (Table 3, runs 1–3). In contrast, block copolymers were selectively produced, when

Table 3
Block copolymerization of p-BuF$_4$PA with the conventional comonomers catalyzed by MoOCl$_4$-n-Bu$_4$Sn-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]
1	p-BuF$_4$PA	ClOc	15 100	1.34 (bimodal)
2	p-BuF$_4$PA	o-Me$_3$SiPA	13 900	1.23 (bimodal)
3	p-BuF$_4$PA	o-CF$_3$PA	12 600	1.18 (bimodal)
4	ClOc	p-BuF$_4$PA	14 900	1.07
5	o-Me$_3$SiPA	p-BuF$_4$PA	9 400	1.12
6	o-CF$_3$PA	p-BuF$_4$PA	8 800	1.06

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

Table 4
Block copolymerization between the novel and conventional comonomers catalyzed by MoOCl$_4$-Et$_3$Al-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]
1	ClPA	ClOc	41 800	1.17
2	ClPA	o-Me$_3$SiPA	36 900	1.22
3	ClPA	o-CF$_3$PA	35 100	1.12
4	2-nonyne	ClOc	112 000	1.16
5	2-nonyne	o-Me$_3$SiPA	117 000	1.13
6	2-nonyne	o-CF$_3$PA	109 000	1.15
7	ClOc	p-BuF$_4$PA	40 100	1.14
8	o-Me$_3$SiPA	p-BuF$_4$PA	25 700	1.06
9	o-CF$_3$PA	p-BuF$_4$PA	18 700	1.07

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

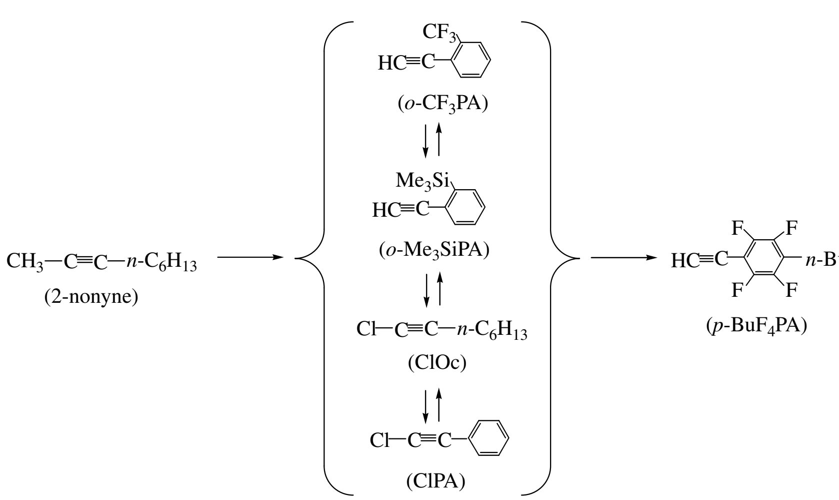
the order of monomer addition was reversed (Table 3, runs 4–6). These results suggest that, whereas the cross propagation from the living poly(p-BuF$_4$PA) to the conventional acetylenes is too sluggish, the living polymers from the conventional acetylenes can initiate the living polymerization of p-BuF$_4$PA effectively.

On the basis of experimental results, Scheme 2 illustrates the suitable orders (arrows) of monomer addition so as to accomplish selective block copolymerizations by using MoOCl$_4$-n-Bu$_4$Sn-EtOH (1:1:2) system. In summary, the following grouping of monomers and order of additions lead to successful block copolymerizations; i.e. first monomer: 2-nonyne; second monomers: ClPA, ClOc, o-Me$_3$SiPA, and o-CF$_3$PA; third monomer: p-BuF$_4$PA. This order is very close to the following order of propagation rate: 2-nonyne $\gg$ ClPA $\geq$ ClOc $\geq$ o-CF$_3$PA $\geq$ o-Me$_3$SiPA $\gg$ p-BuF$_4$PA. A possible explanation for this is as follows. In the case of monomers which show large propagation rates, both the monomer and the propagating end will have large reactivities. When a propagating species with large reactivity is generated from the first monomer, the cross propagation from the propagating species to the second monomer will proceed smoothly, which leads to successful block copolymerization. In the case of the opposite order of monomer addition, the cross propagation is slow compared with the self propagation of the second monomer, which will end up with a broader or bimodal MWD.

3.2. Block copolymerization catalyzed by MoOCl$_4$-Et$_3$Al-EtOH

So far, it has been revealed that not only n-Bu$_4$Sn but also Et$_3$Al and n-BuLi are effective as cocatalysts for the MoOCl$_4$-based living polymerization of substituted acetylenes [7–9]. The most distinct difference among these cocatalysts is seen in the initiation efficiency. Thus we examined block copolymerizations using MoOCl$_4$-Et$_3$Al-EtOH.

Table 4 summarizes only the successful results for the block copolymerizations of the group A monomers with the group B monomers. Fig. 2 depicts the GPC profiles of the products in the attempted block copolymerizations of o-CF$_3$PA with the group A monomers. It is obvious from Fig. 2 that the order of monomer addition drastically influences the block copolymerizations.



Scheme 2.

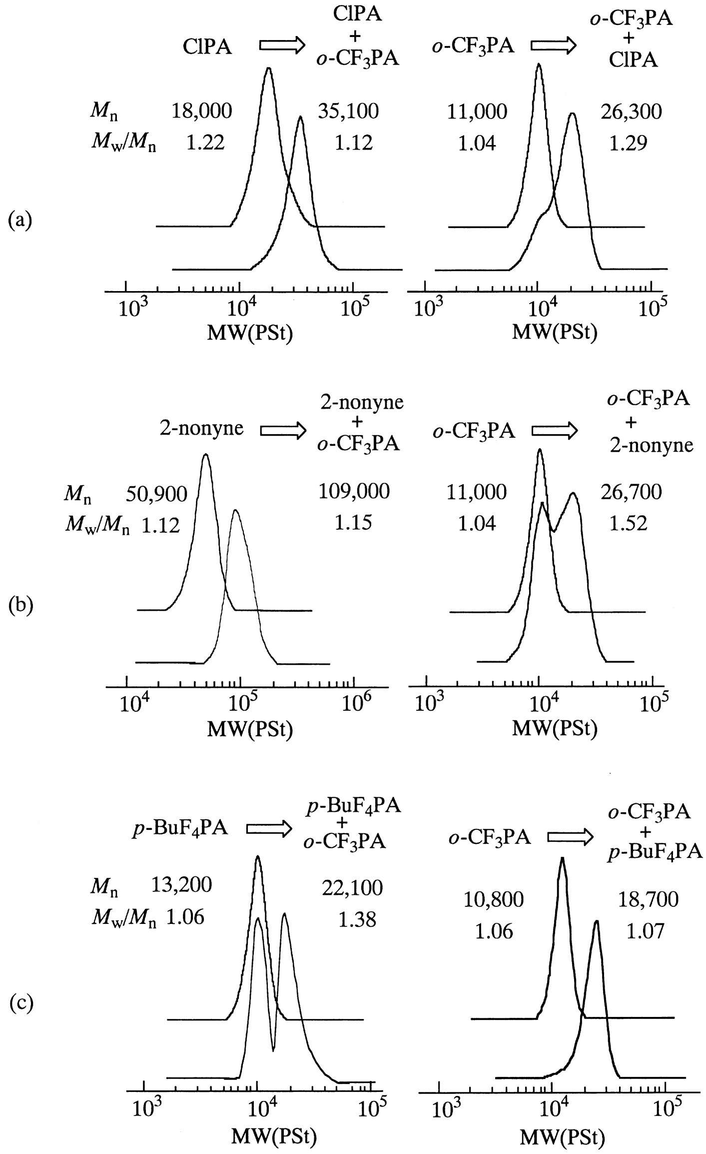
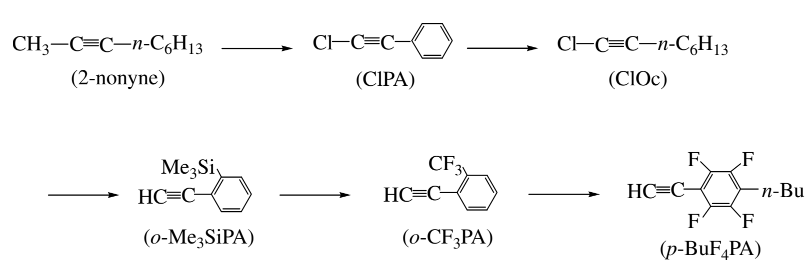


Fig. 2. Block copolymerization of o-CF_3PA with the novel comonomers catalyzed by $MoOCl_4$-Et_3Al-EtOH (1:1:3).

When o-CF_3PA was added to the solution of living poly(ClPA), the corresponding block copolymer was selectively obtained (Table 4, run 3 and Fig. 2(a)). In contrast, when the order of monomer addition was reversed, the product showed a shoulder in the GPC curve due to the homopolymer of o-CF_3PA as a byproduct (Fig. 2(a)). Similarly, living poly(ClPA) undergoes quantitative cross propagation to o-Me_3SiPA and ClOc, leading to the selective formation of block copolymers (Table 4, runs 2 and 3). These block copolymers have relatively high molecular weight as compared to those with the n-Bu_4Sn cocatalyst, which means smaller initiation efficiencies for



Scheme 3.

Table 5
Block copolymerization of p-BuF_4PA with the conventional comonomers catalyzed 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]
1	ClOc	p-BuF_4PA	249 000	1.20
2	o-Me_3SiPA	p-BuF_4PA	231 000	1.18
3	o-CF_3PA	p-BuF_4PA	146 000	1.17

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

Table 6
Ternary block copolymerization using novel comonomers catalyzed 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]	3rd monomer[b]	M_n[c]	M_w/M_n[c]
1	ClOc	ClPA	ClOc	22 000	1.24
2	ClPA	ClOc	ClPA	20 200	1.22
3	o-Me_3SiPA	o-CF_3PA	p-BuF_4PA	15 900	1.10
4	o-CF_3PA	o-Me_3SiPA	p-BuF_4PA	16 400	1.11

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

the $MoOCl_4$-Et_3Al-EtOH system. On the other hand, block copolymers were not selectively formed with the opposite order of monomer addition.

A similar phenomenon was observed in the block copolymerization of 2-nonyne with the group B comonomers. When the polymerization of 2-nonyne was followed by the addition of the group B monomers, the MWDs of the produced block copolymers were relatively narrow, indicating the smooth cross propagation reactions (Table 4, runs 4–6). In contrast, the opposite order of monomer addition led to the formation of dead homopolymers (e.g. Fig. 2(b)). The block copolymerizations of p-BuF_4PA with the group B comonomers were also examined. When p-BuF_4PA was supplied to the solution of living polymers from the group B comonomers, the corresponding block copolymers were selectively produced (Table 4, runs 7–9 and Fig. 2(c)). The opposite order of monomer addition again failed to selectively form block copolymers (Fig. 2(c)). This is the same tendency as in the $MoOCl_4$-n-Bu_4Sn-EtOH system.

Based on results of the preceding [11] and present studies, Scheme 3 depicts the suitable order (arrows) of monomer addition for selective block copolymerization by using the $MoOCl_4$-Et_3Al-EtOH (1:1:3) system. As seen in the scheme, the order of monomer addition affected block copolymerization more than the case with the $MoOCl_4$-n-Bu_4Sn-EtOH system. Thus, block copolymers were selectively formed only when the following order was obeyed: (1) 2-nonyne; (2) ClPA; (3) ClOc; (4) o-Me_3SiPA; (5) o-CF_3PA; and (6) p-BuF_4PA. Another feature of the Et_3Al-containing catalyst as compared to the n-Bu_4Sn-involving counterpart is that the molecular weight of the formed block copolymers is large owing to the low initiation efficiency (cf. Table 4 vs. Tables 1–3).

3.3. Block copolymerization catalyzed by $MoOCl_4$-n-BuLi

According to previous studies [12,13], ClPA and 2-nonyne provide polymers with broad MWD in the presence of $MoOCl_4$-n-BuLi, while p-BuF_4PA polymerizes in a living fashion. Thus it was examined whether p-BuF_4PA and the group B comonomers can produce block copolymers with $MoOCl_4$-n-BuLi or not (Table 5). When p-BuF_4PA was used as second monomer, cross propagation quantitatively occurred to form block copolymers. In contrast, the opposite order of monomer addition led to the failure in the selective formation of block copolymers. It is noteworthy that the monomer combinations in Table 5 afford block copolymers with extremely high molecular weight (M_n 150 000–250 000) by use of $MoOCl_4$-n-BuLi, which is due to the low initiation efficiency of the catalyst.

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

It has been clarified that ClPA provides diblock copolymers with ClOc, o-Me_3SiPA, and o-CF_3PA irrespective of the order of monomer addition in the presence of $MoOCl_4$-n-Bu_4Sn-EtOH. Thus there is a possibility that these monomer combinations afford ABA-type triblock copolymers. As an example, synthesis of ABA- and BAB-type triblock copolymers was attempted with a combination of ClPA and ClOc. Table 6 shows that both triblock copolymers have been successfully obtained (runs 1, 2).

On the other hand, p-BuF_4PA is suited as the second monomer in the binary block copolymerization with o-Me_3SiPA and o-CF_3PA. Thus synthesis of ABC-type triblock copolymers was attempted from these monomers. As seen in Table 6, runs 3 and 4, two kinds of ABC-type triblock copolymers were successfully prepared.

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References

[1] Saunders RS, Cohen RE, Schrock RR. Macromolecules 1991;24:5599.

[2] Park LY, Schrock RR, Stieglitz SG, Crowe WE. Macromolecules 1991;24:3489.
[3] Wallace KC, Liu AH, Davis WM, Schrock RR. Organometallics 1989;8:644.
[4] Schlund R, Schrock RR, Crowe WE. J Am Chem Soc 1989;111:8004.
[5] Fox HH, Wolf MO, O'Dell R, Lin BL, Schrock RR, Wrighton MS. J Am Chem Soc 1994;116:2827.
[6] Kishimoto Y, Eckerle P, Miyatake T, Ikariya T, Noyori R. J Am Chem Soc 1994;116:12131.
[7] Hayano S, Itoh T, Masuda T. Polymer 1999;40:4071.
[8] Kaneshiro H, Hayano S, Masuda T. Macromol Chem Phys 1999;200:113.
[9] Hayano S, Masuda T. Macromolecules 1998;31:3170.
[10] Hayano S, Masuda T. Macromolecules 1999;32:7344.
[11] Iwawaki E, Hayano S, Nomura R, Masuda T. Polymer 2000;41:4429.
[12] Hayano S, Masuda T. J Macromol Sci, Pure Appl Chem 2000;37:853.
[13] Kubo H, Hayano S, Masuda T. J Polym Sci, Part A: Polym Chem 2000;38:2697.
[14] Masuda T, Mishima K, Seki H, Nishida M, Higashimura T. Polym Bull 1994;32:19.
[15] Masuda T, Yoshimura T, Tamura K, Higashimura T. Macromolecules 1987;20:1734.
[16] Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;50:4467.
[17] Carpita A, Lessi A, Rossi R. Synthesis 1984:571.
[18] Brandsma L, Hommes H, de Jong RLP, Verkruijsse HD. Recl Trav Chim Pays-Bas 1985;104:226.
[19] Brandsma L. Preparative acetylenic chemistry, 2. Amsterdam: Elsevier, 1988 (p. 124).