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Living polymerization and block copolymerization of various ring-substituted phenylacetylenes by rhodium-based ternary catalyst

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Summary

Polymerization of several ring-substituted phenylacetylenes, i.e. *p*-methoxy-, *p*-methyl-, *p*-chloro-, and *p*-methoxycarbonylphenylacetylenes by the $[(nbd)RhCl]_2/Ph_2C{=}CPhLi/Ph_3P$ ternary catalyst proceeded in a living fashion to quantitatively provide polymers with low polydispersity indices (M_w/M_n 1.04-1.18). The initiation efficiencies were virtually quantitative. Block copolymerizations proceeded regardless of the combinations and addition orders of these monomers to selectively form the corresponding block copolymers.

Introduction

It is known that catalysts based on group 5 and 6 transition metals and rhodium are able to polymerize substituted acetylenes [1]. Rhodium catalysts are effective in the polymerization of monosubstituted acetylenes, especially phenylacetylene. Rhodium catalysts have two salient features; i.e. one is selective formation of cis-transoid polymers [2], and the other is availability of protic polymerization solvents such as amines and alcohols [3]. Noyori et al. reported the living polymerization of phenylacetylene with rhodium catalysts such as $(nbd)Rh(C{\equiv}CPh)(Ph_3P)_2$/DMAP [4] and $[(nbd)Rh(OMe)]_2/Ph_3P$/DMAP [5], (nbd: bicyclo[2.2.1]hepta-2,5-diene, DMAP: 4-(dimethylamino)pyridine). These catalyst systems require the addition of DMAP to prevent the formation of inactive binuclear complexes, and the initiation efficiencies are not quantitative [6].

Recently, we have reported that the $[(nbd)RhCl]_2/Ph_2C{=}CPhLi/Ph_3P$ ternary catalyst induces living polymerization of phenylacetylene. The initiation efficiency of this system is quantitative and end-functionalized polymers are easily prepared by use of (triphenylvinyl)lithiums having functional groups [7]. Generally speaking, there is a possibility of the formation of block copolymers by sequential polymerization, if several monomers polymerize in a living fashion with the same catalyst. Thus, in the present study, we examined the living polymerization of ring-substituted phenylacetylenes using the $[(nbd)RhCl]_2/Ph_2C{=}CPhLi/Ph_3P$ catalyst, and further attempted the synthesis of block copolymers from them. Phenylacetylene and its derivatives having methoxy, methyl, chloro, and methoxycarbnyl groups at para position were employed as monomers; they are abbreviated as PA, *p*-MeOPA, *p*-MePA, *p*-ClPA, and *p*-MeOCOPA, respectively.

Experimental

$[(nbd)RhCl]_2$ and triphenylphosphine were used as purchased. PA was distilled twice from CaH_2 at reduced pressure. Toluene was washed by the standard method, dried, and distilled twice from CaH_2. Diethyl ether was distilled from sodium/benzophenone ketyl. Ring-substituted PAs were synthesized by applying the literature methods through Pd-catalyzed coupling of the corresponding substituted iodobenzenes with either 2-methyl-3-butyn-2-ol or trimethylsilylacetylene and the subsequent deprotection [8], and purified by distillation or recrystallization.

A mixture of lithium (6.9 mg, 1.0 mmol) and a diethyl ether solution (10 ml) of bromotriphenylethylene (0.1710 g, 0.51 mmol) was irradiated with supersonic wave for 4 h. The resulting yellow solution was used as (triphenylvinyl)lithium solution (50 mM).

Polymerizations were carried out under dry nitrogen in a Schlenk tube equipped with a three-way stopcock. A typical procedure was as follows: The catalyst solution was prepared by adding the ether solution of (triphenylvinyl)lithium (2.0 ml, 1.0 mmol) to a toluene solution (3.0 ml) of $[(nbd)RhCl]_2$ (11.5 mg, 0.025 mmol) and triphenylphosphine (39.4 mg, 0.15 mmol). After catalyst aging for 15 min, polymerization was started by adding a toluene solution of monomer (0.125 M, 4 ml, 0.5 mmol) to 1.0 ml of the catalyst solution. The polymerization was allowed to proceed at 30 °C for 1 h, and then quenched with 0.2 mmol of acetic acid. Monomer conversions were determined by GC. Resulting polymers were precipitated into a large amount of MeOH, filtered, and dried in vacuo at room temperature. Polymer yields were determined by gravimetry. The molecular weights and polydispersity indices (PDIs) of polymers were determined by GPC (eluent THF, columns Shodex KF805L x 3, polystyrene calibration).

Results and Discussion

Living polymerization of ring-substituted PAs

Polymerization of various ring-substituted PAs with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst was examined. All the monomers employed quantitatively polymerized within 1 h, and the corresponding polymers with narrow molecular weight distribution (MWD) (PDIs < 1.2) were obtained in nearly quantitative yields (Table 1). The PDIs of the polymers obtained from monomers having an electron-donating substituent such as *p*-MeOPA and *p*-MePA were about 1.2 while those of the polymers obtained from monomers having an electron-withdrawing substituent such as *p*-ClPA and *p*-MeOCOPA were smaller than 1.1. The initiation efficiencies were 90-100% and nearly quantitative irrespective of the kind of monomers. The resulting polymers except poly(*p*-MePA) were yellow to orange solids and soluble in many organic solvents such as toluene, chloroform, and tetrahydrofuran. Poly(*p*-MePA) was yellow solid and sparingly soluble in these solvents, and the insoluble part turned red in toluene. This is probably because the polymer became insoluble by the main-chain isomerization from cis-

Table 1. Polymerization of PA and para-substituted PAs by $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6)[a]

Monomer	Polymer			
	Yield, %	M_n	M_w/M_n	E_{ini}, %
p-MeOPA	100	7 000	1.18	94.3
p-MePA	90	6 200	1.16	93.5
PA	100	5 100	1.14	100
p-ClPA	97	6 000	1.06	100
p-MeOCOPA	96	8 300	1.04	96.4

[a] Polymerized in toluene at 30 °C for 1 h; $[M]_0 = 0.10$ M, $[[(nbd)RhCl]_2] = 1.0$ mM.

[b] Initiation efficiency.

transoidal structure to cis-cisoidal structure.

Hence the present monomers produced polymers with narrow MWD, multistage polymerization of each monomer was examined in order to confirm that the polymerizations are living systems. Polymerizations were initiated under the conditions shown in Table 1, and monomer feeds were supplied at intervals of an hour. As seen in Figure 1, polymer was quantitatively obtained at every stage for every monomer. Molecular weight of the polymers increased in proportion to monomer consumption, while their PDI remained as small as 1.05-1.20. This indicates that propagating species maintain their activity even after the completion of polymerization, and that the present polymerization of all the substituted PAs are living systems.

The time profiles of the polymerizations were examined. Since the polymerizations were very fast under the conditions of Table 1, 20 equivalent of Ph_3P to $[(nbd)RhCl]_2$ was employed to retard the polymerizations [9]. As shown in Figure 2, the first-order plots of monomers were all linear, indicating that the polymerization rate is proportional to the first order of monomer concentration. The polymerization of PA was faster than those of ring-substituted PAs, and among ring-substituted PAs, those with electron-donating groups polymerized faster than those with electron-withdrawing groups.

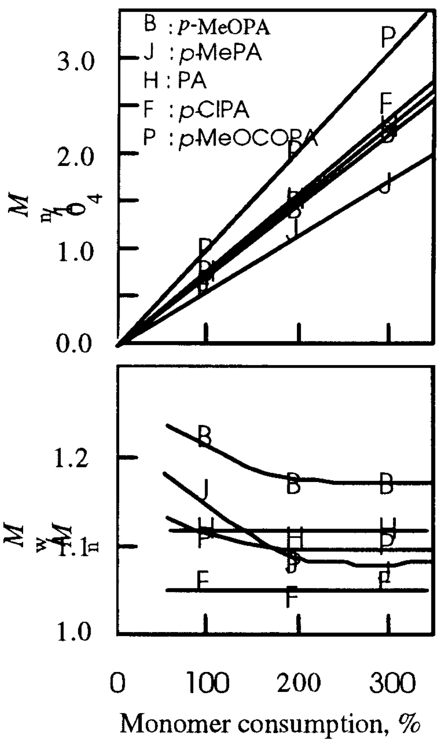

Figure 1. Multistage polymerization of para-substituted PAs (in toluene at 30 °C for 1 h for each stage; $[M]_{0,add}$ = 0.10 M, $[[(nbd)RhCl]_2]$ = 1.0 mM, $[Ph_2C{=}CPhLi]$ = 4.0 mM, $[Ph_3P]$ = 6.0 mM).

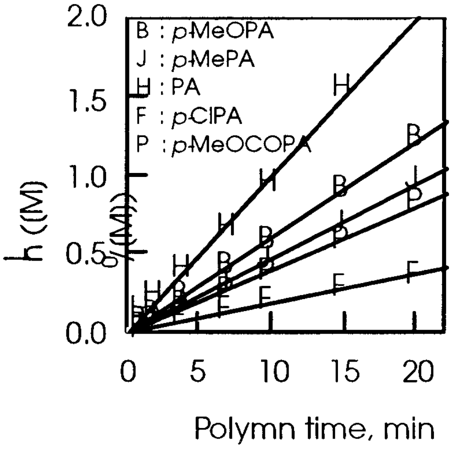

Figure 2. First-order plots for the polymerization of para-substituted PAs (in toluene at 30 °C; $[M]_0$ = 0.10 M, $[[(nbd)RhCl]_2]$ = 1.0 mM, $[Ph_2C{=}CPhLi]$ = 4.0 mM, $[Ph_3P]$ = 20 mM).

Block copolymerization of various ring-substituted PAs

Since it proved that various para-substituted phenylacetylenes polymerize in a living fashion, block copolymerization of these monomers was examined. Polymerization conditions similar to those in Table 1 were adopted except for polymerization time. The periods of time for the first-stage polymerization were as follows: 15 min (PA, *p*-MeOPA), 20 min (*p*-MePA and *p*-MeOCOPA), and 40 min (*p*-ClPA). After the first-stage polymerization, the same amount of second monomer was added and allowed to polymerize for one hour. The reason for employing different polymerization times in the first stage is to start the second-stage polymerization just after the first-stage polymerization had been finished. Monomers were completely consumed in both stages and the resulting polymers were quantitatively obtained.

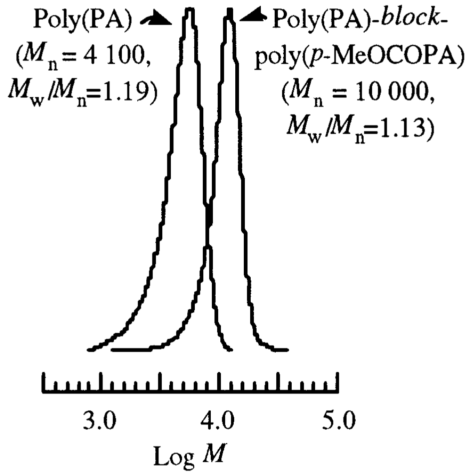

Figure 3. GPC traces of poly(PA) and poly(PA)-*block*-poly(*p*-MeOCOPA) (see Table 2 for conditions).

At first, block copolymerizations were examined by using PA as the first monomer and para-substituted PAs as the second monomers. Figure 3 shows an example of the GPC profiles of first-stage polymer and block copolymer. Poly(PA)-*block*-poly(*p*-MeOCOPA) exhibits no shoulder due to poly(PA), and clearly shifts toward the high molecular weight side as compared to poly(PA). As shown in Table 2, all these monomer combinations provide block copolymers selectively.

Table 2. Block copolymerization of PA with para-substituted PAs by $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6)[a]

Monomer		Polymer		
M_A[b]	M_B	Yield, %	M_n	M_w/M_n
PA	–	100	4 100	1.19
PA	*p*-MeOPA	100	8 600	1.13
PA	*p*-MePA	100	10 300	1.10
PA	*p*-ClPA	100	9 700	1.11
PA	*p*-MeOCOPA	100	10 000	1.13

[a] Polymerized in toluene at 30 °C for 15 min for the first stage and 1 h for the second stage; $[M_A] = [M_B] = 0.10$ M, $[[(nbd)RhCl]_2] = 1.0$ mM.

[b] M_A: First monomer.

Table 3. Block copolymerization of para-substituted PAs with PA by $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6)[a]

Monomer		Polymer		
M_A[b]	M_B	Yield, %	M_n	M_w/M_n
p-MeOPA	–	100	5 900	1.21
p-MeOPA	PA	100	9 800	1.19
p-MePA	–	100	5 300	1.19
p-MePA	PA	100	10 100	1.13
p-ClPA	–	100	7 400	1.06
p-ClPA	PA	100	14 200	1.08
p-MeOCOPA	–	100	8 300	1.04
p-MeOCOPA	PA	100	15 100	1.05

[a] Polymerized in toluene at 30 °C for 15 min (*p*-MeOPA), 20 min (*p*-MePA , *p*-MeOCOPA), 40 min (*p*-ClPA) for the first stage and 1 h for the second stage; $[M_A] = [M_B] = 0.10$ M, $[[(nbd)RhCl]_2] = 1.0$ mM.

[b] M_A: First monomer.

Next, the order of monomer addition was inversed, that is, para-substituted PAs were at first polymerized and then PA was added as the second monomer (Table 3). In all cases, the products showed single GPC peaks with narrow MWD, which supports the exclusive formation of block copolymers.

Finally, block copolymerizations between para-substituted PAs were carried out (Table 4). Even the combinations of monomers with electron-donating and -withdrawing groups such as *p*-MeOPA and *p*-MeOCOPA provided block copolymers with narrow MWD irrespective of the order of monomer addition. Narrower MWD (PDIs ~1.05) was achieved when monomers with electron-withdrawing groups such as *p*-MeOCOPA and *p*-ClPA were used as the first monomers. The MWD depended only on the kind of the first monomer, and not on the kind of the second monomer.

In conclusion, the present study has revealed that PA and its various ring-substituted derivatives, (i.e. *p*-MeOPA, *p*-MePA, *p*-ClPA, and *p*-MeOCOPA), polymerize in a living fashion in the presence of $[(nbd)RhCl]_2/Ph_2C{=}CPhLi/\ Ph_3P$ ternary catalyst, and that they provide block copolymers selectively irrespective of the monomer combination and their addition order.

Table 4. Block copolymerization between para-substituted PAs by $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6)[a]

Monomer		Polymer		
M_A[b]	M_B	Yield, %	M_n	M_w/M_n
p-MeOPA	–	100	5 900	1.21
p-MeOPA	*p*-MePA	100	11 000	1.15
p-MeOPA	*p*-MeOCOPA	97.3	12 000	1.13
p-MePA	–	100	5 300	1.19
p-MePA	*p*-MeOPA	100	11 700	1.12
p-ClPA	–	100	7 400	1.06
p-ClPA	*p*-MeOCOPA	99.5	17 200	1.06
p-MeOCOPA	–	100	8 300	1.04
p-MeOCOPA	*p*-MeOPA	98.9	14 600	1.06
p-MeOCOPA	*p*-ClPA	87.4	15 800	1.04

[a] Polymerized in toluene at 30 °C for 15 min (*p*-MeOPA), 20 min (*p*-MePA , *p*-MeOCOPA), 40 min (*p*-ClPA) for the first stage and 1 h for the second stage; $[M_A] = [M_B] = 0.10$ M, $[[(nbd)RhCl]_2] = 1.0$ mM.

[b] M_A: First monomer.

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