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Living Polymerization of Phenylacetylene Catalyzed by a Cationic Rh Complex Bearing Tetrafluorobenzobarrelene

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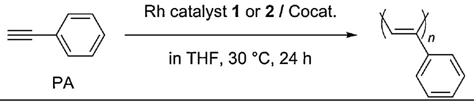
Living polymerization of phenylacetylene (PA) was achieved with new catalyst systems composed of a cationic rhodium complex, [(tfb)Rh(PPh_3)$_2$]BPh_4 (**2**, tfb = tetrafluorobenzobarrelene) and amines as cocatalysts. Applying *i*-PrNH_2 as a cocatalyst, the PDI of the formed poly(PA) was as small as 1.09. Kinetic plots and multistage polymerization proved the livingness of the present polymerization.

Substituted polyacetylenes are promising functional materials for their chemically and physically unique properties.[1,2] Catalysts based on rhodium (Rh) complexes are most commonly used for the polymerization of monosubstituted acetylenes,[2,3] because of their high activity as well as tolerance of polar functional groups of monomers and solvents.[4] Living polymerization of several monomers has been achieved by using classic and well-defined Rh catalysts.[5–9]

Our group has reported a new class of active Rh catalysts that contain a highly π-acidic diene ligand, tetrafluorobenzobarrelene (tfb).[10–12] As compared to conventional catalysts bearing 2,5-norbornadiene (nbd), a series of Rh–tfb catalysts feature high activity in the polymerization of monosubstituted acetylenes such as phenylacetylene (PA) and high molecular weight of the formed polymers. More recently, a zwitterionic Rh–tfb catalyst, (tfb)Rh^+[(η^6-Ph)B^-Ph_3] (**1**), was proven to be another versatile catalyst; catalyst **1** shows of high activity giving high polymer, attributed to the formation of highly active species in a small quantity.[12] In the course of further study on catalyst **1**, we found that its cationic derivative containing two triphenylphosphines (PPh_3), [(tfb)Rh(PPh_3)$_2$]BPh_4 (**2**), gives poly(PA) with a relatively small polydispersity index (PDI). Here we wish to report that new catalysts comprising **2** and various amines as cocatalysts achieve the living polymerization of PA.

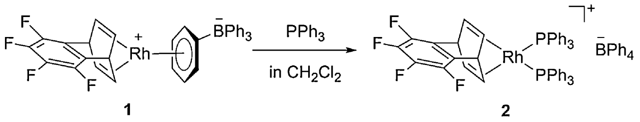
As shown in our previous paper, catalyst **1** polymerizes PA into a high molecular weight polymer, but the PDI of the polymer is 1.80, indicating nonliving character (Entry 1 in Table 1). In contrast, catalyst **2**, synthesized by the reaction of **1** with two equivalents of PPh_3 (Scheme 1),[13,14] itself gave poly(PA) with a relatively small PDI value of 1.4 (Entry 2). Another noteworthy point is an improved initiation efficiency (IE) of catalyst **2** compared to catalyst **1**, as seen from the polymer molecular weights. The phenyl group of BPh_4 in **1** is considered to coordinate in stable form toward ligand exchanging with PA. Catalyst **2** bears two molecules of PPh_3 which have been revealed to coordinate to an Rh center competitively with PA,[9,11] indicating that catalyst **2** should readily react with PA to form active species. It also suggests that the presence of the other coordination compounds would effect control of the polymerization. We finally found conjunction of amines with catalyst **2** remarkably reduce PDIs of the obtained polymers (Entries 3–7), especially when *i*-PrNH_2 was applied, the PDI value of poly(PA) given became as small as 1.09. The formed polymer possessed high stereoregularity with cis-transoidal main chain structure (cis content = 97%) calculated from ^{1}H NMR.

Table 1. Polymerization of PA with Rh complexes **1** and **2**[a]



Entry	Cat.	Cocat.[b]	Conv.[c]/%	Polymer		
				Yield[d]/%	M_n[e]	PDI[e]
1[f]	**1**	None	100	quant	180000	1.80
2	**2**	None	100	95	54000	1.40
3	**2**	Et_3N	100	93	92000	1.17
4	**2**	Et_2NH	100	88	98000	1.15
5	**2**	*n*-BuNH_2	100	90	79000	1.12
6	**2**	*i*-PrNH_2	100	99	100000	1.09
7	**2**	pyridine	100	quant	110000	1.23

[a]In THF, 30 °C, 24 h, $[PA]_0 = 0.50$ M, $[PA]_0/[Rh] = 500$. See experimental details in Supporting Information.[14] [b][Cocat]/[Rh] = 10. [c]Determined by GC ([*tert*-butylbenzene] = 50 mM as an internal standard). [d]MeOH-insoluble part. [e]Estimated by GPC (PSt standard). [f]Data from previous literature.[12a]



Scheme 1. Synthesis of cationic Rh catalyst **2** from **1**.

The rate of the polymerization with catalyst **2** and *i*-PrNH_2 was monitored (Figure 1a). The polymerization proceeded in first order with respect to monomer concentration, which indicates a bimolecular reaction between PA and the propagating species. However, the line did not pass the origin, implying that the initiating species is formed through multiple steps including PA consumption in the initial stage.

Multistage polymerization was examined to gain further information about the living nature. The second-stage polymerization also proceeded practically at the same rate as the first to finally reach completion (Figure 1b). Figure 1c shows M_n's and PDIs of the obtained polymers in another three-stage polymerization. At the end of each stage, aliquots were subjected

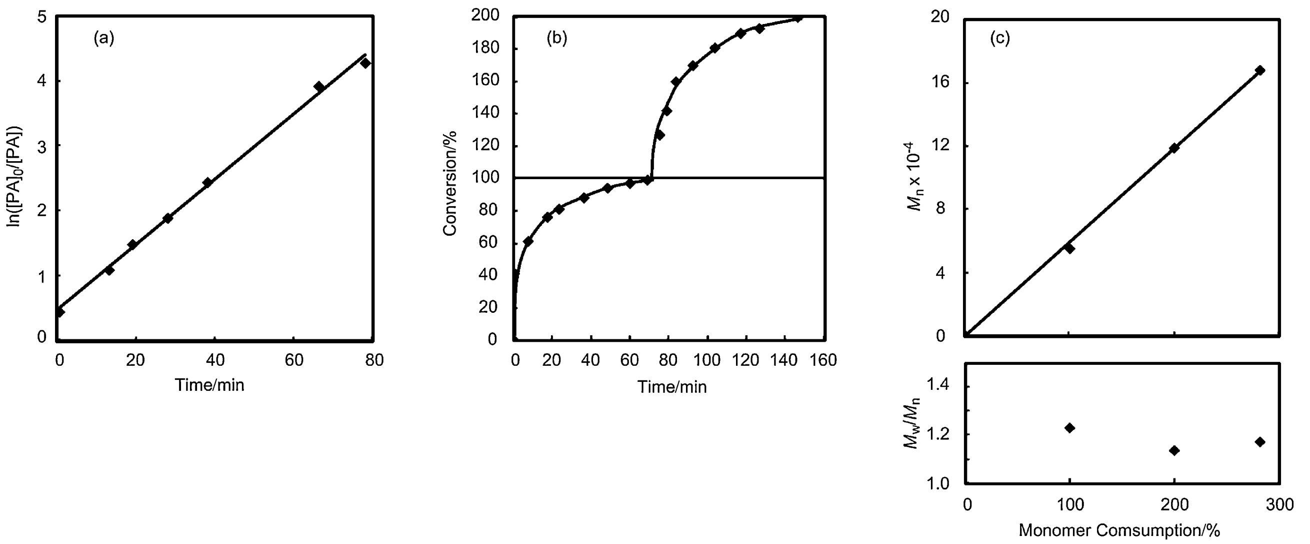


Figure 1. (a) First-order plot for PA polymerization by **2** and *i*-PrNH$_2$, (b) time-conversion curve for multistage polymerization of PA, and (c) M_n plot for multistage polymerization of PA {conditions: see caption a in Table 1 with catalyst **2** and *i*-PrNH$_2$. For (b) and (c), $[PA]_0/[Rh] = 250$ and $[PA]_0 = [PA]_{add} = 0.50$ M}.

to isolation of formed polymer for GPC measurement. The following stages were then started by supplying PA to the remaining polymerization solution. The M_n of the produced polymers increased in proportion to the consumption of monomer [$M_n = 55000$ (1st stage), 119000 (2nd), and 168000 (3rd)], while PDI remained in a range of small value of 1.13–1.23. These results obviously prove that this polymerization is a living polymerization.

Addition of amines such as *i*-PrNH$_2$ is essential in the present living polymerization of PA with catalyst **2**. It is assumed that amines exchange with coordinated PPh$_3$ of **2** in the initial stage of the polymerization and eventually accelerates monomer coordination to the Rh center with liberation of amine. This will promote facile formation of initiating species and in turn propagating species (most likely Rh–alkenyl).[8a,9a] Kishimoto et al. reported the living polymerization catalyst composed of [(nbd)Rh(μ-OMe)]$_2$, PPh$_3$, and 4-dimethylaminopyridine, which gave an NMR-detectable initiating species having a phenylethynyl group.[5] Oro et al. recently displayed that an Rh–alkynyl initiating species in polymerization of PA generates triggered by formation of ammonium cation derived from the amine ligand of a starting Rh complex and a terminal acetylenic proton of PA.[15] In the present system as well, a similar Rh–alkynyl complex may possibly be formed.

In summary, cationic Rh catalyst **2** polymerized PA into a polymer with a relatively small PDI (1.4). Furthermore, living polymerization was achieved by addition of amines such as *i*-PrNH$_2$ as cocatalysts to give poly(PA) with a PDI of around 1.1. The livingness of the polymerization was confirmed by multistage polymerization.

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