Living Polymerization of Phenylacetylene by Novel Rhodium Catalysts. Quantitative Initiation and Introduction of Functional Groups at the Initiating Chain End

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It is known that substituted acetylenes polymerize with various transition metal catalysts.[1] Recently, studies on the polymerization by catalysts based on Rh, a group 9 transition metal, have been increasing.[2] Rh catalysts are effective for the polymerization of certain monosubstituted acetylenes, especially phenylacetylene. Polymerization of phenylacetylene with Rh catalysts selectively produces a stereoregular polymer with a cis−transoidal main chain. However, the Rh catalysts that induce living polymerization have been limited to $(Ph_3P)_2$(nbd)RhC≡CPh/4-(dimethylamino)pyridine[3] and $[Rh(OMe)(nbd)]_2/PPh_3$/4-(dimethylamino)pyridine[4] systems (nbd: 2,5-norbornadiene). These living polymerizations proceed via insertion of the monomer into the Rh−carbon single bond. However, the initiator efficiency is not quantitative (37−72%), and 4-(dimethylamino)pyridine, whose function is unknown, should be added. Further, the initiation reaction by the (phenylethynyl)rhodium complex involves a series of reactions, and the initiating end group of the polymer is not a phenylethynyl group but a hydride. Hence it is impossible to synthesize end-functionalized poly(phenylacetylene)s with this catalyst.

Since the propagating species of these catalyst systems should be vinylrhodiums, we inferred that, if a stable vinylrhodium species is generated from a mixture of rhodium chloride complex, a vinyllithium, and PPh_3, it would induce excellent living polymerization. Here we report on a novel living polymerization of phenylacetylene and the synthesis of an end-functionalized poly(phenylacetylene) by using Rh-based catalyst systems, $[RhCl(nbd)]_2/Ar_2C{=}C(Ph)Li/PPh_3$ (Ar = Ph, 4-$Me_2NC_6H_4$). In a typical run, the polydispersity ratio (M_w/M_n) of the formed polymer was ca. 1.1 and the initiator efficiency with respect to the Rh atom was virtually quantitative. Further, use of (triphenylvinyl)lithiums having functional groups such as the dimethylamino group resulted in the formation of end-functionalized poly(phenylacetylene)s, which quantitatively contained functional groups at the initiating chain end.

As shown in Scheme 1, the polymerization of phenylacetylene by the catalyst[5] prepared from $[RhCl(nbd)]_2$, $Ph_2C{=}C(Ph)Li$, and PPh_3 smoothly proceeded in benzene to quantitatively give a yellow polymer.[6] According to GPC, the number-average molecular weight (M_n) of the polymer was 5400, and the polydispersity ratio was 1.14. The initiator efficiency calculated from this M_n value by assuming that each polymer chain possesses a triphenylvinyl group at the initiating chain end (vide infra) was virtually quantitative.[7] A multistage polymerization experiment was carried out to examine the living nature of the present system. When monomer solutions were added to catalyst solution three times at intervals of 1 h, polymer was quantitatively formed

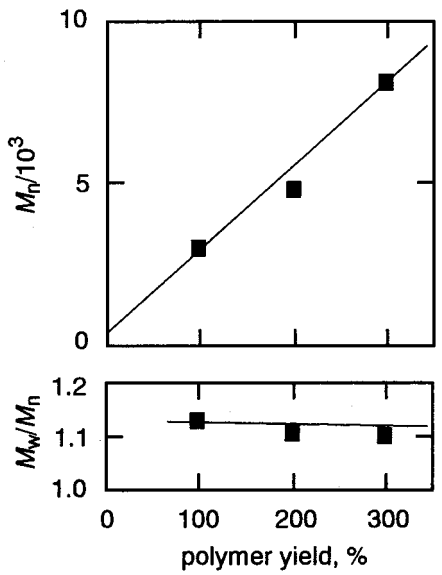
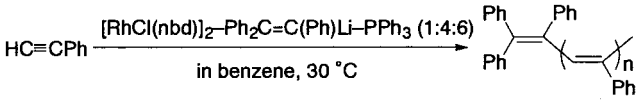


Figure 1. Multistage polymerization of phenylacetylene catalyzed by $[RhCl(nbd)]_2/Ph_2C{=}C(Ph)Li/PPh_3$ (in toluene, 30 °C, the monomer feeds were supplied three times at intervals of 1 h; $[[RhCl(nbd)]_2]$ = 1.0 mM, $[Ph_2C{=}C(Ph)Li]$ = 4.0 mM, $[PPh_3]$ = 6.0 mM, $[monomer]_0 = [monomer]_{added}$ = 50 mM).

Scheme 1



M_w/M_n 1.14, [P*]/[Rh] ca. 100%

in each stage. As seen in Figure 1, the M_n values of the polymer increased in proportion to the polymer yield, while the polydispersity ratios remained as small as ca. 1.1. This means that all the propagating species are active even after the consumption of monomer. The solid line in Figure 1 stands for the theoretical M_n value including end groups. The M_n values agreed with the theoretical ones, indicating that the initiator efficiency is again quantitative. All these results manifest that the present system is a quantitatively initiated living polymerization.

The effect of catalyst components was examined. When *n*-butyllithium was used instead of (triphenylvinyl)lithium, the yield of the polymer decreased to 16%. The M_n increased to 76 000 and the polydispersity ratio became as large as 1.77, meaning it is not a living polymerization. When no PPh_3 was added, the M_n of the polymer was 56 000, and the polydispersity ratio of the polymer increased up to 1.40, which denies living polymerization. Thus, the present system needed both (triphenylvinyl)lithium ([Li]/[Rh] ≥ 1) and PPh_3 ([P]/[Rh] ≥ 3) to exhibit an excellent living nature.

(Triphenylvinyl)lithiums having functional groups were employed to identify the initiating end group of the polymer and synthesize end-functionalized poly(phenylacetylene)s. For instance, when $(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Li$[8] was used and 20 equiv of monomer to the Rh metal was polymerized, polymerization similarly proceeded to quantitatively give a polymer with M_n of 2840 and M_w/M_n of 1.12. In the ^1H NMR spectrum (Figure 2) of this polymer, the vinyl protons of the main

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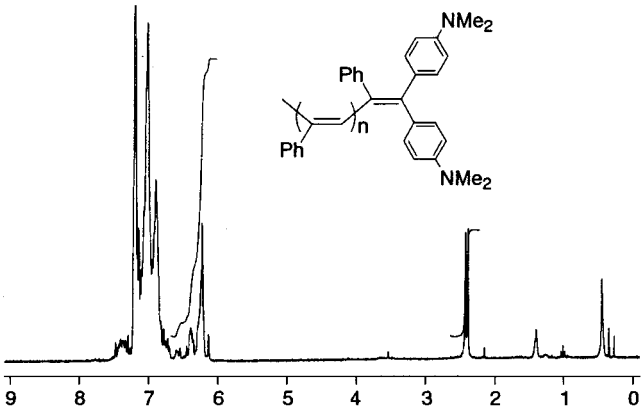
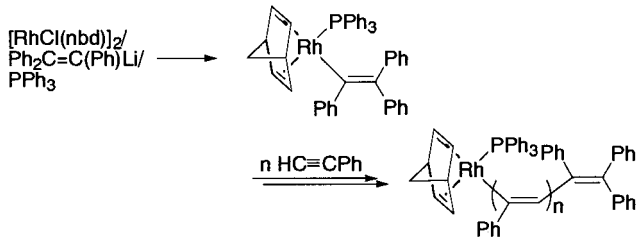


Figure 2. ^{1}H NMR spectrum (270 MHz, C_6D_6) of poly(phenylacetylene) obtained with $[RhCl(nbd)]_2$/$(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Li$/$PPh_3$ (in toluene, 30 °C, 1 h; $[[RhCl(nbd)]_2] = 1.0$ mM, $[(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Li] = 4.0$ mM, $[PPh_3] = 6.0$ mM, $[monomer]_0 = 40$ mM)

Scheme 2



chain are observed at 6.23 ppm as a singlet characteristic of the cis−transoidal structure, and the dimethylamino protons are seen at 2.43 and 2.39 ppm as two singlets. The M_n of the polymer calculated from the intensity ratio of the vinyl protons to the dimethylamino protons, assuming that each initiating chain end possesses one [bis(dimethylamino)triphenyl]vinyl group, was 2630, which is in good agreement with the value obtained by GPC. These findings along with the living nature of the present system reveal that the [bis(dimethylamino)triphenyl]vinyl group has quantitatively been introduced to the initiating chain end of the polymer.

The initiation and propagation mechanisms of the present polymerization are proposed as shown in Scheme 2. A vinylrhodium complex generated from $[RhCl(nbd)]_2$, (triphenylvinyl)lithium, and PPh_3 works as the initiating species.[9] The propagation reaction proceeds via the insertion of phenylacetylene into the Rh−vinyl bond. The similarity between the (triphenylvinyl)rhodium initiating species and the propagating end has probably enabled smooth initiation to achieve living polymerization with high initiator efficiency.

In summary, the present study has revealed that a novel ternary Rh catalyst effects the living polymerization of phenylacetylene to provide poly(phenylacetylene)s with definite initiating end groups. The syntheses of various end-functionalized poly(phenylacetylene)s and block copolymers are underway.

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(5) Supersonic-wave irradiation (2 h) of a mixture of lithium (1.0 mmol) and an ether solution (10 mL) of bromotriphenylethylene (0.50 mmol) at 5−10 °C resulted in the formation of a yellow solution and a white precipitate. The solution was used as (triphenylvinyl)lithium solution (0.50 mM). The catalyst was prepared by addition of the solution of (triphenylvinyl)lithium to a solution of $[RhCl(nbd)]_2$ and PPh_3 ($[[RhCl(nbd)]_2] = 1.0$ mM.; [Rh]:[Li]:[P] = 1:2:3). An excess amount of (triphenylvinyl)lithium was employed to compensate the loss caused by reaction with the moisture in the system.

(6) The polymerization was initiated at 30 °C by addition of a monomer solution to the catalyst solution that was prepared just before use ([phenylacetylene]/[Rh] = 50) and quenched with a small amount of acetic acid after polymerization for 1 h. The polymer was precipitated into a large amount of methanol, filtered off, and dried to a constant weight.

(7) It was assumed that the relative M_n value of poly(phenylacetylene) obtained by GPC using a polystyrene calibration agrees with its absolute value. This assumption has been verified by the fact that the M_n value calculated from the end-group analysis by NMR agreed well with the GPC value (vide infra).

(8) $(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Br$ was prepared by modifying the literature method [Buu-Hoï, Ng. Ph.; Xuong, N. D. *J. Org. Chem.* **1957**, *22*, 302]: $(4\text{-}Me_2NC_6H_4)_2C{=}O$ was allowed to react with $PhCH_2MgCl$ in THF. The reaction mixture was hydrolyzed with dilute sulfuric acid and neutralized with $NaHCO_3$ to afford $(4\text{-}Me_2NC_6H_4)_2C(OH)CH_2Ph$ (olive solid). This alcohol was refluxed in formic acid and then neutralized with $NaHCO_3$ to afford $(4\text{-}Me_2NC_6H_4)_2C{=}CHPh$ (olive solid). This olefin was allowed to react with 1 equiv of bromine in chloroform and neutralized with $NaHCO_3$ to give $(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Br$: olive powder, total yield 10.5%. Mp 179−182 °C. Anal. Calcd for $C_{24}H_{25}N_2Br$: C, 68.41; H, 5.98; N, 6.65. Found: C, 68.66; H, 6.06; N, 6.49. ^{1}H NMR ($CDCl_3$): δ 7.7−7.6 (m, 4H), 7.2−7.1 (m, 2H), 7.05−6.85 (m, 3H), 6.7−6.6 (m, 2H), 6.35−6.25 (m, 2H), 2.54 (s, 6H), 2.35 (s, 6H). $(4\text{-}Me_2NC_6H_4)_2C{=}C(Ph)Li$ was prepared by the method similar to that in note 5 and used for polymerization.

(9) In a preliminary experiment, a Rh complex was isolated from the catalyst solution, whose structure was $(nbd)(Ph_3P)RhC(Ph){=}CPh_2$ according to ^{1}H NMR analysis. This complex in conjunction with PPh_3 induced living polymerization of phenylacetylene. This confirms the mechanism in Scheme 2.

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