Living Polymerization of Phenylacetylenes Initiated by Rh($C{\equiv}CC_6H_5$)(2,5-norbornadiene)[P(C_6H_5)$_3$]$_2$

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Polyacetylenes[1] possessing alternating olefinic bonds along the main chain are of intense interest because of their unique physical properties such as photoconductivity,[2] optical nonlinear susceptibility,[3] and magnetic susceptibility.[4] The presence of aryl or alkyl substituents is crucial for obtaining sufficient stability, appropriate chain conformation and stiffness, and high solubility in organic solvents. Although stereocontrolled, living polymerization[5] is an indispensable tool for designing the highly functional materials based on compositionally pure monodisperse polymers, efficient methods for acetylene derivatives have remained rare. The only example is the metathesis polymerization of alkylated acetylenes, particularly *tert*-butylacetylene with 88–97% cis stereoselectivity achieved by group 6 metal initiators.[6] The Ta–carbene complex-initiated polymerization of 2-butyne is known to proceed with high initiation efficiency, but the stereospecificity is unclear.[7] Recently, this method was extended to the reaction of 1,6-heptadiyne.[8] We have accomplished stereospecific, living polymerization of phenylacetylenes using Rh($C{\equiv}CC_6H_5$)(nbd)[P(C_6H_5)$_3$]$_2$ (**1**, nbd = 2,5-norbornadiene). Although Rh complexes are known to promote polymerization of substituted acetylenes,[9] this is the first example of living, stereospecific polymerization of acetylenes initiated by a well-characterized group 9 metal complex.

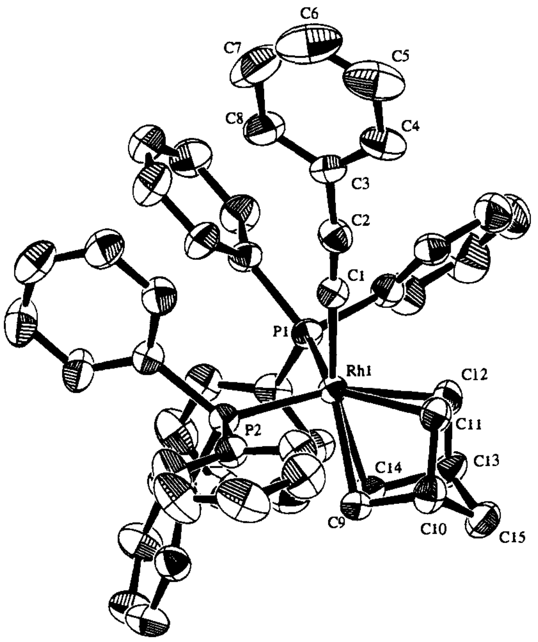
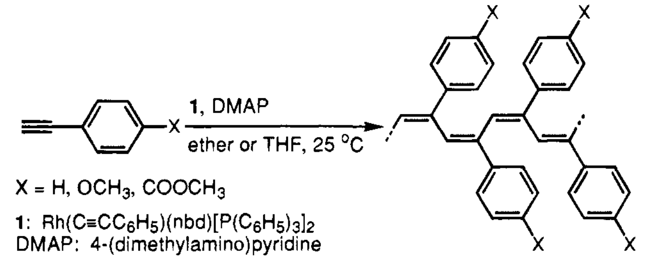


Figure 1. ORTEP plot (50% probability ellipsoids) of the molecular structure of Rh complex **1**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh(1)–C(1), 1.999(7); C(1)–C(2), 1.200(10); Rh(1)–P(1), 2.451(2); Rh(1)–P(2), 2.353(2). Selected bond angles (deg): Rh(1)–C(1)–C(2), 177.2(7); C(1)–C(2)–C(3), 172.9(8); P(1)–Rh(1)–P(2), 109.65(6); P(1)–Rh(1)–C(1), 90.7(2).



Complex **1** was synthesized in 77% yield by reacting [RhCl(nbd)]$_2$, triphenylphosphine, and $LiC{\equiv}CC_6H_5$ (1:4.5:2.5 molar ratio) in ether. The single-crystal X-ray analysis revealed that the Rh metal center has a slightly distorted trigonal bipyramidal coordination geometry with the phenylethynyl group and one olefinic linkage in the axial position as shown in Figure 1. Two triphenylphosphine ligands and another olefinic group from the diene ligand are located in the equatorial plane. The $^{31}P\{^1H\}$ NMR spectrum of **1** taken in THF (85% H_3PO_4 as the external standard) at room temperature shows only a singlet at δ 20.48 ppm, which becomes a doublet coupled to Rh with J_{P-Rh} = 119.3 Hz at −50 °C, indicating that **1** has two magnetically equivalent P nuclei, which is consistent with the crystalline structure, and that, at room temperature, a rapid dissociative equilibrium is set up between **1** and a mono-triphenylphosphine–Rh complex plus free triphenylphosphine.[10]

Polymerization of phenylacetylene (PA) (150 mM) in the presence of **1** (3 mM) and 4-(dimethylamino)pyridine (DMAP) (**1**:DMAP = 1:10) in ether proceeded rapidly at room temperature, resulting in a red-brown precipitate. Treatment of the reaction mixture with acetic acid[11] afforded poly(phenylacetylene) (PPA) in an almost quantitative yield. The polymer

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Table 1. Polymerization of Phenylacetylenes Initiated by Rhodium Complex **1**[a]

		conditions				PPA	
entry	X in PA	solvent	$[PA]_0/[\mathbf{1}]_0$	time, min	% conv	M_n[d]	M_w/M_n[d]
1	H	ether	25	90	94	7700	1.17
2	H	ether	50	117	97	14 900	1.15
3	H	ether	50	35	84	14 200	1.14
4	H	ether	50	15	70	10 100	1.11
5	H	ether	50	10	39	7600	1.09
6	H	ether	50	6	33	4900	1.06
7	H	ether	150	150	97	48 900	1.21
8	H	THF	50[b]	30	97	13 400	1.29
9	H	THF	1000[c]	30	100	205 500	1.23
10	OCH_3	ether	50	120	95	17 100	1.25
11	$COOCH_3$	ether	50	240	86	12 300	1.38

[a] Conditions: $[PA]_0 = 150$ mM, $[DMAP]_0/[\mathbf{1}]_0 = 10$ at 25 °C. [b] $[PA]_0 = 300$ mM, $[\mathbf{1}]_0 = 6$ mM, $[DMAP]_0 = 60$ mM. [c] $[PA]_0 = 600$ mM, $[\mathbf{1}]_0 = 0.6$ mM, $[DMAP]_0 = 6$ mM. [d] Determined by GPC based on polystyrene standards.

obtained by this method with an M_n of 14 900 and an M_w/M_n of 1.15 is soluble in most common aprotic solvents such as toluene, dichloromethane, and THF, but only slightly soluble in ether. The polymer was purified by dissolution in THF and precipitation with methanol to give a fine yellow powder. In THF, under otherwise identical conditions, the polymerization proceeded homogeneously. PPA was obtained after a quenching with acetic acid, followed by the addition of a large volume of methanol. The ^1H NMR spectra of these products in $CDCl_3$ displayed a sharp singlet due to the vinylic protons at δ 5.83 in addition to a set of multiplets at δ 6.62–6.64 (2 H, ortho) and δ 6.93–6.95 (3 H, meta and para), which has tentatively been correlated to the regular head–tail cis–transoidal structure formed by a cis insertion mechanism.[9a] The $^{13}C\{^1H\}$ NMR spectrum of PPA obtained from a 95:5 mixture of $C_6H_5C{\equiv}CH$ and $C_6H_5{}^{13}C{\equiv}{}^{13}CH$ gave two doublets at δ 132.2 and 139.9 ppm with $J_{^{13}C-^{13}C} = 72$ Hz, clearly indicating the presence of the $^{13}C{=}^{13}C$ bond in the polymer chain. This result is consistent with the insertion polymerization mechanism instead of the metathesis pathway. The norbornadiene moiety in **1** was not incorporated in the polymer. Under the same conditions, *p*-methoxy- and *p*-(methoxycarbonyl)phenylacetylene polymerized with **1** to give red-brown polymers with the same stereochemistry but *tert*-butylacetylene polymerized slowly to give a white polymer with an M_n of 23 500 and an M_n/M_w of 2.05 in only 17% yield. Table 1 summarizes the representative results. Judging from the M_n of the product, the efficiency of the polymerization by **1** is estimated to be 33–56%. The polymerization in ether was slower than in THF probably because of the heterogeneity of the reaction system, but it gave a lower polydispersity of the products. The presence of DMAP is crucial to maintain a narrow molecular-weight distribution. For example, the M_w/M_n value of PPA was improved from 1.31 (without DMAP) to 1.15 (with 10 equiv of DMAP per **1**) in the reaction in ether, under the conditions of entry 2 in Table 1. In addition, the GPC profile of the product obtained without DMAP gave a small new peak due to the polymer with higher molecular weight. The lowest M_w/M_n value thus attained was 1.06 (entry 6).

The most significant characteristic of this reaction is the living nature of the polymerization. The M_n value of the products determined by GPC appeared to increase proportionally to the conversion of the parent and substituted PAs in both ether and THF (Table 1, entries 2–6). In addition, the molecular-weight distribution remained within a narrow range throughout the polymerization. A higher M_n value, up to ca. 2×10^5, could be attained by increasing the monomer:catalyst ratio or by decreasing catalyst concentration (entry 9). Direct evidence for the living nature of the polymerization was obtained by isolating a polymer with an active end.[12] Thus, a solid polymer with an M_n of 8000 and an M_w/M_n of 1.28 (Rh:P = 1:1; nbd present; $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 21.9 ppm, $J_{P-Rh} = 179$ Hz), obtained under an argon atmosphere from the polymerization of PA (50 equiv to **1**) in ether, further promotes polymerization. With the addition of 1 equiv of triphenylphosphine, the second polymerization of PA (50 equiv) took place at the same rate as in the first reaction, leading to PPA with final M_n and M_w/M_n values of 15 100 and 1.33, respectively. The clean shift of the GPC peak to the higher molecular-weight region confirmed the near quantitative initiation of the second polymerization by the isolated polymer. The active Rh moiety was removed from the polymer by treatment with acetic acid.[11]

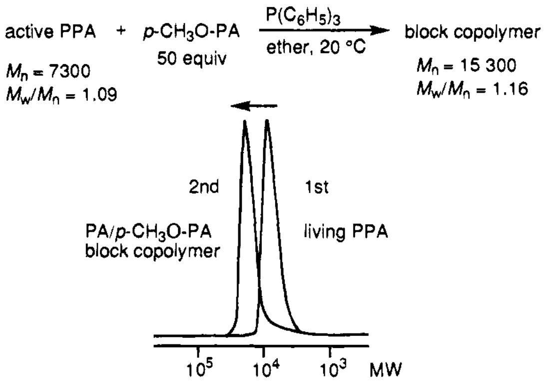

Figure 2. Preparation and GPC profiles of the block copolymer of phenylacetylene and *p*-methoxyphenylacetylene.

The living nature of the Rh-catalyzed reaction allows the synthesis of an AB type block copolymer from the different PAs. Figure 2 shows GPC traces of the block copolymer of PA and *p*-CH_3O-PA. The copolymer possessing an M_n of 15 300 and an M_w/M_n of 1.16 was obtained by reacting the active PPA with an M_n of 7300 and an M_w/M_n of 1.09 and 50 molar equiv of *p*-CH_3O-PA. The ^1H NMR spectrum of the product in $CDCl_3$ gave two sharp singlets at δ 5.83 and 5.75 due to the vinylic protons in the unsubstituted and *p*-methoxy-substituted PPA units, respectively.

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Supplementary Material Available: X-ray structural details for **1**, experimental procedures for the preparation of **1** and the polymerization of PA with **1**, and spectroscopic data of **1** and the obtained homopolymer and block copolymer (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] For an example of the isolation of a living organometallic polymer, see ref 5k.