An Efficient Rhodium(I) Initiator for Stereospecific Living Polymerization of Phenylacetylenes

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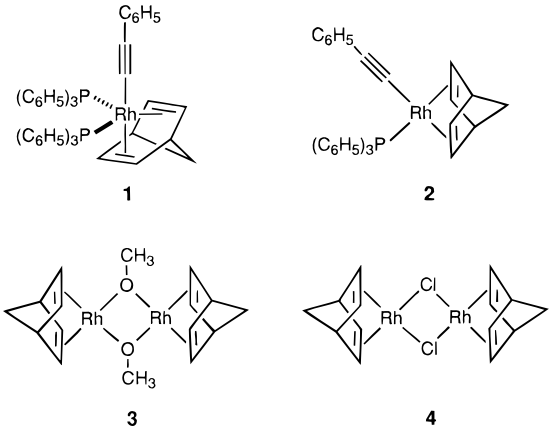
Living polymerization of monosubstituted acetylenes has been extensively investigated, because the resulting stereoregular polymers with a controlled molecular weight are expected to have unique physical properties.[1] Recently, we have observed the polymerization of phenylacetylenes initiated by $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$ (**1**, nbd = 2,5-norbornadiene).[2] Although



this Rh complex acts as an excellent initiator, the reaction rate and the initiation efficiency (I_{eff}) can still be improved. Since the dissociation of one of the two $P(C_6H_5)_3$ ligands from the pentacoordinate complex **1**, giving an active complex $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]$ (**2**), is a prerequisite for the initiation,[2] the presence of the second $P(C_6H_5)_3$ ligand is unfavorable from the reactivity point of view. Such a consideration prompted us to search for tetracoordinate Rh(I) complexes which serve as more reactive initiators. We now report a new Rh system that is easily prepared and displays a much higher reaction rate and I_{eff}.

Polymerization of phenylacetylene (**5a**) occurs rapidly at room temperature in THF containing $[Rh(OCH_3)(nbd)]_2$ (**3**),[3] $P(C_6H_5)_3$, and 4-(dimethylamino)pyridine (DMAP) (Rh:phosphine:amine = 1:1:10) with a **5a**/Rh feed ratio of 50:1. Treatment of the resultant deep red solution with acetic acid followed by a large amount of methanol produced quantitatively poly(phenylacetylene) (PPA) as a yellow fine powder, which has a number-average molecular weight, M_n, of 6900 and a polydispersity, M_w/M_n, of 1.11 determined by GPC. The polymer has the regular head−tail cis−transoidal structure in the main chain, as determined by ^1H NMR spectroscopy ($CDCl_3$, δ 5.83, sharp singlet, vinyl proton).[2] No proton signals arising from the methoxyl group were observed in the ^1H NMR spectrum of an oligomer (M_n = 3400, M_w/M_n = 1.10) obtained from

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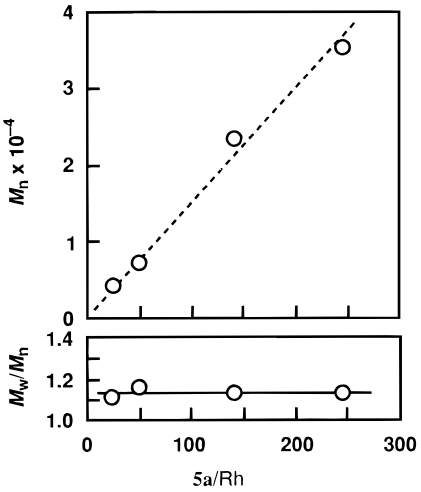
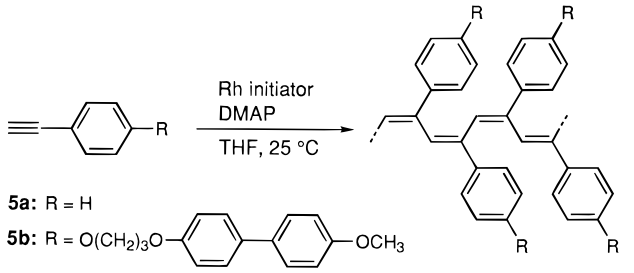


Figure 1. M_n and M_w/M_n values of poly(phenylacetylene)s determined by GPC as a function of the initial **5a**/Rh feed ratio.



$DC{\equiv}CC_6H_5$. A phenylacetylene derivative, **5b**, with a long-chain substituent on the phenyl ring provides a stereoregulated polymer with an M_n of 16 600 and an M_w/M_n of 1.20 in 91% yield.

The reaction with the new Rh initiator proceeding homogeneously in THF is 3−4 times faster than with **1**. The polymerization has proved to be living in nature. As shown in Figure 1, the M_n of the products obtained with 100% conversion of the monomer increased proportionally from the initial **5a**/Rh feed ratio up to 3.5×10^4 with a 250:1 feed ratio, in which the initial concentration of **5a** was kept constant. The M_w/M_n value of the polymer remained within a narrow range, 1.11−1.15. The M_n values indicate that the I_{eff} value of the initiating system, 72%, is approximately doubled compared with the value obtained with **1**, 37%.[2] A higher M_n value, up to 1.9×10^5, can be attained by increasing the **5a**/Rh feed ratio to 1000:1. The living character of the reaction also allows block copolymerization of different phenylacetylenes. Thus, the active PPA with an M_n of 8900 and an M_w/M_n of 1.12, formed from **5a** and the initiator **3** with a **5a**/Rh ratio of 50:1, further promotes polymerization of *p*-methoxyphenylacetylene to give an AB type block copolymer with an M_n value of 23 600 and an M_w/M_n value of 1.28.[4] A clean shift of the GPC peak to a higher molecular weight region confirmed the nearly quantitative initiation of the second polymerization.

The real initiator of the polymerization is a tetracoordinate Rh complex **2**.[2] A combined system consisting of Rh complex **3**, $P(C_6H_5)_3$, and DMAP (Rh:phosphine:amine = 1:1:10) served as the most active initiator for the living polymerization (entry 1 in Table 1). The reaction rate was decreased markedly by increasing the ratio of $P(C_6H_5)_3$ to **3** (entries 2 and 3). The $^{31}P\{^1H\}$ NMR spectrum of a mixture of complex **3**, $P(C_6H_5)_3$, and

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Table 1. Polymerization of Phenylacetylene with the $[Rh(OCH_3)(nbd)]_2/P(C_6H_5)_3$/DMAP System[a]

entry	$P(C_6H_5)_3$/Rh	DMAP/Rh	time (min)	conv[b] (%)	product M_n[c]	product M_w/M_n[c]
1	1.0	10	10	90	6900	1.11
2	1.2	10	12	100	7100	1.17
3	2.0	10	20	98	8100	1.15
4	0	0	6	99	573200[d]	1.55[d]
5	0	10	10	100	15100	1.38
6	2.0	0	40	100	13800	1.33

[a] Conditions: initial [**5a**] = 300 mM; initial [Rh] = 6 mM; in THF at 25 °C. The reaction was initiated by adding a THF solution of the monomer to the Rh complex solution containing additives. [b] Determined by GC analysis of the reaction mixture. [c] Determined by GPC based on polystyrene standards. [d] For THF-soluble part.

5a (Rh:phosphine:**5a** = 1:1:5) in THF-d_8 at −50 °C (δ 34.3 ppm, doublet, J_{P-Rh} = 176 Hz) showed the formation of a tetracoordinate Rh complex **2**.[5,6] Unfortunately, this was unisolable due to instability. By increasing the temperature to 25 °C, complex **2** was converted to an isolable living oligomer bearing a tetracoordinate Rh center, which exhibited a ^{31}P NMR signal in THF-d_8 at δ 19.2 ppm with J_{P-Rh} = 176 Hz.[2] Thus, the reaction proceeds through the same initiation and propagation mechanism as the pentacoordinate complex **1**.

Both $P(C_6H_5)_3$ and DMAP are crucial additives for the living nature of this polymerization. The presence of only $P(C_6H_5)_3$ or DMAP significantly improved the I_{eff} but not the polydispersity, whereas the reaction without these two additives formed a very high molecular weight polymer with an M_n of 5.7×10^5 and an M_w/M_n of 1.55 in addition to THF-insoluble product, indicating that the I_{eff} value of the initiator is very low (entries 4−6 in Table 1). Norbornadiene, probably due to its capability of stabilizing active Rh species,[7−9] is the best diene ligand to attain living polymerization. $[Rh(OCH_3)(cod)]_2$[10] (cod = 1,5-cyclooctadiene) combined with $P(C_6H_5)_3$ and DMAP does not initiate living polymerization, though it produces a high molecular weight PPA with an M_n of 82 500 and an M_w/M_n of 3.77 (Table 2). The isostructured dinuclear complex, $[RhCl(nbd)]_2$ (**4**), in the presence of $N(C_2H_5)_3$ has an extremely high activity but low initiation efficiency.[9,11] Addition of $P(C_6H_5)_3$ completely suppressed the polymerization as shown in Table 2. The methoxyl group in complex **3** is more easily replaced with an alkynyl group than the chloro ligand under the present reaction conditions. This trend probably reflects the relative pK_a values of HCl (−2.2) and CH_3OH (15.5).

Thus, this new initiating system effectively produces stereoregular PPAs with a narrow molecular weight distribution. The Rh complex system promotes the polymerization rapidly with a high initiation efficiency. Most conveniently, the reaction of **5a** can be conducted using an initiator generated *in situ* in THF from commercially available **4**, $NaOCH_3$ (28 wt % CH_3OH solution), $P(C_6H_5)_3$, and DMAP (Rh:$NaOCH_3$:phosphine:amine = 1:1.2:1:10) to give a yellow polymer with an M_n of 11 000 and an M_w/M_n of 1.20 in a quantitative yield (Table 2).

Table 2. Polymerization of Phenylacetylene with Various Rhodium Complexes[a]

initiator system	Rh:P	time (min)	conv[b] (%)	product M_n[c]	product M_w/M_n[c]
3 + $P(C_6H_5)_3$	1:1.2	12	100	7100	1.17
$[Rh(OCH_3)(cod)]_2$ + $P(C_6H_5)_3$	1:2	90	100	82500	3.77[d]
1[e]		30	97	13400	1.29
4 + $P(C_6H_5)_3$	1:1.2	120	0.2		
4 + $NaOCH_3$ + $P(C_6H_5)_3$[f]	1:1	30	100	11000	1.20

[a] Conditions: initial [**5a**] = 300 mM, Rh:DMAP:**5a** = 1:10:50, in THF at 25 °C. The reaction was initiated by adding a THF solution of the monomer to the Rh complex solution containing additives. [b] Determined by GC analysis of the reaction mixture. [c] Determined by GPC based on polystyrene standards. [d] Measured only for THF-soluble fraction. [e] Reference 2. [f] Rh:$NaOCH_3$:$P(C_6H_5)_3$ = 1:1.2:1.

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(4) ^1H NMR (CD_2Cl_2, TMS as internal standard): δ 3.57 (s, CH_3O, 3H), 5.75 (s, olefinic proton, 1H), 5.83 (s, olefinic proton, 1H), 6.47 (br d, $CH_3OC_6H_4$, 2H), 6.64 (m, $CH_3OC_6H_4$, 2H), 6.67 (m, C_6H_5, 2H), 6.93−6.95 (m, C_6H_5, 3H). Similarly, a homopolymer with an M_n of 15 800 and an M_w/M_n of 1.28 was obtained using **5a** and the active polymer with an M_n of 7700 and an M_w/M_n of 1.15.

(5) ^1H NMR at −50 °C (THF-d_8, TMS): δ 1.30 (d, CH_2 of nbd, 1H), 1.47 (d, CH_2 of nbd, 1H), 3.44 (br s, CH=CH of nbd, 2H), 3.74 (br s, CH of nbd, 2H), 5.49 (br s, CH=CH of nbd, 2H), 6.83−7.01 (m, C≡CC_6H_5, 5H), 7.05−7.80 (m, $P(C_6H_5)_3$, 15H).

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