Synthesis of Stereoregular Poly(phenylacetylene)s by Organorhodium Complexes in Aqueous Media

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Most chemical reactions use organic solvents, some of which are toxic and hazardous. Water is a nontoxic and inexpensive natural resource, and replacement of organic solvents in chemical processes by water will undoubtedly contribute to the protection of public health and the living environment. Aqueous polymerizations offer such advantages as simple process design, easy product isolation (e.g., by filtration), low cost of production, hygienic working environment, and considerable reduction of hazardous wastes. Aqueous polymerizations also offer the possibility of developing recyclable or reusable catalyst systems and may enable the preparation of Langmuir−Blodgett (LB) films of functional polymers. Aqueous radical polymerization processes have been widely used on an industrial scale for manufacturing vinyl polymers,[1] but polymerizations by other mechanisms, especially those involving organometallic initiating species, normally need to vigorously exclude moisture from the reaction systems because most of the organometallic complexes are very sensitive to water.[2] Novak and Grubbs have in recent years discovered several "robust" transition-metal catalysts to effect ring-opening metathesis polymerizations (ROMP) in water and have pioneered research efforts in developing aqueous polymerization systems for synthesizing functional polymers.[3] Polyacetylenes are a group of novel conjugating polymers with unique electrical, (nonlinear) optical, optoelectronic, magnetic, chiroptical, (enantio)permselective, and photolithographic properties,[4,5] and development of aqueous catalyst systems for acetylene polymerizations is of great interest from viewpoints of both basic research and practical applications. We here report our efforts in exploring aqueous acetylene polymerization systems: We have developed a group of new organorhodium catalysts that effect stereospecific polymerizations of phenylacetylene in aqueous media (Scheme 1).

Late transition-metal metathesis catalysts are known to be more tolerant of polar substrates than their early transition-metal counterparts,[6] and some ruthenium-, osmium-, and iridium-based complexes have been found to be effective ROMP catalysts in water.[3,7] In acetylene polymerizations, molybdenum-, tungsten-, niobium-, and tantalum-based catalysts are normally used in dry nonpolar solvents such as toluene and carbon tetrachloride. We have, however, noticed that some complexes of late transition metals such as rhodium are synthesized in alcohol/water mixtures and can be used in polar solvents such as methanol and triethylamine.[8] We thus decided to explore the possibility of developing Rh-based aqueous catalyst systems for acetylene polymerizations.

Scheme 1

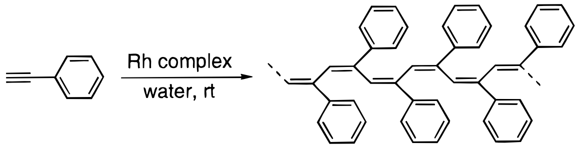

Table 1. Solvent Effect on Polymerization of Phenylacetylenes Catalyzed by $[Rh(nbd)Cl]_2$ (nbd: Norbornadiene)[a]

				polymer		
no.	monomer	solvent	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
1	$HC{\equiv}CPh$	toluene	1.0	1.1	17 200	2.8
2	$HC{\equiv}CPh$	THF	1.0	16.4	62 900	5.5
3	$HC{\equiv}CPh$	water	0.5	58.4[c]		
4	$HC{\equiv}CC_6H_4$-*p*-Me	toluene	1.0	0		
5	$HC{\equiv}CC_6H_4$-*p*-Me	THF	1.0	29.2	17 500	3.2
6	$HC{\equiv}CC_6H_4$-*p*-Me	water	0.2	59.0[d]	22 600[e]	3.2[e]

[a] Polymerized under nitrogen at room temperature; [cat.] = 0.80 mM, $[PA]_o$ = 0.83 M, $[p\text{-MePA}]_o$ = 0.58 M. [b] Determined by GPC in THF on the basis of a polystyrene calibration. [c] Insoluble in THF. [d] THF-soluble part: 2%. [e] For the THF-soluble part.

We first compared the catalytic activity of a well-known Rh complex, $[Rh(nbd)Cl]_2$ (nbd: norbornadiene), in the polymerization of phenylacetylene (PA) in different solvents. When $[Rh(nbd)Cl]_2$ was used in toluene, the polymerization was very slow, yielding only a trace amount (1.1%) of an orange poly(phenylacetylene) (PPA) after 1 h of polymerization (Table 1, no. 1). When THF, a polar solvent, was used, the polymerization became faster. The polymerization became even faster when carried out in water. Unfortunately, however, the PPA produced in the aqueous system was insoluble. Similar but more distinctive results were obtained in the polymerizations of (*p*-methylphenyl)acetylene (*p*-MePA): While no polymer formed in toluene at all, fast polymerization took place in water (cf. Table 1, nos. 4 and 6).

The beauty of organometallic chemistry is that a subtle change in the ligand structure in an organometallic complex may significantly change the complex's catalytic activity and stereoregulating power. When we used $[Rh(cod)Cl]_2$, another well-known Rh complex, to polymerize PA in water, a high molecular weight polymer was obtained in a high yield (Table 2, no. 1). The resulting PPA was completely soluble, enabling us to investigate its molecular structure by spectroscopy. We used ^1H NMR to determine the stereostructure of the PPA according to Simionescu and Percec's method[9] and found that the polymer was highly stereoregular with a *cis* content as high as 94%. Because triethylamine (TEA) has been used as a solvent for acetylene polymerizations by several groups,[8] we checked polymerization of PA initiated by $[Rh(cod)Cl]_2$ in TEA and found that the polymer yield was quite high but that the *cis* content of the polymer was only moderate (Table 2, no. 2). We therefore prepared a number of Rh complexes with nitrogen-containing ligands according to published procedures,[10] and investigated their catalytic activity, especially their stereoregulating power in the acetylene polymerizations. The Rh(cod)(bbpmt) complex initiated the acetylene polymerization and gave a PPA with a *cis* content of 83.2% (Table 2, no. 3). All the other nitrogen-containing Rh complexes we tested yielded PPAs with high *cis* contents. It is worth noting that the $[Rh(cod)(mid)_2]^+PF_6^-$ salt gave a PPA with a high *cis* content (87.5%) in an almost quantitative yield (98.2%) in a short polymerization time (0.7 h).

We have further prepared two water-soluble Rh complexes, $Rh(nbd)(tos)(H_2O)$ and $Rh(cod)(tos)(H_2O)$, according to Kolle's procedure[11] and investigated their

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Table 2. Polymerization of Phenylacetylene by Organorhodium Catalysts[a]

				polymer			
no.	catalyst[b]	solvent	time (h)	yield (%)	M_w[c]	M_w/M_n[c]	% *cis*[d]
1	$[Rh(cod)Cl]_2$	water	0.5	68.3	46 200	2.2	94.0
2	$[Rh(cod)Cl]_2$	Et_3N	24.0	92.4	12 500	4.2	79.7
3	Rh(cod)(bbpmt)	water	20.0	63.2	11 400	2.2	83.2
4	Rh(cod)(pip)Cl	water	0.2	71.7	7 600	2.0	86.0
5	$Rh(cod)(NH_3)Cl$	water	0.2	76.8	23 300	1.8	86.4
6	$Rh(cod)(t\text{-}BuNH_3)Cl$	water	0.2	57.0	6 500	2.2	87.4
7	Rh(cod)(mid)Cl	water	1.5	75.3	12 500	2.0	87.4
8	$[Rh(cod)(mid)_2]^+PF_6^-$	water	0.7	98.2	9 900	2.0	87.5
9	$[Rh(cod)Cl]_2(pda)$	water	1.7	38.5	7 300	1.4	89.8

[a] Polymerized under nitrogen at room temperature; monomer, 0.5 mL; catalyst, 2 mg; solvent, 5 mL. [b] nbd = norbornadiene, cod = 1,5-cyclooctadiene, bbpmt = bis(4-*tert*-butyl)-2-pyridylmethanethiolate, pip = piperidine, mid = *N*-methylimidazole, pda = *o*-phenylenediamine. [c] Determined by GPC in THF on the basis of a polystyrene calibration. [d] Determined by ^1H NMR according to ref 9.

Table 3. Polymerization of Phenylacetylene Catalyzed by Water-Soluble Organorhodium Complexes $Rh(diene)(tos)(H_2O)$[a]

				polymer			
no.	catalyst[b]	solvent	time (h)	yield (%)	M_w[c]	M_w/M_n[c]	% *cis*[d]
1	$Rh(nbd)(tos)(H_2O)$	toluene	1.0	1.1	30 000	3.4	86.0
2	$Rh(nbd)(tos)(H_2O)$	THF	1.0	78.5	72 800	4.2	90.7
3	$Rh(nbd)(tos)(H_2O)$	water	1.0	80.0	216 100	2.8	89.0
4	$Rh(cod)(tos)(H_2O)$	toluene	1.0	2.4	58 600	3.4	94.7
5	$Rh(cod)(tos)(H_2O)$	THF	1.0	70.3	109 000	2.5	99.5
6	$Rh(cod)(tos)(H_2O)$	water	0.5	23.7	73 000	2.5	100.0
7	$Rh(cod)(tos)(H_2O)$	water	1.0	81.9	31 200	5.4	100.0
8	$Rh(cod)(tos)(H_2O)$	(neat)	7.5	20.1	35 400	2.8	82.2

[a] Polymerized under nitrogen at room temperature; $[M]_o = 0.83$ M, [cat.] = 1 mM. [b] nbd = norbornadiene, tos = *p*-toluenesulfonate, cod = 1,5-cyclooctadiene. [c] Determined by GPC in THF on the basis of a polystyrene calibration. [d] Determined by ^1H NMR according to ref 9.

catalytic activity in initiating acetylene polymerizations. Like the $[Rh(nbd)Cl]_2$ complex, $Rh(nbd)(tos)(H_2O)$ was also a poor catalyst in toluene and only about 1% polymer was isolated after 1 h of polymerization (Table 3, no. 1). However, in a polar solvent like THF, this complex performed much better, giving a high molecular weight polymer with a high stereoregularity in a high yield. A PPA with an even higher molecular weight but narrower molecular weight distribution formed when the polymerization was carried out in water (Table 3, no. 3). Similar results were obtained when $Rh(cod)(tos)(H_2O)$ was used as the polymerization catalyst. The noticeable difference is that the $Rh(cod)(tos)(H_2O)$ complex yielded PPAs with higher stereoregularity than did $Rh(nbd)(tos)(H_2O)$ in the same solvent systems. Especially when the $Rh(cod)(tos)(H_2O)$ complex is used in water, stereoregular PPAs with a 100% *cis* content formed in a short polymerization time.[12] Interestingly, however, when the polymerization was carried out neat, the polymer yield was rather low even after a long polymerization time, and the *cis* content of the polymer was also relatively low (Table 3, no. 8).

Figure 1 shows NMR spectra of the PPAs prepared by $Rh(cod)(tos)(H_2O)$ catalyst. For comparison, the spectra of a PPA prepared by a "classical" catalyst system of WCl_6-Ph_3SiH in toluene are also given. The absorption peaks in the ^1H NMR spectra of the PPA prepared by the $Rh(cod)(tos)(H_2O)$ catalyst in water are very sharp (Figure 1B), indicative of the polymer's high stereoregularity (100% *cis*). In the NMR spectrum of the PPA prepared by the Rh catalyst in neat monomer, a new peak appeared at δ 6.78, which is attributable to the absorption by the *trans* polyene protons (Figure 1A).[9] The stereostructural inhomogeneity made the spectrum somewhat broad and accounted for the lower *cis* content of the polymer (82.2%). The spectrum of the PPA prepared by the classical W catalyst system is very broad. The broadening is a result of an atactic polymer. Stereoregularity is not observed with the W system by NMR. The cyclohexadiene units, whose methine protons absorb at δ 3.73 as a small broad peak,[9] also perturb the regularity of the molecular structure of the PPA. The high stereoregularity of the PPA prepared by the aqueous Rh catalyst is also evidenced by the sharp absorption peaks in its ^{13}C NMR spectrum (Figure 1D), while the peaks for the PPA prepared by the W system are much less resolved.

To check whether the Rh catalysts would work in air, we conducted a polymerization catalyzed by $Rh(cod)(tos)(H_2O)$ in an open flask using tap water as the solvent. The result was identical to that obtained under nitrogen within experimental error; that is, we can synthesize a stereoregular PPA in water in an atmosphere of air. This prompted us to explore the possibility of preparing polyacetylene thin films on a water surface in air. Dropping a dilute chloroform solution of PA (1%) onto the water surface of a dilute aqueous solution of $Rh(cod)(tos)(H_2O)$ (50 μM) in an open beaker yielded a thin PPA film (ca. 250 nm) in a few seconds. By removing the formed polymer film and cleaning the water surface by glass plates, the catalyst solution could be reused for the preparation of another piece of new thin PPA film. The aqueous catalyst solution, albeit extremely dilute (20 ppm), could be so repeatedly used at least five times. We could change the film thickness by varying the concentration of the monomer solutions (up to neat monomer). While the thin films floating on the water surface can be deposited onto a solid substrate, the thick film prepared from the concentrated monomer solutions are free-standing (mechanically strong) and can be easily taken out from the water surface by specimen forceps. The aqueous process enables easy preparation of large-area films with uniform thickness without pinholes, which is difficult to achieve with other film preparation methods such as spin coating and solution casting.[13]

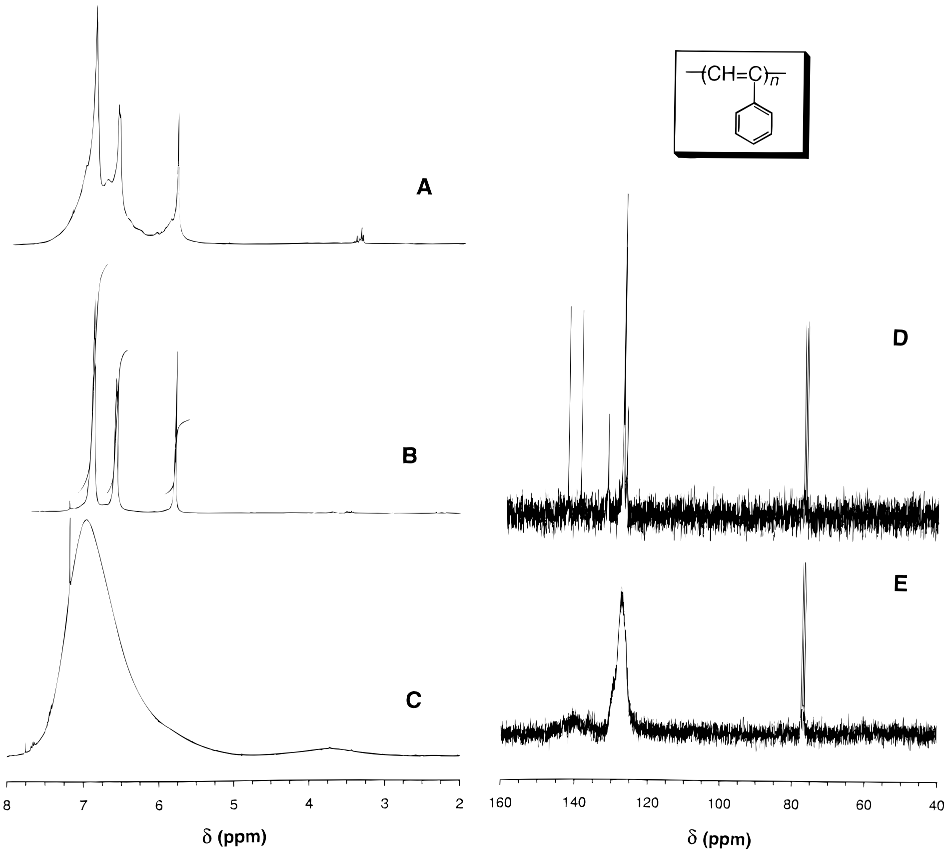

Figure 1. ^{1}H and ^{13}C NMR spectra of poly(phenylacetylene)s (PPAs) prepared by a water-soluble complex of Rh(cod)(tos)(H_2O) (cod = 1,5-cyclooctadiene, tos = *p*-toluenesulfonate) in water (B and D; sample from Table 3, no. 6) and in neat monomer (A; Table 3, no. 8). The spectra for PPA prepared by a "classical" WCl_6-Ph_3SiH catalyst in toluene (C and E) are also shown for comparison. All the spectra were measured in $CDCl_3$ at room temperature.

We have tried to use the water-soluble Rh complexes to polymerize other acetylene derivatives. The polymerization behavior of *p*-MePA was very similar to that of PA. When the polymerizations of *p*-MePA were carried out in toluene, the polymer yields were very low (0.8−1.2%). High molecular weight polymers (M_w 54 000−75 900) were obtained in high yields (67.4−79.8%) when THF was used as a solvent. In this case again, the P(*p*-MePA) prepared by the Rh(cod)(tos)(H_2O) catalyst had a higher stereoregularity (100% *cis*)[14] than that prepared by Rh(nbd)(tos)(H_2O) (90.5% *cis*). Polymerizations initiated by the Rh complexes in water proceeded fast, but unfortunately the P(*p*-MePA)s isolated even after a short polymerization time (15 min) were insoluble. Attempts to use the Rh(cod)(tos)(H_2O) complex to polymerize aliphatic acetylene monomers such as $HC{\equiv}C(CH_2)_5CH_3$, $HC{\equiv}C(CH_2)_2OH$, $HC{\equiv}C(CH_2)_3CO_2H$, and $HO_2CC{\equiv}CCO_2H$ were, however, unsuccessful.[15]

Although much needs to be done to understand the polymerization mechanisms, we suspect that the interaction between the Rh complexes and the aromatic rings might be involved in the formation of the active centers. Thus, the lack of the Rh−aromatic interaction might be responsible for the failure in polymerizing the aliphatic acetylene monomers by the Rh complexes. Toluene is not a good solvent, probably due to the solvent's undesired competitive interaction: The phenyl group in toluene might have partially blocked the way for the PA monomers to coordinate with the Rh complexes.

In summary, in this study, we have developed a number of new Rh-based catalysts that effect acetylene polymerizations in water. Compared with toluene, a commonly-used solvent for acetylene polymerizations,[4] we have found that water is actually a much better solvent (or it may actually act as a cocatalyst): The aqueous polymerization systems are superior in terms of faster reaction and higher stereospecificity. We have successfully synthesized PPAs with 100% *cis* content using a water-soluble Rh complex in open flasks; in other words, we have developed a polymerization system for preparing stereoregular polyacetylenes under a most natural condition: in water in an atmosphere of air.

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(12) In a typical run, a catalyst solution (1 mM) was prepared by dissolving 2 mg of Rh(cod)(tos)(H_2O) in 5 mL of distilled water, to which 0.5 mL of distilled PA was added with vigorous stirring at room temperature under nitrogen. An orange solid formed in ca. 5 min. After 1 h of polymerization, the solid polymer product was separated from the aqueous catalyst solution by filtration and washed with acetone several times. The polymer was dissolved in toluene, and the resulting polymer solution was added dropwise to a large amount of methanol with stirring. The precipitated polymer product was filtered off by a Gooch crucible and dried under vacuum at room temperature to a constant weight. Orange powder, yield: 0.38 g (81.9%). Molecular weights and the polydispersity index of the polymer were estimated by GPC in THF using a set of monodisperse polystyrenes as calibration standards: $M_w = 31\,200$, $M_w/M_n = 5.4$. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.94 (3H, *para* and *meta* aromatic protons), 6.63 (2H, *ortho* aromatic protons), 5.84 (1H, *cis* olefin proton). No peak was observed at δ 6.78, where the *trans* olefin proton absorbs.[9] ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 142.87, 139.31, 131.82, 127.78, 127.55, 126.69. The stereostructure of the polymer was elucidated to be 100% *cis*, using the ^{1}H NMR data by the following equation according to ref 9:

$$\% \, cis = [A_{5.84}/(A_{\text{total}}/6)] \times 100 \tag{1}$$

where A denotes the integrated absorption area and $A_{\text{total}} = A_{5.84} + A_{6.63}\ (+\ A_{6.78}) + A_{6.94}$.

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(14) Polymerized under nitrogen at room temperature for 1 h; $[M]_o = 0.58$ M, [cat.] = 1 mM. Yield: 79.8%. $M_w = 75\,900$, $M_w/M_n = 2.3$. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 6.70 (2H, *meta* aromatic protons), 6.53 (2H, *ortho* aromatic protons), 5.79 (1H, *cis* olefinic proton), 2.13 (3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 140.28, 138.71, 136.03, 131.11, 128.31, 127.58, 20.92. The *cis* content of the polymer was estimated to be 100%, using the ^{1}H NMR data by the following equation:

$$\% \, cis = [A_{5.79}/(A_{\text{total}}/8)] \times 100 \tag{2}$$

where A is the integrated absorption area and $A_{\text{total}} = A_{2.13} + A_{5.79} + A_{6.53} + A_{6.70}$.

(15) Reaction conditions: in water under nitrogen at room temperature for 24 h; $[M]_o = 1$ M, [cat.] = 1 mM. No polymeric products were obtained (yield: 0%).

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