Reusable Rhodium(I)/Cationic Bipyridyl-catalyzed Polymerization of Phenylacetylenes in Water under Aerobic Conditions

Yun-Hua Wang and Fu-Yu Tsai*

Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei 106, Taiwan

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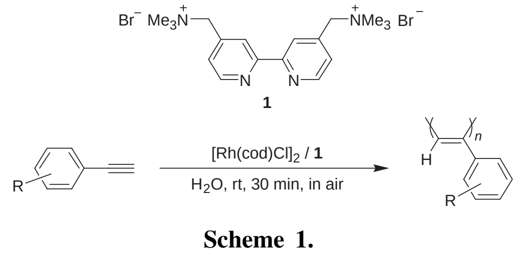
A $[Rh(cod)Cl]_2$ and cationic bipyridyl ligand system was found to be an efficient catalyst for the polymerization of phenylacetylenes in water under aerobic conditions at room temperature. Poly(phenylacetylene) was obtained in high yield with high molecular weight and cis content, and the reused aqueous phase showed activity for recycle run. Mono-substituted phenylacetylenes could also be polymerized by this system in the presence of KOH.

Rhodium complexes are efficient catalysts for the synthesis of cis-transoidal poly(phenylacetylene)s with high molecular weights.[1–13] Recently, aqueous polymerization of phenylacetylenes catalyzed by rhodium-based catalysts has come to be of great interest. Since the use of water as a solvent offers many advantages, such as being cheap, inflammable, and ensuring easy product separation from the reaction mixture. Tang's group has used water soluble $Rh(nbd)(tos)(H_2O)$ and $Rh(cod)(tos)(H_2O)$ to polymerize phenylacetylene and (4-methylphenyl)acetylene in water.[14] Poly(4-carboxyphenyl)acetylene[15–17] and poly(propiolic acid)[18] were prepared in the presence of a base in water by using cationic rhodium complexes as catalysts. On the other hand, the introduction of a water-soluble ligand to rhodium to enable polymerization to proceed in water is one of the best known strategies. Masuda's group employed $Ph_2P(C_6H_4\text{-}m\text{-}SO_3Na)$ as a ligand to introduce a rhodium complex into water for the polymerization of phenylacetylenes.[19]

One of the most important features of the water-soluble catalysts is that recycling and reuse of the catalyst may be possible, which is desirable from the viewpoints of economy and green chemistry. We have previously prepared a water-soluble cationic bipyridine **1**, which acts as an auxiliary ligand, combining with $PdCl_2(NH_3)_2$ to catalyze the Suzuki–Miyaura coupling in water under aerobic conditions and showing excellent activity and recyclability.[20] In this report, we employed this ligand and $[Rh(cod)Cl]_2$ to polymerize phenylacetylenes in the aqueous phase under aerobic conditions, and examined its activity for reuse (Scheme 1).

Because $[Rh(cod)Cl]_2$ is insoluble in H_2O, the catalyst can be conveniently generated in situ by mixing a dichloromethane solution of $[Rh(cod)Cl]_2$ and an aqueous solution of **1** in a 1:2 molar ratio. Typically, $[Rh(cod)Cl]_2$ (2.5 mg, 5.0×10^{-3} mmol) in CH_2Cl_2 (0.2 mL) was mixed with an aqueous solution of **1** (4.6 mg, 1.0×10^{-2} mmol, 2 mL) and stirred at room temperature for 10 min, resulting in a clear, orange-red aqueous phase in the upper layer. The mixture was then heated at 60 °C, after the removal of CH_2Cl_2, the solution was cooled to room temperature. Phenylacetylene (0.22 mL, 2.0 mmol) was added quickly into the aqueous solution with vigorous stirring. After 0.5 h the reddish polymer was collected by filtration and washed with a small amount of H_2O. The combined aqueous solution was then reused in another experiment. The polymer was washed with methanol and acetone several times and then dried in a vacuum at 50 °C overnight. Poly(phenylacetylene) was obtained in 95% yield with M_w 251000 and was highly stereoregular, with a cis content of 90% determined by ^1H NMR (Table 1, Entry 1). The residual catalyst precursor in the collected aqueous solution must have possibility to start the second-time polymerization. Under the same conditions by using the recovered aqueous solution, poly(phenylacetylene) was obtained with M_w 148600 in 76% yield, indicating that the aqueous catalytic system could be separated easily from the polymer by simple filtration and reused (Entry 2). The lower yield of the product obtained using the recovered aqueous solution was attributed to the dilution of the catalyst concentration by H_2O. However, a decrease in catalytic activity after the initial reaction could not be excluded. For comparison, $[Rh(cod)Cl]_2$ was used as a catalyst in the absence of **1** (Entry 3) or the employment of neutral bipyridine as a ligand (Entry 4). Under identical conditions, the yields of poly(phenylacetylene)s and the M_w were much lower, and the PDI of the polymers were broader than those obtained in the presence of **1**. Moreover, the recovered aqueous solution for both reactions showed no activity for further polymerization.



Scheme 1.

Next, we examined the polymerization of 4-ethynylanisole with this catalytic system. Poly(4-ethynylanisole) was obtained in only 10% yield with M_w 3700 after 24 h (Table 2, Entry 1); so, we checked the polymerization of 4-ethynylanisole in the presence of Et_3N and found that by decreasing the amount of

Table 1. Ligand effects on the polymerization of phenylacetylene catalyzed by $[Rh(cod)Cl]_2$ in water[a]

Entry	Ligand	Polymer			
		Yield/%	M_w[b]	M_w/M_n	% Cis[c]
1	**1**	95	251000	2.42	90
2[d]	**1**	76	148600	2.96	93
3	none	73	65600	3.93	96
4	2,2′-bipyridine	70	137600	5.04	81

[a]Conditions: polymerized in H_2O (2 mL) under air at room temperature for 0.5 h, [PA]/[L]/[Rh] = 200/2/1. [b]Determined by GPC for the THF-soluble part on the basis of a polystyrene calibration. [c]Determined by ^1H NMR. [d]Catalyst recycled from the previous run.

Table 2. Base effect on polymerization of 4-ethynylanisole catalyzed by $[Rh(cod)Cl]_2/\mathbf{1}$ in water[a]

Entry	Base/%[b]	Polymer			
		Yield/%	M_w[c]	M_w/M_n	% Cis[d]
1[e]	none	10	3700	2.87	99
2	Et_3N (100)	70	174700	3.42	99
3	Et_3N (50)	84	137100	4.02	97
4	Et_3N (10)	99	111500	3.27	99
5	KOH (100)	99	60600	7.13	99
6	KOH (50)	99	76200	4.76	93
7	KOH (10)	99	179400	2.74	99

[a]Conditions: Polymerized in H_2O (2 mL) under air at room temperature for 0.5 h; [4-ethynylanisole]/[**1**]/[Rh] = 200/2/1. [b]Based on monomer. [c]Determined by GPC for the THF-soluble part on the basis of a polystyrene calibration. [d]Determined by ^{1}H NMR. [e]Reaction time: 24 h.

Table 3. Polymerization of ring-substituted phenylacetylenes catalyzed by $[Rh(cod)Cl]_2/\mathbf{1}$ in water[a]

Entry	Monomer	Polymer			
		Yield/%	M_w[b]	M_w/M_n	% Cis[c]
1[d]	$2\text{-}MeC_6H_4CCH$	50	5300	2.79	92
2	$3\text{-}MeC_6H_4CCH$	87	46700	2.18	99
3	$4\text{-}MeC_6H_4CCH$	99[e]	—	—	99
4	$4\text{-}FC_6H_4CCH$	23	113900	1.93	99
5[f]	$4\text{-}ClC_6H_4CCH$	34	292300	2.24	98
6	$4\text{-}MeOCC_6H_4CCH$	10[e]	—	—	—
7	$4\text{-}EtO_2CC_6H_4CCH$	41	191900	1.97	99
8[g]	$4\text{-}HO_2CC_6H_4CCH$	50[e]	—	—	99[h]

[a]Conditions: Polymerized in H_2O (2 mL) under air at room temperature for 0.5 h; [Monomer]/[KOH]/[**1**]/[Rh] = 200/20/2/1. [b]Determined by GPC for the THF-soluble part on the basis of a polystyrene calibration. [c]Determined by ^{1}H NMR in $CDCl_3$. [d]Reaction time: 24 h. [e]Insoluble in THF. [f]In the absence of KOH. [g]Treatment with KOH (100 mol %) before polymerization and precipitated by aqueous HCl after reaction. [h]Determined by ^{1}H NMR in DMSO-d_6.

base, an increase in the polymer yield was obtained (Entries 2–4). Because polymerization was carried out in water, an inorganic base such as KOH could be used in order to avoid the displeasing odor of Et_3N. We found that the use of 10 mol % KOH based on the monomer gave the highest M_w, yield and cis content with DPI = 2.74 (Entry 7).

Polymerization of ring-substituted phenylacetylenes by our catalytic system was then examined. The reaction of 2-ethynyltoluene under the conditions described in Table 3 was slow, giving a 50% yield of polymer with M_w 5300 after 24 h, presumably due to the steric hindrance of the substituent at the ortho position (Table 3, Entry 1). Polymerization of 3- and 4-ethynyltoluene was much faster giving the corresponding polymers in high yields (Entries 2 and 3). The solubility of poly(4-ethynyltoluene) was similar to the reported result, i.e., insoluble in common organic solvents but partially soluble in $CHCl_3$;[14] as a result the cis content was found to be 99% by ^{1}H NMR. In the case of 4-ethynylhalobenzenes, high molecular weight (M_w = 113900 and 292300) polymers were obtained in 23 and 34% yields, respectively (Entries 4 and 5). Polymerization of 4-ethynylchlorobenzene could be achieved in the absence of KOH. The ring-substituted phenylacetylenes, which have an electron-withdrawing group at the para position, e.g., 4-ethynylacetophenone and ethyl 4-ethynylbenzoate, were also polymerized in the presence of a base, and the insoluble poly(4-ethynylacetophenone) was formed in low yield. Poly(ethyl 4-ethynylbenzoate), which was prepared for study of its nonlinear optical property,[21] was isolated in 41% yield with a high molecular weight and high cis content (Entries 6 and 7). Poly(4-carboxyphenyl)acetylene, used to induce helicity of macromolecules, could also be polymerized by this system.[15–17,22] Polymerization of its potassium salt followed by precipitation in aqueous HCl afforded the polymer in 50% yield with 99% cis-content (Entry 8).

In conclusion, we have successfully employed Rh^I and a water-soluble cationic bipyridyl ligand as a catalytic system for the polymerization of phenylacetylenes in water and in an open flask. The catalyst can be separated easily by simple filtration and the recovered aqueous phase showed activity for further polymerization. We are now attempting to polymerize different monomers in water by a cross-coupling reaction using this ligand and other transition metals.

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