Rhodium-Catalyzed Phenylacetylene Polymerization in Compressed Carbon Dioxide

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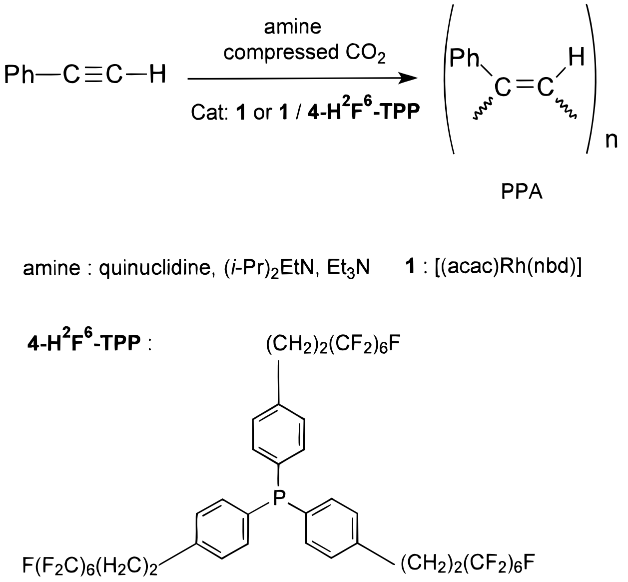
ABSTRACT: Polymerization of phenylacetylene using rhodium catalysts can be carried out with high efficiency in compressed (liquid or supercritical) CO_2. Using the complex [(nbd)Rh(acac)] (nbd = 12,5-norbornadiene, acac = acetyl acetonate) as a catalyst precursor, the polymerization rate in CO_2 is considerably higher than in conventional solvents such as THF or hexane. The resulting polymers consist of THF-soluble (mainly cis-transoidal) and THF-insoluble (mainly cis-cisoidal) species. The polymer characteristics such as stereoregularity and molecular weight are compared to those obtained by polymerization in conventional solvents. Addition of $\{4\text{-}F(CF_2)_6(CH_2)_2C_6H_4\}_3P$ gives rise to a ligand-modified rhodium catalyst with high solubility in compressed CO_2 and leads to an increase in selectivity toward the cis-transoidal polymer.

Introduction

Compressed (liquid or supercritical) CO_2 has been recently recognized as an innovative and ecologically benign reaction medium for chemical syntheses[1] and especially for metal-catalyzed processes.[2] Compared to conventional organic solvents, compressed CO_2 has many advantages such as nonflammability, nontoxicity, and ease of separation of products and/or catalysts from the reaction mixture. Physicochemical properties such as the absence of a gas/liquid phase boundary (in the supercritical state) and possible chemical interactions of compressed CO_2 with catalysts[3] and/or substrates[4] offer additional potential for activity and selectivity control. As for the polymerization in compressed CO_2, DeSimone and co-workers studied mainly radical polymerization and showed that control of the morphology and the microstructure of the resulting polymers is possible.[5] However, few reports have focused on transition-metal-catalyzed polymer synthesis in compressed CO_2: at present, ring-opening metathesis polymerization,[4,6] epoxide/CO_2 copolymerization,[7,8] and oxidative coupling polymerization[9] have been reported. Among them, there is only one example for a well-defined organometallic compound acting as homogeneous catalyst.[4]

Herein we describe rhodium-catalyzed formation of poly(phenylacetylene) (PPA) in compressed CO_2. Various rhodium catalysts are known to promote the polymerization of phenylacetylene (PA) in conventional organic solvents,[10] in neat triethylamine,[10a] or in aqueous solution.[10b] A phosphine-modified Rh(I)−alkynyl complex has been identified as a catalyst for living polymerization of PA quite recently.[11] We now show that both unmodified and phosphine-modified catalysts can be used as initiators for polymerization of PA in compressed CO_2 as an alternative reaction medium. A phosphine ligand with long perfluoroalkyl chain substituents, $\{4\text{-}F(CF_2)_6(CH_2)_2C_6H_4\}_3P$ (4-H^2F^6-TPP),[12] was used to form a phosphine-modified catalytically active species with high solubility in compressed CO_2.



Experimental Section

Materials. All solvents were dried and deoxygenated under an argon atmosphere. Phenylacetylene was dried and distilled over $Na[Et_4Al]$. Triethylamine and diisopropylethylamine were dried and distilled over CaH_2. Quinuclidine (Aldrich) was used as received. The rhodium complex [(acac)Rh(nbd)] (acac = acetyl acetonate, nbd = 2,5-norbornadiene) (**1**) was prepared according to a literature procedure.[13] The "CO_2-philic" phosphine ligand 4-H^2F^6-TPP was prepared as described elsewhere.[12,14]

Polymerization. A stainless steel high-pressure reactor (27 mL volume) equipped with thick glass windows, a PTFE stirring bar, a bore hole for a thermocouple, and needle and ball valves was charged with the complex **1** (7.0 mg, 23 μmol) and 10-fold molar excess of the appropriate amine. The ligand 4-H^2F^6-TPP was added to this mixture if desired. A dosing unit containing PA (0.46 g, 4.5 mmol) was connected to the reactor through the ball valve. Using a compressor, the reactor was filled through the needle valve with a weighed amount of CO_2 (10−24 g) to adjust the desired pressure and density. The liquid CO_2 density was estimated from literature data,[15] and the supercritical CO_2 density was calculated from the reactor

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Table 1. Polymerization of Phenylacetylene Using Catalyst 1 in Various Reaction Media[a]

no.	medium	time (h)	temp (°C)	press. (bar)	yield (%)	THF-soluble: THF-insoluble	stereoregularity (%)[b]	$M_w \times 10^{-4}$	M_w/M_n
1	liqCO_2[c]	1	24	97[e]	65 ± 3	17 ± 2:83 ± 2	78 ± 5	3.1	8.6
2	sc CO_2[d]	1	43	132[e]	70	19:81	82	4.2	9.5
3	THF	1	22	1[f]	0				
4	THF	18	22	1[f]	75	99:1	88	4.9	10.8
5	hexane	1	22	1[f]	25	16:84	85	4.0	11.7
6	hexane	1	21	95[f]	59	19:81	56	1.1	4.2

[a] Conditions: **1**, 23 μmol; quinuclidine, 230 μmol; phenylacetylene, 4.5 mmol. [b] In cis-transoidal PPA as determined by ^{1}H NMR.[18] [c] Density was 0.81 g mL^{-1} according to ref 15. [d] Density was 0.66 g mL^{-1} measured by CO_2 amount per reactor volume. [e] Total pressure after phenylacetylene introduction. [f] Under argon atmosphere.

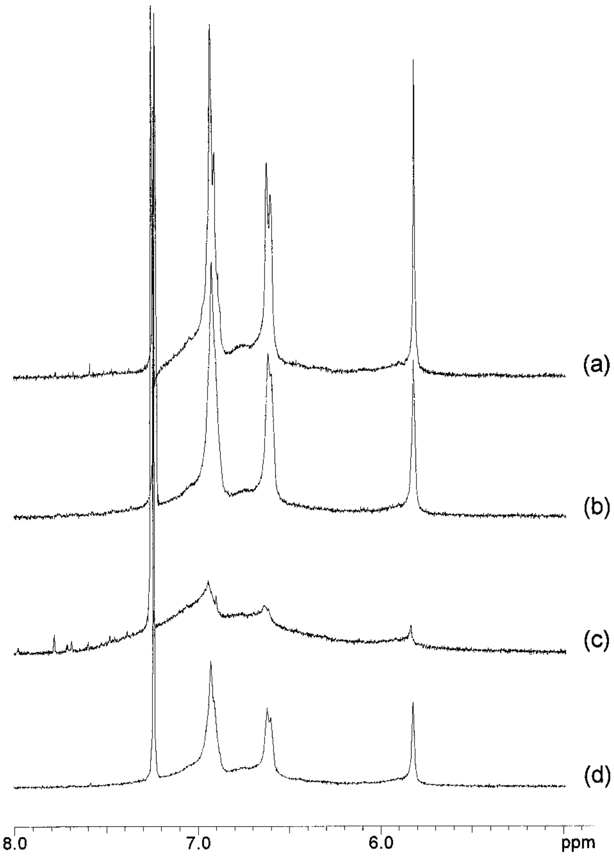


Figure 1. ^{1}H NMR spectra (300 MHz) of cis-transoidal PPA obtained using complex **1** as the catalyst and quinuclidine as a base under various reaction conditions: (a) THF under 1 bar of argon, (b) hexane under 1 bar of argon, (c) hexane under 95 bar of argon, (d) liquid CO_2 (0.81 g mL^{-1}) under 97 bar. The reaction time was 1 h and temperature was 22–24 °C.

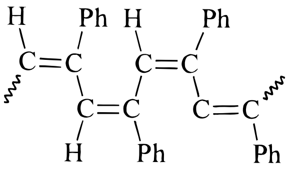
volume and the amount of CO_2 introduced. Upon heating to the desired temperature (21–43 °C) with stirring, the pressure inside the reactor reached 69–170 bar. The dosing unit was pressurized with argon to about 200 bar. Phenylacetylene was introduced into the reactor by opening the ball valve, resulting in a total pressure that was 25 bar higher than the initial value. After the mixture was stirred for a standard reaction time of 1 h, the reactor was cooled to room temperature and then vented.

The residue in the reactor was taken up in THF (15 mL), and acetic acid (1 mL) was added,[16] followed by stirring for several hours. The suspension was transferred into a glass tube and centrifuged to separate THF soluble and insoluble parts. The insoluble part was extracted with THF (3 × 50 mL) under ultrasonic activation. The combined THF fractions were injected into a large amount of MeOH (500 mL). The resulting precipitate was collected by centrifugation and washed with MeOH. Both THF-soluble and insoluble polymers were dried for 12 h under vacuum (1 mbar). The conditions (amount of catalyst, volume of solvent, etc.) in experiments using THF and hexane as solvents were essentially the same as those in the above reaction using CO_2.

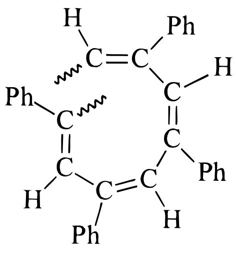
Analysis. NMR spectra were obtained from $CDCl_3$ solutions on a Bruker AM-200 or DPX-300 spectrometer. Chemical shifts are given relative to TMS using the chloroform peak (^{1}H, 7.24 ppm; ^{13}C, 77.0 ppm) as an internal reference. FTIR spectra were measured on a Nicolet 7199 spectrometer in KBr pellets. Gel permeation chromatography (GPC) was carried out at Polymer Standard Service GmbH (Mainz, Germany). THF solutions (100 μL) were eluted at 23 °C at a flow rate of 1.0 mL/min and analyzed using a UV/vis detector (TSP UV 2000, 254 nm) and a diffraction refractometer (Shodex RI71). Molecular weights and molecular weight distributions are reported relative to polystyrene (PS) as a standard.

Results and Discussion

Comparison of Compressed CO_2 with Conventional Solvents. Table 1 summarizes the results of PA polymerization using **1** as a catalyst precursor and quinuclidine as a base under various conditions in compressed CO_2 and in THF or hexane as typical conventional solvents. The complex **1** is well soluble in THF, but no appreciable amounts of polymer were formed within 1 h in this solvent. Extending the reaction time to 18 h and subsequent purification by MeOH yielded PPA as yellow powder (75 % yield). The polymer was fractionized by extraction with THF, and the THF-soluble part (99%) was found to consist mainly of cis-transoidal PPA based on the NMR spectra.[17] The three typical resonances for cis-transoidal PPA appear as fairly sharp and well-resolved signals, indicating a high stereoregularity of the polymer (Figure 1a). Although current published data do not allow a full stereochemical assignment of PPA on the basis of ^{1}H NMR data, the ratio of intensity of the vinylic resonance at δ 5.82 to the total area of proton resonances is frequently used as a qualitative measure for stereoregularity.[18] This analysis results in a stereoregularity value of 88% for the polymer obtained using **1** in THF.



cis-transoidal PPA



cis-cisoidal PPA

In contrast to the situation in THF, complex **1** is very poorly soluble in pure liquid CO_2 and in the quinuclidine/CO_2 mixtures. Before PA introduction, visual inspection in a window-equipped high-pressure reactor at room temperature revealed that the bulk quantity of **1**

Table 2. Polymerization of Phenylacetylene in Compressed CO_2 Using Catalyst 1 in the Presence of Ligand 4-H^2F^6-TPP[a]

no.	P:Rh[b]	amine	CO_2 density (g mL^{-1})	temp (°C)	press.[c] (bar)	yield (%)	THF-soluble: THF-insoluble	stereoregularity (%)[d]	$M_w \times 10^{-4}$	M_w/M_n
1	1:1	quinuclidine	0.80[e]	26	94	76	42:58	90	5.8	10.1
2	1:1	quinuclidine	0.84[e]	29	124	66	26:74	85	4.9	8.1
3	1:1	quinuclidine	0.84[e]	27	134	65	29:71	83	4.4	8.0
4	1:1	quinuclidine	0.88[e]	25	145	60	28:72	74	3.6	8.0
5	1:1	quinuclidine	0.48[f]	43	110	62	25:75	69	5.1	9.4
6	1:1	quinuclidine	0.77[f]	42	150	66	22:78	83	4.3	9.0
7	1:1	quinuclidine	0.82[f]	41	176	70	22:78	74	3.5	8.6
8	1:1	quinuclidine	0.83[f]	41	187	72	24:76	81	4.5	9.4
9	1:1	(i-Pr)$_2$EtN	0.80[e]	27	97	72	23:77	85	3.7	7.7
10	1:1	Et_3N	0.80[e]	27	95	63	40:60	76	4.0	8.7
11	2:1	quinuclidine	0.81[e]	25	100	53	58:42	86		
12	2:1	quinuclidine	0.82[f]	43	195	65	31:69	79		
13[g]	4:1	quinuclidine	0.85[f]	42	190	8	38:62	77		

[a] Conditions: **1**, 23 μmol; quinuclidine, 230 μmol; phenylacetylene, 4.5 mmol; reaction time, 1 h. [b] 4-H^2F^6TPP:Rh catalyst **1** (molar ratio). [c] Total pressure after phenylacetylene introduction. [d] In cis-transoidal PPA as determined by ^{1}H NMR.[18] [e] Liquid CO_2 density was taken from ref 15. [f] Supercritical CO_2 density is given as CO_2 amount per reactor volume. [g] Reaction time, 24 h.

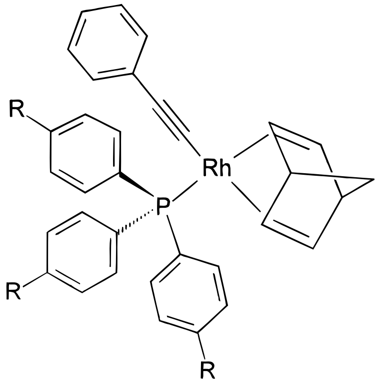
remained as a solid after the amine had dissolved in the liquid CO_2 which was introduced at 72 bar using a compressor. Despite this low solubility, **1** initiated the polymerization of PA very effectively, leading to a 65% yield of PPA within reaction times as short as 1 h. The product consisted of 17% cis-transoidal PPA and 83% of a THF-insoluble fraction. The latter was identified to consist mainly of cis-cisoidal PPA on the basis of its solubility properties, IR spectra, and electron microscopic images.[19,20] The polymerization also occurred very efficiently at conditions beyond the critical point of CO_2 ($T > 31$ °C, $p > 74$ bar). The amine and CO_2 formed a transparent homogeneous supercritical phase under these conditions, but the bulk amount of **1** remained again insoluble as a solid. Nevertheless, polymerization occurred smoothly upon addition of PA, and the polymer precipitated rapidly as bright yellow plates. Independent of the state of the compressed CO_2, the THF-soluble fraction of polymer had a weight-averaged molecular weight (M_w) of approximately 4×10^4 and a fairly broad molecular weight distribution (M_w/M_n).

The high activity *and* the predominant formation of THF-insoluble PPA in compressed CO_2 are in sharp contrast to the polymerization in THF. Hexane is very often quoted as a liquid organic solvent with properties similar to CO_2, because of its similar low polarity, comparable density, and weak solvating abilities. Accordingly, complex **1** proved also very poorly soluble in hexane. In contrast to CO_2, however, the polymerization activity in hexane was low with only 25% conversion after 1 h at room temperature. Surprisingly, application of high pressure of an inert gas (argon) led to an increase in polymerization rate. This polymer had a significantly lower molecular weight and narrower molecular weight distribution than the one prepared under other conditions.

The ratio of THF-soluble to THF-insoluble PPA produced in hexane was very similar to that observed in compressed CO_2 and practically independent of the applied pressure, suggesting a predominant influence of solvent polarity on the stereoselectivity of the polymerization. On the other hand, the stereoregularity of cis-transoidal PPA as estimated from analysis of the NMR spectra was found to be quite sensitive to the reaction conditions. Under normal pressure, the stereoregularity was high in THF or hexane, as indicated by relatively sharp signals in the ^{1}H NMR spectra (Figure 1a,b). Under conditions leading to high polymerization rates in hexane, i.e., under elevated pressure, the polymer had a less well-defined structure, as indicated by very broad, unresolved signals in the ^{1}H NMR spectrum (Figure 1c). It should be noted that pressure-induced cis to trans isomerization has been recently reported for neat PPA.[21] Despite the application of high pressure, however, polymerization using compressed CO_2 gave well-resolved ^{1}H NMR spectra (Figure 1d), indicating high stereoregularity.

Polymerization of PA in Compressed Carbon Dioxide Using Ligand-Modified Rhodium Catalysts. Phosphine ligands have been shown to be very effective modifiers for PA polymerization catalysts, allowing for example control of the stereoregularity and living polymerization systems.[11] Noyori and co-workers have identified complex **2a** as a highly active phosphine-modified rhodium catalysts for PPA formation.[11] Species **2a** is formed in situ from a rhodium precursor, PPh_3 (TPP), and the amine in the polymerization solvent, typically THF. In the present work, the formation of a TPP-modified catalyst for the polymerization in compressed CO_2 was hampered by the low solubility of **1** and especially of the TPP ligand in liquid and supercritical CO_2. Recently, we have demonstrated that the incorporation of perfluoroalkyl chains $(CH_2)_x(CF_2)_yF$ in the aryl moiety increases the solubility of arylphosphines and their complexes in compressed CO_2 dramatically, without strongly affecting the electronic and steric properties of the controlling ligand.[12] The TPP analogue 4-H^2F^6-TPP has been used successfully in catalytic hydroformylation,[12,22] and the concept has been applied to other reactions as well.[2d,23] We therefore anticipated that the use of 4-H^2F^6-TPP during PA polymerization might lead to formation of a phosphine-modified complex **2b**, analogous to Noyori's **2a** but with high solubility in compressed CO_2.

Indeed, a bright orange homogeneous solution was formed from complex **1** and equimolar 4-H^2F^6-TPP in a compressed CO_2/amine mixture. Upon introduction of PA, polymerization occurred rapidly, as indicated by the precipitation of bright yellow plates, which covered the reactor within a few minutes. After 1 h, PPA was isolated in 62−76% yield with M_w of $(3.5-5.8) \times 10^4$ and M_w/M_n of 7.7−10.1 (Table 2, entries 1−10). These values are similar to those obtained with the unmodified precursor, but the presence of the ligand leads to a significant difference in the stereoselectivity of the resulting polymer. The amount of THF-soluble cis-



2a: R = H
2b: R = $(CH_2)_2(CF_2)_6F$

transoidal PPA increased significantly by addition of 4-H^2F^6-TPP in both liquid and supercritical CO_2, as compared to the case of the unmodified catalyst. The increase was most pronounced in liquid CO_2 using sterically less demanding amines (compare Table 2, entries 1, 9, and 10).

The effect of the P/Rh ratio on PPA formation in compressed CO_2 was also studied briefly. Increasing the P/Rh ratio from 1:1 to 2:1 increased slightly the selectivity toward cis-transoidal PPA in liquid and supercritical CO_2 (Table 2, entries 1/11 and 8/12). Further increase of the P/Rh ratio led to a sharp decrease in polymerization activity; using a 4-fold molar excess of 4-H^2F^6-TPP to **1** gave only 8% yield, even when the reaction time was extended to 24 h (Table 2, entry 13). This effect parallels the observation in conventional solvents[11b] and clearly demonstrates the formation of phosphine-coordinated intermediates in compressed CO_2.

Although the ligand 4-H^2F^6-TPP plays an important role in the formation of the active species in compressed CO_2, the stereochemistry and the molecular weight of the resulting PPA differ considerably from those observed with **2a** in the THF.[11] This difference must be mainly due to the change of the reaction medium, if the analogous complex **2b** was formed as the active intermediate in compressed CO_2. Similar considerations apply for the results obtained with the unmodified catalyst **1** in CO_2 and liquid solvent systems. However, it cannot be ruled out at present that the catalytically active intermediates are different in compressed CO_2 and in the organic solvent, and a definite conclusion has to await more detailed mechanistic investigations.

Conclusions

In the present studies, we have investigated the rhodium-catalyzed PA polymerization in compressed CO_2 as a reaction medium. Despite poor solubility of [(acac)Rh(nbd)] (**1**) in compressed CO_2, the polymerization rate was much higher than in THF, where the catalyst precursor **1** is well soluble. The resulting polymer consisted of THF-soluble (mainly cis-transoidal) and THF-insoluble (mainly cis-cisoidal) species. For the soluble fraction, the polymer properties such as stereoregularity and molecular weight were comparable to those obtained in conventional solvents. Using **1** in the presence of 4-H^2F^6-TPP gave rise to a highly soluble and active rhodium catalyst in compressed CO_2 and led to an increase in selectivity toward cis-transoidal PPA. In summary, compressed CO_2 is a possible alternative reaction medium with ecological benefits for PPA formation, allowing also enhanced reaction rates and different stereoselectivities compared to those of typical organic liquids. It will be interesting to see whether these effects apply also for rhodium catalysts other than **1,** including the established systems leading to living polymerization.

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(16) Acetic acid was added to quench the reaction. See ref 11a.

(17) ^1H NMR in $CDCl_3$: δ 5.82 (s, 1H, vinyl proton), 6.60−6.62 (m, 2H, ortho aromatic protons), 6.88−6.93 (m, 3H, meta and para aromatic protons). ^{13}C NMR in $CDCl_3$: δ 126.70, 127.58, 127.80, 131.79, 139.36, 142.90. These values are in good

agreement with those reported for cis-transoidal PPA. See refs 10b, 10e, 10g, and 11.

(18) The stereoregularity in cis-transoidal PPA was estimated from ^{1}H NMR data by the following equation according to refs 10a, 10b, and 10h: cis (%) $= [A_{5.82}/(A_{\text{total}}/6)] \times 100$, where $A_{5.82}$ is the area of the vinyl proton and A_{total} is the total area of the spectrum. However, this procedure does not allow for exact assignment of the stereochemistry of PPA, which has to await further elucidation. Therefore, the resulting value is used here only as a qualitative measure for stereoregularity without direct implications on the exact structure. We gratefully acknowledge helpful comments on stereochemical analysis of PPA by one of the referees.

(19) Generally, PPA has two absorption bands at 740 and 760 cm^{-1} in the IR spectra. The ratio of the intensities of these two bands is a function of the cis content in the polymer. The higher intensity of the band at 740 cm^{-1} compared to that at 760 cm^{-1} supports that this insoluble species is mainly cis-cisoidal PPA. See: Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem.* **1977**, *15*, 2497−2509 and refs 10e and 10h.

(20) The SEM image of the THF-insoluble part showed a much more compact structure than that of the THF-soluble part. This is consistent with the insolubility and the cross-packed structure of cis-cisoidal PPA.

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