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Polymerization of Monosubstituted Acetylenes with a Zwitterionic Rhodium(I) Complex, $Rh^+(2,5\text{-norbornadiene})[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$

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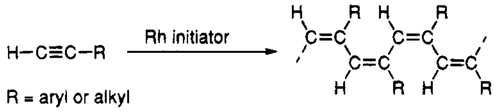
ABSTRACT: $Rh^+(2,5\text{-norbornadiene})[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$, a zwitterionic Rh(I) complex, shows excellent activity for the polymerization of monosubstituted acetylenes under mild conditions. The reaction of phenylacetylene and its *p*- and *m*-substituted derivatives proceeds rapidly to give yellow soluble polymers with a cis configuration of the main polymer chain and with a high number-average molecular weight ($>10^5$) in high yields. The *o*-substituted derivatives give stereoregular red crystalline polymers which are scarcely soluble in organic solvents. The Rh complex has a moderate activity for the polymerization of *tert*-butylacetylene, cyclohexylacetylene, and 3-ethyl-1-pentyne to afford stereoregular cis polymers in quantitative yields.

Introduction

Polymerization of substituted acetylenes promoted by group 5, 6, and 9 transition metal complexes has attracted a great deal of attention.[1] In particular, Rh(I) complexes have been of intense interest because of their potentially high reactivities toward alkynes[2] and capability of inducing stereocontrolled living polymerization.[3] Some Rh(I) complexes such as $[RhCl(diene)]_2$ (diene = 1,5-cyclooctadiene (cod) and 2,5-norbornadiene (nbd)),[4a,d] $[Rh(diene)(N{-}N)]X$ (diene = cod, nbd; N−N = nitrogen-based bidentate ligand; X = PF_6, ClO_4, $B(C_6H_5)_4$),[4a−c] $Rh(cod)[C_5H_4N\text{-}2\text{-}(CH_2)_2P(C_6H_5)(CH_2)_3ZR]PF_6$[4e] (ZR = OC_2H_5, OC_6H_5, $NH(C_6H_5)$, NH(*cyclo*-C_6H_{11})), and $Rh(C{\equiv}CC_6H_5)(nbd)[P(C_6H_5)_3]_2$[3] polymerize phenylacetylenes to give highly stereoregular poly(phenylacetylene)s with a cis−transoidal structure. $[RhCl(diene)]_2$ also initiates cyclopolymerization of 1,5-hexadiyne to give a highly conjugated polymer.[4f] These initiators often require an appropriate additive such as NaOH, $NaOC_2H_5$, or triethylamine to attain high activity. Unfortunately, however, these Rh complexes are not effective for polymerization of simple monoalkylated acetylenes.

We noticed in Alper's earlier findings that the zwitterionic Rh complexes of type $Rh^+(diene)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ exhibit unique selectivities in certain catalytic reactions such as olefin hydroformylation.[5] Alper in fact used a $Rh^+(cod)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$−triethylsilane combined system for polymerization of phenylacetylene. However, the Rh complex without added triethylsilane had only a moderate activity for polymerization even at a higher reaction temperature.[6] We have independently studied related systems and found that the nature of the diene ligand is extremely important for the reactivity.[3] Simple replacement of 1,5-cyclooctadiene by 2,5-norbornadiene in $Rh^+(diene)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ appeared to enhance the reactivity remarkably. Thus, $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (**1a**) acts as an excellent initiator of the polymerization of alkylated and aromatic monosubstituted acetylenes without trialkylsilanes.



Experimental Section

Materials. $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (**1a**)[7] and $Rh^+(nbd)[\{\eta^6\text{-}C_6H_4\text{-}p\text{-}C(CH_3)_3\}B^-\{C_6H_4\text{-}p\text{-}C(CH_3)_3\}_3]$ (**1b**) were prepared by reacting $[RhCl(nbd)]_2$ and $NaB(C_6H_5)_4$ or $LiB[C_6H_4\text{-}p\text{-}C(CH_3)_3]_4$. $Rh^+(dppe)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (**1c**, dppe = 1,2-bis(diphenylphosphino)ethane)[8] was prepared according to the literature procedure. [*o*-Methyl- (**2b**), [*o*-methoxy- (**2c**), [*o*-(trifluoromethyl)- (**2d**), [*m*-methoxy- (**2e**), [*m*-(methoxycarbonyl)- (**2f**), [*p*-methoxy- (**2g**), [*p*-(methoxycarbonyl)phenyl]acetylene (**2h**), and 3-ethyl-1-pentyne (**4b**) were prepared by modified literature methods.[9−11] Commercially available acetylenes such as phenylacetylene (**2a**), 1-phenyl-1-propyne (**3**), *tert*-butylacetylene (**4a**), cyclohexylacetylene (**4c**), (trimethylsilyl)acetylene (**6**), methyl propiolate (**7**), and *N,N*-dimethylpropargylamine (**8**) were dried over CaH_2 and then distilled over CaH_2 before use. THF and CH_2Cl_2 were distilled over sodium benzophenone ketyl and CaH_2, respectively.

Measurement. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM-270 spectrometer with tetramethylsilane as an internal standard. GC analysis was performed on a Shimadzu GC-14A instrument equipped with a CP Cyclodex β 236 M column (0.25 mm i.d. x 25 m). Specific rotation was measured on a JASCO DIP-370 spectrophotometer. Circular dichroism (CD) was performed on a JASCO J-720 spectrophotometer.

Synthesis of (*R*)-(−)-3-Phenyl-1-butyne (5).[12] Optically pure **5** was prepared according to the literature procedures using (*R*)-4-phenyl-2-pentynoic acid as the starting material, which can be prepared in the following procedure. To a suspension of activated zinc (31 g, 0.47 mol) and triphenylphosphine (136 g, 0.52 mol) in CH_2Cl_2 (500 mL) was added a solution of the carbon tetrabromide (156 g, 0.47 mol) in CH_2Cl_2 (250 mL) at 10−20 °C, and the mixture was stirred at room temperature for 15 h. After the addition of a CH_2Cl_2 solution (250 mL) of racemic 2-phenylpropionaldehyde (31.5 g, 0.23 mol) at 0 °C, the reaction mixture was stirred at 10 °C for 2 h and then diluted with hexane (1 L). The resulting precipitate was removed by filtration, and the filtrate was concentrated under vacuum to give crude 2-phenyl-1,1-dibromopropane (65 g). A solution of 1.6 M *n*-butyllithium in hexane (288 mL, 0.46 mol) was added to a solution of the crude dibromide (65 g, 0.23 mol)

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Table 1. Polymerization of Phenylacetylene (2a) with Rh(I) Complexes[a]

entry	catalyst	solvent	temp, °C	time, min	conv, %	yield, %	$M_n/10^4$ [b]	M_w/M_n [b]
1	**1a**	THF	20	1	100	100	11.5	2.87
2	**1a**[c]	THF	23	1	100	100	6.5	2.68
3	**1a**	CH_2Cl_2	22	1	98	100	11.7	2.99
4	**1a**	CH_2Cl_2	−20	180	96	92	20.3[d]	3.92[d]
5	**1a**	CH_2Cl_2[e]	22	1080	86	81	5.3	3.65
6	**1b**	CH_2Cl_2	18	40	77	76	11.3	2.48
7	**1c**	CH_2Cl_2	26	1200	1			
8	$Rh^+(cod)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$	THF	20	270	97	90	3.8	3.02
9	$[RhCl(nbd)]_2$[f]	THF	25	1	100	100	12.2	1.83

[a] Conditions: $[\mathbf{2a}]_0$ = 300 mM, $[Rh]_0$ = 6 mM. [b] Determined by GPC based on polystyrene standards. [c] In the presence of 50 equiv of triethylsilane/Rh. [d] Measured only for the THF-soluble part. [e] $[\mathbf{2a}]_0$ = 600 mM, $[\mathbf{1a}]_0$ = 0.6 mM. [f] In the presence of 100 equiv of triethylamine/Rh.

in THF (1 L) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h, followed by the addition of ca. 300 g of dry ice. Then, the mixture was warmed to 0 °C, poured into water, and extracted with ether to give a crude product. Distillation gave pure 4-phenyl-2-pentynoic acid (racemic form) as a pale yellow oil (33.2 g, 83% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 11.2 (s, 1H), 7.36 (m, 5H), 3.91 (q, 1H, J = 7.3 Hz), 1.57 (d, 3H, J = 7.3 Hz). Optical resolution of racemate was performed according to the literature[13] to give (*R*)-4-phenyl-2-pentynoic acid. The GC analysis showed the enantiomeric excess of **5** to be 99.95%. $[\alpha]_D^{24}$ −20.0 (*c* 3.30, hexane) (lit.[13] $[\alpha]_D^{25}$ −21.8 (*c* 14.2, heptane)).

Polymerizations. The reactions were carried out under an argon atmosphere in a prebaked Schlenk tube. The polymerization was initiated by adding 4 mL of a monomer solution, containing tetralin as an internal standard for GC analysis, to the Rh complex solution (1 mL). After the reaction was quenched by 47 mg of triphenylphosphine, the mixture was poured into 100 mL of methanol. Methanol-insoluble material was collected by filtration, washed with methanol, and then dried under vacuum at room temperature for several hours. Monomer conversion was determined by GC analysis of the reaction mixture.

Characterization of the Polymer Products. Since the polymers obtained above slowly degrade in THF solution,[14] the NMR or GPC analysis was performed immediately after preparation of the samples. The molecular weight distribution of the polymers was determined by size-exclusion chromatography (SEC) in THF at 40 °C on a JASCO GULLIVER system equipped with two polystyrene gel columns (Shodex KF-80M x 2, 8 mm i.d. x 300 mm). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were calculated from the SEC eluograms on the basis of polystyrene calibration. Wide-angle X-ray scattering (WAXS) measurements were carried out using a Rigaku Ru-200B diffractometer. The monochromated X-ray beam was Cu Kα with a wavelength of 0.154 18 nm.

Results and Discussion

Polymerization of Phenylacetylene (2a) with Zwitterionic Rh Complexes. Polymerization of **2a** in the presence of a small amount of **1a** was carried out in common organic solvents such as THF, CH_2Cl_2, methanol, ether, and hexane at room temperature. THF or CH_2Cl_2 is the solvent of choice because of homogeneity of the reaction system. The reaction proceeded exothermally to completion within 1 min, resulting in a dark orange solution. Treatment of the reaction mixture with a large amount of methanol produced a fine yellow precipitate. The methanol-insoluble polymer with M_n values in the range (3−20) × 10^4 and a rather broad molecular weight distribution (M_w/M_n > 2.5) is soluble in most organic solvents such as $CHCl_3$, CH_2Cl_2, THF, and toluene but insoluble in ether. Occasionally, the methanol-insoluble part contained small amounts of THF-insoluble red polymers. Table 1 shows the representative results obtained with several kinds of Rh(I) initiators. The zwitterionic complex **1a** has an excellent activity for the polymerization of **2a**. In contrast to Alper's observation,[6] an addition of triethylsilane (50 equiv/Rh) had no significant influence on the reaction rate. Instead, a decrease in the M_n value of the product was caused (entry 2). Even at −20 °C, the polymerization proceeds to completion within 3 h to give the polymer in a quantitative yield (entry 4). The increase in the monomer to initiator feed ratio from 50:1 to 1000:1 resulted in a slight decrease in the M_n value (entries 3 and 5). The reaction of **1a** with **2a** in a 1:1 molar ratio at room temperature produced the polymer with an M_n of 3.3 × 10^4. These results show the very low initiation efficiency of **1a** (<0.3%) and the predominance of the chain transfer reaction during the polymerization, which causes difficulty in understanding the initiation mechanism.

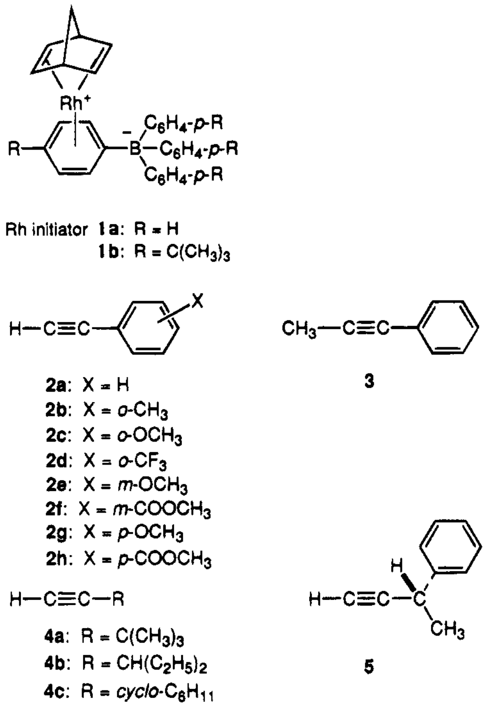

Figure 1. Rh(I) initiators and substituted acetylene monomers.

$Rh^+(nbd)[\{\eta^6\text{-}C_6H_4\text{-}p\text{-}C(CH_3)_3\}B^-\{C_6H_4\text{-}p\text{-}C(CH_3)_3\}_3]$ (**1b**) possessing bulky aryl groups initiates the polymerization of the monomer **2a**, but its activity is lower than that of **1a** (entry 6). It should be noted that $Rh^+(dppe)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (**1c**) with no diene ligand, which is known to catalyze the oligomerization of propyne giving mainly dimers, linear trimers, and cyclic trimers,[15] provides no polymeric product (entry 7).

Table 2. Polymerization of Ring-Substituted Phenylacetylenes with $Rh^+(nbd)[(\eta^6-C_6H_5)B^-(C_6H_5)_3]$ (1a)[a]

entry	monomer	time, min	conv, %	yield, %	$M_n/10^4$ [b]	M_w/M_n [b]
1	**2b**	30	49	35	insoluble	
2	**2c**	30	100	100	insoluble	
3	**2d**	30	53	26	insoluble	
4	**2e**	1	100	100	12.4	2.77
5	**2f**	1	99	100	13.3	2.66
6	**2g**	1	100	100	15.7	1.79
7	**2h**	1	100	100	21.8	2.58
8	**3**	30	0			

[a] Conditions: $[\text{monomer}]_0 = 300$ mM, $[\mathbf{1a}]_0 = 6$ mM, in THF at 19–21 °C. [b] Determined by GPC based on polystyrene standards.

Table 3. Polymerization of Alkylated Acetylenes with $Rh^+(nbd)[(\eta^6-C_6H_5)B^-(C_6H_5)_3]$ (1a)[a]

entry	initiator	monomer	time, min	conv, %	yield, %	$M_n/10^4$ [b]	M_w/M_n [b]
1	**1a**	**4a**	60	98	100	2.8	2.06
2	**1a**	**4b**	60	100	100	0.7	1.80
3	**1a**	**4c**	30	100	100	insoluble	
4	**1a**	**5**	2520	57	55	0.3	1.50
5	$[RhCl(nbd)]_2$[c]	**4a**	60	27	0.6	3.7	1.66

[a] Conditions: $[\text{monomer}]_0 = 300$ mM, $[Rh]_0 = 6$ mM, in THF at 19–21 °C. [b] Determined by GPC based on polystyrene standards. [c] In the presence of 100 equiv of triethylamine/Rh.

The COD-containing zwitterionic complex, $Rh^+(cod)[(\eta^6-C_6H_5)B^-(C_6H_5)_3]$, has moderate activity under the standard polymerization conditions (entries 1 and 8). $[RhCl(nbd)]_2$ has been reported to exhibit a high activity when triethylamine is the solvent[4d] to give polymers with a molecular weight of up to 4.3×10^6. Under the standard conditions in Table 1, the $[RhCl(nbd)]_2$/triethylamine system has an activity similar to that of $Rh^+(nbd)[(\eta^6-C_6H_5)B^-(C_6H_5)_3]$ (entry 9). These results clearly indicate that NBD is the best choice of ligand to attain the high polymerization activity. Although the exact role of the diene ligand remains unclear, the NBD ligand is smaller and has stronger σ-donating and π–back-bonding acceptor capabilities than the COD ligand.[16] Such steric and electronic effects might affect the stability and reactivity of the intermediary Rh complexes.

Polymerization of Ring-Substituted Phenylacetylenes. Table 2 shows the representative results of the polymerization of *o*-, *m*-, and *p*-substituted phenylacetylenes. [*o*-Methyl- (**2b**), [*o*-methoxy- (**2c**), and [*o*-(trifluoromethyl)phenyl]acetylene (**2d**) polymerize rather slowly relative to the parent phenylacetylene to give red products which are soluble in common organic solvents at higher temperatures but not completely soluble at room temperature. The polymerization of [*m*-methoxy- (**2e**), [*m*-(methoxycarbonyl)- (**2f**), [*p*-methoxy- (**2g**), or [*p*-(methoxycarbonyl)phenyl]acetylene (**2h**) with **1a** proceeds rapidly within 1 min at room temperature, resulting in highly stereoregular, soluble yellow polymers in quantitive yield with M_n values on the order of 10^5.

The electronic or steric nature of the substituent at the *m* and *p* positions of the aromatic ring does not significantly affect the polymerization rate and M_n value of the products, while the *o*-substituents lowered the reaction rate, giving insoluble red polymers. The great difference in the solubility of polymers of *o*-substituted phenylacetylenes obtained with **1a** may be attributed to the difference in the structure of the polymer main chain or the crystallinity of the polymers (vide infra). This is in sharp contrast with the polymers synthesized with catalysts such as the group 6 metal complexes, which give soluble poly(**2b**) with a mixture of cis and trans geometry,[17] and $[RhCl(nbd)]_2$, which gives high molecular weight poly(**2c**) with a cis structure.[18] 1-Phenyl-1-propyne (**3**) was inert under our reaction conditions. Attempted copolymerization of **2a** and **3** with **1a** was unsuccessful.

Polymerization of 1-Alkynes with 1a. As listed in Table 3, **1a** initiates the polymerization of *tert*-butylacetylene (**4a**) smoothly but the reaction is slower than that of **2a** under the same reaction conditions to give a white polymer in quantitative yield. The polymer thus obtained is soluble in THF and CH_2Cl_2 and possesses an M_n value of 2.8×10^4 and an M_w/M_n value of 2.06. A $[RhCl(nbd)]_2$/triethylamine (1:100 molar ratio) combined catalyst system, however, has a very low activity toward the monomer **4a** under the identical conditions. 3-Ethyl-1-pentyne (**4b**) also polymerizes with **1a** to yield a soluble, pale yellow polymer with an M_n of 7.3×10^3. Cyclohexylacetylene (**4c**) provides a white product in quantitative yield, which is soluble in common organic solvents at 100 °C but insoluble at room temperature.

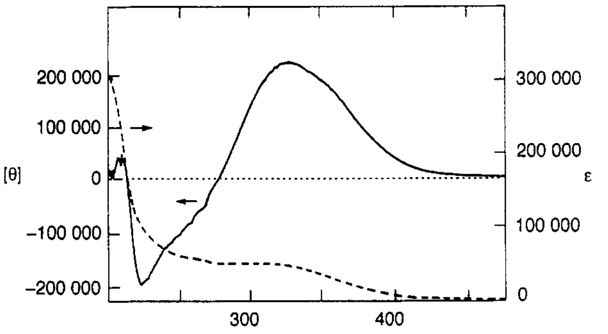

Figure 2. UV/vis and CD spectra of poly[(*R*)-(−)-3-phenyl-1-butyne] taken in THF at room temperature.

The polymerization of (*R*)-(−)-3-phenyl-1-butyne (**5**) with $[\alpha]_D^{24}$ of −20.0 (*c* 3.30, hexane) initiated by **1a** gave a pale yellow product in 55% yield with an M_n value of 3×10^3 and a larger positive $[\alpha]_D^{20}$ value of +548 (*c* 1.0, chloroform). Both the UV/vis and CD transitions shown in Figure 2 are assigned to π–π* transitions of the main chain of poly(**5**) based on the data in the literature.[19] A magnitude in the molar ellipticity ([Θ]) of +220 000 at 329 nm and −200 000 at 230 nm clearly indicates that the chiral side group induces a disymmetric perturbation on the main chain by twisting its conformation with an excess of one screw sense[20,21] which will be discussed in the next section.

In contrast to the reported results,[22–24] (trimethylsilyl)acetylene (**6**), methyl propiolate (**7**), and *N*,*N*-dimethylpropargylamine (**8**) did not produce any polymers under the above described conditions.

Polymer Structure. ^1H NMR spectra of polymers obtained from parent and *m*- and *p*-substituted phenylacetylenes by using **1a** show a sharp singlet due to the vinylic protons of the main chain in the range δ 5.71–5.85, as listed in Table 4. These signals have been tentatively correlated to the regular head–tail cis–transoidal structure[4a] formed by a cis insertion mechanism. We obtained direct evidence for the cis insertion mechanism by the ^{13}C-labeling experiments developed recently.[3] The $^{13}C\{^1H\}$ NMR spectrum of poly(**2a**) obtained from a 95:5 mixture of $HC{\equiv}CC_6H_5$ and $H^{13}C{\equiv}^{13}CC_6H_5$ gives two doublets at δ 132.2 and 139.9

Table 4. ^{1}H NMR Data for Poly(substituted acetylene)s[a]

monomer	polymer, chemical shifts in δ (multiplicity, intensity)	
	vinyl proton	other protons
2a	5.84 (br s, 1H)	6.94 (m, 3H), 6.63 (d, 2H)
2b[b]	5.40 (br s, 1H)	6.81 (t, 1H), 6.69 (m, 2H), 6.22 (d, 1H), 1.79 (br s, 3H)
2c[b]	5.51 (br s, 1H)	6.81 (t, 1H), 6.42 (m, 2H), 6.22 (d, 1H), 3.42 (br s, 3H)
2e	5.85 (br s, 1H)	6.83 (t, 1H), 6.52 (d, 1H), 6. 27 (m, 2H), 3.55 (br s, 3H)
2f	5.71 (br s, 1H)	7.66 (d, 1H), 7.41 (br s, 1H), 7.01 (t, 1H), 6.76 (d, 1H), 3.76 (br s, 3H)
2g	5.76 (br s, 1H)	6.63 (d, 2H), 6.46 (d, 2H), 3.58 (s, 3H)
2h	5.79 (br s, 1H)	7.60 (d, 2H), 6.68 (d, 2H), 3.84 (br s, 3H)
4a	6.18 (br s, 1H)	1.13 (br s, 9H)
4b	5.94 (br s, 1H)	2.47 (br s, 1H), 1.41 (m, 4H), 0.84 (m, 6H)

[a] In $CDCl_3$ at 27 °C. [b] In $CDCl_3$ at 50 °C.

Table 5. Powder Diffraction Data for Poly(substituted acetylene)s

monomer	2θ, deg	interplanar spacing *d*, Å
2a	8.1	10.9
2b	9.2	9.6
2c	9.2	9.6
2d	9.3	9.5
2e	7.6	11.6
2f	6.3	14.2
2g	6.7	13.2
2h	5.4	16.3
4a	9.7	9.2
4b	9.2	9.6
4c	8.1, 9.2	11.0, 9.6
5	8.5	10.4

with $J_{^{13}C-^{13}C} = 72$ Hz, clearly indicating the presence of a $^{13}C{=}^{13}C$ bond in the polymer chain. This result is consistent with the insertion propagation mechanism rather than the metathesis pathway, although the precise initiation mechanism remains unclear.

The ^{1}H NMR spectra of the polymers of *o*-substituted phenylacetylenes **2b**, **2c**, and **2d**, taken in $CDCl_3$ at 50 °C, show a sharp singlet due to vinylic protons at δ 5.40 with poly(**2b**), at δ 5.51 with poly(**2c**), and at 5.28 with poly(**2d**). The spectrum of poly(**4c**) at 100 °C in toluene displays a sharp singlet at δ 6.22. These results indicate that the polymers with low solubility at room temperature have a stereoregular cis structure, which can be contrasted with the products obtained with group 6 catalyst systems. Further heating of poly(**4c**) in toluene at 100 °C generated a small broad signal at δ 6.0–6.1. Cis–trans isomerization of the main chain structure might occur at higher temperature. The spectrum of poly(**5**) taken in $CDCl_3$ at room temperature shows two sharp signals due to vinylic protons at δ 5.58 and 5.91.

The wide angle X-ray scattering (WAXS) of the polymers showed a crystalline peak at $2\theta = 6.3{-}9.7°$ (Table 5), which might be correlated to the (1010) reflection of the pseudohexagonal lattice of rodlike molecules.[18,23,25,26] Interestingly, the interplanar *d* spacing increases when the substituent is replaced from the ortho to meta to para position. A rather sharp signal in the WAXS patterns of the polymers of *o*-substituted phenylacetylenes shows that these polymers have high crystallinity as compared with the parent or *m*- and *p*-substituted phenylacetylenes, which may be related to the low solubility of the polymers. Although Mo complexes are known to cause the cis to trans isomerization of the main chain structure of poly(*tert*-butylacetylene) during the polymerization,[27] the Rh complex **1a** does not change the polymer structure even after standing in solution for up to 24 h. Noticeably, the WAXS measurement of poly(**4a**) showed a sharp signal, as listed in Table 5, revealing that the stereoregular polymer has a crystalline structure. These observations suggest that the polymers of aromatic and alkylated acetylenes have highly stereoregular cis structures and the insoluble polymers have crystalline structures with the same cis geometry.

With regard to three-dimensional structure, although theoretical calculations have predicted that substituted polyacetylenes with a cis–transoidal backbone possess helical structures,[28,29] there have not been enough analytical data on the polymer structure. The ^{1}H NMR and CD spectra of poly(**5**) obtained from optically active monomer **5** suggest that the polymer has a helical cis–transoidal structure as reported for polyacetylenes bearing chiral side groups with a helical conformation of a predominant screw sense.[19,20] The slight decrease in the $[\alpha]_D^{20}$ value from +548 to +504 when the polymer stands in solution for 8 h is probably due to the instability of the helix in solution.

Conclusion

The zwitterionic Rh(I) complex, $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)\text{-}B^-(C_6H_5)_3]$ (**1a**), bearing an NBD ligand and a weakly coordinating tetraphenylborate anion, has been found to be an initiator for the polymerization of 1-alkynes as well as aromatic substituted acetylenes. The polymerization is rapid and quantitative where high molecular weights ($M_n > 10^5$ for aromatic acetylenes, and $M_n \sim 10^4$ for alkylated acetylenes) can be attained. The polymer synthesis can be controlled to produce the cis–transoidal conformation. The NMR spectra in solution as well as the X-ray diffraction patterns suggest the polymers obtained with **1a** have a rodlike helical structure. Complex **1a** is the first example of a halogen-free Rh(I) initiator which has a moderate activity toward the polymerization of simple 1-alkynes to produce high-molecular-weight poly(substituted acetylene)s.

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