Polymerisation of Phenylacetylene Catalysed by a Zwitterionic Rhodium(I) Complex under Hydrosilylation Conditions

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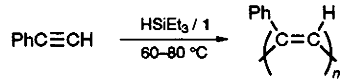
Polymerisation of phenylacetylene occurs in the presence of triethylsilane and $Rh^+(cod)BPh_4^-$ to give stereoregular *cis*-poly(phenylacetylene) with $\bar{M}_w$ of up to 35 000 ($\bar{M}_w/\bar{M}_n$ = 1.7–5.0).

Transition metal catalysed reaction of terminal alkynes with trialkylsilanes in general gives three isomeric alkenylsilanes (α, β-*cis* and β-*trans* adducts).[1] The regio- and stereo-selectivity of the hydrosilylation reaction is dependent on the nature of the metal catalyst (provided reaction conditions are otherwise identical). Many neutral and cationic rhodium(I) complexes were shown to be active hydrosilylation catalysts, some of them being highly selective.[1] Recently, interesting and sometimes unusual properties (especially in terms of regio- and stereo-selectivity) of the rhodium(I) zwitterionic complex, $Rh^+(cod)BPh_4^-$ **1**,[2] have been observed for various transformations.[3] We investigated the reaction of phenylacetylene (PA) with triethylsilane in the presence of complex **1**. However, unexpected and important results were obtained which are the subject of this communication.

When a mixture of PA (1 mmol), Et_3SiH (1 mmol) and catalyst **1** (0.01 mmol) was stirred at 60 °C for 16 h, almost no hydrosilylation occurred (less than 5% of hydrosilylation products were detected by GC and GC/MS analysis). Instead, a red solid material insoluble in the reaction mixture was formed, which was isolated by filtration, washed with ether and dried *in vacuo*. Its ^1H NMR spectrum† is in accord with that of stereoregular poly(phenylacetylene) (PPA) having a *cis*-transoidal structure,[4] GPC analysis of the sample has shown that it is a polymer with $\bar{M}_w$ 10000 ($\bar{M}_w/\bar{M}_n$ = 5.0) (Table 1, entry 1).

The PPA obtained is soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in benzene and insoluble in ether, MeOH, Pr^iOH and DMSO. TGA analysis revealed that the PPA is thermally stable up to 200 °C (5% weight loss occurred at 240 °C). Note that GC analysis of the reaction mixture after removal of PPA revealed that $HSiEt_3$ remained unchanged except for *ca.* 5% which was consumed during hydrosilylation.

These findings prompted us to study the reaction in more detail. The results are summarized in Table 1. First, we examined whether the presence of the hydrosilane is essential. The polymerisation does occur in the presence of catalytic amounts of the silane (1 mol %) and in the absence of $HSiEt_3$ as well. However, in these cases the polymer is obtained both in lower yield and lower $\bar{M}_w$ (entries 2 and 3). It should be noted that longer reaction times do not improve the yield of PPA, thus indicating the termination of the reaction after a certain degree of conversion. When the mixture of PA, $HSiEt_3$ and **1** was stirred at higher temperature (80 °C), *cis*-PPA with $\bar{M}_w$ 17500 ($\bar{M}_n$ 6100) was isolated in 85% yield (entry 4) whereas at 60 °C the yield was only 47% (entry 1). Again, the absence of the silane results in a lower $\bar{M}_w$ and a lower yield (entry 5). Further increase of the reaction temperature causes a drastic decrease in the yield of PPA. Also, *trans*-PPA‡ with low $\bar{M}_w$ is formed in this case (entry 6). More sterically hindered and less reactive (in terms of hydrosilylation) silanes were also evaluated for the polymerisation process. Tris(isopropyl)silane, under identical conditions, behaves similarly to Et_3SiH, and *cis*-PPA with $\bar{M}_w$ 13000 ($\bar{M}_n$ 5700) is formed. However, the yield of the polymer is somewhat lower (entry 7). In the presence of tris(trimethylsilyl)silane or tris(trimethylsiloxy)silane, the yield of PPA is surprisingly low (entries 8 and 9), indeed much lower than in the absence of any silane. Finally, the influence of an added organic solvent on the reaction has been studied. The polymerization was carried out in THF and in benzene and afforded *cis*-PPA in fair yield (entries 10 and 12). THF is definitely the solvent of choice, since it provides the polymer with $\bar{M}_w$ 34700 ($\bar{M}_w/\bar{M}_n$ = 1.85) in 82% yield. In the absence of $HSiEt_3$, the polymer with a lower $\bar{M}_w$ 21400 ($\bar{M}_w/\bar{M}_n$ = 1.8) and a lower yield (64%) is formed (entry 11).



PA *cis*-PPA

The polymerisation of PA has attracted a great deal of attention. The reaction is known to be catalysed mostly by group 5 and 6 transition metal catalysts[7] and Ziegler–Natta catalysts,[5] as well as by palladium[5,8] and nickel complexes.[9] Some rhodium(I) complexes such as $[Rh(cod)Cl]_2$ and $[Rh(cod)(L–L)]^+X^-$ (L–L = bidentate ligand; cod = cyclooctadiene) also polymerise PA to give highly stereoregular *cis*-PPA. Unfortunately, the molecular masses of the polymers obtained were not specified.[4] More recently, Rh^I complex

Table 1 $Rh^+(cod)BPh_4^-$-catalysed polymerisation of phenylacetylene in the presence of trialkylsilane[a]

				cis-Poly(phenylacetylene)[b]				
Entry	Silane	Reaction temp/°C	Reaction time/h	Yield (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Colour
1	$HSiEt_3$	60	16	47[c]	2000	10000	5.0	Red
2	$HSiEt_3$[d]	60	20	37[c]	1600	7000	4.9	Yellow
3	—	60	20	36	1600	6100	3.9	Yellow
4	$HSiEt_3$	80	24	85	6100	17500	2.9	Red
5	—	80	24	56	5100	10900	2.1	Red
6	$HSiEt_3$	100	24	23	1400	3000[e]	2.2	Yellow
7	$HSiPr^i_3$	80	24	43	5700	13000	2.3	Red
8	$HSi(SiMe_3)_3$	80	24	7	4700	10000	2.2	Red
9	$HSi(OSiMe_3)_3$	80	24	3	nd[f]	nd	nd	Red
10	$HSiEt_3$[g]	80	24	82	18700	34700	1.85	Red
11	—[g]	80	24	64	11900	21400	1.8	Red
12	$HSiEt_3$[h]	80	24	68	1500	2600	1.7	Red

[a] Reaction conditions: PA (1 mmol), Et_3SiH (1 mmol), complex **1** (0.01 mmol). [b] Molecular masses were determined by GPC using polystyrene standards. [c] The yield was not changed when longer reaction times (36 or 48 h) were used. [d] 0.01 mmol. [e] *trans*-PPA. [f] nd = not determined. [g] THF (0.2 ml) was used as the solvent. [h] Benzene (0.2 ml) was used as the solvent.

salts $[Rh(cod)\{Py(CH_2)_2P(Ph)(CH_2)_3ZR\}]^+PF_6^-$ (ZR = OEt, OPh, NHPh or cyclohexylamino; Py = 2-pyridyl) were shown to catalyse the polymerisation of PA in dioxane to *cis*-PPA having a high $\bar{M}_w$ (up to 238000).[10] These neutral and cationic Rh^I complexes are well-known and very active hydrosilylation catalysts[1] and no polymerisation occurs when using them in reaction between PA and $HSiR_3$. In conclusion, the zwitterionic complex **1**, unlike its neutral and cationic counterparts, does not induce the hydrosilylation (except trace amounts) of PA but does catalyse its polymerisation, giving rise to the stereoregular *cis*-PPA. While the presence of the hydrosilane is not essential, it does result in the formation of PPA in both higher yield and molecular weight.

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Footnotes

† *cis*-PPA: ^1H NMR ($CDCl_3$) δ 5.82 (s, 1H), 6.60 (m, 2H), 6.90 (m, 3H); a well-defined resonance at δ 5.82 is characteristic of a *cis*-transoidal PPA.[4,5]

‡ ^1H NMR spectrum of *trans*-PPA contains one broad resonance at δ *ca.* 7.[5,6,7b]

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