polymer communications

Acetylene polymerization on Rh(I) complexes

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Acetylene polymerizes under the action of chlorine-bridged Rh(I) complexes such as $[Rh(1,5\text{-}Cod)Cl]_2$ or $[Rh(NBD)Cl]_2$, in the presence of sodium ethoxide as co-catalyst. The microstructure of polyacetylene obtained at different temperatures has been studied by means of i.r. spectroscopy, and its thermal behaviour by t.g.a./d.t.a. The soluble oligomers obtained as secondary products of acetylene polymerization have been studied by u.v. spectroscopy. Moreover, the chlorinated derivative of polyacetylene has been prepared.

(Keywords: polyacetylene; synthesis; rhodium(I) complexes; soluble acetylene oligomers; chlorinated polyacetylene)

Introduction

Due to its peculiar electronic and physical properties polyacetylene is of interest to many synthetic polymer chemists. Up to now various different catalytic systems have been discovered for acetylene polymerization[1,2]. The most known and used polymerization catalysts are Ziegler–Natta systems based on trialkylaluminium and Ti(IV) compounds[3,4], but other systems like Luttinger's catalysts, obtained by reducing Ni(II) or Co(II) salts with $NaBH_4$, are equally effective but less popular[5,6].

Recently other acetylene polymerization catalysts have been reported including systems composed of WCl_6 or $MoCl_5$ and tetraphenyltin[7], and a titanocene complex has also been found to be effective[8]. In this communication, we report that chlorine-bridged Rh(I) complexes, such as $[Rh(1,5\text{-}Cod)Cl]_2$, where 1,5-Cod is *cis,cis*-cycloocta-1,5-diene, are effective polymerization catalysts of acetylene, particularly in the presence of a base like sodium ethoxide which acts as a co-catalyst. Up to now these complexes have been known only as polymerization catalysts for monosubstituted and activated acetylenic monomers[9,10], while to the best of our knowledge they have not been tested and recognized as effective in acetylene polymerization as reported here for the first time.

The polyacetylene obtained with Rh(I) complexes has been identified and studied by i.r. spectroscopy and t.g.a./d.t.a. and compared with published data. The chlorinated derivative of polyacetylene has been prepared to confirm that true polyacetylene was synthesized. Soluble oligomers of acetylene, obtained as secondary products during the polymerization, have been studied by u.v. spectroscopy.

Experimental

The i.r. spectrophotometer and thermogravimetric analyser with differential thermal analyser have been described elsewhere[11].

The u.v. spectrophotometer used was a Perkin Elmer Lambda 5.

Acetylene was purified by passing through a train of gas washing bottles containing aqueous solutions of $K_2Cr_2O_7/H_2SO_4$ and then it was dried in concentrated H_2SO_4 and in an anhydrous $CaCl_2/NaOH$ filled tower.

Rhodium complexes $[Rh\,1,5\text{-}Cod)Cl]_2$ or $[Rh(NBD)Cl]_2$ (where NBD is bicyclo⟨2,2,1⟩hepta-2,5-diene) were prepared from $RhCl_3 . nH_2O$ (Fluka) and 1,5-Cod (Fluka) or NBD (Fluka) according to a published route[12].

Polymerization with $[Rh(1,5\text{-}Cod)Cl]_2$. Polymerization was performed by dissolving a 0.04 M ethanolic solution of $[Rh(1,5\text{-}Cod)Cl]_2$ (0.3 ml) and a 0.1 M methanolic solution of sodium ethoxide (0.15 ml) in a flask containing absolute ethanol (8.0 ml). The flask was evacuated and cooled at −78°C into a dry ice–acetone bath. Then acetylene was admitted into the flask under stirring. Polymerization started only when the mixture was warmed to over −60°C. At this temperature the reaction mixture became red; it was a slurry of solid red polyacetylene flakes in ethanol. Then the reaction mixture was allowed to warm up at room temperature and a further amount of dark polyacetylene was formed as a slurry. The reaction mixture was quickly filtered.

Polyacetylene was washed with acetone and dried *in vacuo*. When polymerization was performed by admitting acetylene at −78°C without stirring the mixture, and by warming the reaction mixture, a thin film of polymer was obtained on the solvent surface. When the polymer was completely dried *in vacuo*, it was shiny and golden-greenish. The film produced was sufficiently thin to allow direct i.r. measurements.

Polymerization with $[Rh(NBD)Cl]_2$. Generally $[Rh(NBD)Cl]_2$ is so effective that it does not require the addition of sodium ethoxide to initiate the polymerization (Rh(I) complexed with 1,5-Cod always needs the addition of co-catalyst). However, the addition of sodium ethoxide easily activates polymerization and enhances the polymer yield.

As an example, a chloroform stock solution of $[Rh(NBD)Cl]_2$ (0.25 ml) was added to absolute ethanol (10.0 ml). The flask was evacuated and cooled at −78°C. Then acetylene was admitted into the flask. The reaction started during the warm-up of the mixture when

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Table 1 Details of the systems studied

Catalyst/Co-catalyst	Molar ratio	Solvent	Temperature (°C)	*Cis* (%)
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:1	benzene	25	30.8
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:1	ethanol	25	26.4
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:2	ethanol	−10	46.1
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:2	ethanol	$-60 < T < -20$	56.0
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:1	ethanol	$-60 < T < -20$	55.2
$[Rh(1,5\text{-}Cod)Cl]_2$/EtONa	1:1	methanol	$-60 < T < -20$	53.3
$[Rh(NBD)Cl]_2$/EtONa	1:2	methanol	$-60 < T < -20$	63.7

temperature was above −45°C, and a slurry of red polyacetylene was formed. By addition of an ethanolic solution of sodium ethoxide (0.15 ml) there was an immediate further formation of red polymer. The polymer was collected as described above.

A summary of runs at different temperatures in different solvents is reported in *Table 1*. Rh(I) complexes used in the present work are effective even for C_2H_2/Rh molar ratios of 500:1. The solvents recovered after polymer filtration are completely transparent but slightly coloured. The coloration is due to the soluble linear and cyclic oligomers of acetylene. These solutions were studied by means of u.v. spectroscopy.

Results and discussion

Rhodium has been known for a long time to be an effective polymerization catalyst for monosubstituted and activated acetylenes, mainly phenylacetylene and its substituted derivatives (e.g. *p*-chlorophenylacetylene). For example, the polymerization of phenylacetylene over $RhCl_3/LiBH_4$, which can be considered a Luttinger catalyst, has been reported[13]. Moreover, it has been pointed out that stable and well characterized Rh(I) complexes are also able to promote phenylacetylene polymerization[9].

We have been intrigued by the fact that low valent rhodium produced *in situ* (Luttinger system) or stabilized by the formation of a stable complex with dienic ligands is able to promote polymerization of phenylacetylene. Hence, we have tried for the first time to see if it is also able to promote acetylene polymerization.

We selected $[Rh(1,5\text{-}Cod)Cl]_2$ and $[Rh(NBD)Cl]_2$ as potential catalysts for acetylene polymerization because they are chlorine-bridged Rh(I) complexes and are very active in promoting phenylacetylene polymerization at room temperature to produce polyphenylacetylene films[11]. The chlorine bridge is easily broken by addition of a base such as sodium ethoxide or even aqueous ammonia to give a derivative which is the active species for acetylenic group polymerization. For $[Rh(NBD)Cl]_2$, the cleavage probably happens spontaneously when acetylene is present, in fact in this case there is no need to add a base as co-catalyst to initiate the acetylenic group polymerization.

Experimental results show that the Rh(I) complexes chosen are effective in acetylene polymerization even at low temperatures. The Rh(I) catalysts used in this study have the advantage over the Ziegler–Natta catalysts of being stable in air and their catalytic activity is not inhibited by the presence of oxygen and/or water. This behaviour is completely analogous to that shown by Luttinger catalysts[5].

The polyacetylene synthesized gives an i.r. spectrum analogous to that reported in the literature[14] and its *cis* and *trans* contents have been calculated from the absorbance ratio between the 1015 cm^{-1} (*trans* CH out-of-plane deformation) and 740 cm^{-1} (*cis* CH out-of-plane deformation) absorption bands (*Table 1*), using a factor of 1.30 for the *cis* band[4]. It has been found that by working at room temperature a *trans*-rich polymer is obtained, while by lowering the polymerization temperature it is possible to increase the *cis* content (*Table 1*). This behaviour is comparable with that found by using other catalysts for acetylene polymerization.

During acetylene polymerization there is a simultaneous formation of soluble oligomers like short chain polyenes and cyclic oligomers such as benzene. The soluble oligomers formed when ethanol was used as the polymerization solvent have been analysed by u.v. spectroscopy. An absorption maximum was found at 230 nm and two shoulders were found at 280 and 340 nm, respectively, followed by very weak shoulders at 540, 590 and 690 nm. In previous work[3] it has been reported that by using a Ziegler–Natta catalyst for acetylene polymerization soluble oligomers are formed as secondary products which give absorption maxima at 240 and 260 nm and a shoulder at 390 nm. Our experimental results are in agreement with this and show that these oligomers should have from three to eight (and sometimes even more) conjugated double bonds.

A t.g.a. run on polyacetylene flakes obtained with Rh(I) catalysts (heating rate 10°C min^{-1} under nitrogen) shows thermal behaviour in agreement with that reported in the literature[15]. A maximum decomposition rate has been detected at 450°C by d.t.a., while a residue of 25% of the original weight of polymer used remained up to 700°C probably due to charring of the sample with the formation of polycyclic aromatic materials.

Polyacetylene freshly obtained over Rh(I) complexes has been chlorinated as a slurry in dichloromethane (by bubbling gaseous chlorine) at 0°C. The chlorinated derivative is soluble in dichloromethane and can be recovered by precipitation in methanol. It is a white solid and could be considered analogous to a poly(1,2-dichloroethylene), if we assume that the original polyacetylene is completely linear and that chlorine undergoes exclusively addition reactions with each double bond without any significant substitution reactions.

Conclusions

It has been shown that Rh(I) complexes are effective as acetylene polymerization catalysts. These complexes are very stable in air and also remain effective in the presence of moisture. Consequently, Rh(I) catalysts have the advantage over the well-known and popular Ziegler–Natta systems of being very easy and safe to handle.

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