

Polymerization of Propadiene. III. Catalyst Systems Based on Various Rhodium(I) Complexes

J. P. SCHOLTEN and H. J. VAN DER PLOEG,* *Polymer Chemistry Laboratory, Twente University of Technology, Enschede, The Netherlands*

Synopsis

The polymerization of propadiene to 1,2-polyallene by various Rh(I) based catalysts is described and discussed. Also the interrelations between these Rh(I) complexes are discussed and an overall reaction scheme is given. A mechanism is put forward in which the formation of a common intermediate from propadiene and different Rh(I) complexes is the rate determining step. It is found that the activity decreases in the order: *cis*-Rh(CO)₂P(C₆H₅)₂Cl > [Rh(CO)₂Cl]₂ > Rh(CO)₃Cl. The complexes Rh[P(C₆H₅)₃]₂(CO)Cl and Rh[P(C₆H₅)₃]₂Cl proved to be inactive in the polymerization of propadiene.

INTRODUCTION

In two previous publications^{1,2} we have dealt with the polymerization of propadiene to structurally homogeneous 1,2-polyallene with catalysts based on alkylated 3*d*-metals and propadiene itself as the stabilizing ligand.

On reviewing the various polymerization methods of propadiene in part I of this series it was noted that Otsuka and his co-workers³ synthesized the 1,2-polymer using a square-planar rhodium(I) complex which was prepared from tetracarbonyl- μ, μ' -dichlorodirhodium(I) and triphenylphosphine, without, however, indicating which species was active. We started our program on 1,2-polyallene with the aim of studying postpolymer reactions. From this point of view the Otsuka route to the polymer seemed attractive, notwithstanding its low yields, because no extreme precautions against air and moisture are necessary, in contrast to the methods involving use of Ziegler and Wilke type catalysts.

In this part of the series we will report on a more detailed investigation of the polymerization of propadiene by some Rh-based catalysts.

We have reinvestigated Otsuka's work and were able to improve the yield appreciably and elucidate the structure of the active catalytic species. In addition, we investigated the activity of some known and hitherto unknown rhodium(I) complexes in the polymerization of propadiene. In most of the polymerization reactions a rather complex mixture of oligomers arose in low yield (1-3%). We could isolate the known tetramer^{4,5} and

* To whom inquiries should be addressed.

pentamer⁶; besides, we were able to isolate a hitherto unknown hexamer and to determine its structure.⁷

EXPERIMENTAL

Starting Materials

Commercial-grade products were used, viz, RhCl_3 hydrate, rhodium(III) chloride hydrate ($\sim 40\%$ Rh) (Fluka); $\text{P}(\text{C}_6\text{H}_5)_3$, triphenylphosphine (BDH); C_3H_4 , propadiene (96%) (Baker); $\text{C}_2\text{H}_5\text{OH}$, ethanol (99.5%) (Shell). All other solvents were used without further purification.

Nomenclature

In order to facilitate the discussion we will refer to the complexes by the symbols shown in Table I.

TABLE I
Symbols Used for the Various Rhodium(I) Complexes

Symbol		
α	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	Tetracarbonyl- μ, μ' -dichlorodirrhodium(I)
β	$\text{Rh}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}\text{Cl}$	Triphenylphosphine <i>cis</i> -dicarbonylchlororhodium(I)
γ	$\text{Rh}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\text{CO})\text{Cl}$	Carbonyl- <i>trans</i> -bis(triphenylphosphine)chlororhodium(I)
δ	$\text{Rh}(\text{CO})_3\text{Cl}$	Tricarbonylchlororhodium(I)
ϵ	$\text{Rh}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\text{Cl}$	Tris(triphenylphosphine)chlororhodium(I)

Synthesis of the Coordination Complexes

Tetracarbonyl- μ, μ' -dichlorodirrhodium(I). This complex was prepared according to the method of Powell and Shaw⁸ from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and carbon monoxide in refluxing ethanol.

Carbonylbis(triphenylphosphine)chlororhodium(I). This compound was prepared according to the procedure of Vallarino,⁹ slightly modified. Ethanol was used instead of benzene as the solvent, because of the instant precipitation of γ in the former solvent.

The compound γ was also prepared according to the method of Evans, Osborn, and Wilkinson¹⁰, directly from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{P}(\text{C}_6\text{H}_5)_3$, and formaldehyde in refluxing ethanol.

Triphenylphosphine-*cis*(dicarbonyl)chlororhodium(I). $\text{Rh}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$ was prepared by the method of Belucco and co-workers.¹¹ Poilblanc and Gallay,¹² however, proved that the Belucco product was a mixture of mono- and binuclear rhodium complexes, and we confirmed this. Therefore, we shall call the mixture of compounds obtained according to the foregoing procedure a Poilblanc mixture.

The complex of the formula $\text{Rh}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3] \text{Cl}$ only exists in a freshly prepared benzene solution for a short period of time and cannot be isolated without rearrangement. Therefore, we used it in solution.

Tricarbonylchlororhodium(I). A 100 ml portion of an ethanolic solution of α was poured into a 250-ml autoclave, which was then closed and flushed with nitrogen. Then carbon monoxide was forced into the autoclave until a pressure of 50 atm was reached. The reaction was carried out at room temperature with continuous stirring for about 6 hr. The excess of carbon monoxide was vented and the autoclave opened. The resulting dark red solution could not be worked up in the usual manner (Belucco), because of the instability of the complex; therefore it was used as obtained.

A suspension of the above-mentioned Poilblanc mixture was treated in the same way with carbon monoxide. The same dark red solution was obtained, as proved by infrared spectroscopy, but also a yellow precipitate which was identified as γ by comparison with an authentic sample.

Trisphenylphosphine Chlororhodium(I). This complex was prepared according to the procedure of Osborne and co-workers¹³ directly from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ by refluxing it with $\text{P}(\text{C}_6\text{H}_5)_3$ in ethanol.

Decarbonylation of Ethanol by $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$ in Alkaline Solution. According to Chatt and Shaw,¹⁴ for Rh(I) complexes γ was refluxed for 16 hr in a 1*N* potassium hydroxide solution in ethanol. The major part of the starting material was recovered, but the green-yellowish filtrate proved to be very active in the polymerization of propadiene. The yields were very small, however, because of the scale of our experiments, and no further identification could be carried out.

Polymerization Experiments

Polymerization was mainly carried out by the following two routes: (1) polymerization at atmospheric pressure, either with or without recirculation of gas; (2) polymerization at the saturated vapor pressure of propadiene.

In all cases a general procedure was used to prepare the catalyst solution. In the cases of α , the Poilblanc mixture, γ , and ϵ , the required amounts of the complex were carefully weighed and dissolved (α) or suspended (γ, ϵ , and the Poilblanc mixture) in ethanol. In the cases of β and δ the required amounts of the complex in solution were pipetted from their solutions of known concentration, assuming a 100% conversion from the starting materials to respectively β and δ .

The reaction mixture was poured into a three-necked flask and the polymerization was carried out according to the method used by Otsuka⁸ for the polymerization of propadiene by rhodium(I) complexes. The low polymer yields and large losses of propadiene make this procedure unattractive.

In order to diminish the losses of propadiene we used a gas-recirculation system as described by Pass and Schramm.¹⁵ The unreacted propadiene is recirculated by a glass plunger pump having a mercury lock on both the

inlet and the outlet side, preventing the back flow of gas. The capacity of the pump can easily be adapted to meet the demand of the experiment.

Before the reaction starts, the reaction vessel system is filled with propadiene, the catalyst is added, and the reaction can proceed. A manometer is attached to the system in order to control constant pressure conditions (1 atm). This method was used to determine the relative reactivity of the various complexes by filtering off the polymer and using the filtrate again in a subsequent polymerization with a known amount of allene.

In order to obtain a faster reaction, a better contact between the poorly ethanol-soluble propadiene and the catalyst solution or suspension in ethanol was desirable. This could be achieved by carrying out the reaction in a stirred double-walled glass autoclave (maximum $T = 200^{\circ}\text{C}$, maximum $P = 12$ atm). The autoclave was filled to half of its volume (500 ml) and closed. It was then flushed with nitrogen, after which liquid propadiene was added under its own pressure. The reactions were carried out at 40°C (unless specified otherwise) and an initial pressure of 3–4 atm (± 15 g of propadiene).

In all cases the polyallene was worked up by an identical procedure. It was filtered off from the reaction medium and washed with acetone to remove catalyst residues, filtered again, and dried at room temperature and a pressure of 10 mm Hg. The yield was 12.0 g (80%).

RESULTS AND DISCUSSION

In order to facilitate the discussion, the preparation and reactions of the complexes to be discussed are presented in Figure 1.

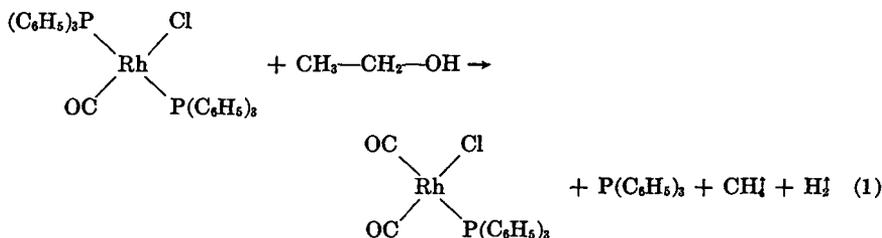
As mentioned in the introduction, our work started with a reinvestigation of Otsuka's work.³ According to this method, the preparation of his catalyst from α and $\text{P}(\text{C}_6\text{H}_5)_3$ in ethanol gives a yellow precipitate suggesting at least that this compound is essential in the observed polymerization. This complex appeared to be γ , according to the infrared spectra, melting point and elemental analysis and has been discussed in various other publications^{10,13}. However, when we isolated the precipitated γ and used it in a separate polymerization experiment it showed hardly any reactivity.

A sample of γ prepared from ϵ and formaldehyde^{10,13} also proved to be an inactive polymerization catalyst. Using Otsuka's method we were not able to confirm his high polymer yields. When the reaction was carried out under pressure the yields were much higher. Using the appropriate temperature and time we were able to obtain yields up to 80–90% polymer. However, the same activity could be obtained by using the filtrate of the reaction mixture for the polymerization.

Residual Polymerization Activity of γ

On refluxing γ for 24 hr in ethanol the polymerization activity was slightly increased; further improvement could be obtained by refluxing for 1–2 hr in a 1*N* potassium hydroxide solution in ethanol.

This can be explained by assuming that decarbonylation of ethanol by γ has taken place according to reaction (1):



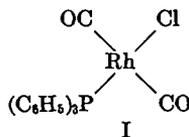
This type of reaction is normal for Rh(III) complexes¹⁴ and is also observed with Rh(I) complexes in allyl alcohol.¹⁵

The proof that solvent decarbonylation has taken place here was the presence of methane in the escaping vapor as shown by gas chromatography. The resulting product β is responsible for the improved activity.

The very low activity of γ itself in ethanol can be explained by assuming that the alkalinity of the glass is sufficient to cause a small production of very active β . In effect, in a reaction vessel prewashed with acid no activity at all could be observed.

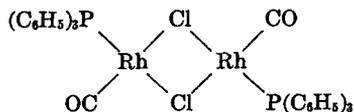
Polymerization Activity of β

In 1969 Belucco and co-workers¹¹ synthesized this complex suggesting it having the transstructure I.



They support their formulation by one CO absorption band in the infrared spectrum at 1980 cm^{-1} and a Rh-Cl band in the far infrared at 295 cm^{-1} . The latter absorption is said to be in agreement with a chloride *trans* to a tertiary arylphosphine in a rhodium(I) complex, based on an article by Bennett.¹⁶

On the other hand, Poilblanc¹² and Steele¹⁸ suggest a dimeric structure II for the compound which we will refer to as β' .



This structure is also in accord with the observed infrared spectra for chlorine-bridged rhodium(I) complexes¹⁶ and elemental analysis. Also this structure is in much better agreement with the molecular weights (865) found by these two workers.

In all our experiments however, we always found two infrared absorptions in the ν_{CO} region: 1990 cm^{-1} (s) and 2080 cm^{-1} (w).

The molecular weights as determined by vapor-pressure osmometry as well as by an ultracentrifuge method resulted in values between that of a monomeric and that of a dimeric structure (700-750). This suggests a mixture of these structure which could be confirmed by thin-layer chromatography (three spots).

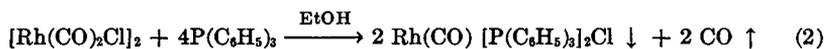
Our view was corroborated by a second publication of Poilblanc and co-workers¹⁹ in which they stated that, depending on the Rh/P(C₆H₅)₃ ratio a mixture of several monomeric and dimeric structures is found (see reaction scheme), when reacting α with P(C₆H₅)₃.

A freshly prepared benzene solution of α and 2 P(C₆H₅)₃, however, showed two equally strong infrared absorptions of ν_{CO} at 2010 cm⁻¹ and 2090 cm⁻¹. These absorptions are identical with those found by Steele and Stephenson when they bubbled carbon monoxide through a benzene solution of β' and can be attributed to the original proposed *cis*-dicarbonyl structure. In benzene solution, relatively rapid disproportionation takes place into the mixture and can be followed in the ultracentrifuge while measuring the molecular weights. Therefore our polymerization experiments with propadiene were carried out with a freshly prepared solution of β . From these experiments it can be concluded that β is a very active polymerization catalyst, about six times as active as the Poilblanc mixture.

Polymerization with α

The foregoing findings however, give no satisfactory explanation for the discrepancy between Otsuka's work and ours. Therefore a closer look into Otsuka's work is necessary.

From his paper it appears that an α /P(C₆H₅)₃ ratio of 1:2 was used. Since we found that in Otsuka's experiment γ precipitated quantitatively, the only conclusion can be that in the solution half of α is still present unreacted. The reaction (2) takes place:



A separate experiment supports this hypothesis, because α appears to be very active for the polymerization of propadiene without adding ligands other than the solvent and propadiene itself. The activity is about one half to one third of that found for β .

The conclusion thus seems justified, that the activity Otsuka observed in his polymerization experiment is due to α and that in his procedure the addition of P(C₆H₅)₃ is superfluous or even disadvantageous.

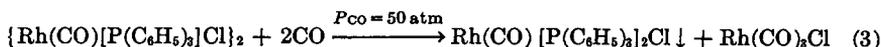
Polymerization with δ

The evolution of carbon monoxide in reaction (2) is clearly observed.

In an attempt to stop this reaction at the stage of β the reaction was carried out under 50 atm carbon monoxide pressure. We obtained a dark-red solution in ethanol, but after removing the surplus of carbon monoxide a yellow precipitate of γ was obtained. This reaction did not lead to any

result, when carried out at normal carbon monoxide pressure. The dark red color of the reaction mixture indicated that the complex in this solution differs from β , which gives a yellow solution.

The same dark-red solution can be obtained by treating a solution of α or a suspension of β' in ethanol in the same way as was shown by infrared spectroscopy. In the case of β' , a yellow precipitate of γ was also obtained. This indicates a disproportionation of β' initiated by carbon monoxide.



The tricarbonyl complex is too instable to be isolated but we have strong reasons to believe that this complex is actually formed. Its presence in solution is corroborated by two strong ν_{CO} absorptions at 2000 cm^{-1} and 2085 cm^{-1} and a medium one at 1880 cm^{-1} . Secondly when nitrogen is passed through any of the solutions of δ saturated with carbon monoxide, α is formed (see Fig. 1). Finally γ could be obtained from δ quantitatively by adding the appropriate amount of $\text{P}(\text{C}_6\text{H}_5)_3$.

This reaction differs from the reaction observed with β' by Steele and Stephenson. They obtained the monomeric β on bubbling carbon monoxide through a benzene solution of β' .

At higher pressures the initiation of the disproportionation reaction is obviously favored. At higher temperatures ($50\text{--}70^\circ\text{C}$), we obtained the already known rhodiumcarbonyl complex $\text{Rh}_4(\text{CO})_{12}$,²¹ although our conditions were much milder. The solutions of δ showed appreciable polymerization activity, although it was less than the activity of α .

Polymerization with ϵ

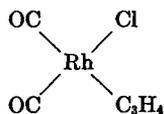
We also investigated the activity of ϵ in ethanol in the polymerization of propadiene. Under the usual conditions no activity could be observed. Otsuka and co-workers,²⁰ however, report an unspecified polymerization activity of the bromo and iodo analogs at higher temperatures in ethanol, and Lindsay and Jones⁵ used ϵ for the tetramerization of propadiene in dichloromethane.

In Table II a comparative summary is given of the various complexes and their activity towards the polymerization of propadiene.

TABLE II
Comparative Polymerization Activity of the Various Rh(I) Complexes

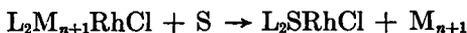
Complex	Yield, g/13.3 mg Rh	propadiene, mole/g-atom rhodium
α	4.4	880
β	10.7	2140
β'	1.6	310
γ	0.02	3
δ	2.7	520
ϵ	0	0

When we look at the three complexes active in the polymerization of propadiene, a possible explanation of the sequence of reactivity $\beta > \alpha > \delta$ could be that a common intermediate is formed. The structure of this common intermediate could be III, and its formation might be the rate-determining step.



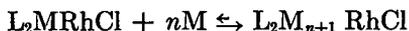
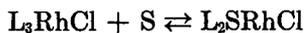
A possible, generalized mechanism can then be formulated.

For a binuclear complex:



where S denotes solvent.

For a mononuclear complex:



In a future publication, in which we will deal with the kinetics and mechanism of the polymerization reactions, support for the "common intermediate hypothesis" will be brought forward, and a solvent effect will be discussed.

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