The monometallic initiation of the metathesis polymerization of cyclopentene

A. J. Amass and M. Lotfipour

Department of Chemistry, University of Aston in Birmingham, Gosta Green, Birmingham, B4 7ET, UK

A detailed study of the monometallic initiation of the polymerization of cyclopentene by WCl_6 has shown that the kinetics of polymerization are extremely complex. The complexity is associated with the formation of a heterogeneous system. Two species have been postulated to act as metathesis catalysts: (i) a toluene soluble species with low activity and (ii) experimental confirmation of a highly active toluene insoluble species that requires the presence of oxygen for its activity.

Keywords

INTRODUCTION

Previous publications[1,2] have described the use of WCl_6 alone as a metathesis catalyst for the polymerization of cyclic alkenes. The initial work suggested that polymerization could be initiated by WCl_6 but subsequent investigations have shown that a substantially more efficient catalyst could be obtained if the obvious reaction products from the reaction between the alkene and catalyst were reacted with oxygen.

The present publication attempts to clarify some of the reactions involved in this system and to establish the location of the active site in polymerizations of this type.

EXPERIMENTAL

Purification of cyclopentene and toluene

The purification procedures, adequately described in ref. 3, were adopted.

Purification of tungsten hexachloride

WCl_6 normally contains hydrolysis products ($WOCl_4$ and WO_2Cl_2) which may be removed by sublimation. A high vacuum sublimation technique was employed where the apparatus was immersed in an oil bath at 120°C, while attached to the high vacuum line. The finger of the apparatus was maintained at a temperature between 70° and 80°C, which prevented the impurities from subliming onto it, so that $WOCl_4$ and WO_2Cl_2 sublimed onto the cooler parts of the apparatus. Pure WCl_6 sublimed onto the hot finger and was transferred to ampoules which were sealed under vacuum.

Solutions of WCl_6 were prepared in toluene and transferred to break-seal ampoules where they were stored until required.

Measurement of rate of polymerization

Polymerization of cyclopentene initiated by WCl_6 alone. The rate of polymerization of cyclopentene, initiated by WCl_6 alone was determined dilatometrically using the apparatus shown in *Figure 1*. The required volumes of cyclopentene and toluene were vacuum-distilled into the

bulb C of the apparatus and while the solution was still frozen, the system was sealed off at point D. After warming the system to room-temperature, the ampoule containing the catalyst was broken and WCl_6 was mixed with the monomer solution. The dilatometer was filled as rapidly as possible sealed from the rest of the apparatus and the dilatometer was suspended in a constant temperature bath. The rate of polymerization was then determined from the contraction/time plot.
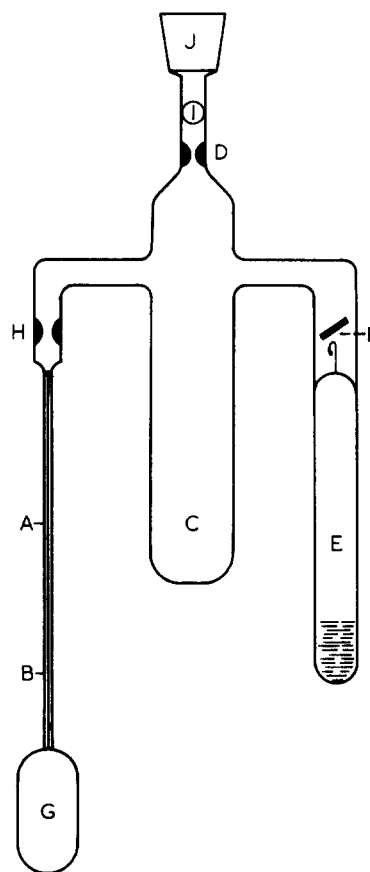

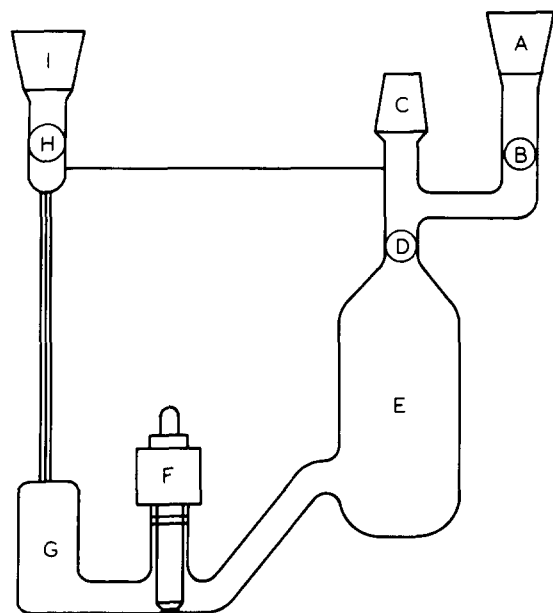*Figure 1* Dilatometer used for WCl_6/cyclopentene studies

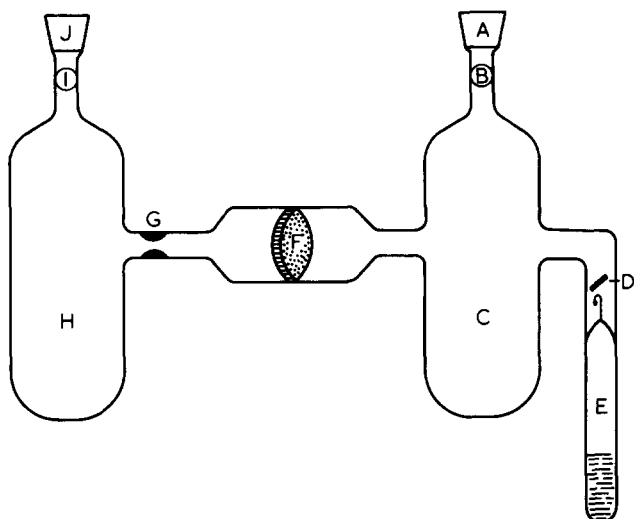Figure 2 Dilatometer used for WCl₆/cyclopentene/oxygen studies

Figure 3 Apparatus for the separation of precipitate

Polymerization of cyclopentene initiated by WCl₆/O₂.
The apparatus shown in *Figure 2* was used for the determination of the rate of polymerization of cyclopentene initiated by WCl₆/O₂ catalyst system. In a typical experiment the required volumes of cyclopentene, toluene and WCl₆ solution were mixed in a pre-reaction vessel and then transferred under vacuum into the bulb E of the apparatus. The solution was then kept for a period of 24 h after which time a known amount of dry oxygen was introduced into the system. The bulb G was filled immediately with the solution and the rate of polymerization was determined dilatometrically in the usual manner under isothermal conditions.

Separation of the precipitate

The reaction of tungsten hexachloride with cyclopentene in toluene is always accompanied by the appearance of an oily precipitate. In order to separate this precipitate from the solution the apparatus shown in *Figure 3* was used. In this experiment the required amounts of cyclopentene and toluene were vacuum-distilled into the bulb C

of the apparatus. The tungsten hexachloride solution in the break-seal was then mixed with the monomer solution and allowed to react for a period of 24 h. After this period of time the clear solution was transferred into the bulb H through the filter F and the oily precipitate, adsorbed on the walls of the bulb C, was repeatedly washed by forward vacuum-distillation of cyclopentene and toluene from the clear solution. After the final washing the apparatus was sealed off at point G.

RESULTS AND DISCUSSION

Kinetics of polymerization of cyclopentene initiated by WCl₆ alone

The principal original objective of this work was to study the extremely active metathesis polymerization initiated by the WCl₆/alkene/O₂ catalyst[2], but it was considered prudent first to complete a study of the less active WCl₆/alkene catalyst in order to distinguish between possible contributions from each system.

In order to study the effect of tungsten hexachloride concentration on the rate of polymerization of cyclopentene, a series of experiments was carried out at constant monomer concentration (9.2 mol. dm⁻³) using the dilatometer shown in *Figure 1*. The conversion-time curves determined in this series of experiments are summarized in *Figure 4*. The ratios shown on this Figure refer to molar ratios of WCl₆ : cyclopentene. A feature of all curves is the non-linearity of the conversion-time dependence obtained. The second important feature of this polymerization is shown in *Figure 5*, which is a plot of the dependence of the initial rate of polymerization on the concentration of tungsten hexachloride.

It can be seen that the rate of polymerization is not constant, even though the percentage conversion of monomer to polymer is less than 3%. It would appear that in this system a series of reactions has to be postulated, most likely between WCl₆ and cyclopentene, and that the product of one of these reactions is a weakly-active catalyst for metathesis. This active species is not the final
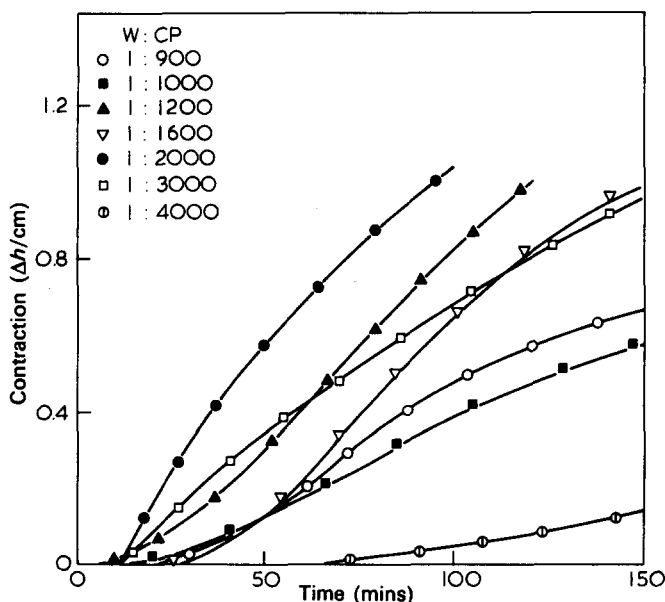

Figure 4 Polymerization of cyclopentene: conversion–time curves for various concentrations of WCl₆ in the absence of oxygen
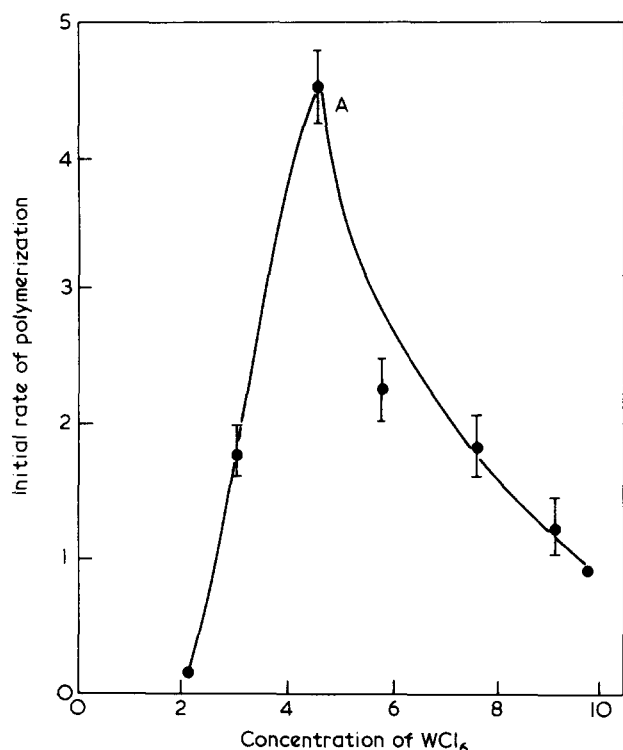
Figure 5 Dependence of the initial rate of polymerization$\times 10^5$ (mol dm^{-3} s^{-1}) of cyclopentene on the concentration of WCl$_6 \times 10^3$ (mol dm^{-3})

product of the reaction sequence but an intermediate, since it is later consumed, leading to the eventual decay of the rate of polymerization.

The dependence of the initial rate of polymerization on the concentration of initiator is shown in *Figure 5*. Within experimental error, indicated on the Figure, the results show that there is a maximum rate of polymerization at a molar ratio of W: cyclopentene of 1 : 2000 when the concentraion of cyclopentene is 9.2 mol dm^{-3}. This behaviour, which was apparent at other concentrations of cyclopentene, could be explained if there are two competitive effects in the system:

(1) the production of an active species and;
(2) the destruction of this species, this reaction involving at least one cyclopentene molecule.

At low concentrations of catalyst the destructive effect occurs at a slow rate and hence the rate of polymerization increases as the concentration of WCl$_6$ increases, whereas at higher concentrations the rate of destruction of the active centre, once it is formed, becomes predominant and this has a dramatic effect upon the rate of polymerization. Even so the shape of the dependence is not explained in this simple manner but it hoped that detailed studies to be presented in another paper will help to explain the relation between the rate of polymerization and concentration of WCl$_6$ in terms of these two types of reaction.

Whenever WCl$_6$ is added to cyclopentene the blue solution turns immediately brown and subsequently produces a brown oily precipitate. This feature is most marked in those polymerizations in which the higher concentrations of tungsten hexachloride are used, whereas at lower concentrations very little precipitate occurs.

Tungsten hexachloride/cyclopentene/oxygen system

A report[2] that the addition of oxygen to the products of the reaction between WCl$_6$ and cyclopentene leads to an
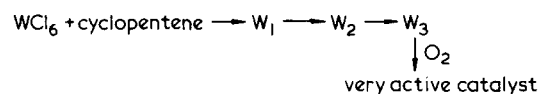
extremely active polymerization catalyst suggested that the activity of this system is associated with the precipitate produced in these reactions. Following the procedure described in the experimental section, attempts were made to undertake a more quantitative study of the polymerization than that carried out by Amass and McGourty[2], who used the percentage conversion after 1 h as an indication of the activity of the catalyst. However, during several experiments the meniscus height in the dilatometer did not change, even though high conversions of monomer had occured consistently in similar experiments carried out as preliminaries to this study; indeed the results of these preliminary studies were similar to those observed by Amass and McGourty[2]. It would appear that the lack of polymerization recorded dilatometrically was due to the fact that the system was devoid of active centres which had remained adhered to the walls of the pre-reaction vessel.

In order to show that the active centre was adhered to the walls of the reaction vessel and produced by reaction of oxygen with the oily precipitate a simple reaction was carried out in the apparatus shown in *Figure 3* and the precipitate was separated from the solution, as described previously. When fresh cyclopentene was vacuum-distilled onto the oily precipitate in the bulb C and dry oxygen was admitted, there was an immediate reaction in section C and the solution became extremely viscous very quickly, whereas the original supernatant liquor, contained in bulb H, remained mobile on addition of oxygen and showed no signs of increased viscosity even after long reaction times (24–36 h). It is therefore apparent that the oily precipitate that is produced on prolonged reaction of WCl$_6$ with cyclopentene is the source of active centres for metathesis polymerization, when oxygen is added to the system. This has presented us with some difficult experimental problems, which we have not yet solved, because using techniques such as dilatometry it is not possible to transfer the active centres from the pre-reaction vessel to the dilatometer bulb. It was hoped that a calorimetric technique would provide a basis for the successful study of this system but again problems were experienced in the experiments attempted.

CONCLUSIONS

Future postulations of the generation of the active centre in the polymerization of cyclic alkenes and the metathesis of linear alkenes must consider the reactions that take place between WCl$_6$, and possibly other transition metal compounds, with the olefinic carbon-carbon double bond. Undoubtedly the studies carried out on the use of WCl$_6$ without oxygen lead us to the conclusion that such reactions exist. The reaction is by no means simple kinetically, although this may have been exacerbated by the insolubility of one of the products in the solvent/monomer system used. The reaction is multi-staged and one of the intermediate products of the sequence is able to act as a weakly-active metathesis catalyst.

It is possible to postulate that there is a general reaction scheme as follows:

WCl$_6$ + cyclopentene ⟶ W$_1$ ⟶ W$_2$ ⟶ W$_3$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ ↓ O$_2$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ very active catalyst

One can now speculate on the nature of some of these reactions and the possible structures of the products.

W_1 would be the structure that is associated with the product formed immediately upon the addition of WCl_6 to the alkene. This species could be a simple complex of the alkene and WCl_6, but in this case one would expect such a reaction to be an equilibrium reaction:

$$WCl_6 + \bigcirc \; = \; \bigcirc\!\!-WCl_6$$
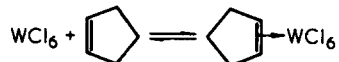
and the position of equilibrium to be temperature dependent. It is worth noting that if this reaction is endothermic, the equilibrium could be forced to the left hand side of the equation by reducing the temperature, particularly down to $-190°C$. Attempts to separate WCl_6 from the reaction mixture by this process have been unsuccessful, so that it can only be concluded that W_1 is not simply a complex of WCl_6 and cyclopentene. It is now plausible to suggest that:

$$\bigcirc + WCl_6 \longrightarrow Cl_xW\underset{H}{-}\!\!\langle\bigcirc \qquad (I)$$
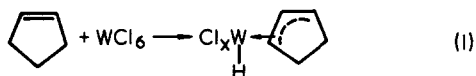
and possibly that W_1 has a structure close to (I)

At this stage it is meaningless to speculate on the structures of W_2, which is considered to be the active species in the absence of oxygen, and W_3, the precipitate that produces an extremely active metathesis catalyst upon reaction with oxygen. The kinetics of the conversions of W_1 to W_2 and W_2 to W_3 are complex and will be the subject of other submissions.

Finally it is confirmed that the final product considered in this scheme; i.e. the precipitate, will react with oxygen to produce an extremely active catalyst for the metathesis of alkenes. A recent paper by Goddard[4] has suggested that molybdenum based catalysts may be monometallic but tungsten metathesis catalysts should require a cocatalyst. It may be that the ring-strain associated with cyclopentene may be sufficient to overcome this requirement. Certainly for cyclic alkenes, it would appear that tungsten can act as a monometallic catalyst, the activity of which is significantly increased by the presence of an oxygen ligand.

REFERENCES

1 Amass, A. J., McGourty, T. A. and Tuck, C. N. *Eur. Polym. J.* 1976, **12**, 93
2 Amass, A. J. and McGourty, T. A. *Eur. Polym. J.* 1980, **16**, 235
3 Amass, A. J. and Tuck, C. N. *Eur. Polym. J.* 1978, **14**, 817
4 Rappe, A. K. and Goddard, W. A. *J. Am. Chem. Soc.* 1982, **104**, 448