

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS  
AS GCE  
F332/01**

**CHEMISTRY B (SALTERS)  
Chemistry of Natural Resources  
ADVANCE NOTICE**

**For issue on or after: 13 MARCH 2015**

**DURATION: 1 hour 45 minutes  
plus your additional time allowance  
MODIFIED ENLARGED 24pt**

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## **NOTES FOR GUIDANCE (CANDIDATES)**

- 1 This leaflet contains an article which is needed in preparation for a question in the externally assessed examination F332.**
- 2 You will need to read the article carefully and also have covered the learning outcomes for Unit F332 ('Chemistry of Natural Resources'). The examination paper will contain questions on the article. You will be expected to apply your knowledge and understanding of the work covered in Unit F332 to answer these questions. There are 20 marks available on the paper for these questions.**
- 3 You can seek advice from your teacher about the content of the article and you can discuss it with others in your class. You may also investigate the topic yourself using any resources available to you.**
- 4 For the examination on 2 JUNE 2015 you will be given a fresh copy of this article, together with a Question Paper. You will NOT be able to bring your copy of the article, or other materials, into the examination.**
- 5 You will not have time to read this article for the first time in the examination if you are to complete the examination paper within the specified time. However, you should refer to the article when answering the questions.**

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## **INSTRUCTION TO EXAMS OFFICER/INVIGILATOR**

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# Catalysis

**Article: Taken from Chemistry Review magazine, published by Philip Allan, February 2014, pages 21–25.**

**In this article, we look at examples of homogeneous catalysis and the variety of catalysts employed in polymerisation reactions to produce polymers with specific structures and physical properties.**

**‘Heterogeneous’ catalysts are widely used in industry: they are in a different phase to the reactants and products so are easily removed from the products. Disadvantages of using certain heterogeneous catalysts are that they are not always specific in terms of the reactions they promote and can produce unwanted by-products. ‘Homogeneous’ catalysts are in the same phase as the reactants. This article will discuss some of their roles and their inherent advantages and disadvantages.**

## Homogeneous catalysis

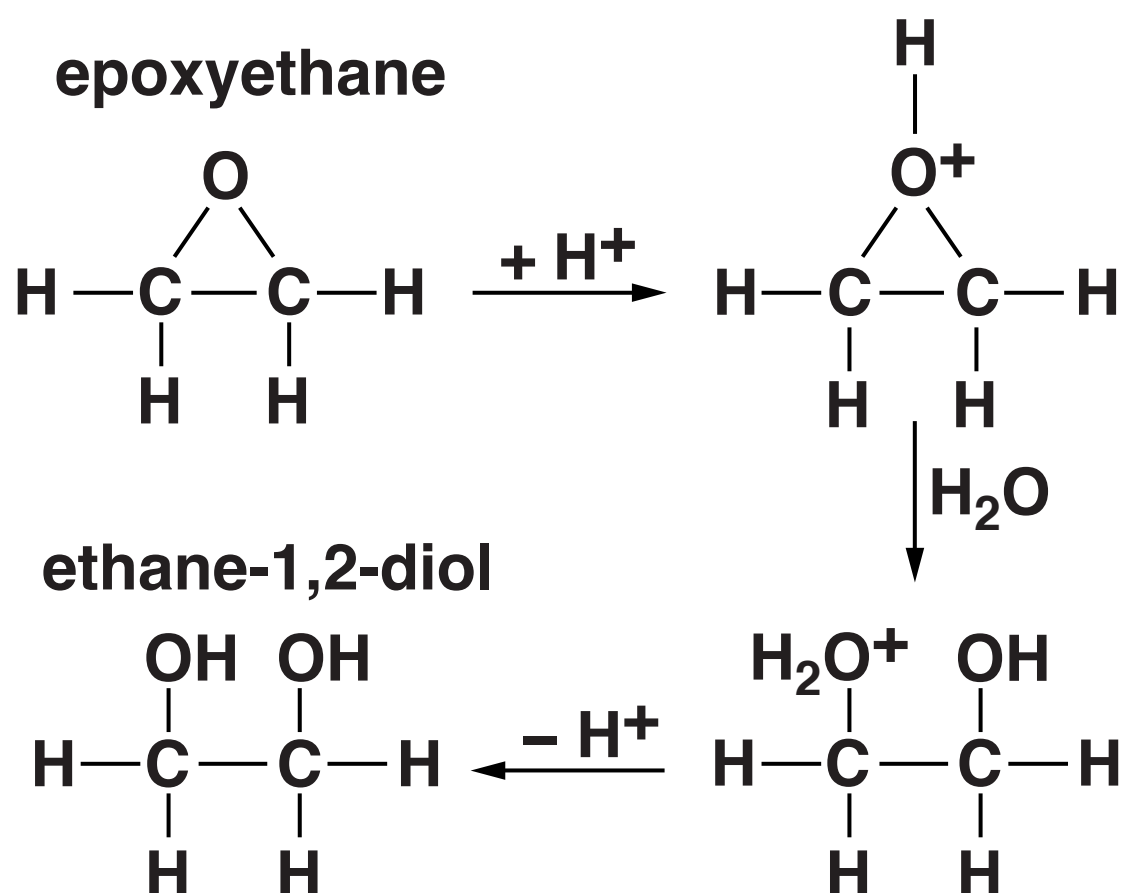
**Homogeneous catalysts are used less frequently in industry than heterogeneous catalysts, as on completion of the reaction they have to be separated from the products, a process that can be expensive. However, there are several important industrial processes that are catalysed homogeneously, often using an acid or base (TABLE 1 opposite).**

TABLE 1 Examples of industrial processes using homogeneous catalysis

MANUFACTURE	CATALYST	EQUATION
Ethane-1,2-diol	Sulfuric acid	$\text{H}_2\text{C}-\overset{\text{O}}{\diagup}\text{CH}_2 + \text{H}_2\text{O} \longrightarrow \text{HOCH}_2\text{CH}_2\text{OH}$
2,2,4-trimethylpentane	Hydrogen fluoride	$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{CH}_2 + \text{H}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3 \longrightarrow \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$
Phenol and propanone	Sulfuric acid	$\text{H}_3\text{C}-\overset{\text{OH}}{\text{O}}-\overset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_5 \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3-\text{CO}-\text{CH}_3$
Bisphenol A	Sulfuric acid	$\text{CH}_3-\text{CO}-\text{CH}_3 + 2\text{C}_6\text{H}_5\text{OH} \longrightarrow \text{HO}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{OH} + \text{H}_2\text{O}$

One example is in the manufacture of ethane-1,2-diol (ethylene glycol, used in antifreeze and as an intermediate in the manufacture of polyesters) from epoxyethane, where the catalyst is a trace of acid (FIG. 1). In the mechanism for this reaction a hydrogen ion is added at the start and lost at the end. This ion functions as a catalyst.

**FIG. 1 A mechanism for the formation of ethane-1,2-diol from epoxyethane**



Two other examples are concerned with the production of 2,2,4-trimethylpentane from 2-methylpropene, again using an acid as the catalyst. One method uses 2-methylpropane (TABLE 1), which yields the alkane in a one-step process. The other method uses only 2-methylpropene:

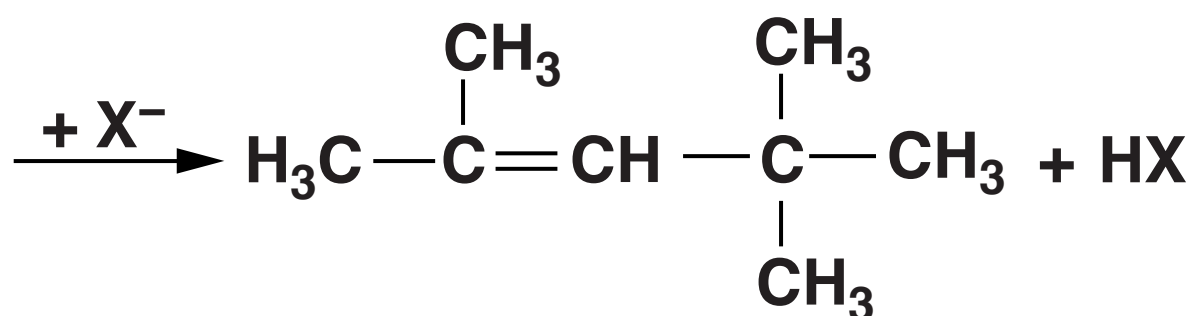
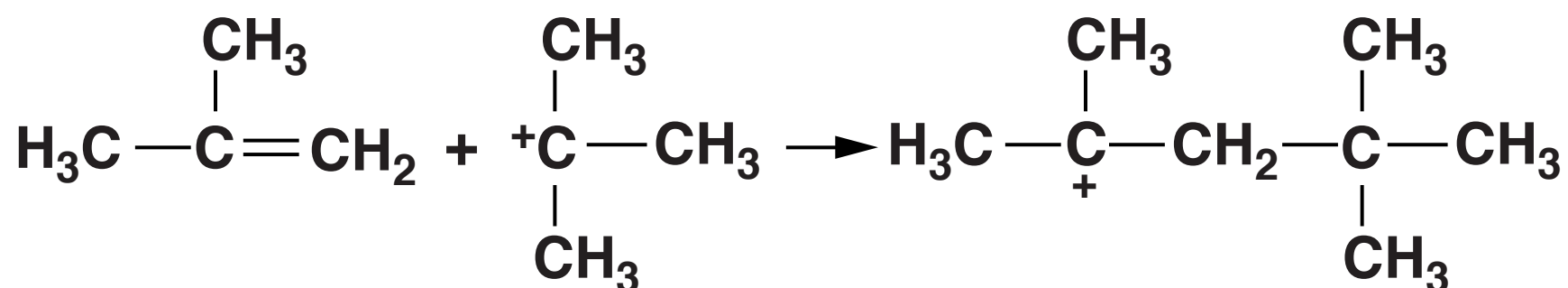
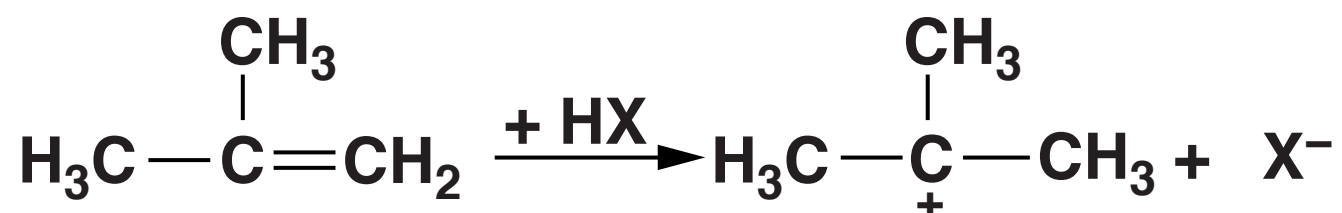
The mechanism of the reaction also involves the addition of a hydrogen ion, from aqueous sulfuric acid, to a reactant (FIG. 2).

The alkene is hydrogenated (using nickel as the catalyst) to 2,2,4-trimethylpentane (isooctane, FIG. 3).

2,2,4-trimethylpentane is often added to petrol to enhance its anti-knock properties, now that methyl t-butyl ether (MTBE) is being phased out.

**FIG. 2 Part of a mechanism for the formation of 2,4,4-trimethylpent-2-ene from 2-methylpropene**

2-methylpropene

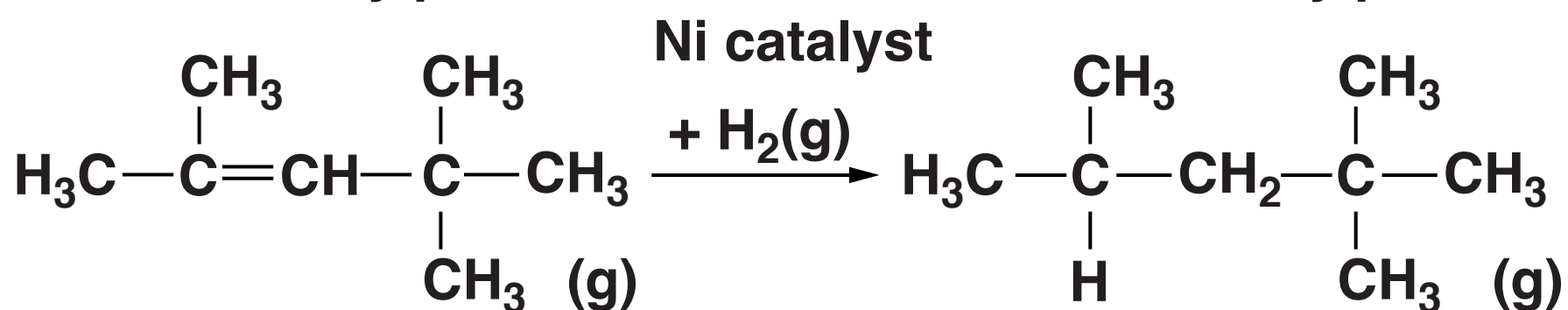


2,4,4-trimethylpent-2-ene

**FIG. 3 The hydrogenation of 2,4,4-trimethylpent-2-ene to 2,2,4-trimethylpentane**

2,4,4-trimethylpent-2-ene

2,2,4-trimethylpentane

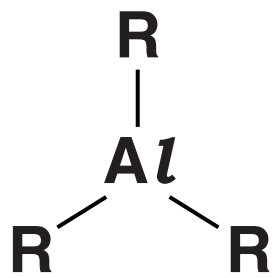


# Catalysts for polymerisation reactions

## Ziegler–Natta catalysts

Ziegler–Natta catalysts are organometallic compounds prepared from titanium compounds with an aluminium trialkyl, which acts as a promoter (FIG. 4).

FIG. 4 Trialkylaluminium (R = alkyl group,  $-(C_nH_{2n+1})$ )



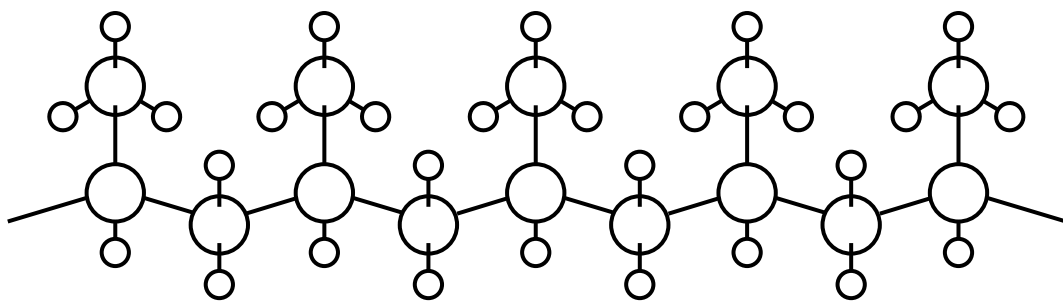
The alkyl groups used include ethyl, hexyl and octyl. Their use makes the polymer molecule ‘grow’ in a linear, unbranched fashion, which makes its properties different from that of branched polymer molecules.

Not only do Ziegler-Natta catalysts allow for linear polymers to be produced, they can also give stereochemical control. Propene, for example, could polymerise in three ways (even if linear) to produce ‘isotactic’ (where all the substituted carbons have the same stereochemical configuration), ‘syndiotactic’ (where the substituted carbons have alternating stereochemical configurations) or ‘atactic’ (where the stereochemistry of the carbons along the chain is random) poly(propene) (FIG. 5).

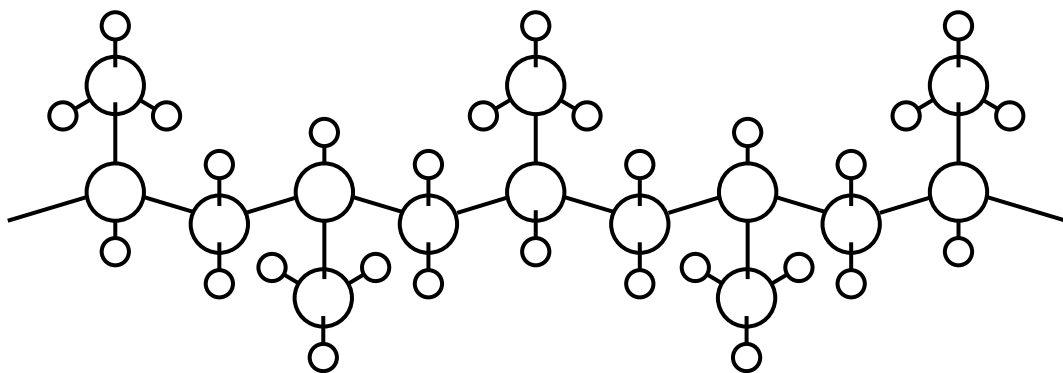


**FIG. 5 Molecular structures of poly(propene)**

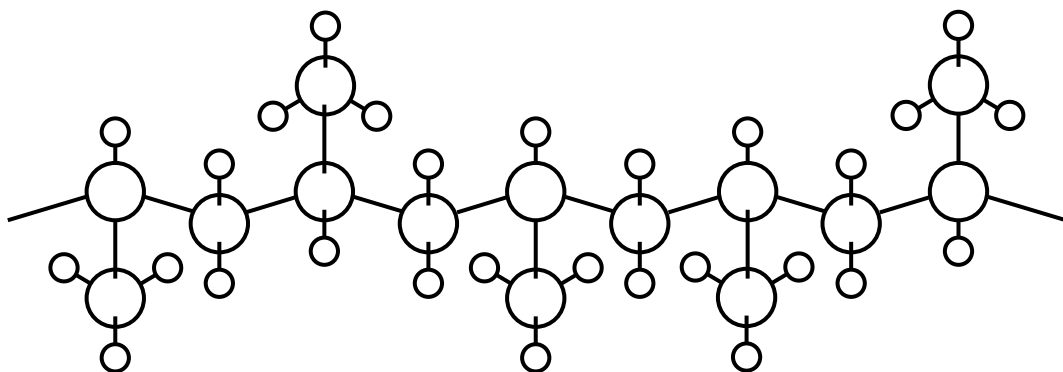
**Isotactic poly(propene)**



**Syndiotactic poly(propene)**



**Atactic poly(propene)**

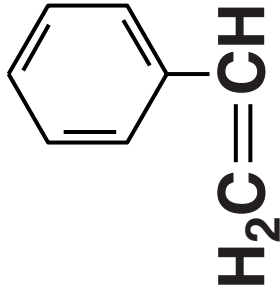
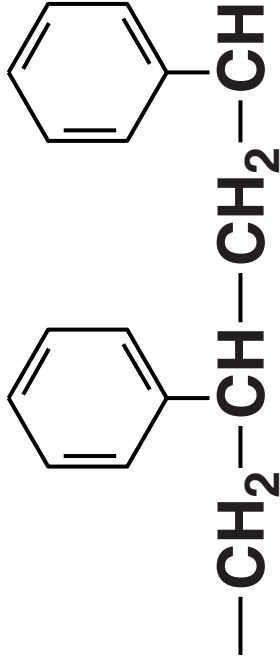


The different stereochemical forms of poly(propene) have different properties. Isotactic poly(propene) is strong, hard and has excellent resistance to stress and cracking. The atactic form is a soft and rubbery polymer. However, the Ziegler–Natta catalyst only allows the propene to react so that isotactic poly(propene) is produced. Even greater control of the polymerisation is obtained using a new class of catalysts, the ‘metallocenes’. Using a metallocene catalyst is the only way currently available commercially for the production of syndiotactic poly(propene). Atactic poly(propene) can be formed by the radical polymerisation of propene.

## **Radical polymerisation**

**Many polymers are produced using radical initiators, which act as catalysts (TABLE 2 opposite).**

TABLE 2 Examples of polymers produced using free radical polymerisation

MONOMER	FORMULA	POLYMER	STRUCTURE
Ethene	$\text{H}_2\text{C}=\text{CH}_2$	Low density poly(ethene) (LDPE)	$\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---}$
Chloroethene	$\begin{array}{c} \text{Cl} \\   \\ \text{H}_2\text{C}=\text{CH} \end{array}$	Poly(chloroethene) (poly(vinyl chloride), PVC)	$\begin{array}{c} \text{Cl} \qquad \text{Cl} \\   \qquad \quad   \\ \text{---CH}_2\text{---CH---CH}_2\text{---CH---} \end{array}$
Propene	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{CH} \end{array}$	Poly(propene) (polypropylene, PP)	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\   \qquad \quad   \\ \text{---CH}_2\text{---CH---CH}_2\text{---CH---} \end{array}$
Propenonitrile	$\begin{array}{c} \text{CN} \\   \\ \text{H}_2\text{C}=\text{CH} \end{array}$	Poly(propenonitrile) (polyacrylonitrile)	$\begin{array}{c} \text{CN} \qquad \text{CN} \\   \qquad \quad   \\ \text{---CH}_2\text{---CH---CH}_2\text{---CH---} \end{array}$
Methyl 2-methylpropenoate	$\begin{array}{c} \text{CO}_2\text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C---CH}_3 \end{array}$	Poly(methyl 2-methylpropenoate) (polymethyl methacrylate, PMMA)	$\begin{array}{c} \text{CO}_2\text{CH}_3 \qquad \text{CO}_2\text{CH}_3 \\   \qquad \quad   \\ \text{---CH}_2\text{---C---CH}_2\text{---C---} \\   \qquad \quad   \\ \text{CH}_3 \qquad \quad \text{CH}_3 \end{array}$
Phenylethene	 $\text{H}_2\text{C}=\text{CH}$	Poly(phenylethene) (poly(styrene))	 $\text{---CH}_2\text{---CH---CH}_2\text{---CH---}$
Tetrafluoroethene	$\text{F}_2\text{C}=\text{CF}_2$	Poly(tetrafluoroethene) (PTFE)	$\text{---CF}_2\text{---CF}_2\text{---CF}_2\text{---CF}_2\text{---}$

**For example, the polymerisation of chloroethene to poly(chloroethene) is started by warming it with a minute trace of a peroxide ( $\text{R-O-O-R}$ , see FIG. 6 opposite).**

**These reactions lead to side chains, so that the molecules of the polymer cannot pack together in a regular way. Thus the branched polymer has a lower melting point and lower density than high density poly(ethene) (HDPE), allowing for different uses of the two polymers. For example, HDPE can be used to make rigid bottles while LDPE is suitable for flexible polythene bags.**

## **Looking forward**

**The search for catalysts will continue to be one of the highest priorities for the chemical industry, as it seeks to run processes at as low a temperature and as near atmospheric pressure as possible, commensurate with a reasonable rate of reaction.**

**Catalysts are sought that will favour one specific reaction over another, thus making the process much more economical. The gains from improving catalysts are both financial and environmental, leading to lower fuel costs and the reduction of harmful waste gases.**

**FIG. 6 A mechanism for the free radical polymerisation of chloroethene to poly(chloroethene).**

<p>The reaction starts with the decomposition of the peroxide.</p>	$\text{R}-\text{O}-\text{O}-\text{R} \longrightarrow 2\text{R}-\text{O}\cdot$
<p>The resulting radicals add to molecules of chloroethene to make new radicals.</p>	$\text{R}-\text{O}\cdot + \text{H}_2\text{C}=\text{CHCl} \longrightarrow \text{R}-\text{O}-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}\cdot$
<p>As more chloroethene molecules are added one at a time, the chain continues to grow.</p>	$\text{RO}-\overset{\text{Cl}}{\underset{ }{\text{CH}}}_2-\text{CH}\cdot + \text{H}_2\text{C}=\text{CHCl} \longrightarrow \text{RO}-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}\cdot$
<p>Termination occurs when, for example, any two radicals react with each other.</p>	$\text{RO}-\overset{\text{Cl}}{\underset{ }{\text{CH}}}_2-\text{CH}-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}\cdot + \cdot\text{CH}-\text{CH}_2-\text{OR} \longrightarrow \text{RO}-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-\text{CH}-\text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}}-\text{CH}-\text{OR}$

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