

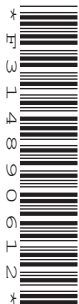
**For issue on or after:
13 March 2012**

AS GCE CHEMISTRY B (SALTERS)

F332 Chemistry of Natural Resources

ADVANCE NOTICE

Duration: 1 hour 45 minutes



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 **23 May 2012** 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.

This document consists of **8** pages. Any blank pages are indicated.

INSTRUCTION TO EXAMS OFFICER/INVIGILATOR

- Do not send this Advance Notice for marking; it should be retained in the centre or destroyed.

Plastic Fantastic

From RSC's Education in Chemistry 'Infochem' supplement, Jan 2005.

You can't miss the addition polymer poly(ethene) (PE, polythene). It's in your house, in the streets and roads, in supermarkets, in your garden and maybe even in you. The list of PE products is endless – shampoo and detergent bottles, gas and plumbing supply pipes, electrical insulation, car wheel arches and petrol tanks, food packaging and crates, and milk, ketchup and healthcare bottles. Poly(ethene) is also used in bullet proof vests, in hip and bone replacements, and as a waterproof coating on skis, sail boards, and canoes. So ubiquitous is this plastic – PE is the most widely used plastic, commanding *ca.* 36 per cent of the total European market – that it's hard to imagine life without it. And yet, like many other products we have come to rely on for our current lifestyles, poly(ethene) was discovered by accident.

A serendipitous discovery

In 1933, Reginald Gibson and Eric Fawcett, two research chemists at ICI's Winnington Laboratory in Cheshire, were working on high pressure and high temperature reactions. They were trying to develop new products for ICI's rapidly growing dyestuffs industry. They tried to react ethene and benzaldehyde (benzenecarbaldehyde) at 2000 atm (1 atm = 101325 Pa) and 170 °C in the hope of producing potential intermediates in the manufacture of dyes.

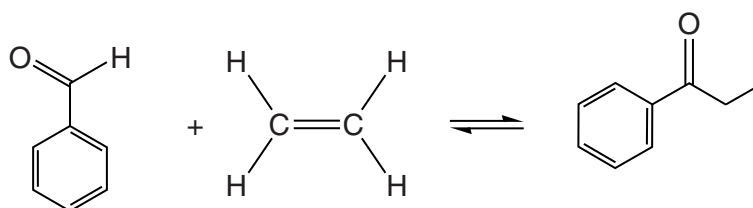


Figure 1: The equation for the reaction expected to occur between benzaldehyde and ethene

The high pressure apparatus had a mercury gas compressor. Benzaldehyde was contained in an inverted glass tube, sealed with mercury and placed in a steel tube in a reaction vessel. The vessel was sealed and put in an oil thermostat, regulated to 170 °C. Ethene was bubbled through the mercury into the benzaldehyde – mercury separated the gas from benzaldehyde rather like a piston.

Gibson and Fawcett started the experiment on Friday afternoon, and left it to run over the weekend. On the Monday morning, they found that the pressure in the system had fallen to *ca.* 500 atm because of a small leak in the oil system. Ethene had expanded and forced the benzaldehyde through the mercury into the oil system. They couldn't replace the benzaldehyde so, having fixed the leak, they restored the pressure by adding more ethene. After a few hours they stopped the reaction and allowed it to cool. No liquid product had formed, but instead a trace amount – 0.2 g – of a waxy solid had formed on the inside wall of the glass tube. Spectroscopic analysis revealed that this contained only hydrogen and carbon in the same ratio as ethene. They had discovered poly(ethene).

Unfortunately, when they tried to repeat the experiment, decomposition of ethene to carbon occurred, which being exothermic caused an explosion, bursting a pressure joint near the oil thermostat and setting it on fire. ICI management immediately stopped high pressure work on ethene until safer premises could be found. That might have been the end of the story but ...

Poly(ethene) – rediscovered

Two years later, and in an isolated building with walls one-foot thick, Michael Perrin, another research chemist, decided to do some more experiments with ethene.

Frank Bebbington, now 94 years old and one of Perrin's research assistants at the time, told *Education in Chemistry*, 'On 20 December 1935 I assembled equipment in a deliberate attempt to polymerise ethylene [ethene] under the same conditions that Gibson and Fawcett had used, but on a smaller scale. Immediately we put the pressure up to 2000 atm the pressure in the reaction vessel started to fall away very slowly, and again we thought there was a small leak in the system. I felt embarrassed because I had assembled the equipment. I compressed more ethylene to take the pressure back up to 2000 atm. At 1.00 pm everybody, except me, went to lunch; I was left to keep the pressure at 2000 atm. When they came back we stopped the experiment, and cooled the vessel. We opened it up, and to our amazement, it contained white powder – 8.5 g of the stuff to be precise. We had rediscovered poly(ethene). We immediately called the research director, Dr J. Swallow, who took the powder in his fingers and said "I wonder if it's a plastic?"

The next couple of attempts to repeat the experiment, however, gave only 0.5 g, 1 g and an explosive decomposition reaction. 'But', says Bebbington, 'once you've made 8.5 g of something, you know you can do it and we were determined to find out how'.

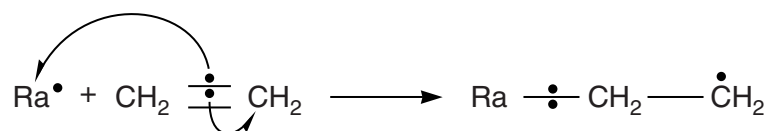
Bebbington remembers, 'after about 200 experiments, we discovered that the key to the successful polymerisation of ethylene [ethene] was an impurity in the ethylene – *ie* oxygen. Too much O₂ – *ca.* 500–1000 ppm (parts per million) – led to decomposition of the ethylene, 20–200 ppm of O₂ gave polyethylene, and no oxygen – no polyethylene'. 'Oxygen', explained Bebbington, 'was acting not as a catalyst but as an initiator because it was being used up during the polymerisation reaction'.

The role of oxygen in the polymerisation process

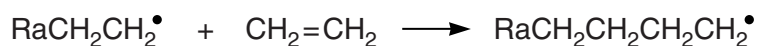
It has since been shown that oxygen reacts with some of the ethene to give an organic peroxide. Organic peroxides are very reactive molecules containing oxygen–oxygen single bonds that are quite weak and that break easily to give free radicals, represented here as Ra•.

The free radical, Ra•, uses one of the electrons in one of the C=C bonds to form a new bond between itself and the left hand carbon atom. The other electron returns to the right hand carbon.

This can be shown using 'half curly arrow' notation:

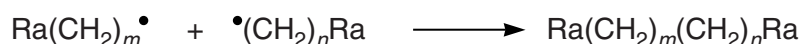


This produces a bigger free radical – lengthened by CH_2CH_2 – that can react with another ethene molecule in the same way:



So now the radical is even bigger. It can react with another ethene – and so on and so on. The polymer chain gets longer and longer.

The chain doesn't grow indefinitely. Sooner or later two free radicals will collide together.



That immediately stops the growth of two chains and produces one of the final molecules in the poly(ethene). It is important to realise that the poly(ethene) is going to be a mixture of molecules of different sizes, made in this sort of random way.

Moving on

By April 1936 the first pound of poly(ethene) had been made. It was sent to the Nobel Division of ICI in Ardeer, Scotland, where the only injection moulding machines existed, and a few small pill boxes were made. Back at Winnington, Perrin and his team made more poly(ethene) and started testing their new material. The PE that they had made was low density polyethene (see Figure 2). Its excellent insulating properties at high frequencies soon attracted the telephone industry, which was quick to spot it as a replacement for gutta-percha to insulate telephone cables. (Gutta-percha – latex from rubber trees in the Far East – was becoming increasingly difficult to obtain because of the imminent war.) On 1 September 1939 poly(ethene) became an official product of ICI.

During World War II all PE was made for the Government, specifically for high frequency experimental radar cable. The successful development of radar is said to have shortened the war by years. A poly(ethene) tube, called Pluto, was also laid across the Channel for transferring petrol from the UK to France.

Since its discovery over 70 years ago, there have been many improvements to the synthesis of poly(ethene). These have centred on the development of several types of catalyst – notably Ziegler–Natta catalysts in the 1950s and metallocene catalysts in the 1970s – so that the polymerisation can be done at lower pressures and temperatures, thus using less energy and making the process more environmentally acceptable.

Poly(ethene) – it's so useful

In its simplest form poly(ethene) consists of a long backbone of carbon atoms with two hydrogen atoms attached to each. This is called linear poly(ethene) or high density poly(ethene) (HDPE). Sometimes the hydrogen atoms are replaced by other PE molecules, which gives branched or low density poly(ethene) (LDPE) – the molecules don't pack together so well.

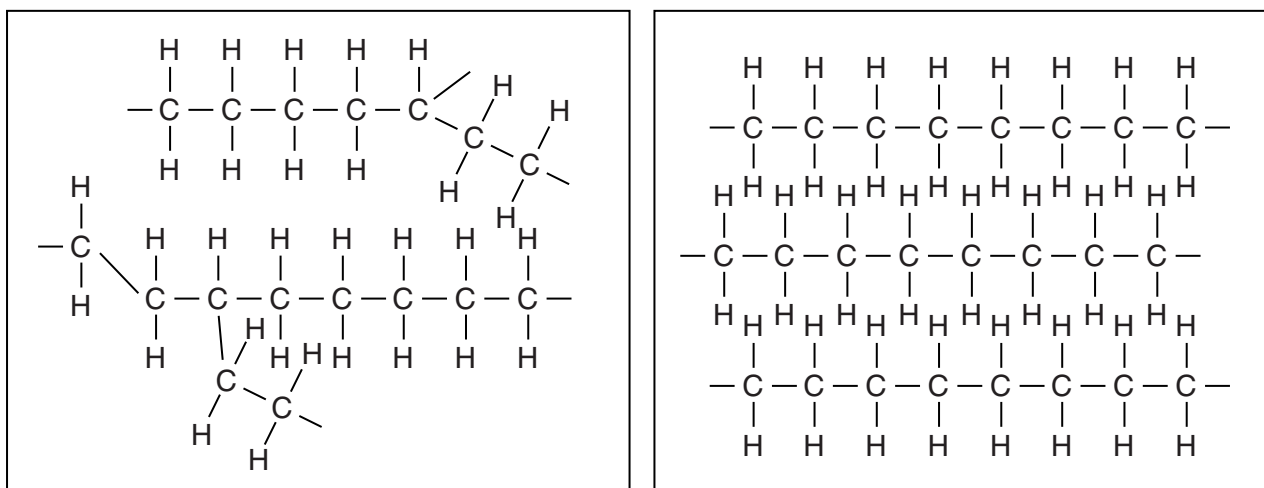


Figure 2: Part of the structure of the polymer chain in LDPE (left) and HDPE (right)

Approximately two thirds of all injection moulded PE items are made from HDPE – industrial containers, such as crates and pallets, gas and water pipes, canoes, car parts, and food containers, carbonated bottle bases and caps; LDPE is used mainly for food packaging films, waterproof films, and electrical cable insulation.

As well as poly(ethene), many other polymers can be made from alkene monomers. These include poly(propene), which is used to make drain pipes and crates and poly(chloroethene), or PVC, which is used to make the coating for electrical wires.

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