

ADVANCED SUBSIDIARY GCE

CHEMISTRY B (SALTERS)

F332/ADVANCE NOTICE

Chemistry of Natural Resources: Advance Notice article

For issue on or after:

13 MARCH 2011

Friday 27 May 2011

Afternoon

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** You will **not** be able to bring your copy of the article, or other materials, into the examination. The examination paper will contain a fresh copy of the article as an insert.
- 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

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Polymers on the move

Adapted from an article in the RSC's Education in Chemistry, November 2007

With transport being one of the major sources of anthropogenic CO₂ emissions, and transport costs being so sensitive to fuel prices, there is an urgency for car and aircraft manufacturers to reduce the weights of their products, and replace metals wherever possible with plastics and composites. *David Birkett*

The oil price shock of the 1970s led to the first big increase in the use of plastics in transport. Metal bumpers, wooden dashboards, leather-covered steel steering wheels, and glass headlamp covers were soon replaced by plastics, such as

ABS – acrylonitrile (2-propenenitrile) butadiene styrene – a tough plastic made by polymerising 2-propenenitrile and styrene (phenylethene) in a preformed latex of polybutadiene rubber.

Polymer	Properties and Uses				
	Impact strength /kJm ⁻²	Maximum use temperature /°C	Density /gcm ⁻³	General	Uses
Acrylonitrile butadiene styrene (ABS)	14–55	75–95	1.04–1.07	Rigid, tough, excellent for injection moulding	Car fascia panels
Fluoroplastics (PTFE, FEB)	13 – no break	205–280	1.17	Exceptional anti-stick/low friction characteristics	Engine gaskets and bearings
Nylons	4.0–5.0	80–110	1.13	Rigid, tough, hard-wearing	Carburettor parts, gear wheels
Poly(propene)	5–20	80	0.902	Extremely tough, exceptional fatigue resistance	Car accelerator pedals
Poly(chloroethene) (PVC)	2.0–45	60	1.38	Flexible, durable, good impact strength	'Imitation leather' fabrics

Table 1 Properties and uses of some polymers used in car manufacture

(Information from: 'Plastics, a guide to some workshop practices and industrial processes'
Published in 1994 by ICI and York University Polymer Industry Education Centre ISBN: 1 85342 700 4)

Polybutadiene is made from the monomer buta-1,3-diene. The polymerisation reaction occurs by the two double bonds opening up, providing linking points to other monomer units and creating a new double bond between the central pair of carbon atoms.

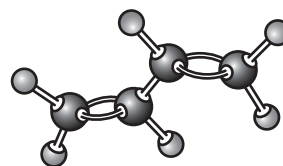


Fig. 1 A model of the buta-1,3-diene monomer

Windscreens used to sit loosely in rubber surrounds until chemists discovered that bonding them in place with polyurethane adhesives meant that the strength of glass could contribute to the roll-over strength of a car, so that there was room to reduce the body weight. The rubberised hair in seat cushions was replaced with polyurethane foam and new applications for plastics and elastomers appeared such as cup holders and sound insulation foam under the bonnet.

Not all were inspired by the desire to reduce the weight of the vehicles – often lower cost or greater design flexibility were more important – but the overall effect was improved fuel efficiency. By 1977 plastics contributed 4.6 per cent of the average weight of a vehicle.



In-flight polymers: using plastics will save fuel

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Sticky problems

Interestingly, vehicle paints were traditionally based on several layers of different high molecular mass polymers dissolved in solvents. However, because of concerns with solvent emissions, these have now largely been replaced by water-based paints

(where the applied polymer is typically of lower molecular mass) or powder coatings (where the polymer is applied electrostatically as a powder to the vehicle and melted later).

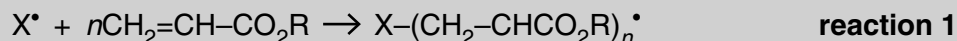
When all the layers have been applied, the vehicle is heated to $>150^{\circ}\text{C}$ to increase the molecular mass of some of the layers or to melt others, and allow them to form a continuous coating. Moves to reduce the energy consumption of this step by lowering the bake temperature would probably lead to problems with the final performance of the adhesives.

However, as more and more of the steel bodywork of the typical car is replaced by plastics or composites the nature of the paint system will have to change. Corrosion protection will become less important, but protection against ultraviolet light degradation of the plastic will be an issue. Paints designed to adhere to metals will generally adhere much less well to polymeric substrates. And, since a $150\text{--}180^{\circ}\text{C}$ bake is not possible for many of the cheaper plastics, some designers are leaving the plastic unpainted, relying on added pigments for colour and ultraviolet protection. If the paint bake cycle is eliminated, the adhesives holding the car together will have to be redesigned, and it may not be possible to maintain the same high-temperature performance under the bonnet.

This leads on to considerations of how plastic panels, particularly the notoriously hard to bond polyalkenes such as poly(propene), will be fixed to one another or to the remaining metal structures. In recent years several adhesive manufacturers have developed two-part acrylic (esters of propenoic or methyl propenoic acid) adhesives that can bond polyalkenes very well (see **Box 1**).

Box 1 Bonding polyalkenes

There is a broad class of adhesives known as acrylics, based on esters of acrylic (propenoic) or methacrylic acid: $\text{CH}_2=\text{CH}-\text{CO}_2\text{R}$ or $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}_2\text{R}$. These are polymerised by a free radical initiated polyaddition:



Traditionally the free radical, X^\bullet , is generated by the reaction of a hydroperoxide, such as cumene hydroperoxide, $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OOH}$, with a reducing agent such as a substituted hydrazine, a dihydropyridine or a thiourea. The resulting free radical, $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O}^\bullet$, is of the alkoxy type.

Acrylic adhesives bond a wide range of plastics, for instance polycarbonate or ABS, but are ineffective on poly(ethene) or poly(propene) because they can't get a chemical 'grab' on the unreactive surfaces.

However, in the late 1990s a new class of acrylic adhesives began to appear where the free radicals were generated by a different mechanism involving trialkyl boranes, R_3B (generally stabilised by complexing with an amine) and traces of atmospheric oxygen. This reaction produces alkyl radicals, e.g. $\text{CH}_3\text{CH}_2^\bullet$, which are much more reactive than alkoxy radicals and can abstract a hydrogen from a polyalkene surface:



The radical on the surface can now initiate polymerisation of the acrylic monomer, but now the growing chain is chemically bound to the surface.

These are finding application in the car industry but the products are relatively new, so there are no long-term data on the durability of the bonds.

Scrap heap challenge

A factor that is becoming increasingly important for car designers to consider is the recyclability of the materials they use. Most of the steel from scrapped cars is already recycled, but polymers present problems. Simple thermoplastics such as nylon or polycarbonate, once segregated, can be



Plastics pose a challenge for the environment

© Alan Schein/Alamy

melted down and reused, albeit in less stringent applications, but composites, for instance glass-reinforced poly(propene), or thermosets, such as vulcanised rubber, present difficulties.

Consider, for example, polyurethane foam seating, one of the biggest uses of synthetic polymers in cars.

The cushions from an old car will generally have been compressed or otherwise damaged, so can't be reused. The foams can't be melted down without decomposing, so what can we do?

Three approaches are being used, but none of them is wholly satisfactory.

- Digest the foam in ethylene glycol (ethane-1,2-diol) to yield polyols suitable for synthesising rigid insulating poly-urethane foam.
- Chop the foam up and compress it, and use the resulting material in, for instance, carpet backing.
- Recover some of the energy used to make the foam by burning it in an incinerator.

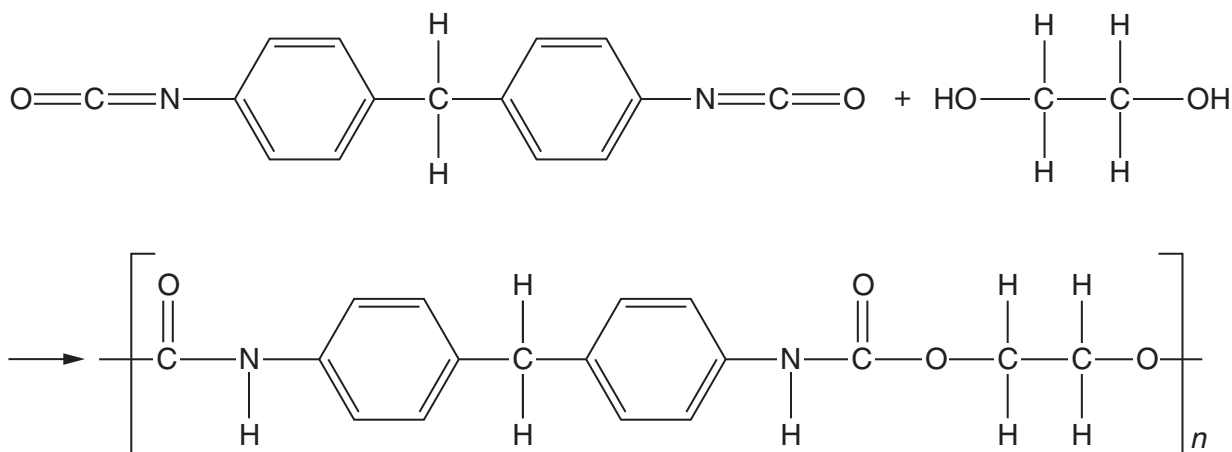


Fig. 2 An example of the formation of a polyurethane repeating unit from its monomers

The first two methods require markets for the products and the third method produces gases that are not particularly environmentally friendly.

Long-term forecast

Even if fuel costs fall in the near future, petroleum will eventually become scarce and replacement liquid fuels (biofuels, oil-from-coal or synthetic fuels using hydrogen from the electrolysis of water) are more expensive without subsidy. The long-term forecast is therefore for relatively high fuel costs. Pressures from green activists, governments

and customers for lower carbon emissions from transport are more likely to increase rather than relax.

Weight reduction will therefore continue to be a key objective of manufacturers, and plastics and composites will play an ever increasing role. On the other hand, most plastics are oil-based, so their own costs will also increase. As the polymer content of cars increases, recyclability of the materials will also need to be built in. Whichever way you look, there's an interesting road ahead for polymer chemistry.

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