Design polymers

Scopes:

- the properties and structures of polymers based on their methods of formation for both addition and condensation polymers
- the presence of side-chains and intermolecular forces affect the properties of polymeric materials - example spider silk.

Addition Polymers

Polymers made from alkenes contain only carbon and hydrogen atoms.
The physical properties of polymers are determined by the intermolecular forces present in the polymer.
The electronegativity difference between carbon and hydrogen is small.
The only intermolecular forces present in these polymers are van der Waals' forces.
The properties of addition polymers can be modified in a number of ways.

- the polymer chain length – in general, the longer the polymer chains, the stronger the van der Waals' forces.
- the number of side-chains – in general, unbranched chains can pack together better than polymers with lots of side-chains. (eg. poly(ethene))
- types of bonding – eg. the presence of chlorine atoms in poly(chloroethene) results in some permanent dipole interactions between carbon and chlorine because of the polarity of the carbon-chlorine bond.

Poly(ethene)

If side-chains are present, it is more difficult for the polymers to line up and resulting in weaker intermolecular forces.

The role of side-chains is shown in the case of low-density poly(ethene) (LDPE) and high-density poly(ethene) (HDPE).

LDPE has extensive random branching on its polymer chains.

LDPE is a plastic of low density which softened at a relatively low temperature.

The soft bags are made from LDPE, which has lots of side-chains and is relatively weak and easy to deform.

HDPE has straight polymer chains.

These could pack together more closely, resulting in stronger van der Waals' forces between polymer chains.

HDPE is less flexible, has higher melting point and is a stronger plastic than LDPE.

HDPE is used to make bottles for milk and fruit juices.

Exercise 1

Using the concept of intermolecular forces, explain why HDPE could be used to make containers that can be sterilised by boiling water but LDPE cannot.

Workings

As HDPE has fewer side-branches between polymer chains, its polymer chains can pack closer together compared to those in the highly branched LDPE polymer chains.

HDPE has stronger van der Waals' forces than LDPE. These stronger van der Waals' forces cause HDPE to have a higher softening temperature, so it can withstand a temperature of 100°C without losing its shape.

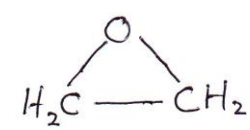
Polyethylene glycol (PEG)

PEG is used to coat the gold nano-cages and liposomes that can be used in drug delivery.

Varying reaction conditions can produce different class of PEG.

The skeletal formula of PEG is:

PEG is made from monomers of epoxyethane:



Epoxyethane is a reactive cyclic molecule, written as CH_2CH_2O.

It is reacted with 1,2-ethanediol to produce PEG.

The polymerisation of epoxyethane is shown by this equation:

$$HOCH_2CH_2OH + n(CH_2CH_2O) \longrightarrow HO(CH_2CH_2O)_{n+1}H$$

The catalysts used and the ratio of reactants affect the size of the polymer chains.

By varying the molecular mass of the polymer, a whole range of products is made.

They are often used as liquids or low melting point solids.

Their solubility in water, and in many non-polar solvents, is one of their advantages over other polymeric materials — their use in drug delivery.

Their molecular mass is given after their name, e.g. PEG 400 or PEG 10000

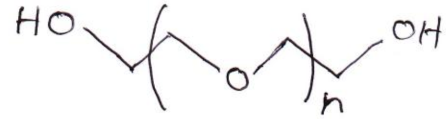
PEG 200 and PEG 2000 were used to help preserve the timbers of the Mary Rose — a ship that sank about 500 years ago and was raised from the seabed in 1982.

Spraying the wood with PEG 200 started in 1994 and the switch to the more waxy PEG 2000 began in 2004.

The water in the timbers is replaced by PEG and the remains of the ship can then be slowly dried out without crumbling away.

Exercise 2.

Skeletal formula of PEG is:



Give structural formula for PEG.

Workings

$HOCH_2 [CH_2OCH_2]_n CH_2OH$

Exercise 3

Which type of intermolecular forces will PEG form with water?

Workings

hydrogen bonds

Exercise 4

Is PEG an addition or a condensation polymer? Explain your answer.

Workings

An addition polymer because the polymer is the only product of the reaction and no small molecule is released.

(It is an unusual polymer as its monomers are not alkene.)

Exercise 5

Consider between PEG 200 and PEG 2000.

a. Explain which will have the higher melting point?

b. What will be the strongest type of intermolecular forces between the polymer chains?

c. Given that a sample of PEG was made in this reaction:

$$HOCH_2CH_2OH + n(CH_2CH_2O) \longrightarrow HO(CH_2CH_2O)_{n+1}H$$

How would you vary the proportion of reactants to produce PEG 200 instead of PEG 2000?

Workings

a. PEG 2000 will have the higher melting point.

b. The strongest forces between the polymer chains will be permanent dipole-dipole attraction.

c. Increase the concentration of $HOCH_2CH_2OH$, as this terminates the chains.

Exercise 6

Which instrumental technique (mass spectrometry, NMR spectroscopy or X-ray crystallography) would you recommend to check the relative molecular mass of the PEG formed?

Workings

mass spectrometry.

Exercise 7

a. How many main peaks would you expect to see in the low-resolution NMR spectrum of ethane-1,2-diol, $HOCH_2CH_2OH$? Explain your answer.

b. How would you expect the peaks in part a. to be affected if D_2O was used as the solvent to obtain the NMR spectrum.

c. What splitting pattern would you expect the peaks in part a. to show in high-resolution NMR?

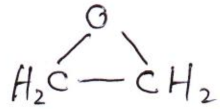
Workings

a. Two peaks.
One for the two equivalent $-OH$ protons and one for the four equivalent protons in the two $-CH_2-$ groups.

b. The $-OH$ peak would disappear.

c. The $-OH$ peak would not be split but the $-CH_2-$ peak would be a triplet.

Exercise 8

How many main peaks would you expect to see in the low-resolution NMR spectrum of epoxyethane, 

?

Explain your answer.

Workings

One peak as all four protons (^1H atoms) in epoxyethane are equivalent.