Plastics Topics – Polymer structures

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Plastics Topics – Polymer structures

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Polymers

Polymers are long chain molecules, i.e., they are made up of many ‘monomers’, where the ‘monomer’ is the repeating element of the long chain. Understanding the structure of the monomer is the key to understanding the structure and, more importantly, the properties of the resulting polymer.

This publication aims to outline most of the monomers for the common polymers.

1. Polymers versus plastics

We take a very simple view on the terminology of ‘polymers’ and ‘plastics’ and do not regard these words as interchangeable (although some do).

- A polymer is a long chain molecule in the pure state, i.e., a collection of long chain molecules. Very few polymers are processed in this pure state. Most are compounded with additives, processing aids and, at a minimum, colouring agents.
- A plastic is a polymer when it has been compounded with these additives and is ready for processing.

2. Drawing the structures

The conventions for drawing and naming chemicals are well laid down by international organisations and these are very suitable for the chemists who are familiar with them.

However, many people in the plastics industry do not have a chemistry background and find the standard diagrams hard to read and understand.

As an example, the structure of PA 6 (Nylon 6) should be written as:

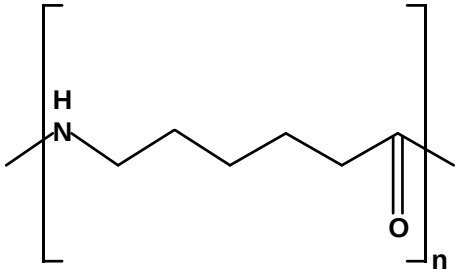


Figure 1: PA 6

This does not show the carbon and hydrogen atoms as they are assumed to be present at the intersections of the lines. An alternative representation of the structure to show the location of the carbon and hydrogen atoms would be:

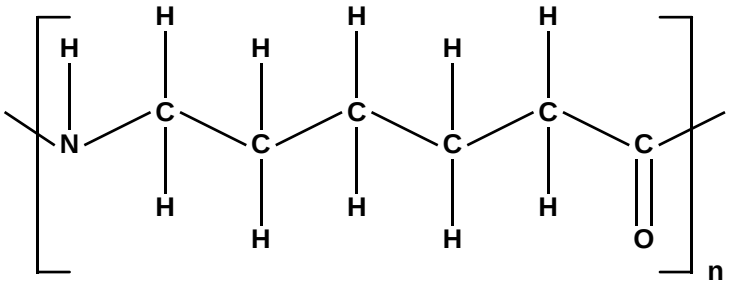


Figure 2: PA 6 – alternative representation 1

This shows the angular nature of the carbon-carbon bonds bends as well as all the individual atoms.

It is also possible to draw this same structure as:

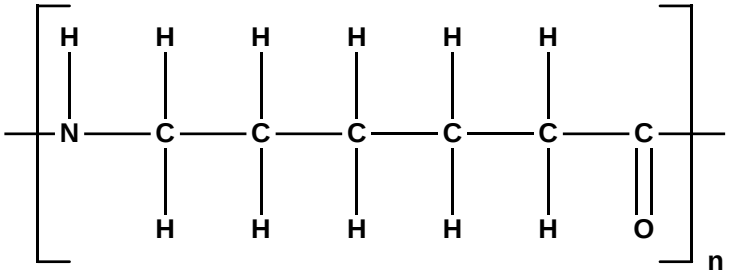


Figure 3: PA 6 – alternative representation 2

This does not show the angular nature of the carbon-carbon bonds but does show all the individual atoms.

For some structures, such as PA 6, the repeated CH_2 features can be shortened to give the representation:

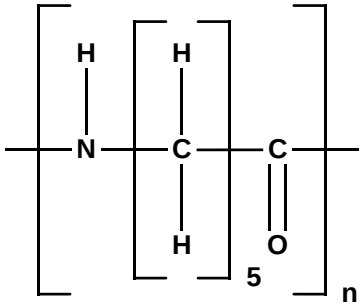


Figure 4: PA 6 – alternative representation 3

In this document, as a general rule, we will use the simple form shown in Figure 3 as this is easy to understand and visualise for non-chemists. We will sometimes use the form shown in Figure 4 when the number of repeating units is large and the structure becomes unnecessarily complex.

3. The benzene ring

The benzene ring appears in many polymer structures and the full representation of the benzene ring is as shown in Figure 5

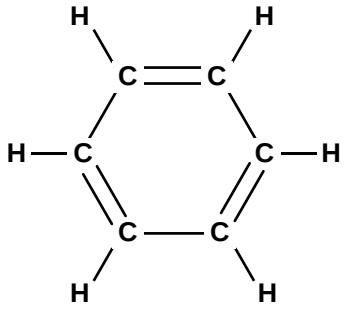


Figure 5: The 'classic' structure of the benzene ring

This shows the 'ring' of 6 carbon atoms with the associated double bonds and hydrogen atoms. The 'shorthand' form of this is much easier to draw and this is shown in Figure 6:

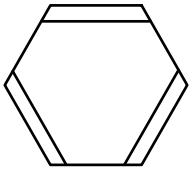


Figure 6: Short form of the classic structure

This representation is now regarded as largely incorrect because the double bonds and the hydrogen atoms are as not clearly delineated as this drawing would imply. In fact, the hydrogen atoms exist more as a cloud and the current preferred representation is shown in Figure 7:

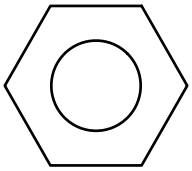


Figure 7: Closer to reality?

This is the representation that will be used in all polymers containing a benzene ring structure.

4. Where do we start?

The repeating nature of the monomer and the length of some of the monomers means that it is possible for monomers to look very different but to be exactly the same. Simply 'starting' the monomer at a different position can make the representations look very different (although they are exactly the same when continuously repeated). Two representations of PC (polycarbonate) are shown below:

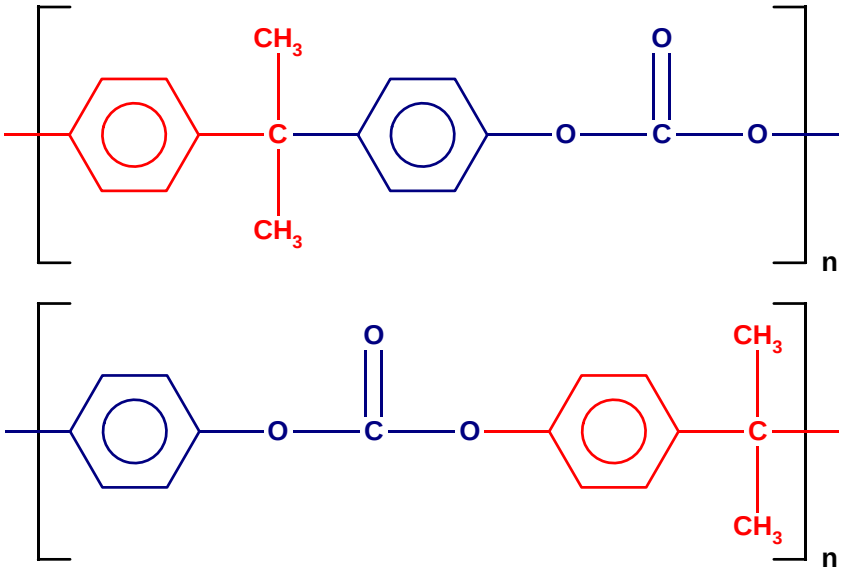


Figure 8: Two views of Polycarbonate

These monomers look very different but are identical when repeated in the polymer chain. Readers are advised to be wary of where the monomer starts when looking at the structure drawings.

5. Homopolymers and copolymers

Homopolymers consist of a single monomer (A) that is repeatedly joined together to form the long chain of the polymer molecule:

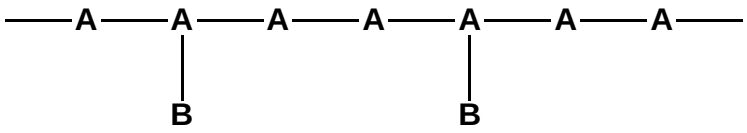
—A—A—A—A—A—A—A—

Copolymers consist of two different monomers (A and B) that are alternated when joined together to form the long chain of the polymer molecule:

—A—B—A—B—A—B—A—

In some copolymers the ratio of A to B is not 1:1, i.e., the B molecule is repeated less often than the A molecule and we will indicate this where this is the case.

Graft copolymers are copolymers with a branched structure in the long chain of the polymer molecule:



Terpolymers consist of three different monomers (A, B and C) that are alternated when joined together to form the long chain of the polymer molecule:

It is also possible that terpolymers will not have a ratio 1:1:1 and we will indicate where this is the case.

6. Isotactic, atactic and syndiotactic

The structure is not only important in terms of the atoms that make it up but the actual layout of the atoms around the main backbone carbon chain can be also be significant. The repeating structure of PS is shown below in two forms, the atactic and the syndiotactic

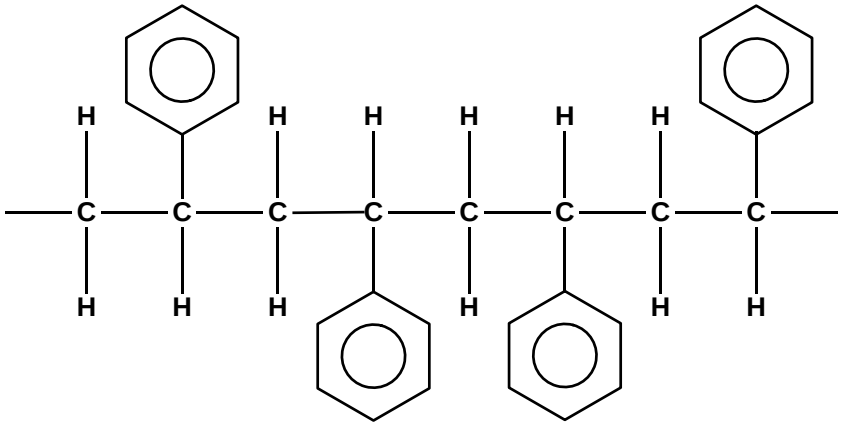


Figure 9: Atactic PS – irregular structure and cannot pack to form crystals

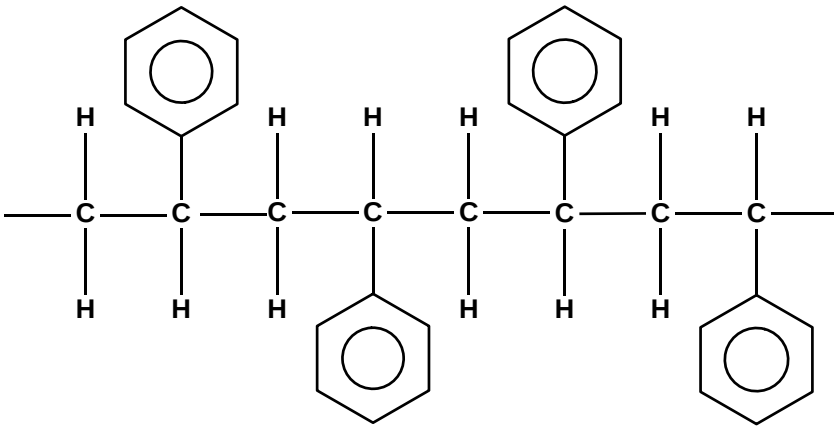


Figure 10: Syndiotactic PS – regular structure and can pack to form crystals

Where the forms vary significantly then this will be indicated.

The Periodic Table of Thermoplastics

The general layout of this document will follow the Periodic Table of Thermoplastics (see right for a simplified version). A full version is available for free download from www.tangram.co.uk.

This was developed by Tangram Technology Ltd. to provide a framework for looking at and classifying the main families of thermoplastics. This will also be used as a framework for the polymer structures. As a general rule, we will move along the rows and then down to the columns but polymers from a single family will all be treated together. As with the Periodic Table of Thermoplastics, polymers will be colour coded to indicate the broad family to which they belong.

Polymer structures are very complex and many of the structures are difficult to ascertain with a high degree of confidence. If we have made any mistakes then we would be glad to hear from readers with corrections and/or suggestions for additional structures to include.

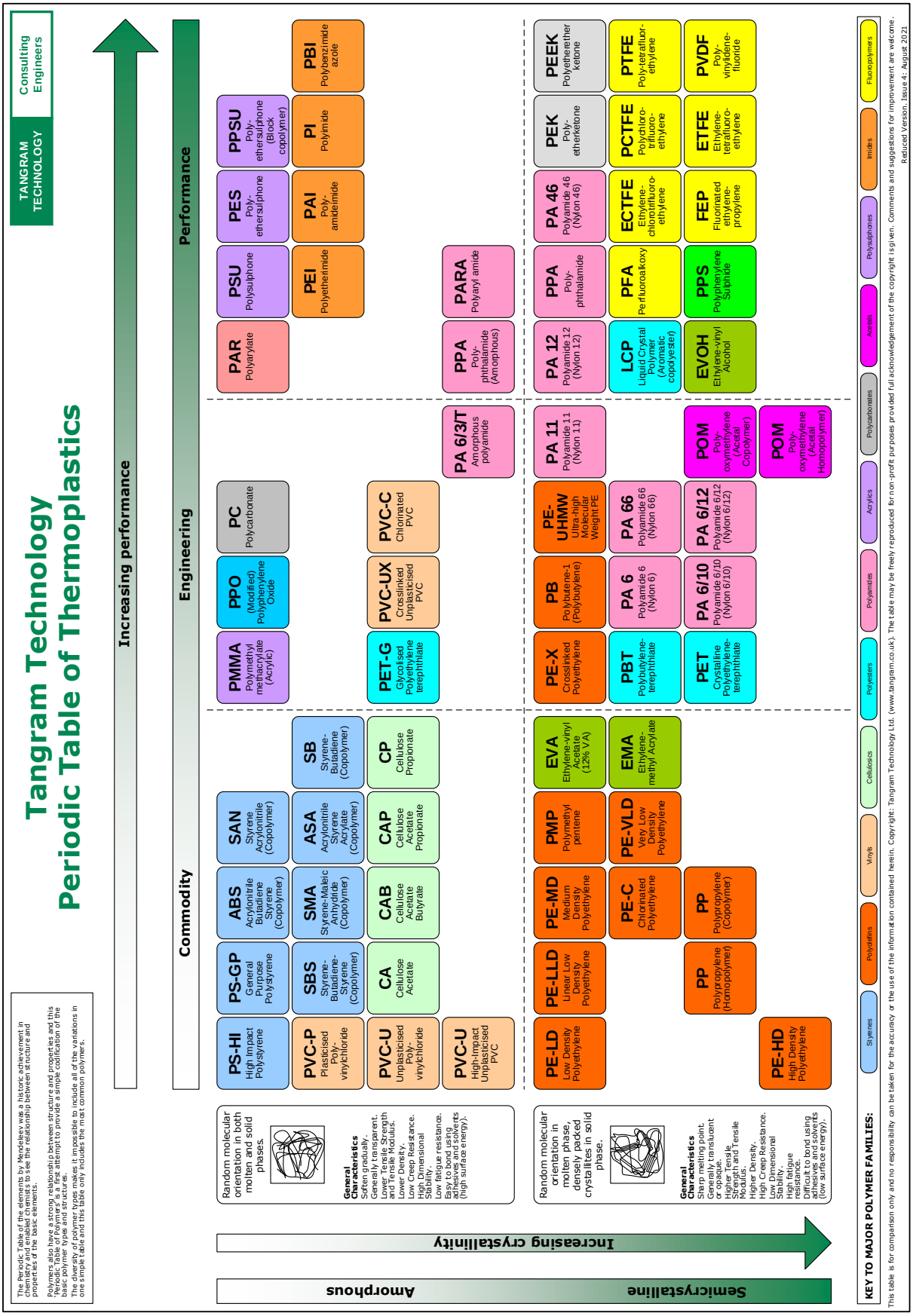
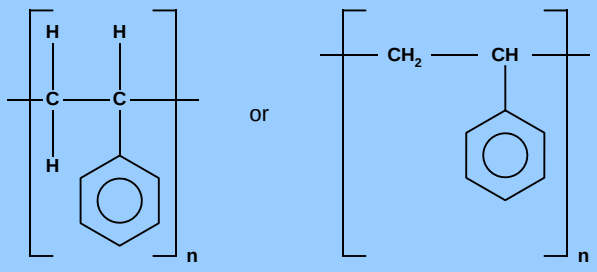


Figure 11: Reduced version of the Periodic Table of Thermoplastics

Styrenes – Amorphous/commodity

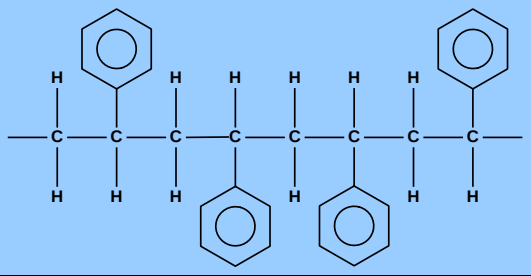
Homopolymers

PS – Polystyrene



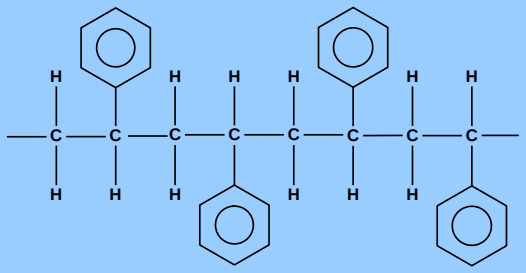
Atactic PS

Random distribution of the benzene rings, irregular structure and cannot pack to form crystals.



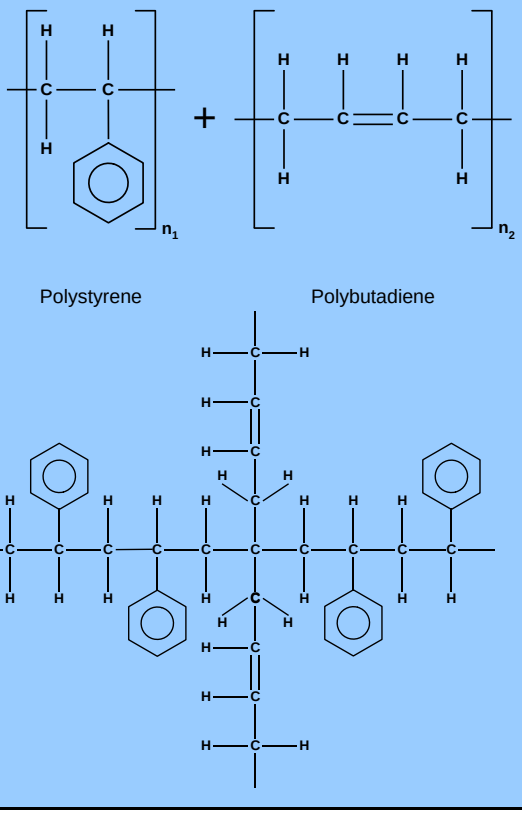
Syndiotactic PS

Regular distribution of the benzene rings and can pack to form crystals. Therefore, not an amorphous but a crystalline polymer.



High impact PS

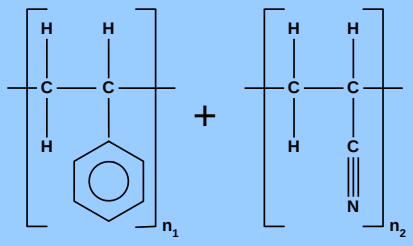
PS-HI is a graft copolymer where the butadiene is generally at right angles to the main PS backbone chain. This adds considerable extra impact resistance to the normally brittle PS.



Styrenes – Amorphous/commodity

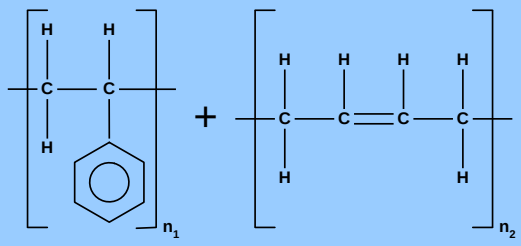
Copolymers

SAN – Styrene acrylonitrile copolymer



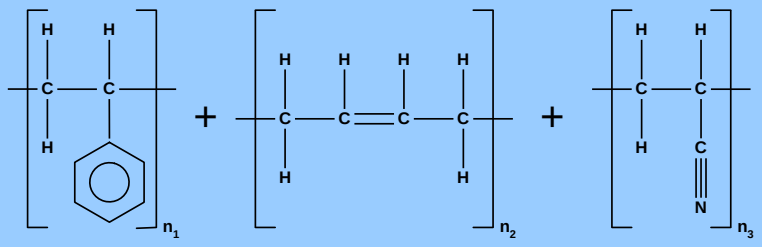
Polystyrene Acrylonitrile

SB – Styrene butadiene copolymer



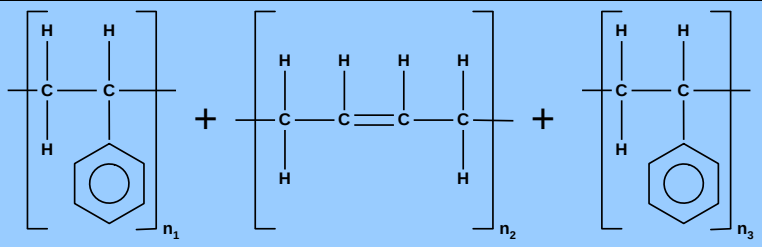
Polystyrene Polybutadiene

ABS – Acrylonitrile butadiene styrene copolymer



Polystyrene Polybutadiene Acrylonitrile

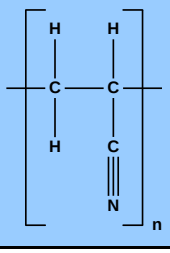
SBS – Styrene butadiene styrene copolymer



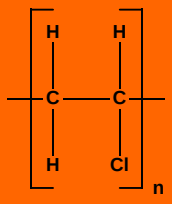
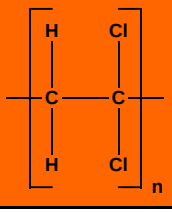
Polystyrene Polybutadiene Polystyrene

Acrylonitrile

Mainly used as copolymers (with methyl acrylate or methyl methacrylate) or as part of styrene copolymers such as SAN or ABS.

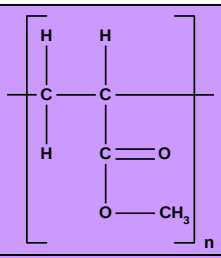
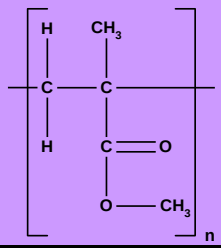


Vinyls – Amorphous/commodity

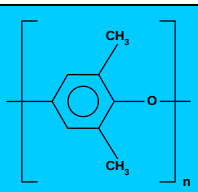
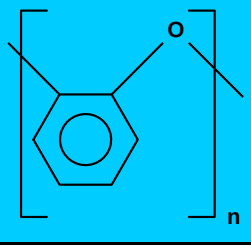
PVC – Polyvinyl chloride Available in plasticized and unplasticized formats when compounded. Also available as cross-linked (PVC-UX) to form a more rigid matrix.	
PVDC – Polyvinylidene chloride	

Plastics Topics – Polymer structures

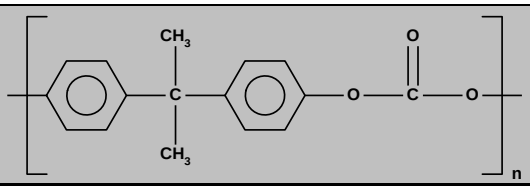
Acrylics – Amorphous/engineering

PMMA – Poly (methyl methacrylate) Hard and brittle	
Poly (methyl acrylate) Soft and rubbery	

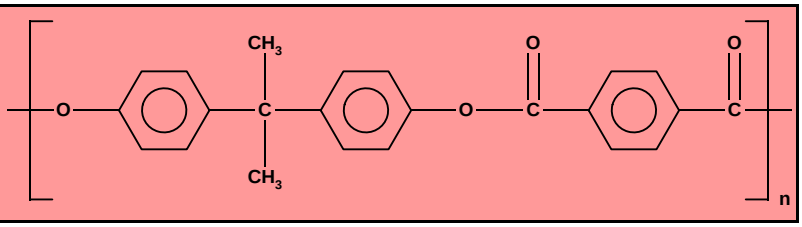
Polyphenylenes – Amorphous/engineering

PPE – Polyphenyl ether	
PPO – Polyphenylene oxide Not strictly an oxide but actually an ether.	

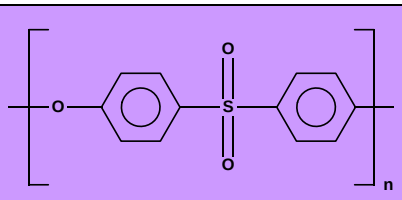
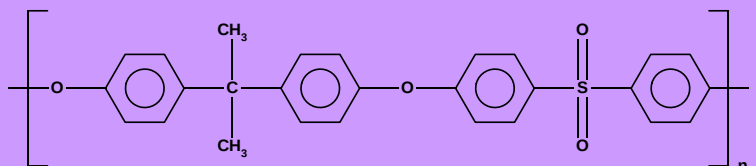
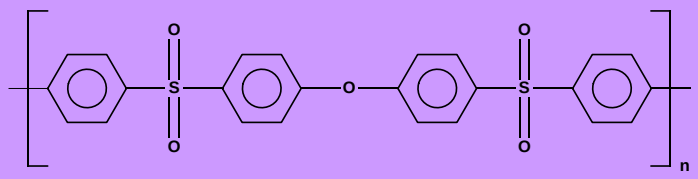
Polycarbonates – Amorphous/engineering

PC – Polycarbonate	

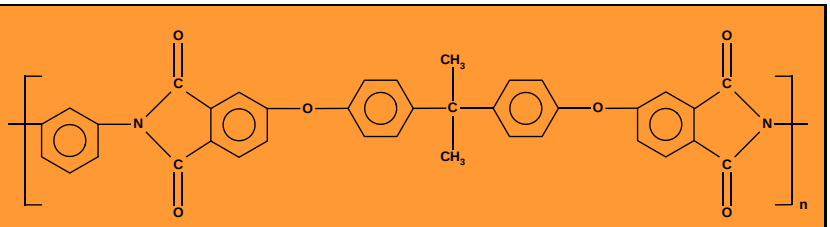
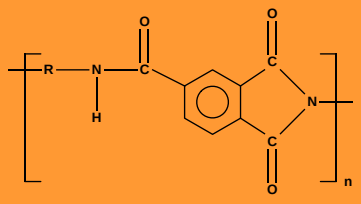
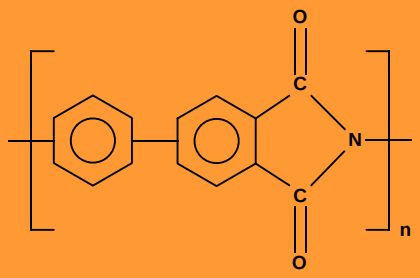
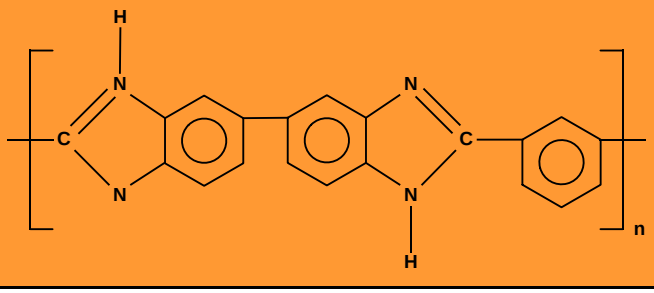
Polyarylates – Amorphous/engineering

PAR – Polyarylate	

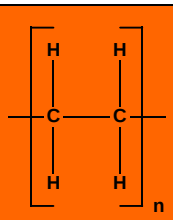
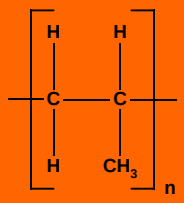
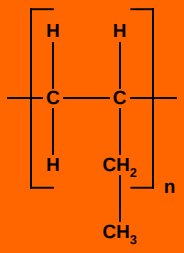
Polysulphones – Amorphous/performance

PES – Polyethersulphone: The general structure of the Polysulphones:	
PSU – Polysulphone	
PPSU – Polyphenylsulphone	

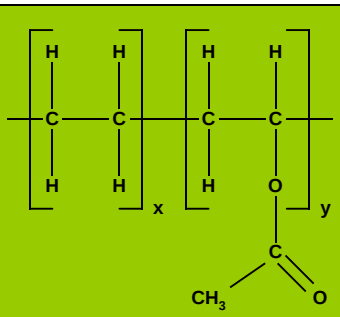
Polyimides – Amorphous/performance

PEI – Polyetherimide	
PAI – Polyamideimide	
PI – Polyimide	
PBI – Polybenzimideazole	

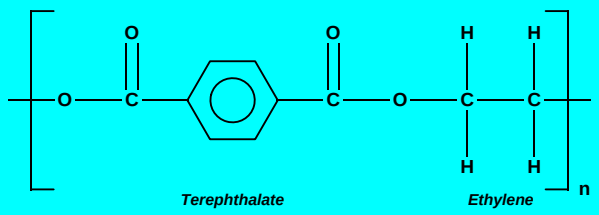
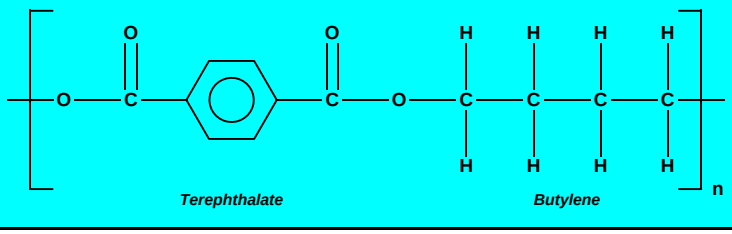
Polyolefins – Crystalline/commodity

PE – Polyethylene	
PP – Polypropylene	
PB – Polybutylene This is more accurately a crystalline engineering polymer but belongs to the polyolefin family and is presented here for completeness.	

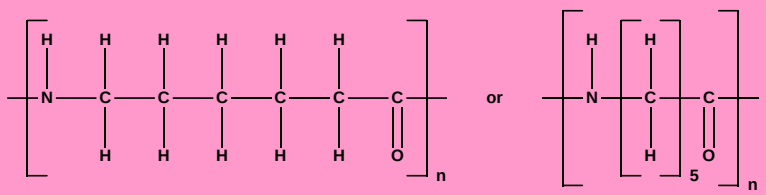
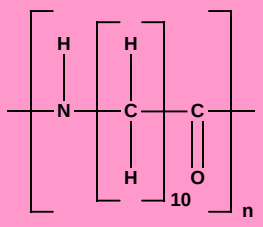
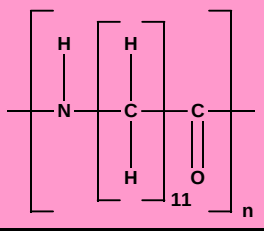
Vinyl acetate – Crystalline/commodity

EVA – Ethylene vinyl acetate. Random copolymer.	

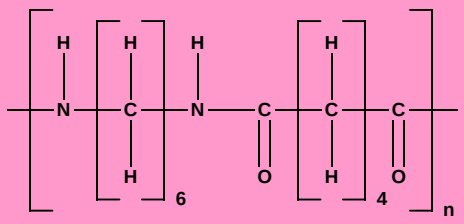
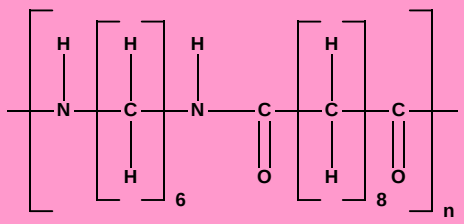
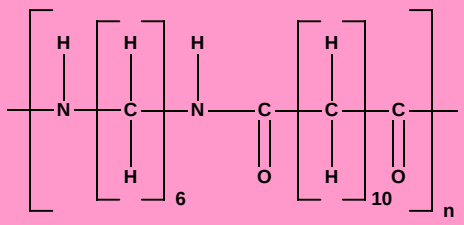
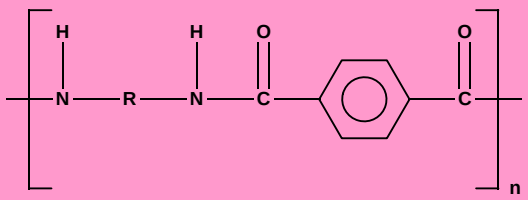
Polyesters – Crystalline/engineering

PET – Polyethylene terephthalate	
PBT – Polybutylene terephthalate	

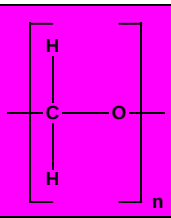
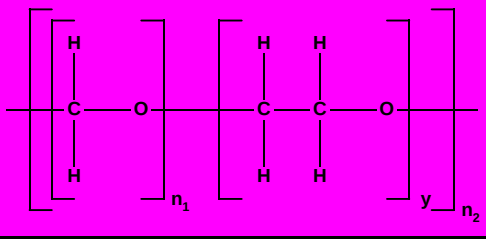
Polyamides – Crystalline/engineering

Homopolymers	
PA 6 – Polyamide 6 (Nylon 6) There are 5 repeating CH_2 elements but there are a total of 6 carbon atoms in the monomer.	
PA 11 – Polyamide 11 (Nylon 11)	
PA 12 – Polyamide 12 (Nylon12)	

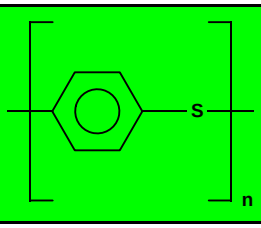
Polyamides – Crystalline/engineering

Copolymers	
PA 6/6 – Polyamide 6/6 (Nylon 6/6) 6 carbons in copolymer chain.	
PA 6/10 – Polyamide 6/10 (Nylon 6/10) 10 carbons in copolymer chain.	
PA 6/12 – Polyamide 6/12 (Nylon6/12) 12 carbons in copolymer chain.	
PPA – Polyphthalamide (PA 6/3/T)	

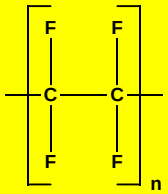
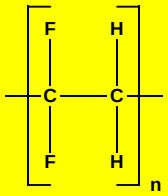
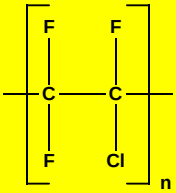
Polyoxymethylenes – Crystalline/performance

POM – Polyoxymethylene Acetal copolymer	
POM – Polyoxymethylene Acetal homopolymer. Where n_1 and n_2 are statistically distributed in the copolymer.	

Polysulphides – Crystalline/performance

PPS – Polyphenylene sulphide	

Fluoropolymers – Crystalline/performance

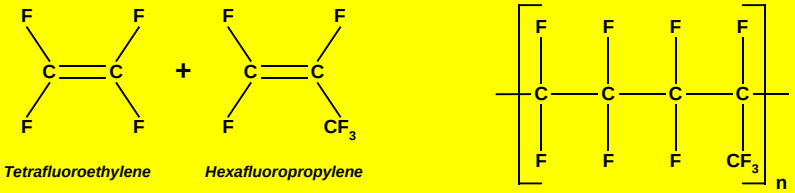
Homopolymers	
PTFE – Polytetrafluoroethylene	
PVDF – Polyvinylidene fluoride	
PCTFE – Polychlorotrifluoro-ethylene	

Fluoropolymers – Crystalline/performance

Copolymers

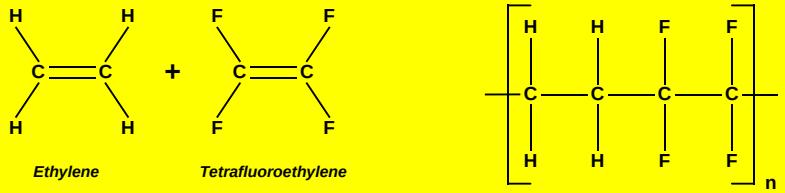
FEP – Fluorinated ethylene propylene

Copolymer of tetrafluoroethylene and hexafluoropropylene



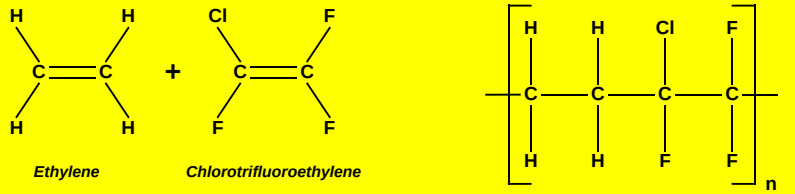
ETFE – Ethylene-Tetrafluoroethylene copolymer

Copolymer of ethylene and tetrafluoroethylene

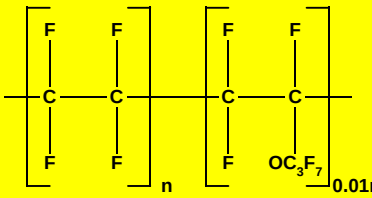


ECTFE – Polyethylene chlorotrifluoroethylene

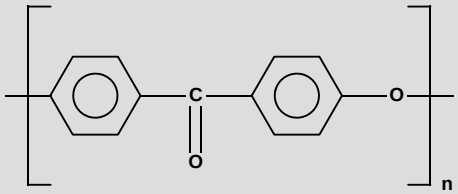
(Ethylene-Chlorotrifluorethylene copolymer)



PFA – Perfluoroalkoxy



Polyether ketones – Crystalline/performance

PEK – Polyetherketone The general structure of the polyether ketones:	
PEEK – Polyether ether ketone B