



Plastics Topics – Polymer structures

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Plastics Topics – Polymer structures

Contents:

Polymers	3
1. Polymers versus plastics	3
2. Drawing the structures	3
3. The benzene ring	4
4. Where do we start?	5
5. Homopolymers and copolymers	5
6. Isotactic, atactic and syndiotactic	6
The Periodic Table of Thermoplastics	7
Styrenes – Amorphous/commodity	9
Homopolymers	9
PS – Polystyrene	9
Atactic PS	9
Syndiotactic PS	9
High impact PS	9
Styrenes – Amorphous/commodity	10
Copolymers	10
SAN – Styrene acrylonitrile copolymer	10
SB – Styrene butadiene copolymer	10
ABS – Acrylonitrile butadiene styrene copolymer	10
SBS – Styrene butadiene styrene copolymer	10
Acrylonitrile	10
Vinyls – Amorphous/commodity	11
PVC – Polyvinyl chloride	11
PVDC – Polyvinylidene chloride	11
Acrylics – Amorphous/engineering	12
PMMA – Poly (methyl methacrylate)	12
Poly (methyl acrylate)	12
Polyphenylenes – Amorphous/engineering	12
PPE – Polyphenyl ether	12
PPO – Polyphenylene oxide	12
Polycarbonates – Amorphous/engineering	12
PC – Polycarbonate	12
Polyarylates – Amorphous/engineering	12
PAR – Polyarylate	12
Polysulphones – Amorphous/performance	13
PES – Polyethersulphone:	13
PSU – Polysulphone	13
PPSU – Polyphenylsulphone	13
Polyimides – Amorphous/performance	14
PEI – Polyetherimide	14
PAI – Polyamideimide	14

Plastics Topics – Polymer structures

PI – Polyimide	14
PBI – Polybenzimidazole	14
Polyolefins – Crystalline/commodity	15
PE – Polyethylene.....	15
PP – Polypropylene	15
PB – Polybutylene.....	15
Vinyl acetate – Crystalline/commodity	15
EVA – Ethylene vinyl acetate.....	15
Polyesters – Crystalline/engineering	16
PET – Polyethylene terephthalate	16
PBT – Polybutylene terephthalate	16
Polyamides – Crystalline/engineering	16
Homopolymers.....	16
PA 6 – Polyamide 6 (Nylon 6).....	16
PA 11 – Polyamide 11 (Nylon 11).....	16
PA 12 – Polyamide 12 (Nylon12).....	16
Polyamides – Crystalline/engineering	17
Copolymers.....	17
PA 6/6 – Polyamide 6/6 (Nylon 6/6).....	17
PA 6/10 – Polyamide 6/10 (Nylon 6/10)	17
PA 6/12 – Polyamide 6/12 (Nylon6/12)	17
PPA – Polyphthalamide (PA 6/3/T).....	17
Polyoxymethylenes – Crystalline/performance	18
POM – Polyoxymethylene	18
POM – Polyoxymethylene	18
Polysulphides – Crystalline/performance	18
PPS – Polyphenylene sulphide.....	18
Fluoropolymers – Crystalline/performance	19
Homopolymers.....	19
PTFE – Polytetrafluoroethylene.....	19
PVDF – Polyvinylidene fluoride	19
PCTFE – Polychlorotrifluoro-ethylene	19
Fluoropolymers – Crystalline/performance	20
Copolymers.....	20
FEP – Fluorinated ethylene propylene	20
ETFE – Ethylene-Tetrafluoroethylene copolymer.....	20
ECTFE – Polyethylene chlorotrifluoroethylene	20
PFA – Perfluoroalkoxy	20
Polyether ketones – Crystalline/performance	21
PEK – Polyetherketone.....	21
PEEK – Polyether ether ketone B.....	21

Plastics Topics – Polymer structures

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:

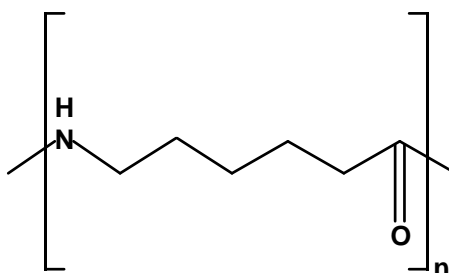


Figure 1: PA 6

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:

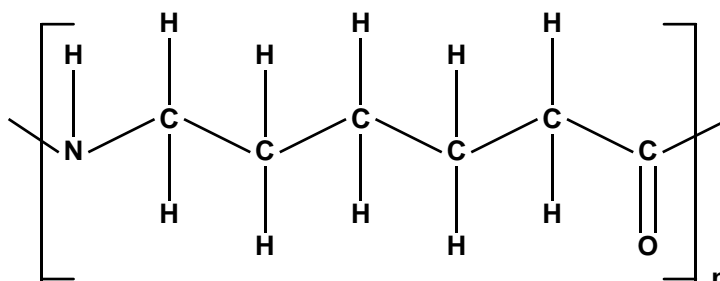


Figure 2: PA 6 – alternative representation 1

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

It is also possible to draw this same structure as:

Plastics Topics – Polymer structures

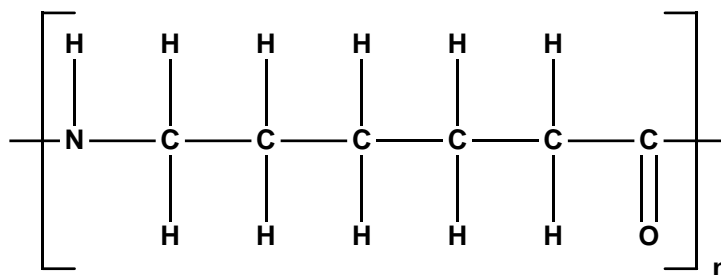


Figure 3: PA 6 – alternative representation 2

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 CH₂ features can be shortened to give the representation:

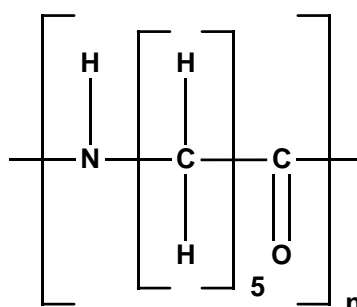


Figure 4: PA 6 – alternative representation 3

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

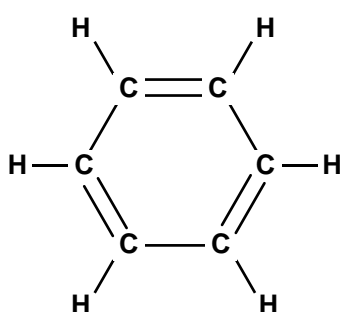


Figure 5: The 'classic' structure of the benzene ring

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:

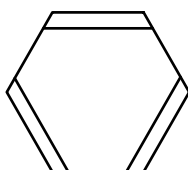


Figure 6: Short form of the classic structure

Plastics Topics – Polymer structures

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:

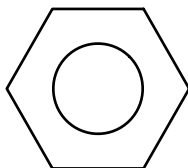


Figure 7: Closer to reality?

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:

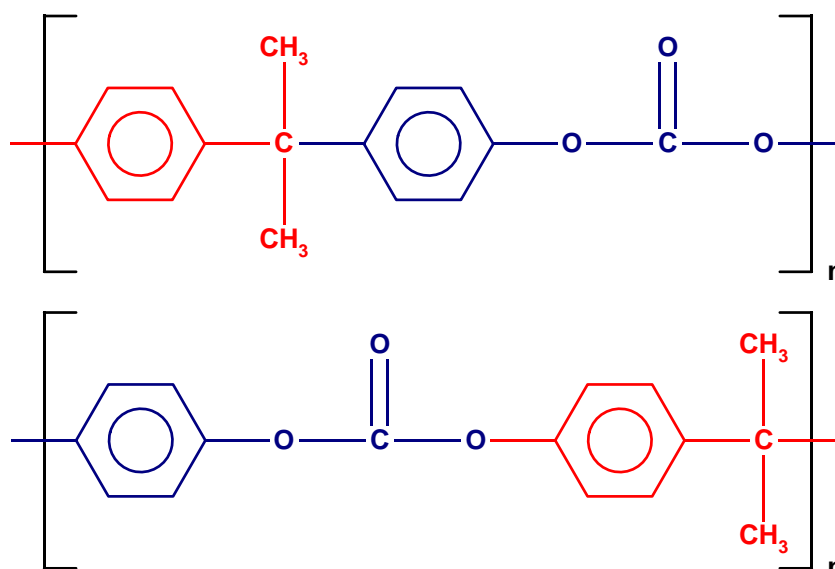


Figure 8: Two views of Polycarbonate

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:



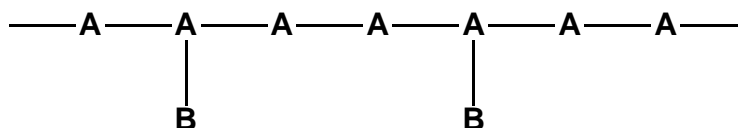
Copolymers consist of two different monomers (A and B) that are alternated when joined together to form the long chain of the polymer molecule:



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:

Plastics Topics – Polymer structures



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

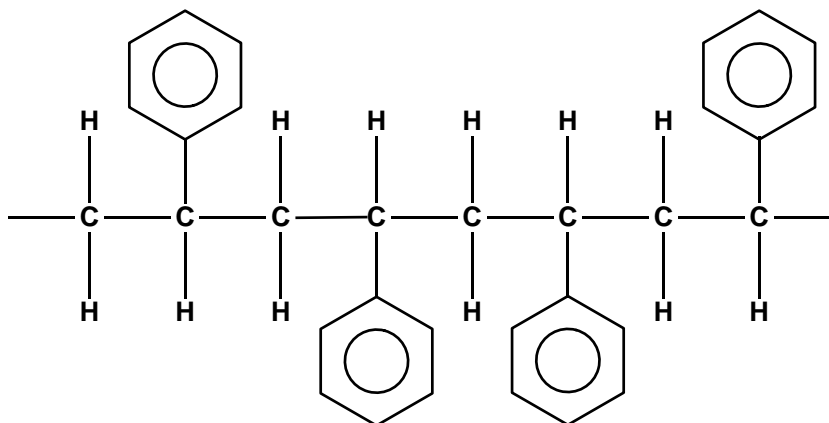


Figure 9: Atactic PS – irregular structure and cannot pack to form crystals

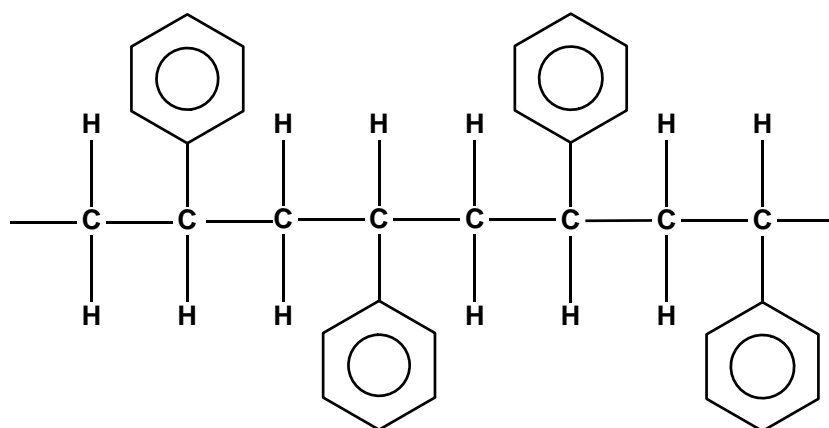


Figure 10: Syndiotactic PS – regular structure and can pack to form crystals

Where the forms vary significantly then this will be indicated.

Plastics Topics – Polymer structures

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.

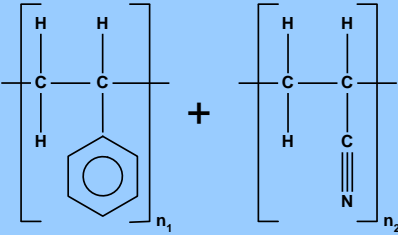
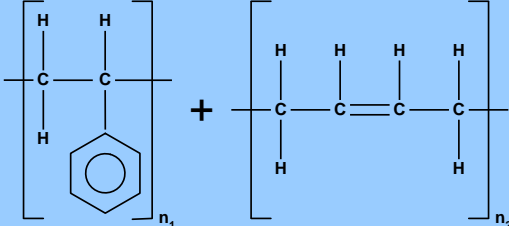
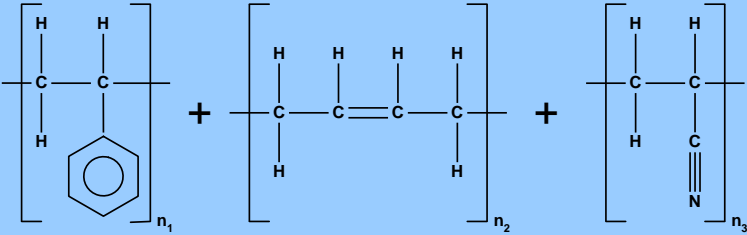
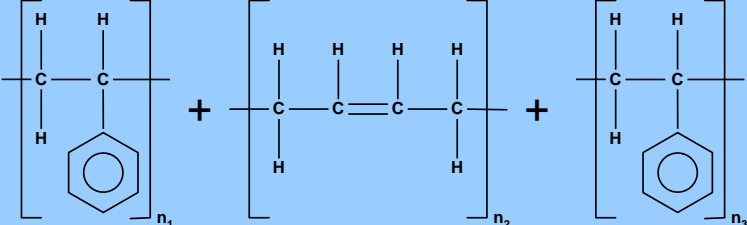
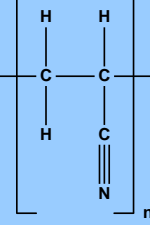
Plastics Topics – Polymer structures

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.	<p style="text-align: center;">Polystyrene Polybutadiene</p>

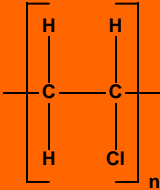
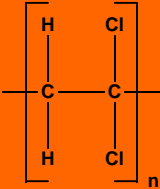
Plastics Topics – Polymer structures

Styrenes – Amorphous/commodity

Copolymers	
SAN – Styrene acrylonitrile copolymer	 <p>The diagram shows the chemical structures of Polystyrene and Acrylonitrile. Polystyrene is represented as a chain of carbon atoms with hydrogen atoms and a phenyl ring attached. Acrylonitrile is represented as a chain of carbon atoms with hydrogen atoms and a cyano group (C≡N) attached. The structures are shown with their respective subscripts n_1 and n_2.</p> <p>Polystyrene Acrylonitrile</p>
SB – Styrene butadiene copolymer	 <p>The diagram shows the chemical structures of Polystyrene and Polybutadiene. Polystyrene is represented as a chain of carbon atoms with hydrogen atoms and a phenyl ring attached. Polybutadiene is represented as a chain of carbon atoms with hydrogen atoms and a double bond between two of the carbons. The structures are shown with their respective subscripts n_1 and n_2.</p> <p>Polystyrene Polybutadiene</p>
ABS – Acrylonitrile butadiene styrene copolymer	 <p>The diagram shows the chemical structures of Polystyrene, Polybutadiene, and Acrylonitrile. Polystyrene is represented as a chain of carbon atoms with hydrogen atoms and a phenyl ring attached. Polybutadiene is represented as a chain of carbon atoms with hydrogen atoms and a double bond between two of the carbons. Acrylonitrile is represented as a chain of carbon atoms with hydrogen atoms and a cyano group (C≡N) attached. The structures are shown with their respective subscripts n_1, n_2, and n_3.</p> <p>Polystyrene Polybutadiene Acrylonitrile</p>
SBS – Styrene butadiene styrene copolymer	 <p>The diagram shows the chemical structures of Polystyrene, Polybutadiene, and Polystyrene. Polystyrene is represented as a chain of carbon atoms with hydrogen atoms and a phenyl ring attached. Polybutadiene is represented as a chain of carbon atoms with hydrogen atoms and a double bond between two of the carbons. The structures are shown with their respective subscripts n_1, n_2, and n_3.</p> <p>Polystyrene Polybutadiene Polystyrene</p>
Acrylonitrile Mainly used as copolymers (with methyl acrylate or methyl methacrylate) or as part of styrene copolymers such as SAN or ABS.	 <p>The diagram shows the chemical structure of Acrylonitrile, represented as a chain of carbon atoms with hydrogen atoms and a cyano group (C≡N) attached. The structure is shown with its subscript n.</p>

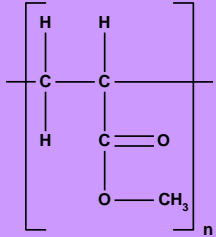
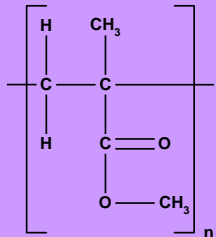
Plastics Topics – Polymer structures

Vinyls – Amorphous/commodity

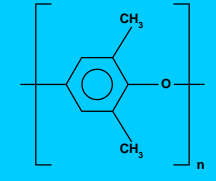
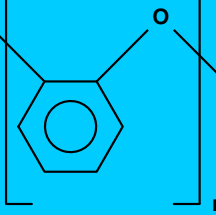
<p>PVC – Polyvinyl chloride</p> <p>Available in plasticized and unplasticized formats when compounded.</p> <p>Also available as cross-linked (PVC-UX) to form a more rigid matrix.</p>	 <p>The diagram shows the repeating unit of Polyvinyl chloride (PVC) enclosed in large square brackets with a subscript 'n'. Inside the brackets, two carbon atoms are connected by a horizontal line. The left carbon atom is bonded to two hydrogen atoms (H) above and below it. The right carbon atom is bonded to a hydrogen atom (H) above it and a chlorine atom (Cl) below it. Horizontal lines extend from the left and right sides of the carbon atoms, indicating the continuation of the polymer chain.</p>
<p>PVDC – Polyvinylidene chloride</p>	 <p>The diagram shows the repeating unit of Polyvinylidene chloride (PVDC) enclosed in large square brackets with a subscript 'n'. Inside the brackets, two carbon atoms are connected by a horizontal line. The left carbon atom is bonded to two hydrogen atoms (H) above and below it. The right carbon atom is bonded to two chlorine atoms (Cl) above and below it. Horizontal lines extend from the left and right sides of the carbon atoms, indicating the continuation of the polymer chain.</p>

Plastics Topics – Polymer structures

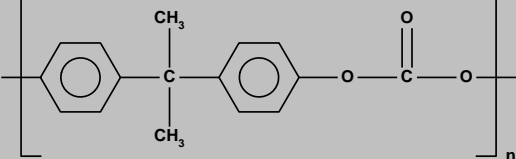
Acrylics – Amorphous/engineering

<p>PMMA – Poly (methyl methacrylate) Hard and brittle</p>	
<p>Poly (methyl acrylate) Soft and rubbery</p>	

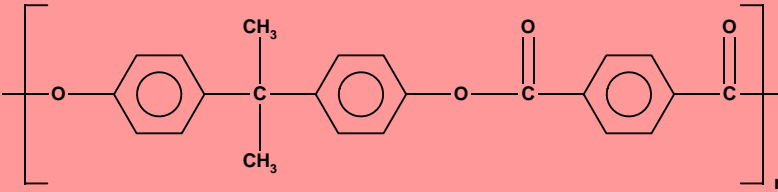
Polyphenylenes – Amorphous/engineering

<p>PPE – Polyphenyl ether</p>	
<p>PPO – Polyphenylene oxide Not strictly an oxide but actually an ether.</p>	

Polycarbonates – Amorphous/engineering

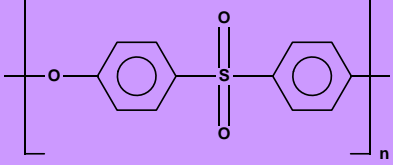
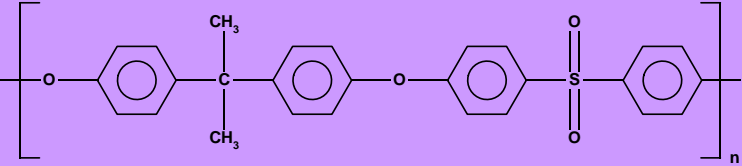
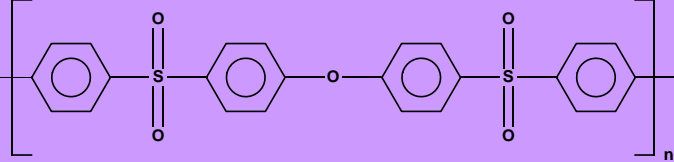
<p>PC – Polycarbonate</p>	
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Polyarylates – Amorphous/engineering

<p>PAR – Polyarylate</p>	
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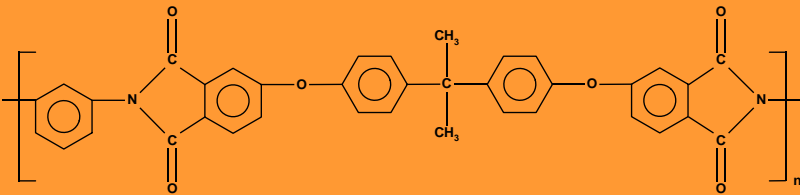
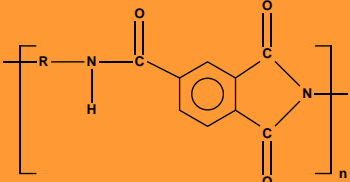
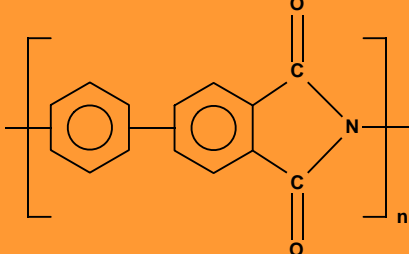
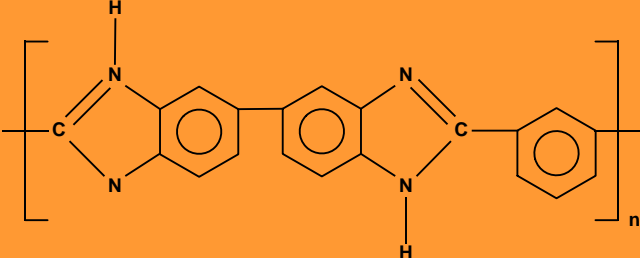
Plastics Topics – Polymer structures

Polysulphones – Amorphous/performance

<p>PES – Polyethersulphone: The general structure of the Polysulphones:</p>	 <p>The diagram shows the repeating unit of Polyethersulphone (PES) enclosed in large square brackets with a subscript 'n'. The unit consists of an oxygen atom (O) connected to a benzene ring, which is then connected to a sulfur atom (S) double-bonded to two oxygen atoms (O). This sulfur atom is further connected to another benzene ring, which is finally connected back to an oxygen atom, completing the chain.</p>
<p>PSU – Polysulphone</p>	 <p>The diagram shows the repeating unit of Polysulfone (PSU) enclosed in large square brackets with a subscript 'n'. The unit consists of a benzene ring connected to a carbon atom (C) which is bonded to two methyl groups (CH₃). This carbon atom is also connected to another benzene ring, which is then connected to an oxygen atom (O). This oxygen atom is connected to a third benzene ring, which is then connected to a sulfur atom (S) double-bonded to two oxygen atoms (O). This sulfur atom is finally connected to a fourth benzene ring, which is connected back to the first oxygen atom, completing the chain.</p>
<p>PPSU – Polyphenylsulphone</p>	 <p>The diagram shows the repeating unit of Polyphenylsulfone (PPSU) enclosed in large square brackets with a subscript 'n'. The unit consists of a benzene ring connected to a sulfur atom (S) double-bonded to two oxygen atoms (O). This sulfur atom is connected to a second benzene ring, which is then connected to an oxygen atom (O). This oxygen atom is connected to a third benzene ring, which is then connected to another sulfur atom (S) double-bonded to two oxygen atoms (O). This second sulfur atom is finally connected to a fourth benzene ring, which is connected back to the first sulfur atom, completing the chain.</p>

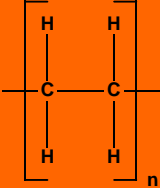
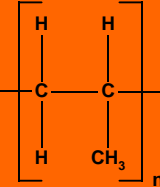
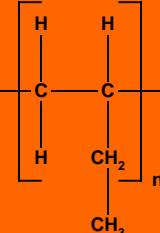
Plastics Topics – Polymer structures

Polyimides – Amorphous/performance

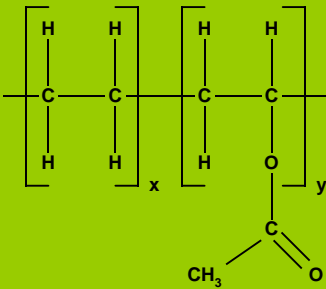
PEI – Polyetherimide	 <p>The structure shows a repeating unit of a polyetherimide. It consists of two benzimidazole rings (each with two carbonyl groups) connected to a central ether linkage. The ether linkage is part of a chain containing a central carbon atom bonded to two methyl groups (CH₃) and two phenyl rings. The entire unit is enclosed in brackets with a subscript 'n'.</p>
PAI – Polyamideimide	 <p>The structure shows a repeating unit of a polyamideimide. It features a benzimidazole ring with two carbonyl groups. One of the carbonyl groups is part of an amide linkage (-NH-CO-) where the nitrogen is bonded to an 'R' group. The other carbonyl group is part of the imide ring. The unit is enclosed in brackets with a subscript 'n'.</p>
PI – Polyimide	 <p>The structure shows a repeating unit of a polyimide. It consists of a benzimidazole ring with two carbonyl groups, where one carbonyl group is part of the imide ring and the other is part of the polymer backbone. The unit is enclosed in brackets with a subscript 'n'.</p>
PBI – Polybenzimidazole	 <p>The structure shows a repeating unit of a polybenzimidazole. It consists of two benzimidazole rings connected at their 2-positions. Each benzimidazole ring has a hydrogen atom on its nitrogen. The units are enclosed in brackets with a subscript 'n'.</p>

Plastics Topics – Polymer structures

Polyolefins – Crystalline/commodity

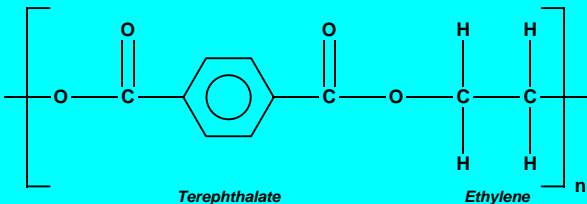
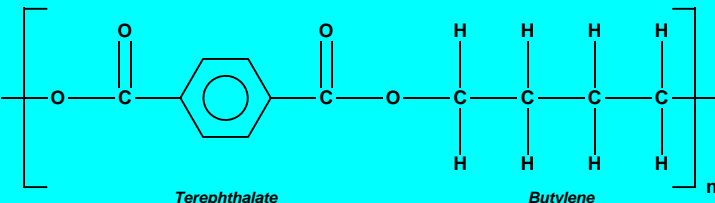
PE – Polyethylene	
PP – Polypropylene	
PB – Polybutylene This is more accurately a crystalline engineering polymer but belongs to the polyolefin family and is presented here for completeness.	

Vinyl acetate – Crystalline/commodity

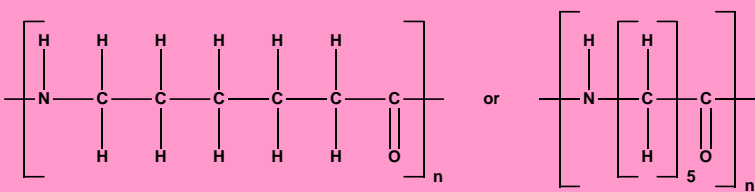
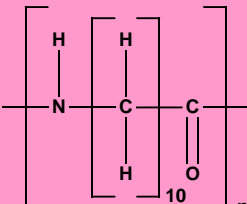
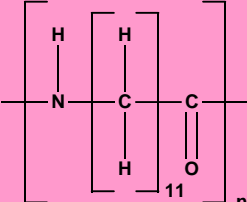
EVA – Ethylene vinyl acetate. Random copolymer.	
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Plastics Topics – Polymer structures

Polyesters – Crystalline/engineering

<p>PET – Polyethylene terephthalate</p>	 <p>The diagram shows the repeating unit of PET. It consists of a terephthalate group (a benzene ring with carbonyl groups at the 1 and 4 positions) linked via ester bonds to an ethylene group (two carbon atoms with four hydrogen atoms). The entire unit is enclosed in brackets with a subscript 'n'.</p>
<p>PBT – Polybutylene terephthalate</p>	 <p>The diagram shows the repeating unit of PBT. It consists of a terephthalate group (a benzene ring with carbonyl groups at the 1 and 4 positions) linked via ester bonds to a butylene group (four carbon atoms with eight hydrogen atoms). The entire unit is enclosed in brackets with a subscript 'n'.</p>

Polyamides – Crystalline/engineering

<p>Homopolymers</p>	
<p>PA 6 – Polyamide 6 (Nylon 6)</p> <p>There are 5 repeating CH₂ elements but there are a total of 6 carbon atoms in the monomer.</p>	 <p>The diagram shows two representations of the PA 6 repeating unit. The first is a full structural formula showing a nitrogen atom bonded to a hydrogen atom, followed by a chain of six carbon atoms, with the last carbon being a carbonyl group. The second representation is a simplified version where the five methylene groups are grouped together in a bracket with a subscript '5', and the carbonyl group is shown as a carbon atom double-bonded to an oxygen atom. Both are enclosed in brackets with a subscript 'n'.</p>
<p>PA 11 – Polyamide 11 (Nylon 11)</p>	 <p>The diagram shows the PA 11 repeating unit. It consists of a nitrogen atom bonded to a hydrogen atom, followed by a chain of ten carbon atoms, with the last carbon being a carbonyl group. The ten methylene groups are grouped together in a bracket with a subscript '10'. The entire unit is enclosed in brackets with a subscript 'n'.</p>
<p>PA 12 – Polyamide 12 (Nylon 12)</p>	 <p>The diagram shows the PA 12 repeating unit. It consists of a nitrogen atom bonded to a hydrogen atom, followed by a chain of eleven carbon atoms, with the last carbon being a carbonyl group. The eleven methylene groups are grouped together in a bracket with a subscript '11'. The entire unit is enclosed in brackets with a subscript 'n'.</p>

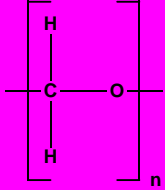
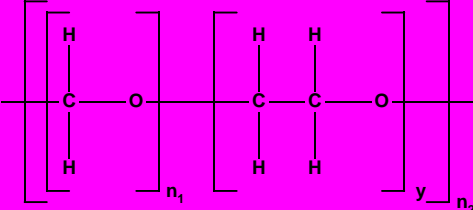
Plastics Topics – Polymer structures

Polyamides – Crystalline/engineering

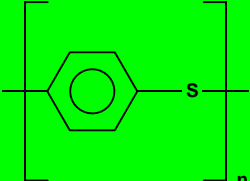
Copolymers	
<p>PA 6/6 – Polyamide 6/6 (Nylon 6/6) 6 carbons in copolymer chain.</p>	<p>The diagram shows the repeating unit of PA 6/6. It consists of a nitrogen atom bonded to two hydrogen atoms, followed by a methylene group (CH₂) enclosed in brackets with a subscript 6, then another nitrogen atom bonded to two hydrogen atoms. This is followed by a carbonyl group (C=O), a methylene group (CH₂) enclosed in brackets with a subscript 4, and another carbonyl group (C=O). The entire unit is enclosed in large brackets with a subscript n.</p>
<p>PA 6/10 – Polyamide 6/10 (Nylon 6/10) 10 carbons in copolymer chain.</p>	<p>The diagram shows the repeating unit of PA 6/10. It consists of a nitrogen atom bonded to two hydrogen atoms, followed by a methylene group (CH₂) enclosed in brackets with a subscript 6, then another nitrogen atom bonded to two hydrogen atoms. This is followed by a carbonyl group (C=O), a methylene group (CH₂) enclosed in brackets with a subscript 8, and another carbonyl group (C=O). The entire unit is enclosed in large brackets with a subscript n.</p>
<p>PA 6/12 – Polyamide 6/12 (Nylon 6/12) 12 carbons in copolymer chain.</p>	<p>The diagram shows the repeating unit of PA 6/12. It consists of a nitrogen atom bonded to two hydrogen atoms, followed by a methylene group (CH₂) enclosed in brackets with a subscript 6, then another nitrogen atom bonded to two hydrogen atoms. This is followed by a carbonyl group (C=O), a methylene group (CH₂) enclosed in brackets with a subscript 10, and another carbonyl group (C=O). The entire unit is enclosed in large brackets with a subscript n.</p>
<p>PPA – Polyphthalamide (PA 6/3/T)</p>	<p>The diagram shows the repeating unit of PPA. It consists of a nitrogen atom bonded to two hydrogen atoms, followed by an 'R' group, then another nitrogen atom bonded to two hydrogen atoms. This is followed by a carbonyl group (C=O) bonded to a benzene ring, which is in turn bonded to another carbonyl group (C=O). The entire unit is enclosed in large brackets with a subscript n.</p>

Plastics Topics – Polymer structures

Polyoxymethylenes – Crystalline/performance

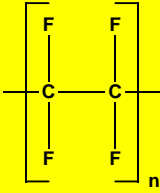
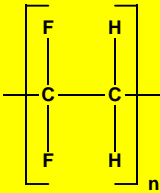
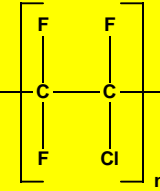
<p>POM – Polyoxymethylene Acetal copolymer</p>	 $\left[\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{O}- \\ \\ \text{H} \end{array} \right]_n$
<p>POM – Polyoxymethylene Acetal homopolymer. Where n_1 and n_2 are statistically distributed in the copolymer.</p>	 $\left[\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{O}- \\ \\ \text{H} \end{array} \right]_{n_1} \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\text{O}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_{n_2}$

Polysulphides – Crystalline/performance

<p>PPS – Polyphenylene sulphide</p>	 $\left[\text{C}_6\text{H}_4-\text{S} \right]_n$
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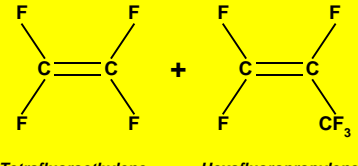
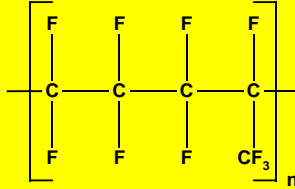
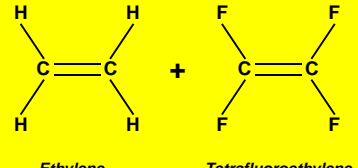
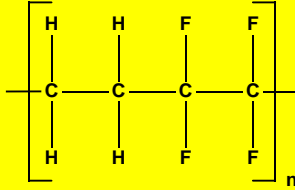
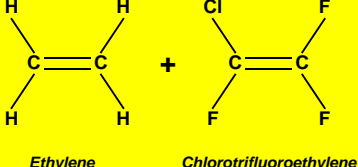
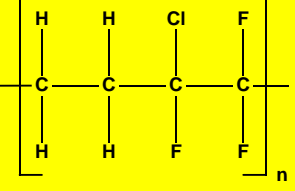
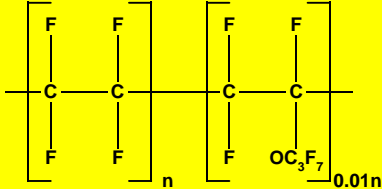
Plastics Topics – Polymer structures

Fluoropolymers – Crystalline/performance

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

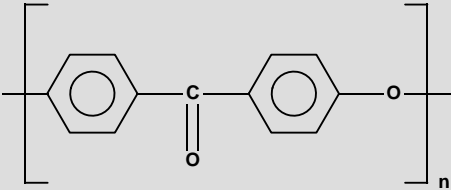
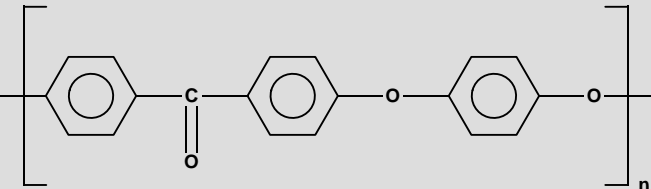
Plastics Topics – Polymer structures

Fluoropolymers – Crystalline/performance

Copolymers		
<p>FEP – Fluorinated ethylene propylene Copolymer of tetrafluoroethylene and hexafluoropropylene</p>	 <p><i>Tetrafluoroethylene</i> <i>Hexafluoropropylene</i></p>	
<p>ETFE – Ethylene-Tetrafluoroethylene copolymer Copolymer of ethylene and tetrafluoroethylene</p>	 <p><i>Ethylene</i> <i>Tetrafluoroethylene</i></p>	
<p>ECTFE – Polyethylene chlorotrifluoroethylene (Ethylene-Chlorotrifluoroethylene copolymer)</p>	 <p><i>Ethylene</i> <i>Chlorotrifluoroethylene</i></p>	
<p>PFA – Perfluoroalkoxy</p>		

Plastics Topics – Polymer structures

Polyether ketones – Crystalline/performance

<p>PEK – Polyetherketone The general structure of the polyether ketones:</p>	 <p>The diagram shows the repeating unit of a polyetherketone (PEK) polymer. It consists of a benzene ring connected to a carbonyl group (C=O), which is further connected to another benzene ring, and finally to an oxygen atom. The entire unit is enclosed in large square brackets with a subscript 'n' at the bottom right, indicating the polymer chain length.</p>
<p>PEEK – Polyether ether ketone B</p>	 <p>The diagram shows the repeating unit of a polyether ether ketone (PEEK) polymer. It consists of a benzene ring connected to a carbonyl group (C=O), which is further connected to a benzene ring, an oxygen atom, another benzene ring, and a second oxygen atom. The entire unit is enclosed in large square brackets with a subscript 'n' at the bottom right, indicating the polymer chain length.</p>