I find searching for polymeric structures difficult and I get results I don't fully understand. Can you explain how polymeric structures are defined so I can tailor my searches to be more effective?

Polymers and extended structures are defined within the CSD with the use of the polymeric bond, drawn as a zigzag line in the 2D diagram. When a substructure search is performed, the search will be conducted by attempting to find a match between the sketched atoms and the atoms which make up the smallest (crystallographic) repeating unit of each structure in the database, as illustrated in the 2D diagram of the entry. The smallest repeating unit of a structure in the database is very often the asymmetric unit as defined by the crystallographer, with the addition of polymeric bonds at the end points to fully define the structure. So, connections to atoms outside the smallest repeating unit are defined using a polymeric bond type in an attempt to overcome the problem of differently defined asymmetric units in related structures.

Therefore, if you are searching for any structure where, for example, the metal coordination sphere is completed by polymeric ligand atoms, or you have drawn an extensive substructural unit of an organic polymer (which may include atoms not in the smallest repeating unit) it is wise to make the bond type of the relevant bonds "ANY" or "POLYMERIC". Definition of the type of bond that extends the substructure from the smallest repeating unit as "single" for example, will lead to relevant structures being missed.

The following are some additional hints for searching for metal-coordination polymers structures or organic polymers.

Metal-coordination polymers

The ligands of metal-containing polymers are always fully defined, as is the complete metal coordination sphere. So:

- Draw any connections between the metal and the ligand atoms with a bond type "ANY". This will ensure that structures in which the coordination sphere is completed with polymeric bonds (i.e. atoms outside the smallest repeating unit) will be found.
- If you want to find polymeric structures containing a particular ligand, sketch the ligand and combine this search with a search for a polymeric bond type (between atoms of "ANY" type).
- If you are in doubt as to how the smallest repeating unit is defined for the types of structure you want to search for, start with the simplest substructure as possible – for example, if you are interested in finding Zn phosphate containing polymeric structures, firstly draw only the Zn atom coordinated to a phosphate ligand and combine it with a search for a polymeric bond. You can progressively narrow the search by adding further connectivity – this way you can be sure that you will not miss relevant structures.

An Example

Below is a diagram of the structure we want to find in the database:
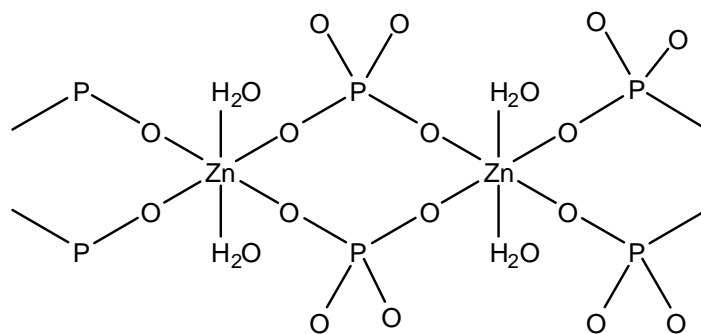
The structure is an extended structure – for clarity, only part of the structure is shown. In this example we are ignoring the issue of bond typing for the phosphate ligand and all P-O bonds are shown with a single line.

The smallest repeating unit may be defined within the CSD in one of two ways – both **maintain a full metal coordination environment and complete ligands** and these are shown below:
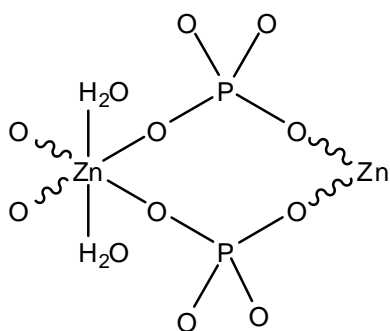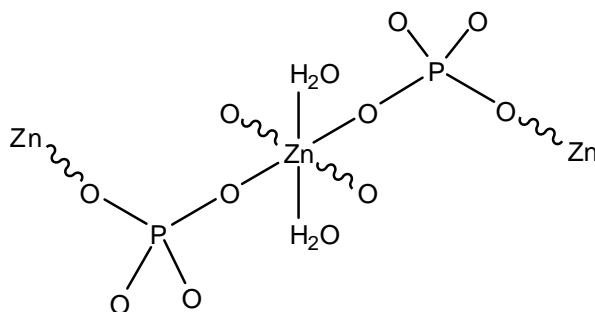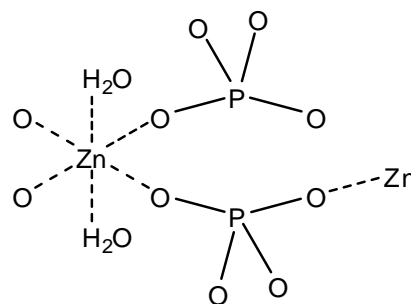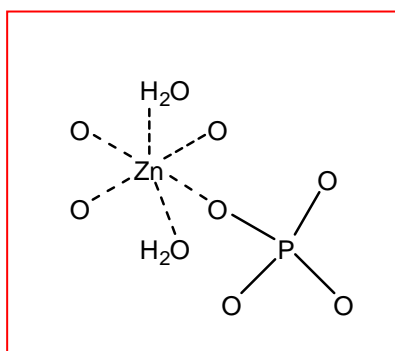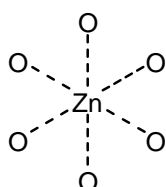

A   B
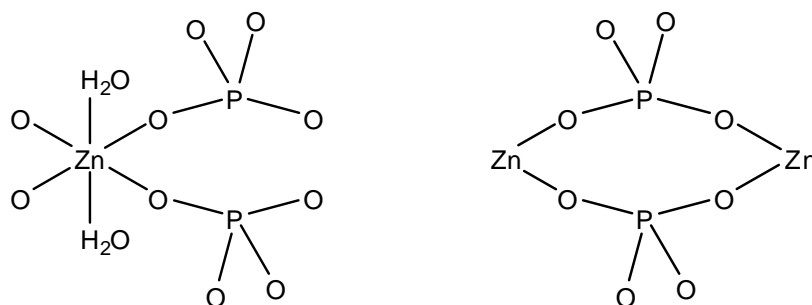
〜〜〜 Polymeric bond type

The following substructures, sketched in ConQuest, would find the target structure:

-------- "ANY" bond type

The substructure highlighted in red is a very "safe" search since it contains the full metal coordination sphere, a complete water ligand and a complete phosphate ligand and it does not extend the substructure beyond the smallest repeating unit. Note all connections between the metal and the ligands are made with bond type "ANY". This is to ensure that structures in which these connections are defined as "POLYMERIC" are found.

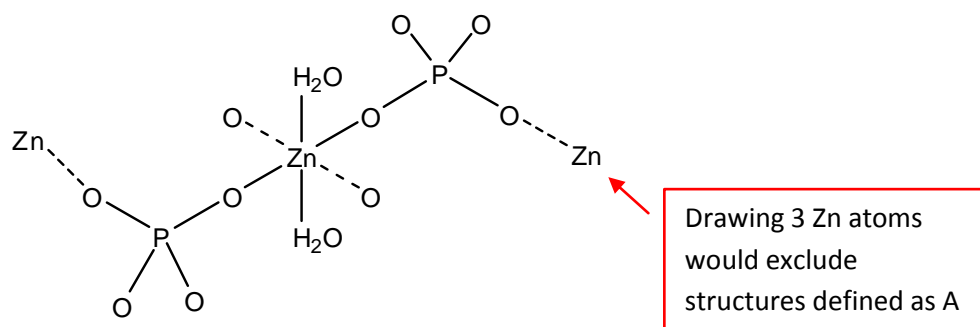The following are examples of substructures that **would not** find the target structure

In both the above structures, defining all Zn-O bonds as single bonds will cause the search to fail as some of these bonds are defined as "POLYMERIC" bonds in the target structure.

The following substructure search would **fail** to find the structure, if the structure has been defined as **B** (see above).
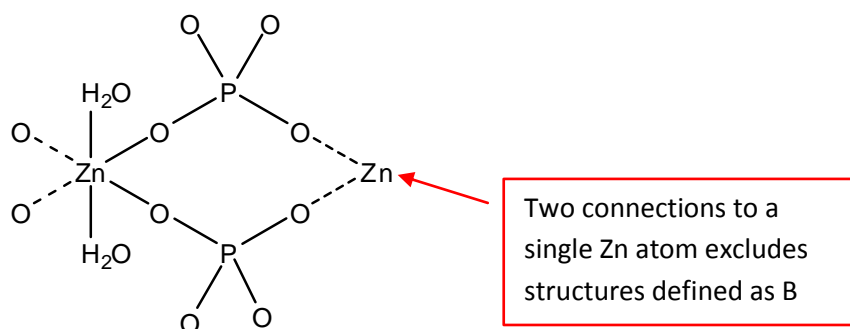
Two connections to a single Zn atom excludes structures defined as B

The following substructure search would **fail** to find the structure, if the structure has been defined as **A** (see above).

H_2O O   O

P

Zn

O   O   O

Zn   O

O   Zn

O   O

P

H_2O

O   O

Drawing 3 Zn atoms would exclude structures defined as A

Therefore to maximise your chances of finding relevant structures limit your substructure search to the metal's immediate coordination environment and one fully defined ligand of each type present – in the above example a phosphate and a water.

Organic polymers

As for the metal containing polymers, it is wise, when searching for organic polymeric structures, to search for the smallest possible chemical unit of the polymer of interest. If this results in too many hits, the above search can be refined by combining it with a search for some or all of the following:

- restricting the allowed elements,
- using the "ORGANIC POLYMER" flag found in the Chemical Class pane of the Name/ Class dialogue

If you want to search for an extended structural subunit, generate all hydrogens where appropriate and set all bond types to "ANY", or use "VARIABLE" bond types. By defining all bond types as "ANY" or "VARIABLE", you do not have to know, *a priori*, how the smallest repeating unit of the structure has been defined within the database. If there are areas of the structure for which you are confident of the bonding (*i.e.* the bonds are unlikely to be defined as polymeric) then the bond type can be specified in the usual way.