Question: Thermosetting polymers are cross-linked and so do not show a glass transition temperature in the same was as either thermoplastics or elastomers.

Answer: The statement is partially right.

To properly answer this question it is important in a first place to describe what a cross-linked polymer is, and then explain the difference between thermosets, thermoplastics and elastomers.  
In the end, the influence of the cross-linking on the glass temperature will be shown.

All the kinds polymers mentioned just above are made of very long molecules with a covalent bonding between their carbon atoms. When only secondary chemical bonds exist between these chains, like Van der Waals and hydrogen ones, the material is called a thermoplastic. Also, when heat is applied to the material, secondary bonds melt and chains are free to slip.

On the contrary, cross-linked chains are one of the characteristic properties of thermosetting polymer. These types of bonds are much stronger because they can be either covalent or ionic. They can be made chemically by mixing resin and a hardener agent which react together when heated; or by irradiation of a thermoplastic (figure1)[[1]](#footnote-2). The resulting polymer is called a thermoset and is usually described as a network material.

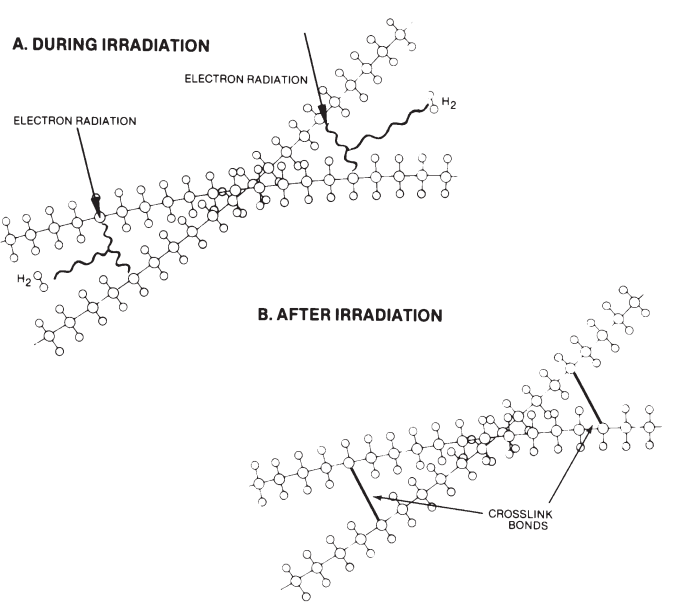


Figure1: Irradiation cross-linking

The third type of polymer exists: the elastomers. Considering the cross-linking property, they can be described as a mix between a thermoset and a thermoplastic. Indeed, they are cross-linked but they have very few of these bonds: only one every hundred or more monomer units[[2]](#footnote-3).

Now that the description of every material is done, the influence of that kind of bonding on the glass temperature is going to be discussed.

When a polymer is heated, it passes through different mechanical states. For a thermoplastic we can easily separate three of them: plastic, viscoelastic, and viscous (at high temperatures). The glass temperature, TG, is the temperature at which secondary bonds start to melt. As it has been said before thermoplastics do not have any covalent cross-linking between their chains, and above TG, without their secondary bonds, they are likely to slip on each other: the polymer is in his viscoelastic state. If the temperature continue rising, all the Van der Waals and hydrogen bonds melt and the material quickly become liquid.

If the elastomers are now considered: above TG their long carbon chains are still linked to each other by strong covalent cross-links which do not melt like secondary bonds. But as it has been explained before, the number of cross-links is very small and as a consequence chains still linked to each other are capable of elastics extensions of 300% or more[[3]](#footnote-4). The structure of the material cannot be destroyed but the mobility is not completely forbidden.

On the contrary, molecules in thermosetting polymers are not capable of any mobility. Indeed if a large amount of unit on the polymer chain is cross-linked to another chain, the covalent bonds form a very hard 3D network. Also, if the secondary bonds are melted above TG, molecules under stress simply cannot move because of the too large number of covalent bonding.

As a conclusion, it has just been proven that this statement is just wrong on small details. It is true that all thermosets are cross-linked polymers. But, as we said before, elastomers have also some of their chains linked but with a very low the density of these bonds. Second, every material has a glass temperature where its secondary bonds start to melt; but the mechanical comportment beyond this point is just different depending on the material. Indeed, if the polymer is highly cross linked like for thermoplastic, nothing happens above TG (and before decomposition). If it is an elastomer, the material is going to have a long rubbery state above TG and if it is a thermoplastic, it will quickly become liquid above TG.

1. www.r-scc.com/PDF/Tech-electronics.pdf, viewed Nov 11 2008 [↑](#footnote-ref-2)
2. Ashby, M. F., Jones D. R., (2005), *Engineering Materials 2*, Butterworth Heinemann, p. 269 [↑](#footnote-ref-3)
3. Ashby, M. F., Jones D. R., (2005), *Engineering Materials 2*, Butterworth Heinemann, p. 269 [↑](#footnote-ref-4)