100525 Quiz 7 Introduction to Polymers

1) We looked at Ziegler-Natta polymerization briefly.
   a) What two compounds would you mix to make a Ziegler-Natta catalyst system?
   b) Why does one of these include a transition metal?
   c) Is Ziegler-Natta polymerization carried out in the bulk or in solution?
   d) Why was there a problem with polymerization of propylene by free radical mechanisms?
   e) Why does Ziegler-Natta polymerization result in isotactic polypropylene?

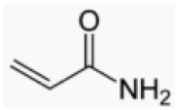
2) a) Name and draw the structure of the monomers used for ATRP polymerization in class.
   b,c) Explain how ATRP is a living polymerization, that is, give the mechanism for the extension of the lifetime of the free radical including chemical species involve in the synthesis done in class.
   d) In the ATRP reaction the reaction mixture turned first blue, then green then back to blue. Explain these color changes.
   e) Why was vitamin C added to the reaction mixture? Is this always necessary for an ATRP polymerization?

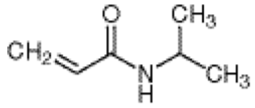
3) a) Describe the structure of ferrrocene.
   b) How is this structure modified by the addition of substitutent groups (such as Cl) on the pentadiene rings?
   c) Sketch the structure of a zirconia metallocene catalysts.
   d) Explain the mechanism of polymerization using this zirconia catalysts
   e) Are metallocenes heterogeneous or a homogeneous catalysts?

ANSWERS: 100525 Quiz 7 Introduction to Polymers

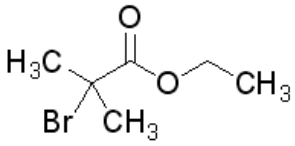
1) a) $TiCl_3$ and $Al(C_2H_5)_2Cl$ or $TiCl_4$ $Al(C_2H_5)_3$ or VCl_4 and $Al(C_2H_5)_2Cl$.
b) 6 bonding orbitals with only 5 filled leaves one for coordination with a vinyl bond. Transition metals have multiple oxidation states, this is why they are used as catalysts.
c) It is carried out in solution as described by the UBC web page, http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/UBCWassellExperiment%209.htm, although they do not give the solvent used. This is either p-xylene or dichlorobenzene at high temperature (135C).
d) Polypropylene can not propogate with a free radical mechanism because the methyl side group can hold a free radical more easily than the vinyl group.
e) The Cossee-Arlman mechanism is highly sterically restricted. The monmer only fits into the catalyst site in one orientation with respect to the growing chain.

2) a)

Monomer 1 Acrylamide 

Monomer 2 n-isopropylacrylamide 

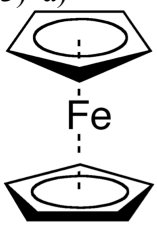
b,c) In ATRP an organohalide (RX) and a transition metal (Mt)/ligand complex (Lm) are in equilibrium with a radical R•. The radical initiator reacts with a monomer to produce a propagating polymeric species. The halide/radical equilibrium serves to protect the radical from recombination since the radical is only present a small amount of the time in an unprotected, propagating form and spends most of the time protected by the organohalide group.
In class the organohalide was



Ethyl Bromo isobutyrate
The transition metal came from
Cupric Bromide Cu(II)Br
The ligand was

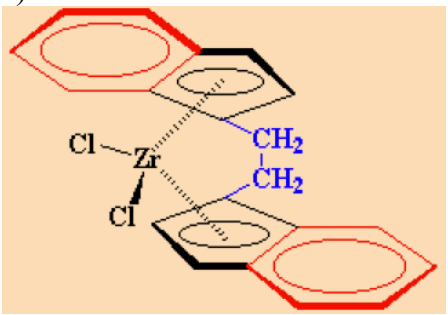
PMDETA N,n,n',n',n-Pentamethyldiethylenetriamine
d) When PMDTA is added the solution turns blue because the Cu(II) ligand complex is formed. With addition of ascorbic acid the solution turned dark blue/black/ or green depending on the amount of reducing agent. This is conversion of Cu^{+2} to Cu^{+} with formation of the protected free radical in the activated state. The color is determined by the equilibrium between activated and deactivated state. Oxygen in air gradually dissolves in the solution from the air and oxidizes Cu^{+} to Cu^{+2} causing the color to return towards blue.
e) Vitamin C is ascorbic acid see question d. It is a reducing agent and it removes dissolved oxygen from the water. It would not have been necessary if the water was degassed and if the reaction were run under an inert gas (dry Nitrogen).

3) a)

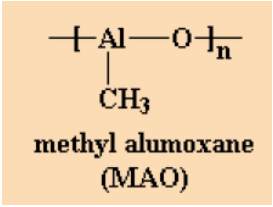


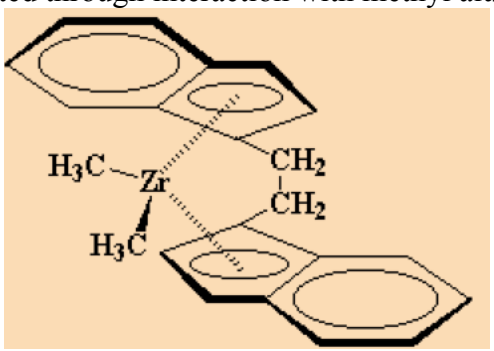
b) The two pentadiene rings will tilt with respect to each other allowing access to the caged metal atom for approaching chemical species.

c)

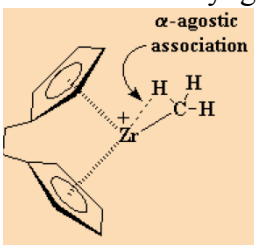


d) The molecule in part c is methylated through interaction with methyl alumoxane:

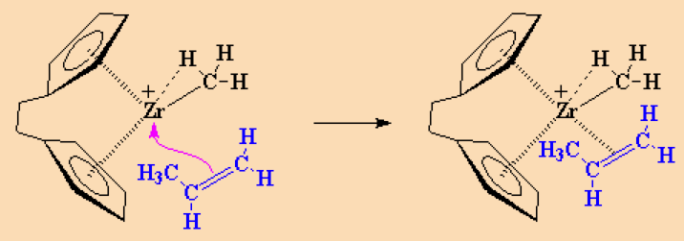




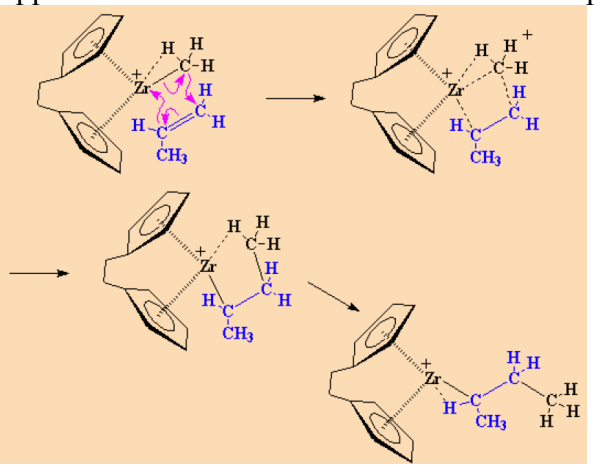
One labial methyl group leaves forming an α-agostic association,



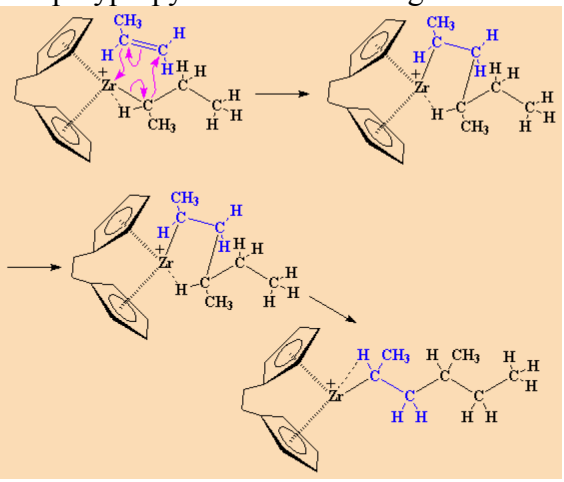
The positive charge on the zirconia atom associates with the unsaturated bond of an alkene monomer,



Rearrangement of the bonds leads to a 4 and then a 5 member cyclic structure that decomposes to the polymer chain allowing for a further a-agostic bond and the next monomer addition at the opposite side of the zirconia metallocene complex.



For polypropylene this switching of the reaction orientation leads to isotactic polymer,



e) Metallocenes are homogeneous catalysts.