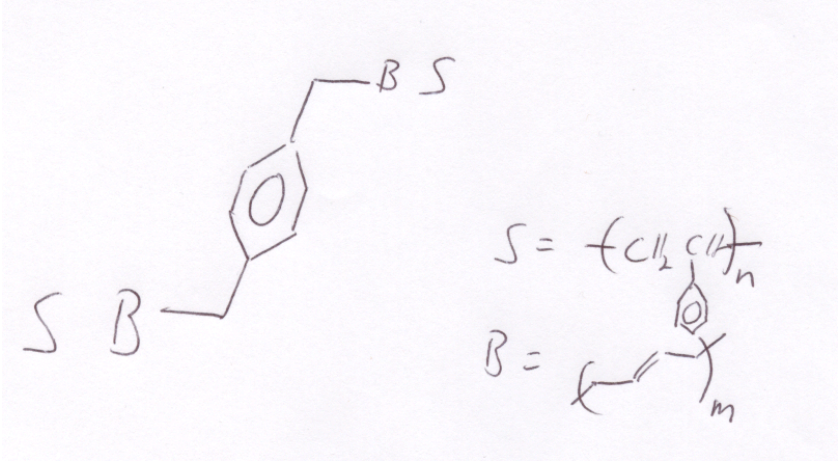
090313 Quiz 9 Introduction to Polymers (Chemistry)

This week we ran an ATRP polymerization and discussed anionic and cationic polymerization as well as the nomenclature for stereochemistry of polymers.

1) 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?

2) a) Describe the basic unit of stereochemistry in polymers and the possible states that this basic unit can display.
b) What is the smallest stereochemical unit that can be measured and explain why this is the smallest measurable stereochemical unit.
c) Describe the states that the stereochemical unit of part b can display.
d) PVME (polyvinylmethylether) polymerized cationically at very low temperatures is predominantly isotactic. Polyisobutylene polymerized under identical conditions is not. Explain why.
e) Describe an atactic polymer and describe a stereochemically random polymer.

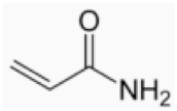
3) a) Why is there no real termination for ionic polymerizations (i.e. no coupling or disproportionation)?
b) Briefly outline how you would produce Kraton Rubber which is a block copolymer

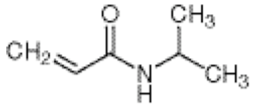


with the structure:
c) How would you make a 4-arm star polymer of polystyrene using a similar polymerization to part *e*?
d) Name a typical initiator for anionic polymerization.
e) Why are the number of monomers that can possibly be polymerized by anionic and cationic polymerization extremely limited? Give examples of monomers that can be polymerized by these two mechanisms and show the propagating species.

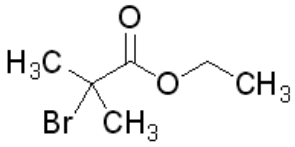
Answers: 090313 Quiz 9 Introduction to Polymers (Chemistry)

1) a)

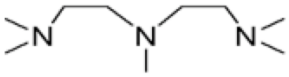
Monomer 1 Acrylamide 

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



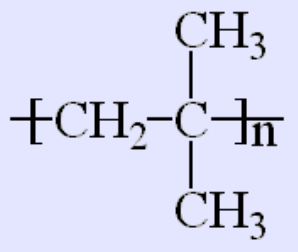
Ethyl Bromo isobutyrate
The transition metal came from
Cupric Bromide Cu(II)Br
The ligand was



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).

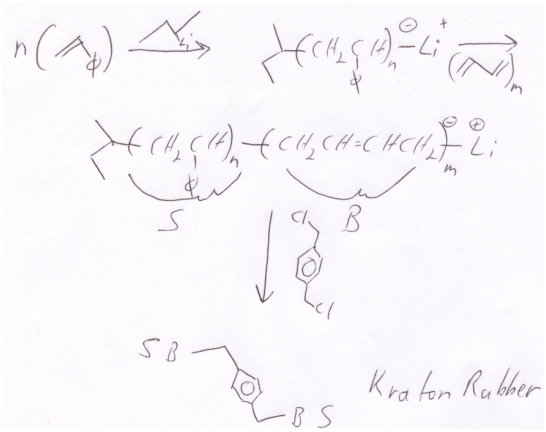
2) a) The basic unit is a diad and it can be meso (same orientation of substitution) or racemic (mixed state of substitution).
b) NMR measures only triads since it measures the perturbation of nuclear spin at a particular substitutent group by neighboring mer units (substitutent groups). Since a given substitutent group is equal distance to two other groups it can only measure a group of 3 at the smallest size. Larger groups can be measured. A group of 3 mer units is called a triad.
c) isotactic mm, syndiotactic rr, heterotactic mr or rm.
d) Polyisobutylene is symmetrically substituted so it does not display tacticity.



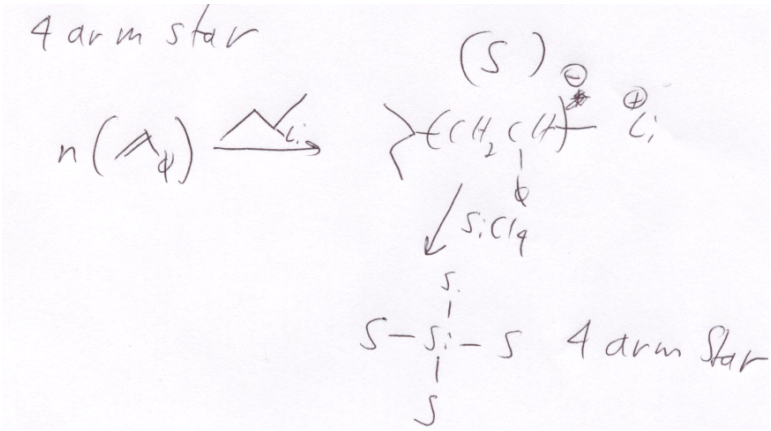
e) A stereochemically random polymer contains 50% racemic and 50% meso diads; 25% isotactic, syndiotactic and 50% heterotactic triads; etc for higher order tacticities. An atactic polymer doesn't crytallize but there isn't a fixed tacticity value.

3) a) The propogating species is charged and two of these groups repel each other electrostatically.

b) This is produced anionically in a living polymerization that is used on an industrial scale.



c)



d) sec-butyl lithium or tert-butyl lithium (t-butyl lithium).