CREATE RAFT

1. Based on this reading, what is your definition of degenerative transfer?

Group 1: Thermodynamically neutral process in which a chain capping agent can be added to the end of a growing radical chain in order to reduce chain transfer and termination reactions
Group 2: Thermodynamically neutral reversible transfer of a radical between two chains.
Group 3: A bimolecular chain transfer event that transfers the radical chain end from the growing polymer to a chain transfer agent. Importantly, the transfer event is reversible and is used to control MWD.
Group 4: A polymerization where a n group is reversibly added to identical chains in a thermodynamically neutral process so both chains can grow equally.
Group 5: Thermodynamically neutral reversible transfer of radical between two chains where the probability of adding a monomer is equal in either state
Group 6: Thermodynamically neutral process of initiating the radical.
Group 7: Thermodynamically neutral and reversible process involving the transfer of an atom from a covalent dormant species to an initiator, transfering one radical from one species to another.
Group 8: Thermodynamically neutral addition step that causes growing radicals to become dormant species by adding nonradical end group and vice versa...
Group 9: Thermodynamically neutral way of doing a living polymerization by atom transfer between a capped chain and a radical chain.
Group 10: The growing radical becomes capped by the transfer of an atom from the transfer agent causing it to become dormant, while the transfer agent becomes a radical that undergoes propagation; thermodynamically neutral

2. To achieve a polymerization with living characteristics, should the rate of propagation or degenerative transfer be faster?

Group 1: Degenerative Chain transfer must be faster
Group 2: Degenerative transfer must be faster.
Group 3: Degenerative transfer must be faster than the rate of propagation.
Group 4: Degenerative transfer
Group 5: Degenerative transfer should be faster
Group 6: Degenerative transfer should be faster than the rate of propagation.
Group 7: Degenerative transfer should be faster.
Group 8: Degenerative transfer should be fastest
Group 9: Degenerative transfer should be faster than the rate of propagation.
Group 10: Degenerative transfer should be faster than the rate of propagation to avoid side chain reactions

3. How do you think this polymerization is initiated?

Group 1: POlymerization is initiated by the homolytic cleavage of a labile bond which exposes a radical

Group 2: Small amount of traditional radical initiator, excess of CT agent.

Group 3: Polymerization is initiated with a small amount of radical initiator, such as thermal or photoinitiation.

Group 4: Start with a small amount of the radical and then add heat to the reaction.

Group 5: add a small amount of initiator in with your monomer and chain transfer agent (ex: AIBN) then you would heat to initiate the AIBN, and then there would be homolytic cleavage of your chain transfer agent to begin the polymerization

Group 6: A small amount of free radical initiator (like AIBN) is added to generate the initial radical species, which adds to the monomer, then the transfer of iodine can lead to radical propagation

Group 7: Polymerization is initiated by the the presence of a radical which can be formed by heating a reacting or through photoinitiation.

Group 8: Chain transfer agent needs to be in excess compared to initiator… The same a CRP: reactive alkyl halide or AiBN to generate a radical species that will lead into propagation.

Group 9: This polymerization is most likely initiated by a small amount of thermal initiator with homolytic cleavage (e.g. AIBN) in order to generate the radical chain ends necessary to induce degenerative transfer.

Group 10: small amount of initiator with a chain transfer agent, then same amounts of monomer, initiating solvents, and temperatures. Initiation can be: decomposition of initiators, initiation via an external source, or thermal initiation

4. In the last paper about degenerative chain transfer, the chain transfer agent (CTA) was a single atom (iodine). In this introduction, the CTA is changed to a thiocarbonyl group. What implications on the mechanism of polymerization might this have?

Group 1: The activation energy will be lower, which will allow the transfer agent to transfer more quickly. This will lead to a more controlled polymerization.

Group 2: This makes the chain transfer step have three states (R-bound CTA, Polymer-bond CTA, thioester-carbon-centered radical), and the reaction coordinate would look like a McDonald's M. The transfer would have a lower activation energy because thiocarbonyls are less stable, so we could expect faster chain transfer rates.

Group 3: There would be three states, the polymer-bound X, the X compound, and a radically bonded intermediate that would be lower in energy than the polymer X and the radical. However, it would not be so much lower in energy that it would be kinetically impossible to move from one state to another.

Group 4: There is a resonance where the radical can be on the carbon of the thiocarbonyl which is more stabilized and that would lower the activation energy to transfer the radical potentially making the rate at which the radical jumps back and forth between chains faster

Group 6:The activation energy would be lower due to resonance of the thiocarbonyl. Rxn goes to a two step process 1st step - radical from diff chain end adds to the sulfur with double bond causing formation of radical on central carbon bonded to both sulfurs. 2nd step - kicks off the original chain end to reform a double bond.
Group 7:
Group 5: Due to the higher chain transfer constant of the thiocarbonyl the activation energy of the mechanism will be lower allowing for a higher rate of chain transfer and thus more controlled polymerization.
Group 8: The thiocarbonyl reagent allows for a low activation energy of transfer between the radical propagating chain end and chain transfer agent. The mechanism also involves a three step process where in the 2nd step is slightly higher in energy compared to the 1st and 3rd species. Low activation energy allows for rapid chain transfer, therefore allowing for all chain ends to propagate at a similar rate, resulting in low dispersity. Sulfur is an exceptionally stable radical, allowing for these low, activation energy mechanistic steps.
Group 9: The endpoints of the energy diagram would still be the same, but in the mechanism there is a step where the radical is stabilized on the carbon of the thiocarbonyl, which would be lower in energy. There would be two energy barriers, one for the radical addition onto the thiocarbonyl and one for the thiocarbonyl to start the new chain