Polymer Chemistry Exam #2 Solutions May 2014

1. For emulsion and suspension polymerization, answer the following questions.

(a) What is the differences in initiator, additive, and status of product between suspension polymerization and emulsion polymerization?

suspension ~ monomer-soluble [water-insoluble] initiator, stabilizer additive, beads product
emulsion ~ water-soluble initiator, surfactant additive, latex [water colloid] product

(b) What are the three [3] intervals [periods] in emulsion polymerization?

(particle) nucleation, (particle) growth, completion

(c) How does the rate of polymerization change in the three intervals of emulsion polymerization? Explain.

interval I [nucleation] ~ Rp increases as the # of particles N increases
interval II [growth] ~ Rp constant as monomer fed to particle at a constant rate ([M] constant)
interval III [completion] ~ Rp down as monomer being used up ([M] down)

(d) The rate and degree of polymerization of emulsion polymerization can be increased at the same time. Explain how and why it is possible in emulsion polymerization. Explain also why it is not possible in suspension polymerization.

In suspension polymerization there is no reaction variable that can increase Rp and xn at the same time, as raising [I] or temperature results in the decrease in xn. In emulsion polymerization the use of more surfactant results in the increase in Rp and xn, both of which are dependent on # of particles.

2. For RAFT polymerization, answer the following questions.

(a) RAFT polymerization is much faster than NMP or ATRP. Explain why.

Concentration of radical in RAFT, which is similar to conventional radical polymerization, is much higher than that in NMP or ATRP, which is kept very low.

(b) RAFT polymerization of styrene requires more reactive RAFT agent than that of vinyl chloride does. Explain why.

Propagating styrene radical, with better radical-stabilizing phenyl substituent, is less reactive than vinyl chloride radical, and can only be captured by more reactive RAFT agent.

3. For cationic polymerization, answer the following questions.

(a) Methyl vinyl ether [CH_2=CH-OMe] is polymerized by cationic initiators, and not by anionic initiators. Explain why in some detail regarding the structure of the monomer.

Cationic polymerization favors the vinyl monomer with electron donating substituent. Methoxy group is an inductively electron withdrawing and resonance electron donating group. The resonance (stabilizing carbocation) effect overweighs the inductive effect.

(b) Cationic polymerizations are not living polymerizations. Explain why in terms of the structure of propagating species.

The positive charge in cationic propagating species is delocalized by hyperconjugation to the H at the beta position to the charged carbon, which makes the H be easily abstracted as proton in termination and/or chain transfer reactions.

(c) The polymerization of methyl vinyl ether can be living-like [reversible-deactivation] by adding a Lewis base. Explain how it works.

The Lewis base donates (lone-pair) electrons to propagating (charged) terminal carbon, and stabilize the carbon-counter ion bond. Then monomer inserts into the bond in a controlled manner. See p130, Textbook.

(d) Cationic polymerization of styrene is much faster than radical polymerization of the same monomer. Explain why.

Formation of initiating species is much faster in cationic polymerization, which gives much higher concentration of propagating chain.

4. SIS triblock copolymer is a chain with styrene block – isoprene block – styrene block.

(a) SIS behaves as an elastomer like crosslinked isoprene at room temperature. Explain how.

S block and I block are phase-separated to form a thermoplastic elastomer, where glassy (solid) S phase acts as a (physical) cross-linking point in rubbery I phase at room temperature.

(b) What kind of initiator(s) would you use to prepare SIS?

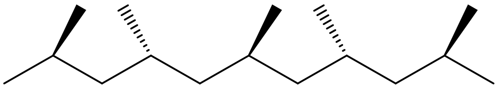
anionic initiators to insure living (co)polymerization. either BuLi or Na + naphthalene

(c) Would you run the polymerization of (b) in polar or non-polar solvent? Explain why.

nonpolar solvent to promote (cis-)1,4-polymerization of isoprene. In polar solvent proportion of 1,2- or 3,4-polymerization is too high, which results in the loss of flexibility of chain.

5. Regarding the tacticity control during polymerizations, answer the following questions.

(a) Draw the structure of syndiotactic poly(vinyl chloride), showing five repeat units.



(b) Match the following terms to either (A) radical or (B) ionic polymerization; (1) chain-end control, (2) catalyst-site control, (3) meso sequence (4) racemic sequence, (5) syndiotactic, and (6) isotactic.

(A) – 1 – 4 – 5 (B) – 2 – 3 – 6

(c) Explain your answer to (b).

In radical polymerization tacticity is determined by the interaction between substituents of terminal monomer unit and incoming monomer (at the chain end), which favors alternating [racemic] and syndiotactic placement.

In ionic polymerization tacticity is determined by the interaction among terminal unit, counter-ion, and incoming monomer (at the catalyst site), in which monomer attached with the same face [meso] every time to give isotactic placement.

(d) Discuss the effect of larger counter-ion and more polar solvent on the stereoregulation in ionic polymerization.

Larger counter-ion is more loosely bound to chain end, and gives less regulation on incoming monomer and less meso (iso) placement.

More polar solvent separate counter-ion from chain end, and gives less regulation on incoming monomer and less meso (iso) placement.

6. Answer the following questions briefly.

(a) It is observed in a coordination polymerization that ethylene is polymerized faster than propylene is. Should the propagating species of this polymerization be radical, cationic, or anionic? Explain.

anionic. Electron-donating methyl group let the propagating anionic species of propylene less reactive than that of ethylene.

(Actually, the propagating species in typical Ziegler Natta polymerization is considered to be anionic.)

(b) How is the structure of LLDPE different from LDPE? What is the difference originated from?

LDPE contains long and short chain branches, while LLDPE contains only short chain branches. The difference is originated from the difference in the mechanism of branch formation; the branches of LDPE by (inter- and intra-molecular) chain transfer to polymer, and those of LLDPE by copolymerization with short alpha-olefins.

(c) How is the structure of LLDPE prepared with $TiCl_4$ different from that prepared with Cp_2TiCl_2? What is the difference originated from?

Compared with LLDPE by ZN catalyst, that by metallocene catalyst has narrower molar mass distribution and more even distribution of branches. The difference is originated from the difference in characteristics of catalyst; multi-site ZN catalyst and single-site metallocene catalyst.