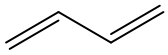
Polymer chemistry and macromolecular engineering
Fall 2024
Assignment 4

1) What are the main differences between ionic and radical chain polymerization? (state three differences)

2) Consider the cationic polymerization of 1,3-butadiene ([M] = 3 M) using $AlCl_3$ as initiator and $(CH_3)_3CCl$ as co-initiator. The rate constants for initiation, propagation and termination are $k_i = 60 \times 10^{-3}\ M^{-1}s^{-1}$, $k_p = 2.5\ M^{-1}s^{-1}$ and $k_t = 5 \times 10^{-3}\ s^{-1}$, respectively.



1,3-butadiene

a) The polymerization of 1,3-butadiene can proceed via two different pathways: 1,2–polymerization and 1,4–polymerization. Draw all possible isomeric repeating units of polybutadiene.

b) Derive the rate of polymerization (R_p) equation.

c) Calculate the degree of polymerization of polybutadiene. Assume that there are no chain transfer reactions occurring.

d) Now consider that a transfer agent was added to the reaction at a concentration of 30 mM. The rate constant of the chain transfer to the transfer agent (k_{trs}) is 1.5 $M^{-1}s^{-1}$. What is the new degree of polymerization?

3) For the synthesis of polystyrene, 5 g styrene (M=104.15 g/mol) is dissolved in 250 mL THF. The polymerization is initiated using sodium naphthalene. The concentration of anions initiating the polymerization ($[M^-]$) is 0.01M. After 2h, the polymerization is stopped at a conversion of p = 0.95 by the addition of water.

a) Illustrate the initiation, propagation and termination of the polymerization.

b) Calculate the dissociation constant of sodium polystyrene, if $k_p^{\pm} = 0.3$ L mol^{-1} sec^{-1} and $k_p^- = 75$ L mol^{-1} sec^{-1}.

c) The same reaction is carried out in the presence of 0.05M sodium tetraphenylborate. The parameters of this polymerization are as follows: $k_p^{\pm} = 1.5 \times 10^{-3}$ $Lmol^{-1}sec^{-1}$ and $k_p^- = 5000$ $L.mol.sec^{-1}$. Calculate the dissociation constant of sodium tetraphenylborate $K_{D\ sodiumtetraphenylborate}$.