

Kinetics & Reactor Design I: Kinetics

Continuing Ed workshop by Richard Skeirik, PE

Polymer Kinetics Exercise

Consider the cationic chain polymerization:

$M + H^+ \rightarrow P_1^+$	Monomer is initiated P_1 is formed
$M + P_1^+ \rightarrow P_2^+$	P_1 is consumed P_2 is formed
$M + P_2^+ \rightarrow P_3^+$	P_2 is consumed P_3 is formed
$M + P_n^+ \rightarrow P_{n+1}^+$	P_n is consumed P_{n+1} is formed
$OH^- + P_n^+ \rightarrow P_{n+1} + H_2O$	P_n is consumed Dead polymer is formed

Start simple. Write the rate expression for H^+

$$R(H^+) =$$

In a closed reactor, if you put in x moles of H^+ , how many polymer chains can be formed?

P_1 appears in two reactions. Write its rate equation:

$$R(P_1) =$$

Now, try to write, one under the other, the rate equations for P_1 through, say P_4 .

Now add the left sides (total rate for the the four Ps) and the right sides.

$$R(P_1 \text{ through } P_4) =$$

What will happen if you continue for longer and longer P?

(Continued on back)

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Now, one polymer chain gets initiated right away. Another gets initiated later. Then you quench the polymerization with water. Which chain will be longer? What if both chains are initiated right away? Which will be longer?

Now imagine all the acid goes in at one shot, and very quickly it all initiates a monomer. Later you quench the reaction. What chain lengths do you think you'll find? Hint: this is called a very narrow molecular weight distribution.