Bulk Polymerization Standard Operating Procedure (SOP)

By Devin Roach

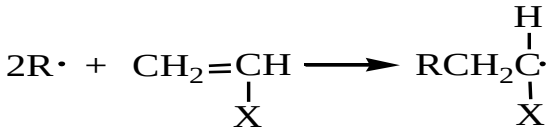
What is bulk polymerization?:

Bulk polymerization is a common method for polymer fabrication on an industrial scale. In general, the initial material consists of mostly of pure monomer. Initiator is then added and the reaction begins upon exposure to heat or other free energy. As the reaction proceeds the polymer mixture will become more viscous as the chain length and molecular weight increases. Here, we will rely on addition (chain-growth) polymerization.

Polymerization Scheme Overview:

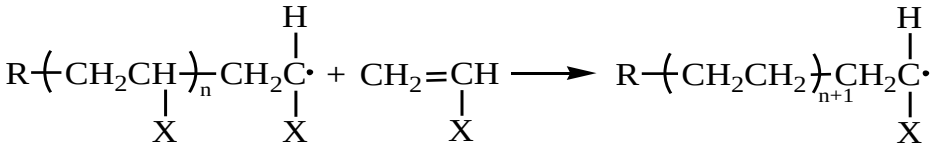
Free radical polymerization consists of three steps: Initiation, Propagation and Termination. At the initiation stage of chain-growth free radical polymerization of styrene monomers, the initiator, I, forms free radicals species: R, which then couples with one electron of the carbon-carbon double bonds of the styrene monomer to form another radical (see scheme 1.1). These bonds are particularly susceptible to radical attack because of their relatively low stability and resonance stabilization of the resulting radical throughout the phenyl group. In the next stage, propagation, the newly formed radical reacts with another monomer to form another radical, resulting in a polymer that is one unit longer (see scheme 1.2). The process is then repeated to form a chain of monomers, or the polymer. The propagation step is terminated when two radicals combine together to form a neutral species, known as coupling or combination (see scheme 1.3a); or disproportionation, in which hydrogen transfer results in the formation of two molecules: one saturated and one unsaturated end group (see scheme 1.3b).

Initiation Step



--- (Scheme 1.1)

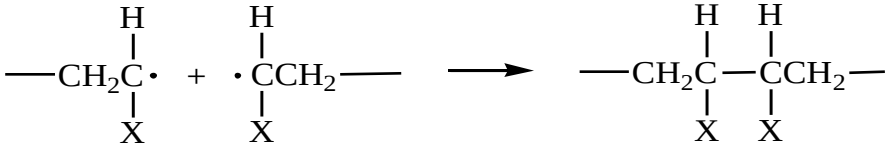
Propagation Step



---(Scheme 1.2)

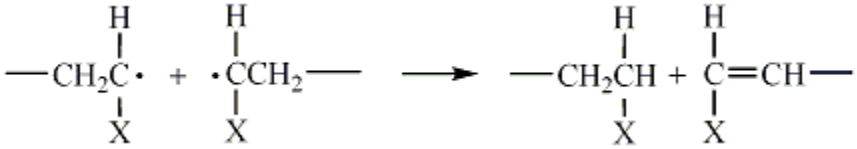
Termination Step

Combination or Coupling



---(Scheme 1.3a)

Disproportionation



---(Scheme 1.3b)

Materials:

1. Styrene monomer (from Sigma Aldrich).
2. Azobisisobutyronitrile (AIBN) 12wt% in Acetone (from Sigma Aldrich).

Safety tips and equipment:

- Put on glasses, gloves, and lab coats upon entering the lab.
- Perform work under the hood to avoid ingesting volatile chemicals.
- Take care when using the hot oil bath.

Procedure:

1. Measure 15mL of bulk styrene in a graduated cylinder.
2. Pass the styrene through a silica column to remove the inhibitors normally included.
   (Note: perform this process under the hood, styrene monomer is harmful to inhale)
3. Next, measure 5mL of AIBN in Acetone.
4. Gently mix the AIBN into the filtered styrene using a glass rod.
   (Note: AIBN is a volatile chemical so mix under the chemical hood)
5. Place the mixture in 80˚C in an oil bath.
6. Let the reaction proceed for 20 minutes occasionally stirring with the glass rod.
   (Note: the viscosity of the mixture should be increasing. Pull the glass rod out of the mixture to form a fiber as a check)
7. Remove the mixture from the hot plate and let cool to room temperature.
8. Use the glass rod to pull a fiber out of the mixture and let that cool. Observe that the fiber now breaks in a brittle manner.

How can we take this further?

Many interesting experiments can be performed using this same basic procedure. For example, the initiator concentration can be varied. The resulting molecular weight will be

changed. In addition, the effect of the different termination steps described in Scheme 3a&b can be observed. The same reaction procedure can be used to create Nylon-6,6.

The resulting molecular weight of the polymer can be observed using size exclusion chromatography (SEC). Other methods such as ^{1}H NMR spectroscopy can be used to determine the conversion of the monomers.