Experimental investigation of the kinetics of nitroxide - mediated free radical polymerization (NMRP); Styrene and styrene - divinylbenzene

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1. Introduction / Objectives

Controlled radical polymerization (CRP) has become a promising technique for producing polymers with highly controlled structures and polydispersity index close to 1.1. The basic principle consists of introducing into the reacting system a species, a stable nitroxide radical, able to trap the propagating radical in a nonpropagating species, as represented below:

$$P_\bullet + X \underset{K\,deact}{\overset{K\,act}{\rightleftharpoons}} P - X$$

(Active)   (Dormant)

$P_\bullet$ represents the propagating radical, P-X the dormant (trapped) radical, and X is the controller .

Experiments were carried out in bulk using 2, 2, 6, 6–tetramethyl-1-piperidinyloxy (TEMPO) as controller and dibenzoyl peroxide (BPO) as initiator. The objectives were:

➢ To observe the effect of TEMPO/ BPO ratio and polymerization temperature on conversion, molecular weights and polydispersity.
➢ To generate a source of reliable experimental data for parameter estimation and model validation purposes.
➢ To examine the NMRP of styrene in the presence of cross linking agent, divinylbenzene (DVB)

2. Effect of (TEMPO/ BPO) Ratio

➢ The larger the ratio (the more TEMPO in the recipe), the slower the polymerization .
➢ Existence of an apparent induction time at (TEMPO/ BPO) = 1.5 .Related to the time needed to reach an equilibrium between activation and deactivation of polymer radicals, which lasts about 2.5 hrs at those conditions.
➢ A complete replicate has been carried out at (TEMPO/BPO) = 1.1 to obtain an idea of the reproducibility of our data.

Figure 1. Effect of (TEMPO/ BPO) ratio on rate of polymerization. STY homopolymerization at 120 °C.

➢ As expected for typical CRP, the molecular weight trends are linear.
➢ Higher values of the number average molecular weights, Mn, are obtained when the (TEMPO / BPO) ratio is decreased.

Figure 2. Effect of (TEMPO/BPO) ratio on the number average molecular weight. STY homopolymerization at 120º C.

➢ The experimental data do not show much difference for various ratios. Very low values, between 1.07 and 1.2, are obtained.
➢ Frequent sampling in the beginning of the experiment was done for (TEMPO/BPO) =1.5 to capture and verify the trends predicted by a mathematical model.

Figure 3. Effect of TEMPO/BPO ratio on PDI. STY homopolymerization at 120°C.

3. Effect of Temperature

➢ As expected, the polymerization proceeds faster at a higher temperature.

Figure 4. Effect of temperature on the kinetics of the reaction.

➢ A slight reduction in the values of Mn and Mw is observed at 130 °C.

Figure 5. Effect of temperature on molecular weights.

4. STY/DVB Copolymerization

➢ Level of DVB does not have a large effect on the overall rate of polymerization, although the rates of reaction with added DVB are slightly faster than the rates seen with no DVB.

Figure 6. STY/DVB Copolymerization with (TEMPO/BPO =1.1), T= 120 °C, and different levels of DVB.

Figure 7. Molecular weight development (Mn and Mw vs. conversion) for nitroxide-mediated radical copolymerization of STY/DVB (DVB = 1 and 1.5 wt%).

Figure 8. PDI with respect to conversion for nitroxide-mediated radical copolymerization of STY/DVB (DVB = 1 and 1.5 wt %).

➢ At the start of the polymerization the molecular weights are low, as seen with NMRP homopolymerization of styrene.
➢ The number average molecular weight shows a steady increase with conversion. In contrast, the weight average molecular weight of the samples increases abruptly with conversion, prior to the gelation point. Subsequently, there is a drop in the weight average molecular weight (observed also as a decrease on PDI in Figure 9). This is because only the soluble fraction of the produced material is being analyzed and typically this will be lower molecular weight material.
➢ The expected behavior of the gel content increasing very rapidly after the gelation point at high conversions was obtained.
➢ Compared to the copolymerization of STY/DVB using conventional free radical polymerization (insert), the NMRP reaction leads to a gelation point significantly shifted from about 7 to 50% monomer conversion .This relates to the manner of molecular weight buildup in NMRP where the initial chain lengths are small, giving a reduced probability of crosslinks

Figure 9. Gel content values vs. conversion for STY/DVB copolymerization initiated with (TEMPO/BPO = 1.1) at 120 °C

5. Immediate Future Steps

➢ Complete experiments for (TEMPO/ BPO) ratio verifications at 130 ° C.
➢ Further experiments for Sty / DVB with frequent sampling.
➢ Continue the experimental investigations of NMRP at higher temperatures (150- 220 ° C)