MATSE 473

Lab 4:
Cationic Polymerization of Styrene

Due 2/10/17

Group 4:

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Introduction

In this lab polystyrene was synthesized using cationic polymerization. Polystyrene is a very common plastic that is used for many different applications such as in packaging and appliances. Cationic polymerization is a high-yield method of synthesizing polystyrene that is similar to ionic polymerization, except it is initiated by a cation rather than an anion. This method of polymerization is the most popular way to synthesize polyisobutylene and other butyl rubbers.

Mechanism

Polystyrene is created using cationic polymerization catalyzed by aluminum trichloride in the presence of a small amount of water. In solution, the missing electron pair of the aluminum trichloride is attracted to the electron pairs on the water molecules, forming a bond. Once bonded with the aluminum trichloride, the electronegative oxygen pulls electrons away from its hydrogens, making them slightly positive. This makes them very susceptible to detach and react with the styrene monomers. This splits up the double bond within the styrene, causing the other carbon to have a missing electron. This positively charged carbon then reacts with the double bond within other styrene monomers. As this pattern continues it forms the polymer chain. See figures 1 below for a diagram of the initiation and propagation, only in this case the monomer is isobutylene instead of styrene. The chain will continue to grow until there is no more monomer or the reaction ends due to chain transfer. This is why the reaction should be run at a relatively low temperature, as the energy barrier for this chain transfer is relatively low.

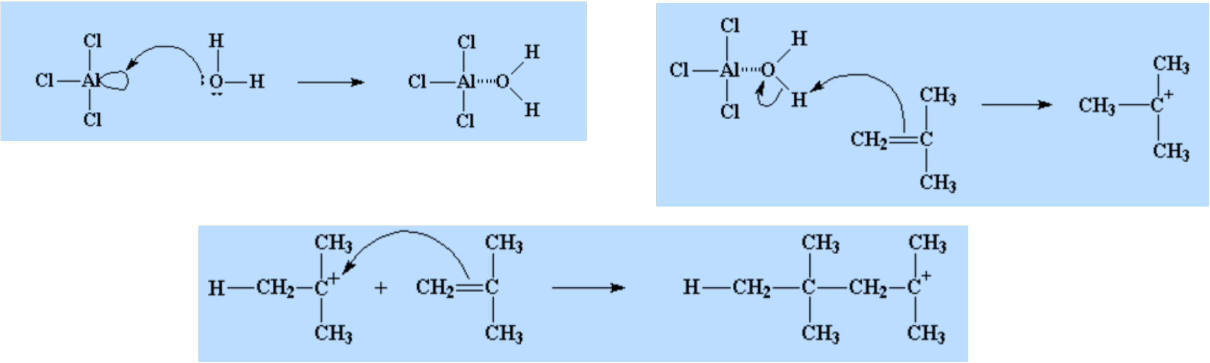

Figure 1: Initiation and propagation of the cationic polymerization of isobutylene.

Source: http://pslc.ws/macrog/cationic.htm

Operational Procedure

The polystyrene was prepared under a hood in a 100 ml two-necked flask connected to a condenser. The first step was to add 40 ml of methylene dichloride as a solvent. Second, 0.15 g of aluminum chloride was added to the solution and mixed for several minutes until it dissolved. Once this was done, the solution was lowered into an ice and salt bath cooled to -10 °C, the open neck was plugged, and the flask and its contents were gassed with nitrogen. After a few minutes of purging, a solution of 5 ml of polystyrene and 10 ml of methylene dichloride was added. This mixture was then allowed to mix for an hour. Once done, a few ml of methanol was slowly added to the flask. Next, the entire contents of the flask were dumped into a beaker with about 250 ml of methanol. This mixture was then vacuum filtered to isolate the solid polymer. Methanol was again added to the powder for two more cycles of additional vacuum filtering to ensure all catalyst was washed out. Once this was complete the polymer powder was collected and dried overnight.

Observations and Results of the Experiment

Upon adding the catalyst to the monomer solution, it slowly began turning an orange color over the course of about 15 minutes. The moment the polymer solution was added to the methanol there was a clear indicator that the reaction had been successful. White solid polymer could immediately be seen precipitating out of the solution. This is due to the addition of methanol changing the solubility of the polymer in the solution. While polystyrene is entirely soluble in methylene dichloride and therefore could not be seen, it is insoluble in methanol, causing it to precipitate. This precipitate was collected, rinsed, and dried resulting in a total of 3.942 grams of polymer.

Laboratory Discussion and Conclusions

5 ml of styrene was used to prepare the polystyrene. Using a density of 0.909 g/cm^3, this results in an initial weight of 4.454 g. This means a yield of 3.942 g polystyrene would be an 88.5% conversion. The leftover unpolymerized styrene monomers must have not been able to come into contact with the polymerizing chains, or the more likely scenario is that some of the polymer powder did not make it to the final bag and was lost throughout the processing steps.

By using the amount of monomer and catalyst used we can determine the theoretical molecular weight of the synthesized polystyrene. Styrene has a density of 0.909 g/ml and a molecular weight of 104.15 g/mol. This means the 5 ml added for this procedure equals 0.0436 mols of styrene. The amount of catalyst added was 0.15 grams. Since the density of aluminum trichloride is 2.48 g/ml, this equals a volume of 0.372 ml. Adding the volume of the monomer and the catalyst together gives us 0.00537 L. If we divide the mols of styrene by this volume, we get a molar concentration of styrene to be 8.116 mols styrene per liter of monomer plus catalyst. Next we must calculate the mols catalyst used. Using a molecular weight of 133.34 for aluminum trichloride, this can be determined to equal 0.001125 mols catalyst. Like with styrene, this number is divided by the total volume to get a molar concentration of the catalyst which equals 0.2095 mols/L. Using the equation molecular number average (Mn) = mols monomer divided by mols catalyst, Mn can be determined to equal 8.116 divided by 0.2095 or 38.74. By multiplying this number by the molecular weight of styrene (104.15), the theoretical molecular weight for this polymerization technique can be determined to be 4034.76 g/mol.

Overview/Comments

As expected, polystyrene was synthesized from its styrene monomer using cationic polymerization. The reaction as run at a low temperature in order to improve reactivity and increase molecular weight. The percent conversion was fairly high at about 88.5%. This number can most likely only be significantly improved through the use of better processing techniques and polymer collection.

Works Cited:

1. http://pslc.ws/macrog/cationic.htm