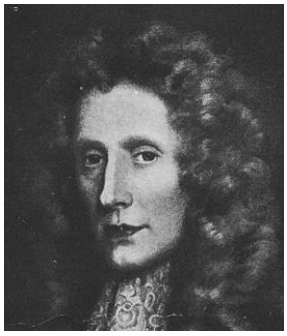
Fig. 11-1



Sir Robert Boyle (1627-1691)
http://en.wikipedia.org/wiki/Robert_Boyle

Experiment 11

VACUUM DISTILLATION, POLYMERIZATION OF STYRENE

Text Topics and New Techniques

Polymerization, vacuum distillation

Discussion and Techniques

Some attribute the change from the secrecy prone field of alchemy to the science of chemistry to Sir Robert Boyle. Boyle believed in the sharing and publication of experimental results and the use of the results to develop logical explanations. One of his most famous works, *The Sceptical Chymist*, was published in 1661 and is available on the Internet (http://oldsite.library.upenn.edu/etext/collections/science/boyle/chymist/). Boyle is probably known best to students for his experiments with gases that resulted in Boyle's Law (PV = constant). Although Boyle did not invent the vacuum pump, he was one of the first to use the pump to perform experiments in a vacuum. Boyle was probably also the first to perform a distillation under reduced pressure (a vacuum distillation). Today's experiment will use a vacuum distillation to purify the very commercially important compound, styrene.

As many organic compounds have a tendency to decompose at high temperatures, distillations above 200°C should generally be avoided if other options are available. Fortunately, there is a way to reduce the boiling point. Recall that boiling occurs when the vapor pressure of a substance equals the confining pressure. If the pressure in the system is reduced, the substance will boil below its atmospheric pressure boiling point. The most convenient way to reduce the pressure is to connect the system to an aspirator. An aspirator is capable of reducing the pressure from atmospheric pressure down to the vapor pressure of the water at the temperature of the water. This means if the system is leak free that the pressure in the system will be reduced to about 18 mm pressure. Knowing the system pressure, it is possible to use various methods to estimate the boiling point at reduced pressure from the atmospheric pressure boiling point. One method to determine the reduced pressure boiling point is to use the Clausius-Clapeyron equation and an empirically adjusted Trouton's rule. Assuming the system pressure is about 18 mm. the result of this calculation and adjustment is:

$$\mathbf{T_w = 0.78\,T_a - 60}$$

T_w = boiling point at water aspirator pressure in Celsius
T_a = boiling point at atmospheric pressure (760 mm) in Celsius

The apparatus for a vacuum distillation is very similar to the apparatus for a simple distillation. The biggest difference is that the vacuum distillation adapter (often used for simple distillations as well) is connected via a trap to an aspirator using thick walled rubber tubing. To prevent bumping in atmospheric distillations, boiling chips are usually added. However, boiling chips are usually ineffective at reduced

pressure. Bleed or capillary tubes are often inserted into the distilling flask but it is a challenge to adjust the bleed rate. The simplest method to reduce bumping is to use magnetic stirring. The stirrer will work through the heating mantle if the stirrer unit is close enough to the stirring bar. Perhaps the biggest challenge is cutting fractions as it is undesirable to break the vacuum to change flasks. Different types of fraction cutters that can be used without breaking the vacuum have been designed. Note that fraction cutters replace the vacuum distillation adapter and are designed so they can direct the distillate into different receivers. Finally, be sure to lightly grease all the joints to prevent leaks.

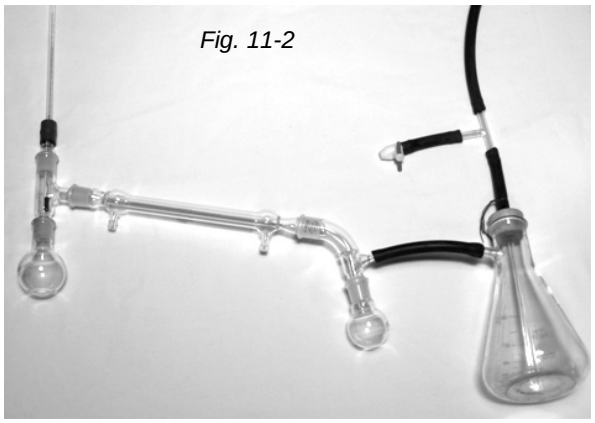
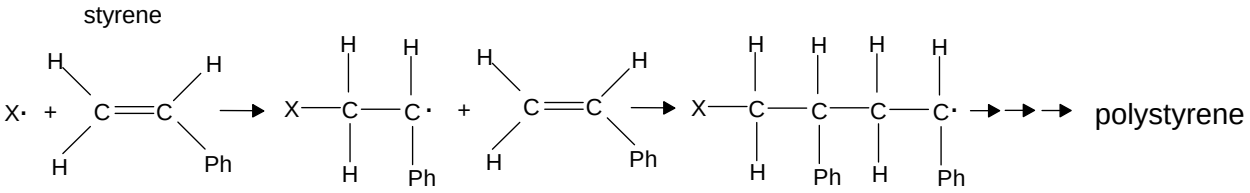


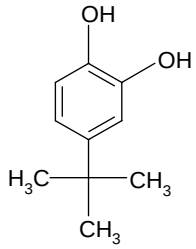
Fig. 11-2

Today, you will perform a vacuum distillation of one of the most important starting materials for plastic synthesis. We are engulfed in a world of plastic with a considerable amount of the plastic derived from various forms of polystyrene such as styrofoam. Polystyrene results when hundreds of styrene molecules are joined using a free radical to initiate a chain reaction.

free radical initiator X–X → 2 X•, Ph = phenyl (benzene minus a hydrogen ring)



Commercially available styrene usually contains a free radical inhibitor such as 4-*t*-butylcatechol. The inhibitor substantially decreases the rate at which styrene polymerizes while sitting in a bottle on the stockroom shelf. Before polymerization of styrene is performed, the 4-*t*-butylcatechol can be removed either by extraction or vacuum distillation. Since 4-*t*-butylcatechol is an aromatic alcohol, like phenol, it has the properties of a weak acid and can be extracted from an organic solvent into an aqueous base solution. Alternatively, the styrene can be distilled leaving the 4-*t*-butylcatechol behind in the distillation flask. Since styrene has a tendency to polymerize at its atmospheric pressure boiling point, styrene needs to be distilled under vacuum to lower its boiling point.



4-*t*-butylcatechol

Procedure

Purification using vacuum distillation. Set up a simple distillation apparatus with a 25 mL flask containing about 10 mL of styrene and a magnetic stirring bar mounted in a heating mantle on top of a magnetic stirring device. Be sure to lightly grease all joints to form leak-proof seals. The glass between the distilling flask and the thermometer should be wrapped with glass wool to provide insulation. After the instructor checks the setup, **establish a vacuum before turning on the heating mantle.** Also turn on the stirrer to a rapid rate. This distillation has a tendency to foam and the heat must be gradually turned up until boiling is achieved. Do not continue to raise the temperature after boiling is achieved or foaming will occur. Distill until most but not all of the styrene has distilled over. Locate the literature atmospheric pressure boiling point of styrene and use the formula on a previous page to calculate the expected boiling point at water aspirator pressure (about 18 mm). Record the temperature at which you collect distillate and stop the distillation when there is still a small amount of liquid in the distilling flask. Verify that the liquid is styrene by running an ir, nmr and/or refractive index of your distillate. Store the remaining distilled styrene in a tightly stoppered container in a refrigerator for possible use in ***Experiment 14.***

Purification using extraction. Transfer about 10 mL of commercial styrene to a separatory funnel and add 20 mL of 1 M NaOH to the funnel. Shake the mixture with frequent venting and allow the layers to separate. Draw off the base solution and appropriately discard it. Wash the styrene layer a couple of times with water to remove residual NaOH. Dry the styrene over calcium chloride for several minutes.

Polymerization of styrene. To six 13 x 75 mm test tubes, add about 1 mL styrene samples, a couple of boiling chips and additive as directed below.

#	Tube 1
1	commercial styrene directly from commercial bottle
2	commercial styrene directly from commercial bottle + 1 drop of *t*-butyl peroxybenzoate
3	extracted styrene
4	extracted styrene + 1 drop of *t*-butyl peroxybenzoate
5	vacuum distilled styrene
6	vacuum distilled styrene + 1 drop of *t*-butyl peroxybenzoate

In a hood, heat the test tubes in a sand bath until they are boiling and observe. Be very careful not to boil the liquid out of the tube. After a couple minutes of boiling, allow the tubes to cool and report your observations about the contents of the test tubes.

Option: Infrared spectrum of polystyrene. ***Experiment 31*** includes the determination of the ir spectra of polymers. As an interesting option, determine the ir of polystyrene and compare it to a reference spectrum.

References

Roberts, R. M.; Gilbert, J. C.; Rodewald, L. B.; Wingrove, A. S. *Modern Experimental Organic Chemistry*, Saunders, 4th ed., **1985**, 619-625.
Nimitz, J. S. *Experiments in Organic Chemistry*, Prentice-Hall, 1991, 422-429.

Prelaboratory Preparation - *Experiment 11*

First, be sure to list all the goals of the experiment. Look up the atmospheric pressure boiling point of styrene and calculate the predicted boiling point for styrene at 18 mm pressure. Decide how you will verify that the liquid is styrene. Write the structure of *t*-butyl peroxybenzoate and the reaction for its decomposition.

Observations

Report all relevant observations including boiling points and spectra.

Conclusions

This section should include the following:

1. Was the liquid you distilled and extracted styrene? Explain your answer.
2. Were the goals of the experiment achieved? Explain your answer.
3. Compare the calculated 18 mm boiling point for styrene with your observed value. Account for any differences.
4. Evaluate the usefulness of vacuum distillations. Comment on when a vacuum distillation should be used (e.g., size of sample, boiling point of sample, etc.).
5. Write a reaction for the polymerization of chloroethene (vinyl chloride) to polyvinyl chloride.
6. Discuss the effects of inhibitors and free radical initiators on the polymerization of styrene. Base your discussion on your observations.