INHIBITION OF THE THERMAL POLYMERIZATION OF STYRENE

by

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Date

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TITLE I

INTRODUCTION

It is the purpose of this thesis to further study the inhibition of the thermal polymerization of styrene along the same lines as Cohen (1), and wherever necessary to improve and correct his work.

Chloranil is the inhibitor to be studied and the spectrophotometer used by Cohen (1), is abandoned in favor of an electrophotometer for colorimetric determinations. Complete calibration curves for the electrophotometer with chloranil in styrene solutions are included.

With the experimental methods on a sound basis, the overall problem is again attacked by attempting to repeat the work of Schultz, Kammerer and Lorentz (11), using chloranil in place of benzoquinone. Experimental data and curves are given to show the disappearance of inhibitor with time and also the per cent polymer formed near the end of the induction period.

An extensive literature search has been made as a major part of this work and some of the more pertinent references are given in the bibliography.

TITLE II

ACKNOWLEDGEMENT

The author hereby expresses his gratitude to Dr. Howard E. Sheffer for his many hours spent with the author discussing journal articles, explaining the fundamental theory of this work and advising on experimental technique.

TITLE III

EXPERIMENTAL METHODS

This title is subdivided into four sections which are to explain methods tried by the author for the purpose of putting this work on a quantitative and reproducible basis.

Section 1. Improvement of the constant temperature bath.

Upon making a preliminary run following the procedure of Cohen (1), it was noticed that identical samples, being submerged in the constant temperature oil bath for the same length of time, were of different colors. This difficulty of poor circulation in the oil bath was overcome by using two rapid mechanical agitators arranged to give the optimum propulsion.

The temperature constancy throughout the oil bath was verified by placing a series of ten calibrated thermometers at various spots in the bath and obtaining identical readings.

Section 2. Purification of reagents.

In order to obtain quantitative results it is necessary to use pure reagents. To remove commercial inhibitor, Dow N-99 styrene was vacuum distilled under nitrogen at approximately 52° C and under 26 to 30 millimeters pressure. An attempt was made to ascertain the purity of the distilled styrene by means of the refractive index--a method used by Goldfinger, Skeist, and Mark (2). However, by using a Carl Zeiss, Jena #9330 refractometer, no difference could be noticed between the refractive indices of the distilled and undistilled styrene.

Since tertiary butyl catechol, the commercial inhibitor, is so much higher boiling than styrene, it was assumed without proof that styrene, distilled as described above, is adequately free of inhibitor for this work. Late in this work there came to the attention of the author a seemingly simple colorimetric test (3), for tertiary butyl catechol and the reference is included for the convenience of future workers.

It is further desirable to utilize pure inhibitor. Many of the common methods of sublimation (4), were tried but none were applicable to chloranil. One method by which small amounts of chloranil may be sublimed consists in using a 250 milliliter beaker in which a one inch watch glass is suspended by wires about an inch from the bottom. The beaker is covered with a four inch watch glass which is kept cool by allowing carbon tetrachloride to evaporate from it. The chloranil is placed in the bottom of the beaker, and upon heating, the vapors rise, condense on the bottom of the large watch glass and drop into the small suspended receptacle.

A private communication from the manufacturers of Eastman White Label chloranil states that their product is 98% pure. It was therefore thought justifiable to use the inhibitor without further purification. However, the above communication recommended recrystallization from acetone. This method offers fluffy, light yellow crystals in good yield. Melting point determinations in sealed melting point tubes about two centimeters long indicated that the melting point of chloranil was raised several degrees by recrystallization but this is no criteria for purity. The melting point varies widely with but small variations in length of the sealed tube or amount of sample and the value obtained (302-310° C), cannot be justifibly compared with the handbook value (289° C), without comparing experimental methods.

Section 3. Colorimetric determinations.

The next phase of this work was to check Cohen's (1) statement that chloranil in styrene solutions obey Beer's law. Complete absorption curves for several concentrations of chloranil were obtained using the Cenco-Sheard spectrophotometer. The curves agree qualitatively with those of Cohen (1) and for future reference, data for these curves will be included at the end of this section in table I.

In order to obtain the Beer's law curve of optical density versus concentration of chloranil in styrene solution, a series of solutions of known concentration was prepared and the optical density readings taken at various wave lengths (480 mu. for dilute solutions and 520 and 550 mu. for the more concentrated solutions.)

However, it was found impossible to attain reproducible results with the Cenco-Sheard spectrophotometer. By just varying the slit and diaphram, for example, two completely different optical density values may be obtained for the same solution.

Therefore at this point it was decided to change to the

Fisher electrophotometer for future colorimetric determinations of inhibitor. This change is perfectly justifiable since we are not concerned with the one advantage of the spectrophotometer, that is, the narrow wave band. The only thing pertinent here is to have an instrument that will measure light absorption reproducibly over a defined range of concentration.

Two calibration curves (optical density versus inhibitor concentration) were prepared for the Fisher electrophotometer, one for the more concentrated solutions using the green filter and another for weaker solutions using the blue filter. The data are given below and plotted on curves 1 and 2. For several of the more dilute solutions, a Roller-Smith precision balance was used to insure accurate weighing of the chloranil samples.

The data were obtained by making up standard solutions using commercial styrene. This was shown to be permissible by preparing two solutions from distilled styrene and two from commercial styrene. All four readings were identical proving that the <u>tertiary</u> butyl catechol does not influence the color of the chloranil in styrene solutions. These identical readings also show that chloranil in styrene solutions can be prepared reproducibly.

The data in Table II resulted from two completely separate sets of solutions prepared on separate days. Optical density readings were taken for both sets on the Fisher electrophotometer and on the Cenco-Sheard spectro-