

## Note on the Development of Methods for Studying the Polymerisation of Styrene and Acrylonitrile by Positive Gaseous Ions

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It has been argued that positive gaseous ions, due to their very high electron affinity, act radiation-like and are thereby capable of breaking covalent chemical bonds. Accordingly these ions might be assumed to be precursors to reactive entities characteristic for radiation chemistry, e.g. free radicals. Thus, upon bringing positive gaseous ions into contact with liquids containing monomers, one would expect polymerisation to occur. It is thought that the polymerisation produced by ionizing radiations proceed in some cases *via* free radicals and in other cases (often at low temperatures) *via* ionic species <sup>2,3</sup>.

We have developed methods for studying the polymerisation of styrene and acrylonitrile by positive gaseous ions. For styrene, some positive evidence has been found. It seems, however, that emphasis has to be placed primarily on the design of the apparatuses and the methods by which basic studies can be made. We shall discuss such points by referring to Fig. 1 which shows a modification of an apparatus developed for studies on aqueous solutions <sup>4</sup>.

One of the main methodological problems is that the liquid phase has to be sufficiently conductive to allow the passage of unipolar charges through the system. For this purpose, one has to select solutions which contain some electrolyte, but the latter should be chosen so as not to inhibit the polymerisation too much. For styrene it was found possible, after performing the conventional extraction of inhibitors by means of a dilute NaOH solution, to add alcohol (about 25 %), water (about 1.3 %)

and CaCl<sub>2</sub> (less than 0.1 %) to give a solution of sufficient conductivity. Due to these additions, the radiation chemical G-value is reduced — this can be elucidated by means of  $\gamma$ -ray induced polymerisations of samples of the solution. Using this solution in the apparatus of Fig. 1, it was found possible to achieve corona currents of some  $\mu$ A with helium flushing through the space over the section I of the apparatus. It was found possible to maintain stable conditions over a period of many days. The formation of polystyrene was detected by precipitating with methanol after cooling with ice.

For acrylonitrile the conductivity problem is easier since it is soluble in water. A distillation of the monomer under oxygen-free conditions served to remove inhibitors. Samples of the monomer were dissolved in distilled water which had been previously redistilled twice in a quartz apparatus. The solution was made 5 % in acrylonitrile and then 0.1 % in CaCl<sub>2</sub> in order to increase the conductivity sufficiently so as to allow currents of the order of some  $\mu$ A to be used. In addition, a radiation polymerisation by means of gamma rays was performed in the same way as that described by Dainton <sup>5</sup>.

The helium gas used was 99.99 % pure, the possible impurities stated being N<sub>2</sub> 0.01 %, O<sub>2</sub> 0.0005 %, H<sub>2</sub> 0.0005 %. The gas was purified using a 1 m tube containing granular copper \* at 175°C. This removed traces of oxygen from the gas but not nitrogen. It is therefore possible that some charge transfer from helium to nitrogen may have taken place.

Positive evidence has been obtained with styrene but the yield was small. A clear turbidity in the contents from cell 1 was observed upon methanol treatment but nothing occurred in the samples from cells 2, 3 and 4. The yield was 0.2 mg and the total number of  $\mu$ Ah was 34 as found by a recorder. The voltage used was  $\sim$  5kV and the current a few  $\mu$ A. The helium flow-rate was about 15 ml/min. The anode light was confined to the tungsten wire and no sparking was detected. Some difficulties due to alcohol evaporation were encountered in the experiments. This caused a

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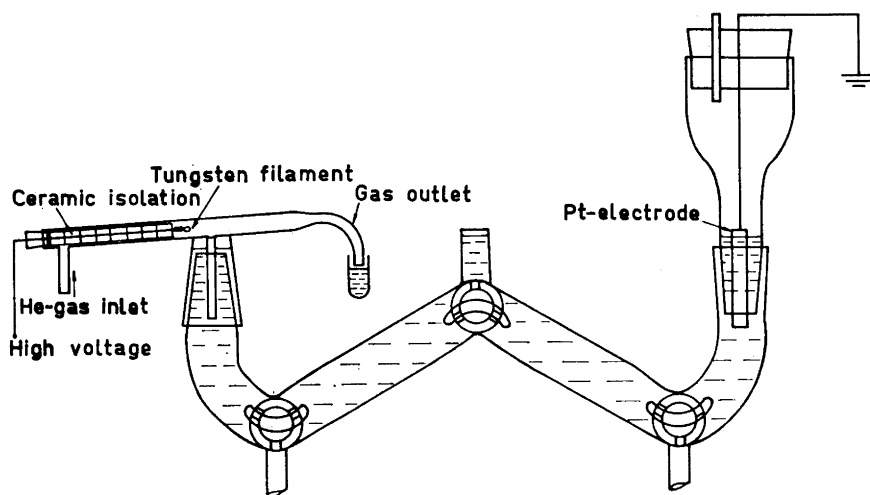


Fig. 1. Glass apparatus for positive gas ion production and performance of radiation-like polymerisation reactions. A series resistor of 100 Mohm is placed between H.T. generator (0–10 keV) and anode filament. The platinum cathode is connected to a current recording device. The left side of the apparatus is denoted cell 1, the next part cell 2 etc. The part on the right containing the platinum electrode is denoted cell 4.

gradual decrease in ion current due to the decrease in level. The molecular weight of the product is not known but, if it is assumed to be 100 000, we arrive at an M/N value (M total number of molecules produced, N total number of ions) of  $\sim 0.02$ .

It is hoped that further experiments with the methods described will contribute to an understanding of the initiation process involved in polymerisations of this type. The presence of OH groups in the polymers will be investigated using the method of Dainton<sup>5</sup> in order to prove or disprove the formation of OH-radicals by the positive ions.

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