

454. The Propagation of Reaction Chains in the Polymerisation of Styrene.

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Styrene has been polymerised in the presence of oxygen, nitrogen, hydrogen, and mixtures of oxygen with nitrogen and oxygen with hydrogen severally. By using special apparatus, the progressive viscosity and density changes resulting from polymerisation could be measured on the same sample without unsealing the reaction vessel.

A simple mathematical treatment is proposed, which combines the viscosity and density measurements, to give a measure of the molecular weight of the polymer being formed during the reaction. This molecular weight decreases in a characteristic way with increasing partial pressure of oxygen. No significant difference could be detected between the action of hydrogen and nitrogen, when pure. When acting as a diluent for the oxygen, some evidence was obtained that the hydrogen takes part in the chemistry of the polymerisation.

Calculated molecular weights are used to follow the propagation of reaction chains in the polymerisation of styrene. The effect of the partial pressure of oxygen is tentatively interpreted by a mechanism in which oxygen acts as a chain breaker, as well as initiating chains through the formation of peroxides.

OXYGEN appears to act sometimes as a promoter and sometimes as an inhibitor in addition polymerisation. The mechanism of promoter action is almost certainly related to peroxide formation. The inhibiting action has been explained by Barnes (*J. Amer. Chem. Soc.*, 1945, **67**, 217) as being due to preferential reaction of carriers in the reaction chain, with oxygen rather than with further molecules of monomer. The general effect observed is an initial induction period, followed by polymerisation catalysed by the vinyl peroxide formed during the induction period.

So far as is known, nitrogen molecules have no specific effect on the course of the polymerisation reaction. To investigate this more fully, comparative experiments were carried out in which the nitrogen was replaced by hydrogen. If energy transfer plays an important part in the propagation of the reaction chains, hydrogen might be expected to behave differently from nitrogen. Hydrogen has been shown to be about as effective in causing the activation of organic molecules in unimolecular decompositions as the organic molecules themselves (cf. Oldenberg and Frost, *Chem. Reviews*, 1937, **20**, 99) and would probably facilitate the degradation of vibrational energy in colliding with an activated reaction product. However, no evidence for any specific difference between pure nitrogen and pure hydrogen could be obtained, at least under the conditions of the experiments described below. When the hydrogen is used as a diluent for the oxygen, there is some evidence that, unlike nitrogen, it takes part in the chemical reactions.

The reaction was studied by measuring *both* density and relative viscosity of the styrene during polymerisation. Relative viscosity has often been used as a measure of the extent of polymerisation, on the basis of the Arrhenius equation $\log \eta_r = kc$, where η_r is the relative viscosity, and c is the concentration of polymer dissolved in the monomer (*e.g.*, Foord, *J.*, 1940, 48). However, the constant k depends on the molecular weight and degree of branching of the polymer in solution. If these factors alter in the course of polymerisation, the use of the Arrhenius equation by itself would give misleading information. A more general relationship between viscosity and concentration is the Mark equation, $KM^\alpha = [\eta] \approx (\ln \eta_r)/c$, where $[\eta] = \lim_{c \rightarrow 0} (\ln \eta_r)/c$ is the intrinsic viscosity, M the molecular weight of the polymer, and K and α are constants which depend to some extent on the degree of branching of the polymer molecules.

This relationship may be combined with density measurements as follows. Both experiment and theory indicate that the mass of polymer formed controls density changes, which do not

appear to be influenced to any great extent by the molecular weight or degree of branching of the polymer molecules.

Starkweather and Taylor (*J. Amer. Chem. Soc.*, 1930, 52, 4708) showed that for vinyl acetate the extent of polymerisation is proportional to the volume contraction per cent., or to the increase in density divided by density, for

$$\text{Volume contraction, \%} = (\rho_t - \rho_0)/\rho_t = \Delta\rho/\rho_t$$

where ρ_0 = the density of monomer, ρ_t = density of partly polymerised monomer in time t , and $\Delta\rho$ = increase in density. For a small change in density $\Delta\rho/\rho_t \approx \Delta\rho/\rho_0$, so that in the initial stages of polymerisation the increase in density should measure the extent of reaction. Giguère (*J. Polymer Chem.*, 1947, 2, 296) has shown this to be true up to 25% conversion by preparing solutions of polystyrene in monomer and measuring their density.

We may derive this theoretically: Let the volume of a styrene molecule be V c.c., its mass m g., and the initial number of molecules N ; then initial density $\rho_0 = m/V$. Suppose that after time t , n new chemical bonds are formed by the polymerisation reaction. If the contraction in volume (v) per bond formed is constant and does not depend on the way the monomer units are joined together in the polymer molecule (*i.e.*, neglecting corrections for branching, etc.; cf. the general evidence of the parachor, Sugden, "Parachor and Valency", 1930, p. 33), then

$$\begin{aligned} \text{Volume contraction at time } t &= nv \text{ c.c.} \\ \text{Density at time } t &= Nm/(NV - nv) \\ &= \rho_0 \left(1 - \frac{nv}{NV}\right) \\ \text{Therefore} & n = NV\Delta\rho/v\rho \\ \text{Weight of polymer formed} &= nm \text{ g.} \\ \text{Concentration of polymer} &= nm/(NV - nv) \\ &= m\Delta\rho/\rho_0 v = k\Delta\rho \text{ g./c.c.} \end{aligned}$$

which is the relation observed by Giguère, and by Starkweather and Taylor.

Combining this with Mark's relationship we have

$$(\log \eta_r)/\Delta\rho = K'M^a = \text{"Structure function"}$$

where K' is a constant and the other symbols are as before. Simultaneous measurement of viscosity and density during polymerisation permits evaluation of the "Structure function" $(\log \eta_r)/\Delta\rho$. From its variation can be seen how far the molecular weight and structure of the polymer alter during the course of the polymerisation.

The results of various polymerisation experiments are recorded in Figs. 1—4. Important features of these results are now discussed.

(i) Three experiments under pure nitrogen and two under pure hydrogen (Figs. 1A, 2A, 3A), showed that the behaviour of these two gases is similar, so far as the present experiments go. It will be seen that the curves obtained for one of the experiments in the presence of nitrogen lie well below those obtained for the other experiments with nitrogen or hydrogen present (Figs. 1A, 2A, and 3A). In this case there was evidence that the course of the reaction was substantially different since the styrene became opalescent when the polymerisation vessel was being sealed off. This experiment has not been included in the average below.

Both $\Delta\rho$ and $\log \eta_r$ increase linearly with time and the average slope for all the experiments was

$$\begin{aligned} & (t \text{ in minutes}) \\ d(\log \eta_r)/dt &= 0.00205 \pm 0.00009 \\ d(\Delta\rho)/dt &= (3.40 \pm 0.12) \times 10^{-6} \end{aligned}$$

On the other hand, the $\log \eta_r$ curve for polymerisation under oxygen (Fig. 1A) indicates a considerable induction period, whereas the $\Delta\rho-t$ curve indicates hardly any induction period (Fig. 2A). As explained above, this is because, in addition to increasing the number of chemical bonds, as shown by $\Delta\rho$, the course of polymerisation involves changes of molecular weight and structure of the polymer. Viscosity is much more sensitive to these changes than is density.

(ii) Various mixtures of oxygen with nitrogen give curves lying between those obtained for the pure gases (Figs. 1B, 2B, 3B). So far as could be ascertained from a single series of experiments, hydrogen and nitrogen do not behave in the same way in the presence of oxygen.

FIG. 1A.

Viscosity increase with time for polymerisation in the presence of pure nitrogen, pure hydrogen, and pure oxygen.

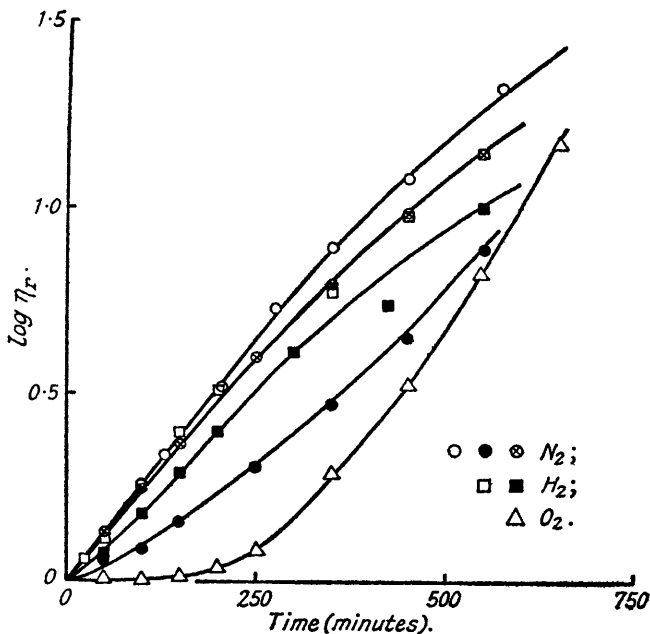
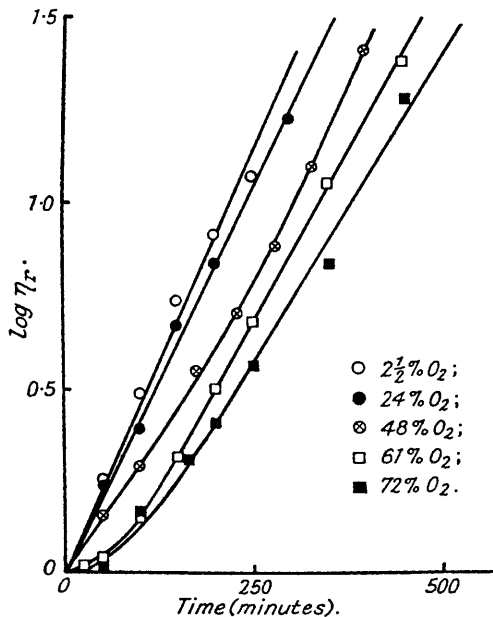


FIG. 1B.

Viscosity increase with time for polymerisation in the presence of mixtures of oxygen with nitrogen.



The difference is shown in Figs. 2B and 3B. The values of $\log \eta_r$ are not plotted in this case, to avoid confusing Fig. 1B, but these can be obtained from Figs. 2B and 3B by taking the ratios.

Some oxygen is consumed during the polymerisation, since on opening the viscometer at the completion of experiments with oxygen present there was an inrush of air, particularly noticeable

FIG. 2A.

Density increase with time for polymerisation in the presence of pure nitrogen, pure hydrogen, and pure oxygen.

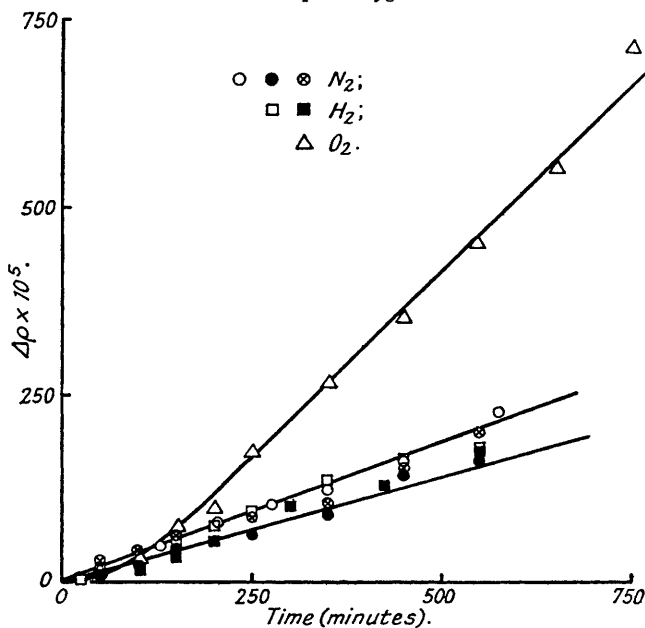


FIG. 2B.

Density increase with time for polymerisation in the presence of mixtures of oxygen with nitrogen, and oxygen with hydrogen.

Nitrogen mixtures:

- $2\frac{1}{2}\% O_2$; ● $24\% O_2$; ⊗ $48\% O_2$;
- $61\% O_2$; ■ $72\% O_2$;

Broken curve calculated for $7\% O_2$.

Hydrogen mixture: ▲ $7\% O_2$.

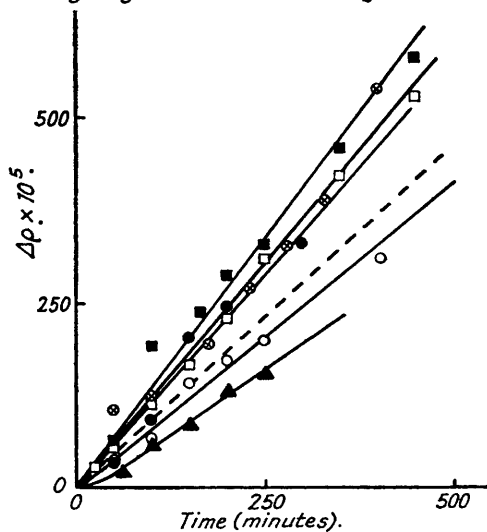


FIG. 3A.
Comparison between the effect of pure nitrogen and pure hydrogen on the structure function.

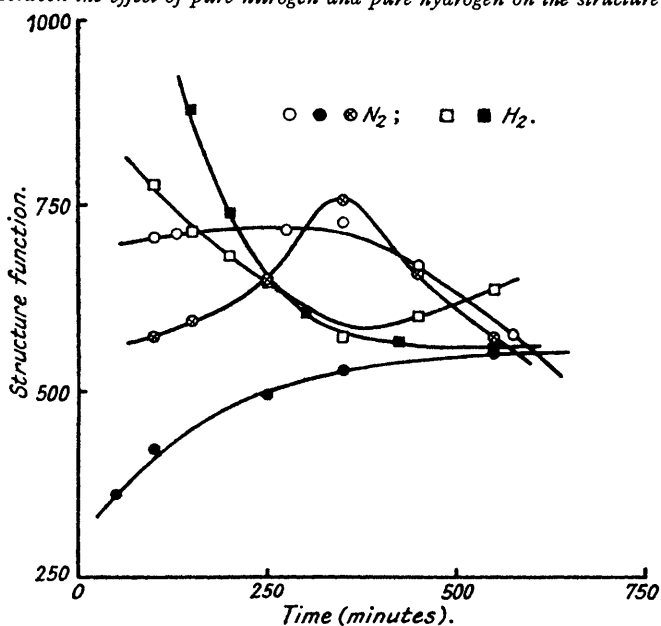
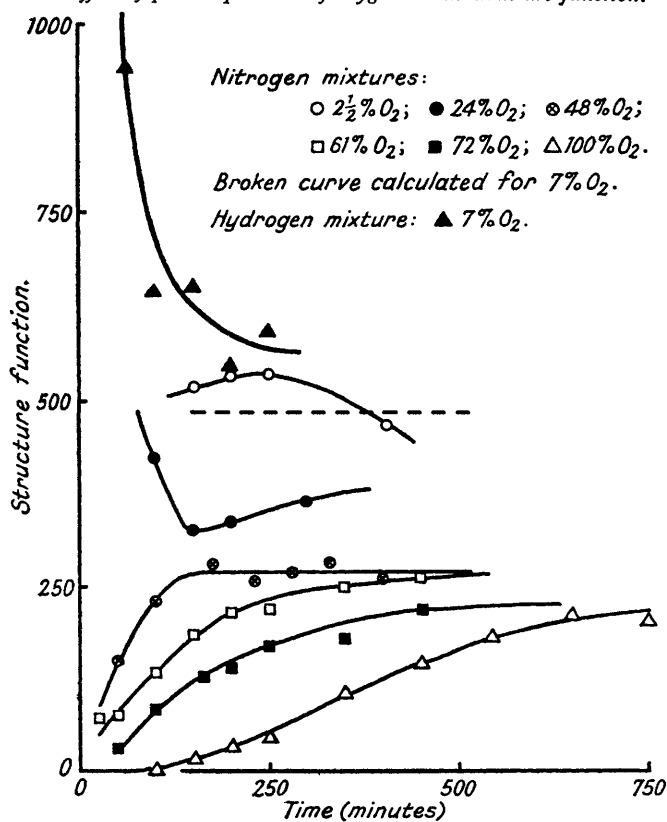


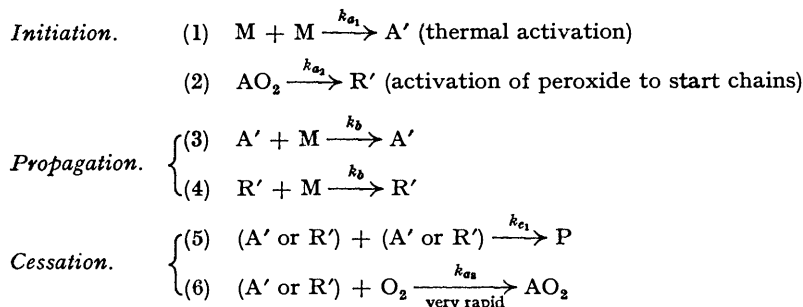
FIG. 3B.
The effect of partial pressure of oxygen on the structure function.



in experiments where more than 24% oxygen was used. This indicates consumption of oxygen during the reaction, which is to be expected if peroxides are formed.

Fig. 3 shows the plot of $(\log \eta_r)/\Delta\rho$ against time. So far as this "Structure function" measures the molecular weight of the polymer being formed, it appears that the molecular weight increases from zero to an asymptotic limit (Fig. 3B) provided that the atmosphere contains 48% oxygen or more. With less than this amount of oxygen present the molecular weight is higher (cf. also Fig. 3A). For each concentration of oxygen the limiting molecular weight is more or less constant. Plotting the partial pressure of oxygen against the *average value* of the limiting molecular weight gives a smooth curve (Fig. 4) falling steeply at low partial pressures of oxygen and flattening out at higher partial pressures.

Discussion.—Polymerisation in the presence of oxygen. A curve of this type (Fig. 4) may be interpreted by the following mechanism: Let M represent a monomer molecule, P an inactive polymer molecule, and A' and R' active growing polymer molecules. These can each have a molecular weight varying with time, but otherwise differ from one another merely in their origin. Then we may have the following series of reactions:



Active centres are formed either thermally or from the decomposition of peroxides according to equations (1) and (2). Owing to the preferential reaction of the active centres with oxygen [reaction (6)] little or no polymer will be formed until the concentration of dissolved oxygen has fallen to a low value. The concentration of the peroxide will therefore increase until substantially all the oxygen has been combined. The molecular weight of the polymer will then start to increase rapidly as the second cessation reaction will then become relatively unimportant. In the above experiments the volume of styrene and the volume of the gaseous atmosphere were kept approximately constant so the ultimate concentration of peroxide formed may be taken as proportional to the initial partial pressure of oxygen in the polymerisation vessel. On the basis of this assumption the limiting value

$$[AO_2] = Kp_{O_2} \dots \dots \dots (7)$$

Other workers have shown that the concentration of peroxide catalysts remains sensibly constant during polymerisation owing to their slow unimolecular decomposition. A steady state is reached when (A' and R' being treated as kinetically equivalent)

$$\text{Rate of initiation} = \text{rate of cessation}$$

$$k_{a1}[M]^2 + k_{a2}Kp_{O_2} = k_{c1}[A']^2 \dots \dots \dots (8)$$

i.e., only reactions (1), (2), and (5) are taken into account in the steady state.

$$\text{Chain length} = \frac{\text{Rate of propagation}}{\text{Rate of cessation}} \dots \dots \dots (9)$$

$$= \frac{k_b[A'][M]}{k_{c1}[A']^2} = \frac{k_b[M]}{k_{c1}[A']}$$

Substituting from equation (8), we have

$$\text{chain length} = k_b[M] / \sqrt{k_{c1}(k_{a1}[M]^2 + k_{a2}Kp_{O_2})} = \frac{K_1}{\sqrt{1 + K_2p_{O_2}}}$$

The chain length, *i.e.*, the average molecular weight once a steady state has set in, should thus behave as is actually observed in Fig. 4, in which the limiting molecular weight is controlled by the initial partial pressure of oxygen used.

Effect of hydrogen in the presence of oxygen. The data so far available require further experimental substantiation before a definite interpretation can be given. However, the possibility of interference with the normal polymerisation chains, by processes involving the chemical interaction of hydrogen such as $\text{AO}_2 + \text{H}_2 \longrightarrow \text{A}\cdot\text{O}\cdot\text{OH} + \text{H}$, is of considerable interest, and should be kept in mind in other experiments on polymerisation. Such a possibility of chemical interaction with the radicals in solution is not necessarily limited to hydrogen. For example, hydrocarbons such as ethylene can be considered from this standpoint.

By controlling the temperature and partial pressure of oxygen used, the average molecular weight of the product may likewise be controlled, as is shown by Fig. 4.

The general rise of molecular weight with time when the partial pressure of oxygen exceeds about 24% (Fig. 3B) also agrees with the simple mechanism outlined. However, when the

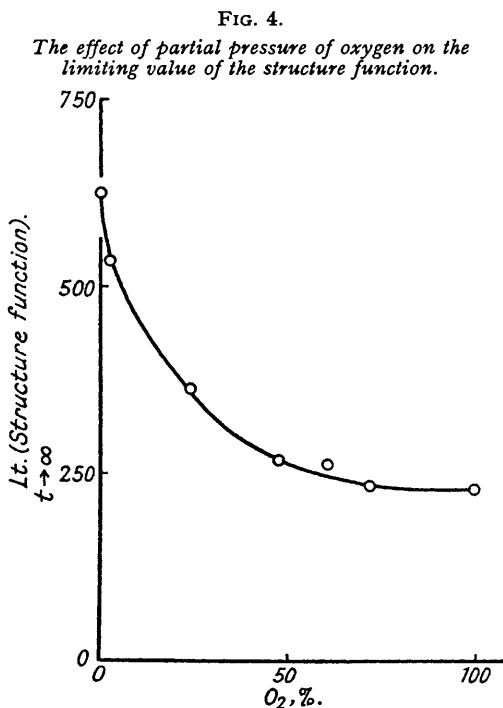
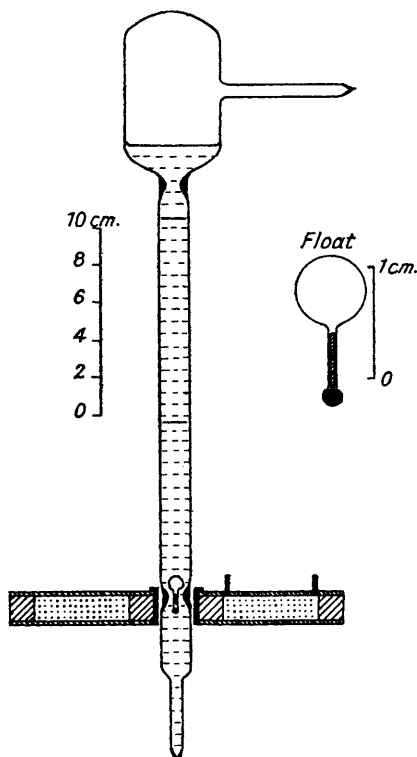


FIG. 5.
Densitometer-viscometer in position for viscosity measurement.



partial pressure of oxygen is less than about 24%, the course of polymerisation, at the temperature used, is more erratic, and high *initial* molecular weights are frequently found. These high initial molecular weights appear to be due to the absence of reaction (6) which suppresses polymer molecular weight in the early stages, when sufficient oxygen is present. In the absence of this reaction, the polymer molecules grow until they interfere with one another. But the reproducibility of the growth process is poor, as might be expected from the fact that chain stopping and chain starting depend on chance impurities.

An independent check on the above conclusions was obtained as follows. In some experiments the polymer formed was precipitated from benzene solution by the dropwise addition of excess of methylated spirits (Foord, *loc. cit.*). The polymer was filtered off and dried. An approximate value of the intrinsic viscosity was obtained by measuring the relative viscosity of solutions of the polymer in toluene (0.1—0.2%). The following results were obtained :

Gas present during polymerisation.	[η].	Gas present during polymerisation.	[η].
61% O ₂ in N ₂	1.13	48% O ₂ in N ₂	1.52
Pure H ₂	2.66		

These results confirm the general trend towards increased molecular weight as the partial pressure of oxygen decreases.

EXPERIMENTAL.

Nitrogen.—Nitrogen as supplied by the British Oxygen Co. contained 1–2% of oxygen as the chief impurity. This was removed by the method employed by Mackle and Ubbelohde (this vol., p. 1161).

Oxygen.—The oxygen was also supplied by this firm, and was used without further purification.

Hydrogen.—Hydrogen was generated by electrolysis of a saturated solution of barium hydroxide, nickel electrodes being used. Purification was accomplished by passing the gas through two successive tubes packed with platinised asbestos electrically heated to 600°. The first tube served to remove traces of catalytic poisons which may have been present, and both tubes caused any adventitious oxygen to be oxidised to water. The purified hydrogen was dried by passing through concentrated sulphuric acid. Any sulphuric acid spray was removed by diffusion through potassium hydroxide pellets and chemically pure glass-wool.

Styrene.—On receipt, this contained quinol as inhibitor, together with an undetermined amount of phenylacetylene, a common impurity in commercial styrene. The scheme used for purification was essentially that of Price and Adams (*J. Amer. Chem. Soc.*, 1945, **67**, 1674). Quinol was removed by successive shaking with 10% sodium hydroxide solution. By stirring vigorously with Nessler's reagent (Johnson and McEwen, *ibid.*, 1926, **48**, 469) the phenylacetylene was removed. The product was allowed to stand over calcium chloride, and before use the styrene was fractionated from potassium hydroxide pellets under pure nitrogen at reduced pressure. The middle fraction was collected and redistilled as before, the fraction coming over at 45–46°/20 mm. being accepted as pure styrene.

The Viscometer-Densitometer.—Densities were measured by a magnetic balance method, the buoyancy force on a small glass float being counterbalanced by the magnetic force on a small piece of iron sealed into the float. Relative viscosities were obtained from the density of the liquid and the time of rise of the float between two marks on the viscometer tube. Since density and viscosity measurements do not appear to have been made simultaneously on a polymerising system, the method will be given in some detail.

Construction of the Apparatus.—The float. Pyrex tubing was drawn out to give a uniform capillary of about 2 mm. bore, and into this capillary was inserted a thin strip of "Stalloy" transformer core metal, chosen for this work because of its extremely low magnetic retentivity. One end of the capillary was sealed, and a small bulb of about $\frac{1}{4}$ in. diameter blown on the end. The other end of the capillary was thickened slightly and then sealed off giving the float a total length of about $\frac{3}{8}$ in. (Fig. 5). The density of the float was adjusted by adding small pieces of molten glass to the tail until the float just failed to sink in monomeric styrene at 25°. This ensured a high sensitivity for our work.

Densitometer-Viscometer. The vessel in which the polymerisation took place was a cylindrical bulb made from 2-in. Pyrex tubing. Joined to its were a $\frac{3}{8}$ in. diameter side-arm for filling, and a uniform $\frac{3}{8}$ in. (outside diameter) tube in which the measurements of density and viscosity were made. The float was inserted into this tube and kept in position by the constrictions as shown. Fig. 5 shows the apparatus in position for measurements of density and viscosity. During polymerisation, the apparatus was inverted so that the solution flowed into the large bulb.

Coil. Two thousand turns of 30 s.w.g. copper wire (enamelled and cotton-covered) were wound on a former made from a core of aluminium tubing of $\frac{3}{8}$ in. inside diameter and two plywood discs each 7 in. in diameter. The centre was reinforced by a circular block of wood fitting the aluminium core tightly. As the coil was intended to be immersed in a thermostat, the former was soaked in "Akard" bakelite lacquer and stoved for 3 hours in a vacuum oven. This was repeated after winding on the wire. The external leads were rubber-covered wire, and where they entered the coil the joins were well covered with "Picein" wax. The whole coil was finally given a thick coat of a mixture of one part bee's wax and one part resin, together with a little magnesium carbonate as filler. To concentrate the magnetic field of the coil, a ring of soft iron, of $\frac{3}{8}$ in. inside diameter, was attached to the upper end of the aluminium core. This served to give a sharper balance point in the density determination. The coil was clamped horizontally in a thermostat at 25° ± 0.02°. The current passing through the coil was measured by a linear scale milliammeter having a range of 150 ma.

Density calibration. Before insertion in the densitometer-viscometer the float was calibrated. The density ρ is given by $\rho = d + ki^2$, where d = density of the float, i = current through the coil, and k = constant. Several mixtures of ethyl acetate and chloroform containing up to about 5% of chloroform were prepared, and their density determined at 25° ± 0.02° with a pycnometer. A $\frac{3}{8}$ in. Pyrex tube sealed at one end was filled with one of these mixtures and clamped vertically in the thermostat through the centre of the coil. The float was dropped in, and 15–20 minutes allowed for the temperature to reach 25°. The current in the coil was switched on and adjusted to a value of about 120 ma. by means of the sliding resistance in parallel with it. The float was drawn down the tube by means of a magnet until it was held by the magnetic field of the coil. The current was then decreased slowly until the magnetic force just failed to balance the buoyancy force when the float commenced to rise to the surface. The current flowing when this occurred was noted and the procedure repeated several times for consistent results. Density ρ and i^2 gave a linear plot from which the constants d and k were calculated by standard probability methods. The float actually used for most of the experiments recorded here measured density according to the equation $\rho = 0.89509 + 1.562 \times 10^{-6} i^2$, where i was measured in milliamps.

The Polymerisation Experiments.—Freshly distilled styrene was quickly sucked into the inverted viscometer-densitometer and the air was displaced by the gas under which it was required to carry out the polymerisation. In the case of gases which were available in quantity (oxygen and nitrogen) this was done by blowing the gas through the vessel for about 10 minutes before sealing it off. For hydrogen and for the mixture of oxygen and hydrogen, which was prepared in a gasometer of 2 l. capacity, the vessel was evacuated and refilled with the gas, the process being repeated about a dozen times before

sealing off. About the same volume of styrene was taken (45 c.c.) in each experiment, so that the volume of the gas in the polymerisation vessel was about the same (120 c.c.) each time.

During polymerisation, carried out in a thermostat at $65^{\circ} \pm 0.07^{\circ}$, the viscometer was removed at known intervals, the reaction arrested by chilling, and measurements were taken at 25° . On reimmersion at 65° two minutes were allowed for the heating up, in plotting the data.

Measurements.—20—25 Minutes were allowed for the styrene to attain temperature equilibrium, with the viscometer clamped vertically through the centre of the coil (Fig. 5) by means of non-magnetic clamps. Density measurements were made as already described for the calibration of the float, the float being kept in the wide part of the viscometer tube away from the constrictions. As the viscosity of the styrene increased during polymerisation it became more and more difficult to obtain an accurate estimate of the density. This difficulty was overcome to some extent by attaching an electric buzzer to the bulb of the densitometer-viscometer. The vibration helped to overcome the friction between the float and the viscometer tube. Several readings were taken and the mean was used in the calculation of density. To measure the relative viscosity of the partly polymerised styrene, the viscometer tube was withdrawn slightly from the coil until the tail of the float slid through the constriction. This served to centre the float so that it rose freely without touching the sides when the current through the coil was switched off. The time of rise between two marks on the viscometer was noted. This operation was also repeated several times, and the mean time of rise t used to calculate the relative viscosity $\eta_r = i^2 t / i_0^2 t_0 = \rho_0 t / \rho t_0$.

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