310. *The Polymerisation of Vinyl Compounds by the Sulphite Radical.*

By B. DUDLEY SULLY.

The polymerisation of styrene in emulsion by means of monothionic acid radicals generated by the oxidation of sodium sulphite in the aqueous phase is described. The polymerisation is catalysed by the presence of traces of copper in a manner parallel to the known effects of similar quantities of copper in the aerial oxidation of sulphite solutions. The proposed mechanism is in agreement with current theories for both the oxidation of sulphite and the reaction of the bisulphite ion with styrene in the presence of an excess of gaseous oxygen. It is also shown that when the partial pressure of oxygen approaches zero each atom of oxygen produces several molecules of polymer, and the effect is explained by chain transfer between the growing radical and the sulphite ions in solution. The polymer molecules formed have sulphonic acid end-groups.

THIS research began with the observation that addition of sodium sulphite to an emulsion of styrene in water markedly increased the rate of polymerisation. Further experiment showed that the rate of polymerisation increased with rising temperature, being a maximum, at atmospheric pressure, at 90°. This paper describes the polymerisation of styrene but the same technique can be applied to other polymerisable vinyl compounds such as vinyl acetate and methyl methacrylate. For example, vinyl acetate can be polymerised quite rapidly at room temperature although, as with all emulsion techniques applied to ester monomers, the product may be partly hydrolysed unless the pH of the emulsion is kept within certain limits.

The procedure in its simplest form as applied to styrene is illustrated by the following experiment : 50·0 g. of styrene (freshly distilled) containing 0·5 g. of oleic acid were emulsified with twice the weight of distilled water containing 0·50 g. of hydrated sodium sulphite. The emulsion was stirred in a flask at 90·0° ± 0·1° (thermostat) and was vented to the atmosphere through a narrow-bore glass tube about 6 in. long. In this way air could very slowly diffuse into the flask, aided to some extent by the expansion and contraction of the vapour above the emulsion caused by slight variations in the temperature of the bath. The sodium sulphite used contained 8 p.p.m. of copper and 15 p.p.m. of iron. After approximately 17 hours' stirring, polymerisation was complete and there was no residual odour of styrene. During the polymerisation about 13 g. of the styrene coagulated prematurely to a hard mass that adhered to the stirrer. The Staudinger molecular weight of the product isolated by coagulation with butanol and acetic acid, washing with distilled water and drying in an oven, was 390,000. An experiment at 80° under the same conditions gave similar results. The procedure was improved in later experiments by the following changes. (1) The oleic acid was replaced by stearic acid (this improved the colour of the product after moulding). (2) Alkali or buffer salts were added, to lessen the variation in pH that results from such causes as the formation

of benzaldehyde or the oxidation of the sulphite. (3) Protective colloids, *e.g.*, gelatin or methyl cellulose, were added to the emulsion to increase its stability. (4) The presence of protective colloids, particularly gelatin, tends to reduce the catalytic activity of the sulphite and so increase the time of polymerisation. It was realised that the oxidation of sulphite is also inhibited by the presence of gelatin and, on the assumption that the chain oxidation of the sulphite was the starting point of the polymerisation, 10 p.p.m. of cupric copper were added to increase the rate of chain initiation. Experiments 1 and 2 show the inhibiting effect of gelatin and the manner in which it is overcome.

In another series of experiments attempts were made to measure the absorption of oxygen by connecting the reaction vessel to a gas burette, but the results were not conclusive because there was a considerable apparent absorption of gas when polymerisation was nearly complete owing to removal of the partial pressure exerted by the monomeric styrene. On an industrial scale commercial nitrogen containing 0·1% of oxygen has been used to obtain a controlled oxidation of the sulphite.

The remaining experiments (nos. 3—15) were made with particularly rigid control of oxygen and oxidising impurities. A review of these experiments shows that the coupling between the oxidation of the sulphite and the polymerisation of the styrene is not so rigid as was at first thought, and leads to the conclusion that the intermediate active state is capable of separate existence for an appreciable time. In order to examine the effect of oxygen and oxidising agents it was clear that special consideration would have to be given to the purification of the styrene before polymerisation. Earlier experience had shown that by vacuum-distillation alone it is particularly difficult to obtain with absolute certainty styrene perfectly free from oxidation products, a difficulty apparently caused by very small leaks in the apparatus. The presence of aldehydic impurities in most samples of styrene distilled *in vacuo* in the laboratory can be shown by the change in colour when a sample is shaken with a small proportion of aqueous neutral 5% hydroxylamine hydrochloride solution containing methyl-orange. The best styrene samples from the point of view of oxygen impurities were prepared by steam-distillation. At first premature polymerisation caused considerable difficulty, but this was later eliminated by steam-distillation from a solution of ferrous sulphate in the presence of sulphur. Using the apparatus shown in Fig. 1 it was possible to work in the complete absence of air and the styrene could be steam-distilled under reflux and run into the polymerisation solution as and when required. At no time did polymerisation cause difficulty when this method was used.

<div align="center">EXPERIMENTAL.</div>

The polymerisation system for experiments 1 and 2 had the following composition in parts by wt. : styrene 100, anhydrous sodium sulphite 1·0, stearic acid 0·5, gelatin 0·3, anhydrous sodium carbonate 0·05, and distilled water 300. The apparatus, a three-necked flask fitted with a thermometer and an efficient stirrer, was cleaned with chromic–sulphuric acid to remove traces of inhibitors. Recently distilled styrene containing quinol was de-stabilised by washing with (1) aqueous sodium hydroxide until no colour was developed in the alkali after keeping for ½ hour, (2) distilled water, (3) 0·1N-potassium dichromate acidified with acetic acid, and finally (4) several quantities of distilled water until neutral. The emulsion was prepared within 1 hour of de-stabilising the styrene and was heated in a water-bath thermostatically controlled to 90·0° ± 0·1°. A temperature of 60° was reached in less than 5 minutes and time readings were referred to this point as zero. Samples of the emulsion were drawn at zero time and at 15-minute intervals until polymerisation had commenced as shown by the formation of an opalescence on dilution with an excess of methanol. After the induction period had been determined further samples were taken at hourly intervals. The amount polymerised was determined by precipitating the emulsion with a ten-fold excess of methanol acidified with hydrochloric acid to N/100. The polymer was washed with methanol, followed by N/1000-acetic acid and a further quantity of methanol, after which it was dried at 80° and weighed. The rate of oxidation of the sulphite was estimated by diluting a sample of the emulsion with ten times its weight of distilled water, neutralising with acetic acid, and titrating with N/10-iodine (starch).

Experiment 1.—No added copper catalyst.

Time (hrs.)	0	1	2	2·25	3	4	5	22
Temp.	60·0°	89·8°	89·5°	89·3°	89·5°	89·8°	89·5°	89·5°
Wt. polymerised, %	0	0	0	trace	0·20	—	2·5	39·4
Sodium sulphite (parts by wt.)	1·000	0·930	0·920	—	0·870	0·850	0·805	0·426

Experiment 2.—Conditions as in expt. 1 except for the addition of copper sulphate equivalent 10 p.p.m. of metallic copper, calc. on the wt. of styrene.

Time (hrs.)	0	0·25	0·5	1	2	2·5	3	3·5	4	5	6
Temp.	60°	87°	89·8°	89·2°	90·0°	90·0°	90·2°	90·8°	91·0°	90·1°	89·8°
Weight polymerised, %	0	trace	2·4	8·56	22·5	—	46·6	—	82·8	100	—
Sodium sulphite (parts by wt.)	1·000	0·944	0·895	0·845	—	0·760	0·730	0·674	0·654	0·495	0·332

The molecular weight of the polymer formed in expt. 2 as determined by the Staudinger viscosity method was 117,000. It will be observed that during the polymerisation 0·4 g. of sodium sulphite was oxidised and on the assumption that one molecule of sulphite would on oxidation lead to the formation of one molecule of polystyrene the number-average molecular weight is $100 \times 126/0\cdot4 = 31,500$, which is not inconsistent with available data. Other similar experiments showed that the rate of polymerisation was influenced by the pH of the sulphite solution in a manner parallel with the influence of pH on the rate of oxidation of sulphite solutions by gaseous oxygen.

Experiments 3—15.—Materials used were :

(a) *Styrene.* Pure styrene stabilised with quinol and sulphur, n_D^{20} 1·54697.

(b) *Sodium sulphite, anhydrous.* Iron content 30 p.p.m.; copper content 15 p.p.m.

(c) *Copper sulphate,* N/10. Standardised by Foote's method (*J. Amer. Chem. Soc.*, 1938, **60**, 1349).

(d) *Stearic acid.* Good-quality commercial acid having an iodine value less than 5 and a faint yellow colour when molten [Type S.D.S., Prices (Bromborough) Ltd.].

(e) *Distilled water.* Obtained by distillation of town water with sodium chromate using an aluminium condenser, it contained up to 10 p.p.m. of aluminium.

(f) *Ferrous sulphate.* AnalaR grade.

(g) N-*Sodium hydroxide.* Standard laboratory analytical reagent.

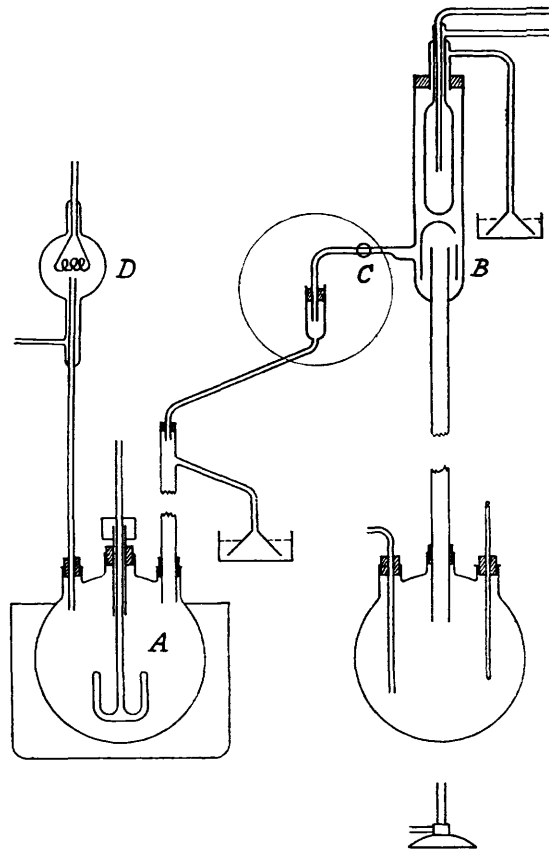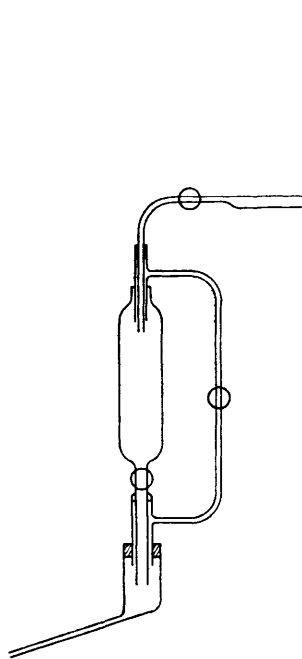FIG. 1.   FIG. 2.

Apparatus. The apparatus (Fig. 1) consisted of a three-necked flask (*A*) fitted with a glass stirrer in a stainless steel bearing with a rubber gland and an inlet for the styrene. The whole was immersed in a bath at 91·0° (thermostat). The styrene was steam-distilled in a current of hydrogen (30 ml./min.) through a specially designed column containing a separator (*B*) in the head, whereby the aqueous layer was returned to the top of the column and the styrene layer was run as required, through a stop-cock (*C*), directly into the polymerisation flask (*A*). The air in the apparatus was displaced by hydrogen from a cylinder, from which the last trace of oxygen was removed by passage through the heated filament of a 60-watt electric lamp (*D*).

General procedure. Styrene was added to the distillation flask, together with an aqueous solution of ferrous sulphate. The mixture was prevented from bumping by adding a few pieces of alumina and a little stearic acid to emulsify the styrene. The column was a Dufton spiral, 5 ft. long, and equivalent to 5—10 theoretical plates. The average composition was : styrene 160 ml.; ferrous sulphate 10 g.; stearic acid 0·5 g.; water 400 ml. The air in the flask and column was displaced with purified

hydrogen through a water seal before the heating was commenced. A manometer in the gas supply to the burner facilitated the day-to-day reproduction of the same conditions of reflux.

The polymerisation flask (*A*) contained the aqueous catalyst solution, the standard composition being sodium sulphite (anhydrous) 3·0 g., stearic acid 1·2 g., 0·1M-copper sulphate 0·6 ml., N-sodium hydroxide 1·2 ml., and distilled water 600 ml. The stearic acid was added first, followed immediately by the sodium sulphite dissolved in the full amount of water. The copper sulphate solution, followed by the sodium hydroxide, was added after the sulphite solution had reached the temperature of the thermostat (90°). The mixture was left in the thermostat with occasional stirring for an average of 17 hours before addition of the styrene, and during this time the last trace of oxygen was presumed to be absorbed by the sulphite. Continuous stirring was commenced about 1 hour before the first addition of the styrene. In order to standardise the conditions the styrene was boiled under total reflux for 3 hours before it was added to the sulphite solution. After polymerisation the emulsion was not exposed to air until it was quite cool, to avoid degradation. Prematurely coagulated polystyrene was removed by filtration through muslin. The emulsion was acidified with concentrated hydrochloric acid, and the coagulated polystyrene filtered off and washed with distilled water until free from traces of chlorides and sulphate.

Experiment 3. Styrene (100 ml.), and water (400 ml.) containing hydrated ferrous sulphate (10 g.) were boiled under total reflux for 3 hours in a current of hydrogen (30 ml./min.). The aqueous catalyst solution contained sodium sulphite (anhydrous; 3·0 g.), 0·1N-copper sulphate (0·6 ml.), stearic acid (1·2 g.), N-sodium hydroxide (1·2 ml.), and water (600 ml.). This mixture was left overnight at 91·0° and then stirred for 15 minutes; at the end of the refluxing period the styrene was added at a steady rate during 45 minutes. Stirring was continued for a further 2 hours and the emulsion was cooled overnight. Hydrogen (60—70 ml./min.) was passed through the polymerisation flask throughout the experiment. On pouring of the emulsion through muslin, 1 g. of prematurely coagulated material was obtained as a single piece. The emulsion (710 g. containing 12·3% of solid, determined by evaporation) was coagulated with hydrochloric acid. The resulting polystyrene after washing was dried in a vacuum oven at 100°. The dry polymer had a Staudinger molecular weight of 605,000 and the viscosity of a 5% solution in benzene at 20° was such that a ⅛ in. steel ball took 47 seconds to fall through 6 cm.

Experiment 4. In this experiment no copper catalyst was added, the only copper metal present being that contained as impurities in the components, particularly the sodium sulphite. The general conditions were as in expt. 3. The resulting emulsion contained 12·7% of polystyrene and 1 g. of prematurely coagulated material. The product, isolated as before, had a Staudinger molecular weight of 583,000 and the viscosity of a 5% solution measured as in expt. 3 was 36 seconds.

Experiment 5. This experiment was made to determine the activity of sodium dithionate as a catalyst for polymerisation. The sodium dithionate was recrystallised 3 times from water and was free from chloride and sulphate. The general conditions were similar to those of expt. 3. A solution containing sodium dithionate (3·0 g.) and stearic acid (1·2 g.) in water (600 ml.) was kept at 91° for 45 hours in a current of hydrogen (60—70 ml./min.). N-Sodium hydroxide (1·2 ml.) was then added. The styrene was boiled under reflux for 3 hours and then distilled into the polymerisation flask during 105 minutes. After a further 4 hours the emulsion was allowed to cool overnight. Next morning the styrene had separated and appeared to be only slightly polymerised. A small proportion remained emulsified in the water but contained only 16% of polystyrene, the remainder being unchanged monomer.

Experiment 6. Expts. 6, 7, and 8 were made to determine whether it is necessary to have the copper catalyst present in the emulsion throughout the polymerisation or whether the monothionic acid radicals or radical ions have an appreciable life before dimerisation. The general conditions were as in expt. 3. Sodium sulphite (anhydrous; 3·0 g.), 0·1N-copper sulphate (10·0 ml.), and N-sodium hydroxide (3·2 ml.) were dissolved in water (600 ml.) at 70° and the solution was filtered in air through a Buchner funnel to remove the cuprous precipitate. It was then poured immediately into the polymerisation flask which already contained stearic acid (0·5 g.) and from which all air had been displaced by a current of hydrogen. The styrene, which had been boiling under reflux for 3 hours, was added at a constant rate during 2 hours. The product had a Staudinger molecular weight of 394,000 and the viscosity of a 5% solution measured as in expt. 3 was 30 seconds.

Experiment 7. This experiment was similar to the previous but the apparatus was modified so that the mixing and filtration of the sodium sulphite solution after the addition of the copper could be carried out in an atmosphere of purified hydrogen, at 90°. The polymerisation proceeded exactly as before and the product had a Staudinger molecular weight of 533,000.

Experiment 8. This experiment was again similar to experiment 5 but 50 ml. of styrene monomer were added to the sulphite solution after the addition of the copper sulphate solution. The temperature was 90° throughout. The styrene monomer separated all the precipitated cuprous oxide by a kind of flotation process so that on filtration through paper in an atmosphere of purified hydrogen every detectable trace was removed. Styrene added to the filtrate polymerised as readily as before and the polymer produced gave a clear moulding free from copper. It appears that the sulphite radicals remain in the solution and will catalyse the polymerisation even after the removal of the metals.

Experiment 9. A solution containing sodium sulphite (anhydrous; 3·0 g.), stearic acid (1·2 g.), N-sodium hydroxide (1·4 ml.), and 0·1N-copper sulphate (1·0 ml.) in air-free water (600 ml.) was allowed to remain in a hydrogen atmosphere for 48 hours at 90° in an unsuccessful attempt to prevent polymerisation by allowing the sulphite radicals to dimerise. Styrene was added during 2 hours and was completely polymerised in a further hour. The emulsion contained 13·0% of polymer after passing through a muslin screen which retained 1 g. The Staudinger molecular weight was 722,000 and the viscosity of a 5% solution measured as before was 94 seconds.

Experiment 10. This experiment was similar to expt. 3, except that the catalyst solution was kept at 90° for 17 hours before addition of the styrene and commercial nitrogen was used as the inert gas. The styrene polymerised readily to a Staudinger molecular weight of 583,000.

In the remaining experiments the apparatus was so modified that the styrene could be collected and

measured before being added to the sulphite solution. To do this the portion of the apparatus enclosed in the circle in Fig. 1 was modified as shown in Fig. 2. Care was still taken to ensure that oxygen contamination was eliminated by thorough purging of the apparatus with measured volumes of purified hydrogen.

Experiment 11. The general conditions were similar to those described in the previous experiments but the amount of copper catalyst was reduced. Stearic acid (1·2 g.) and hydrated sodium sulphite (6·0 g.) were weighed into the polymerisation flask. The air in the flask was displaced with hydrogen, and then 600 ml. of boiling distilled water containing N/100-copper sulphate in 1% acetic acid (0·18 ml.) and N-sodium hydroxide (2·0 ml.) were added. The solution was left overnight in contact with purified hydrogen. The styrene was first boiled under reflux in hydrogen for 2¼ hours and then 120 ml. were collected in a current of hydrogen and run into the caatalyst solution during 1¾ hours. Polymerisation was complete about ½ hour after the last drop had been added, and the emulsion was allowed to cool overnight. The emulsion contained 15·6% of polymer and 7 g. of coarse particles retained by a muslin screen.

Experiment 12. Stearic acid (1·2 g.) and hydrated sodium sulphite (6·0 g.) were added to the flask as in the previous experiments, followed by 600 ml. of boiling distilled water containing N/100-copper sulphate in 1% acetic acid (0·18 ml.) and N-sodium hydroxide (10 ml.). After 3 hours' refluxing in hydrogen, 200 ml. of the styrene were collected and run into the polymerisation solution during 3 hours. 45 Minutes after the last drop of styrene had been added the unpolymerised material was distilled off in a current of hydrogen. After recovery of 33 ml. of styrene in this way the mixture was left to cool overnight. Distillation was recommenced the next morning and a further 16 ml. of styrene were obtained, making a total of 49 ml. The final emulsion (650 g.) was alkaline to phenolphthalein and contained 18·6% of polymer having a Staudinger molecular weight of 455,000.

In the next experiment the general quantities and conditions were as in expt. 12, but the reaction time was considerably extended in an endeavour to complete the polymerisation. However, the proportion of styrene polymerised was not greatly increased by prolonged contact with sulphite solution, owing presumably to the removal of the sulphite radicals by the formation of polystyrene.

Experiment 13. The catalyst solution prepared as in the previous experiment was stirred for 2¼ hours before addition of the styrene, whereas previously the solution was left overnight. The styrene was added initially at the rate of 5 drops per minute and then at a slower rate overnight. By the next morning 80 ml. had been added. During the following day the remainder of the styrene was added, making a total of 200 ml. Since the polymerisation was not complete at the end of the day it was allowed to continue overnight. Next morning 32 ml. of unpolymerised styrene were recovered by distillation in a current of hydrogen. Coarse particles (27 g.) were separated by pouring the emulsion (710 g.) through a muslin screen. The Staudinger molecular weight of the product was 290,000 and the viscosity of a 5% solution in benzene measured as before was 3 seconds.

Experiment 14. Hydrated sodium sulphite (6·0 g.) and stearic acid (3·0 g.) were added to the flask immersed in the bath at 90° and the air was displaced with hydrogen. N/100-Copper sulphate (0·54 ml.) and N-sodium hydroxide (7·5 ml.) were added in cold distilled water (375 g.). The mixture was left overnight without stirring, in an atmosphere of purified hydrogen. Next day the solution was stirred for 4 hours, after which 75 ml. of styrene were added in 10 minutes, and were polymerised in about 30 minutes. 75 Ml. of distilled water saturated with air at 24° were next added, followed by a further 75 ml. of styrene which were run in during 15 minutes. This second portion was polymerised in a further hour, and so again 75 ml. of air-saturated water were added, followed by 75 ml. of styrene which were polymerised in about 1½ hours. A further 75 ml. of air saturated distilled water were then added, followed by 75 ml. of styrene. In this way a total of 300 ml. of styrene were added to 600 ml. of catalyst solution. After cooling overnight unchanged monomer (26 ml.) was recovered by distillation in hydrogen. The emulsion (785 g.) contained 29·1% of polymer. When the mixture was poured through muslin a single piece of polymer (10 g.) was separated. The Staudinger molecular weight was 528,000 and the viscosity of a 5% solution measured as before was 42 seconds.

Experiment 15. In this experiment the pH of the emulsion was stabilised by the use of borax, phosphate buffers having been found to interfere with the polymerisation (probably by the formation of complex salts with the copper catalyst).

Hydrated sodium sulphite (6·0 g.) and stearic acid (3·0 g.) were weighed into the polymerisation flask immersed in a bath at 90° as before, and the air was displaced with purified hydrogen. Distilled water (375 g.) containing AnalaR borax (0·60 g.) and N/10-copper sulphate (0·27 ml.) was added and the whole left in the bath overnight. Next morning the solution was stirred whilst the styrene was boiled under reflux for 2¾ hours, after which the first 75 ml. of styrene were collected and added as in the previous experiments during 90 minutes. After all had been added, 75 ml. of air-saturated distilled water were run in. This process of alternate addition was repeated as in expt. 14 until a total of 300 ml. of styrene had been added and the total weight of water including that present initially was 600 ml. After 6 hours from the first addition of styrene the flask was removed from the bath and allowed to cool overnight. Next morning unchanged styrene (40 ml.) was recovered by distillation at 90° in a current of hydrogen. The polymer content of the emulsion was 27% and the coarse particles, separated on pouring through muslin, weighed 5 g. The Staudinger molecular weight of the polymer isolated as before was 527,000. The viscosity of a 5% benzene solution was 29 seconds.

All molecular weights were determined by the Staudinger viscosity method at a concentration of 0·1% of the polymer in dry benzene and a value of 1·8 × 10⁻⁴ for the Staudinger constant was used.

DISCUSSION.

Polymerisation experiments of the kind described are very susceptible to the presence of traces of impurities and very rigid control is necessary before they can be considered quan-

titatively. The purest obtainable monomer was used to reduce the possibility of chain termination by reaction with an impurity. Interpretation of the experiments would be greatly simplified if it were possible to polymerise the styrene in a special solvent or with some addition functioning as a chain-terminating agent so that throughout the experiment all the polymer chains would be terminated by a controllable mechanism. At present, however, it is uncertain whether any agent exists which will affect only the chain-terminating mechanism without at the same time having an effect on the chain-initiating mechanism. Thus alcohols which cause chain termination also inhibit the oxidation of sulphite.

The oxidation of sulphite solutions by gaseous oxygen or air was first studied by Bigelow (*Z. physikal. Chem.*, 1898, **26**, 493) who showed that various organic compounds containing a hydroxyl group (*e.g.*, benzyl alcohol, butan-2-ol, allyl alcohol, mannitol, and glycerol) acted as powerful negative catalysts; he also showed that the rate of oxidation was very sensitive to the previous history of the water in which the sulphite was dissolved. Titoff (*ibid.*, 1903, **45**, 641) showed that the oxidation was very sensitive to the presence of copper and to a lesser extent of iron. One part of copper in 16×10^9 parts of water accelerated the reaction about 30%; in later work he used known amounts of copper and was then able to obtain reproducible results. Bäckström (*J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Trans. Faraday Soc.*, 1928, **24**, 601) was the first to recognise the oxidation of sulphite as a chain reaction in which an active centre serves as the starting point for the oxidation of a large number of molecules. According to Semenoff ("Chemical Kinetics and Chain Reactions," Oxford Univ. Press, 1935, p. 383) it is considered by some that in the absence of both light and catalysts the oxidation of sulphite would not proceed at all. Similar conditions govern the polymerisation of styrene emulsions in sulphite solution, and in the same way it has been found impossible to purify the ingredients to such an extent that the initial polymerisation is completely inhibited.

The chain mechanism for the oxidation of sulphite involves the formation of unstable intermediate compounds either by the step-wise reduction of oxygen or by the oxidation of the sulphite ion. The latter mechanism, reviewed by Hammett ("Physical Organic Chemistry," New York, 1940, p. 370 *et seq.*), is more in accordance with the polymerisation reaction. Fuller and Crist (*J. Amer. Chem. Soc.*, 1941, **63**, 1644) found that the reaction of sodium sulphite solutions saturated with oxygen was strictly of the first order with respect to sulphite-ion concentration and was also directly dependent on the cupric ion concentration when this exceeds 10^{-9}M. From an analysis of the latter effect it was claimed that there was a primary process independent of the heavy-metal ion. It was also found that the rate is independent of the pH between 8·8 and 8·2 and decreases in a complicated manner between 5·9 and 3·2. When a solution of sodium sulphite is oxidised with an excess of oxygen only a small proportion of dithionic acid is formed, which indicates that the oxygen reacts more rapidly with the sulphite radicals than with the reduced copper. On the other hand, it has been found that the reaction of sodium sulphite with a cupric copper salt in the absence of oxygen produces a complex salt of copper which undergoes electron transfer and forms sulphite radicals, about half of which dimerise to dithionic acid.

Compounds of sodium hydrogen sulphite and styrene have been prepared by several workers. Kharasch, Schenck, and Mayo (*ibid.*, 1939, **61**, 3092) and Kharasch, May, and Mayo (*J. Org. Chem.*, 1938, **3**, 175) have studied the reaction in detail and have isolated three different compounds, *viz.*: $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot SO_3H$, $C_6H_5 \cdot CH{:}CH \cdot SO_3H$, and $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot SO_3H$. These are formed simultaneously by passing oxygen into a vigorously stirred mixture of styrene with a stoicheiometric excess of alkali hydrogen sulphite. A free-radical mechanism was proposed for their formation by Kharasch and his co-workers (*locc. cit.*), who further noted that no polymer was formed during the preparation, and the present work shows that this is explained without doubt by the presence of an excess of gaseous oxygen which combines with the activated styrene radicals and prevents chain growth. The following mechanism for the polymerisation of styrene is consistent with the data for the oxidation of aqueous sulphite solutions and also with the mechanism proposed by Kharasch and his co-workers for the formation of the styrene sulphonic acid compounds :

(1) The bivalent sulphite ion loses an electron and becomes a univalent sulphite free radical, *e.g.*, monothionic acid free radical or monothionic acid free-radical ion. In the presence of bivalent copper this is explained by the formation of a complex cupric sulphite, followed by the transfer of an electron from the sulphite ion to the copper ion, as in the formation of free iodine from cupric iodide. In both cases the cupric copper is reduced to the cuprous state.

$$Cu^{++} + SO_3^{--} = Cu^{+} + SO_3^{-} \text{ *}$$

5 D
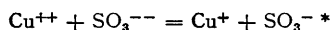
(2) The monothionic acid free radical (or free-radical ion) combines with styrene monomer to form a free radical complex.

$$C_6H_5—CH{=}\ddot{C}H_2 + SO_3^- * = C_6H_5—H\dot{C}{=}\overset{SO_3^-}{C}H_2 *$$
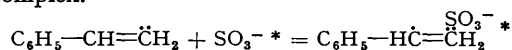
(3) The free radical complex combines with more styrene and the chain grows into a giant polymer radical by the accepted mechanism.

(4) The giant polymer radical continues to add styrene molecules linearly until it either gains or loses an electron. This may occur in various ways, *e.g.*: (*a*) Reaction with another polymer radical leading to complete termination of chain growth either by disproportionation to two neutral molecules or by dimerisation. A sulphite radical in the aqueous phase could also react similarly with a polymer radical. (*b*) Reaction with another neutral molecule. In this case the chain growth does not stop but undergoes transfer since the resulting product will still have an odd electron. The neutral molecule may be another " dead " molecule which may lose an electron from the middle of the chain leading to chain branching. The evidence adduced later in this work suggests that the most frequent reaction is the acquisition of an electron from a sulphite ion in the aqueous phase. This terminates the growth of the polymer molecule and creates another sulphite radical which in turn starts the growth of another chain.

(5) New chains are started when the trace of molecular oxygen in the gaseous phase oxidises the colloidal cuprous hydroxide back to the cupric state in which form it can react again with the sulphite ion as in (1). From this it will be seen that by the most efficient use of the oxygen in the gas space one molecule of oxygen will generate four sulphite free radicals :

$$4CuOH + 4H_2O + O_2 = 4Cu(OH)_2 + 2H_2O$$
$$Na_2SO_3 + Cu(OH)_2 = CuOH + NaOH + NaSO_3 *$$
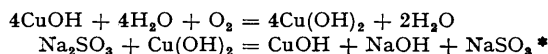
One of the features of the sulphite method of polymerisation is that it is particularly easy to obtain products of unusually high molecular weight. Several factors appear to contribute to this technically desirable effect, of which perhaps the most important is that the oxygen content of the emulsion is maintained at a very low value on account of its rapid reaction with the sulphite. From a general consideration it is believed that the presence of molecular oxygen is the most common factor leading to the formation of polymer molecules of low molecular weight, and the usual peroxide catalysts have obvious disadvantages in this respect. The molecular weight of the polymer may be varied by controlling the rate of oxidation of the sodium sulphite, as, for example, by passing at a measured rate through the emulsion a current of commercial nitrogen containing 0·1% of oxygen.

Several unsuccessful attempts were made to prepare a sulphite–styrene emulsion under conditions which would eliminate the initial oxidation of the sulphite, so that the polymerisation of the styrene would be completely inhibited until a trace of oxygen was admitted, but in every case the styrene polymerised to some extent before the admission of the oxygen. Attempts were also made to stir the sulphite solution in a closed system (expts. 9 and 10) so that the last trace of oxygen would be absorbed and then to allow a further lapse of time to permit the sulphite radicals to dimerise. This also was unsuccessful, for on adding the oxygen-free styrene once again a certain proportion polymerised.

The quantitative aspect of the dimerisation of a sulphite free-radical ion is interesting. If a sulphite free-radical ion dimerises immediately on collision with another similar free radical, as would be expected if the energy of activation for the combination were zero, then the concentration of radicals would decrease at a rate which at any instant is proportional to the square of the concentration at that instant (second-order reaction). Calculation on this basis shows that if at zero time the concentration is 100 and if after one minute this is reduced to 10, then the concentration after t minutes is $100/(9t + 1)$. It follows that in spite of the initial rapid reaction the amount present after one hour is still 0·185 and after 24 hours 0·0077.

On the other hand, for a unimolecular reaction in which the concentration decreased from 100 to 10 in the first minute the concentration after time t is $100 \times 0·1^t$, so that the concentration remaining would be 0·1 in 3 minutes and 0·001 in 6 minutes. The energy of activation required for the dimerisation will not be zero owing, amongst other things, to the repelling effect of the charge on the ions which would hinder their collision. In the light of these considerations the experimental results are not altogether unexpected.

Although efforts to eliminate the radicals by mutual recombination did not succeed it was found that, unless the sulphite solution was reactivated with air or oxygen, only a limited proportion of styrene could be polymerised. Thus, in experiments 12 and 13 with the purest obtainable monomer it was found that a sulphite solution will only polymerise about one-

seventh of its weight of styrene, after which the reaction practically ceases. With very impure styrene only a small concentration of polymer can be obtained. The reaction of the sulphite free-radical ions with the styrene is probably kinetically of the first order, owing to the excess of styrene, so that the removal of the free radicals by this mechanism is readily understood.

Experiments 13, 14, and 15 show that after the removal of the free radicals from the solution by polymer formation the oxygen contained in one volume of air-saturated water at room temperature will regenerate sulphite free-radical ions in a quantity sufficient to polymerise one volume of styrene. One litre of air-saturated water at 25° contains 6·0 ml. of oxygen (N.T.P.). If one atom of oxygen leads to the formation of two sulphite free radicals, it follows that the lower possible number average molecular weight of the product is numerically equal to the weight of polymer produced by 8 g. of oxygen, *i.e.*, $22,400 \times 904/(6 \times 4) = 850,000$ approx. (the density of styrene is 904 g./l.). There is little doubt that the number average molecular weight is much less than this. It seems therefore that with the purest obtainable styrene there is considerable reaction between the growing polymer molecules and sulphite ions in solution. These sulphite ions terminate the growth of the polymer molecule by a chain-transfer mechanism in which an electron is given up by the sulphite to the growing polymer chain in the same way as it can give up an electron to cupric copper. This produces another sulphite free radical which will initiate the formation of another polymer chain.

The probability of such a reaction occurring is high, since the sulphite ions are relatively numerous and furthermore they donate an electron with relative ease. In this way several polymer molecules each containing a sulphonic acid end-group can be produced from a single molecule of oxygen as the initiating step, and the minimum amount of gaseous oxygen required to oxidise the trace of copper and so continue the polymerisation is reduced to that necessary to replace the radicals that are lost by dimerisation. Further support for this view is obtained from an estimation of the number of sulphonic acid end-groups by neutralisation with alkali and then titration with hydrochloric acid in benzene, using the viscosity of the solution to determine the end-point (Sully, *Nature*, 1947, **159**, 882). This method which is applicable to polymers of the highest molecular weight indicates a number average molecular weight of 30,000, so that under conditions of minimum oxygen consumption it seems that $850,000/30,000 = 28$ molecules of polymer each containing a sulphonic acid end-group are formed from each initiating radical. However, the quantitative interpretation of the end-group titrations is as yet not quite clear and the results must be accepted with caution.

The work described above [cf. B.P. 582,134, 582,327, 587,455, and 608,635 (Sully and A. Boake, Roberts, and Co.)] forms part of an independent discovery of the so-called redox system of polymerisation. The sulphite–oxygen system described is simpler than other systems involving peroxides, so that the mechanism was appreciated at an early date. Furthermore the radicals are utilised more efficiently in the polymerisation, so that the experiments permit a quantitative interpretation not possible with systems involving peroxides in which several species of initiating radicals may be formed.