[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Catalysis of Polymerization by Ozonides. II[1]

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A study of the polymerization of dienes in the presence of ozonides led to experimentation directed primarily toward ascertaining: 1, the characteristics of the polymerization of styrene in the presence of ozonides as compared with those in the presence of other catalysts; 2, the relative activity of oxygen and ozonides as catalysts for polymerization; 3, whether an interruption of the polymerization process rendered a given polystyrene chain incapable of further addition of styrene.

Experimental Methods

The course of the polymerization was followed in three ways. 1. An aliquot from the reaction mixture of styrene and ozonide was removed from time to time and the viscosity of a 10% solution of it in benzene determined.[1] 2. Similarly, aliquots (0.5–1.0 g.) of the reaction mixture were dissolved in dioxane (10–15 ml.) and the polystyrene precipitated by the rapid addition of 95% alcohol (150–175 ml.). After one to two days the polystyrene was filtered off, washed and dried to constant weight at 45° (20 mm.) over calcium chloride. (A better separation of polystyrene was obtained with dioxane than with benzene.) The method left less than 2–3% of polystyrene in solution as evidenced by the residue from the evaporation of the alcoholic solution at 50° (20 mm.). 3. The specific viscosity of the polystyrene so obtained was determined as follows: such a weight of solid was dissolved in benzene as would give a solution containing 26 g. of polystyrene (equivalent to 0.25 mole of styrene) per liter of solution. The flow time of this solution through a viscometer divided by the flow time of benzene gave the relative viscosity. This value less 1 gave the specific viscosity of the polystyrene. Staudinger and associates[2] showed that the specific viscosity of polystyrene is indicative of the size of the molecule and the values have in general been so interpreted in this paper.

Characteristics of Polymerization of Styrene.[3]—There are represented in Fig. 1 the typical changes that took place in the viscosity of the solution, in the amount of polystyrene, and in its specific viscosity, during the course of the reaction. It may be seen that for about four weeks there was almost a linear increase in both the amount and specific viscosity of polystyrene formed. The viscosity of the solution increased rather slowly for about three weeks and then much more rapidly for the fourth week.

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(1) Houtz and Adkins, THIS JOURNAL, **53**, 1058 (1931).

(2) Staudinger, Brunner, Frey, Garbsch, Signer and Wehrli, *Ber.*, **62**, 241 (1929).

(3) *Cf.* Carothers, *Chem. Rev.*, **8**, 394 (1931). Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932, pp. 157–253.

This is presumably due to the fact that during the earlier period the polymers were not such long chains as they were later, so that a given amount of polymerization produced a much less marked change in the viscosity of the solution. Apparently no more than 92–93% of the styrene underwent polymerization.

The trend of the curve indicating the specific viscosity of the polystyrene is downward after a certain length of time. This is shown more clearly by the data plotted in Fig. 2 for a polymerization at a higher temperature (25°) and with a different catalyst. These data show that while the amount of polystyrene steadily increased to a maximum, the viscosity of the solution and especially the specific viscosity *decreased*, after reaching a maximum, to approximately 75% of that value.

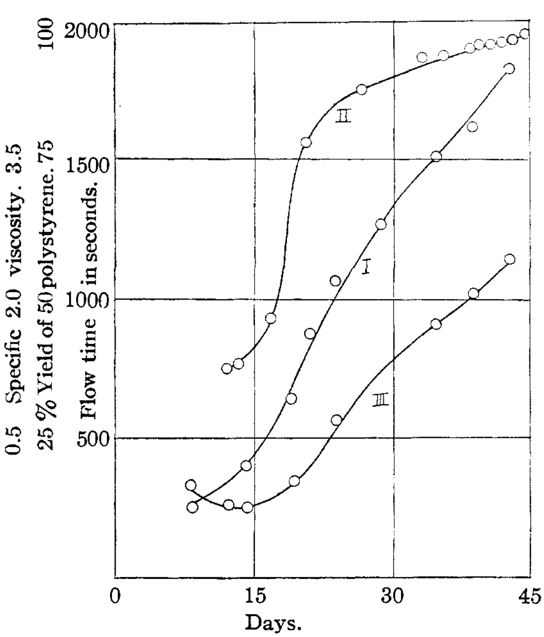

Fig. 1.—Polymerization of styrene at 15° with 2% of diisobutylene ozonide: I, percentage yield of polystyrene; II, flow time of a 10% solution of the reaction mixture in benzene calculated for a viscometer showing a value of 45.7 seconds for benzene; III, specific viscosity of the polystyrene. The data plotted above and in Fig. 2 are for single reaction mixtures; however, all characteristics of the polymerization have been duplicated both under the same conditions and with different catalysts.

The specific viscosity of polystyrene produced varied according to the environment during the reaction. For example, polystyrene produced in an atmosphere of nitrogen at 100° for twenty-two to thirty-two hours had a specific viscosity of 19.1–19.3, while in oxygen under similar conditions it was 6.6 to 5.2. Under nitrogen but with diisobutylene ozonide or with benzoyl peroxide as a catalyst, the maximum specific viscosity was 1.4 to 1.3. As indicated in Figs. 1 and 2, the specific viscosity rose to a value of approximately 4 in the presence of diisobutylene ozonide as a catalyst at 15°. The polystyrene formed under nitrogen without an added catalyst was quite different in physical properties from other samples of polystyrene. Most of the polystyrene produced under nitrogen could be lifted out on a stirring rod as a tough, doughy mass. Staudinger observed that the specific viscosity of polystyrene decreased with increase in the temperature of formation. He reported values of 5.95 for 15°, 2.18 at 75°, and 1.21 at 115° for polystyrene formed in the absence of an added catalyst.

It should be noted that the samples of polystyrene were not homogeneous with regard to molecular size. If the precipitant (alcohol) was added slowly the polymer first precipitated sometimes had a specific viscosity 150% as great as that of the material precipitated later. Since it was impossible to grind the polymer in a mortar it was advisable to bring about the precipitation very rapidly so that a more representative sample might be obtained for the determination of the average specific viscosity.

Oxygen versus Peroxides and Ozonides as Catalysts for Polymerization.—Staudinger and Lautenschlager[4] reported that oxygen is a much more active catalyst for the polymerization of styrene at 80° than is benzoyl or diphenylethylene peroxide. They state that this is to be expected since oxygen is less available from a peroxide than from the gas. They state that the only way a peroxide could catalyze the polymerization of another compound would be to yield oxygen to it, forming a peroxide of it which would then undergo polymerization. This conclusion is so contradictory to those arrived at in this Laboratory that the matter was tested further. Staudinger and Lautenschlager heated 10-g. portions of styrene at 80° for ten, fifteen, twenty or twenty-five hours with an unspecified amount of oxygen or of benzoyl or diphenylethylene peroxide. They then determined the extent of polymerization by evaporating the excess styrene at 80° in a "high vacuum" for an unspecified length of time. In order to test out their conclusion a series of experiments was performed.

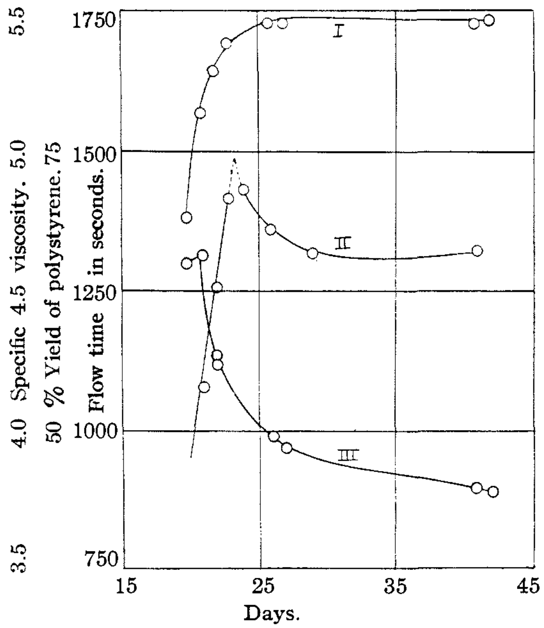

Fig. 2.—The later stages in the polymerization of styrene at 25° with 2% pinene ozonide: I, percentage yield of polystyrene; II, flow time of solution of reaction mixture in benzene; III, specific viscosity of polystyrene.

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[4] Staudinger and Lautenschlager, *Ann.*, **488**, 1 (1931).

One-gram samples of styrene were heated at 80° in a thermostat in 20 × 2.5 cm. test-tubes. Before sealing the tubes, they were immersed in an ice–salt mixture, so that an appreciable pressure would be developed on heating to 80°. One tube of each set of six contained oxygen, one carbon dioxide, and the others benzoyl peroxide in three different concentrations (0.1, 1.0, 3.0%) in an atmosphere of carbon dioxide. The volume of each tube was about 60 cc. Considering the initial temperature to be $-15°$ upon sealing there would be 0.078 mole of oxygen available for each mole of styrene if the pressure were to be reduced to one atmosphere in the tube by oxygen absorption. Considering one atom of oxygen in each molecule of benzoyl peroxide to be available, 0.00325 mole of oxygen would be available per mole of styrene, in the tubes containing 0.1% benzoyl peroxide. That is to say, twenty-five times as much oxygen was available to the styrene in the oxygen tube as in the 0.1% benzoyl peroxide tube. Also, since oxygen was bubbled through the styrene immediately before each sample for an oxygen tube was weighed out, free oxygen should have ample opportunity to demonstrate its superiority as a polymerization catalyst. The amount of polymerization under these conditions after ten and twenty hours was as follows: with oxygen 6 and 48%, with carbon dioxide 10 and 15%, with 0.1% benzoyl peroxide 45 and 80%, with 1% benzoyl peroxide 94% at both times. These data show that benzoyl peroxide is a much more active catalyst than oxygen. Other experiments showed that diisobutylene ozonide is much more active than benzoyl peroxide as a catalyst for the polymerization of styrene. Similar results were obtained when the polymerizations were carried out at 25 and 100° in a benzene solution which was vigorously agitated in order to ensure intimate contact of styrene and oxygen.

Another experimental finding may also be noted here, which may have a bearing upon the hypothesis that peroxides and ozonides catalyze polymerization through the liberation of oxygen. Diisobutylene ozonide, for example, did *not* produce oxygen in any considerable amount when it decomposed. Fifteen grams of the ozonide produced 200 cc. of gas at room temperature within seven days and 500 cc. within a month. The gas analyzed approximately 17% carbon dioxide, 2% unsaturated compounds, 1% oxygen, 23% carbon monoxide, 43% methane and 14% hydrogen.

The stability of diisobutylene ozonide in the presence of unsaturated compounds should be noted. As previously reported this ozonide explodes if heated above about 60° and loses practically all of its catalytic activity if allowed to stand more than four or five days at room temperature. In striking contrast to these statements are the observations that diisobutylene ozonide, dissolved in an unsaturated hydrocarbon, was active as a catalyst for many days at 100°, and with indene at room temperature for several months.[1]

Samples of styrene occasionally vary a great deal with respect to their sensitivity toward polymerization, even when great care is exercised in their preparation and distillation. Samples of styrene which have been in contact with air for some time are very reactive and presumably the high sensitivity toward polymerization is due to the oxygen content. For example, a sample of styrene which had stood for six months in contact with air was as much polymerized after twelve days at 25° in the presence of 4% of its weight of pinene ozonide as was freshly distilled styrene after seventeen days under the same conditions. However, the "old" styrene is not an active catalyst for polymerization, for when 3% of it was added to freshly distilled styrene the resulting mixture polymerized at the same rate as did freshly distilled styrene. Furthermore, polystyrene is not a catalyst for polymerization, for when 1 part of polystyrene was added to 20 parts of freshly distilled styrene the polymerization of the latter was not accelerated.

Addition of Styrene to Polystyrene.—Experiments were conducted with the object of ascertaining whether polystyrene after being precipitated and dried was able to add styrene with the formation of polystyrene of greater molecular weight. To this end samples of polystyrene were prepared, precipitated and dried as in the method described for the gravimetric determination of polystyrene. These samples (*a*, *b* or *c*) of polystyrene of known specific viscosity were then mixed with styrene. After an appropriate length of time for reaction the new polystyrenes (*d*, *e* or *f*) were precipitated, dried, weighed and their specific viscosities determined. Styrene was allowed to polymerize under exactly the same conditions, the polystyrenes (*g*, *h* or *i*) precipitated, weighed and the specific viscosities determined. Mixtures were then made up of polystyrenes (ag, bh and ci) in such a ratio as to be identical with the polystyrenes (*d*, *e* or *f*) *if* styrene had not reacted with polystyrene (*a*, *b* or *c*). The specific viscosities of these mechanical mixtures were then determined. The significant data are recorded in Table I.

If the polystyrene produced from a mixture of polystyrene and styrene had a higher specific viscosity than did the original polystyrene (or the polystyrene produced from styrene alone under similar conditions), then addition of styrene to the original polystyrene *must* have taken place. This is seen to be the case in experiments 1 and 3 of Table I. However, this comparison does not give an accurate indication of the extent of the addition of styrene to polystyrene. Such a comparison may be made between the specific viscosity of the product and of the mechanical mixture referred to above. In experiment 1 the increase was from 11.6 to 15.6, in 3 from 11.5 to 11.9, and in 5 from 2.22 to 2.45. It is thus clear that in all three cases (involving different temperatures, times and catalysts) there was a reaction of styrene with the dried polystyrene.

TABLE I

ADDITION OF STYRENE TO POLYSTYRENE

	Reactants		Time,	Polystyrene after	% Styrene	Sp. viscosity	
	Name	g.	hrs.	reaction, g.	polymerized	Product	Mixture
1	Polystyrene[a]	0.317	13	0.636[d]	49.7 ± 0.8	15.5 ± 0.12[d]	11.6
	Styrene	.641	(100°)				(ag)
2	Styrene	1.467	13	.474[g]	32.4 ± .3	13.0 ± .3	..
			(100°)				
3	Polystyrene[b]	0.265	6	.600[e]	28.3 ± .4	11.9 ± .1[e]	11.5
	Styrene	1.181	(100°)				(bh)
4	Styrene	3.290	6	.660[h]	20.0 ± .5	11.2 ± .3[h]	..
			(100°)				
5	Polystyrene[c]	0.280	72	.359[f]	13.1	2.45 ± .03[f]	2.22
	Styrene	.603	(25°)				(ci)
	Pinene ozonide	.024					
6	Styrene	1.808	72	.233[i]	12.9 ± .2	2.43 ± .06[i]	..
	Pinene ozonide	0.054	(25°)				

[a] Specific viscosity 10.5, prepared in 5.5 hrs. at 100° without added catalyst. [b] Specific viscosity 11.5. prepared in 6.0 hrs. at 100° without added catalyst. [c] Specific viscosity 2.20, prepared in 5 days at 25° with pinene ozonide as a catalyst. [d] to [i] See text

Polymerization of Various Compounds.—The catalytic activity of an ozonide in nitrogen for several compounds was tested qualitatively by measuring viscosities before and after standing in contact with the catalyst in sealed tubes. These experiments were carried out chiefly for the purpose of ascertaining whether the catalytic activity of diisobutylene ozonide was limited to non-oxygenated compounds. Benzalacetone in benzene solution with 1% of diisobutylene ozonide showed no viscosity change in seventy days at room temperature, nor in eight days at 100°. A 10% solution of dibenzalacetone in benzene with 1% of diisobutylene ozonide showed a 5% increase in viscosity in eight days at 100°. The blank samples showed no increase. A gummy residue, insoluble in alcohol, was found in the tubes containing the catalyst. Crotonalacetone showed a 205% viscosity increase in eight days with 3% diisobutylene ozonide at 100°, and a 100% increase without catalyst. 2,4-Hexadienal increased in viscosity on heating in air, but 3% of diisobutylene ozonide showed no additional effect. Sorbic acid in dioxane was not affected by the catalyst, either at 23 or at 100°. Ethyl sorbate showed 70% increase in viscosity with 3% pinene ozonide, and 24% increase without catalyst in seventy-six days at 23°. In nine days at 100°, its viscosity increased six-fold without catalyst and ten-fold with 3% pinene ozonide. On heating 1,3-cyclohexadiene at 100° for thirty days a polymer formed which was insoluble in the monomer.[5] There was 50% more gummy residue left after evaporation of the sample containing ozonide than was found in the case of the blank.

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[5] Hoffman and Damm, *Mitt. schles. Kohlenforschungsinst. Kaiser-Wilhelm Ges.*, **2**, 97 (1925); *Chem. Abstracts*, **22**, 1249 (1928).

Cyclohexene Ozonide.—One of the original objects of this investigation was to ascertain the relative merits of various ozonides as catalysts for polymerization, so the properties of cyclohexene ozonide were investigated. Harries[6] prepared two solid cyclohexene ozonides in carbon tetrachloride solution which he believed to be polymers. In addition to these solid polymers a liquid ozonide of low molecular weight has now been obtained as follows. Ozone was passed into a solution of 6 g. of cyclohexene in 125 cc. of chloroform. An insoluble solid (A) immediately formed. When quantitative absorption of ozone ceased the product was filtered, and the filtrate treated with 2 to 3 volumes of petroleum ether. A granular solid (B) separated which was apparently a mixture, since it melted over a wide range. The insoluble solid (A) was amorphous, paper-like in appearance. It did not dissolve in ether, alcohol, cyclohexane, chloroform, nor acetic acid. It was slightly soluble in benzene and in dioxane. Molecular weight determinations on the soluble solid (B) gave values in benzene of 2100, 2270, 3650, 2185, 2970, 2640; and in dioxane 1515, 1120, 1270, 1200 and 1250. When allowed to stand in a chloroform solution it changed into a substance insoluble in chloroform. Both of these materials (A and B) were found to be practically inactive for the polymerization of styrene, although the (B) solid showed a slight activity toward styrene during a thirty-day interval. When cyclohexene was ozonized in glacial acetic acid, a liquid ozonide (C) was obtained which had a molecular weight of about 450 in freezing dioxane. In nine days at room temperature, 2% of the liquid cyclohexene ozonide (C) in styrene caused the formation of 14.9% polystyrene while 2% of diisobutylene ozonide caused 83.8% of the styrene to polymerize.

Correlation of Results.—The results presented in this paper are in disagreement at two points with those reported by Staudinger and his associates. First, contrary to their observations, peroxides and ozonides have been found to be much more active than oxygen as catalysts for the polymerization of styrene. Second, the polystyrene produced at higher temperatures in this Laboratory in the presence of oxygen had three or four times as large a specific viscosity as did that produced under similar conditions by Staudinger, while the polystyrene produced under nitrogen at 100° had a specific viscosity three or four times as high as the highest specific viscosity observed by him even for polystyrene produced at temperatures as low as 15°. It proved impractical in this Laboratory to polymerize styrene at 15°, for the styrene remained unchanged at room temperatures in contact with air for a year. These results suggest the possibility that the samples of styrene used by Staudinger contained a catalyst which gave a more rapid polymerization and therefore shorter chains than did that used in this Laboratory.

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(6) Harries, *Ann.*, **410**, 21 (1915).

A significant fact in regard to the correlation of specific viscosity and length of the polystyrene chain has become evident.[2] The lower specific viscosity of polystyrene produced in thirty-five days as compared with that produced in twenty days (Fig. 2), for example, can hardly be due to a decrease in the length of chain and the breaking of carbon to carbon linkages at 25°, but must rather be due to some other change in dimensions or other characteristics of the polystyrene "molecule." There can be no reasonable doubt that there is, as Staudinger pointed out, a correlation of specific viscosity with length of chain, but at least with the polystyrenes of higher specific viscosity, some other factor apparently *in part* determines the observed value of the latter constant. The specific viscosities referred to in this paragraph are several times as large as those for which Staudinger showed a correlation between specific viscosity and molecular weight.

It appears to the authors that the polymerization of styrene may involve two rather distinct phenomena. The one is the initiation of the reaction or starting of chains, the other is the increase in the length of these chains. It is certain that ozonides, peroxides, salts, etc., catalyze the initiation of chains; however, there is no evidence so far as the authors are aware as to whether or not these catalysts increase the rate of lengthening of these chains. If little catalyst is present the chains become very long even at 100°. If many chains have been begun as in the presence of an active catalyst, then all the available styrene is used up before any of the chains become very long.

The evidence presented in this paper in regard to the capacity of dried polystyrene to add styrene indicates that the polymerization of styrene is not a process that must proceed to completion without interruption. The lengthening of the carbon chain may be stopped by precipitating and drying the polystyrene. The polystyrene will later react with styrene if it is available and the chain thus become longer. In the presence of pinene ozonide there was relatively little addition of styrene to polystyrene or increase in amount of polymerization of styrene in the presence of polystyrene. This is understandable because the catalyst initiated so many chains and the lengthening process is so slow at 25° that by far the greater part of the styrene went to form new chains rather than to prolong those already started.

More styrene reacted within a given length of time in the presence of polystyrene than in its absence, even though polystyrene is not a catalyst for the reaction. This is shown by a comparison of experiments 1 and 2, and 3 and 4 in Table I. In each case approximately 50% more styrene was polymerized in the mixture containing polystyrene than in the mixtures which originally contained no polystyrene. This indicates that the rate of the reaction of styrene is a function of the amount of polystyrene available for addition. All of these facts indicate that the addition of styrene to polystyrene is a normal addition reaction which requires no special hypothesis.

There is no evidence available that seems to the authors to show that the polymerization of styrene by ozonides or peroxides *depends* upon the transfer of oxygen from the latter to the styrene, or that the decomposition of the ozonide or peroxide is an essential step in the mechanism of polymerization. There is, of course, ample evidence that oxygen does add to alkene linkages and that ozonides polymerize, as shown for cyclohexene ozonide in this paper and as has been previously pointed out by numerous investigators. The role of the ozonide appears on the basis of the experimental results available to be no different from that of a metallic chloride such as tin for the catalysis of polymerization. Presumably the catalysts form a molecular complex with the styrene which is more labile toward polymerization than is styrene alone.

Summary

The course of the polymerization of styrene under a variety of conditions has been followed by determination of the viscosity of the solution and of the weight and specific viscosity of polystyrene produced. The specific viscosity of the polystyrene was shown to reach a maximum after which there was a material decrease in the value of this physical constant. The polystyrene chains of greatest length, as measured by the specific viscosity, were formed under nitrogen at 100°. Certain peroxides and especially diisobutylene ozonide were shown to be a much more active catalysts than oxygen for the polymerization of styrene. Polystyrene after precipitation and drying retained its capacity to add styrene with the formation of chains of greater length. The significance of these facts in regard to the mechanism of catalysis and polymerization of styrene has been discussed. Certain experimental findings in regard to the characteristics of cyclohexene ozonide have been presented. The activity of diisobutylene ozonide for the catalysis of the polymerization of benzalacetone, dibenzalacetone, crotonalacetone, 2,4-hexadienal, ethyl sorbate and cyclohexadiene-1,3 has been demonstrated.

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