[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WESTERN RESERVE UNIVERSITY]

The Polymerization of Styrene in Thymol Solution

BY J. K. MOORE, R. E. BURK AND H. P. LANKELMA

The work of Burk and Thompson[1] in which styrene was polymerized after drastic purification indicated the futility of attempting to free it from traces of catalytic oxygen or oxygen compounds by purification alone. In the present research reasonably pure styrene was polymerized in solution in an effective oxidation inhibitor, thymol, which would maintain the reaction free of oxygen during the polymerization. Thymol is an inhibitor of considerable power and also offers the interesting possibility of acting as an acceptor for free radicals, assumed by some to be intermediates in the polymerization of styrene. Thus, if free radicals are present, they could react with the phenolic hydrogen, with tertiary hydrogen, with primary hydrogen or with aromatic hydrogen, these representing a graded series of hydrogen atoms with respect to probable reactivity. Such removal of hydrogen in the standard fashion of a free radical[2] then creates a free radical from the thymol molecule from which the hydrogen had been removed. This radical could then enter into a polymerization chain with styrene.

Experimental

Styrene obtained from the Dow Chemical Company was first washed with 0.1 *N* sodium hydroxide until all phenolic substances[3] were removed. It was then extracted with dilute ammoniacal silver oxide[4] until no more acetylide was formed. This product was dried with anhydrous calcium sulfate and distilled in a concentric tube column[5] under conditions which correspond to an efficiency of about 20 plates. According to the vapor pressure data of Stanley,[6] Patnode and Scheiber,[7] Linder[8] and Stuckey and Saylor[9] this fractionation should have been adequate to remove most of the ethylbenzene, believed to be the principal impurity. The boiling point of the product, 27° at 4.6 mm., agreed well with the vapor pressure data of Linder.[8] The refractive index $n^{20}\mathrm{D}$ of the product was 1.5463 ± 0.0002, in fair agreement with the values of Patnode and Scheiber.[7]

The thymol used melted at 49.7–50°. This material was dissolved in aqueous sodium hydroxide, filtered, precipitated with hydrochloric acid and vacuum distilled. The middle portion used in experimentation distilled at 159–160° at 90–92 mm. pressure and again had a melting point of 49.7–50°.

The reaction proper was carried out in glass ampules using solution volumes 100–300 cc. These were flushed with dry nitrogen, cooled to dry-ice temperature, and sealed off. Temperatures were accurate to ±0.1°. The contents after polymerization were subjected to vacuum distillation in the equipment described above. This was found to be quantitative in separating unchanged styrene from dimeric and more highly polymerized styrene. This was made possible by the low holdup of the column which was of the order of 0.3 g. The reacted styrene was then obtained by difference. Polymer and thymol were then separated by the use in proper succession of precipitation with methyl alcohol, caustic extraction, dilution with benzene and distillation. Material balances on both polymer and thymol are seen to be reasonably good.

The course of the polymerization at 145° is shown in Fig. 1 at 100° in Fig. 2. It will be noted that a third order reaction course was followed. This was quite reproducible. A fraction of the data supporting these curves is shown in Table I.

TABLE I

STYRENE POLYMERIZATION IN THYMOL SOLUTION

Concn. of styrene in all experiments 44.2 mole per cent. (3.10 moles/l.).

Time, hr.	% Polymn. (by wt.)	Third order vel. const. $\times 10^3$ moles/l./hr.	Time, hr.	% Polymn. (by wt.)	Third order vel. const. $\times 10^3$ moles/l./hr.
a.	Temp. 145°		b.	Temp. 100°	
13	36.0	5.77	40	8.3	0.246
31	48.6	4.67	90	16.2	.245
42	56.3	5.37	120	18.8	.224
48	56.6	4.67	158	23.6	.235
60	64.6	5.98	230	28.0	.210
100	72.9	6.56	Best value		.230
136	72.95	4.85			
160	72.8	4.07			
205	81.2	6.93			
Best value		5.50			

For molecular weight determination of the polymeric material it was first hydrogenated in benzene solution, using as a catalyst platinum black.[10] The technique employed produced quantitative hydrogenation without concurrent polymerization when monomeric styrene was used. Benzene and ethylbenzene were removed from the thymol

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[1] R. E. Burk and H. E. Thompson, THIS JOURNAL, **57**, 711 (1935).

[2] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," the Johns Hopkins Press, Baltimore, Md., 1935.

[3] Private communication, Dow Chemical Company (1938).

[4] F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 65.

[5] M. L. Selker, R. E. Burk and H. P. Lankelma, *Ind. Eng. Chem., Anal. Ed.*, **12**, 352 (1940).

[6] H. M. Stanley, *Chemistry and Industry*, 93 (1938).

[7] W. Patnode and W. J. Scheiber, THIS JOURNAL, **61**, 3449 (1939).

[8] E. G. Linder, *J. Phys. Chem.*, **35**, 531 (1931).

[9] J. M. Stuckey and J. H. Saylor, THIS JOURNAL, **62**, 2922 (1940).

[10] H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 53–59, 452–458.

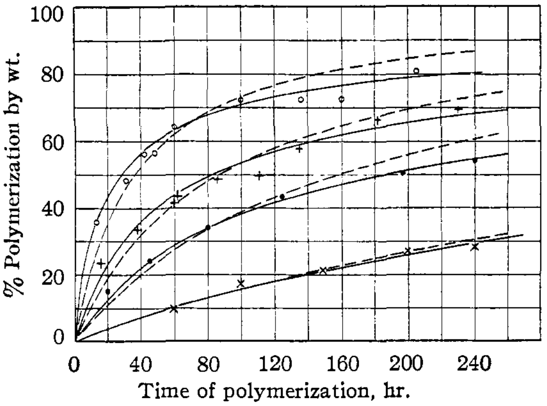

Fig. 1.—Polymerization of styrene at 145° in solution in thymol: O, 44.2 mole% styrene; +, 31.6 mole% styrene; ●, 20.0 mole% styrene; ×, 10.0 mole% styrene; — — —, second order curve; ———, third order curve.

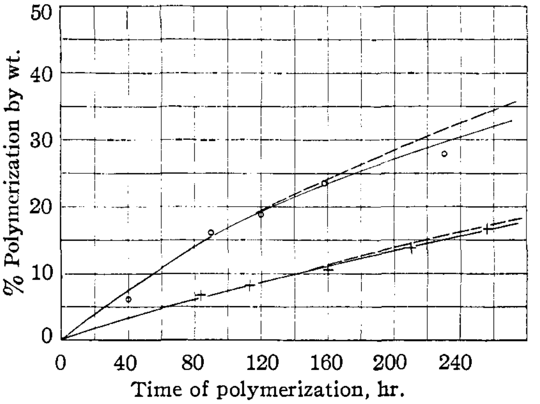

Fig. 2.—Polymerization of styrene at 100° in solution in thymol: O, 44.2 mole% styrene; +, 31.6 mole% styrene; — — —, second order curve; ———, third order curve.

solution of hydrogenated polymer by distillation and the residue was then redissolved in benzene for extraction. Otherwise, difficulty was experienced in removing ethylbenzene. Thymol was removed from this solution by repeated extraction with a solution of potassium hydroxide in 50% methyl alcohol solution. Benzene was finally evaporated from the hydrogenated polymer to constant weight and the polymer then redissolved in a known amount of pure benzene for freezing point measurements. Molecular weights obtained are shown in Table II and are seen to be substantially constant within the accuracy of measurements.

Interpretation

The rate of styrene polymerization using the above technique was quite reproducible. This is reasonable evidence that adventitious oxygen is not an important factor in catalyzing the reaction.

TABLE II

THE MOLECULAR WEIGHT OF THE HYDROGENATED POLYMER

Concn. mole % styrene	Temp. of polymn., °C.	Time, hr.	% Polymn. (by wt.)	m^a	n^b
44.2	145	15	37.5	1350	5.4
		48	59.5	1085	6.6
		160	76.0	1260	9.5
	100	205	27.0	1540	4.7
31.6	145	35	33.5	910	3.6
		108	55.0	650	3.9
		205	65.0	715	4.8
	100	108	8.0	990	1.68
		205	14.0	900	2.07
20.0	145	48	25.0	895	2.90

[a] m is the molecular weight (number average) of the hydrogenated polymer. [b] n is the number of units of monomer in the average molecule present at any time (including monomer).

Reasonably satisfactory point to point velocity constants were obtained for the third order law as will be seen in the last column of Table I. They were substantially better than the second order constants. The third order character of the reaction was also revealed more critically by plotting the reciprocal of the square of the initial concentration of styrene against time. This yielded excellent linear plots as may be seen in Fig. 3, both at 100 and 145°. A similar plot with the reciprocal of the initial concentration of monomer plotted against reaction time, which should give linear graphs for a bimolecular reaction, failed to do so by a wide margin. The

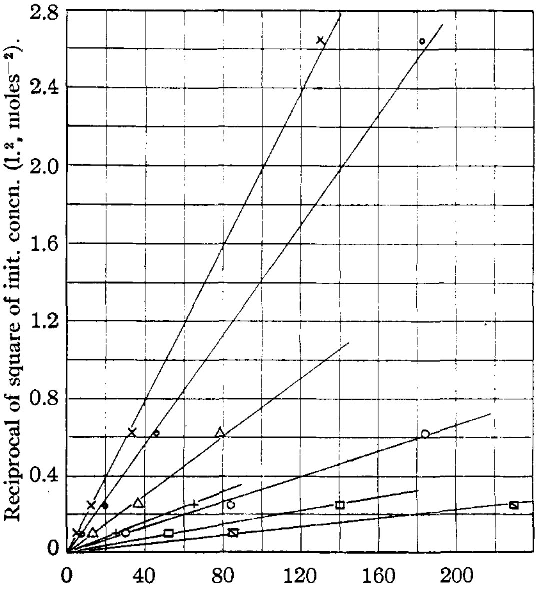

Fig. 3.—Third order half-life data: O, 0.50 life at 145°; △, 0.33 life at 145°; ○, 0.25 life at 145°; ×, 0.20 life at 145°; ⊠, 0.15 life at 100°; □, 0.10 life at 100°; +, 0.05 life at 100°.

reaction is thus seen to be third order under the conditions used.

The molecular weight of the polystyrene varied and increased with time when attempts were made to determine it in the unhydrogenated state. On the other hand, the hydrogenated polymer had a molecular weight (number average) of the order of 1000 as may be seen from Table II. It is evident that the molecular weight did not increase with increase in the fraction polymerized. If anything, the reverse tendency existed, although it is doubtful whether the determinations were sufficiently accurate to justify that conclusion.

While oxygen catalysis has been eliminated, the third order character and the molecular weight of the polymer certainly cannot be accounted for on the basis of an orthodox uncatalyzed thermal reaction.[11,12] It was suspected that the thymol solvent was itself acting as a mild catalyst for the reaction. This idea was strengthened by attempts to use certain antioxidants more powerful than thymol. Thus when *t*-butylcatechol was used as a solvent, polymerization occurred more rapidly than when thymol was used and the product was quite viscous, indicating a higher degree of polymerization. Polymerization was complete in this instance in fifty to sixty hours, using 30–40 mole per cent. styrene solutions in *t*-butylcatechol at a temperature of 145°. This interpretation implies merely that these inhibitors are exhibiting in varying degree the usual catalytic powers to be expected for an acid.[13]

In this instance the weak acid thymol would form an active complex with styrene monomer and the acid would remain associated with the growing polymer. Polymerization would terminate with the dissociation of the catalyst and the molecular weight would be determined by the mean life of the complex, which would be essentially constant at a given temperature irrespective of the fraction polymerized.

The termolecular character of the reaction can be accommodated by the mathematical development of Breitenbach[14] and Mark.[15] Thus a reaction with a second order chain-initiating action and a first order chain-terminating mechanism would have an over-all third order. This raises the question concerning an allowable second order chain-initiating mechanism. However, this should be possible because of the associated character of phenolic compounds. Thus the reaction

$$T_x + 2M \longrightarrow MT + MT_{x-1}$$

where M is the monomeric styrene and T is monomeric thymol, may proceed more readily than

$$T_x + M \longrightarrow MT + T_{x-1}$$

The alternate interpretation of the reaction mechanism would be that free radicals, in the sense of molecules containing carbon atoms with an odd number of electrons, are formed and that chain propagation and termination then follow an appropriate radical chain mechanism as outlined by others.[15,16,17] On the other hand, our solvent, thymol, was chosen in part with such a possible mechanism in view. Thus, thymol contains phenolic, tertiary, primary and aromatic hydrogen, representing various degrees of ease of reaction with free radicals. If the free radical chains were terminated solely by reaction with thymol, free radicals would be produced from the participating thymol molecules and these would in turn initiate new chains. Under these conditions each polymer molecule would contain thymol. With this in view, special attention was paid to the material balance on both thymol and the polymer. It is noted in Table III that the material balances on polymer and on thymol of proper melting point were excellent.

TABLE III

REACTION OF STYRENE AND THYMOL

Concentration of all samples 31.6 mole % styrene or 24.35% styrene (by wt.).

Reaction time, hr.	Temp., °C.	% Polymn. from distn. data	Weight of polymer		%	Weight of thymol		%
			Calcd.	Found		Calcd.	Found	
0	...	0.0	0.0	0.0		95.6	95.4	99.8
58	100	7.8	1.9	...		89.3	88.5	99.2
153	100	16.0	4.02	4.11	102.2	83.3	83.5	100.3
113	100	6.6	1.45	1.50	105.0	76.2	77.2	101.3
256	100	17.6	4.62	4.64	100.4	85.6	85.9	100.3
25	145	48.5	10.95	10.67	97.3	71.75	71.2	99.2
48	145	63.6	16.1	15.8	98.2	79.9	80.1	100.3
96	145	66.9	16.9	...		79.8	77.8	97.5

Thus no evidence was afforded for the idea that the growing polymer chains consisted of free radicals of the odd electronic type. Had this mechanism followed, however, the polymer should have contained some 12.7% thymol. If chain growth were terminated in some other way, this evidence could be disregarded.

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(11) G. S. Whitby, *Trans. Faraday Soc.*, **32**, 315 (1936).

(12) G. S. Whitby and M. Katz, This Journal, **50**, 1160 (1928).

(13) F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(14) J. W. Breitenbach, *Monatsh.*, **71**, 275 (1938).

(15) H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publ., Inc., New York, N. Y., 1940.

(16) P. J. Flory, This Journal, **59**, 241 (1937).

(17) H. Staudinger, "Die Hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

No induction period was observed in the reaction. The energy of activation calculated from the termolecular velocity constants at 145 and 100° was 21,800 ± 500 cal.

Summary

1. The rate of polymerization of purified styrene in thymol solution is strictly reproducible and follows a third order law.

2. No induction period exists.

3. The energy of activation is estimated to be 21,800 calories.

4. The average molecular weight of the polymer is approximately constant and in the neighborhood of 1000.

5. Interpretation of these experimental facts has been presented.

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The Sorption of Hydrogen by Metals. Temperature Variation Experiments

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Introduction

In 1927 the author pointed out[1] that in the sorption of hydrogen on massive copper it seemed possible that the process of solution was at play. This conclusion resulted from the observation of a low-pressure increase followed by a high-pressure decrease in the sorption of the gas when the copper had been poisoned with carbon monoxide. In another study[2] in which a thin coating of copper upon inert diatomite brick was employed a small amount of this poison did not cause the high-pressure decrease in hydrogen adsorption; this seemed to imply that here was a case of true adsorption without any secondary process. Further light was thrown upon the subject in a different attack by Benton and White[3] who revealed that when massive copper sorbs hydrogen at −78.5°, the temperature is raised to 0° and again is brought to −78.5°, a series of sorptions result showing, first an initial adsorption at −78.5°, second, some rapid desorption at 0° followed by a slow secondary process of sorption (solution) at 0°, and finally readsorption when the temperature is returned to −78.5°. More recently the writer[4] carried out experiments with a like temperature variation on a supported nickel sample; in this case the slow secondary action at 0° was quite small, and this is in accord with the fact that little or no diffusion or solution could be expected when practically all of the adsorbent is represented by surface.

To the present these experiments on supported nickel constitute the only such study made with thin coatings of a metal. The present work was undertaken to obtain additional data with other metals, in both the massive condition and the supported state (each form of a given metal being prepared by identical procedure), the behavior of which, when compared among themselves, and with that of the previously mentioned supported nickel and with the massive copper of Benton and White, should point to rather definite conclusions regarding the secondary action.

Experimental

The apparatus, purification of hydrogen[5] and of helium,[4] used as a reference gas, have been described. The metals employed were cobalt and platinum. Massive cobalt was prepared by calcining cobalt nitrate at 350° and reducing in a silica tube at 650 to 700°. The metal was then partially reoxidized at 400° and reduced at 450 to 500°. This treatment was repeated in an effort to secure a final reduction at a lower temperature but it was necessary to reduce again at 450 to 500° before the reduction was practically completed.

The supported cobalt in the ratio of two moles of metal to 1000 g. of brick was prepared in a manner similar to the massive cobalt except that the nitrate was first dissolved and absorbed by the inert brick granules.

For the platinum examples the method of Willstätter[6] was used. The powdery platinum black for the massive sorbent was pressed while wet so as to obtain a granular form instead of a fine

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[1] Griffin, THIS JOURNAL, **49**, 2136 (1927).

[2] Griffin, *ibid.*, **57**, 1206 (1935).

[3] Benton and White, *ibid.*, **54**, 1379 (1932).

[4] Griffin, *ibid.*, **61**, 272 (1939).

[5] Pease, *ibid.*, **45**, 1196 (1923).

[6] Willstätter, *Ber.*, **45**, 123 (1921).