seal broken. The contents of the tubes were dissolved in methyl ethyl ketone containing hydroquinone, and this solution was slowly added with stirring to a 3 times excess of methanol. The precipitated polymer was filtered, washed copiously with methanol and allowed to dry to constant weight in a vacuum oven at 60°.

Chlorine Analysis.—The per cent. chlorine was determined using the Parr bomb.

Results and Discussion

The experimental data are summarized in Table I. The copolymerization rate constants were calculated according to the method of Alfrey and Goldfinger[1] in the usual manner.

TABLE I

DETERMINATION OF r_1 AND r_2 THE COPOLYMERIZATION RATE CONSTANTS SYSTEM 2,5-DICHLOROSTYRENE–METHYL ACRYLATE

Monomer composition				Polymer composition (Exp.)	
Mole fraction 2,5-di-chloro-styrene	Mole fraction methyl acrylate	Yield, %	Chlorine, %	Mole fraction 2,5-di-chloro-styrene	Mole fraction methyl acrylate
0.90	0.10	4.4	39.95	0.950	0.050
.75	.25	3.0	39.15	.913	.087
.50	.50	3.7	37.20	.829	.171
.25	.75	4.4	32.15	.643	.357
.10	.90	4.9	22.30	.371	.629
.05	.95	4.3	14.15	.206	.794

The smooth curve in Fig. 1 represents the theoretical curve calculated from the values $\alpha = 0.25$ and $\beta = 0.15$. These correspond to the values, according to the latest nomenclature,[2] $r_1 = 4$ and $r_2 = 0.15$, respectively. The encircled points are experimentally determined from the data in Table I.

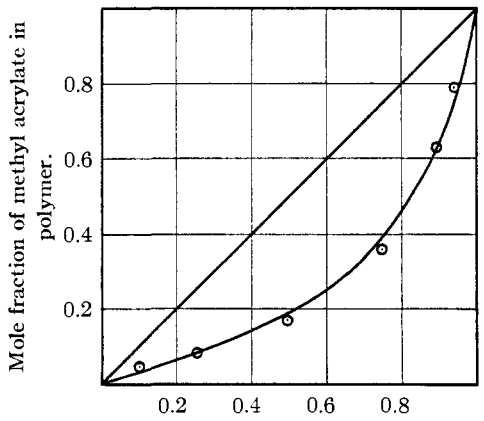

Fig. 1.—Copolymerization composition curve.

The value $r_1 = 4$ indicates that the 2,5-dichlorostyrene monomer adds to the 2,5-dichlorostyrene free radical four times as fast as the methyl acrylate monomer adds. The value $r_2 = 0.15$ indicates that the methyl acrylate monomer adds to the methyl acrylate free radical 0.15 as fast as the 2,5 dichlorostyrene monomer adds to the methyl acrylate free radical.

(1) T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
(2) Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y. RECEIVED OCTOBER 20, 1947

The Preparation of 2,3,5-Triphenyltetrazolium Chloride

BY A. M. MATTSON, C. O. JENSEN AND R. A. DUTCHER

Synthesis of 2,3,5-triphenyltetrazolium chloride by the method of Pechman and Runge as modified by Bamberger and Billeter and by Kuhn and Jerchel[1] resulted in poor yields of preparations which had a greater chloride content than the desired monobasic compound. A better yield of the compound with the theoretical chloride content and a saving of time were achieved by modifying the previous procedures.

Experimental

Triphenylformazan.—Twenty-one and two-tenths grams (0.2 mole) of freshly distilled benzaldehyde was dissolved in 125 ml. of methanol. To this solution 21.6 g. (0.2 mole) of phenylhydrazine was added during mechanical agitation. The hydrazone, dissolved in one liter of methanol, was added to a solution of 50 g. of sodium hydroxide and 70 g. of sodium acetate in one liter of methanol. To this solution, cooled to 20°, benzenediazonium chloride prepared from 18.6 g. of aniline (0.2 mole), 50 ml. of concentrated hydrochloric acid, 50 ml. of water and 14–15 g. of sodium nitrite, was added slowly during agitation. Formazan was precipitated as small red crystals. A yield of 15.8 g. (23%) of triphenylformazan was obtained, m. p. 170°.

2,3,5-Triphenyltetrazolium Chloride.—Fifteen grams (0.05 mole) of triphenylformazan were dissolved in 100 ml. of chloroform and the solution was cooled to 20°. Lead tetraacetate (30 g.) was added until the red color disappeared. The chloroform was evaporated and the residue taken up in water. Hydrochloric acid was added and the lead chloride was removed by filtration. The monobasic triphenyltetrazolium chloride was removed from the filtrate by three successive extractions with chloroform (water–chloroform ratio of 3:1), leaving the more acid salt in the water. The chloroform solution was concentrated on the steam-bath. Addition of ether to this solution precipitated the tetrazolium salt in long, silky needles. Nine and seven-tenths grams (57.7% based on formazan) of 2,4,5-triphenyltetrazolium chloride was obtained, m. p. 245° (d.) (Pechman and Runge 243°).

(1) Pechman and Runge, *Ber.*, **27**, 2920 (1894); Bamberger and Billeter, *Helv. Chim. Acta*, **14**, 232 (1931); Kuhn and Jerchel, *Ber.*, **74B**, 941 (1941).

FREAR LABORATORIES
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
RECEIVED OCTOBER 6, 1947

Effects of Inhibitors on the Polymerization of Styrene[1]

BY FRANK R. MAYO AND R. A. GREGG

Inhibitors of free radical polymerization are regarded as materials which, by transfer or addition, are converted to radicals so stable they do

(1) This paper was presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September 15, 1947.

not add to double bonds. This note will show that benzoquinone is not an inhibitor in this sense and that even the stable radical triphenylmethyl adds readily to styrene.

Foord[2] and Goldfinger, Skeist and Mark[3] found the period of inhibition of styrene polymerization by benzoquinone was proportional to the initial quinone concentration. Assuming the consumption of inhibitor to be a direct measure of the rate of chain initiation, they calculated the activation energy for chain initiation. Since the present work shows that most of the quinone radicals add to styrene, the above assumptions are not justified. At 100°, the rate of uncatalyzed polymerization of styrene is 2.23% per hour yielding a polymer of degree of polymerization 4030.[4] The total moles of polymer per gram per hour is 5.32×10^{-8}, and is equal to the maximum number of chains which could have been initiated. At 100°, 10^{-4} g., 9.3×10^{-7} mole, of benzoquinone inhibits the polymerization of 1 g. of styrene for one hour.[3] Hence, at least 17 molecules of quinone are consumed per radical chain initiated.

Since the inhibition period, the time required to consume quinone, is directly proportional to the initial concentration of quinone, its rate of disappearance is independent of its concentration and quinone cannot be reacting directly with monomer. Let us consider the possible reactions, denoting monomer and quinone by M and Q, and the derived radicals by M* and Q*

$$2M \longrightarrow 2M^* \quad (1)$$
$$M^* + Q \longrightarrow Q^* \quad (2)$$
$$Q^* + M \longrightarrow M^* \quad (3)$$
$$2Q^* \longrightarrow \text{non-radical products} \quad (4)$$
$$Q^* + M^* \longrightarrow \text{non-radical products} \quad (4a)$$
$$2M^* \longrightarrow \text{non-radical products} \quad (4b)$$

If we assume the mechanism to be described completely by Equations 1, 2, 3 and 4, then

$$-dQ/dt = M^2(2k_1 + k_3\sqrt{k_1/k_4}$$

The rate of disappearance of quinone should then be independent of the quinone concentration, as observed, and about 16 out of 17 quinone radicals react by Equation 3 instead of Equation 4. At higher radical concentrations Equation 4 may predominate since it is of second order while Equation 3 is of first order with respect to radicals.[5] Equation 2 may represent either chain transfer or addition of quinone to the chain (copolymerization). Reaction 4b must be unimportant or quinone would not be an inhibitor. If the termination step were 4a, then the rate of disappearance of quinone would depend on the quinone concentration.

It is desirable to have an inhibitor which will not initiate or continue chains, each molecule of which will terminate one reaction chain. Then the rate of chain initiation could be determined and, from our data,[4] the number of polymer molecules formed per chain initiated, *i. e.*, the extent of chain transfer with styrene monomer.[6] Hence, we investigated the radical triphenylmethyl hoping it would terminate chains without starting any.

Hexaphenylethane was dissolved in styrene and heated in narrow diameter tubes sealed under nitrogen. The length of the inhibition period was determined from the viscosity of the reaction mixture, measured as the time for a bubble to traverse a measured distance in the tube. Figure 1 shows that the solution viscosities after the induction period follow essentially the same course as in the blank run. The induction periods were taken as

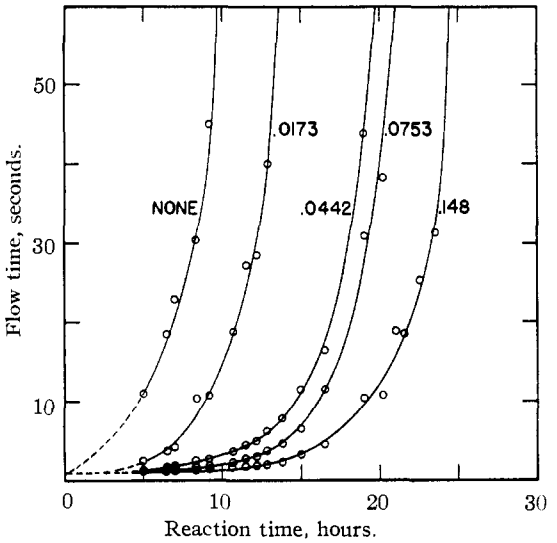

Fig. 1.—Polymerization of styrene at 100° with various initial concentrations of hexaphenylethane, as indicated in moles/liter.

the times required for the solutions to attain a "bubble time" of thirty seconds, minus the eight and three-tenths hours required to reach this stage in the blank. The essential data and conclusions are summarized in Table I and Fig. 2. The results show that the inhibition period increases with the initial concentration of inhibitor, but less rapidly; a large concentration of inhibitor is relatively less effective than a small concentration.

TABLE I

INHIBITION OF THE POLYMERIZATION OF STYRENE AT 100° BY HEXAPHENYLETHANE

Inhibitor moles/l.	Inhibition period, hours	Hours per unit inhibitor concentration
None	None	240–300[a]
0.0173	3.9	225
.0442	9.7	219
.0753	10.9	145
.148	15.0	101

[a] Estimated from Fig. 2.

(2) Foord, *J. Chem. Soc.*, 48 (1940).
(3) Goldfinger, Skeist and Mark, *J. Phys. Chem.*, **47**, 578 (1943).
(4) Gregg and Mayo, THIS JOURNAL, in press.
(5) *Cf.* Cohen, *ibid.*, **69**, 1057 (1947).
(6) While this attempt failed, the transfer constant of polymerizing styrene with styrene monomer has been determined and will be published shortly.

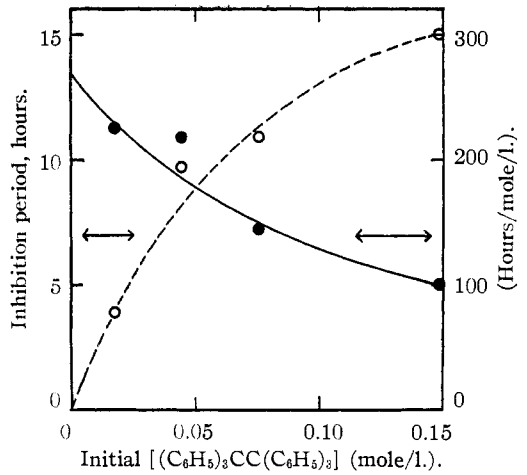

Fig. 2.—Inhibition periods in the polymerization of styrene, in hours (broken line), and in hours per unit concentration of hexaphenylethane (solid line).

This result may be due to the disappearance of hexaphenylethane in a side reaction, such as the addition to styrene; the addition of tri-biphenylmethyl to styrene to give a 2:1 product has been observed.[7] However, since our data are not consistent enough to permit analysis of the kinetics, the inhibition period per unit concentration of inhibitor has been plotted against the concentration of inhibitor in Fig. 2 and extrapolated to estimated zero concentration of inhibitor. Making the reasonable assumption that this extrapolation minimizes complications due to side reactions which consume hexaphenylethane, the results show that the induction period is of the order of two-hundred-forty to three-hundred hours per mole of substituted ethane initially present. Thus, such a solution would consume about 1/270 or 0.0037 mole of hexaphenylethane per hour. Normally, $5.32 \times 10^{-8} \times 905 = 4.8 \times 10^{-5}$ mole of polymer per liter per hour would have been produced. Hence, about 77 molecules of hexaphenylethane disappear (at zero ethane concentration) for each molecule of polystyrene that would have been formed in its absence. It follows that triphenylmethyl radicals must start nearly as many chains as they stop. The addition of hexa-arylethanes to double bonds seems to be the result of an initiation of "polymerization" by free radicals, and an even more effective termination by the same kind of radicals or by undissociated ethane, so that only *very* low molecular weight polymer is formed while triarylmethyl radicals, or undissociated ethane, remain.

We consider that this work leads to the following conclusions: Any free radical may start or terminate the polymerization of a styrene chain. Neither benzoquinone nor hexaphenylethane is suitable for measuring the spontaneous rate of chain initiation, nor for calculating its activation energy. Whether a source of free radicals will behave as a catalyst or an inhibitor depends on the balance between the rate of addition of these radicals to monomer, the rate of interaction of radicals and the rate of growth of the polymer radicals at the chosen temperature. If the radicals do not add rapidly or if they are supplied too fast, then a high radical concentration results and chain growth is restricted. If the radicals add very rapidly, or are supplied slowly enough, polymerization will result. These statements mean simply that the dividing line between catalysts and inhibitors is not clear cut; the differences between them are quantitative rather than qualitative.

(7) Marvel, Dec and Corner, THIS JOURNAL, **67**, 1855 (1945).

GENERAL LABORATORIES
UNITED STATES RUBBER COMPANY
PASSAIC, NEW JERSEY RECEIVED SEPTEMBER 12, 1947

The Periodate Oxidation of Some Dihydroxyaminoalkanes[1]

BY J. F. MEAD AND E. A. BARTRON

It has been reported previously[2] that two of the contiguously substituted dihydroxyaminoalkanes and possibly dihydrosphingosine[3] can be partially identified by the periodate or lead tetraacetate oxidation of the N-acetyl derivatives with measurement of the amount of oxidizing agent consumed.

A simpler method applicable to a wide variety of related compounds is the periodate oxidation[4] of the amino glycols themselves, with isolation of at least two of the oxidation products.

The reactions of the various types of isomeric compounds with periodate can be represented as follows

Type I $R—CHNH_2—CHOH—CH_2OH + 2IO_4^- \longrightarrow R—CHO + HCOOH + HCHO + NH_3 + 2IO_3^-$

Type II $R—CHOH—CHNH_2—CH_2OH + 2IO_4^- \longrightarrow R—CHO + HCONH_2 + HCHO + 2IO_3^-$

Type III $R—CHOH—CHOH—CH_2NH_2 + 2IO_4^- \longrightarrow R—CHO + HCOOH + HCHO + NH_3 + 2IO_3^-$

Type IV $CH_2OH—C(R)NH_2—CH_2OH + 2IO_4^- \longrightarrow R—CONH_2 + 2HCHO + 2IO_3^-$

Type V $CH_2OH—C(R)OH—CH_2NH_2 + 2IO_4^- \longrightarrow R—COOH + HCHO + NH_3 + 2IO_3^-$

It will be noticed that if R is different from H (as in the case of sphingosine) all five types give different products except I and III, which can be distinguished by oxidation of the N-acetyl derivatives[2] and measurement of the amount of formaldehyde produced.

In testing the method, the simplest substrates were used, and the products isolated or identified were those most easily isolated or determined quantitatively. As can be seen from Table I, the

(1) This work was supported by grant No. 840 (Penrose Fund) of the American Philosophical Society.

(2) C. Niemann, A. A. Benson and J. F. Mead, *J. Org. Chem.*, **8**, 397 (1943).

(3) After completion of this note a paper appeared by Carter, Glick, Norris and Phillips, *J. Biol. Chem.*, **170**, 1 (1947), who oxidized dihydrosphingosine to obtain formaldehyde, formic acid and ammonia.

(4) E. L. Jackson, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1944, Chap. 8, p. 341.