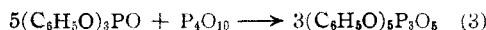


monoethyl monofluorophosphate of high purity,  $n_D^{20}$  1.3668,  $d_4^{20}$  1.3185.

*Anal.* Calcd. for  $C_2H_5O_3PF$ : F, 14.84; P, 24.2; neut. equiv., 128.05. Found: F, 14.8; P, 24.8; neut. equiv., 128-129.

**Hydrogen Fluoride and Phenyl Polyphosphate.**—The phenyl polyphosphate was prepared by treating 15.6 g. (0.055 mole) of phosphoric anhydride with 90 g. (0.276 mole) of triphenyl orthophosphate, according to the equation<sup>13</sup>



Then 91 g. of this crude phenyl polyphosphate was mixed with 7.5 g. of anhydrous hydrogen fluoride; 21.2 g. of crude diphenyl monofluorophosphate was recovered by distillation at 1-2 mm., and redistillation of an intermediate fraction gave 3.8 g. of the relatively pure ester, b.p. 117-120° at 0.1-0.5 mm., reported<sup>14</sup> 115-118° at 0.4 mm.

*Anal.* Calcd. for  $C_{12}H_{10}O_5PF$ : F, 7.53. Found: F, 7.59.

**Half-esters of Monofluorophosphoric Acid, and Their Salts.**—One-tenth molar aqueous solutions of potassium monoethyl monofluorophosphate hydrolyzed to the fluoride and monoethyl orthophosphate at a rate of less than 0.1% per hour at 100° at pH 7-9, and less than 0.25% per hour at room temperature at pH 1 (HCl).

This great hydrolytic stability was reflected in toxicity tests with rats. LD<sub>50</sub> values greater than 250 mg./kg. were found for sodium salts of both monoethyl and monoisopropyl monofluorophosphates by intraperitoneal injection.

Fitch<sup>9</sup> found the relative molar activity of sodium salts of monoethyl and monoisopropyl monofluorophosphates against cholinesterase to be  $2.5 \times 10^{-6}$  and  $7.5 \times 10^{-6}$ , respectively, compared with DFP as unity.

(13) W. H. Woodstock (to Victor Chemical Works), U. S. Patent 2,402,703, June 25, 1946.

(14) N. B. Chapman and B. C. Saunders, *J. Chem. Soc.*, 1010 (1948).

**Acknowledgment.**—This investigation was carried out under a research fellowship sponsored by the Ozark-Mahoning Company, Tulsa, Oklahoma. It was made possible only by the active interest taken in the research problem by Dr. Hoke S. Greene, Dean of the Graduate School, to whom the authors wish to express their deepest appreciation.

### Summary

1. The reaction of anhydrous hydrogen fluoride with polyphosphoric acid esters has been studied as a means of preparing esters of monofluorophosphoric acid,  $(HO)_2POF$ . In this reaction the P-O-P bridges of the polyphosphate chain are split in rapid succession, from one end of the chain to the other, by molecules of hydrogen fluoride, with a fluorine atom becoming attached, in each step, to the phosphorus atom which is split from the end of the chain.

2. Two types of esters of monofluorophosphoric acid have been prepared: (a) the known neutral esters,  $(RO)_2POF$ , and (b) the hitherto unreported acidic half-esters,  $(RO)(HO)POF$ , and their alkali salts.

3. In contrast to the neutral esters, salts of the acidic half-esters, *i. e.*, of monoalkyl monofluorophosphates, showed very little toxicity and practically no anti-cholinesterase activity. The alkali salts were effective in preventing the growth of certain molds on solid agar media.

CINCINNATI, OHIO

RECEIVED JANUARY 3, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

## Cyclic Sulfones. II. The Polymerization of Styrene in the Presence of 3,4-Diphenylthiophene-1-dioxide and 3,4-Di-(*p*-chlorophenyl)-thiophene-1-dioxide<sup>1</sup>

BY C. G. OVERBERGER,<sup>2</sup> HARRY J. MALLON AND RALPH FINE

This paper describes the polymerization of styrene catalyzed by benzoyl peroxide in the presence of 3,4-diphenylthiophene-1-dioxide (III, R =  $C_6H_5-$ ) and 3,4-di-(*p*-chlorophenyl)-thiophene-1-dioxide (III, R = *p*-ClC<sub>6</sub>H<sub>4</sub>-) and a study of the retarding properties of these dioxides when present in small concentrations.

We have found that when styrene is polymerized to low conversions with benzoyl peroxide as the catalyst in the presence of small quantities of these thiophene dioxides, the molecular weight

of the polystyrene is markedly reduced below that of control experiments, some retardation of the polymerization rate occurs, and the polymer chain contains sulfur in the case of III, R =  $C_6H_5-$ , and sulfur and chlorine (in approximately the correct ratio) in the case of III, R = *p*-ClC<sub>6</sub>H<sub>4</sub>-. When styrene is polymerized in the presence of small quantities of the 3,4-disubstituted thiophenes, the molecular weight of the polystyrene is not appreciably reduced, no retardation is noted, and the polymers contain no sulfur and chlorine.

For the experiments using 3,4-diphenylthiophene-1-dioxide, the rate at low conversions was measured using the dilatometer<sup>3</sup> technique. Although some error is involved due to variations in polymer density for very low molecular weight polymers, we feel that this method is much more satisfactory than precipitation procedures all of

(1) For the first paper in this series, see THIS JOURNAL, **72**, 2856 (1950). Part of the work described in this manuscript was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program. Presented in part before the Division of Organic Chemistry of the American Chemical Society at Chicago, September, 1946. A portion of this paper comprises parts of these presented by Harry J. Mallon and Ralph Fine in partial fulfillment of the requirements for the Master of Science degree in the graduate School of the Polytechnic Institute of Brooklyn.

(2) Department of Chemistry, Polytechnic Institute of Brooklyn.

(3) Goldfinger and Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

which result in the loss of some low molecular weight polymer.

Table I summarizes the molecular weight data obtained when  $R = p\text{-ClC}_6\text{H}_4\text{-}$  and  $R = \text{C}_6\text{H}_5\text{-}$ . Figures 1 and 2 indicate the rate curves obtained with the use of dilatometer with different concentrations of III,  $R = \text{C}_6\text{H}_5\text{-}$ .

TABLE I

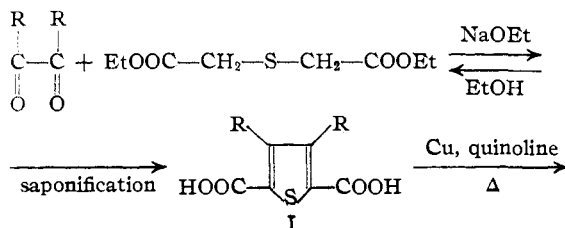
MOLECULAR WEIGHTS OF POLYSTYRENE PREPARED WITH AND WITHOUT THE PRESENCE OF RETARDERS

| Dioxide or thiophene, <sup>a</sup> g. | Moles liter <sup>-1</sup> × 10 <sup>-3</sup> | [ $\eta$ ] | Mol. wt. / × 10 <sup>3</sup> |
|---------------------------------------|--|------------|------------------------------|
| 0.2 <sup>b</sup>                      | 18.4 Control                                 | 0.26       | 41                           |
|                                       |  | .34        | 63                           |
| .3 <sup>b</sup>                       | 27.0 Control                                 | .23        | 34                           |
|                                       |  | .335       | 62                           |
|                                       |  | .217       | 30                           |
| .4 <sup>b</sup>                       | 36.0 Control                                 | .335       | 62                           |
|                                       |  | .198       | 26                           |
|                                       |  | .301       | 53                           |
| .5 <sup>b</sup>                       | 46.2 Control                                 | .34        | 63                           |
|                                       |  | .335       | 62                           |
|                                       |  | .305       | 53                           |
| .2 <sup>c</sup>                       | 20.1 Control                                 | .34        | 63                           |
|                                       |  | .335       | 62                           |
|                                       |  | .314       | 56                           |
| .4 <sup>c</sup>                       | 39.8 Control                                 | .288       | 49                           |
|                                       |  | .315       | 56                           |
|                                       |  | .249       | 36.2                         |
| .10 <sup>d</sup>                      | 7.48   | .248       | 36.4                         |
|                                       |  | .221       | 30.0                         |
| .20 <sup>d</sup>                      | 15.0   | .210       | 27.8                         |
|                                       |  | .205       | 23.3                         |
| .30 <sup>d</sup>                      | 22.5   | .198       | 22.0                         |
|                                       |  | .163       | 18.4                         |
| .40 <sup>d</sup>                      | 29.9   | .168       | 19.3                         |
|                                       |  | .289       | 46.5                         |
| .60 <sup>d</sup>                      | 44.9   | .286       | 45.6                         |
|                                       |  | .271       | 41.7                         |
| .70 <sup>e</sup>                      | 61.0   | .291       | 46.9                         |
|                                       |  | Control    |                              |

<sup>a</sup> 20 g. of purified styrene (see experimental section) and 0.2 g. of benzoyl peroxide were used in all experiments. <sup>b</sup> 3,4-Di-(*p*-chlorophenyl)-thiophene-1-dioxide. <sup>c</sup> 3,4-Di-(*p*-chlorophenyl)-thiophene. <sup>d</sup> 3,4-Diphenylthiophene-1-dioxide. <sup>e</sup> 3,4-Diphenylthiophene. <sup>f</sup> Determined by equation of ref. 13.

### Preparation of Thiophene Dioxides

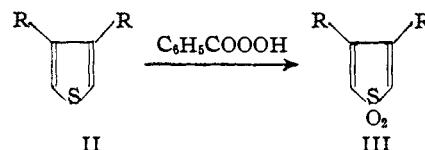
I. Discussion.—The procedure employed to prepare these dioxides was similar to that of Hinsberg<sup>4</sup> and Backer<sup>5,6</sup> and co-workers, and is outlined below.



(4) Hinsberg, *Ber.*, **43**, 901 (1910); (b) **45**, 2413 (1912); (c) **48**, 1611 (1915).

(5) Backer, Bolt and Stevens, *Rec. trav. chim.*, **56**, 1063 (1937).

(6) Backer and Stevens, *ibid.*, **59**, 423 (1940).



Some improvements in the original procedures have been made. A study of the decarboxylation step with acid, neutral and basic reagents resulted in the use of copper powder and quinoline<sup>7,8</sup> as the preferred reagent. An optimum yield in the oxidation step where  $R = p\text{-ClC}_6\text{H}_4\text{-}$  was obtained with the use of a 1.8 mole excess of perbenzoic acid at 60° with stirring for fifteen hours.

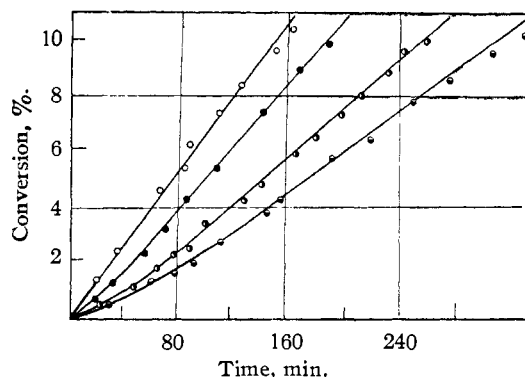


Fig. 1.—Dilatometer rate curves for the polymerization of styrene in benzene in the presence of 3,4-diphenylthiophene-1-dioxide: ○, control with no dioxide; ●, 0.1 g. dioxide; ○, 0.4 g. dioxide; ●, 0.8 g. dioxide.

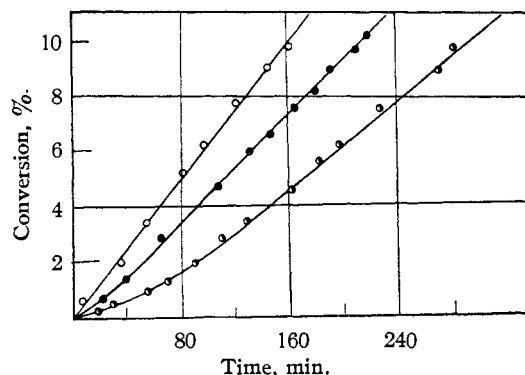


Fig. 2.—Dilatometer rate curves for the polymerization of styrene in benzene in the presence of 3,4-diphenylthiophene-1-dioxide: ○, 0.7 g. of thiophene; ●, 0.2 g. dioxide; ○, 0.6 g. dioxide.

### II. Experimental<sup>9</sup>

Diethyl Thiodiglycolate.—The procedure was similar to that described in a patent of Kyrides, Groves and Zienty<sup>10</sup> although these investigators did not specifically report the preparation of this compound. The procedure was

(7) Shepard, Winslow and Johnson, *THIS JOURNAL*, **52**, 2083 (1930).

(8) Walling and Wolfstirn, *ibid.*, **69**, 852 (1947).

(9) All melting points are corrected.

(10) Kyrides, Groves and Zienty, U. S. Patent 2,262,686, November 11, 1941.

modified in that the product was worked up and isolated in a different way. To 248 g. (2.02 moles) of ethyl chloroacetate dissolved in 1250 ml. of acetone, 311 g. (1.29 moles) of sodium sulfide nonahydrate was added slowly with stirring. Heat was applied to initiate the reaction and was discontinued when the reaction started. The reaction was allowed to proceed for three hours with stirring at which time it had subsided and cooled. After removal of the sodium chloride by filtration, the acetone layer was separated and the aqueous layer extracted with ether. After drying the combined acetone and ether layers, and removal of the acetone and ether by distillation under reduced pressure, the product was distilled further under reduced pressure through a 10" helices-packed column under nitrogen. The product, a water-white, oily, unpleasant smelling liquid boiled at 105° (3 mm.), 110° (4 mm.), 115° (5 mm.), 138° (15 mm.),  $n_{D}^{25}$  1.4619, 119.5 g. (57%). Backer and Stevens<sup>6</sup> reported a b. p. of 135–136° (10 mm.) and 145–146° (15 mm.) for this compound prepared by the esterification of thiodiglycolic acid (62%).

**3,4-Di-(*p*-chlorophenyl)-thiophene-2,5-dicarboxylic Acid.**—This procedure was very similar to that for the preparation of 3,4-diphenylthiophene-2,5-dicarboxylic acid<sup>6</sup> except that anhydrous ethanol was used instead of methanol and an atmosphere of nitrogen was maintained over the reaction flask. From a solution of 300 ml. of anhydrous ethanol containing 30.7 g. (0.15 mole) of diethyl thiodiglycolate, 42.2 g. (0.15 mole) of *p,p'*-dichlorobenzil, and a solution of 12 g. (0.52 g. atom) of sodium dissolved in 188 ml. of anhydrous ethanol, there was obtained in 72 hours, with occasional shaking, on recrystallization from 95% ethanol with Norite, 34.5 g. (59%) of yellow plates, m. p. 299–300°, neutral equiv., calcd., 196; found, 195. *Anal.*<sup>11</sup> Calcd. for  $C_{18}H_{10}Cl_2O_4S$ : C, 54.97; H, 2.56. Found: C, 55.18; H, 2.76. This procedure was likewise used to prepare 3,4-diphenyl-2,5-dicarboxylic acid.<sup>6</sup>

**3,4-Di-(*p*-chlorophenyl)-thiophene.**—The procedure of Backer and Stevens<sup>6</sup> gave only a 26% yield of the decarboxylated product. The following procedure gave more satisfactory results, and is similar to a procedure used to decarboxylate cinnamic acids described by Walling and Wolfstirn.<sup>8b</sup>

A mixture of 47.3 g. (0.121 mole) of 3,4-di-(*p*-chlorophenyl)-thiophene-2,5-dicarboxylic acid and 142 g. of redistilled quinoline was heated with an open flame to dissolve the solid. To this was added 4.73 g. of copper powder (10% of the weight of the dicarboxylic acid) and a vigorous evolution of carbon dioxide occurred. Heating was continued intermittently over a period of two hours to keep the solution at a low boil, about 209°, until no further evolution of carbon dioxide was detected (lime water test). The mixture was filtered hot to remove the copper and the filtrate neutralized with cooling with 358 ml. of 3 *N* hydrochloric acid. The brown precipitate was removed by filtration and washed several times with 100-ml. portions of 1 *N* hydrochloric acid, then with a large quantity of water until the washings were neutral. The crude brown crystals were recrystallized from absolute ethanol (Norite). The crystalline product, golden plates, melted at 136–137°, 16.8 g. (45%). Attempts to decarboxylate the acid in aqueous mineral acid were unsuccessful. *Anal.* Calcd. for  $C_{16}H_{10}Cl_2S$ : C, 62.96; H, 3.30. Found: C, 63.19; H, 3.24. Using a similar procedure, an 80% yield of 3,4-diphenylthiophene was obtained; compare 65%, ref. 6; 56%, ref. 5.

**3,4-Di-(*p*-chlorophenyl)-thiophene-1-dioxide.**—The procedure for preparing this compound was based on that used by Backer, Bolt and Stevens<sup>6</sup> to prepare 3,4-diphenylthiophene-1-dioxide. In order to obtain any 3,4-di-(*p*-chlorophenyl)-thiophene-1-dioxide, new experimental conditions were required. Perbenzoic acid was prepared according to "Organic Syntheses."<sup>12</sup> In a 2-l., round-

bottomed flask equipped with a reflux condenser were added 20.6 g. (0.0675 mole) of 3,4-di-(*p*-chlorophenyl)-thiophene and 150 ml. of chloroform. To this was added a solution of 26.08 g. (0.189 mole) of perbenzoic acid in 538 ml. of chloroform solution. The reaction mixture was allowed to reflux gently overnight (15 hours). The solution was neutralized by washing with three 250-ml. portions of sodium bicarbonate solution and washed with equal parts of water. To this solution was added 150 ml. of absolute ethanol and the chloroform-ethanol solution was concentrated under reduced pressure. Solid precipitated as the chloroform content of the solution was reduced; the flask was then chilled in Dry Ice and the solid removed. Two recrystallizations of the initial yellow crystals from absolute ethanol using "Norite" gave white flaky crystals, m. p. 179°, dec., 4.0 g. (18%). *Anal.* Calcd. for  $C_{16}H_{10}Cl_2O_3S$ : C, 56.98; H, 2.98. Found: C, 56.81; H, 2.86.

The above procedure represents the best of a series of thirteen experiments with variations in mole ratios and conditions. The use of 30% hydrogen peroxide in a molar ratio of 6:1 in glacial acetic acid gave a 7.2% yield by initial heating followed by standing for one week.

A 55% yield of 3,4-diphenylthiophene-1-dioxide was obtained using the procedure of Backer, Bolt and Stevens, m. p. 167–167.5° dec. (171°, dec., 40%).<sup>6</sup>

### Polymerization. I. Experimental

**Polymerization of Styrene—with 3,4-Di-(*p*-chlorophenyl)-thiophene-1-dioxide.**—The styrene was carefully fractionated under nitrogen through a 12-plate, helices-packed column; the benzoyl peroxide was recrystallized from chloroform and the benzene likewise fractionally distilled.

A solution of 20 g. of styrene, 0.2 g. of benzoyl peroxide and the dioxide were placed in a soft glass tube having a constricted neck. The solution was made up to a volume of 32.8 ml. by the addition of benzene. The contents of the tube were then frozen under nitrogen, the tube was sealed and allowed to come to room temperature. The tube was then placed in a bath at a temperature of 70 ± 0.1° and the polymerization allowed to proceed for two or three hours. The controls were experiments conducted in a similar way; the addition of 10 ml. of benzene gave a total volume of 32.8 ml. At the end of the two- or three-hour period, the tube and its control were removed, the solutions frozen, the tubes opened and the contents allowed to come to room temperature. The polymers were precipitated as a powder by dropping the solution slowly into 400 ml. of methanol with stirring. After 10 or 15 minutes the precipitated polymer was removed by filtration, redissolved in a minimum amount of methyl ethyl ketone and precipitated again in 400 ml. of methanol. The polymers were digested at 65° for five to seven hours in 250 ml. of absolute ethanol. The polymer was then removed by filtration and dried in vacuum for twelve hours, and weighed. Only a trace of material of any kind was ever recovered on evaporation under reduced pressure of the ethanol used for digestion. The polymerization experiments in which the 3,4-di-(*p*-chlorophenyl)-thiophene was used were carried out in the same manner.

Molecular weights (Table I) of all polymers were obtained from intrinsic viscosity determinations using the equation of Goldberg, Hohenstein and Mark.<sup>13</sup>

Using the above technique a typical experiment employing 0.2 g. of 3,4-diphenylthiophene-1-dioxide gave 4.8 g. (24%) of polymer in three hours. *Anal.* Found: chlorine, 0.59%; sulfur, 0.20% [polymer digested for 5 hours in absolute ethanol]; sulfur, 0.21% [polymer digested for an additional 5 hours]; chlorine, 0.35%; sulfur, 0.16% [polymer digested for an additional 10 hours]; chlorine-sulfur ratio, theo. 2.22. Found: 2.95, 2.62, 2.19. A control experiment gave 6.5 g. (32.5%) of polymer in three hours. An experiment using 0.5 g. of dioxide gave 1.54 g. (7.7%) of polymer in two hours. *Anal.*

(11) Analyses by Mr. H. S. Clark, Urbana, Illinois.

(12) Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 431.

(13) Goldberg, Hohenstein and Mark, *J. Polymer Sci.*, **2**, 508 (1947).

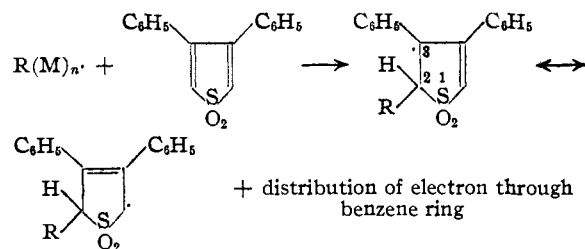
Found: chlorine, 1.43%; sulfur, 0.69%; chlorine-sulfur ratio; theo., 2.19; found, 2.07. Additional experiments gave similar results. When the thiophene was substituted in place of the thiophene dioxide no chlorine or sulfur was found in the polymer chain.

**With 3,4-Diphenylthiophene-1-dioxide.**—The rate curves were determined with the use of a dilatometer. The general method and theory have been described by Goldfinger and Lauterbach.<sup>8</sup> The apparatus consisted of a glass bulb to which was attached a stopcock equipped with a reservoir to introduce the sample and a capillary tube equipped with a small water condenser. The volume of the dilatometer as calibrated with mercury was 35.214 ml. The cross sectional area of the capillary was likewise calibrated with mercury (0.032 ml./cm.). A calibration curve for the dilatometer was determined as described by Goldfinger and Lauterbach. The benzoyl peroxide (0.2 g.), the dioxide and 20 g. of styrene were made up to 50 ml. with benzene, in a volumetric flask. This solution was introduced into the dilatometer, previously flushed with oxygen-free nitrogen, through the stopcock until nearly all the bulb and capillary were full. The bulb was then placed in a constant temperature bath at  $70 \pm 0.1^\circ$ . At the end of five minutes, the charge was carefully drawn into the capillary to the desired mark by reducing the pressure at the end of the capillary tube. The stopcock was then closed and readings were taken at approximately fifteen-minute intervals by means of a cathetometer. The polymers were precipitated and reprecipitated as described previously. In these experiments longer digestion periods (24 hours) were used. The molecular weight data are tabulated in Table I. Using the above technique a typical experiment employing 0.20 g. of dioxide gave a yield determined by precipitation of 6.2%, compared with a 9.7% dilatometric conversion (Fig. 1) in an equivalent time. *Anal.* Sulfur, 0.09. Using 0.4 g. of dioxide the yield determined by precipitation was 5.9% compared with a 9.8% dilatometric conversion in an equivalent time. *Anal.* Sulfur, 0.44. Six additional experiments gave similar results.

When the thiophene was substituted in place of the thiophene dioxide no sulfur was found in the polymer chain.

Low conversion polymers (below 2%) prepared by the polymerization of styrene in the presence of 3,4-diphenylthiophene-1-dioxide likewise contained sulfur.

**Results and Discussion of Polymerization Experiments.**—The most likely reaction which may occur between the thiophene dioxide and the growing polymer radical is indicated. The reso-



nance in the thiophene ring has been markedly reduced by the formation of the sulfone and the double bond<sup>14</sup> is more susceptible to radical

(14) This double bond should be similar in reactivity to a cinnamic acid. If the styrene-polymer radical has some polar character as has been suggested by Price ("Mechanism of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 96) this addition should also be favorable since the sulfone group is withdrawing electrons from the 2-3 bond making it susceptible to attack by radicals of high electron density. From the viewpoint of Walling, Briggs, Wolfstirn and Mayo, *THIS JOURNAL*, **70**, 1587 (1948), there are possibilities for resonance in the ion radical transition state resulting from a one electron transfer.

addition, whereas in the 3,4-substituted thiophene itself, there is considerable resonance, the 2,3-bond has more single bond character and is not susceptible to radical attack.<sup>15</sup> The addition of the polymer radical should give the intermediate radical as indicated, the most stable radical that can result from the addition. Similar considerations to account for the observed orientations of free radicals on addition to olefins have been advanced by Mayo and Walling,<sup>16</sup> and Koelsch and Boekelheide.<sup>17</sup> This radical may be more stable due to the resonance possibilities than is the growing chain which ends in a styrene radical and this along with steric factors probably accounts for the retarding properties of the dioxides. Price<sup>18</sup> has suggested a similar mechanism to explain the retardation of free radical polymerizations by nitrobenzene.

From Figs. 1 and 2, it can be seen that there is much more retardation of rate for about the first hour with some continued small retardation for the next two hours. The amount of retardation depends to some extent on the concentration of the dioxide. The molecular weight is possibly reduced by termination of the relatively stable radical adduct by disproportionation with another polymer radical or by a bimolecular reaction with styrene to give a new free radical and a terminated chain which contains a dioxide residue. This latter type of reaction has been suggested by Mayo<sup>19</sup> to account for the weak chain transfer properties of benzene and by Price and Read<sup>20</sup> to account for the chain transfer properties of chloranil.

Since at the higher concentrations of dioxide more than one thiophene dioxide residue was found per polymer molecule, some copolymerization probably occurs. A termination step of the radical adduct which may occur by coupling with itself or other growing chains might also account for the introduction of dioxide units into the chain.

**Acknowledgment.**—The senior author wishes to thank Dr. C. S. Marvel and Dr. Turner Alfrey for their advice and helpful criticism.

### Summary

3,4-Di-(*p*-chlorophenyl)-thiophene-1-dioxide has been prepared and characterized.

3,4-Diphenylthiophene-1-dioxide and the chloro derivative function as retarders when present in small amounts for the polymerization of styrene catalyzed by benzoyl peroxide. They likewise reduce the molecular weight of the polymer.

BROOKLYN, N. Y.

RECEIVED JANUARY 26, 1950

(15) Wheland ("The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 70) gives a value of 29 kcal. for the resonance energy of thiophene.

(16) Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

(17) Koelsch and Boekelheide, *THIS JOURNAL*, **66**, 412 (1944).

(18) Price and Durham, *ibid.*, **65**, 757 (1943).

(19) Mayo, *ibid.*, **65**, 2324 (1943).

(20) Price and Read, *J. Polymer Sci.*, **1**, 44 (1946).