stant for polymerization indicate that the reactions of the growing polymer radical are independent of average chain length over the range 100 to 10,000 styrene units. The results establish the validity of a simple and accurate method for comparing the reactivities of solvents in general with the free radicals which occur in polymerizing systems.

Number average molecular weights of the products of thermal polymerizations of styrene at low conversions have been determined by osmotic pressure measurements and by chlorine analyses; they bear a simple relation to the intrinsic viscosities of the unfractionated polymers.

PASSAIC, N. J. RECEIVED JULY 19, 1947

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. IV. Vinylthiophenes[1,2]

BY G. BRYANT BACHMAN AND LOWELL V. HEISEY

The desirable polymerization and copolymerization characteristics of the chlorinated styrenes[3] and alpha-methylstyrenes[2b] have suggested studying their analogs in the thiophene series. We have synthesized a representative group of compounds with one, two or three chlorine or bromine atoms and an alpha- or beta-vinyl or isopropenyl group substituted on the thiophene nucleus. These compounds have been found to polymerize and copolymerize similarly to the corresponding benzene compounds, the rates increasing with the number of chlorine atoms present on each thiophene nucleus. The polymers were all somewhat colored, however, in spite of careful purification of the monomers. This seems to be inherent in the alpha-halothiophenes themselves. Even 2-chlorothiophene, which is color stable in stoppered tubes at 70° for days, colors within a few hours at this temperature in the presence of peroxides.

The preparation of vinylthiophenes is a problem very similar in nature to that of preparing vinylbenzenes except that the thiophene nucleus is more reactive, less stable, and subject to different rules of orientation than the benzene nucleus. We have been especially interested in observing the results of exchange metallation in the thiophene series. Either an alpha-hydrogen or an alpha-halogen may be replaced by lithium when treated with alkyllithium compounds. Thus 2-chloro-, 2,5-dichloro- and 2,3,4,5-tetrachlorothiophenes gave the corresponding metallo-derivatives with lithium in the 2-position and chlorine in the 5-, 5- and 3,4,5-positions, respectively. Magnesium reacted with 2,5-dibromothiophene normally, but with 2-bromo-5-chloro- and with 2,3,4,5-tetrachlorothiophenes it reacted well only in the presence of a co-halide (ethyl bromide). These lithium reagents and the corresponding Grignard reagents gave alcohols (Table I) with acetaldehyde, propionaldehyde, or acetone which were readily dehydrated to the desired vinylthiophenes (Table II). Some of the tertiary alcohols dehydrated spontaneously during isolation. Other vinylthiophenes were prepared from the corresponding methyl thienyl ketones by reduction or by reaction with methylmagnesium halide followed by dehydration of the resulting alcohols.

α-Methylstyrenes with ortho halogen atoms have been shown[2b] not to polymerize or copolymerize freely, a fact which is attributed to the steric hindrance to free rotation of the isopropenyl group provided by the ortho substituent. This hindrance is not as extreme in the thiophene series. The angles between adjacent positions amount to about 72° for five-membered rings and only about 60° for six-membered rings. Models show that the isopropenyl group in 2,5-dichloro-3-isopropenylthiophene is free to rotate about a full circle, and in agreement with the model and the theory this vinyl compound copolymerizes satisfactorily with butadiene in an emulsion system. That it is a borderline case is indicated by the fact that its bulk polymer with maleic anhydride and its emulsion polymer with styrene were obtained in only small yields (about 5%).

Acknowledgment.—We wish to express our appreciation to the Purdue Research Foundation and to the General Tire and Rubber Company for financial support in the form of a fellowship.

Experimental

Unsubstituted Vinylthiophenes.—2-Vinylthiophene has been previously reported.[4] 2-Isopropenylthiophene was prepared by adding 2-acetylthiophene to an ether solution of methylmagnesium bromide (a different method from that used by Thomas[5]), and steam distilling the unstable hydrolyzed product with 2% sulfuric acid.

Anal. Calcd. for C_6H_6S: C, 67.7; H, 6.5. Found: C, 67.7; H, 6.5.

5-Bromo-2-vinylthiophenes.—2,5-Dibromothiophene,[6] 182 g. (0.75 mole), in 250 ml. of dry ether was converted to the mono-Grignard reagent with 18.3 g. (0.75 mole) of magnesium. Benzene, 200 ml., caused the ether-insoluble red oil to dissolve. Addition of acetaldehyde 34 g. (0.77 mole) or acetone 43.5 g. (0.75 mole) and hydrolysis with dilute acetic acid gave the corresponding alcohols mixed

---

[1] From the Ph.D. thesis of L. V. Heisey, Purdue University, June, 1947. Present address: McPherson College, McPherson, Kansas.

[2] For previous papers in this series see, (a) Bachman and Lewis, THIS JOURNAL, **69**, 2022 (1947), and (b) Bachman and Finholt, *ibid.*, **70**, 622 (1948).

[3] Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944).

[4] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[5] Thomas, *Bull. soc. chim.*, **5**, 732 (1908); *Compt. rend.*, **146**, 642 (1908).

[6] Steinkopf and Köhler, *Ann.*, **532**, 250 (1937).

TABLE I

CHLORINATED THIOPHENE ALCOHOLS

Name[a]	Yield,[b] %	B. p., °C., mm.	n^{25}_D	d^{25}_{25}	Formula	Chlorine, %	
						Calcd.	Found
T—CHOHCH$_3$							
(2),5-Cl	A(81), B(71), C(27)	85–87 (2)	1.5556	1.264	C_6H_7OSCl	21.8	21.7
(3),2,5-diCl	B(90)	95–97 (1)	1.5630	1.413	$C_6H_6OSCl_2$	36.0	35.6
(2),3,4,5-triCl	C(87), D(79)	109–112 (2)	....[c]	...	$C_6H_5OSCl_3$	45.9	46.0
T—C(CH$_3$)$_2$OH							
(2),5-Cl	A(67), C(95)	83–85 (1)	1.5362	1.226	C_7H_9OSCl	20.1	19.9
(3),2,5-diCl	E(93)	104–105 (2)	1.5560	1.358	$C_7H_8OSCl_2$	33.6	33.3
(2),3,4,5-triCl	D(77)	118–122 (2)	....[d]	...	$C_7H_7OSCl_3$	43.3	42.8
T—CHOHC$_2$H$_5$							
(2),5-Cl	A(68)	100–101 (1)	1.5408	1.232	C_7H_9OSCl	20.1	19.8

[a] T stands for thienyl. Parenthetical numbers give positions of hydroxyalkyl groups. [b] Methods of preparation: A, hydrogen–lithium interchange followed by addition of RCOR′; B, reduction of acetylthiophene; C, preparation of thiophene–Grignard reagent followed by addition of RCOR′; D, halogen–lithium interchange followed by addition of RCOR′; E, acetylthiophene and CH_3MgX. [c] Solid, m. p. 52.5–53.5°. [d] Solid, m. p. 78.5–79.5°.

TABLE II

VINYLTHIOPHENES

Substituents[a]	Method[b] and yield, %	B. p., mm.	d^{25}_{25}	n^{25}_D	Formula	Analyses, %	
						Calcd.	Found
T—CH=CH$_2$							
(2),5-Br	A(34)	64–65 (5)	1.668	1.6160	C_6H_5SBr	S, 16.96	16.81
(2),5-Cl	B(72), C(48)	56–57 (7)	1.199	1.5780	C_6H_5SCl	Cl, 24.5	24.3
(3),2,5-diCl	B(64)	55–56 (1)	1.361	1.5908	$C_6H_4SCl_2$	Cl, 39.6	39.2
(2),3,4,5-triCl	B(70), C(0)	83–84 (1)	1.502	1.6106	$C_6H_3SCl_3$	Cl, 49.8	49.8
T—C(CH$_3$)=CH$_2$							
(2),none	D(59)	66–67 (20)[c]	1.022	1.5586	C_7H_8S	C, 67.7 H, 6.50	67.7 6.50
(2),5-Br	A(53)	84–85 (3)	1.631	1.6038	C_7H_7SBr	S, 15.79	15.61
(2),5-Cl	C(84), D(51)	78–79 (10)	1.182	1.5720	C_7H_7SCl	Cl, 22.4	22.3
(3),2,5-diCl	B(83)	77–78 (1)	1.306	1.5831	C_7H_6SCl	Cl, 36.7	36.4
(2),3,4,5-triCl	B(63)	93–94 (2)	1.446	1.5920	$C_7H_5SCl_3$	Cl, 46.8	46.7
T—CH=CHCH$_3$							
(2),5-Cl	B(47)	80–82 (7)	1.157	1.5787	C_7H_7SCl	Cl, 22.4	22.1

[a] T stands for thienyl. Parenthetical numbers give positions of vinyl groups. [b] Methods of preparation: A, spontaneous dehydration of the alcohol prepared from 5-bromo-2-thienylmagnesium bromide and RCOR′; B, dehydration of the corresponding alcohol over activated Al_2O_3 at 300°; C, dehydration of the corresponding alcohol by heating with $KHSO_4$; D, dehydration of the alcohol from 2-acetylthiophene and CH_3MgX. [c] Reported by Thomas,[5] b. p. (727 mm.) 166–167°.

with their dehydration products. The mixtures were steam distilled with 2% sulfuric acid and the vinyl derivatives rectified and isolated with 34% and 53% yields, respectively. Their properties are listed in Table II.

2-Bromo-5-chlorothiophene.—2-Chlorothiophene, 118.6 g. (1.0 mole), in carbon disulfide, 200 ml., was brominated with 160 g. (1.0 mole) of bromine at 0°. After twenty-four hours the mixture was decolorized with 5% sodium sulfite solution, the solvent removed, and the residue heated on a steam cone with 5% sodium hydroxide solution for four hours. Rectification of the product through a short column gave 147 g. (74.6% yield) of a colorless liquid, b. p. (18 mm.) 69.5–70.0°; m. p. −22° to −20°; n^{25}_D 1.5924; d^{25}_{25} 1.803.

Anal. Calcd. for C_4H_2SClBr: C, 24.33; H, 1.00. Found: C, 24.31, 24.42; H, 1.19, 1.30.

5-Chloro-2-vinylthiophenes:—**(A) From 2-Chlorothiophene.**—A solution of 11.9 g. (0.1 mole) of 2-chlorothiophene in 25 ml. of dry ether was added at 0° to a solution of butyllithium prepared from 1.80 g. (0.26 mole) of lithium and 11.1 g. (0.12 mole) of *n*-butyl chloride in 45 ml. of dry ether. The resulting light yellow suspension was refluxed for six hours and then carbonated with Dry Ice to determine the structure of the lithium compound. A 10.4-g. yield (65%) of 5-chloro-2-thiophenecarboxylic acid,[7] m. p. 150–152°, was obtained. Similar solutions prepared with five to ten times as much of each reactant were treated with one and a half molar quantities of acetaldehyde, propionaldehyde and acetone, respectively, at 0°. The resulting mixtures were stirred for two hours at room temperature, hydrolyzed by dropwise addition of 10% aqueous sodium carbonate, and the organic materials separated, ether-extracted and fractionated under reduced pressure. The alcohols were colorless oily liquids.

Attempts to convert 2-chlorothiophene to 5-chloro-2-thienylmagnesium bromide by exchange metallation with ethylmagnesium bromide in boiling ether or benzene were unsuccessful. No ethane was evolved within two hours and carbonation with Dry Ice gave only propionic acid and recovered dichlorothiophene.

(B) **From 2-Acetyl-5-chlorothiophene.**—Reduction of 2-acetyl-5-chlorothiophene with aluminum isopropoxide and fractional distillation of the product gave a 71% yield of 5-chloro-2-(1′-hydroxyethyl)-thiophene.

---

[7] "Thiophene Chemicals," Socony-Vacuum Oil Co., Inc., New York, N. Y., 1946.

Treatment of 2-acetyl-5-chlorothiophene with methylmagnesium halide gave 5-chloro-2-isopropenylthiophene but none of the corresponding alcohol.

(C) **From 2-Bromo-5-chlorothiophene.**—The Grignard reagent from 29.0 g. (0.4 mole) of 2-bromo-5-chlorothiophene in 150 ml. of ether was treated with 26 g. (0.6 mole) of acetaldehyde in 100 ml. of ether and 150 ml. of benzene. The mixture was refluxed half an hour, worked up and distilled to obtain 6 g. (0.04 mole) of 5-chloro-2-vinylthiophene, 15 g. (0.11 mole) of 5-chloro-2-(1′-hydroxyethyl)-thiophene and 1.0 g. (0.02 mole) of 5,5′-dichloro-2,2′-dithienyl, m. p. 107–109.[8] Later attempts to prepare this Grignard reagent directly were unsuccessful, and it was found better to use a cohalide (ethyl bromide).

(D) **From 2,5-Dichlorothiophene.**—Carbonation of 5-chloro-2-thienyllithium prepared from about 0.3 mole of butyllithium and 30.6 g. (0.2 mole) of 2,5-dichlorothiophene gave a 63% yield of 5-chloro-2-thiophenecarboxylic acid, indicating the feasibility of preparing 5-chloro-2-vinylthiophenes by this approach. The method was not applied, however, because satisfactory results were obtained by the simpler syntheses already indicated.

The alcohols prepared by these syntheses were dehydrated as indicated in Table II. Dehydrations over alumina were accomplished in a furnace which consisted of a vertical, electrically heated, 25 mm. × 50 cm. Pyrex reaction tube packed with 4–8 mesh alumina. The top of the tube had two dropping funnels, one for the alcohol and the other for solvent to flush the system. The bottom of the reaction tube was connected to a water aspirator through a water-cooled condenser and a trap immersed in a Dry Ice–trichloroethylene bath. The alumina was activated before use by drawing a slow stream of air through it at 500° overnight.

The dehydrations were conducted by dissolving the alcohols in an equal volume of dry benzene and passing the solution through the furnace at 300° and 30–100 mm. at the rate of 100 ml. per hour. A similar amount of benzene was passed through the furnace after the main fraction to flush the system, and one hour was allowed for drainage before the product was removed.

Dehydrations with potassium hydrogen sulfate catalyst were done at a pressure which permitted dehydration but not distillation of the alcohol. The yields by this method were good only for the tertiary alcohols.

Trinitrobenzene was regularly used as an inhibitor to polymerization in distilling the vinyl compounds.

The 2,5-Dichloro-3-vinylthiophenes.—3-Acetyl-2,5-dichlorothiophene was prepared by the method of Steinkopf and Köhler[6] but their yield (16%) was greatly improved (to 84%) by using carbon disulfide as solvent instead of petroleum ether. The Perrier technique[4] gave only 57% yields in carbon disulfide. Hypochlorite oxidation of the above ketone gave 2,5-dichloro-3-thiophenecarboxylic acid.[8a]

Aluminum isopropoxide reduction of 3-acetyl-2,5-dichlorothiophene gave on distillation 2,5-dichloro-3-(1′-hydroxyethyl)-thiophene (90%). Treatment of the ketone with methylmagnesium halide gave 2,5-dichloro-3-(2′-hydroxyisopropyl)-thiophene (93%).

The above alcohols were dehydrated satisfactorily to the corresponding vinyl compounds in the vapor phase over alumina at 300°.

The 3,4,5-Trichlorovinylthiophenes.—2,3,4,5-Tetrachlorothiophene, 5.56 g. (0.025 mole), was added to a filtered solution of butyllithium (0.03 mole) in 50 ml. of ether. Refluxing for four hours, carbonation with Dry Ice, and isolation of the product gave 3.2 g. (55.4% yield) of 3,4,5-trichloro-2-thiophenecarboxylic acid, m. p. 223–224° (reported,[9] m. p. 224°).

Conversion of 2,3,4,5-tetrachlorothiophene to a Grignard reagent using a cohalide (C_2H_5Br) proceeded less satisfactorily. Reaction of either metallo derivative with acetaldehyde or with acetone instead of Dry Ice gave the desired alcohols. These were dehydrated at 300° over alumina. Other methods were unsuccessful.

Polymerization Studies.—Small samples of the vinyl compounds described were polymerized alone and with styrene, methyl methacrylate, vinyl acetate and maleic anhydride by heating at 70° in 3-inch test-tubes with 0.5% of benzoyl peroxide. The propenyl compound did not polymerize or copolymerize. The isopropenyl compounds did not polymerize alone but did copolymerize. However those compounds with the isopropenyl group in the 2-position and with a halogen in the 5-position polymerized on long exposure to sunlight. It is believed that this is the result of a partial photochemical decomposition yielding hydrogen halides which are known to catalyze the polymerization of isopropenylbenzene. The vinylthiophenes polymerized and copolymerized normally.

Rubbery copolymers with butadiene were prepared in a typical GR-S type emulsion system containing: butadiene 7.5 g., olefin 2.5 g., water 17.5 g., potassium persulfate 0.03 g., lauryl mercaptan 0.06 g. and soap 0.5 g. These copolymerizations were run in sealed tubes rotating in a water-bath at 40° until no further change occurred as evidenced by cessation of fall of the liquid meniscus in the tube. Evidence of copolymerization was determined by the amount and character of the precipitated and acetone-extracted copolymer. Satisfactory rubbers were obtained from all of the vinyl compounds except the 5-chloro-2-propenylthiophene, which did not copolymerize, and the 3,4,5-trichloro-2-isopropenylthiophene, which was not studied.

The copolymers of 2,5-dichloro-3-isopropenylthiophene were of especial theoretical interest and were therefore purified and analyzed. The product with styrene, obtained through an emulsion polymerization at 40–60° for three weeks, was precipitated with aqueous sodium chloride, washed with methanol, and extracted continuously with acetone for eight hours. The residue (5%) was a white powder.

Anal. Calcd. for $(C_8H_8 \cdot C_7H_6SCl_2)_x$: Cl, 23.9. Found: Cl, 21.47, 21.24.

The product with maleic anhydride, obtained through a bulk polymerization of the reactants at 70° for one month, was extracted continuously with benzene for six hours. The residue (5%) was a white powder.

Anal. Calcd. for $(C_4H_2O_3 \cdot C_7H_6SCl_2)_x$: Cl, 25.4. Found: Cl, 19.08, 18.84.

The product with butadiene, obtained in 90% yield in sixty-six hours as described above, was a brown rubbery solid.

Anal. Calcd. for $(3C_4H_6 \cdot C_7H_6SCl_2)_x$: Cl, 9.01. Found: Cl, 9.27, 9.14.

These data indicate that copolymerization occurred.

Summary

A number of halogenated thiophene alcohols have been prepared and dehydrated to the corresponding vinyl halogenated thiophenes in order to study the polymerization and copolymerization characteristics of these olefins.

LAFAYETTE, INDIANA RECEIVED DECEMBER 15, 1947

---

[8] Thöl and Eberhard, *Ber.*, **26**, 2945 (1893).

[8a] Recently described by Hartough and Conley, THIS JOURNAL, **69**, 3097 (1947), m. p. 147–148°.

[9] Steinkopf, Jacob and Penz, *Ann.*, **512**, 136 (1934).