## Experimental Section

**Materials. THF and ECH.** Commercial reagents were purified as described in our previous paper.[1]

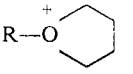
**Methylene Dichloride.** For uv measurements, commercial reagent was treated with concentrated sulfuric acid, washed with water, dried over calcium chloride and distilled. For use in polymerizations it was further dried over phosphorus pentoxide and finally distilled over calcium hydride, bp 40°.

**$SnCl_4$ and $AlEtCl_2$.** Commercial reagents were purified by distillation under reduced nitrogen pressure, bp 59° (112 mm) and 70° (8 mm), respectively.

**$BF_3$–THF.** The complex was synthesized by passing $BF_3$ gas into anhydrous THF at 0° and purified by distillation under reduced nitrogen pressure, bp 70° (4 mm) [lit.[9] bp 69° (4 mm)].

**Polymerization and Determination of [p*].** Polymerization was carried out at 0° under a nitrogen atmosphere. The reaction was initiated by the addition, by means of a syringe, of the Lewis acid catalyst to 10 ml of monomer containing ECH at 0°. $BF_3$ was added as its THF complex. After a desired time of reaction, the polymerization system was terminated by the addition of a THF solution of an equimolar amount (to the catalyst) of sodium phenoxide. The mixture was allowed to react for 1 min at 0° and then decomposed by an aqueous solution of sodium hydroxide. Then the uv analysis of the phenyl ether at the polymer end was carried out as described previously.[3]

It was shown by using $(C_2H_5)_3O \cdot BF_4$ that the reaction of sodium phenoxide with the trialkyloxonium ion proceeds quantitatively within a period of time less than 20 sec. The reactivity of cyclic trialkyloxonium ion of the type



toward phenoxide ion is considered to be even higher than that of $(C_2H_5)_3O^+$. Hence, the above result is taken to indicate that the reaction of sodium phenoxide with the propagating species, eq 3, proceeds very rapidly in comparison with the rate of the change of [p*] in the polymerization.

By reference experiments, it was also established that, under the present experimental conditions, no phenyl ether is formed by the reaction between sodium phenoxide and Lewis acid catalysts. Furthermore, the formation of phenyl ether by the reaction of sodium phenoxide with ECH was shown to be negligible under these conditions.

(9) R. C. Osthoff, C. A. Brown, and J. A. Hawkins, *J. Amer. Chem. Soc.*, **73**, 5480 (1951).

# Monomer Syntheses, Polymerization, and Copolymerization of Vinylthiazoles[1]

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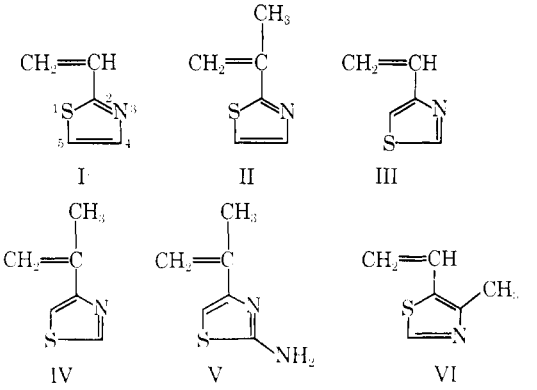
*Received May 29, 1968*

ABSTRACT: The syntheses of a number of vinyl and isopropenylthiazoles are described. Five of these monomers were found to undergo radical polymerization, and the 2-isopropenylthiazole monomer was found to polymerize readily anionically. The nmr spectra of the isopropenylthiazoles in the methyl group region show three distinct signals which are discussed. Reactivity ratios for the copolymerization of 2-vinyl- and 4-vinylthiazole have been determined. 2-Vinylthiazole is much more reactive than the 4-vinyl monomer, and reasons for this are discussed in terms of expansion of the sulfur octet.

There is little literature concerning the synthesis and polymerization behavior of vinyl- or isopropenylthiazoles. This study was prompted by three factors: a desire to know more about the effect of the heterocyclic aromatic thiazole nucleus on monomer reactivity; the hope of determining polymer stereoregularity as a function of initiator type and other reaction variables by the use of nmr; and an interest in quaternized thiazole polymers as catalysts for reactions catalyzed by thiamine.[3] The first two aspects are commented on here, and the third is discussed in the following paper.

Literature reports of the polymerization of the known thiazole monomers are confined to the 2- and 5-vinyl derivatives. 4-Methyl-5-vinylthiazole is reported as yielding only viscous oils with benzoyl peroxide but hard copolymers with maleic anhydride.[4] The 2-vinyl-4-methyl- and 2-isopropenyl-4-methylthiazoles yield radical-initiated homopolymers[5] and radical-initiated copolymers with butadiene or styrene.[6] No reactivity ratios were reported.

**Monomer Syntheses.** Monomers I–VI were synthesized.




(1) A portion of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; *Polym. Preprints*, **8** (1), 363 (1967).

(2) Continental Oil Co. Fellow, 1966–1967.

(3) The catalytic activity of thiamine is known to be due to the presence of the quaternized thiazole ring: R. Breslow and E. McNelis, *J. Amer. Chem. Soc.*, **81**, 3080 (1959).

(4) G. B. Bachman and L. V. Hersey, *ibid.*, **71**, 1985 (1949).

(5) D. L. Schoene, *ibid.*, **73**, 1970 (1951).

(6) D. L. Schoene, U. S. Patent 2,515,318 (1950); *Chem. Abstr.*, **44**, 8699 (1950); U. S. Rubber Co., British Patent 609,467 (1949); *Chem. Abstr.*, **43**, 2805 (1949).

TABLE I
RADICAL POLYMERIZATIONS OF VINYL- AND ISOPROPENYLTHIAZOLES[a]

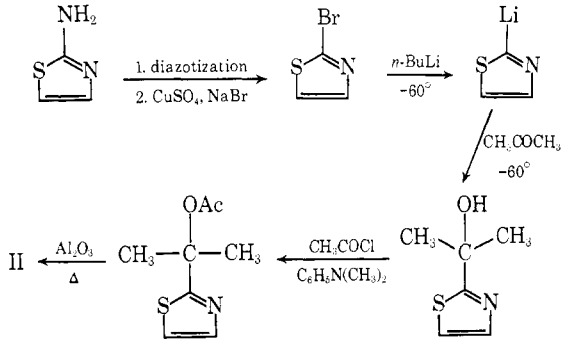
| Run no. | Monomer | Initiator, wt % | Temp, °C | Time, hr | Conversion, % | Softening pt, °C | $\eta_{inh}$[b] |
|---|---|---|---|---|---|---|---|
| 1 | I | 0.64 | 80 | 5 | 73% | 115–135 | 0.95 |
| 2 | II | 1.4 | 90 | 36 | 32 | 150–170 | 0.06 |
| 3 | III | 1.6 | 80 | 12 | 100[c] | 110–130 | 0.14 |
| 4 | III | 1.0 | 80 | 0.8 | 61[d] | | |
| 5 | IV | 0.71 | 80 | 36 | 26 | 130–170 | 0.07 |
| 6 | VI | 1.3 | 90 | 12 | 48 | 150–180 | 0.03 |

[a] Polymerization in bulk using azobisisobutyronitrile. [b] Inherent viscosities in dimethyl sulfoxide at 30.0°, 0.5 g of polymer/100 ml of solvent. [c] Approximtely 90% of this polymer was insoluble in all common solvents. [d] All but a trace of this polymer was soluble in common solvents.

2-Vinylthiazole (I) was previously reported,[5] although analytical results indicated that it was slightly impure. The literature preparation of I was repeated, and the compound was obtained in a pure form.

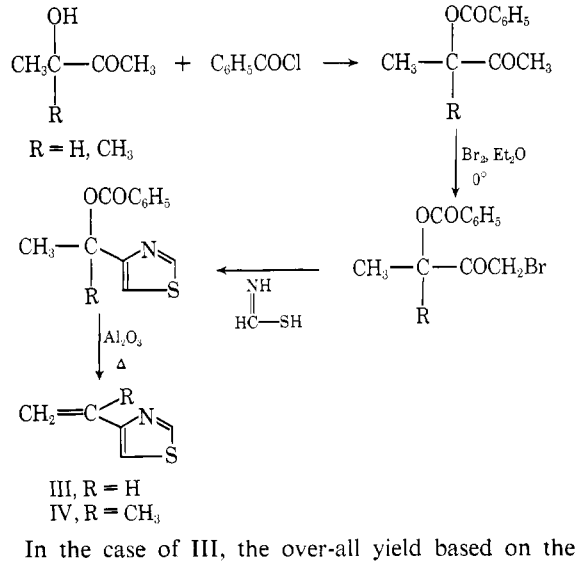
2-Isopropenylthiazole was prepared starting with 2-aminothiazole as shown in Scheme I. The over-all yield for the four steps was 30%.

SCHEME I



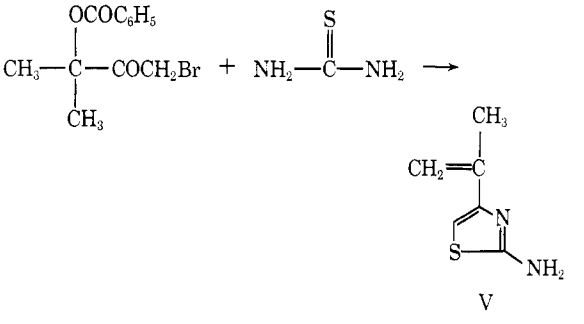

4-Vinyl- and 4-isopropenylthiazoles (III and IV) were synthesized by a parallel series of reactions starting with 3-hydroxy-2-butanone and 3-hydroxy-3-methyl-2-butanone, respectively (Scheme II).

SCHEME II




In the case of III, the over-all yield based on the hydroxybutanone was 34%. In the 4-isopropenylthiazole (IV) synthesis, the monomer was usually isolated by simple vacuum distillation of the *t*-benzoate. The over-all yield of IV based on hydroxybutanone was 24%.

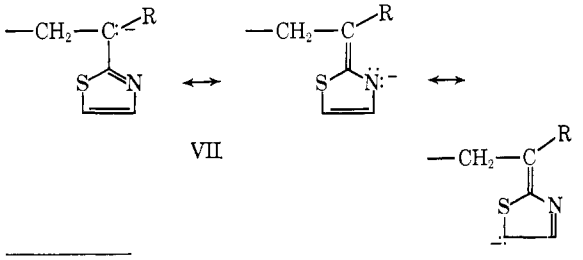
2-Amino-4-isopropenylthiazole was obtained directly by treatment of 1-bromo-3-benzoxy-3-methyl-2-butanone with thiourea.




4-Methyl-5-vinylthiazole (VI) was prepared by a modification of the method of Buchman and Richardson.[7]

**Polymerization of Monomers.** All of the thiazole monomers (with the exception of V which was not investigated) could be polymerized to solid polymers which were generally soluble in common solvents such as benzene, chloroform, dimethyl sulfoxide and dilute hydrochloric acid. Only in the case of 4-vinylthiazole (run 3, Table I) at very high conversions did insolubility arise. The same monomer when polymerized for a shorter period of time gave only a trace of insoluble material. Analyses and spectra were in accord with the expected normal mode of polymerization. Anionic polymerization initiated by *n*-butyllithium was successful in the case of 2-isopropenylthiazole (Table II).

Attempted polymerizations in the case of 4-vinyl- or 4-isopropenylthiazoles using *n*-butyllithium gave only traces of polymer under similar conditions. Simple valence bond considerations of the anion derived from a 2-substituted thiazole (VII) indicate that the anion




(7) E. R. Buchman and E. M. Richardson, *J. Amer. Chem. Soc.*, 67, 395 (1945).

TABLE II
ANIONIC POLYMERIZATION OF 2-ISOPROPENYLTHIAZOLE

| Monomer | Amt, mmol | Initiator[a] | Amt, mmol | Time, hr | Temp, °C | Conversion, % | Softening pt, °C | $\eta_{inh}$[b] |
|---|---|---|---|---|---|---|---|---|
| II | 48 | *n*-BuLi | 0.48 | 36 | 25 | 51 | 170–200 | 0.22 |
| II | 16 | $C_6H_5MgBr$[c] | 0.28 | 1 | 25 | 100 | 170–185 | |
| II | 16 | $C_6H_5MgBr$[c] | 0.28 | 1 | 0 | 100 | 175–190 | |

[a] *n*-Butyllithium (1.6 *M*) in hexane. [b] In dimethyl sulfoxide (30°), 0.5 g of polymer/100 ml of solvent. [c] Phenylmagnesium bromide was added as a 0.7 *M* solution in toluene to monomer in 10.0 ml of toluene.

TABLE III[a]
COPOLYMERIZATION OF STYRENE ($M_1$) AND 4-VINYLTHIAZOLE ($M_2$)

| Run no. | Molar ratio $M_1/M_2$ in feed | Time, min | Conversion, % | % S in copolymer |
|---|---|---|---|---|
| 1 | 0.11 | 13 | 9.4 | 25.03 |
| 2 | 0.32 | 17 | 12.3 | 21.56 |
| 3 | 0.43 | 16 | 11.8 | 20.03 |
| 4 | 0.66 | 17 | 11.8 | 18.47 |
| 5 | 1.00 | 20 | 13.9 | 15.62 |
| 6 | 1.47 | 17 | 10.0 | 13.07 |
| 7 | 2.28 | 18 | 11.2 | 10.08 |
| 8 | 3.00 | 17 | 11.0 | 8.98 |
| 9 | 9.00 | 17 | 11.0 | 3.68 |

[a] See Experimental Section for further details.

TABLE IV[a]
COPOLYMERIZATON OF STYRENE ($M_1$) AND 2-VINYLTHIAZOLE ($M_2$)

| Run no. | Molar ratio $M_1/M_2$ in feed | Time, min | Conversion, % | % S in copolymer |
|---|---|---|---|---|
| 1 | 0.17 | 11 | 11.7 | 25.84 |
| 2 | 0.33 | 17 | 14.8 | 27.06 |
| 3 | 0.45 | 17 | 12.8 | 25.31 |
| 4 | 0.67 | 19 | 13.0 | 24.16 |
| 5 | 1.00 | 20 | 10.5 | 23.13 |
| 6 | 1.50 | 22 | 9.2 | 20.73 |
| 7 | 2.08 | 23 | 10.5 | 18.80 |
| 8 | 3.00 | 20 | 9.1 | 17.13 |
| 9 | 5.38 | 22 | 10.1 | 12.25 |

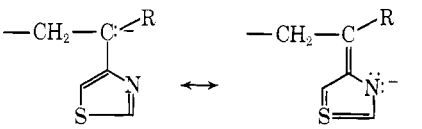
[a] For further details, see Experimental Section.

TABLE V
REACTIVITY RATIOS FOR STYRENE ($M_1$) AND VINYLTHIAZOLES OR OTHER VINYL AROMATIC MONOMERS ($M_2$)

| Monomer | $r_1$ | $r_2$ | $r_1r_2$ |
|---|---|---|---|
| 2-Vinylthiazole | 0.14 | 3.32 | 0.46 |
| 4-Vinylthiazole | 0.66 | 0.82 | 0.54 |
| 2-Vinylpyridine | 0.55 | 1.14 | 0.63[a] |
| 4-Vinylpyridine | 0.55 | 0.52 | 0.29[a] |
| 4-Vinylpyrimidine | 0.17 | 1.20 | 0.20[a] |
| 2-Vinylthiophene | 0.35 | 3.10 | 1.0[a] |
| 2-Vinylquinoline | 0.49 | 2.09 | 1.0[a] |

[a] Values from "Polymer Handbook," J. Brandrup and E. Immergut, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, Chapter II.

should be delocalized with negative charge on the electronegative nitrogen atom. In accord with this 2-isopropenyl-4-methylthiazole is known to undergo Michael additions.[8] In contrast, the anion derived from the 4-derivatives can have negative charge delocalized onto nitrogen only by expansion of the sulfur octet (VIII).



VIII

The nmr spectra of the polymers in $CDCl_3$ obtained from 4-isopropenyl- and 2-isopropenylthiazole showed well-resolved methyl group peaks due to syndiotactic, heterotactic, and isotactic triads in the polymer chain. Poly(4-isopropenylthiazole), prepared using azobisisobutyronitrile, showed peaks at $\tau$ 9.9, 9.4, and 9.0, the largest peak being at $\tau$ 9.9. Using the same initiator the polymer from 2-isopropenylthiazole showed methyl group peaks at $\tau$ 9.6, 9.1, and 8.6, the largest being at $\tau$ 9.6. Poly(2-isopropenylthiazole) prepared anionically with *n*-butyllithium or phenylmagnesium bromide showed the same three methyl group peaks as the radical initiated polymer but in these instances the largest peak was at $\tau$ 9.1 indicating a different triad composition for this polymer. The very high-field methyl group signal at $\tau$ 9.9 or 9.6 would seem to indicate that the polymer exists in a conformation such that in one of the triad configurations the methyl group is forced close to the face of one or more thiazole rings. A similar situation has been reported in the case of poly($\alpha$-methylstyrene). Two groups have investigated the latter polymer and have made different triad assignments to the methyl group signals.[9,10] Further discussion of this point will be deferred to a future paper.

**Copolymerization Results.** Copolymerizations of 2-vinyl- and 4-vinylthiazoles with styrene were carried out at 80° using azobisisobutyronitrile as initiator. Results are presented in Tables III and IV. Because conversions were somewhat high, monomer concentrations were averaged by the standard method.[11]

Reactivity ratios were determined by the Mayo–Lewis method and the Fineman–Ross method as shown in Figures 1–4. Results are tabulated in Table V

(8) T. Shono, S. Kodama, and R. Oda, *Kogyo Kagaku Zasshi*, **58**, 917 (1955); *Chem. Abstr.*, **50**, 13017 (1956).
(9) S. Brownstein, S. Bywater, and D. Worsfold, *Makromol. Chem.*, **48**, 127 (1961).
(10) Y. Sakurada, *et al.*, *J. Polym. Sci., Part B*, **1**, 633 (1963).
(11) T. Alfrey, Jr., J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, p 14.

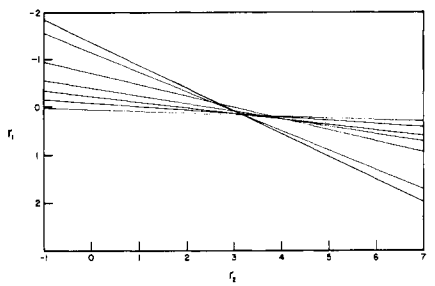


Figure 1. Mayo–Lewis plot for styrene and 2-vinylthiazole.

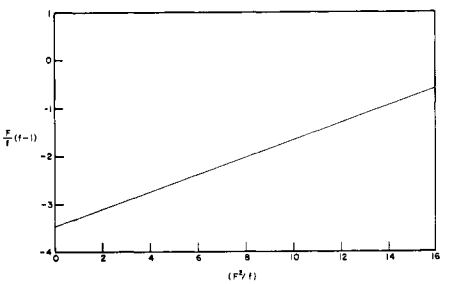


Figure 2. Fineman–Ross plot for styrene and 2-vinylthiazole.

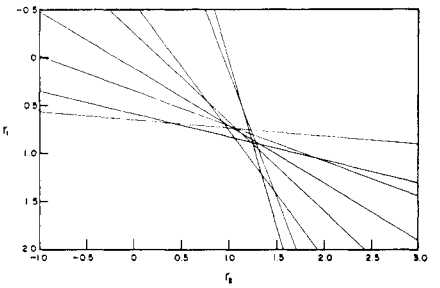


Figure 3. Mayo–Lewis plot for styrene and 4-vinylthiazole.

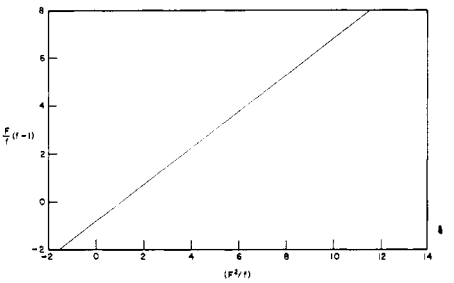
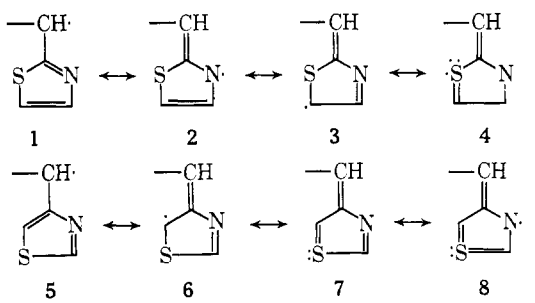


Figure 4. Fineman–Ross plot for styrene and 4-vinylthiazole.

along with some other heterocyclic aromatic monomers for comparison.

The most striking observation from this work is the much greater reactivity of 2-vinylthiazole toward its own radical or to a styryl radical than the case of 4-vinylthiazole. 4-Vinylthiazole monomer is less reactive to its own radical than styrene. The 2-vinylthiazole radical is more highly resonance stabilized than the 4-vinyl analog, and one may discuss this in terms of resonance structures available to the two radicals.



Structures **1–3** for the 2-vinylthiazole radical do not involve expansion of the sulfur octet. However, for the radical derived from 4-vinylthiazole only two structures are involved which do not involve expansion of the sulfur octet. In an open chain compound, a structure similar to **7** has been invoked to explain the high $Q$ values for a vinyl sulfide.[12a] Furthermore, a structure similar to **8** has been suggested to play a role in the fact that there is stronger conjugation of sulfur in the thiophene ring than of oxygen in the furan ring.[12b]

It would appear in the present case that, although structures **7** and **8** may play some role in stabilizing the radical from 4-vinylthiazole, this role is of minor importance relative to structures which do not require such sulfur expansion. Further work will be required to assess quantitatively these observations.

(12) (a) C. C. Price and J. Zomlefer, *J. Amer. Chem. Soc.*, **72**, 14 (1950); (b) D. S. Tarbell and P. Hoffman, *ibid.*, **76**, 2451 (1954).

## Experimental Section

Melting points are uncorrected. Polymer softening temperatures were recorded as the range in which the polymers turned to a clear melt between the cover glasses of the Fisher-Johns apparatus. Nmr spectra were taken with a Varian A-60 spectrometer using tetramethylsilane as internal or external standard. Nmr spectra are presented in $\tau$ units, with peak description and integration in parentheses, followed by assignment. The solvent used is also presented in parentheses preceding the $\tau$ values. Microanalyses and molecular weight determinations were performed by Micro-Tech Laboratories of Skokie, Ill. Viscosities were determined at 30° using Cannon–Fenske viscometers.

**2-Benzoxypropionitrile.** The procedure of Olin and Johnson was used.[13] The product boiling at 100–104° (1.0 mm) (lit.[13] bp 142° (12 mm)) was redistilled yielding 229 g (86%) of clear colorless oil. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.24 (doublet, 3 H) assigned to the methyl group, 4.19 (quartet, 1 H) assigned to the methine proton, and 2.33 and 1.62 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta*, *para* protons and the *ortho* protons of the phenyl ring, respectively.

**2-Benzoxythiopropionamide.** Hydrogen sulfide gas was bubbled for 20 hr through a solution of 129 g (0.737 mol) of 2-benzoxypropionitrile in 400 ml of ethanol containing 10 ml of triethanolamine. Removal of solvent under vacuum yielded a crystalline solid which was washed with 100 ml of cold ethanol and dried in a vacuum oven at 60° (6 mm). The yield of product, mp 100–102° (lit.[13] mp 104°), was 140 g (90%). The nmr spectrum ($CDCl_3$) showed peaks at $\tau$ 8.24 (doublet, 3 H) assigned to the methyl group, 4.17 (quartet, 1 H) assigned to the methine proton, and 2.70–1.60 (mainly two broad multiplets, 7 H) assigned to the phenyl ring protons and the protons of the thioamide group.

(13) J. Olin and T. Johnson, *Rec. Trav. Chim. Pays-Bas*, **50**, 72 (1931).

**2-(1-Benzoxyethyl)thiazole.** The procedure of Schoene[5] was used. Distillation yielded 106 g (68%) of product, bp 127–147° (0.8 mm) (lit.[5] bp 137–142° (2.0 mm)). The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.16 (doublet, 3 H) assigned to the methyl group, 3.53 (quartet, 1 H) assigned to the methine proton, and 2.75–1.65 (mainly three multiplets, 7 H) assigned to the aromatic protons of the phenyl and thiazole rings.

**2-Vinylthiazole.** Schoene's procedure was again used.[5] Distillation yielded 52% of clear colorless liquid, bp 50° (10 mm) (lit.[5] bp 46–47° (1.0 mm)). An analytical sample, purified by distillation on a spinning-band column, had bp 52.5° (10 mm), $n^{25.5}$D 1.5628 (lit.[5] $n^{20}$D 1.5435). The nmr spectrum ($CCl_4$) had peaks at $\tau$ 4.7–3.8 (multiplet, 2 H) assigned to the two $\beta$ protons of the vinyl group, 3.3–2.8 (multiplet, 2 H) assigned to the $\alpha$ proton of the vinyl group and to $H_5$ of the thiazole ring, and 2.30 (doublet, 1 H) assigned to $H_4$ of the thiazole ring.

*Anal.* Calcd for $C_5H_5NS$: C, 54.05; H, 4.50; S, 28.83. Found: C, 54.31; H, 4.57; S, 28.57.

**2-Bromothiazole.**[14] The method of Ganapathi and Venkataraman[14] was employed to prepare 2-bromothiazole, except that the product was extracted with ethyl ether rather than steam distilled. Distillation yielded 59% of product, bp 73° (15 mm), $n^{25}$D 1.5905 (lit.[15] bp 64–65° (15–20 mm), $n^{25}$D 1.5912). The nmr spectrum ($CCl_4$) showed two doublets at $\tau$ 2.50 and 2.26, 1 H each, assigned to $H_5$ and $H_4$, respectively, on the thiazole ring.

**2-(2-Hydroxy-2-propyl)thiazole.** An ethereal solution of *n*-butyllithium prepared from 17.0 g (2.43 mol) of lithium wire, 137 g (1.00 mol) of 1-bromobutane, and 800 ml of ethyl ether was cooled to −70° with a Dry Ice–acetone bath, and a solution of 164 g (1.00 mol) of 2-bromothiazole in 400 ml of ethyl ether was added, the temperature being maintained below −60°. After completion of addition, the deep red solution was cooled to −70°, and a solution of 58.0 g (1.00 mol) of acetone in 200 ml of ethyl ether was added at a rate which again permitted the temperature to remain below −60°. The mixture was stirred at −70° for 0.5 hr; the bath was removed and the mixture allowed to warm to −10° with stirring before being poured into 2 l. of cracked ice and water containing 200 ml of concentrated hydrochloric acid. The layers were separated when the ice had melted; the aqueous layer was made basic with 30% ammonium hydroxide solution, and extracted ten times with a total of 2 l. of ethyl ether. The original ether layer was shaken with a portion of the basic aqueous layer, and all ether solutions were combined for drying over potassium carbonate. Removal of solvent and vacuum distillation yielded a clear colorless oil, bp 95–98° (10 mm), which solidified on standing. An analytical sample, twice recrystallized from petroleum ether (bp 30–60°), had mp 38–42°. The yield of 2-(2-hydroxy-2-propyl)thiazole was 100 g (70.0%) after one recrystallization from petroleum ether (bp 30–60°) and vacuum drying at 32° (10 mm) for 2 hr. The nmr spectrum ($CCl_4$) of the carbinol showed peaks at $\tau$ 8.44 (singlet, 6 H) assigned to the geminal methyl groups, 5.15 (broad singlet, 1 H) assigned to the hydroxyl proton, 2.97 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, and 2.55 (doublet, 1 H) assigned to $H_4$ on the thiazole ring.

*Anal.* Calcd for $C_6H_9NOS$: C, 50.35; H, 6.30; S, 22.38. Found: C, 50.23; H, 6.41; S, 22.27.

**2-(2-Acetoxy-2-propyl)thiazole.** The acetate was prepared from 100 g (0.700 mol) of 2-(2-hydroxy-2-propyl)thiazole, 90.0 g (0.744 mol) of N,N-dimethylaniline, 63.5 g (0.814 mol) of acetyl chloride, and 300 ml of ethyl ether, according to the procedure of Vogel[16] for the preparation of *t*-butyl acetate. The acetyl chloride was added to the solution of the other reactants at a rate permitting gentle reflux, with heat being applied by steam bath to maintain reflux for 1 hr after completion of addition. With violent stirring, 300 ml of water was added slowly through the addition funnel. The ether layer was separated and combined with the 500 ml of ether solution obtained from extraction of the aqueous layer with four 125-ml portions of ethyl ether, the total ether solution being dried over potassium carbonate. Solvent was removed *in vacuo* and vacuum distillation yielded one fraction, bp 45–50° (0.2–0.4 mm), of clear colorless oil, 114 g (88.3%), $n^{27}$D 1.4969. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.27 (singlet, 6 H) assigned to the geminal methyl groups, 8.13 (singlet, 3 H) assigned to the acetyl methyl group, 2.94 (doublet, 1 H) assigned to $H_5$ on the thiazole ring.

*Anal.* Calcd for $C_8H_{11}NO_2S$: C, 51.89; H, 5.95; S, 17.30. Found: C, 51.88; H, 5.92; S, 17.51.

**2-Isopropenylthiazole.** Using a 20-mm i.d. column, 37.5 cm in length, packed with 4–6 mesh activated alumina, 58.4 g (0.316 mol) of 2-(2-acetoxy-2-propyl)thiazole was pyrolyzed at 440° (6.0 mm). The same method of isolation used for 2-vinylthiazole yielded 32.4 g (82.0%) of product, bp 54–60° (4–10 mm). Redistillation on a spinning-band column produced an analytical sample, bp 62.5° (9.5 mm), $n^{27}$D 1.5532, as a clear colorless oil which rapidly turned yellow on standing. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 7.78 (singlet with fine splitting, 3 H) assigned to the methyl group, 4.73 and 4.18 (two singlets with fine splitting, 1 H each) assigned to the $\beta$ protons of the isopropenyl group, 2.82 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, and 2.28 (doublet, 1 H) assigned to $H_4$ on the thiazole ring.

*Anal.* Calcd for $C_6H_7NS$: C, 57.60; H, 5.60; S, 25.60. Found: C, 57.33; H, 5.78; S, 25.33.

**3-Benzoxy-2-butanone** was prepared by the method of Diels and Stepan.[17] Distillation yielded 119 g (72%) of product, bp 108–118° (1.5 mm) (lit.[17] bp 140–141° (8 mm)). The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.77 (doublet, 3 H) assigned to the $C_4$ methyl group, $\tau$ 8.10 (singlet, 3 H) assigned to the $C_1$ methyl group, 4.94 (quartet, 1 H) assigned to the methine proton, and 2.73 and 2.12 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta*, *para* protons and the *ortho* protons of the phenyl ring, respectively.

**1-Bromo-3-benzoxy-2-butanone** was also prepared by Diels and Stepan;[18] their procedure, with variations, is repeated here. Two portions of 3-benzoxy-2-butanone (37.8 g (0.197 mol) and 45.3 g (0.226 mol)), each dissolved in an equivalent weight of chloroform, were cooled in ice water baths. Equimolar amounts of bromine (32.0 g (0.200 mol) and 38.4 g (0.240 mol)), each dissolved in an equivalent weight of chloroform, were added over 10–15-min periods. When the bromine color had almost disappeared, aspirator vacuum was applied to remove hydrogen bromide. The two solutions were combined and solvent was removed, leaving a crystalline solid which was recrystallized from methanol. The methanol solution yielded two crops of product, totalling 67.1 g (56%), mp 70–72° (lit.[18] mp 72–73°). The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.42 (doublet, 3 H) assigned to the $C_4$ methyl group, 5.95 (singlet, 2 H) assigned to the $C_1$ methylene group, 4.47 (quartet, 1 H) assigned to the methine proton, and 2.50 and 1.90 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta*, *para* protons and the *ortho* protons of the phenyl ring, respectively.

(14) K. Ganapathi and A. Venkataraman, *Proc. Indian Acad. Sci., Sect. A*, **22**, 362 (1945).
(15) H. Beyerman, P. Berben, and J. Bontekoe, *Rec. Trav. Chim. Pays-Pas*, **73**, 328 (1954).
(16) A. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1959, p 383.
(17) O. Diels and E. Stepan, *Ber.*, **40**, 4340 (1907).
(18) O. Diels and E. Stepan, *ibid.*, **42**, 1788 (1909).

Higher yields were obtained by the addition of undiluted bromine to an ethyl ether solution of the benzoate. 3-Benzoxy-2-butanone (113 g, 0.589 mol) was dissolved in 133 g of ethyl ether and the solution cooled to 0° with an external ice water bath. Bromine (104 g, 0.650 mol) was added over a 15-min period. Hydrogen bromide and solvent were removed under aspirator vacuum, leaving the solid product, 111 g (70%), after washing with ether and vacuum drying. The product was identical in every respect with that prepared in chloroform solution.

**Thioformamide.** The procedure of Erlenmeyer and Menzi[19] was used with the exception that the supernatant ethyl ether layer was exchanged periodically with fresh anhydrous ethyl ether. This resulted in an improvement of the yield from 24 to 35%.

**4-(1-Benzoxyethyl)thiazole.** A cold solution of thioformamide (7.5 g 0.12 mol) in 175 ml of ethyl ether was combined with a solution of 1-bromo-3-benzoxy-2-butanone (20 g, 0.074 mol) in 125 ml of ethyl ether and 50 ml of benzene and the mixture heated at reflux for 6 hr. The organic layer was decanted and 200 ml of water added to the solid residue, which dissolved as the aqueous mixture was made basic with 10% sodium hydroxide solution. The oil which separated was collected by extracting three times with 100-ml portions of ethyl ether. The original organic layer was shaken with the basic aqueous layer and combined with the ether extraction, followed by drying over sodium sulfate. Removal of solvent and vacuum distillation yielded 14.2 g (82%) of product, bp 130–132° (0.4 mm), $n^{27}D$ 1.5677, a clear orange oil. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.25 (doublet, 3 H) assigned to the methyl group, 3.59 (quartet, 1 H) assigned to the methine proton, 2.70–2.40 (multiplet, 4 H) assigned to the *meta, para* protons of the phenyl ring and $H_5$ on the thiazole ring, 2.00–1.70 (multiplet, 2 H) assigned to the *ortho* protons of the phenyl ring, and 1.19 (doublet, 1 H) assigned to $H_2$ on the thiazole ring.

*Anal.* Calcd for $C_{12}H_{11}NO_2S$: C, 61.80; H, 4.72; S, 13.73. Found: C, 61.95; H, 4.85; S, 13.55.

**4-Vinylthiazole.** Using the pyrolysis apparatus described above, 75.1 g (0.322 mol) of 4-(1-benzoxyethyl)thiazole was pyrolyzed under the same conditions. The method of isolation used before yielded 28.3 (80%) of product, bp 58–59° (10 mm), which was stored over hydroquinone in a refrigerator. Redistillation through a spinning-band column yielded pure product, bp 58.5° (10 mm), $n^{26.5}D$ 1.5729. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 4.71, 4.53, 3.99, and 3.70 (four doublets, 2 H) assigned to the $\beta$ protons of the vinyl group, 3.40–2.93 (four singlets, 1 H) assigned to the $\alpha$ proton of the vinyl group, 2.81 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, and 1.16 (doublet, 1 H) assigned to $H_2$ on the thiazole ring.

*Anal.* Calcd for $C_5H_5NS$: C, 54.05; H, 4.50; S, 28.83. Found: C, 53.70; H, 4.24; S, 28.78.

**3-Benzoxy-3-methyl-2-butanone.** 3-Hydroxy-3-methyl-2-butanone (100 g, 0.980 mol) was treated with 138 g (0.979 mol) of benzoyl chloride in 400 ml of pyridine according to the procedure used above for 3-benzoxy-2-butanone. The identical isolation procedure yielded 149 g (74%) of product, bp 88–90° (0.3 mm) (lit.[20] bp 140–142° (10 mm)). The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.42 (singlet, 6 H) assigned to the geminal methyl groups, 7.90 (singlet, 6 H) assigned to the $C_1$ methyl group, and 2.57 and 1.98 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta, para* protons and the *ortho* protons of the phenyl ring, respectively.

**1-Bromo-3-benzoxy-3-methyl-2-butanone.** 3-Benzoxy-3-methyl-2-butanone (190 g, 0.922 mol) was dissolved in 140 g of ethyl ether and the solution cooled to 0° with an external ice water bath. Bromine (176 g, 1.10 mol) was added over a 20-min period, with hydrogen bromide and solvent being removed by aspiratory vacuum 10 min after completion of addition. The residual oil was vacuum distilled, yielding 224 g (85%) of product, bp 114–125° (0.1–0.2 mm). The nmr spectrum of this compound indicated that it was slightly impure. It was successfully used, however, in the next step.

**4-Isopropenylthiazole.** A solution of 111 g (0.389 mol) of 1-bromo-3-benzoxy-3-methyl-2-butanone in 150 ml of ethyl ether was combined with a solution of 28.9 g (0.474 mol) of thioformamide in 425 ml of ethyl ether. The mixture was heated under reflux for 13 hr, filtered, and the solid residue combined with 250 ml of water. The aqueous mixture was made basic with 10% sodium hydroxide solution and extracted four times with a total of 500 ml of ethyl ether. The original ether layer was shaken with the basic aqueous layer, combined with the extract, and dried over sodium sulfate. Removal of solvent and vacuum distillation yield 18.7 g (38.4%) of clear colorless oil, bp 66–80° (6.0 mm). This material was redistilled through a spinning-band column, yielding pure product, bp 68.5° (6.3 mm), $n^{26.5}D$ 1.5612. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 7.94 (singlet, 3 H) assigned to the methyl group, 4.88 and 4.07 (two singlets with fine splitting, 1 H each) assigned to the $\beta$ protons of the isopropenyl group, 2.97 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, and 1.38 (doublet, 1 H) assigned to $H_2$ on the thiazole ring.

*Anal.* Calcd for $C_6H_7NS$: C, 57.60; H, 5.60; S, 25.60. Found: C, 57.37; H, 5.70; S, 25.48.

A higher boiling fraction, bp 80–81° (6.3 mm), was isolated in good purity from the spinning-band distillation of 4-isopropenylthiazole. This compound, a clear colorless oil, $n^{26}D$ 1.5783, showed nmr peaks ($CCl_4$) at $\tau$ 8.20 (singlet, 6 H) assigned to the geminal methyl groups, 7.40 (broad singlet, 1 H) assigned to the hydroxyl proton, 2.82 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, and 1.22 (doublet, 1 H) assigned to $H_2$ on the thiazole ring. It is presumably the carbinol, 4-(2-hydroxy-2-propyl)thiazole, arising from the hydrolysis of 4-(2-benzoxy-2-propyl)thiazole, the non-isolated intermediate in the synthesis of 4-isopropenylthiazole.

The reduction of 4-isopropenylthiazole to 4-isopropylthiazole in the presence of platinum oxide in acetic acid solution in a Parr low pressure hydrogenation apparatus was unsuccessful. There was no hydrogen uptake over a 72-hr period.

**4-(2-Benzoxy-2-propyl)thiazole.** Thioformamide (40 g, 0.66 mol) was condensed with 1-bromo-3-benzoxy-3-methyl-2-butanone (160 g, 0.56 mol) in 900 ml of refluxing ethyl ether for 6 hr with stirring. After filtration, the solid residue was dissolved in 400 ml of distilled water. Basification of the aqueous solution with 10% sodium hydroxide solution caused the precipitation of a white crystalline solid, crude mp 66–72°. The aqueous solution was extracted three times with 125-ml portions of ethyl ether which was combined with the original reaction solvent after the latter had been shaken with the basic aqueous solution. The combined ether layers were dried over sodium sulfate. Solvent removal and vacuum distillation yielded 14.6 g (21%) of 4-isopropenylthiazole, bp 53° (3.5 mm). The crystalline solid was recrystallized from ethyl ether yielding 49.5 g (36%) of 4-(2-benzoxy-2-propyl)thiazole. The nmr spectrum ($CCl_4$) showed peaks at $\tau$ 8.04 (singlet, 6 H) assigned to the geminal methyl groups, 2.77 (doublet, 1 H) assigned to $H_5$ on the thiazole ring, 2.63 and 2.00 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta, para* protons and the *ortho* protons on the phenyl ring, respec-

(19) H. Erlenmeyer and K. Menzi, *Helv. Chim. Acta*, **31**, 2071 (1948).

(20) R. McGill, U. S. Patent 219,172 (1939); *Chem. Abstr.*, **34**, 5463 (1940).

tively, and 1.40 (doublet, 1 H) assigned to $H_2$ on the thiazole ring.

*Anal.* Calcd for $C_{13}H_{13}NO_2S$: C, 63.16; H, 5.26; S, 12.96. Found: C, 63.40; H, 5.37; S, 12.95.

**4-Methyl-5-vinylthiazole** was prepared from thiamine according to published procedures.[7,21] The nmr spectrum showed signals at $\tau$ 7.59 (singlet, 3 H) assigned to the methyl group, 4.71 (multiplet, 2 H) assigned to the $\beta$ protons of the vinyl group, 3.18 (quartet, 1 H) assigned to the $\alpha$ proton of the vinyl group, and 1.43 (singlet, 1 H) assigned to $H_2$ on the thiazole ring.

**2-Amino-4-(1-benzoxyethyl)thiazole.** 1-Bromo-3-benzoxy-2-butanone (14.0 g, 0.0517 mol) and thiourea (5.3 g, 0.070 mol) were condensed in 125 ml of benzene heated under reflux for 5 hr, during which time 0.9 ml of water was collected in a Dean–Stark trap. The mixture was cooled on an ice water bath; the benzene layer was separated and the residual solid was dissolved in 200 ml of water. The resultant aqueous solution was made basic with 10% sodium hydroxide solution, causing the precipitation of a white solid which was collected by suction filtration and washed with water. The crude yield after vacuum drying was quantitative. An analytical sample, recrystallized three times from 100% ethanol, had mp 164.5–166.0°. The nmr spectrum (dimethyl sulfoxide-$d_6$) showed peaks at $\tau$ 8.37 (doublet, 3 H) assigned to the methyl group, 6.37 (singlet, 2 H) assigned to the amino group, 3.96 (quartet, 1 H) assigned to the methine proton, 3.34 (singlet, 1 H) assigned to $H_5$ on the thiazole ring, and 2.33 and 1.88 (two multiplets, 3 H and 2 H, respectively) assigned to the *meta*, *para* protons and the *ortho* protons of the phenyl ring, respectively.

*Anal.* Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.06; H, 4.84; S, 12.90. Found: C, 57.96; H, 4.97; S, 12.81.

**2-Amino-4-isopropenylthiazole.** A mixture of 1-bromo-3-benzoxy-3-methyl-2-butanone (84.5 g, 0.297 mol) and thiourea (25.0 g, 0.329 mol) in 500 ml of benzene was heated at reflux for 5.5 hr, after which time a large yellow mass formed, preventing further stirring. The organic layer was removed by filtration and 200 ml of water was added to the solid residue. An insoluble yellow gum was separated from the aqueous phase and set aside. The aqueous phase was made basic with 10% sodium hydroxide solution and extracted three times with 50-ml portions of benzene. Drying of the benzene extract over sodium sulfate, followed by solvent removal, yielded 10 g of gummy brown solid. This was subjected to vacuum sublimation at 25° (0.05 mm), yielding 1.5 g (3.6%) of 2-amino-4-isopropenylthiazole, mp 78–80° (capillary). Removal of solvent from the original organic layer led to the recovery of small amounts of starting materials. The nmr spectrum ($CDCl_3$) of the 2-amino-4-isopropenylthiazole showed peaks at $\tau$ 7.97 (singlet with fine splitting, 3 H) assigned to the methyl group, 4.90 and 4.30 (two singlets with fine splitting, 1 H each) assigned to the vinylic protons, 4.12 (broad singlet, 2 H) assigned to the amino group, and 3.63 (singlet, 1 H) assigned to $H_5$ on the thiazole ring.

*Anal.* Calcd for $C_6H_8N_2S$: C, 51.43; H, 5.71; S, 22.86. Found: C, 51.70; H, 5.54; S, 22.98.

The gummy yellow solid was extracted with ethyl acetate, yielding a hard tan powder which was insoluble in water and the common organic solvents, but soluble in dilute hydrochloric acid. This substance was not characterized further.

**Polymerizations of Vinyl and Isopropenylthiazoles.** The monomers were purified prior to use by distillation through a spinning-band column. The purified monomers each showed a single peak on the vapor phase chromatograph (2-m column of 20% QF-1 on 60–80 firebrick, at 125°). Polymerizations were run in bulk in 15-ml, one-necked flasks, fitted with micromagnetic stirrers and stopcock adapters. The polymerization equipment was dried in a 110° oven, and allowed to cool in a glove box under nitrogen. Monomer samples were degassed through three freeze–thaw cycles, prior to addition of initiators in the ionic polymerizations, and after the addition of initiator in the free radical polymerizations. All additions and transfers were made under a nitrogen atmosphere. The polymers were precipitated by pouring into ligroin (bp 66–75°) and were reprecipitated from benzene or chloroform solutions into ligroin, followed by vacuum drying at 60°. Insoluble products were separated and dried under the same conditions. Inherent viscosities were taken on 0.5% solutions in benzene or dimethyl sulfoxide at 30°. A summary of the polymerization is presented in Table I. The analytical data are presented for those polymers prepared, using azobisisobutyronitrile as a free radical initiator.

*Anal.* Calcd for $(C_5H_5NS)_n$: C, 54.05; H, 4.50; S, 28.83. Found for poly(2-vinylthiazole): C, 54.08; H, 4.82; S, 28.36. Found for poly(4-vinylthiazole): C, 54.07; H, 4.84; S, 28.36.

*Anal.* Calcd for $(C_6H_7NS)_n$: C, 57.60; H, 5.60; S, 25.60. Found for poly(2-isopropenylthiazole): C, 57.14; H, 5.87; S, 24.47. Found for poly(4-isopropenylthiazole): C, 57.42; H, 6.05; S, 25.40.

**Copolymerizations of 2-Vinyl- and 4-Vinylthiazole with Styrene.** The thiazole monomers were purified as above. Commercial styrene was stirred with 10% aqueous potassium hydroxide, washed with water until the wash liquid was neutral, dried over sodium sulfate, and vacuum distilled prior to use from calcium hydride at 34° (6.0 mm). In general, a combined total of 20 mmol of comonomers was used for each copolymerization. The copolymerizations were carried out in 15-ml flasks, cleaned and fitted as above, with all weighings, transfers, and additions being made under a nitrogen atmosphere. Azobisisobutyronitrile (10 mg per copolymerization) was used as the initiator at a copolymerization temperature of 80°. Copolymers were precipitated at low conversions by pouring into ligroin (bp 66–75°) and were purified for sulfur analyses by lyophilization from benzene. The copolymerization data are presented in Tables III and IV.

(21) (a) R. Williams, *et al.*, *J. Amer. Chem. Soc.*, **57**, 536 (1935); (b) M. Thiel, F. Ansinger, and W. Stengler, *Ann.*, **619**, 168 (1958).