reaction occurred. When XX (2.22 g., 0.00725 mole) was dissolved in a hot mixture of 1:1 dimethylformamide–water and heated under reflux for 16 hr., the monoacetyl compound was obtained on cooling in 1.20 g. yield (63%) of melting at 305° dec. Crystallization from dimethylformamide gave material melting at 317° dec. which was dried at 150° for analysis.

Anal. Calcd. for $C_9H_8N_6O_4$: C, 40.91; H, 3.05; N, 31.81. Found: C, 40.96; H, 3.13; N, 31.73.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis of Polymers Containing Recurring Thiazole Rings

J. E. MULVANEY AND C. S. MARVEL

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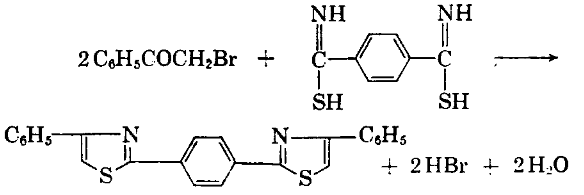
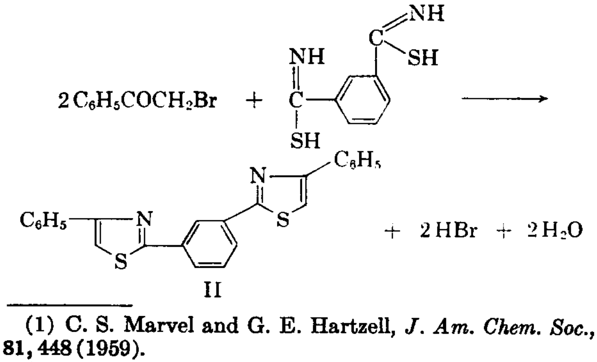
Polymers with molecular weights in the 5000 to 6000 range, one of which is a film-forming material and all of which show fair stability at 300°, have been obtained by condensing *p*-bis(bromoacetyl)benzene with dithioamides.

With the continuing[1] objective of preparing new and thermally stable high molecular weight materials containing aromatic units, a number of new polymers have been synthesized containing benzene rings and thiazole rings in a polymer chain backbone. The thiazole nucleus is more resistant to electrophilic substitutions such as sulfonation[2] than benzene itself.

A preliminary study showed that the model compounds 1,4-bis(4-phenyl-2-thiazolyl)benzene (I) and 1,3-bis(4-phenyl-2-thiazolyl)benzene (II) could be prepared as shown below in good yields by use of refluxing dimethylformamide as a solvent. The condensation of halomethylketones and thioamides has long been known[3] as a general method of preparing thiazoles. Our results encouraged us to believe that similar reactions with bis-α-bromoketones might afford the high yield[4] necessary to produce high molecular weight condensation polymers. Reactions of dithioamides and bis-α-haloketones have been carried out by Erlenmeyer[5] to yield presumably polymeric materials, other than the ones reported here, but the products were not fully characterized.



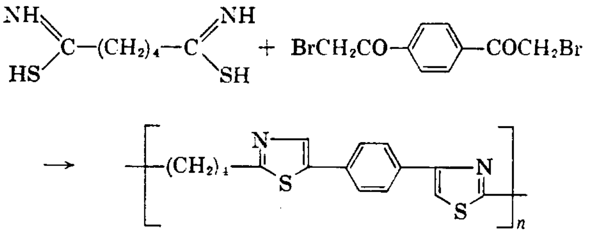
I



II

Three new thiazole polymers have been prepared and are described below. The dithioamides were made from the corresponding dinitriles by the addition of hydrogen sulfide, and the *p*-bis(bromoacetyl)benzene was prepared by treatment of *p*-diacetylbenzene with bromine in acetic acid.

A polymer (III) was synthesized by condensing dithioaldipamide and *p*-bis(bromoacetyl)benzene in acetic acid as indicated:



III

Polymer III exhibits what appears to be a polyelectrolyte effect in formic acid, displaying inherent viscosities of 3.50, 4.67, and 5.53 at concentrations of 0.239, 0.122, and 0.067 g./100 ml., respectively. However, assuming one bromine atom per chain

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[1] C. S. Marvel and G. E. Hartzell, *J. Am. Chem. Soc.*, 81, 448 (1959).

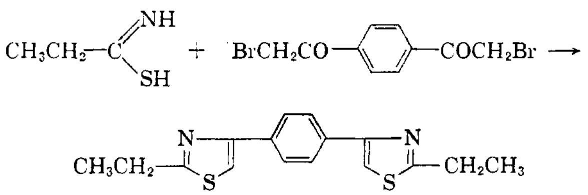
[2] R. H. Wiley, *Organic Chemistry*, ed. H. Gilman, John Wiley and Sons, Inc., New York, Vol. IV, p. 799, 1953.

[3] R. H. Wiley, D. C. England, and L. C. Behr, *Org. Reactions*, VI, 367 (1951).

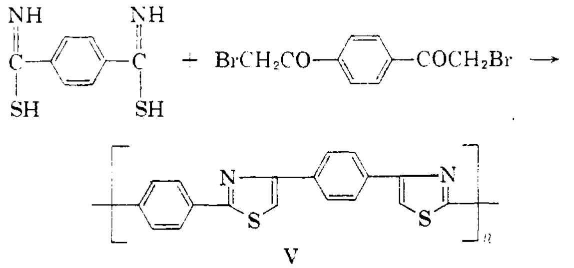
[4] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Chapter 3.

[5] (a) H. Lehr and H. Erlenmeyer, *Helv. Chim. Acta*, 27, 489 (1944). (b) G. Bischoff, O. Weber, and H. Erlenmeyer, *Helv. Chim. Acta*, 27, 947 (1944). (c) H. Erlenmeyer, W. Büchler, and H. Lehr, *Helv. Chim. Acta*, 27, 969 (1944). (d) H. Erlenmeyer and M. Erne, *Helv. Chim. Acta*, 29, 275 (1946). (e) H. Erlenmeyer and K. Degen, *Helv. Chim. Acta*, 29, 1080 (1946). (f) H. Erlenmeyer and W. Büchler, *Helv. Chim. Acta*, 29, 1924 (1946).

from bromoacetyl end groups, the bromine value (1.25%) indicates a number average molecular weight of about 6400 for this polymer or approximately thirty recurring units. It is insoluble in most organic solvents, but soluble in strong acids such as sulfuric, hydrochloric, or formic. A film is obtained by casting a formic acid solution. The polymer loses only 4.2% of its weight during twenty-four hours at 290–300°. In addition to the correct elemental analysis, further evidence for the structure is indicated by a comparison (Table I) of the ultraviolet spectra of Polymer III and model compound IV (prepared as shown below).


IV

The fully aromatic polymers V and VI were synthesized according to the equations:


V

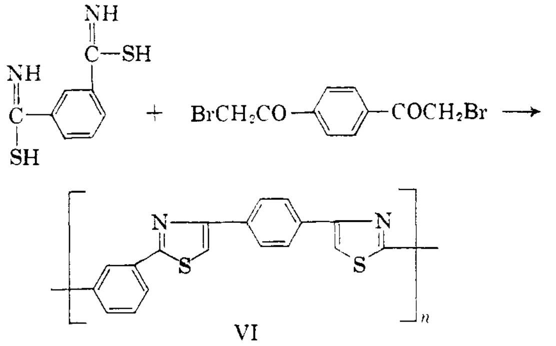

VI

TABLE I

Comparison of Ultraviolet Spectra[a] of Polymers III, V, and VI with Model Compounds I, II, and IV (in mμ)

Compound	λ_{max1}	$(E_{1\,cm.}^{1\%})$	ϵ	$\lambda_{max2}(E_{1\,cm.}^{1\%})$	ϵ
Polymer III	282	(1010)		—	
Model compound IV	279	(840)	25,200	—	
Polymer V	282	(647)		375 (878)	
Model compound I	261	(537)	23,600	377 (606)	26,700
Polymer VI	277	(790)		332 (768)	
Model compound II	254	(858)	36,700	332 (512)	22,500

[a] In concentrated sulfuric acid.

The best solvent found so far for polymerization is refluxing dimethylformamide. However, even in this solvent the polymer begins to precipitate shortly after reaction commences. Both polymers V and VI are insoluble in the common organic solvents. They are soluble in sulfuric acid and slightly soluble in trifluoroacetic acid. Both polymers have been obtained as yellow powders. Polymer V has an inherent viscosity of 0.12 in sulfuric acid and polymer VI has an inherent viscosity of 0.095 in the same solvent. On the basis of the bromine content of polymer V (~1.5%) and again assuming one bromomethylketo end group per polymer chain, one arrives at a molecular weight of approximately 5300 for polymer V (about sixteen recurring units), and 5800 for polymer VI (1.38% Br). Neither V nor VI melts at 350°; both only darken slightly at this temperature. The ultraviolet spectra of polymers V and VI are compared with spectra of model compounds I and II in Table I.

EXPERIMENTAL[6]

Preparation of dithio-1,4-benzenedicarboxamide. The method used was the general procedure of Fairfull, Lowe, and Peak.[7] From a solution of 10 g. (0.077 mole) of terephthalonitrile (recrystallized from benzene, m.p. 226–227°) and 7.8 g. (0.077 mole) of redistilled triethylamine in 300 ml. of pyridine through which dried hydrogen sulfide was passed for 2.7 hr., there was obtained 15 g. (99%) of dithio-1,4-benzenedicarboxamide, m.p. 269–273° dec. One recrystallization from nitrobenzene raised the m.p. to 272–274° dec. (lit.,[8] m.p. 263°).

Anal. Calcd. for $C_8H_8N_2S_2$: C, 48.94; H, 4.11; N, 14.27. Found: C, 49.20; H, 3.69; N, 14.15.

Preparation of dithio-1,3-benzenedicarboxamide. The same procedure was used as that given for dithio-1,4-benzenedicarboxamide (above). From 4.0 g. (0.031 mole) of isophthalonitrile, there was obtained 4.3 g. (71%) of dithio-1,3-benzenedicarboxamide, m.p. 200–201° dec. (lit.,[9] m.p. 199–200 dec.), λ_{max} 230 mμ, ε 21,700; 298 mμ, ε 13,300 in ethanol.

Preparation of dithioadipamide. The general procedure[7] was again used here. From 21.6 g. (0.20 mole) of adiponitrile there was obtained 7.2 g. (20%) of dithioadipamide, m.p. 180–182° (lit.,[10] m.p. 180°), λ_{max} 265 mμ, ε 30,400, in ethanol.

Preparation of thiopropioamide. The procedure of Kindler[11] was used except that the reaction was carried out at atmospheric pressure. A 20% yield of thiopropioamide was obtained, m.p. 41–42° (lit.,[11] m.p. 42–43°).

Preparation of p-bis(bromoacetyl)benzene. The procedure was that of Ruggli and Gassenmeier.[12] From 5.0 g. (0.031 mole) of *p*-diacetylbenzene there was obtained 7.9 g. (80%)

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[6] Melting points are uncorrected. Microanalyses were performed by Mr. J. Nemeth of the University of Illinois and by the Clark Laboratories and the Micro-Tech Laboratories.

[7] A. E. S. Fairfull, J. L. Lowe, and D. A. Peak, *J. Chem. Soc.*, 742 (1952).

[8] G. Luckenbach, *Ber.*, **17**, 1430 (1884).

[9] G. Luckenbach, *Ber.*, **17**, 1429 (1884).

[10] H. Erlenmeyer and G. Bischoff, *Helv. Chim. Acta*, **27**, 412 (1944).

[11] K. Kindler, *Ann.*, **431**, 201 (1923).

[12] P. Ruggli and E. Gassenmeier, *Helv. Chim. Acta*, **22**, 496 (1939).

of *p*-bis(bromoacetyl)benzene, m.p. 160–165°. Recrystallization from ethanol (Darco) increased the m.p. to 176–178° (lit.,[13] m.p. 177–178°), λ_{max} 265 mμ, ε 17,800.

Preparation of 1,4-bis(2-ethyl-4-thiazolyl)benzene (IV). A solution of 1.0 g. (0.011 mole) of thiopropioamide and 1.77 g. (0.0056 mole) of *p*-bis(bromoacetyl)benzene in 40 ml. of dimethylformamide was refluxed overnight. After removal of most of the solvent under reduced pressure, there was obtained 1.1 g. of crude product, m.p. 94–97°. Two recrystallizations from dimethylformamide (Darco) gave 1.0 g. (44%) of IV, m.p. 114–116°. See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{16}H_{16}N_2S_2$: C, 64.0; H, 5.33; N, 9.33. Found: C, 63.75; H, 5.29; N, 9.13.

Preparation of 1,4-bis(4-phenyl-2-thiazolyl)benzene (I). A solution of 3.270 g. (0.0166 mole) of dithio-1,4-benzenedicarboxamide and 6.637 g. (0.0333 mole) of phenacyl bromide in 150 ml. of purified dimethylformamide was heated under reflux for 18 hr. After cooling the product crystallized in the form of plates. More solid was obtained by diluting the mother liquor with 500 ml. of water. The combined solids were washed with methanol and dried in a vacuum oven at 60° to give 4.77 g. (96.9%) of I, m.p. 225–226°. One recrystallization raised the m.p. to 229–230° (lit.,[7] m.p. 225°). See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{24}H_{16}N_2S_2$: C, 72.69; H, 4.04; N, 7.08. Found: C, 72.48; H, 3.86; N, 6.89.

Preparation of 1,3-bis(4-phenyl-2-thiazolyl)benzene. A solution of 1.635 g. (0.0083 mole) of dithio-1,3-benzenedicarboxamide and 3.318 g. (0.0166 mole) of *p*-bis(bromoacetyl)benzene in 75 ml. of purified dimethylformamide was heated under reflux for 18 hr. Working up the product in the same manner as described above for compound I, there was obtained a 3.21 g. (97.5%) yield of II, m.p. 167–169°, which, after recrystallization from carbon tetrachloride, had m.p. 170°. See Table I for ultraviolet spectra.

Anal. Calcd. for $C_{24}H_{16}N_2S_2$: C, 72.69; H, 4.04; N, 7.08. Found: C, 72.55; H, 4.17; N, 6.84.

Preparation of thiazole polymer III. To a hot solution of 3.700 g. (0.0210 mole) of dithioadipamide in 425 ml. of acetic acid, there was added 6.720 g. (0.0210 mole) of *p*-bis(bromoacetyl)benzene in 250 ml. of hot acetic acid. A yellow precipitate began to form immediately. After heating with stirring at 80° for 24 hr., the solid was collected on a filter and reprecipitated twice from formic acid into a large excess of ethanol. The solid powder was ground and dried at 60° (1 mm.). Ultraviolet spectra and other properties of this polymer are mentioned in the discussion section of this paper.

Anal. Calcd. for $(C_{16}H_{14}N_2S_2)_n$: C, 64.41; H, 4.72; N, 9.38; S, 21.45. Found: C, 63.65; H, 4.75; N, 9.04; S, 20.59; Br, 1.25, 1.26.

Preparation of thiazole polymer V. A solution of 3.200 g. (0.01000 mole) of *p*-bis(bromoacetyl)benzene and 1.963 g. (0.01000 mole) of dithio-1,4-benzenedicarboxamide in 300 ml. of purified dimethylformamide was refluxed for 105 hr. with stirring. The reactants were initially soluble, but a fine yellow powder began to form within a few minutes after mixing. At the end of the reaction period, the solid was collected on a filter, washed with methanol, and dried overnight in a vacuum oven yielding 2.810 g. of fine yellow powder. The inherent viscosity was 0.12 in sulfuric acid at 25° (0.24 g./100 ml.). Ultraviolet spectra and other properties of this polymer are mentioned in the discussion section of this paper.

Anal. Calcd. for $(C_{18}H_{10}N_2S_2)_n$: C, 67.90; H, 3.17; N, 8.80. Found: C, 66.46; H, 3.92; N, 8.69; Br, 1.38, 1.65.

Preparation of thiazole polymer VI. A solution of 3.200 g. (0.0100 mole) of *p*-bis(bromoacetyl)benzene and 1.963 g. (0.0100 mole) of dithio-1,3-benzenedicarboxamide in 300 ml. of dimethylformamide was heated under reflux with stirring for 216 hr. Although the reactants were initially miscible, a fine yellow powder began to form shortly after they were mixed. At the end of the reaction period, 2.58 g. of a fine yellow powder was obtained by filtration. Addition of the mother liquor to 1 l. of methanol caused the precipitation of an additional 0.278 g. of yellow powder. This material showed the same ultraviolet maxima as the initial precipitate.

Anal. Calcd. for $(C_{18}H_{10}N_2S_2)_n$: C, 67.90; H, 3.17; N, 8.80. First precipitate: C, 64.90; H, 3.60; N, 8.44; Found: Br, 1.38. Second precipitate: C, 66.01; H, 3.68; N, 8.46; Br, 2.37.

The inherent viscosity in sulfuric acid was found to be 0.095 at 25° (0.24 g./100 ml.).

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It is a pleasure to acknowledge the help of Mrs. N. S. Fan, Mr. R. R. Haynes, and Mr. H. Schauble in the synthesis of intermediates.

URBANA, ILL.

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[13] F. Kröhnke and I. Vogt, *Chem. Ber.*, **86**, 1132 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Reactions of 2-Benzhydrylphenylacetic Acid; A New Pyrone Synthesis[1]

R. L. LETSINGER, J. D. JAMISON,[2] AND A. S. HUSSEY

Received April 20, 1960

In contrast to 8-benzhydryl-1-naphthoyl chloride, which isomerizes with 1,5-phenyl migration under Friedel-Crafts conditions, 2-benzhydrylphenylacetyl chloride cyclizes to a seven-membered cyclic ketone (IV) in the presence of aluminum or stannic chloride. When heated with a mixture of acetic acid and polyphosphoric acid both 2-benzhydrylphenylacetic acid and ketone IV afford a substituted 4-pyrone (VI) in good yield.

In a previous paper it was reported that 8-benzhydryl-1-naphthoyl chloride (Ib) rearranged in the presence of stannic chloride to a substance which on hydrolysis gave (>90%) 1-phenylhydroxy-

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[1] Presented at the 137th Meeting of the American Chemical Society, Cleveland, April 1960.

[2] Standard Oil Co. of Indiana Fellow, 1958–59.