

typical diene synthesis. The adduct formed by this reaction was subjected to oxidation with concentrated nitric acid to produce mellitic acid.

Because thiophene and its simple derivatives do not react as dienes in a diene synthesis, an attempt was made to see if the positive inductive effect of four methylol groups on the thiophene ring could enhance the dienic character of thiophene sufficiently to enable it to react in a diene synthesis. Tetramethyl thiophenetetracarboxylate was prepared by a method employed by Michael.² This was reduced to tetramethylolthiophene by the use of lithium aluminum hydride. This compound failed to react with either maleic anhydride or dimethyl acetylenedicarboxylate in a diene synthesis.

EXPERIMENTAL³

Tetramethylolfuran. The tetraethyl ester of furan tetracarboxylic acid was reduced with lithium aluminum hydride to produce tetramethylolfuran. Eleven grams of lithium aluminum hydride were pulverized in a mortar and then suspended in 200 ml. of anhydrous ether in a 1000-ml., three-neck, round-bottom flask, fitted with a reflux condenser and a mechanical stirrer. Thirty-four grams of the tetraethyl ester of furan tetracarboxylic acid were warmed in a water bath to liquefy the ester and a few milliliters of ether were added to keep it in the liquid state. The ester was placed in a small separatory funnel and added drop-wise with caution to the hydride suspension which was cooled in an ice water bath. The rate of ester addition was adjusted to gentle reflux of the reaction mixture. After the ester had reacted, enough water was cautiously added to decompose the excess hydride, after which a large volume of water was added. The resulting aqueous layer contained a thick orange solid in suspension. The water layer was filtered to remove the aluminum and lithium salts and the filtrate, now strongly basic, was adjusted to a pH of approximately nine with phosphoric acid. The solution was again filtered, removing lithium and aluminum phosphates, and then evaporated on a steam bath to a volume of about 200 ml. The solution was allowed to go to virtual dryness at room temperature. The residue was treated with 95% ethyl alcohol to extract preferentially the organic portion. The ethyl alcohol was evaporated to 17 g. of a dark brown sirup, representing crude tetramethylol furan. Crystal formation occurred very slowly at a temperature of 0°. These crystals were removed mechanically and recrystallized from water using decolorizing charcoal to yield 8 g. (45%) of white crystals which melted at 123–124°.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.08%; H, 6.39%. Found: C, 50.93%; H, 6.46%.

Mellitic acid. Mellitic acid was prepared by addition of maleic anhydride to tetramethylol furan followed by oxidation of the adduct with nitric acid. About 5 g. of crude tetramethylol furan were placed in an 8-inch test tube. Four grams of finely ground maleic anhydride were added in the dry state to the test tube. About 5 ml. of dry benzene at a temperature of 23° was added and shaken gently to obtain a homogeneous mixture. During the next 5 min. the reaction temperature rose to 33°. The mixture was allowed to stand for 1 hr. after it returned to room temperature. The mixture was removed as a water suspension and added dropwise through a reflux condenser to 70 ml. of a boiling 1:1 by volume mixture of concentrated nitric and fuming nitric acid. Boiling was maintained for 1 hr. after addition and then the clear yellow solution was evaporated to dryness on a steam bath. The yellow residue was crystallized once from con-

centrated nitric acid and then from water using decolorizing carbon. White crystals melting at 284–286° were obtained. The yield was not determined because of subdivision of the diene adduct in other purification attempts.

Tetramethylolthiophene. A modification of the reduction technique for the production of tetramethylolfuran was required in the preparation of tetramethylolthiophene because the ester which was used as starting material is relatively insoluble in ether. Lithium aluminum hydride (2.75 g., 0.07 mole) was pulverized and suspended in 300 ml. of absolute ether in a 500-ml. round-bottom flask which was attached to a Soxhlet extraction tube containing tetramethyl thiophenetetracarboxylate (10.0 g., 0.03 mole). The reduction was run at reflux temperature for 12 hr. until no solid remained in the extraction thimble. Water was added to decompose the excess hydride. The reaction mixture was poured into ice water and the ether layer separated from the aqueous mixture. The aqueous portion was filtered with suction, the filtrate was evaporated on a steam bath to dryness, and the residue was extracted with 95% alcohol. The resulting brown solution was evaporated at room temperature to a viscous mass.

The product was isolated by use of Permutit Q cation exchange resin and Dowex 2 anion exchange resin.

Twenty ml. of an aqueous solution of the reaction mixture (5% by volume) was adjusted to a pH of approximately four with hydrochloric acid. This solution and the washes were allowed to run through the cation column at the rate of 2.5 ml./minute. After the solution had passed over the resin the column was washed with 50 ml. of distilled water, 20 ml. of 95% ethyl alcohol, and again with 150 ml. of distilled water. The filtrate obtained from the cation column was passed through the anion column at the rate of 2.5 ml./minute. The column was then washed, at the same rate of flow, with 20 ml. of distilled water and 100 ml. of distilled water saturated with carbon dioxide. The filtrate was colorless. The deionized filtrate was evaporated on a steam bath to a volume of 25 ml. and allowed to go to dryness at room temperature. The residue, two grams (33%), was a white substance which melted at 102–103°.

Anal. Calcd. for $C_8H_{12}O_4S$: C, 47.06; H, 5.88; S, 15.69. Found: C, 46.94; H, 5.97; S, 15.98.

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Attempts to Copolymerize Pyrene with 1,3-Butadiene and with *p*-Chlorostyrene¹

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Some preliminary experiments on the copolymerization of pyrene with 1,3-butadiene in an emulsion system were reported by Marvel and Anderson.² The polymers obtained showed ultraviolet absorption maxima at 342, 301.5, and 260 $m\mu$ and on this basis it was concluded that copolymerization had occurred. In this further work on the problem with

(1) The work discussed herein was performed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman and Lt. Paul D. Shaw, project engineers.

(2) C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **76**, 5434 (1954).

(2) Michael, *Ber.* **23**, 1633 (1895).

(3) All melting points are uncorrected.

a better grade of pyrene, the earlier experiments could not be duplicated.

Pure pyrene (m.p. 149.5–150°) was prepared by the zone melting technique³ and was used in these emulsion copolymerization experiments with 1,3-butadiene and *p*-chlorostyrene. The purified polymers, when analyzed for carbon and hydrogen, proved to be only polybutadiene and poly-*p*-chlorostyrene, respectively. The butadiene polymers did show weak ultraviolet absorption, which appears to be due to small amounts of pyrene which were not removed in the purification. The pyrene contaminations are estimated at $0.031 \pm 0.005\%$ in these polymers.

EXPERIMENTAL

Pyrene. A 22-mm. diameter Pyrex tube *ca.* one meter in length was sealed off at one end and filled with 261.5 g. of crude pyrene (Gesellschaft für Teerverwertung "pure" grade) by melting it to a solid plug *ca.* 81 cm. long. The tube was clamped vertically.

The heater was a 1-cm. long helix of nichrome wire attached to a five volt transformer. The transformer was attached over pulleys to a counterweight. The string connecting the two also was wrapped around a 0.5-inch diameter shaft, which was connected to a one revolution per hour synchronous motor.

The pyrene was heated at such a rate that a 3–5 cm. length was liquid at all times. It was necessary to shield the heater with aluminum foil to protect against air currents in the room. Moving at a rate of 1.6 inches down the tube per hour, the heater required between 19 and 20 hr. per pass. After fifteen passes had been made, the material was removed in fractions, starting from the top of the tube:

| Fraction | Approximate Weight, G. | Color (When Melted) | M.P. (°C.) (Corr.) |
|----------|------------------------|---------------------|--------------------|
| 1 | 15 | Colorless | 149.5–150 |
| 2 | 70 | Very pale yellow | 149–150 |
| 3 | 90 | Pale yellow | 148.5–149.5 |
| 4 | 90 | Dark | (Discarded) |

Fraction 1 was used for all polymerization work.

***p*-Chlorostyrene.** This compound was prepared from *p*-chloroacetophenone, using the procedure of Marvel and Schertz,⁴ b.p. 40–41°/2.6 mm., n_D^{20} 1.5649.

Pyrene-butadiene copolymerizations. These copolymerizations were conducted in emulsion in 4-ounce screw-cap bottles sealed with acrylonitrile rubber gaskets. Each charge contained 28 ml. of a 2.86% solution of Office of Rubber Research soap (specification L.M. 2.3.0.5.2), 1.50 g. of pyrene, 7.5 ml. of benzene, 1.5 ml. of a 3% aqueous solution of potassium persulfate, and 13.5 g. of butadiene, in addition to a variable amount of technical lauryl mercaptan (Hooker Electrochemical Co.) as a modifier. The bottles were tumbled end-over-end at 29 revolutions per minute for a specified period in a constant temperature bath at $50 \pm 1^\circ$. Table I lists the variables for these polymerizations. The polymers were isolated by addition of 5 ml. of a 4.2% solution of sulfuric acid saturated with sodium chloride after first protecting against air oxidation by the addition of 5 ml. of a satu-

(3) E. F. G. Herington, R. Handley, and A. J. Cook, *Chem. & Ind. (London)*, 292 (1956).

(4) C. S. Marvel and G. L. Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).

rated methanol solution of *N*-phenyl- β -naphthylamine. The polymers were purified by washing well with water, drying, and repeated precipitation (usually ten times) from benzene solution into methanol. The insoluble (cross-linked) material was separated out from the first solution before precipitation by filtration through 200-mesh wire screen. Only samples 10 and 11 showed complete solubility. The elemental analyses shown in Table II are the average of two values. The ultraviolet absorption spectra were obtained with a Cary recording spectrophotometer, Model 11, using solutions in tetrahydrofuran. The solvent was purified by passage through a column of Linde Molecular Sieves, Type 13X.

TABLE I
PYRENE-BUTADIENE POLYMERIZATION VARIABLES

| Sample | Modifier, Mg. | Hours Tumbled | Conversion, % ^a | η (0.25% in Benzene) |
|--------|---------------|---------------|----------------------------|---------------------------|
| 5 | 45 | 88 | 87.5 | ^b |
| 6 | 45 | 36 | 33.1 | 1.21 |
| 7 | 45 | 48 | 46.3 | 1.65 |
| 8 | 60 | 37 | 44.3 | 1.13 |
| 9 | 60 | 43 | 52.6 | 1.03 |
| 10 | 90 | 30 | 42.6 | 0.350 |
| 11 | 120 | 30 | 40.2 | 0.444 |

^a No correction was made for fatty acid or *N*-phenyl- β -naphthylamine inclusion. ^b Essentially only crosslinked material was obtained.

Elemental analysis on the soluble portions of these polymers after purification indicated the materials all to be only polybutadiene (see Table II).

TABLE II
COMPOSITION OF PYRENE-BUTADIENE COPOLYMERS

| Sample | Elemental Analysis (Average Values) | | C/H Ratio |
|-----------|-------------------------------------|-------|-----------|
| | % C | % H | |
| 6 | 88.01 | 10.97 | 8.023 |
| 7 | 87.51 | 10.98 | 7.970 |
| 8 | 88.52 | 11.15 | 7.939 |
| 9 | 88.57 | 11.10 | 7.979 |
| 10 | 86.95 | 10.92 | 7.962 |
| 11 | 87.48 | 10.91 | 8.018 |
| Butadiene | 88.82 | 11.18 | 7.945 |
| Pyrene | 95.02 | 4.98 | 19.1 |

These polymers (5–6 g./l. in tetrahydrofuran) showed weak ultraviolet absorption maxima at 335, 318, 300, 271, and 260 $m\mu$, values differing from those observed by Marvel and Anderson,² but very similar to the spectrum of pyrene in ethanol. The spectrum of pyrene in tetrahydrofuran (1.86 mg./l.) showed maxima at 334, 318, 305, 271, 260, and 237 $m\mu$. Using the 335- $m\mu$ maximum and assuming Beer's law is applicable, it was calculated that each of these polymers contained pyrene as a contamination in the range of 0.031 ± 0.005 weight per cent. This level of pyrene at the end of the purification process is entirely reasonable.

Pyrene-*p*-chlorostyrene copolymerization. Only one polymer was prepared, using the same recipe as above, except substituting 15.0 ml. of *p*-chlorostyrene for the butadiene, and using 25 mg. of modifier. The polymerization was of 88 hr. duration and the uncorrected conversion was 107%. The inherent viscosity (0.25% in benzene) was 0.842.

Anal. Calcd. for $(C_{12}H_7Cl)_x$: C, 69.33; H, 5.09; Cl, 25.58. Found: C, 69.51; H, 5.37; Cl, 25.65. C, 68.90; H, 5.23.