CHARACTERISTICS OF DIALKYL ALKYLTHIOBORONATES AND TRIALKYLBORATES

Compound	Yield, %	B.p. (mm.), °C.
Ethylene *n*-butyl thioboronate	45	84 (6)
Ethylene *i*-butyl thioboronate	38	83 (6.5)
Di-*n*-amyl-*n*-butyl thioboronate	29	132 (0.5)
Di-*n*-amyl-*t*-butyl thioboronate	72	122 (0.2)
Di-*n*-butyl-*s*-butyl thioboronate	63	105 (0.8)
Di-*n*-butyl-*n*-hexyl thioboronate	58	119 (0.3)
Tri-*n*-amyl thioborate	65	164 (0.4)
Tri-*n*-butyl thioborate	70	147 (1.0)

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A NEW METHOD FOR THE PREPARATION OF CRYSTALLINE POLYVINYL CHLORIDE

Sir:

We have prepared crystalline polyvinyl chloride with conventional free-radical catalysts at 50° using aliphatic aldehydes as polymerization media. Although all aliphatic aldehydes tried have produced this stereoregulating effect, *n*-butyraldehyde and 2-ethylhexylaldehyde appear to give the best results. As is to be expected from the chain transfer activity of aldehydes, very low molecular weight polymers are produced, *e.g.*, approximately 5,000. The reaction is carried out at 50° using a mole to mole ratio of monomer to aldehyde and a millimole of free-radical catalyst per mole of monomer. A typical polymerization using 72.0 g. of *n*-butyraldehyde, 62.5 g. of vinyl chloride, and 0.16 g. of azodiisobutyronitrile in 9 hours yields 9.13 g. of polyvinyl chloride. The crystalline material in tetrahydrofuran gives a cloudy solution which does not clear up on heating. The same effect is noted with cyclohexanone but on heating to 120° the solution becomes clear.

The crystallinity, and hence stereoregularity, of the polymers was investigated using X-ray diffraction and infrared absorption methods. The regular sequences in polyvinyl chloride crystallize readily so that changes in crystallinity are directly related to changes in regularity. The unoriented X-ray pattern of the polyvinyl chloride prepared in *n*-butyraldehyde possesses sharp lines with "d" spacings at 5.16 (m), 4.66 (s), 3.65 (m), 3.44 (m), 2.84 (m), 2.56 (w), 2.28 (m), 2.07 (w), 1.78 (vw), 1.59 (vw), 1.40 (vw), 1.25 (vw), 1.14 (vw) Å. (letters in parentheses indicate relative intensities where s = strong, m = medium, w = weak, vw = very weak). These values agree well with those reported by Fordham, Burleigh and Sturm.[1] The lines with "d" spacings at 3.65, 1.40, 1.25, and 1.14 Å., however, have not been reported previously.

With regard to the infrared absorption spectrum of polyvinyl chloride, the ratio of the absorbance at 635 cm.$^{-1}$ to that at 692 cm.$^{-1}$ has been used as a measure of crystalline syndiotactic units in the polymer.[2-6] Table I gives the D_{635}/D_{692} ratio for polyvinyl chloride prepared in bulk at high and low temperatures and in *n*-butyraldehyde at high temperature.

TABLE I

INFRARED ABSORPTION DATA

Polyvinyl Chloride Prepared in	D_{635}/D_{692}
Bulk at +50°	1.5
Bulk at −70°	2.6
n-Butyraldehyde at +50°	4.3

An increase in the absorbance ratio is indicative of increased crystallinity. The infrared absorption measurements were made using films cast on potassium bromide discs from tetrahydrofuran or cyclohexanone solutions; for the polymer prepared in *n*-butyraldehyde the film was cast from a cyclohexanone solution at 120°. Based on the above evidence, we have assigned the syndiotactic structure to this polyvinyl chloride.

The stereoregulating effect of aliphatic aldehydes on the free-radical polymerization of vinyl chloride is not yet understood. Study of the mechanism of this effect is in progress.

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A NOVEL SYNTHESIS OF BENZOCYCLOBUTENE DERIVATIVES[1]

Sir:

About a year ago we reported[2] the formation of a stable dipositive carbonium ion from trichloromethylpentamethylbenzene (I). We now wish to record another unusual and useful reaction of this and related substances.

I is a colorless, crystalline solid, m.p. 94.5–95.0°. It was observed that at or slightly above its melting point, *I evolved hydrogen chloride.* In a quantitative experiment, 1.074 g. (4.05 mmoles) of I was heated at 110–125° in a dry nitrogen stream which subsequently passed through standard sodium hydroxide. In the first hour, 3.76 mmoles of hydrogen chloride was collected. Two more hours netted 0.50 mmole, and after three additional hours, only 0.03 mmole more of hydrogen chloride was produced (a total of 105.9% of the theoretical for one mole). On cooling, there was isolated a crystalline solid II, m.p. 73–74° (from pentane). *Anal.*[3] Calcd. for $C_{12}H_{14}Cl_2$:

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[3] All analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Michigan.