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Polymerization of Beta-Methallyl Alcohol and its Lower Aliphatic Esters

BY J. D. RYAN AND F. B. SHAW, JR.

An investigation of the physical properties and polymerization tendency of β-methallyl alcohol and its lower aliphatic esters has been made in the hope that these materials may serve as monomers for the production of high molecular weight solid resinous materials. While β-methallyl halides (3-halogen-2-methyl-propene) have undergone considerable study[1,2] only a few physical constants of β-methallyl alcohol, β-methallyl acetate and β-methallyl isobutyrate[3] have been recorded.

β-Methallyl Alcohol.—This material, kindly furnished by the Shell Development Company, is a water-white, limpid liquid with a disagreeable odor; its vapors produce a sharp and irritating effect on the nose and eyes: b. p. 114° at 760 mm. and d^{20}_{20} 0.8524; refractive indices at 20, 25, and 30°, are 1.4252, 1.2432 and 1.4211, respectively.

Water at 20° dissolves 19.4% of the alcohol, while the alcohol itself dissolves 33.8% of water at the same temperature, both measurements by weight. Water and β-methallyl alcohol form a mixture boiling constantly at 92°, containing 59.8% methallyl alcohol by weight.

Poly-β-methallyl Alcohol.—β-Methallyl alcohol has a definitely low polymerization tendency. When carefully purified and refluxed either in a glass or metal system with or without aeration, it showed no significant increase in refractive index after seventy-five hours.

When irradiated for eighteen days in a clear quartz tube, β-methallyl alcohol gave a liquid polymer of extremely high viscosity having a refractive index of 1.507 at 30°.

A number of catalysts in conjunction with heat were employed for polymerization of β-methallyl alcohol and it was found that lower polymers are obtained by this method than by the use of ultraviolet light. To illustrate, after refluxing the alcohol in benzene solution in the presence of small amounts of benzoyl peroxide for two hundred hours, a polymer having a refractive index of 1.427 was obtained while under similar conditions using perchloric acid as the catalyst, a polymer having a refractive index of 1.469 was obtained, both measurements at 30°. Other catalysts, such as β-naphthalenesulfonic acid, sodium bisulfate, and zinc chloride, gave products having slightly lower refractive indices than that obtained with perchloric acid.

The poly-β-methallyl alcohols are water-white liquids ranging in viscosity from that of the monomer to highly viscous molasses-like polymers which are distillable at ordinary pressures without decomposition even as high as 300°.

(1) Vaughan and Rust, THIS JOURNAL, **61**, 215 (1939).
(2) Kharasch, Nudenberg and Sternfeld, *ibid.*, **62**, 2034 (1940).
(3) Groll and Hearne, U. S. Patent 2,164,188 (1939).

β-Methallyl Aliphatic Esters.—The best method of preparing the lower aliphatic esters of β-methallyl alcohol was found to be the reaction of the desired acid anhydride on the alcohol, at reflux temperature, the yield being 95%. Only small yields are obtained by allowing the alcohol and the aliphatic acid to interact. The use of acid chlorides or the common esterification catalysts favors the formation of low polymers of the alcohol and the esters, making purification difficult and impairing yields.

TABLE I

PHYSICAL PROPERTIES

β-Methallyl-	B. p., °C. 760 mm.	d^{20}_{20}	n_D 20°	n_D 25°	n_D 30°	Equiv. wt. Calcd.	Equiv. wt. Found
Formate[a]	103	....	1.4135	1.4110	1.4086	100	99
Acetate	124	0.9239	1.4129	1.4104	1.4080	114	114
Propionate	142	.9143	1.4170	1.4150	1.4125	128	129
n-Butyrate	161	.8950	1.4230	1.4201	1.4172	142	143

[a] Prepared from 85% formic acid in low yield.

Polymerization of β-Methallyl Esters.—These, like β-methallyl alcohol, show little tendency to polymerize by the action of heat alone, or even after prolonged refluxing in the presence of solvents. They also tend to polymerize to the greatest extent when irradiated with ultraviolet light, the resulting polymers having a higher molecular weight than those obtained with catalysts.

Samples of the β-methallyl formate, acetate, propionate and *n*-butyrate were irradiated in a clear quartz tube for twenty-five days. In all cases liquid polymers were formed, the refractive indices of which are as follows: poly-β-methallyl formate, 1.483; acetate, 1.470; propionate, 1.461; *n*-butyrate, 1.456. It is of interest to note that the addition of aldehydes to the monomeric esters failed to inhibit their polymerization as proved by following the course of the polymerization by refractive index measurements. Determination of molecular weight by a cryoscopic method on one of the poly-β-methallyl acetate products (n_D 1.471, d^{20}_{20} 1.074) gave a result of 652 indicating the mixture of polymers averages a hexamer.

Summary

Some physical properties and the polymerization characteristics of β-methallyl alcohol and several of its lower aliphatic acid esters have been described. Poly-β-methallyl alcohols and poly-β-methallyl lower aliphatic esters are viscous liquids rather than high molecular weight resinous solids.

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