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Abstract

Full Text

Lead-Organic Methacrylates

D. A. KOCHKIN

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Earlier we described the synthesis and properties of organotin methacrylates $R_3SnOOCC(CH_3)=CH_2$ and $R_2Sn(OOCC(CH_3)=CH_2)_2$, and polymers made from them, which are mechanically strong glass-like materials ([1–3]). The indicated monomers copolymerize with unsaturated substances.

In order to obtain aryllead methacrylates, we studied the reactions of triphenylplumbanol $(C_6H_5)_3PbOH$ and diphenylplumbanone $(C_6H_5)_2PbO$ with methacrylic acid. As a result of these investigations, one representative of lead-containing methacrylates $R_2Pb(OOCC(CH_3)=CH_2)_2$ was obtained: diphenylplumbylene dimethacrylate $(C_6H_5)_2Pb(OOCC(CH_3)=CH_2)_2$, polymers from it, and also copolymers. The indicated compounds have not been described in the literature; a patent description ([4]) contains a brief mention of the possibility of the reaction of trimethylbromoplumbane with the potassium salt of methacrylic acid. No description of the method of preparation or of the properties of the products is given.

The synthesis of diphenylplumbylene dimethacrylate was carried out analogously to organotin derivatives by the following reaction:

$$R_2SnO + 2CH_2=C(CH_3)COOH \rightarrow R_2Sn(OOCC(CH_3)=CH_2)_2, \quad (1)$$

$$R_2PbO + 2CH_2=C(CH_3)COOH \rightarrow R_2Pb(OOCC(CH_3)=CH_2)_2. \quad (2)$$

However, in the case of the interaction of triphenylplumbanol and methacrylic acid, a very interesting formation was observed of only diphenylplumbylene dimethacrylate $(C_6H_5)_2Pb(OOCC(CH_3)=CH_2)_2$, and not triphenylplumbyl methacrylate $(C_6H_5)_3PbOOCC(CH_3)=CH_2$, as would be expected according to the analogous reaction of triarylstannols and methacrylic acid (3), established earlier ([1]),

$$R_3SnOH + HOOCC(CH_3)=CH_2 \rightarrow R_3SnOOC(CH_3)=CH_2. \quad (3)$$

This is apparently connected with the cleavage of one phenyl group of triphenylplumbanol with its replacement by a methacrylic residue (4):

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$$(C_6H_5)_3PbOH+2HOOCC(CH_3)=CH_2 \rightarrow (C_6H_5)_2Pb(OOCC(CH_3)=CH_2)_2+C_6H_6+H_2O. \quad (4)$$

An analogous reaction of triarylplumbanols with organic acids was confirmed by the example of their interaction with nicotinic acid

$(C_6H_5)_3PbOH+2$[[unclear: pyridine-ring structural formula]]$COOH \longrightarrow$ ([[unclear: pyridine-ring structural fo

Of the lead-containing methacrylates whose synthesis is possible by an analogous method, the greatest interest is presented by diphenylplumbylene dimethacrylate, which is the most stable compound and is readily obtained as a result of the indicated reactions. This monomer polymerizes and copolymerizes with unsaturated compounds, for example with

methyl methacrylate. The copolymer of diphenylplumbylene dimethacrylate with the latter is a transparent, glass-like material with a softening temperature above 200°. The properties of the compounds obtained are being investigated.

Experimental Part

$(C_6H_5)_4Pb$. Tetraphenyllead was obtained by the interaction of a Grignard reagent and lead dichloride according to the previously described method (5), in a yield of 45.4% of theory.

$(C_6H_5)_3PbCl$ and $(C_6H_5)_2PbCl_2$. When gaseous hydrogen chloride is passed through a boiling chloroform solution containing 19 g of tetraphenyllead, triphenylchloroplumbane and a crystalline precipitate of diphenyldichloroplumbane are formed. The chloroform layer contains triphenylchloroplumbane. There were obtained 8.6 g of triphenylchloroplumbane (m.p. 203°) and 5.8 g of diphenyldichloroplumbane. The latter is sparingly soluble in chloroform and precipitates from the solution.

Triphenylplumbanol $(C_6H_5)_3PbOH$ and **diphenylplumbanone** $(C_6H_5)_2PbO$. Triphenylplumbanol was obtained by hydrolysis of triphenylchloroplumbane with a saturated alcoholic alkali solution. From 9.4 g (0.02 g-mole) of triphenylchloroplumbane there were obtained 7.2 g of triphenylplumbanol. Yield 80% of theory. $(C_6H_5)_3PbOH$ is a crystalline substance, readily soluble in hot benzene, alcohol, chloroform, and ether; insoluble in water.

Found, %: C 47.23; 47.35; H 3.34; 3.30
$C_{18}H_{16}PbO$. Calculated, %: C 47.59; H 3.54

On hydrolysis of 8.6 g of diphenyldichloroplumbane, dissolved in a mixture of methyl and ethyl alcohols, with a saturated solution of alcoholic alkali (2.1 g KOH in 30 ml of ethyl alcohol), after subsequent dilution of the reaction mixture with water, 6.6 g of diphenylplumbanone were obtained in the form of a bulky

white precipitate. Yield 90% of theory. Diphenylplumbanone does not melt and is sparingly soluble in ordinary solvents.

$(C_6H_5)_2Pb(OOCC(CH_3) = CH_2)_2$: a) **From diphenylplumbanone.** Into a three-necked flask equipped with a stirrer were placed 11.3 g (0.03 g-mole) of diphenylplumbanone, 50 ml of water, and, with stirring, 5.9 ml (0.07 g-mole) of freshly distilled methacrylic acid (b.p. 35°/2 mm) was added. The reaction mass foamed slightly. Stirring was continued for 2 hours and the mixture was left overnight. The crystals that separated were filtered off and washed with several portions of hot water (in order to remove residues of methacrylic acid). There were obtained 10.7 g of diphenylplumbylene dimethacrylate; yield 67% of theory; readily soluble in hot benzene and dioxane; less soluble in alcohol and ether; insoluble in water; on heating above 225° it melts and polymerizes.

Found, %: C 45.41; 45.48; H 3.93; 3.91; Pb 38.53; 38.64
$C_{20}H_{20}PbO_4$. Calculated, %: C 45.18; H 3.79; Pb 38.98

b) **From triphenylplumbanol.** Into a flask were placed 4.5 g (0.01 g-mole) of triphenylplumbanol, 30 ml of water, and 3.4 ml (0.04 g-mole) of freshly distilled methacrylic acid. The reaction products, with constant stirring, were heated at 60° for 2 hours and left overnight. The crystalline precipitate was filtered off and washed with several portions of hot water (30–40 ml) and dried in a vacuum desiccator to constant weight. After recrystallization from hot benzene, 3.2 g of diphenylplumbylene dimethacrylate were obtained. Yield 60.3% of theory.

Polymerization of diphenylplumbylene dimethacrylate. 2 g of diphenylplumbylene dimethacrylate were dissolved in 30 ml of benzene and about 0.1 g of benzoyl peroxide or azobisisobutyric acid was added. The reaction mixture was heated at the boiling point of benzene for 3 hours.

After this the benzene was distilled off and the solution was concentrated to 1/3 of its volume. This gave a thick, viscous mass, which polymerized after only 5 hr of heating in a thermostat at 90–100° to a solid polymeric material.

Copolymerization of diphenylplumbylene dimethacrylate with methyl methacrylate. Into an ampoule were placed 10 g of diphenylplumbylene dimethacrylate, 10 g of methyl methacrylate, and about 0.1 g of benzoyl peroxide or azobisisobutyric acid. The ampoule with the contents was sealed and heated in a thermostat for 3 hr at 40–50°, then 3 hr at 60–70°, and 106 hr at 120–130°. A solid, mechanically strong, slightly turbid copolymer was obtained, which had a softening point above 180°. The specific impact toughness of the specimen was 18–19 kg/cm^2.

Fig. 1. Thermomechanical properties of copolymers of diphenylplumbylene dimethacrylate with methyl methacrylate (1:1)

Some thermomechanical properties of the specimen obtained are presented in Fig. 1. The tests were carried out on a consistometer. According to the data obtained, the material undergoes significant deformation only above 180–190°.

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Fig. 1. Thermomechanical properties of copolymers of diphenylplumbylene dimethacrylate with methyl methacrylate (1:1)

Figure 1: Fig. 1. Thermomechanical properties of copolymers of diphenylplumbylene dimethacrylate with methyl methacrylate (1:1)

The copolymer of diphenylplumbylene dimethacrylate with methyl methacrylate strongly absorbs X-rays.

Thus, by the interaction of triphenylplumbanol and diphenylplumbanone with methacrylic acid, a lead-containing methacrylate—diphenylplumbylene dimethacrylate—was obtained. It was established that diphenylplumbylene dimethacrylate $(C_6H_5)_2Pb(OOCC(CH_3) = (CH_2))_2$ polymerizes and copolymerizes with unsaturated monomers to form polymeric materials.

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Note: Figure translations are in progress. See original paper for figures.

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