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SYNTHESIS AND POLYMERIZATION OF DIFURYLMETHYL- AND DIMETHYLFURYLVINYLSILANE

S. S. Dyankov and D. M. Shopov

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Difurylmethyl- and dimethylfurylvinylsilanes are synthesized. With 2% of ethyllithium they give solid polymers, unchanged on heating to 350°. Views, based on IR spectra, are offered regarding their structures.

Many furan plastics have found application as thermostable and anticorrosion coatings, bonding materials, glues, and moulding compositions. Stable rubbers are obtained from copolymers of vinylfuran and butadiene. Some polymeric materials based on furyloxysilanes are also being brought into production.

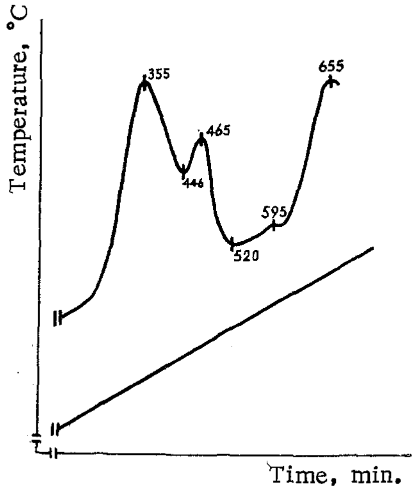


Fig. 1. Thermogram of the polymer of dimethylfurylvinylsilane.

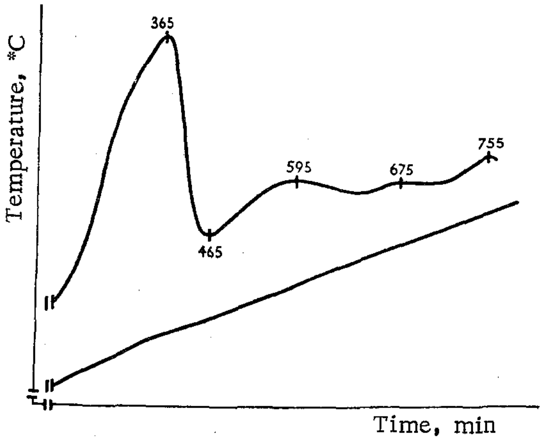


Fig. 2. Thermogram of the polymer of difurylmethylvinylsilane

We previously synthesized some furan organosilicon derivatives with the α-carbon atom in the furan ring directly linked to a silicon atom [1]. The present paper deals with preparation of difurylmethylvinylsilane and dimethylfurylvinylsilane, and the question of their polymerization. These compounds were prepared by reacting furyllithium with methyldichloro- and dimethylethoxyvinylsilane in yields, respectively, of 50.0 and 58.5%.

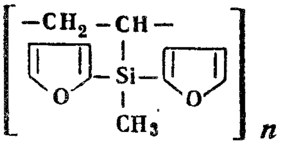
No solid polymer was obtained when dimethylfurylvinylsilane was polymerized with ethyllithium. Difurylmethylvinylsilane gave less than 1% of solid polymer.

The possibility of preparing polymers involving the furan ring using catalytic amounts of ethyllithium was checked with furan, 2-methylfuran, and 2-trimethylsilylfuran, these conditions being the same as in runs with freshly-distilled monomers, i.e. temperature 20° and 50°, amount of ethyllithium 0.5, 1, 2, and 4%, time 2, 8, and 24 hr. For all runs in this series the starting compounds were isolated pure.

Solid polymers could be obtained only if moisture was carefully removed from the starting monomers. With 2 mole % ethyllithium, after only 2 hr at 20°, the yields of solid polymer from difurylmethylvinylsilane and dimethylfurylvinylsilane were, respectively, 60 and 21%.

Comparison of IR spectra of monomers and polymers showed that the following disappear from the spectra of the polymers: absorption at 956 cm^{-1} corresponding to the group (Si–CH=CH$_2$ [2], the 3013 and 3055 cm^{-1} frequencies of the valence vibrations of the vinyl group, and the assumed overtone of some vinyl group vibrations at 1916 cm^{-1} [3]. The out-of-plane deformation vibrations of the C–H group in –CH=CH$_2$ at about 990 cm^{-1}, and vibrations of a double bond at about 1600 cm^{-1}, for vinylfurylsilanes, overlap with the vibrations of the furan ring [4] in the same regions. The spectra of all our silicon-substituted furans without alkenyl groups [1], exhibit absorptions at 1007 and 1590 cm^{-1}. However, for the polymers, the absorption at 1598 cm^{-1} disappears. The furan ring maxima (597–900 ~ 1007, 1072, 1155–1180, 1208, 1270, 1380, 1458, ~ 1490 and 3115 cm^{-1}), and the 1252 cm^{-1} band corresponding to the Si-Me group, are unchanged. The spectra of the polymers also show absorption at 1342 cm^{-1} (> CH ~ ?) and 2850 and 2920 cm^{-1} (–CH$_2$–).

The IR spectra data, as well as experiments with furan and its 2-substituted derivatives, give reason to think that the solid polymers obtained are basically constructed of units of the following types:



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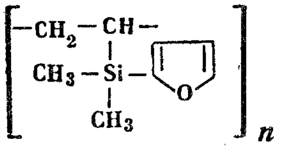

The polymers isolated formed white powders, sparingly soluble in cyclohexane, benzene, and chlorobenzene, which did not melt even at 300°. The same sparingly soluble polymer was also obtained from diphenylmethylvinylsilane and lithium alkyls [5].

With a view to determining the heat stabilities of the polymers prepared by differential thermal analysis, their heating curves in air were measured. The polymers were unchanged up to 340–350°. The thermograms obtained (Figs. 1 and 2) show that polymethylfuryl and polydifurylmethylvinylsilane show exothermic effects at, respectively, 355° and 365°. The IR spectrum of a specimen of difurylmethylvinylsilane polymer heated to 370° showed a change in the maximum at 1252 cm^{-1} (Si–Me), appearance of a wide band in the 1007-1180 cm^{-1} region, and absorption at 1600 cm^{-1}. We think that at those temperatures splitting off of methyl groups starts, and that there is some breaking of the basic polymer chains.

From the IR spectra of specimens of difurylmethylvinylsilane polymers heated to the corresponding temperatures, it is considered that deeper destruction starts at 445° and 465° (endothermic effects), and that at 465° and 595° (exothermic effects) combustion has already begun.

Experimental

Preparation of monomers. The furylvinylsilanes were prepared from furyllithium and the appropriate methyl-(chloro) ethoxyvinylsilanes. Furyllithium was prepared by the method of [1], using 2.4 g at Li and 1 mole furan. The resultant solution was filtered, and run into the appropriate silane, after which the reactants were heated together for 6–8 hr, and the product worked up in the usual way. After distilling off the ether, a wide cut was taken, and this was distilled over Na through a column.

Dimethylfurylvinylsilane. Prepared from 60 g (0.51 mole) dimethylethoxyvinylsilane, yield 44.5 g (58.5%). Liquid, bp 149–150°, n_D^{20} 1.4670, d_4^{20} 0.9040. Found: C 63.00; H 7.50; Si 18.68%. Calculated for $C_8H_{12}SiO$: C 63.20; H 7.90; Si 18.40%.

Difurylmethylvinylsilane. Prepared from 35.2 g (0.25 mole) dichloromethylvinylsilane. Yield 26.0 g (50.0%). Liquid, bp 101–102° (5 min); n_D^{20} 1.5190; d_4^{20} 1.0466. Found: C 64.69; H 5.88; Si 13.51%. Calculated for $C_{11}H_{12}SiO_2$: C 64.70; H 5.91; Si 13.70%.

Polymerization of the furylvinylsilanes. The catalyst, ethyllithium, was used as a solution in n-heptane (concentration 0.157 mole/*l*).

To obtain solid polymers, the monomers were first dried over Na in ampuls pumped down to 1×10^{-3} mm.

All runs were made in a reactor under argon, with constant stirring, or in ampuls. The polymer was precipitated with MeOH, washed a few times, and vacuum-dried.

The heating curves were determined using an automatic recording differential thermal analysis instrument. Heating was in air, and the rate was 8–10°/min. Al_2O_3 was the standard.

IR spectra were measured over the 400-3200 cm^{-1} range, with a UR-10 instrument, using Nujol suspensions or material tabletted with KBr. Layer thickness 0.005 cm.

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Institute of Organic Chemistry, Bulgarian AS, Sofia