ORGANOSILICON COMPOUNDS CONTAINING THE FURAN RING

XIV. Photosensitive Polymers Based on Organosilicon Esters of 3-(2'-Furyl) Acrylic Acid and Cinnamic Acids*

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Hydrolysis of organosilicon esters of 3-(2'furyl)acrylic or cinnamic acids, and cohydrolysis with organyltrialkoxysilanes gives organosilicon resins, which solidify when illuminated with UV light.

In the photolithographic method of making semiconductor devices, light-sensitive organosilicon coverings play a definite part [2]. They can be obtained either from the usual organosilicon lacquers (e.g. K-1), by adding photosensitive compounds, or from film-forming organosilicon resins, containing, joined by a Si—C bond, functional groups prone to photopolymerize. Examples of such groups are acrylo, cinnamyl, and styryl, etc. [3]. Their light-sensitivities are considerably enhanced by photosensitizers [4], among them various unsaturated furan derivatives [5]. Linking of these two types of light-sensitive groups in a molecule of appropriate organosilicon monomers should have an altogether favorable effect on the tendencies of the resins to photopolymerize.

Organosilicon esters of 3-(2'-furyl)acrylic acid [6] are such monomers. To prepare light-sensitive polymers from them, trialkoxysilylmethyl esters of 3-(2'furyl)acrylic acid, or mixtures thereof with organylalkoxysilanes, diorganyldialkoxysilanes, or tetraalkoxysilanes dissolved in ether, were treated with water in the presence of alkaline catalysts (ammonia), or without them. When 20% toluene solutions of the resins are introduced by centrifuging onto the surface of glass, copper, germanium, or other materials, and dried out, they give light-sensitive coatings, passing over to the insoluble state when illuminated with UV light (e.g. by a PRK-4 lamp).

Quick-forming photosensitive films were prepared similarly from trialkoxysilylmethyl esters of cinnamic acid. The thermomechanical properties of such films can be varied over a wide range by varying the mole rations of the reactants, and the natures of the groups R in $RSiX_3$ or R_2SiX_2 (X = Cl, alkoxy) used for cohydrolysis with the organosilicon esters of cinnamic acid to make the resins.

EXPERIMENTAL

Hydrolysis of trimethoxysilylmethyl ester of 3-(2'-furyl)acrylic acid. A 3-necked flask fitted with a mechanical stirrer, dropping funnel and reflux condenser, was charged with 10 g trimethoxysilylmethyl ester of 3-(2'-furyl)acrylic acid and 60 ml diethyl ether, and 2.8 ml water added with vigorous stirring. After stirring for 3 hr, the reaction products were left overnight (16 hr). Then 4 ml 30% ammonia was added, the mixture stirred for 8 hr, neutralized with AcOH, the ether layer separated, and dried over $MgSO_4$. Distilling off the solvent gave 4 g light-sensitive resin.

Similarly 24 g trimethoxysilylmethyl ester of cinnamic acid (in 35 ml ether), 5.4 ml water, and 2.5 ml concentrated ammonia gave 16 g light-sensitive resin. After drying, the reduced viscosity of a 0.5% toluene solution at 19° C was 0.079, and that of a 0.72% toluene solution was 0.102.

Cohydrolysis of the trimethoxysilylmethyl ester of 3-(2'-furyl)acrylic acid with phenyltrimethoxysilane. 3 ml Water was added to a vigorously stirred solution of 6.3 g trimethoxysilyl ester of 3-(2'-furyl)acrylic acid and 2 g phenyltrimethoxysilane in 50 ml ether, and the whole then stirred for 12 hr. The ether solution was separated off and dried over $MgSO_4$, the ether distilled off, giving 2.5 g residue, a light-sensitive resin. The reduced logarithmic viscosity of a 0.79% toluene solution was 0.046 at 20° C.

Cohydrolysis of the trimethoxylsilylmethyl ester of cinnamic acid, with phenyltrimethoxylsilane. 4.2 g Phenyltrichlorosilane was added dropwise to 12.8 g MeOH which was well stirred. Then a solution of 22.6 g trimethoxysilylmethyl ester of cinnamic acid was added, dissolved in 60 ml ether, and 8 ml water added dropwise. The whole was then stirred for an hour, and neutralized with 50% NaOH. The ether layer was separated off, washed with 10% NaCl, and dried over $MgSO_4$. The solvent was taken off under a water-pump vacuum. Yield 20 g photosensitive resin. After drying a 0.88% toluene solution had a reduced logarithmic viscosity of 0.055 at 20° C.

*For Part XIII see [1].

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