

Certain Condensations of Polyamines and Polyfunctional Compounds*

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The purpose of this investigation was to study the reactions of diamines and other polyamines with such polyfunctional compounds as 2,2'-dichloroethyl ether, 1,4-dibromo-2-butene, chloroacetyl chloride and silicon tetrachloride. The results from such condensations have yielded fiber producing compounds, rubber-like products, and resins.

Experimental

Hexamethylenediamine and 2,2'-dichloroethyl ether:

Eighty-seven grams of hexamethylenediamine (0.75 mole), dissolved in 100 ml. of 50% ethyl alcohol, was placed in a three-necked flask equipped with a dropping funnel, condenser, and a mechanical stirrer. One hundred and eight grams of 2,2'-dichloroethyl ether (0.75 mole) in 100 ml. of ethyl alcohol was added dropwise with continued stirring and gentle heating. After the complete addition (2½ hours), vigorous stirring and refluxing were continued for 7 hours. The reaction product, when cooled, could be pulled into fibers. The alcoholic solution was evaporated and the product became solid (m.p. 159°C.). When the solid was heated on a steam cone, it softened sufficiently so that it could be drawn into fibers. The fibers, however, were somewhat brittle and soluble in water.

When pyridine and ethyl alcohol were used as solvents for the condensation, a viscous, orange-brown product was obtained which could be drawn into fibers 10 feet long before breaking.

Hexamethylenediamine and 1,4-dibromo-2-butene:

Fifty-four grams of 1,4-dibromo-2-butene in 100 g. of dibutyl ether was added dropwise over a period of several hours to a refluxing solution of 38 g. of hexamethylenediamine in 100 g. of dibutyl ether with vigorous stirring. A gummy precipitate began to form and it increased as the 1,4-dibromo-2-butene solution was added. When the addition was almost completed, the solution became difficult to stir. The product was filtered and dried. The product had no sharp melting point but decomposed on heating. It was insoluble in water, benzene, chloroform, and pyridine and only slightly soluble in hydrochloric acid. A sample of the product, when placed in a hydraulic press at 5000 lbs./sq. in. and 150°C.,

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yielded a disc which was slightly pliable. It lacked the strength of the common thermosetting plastics.

Hexamethylenediamine and chloroacetyl chloride:

Twenty-nine grams of chloroacetyl chloride (0.25 mole) in 100 g. of dibutyl ether was added dropwise over a period of several hours to 29 g. of hexamethylenediamine (0.25 mole) in 100 g. of dibutyl ether under reflux. As the addition was continued, a precipitate began to cling to the sides of the flask and stirring became difficult. When the product began to darken, further heating was discontinued. The solution was cooled and the solid product was filtered. The product was suspended in 100 ml. of a 10% caustic solution and vigorously stirred. The suspended product was filtered and as much of the aqueous solution as possible was pressed out and the residue was washed with acetone and air dried. The product had the appearance of sponge rubber. It had a slight resiliency and a certain toughness to stretching. It was insoluble in water, pyridine, carbon disulfide, petroleum ether, glacial acetic acid, ethanolamine, tetraethylenepentamine, 2-nitropropane-butanol mixture, acetone, alcohol and ether. It was soluble in formamide. Suspension of the product in acetone and then extrusion resulted in a fiber with slight resiliency.

1,3-Diaminobutane and silicon tetrachloride:

One gram of silicon tetrachloride was added dropwise to one gram of 1,3-diaminobutane with vigorous stirring. The reaction was violent. The solution turned orange in color and became very viscous. When the product was cooled, it became a clear glassy resin. The product could be drawn into fibers when warmed to the softening point. The fibers, however, were brittle and very hygroscopic.

Tetraethylenepentamine and silicon tetrachloride:

Two grams of silicon tetrachloride was added dropwise to two grams of tetraethylenepentamine with vigorous stirring. The solution became viscous and formed a putty-like material. The putty could be bounced, but it did not show any flattened surfaces from the violent contacts.