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Preparation of Highly Fluorinated Diols Containing Ether Linkages

New hydroxy-terminated perfluoroethers and polyurethane resins derived from ethers possess outstanding chemical resistance and good thermal properties, and can be used in numerous industrial applications as potting compounds, coatings, and seals. The hydroxy-terminated ethers are also useful as intermediates in the synthesis of highly fluorine substituted elastomers and adhesives.

Basically, the precursor materials are prepared by the reaction of perfluorinated diacid fluorides with hexafluoropropylene epoxide in the presence of a suitable catalyst, such as cesium fluoride. The precursors constitute a fraction of the products obtained from the reaction. A specific example of forming the precursors involves the reaction of hexafluoropropylene oxide with perfluoroglutaryl fluoride in the presence of cesium fluoride and a suitable solvent.

The precursor acid fluoride-terminated ethers are converted to diols by reaction with a reducing agent such as an alkali metal borohydride or an aluminum hydride. Reduction takes place in the presence of an inert solvent such as dioxane or diethylene glycol dimethyl ether. The diacid fluoride starting material is usually added by drops to the solution of the solvent and reducing agent. The temperature at which the reduction is carried out is not critical. Normally the reactants are heated to a temperature not in excess of the boiling temperature of the solvent. The reactants are stirred during the reaction for a period up to three hours, after which water is added to remove any excess borohydride present. This step is followed by a separation of the diols from solution.

The diols produced can then be used in reactions with suitable diisocyanates to form new polyurethanes. Any diisocyanate conventionally used to produce polyurethane resins is suitable. These include toluene diisocyanate and mixtures of its isomers such as the 2, 4 and 2, 6 isomers, as well as diphenylmethane-4, 4'-diisocyanate. It is particularly desirable to use a diisocyanate selected to give a maximum number of fluorine atoms, such as tetrafluoro-m-phenylene diisocyanate, tetrafluoro-p-phenylene diisocyanate, perfluorotrimethylene diisocyanate, 1-chloro-2, 4-diisocyanate-3, 5, 6-trifluorobenzene and similar compounds; the extremely good thermal properties and nonflammability of the diols can be attributed to the presence of fluorine atoms in the polymer chains.

The resultant polymers range from sticky semi-solids to tough, brittle sheets depending upon the amount of diisocyanate used in the extension and cross-linking reaction between it and the diols. Although the hardness of the resultant polymers increases with the increasing ratio of diisocyanate to diol, the glass temperature of the resultant polyurethanes is not adversely affected. A mole ratio of diisocyanate to diol from 1:1 up to 3:1 may be used. The preferred mole ratio range is from 1:1 to 2:1.

The time and temperature of the polymerization reaction are dependent upon the molecular weight of the prepolymer and type of diisocyanate used. Completion of polymerization for the given diol-diisocyanate can be determined by the increase in viscosity of the melt polymer. Generally the temperature of curing can vary from 25° to 100°C, while the time of the cure can range from 10 to 30 minutes.

(continued overleaf)

Note:

Requests for further information may be directed to:

Technology Utilization Officer
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Patent status:

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