

Polysilphenylenes

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Research Objective: The motivation for this work is to develop novel fire retardant elastomers based on vinyl substituted silphenylene siloxane copolymers.

Approach: The motivation to investigate flame retardant elastomers by substituting a silphenylene siloxane polymer backbone with a high number of vinyl groups is the following: Vinyl substituted siloxanes can be cured by addition of a multifunctional Si-H compound under catalysis with a variety of platinum complexes. The hydrosilylation reaction of the double bonds with the Si-H cross-linker will then generate a network structure. Depending upon the ratio of cross-linker to vinyl groups, the cross-link density of such a system can be controlled over a broad range. Materials can thus be obtained with properties ranging from a slightly cross-linked elastomer to a highly cross-linked resin type structure. For elastomers, our concept is to transform a polymer with high vinyl content by hydrosilylation of a small amount of all vinyl groups present. The bulk of the unsaturated functionalities will then remain and be available to thermally cross-link at temperatures higher than the application temperature of the elastomer, i.e. in case of a fire. The resulting resin structure will then guarantee high char yields and, hence, good flame retardancy.

Accomplishment Description: The synthesis of a series of vinyl substituted silphenylene siloxane polymers of high molecular weight is described. ^{29}Si NMR spectroscopy indicates that the polymers possess an exactly alternating microstructure of the silphenylene and siloxane moieties. The materials are completely amorphous with glass transition temperatures between -60°C and -86°C . All polymers degrade thermally only above 500°C under both oxidative or inert atmosphere. The char yields at 900°C increase with increasing vinyl content from 30 percent up to almost 70 percent. Cross-linking of a small fraction of vinyl groups by hydrosilylation gives materials with elastomeric properties. Dynamic mechanical experiments indicate that the bulk of vinyl groups cross-links thermally at temperatures above 230°C . Therefore, the temperature window for possible applications of these materials as fire-safe elastomers extends from about -86°C to approximately 230°C .

Significance: A series of strictly alternating vinyl substituted (i.e. cross-linkable) silphenylene siloxane copolymers with systematically varying vinyl content has been synthesized. The polymers are completely amorphous gums with glass transition temperatures ranging from -86°C to -59°C as a function of vinyl content and volume fraction of highly mobile siloxane units. The materials degrade thermally above 500°C . As the vinyl content increases, both the onset temperature of major degradation and the char yield at 900°C shift to higher values.

Expected Results: One of the polymers has an extremely high degradation temperature of over 600°C and a char yield of almost 70 percent in air, which makes it a promising candidate for potential applications as a flame retardant elastomer. The reason for the

remarkable thermal stability is ascribed to a cross-linking reaction of the vinyl functionalities, which occurs slightly below the onset of siloxane redistribution reactions around 300°C.

References: Dvornic, P.R., Lenz, R.W., High Temperature Siloxane Elastomers, (Huethig & Wepf Verlag, New York, 1990).

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