ANNOTATION

Igor S. Sirotin

Synthesis of new oligomers and polymers with phosphazene and benzoxazine heterocycles for use as resins for composite materials with reduced flammability

Scale-up ready methods for synthesizing chlorophosphazene precursors and aryloxyphosphazenes containing epoxy and benzoxazine functional groups have been developed. A series of new diamine benzoxazine monomers has been synthesized. Some dibenzoxazines were obtained for the first time and are non-flammable. Relationships between the conditions of the above reactions, yields and structures and properties of the products have been established, and more than 50 individual compounds have been identified using NMR spectroscopy, MALDI-TOF mass spectrometry and other analysis methods. Rheological, thermochemical and spectral methods have been used to find mathematical models and processing recommendations for obtaining thermosetting polymer matrices based on the synthesized compounds. The obtained results significantly expands the range of epoxies and benzoxazines available for practical use and represents a solution to a major scientific problem – the creation of effective and easily adaptable to existing manufacturing methods for synthesizing new resins components for limited flammability, self-extinguishing or completely non-flammable polymer matrix composite materials. The analysis of the obtained phosphazene-containing epoxy and benzoxazine oligomers performed using a complex of modern physicochemical methods allows us to draw a conclusion about the purity and quantitative yield of the products, as well as the possibility of regulating the content of the phosphazene component to 60-70%, which allows us to consider the developed methods are engineering-ready. The conducted studies of the polymerization processes of various benzoxazines allow us to conclude that electron-donating substituents in the meta-position of the amine increase, and in the ortho- and para-positions of phenol or amine – decrease the reactivity of the monomer and the properties of the polymer. The refined schemes and established temperature-time characteristics of chain growth, transfer and termination proposed on the basis of solid-state MAS NMR ^{13}C spectroscopy of dibenzoxazines with different degrees of curing make it possible (1) to explain the facts of formation of polyimine structures, destruction and loss of mass during polymerization, caused, among other things, by deamination in the chain and restoration of iminium or quinomethide end groups, (2) to form the prerequisites for a justified molecular design of monomers and development of benzoxazine binders with minimization of side processes and improvement of polymer properties. The established features of catalytic synthesis of chlorocyclophosphamides make it possible to regulate the yield of both cyclic trimers and tetramers (up to 75% and 27%, respectively) and higher homologues (up to 50%). Eugenol derivatives were synthesized from chlorophosphazene precursors $[PNCl_2]_4$ and a mixture of $[PNCl_2]_{n=3-10}$, by epoxidation of which with m-chloroperbenzoic acid new epoxyphosphazenes with a molecular weight of over 1400 and an epoxy equivalent weight of over 265% were obtained. The effects revealed from their introduction into matrices are comparable to analogs based on hexachlorocyclophosphazene, which allow us to conclude that a mixture of chlorocyclophosphazenes is applicable as a precursor for thermosetting plastic modifiers. The established patterns of polymer formation based on the synthesized monomers and oligomers and the structure-property relationships allow us to propose new approaches to the development of fire-resistant or completely non-flammable resins for polymer matrix composite materials of the following types: epoxyphosphazene-amine, benzoxazine and epoxy-benzoxazine, or their combinations. The test of the proposed approaches has shown their practical applicability for obtaining non-flammable composite materials while maintaining or improving their physical, mechanical and thermal characteristics.