ABSTRACT

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INVESTIGATION OF THE PATTERNS OF FORMATION AND STRUCTURE OF POLYBENZOXAZINES

The relevance of the research topic is that benzoxazines are heterocyclic compounds capable of polymerization with ring opening to form, depending on the functionality, linear or cross-linked polymers. Polybenzoxazines have low flammability, high thermal and chemical resistance, high strength and elastic modulus, low moisture absorption and low shrinkage during curing. These properties make them an excellent alternative to traditional thermosetting materials such as phenol-formaldehyde and epoxy resins.

Despite the fact that a large number of benzoxazine monomers of various structures have been synthesized to date, the structure of the three-dimensional polymers formed during their curing has not yet been fully established. And although there is a general idea of the polymerization mechanism and the resulting structure of the polymers, the study of the chemical structure of polybenzoxazines is still ongoing.

The aim of the work is to study the processes of thermal polymerization of benzoxazines and the patterns of formation of the chemical structure of polybenzoxazines based on aromatic diamines and phenol homologues.

Research objectives:

1. Synthesize a series of benzoxazine monomers based on diaminodiphenylmethane isomers to identify the influence of the position of the amino group in the initial diamine on the reactivity of the monomers and the thermomechanical characteristics of the resulting polybenzoxazines;
2. Synthesize a series of benzoxazine monomers based on 4,4'- diaminodiphenylmethane and phenol (two reactive positions), cresols (one reactive position), 2,4 dimethylphenol (reactive positions blocked),

compare their reactivity and establish the possibility of polymerization occurring at the arylamine fragment;

3. Identify possible deamination processes during polymerization found in model monobenzoxazines but not described for dibenzoxazines;
4. Explain the formation of imine bonds in the structure of polydibenzoxazines based on 4,4'-diaminodiphenylmethane and phenol homologues;
5. Compare the chemical structure formed during thermal polymerization of difunctional benzoxazines based on (a) 4,4'-diaminodiphenylmethane and homologues of phenol, (b) bisphenol A and aniline.

The scientific novelty of the work is that two previously undescribed difunctional benzoxazine monomers based on 3,3'- and 3,4'-diaminodiphenylmethane have been synthesized. The chemical structure of network polybenzoxazines based on 4,4'-diaminodiphenylmethane and phenol homologues has been established using solid-state NMR spectroscopy with ^{13}C magic-angle spinning as a function of curing time and degree at 180 °C. A scheme for thermal polymerization of benzoxazines has been proposed for the first time, including chain transfer and termination processes and explaining the formation of polyimine-type structures.

The theoretical and practical significance of the work lies in the fact that the established patterns and temperature-time characteristics of the polymerization of benzoxazine monomers depending on their structure clarify the existing knowledge about the polymerization of 1,3-oxazine heterocycles and the chemical structure of the resulting polybenzoxazines, allow us to move on to a substantiated molecular design of new benzoxazine monomers, and also provide additional opportunities for regulating the polymerization processes of benzoxazines, which is necessary to expand the range of binders for polymer composite materials based on them.

The provisions submitted to the defense:

1. Synthesis of new benzoxazines based on 3,3'- and 3,4'-diaminodiphenylmethane and thermomechanical properties of polymers based

on them in comparison with polydibenzoxazine based on 4,4'- diaminodiphenylmethane.

2. Chemical structure of cross-linked polybenzoxazines based on 4,4'-diaminodiphenylmethane and phenol homologues formed during thermal polymerization.

3. Scheme of polymerization of dibenzoxazines, including processes of chain transfer, termination and formation of polyimine-type structures.