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« Synthesis and application of branched polymers based on polyvinyl alcohol»

Relevance of the theme. The search for new approaches that provide simultaneous achievement of biocompatibility, high mechanical strength, ability to limited swelling in water and manufacturability of product molding is a topical topic of research. To ensure these characteristics, this paper proposes an approach based on the formation of hydrogels based on chain branching products of polyvinyl alcohol as a result of its interaction with epichlorohydrin in an alkaline medium. In this case, film materials with high biocompatibility, significant mechanical strength, and the ability to swell in water at physiological temperatures can be obtained by foeming from aqueous media under conditions that ensure unhindered removal of residual amounts of the crosslinking agent and its hydrolysis products. The kinetic regularities of the synthesis of branched chains under the conditions of modification of linear polyvinyl alcohol with epichlorohydrin in an alkaline medium have been established, which make it possible to predict the properties of the resulting macromolecular products.

Degree of development of the them. The development of materials with high biocompatibility, sufficient mechanical strength for use in biomedical fields, the ability to swell in water, and the manufacturability of product molding is known to be difficult. Although many hydrogels have biocompatibility and the ability to swell in water, the complexity of product molding and the low mechanical strength of this class of materials in the swollen state limit the possibility of their application to create biomedical products. At the same time, it is known that chemical gels of polyvinyl alcohol, along with limited swelling in water and biocompatibility, are characterized by high physical and mechanical characteristics. On the contrary, the main obstacles in the creation of biocompatible materials based on chemically cross-linked polyvinyl alcohol are the need for thorough purification from unreacted cross-linking agents and the complexity of product molding. The transition to physical gels of polyvinyl alcohol makes it possible to avoid the use of cross-linking agents, as well as to ensure high manufacturability of product molding, but at the cost of a significant decrease in mechanical strength. Taking into account the noted circumstances, this dissertation work is aimed at establishing the patterns of synthesis of branched polymers based on polyvinyl alcohol and searching for promising areas for their application.

The purpose of the work is determination of the regularities of branching of linear polyvinyl alcohol under conditions of modification of its chains with epichlorohydrin in an alkaline medium for the synthesis of polymers promising as materials for medical and biological purposes.

The main tasks:

- establishing the mechanism and kinetic regularities of chain branching of linear polyvinyl alcohol under conditions of modification with epichlorohydrin in alkaline aqueous solutions;
- quantitative description of the kinetic data and calculation of the kinetic parameters of the stages leading to chain branching of polyvinyl alcohol, as well as the main side reactions;
- establishment of rheokinetic regularities of chain branching of polyvinyl alcohol when interacting with epichlorohydrin in an alkaline medium under various temperature and concentration conditions;
- establishing regularities of swelling of films in water formed from branched polyvinyl alcohol in various temperature and concentration conditions;
- development of approaches to obtaining biocompatible and hemocompatible materials based on branched polyvinyl alcohol.

Scientific novelty.

- for the first time, taking into account the side reactions of the hydrolysis of epoxy groups of epichlorohydrin and glycidyl groups associated with the polymer chain, a kinetic model of chain branching of polyvinyl alcohol upon interaction with epichlorohydrin in an alkaline medium was proposed and its parameters were determined;
- a decrease in the rate of hydrolysis of epichlorohydrin in the presence of polyvinyl alcohol was established, which is associated with a decrease in the frequency factor due to an increase in the viscosity of the reaction system;
- it has been shown that the hydrolysis of glycidyl groups associated with the chain of polyvinyl alcohol is limited by the diffusion of hydroxide ions into macromolecular coils and is characterized by a low activation energy and a small pre-exponential factor;
- taking into account side reactions, the theoretical ratio for calculating the number average molecular weight of the products of polyvinyl alcohol chain branching under the action of epichlorohydrin in an alkaline medium and showing its adequacy to experimental data, as well as a method for determining the rate constant for the reaction of alcoholate ions of polyvinyl alcohol and glycidyl groups associated with a chain of polyvinyl alcohol;

- it has been shown that polyvinyl alcohol chain branching has no significant effect on the degree of crystallinity, but causes a decrease in the size of ordered regions;

  the existence of a threshold concentration, temperature and molecular weight of the initial linear polymer, at which a physical network of entanglements is formed in the process of interaction of polyvinyl alcohol with epichlorohydrin in an alkaline medium, has been established.

Theoretical and practical significance. The theoretical significance of the work is that a quantitative approach has been developed to describe the kinetics of chain branching of polyvinyl alcohol upon interaction with epichlorohydrin, taking into account side reactions, and methods for determining the parameters of the kinetic model (rate constants) have also been proposed. The practical significance of the work is that it has been shown the possibility of forming films based on branched polyvinyl alcohol, capable of limited swelling in water at physiological temperatures, retaining significant strength in the swollen state, showing biocompatibility and hemocompatibility. The obtained films may be of interest for the manufacture of endoprostheses of blood vessels, substrates for cell culture and postoperative bandages (barrier materials).

The main provisions for the defense:

- kinetic regularities and the mechanism of chain branching of polyvinyl alcohol when interacting with epichlorohydrin in an alkaline medium;
- experimental regularities of changes in the viscosity of the reaction system in the process of chain branching of polyvinyl alcohol of various molecular weights at various concentrations of reagents and temperatures;
- regularities of swelling of films based on branched polyvinyl alcohol obtained at different ratios of reagents, temperatures, concentrations and molecular weights of the initial linear polyvinyl alcohol;
- consideration of biocompatibility, hemocompatibility and mechanical strength of obtained films based on branched polyvinyl alcohol.