

# Synthesis and properties of lignin-highly branched polymeric systems

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*Abstract – Branched water-soluble surface-active polymers based on lignin were obtained. A simple and convenient method of modifying the natural polymer as a result of low-temperature radical polymerization is proposed, which allows obtaining branched copolymers with grafted chains of functional polymers. Using this synthetic approach and changing the functional composition of the grafted copolymer, it is possible to easily adjust the colloidal-chemical properties of lignin-containing polymers.*

Keywords – lignin, radical polymerization, branched polymers, surfactants, colloidal structures.

## Introduction

Lignin is the most common natural aromatic polymer on earth and is a large and renewable reservoir (source) of raw materials for the synthesis of polymeric materials and chemicals [1]. This biopolymer makes up approximately 30-50% of the mass of raw materials for paper production (lignocellulose). According to the US Energy Bureau, about 70 million tons of technical lignin, which are a by-product of pulp processing industries, is produced annually in the world [2]. Since interest in biofuels is growing, for which vegetable raw materials are used, cellulose, in particular, so the amount of technical lignin is increasing [3, 4]. Therefore, the search for new areas of application of lignin is relevant and promising. Lignin has the potential for producing various classes of engineering plastics due to the presence of reactive functional groups, a wide variety of modification options, moderate biodegradability, and compatibility with organic reagents and solvents [5, 6, 7]. Researchers pay a lot of attention to the production of polymer composite materials with the participation of lignin, where this polymer is used as a reagent and filler. Stitched polyurethane compositions, epoxy resins are obtained on its basis [6, 8, 9]. Some methods of direct chemical modification of lignin are also described in the literature, for example, the methods of introducing amino and epoxy groups into the composition of lignin using the reactions of adding of bifunctional (epoxide- or amine-containing) compounds to the hydroxyl groups of lignin [10]. A promising method of lignin modification is the grafting of polymer chains by the method of radical polymerization [5]. To obtain the primary (initiating) radical on lignin, the photolysis [11], gamma irradiation [12], oxidation of lignin with hydroperoxides [13], and redox systems involving metal cations and hydroperoxides [14, 15] are used. Recently, more and more works have appeared on the modification of lignin by methods of controlled radical polymerization, which is carried out in several stages with the preliminary preparation of a macroinitiator based on lignin [16, 17, 18].

## Results

We have proposed a new method of lignin modification based on the grafting of functional polymers and copolymers as a result of a radical polymerization reaction initiated by a redox

system based on Ce(IV) salts and hydroxyl fragments of lignin. The statistical graft copolymer was obtained by radical polymerization in acetone or DMF at room temperature. The N-vinylpyrrolidone (NVP) was used to ensure water solubility and glycidyl methacrylate (GMA) to introduce side reactive epoxy fragments into the lignin structure (Fig. 1). A large number of aliphatic hydroxyl groups contained in the structure of lignin allow it to be used together with Cerium salt as a component of the redox initiating system. It is shown that lignin effectively initiates polymerization at a concentration of 5-30% of the mass fraction of monomers, and the conversion is 40-60% according to the results of gravimetric analysis. The structure of polymers was confirmed by the method of elemental analysis, NMR and IR spectroscopy.

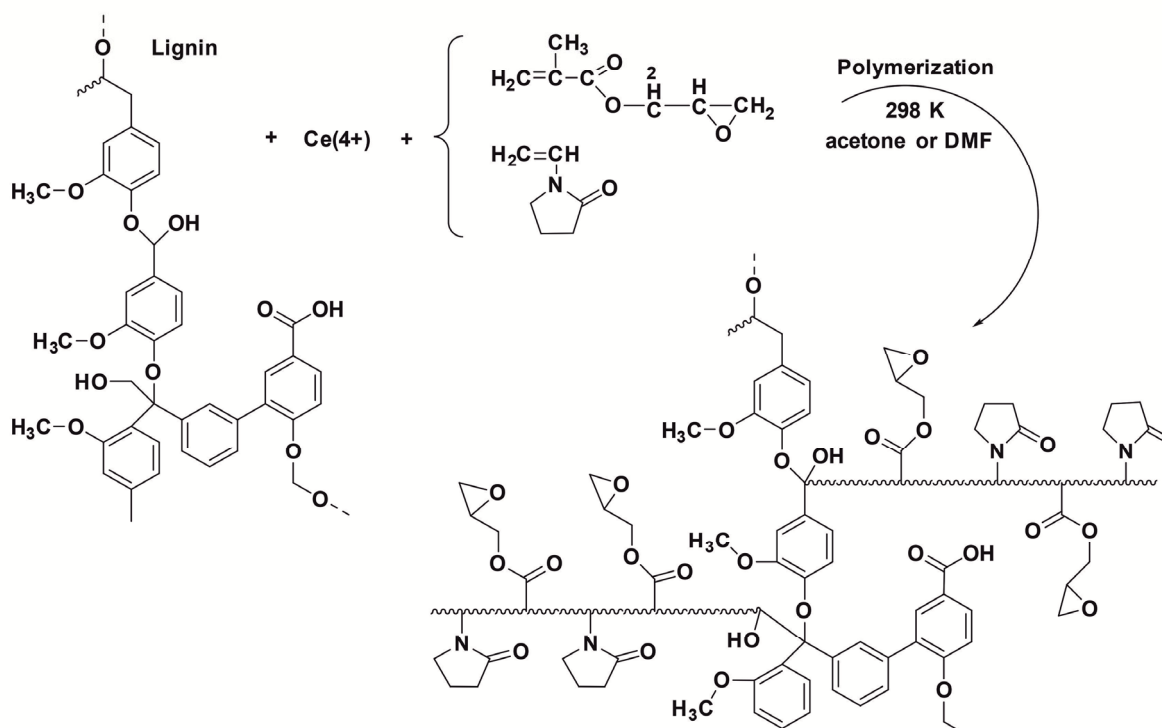


Fig. 1. The scheme for obtaining of the lignin-containing copolymer with grafted functional polymer chains.

The grafting of poly(NVP-co-GMA) chains allows not only to improve the solubility of the lignin-containing copolymer in water (the original Protobind 1000 brand lignin dissolves only in an alkaline medium at pH 10), but also to enhance the surface activity of such copolymers. In Fig. 2, the surface tension isotherms of aqueous solutions of lignin and its derivatives with grafted poly(NVP-co-GMA) chains are presented. It can be seen (Fig. 2), the increase in hydrophobic GMA units in the grafted copolymer leads to a significant change in the colloidal and chemical properties of lignin-containing copolymers. The size of micellar structures, as well as their polydispersity, decrease after the grafting of poly(NVP-co-HMA) chains. Moreover, the increase in content of the hydrophobic GMA monomer units leads to the controlled increase in the surface activity of the lignin-containing copolymer and a decrease in the size of the micellar structures formed by the molecules of this polymer.

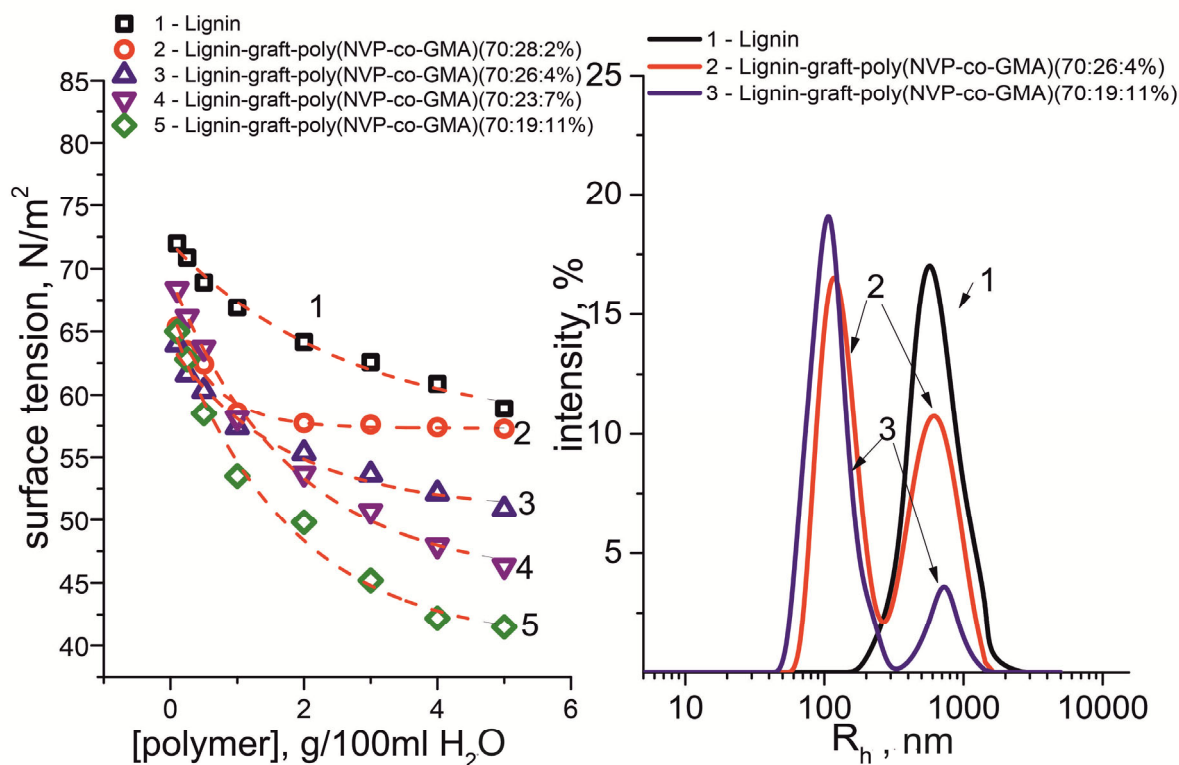


Fig. 2. Surface tension isotherms of aqueous solutions of lignin (1) and lignin-graft-poly(NVP-co-HMA) copolymers with grafted chains of different composition (2-5) (left), and hydrodynamic radii of micellar structures formed by lignin molecules (1) and its derivative copolymers of lignin-graft-poly(NVP-co-HMA) (2-3) in aqueous solution (right).

The presence of reactive epoxy fragments in the modified lignin made it possible to attach hydroxyl-containing polymethyloxazoline chains. The addition reaction was carried out under mild conditions at 313K, in the presence of boron trifluoride etherate as a catalyst. The efficiency of polymethyloxazoline chain grafting was monitored by <sup>1</sup>H NMR and thin-layer chromatography (TLC) methods.

### Conclusions

A method of synthesis of functional branched copolymers based on lignin has been developed. By changing the composition of the monomer mixture and the monomer/lignin ratio, it is possible to control the properties, in particular, colloidal and chemical properties, of the obtained copolymers. The proposed method of lignin modification allows grafting polymer chains with various reactive fragments, which makes it possible to further modify lignin-containing copolymers and obtain macromolecules of complex architecture.

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