Kinetic regularities of dispersion oxidative polymerization of aniline in aqueous solutions of branched polyvinyl alcohol

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Relevance of the research topic. Ensuring the stability of aqueous polyaniline (PANI) dispersions formed during the oxidative polymerization of aniline in an acidic medium requires the use of macromolecular stabilizers. To obtain aggregatively stable PANI suspensions, linear nonionic polymers such as poly(N-vinyl-2-pyrrolidone), polyethylene glycol, and polyvinyl alcohol (PVA) are commonly used, providing a steric stabilization effect. However, the size of the resulting PANI particles is usually quite large (300–500 nm), which limits their applicability in nanotechnology. Reducing the particle size of the dispersed phase in the products of oxidative polymerization of aniline is achieved by increasing the concentration and viscosity-average molecular weight of water-soluble macromolecular stabilizers, although both approaches demonstrate limited effectiveness. The efficiency of PANI steric stabilization can be enhanced by significantly increasing the density of Kuhn segments within the macromolecular coil of polymer stabilizers; however, this requires chain branching. Previously, a series of studies on the synthesis of branched PVA was carried out at the Department of Biomaterials of the D.I. Mendeleev University of Chemical Technology of Russia; however, a systematic investigation of its colloid-chemical properties and ability to provide steric stabilization of particles has not been conducted. Therefore, this dissertation is devoted to solving the urgent problem of establishing the colloid-chemical properties of aqueous solutions of branched PVA of various molecular weights, as well as its use for stabilizing polymer particles formed during their synthesis, including under the conditions of oxidative polymerization of aniline. The developed approach made it possible to form PANI-containing particles with a size of less than 200 nm, which may be important

for their processing and the production of functional nanomaterials. In addition, branched PVA had a significant effect on the rate of the non-catalytic and catalytic stages of oxidative polymerization of aniline. The latter circumstance made it possible to clarify the mechanism of oxidative polymerization of aniline in the presence of water-soluble branched polymers.

The goal of this work is to establish the colloid-chemical properties of aqueous solutions of branched polyvinyl alcohol of various viscosity-average molecular weights and the kinetic regularities of dispersion oxidative polymerization of aniline in aqueous solutions of branched polyvinyl alcohol.

The tasks of the research

1. To develop an approach for calculating the viscosity-average molecular weights of synthesized branched PVA macromolecules and to verify their values by comparing the sizes of macromolecular coils determined by viscometry and dynamic laser light scattering;
2. To experimentally obtain surface tension isotherms at the «aqueous solution of branched PVA–air» interface by the tensiometric method and to interpret their profile;
3. To experimentally obtain wetting isotherms of the Teflon surface by aqueous solutions of synthesized branched PVA macromolecules using the goniometric method. Based on the experimental wetting isotherms, to construct isothermal dependencies of the work of adhesion and the work of wetting of the Teflon surface on the concentration of aqueous solutions of branched PVA of various viscosity-average molecular weights;
4. To determine the effect of the concentration and viscosity-average molecular weight of dissolved branched PVA on the rate constants and activation energies of the catalytic and non-catalytic stages of the oxidative polymerization of aniline;
5. To establish the effect of the viscosity-average molecular weight of branched PVA on the size of particles formed as a result of oxidative polymerization of aniline;

6. To demonstrate the fundamental possibility of using branched PVA as a steric stabilizer in the radical suspension polymerization of styrene.

The scientific novelty of the work:

1. An iterative method for calculating the viscosity-average molecular weights of products of linear PVA chain branching as a result of its chemical modification with epichlorohydrin in an alkaline medium has been developed;

2. It has been shown that with an increase in the viscosity-average molecular weight of branched PVA, its surface activity increases; however, a subsequent increase in the concentration of branched PVA leads only to a slight decrease in the surface tension of its aqueous solutions, which is presumably associated with the shielding of the «water–air» interface by adsorbed branched macromolecules;

3. A hypothesis has been put forward that the change in the wetting inversion point of the Teflon surface by aqueous solutions of linear and branched PVA is determined by the ratio of the factors of shielding the interfacial surface by already adsorbed branched macromolecules and the increase in the density of polar hydroxyl groups within the macromolecular coil as a result of chain branching;

4. It has been found that with an increase in the viscosity-average molecular weight of PVA caused by chain branching, a decrease in the size of particles of oxidative polymerization products of aniline in aqueous solution is observed, which may be a consequence of the increased density of hydroxyl groups within the macromolecular coil. The fundamental possibility of using highly hydrolyzed branched PVA as a steric stabilizer in the suspension polymerization of styrene has been demonstrated;

5. An increase in the values of the rate constants of the catalytic stage of oxidative polymerization of aniline with increasing concentration and viscosity-average molecular weight of branched PVA dissolved in the reaction system has been discovered and explained;

6. Assuming the formation of hydrogen bonds between the hydroxyl groups of PVA residues and the amino groups of the monomer, an equation has

been derived explaining the experimentally established inversely proportional relationship between the rate constant of the non-catalytic stage of oxidative polymerization of aniline and the concentration of branched PVA in the reaction system;

7. An increase in the activation energy of the catalytic stage of oxidative polymerization of aniline by 8–12 kJ/mol, as well as a change in its overall kinetic order from first to second upon increasing the temperature from 5°C to 15°C during the reaction in an aqueous solution of branched PVA, has been discovered.

Theoretical and practical significance of the work:

1. An iterative method for calculating the viscosity-average molecular weights of branched PVA has been developed;

2. The regularities of adsorption of branched PVA from aqueous solutions have been established;

3. The kinetic regularities of dispersion oxidative polymerization of aniline in the presence of branched PVA have been established;

4. The possibility of obtaining aqueous PANI and polystyrene dispersions using branched PVA as a stabilizer has been demonstrated.

The main provisions for the defense:

1. The iterative method for determining the viscosity-average molecular weights of synthesized branched PVA macromolecules and its verification by comparing the sizes of macromolecular coils calculated by the viscometric method and determined by dynamic laser light scattering;

2. The regularities of changes in surface tension at the «aqueous solution of branched PVA–air» interface depending on the concentration and viscosity-average molecular weight of branched PVA in aqueous solution, as well as the regularities of wetting of the Teflon surface by aqueous solutions of synthesized branched PVA macromolecules of various viscosity-average molecular weights and concentrations;

3. The kinetic regularities of oxidative polymerization of aniline in aqueous solutions of branched PVA of various viscosity-average molecular weights and concentrations;

4. The use of branched PVA to ensure the stabilization of aqueous PANI and polystyrene dispersions.