

POLYVINYLPIRROLIDONE AS A REACTING MODIFIER IN POLYMER CHEMISTRY

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Polyvinylpyrrolidone (PVP) is used by itself as a sorbent, a thickener of cosmetic ointments, and for encapsulation of medical drugs. Due its high surface energy, PVP is also an attractive (a promising) substance in the formation of metal nanopowders as well as silicate nanopowders from corresponding solutions. PVP keeps adsorbed drugs on the pyrrolidone rings of the macromolecule.

Macromolecule of polyvinylpyrrolidone in a free state has a helicoidal structure with pyrrolidone rings outside, that promotes the interaction of the peptide groups with substances by complex formation.

Polyvinylpyrrolidone is characterized by high complexation ability. It forms complexes with organic and inorganic electron-donor as well as electron-acceptor compounds. Complexes form highly polarized peptide groups of the pyrrolidone rings due to mesomeric effect. Specific role is played by complexes of PVP with vinyl monomers which polymerize in the presence of PVP.

Important and notable property of PVP is the ability to form complexes. This ability significantly influences the kinetic of polymerisation and the formation of a polymeryc matrix structure in the process of hydrogel synthesis.

As it has been shown PVP can form charge-transfer complexes with water-soluble vinyl monomers. The results of spectral analysis and quantum mechanical calculations with the application of package Chem 3D shows that $-C=C-$ bond of a monomer molecule, negative charge of which significantly changes, and nitrogen atom of the pyrrolidone cycle ($-N-$), the charge of which increases from +0,35 to +0,42, both participate in the formation of a complex.

The complex was characterized by the constant of complex stability (Kst), and its value increases with the presence of water or primary alcohol groups. Based on this information, the structure of a charge-transfer complex (CTC) with, for example, 2-hydroxyethyl methacrylate (HEMA) was substantiated.

The impact of the complexation on both the polymerization kinetics and the formation of a copolymer structure initiated by radical initiators has been studied. The activating effect of iron (II) and iron (III) sulfates has been revealed for the initiator-free polymerization of the formulation. An analytical approach to determining the molecular weight of the chain fragments located between two neighboring cross-linking nodes in the polymer network (M_n) has been developed depending on the values of the stability constant (Kst) for the charge-transfer complexes.

The rate constant of the polymerisation significantly depends on Kst of CTC. The polymerization rate increases with the increase of Kst of CTC with the maximum at the equimolar ratio of a proton donor (H_2O) and segments of PVP.

The results prove the matrix mechanism of polymerization – local concentration of monomer molecules activated with CTC on the chains of PVP.

Degree of grafting of PVP depends on the nature of a complex-forming solvent and the nature of an initiator of polymerization of HEMA:PVP compositions.

Matrix effect increases with the increase of hydroxyl group number in the solution and with the increase of the molecular weight of a proton donor. As a result, CTC with polyvinyl alcohol as a proton donor was found to have significant activating ability.

This method allowed to obtain hydrogels with higher mechanical resistance based on the combined matrix PVP:PVA. Complex based on the PVA and PVP shows the highest efficiency at the ratio of 2:1.

By free-radical thermo polymerisation of water soluble hydroxyalkylen (meth)acrylates in aqueous solution using water-soluble or alcohol soluble peroxide initiators, at the temperature of 50...70 °C. In this case, network structural parameters and water amount in the hydrogel depend on the amount of water in the reaction mass.

Based on the reactivity of HEMA:PVP composition, a stable hydrogel can be formed in the process of polymerisation in water solution when the amount of aqueous is 2-3 times higher than the mass of composition, that forms polymeric matrix. Resulting hydrogel doesn't release excess of water due to its high sorption ability of PVP-based polymeric matrix and significantly smaller ratio of macrochains crosslinks. However under the major excess of water resulting hydrogel has lower mechanical resistance.

At the same time is possibility of obtaining of homogenous blend of polycaproamide (PA-6) with PVP. This blend is characterized by a high degree of crystallinity and the higher temperature of crystallization.

Authors propose obtaining a nanocomposite based on the blend polypropylene – polycaproamide (PP/PA-6) with enhanced temperature resistance, using the positive effect of PVP and (montmorillonite) MMT on obtaining a homogeneous mixture and improving temperature characteristics of the composite. For this purpose, it is proposed at first to obtain a nanocomposite based on PA-6 with MMT, which is intercalated by PVP. Next, to obtain a blend based on PP and the synthesized nanocomposite. It is assumed that the application of MMT, intercalated by PVP, will contribute to the enhancement of thermostability of PA-6. At the same time PVP associated with PA-6, will contribute to an increase in the compatibility of polypropylene with polyamide, which will exclude the use of reactive compatibilizers with a complex chemical structure.

In the course of thermo gravimetric studies it was established that blends of PVP with PA-6, modified by the MMT/PVP mixture are distinguished by rather high thermal resistance.