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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF WATER-SOLUBLE AND WATER-SWELLING POLYMERS BASED ON VINYL ETHERS

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The scientific and technological aspects of water-soiuble and water-swelling polymers to be synthesized from the domestic raw materials of Kazakhstan are described. The application area of polymeric reagents in medicine, biotechnology, agriculture, enhanced oil recovery, ecology is also considered.

synthesis of vinyl ether monomers

The basic raw material to synthesize vinyl ether monomers is acetylene that is produced "Carbide"company in Kazakhstan and mono- or diatomic alcohols (or aminoalcohols) that are purchased mainly from Russia. The main scheme of production of vinyl ethers is as follows : calcium carbide→ acetylene→vinyl ethers (butyl vinyl ether, isobuty vinyl ether, and vinyl ether of ethyleneglycol, vinyl ether of ethyleneglycol, divinyl ether of diethyleneglycol, vinyl ether of monoethanolamine). At present "Carbide" company is able to produce vinyl. ethers about 1000 tons per year. The cost of monomers ranges from 1400 to 2000 $ per 1 ton.

Synthesis of water-soluble and water-swelling polymers[1]

The above-mentioned monomers behave a low activity in the course of radical initiated polymerization owing to donation of a lone pairs of electrons from oxygen to double bond.
For instance in the presence of radical initiators the oligomer products with the molecular weight $(1-2) \cdot 10^3$ are mainly formed, in the presence of acid catalysts the formation of polyacetales or stable complexes of ammonium type is occurred. In this connection the attention of researchers has been paid to find an available procedure to involve such monomers into the polymerization process. It is proved to be that the gamma-irradiation method is more effective to obtain both water-soluble and water-swelling (co)polymers. The formation of branched and a crosslinked structure under the action of gamma-irradiation mainly is connected with elemental reaction of chain transfer to the polymer. From the spin-trapping data it follows that polymers of vinyl ethers exhibit a high activity in the elimination reaction of hyldrogen from both main chain and side substitutes [2].

Gamma-irradiation technology of producing of water-soluble and water-swelling polymers

At present "Medpolymer" Ltd. venture established at the Department of High Molecular Compounds of Kazakh State National University produces with the help of small gamma-irradiation facility "RHM- γ-20"(working volume is 2 liters, irradiation dose is 170 rad/s) about 1 ton of wet gels per year. It is expected that the application of gamma-irradiation module with working volume 2 m^3 will considerably increase the efficiency of polymer production up to 100 tons per year. The basic technological lines or operations(blocks) to be mounted at the territory of National nuclear Center of the Republic Kazakhstan (Almaty) consist of:

· Rectification column and distilling apparatus for purification of monomers;

· Irradiation of reaction mixture by gamma-irradiation $source^{60}C_o$;

· Purification of polymer reagents;

· Producing of commercial produts.

The cost of final products will approximately be 2500-3000 $ per 1 tonn.

Stimuli-responsive characteristics of hydrogels [3-5]

Polymer materials that can reversibly respond to external conditions (pH, temperature, ionic strength, electric current, light etc.) are called as stimuli-responsive, "smart" or "intelligent" material. These properties stimulated research on the feasibility of such materials as artificial muscles, drug delivery systems, sensors, actuators, pumps etc. The ability of both linear and crosslinked polymers based on vinyl ethers to undergo phase or volume transitions in response to temperature, solvent and ionic composition, pH and DC electric field has been shown.

Application of hydrogels in medicine and biotechnology [6-8]

Polymeric hydrogels due to a unique physico-chemical and medical-biological properties (the ability to absorb biological liquids, biocompatibility, soft tissue-like consistence, porous st커cture, permeability with respect to large and small molecules, compatibility with blood, nontoxity etc.) nowadays already find wide and effective application in various ares of medicine, pharmacology, biology and biotechnology. Nowadays << Polygel >> is successfully used in a number of clinics and medical scientific centers of the Republic of Kazakhstan. Some aspects of the Republic of Kazakhstan. Some aspects of biomedical application of hydrogels based on vinyl ethers of glycols are considered below.

Poymer hydrogels as ointments and contact medium for ultrasonic diagnostics

Medical-biological tests of hydrogels on the basis of vinyl ethers show that they have not any irritating and toxicity action and good compatibility with tissue. It has been established that they can serve as carrier of sulfanilamide drugs, antibiotics, anesthetics, antiseptics and biological active substances. Microbiological tests show that hydrogels do not influence into the activity of drugs. Experiments on animals have shown that the hydrogel-based ointments are more effective than analogous fatty and hydrocarbon ones. The treatment of burned wound by hydrogel ointments enhances the healing up to 5-7 days in comparison with control experiments. This is connected with aspiration-drainage function of hydrogels, e.g. sorption of purulent exudate and phlogogenic liquids that promotes fast clearing and accelerated healing. << Polygel >> composition is used now as contact medium for ultrasonic diagnostics and lithotropcy of gastrolith and kidneys.

Implants and autonomic skin tensile systems

One of major areas of application of hydrogels is using them as materials for endoprothesis of soft tissue in regenerating and plastic surgery. Clinical tests provided at the Institute of Surgery (Moscow) (in vitro and in vivo) show that hydrogels maintain their structure during several years with respect to infected media (staphylococcus, streptococcus). Control tests showed that polyhydroxyethylmethacrylate and polyacrylamide gels are unstable and degrade in such infected media. Hydrogels based on vinyl ethers of glycols was also used as implants-protechors and autonomic skin-tensile materials. At definite conditions the skin-tensile effect reaches up to 15 times that allows to obtain the donor part of skin. Hystological and morphological show that at the initial state the increasing of skin surface occurs as a result of swelling pressure of implant and after 2-3 months this process proceeds mainly as result of growth the connective tissue around the implanted skin-tensile. Last years we have worked out the hydrogel composition for correction of volume and form of various anatomic organs and soft tissue. Hydrogel with required consistency can be injected into the necessary part of organism with the help of syringe. The positive cosmetic effect has already been obtained on dogs, rabbits. The atraumatic effects and the absence of afteroperation hems are the main advantage of hydrogel implants. The realization of manipulations is possible under the local anesthesia in ambulatory conditions.

Drainage, embolization and abturation materials

A new type of hydrogel drainages for treatment of abscess and phlegmon of soft tissue were obtained on the basis of untoxic and biocompatible crosslinked polymers of vinyl ethers of glycols. Drainage is represented as atraumatic plate with site 3x3x20 mm constructed from the soft, elastic hydrophilic polymer material possessing high sorption ability with respect to biological liquids (the swelling degree is 100 g/g); the destructive stress up to 3 kG/cm^2, the relative expansion is about 120%. Drainage provides an active osmosis of purulent substrate and oedematic liquids and prevents in긔ammation of soft tissue. Clinical tests show that the application of drainage promotes an essential shortening of surgical treatment of abscess and phlegmon. An ability of hydrogel to swell in blood allows using them in vascular surgery. Emboli made from hydrogel in blood vessel swells during several minutes, providing the effective embolization and termination of a bleeding. One of a urgent problem in pulmanology is the treatment of primary and afteroperational insolvency of lungs and bronchial fistulas. Existing methods of conservative treatment of these pathologies are directed on obturation of a zone of infiltration of air into the pleuritic cavity. Hydrogels containing chlorhexydine (antiseptic) provides the sealing, and does not cause irritation of bronchus and reflector cough; behave adhesive and hydrophilic properties, static character, i.e. they are not displaced in bronchial tree; render the local medical operation during long time. Finally the realization of manipulation does not require high qualification and special equipment. Immobilization of catalase within "intelligent" hydrogels has lead to regulate "on/off" activity of enzyme. concentration and fractionation of proteins using stimuli-sensitive character of hydrogels is in progress.

Application of hydrogels as moisture absorbers in agriculture [9]

The preliminary experiments on application of hydrogels as regulator of water regime showed that about 50-100 Kg of dry gel with the swelling degree 100 g/g is enough to treat 1 hectare of soil if the cultivation zone is dry and about 20 Kg of dry gel if the cultivation zone is meliorate. Table shows the effect of hydrogels on the biometrics parameters of food grains.

Hydrogel amount, g/kg	Vegetation period, days	Plant height, cm	Dry biomass, mg
No gel	7	7,5±0,6	14±0,3
11	12	9,5±0,7	16±0,6
28	14	13,5±1,2	21±0,6

Enhanced oil recovery with the help of hydrogels

It is well known that water-soluble and water-swelling polymers are especially suited for various oilfield applications including a number of enhanced oil recovery (EOR) processes. Polymeric reagents based on vinyl ethers of glycols can be used as drilling mud additives for fluid loss control, shale stabilization, flocculation, filtration control etc. under harsh conditions of high temperature (25-150 ℃ and high salinity (10%) and/or hardness.

Application of water-soluble and water-swelling polymers to solve some ecological problems [10]

There are several ecological problems connected with rehabilitation of soil and water from radionuclides in Kazakhstan (Semipalatinsk region) as well as with purification of industrial waste. The ability of interpolymer complexes (IPC) - products of interaction of two macromolecules - to form thin films on the surface of soil can be applied for protection of soil from water and wind erosion. The preliminary experiments showed that the sand soil treated by 1% aqueous solution of IPC does not erode at the velocity of wind 10-15 m/s. The aggregated soil keeps the rainfall up to 550-650 mm and the temperature variation from -30 to +30 ℃ more than 1 year. The average value of erosion of the aggregated soil is less than 0.2% whereas the erosion of untreated one reaches up to 74%. It has been shown that cationic and amphoteric (linear and crosslinked) polymers are able to bind heavy metal ions in both cationic and anionic forms. Such sorbents can be used for recovery of heavy metal ions including radionuclides from the industrial waste. Cyclic swelling and shrinking properties of polyelectrolyte hydrogels under the action of direct current are effective way to purify of waste waters from the inorganic and organic pollutants.

Conclusion

One can expect that the producing of water-soluble and water-swelling polymers from the domestic raw monomers of Kazakhstan will provide to solve successfully some scientific, technological and industrial problems.

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