

DESIGN OF "INTELLIGENT" POLYMER MATERIALS BASED ON VINYL ETHERS

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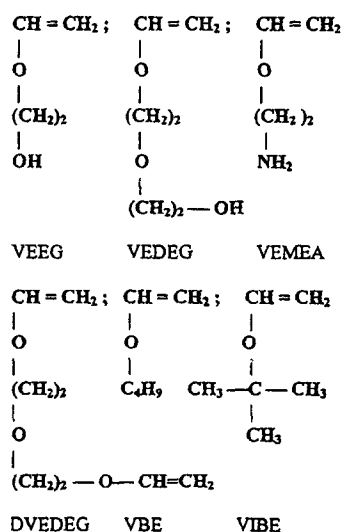
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Vinyl ethers of glycols and aminoalcohols are specific and perspective monomers to synthesize polymer materials that can reversibly respond to external conditions. Some fundamental aspects and application area of "intelligent" polymer materials are summarized below:

Synthesis of linear and crosslinked poly(vinyl ethers)

Nonionic, cationic, anionic and amphoteric (co)polymers have been synthesized by gamma-irradiation polymerization of vinyl ethers [1].



where VEEG, VEDEG, VEMEA, DVEDEG, VEE and VIBE are abbreviations of vinyl ether of ethyleneglycol, vinyl ether of diethyleneglycol, vinyl ether of ethanolamine, divinyl ether of diethyleneglycol, vinyl butyl ether and vinylisobutyl ether respectively.

During 10 years our research group have intensively been working on radiation chemical synthesis and characterization of (co)polymers of vinyl ethers of glycols and aminoalcohol. An idea to apply a radiation induced polymerization method offers some advantages: it is a simple and additive-free process at all temperatures, the degree of crosslinking can easily be controlled by irradiation conditions. The radiation methods are especially attractive for synthesis of hydrogels with potential biomedical application because it is possible to combine into one step two processes: the synthesis and sterilization of the product, and to get with good mechanical characteristics. The reactivity of vinyl ether monomers and quantitative information about monomers and quantitative information about the kinetics and mechanism of radical reactions were obtained by spin-trapping method[2].

Thermo-, pH- and electrosensitive hydrogels

The preparation methodology of temperature and pH-sensitive hydrogels with balanced hydrophilic/hydrophobic groups has been worked out[3]. The aqueous solution of linear copolymers

consisting of VEEG (VEDEG) and VBE exhibit either low or upper phase transition temperatures due to the destruction of hydrogen bonds and the enhancement of hydrophobic interaction in aqueous solution (Fig.1).

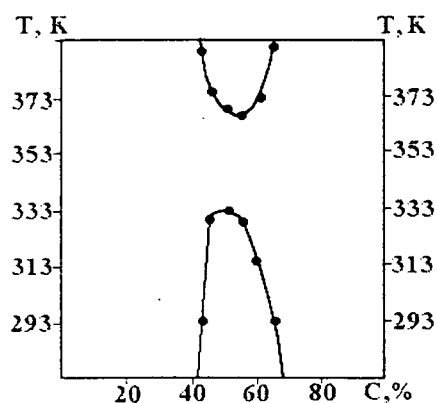


Fig. 1 Phase diagram of VEEG-VBE in water

The phase separation temperature decreases with the increasing of the molar part of butyl radicals in copolymers as a result of strengthening of hydrophobic interactions between butyl fragments. The swelling equilibria of a series of poly(butyl vinyl ether-co-acrylic acid) hydrogels at different pH values have been studied. Swelling degree of copolymers is low at low pH because carboxylic groups uncharged and high at high ionization degree of carboxylic groups. Moreover the swelling degree become lower and the inflection points shift to higher pH value when the content of vinyl butyl ether in copolymers increases. This is due to the stabilization of collapsed structure of gels by hydrophobic interactions of butyl radicals.

The combination of the temperature-sensitivity with pH-sensitivity in one and the same materials has lead to design a new family of "hydrid intelligent" polymers [4]. For polyampholyte hydrogels the swelling-deswelling, deformation and oscillation-relaxation phenomena leading to periodic change of mass, size and

shape of the specimen under the influence of DC electric field have been found. The time dependence of mass change of polyampholyte gels under the influence of DC electric current is shown in Fig.2.

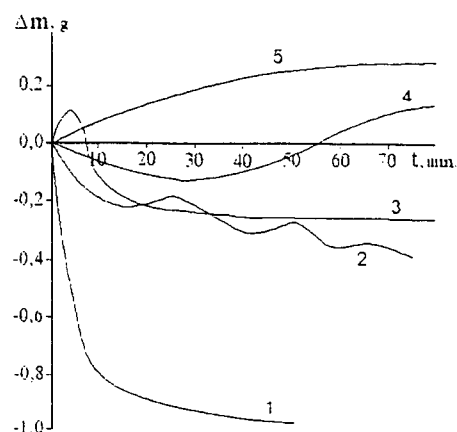


Fig.2. Kinetic curves of relative mass change of polyampholyte gels under the influence of electric current

In cationic (pH = 3,0, curve 1) and anionic (pH = 6,2, curve 3) forms hydrogel gradually shrinks [5]. Under the action of DC electric field the redistribution in double electric layer occurs and the shrinking of the specimen from both side takes place. Ampholytic gel specimen swells at the isoelectric point (IEP) (Fig.2, curve 5). This phenomenon observed for the first time can be interpreted as follows : at the IEP the neutral network under the action of DC is polarized. As a result at the ends of specimen adjoining to cathode and anode sides the density of network charge is increased. The increased charges should be compensated by outer counterions that in turn cause a water flow inside the system and swelling. At the IEP, at intermediate values of ionic strength $2 \cdot 10^{-2} < \mu < 7,5 \cdot 10^{-3}$ polyampholyte gels oscillates (Fig.2, curves 2,4). These types of curves can be represented as sequential realization of :

- relaxation phenomenon, when Δm depends on time exponentially and consequently there is linear dependence between dm/dt and Δm (Fig.3);

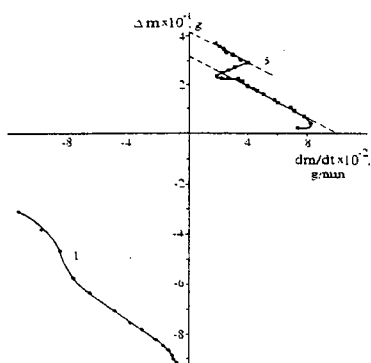


Fig.3 Phase portraits of curves 1 (1) and 5 (5), taken from Fig.2.

- oscillation phenomenon, when Δm depends on time harmonically. In this case phase portrait in coordinates $dm/dt = f(\Delta m)$ is ellipsoidal (Fig. 4).

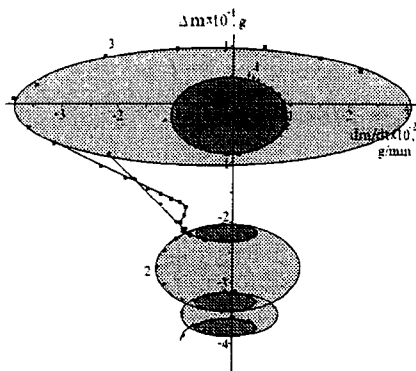


Fig. 4. Phase portraits of curves 2 (2) 3 (3) and 4 (4), taken from Fig. 2.

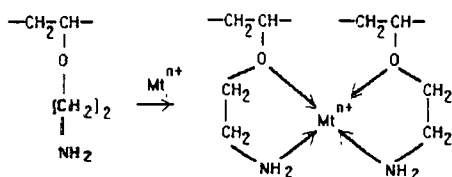
The oscillation-relaxation regimes are characterized by numerical values of $1/\tau$ (where τ is relaxation period). For relaxation movement this parameter is equal to tangent of slope of linear part, for oscillation movement - to the ratio of semiaxis of ellipse.

Interpolymer complexes and membranes

An introduction of butyl vinyl ether fragments into the structure of VEEG promotes the complexation process with respect to poly(carboxylic acids) and vice versa PolyVEEG can also interact with copolymers of VBE and acrylic acid [6]. The combination of electrochemical, hydrodynamic and spectroturbidimetric methods shows that the stoichiometric interpolymer complexes (IPC) stabilized by cooperative system of hydrogen bonds are formed. The heating of IPC films at 383 K during 4 hours leads to the formation of insoluble but swellable in polar solvents membranes crosslinked by ester bonds. Two-dimensional interpolymer membranes was obtained by carrying out the interpolymer reactions on a dimeric interface [7,8]. The mechanism of IPC formation on the dimeric interface is similar to the process taking place in aqueous solution. However, the interface layer limits a fully mixing of the components and the reaction rate is controlled by diffusion of interacting macromolecules towards the interface. Complexation of organophilic polymers with Cu^{2+} ions is accompanied by the formation of interfacial blue film with the maximal absorbency at $\lambda = 680-700$ nm. table represents IR and Raman spectra of polymer-copper complex.

Bond	Frequency, cm^{-1}		
	IR	Raman	IR(complex)
$\nu_s(\text{C-O-C})$	1090	1090	1060
$\nu_{as}(\text{C-O-C})$	1210	1210	1200
$\nu(\text{C-N})$	1325	1323	1320
$\delta(\text{C-H})$	1465	1466	1465
$\nu_s(\text{N-H})$	3315	3320	-
$\nu_{as}(\text{N-H})$	3387	-	3350

Shifting of C-O-C and NH bands to lower frequency region confirms the participation of oxygen and nitrogen atoms in complexation reaction. Parameters of ESR spectra ($g_{\perp} = 2,033$, $g_{\parallel} = 2,260$, $A_{\parallel} = 170$ Oe) suggest the participation of copper(II) ions in five-membered chelate cycle as shown below:



Thin films and membranes prepared from the IPC can be applied in membrane technology to separate water-organic and organic-organic mixtures by pervaporation method.

Ion-conducting elastomeric materials

One can expect that polymers based on vinyl ether monomers will also be able to solvate alkali metal ions through donor-acceptor interactions similar to poly(ethyleneglycol). Moreover, divinyl ether of diethyleneglycol itself which repeats ethyleneoxide fragments can give gel structures with wide spectrum of morphology. Such three-dimensional macromolecular architectures can simply be converted into the solid elastomeric electrolytes by an introduction of specific alkaline salts within their structure (either during polymerization process or soaking of the prepared

gels in concentrated solution of desired salts in selected polar organic solvents).

Elastomeric polymeric electrolytes with ionic conductivity 10^{-7} S/cm have been obtained by incorporating of sodium perchlorate into the three-dimensional structure polyDVEDEG.

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