

# EFFECT OF MAGNETIC FIELD ON THE STRUCTURE FORMATION AND PROPERTIES OF HYDROXYETHYLMETHACRYLATE / POLYVINYLPIRROLIDONE COPOLYMERS

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## Abstract

*The effect of a permanent magnetic field on the polymerization kinetics and structural parameters of a hydrogel network on the basis of 2-hydroxyethylmethacrylate with polyvinylpyrrolidone compositions has been investigated. It has been shown that the magnetic field activates matrix polymerization of mentioned compositions and assists in the structure formation of copolymers with a smaller crosslink density. The efficiency of the developed polymeric materials for production of ultrathin contact lenses "Glipox" has been confirmed.*

**Keywords:** polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, magnetic field, matrix polymerization

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## Introduction

The polyvinylpyrrolidone (PVP) / 2-hydroxyethylmethacrylate (HEMA) cross-linked copolymers are successfully applied in biomedical practice, including the manufacture of endoprostheses, contact lenses, implants, dental compositions etc. [1]. They are obtained, basically, via thermo-, photo- and radiation polymerization in the presence of initiators or without them [2,3]. The main regularities of such syntheses and reactions topological schemes were developed at the Department of Chemical Technology of Plastic Processing of the Lviv Polytechnic National University; the possibility of polymerization process activation both under homogeneous conditions and on the phase boundary has been revealed as the result of the charge-transfer complex formation into the system of monomer – polymeric matrix – protophobic solvent.

It is foreseen that under polymerization the reactivity of polymeric matrix may be strengthened by orientational, diffusive and solvation effects generated by external energy fields, permanent magnetic field in particular. At the same time the polymerization processes under the influence of the magnetic field (MF) have not been studied thoroughly, though they are important both from scientific and practical points of view. Therefore, the researches in this direction foresee the deepening of theoretical conceptions about polymer formation and enhancement of possibilities for synthesis of new polymers and modification of existing ones resulting in the new non-traditional syntheses of perspective hydrogel materials on the basis of PVP copolymers.

## Aim of the work

The aim of this work is to investigate the effect of the permanent magnetic field on the polymerization kinetics, structure formation and properties of HEMA / PVP copolymers.

## Materials and methods

HEMA (Bisomer) used for polymerization was purified by vacuum distillation (residual pressure is 130 N/m<sup>2</sup>, T<sub>boil</sub> = 351 K). Also ethylene glycol dimethacrylate (DMEG; Merck) (T<sub>boil</sub> = 343 K under the residual pressure of 400 N/m<sup>2</sup>) and high purified polyvinylpyrrolidone (PVP; AppliChem GmbH) with mol. wt. 28·10<sup>3</sup> were used. Benzoyl peroxide (BP), having been recrystallized twice from methanol, was used as the initiator of polymerization.

The permanent magnetic field was created by the powder magnets "Niomax" on the basis of ferrum-neodymium-boron Fe<sub>14</sub>Nd<sub>2</sub>B which were characterised by the following properties: the residual magnetic induction, B<sub>r</sub> = 1.15 T; the coercive force on magnetization, jH<sub>c</sub> = 400 kA/m; the maximum magnetic energy, (BH/2)<sub>max</sub> = 240 kJ/m<sup>3</sup>. Magnets had the form of disks with a diameter of 97 mm and thickness of 20 mm which were clasped by magneto-conductor with one mobile pole. The intensity of magnetic field was regulated by a free clearance between disks.

Structural parameters of the polymeric net in hydrated state were estimated by means of the molecular weight of macrochain section (M<sub>n</sub>) between neighboring cross-linking nodes or by means of cross-linking density (ν = 1/M<sub>n</sub>) determined using module of high elasticity.

The molecular weight of chain section between neighboring cross-linking nodes was calculated by the following formula [4]:

$$M_n = \frac{L^5 \rho_p v_s}{0,5 - \mu}$$

where:

L – coefficient of linear swelling;

ρ<sub>p</sub> – polymer density, kg/m<sup>3</sup>;

v<sub>s</sub> – molar volume of the solvent, m<sup>3</sup>·kg<sup>-1</sup>·mol<sup>-1</sup>;

μ – parameter of polymer-liquid interaction

$$\mu = 0,5 - \frac{v_s \sigma_\infty L^4}{RT(\lambda^2 - \lambda^{-1})}$$

σ<sub>∞</sub> – equilibrium tension, kgf/m<sup>2</sup>

$$\lambda = 1 + \varepsilon, \quad 0 < \varepsilon < 0,3,$$

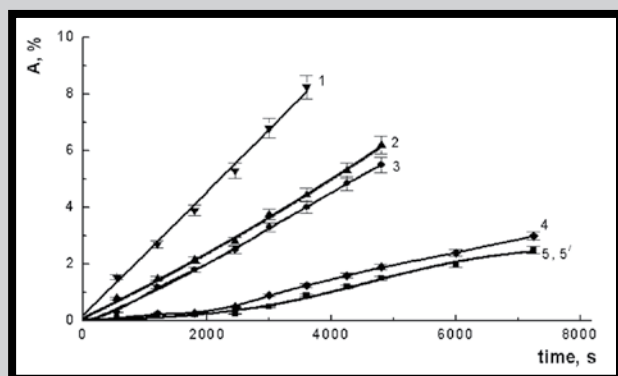
ε – equilibrium tension strain.

Polymerization kinetics was investigated using dilatometric analysis [5], composition of copolymers were investigated by the procedures described in [6] and permeability of polymers for water and NaCl was investigated by the procedure offered by Karelin [7].

## Results and discussion

HEMA polymerization was studied in the presence of PVP at the ratio HEMA:PVP = 10:0...7:3 weight parts (wt.p.) in the range of magnetic field intensity H = 0...310 kA/m and temperatures 303...333 K. The influence of MF on homopolymerization kinetics of HEMA was studied previously at the ratio monomer : initiator = 10:0,03 wt.p. at 313 K. It was determined that homopolymerization of HEMA both in a magnetic field, and without it proceeds with the same rate (FIG. 1, curve 5 and 5'), i.e. it is possible to ascertain that MF does not influence the HEMA homopolymerization.

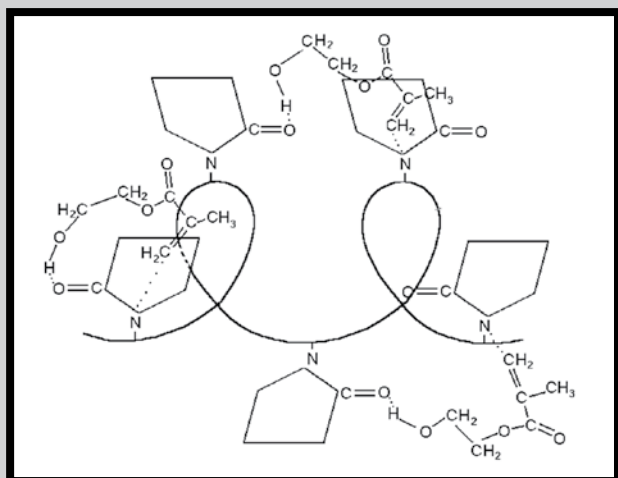
At the same time, MF accelerates polymerization in the case of PVP-containing compositions with peroxide as well as without it. The polymerization rate increases proportionally to the increase of polymeric matrix amount in the composition, the same as for thermoinitiated polymerization (FIG. 1).



**FIG. 1. Dependence of polymer A yield upon mixture composition.**

[PB] = 0.3%. HEMA:PVP mixture composition, wt. p.: 1 - 7:3; 2 - 8:2; 3,4 - 9:1; 5,5' - 10:0; MW<sub>pvp</sub> = 28000; Intensity of magnetic field H, kA/m: 1...3, 5 - 310; 4, 5' - 0; T = 313 K.

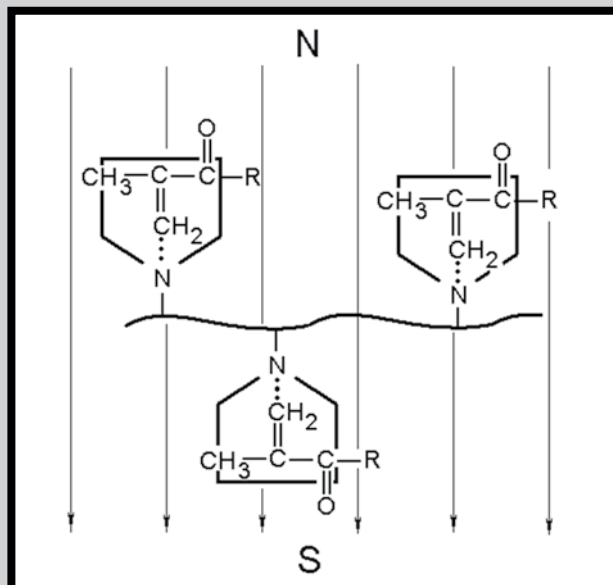
The mentioned phenomena may be explained using previously determined mechanism of matrix polymerization of (meth)acrylates in the presence of PVP. The process evidently is accompanied by monomer molecules salvation over PVP-matrix with the charge-transfer complex formation [8] (SCHEME 1).



**SCHEME 1. Complexation between HEMA and PVP.**

The dissociation of double bond in monomer molecules is facilitated and the polymerization rate increases due to the complex formation. On the other hand, probably [9], the orientation in the magnetic field is caused, mainly, by the anisotropy of molecules diamagnetic susceptibility. The single bond has the greatest diamagnetic susceptibility when the field is directed along a bond axis; therefore the molecule is orientated perpendicularly to a field. On the contrary, the double bond has the greatest value when the field is directed perpendicularly to a bond axis and the molecule is orientated in parallel to the magnetic field. In the article [9] it was supposed that the peptide bond should have the anisotropy of a diamagnetic susceptibility because it partially has the character of the double bond due to the presence of two resonance structures. Thus, the peptide bond anisotropy has the same sign and almost the same value as the double bond.

Taking into account all above mentioned and the similarity of the peptide bond with the bond in the PVP macromolecule, it is possible to foresee that the plane of the single bond in the PVP macromolecule tends to be oriented perpendicularly to MF, and the bond connecting a cycle with the main chain is parallel to MF (as well as the plane of the double bond C=C in the monomer) (SCHEME 2).



**SCHEME 2. The components orientation of monomer-polymer composition in MF.**

Also it is possible to foresee that aggregation of monomer molecules near the polymeric matrix would be easier owing to such orientation under MF influence. This fact, in turn, facilitates the access of monomer molecules to the active groups of PVP macromolecules strengthening in such a way the complexation, which is the factor of polymerization acceleration [8]. As a result of the oriented placing of macromolecules the mobility of formed associates decreases, the best kinetic conditions of chain growth are created, and also the initial conditions of the structure formation of (co)polymers with the arranged distribution of macrochains are established.

During polymerization in the solution the nature of a solvent and its properties, among which dielectric constant ( $\epsilon$ ) is the determining factor, have the great influence on the polymerization rate (TABLE 1). The researches have shown that the polymerization rate of the HEMA / PVP compositions decreased in the following row: water ( $\epsilon = 78.3$ ) > dimethyl sulfoxide (DMSO) ( $\epsilon = 46.6$ ) > ethylene glycol (EG) ( $\epsilon = 37.7$ ) > butanol ( $\epsilon = 17.7$ ).

**TABLE 1. Effect of magnetic field intensity (H) and solvent dielectric constant ( $\epsilon$ ) on the polymerization rate (V) of compositions with PVP (T = 313 K).**

№	Composition *	H, kA/m	$\epsilon$	V, mol·dm <sup>-3</sup> ·s <sup>-1</sup>
1	HEMA:PVP	0		4.7·10 <sup>-5</sup>
2		310		11.4·10 <sup>-5</sup>
3	HEMA:PVP:H <sub>2</sub> O	310	78.3	8.8·10 <sup>-6</sup>
4	HEMA:PVP:DMSO	310	46.6	5.2·10 <sup>-6</sup>
5	HEMA:PVP:EG	310	37.7	2.3·10 <sup>-6</sup>
6	HEMA:PVP:butanol	310	17.7	1.3·10 <sup>-6</sup>

\* – HEMA:PVP: solvent :PB = 9:1:10:0,02 wt. p.

**TABLE 2. Structural characteristics of the net and properties of copolymers synthesized in MF (T = 313 K, [PB] = 0.3 mas.%).**

HEMA:PVP, wt. p.	MF intensity, kA/m	M <sub>n</sub> , kg·mol <sup>-1</sup>	v=10 <sup>2</sup> /M <sub>n</sub> , mol·kg <sup>-1</sup>	D <sub>NaCl</sub> ·10 <sup>12</sup> , m <sup>2</sup> /s	F*, MPa	T <sub>v</sub> *, K
10 : 0	0 310	6.2±1.0 17.3±2.0	16.1 5.8	0.83 0.94	200±5 278±5	357±1 378±2
9 : 1	0 310	7.0±1.0 9.5±1.0	14.3 10.5	0.89 1.00	219±5 258±5	365±1 377±1
8 : 2	0 310	11.3±1.0 11.9±1.5	8.9 8.4	2.11 2.61	288±5 333±8	369±1 383±2
7 : 3	0 310	11.7±1.5 14.6±1.5	8.6 6.9	3.49 4.17	296±7 340±8	372±1 385±2

M<sub>n</sub> - molecular weight of the net fragment; v - cross-linking density; D<sub>NaCl</sub> - coefficient of NaCl diffusion through the hydrogel; F - surface hardness; T<sub>v</sub> - heat resistance by Vicata,  
\* - properties in the solid state, others - in the equilibrium swelling state.

On the basis of experimental investigations the basic kinetic parameters of the polymerization reaction (rate constants, reaction orders, activation energy) for the composition HEMA:PVP = 9:1 wt.p. in MF have been calculated. The effective activation energy of the process in DMSO is 46 ± 2, in water – 39 ± 2 kJ/mol. These values are considerably lower in comparison with polymerization of such systems without MF (67 and 57 kJ/mol, respectively). The received values testify the active role of solvents in the polymerization process in MF, with changes depending on their dielectric constant.

At the same time, it has been established that MF essentially influences the crosslinking during HEMA homopolymerization. In the MF crosslinking density considerably decreases compared with polymerization of PVP-compositions (TABLE 2), though MF practically does not affect the homopolymerization kinetics of HEMA.

The obtained dependences correlate with above mentioned orientation scheme of the components of monomeric composition in the magnetic field and are caused by MF effect on the aggregation of monomer molecules due to the polarising and orientational phenomena. Since the planes of C=C double bonds of HEMA, as well as of ethylene glycol dimethacrylate (DMEG) which is responsible for the formation of the structural network at HEMA polymerization are oriented in parallel to the external magnetic field, the best kinetic conditions of chain growth in the reaction of binary copolymerization of HEMA with DMEG are created. Therefore the part of the latter component decreases in crosslinking reaction and copolymer with less crosslinking density (higher value of M<sub>n</sub>) and the better operational properties is formed (TABLE 2).

The copolymers operational properties and their interdependence with the structure and obtaining conditions have been examined in order to develop the synthesis technology for the production of medical wares, including contact lenses. It has been established that MF with the intensity of 310 kA/m increases sorption ability by 10...15 % and permeability of copolymers for water and soluble low-molecular substances (TABLE 2), which is one of the basic characteristics for estimation of duration and ophthalmic comfort of the lenses. The increase of surface hardness of the synthesised in MF copolymers (which determines their fitness for mechanical treatment) compared with those obtained via thermopolymerization (from 200 to 278 MPa for homopolymer and from 210...296 to 231...340 MPa for copolymers depending on their composition), is determined by the fact that under MF conditions the polymer with a more ordered and less defective structure is formed. The researches have confirmed the possibility to obtain hydrophilic polymers with the increased physico-mechanical properties in the constant MF with the following mechanical treatment.

The results of the investigations concerning the MF effect on the structure formation of copolymers have been used to obtain hydrophilic polymers necessary for production of ultrathin contact lenses "Glipox" and accommodative crystalline lenses. The properties of the "Glipox" material are given in TABLE 3.

The lenses have successfully passed the industrial and toxicological tests. They are stable to the action of detergents and disinfectants and stand sterilization in water without changing their optical and physico-mechanical properties. The lenses are produced with a refraction from – 25 to +18 D, the thickness in the centre – from 0.04 to 0.10 mm depending on the refraction. Thus it is necessary to pay attention to the important property of lenses to keep the form without curling and high optical properties even at the least thickness.

**TABLE 3. Technical characteristics of the contact lenses "Glipox" in equilibrium swelling state.**

Technical features and its value	Value
Minimal thickness of the lens in the centre, mm	0.04
Tenacity, MPa	6.9
Elasticity, %	69
Water content, %	38
Permeability of light, %	96
Permeability* of NaCl, mol·m <sup>-2</sup> ·h <sup>-1</sup>	264
* Permeability* of water, m <sup>3</sup> ·m <sup>-2</sup> ·h <sup>-1</sup>	76.3·10 <sup>-3</sup>
* – for minimal thickness	

## Conclusion

It has been determined the active effect of permanent magnetic field on the polymerization kinetics of HEMA / PVP compositions and the formation of more ordered structure of copolymers with less crosslinking density and better properties. It has been used for technological implementation of polymeric material "Glipox" used for ultrathin contact lenses.

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