

*Volodymyr Skorokhoda, Yuriy Melnyk, Natalia Semenyuk
and Oleh Suberlyak*

STRUCTURE CONTROLLED FORMATION AND PROPERTIES OF HIGHLY HYDROPHILIC MEMBRANES BASED ON POLYVINYLPIRROLIDONE COPOLYMERS

*Lviv Polytechnic National University,
12, S. Bandera str., 79013 Lviv, Ukraine; vskorohoda@yahoo.com*

Received: August 29, 2011 / Revised: September 19, 2011 / Accepted: December 20, 2011

© Skorokhoda V., Melnyk Y., Semenyuk N., Suberlyak O., 2012

Abstract. Polymerization of hydroxyalkyl(meth)acrylates with polyvinylpyrrolidone has been investigated. Thus highly hydrophilic membranes have been obtained and several properties have been investigated including polymerization rate, viscosity, extinction, water permeability of the membranes, their tensile strength and tensile elongation at break. Parameters characterizing complex formation between monomer and polyvinylpyrrolidone are related to structural parameters of resulting copolymer networks. Effective methods of controlling structures as well as properties of highly hydrophilic membranes have been defined.

Keywords: membrane, polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, penetrability, hydrophilicity.

1. Introduction

Polyvinylpyrrolidone (PVP) and hydroxyalkyl (meth)acrylates (HAMA) cross-linked copolymers are widely used in biomedicine, namely for the production of corrective contact lenses, (hemo)dialysis membranes, implants, leather substitutes, systems of drugs controlled release, and more [1, 2]. The operational and technological properties of such copolymers are determined by their structures and network structural parameters. Therefore the search for effective methods of controlled formation of PVP copolymers structure is of significant scientific and practical interest.

Our important aim was determination of factors controlling structures and properties of PVP/HAMA copolymers.

2. Experimental

2-hydroxyethylmethacrylate (HEMA; Bisomer) was purified by distillation under vacuum (residual pressure 130 N/m², boiling temperature 351 K). High-purified PVP (AppliChem GmbH) with molecular weight of (10–28)·10³ was used. Polymerization was initiated by potassium persulphate which was twice recrystallized from an aqueous solution. Hydrogel membranes were obtained combining the membrane formation stage and polymerization stage in the solution of one or more solvents (mostly in water). Before the experiments membranes were hydrated in water until the equilibrium state was achieved.

The composition and structural parameters of hydrogel network (molecular mass of network internodal fragment M_n) were investigated in accordance with procedures developed earlier [3]. The graft efficiency f was calculated as the ratio of grafted PVP amount to the total amount of PVP in the initial mixture.

Average molecular mass of chain sections between adjacent cross-link nodes was determined using the following formula [4]:

$$M_n = \frac{L^3 r_p n_s}{0.5 - m} \quad (1)$$

where L is the coefficient of linear swelling; r_p is polymer density in kg/m³; n_s is a molar volume of the solvent in m³/(kg·mol); m is a parameter characterizing polymer + liquid interactions. We have

$$m = 0.5 - \frac{n_s S_\infty L^4}{RT(I^2 - I^{-1})} \quad (2)$$

where S_{v} is the equilibrium tension in kgf/m^2 ; R is the gas constant and T is the thermodynamic temperature. We further have

$$l = 1 + e, \quad 0 < e < 0.3 \quad (3)$$

where e is the equilibrium tension strain.

Complex formation between HEMA and PVP was studied by means of optical density change D depended upon the components ratio [5]. A strong dependence of optical density upon the components ratio indicates complex formation with charge transfer [4]. To determine the coefficient of complex stability K_c , the relation $[\text{PVP}] \cdot l/D = f(1/[M])$ was plotted; here $[\text{PVP}]$ is PVP concentration, l is the thickness of the absorbent layer, $[M]$ is a monomer concentration. The intercept of the line at the ordinate axis corresponds to the inverse value of the extinction coefficient l/ε while the slope represents $1/\varepsilon \cdot K_c$.

Mechanical properties were determined using a break method by means of Kimura Machinery tester model 050/RT-6010, according to the procedure described in [6]. The machine has a round pin indenter for the film break what allows working in aqueous media. Diffusive permeability of synthesized membranes for water and a model substance dissolved in it without external pressure was determined using a laboratory osmometer according to a procedure described by Karelin [7].

The solutions viscosity was determined in accordance with standards using a VPG-2 viscosimeter at 293 K.

3. Results and Discussion

Pavlyuchenko and Ivanchev [1] discussed possibilities of network copolymers synthesis based on PVP and HAMA with a structure (composition and density of the network) control exercised by varying the composition of the starting materials. The structure largely determines physical, mechanical and more importantly the sorption-diffusion properties of the polymers. In turn, these properties determine practical applications as membranes for a variety of purposes. Essentially, the copolymer structure is determined by PVP concentration in the initial mixture. PVP partially reacts during polymerization and partially is washed out during hydration. As a result of PVP washing out and structure "loosening" related to its increased concentration in the initial mixture, the copolymers porosity increases and affects the penetration. However, such a method of porosity control leads to non-uniformity of porosity throughout the volume because of regular conversion heterogeneity and possible local fluctuations of PVP macromolecules in a monomer medium. Moreover, such a method of the porosity increase is non-efficient because of over expenditure of expensive PVP.

The other prevailing method of hydrogels porosity control is polymerization in the presence of varying amounts of solvent. In such a case the porosity essentially depends on the solvent amount in the initial mixture keeping the PVP monomer amount constant; we have discussed this situation in an earlier paper [6]. The network density is represented by the molecular mass of the internodal fragment M_n ; see again Eq. (1). M_n is a measure of penetration if structural defects are absent. The defects may be formed at low concentrations of the solvent. However, if the solvent content exceeds the maximum absorption capability by polymeric matrix via swelling, a phase separation is observed. The result is film blooming that limits the synthesized polymers application in those cases when high transparency (e.g. for contact lenses) is needed along with a good penetration. A solvent which is non-absorbed by the polymeric matrix during segregation process is found in its free state forming additional cells ("defects") - the amount and sizes of which depend upon the volume of dispersive medium. The sizes of "defective" pores are not easily controlled and depend only upon physical factors- as it was discussed earlier [6].

Once formed, effective pores cause the increased penetration because their sizes, as a rule, considerably exceed the sizes of capillaries in the polymeric matrix. Therefore, the solvent free volume is the channel, through which a great amount of diffusing compound diffuses. Thus, compounds with larger molecular sizes can penetrate through the channel decreasing the impedimental and selective ability of membranes. At some moment the membrane turns into an usual filter.

We have found that in the presence of PVP polymerization of hydroxyalkyl(meth)acrylates proceeds *via* complex formation stage - with a considerable influence on the polymerization rate. We summarize these results in Table 1.

A change of solution colour has been observed by Rzaev [5] before; it provided a qualitative confirmation of the complex formation with the charge transfer. The reagents mixing in HEMA + PVP system provided a yellow colour. Infrared (IR) spectroscopy also confirms the complex formation with the charge transfer. Both splitting and shifting of the absorption bands typical for the monomer double bond (from 1620 to 1630 cm^{-1}) and PVP tertiary nitrogen (from 1275 to 1290 cm^{-1}) reveal that those groups take part in the complex formation.

For quantitative determination of complex formation constants, we have investigated changes in the optical density as a function of the components ratio. The resulting constants of complex stability and extinction coefficients are also listed in Table 1. The resulting values of the complex formation constants, namely $K_c < 5$, indicate that the components forming the complex may initiate the copolymerization [5].

The HEMA + PVP system plays a role of high performance initiator even in the absence of additional traditional initiators of peroxide type or azocompounds. The initiation practically does not depend on the viscosity of the reaction mixture; viscosity changes are related to the solvent nature (Table 1). In such a case the polymerization proceeds *via* complex-radical matrix mechanism with the formation of some cross-linked copolymers – as discussed by us before [8].

The complex formation affects not only the polymerization kinetics but also the composition of the synthesized copolymers (via graft efficiency) and structural parameters of the networks. These results are presented in Fig. 1.

The present results confirm our earlier suggestion [9]: pretreatment of the initial mixture provides a control of structure and properties of the network formed. The synthesis is carried out in the solvent amount corresponding to its content in the polymer at equilibrium swelling state. Then, choosing the solvent nature it is possible to control the network density by the change of complex formation constants between HAMA and PVP. In such a case the membrane porosity is directionally affected by the density of the polymeric matrix – with a controlled change of penetrability as a result; Tables 2 and 3 testify to this.

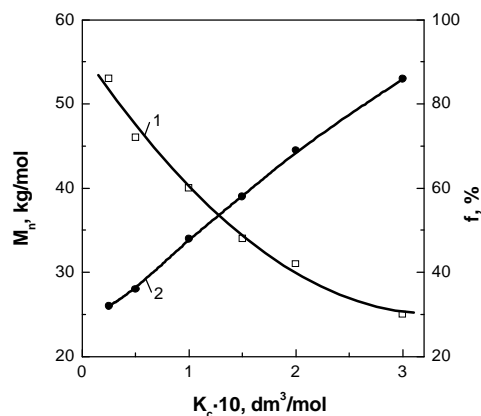


Fig. 1. Dependence of the mass between crosslinks M_n (curve 1) and graft efficiency f (curve 2) upon the constant K_c of complex formation between HEMA and PVP

Table 2 also contains results of tensile testing, namely the tensile strength and the tensile elongation at break e_b . We recall that the latter property is inversely proportional to the material brittleness B as defined in [10] and reviewed in [11]. Changes in the tensile strength are small while changes in e_b are somewhat larger, with the highest value for Material 6. Interestingly, Materials 6 and 7 have the highest values of water permeability.

Table 1

Effect of solvent nature on the complex formation parameters and polymerization rate V_p for HEMA/PVP systems

No. of exp.	Solvent	Constant of complex stability, dm^3/mol	Extinction coefficient, $\text{dm}^3/\text{mol}\cdot\text{cm}$	Viscosity* ($h \cdot 10^3$), Pa·s	$V_p^* \cdot 10^4, \text{mol}/\text{dm}^3 \cdot \text{s}$ (at 333 K)
1	Dimethylsulphoxide	0	–	2.4	0
2	Cyclohexanol	0.06	20.8	17.6	0.6
3	Butanol	0.12	10.0	2.1	0.8
4	Ethylene glycol	0.17	5.6	14.4	1.1
5	Diethylene glycol	0.21	2.1	22.3	1.5
6	Water	0.28	5.3	5.3	3.8

* HEMA:PVP:solvent = 9:1:10 mass parts (without an initiator)

Table 2

Effect of solvent nature and amount on the properties of polymeric hydrogels

No of exp.	Mixture composition, mass parts				Internodal molecular mass, kg/mol	Optical transmission coefficient, %	Tensile strength ($\sigma \cdot 10^3$), MPa	Elongation at break, %	Coefficient of water permeability ($K \cdot 10^4$), $\text{m}^3/\text{m}^2 \cdot \text{h}$
	HAMA*	PVP	H ₂ O	DMSO					
1	80	20	100	0	24	95	40	235	52
2	80	20	99	1	25	95	40	235	53
3	80	20	90	10	31	95	41	240	57
4	80	20	80	20	41	95	41	245	63
5	80	20	70	30	52	95	42	250	70
6	80	20	60	40	65	95	42	255	76
7	80	20	40	60	67	–	–	–	77
8	80	20	80	20	38	96	43	230	57
9	80	20	80	20	44	94	40	240	70

* 2-hydroxyethylmethacrylate is used as HAMA in experiments 1–7; 2-hydroxypropylmethacrylate is used in experiment 8 while 2-hydroxypropylacrylate in experiment 9.

Sorption-diffusion properties of hydrogel membranes

№ 3/II	Mixture composition, mass parts				Water content, %	Coefficient of water permeability ($K \cdot 10^4$), $\text{m}^3/\text{m}^2 \cdot \text{h}$	Penetration coefficient*, $\text{mol}/\text{m}^2 \cdot \text{h}$		
	HEMA	PVP	H ₂ O	DMSO			NaCl	Carbamide	Saccharose
1	100	–	100	–	40	5	80	13	5
2	80	20	100	–	48	52	181	36	14
3	80	20	95	5	48	55	193	–	–
4	80	20	90	10	47	57	212	–	–
5	80	20	80	20	47	63	240	–	–
6	80	20	200	–	55	74	234	59	30
7	80	20	300	–	61	90	263	60	31
8	70	30	100	–	53	71	232	59	30
9	50	50	100	–	61	102	274	65	33

* for $\delta = 200 \mu\text{m}$; optical transmission coefficient is 90 – 96 % for experiments 1–5, 8 and 9; opaque membranes have been obtained in experiments 6 and 7.

We have studied a change of the network density in the interval which affects, first of all, the membrane penetrability for low molecular mass compounds; the impedimental action is slightly affected for the high molecular mass compounds. An increase of the total porosity with the dilution of the reaction medium practically does not change the density of copolymer network synthesized in the same solvent. These facts confirm our conclusions reached above.

The largest effect on the network structural parameters and penetrability is observed adding a small amount of dimethylsulphoxide (in the medium of which complex formation between monomer and PVP is not observed) to water. An increase of dimethylsulphoxide content above 40 mas % of the total solvent amount does not change these parameters (Table 2, Materials 5 and 6). Exchange of HEMA for 2-hydroxypropylmethacrylate favors formation of a more dense network with lower penetrability – as seen in Table 2 for Materials 3 and 7.

At the same time, the hydrogel membranes based on HEMA/PVP copolymers have higher sorption properties compared with HEMA copolymers and higher penetrability for water and several low molecular mass compounds (Table 3).

It is interesting that the mass between crosslinks does not directly depend upon the solvent polarity; see Table 3. One would expect such a dependence of the given “loosing” effect on the PVP molecules. However, when the solvent amount exceeds its maximum sorption by the polymeric matrix at swelling equilibrium, the already mentioned phase separation occurs (Table 3, Materials 6 and 7).

4. Conclusions

Thus, the control of the initial mixture composition *via* complex formation is an effective method of structure and penetration control for hydrogel membranes based on hydroxyalkylmethacrylates and polyvinylpyrrolidone. Such membranes may be recommended for encapsulation and creation of prolonged forms of drugs controlled release [12], hemodialysis, as well as for fractionating and concentrating of high molecular mass compounds, including biological media.

References

- [1] Pavlyuchenko V. and Ivanchev S.: *Vysokomol. Soed.*, 2009, **51**, 1075.
- [2] Suberlyak O., Skorokhoda V. and Melnyk J.: *Eng. Biomater.*, 2009, **XII**, 5.
- [3] Skorokhoda V., Semenyuk N. and Suberlyak O.: *Polym. Zh.*, 2006, **2**, 155.
- [4] Shvarts A. And Grigorovskaya V.: *Colloid. Zh.*, 1965, **1** 30.
- [5] Rzaev Z.: *Polymery i Sopolimery Maleinovo Angidrida*. Elm, Baku 1984.
- [6] Suberlyak O., Melnyk J. and Skorokhoda V.: *Khim. Prom. Ukrainy*, 2008, **2**, 29.
- [7] Dubyaga V., Perepechkin L. and Katalevskiy E.: *Polymernye Membrany*. Khimiya, Moskva 1981.
- [8] Skorokhoda V., Melnyk J. and Suberlyak O.: *Nauk. Zapysky NaUKMA*, 2007, **66**, 33.
- [9] Suberlyak O., Melnyk J. and Skorokhoda V.: *Khim. Prom. Ukrainy*, 2009, **4**, 26.
- [10] Brostow W., Hagg Lobland H.E. and Narkis M.: *J. Mater. Res.* 2006, **21**, 2422.
- [11] Brostow W., Kovacevic V., Vrsaljko D. and Whitworth J.: *J. Mater. Ed.* 2010, **32**, 273.
- [12] Babu R.J., Brostow W., Kalogeris I. and Sathigari S.: *Mater. Letters* 2009, **63**, 2666.

**ОСОБЛИВОСТІ НАПРАВЛЕНОГО ФОРМУВАННЯ
СТРУКТУРИ І ВЛАСТИВОСТІ
ВИСОКОГІДРОФІЛЬНИХ МЕМБРАН НА ОСНОВІ
КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ**

***Анотація.** Досліджено полімеризацію композиції гідроксіалкіл(мет)акрилатів з полівінілпіролідоном і синтезовані високогідрофільні мембрани на їх основі. Досліджено основні властивості одержаних кополімерів, у т.ч. фізико-*

механічні та проникність. Виявлено взаємозв'язок параметрів комплексоутворення між мономером та полівінілпіролідоном у вихідній композиції зі складом і структурними параметрами сітки кополімерів. Виявлені ефективні способи направлено формування структури і регулювання властивостей досліджуваних високогідрофільних мембран.

***Ключові слова:** мембрана, полівінілпіролідон, 2-гідроксіетилметакрилат, проникність.*