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**POLYMERIC HYDROGELS
ON THE BASE OF POLYMETHYL
VINYL ETHER OF MALEIC ACID CROSS LINKED
WITH POLYPROPYLENE GLYCOL**

Abstract. It was experimentally studied kinetics and equilibrium of etherification reaction of polymethyl vinyl ether of maleic acid cross-linked with polypropylene glycol. In the result section of this study it was proved that significant changes in physical-chemical properties of the system occur in the course of reaction, and these changes lead to the changes of rate constants Thermodynamic and kinetic parameters of the etherification process of polymethyl vinyl ether of maleic acid cross-linked with polypropylene glycol were determined.

Keywords: hydrogel, equilibrium constant, polymer, reaction rate, etherification.

The history of gels investigation began from their first naming in the work of Lim and Wichterle [1] in the 1960-s of XX century. And the monography of S.P. Papkov published in 1974 year became the first scientific work entirely devoted to polymeric gels. Then in 1974 year T.Tanaka in his work «Collaps of gels and the critical end point» declared his point of view on many questions being relevant at that stage of evolution of the sphere of polymers investigation [2].

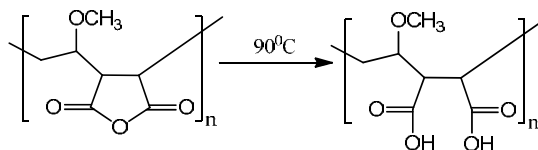
Now we can express firm confidence that there is a gulf between us and the first investigators of gels properties, if only because in the theory of P.N. Herman and P.J. Flory the first gel definition described gels as soft or solid-like materials that characteristic is the absence of equilibrium elastic modulus. Hydrogels take a definite position in the classification of polymeric biomaterials produced on the base of organic substances. Hydrogels are traditionally determined as «two- or multicomponent systems that contain in their structures spatially cross-linked three dimensional net of polymeric chain and aqueous solution filling the space between macromolecules» [3].

There is a wide range of spheres where polymers are used but there is no literature data about the kinetics of etherification reaction of polymethyl vinyl ether of maleic acid with polypropylene glycol. This study is necessary for the choosing and the estimation of optimal conditions for the carrying out of this process.

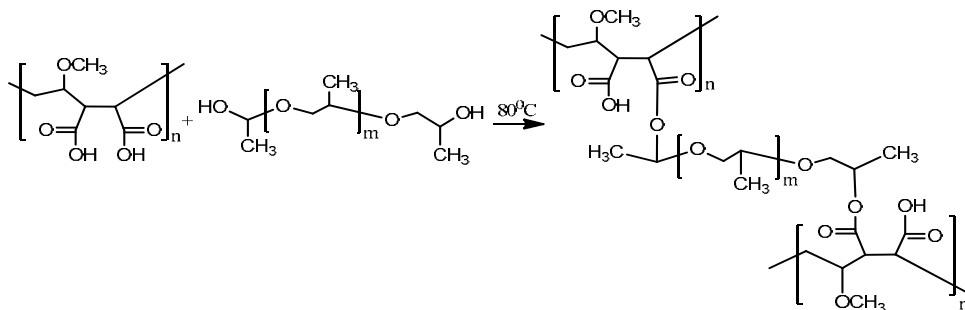
The aim of this work is the development and the creation of scientific basis of hydrogels synthesis on the base of polymethyl vinyl ether of maleic acid cross-linked with polypropylene glycol.

Experimental

Poly(methyl-vinyl-co-maleic acid) or polymethylvinyl maleic acid ether (PMVE-MA) was obtained by hydrolysis polymethylvinyl ether of maleic anhydride (PMVE-MAH):



Process was held on assembly of round-bottomed flask with volume of 100 ml and backflow condenser. Base mixture was prepared of 0.6500 g of PMVE-MAH and 20 ml of distilled water. Hydrolysis was carried at the temperature of 90°C during 2 hours. Gradually water solution of polypropylene glycol (PPG) was added to generated polymethylvinyl maleic acid ether (PMVE-MA) up to obtaining of homogenic mixture. Excess water was drained with rotary evaporator. Reaction mixture was firmed for 24 hours at 80°C. In the result of etherification reaction between polymethylvinyl maleic acid ether and polypropylene glycol gel PMVE-MA with PPG was formed [4]:



The number of carboxylic groups in hydrogel was calculated with the use of titration method of acids mixture [4]. 0.1 N alcoholic solution of potassium hydroxide was used as the titrant.

Product yield was determined by the next formula [5, 6]:

$$x = \frac{AN_0 - AN_c}{AN_0} \cdot \beta \cdot 100\% , \quad (1)$$

where AN_0 – is initial acid number of reaction mixture, mg KOH/g; AN_c – is current acid number of reaction mixture, mg KOH/g; β – molar ratio of PMVE-MA/PPG.

Average initial reaction rate v_0 (mol/l·h) was determined as arithmetic mean value computed according following formula (2):

$$v_0 \cong c_0 \cdot \frac{x_i}{100} \cdot \frac{1}{t}, \quad (2)$$

where c_0 – initial concentration, mol/l; t – the time from the beginning of reaction till the sampling; x_i – yield of PMVE-MA with PPG in i -the sampling, %. Equilibrium constant of the studied etherification reaction was described by the equation (3) [6]:

$$K_c = \frac{\left(\frac{\bar{x}}{100}\right)^2}{\left(\beta - \frac{\bar{x}}{100}\right) \cdot \left(1 - \frac{\bar{x}}{100}\right)} \quad (3)$$

Experiments were carried out with the excess of polymethylvinyl maleic acid ether (PMVE-MA).

Results and discussion

Dependence $\lg(K_c)$ from temperature (t) is presented in figure 1. Values of equilibrium constants calculated according to experimental data are given in table 1.

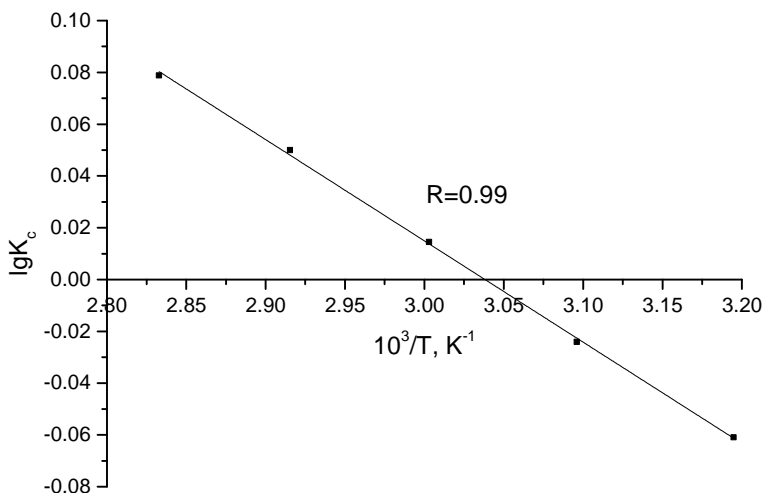


Figure 1 – Dependence of the logarithm of concentration equilibrium constant of the reaction from temperature

Enthalpy and entropy of reaction are equal to $\Delta H^0=61.13$ kJ/mol; $\Delta S^0=-161.91$ J/(mol·K), i.e. temperature increasing leads to shift of equilibrium towards products.

Table 1 – Values of equilibrium yield of PMVE-MA with PPG and equilibrium constant of reaction at variable temperature

Temperature, °C	Yield PMVE-MA with PPG, %	Constant of reaction
40	58	0.869±0.02
50	60	0.946±0.02
60	65	1.034±0.01
70	67	1.122±0.03
80	70	1.199±0.05

Kinetic curves of etherification of polymethyl vinyl ether of maleic acid with polypropylene glycolis are given in figure 2.

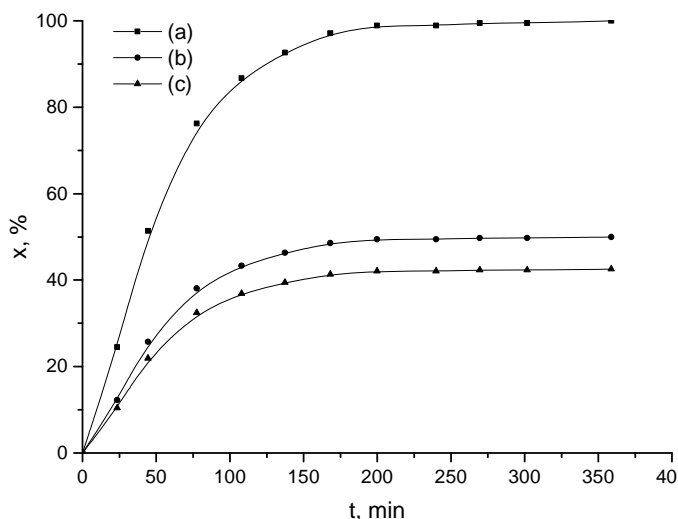


Figure 2 – Kinetic curves of etherification of PMVE-MA with PPG at variable temperature: (a) – 80°C; (b) – 60°C; (c) – 40°C

It is evident (figure 2) that reaction rate expectably increases with the rise of temperature. Moreover, limiting degree of substitution was achieved in 4÷6 hours at the whole interval of the change of reaction temperature. Observed increase of temperature is accompanied with the increase of limiting degree of substitution and the phenomenon is probably related to viscosity reduction of reaction medium.

Activation energy of the etherification process of polymethyl vinyl ether of maleic acid with polypropylene glycol was determined by the use of Arrhenius equation (4) in following studies (figure 3).

$$k_r = A \exp(-E^\# / RT), \quad (4)$$

where T – temperature, K; A – pre-exponential factor; $E^\#$ – activation energy, J/mol; R – gas constant, value is 8.31441 J/(mol·K).

The logarithmical form of equation takes the following form (5):

$$\ln k_r = \ln A - E^\# / RT \quad (5)$$

or,

$$\lg k_r = \lg A - E^\# / 2.303RT .$$

The constants of etherification reaction rate are given in table 2.

Table 2 – The constants of direct reaction rate at variable temperature

№	Temperature a, °C	k_r , L ² /(mol ² ·h)
1	40	8.03±0.2
2	50	18.15±0.6
3	60	37.95±1.1
4	70	80.3±0.9
5	80	128.15±0.5

Arrhenius dependence for the constant of etherification reaction rate of polymethyl vinyl ether of maleic acid with polypropylene glycol is presented in figure 3.

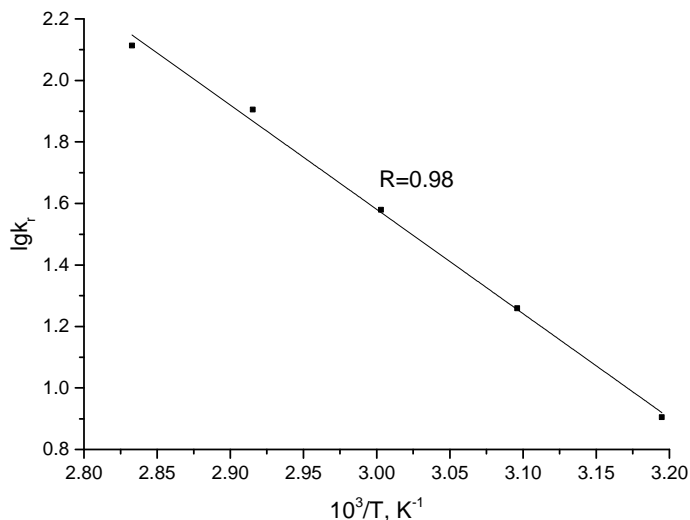


Figure 3 – Dependence $\lg k_r$ from reciprocal temperature for etherification reaction of PMVE-MA with PPG

It was estimated that the energy of activation for the product of etherification of polymethyl vinyl ether of maleic acid with polypropylene glycol is equal to 64.86 kJ/mol.

Conclusions. There through it was found that 80°C (conversion degree is 98%) is the optimal condition for producing the maximum yield of reaction product and minimizing the energy expenditure requested for reaction. Also it

was determined that activation energy for the product of etherification of polymethyl vinyl ether of maleic acid with polypropylene glycol is equal to 64.86 kJ/mol accordingly.

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Резюме

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ПОЛИПРОПИЛЕНГЛИКОЛЬМЕН ТІГІЛГЕН ПОЛИМЕТИЛВЕНИЛЭФИРМАЛЕИН ҚЫШҚЫЛЫ НЕГІЗІНДЕГІ ПОЛИМЕРЛІ ГИДРОГЕЛЬ

Полипропиленгликольмен тігілген полиметилвинил эфир малеин қышқылы негізіндегі этерификация реакциясының тепе-теңдігі және кинетикасы тәжірибие жүзінде зерттелген. Зерттеу нәтижесінде көрсетілгендей, реакция барысында жүйенің физико-химиялық күйі өзгеріске ұшырайды да, реакцияның жылдамдығына әсер етеді. Полипропиленгликольмен тігілген полиметилвинил эфир малеин қышқылы

негізіндегі этерификация процессінің кинетикалық және термодинамикалық параметрлері анықталды.

Түйін сөздер: гидрогель, тепе-теңдік константасы, полимер, реакция жылдамдығы, этерификация.

Резюме

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ПОЛИМЕРНЫЕ ГИДРОГЕЛИ НА ОСНОВЕ ПОЛИМЕТИЛВИНИЛОВОГО ЭФИРА МАЛЕИНОВОЙ КИСЛОТЫ, СШИТОГО ПОЛИПРОПИЛЕНГЛИКОЛЕМ

Экспериментально исследована кинетика и равновесие реакции этерификации полиметилвинилового эфира малеиновой кислоты, сшитого полипропиленгликолем. В результате исследования было показано, что в ходе реакции происходят значительные изменения физико-химических свойств системы, которые ведут к изменениям констант скоростей. Установлены термодинамические и кинетические параметры процесса этерификации полиметилвинилового эфира малеиновой кислоты с полипропиленгликолем.

Ключевые слова: гидрогель, константа равновесия, полимер, скорость реакции, этерификация.