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PREPARATION OF HYDROGELS VIA CROSS-LINKING OF POLY(ACRYLAMIDE-CO-2-ACRYLAMIDO-2-METHYL-1-PROPANE SODIUM SULFONATE) WITH AMMONIUM PERSULFATE¹

Изучено гелеобразование поли-2-акриламида-2-метилпропансульфоната натрия в водных растворах в присутствии персульфата аммония (ПСА) в качестве сшивающего агента при температурах 60–80 °С. Установлено, что минимальная концентрация раствора полимера, достаточная для формирования консистентного геля, составляет около 1,5 мас. %. При этом гель образуется только при концентрации ПСА 0,35 % по отношению к массе полимера и имеет низкие величины водопоглощения и гель-фракций. Показано, что лучшими свойствами с точки зрения консистенции, водопоглощения и величин гель-фракций обладают гели, полученные при концентрации полимера в растворе 2 %. При этом увеличение концентраций и полимера, и ПСА приводит к получению более прочного геля. Установлено, что увеличение концентрации полимера в растворе с 1,5 до 2 % позволяет снизить минимальную концентрацию ПСА, необходимую для начала гелеобразования. Водопоглощение гидрогелей, полученных при концентрации полимера 2 %, снижается с увеличением концентрации ПСА, в то время как величины гель-фракций практически не меняются. Показано, что повышение температуры гелеобразования с 60 до 70 °С приводит к снижению времени начала формирования геля в 2,5–3,0 раза.

Ключевые слова: гидрогель; гель-прочность; вязкость; водопоглощение; гель-фракция.

A series of hydrogels were prepared by cross linking of poly(2-acrylamido-2-methylpropane sodium sulfonate) in aqueous solutions in presence of ammonium persulfate (APS) as a cross linking agent at 60–80 °C. It was shown that the minimum concentration of the polymer solution, sufficient to form a consistent gel is about 1,5 wt %. Gel in this case is formed only at APS concentration of 0,35 % per weight of polymer and has low water absorption and gel fraction. It can be said that, gels obtained with 2 % polymer solutions exhibit the best properties in terms of consistency, water absorption and gel fraction values. It was determined that, the increase in polymer and APS concentrations results in a stronger gel. Furthermore, an increase in polymer concentration of solutions from 1,5 to 2 % reduces the minimum concentration of APS needed to start gelation. The water absorption of hydrogels, obtained with 2 % polymer solutions, is decreased with increasing the concentration of APS, whereas the gel fraction values remain almost unchanged. It was shown that, increasing in temperature from 60 to 70 °C leads to reduction in the start time of gelation by the factor of 2,5–3,0.

Key words: hydrogel; gel strength; viscosity; water absorption; gel fraction.

In recent years acrylamide homopolymers and copolymers are widely used in various industries: water treatment, paper processing, extraction and processing of minerals, medicine, agriculture, construction and oil industry [1]. In the oil industry, these polymers are used in particular to reduce excessive water production in oil wells. Non hydrolyzed and partially hydrolyzed polyacrylamides (HPAM), with varying degrees of hydrolysis and molecular weights are being used for this purpose. Anionic acrylamide copolymers such as poly(acrylamide-co-sodium acrylate), poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid), and poly(acrylamide-co-2-acrylamido-2-methylpropane sodium sulfonate) (PAMPS) have considerable importance in enhanced oil recovery (EOR)/improved oil recovery (IOR) [2]. Among these copolymers, PAMPS is of more special interest because of its strongly ionizable sulfonate groups and completely

¹ Статья публикуется в авторской редакции.

dissociation in the whole pH range. These polymers are injected together with a cross-linker, mainly Cr^{3+} or Al^{3+} containing compounds to the target zones of reservoirs. After allowing sufficient time, the injected cross-linkable solution, referred to as gelant, is converted into a cross-linked network (gel), which behaves as a flow diverting or blocking agent [3]. It is proved that complex formation between chromium(III) cation and carboxylate groups is a driving force of this interaction. Depending on the reagents ratio, the complex contains two or three carboxylate groups. The amide units are not involved in any specific reaction with the cation [4]. Although in contrast to formerly used chromium(VI) cross-linking systems, chromium(III) ones are not toxic, environmental considerations and limitations related to water pollution caused by heavy metals have increased the tendency to use other types of cross-linkers like double bond-containing ones, specially N,N'-methylenebisacrylamide. A chemical-bonded hydrogel has permanent properties due to the covalent nature of the cross-link entity [5]. Ammonium persulfate (APS) and potassium persulfate (KPS) are water soluble thermal initiators which are used frequently in both solution and inverse-suspension polymerization processes of hydrogels synthesis [3]. Preparation of cross-linked poly(vinylpyrrolidone)/poly(vinyl alcohol) hydrogels in aqueous solution at 80 °C in presence of KPS as cross-linker has been reported [6]. Thermal aging behavior of HPAM polymers in presence of KPS as residual initiator of polymerization has been studied and reported the increase of molecular weight at 60–80 °C, based on capillary viscometric data [7]. But they did not suggest any explicit reason for this increasing. PAMPS has higher thermal stability and salt resistance than HPAM. In addition, it is used in EOR/IOR applications up to 120 °C [3]. Thermal aging of a medium molecular weight PAMPS over short-time periods at moderate temperatures and low concentrations of KPS has been reported to decrease the intrinsic viscosity [8]. Application of persulfates as cross-linking agent for HPAM and PAMPS has not been investigated yet. But it seems possible to cross-link this type of polymers with high concentrations of persulfate (as cross-linker) and obtain hydrogels which can satisfy the EOR/IOR requirements in the medium-temperature oil reservoirs.

The aim of current work is to prepare hydrogels based on PAMPS, using APS as a free radical cross-linking agent, at 60–80 °C. An alphabetical coding method is applied to determine the strength of gels and kinetics of gel formation, using bottle test and viscometric data. Gel fraction (δ) and equilibrium water absorption (A) are measured using gravimetric method. FTIR spectroscopy is applied to characterize chemical structure of obtained networks. Mechanism of gel formation will be discussed based on experimental results, evidences and comparison with other works.

Materials and methods

Materials. PAMPS with an average molecular weight of 8 million, sulfonation degree of 25 % and water content of less than 10 wt %, was provided by SNF Co (France) under the trade name of AN125 in powder form. This polymer is the one which used in [3] and [8]. APS was the product of Applichem (P. A. grade) and used in solid form (after recrystallization). Distilled water was used as solvent to prepare gelant solutions.

Samples preparation and characterization. The polymer gels were prepared according to the following two steps: PAMPS (here after is referred to as «polymer») solutions at different concentrations were prepared by adding distilled water to polymer powder followed by gentle stirring for 8 hours, using a (Griffin & George Minimag stirrer SWT-180-010K (UK)). After that, they were held without stirring overnight until a homogeneous solution was obtained. APS as cross-linker was magnet-stirred in required amounts with polymer solutions at room temperature for 10 min to obtain gelant solutions (mixture of copolymer and cross-linker). The obtained gelant solutions were poured into wide mouth glass bottles (70 ml). Then, the bottles were kept in an oven at 60, 70, and 80 °C as long as it was required. The gel formation process was monitored based on the Sydansk's gel strength code by observing the appearance of the gel structure on the wall of the bottle when the bottle is inverted [9]. A comprehensive series of bottle tests were conducted at mentioned temperatures in order to select suitable reactants concentration for the polymer gel treatment. The final objective of these screening tests was to determine the limit of concentration of gel components which leads to gel formation. Based on the screening work, suitable systems were selected for extensive investigations of gel fraction and degree of swelling.

Viscosity measurements. To represent the degradation of non gel forming samples in a quantitative manner, some viscosity measurements were conducted using Rheotest (Germany), a coaxial viscometer with the spindles N and S1, according to instruction manual of it. Viscosity of the prepared gelants was measured in a shear rate domain of 10 to 1000 s^{-1} .

Equilibrium water absorption and gel fraction. After obtaining gels with strength codes higher than G, they were vacuum dried at moderate temperature (40 °C) in order to avoid thermal decomposition, until constant weight. Then approximately 40 mg of each hydrogel was immersed into 500 ml distilled water for 48 hours to reach the equilibrium swelling at room temperature. Then excess liquid was filtered through acrylic/polyester

gauze with fine mesh. Swollen gel was weighed after 15 min remaining on filter and removing the water on the surface with tissue paper, and the water absorption (A) was calculated using equation:

$$A = (W - W_0) / W_0,$$

where W and W_0 are the weights of the water – swollen gel and dry absorbents, respectively. Absorption is expressed in grams of water retained in the gel by one gram of dried gel. The tabulated results are the arithmetic mean of 3 experiments. The precision of this method has been determined to be around $\pm 3,5\%$ [10]. Drained gels were held in oven at $70\text{ }^{\circ}\text{C}$ until constant weight (W_1), and the gel fraction (δ) was calculated using equation:

$$\delta = (W_1 / W_0) \cdot 100.$$

FTIR spectroscopy. FTIR spectra were recorded on a Bruker ALPHA spectrometer, equipped with measuring module of diamond crystal. Samples were thin films of hydrogels, vacuum-dried at $40\text{ }^{\circ}\text{C}$.

Results and discussion

It is showed that AN125 in 0,2 wt % aqueous solution and KPS/polymer weight ratio of 0,04 at $60\text{ }^{\circ}\text{C}$ undergo thermal degradation, caused by decomposition of KPS to free radicals [8]. Results of screening tests show that, before polymer concentration of 1,5 wt %, and up to APS/polymer weight ratio of 0,30, viscosity decreases during thermal treatment. As it is shown in fig. 1, *a*, shear viscosity is decreased during thermal aging over a wide range of shear rates ($145,8\text{--}437,4\text{ s}^{-1}$) in 1,5 wt % solution of AN125 containing APS/polymer weight ratio of 0,20. As APS/polymer weight ratio is increased from 0,20 to 0,25 at polymer concentration of 1,5 wt %, the extent of degradation is increased and consequently the shear viscosity is decreased. This behavior is not limited to shear rate of $145,8\text{ s}^{-1}$ and takes place over the whole range of mentioned shear rates. The similar behavior is observed in aging of 2 wt % aqueous solution (fig. 1, *b*). Although the trend of changes in viscosity against shear rate and APS/polymer ratio in fig. 1, *a*, and fig. 1, *b*, is more or less similar, the viscosity almost remains constant or slightly increases in second hour of thermal treatment in fig. 1, *b*. Probably here a competition between network formation and polymer destruction takes place in which the higher extent of network formation results in viscosity increment in second hour of thermal treatment, and the higher extent of degradation in third hour leads to viscosity depression. Based on viscometry data and results of bottle tests it can be concluded that the APS/polymer weight ratios, approximately 0,30 and 0,25 are thresholds of gel formation for polymer concentration of 1,5 and 2 wt %, respectively.

Kinetics of gel formation process in this study has been qualitatively tabulated, together with the properties of prepared hydrogels (table 1). It is clearly observed that the onset and rate of gel formation strongly depends on concentration of polymer solution and APS/polymer ratio. The minimum concentration of polymer solution for consistent gel formation is 1,5 wt %. This minimum polymer concentration provides the sufficient distance between polymer chains to initiate cross-linking reaction with APS molecules. At constant weight percent of polymer, increasing the amount of APS decreases the time to obtain stronger gel. Also, at constant APS/polymer ratio, higher concentration of polymer solution results in a similar effect. Results of bottle tests and viscometry suggest that increasing the concentration of polymer solutions shifts the threshold of gel formation to the lower APS/polymer ratios. It can be said that higher polymer concentration increases the probability of effective collisions between polymer chains and APS. Consequently lower concentration will be needed to start cross-linking. Results of screening tests suggest that formation of consistent gel in our study takes place over a narrow range of AN125 and APS concentrations. At polymer concentration of 1,5 wt % only a relatively consistent gel with low A and δ is formed with APS/polymer weight ratio of 0,40. Increasing the polymer concentration to 2 wt % broadens the range of APS/polymer ratio for preparation of consistent gels with measurable A and δ . Also it is clear that the value of A is decreased with increasing the APS/polymer ratio. Increase in the value of A because of change in polymer concentration from 1,5 to 2 wt % at APS/polymer weight ratio of 0,40 is obvious. Trend of changes in values of A versus APS concentration is in accordance with well-known patterns [10]. Similar behavior has been reported for effect of KPS concentration on A in PVA/PVP based hydrogels [6]. Gel fraction is increased because of increase in polymer concentration but is remained approximately unchanged all over the gel formation range at polymer concentration of 2 wt %. It seems that the extent of chain destruction, which has been studied by [7, 8], and chain cross-linking controls A , δ , and gel strength. At polymer concentration of 1,5 wt %, chain destruction plays dominant role and no gel is formed, except a narrow range of APS concentration which results in a relatively weak gel. At polymer concentration of 2 wt %, role of chain cross-linking dominates. Thus gel formation takes place over a broader range of APS concentration and

leads to stronger gels. Increase in APS/polymer ratio increases the cross link density and consequently reduces A . But simultaneously increases the extent of chain destruction which first prevents ascending of δ , keeps it constant and finally prevents consistent gel formation.

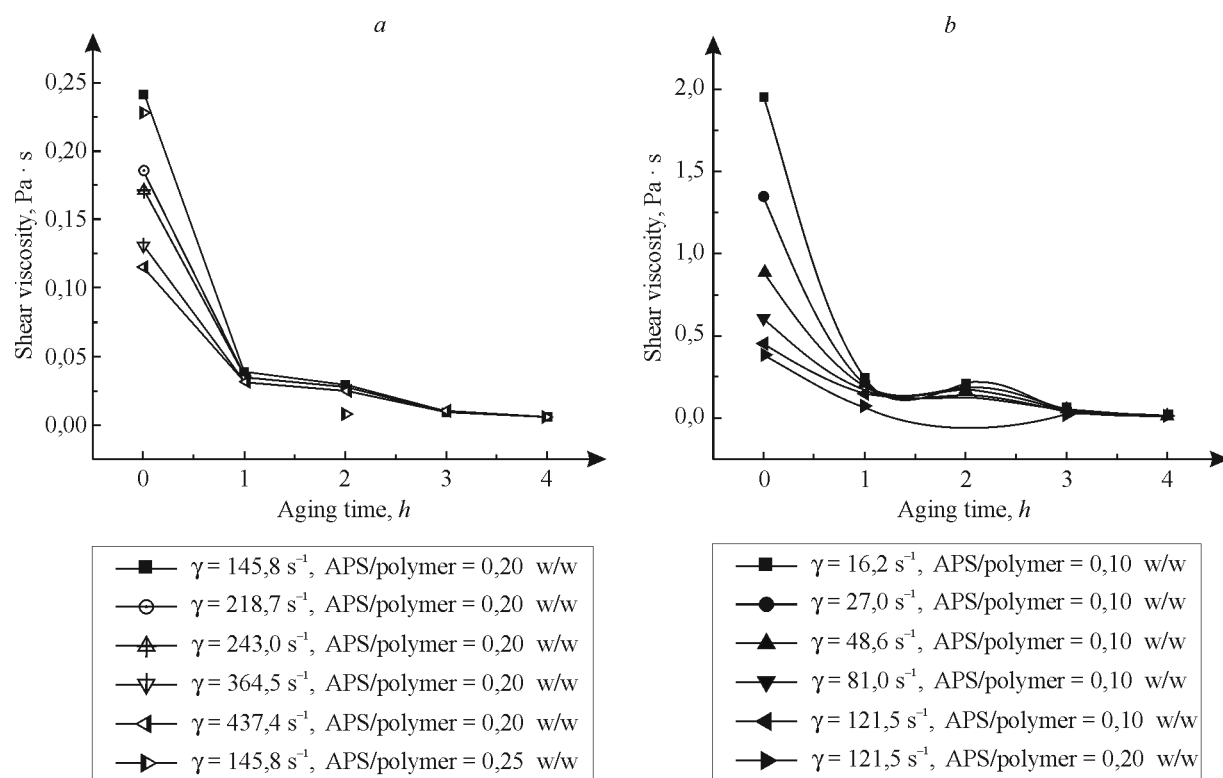


Fig. 1. Viscosity behavior of 1,5 wt % (a) and 2 wt % (b) solutions of AN125, containing different APS/polymer ratios, during thermal aging at 60 °C

Table 1

Effect of AN125 and APS concentrations on strength and properties of gels, prepared at 60 °C

Aging time, <i>h</i>	Concentration of AN125, wt %							
	1,5				2			
	APS/polymer weight ratio							
	0,30	0,35	0,40	0,45	0,30	0,35	0,40	0,45
	Gel strength code							
1	C	C	C	C–D	D–E	D–E	D–E	E
2	D	D	D	D	E–F	E–F	E–F	F
3	D	E	E	D	F	F–G	E–F	F
4	D	E–F	E–F	D	F–G	F–G	F–G	F
5	D	F	F	D	F–G	G	F–G	F
6	D	F	F–G	D	F–G	G	G	F
7	D	F	G	D	G	G–H	G	F
8	D–E	F	G	D–E	G	H	G–H	F
<i>A</i> , g _{H₂O} / g _{hydrogel}	–	–	285 ± 10	–	871 ± 31	708 ± 24	585 ± 20	–
δ, %	–	–	25 ± 1,2	–	48,3 ± 0,5	45,1 ± 1,5	46,6 ± 1,9	–

Note. Dash – no gel is formed.

FTIR spectrum of a typical hydrogel sample is presented in fig. 2. These spectrum clearly mark a stretching vibration of amide $C=O$ at 1650 cm^{-1} . The shoulder of carboxylate groups in AN125 which appears at 1600 cm^{-1} , is changed to a sharp stretching vibration in hydrogel, due to partial hydrolysis of acrylamide groups. The vibration of methylene groups is observed at 1420 cm^{-1} . The observed absorbance at 1045 cm^{-1} is characteristic of symmetric stretching of SO_3 groups. The characteristic absorbance of asymmetric stretching of SO_3 at 1175 cm^{-1} in the spectra of AN125 is not observed in the spectra of hydrogel. Instead, observed shoulder in the spectra of AN125 at 1100 cm^{-1} is converted to a strong peak in hydrogel, which may be attributed to the symmetric stretching vibrations of $C-O-C$ bonds. The increase in the absorbance at 1250 cm^{-1} in hydrogel, compared with the one of AN125 spectra can be interpreted to the interaction of stretching vibrations of CH and $C-O-C$ bonds [11]. Formation of $C-O-C$ bonds has been reported already for PVA/PVP based hydrogels, cross-linked with KPS [6]. An imide structure has been proposed to be an intermediate in the low pH hydrolysis of poly(acrylamide), yielding short blocks of carboxylic groups distributed along the polymer chains [2]. Dominance of imide formation in acidic hydrolysis of polyacrylamide aqueous solutions is also confirmed in [12]. In neutral and basic pH, both hydrolysis to acrylate and imide formation do occur, but hydrolysis is favored [13]. The increase in the molecular weight of HPAM copolymers during thermal treatment at $60\text{--}80\text{ }^{\circ}\text{C}$ is attributed to intermolecular imidization of polymer chains [7]. It is showed that the formation of a broad peak between $1640\text{--}1750\text{ cm}^{-1}$ suggests imide formation [14]. Absence of a broad peak in this region confirms the absence of intramolecular or intermolecular imidization and dominance of hydrolysis and free radical cross-linking via APS decomposition, formation and combination of macroradicals.

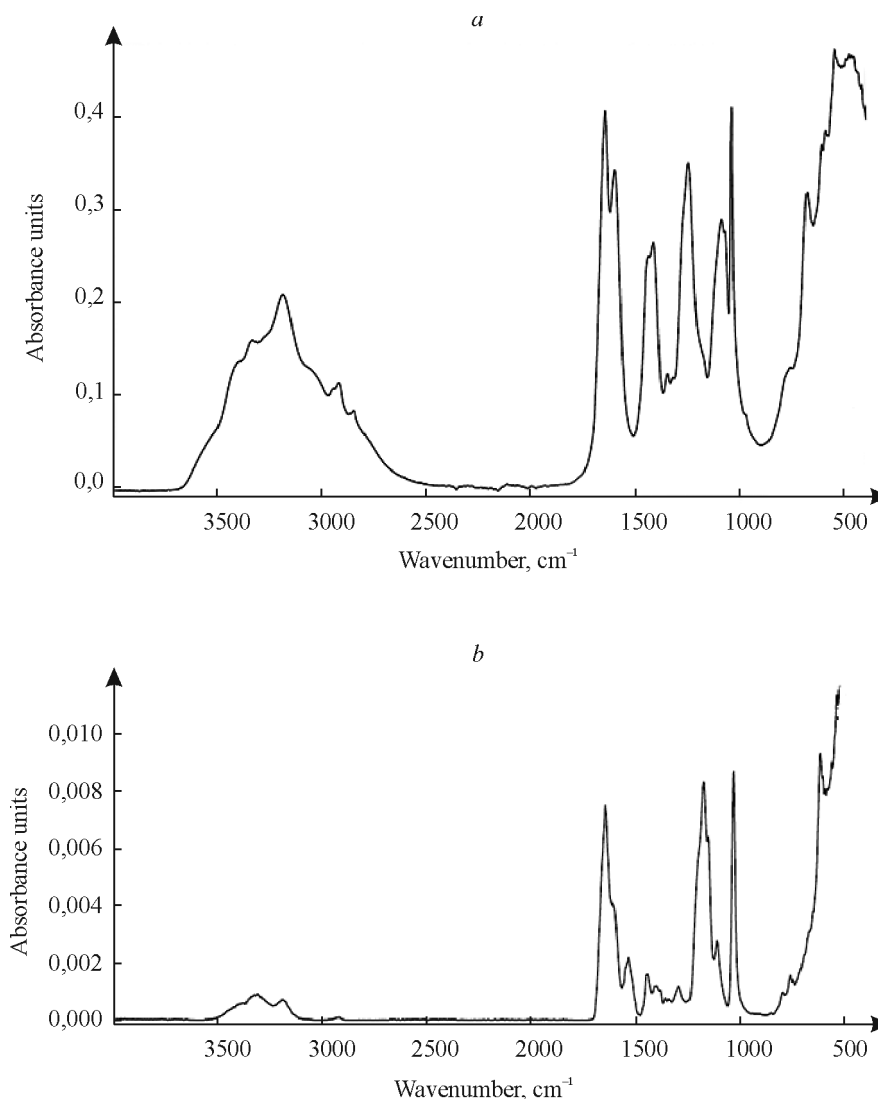


Fig. 2. IR spectra of hydrogel, based on 2 wt % solution of AN125 and APS/polymer weight ratio of 0,40, cross-linked at $60\text{ }^{\circ}\text{C}$ (a) and spectra of AN125 (b)

Effect of temperature on kinetic of gel formation is presented in table 2. It is obvious that increase in aging temperature from 60 to 70 °C reduces the conversion time of gelant solutions to consistent gel in 2,5–3,0 times. However increase in aging temperature from 70 to 80 °C increases the extent of polymer degradation and no consistent gel is formed at 80 °C. A gel, prepared at 60 °C based on the 2 wt % polymer solution and cross-linker/polymer weight ratio of 1/3 may be considered as optimum gel in terms of gel strength, water absorption and gel fraction.

Table 2

**Effect of temperature and concentration of cross-linker
on conversion time of 2 wt % AN125 solution to consistent gel**

APS/polymer weight ratio	Consistent gel formation time at 60 °C, h	Consistent gel formation time at 70 °C, h	Consistent gel formation time at 80 °C, h
0,30	8	3	–
0,35	7	2,5	–
0,40	6	2	–

Note. Dash – no gel is formed.

APS can be used as a cross-linker for preparing hydrogels based on aqueous solutions of medium molecular weight PAMPS copolymers at moderate temperatures. Onset of gel formation, consistency of obtained gels, time to obtain the stronger gel, water absorption and gel fraction depend on polymer concentration, amount of cross-linker, and temperature. Gel formation proceeds via competition between free radical cross-linking and free radical polymer degradation. The extent of chain destruction and chain cross-linking determines water absorbency, gel fraction, and strength of prepared hydrogels. In order to optimize the stability and swelling properties of these hydrogels for using in EOR/IOR applications, further studying the effects of pH, temperature, and concentration of different ions can be the next steps of present study.

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