SPECTRAL ANALYSIS OF WATER GELS BASED ON POLY(ACRYLAMIDE) PREPARED BY DIFFERENT WAYS

V.V. Lopatin, A.A. Askadskii, A.S. Peregudov**

Federal State Unitary Company 'Research Institute of Rubber and Latex Articles, 42 Krasnobogatyrskaya Street, Moscow, Russia
**A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, 28 Vavilov Street, Moscow 11991, B-334, Russia*

Introduction

In the previous work [1], we described the experimental and calculated results for network structures of the polyacrylamide gels obtained with the different prehistory. We investigated the original gel obtained by copolymerization of acrylamide (AA) with small amount of N,N`-methylene-bis-acrylamide (MBAA) in presence of ammonium persulfate (sample 20/1). The sample 20/2 was obtained on the second stage of the process by γ-irradiation of the gel 20/1. The sample 20/3 was obtained after sterilization of the original copolymer at 120 °C and pressure 1.2 atm. for 40 min. The sample 20/4 was obtained at the second treatment by the γ-irradiation. The data of the thermo-mechanical analysis and the calculation of the polymer network properties, published in [1], showed that as the result of the gel γ-irradiation, it is possible to form additional small amount of crosslinking (up to 9%) of the repeating units of the neighboring chains of polyacrylamide. In this work, we conducted the detailed spectral analysis of the chemical transformations, which can occur at γ-irradiation.

Results and Discussion

First of all, we obtained the IR-spectra of all four samples of the copolymer AA and MBAA. The measurements were conducted on the carefully dried samples (but not on the gels containing only small amount of copolymer) to keep the copolymer concentration in the samples approximately equal to 100%. Because the dried gels were very hard glass-like mass, they were mechanically treated to form the powder-like samples, which were used to prepare the tablets with KBr or the suspension in the vaseline oil.
The spectra were obtained by using the IR Furrier spectrometer "Magna-750 IR" made by Nicolet company. The spectrometer had the spectral resolution 2 cm^{-1}. At using the EVM-program Omnic, from the spectra of the tablets, the KBr spectrum was subtracted.
The analysis showed that the spectra of each sample, determined with KBr and in vaseline oil, are identical. However, the spectra in the vaseline oil contain additional bands belonging to the oil. Because of this, the data in Fig.1 show the spectra of all four samples obtained only on tablets with KBr.
From the data in Fig.1, it is seen that the spectra contain wide barely visible bands characteristic for the networking polymers. Based on the assumed scheme of the synthesis [1], the samples 20/1 and 20/2 should vary in that that in the first sample the primary and the secondary aminogroups should be present, and the secondary groups should be a small amount, while in the rest of the samples, it should be a significant amount of the secondary aminogroups. However, the spectra of all samples are identical. In the spectra, it is observed the wide and very intensive absorbency with a complex contour in the area of 3400-3100 cm^{-1}, which is characteristic to the valent vibration of the NH-group. The complex contour of the band is connected with the strong intermolecular hydrogen bonds, the formation of which is unavoidable in the solid state. Because of this, it is impossible to determine whether there are differences in the chemical structure of the investigated polymers based on the shape of the spectra in the area of the valent vibrations of the NH-groups. In the spectra, there is also an intense band Amid I in the area of 1650 cm^{-1}, but there is no band Amid II at 1550 cm^{-1}, which should be observed for the primary amides. It should be assumed that in the investigated

samples, there are no primary amino-groups, however, due to the fact that the polymer is crosslinked, the band Amid I has also the wide and complex contour, and the band Amid II can be masked under wide band Amid I. The samples 20/3 and 20/4 differ by the conditions and longevity of the radiation and thermal treatment. However, it is known that the radiation treatment usually leads to the change of the physical properties of gels, such as ability to swell, the crystallinity state change, and so on. Such changes can be often observed in the spectra, however, they are very fine effects, which are difficult to detect in the spectra of the polymers having very wide and unclear bands.

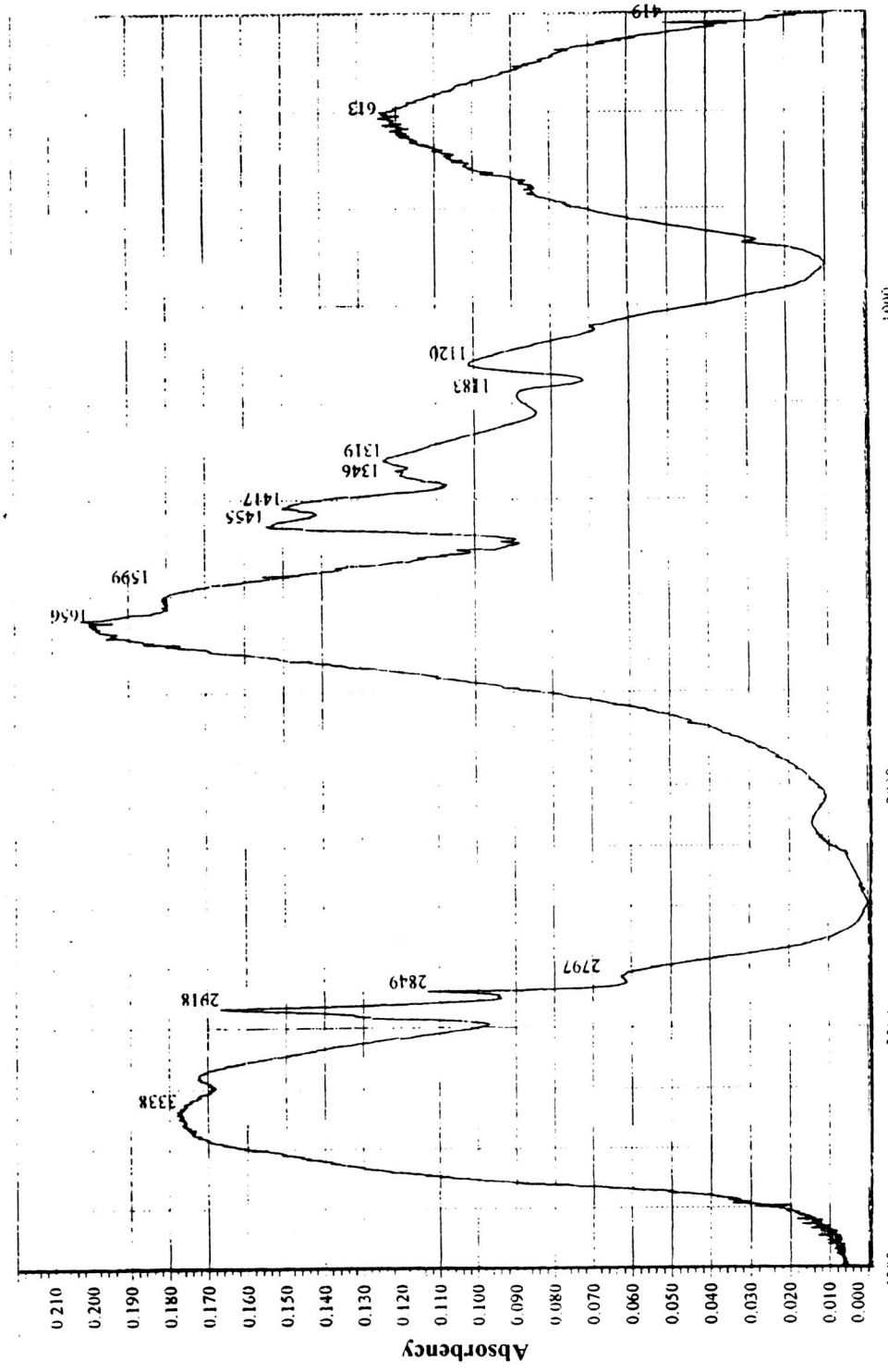


Figure 1a. IR-spectrum of the sample 20/1

The measured spectra were compared with the available in the computer data base with the spectra of the investigated polymers. The closest coincidence of the available in the data base spectra with the measured spectra was found to be the spectra of polyacrylamides from Hercules, Inc.

For the more detailed analysis of the network structure of the polymers underwent the γ-radiation, we investigated their spectra NMR ^{1}H and ^{13}C, which were recorded on the spectrometer AMX-400 made by

Brucker firm with working frequencies 400.13 and 100.61 MHz, correspondingly.

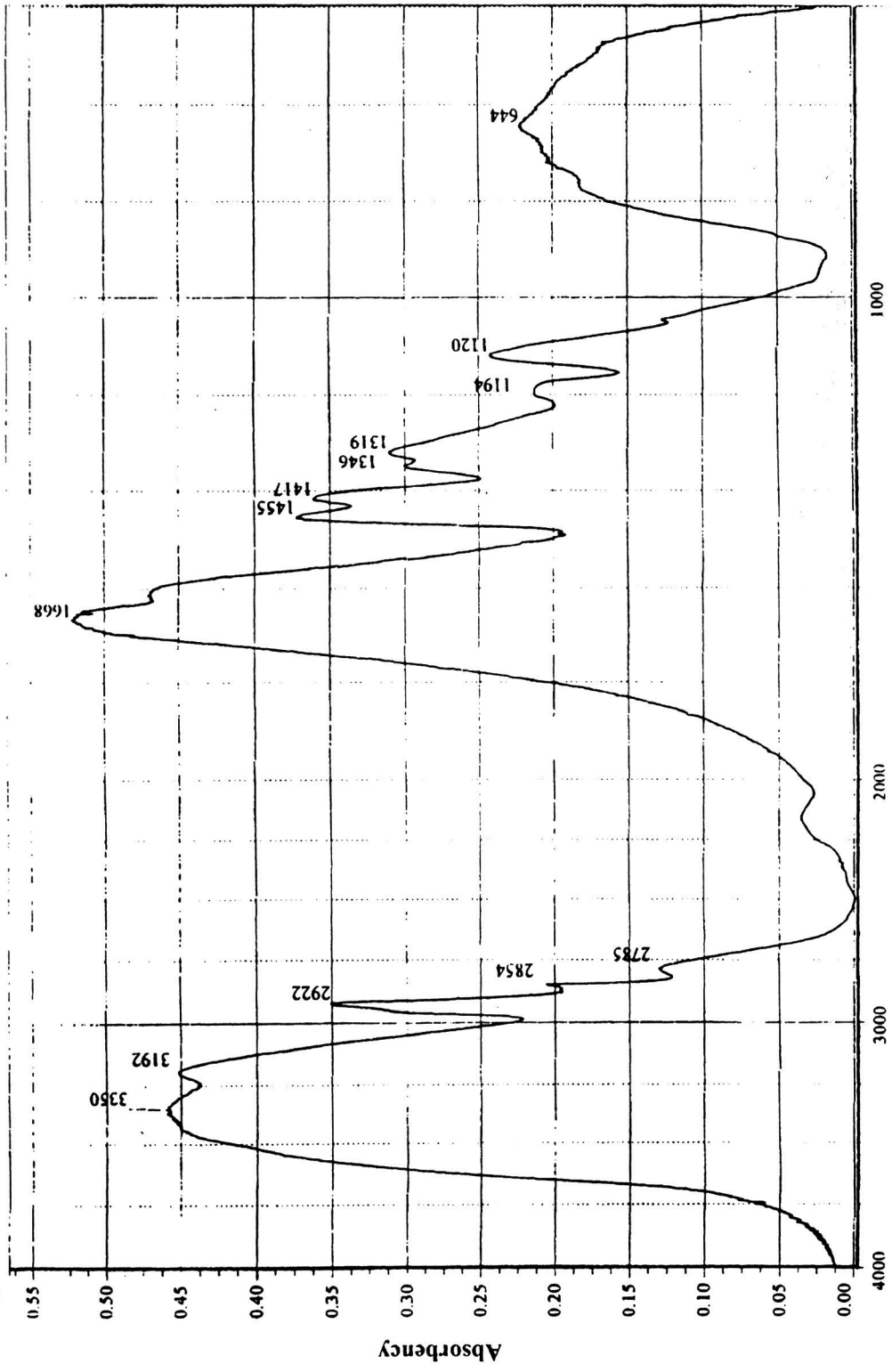
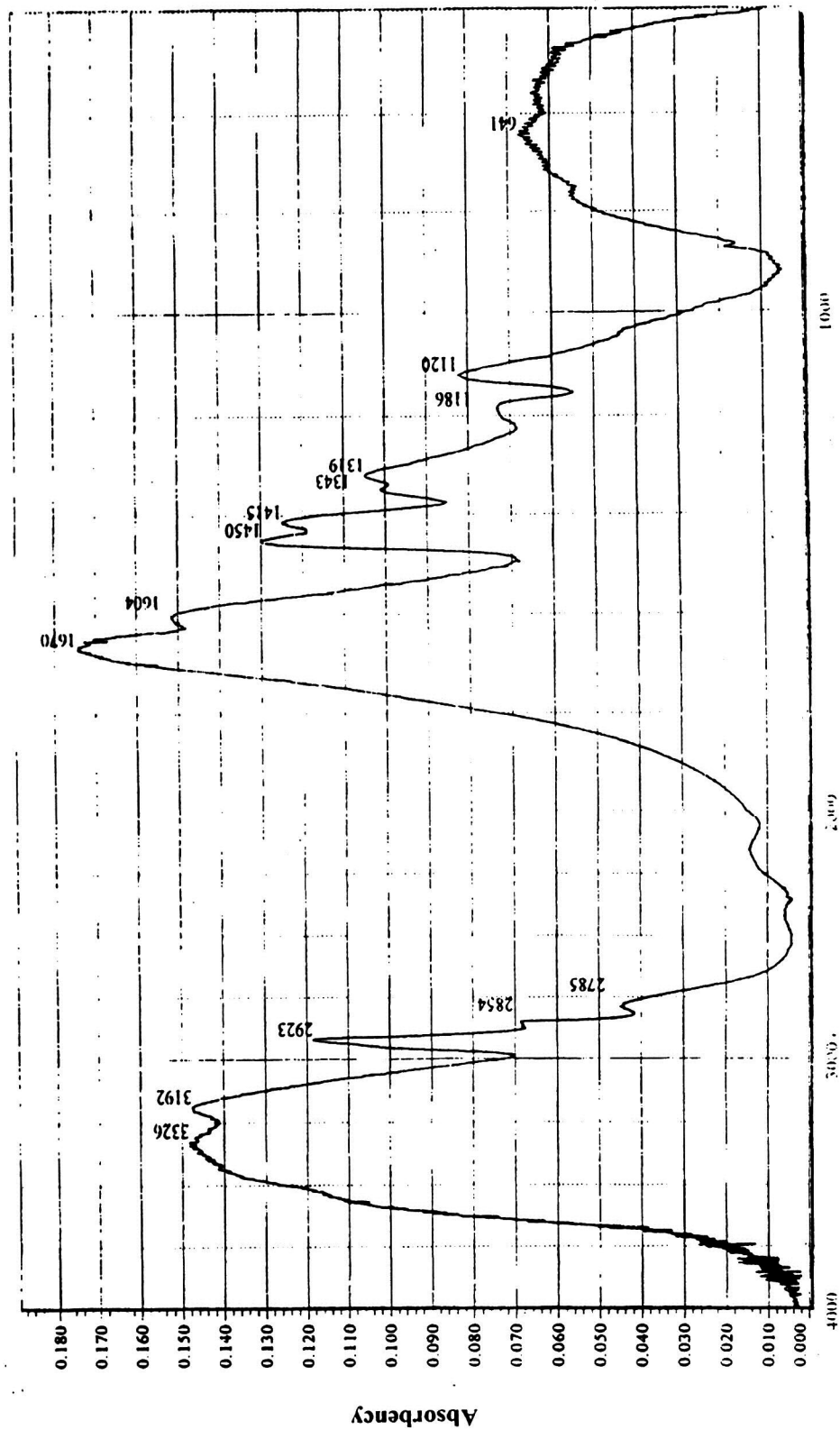


Figure 1b. IR-spectrum of the sample 20/2.



Wave Number, cm^{-1}

Figure 1c. IR-spectrum of the sample 20/3.

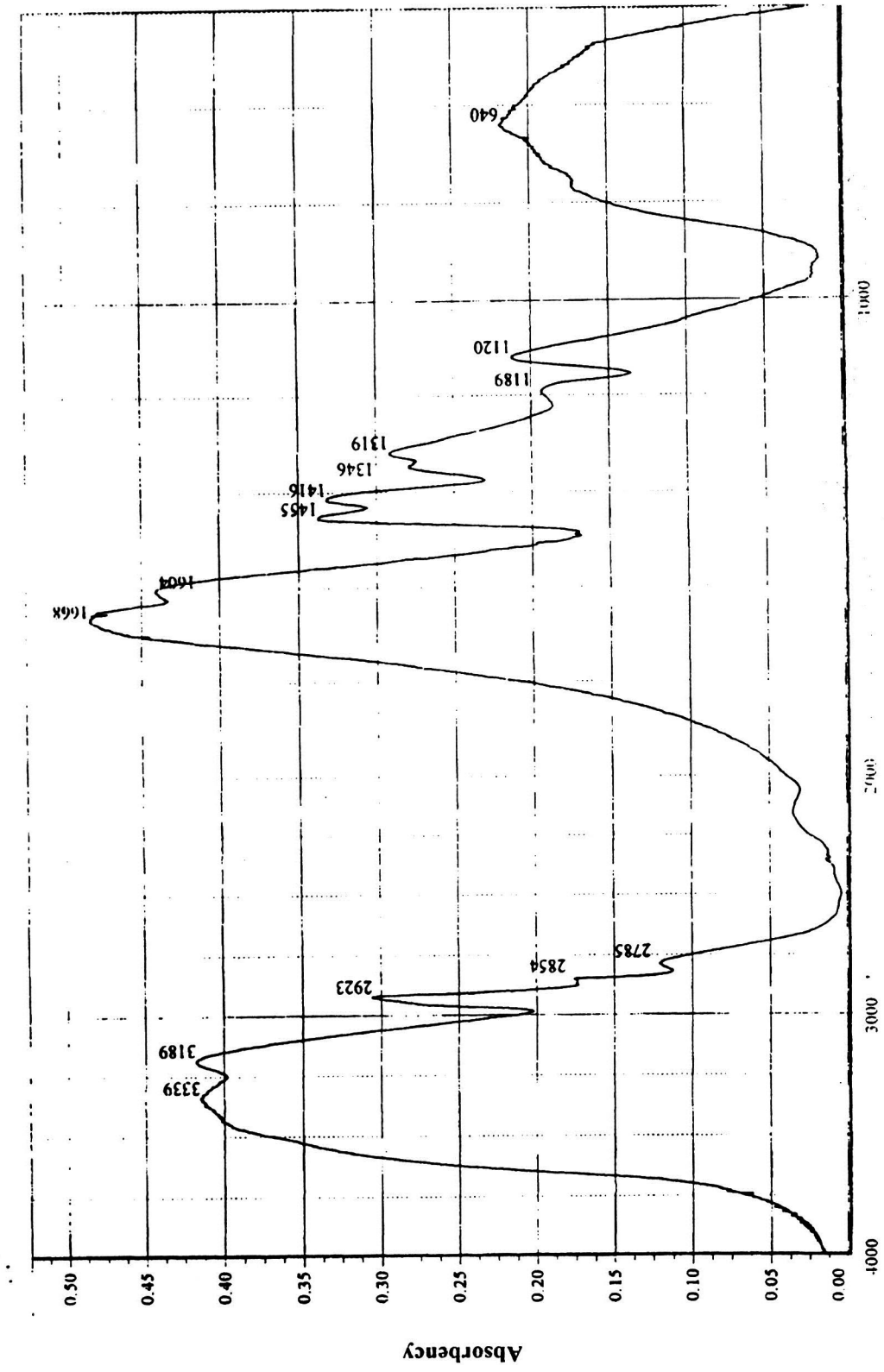


Figure 1d. IR-spectrum of the sample 20/4.

The PMR spectrum of the original polyacrylamide in D_2O (Fig.2) contains two groups of the widened signals at 1.5 and 2.0 m.d. with the ratio of the integral intensities 2:1, which are related to CH_2- and CH-fragments

of the polymer chain. The widening of the signals is, probably, connected with the steric stress in the polymer. Because of this, these fragments occur in a different magnetic surrounding caused by the anisotropy effects of the neighboring groups.

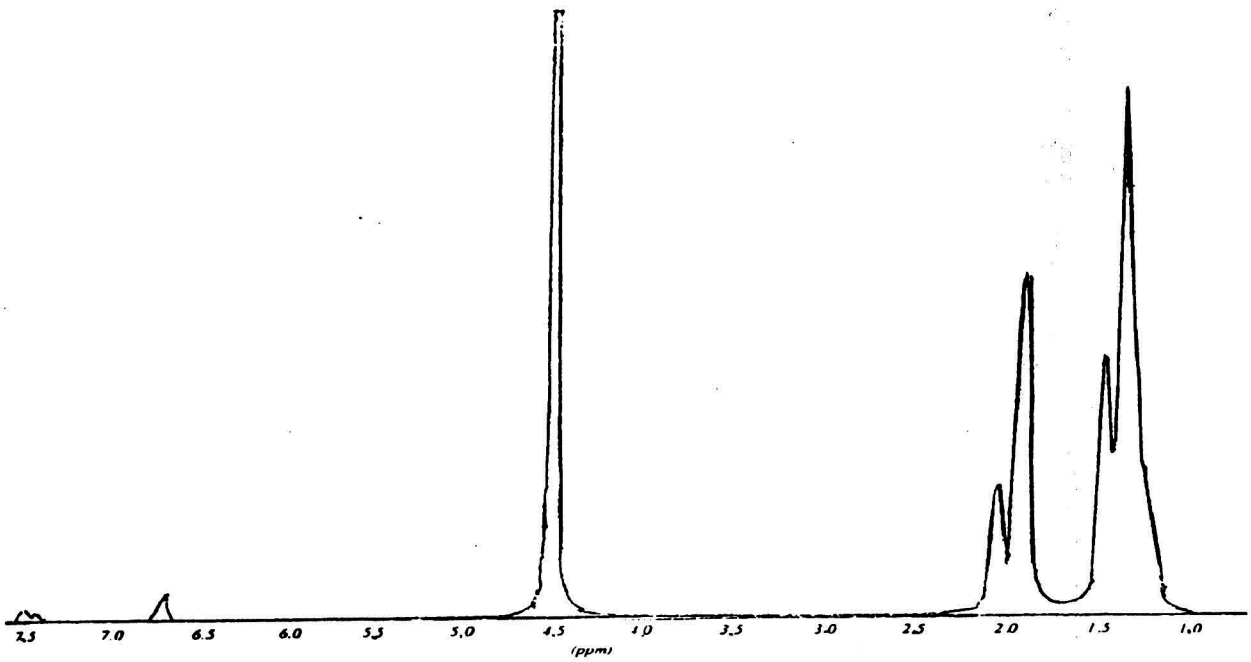


Figure 2. PMR-spectrum of the original gel based on polyacrylamide in D_2O.

In the PMR spectrum, it is also observed the widened signals of significantly intensity at 6.7 and 7.4 m.d., which can belong to the olefin protons of the original monomer, and also to the products of polymerization. The content of these protons is less than 3%.

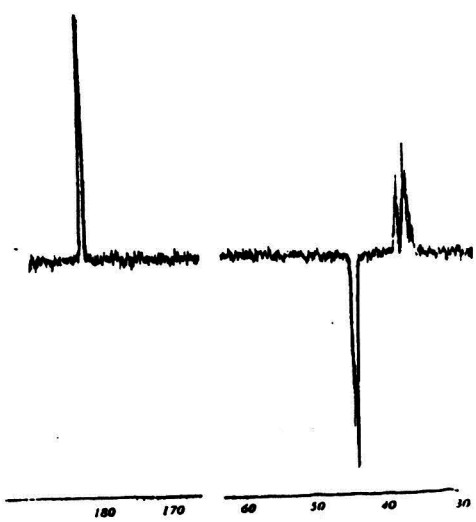


Figure 3. Spectrum NMR ^{13}C of the original gel based on polyacrylamide in D_2O obtained in the regime of the J- modulated spin echo.

The NMR ^{13}C spectrum of the original polyacrylamide in D_2O (Fig.3) obtained in the regime of the J-modulated spin echo (as a reference signal)contains a set of signals of CH_2-groups at 36-38 m.d., a set of signals of CH-groups at 43.5 - 44.3 m.d., and the widened signal at 182 m.d. related to the nuclei of the polymer carbonyl carbons.

Due to the fact that as the result of the short-term γ-irradiation, the changes in the spectra are insignificant, we conducted the prolonged irradiation, which allowed to determine the changes in the structure of the investigating polymers. After 2-hrs irradiation, the NMR spectra changed noticeably, what can witness the presence of the structure changes at irradiation.

The NMR ^{13}C spectrum on Fig.4 was obtained on the sample after long irradiation. It was determined in the usual regime. From Fig.4a, it is seen that at the base of the set of signals of the carbons of the CH-group nuclei at 44 m.d., the wide shoulders are appeared. They witness the formation of new CH-groups in another structural surrounding compared with the original polymer. In the spectra, it is also observed a very wide signal with the center at approximately 120 m.d (Fig.4b). The appearance of this signal can be connected with partial content of the alkene structures, formed at the prolonged γ-irradiation. The existence of such structures can be related with either formation of the free

acrylic acid or by separation of hydrogen from the repeating units of the main polyacrylamide chain with their transformation according to the Scheme 1 below.

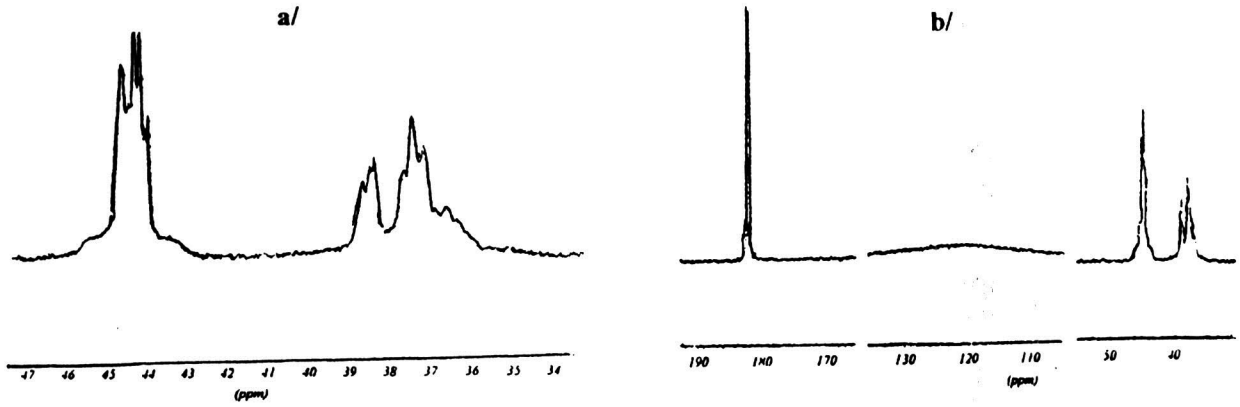
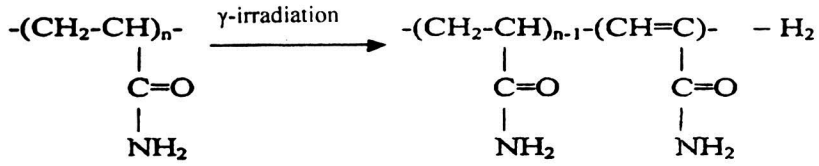


Figure 4 (a/ and b/). The NMR ^{13}C spectrum of the gel after prolonged γ-irradiation

Scheme 1.



To analyze the mechanism of the alkene structures formation, in the gel containing 3.5 % of MBAA, a certain amount of the acrylic acid (5%) was added, and then, the NMR ^{13}C spectrum of the system was taken. It was found that the spectrum did not show such shoulders, and the spectral picture was unchanged. Hence, the appearance of the wide signal can be related with formation of the structures according to the Scheme 1 above.

Conclusions

Thus, the experiments and calculations show that as the result of the γ-irradiation, the residual monomers in the original gel polymerize. It also occurs the formation of the crosslinked network in a very small concentration. The formation of the structures containing the >C=C< bonds is also occurs.

References

1. *Lopatin V.V., Askadskii A.A. // Russian Polymer News, v.8, No.3, 2003, pp.47-53.*