Obtaining a copolymer of polyhexamethylene guanidine hydrochloride and polyvinyl alcohol

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Abstract. The possibility of obtaining a polymer gel based on polyhexamethylene guanidine hydrochloride and polyvinyl alcohol under conditions of acid catalysis is considered. It was shown that the use of formaldehyde as a crosslinking agent leads to the formation of methylene bridges between the hydroxyl groups of polyvinyl alcohol and the amino groups of polyhexamethylene guanidine hydrochloride. The study of samples obtained by IR spectroscopy revealed the presence of corresponding signals of functional groups at 2780 cm⁻¹ (isolated methylene group between nitrogen and oxygen atoms) and 1580 cm⁻¹ (characteristic band of the guanidine group).

1. Introduction
The development of the chemistry of macromolecular compounds opens up significant opportunities for the use of polymeric materials in various fields, including medicine. A special place is occupied by polymer gels, which can act as the basis of many drugs, carriers of medicinal substances, and also as independent means [1, 2]. At the same time, the creation of a universal framework that can act both as a carrier matrix and as an independent means is definitely relevant. Polyhexamethylene guanidine hydrochloride and polyvinyl alcohol can be considered as components of such a polymer gel. Both polymers are gelling and biocompatible, as well as water-soluble [3, 4]. The presence of a high antimicrobial activity of polyhexamethylene guanidine hydrochloride will give such a gel its own activity, and the film-forming ability of polyvinyl alcohol will make it possible to use such a gel as an independent agent for external use.

This work proposes a method for producing a copolymer of polyvinyl alcohol and polyhexamethylene guanidine hydrochloride for use as antimicrobial coatings or disinfectants with prolonged action.

2. Materials and Methods
Polyhexamethylene guanidine hydrochloride (PHMGhch) was obtained by polycondensation (Figure 1) in melt of guanidine hydrochloride and hexamethylene diamine at a temperature of T=165°C for 3 hours. Guanidine hydrochloride was made by “Across Organics” and used without previous cleaning (99%, Tm=185-189°C, [H2O]≤0.2%). Hexamethylene diamine was cleaned by distilling method at a temperature of 205°C fraction was made at a temperature 202-205°C [3].
To obtain the gel, we used chemically pure polyvinyl alcohol (PVA). The synthesis was carried out in solution in the presence of hydrochloric acid as a catalyst. A 10% PVA solution was poured into a round-bottom flask and heated to 60 °C, then formalin solution and hydrochloric acid were added and the temperature was again brought to 60 °C, after which the PHMGhch solution was loaded with vigorous stirring. The reaction mixture was maintained under these conditions for 1.5 h, after which turbidity was first observed, and then the formation of white flakes, which quickly adhered to each other. The reaction product was extracted and washed repeatedly with distilled water (more than 10 times) until the smell of formaldehyde disappeared and the pH was neutral. IR spectra were obtained using the equipment of the Collective Use Center of Baikal Institute of Nature Management, Siberian branch, Russian Academy of Sciences.

3. Result and Discussion
The high antimicrobial activity of PHMGhch, together with its gelation property, opens up wide possibilities for the use of this class of polymers in the field of medicine. The sorption activity of the PGMGhch hydrogel [5] in relation to medicinal substances of both plant and synthetic origin makes it possible to create a complex agent for the treatment of skin lesions. Currently, gels and ointments are widely used for the treatment of wound surfaces, while in the case of the treatment of such injuries in the field, it may be necessary to use an agent with a prolonged effect of action. Therefore, traditional drugs may not be suitable due to regular application to the wound surface. One of the approaches to solving this problem can be the preparation of a copolymer of PVA and PGMGhch.

The synthesis of a copolymer of PVA and PGMGhch was carried out under conditions of acid catalysis. The basis was the synthesis of polyvinylformal (PVF) [6], which is also carried out in the presence of hydrochloric acid, resulting in the formation of a formal with an isolated methylene group between oxygen atoms, exhibiting signals in the IR spectrum in the region at 2780 cm⁻¹ [7].

It is known that formaldehyde interacts with both amines and alcohols, on the basis of which it was assumed that the reaction can proceed according to the following scheme (figure 2)[8]:

![Figure 2. Proposed scheme for the synthesis of PHMGhch and PVA gel.](image-url)
The resulting product was investigated by IR spectroscopy. Figure 3 shows that in the region of 2780 cm\(^{-1}\) there is a characteristic signal for an isolated methylene group between oxygen and nitrogen atoms.

Figure 3. IR spectrum: 1) copolymer PVA:PHMGhch; 2) PVF; 3) PVA.

Figure 4 shows IR spectra of the copolymer PVA:PHMGhch and PHMGhch. A specific absorption band of the guanidine group is present in the region of 1600 cm\(^{-1}\), which may indicate their presence in the structure of the compound. In the region of absorption of free amino groups in the copolymer, a broad band is observed, which by its nature more closely resembles the absorption of hydroxyl groups, which is associated with the overlap of their signals. A similar pattern can be observed in the region of bending vibrations at 1000 cm\(^{-1}\).

Figure 4. IR spectrum: 1) PHMGhch; 2) copolymer PVA:PHMGhch.

Thus, when comparing IR spectra of starting compounds and the reaction product, it was found that the latter contains specific signals that allow indirectly asserting the interaction with the formation of the PVA: PHMGhch copolymer.
With repeated washing with distilled water, the resulting product swelled with each successive time. Washing was carried out to constant weight. The equilibrium degree of swelling was determined by the gravimetric method, which was 19 g / g, which is less than the PHMGhch hydrogel [3]. This is probably due to the fact that during the formation of a bond between PHMGhch and PVA, a parallel reaction of PVF formation occurs, which is also indirectly confirmed by swelling in dioxane, which is a solvent for PVF.

It was previously established [5] that the PHMGhch hydrogel obtained by crosslinking the terminal amino groups with formaldehyde undergoes degradation upon prolonged exposure to an aqueous medium. The destruction proceeds with the formation of PHMGhch fragments and, probably, formaldehyde in the gem-diol form. To exclude the likelihood of the formation of the PHMGhch hydrogel and PVF separately, the resulting copolymer was placed in distilled water for 14 days. So, in figure 5 shows the absence of fundamental differences, which may indicate the formation of the compound shown in the scheme of the proposed reaction.

![IR spectrum](image)

**Figure 5.** IR spectrum: 1) PVA / PHMGhch copolymer 2) PVA / PHMGhch copolymer after 14 days in distilled water.

### 4. Conclusion

As a result of the work done, a copolymer of polyhexamethylene guanidine hydrochloride and polyvinyl alcohol was synthesized. The resulting compound was an elastic, water-swellable polymer gel with an equilibrium swelling rate of 19 g / g. The structure of copolymer was indirectly confirmed by IR spectroscopy. It was shown that at 1580 cm\(^{-1}\), there is a clear specific band of the guanidine group, the intensity of which remains after 14 days of being in distilled water. The presence of a signal at 2780 cm\(^{-1}\) confirms the presence of an isolated methylene group between the oxygen and nitrogen atoms, which binds polyvinyl alcohol and polyhexamethylene guanidine hydrochloride. In the future, it is planned to study the sorption properties of the obtained copolymer using the example of extracts of medicinal plants.

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