

Hydrogels of Polysaccharide Carboxymethyl Hydroxypropyl Guar Crosslinked by Multivalent Metal Ions

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Abstract—Hydrogels of polysaccharide carboxymethyl hydroxypropyl guar crosslinked by chromium(III) ions are synthesized. The effect of crosslinker concentration on the mechanical behavior of the gels is studied, and the amount of chromium compounds able to interact with polymer chains and the amount of carboxyl groups of the polymer involved in crosslinking are compared. It is shown that the elastic modulus of the gels attains a constant value when not all but only about 10% functional groups interact with chromium compounds. At high concentrations, crosslinker molecules basically bind to one functional group; as a result, the gel recharges. This binding proceeds until all carboxyl groups are filled.

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INTRODUCTION

One of the key methods of obtaining hydrogels involves the crosslinking of polymer macromolecules. This is the single method for producing nontoxic, biocompatible, and biodegradable gels from natural polymers. Many of these polymers are polyanions; therefore, cations of multivalent metals are often used as crosslinkers [1–3]. Gels crosslinked by multivalent cations have found use in many fields, for example, in biomedical applications [4] to replace damaged tissues [5], because they can serve as a matrix for the controlled growth of cells [6]; for 3D-printing of biocompatible materials [7]; and for creation of artificial leather [8] and soft robotics components [9]. They are also used as thickeners in the food [10] and oil-producing industries [11, 12] and as absorbents of toxic metal ions (Cu²⁺, Cd²⁺, Cr⁶⁺, etc.) [13] in water purification. Control over crosslinking makes it possible to attain the optimum mechanical properties of gels for each particular application.

Networks with a tailored architecture (with a given amount of intermolecular crosslinks and loops) can be obtained only using specially synthesized macromolecules with a strictly determined chemical structure, for example, with terminal functional groups and the known number of branches [14–16]. Polysaccharides and their derivatives usually possess a more complex architecture, that is, the presence of randomly bound side chains, the statistical distribution of functional groups along the chain, and their different positions.

Accordingly, networks produced by the crosslinking of polysaccharides are characterized by a much more complex structure: they may contain more or less densely crosslinked regions [17] and defects [18] and even be microphase separated [19]. The structure and mechanical properties of polysaccharide networks primarily depend on the character of interaction between a crosslinker and polysaccharide functional groups, including the chemical nature and energy of the bond formed and the crosslinker functionality determined by the charge of corresponding ions.

For anionic polyelectrolytes, various cations may serve as crosslinkers: divalent (Ca²⁺, Mg²⁺, Ba²⁺) [20, 21], trivalent (Fe³⁺, Al³⁺, Cr³⁺) [22], and tetravalent (Ti⁴⁺ and Zr⁴⁺) [23, 24]. They can form crosslinks with strongly different energies. For example, the study of xanthan gels showed that crosslinks formed by Al³⁺ ions are stronger (51 *kT*) than crosslinks formed by chromium Cr³⁺ ions (20 *kT*) [22]. At the same time, in poly(acrylic acid) gels, Al³⁺ and Fe³⁺ ions form crosslinks with a much lower energy capable of self-recovery upon rupture [25, 26].

One of the most interesting cases is polyelectrolyte crosslinking by chromium(III) ions, because crosslinking proceeds fairly slowly (the gelation time may be several minutes or even hours [27, 28]). This makes it possible to obtain an evenly crosslinked network within the entire volume of the gel, in contrast, for example, to crosslinking by Ca²⁺ and Al³⁺ ions occur-

ring almost instantaneously [29, 30]. This behavior of chromium ions is associated with the structure of chromium compounds in aqueous solutions. At different pH values, chromium ions $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ coexist with $\text{Cr}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ and $\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4^+$ hydroxides. These monomers may associate to form oligomers (olates), which serve as effective crosslinkers [31]. Moreover, chromium crosslinks are not of electrostatic but predominantly of coordination covalent nature [32]. As a consequence, they are fairly strong and do not break down spontaneously. The kinetic features of polyelectrolyte gelation in the presence of chromium ions were studied in detail [28, 33, 34]. At the same time, little attention was paid to the mechanical properties of gels after synthesis. For example, the study of the swelling behavior of xanthan and partially hydrolyzed polyacrylamide gels revealed that, as the concentration of chromium added in synthesis increases, the amount of chromium ions bound by the gel first increases and then assumes a constant value [18, 35]. It was observed that not all carboxyl groups of the polymer are filled with ions; however, the reasons behind this behavior remained unclear and the formation of various monomeric and oligomeric chromium compounds was not taken into account.

As was shown in [36], with an increase in the concentration of chromium ions, the elastic modulus of xanthan gels initially increases and then reaches a plateau. These authors believe that this circumstance may be explained by the fact that only a limited amount of chromium ions smaller than the amount of carboxyl groups (approximately one chromium ion per six xanthan monomer units) can attach to polymer chains owing to electrostatic repulsion between ions bound and not bound to chains. It was assumed that all bound chromium ions form crosslinks, while ions not forming crosslinks (bound to one carboxyl group) were disregarded.

It was found that the value of pH influences the mechanical properties of gels [37]. For example, at low pH values (usually below 2), no gelation occurs because the carboxyl groups of the polymer are fully protonated, which hinders their interaction with metal ions. At high pH values (usually above 6), ions are transformed into insoluble hydroxides, which also cannot induce crosslinking.

This work concerns the synthesis and investigation of the mechanical properties of gels based on the guar derivative, high molecular weight polysaccharide carboxymethyl hydroxypropyl guar (CMHPG) containing semiflexible chains (their inherent persistence length is about 10 nm [38]); as a consequence, the CMHPG-based gels are not brittle even at high crosslinker concentrations. The hydrogels of guar and hydroxypropyl guar (HPG) were extensively studied, and in the overwhelming majority of papers, borate ions were used as crosslinkers [38–40]. At high pH

values, they can form dynamic covalent bonds with the hydroxyl groups of polymer chains, thereby inducing crosslinking [38]. Crosslinks formed by borate ions have an extremely low energy, about 5–20 kT [41]. Guar and HPG were crosslinked by metal ions, for example, Ti^{4+} [42] or Zr^{4+} [43]. It is believed that metal ions participate in the reaction of ligand exchange with hydroxyl groups of the polymer [44]; however, the authors of [45] suppose a more complex mechanism of crosslinking, including the formation of colloidal metal particles. The crosslinking of guar derivatives containing carboxyl groups (CMHPG and carboxymethyl guar) by metal ions was described only in single publications [46, 47]. For example, it was shown that the ions of trivalent metals (Al^{3+} and Fe^{3+}) are more effective for preparing microgranules of crosslinked carboxymethyl guar than the ions of divalent metals (Ba^{2+} , Ca^{2+} , etc.) [47].

The goal of this work is to gain insight into the relationship between the laws controlling the crosslinking of CMHPG by metal ions at the molecular level and the mechanical properties of the resultant gels.

EXPERIMENTAL

Materials

In this work, CMHPG of the POLYFLOS CH410P brand (Lamberti) and chromium(III) chloride hexahydrate (Sigma-Aldrich, purity > 98%) were used. According to viscometry, the molecular weight of CMHPG was 1.6×10^6 . Solutions were prepared using deionized distilled water obtained on a Milli-Q system (Millipore Waters), and in NMR experiments, deuterated water (AstraKhim, Russia; isotopic purity > 99.9%) was used.

Polymer Purification

The aqueous solution of CMHPG (0.5 wt %) was subjected to vacuum filtration through Robu ceramic filters with a pore diameter of 16–40 μm to remove water-insoluble impurities. The polymer was then reprecipitated in ethanol (polymer solution : ethanol = 1 : 10, vol), and the resulting precipitate was dissolved in water and lyophilized. The purified polymer dissolved to form completely transparent aqueous solutions, and the viscosity of solution did not decrease with time.

Sample Preparation

The aqueous solution of CMHPG with the desired concentration was initially prepared under stirring on a magnetic stirrer for a day. Afterwards, a crosslinker (CrCl_3) solution (0.6 wt %) was added, and the mixture was vigorously stirred with a spatula for 10–20 s and allowed to rest for a day. The CrCl_3 solution was

prepared 2 to 3 days before use so that the hydrolysis of chromium ions was complete [48].

Mechanical Properties

The mechanical properties under shear deformation were studied on a Physica MCR 301 rotational rheometer (Anton Paar, Austria). For this purpose, cylindrical gel samples with a height of 8 mm and a diameter of 25 mm were synthesized. The plate–plate geometry of the measuring cell with a diameter of 25 mm was used. The temperature, which was controlled using Peltier elements, was set to $20.00 \pm 0.05^\circ\text{C}$. To avoid evaporation of the solvent from the sample during measurements, a casing with Peltier elements was used. Experiments were carried out in the oscillation mode, in which the frequency dependences of the storage modulus G' and the loss modulus G'' were measured in the range of external impact frequency $\omega = 0.04\text{--}50\text{ s}^{-1}$. All measurements were performed in the linear viscoelasticity mode (at a strain amplitude of $\gamma = 1\text{--}5\%$), in which the storage and loss moduli were amplitude independent. The experimental procedures were described in detail in [49–51].

The compression modulus of gels E was determined on a lab installation which made it possible to measure load (force) F in the range of 0–6 N (accuracy, 0.001 N) and strain in the range of 0–30 mm (accuracy, 0.01 mm). The compression rate was 0.6 mm/min. For compression experiments, cylindrical gel samples with a height of 10 mm and a diameter of 10 mm were synthesized. The value of E was calculated according to the relation of the classical theory of elasticity of polymer networks [52]

$$\sigma = E/3(\lambda - 1/\lambda^2),$$

where σ is stress ($\sigma = F/S_0$, F is the applied force, and S_0 is the cross-sectional area of the undeformed sample), and λ is the relative strain (ratio of the heights of the gel in the deformed and undeformed states).

Nuclear Magnetic Resonance Spectroscopy

^1H NMR spectra were measured on a Bruker AV-600 spectrometer using D_2O as a solvent. The experimental technique was described in detail in [53, 54]. Spectra were taken at 70°C in order to reduce the viscosity of the sample and the broadening of lines, to shift signals of the solvent to the strong field (4.3 ppm), and to register signals due to C1 protons of saccharide rings situated in the range of 4.5–5.3 ppm. The sample was placed in a standard quartz ampoule (Norell) with a diameter of 5 mm. The data were processed using the Bruker TopSpin software program, including phase and baseline correction. The signal of the solvent served as a reference for determining chemical shifts.

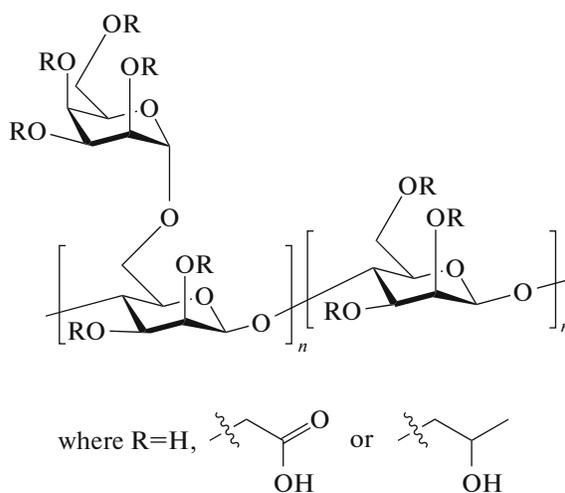
^{13}C NMR spectra were measured on a Bruker AvanceII-300 spectrometer (7.0 T; frequency, 75.5 MHz) using D_2O as a solvent. The internal secondary standard was dimethyl sulfoxide- d_6 (39.5 ppm for ^{13}C nuclei). The viscosity of the sample was decreased by adding 0.5 mL of 3% NaOH solution in D_2O to the initial substance (15 mg). Spectra were measured at a temperature of 50°C and 15-h accumulation of the signal with a 3-s delay between pulses. For quantitative interpretation of the ^{13}C NMR spectra, an inverse gated (IGATED) decoupling pulse sequence was used which allows one to avoid a disproportionate change in the signals of separate groups related to the nuclear Overhauser effect.

X-ray Fluorescence Analysis

X-ray fluorescence analysis (XRF) [55] was carried out on a VRA-30 spectrometer (Carl Zeiss, Germany) in a vacuum chamber. Fluorescence was excited using an X-ray tube with a molybdenum anode at a voltage of 40 kV and a current of 20 mA. To prepare the samples, the gels were dried, ground to the powdery state, and pressed into pellets. A LIF200 analyzing crystal, 0.17° collimator, and SD + FD detectors were used. Measurements were carried out two to three times, and the content of chromium atoms in the sample was averaged.

RESULTS AND DISCUSSION

In this work, CMHPG hydrogels crosslinked by chromium(III) ions were studied. The main chain of CMHPG molecules is composed of mannose units to which side galactose units are attached randomly. The structural formula of carboxymethyl hydroxypropyl guar is outlined below.



Part of the OH groups were replaced with carboxymethyl and hydroxypropyl groups. The polymer concentration was 1 wt % (52 mmol/L of monosaccharide residues), which corresponds to the semidilute

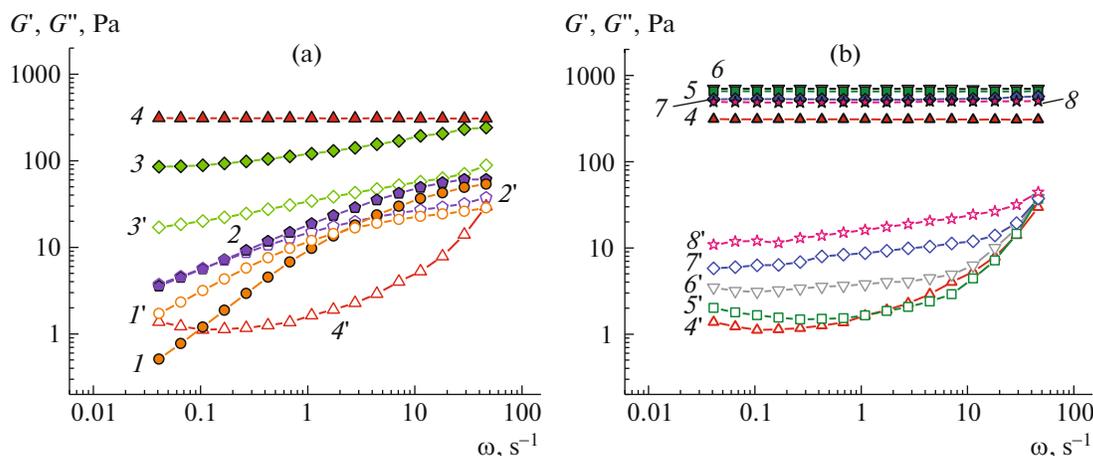


Fig. 1. Frequency dependences of ($1-8$) the storage modulus G' and ($1'-8'$) the loss modulus G'' for aqueous solutions containing 1 wt % CMHPG and different concentrations of the crosslinker CrCl_3 added during the synthesis. $C_{\text{Cr}} = (1, 1')$ 0, ($2, 2'$) 0.11, ($3, 3'$) 0.22, ($4, 4'$) 0.78, ($5, 5'$) 2.2, ($6, 6'$) 5.6, ($7, 7'$) 9.0, and ($8, 8'$) 11.2 mmol/L. $T = 20^\circ\text{C}$. Color figures are available in the electronic version.

regime. At the given concentration, CMHPG macromolecules can be crosslinked to form a spatial network via the interaction of chromium ions with carboxymethyl groups of various polymer chains. Studies were carried out at the CrCl_3 concentration $C_{\text{Cr}} = 0-11.2$ mmol/L.

The mechanical characteristics of the gels, that is, the frequency dependences of the storage modulus G' and the loss modulus G'' , are shown in Fig. 1 for various crosslinker concentrations. In the absence of the crosslinker, the polymer forms a solution with weak viscoelastic properties: in the high frequency region, $G' > G''$; that is, the elastic response to the mechanical impact prevails; and in the low frequency region, $G' < G''$; that is, viscous properties predominate. The elastic response and the presence of a weakly defined plateau on the $G'(\omega)$ plot indicate the existence of entanglements between macromolecules. The solution flows, and its viscosity at zero shear rate is 32 Pa s.

Upon addition of small crosslinker concentrations (up to 0.11 mmol/L), the general shape of the curves is preserved (Fig. 1a); however, the slope of the curve $G'(\omega)$ at low frequencies increases, which indicates the approaching gelation. At a crosslinker concentration of 0.11 mmol/L, curves $G'(\omega)$ and $G''(\omega)$ become parallel, and it may be assumed that this concentration corresponds to the gelation point [56], that is, formation of the network throughout the solution volume. Note that, at crosslinker concentrations below 0.22 mmol/L, the loss modulus G'' increases. This is evidence for a rise in viscosity due to crosslinking between macromolecules and an increase in the dissipation energy under mechanical deformation. The growth of G'' continues at concentrations that are somewhat higher than the concentration at the gelation point, because apparently not all macromolecules are involved in the formation of the network and it

contains a large amount of the sol fraction. At higher crosslinker concentrations (up to 11.2 mmol/L), a plateau is observed within the entire studied frequency region $G' > G''$ and on the plot of $G'(\omega)$, which suggests gelation. In this concentration range, G'' is lower than that at a crosslinker concentration of 0.22 mmol/L. This fact indicates a considerable reduction in the role of viscous relaxation processes, which is probably associated with the presence of the fully formed network, into which a greater part of macromolecules are incorporated. Indeed, at crosslinker concentrations less than 0.78 mmol/L, the shape of the curves of $G'(\omega)$ and $G''(\omega)$ changes appreciably, which indicates gradual formation of the network and the incorporation of a larger amount of macromolecules into it. In the crosslinker concentration range of 0.78–11.2 mmol/L, the shape of the curves of $G'(\omega)$ and $G''(\omega)$ remains almost unchanged (Fig. 1b), which provides evidence for gel formation. However, in this case, the loss modulus G'' grows to some extent; that is, the dissipation of mechanical energy becomes more pronounced during the deformation process. Hence, at high crosslinker concentrations, despite a slight change in the storage modulus, the structure of the gels changes. It appears that defects are formed in the network which are not elastically active elements and are capable of moving, for example, free ends; as a result, stress relaxation occurs [57].

Plots $G'(\omega)$ and $G''(\omega)$ have no intersection points and are typical of chemically crosslinked gels. This fact shows that crosslinks formed by chromium ions are fairly strong and do not break down once formed. A similar behavior is observed, for example, for xanthan crosslinked by chromium ions [19]. The authors of [58] assume that chromium crosslinks are of partially electrostatic and partially coordination covalent

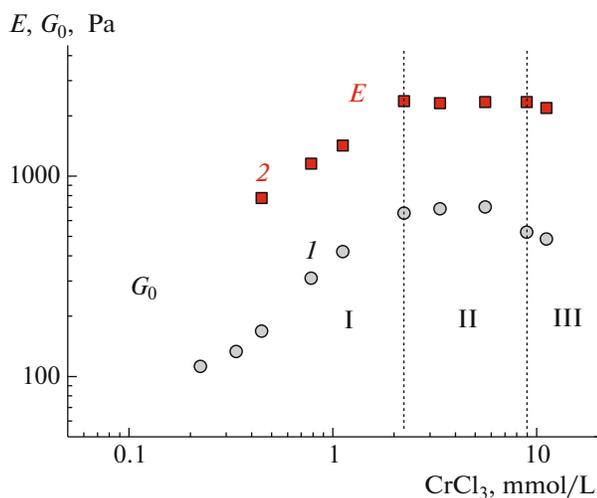


Fig. 2. The shear modulus G_0 (1) and the compression modulus E (2) as a function of the concentration of the crosslinker CrCl_3 added during the synthesis for aqueous solutions containing 1 wt % CMHPG. $T = 20^\circ\text{C}$. Here and in Fig. 5, vertical dashed lines denote boundaries of three crosslinker concentration regions discussed in the text.

nature, as confirmed by high values of their energy (42 kJ/mol) [22].

There are three regions on the dependence of the shear modulus G_0 on crosslinker concentration (Fig. 2). At low crosslinker concentrations ($C_{\text{Cr}} < 2.2$ mmol/L), the plateau storage modulus increases (for crosslinker concentrations, at which no plateau is observed, the values of G' at 0.7 s^{-1} are taken as G_0). At intermediate crosslinker concentrations ($2.2 \text{ mmol/L} < C_{\text{Cr}} < 9$ mmol/L), G_0 remains almost invariable. Finally, at high crosslinker concentrations ($C_{\text{Cr}} > 9$ mmol/L), G_0 decreases slightly.

The gels in all three regions were studied in compression experiments (experiments were conducted at crosslinker concentrations above 0.45 mmol/L, because at lower concentrations the gels are cross-linked so slightly that they change shape under their own weight). Figure 3a shows the compression curves obtained at various chromium concentrations. From the initial portion of the curves (Fig. 3b), the values of the compression modulus E were determined (Fig. 2). It is seen that the compression modulus obeys the same dependence on C_{Cr} as the shear modulus G_0 . Note that, at crosslinker concentrations above 2.2 mmol/L, the slope of compression curves remains more or less the same in the small strain range (Fig. 3b), which corresponds to a constant shear modulus. At the same time, in the entire crosslinker concentration range, the gels are capable of large reversible deformations—they may be compressed by 90–95% without breakdown.

It is important to note that in this work the mechanical properties of the gels after synthesis, which are not equilibrium swollen, were investigated. Our results correspond to the constant polymer concentration in the gels. The equilibrium degree of swelling α^3 decreases with an increase in the degree of crosslinking (see below), because for polyelectrolytes in a good solvent $\alpha^3 \sim N^{3/2}$ [59]. As a consequence, at low degrees of crosslinking, the elastic modulus of equilibrium swollen gels is smaller than that for the gels after synthesis. For example, at a crosslinker concentration of 0.45 mmol/L, the degree of swelling is on the order of 39; that is, the polymer concentration ϕ in the equilibrium swollen gel is smaller than that in the gel after synthesis; as a result, the elastic modulus decreases upon swelling (since, e.g., for polyelectrolyte gels in the absence of

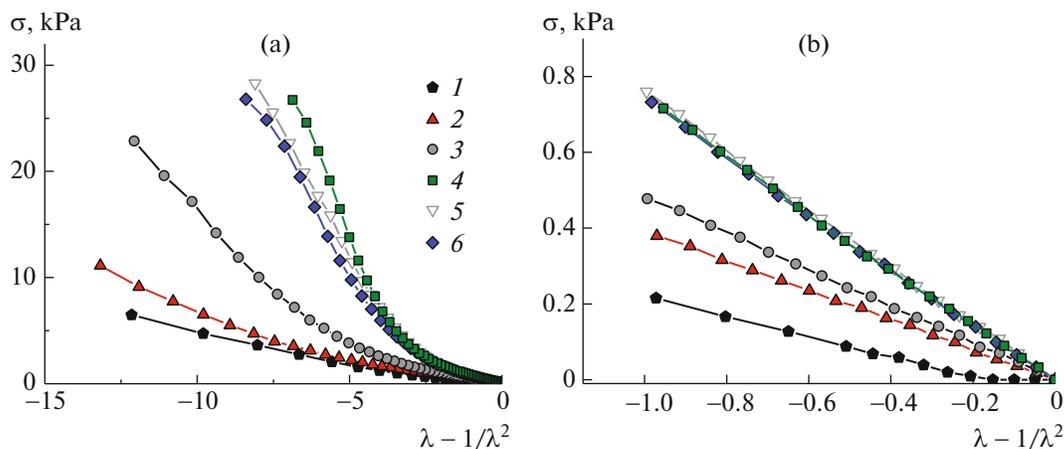


Fig. 3. (a) Plots of stress σ vs. $\lambda - 1/\lambda^2$ and (b) their initial regions for hydrogels containing 1 wt % CMHPG and different concentrations of the crosslinker CrCl_3 added during the synthesis. $C_{\text{Cr}} = (1)$ 0.45, (2) 0.78, (3) 1.1, (4) 2.2, (5) 5.6, and (6) 9.0 mmol/L. $T = 20^\circ\text{C}$.

Table 1. pH values of gels and the fraction of various chromium compounds with varying concentration of the added crosslinker CrCl₃ [64]

[CrCl ₃], mmol/L	pH	Cr(H ₂ O) ₆ ³⁺ , mol %	Cr(OH)(H ₂ O) ₅ ²⁺ , mol %	Cr(OH) ₂ (H ₂ O) ₄ ⁺ , mol %	Cr ₂ (OH) ₂ ⁴⁺ , mol %	Cr ₃ (OH) ₄ ⁵⁺ , mol %
0.45	5.30	1	9	16	0	74
0.78	5.10	2	11	14	1	72
1.10	4.90	4	13	12	3	68
2.20	4.60	9	16	9	3	63
3.40	4.30	15	18	5	4	58
5.60	3.75	29	19	2	5	45
9.0	3.40	44	16	0	4	36
11.20	3.35	50	14	0	3	33

salt, $G_0 \sim \phi^{5/6}$ [60]). Thus, with an increase in the degree of crosslinking, a difference between the elastic moduli of the equilibrium swollen gels and the gels after synthesis becomes less distinct. In what follows, the elastic moduli of the gels after synthesis are considered.

To explain the mechanical behavior of the gels, it is necessary to gain insight into the features of CMHPG crosslinking at the molecular level. The process of crosslinking depends, first, on the amount of CMHPG functional groups accessible for crosslinking and, second, on the structure and type of compounds formed by chromium ions in solution.

The total amount of functional carboxymethyl groups of the polymer was assessed by NMR spectroscopy. The peaks in the spectra were assigned in accordance with [61]. According to the ¹H NMR spectrum (Fig. 4a), the amount of hydroxypropyl groups per monosaccharide residue was calculated from the ratio of areas of peaks at 3.07 ppm (the signal of –CH₃ protons of the hydroxypropyl group) and 4.5–5.3 ppm (the signal of C1 protons bound to two oxygen atoms). It amounted to 0.41. From the IGATED ¹³C NMR spectrum (Fig. 4b), the ratio of the amounts of carboxymethyl (175–180 ppm) and hydroxypropyl groups (15–20 ppm) was estimated to be 0.25. Hence, it follows that the amount of carboxymethyl groups per monosaccharide residue is 0.1 and their total concentration is 5.3 mmol/L. It is known that only deprotonated carboxyl groups –COO[–] are involved in interaction with chromium ions, which is explained by the fact that the replacement of protons with chromium compounds is hardly possible [62]. The amount of deprotonated groups decreases with decreasing pH, which occurs with increasing crosslinker concentration in the gels because during their preparation the polymer aqueous solution (pH 5.5) is mixed with the CrCl₃ solution (pH ~ 2.8). The pH values of the gels at various CrCl₃ concentrations are given in Table 1. The inherent dissociation constant of carboxymethyl groups p*K* is about 3.4 [63]. Note that carboxymethyl

groups are fairly far apart, which excludes their mutual influence during dissociation. Taking these data into account, the concentration of deprotonated groups at various crosslinker concentrations was calculated (Fig. 5b).

As regards chromium ions, in aqueous solutions they form several compounds. A Cr³⁺ ion coordinates to six water molecules and exists as Cr(H₂O)₆³⁺. This compound prevails at pH < 2 [64]. At higher pH values, hydrolysis occurs to yield hydroxide ions Cr(OH)(H₂O)₅²⁺ and Cr(OH)₂(H₂O)₄⁺ and hydroxide Cr(OH)₃, which is insoluble in water. Different monomer ions form stable oligomers with each other (olates), such as Cr₂(OH)₂⁴⁺, Cr₃(OH)₄⁵⁺, etc. The fractions of each hydroxide ion and olate change with varying pH. They were calculated in accordance with [64] (Table 1). The crosslinking of carboxyl groups by various chromium ions proceeds via the reaction of ligand exchange, in which coordinated water molecules are replaced with polymer COO[–] groups [31]. Given this, different chromium ions have different ability to attach to carboxyl groups and different efficiency of crosslinking. For example, monomer ions cannot crosslink carboxyl groups [22], since they are weakly bound to them. On the contrary, olates can form crosslinks [32].

The amount of chromium ions bound to CMHPG molecules was estimated as follows. The gels were placed in a large amount of the solvent; as a result, ions not bound to polymer chains left them and passed to the external solution. Afterwards, the gels were dried and the amount of chromium ions remaining in them was estimated by X-ray fluorescence analysis. A comparison of the amount of chromium atoms bound to the gel with the total amount of added salt CrCl₃ (with concentration C_{Cr}) is presented in Fig. 5a.

The total amount of chromium compounds (various monomers and oligomers) bound to polymer chains was calculated from the amount of the bound

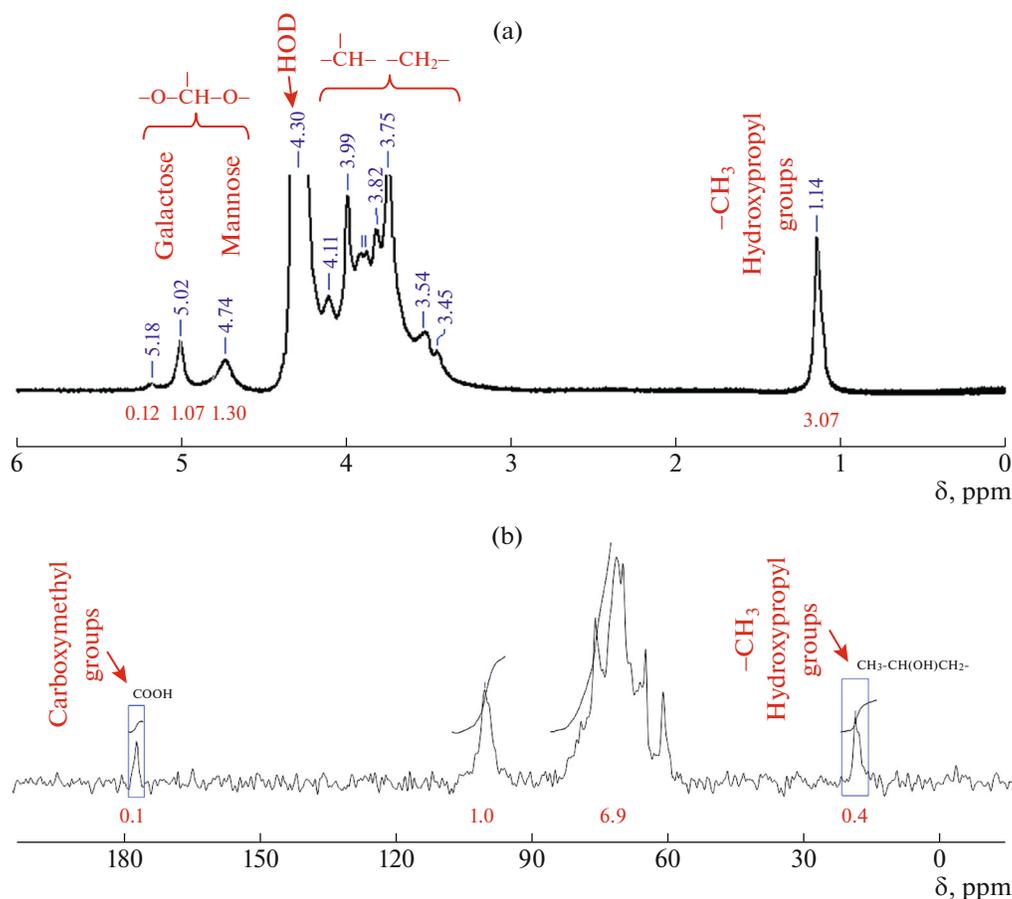


Fig. 4. (a) ^1H NMR spectra of 0.8% CMHPG solution in D_2O at 70°C and (b) IGATED ^{13}C NMR spectrum of 3% CMHPG solution in D_2O at 50°C . The peaks are assigned in accordance with [61].

chromium atoms and the fractions of each of the compounds formed at different pH values (Table 1). The amount and full charge of the bound compounds are compared with the amount of deprotonated carboxyl groups of the polymer in Fig. 5b.

It is seen that, at low C_{Cr} (<2.2 mmol/L, region I) corresponding to the region of growth of the elastic modulus in Fig. 2, almost all chromium is bound to the gel (Fig. 5a). This occurs because in this region the amount of deprotonated COO^- groups to which the ions can bind is much larger than the total amount of chromium (Fig. 5b). In this situation, chromium monomers and oligomers can bind to several COO^- groups of different macromolecules, forming intermolecular crosslinks contributing to the elasticity of the gel; to several COO^- groups of a single macromolecule, forming loops; and to one COO^- group [18]. The effective amount of chromium compounds yielding transverse crosslinks (Fig. 5c) was estimated from the compression modulus E according to the formula [65]

$$v_{\text{cr}} = \frac{E}{3RT(f/2)},$$

where R is the universal gas constant, T is temperature, and f is the functionality of crosslinks. The value of f was taken to be 4 under the assumption that one chromium compound can bind basically to two COO^- groups [58]. As is clear from Fig. 5c, only a small fraction (5–10%) of chromium compounds form transverse crosslinks. This is most likely associated with the fact that the amount of COO^- groups is much higher than the amount of points of contact between polymer chains involved in crosslinking. During crosslinking, chromium ions are bound to COO^- groups first found by them and then they cannot detach from them because of a high binding energy. Thus, they are statistically distributed between crosslinks and other sections of the network. It can be assumed that the amount of loops is small, because the polymer solution exists in the semidilute regime with entanglements (see above) and the majority of chromium compounds are bound to only one COO^- group.

At intermediate C_{Cr} values (2.2–9.0 mmol/L, region II) corresponding to the constant elastic modulus, not all chromium but only a certain fraction of it is bound to the gel (Fig. 5a). The absolute amount of the bound chromium increases with increasing C_{Cr} ;

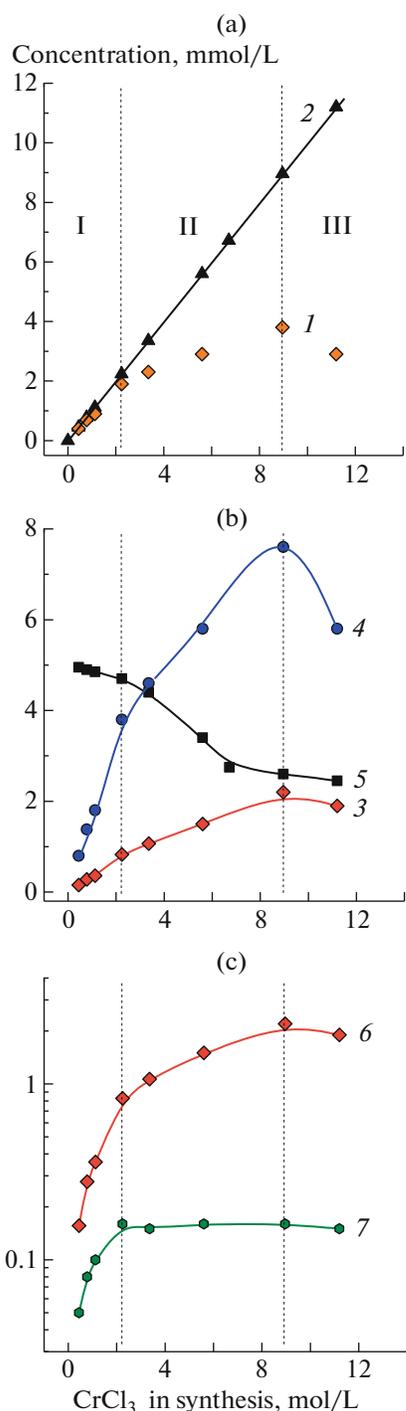


Fig. 5. (a) Concentration of (1) chromium atoms bound to the gel and (2) CrCl_3 added during the synthesis, (b) (3) amount and (4) charge of chromium compounds bound to the gel and (5) the amount of deprotonated carboxyl groups of CMHPG, and (c) the amount of chromium compounds (6) bound to the gel and (7) forming crosslinks as a function of the concentration of CrCl_3 added during the synthesis. The CMHPG concentration is 1 wt %. $T = 20^\circ\text{C}$.

that is, chromium ions continue to bind to polymer chains. This turns out to be possible because the amount of bound compounds in the region under

consideration is still smaller than the amount of deprotonated COO^- groups (Fig. 5b). It may be assumed that the elastic modulus and the amount of compounds involved in crosslinking cease to grow (Fig. 5c), because all points of contact between polymer chains involved in crosslinking are filled [66] and chromium ions further bind primarily to one COO^- group. This circumstance contributes to a change in the structure of the gels and the appearance of a large amount of defects. As a result, the loss modulus and the dissipation of energy under shear deformation increase (Fig. 1b). Since the charge of the carboxyl group is -1 and the charge of almost all chromium compounds is above $+1$ (Table 1), the recharge of functional groups proceeds during binding. As follows from Fig. 5b, at the boundary of regions I and II, the full charge of chromium compounds bound to chains is close to the full charge of carboxyl groups. Hence, in the second region, switching of the full charge of polymer chains from negative to positive and recharge of the gel as a whole occur. It appears that such a recharge is responsible for the situation that, even though accessible functional groups are present, not all added positively charged chromium ions are bound to the gel. Their binding is hampered by the repulsion of like-charged polymer chains [36, 67].

Finally, in the third region ($C_{\text{Cr}} > 9$ mmol/L), the amount of chromium compounds bound to the gel becomes close to the total amount of COO^- groups (it appears that the amount of carboxyl groups is somewhat higher because several carboxyl groups are "consumed" by a fraction of chromium ions). Thus, all functional groups of the polymer are filled. A small decrease in the amount of chromium bound to the gel (Figs. 5a, 5b) and in the elastic modulus (Fig. 2) is due to the fact that the amount of deprotonated carboxyl groups tends to decrease with an increase in C_{Cr} .

CONCLUSIONS

In this study, CMHPG hydrogels crosslinked by chromium (III) ions are obtained for the first time and the effect of crosslinker concentration on their properties is investigated. It is shown that at low concentrations the whole crosslinker is bound to polymer chains and only part of it forms intermolecular crosslinks. This is the reason behind a rise in the elastic modulus. At intermediate crosslinker concentrations, the amount of intermolecular crosslinks does not increase and the highest elastic modulus of the gel is reached at crosslinker concentrations considerably smaller than the total amount of accessible functional groups. This can be explained by the fact that, when a large amount of ions are bound to macromolecules, the recharge of polymer chains occurs; as a result, the binding of a large amount of ions becomes more difficult. Finally, at high crosslinker concentrations, all functional groups are filled and the properties of the gel are deter-

mined by the amount of deprotonated carboxyl groups. Regularities revealed in this study are of importance from both the point of view of fundamental polymer science for understanding the relationship between the process of crosslinking at the molecular level and the structure of the obtained networks and the practical standpoint for optimizing the mechanical properties of polyelectrolyte hydrogels crosslinked by metal ions.

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