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Interaction of Carboxylated Polyacrylamide with Chromium(III) Acetate: ^{13}C NMR Study of Mechanism

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Abstract—The interaction of chromium(III) acetate with poly(acrylamide-co-acrylic acid) in aqueous medium leads to formation of three-dimensional network of crosslinked macromolecules. Formation of the complex between chromium(III) cation and carboxylate groups is a driving force of the interaction. Depending on the reagents ratio, the complex contains two or three carboxylate groups. The amide units are not involved in any specific interaction with the cation.

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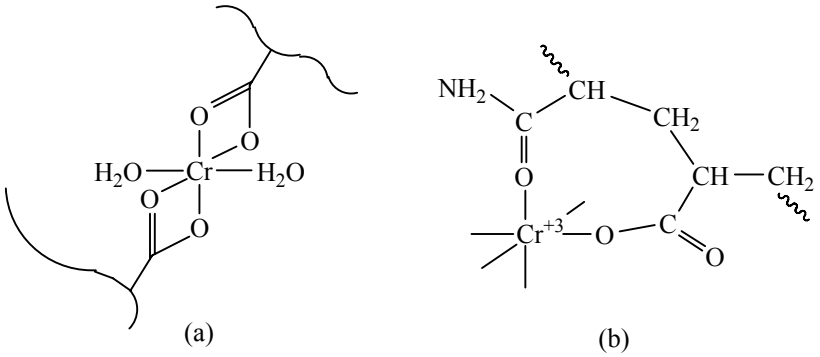
Carboxylated polyacrylamide is a copolymer consisting of acrylamide and acrylic acid units. It is widely used in preparation of polyelectrolyte hydrogels capable of efficient water absorption [1–7]. In the hydrogel, the ionizable polyelectrolyte chains are crosslinked into three-dimensional network structure. The crosslinks can be either covalent (chemical) or physical. Chemical crosslinking is achieved by copolymerization in the presence of bifunctional monomer or by recombination of macroradicals generated by ionizing radiation or by low molecular weight radical initiators. Polymer interaction with transition metal ions is among numerous methods of physical crosslinking, in this case the polymer functional groups act as ligands forming donor-acceptor or ionic complexes with the metal ion [8–11].

Chromium(III) acetate is known as an efficient crosslinker of carboxylated polyacrylamide [8, 9]. In the presence of this salt, the gel is formed in the aqueous solution of the copolymer in a wide range of pH. The gelation time is temperature-dependent; it can be easily altered by changing the components ratio as well. In contract to chromium(VI) compounds, chromium(III) ones are not toxic. The hydrogel based on carboxylated polyacrylamide and chromium(III) acetate is widely applied in oil extraction to enhance the recovery from oil reservoirs [8, 9].

Despite evident practical importance of such hydrogels, the mechanism of crosslinking via interaction of copolymer functional groups with chromium(III) cation has not been clear. It is assumed [8, 9] that in the aqueous solutions (pH of 2 to 9) chromium acetate exists in the form of complex compound with metal cation coordination number of 6. In the inner sphere of the complex, six water molecules are located. The interaction with polymer functional groups is in fact the ligand exchange reaction (water molecules are exchanged to the polymer functional groups) with formation of donor-acceptor bond due to chromium cation unoccupied orbitals and lone electron pairs of the functional group atoms. However, it has remained unclear so far, whether the crosslink is formed by carboxylate or amide groups; the stoichiometry of the interaction has not been confirmed as well. The possible interaction mechanisms have been suggested in [8] (see Scheme 1). One of the suggested mechanisms (Scheme 1a) presumes that chromium(III) cation is bound to two carboxylate groups of the polymer, and to two water molecules. In this case, carboxylate groups act as bidentate ligands.

Scheme 1.



Alternatively (Scheme 1b), amide groups of the polymer can participate in the complex formation; in the latter case chromium cation is bound to carboxylate group and oxygen atom of the adjacent amide group.

It is commonly assumed that carboxylate groups of the polymer play the decisive part in the complex formation [8–11]. To date, the only experimental evidence of this has been the weakening of IR absorption bands assigned to carboxylate C=O stretching in the spectra of the products of copolymer interaction with chromium(III) acetate [10, 11]. We have failed to find any quantitative study proving that carboxylate group is the only function interacting with chromium(III); reliable data on the complex stoichiometric composition has not been found as well.

To fill the gap, this work aimed to directly determine the nature of the polymer ligand groups binding to chromium(III) cation and to quantify the formed complex composition. In order to answer the posed questions, we took advantage of ^{13}C NMR spectroscopy, more accurate quantitative method as compared to IR spectroscopy [12]. Indeed, the formation of donor-acceptor bond between chromium(III) cation and carboxylate group of the polymer should have resulted in significant changes of ^{13}C chemical shift of the signals assigned to acrylate unit. Moreover, due to paramagnetism of Cr(III), the decrease of intensity of the signals of carboxylate groups as well as of acrylate CH could be anticipated. At the stoichiometric ratio of Cr(III) and carboxylate groups, ^{13}C signal of the latter should have completely disappeared. Similarly, the intensity of the signals assigned to amide groups and CH of acrylamide units should have decreased, provided that acrylamide units are the binding sites for chromium(III) cation. Not only the chemical nature of the interacting polymer units could be elucidated from the comparison of ^{13}C NMR spectra of the initial polymer and those of the formed hydrogel; determination of the stoichiometric ratio of the interacting components was among the goals of the work.

The peculiarities of the complex formation in the studied systems were definitely due to polyelectrolyte nature of the reacting ligand. In particular, negative charge on the polymer carboxylate group facilitated its interaction with the positively charged Cr(III) ion [13]. The macromolecular nature or the ligand enhanced the interaction efficiency, however, slowing down the ligand exchange reaction.

Evidently, the hydrogel could be formed upon Cr(III) interaction with the polymer if the resulting chromium complex included two or more of the polymer functional groups. Even though Cr(III) coordination number could be up to 6, the formation of complex by Cr(III) ion and more than three carboxylate groups of the polymer was hardly possible. This was majorly due to steric hindrance of the bulky polymer chains. Furthermore, the addition of the charged low-field carboxylate ligand to the Cr(III) cation already bound to three carboxylate groups could not be efficient. The interaction of neutral acrylamide groups with Cr(III) was not efficient as well (see details below).

The decrease of intensity of the ^{13}C NMR signal of carboxylate groups due to complex formation was determined by the reagents ratio, in addition to the stoichiometric complex composition. For instance, at 1 : 1 initial ratio of Cr(III) and carboxylate groups (excess of chromium), the signal of unbound carboxylate group should have disappeared at any of the possible complex compositions (1 : 1, 1 : 2, or 1 : 3). At lower ratio of [Cr(III)] : [COO^-], the changes in

spectra would reflect the complex composition (see the anticipated results in the table).

From the tabulated data it followed that the forming complex stoichiometry was to be defined most accurately at the initial components ratio of [Cr(III)] : $[COO^-]$ = 1 : 3. In that case the gap between the NMR signal intensity anticipated in the cases of different complex composition was the largest.

In the ^{13}C NMR spectrum of the initial uncrosslinked polymer two structured signals were observed in the range of 179–185 ppm (Fig. 1a): at δ of 183.9 and of 180.8 ppm. Those bands were assigned to the carboxylate and amide groups, respectively, following the assignment of the similar signals in the spectrum of the product of polyacrylonitrile fiber alkaline hydrolysis [12]. The integral intensities ratio of the two mentioned bands was of 3 : 97 in the case of the unreacted polymer.

In the range of 20–50 ppm of the same spectrum (Fig. 1b), four structured signals were observed, at 46 ppm (minor, CH of acrylate units), 43 ppm (CH of acrylamide units), 38 ppm (CH_2), and 34–38 ppm (CH_2). The presented assignments were made according to the chemical shift values taking into account the DEPT spectra. The integral intensities ratio of the signals assigned to CH of acrylate and acrylamide units was of 3 : 97. Thus, from both pairs of signals it followed that the content of carboxylate groups in the initial polymer was of 3 mol %.

Figure 2a shows the ^{13}C NMR spectrum of the crosslinked polymer (179–185 ppm range). In the spectrum, two broadened partially overlapping signals were revealed. More intense signal was observed at δ = 180.8 ppm, and the weaker signal was located at δ = 180 ppm; the signal of free carboxylate groups at 183.9 ppm was absent. Basing on the chemical shifts, the major signal was assigned to the amide group, and the weaker signal was assigned to the carboxylate of sodium acetate. The integral intensities ratio, 97 : 3, confirmed that upon crosslinking all carboxylate groups were included into the forming complex of the [Cr(III)] : $[COO^-]$ = 1 : 3 composition. Noteworthily, the chemical shift of the amide carbonyl signal remained the same, and the signal was noticeably broadened. That pointed at the non-specific interaction of Cr(III) with amide groups changing the relaxation properties of the latter. Thus, the amide groups did not participate in the complex formation at the initial ratio of [Cr(III)] : $[COO^-]$ = 1 : 3 or less.

Anticipated decrease of carboxylate NMR signal at varied components ratio and at different theoretical complex stoichiometry

Initial ratio [Cr(III)] : $[COO^-]$	I_g/I_p[a] at different complex stoichiometry [Cr(III)]:$[COO^-]$		
	1 : 1	1 : 2	1 : 3
1 : 1	0	0	0
1 : 2	1/2	0	0
1 : 3	2/3	1/3	0
1 : 4	3/4	1/2	1/4

[a] I_g and I_p are intensities of carboxylate group NMR signal in the case of the hydrogel and the linear polymer, respectively.

The above conclusion was confirmed by the analysis of the hydrogel spectrum in the range of 20–50 ppm. In particular, three signals were observed in that range: at δ = 43 ppm (intense, CH of acrylamide units), at δ = 34–39 ppm (intense, CH_2), and at δ = 23 ppm (minor, sodium acetate CH_3). The assignments made were based on the chemical shifts and the analysis of DEPT spectrum. The signal of acrylate units CH at δ = 46 ppm was absent. The integral intensities ratio of the signals assigned to acrylamide units CH and sodium acetate CH_3 was of 97 : 3.

Thus, it was proved that in the hydrogel prepared via the interaction of Cr(III) with the polymer the crosslinking complex indeed contained two or three carboxylate groups depending on the initial components ratio (exactly three carboxylate groups were found in the complex at the initial ratio of [Cr(III)] : $[COO^-]$ = 1 : 3 or less). The amide units were not involved in any specific interaction with the cation. In the case of soluble product formation instead of the hydrogel, the chromium(III) complex included only one carboxylate group.

The suggested scheme of hydrogel formation is illustrated in Scheme 2. As shown in Scheme 2, carboxylate groups acted as bidentate ligands in the reaction. Possibly, that form was in equilibrium with the monodentate carboxylate ligand, due to ligand exchange with water molecules (Scheme 3). However, the bidentate form of carboxylate should interact with the cation more efficiently, and the shown equilibrium is likely shifted to the left.

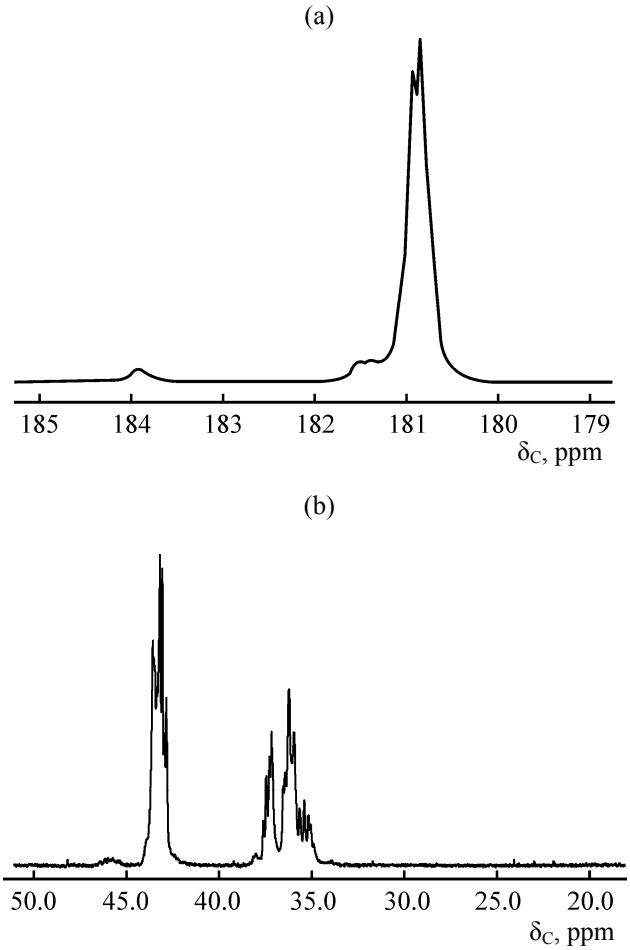


Fig. 1. ^{13}C NMR spectrum of the linear polymer in the range of (a) 179–185 ppm and of (b) 20–50 ppm.

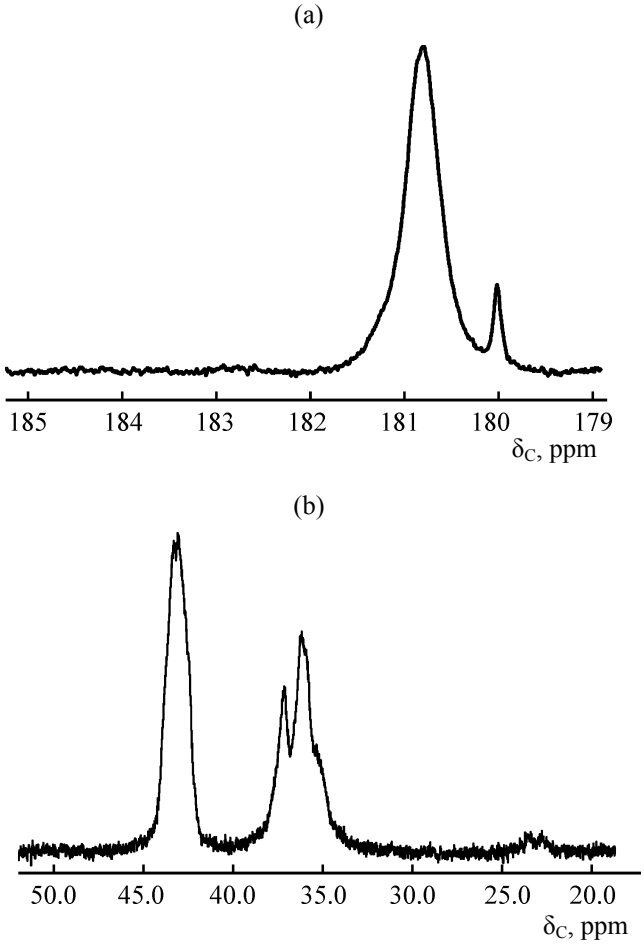


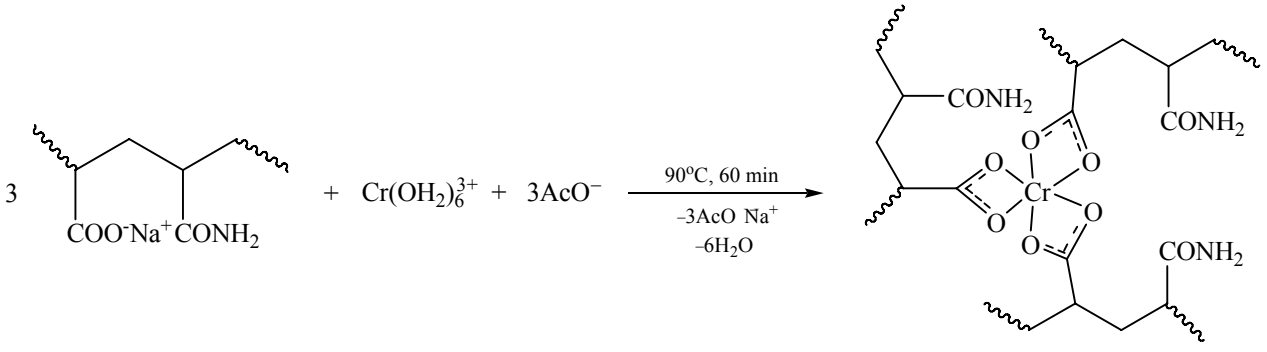
Fig. 2. ^{13}C NMR spectrum of the crosslinked polymer in the range of (a) 179–185 ppm and of (b) 20–50 ppm.

EXPERIMENTAL

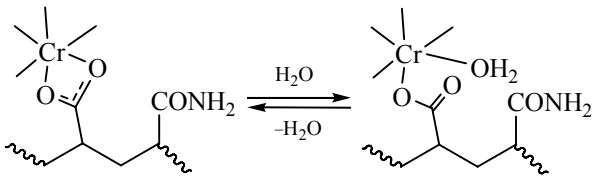
The polymer studied was Alcoflood 254S, carboxylated polyacrylamide (BASF, Germany). It is a polyanionic water-soluble linear copolymer of acrylamide and sodium acrylate. The carboxylate groups content in the polymer was of 3 mol %, the viscosity-average molecular mass was of 5×10^5 Da. Chromium(III) acetate (Petrokhim) was used in the form of 44 wt % aqueous solution.

The linear polymer was studied in the form of 10 wt % solution in deuterated water, prepared by dissolving 0.1 g of the polymer in the corresponding amount of water.

Scheme 2.



Scheme 3.



To prepare the hydrogel sample, chromium(III) acetate was added to solution of the linear polymer in deuterated water in the ratio of [Cr(III)] : [COO^-] = 1 : 3. The mixture was stirred till homogenization, and the so prepared solution was heated at 90°C during 60 min.

The samples for NMR studies were prepared directly in the 5 mm ampoules (Sigma-Aldrich). ^{13}C NMR spectra were recorded with Avance-500 (Bruker) spectrometer at 125.8 MHz. The relative error of the functional groups quantitative determination was less than 7% at p of 0.95.

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