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Preparation and Properties of Polyfluorinated Acrylamide-Sodium Acrylate Copolymers

A. I. Rakhimov, D. A. Vershinin, A. V. Miroshnichenko, and O. S. Rakhimova

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia
e-mail: organic@vstu.ru

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Abstract—Preparation and properties of diluted aqueous solutions of a copolymer of polyfluorinated acrylamide and sodium acrylate have been studied. The polyfluorinated groups were introduced into the polymer via the reaction with 2,2,3,3,4,4,5,5-octafluorohexyl sulfurochloridite. It is shown that the introduction of polyfluoroalkyl fragments decreases the solutions viscosity and freezing point due to intermolecular interactions. The analysis of possible cluster structures formed by the functional groups has been performed.

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At present, polyfluorinated organic substances are widely applied due to a complex of specific utilitarian properties. Polyfluoroalkylated long-chain oligomers may be applied to polymer compositions to improve their chemical, thermal resistance, and wear resistance.

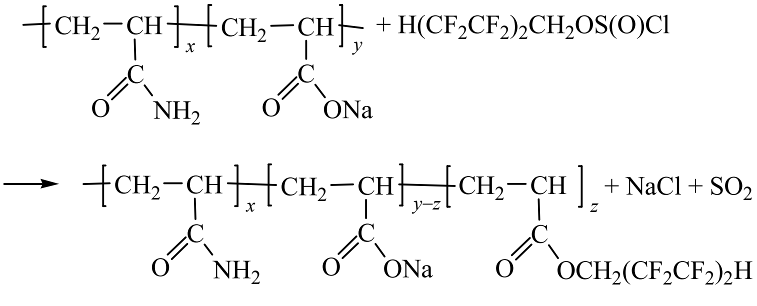
In this work the influence of introduction of polyfluoroalkyl groups on the physicochemical properties of acrylamide-sodium acrylate copolymer was studied, and potential applications of the copolymer solution were analyzed.

In our previous works [1–4] it has been shown that polyfluoroalkyl sulfurochloridites are unique polyfluoroalkylating reagents capable of transforming carboxylic acid salt into ester of polyfluorinated alcohol.

In this work, having used 2,2,3,3,4,4,5,5-octafluorohexyl sulfurochloridite as an example, we demonstrated that the same reaction might be applied to introduce polyfluoroalkyl groups into copolymer of acrylamide and sodium acrylate.

Fluorine-containing copolymer was prepared from the copolymer of acrylamide and sodium acrylate (molecular weight 1.2×10^6, x = 60%, y = 40%) and 2,2,3,3,4,4,5,5-octafluorohexyl sulfurochloridite, at the reagents ratio of 1:5. In a typical experiment, 1 g of the initial copolymer was loaded into a stirred reactor, 10 ml of dimethylformamide DMF was added, and then 5 g of 2,2,3,3,4,4,5,5-octafluorohexyl sulfurochloridite was introduced. The reaction temperature was minus 10°C during the first 10 min, then the reaction mixture was heated up to 40°C and incubated during 60 min at this temperature. After incubation, DMF was partially removed from the reaction mixture, and the obtained precipitate was filtered off and dried.

This process involving sodium acrylate groups was performed similarly to the procedure described in [5–7]. The general reaction scheme is as follows.



Fluorine content in thus prepared copolymer was 3.7 wt % (as determined by direct potentiometry with the fluoride selective electrode after the sample combustion, dissolution, and titration). The melting point of the product was 160°C. In the IR spectrum of the product the following bands were observed (cm^{-1}): 2916, 2368, 1750, 1660, 1417, 1094.

It should be noted that in the IR spectrum of the prepared copolymer, in contrast to that of the initial one, an intensive band at 1760 cm^{-1} was observed. This proved that 2,2,3,3,4,4,5,5-octafluorohexyl sulfurochloridite reaction with sodium acrylate units proceeded similarly to its interaction with monocarboxyl acids sodium salts [6] and with sodium salts of ε-aminocaproic acid oligomers [8].

The fluorine content corresponding to a single octafluoropentyl fragment introduced into the copolymer is 0.013 wt %. Thus, approximately z = 6.6 wt % of sodium acrylate groups participated in the reaction, and about 300 fluorinated groups per single macromolecule were present in the copolymer.

Apparent viscosity of solutions was measured using VPZh-1 capillary glass viscometer. The viscosity thus measured was reported in seconds and equaled the flow time of 25 ml of solution at 22°C through the 1.52 mm capillary. Aqueous copolymers solutions concentration was either 0.1 or 0.3 wt %. Effect of solution concentration on viscosity is shown below for both initial and modified copolymers.

Concentration, wt %	Apparent viscosity, s	
	initial oligomer	polyfluorinated oligomer
0.3	83	16
0.1	59	10
water	4	

It is seen that the measured viscosity was reduced upon fluoroalkylation of the copolymer: 5.9 times lower for 0.1 wt % solutions and 5.2 times lower for 0.3 wt % solutions. Evidently, the introduction of the polyfluorinated fragments significantly affected water cluster structure as compared with the initial copolymer [9]. Probably, the introduction of about 300 $H(CF_2CF_2)_2CH_2$ groups into each macromolecule decreased molecular weight of cluster structures formed with the aid of the copolymer functional groups.

Unlike aqueous sodium acetate (the freezing point of about 8 wt % solution is –10°C), aqueous initial copolymer solution froze at –18°C, while freezing point of the fluorinated copolymer solution was even lower, –21°C [10].

To compare the effect of sodium carboxylate groups on the cluster structures with that of metal chlorides, analysis of the possible cluster structures formed with the aid of these groups was performed by means of the *ab initio* quantum-chemical method with the 6-31G basis set. Electron structures of the following objects were analyzed: water dimer, water tetramer, sodium acetate, sodium formate, sodium chloride, and the associates of mentioned salts with water dimer (formed upon interaction of the salts with water clusters). The non-empirical method accounted for all electron-nucleus interactions in the given molecules. Electronic and geometric structures of sodium acetate and sodium formate complexes with water dimer were found to be identical.

In the associates of sodium salts with water dimer (elementary unit of the cluster), a 6-membered cyclic structure was formed between the contact ion pair of the sodium salt molecule and water dimer (see figure). Values of partial atomic charges, bonds lengths, bond angles, and hydrogen atom rotation barriers were compared in cases of the initial dimers and their complexes; and full energies of complexes formation were determined.

Valence H–O bonds were longer in the complexes (0.098 nm) that those in the initial dimers (0.096 nm). The bond angle in the dimer equaled 180°, while in structures containing NaCl or carboxylates it decreased to 159.5° and 158.1°, respectively.

Important information on the bonds polarization leading to the bond angle change in the dimer was obtained from the partial atomic charges on hydrogen and oxygen atoms of both water molecules in the complex. In the NaCl complex the positively charged sodium interacted with oxygen atom of the dimer resulting in the decrease of partial negative charge on the oxygen (from –0.88 in an isolated dimer to –0.95 in the complex). This was accompanied with the polarization of the valence H–O bond. As a result, the oxygen atom connected via a hydrogen bond also became more negatively charged (its partial charge decreased from –0.83 to –0.91). Hydrogen atoms of water molecules in the complex gained higher positive charge: the hydrogen atom bound with chlorine possessed a partial charge of +0.48 instead of +0.43 in the isolated dimer, the partial charge on the hydrogen associated with the water molecule changed from +0.47 to +0.54. Partial charges on atoms upon formation of a complex with sodium acetate changed somewhat more significantly. Both hydrogen atoms (associated with the carboxylate oxygen and participating in the hydrogen bond formation with the other water molecule) have a charge of +0.54. Evidently, the polarization of water dimer bonds occured in complexes with sodium acetate and sodium formate.

The energy gain due to complex formation was estimated according to the following equation.

$$\Delta E = \Sigma E_{\text{init}} - \Sigma E_{\text{comp}}.$$

Even though the calculated ΔE values were close, the complexes could be arranged into the following series according to their stability: ΔE_{HCOONa} (–38.4) > $\Delta E_{\text{CH}_3\text{COONa}}$ (–38.3) > ΔE_{NaCl} (–38.1) (kcal mol^{-1}).

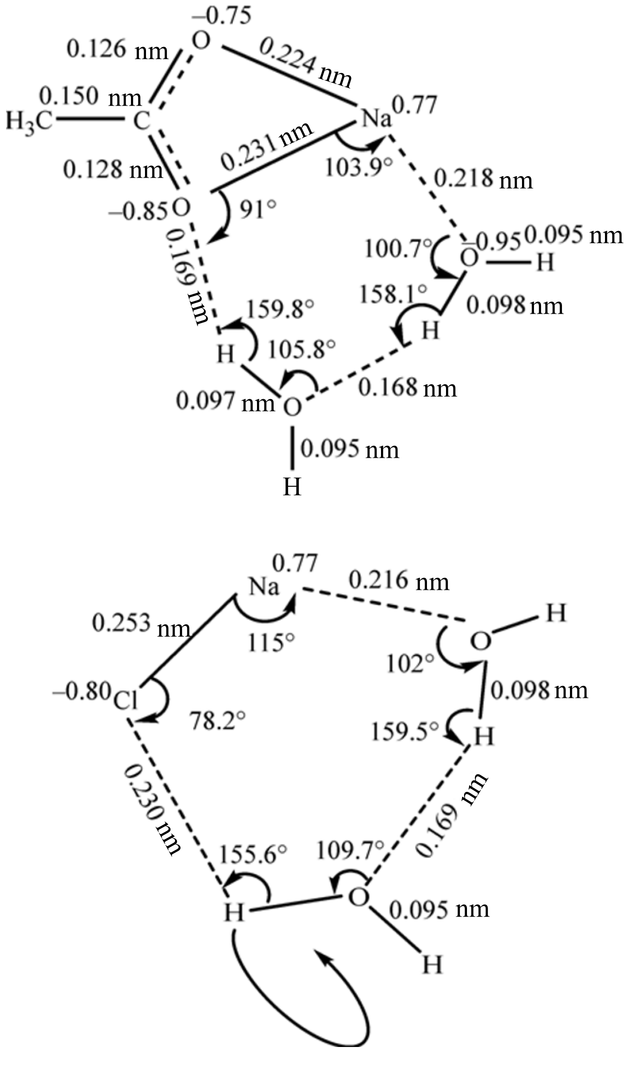
The cyclic tetramer formation from a pair of dimers was less favorable ($\Delta E_{\text{tetramer}} = -26.7$ kcal mol^{-1}), thus, clusters decay with the formation of stable salt complexes was possible.

The energy barrier to the rotation of the chlorine-bound hydrogen atom around the nonvalence H···O bond in the complex with NaCl was quite low (2.8 kcal mol^{-1}). This barrier was almost twice higher in case of the H···O group bound to oxygen atom of acetate or formate fragment. This difference might be important at low temperature, so that stable complexes could embed into the water cluster structure and affect the polarity of the spatial polycluster water structure.

The analysis presented above explained the significant effect of the sodium carboxylate groups on the properties of low-concentrated solutions of the studied acrylamide-sodium acrylate copolymers. In case of polyfluoroalkylated derivative, the solutions freezing temperature and viscosity were low; thus, they might be recommended for various technical applications.

The characteristics of the 0.1 wt % solution of the polyfluorinated copolymer were as follows.

Density	1010 kg m^{-3}
Apparent viscosity	10 s
Freezing point	20°C
Freezing point	7



Complexes of acetate and sodium chloride with two water molecules.

Testing of this solution showed that it is multipurpose and does not contain any expensive reagents like carboxymethyl cellulose. It maintained its stability up to 100 days; the apparent viscosity (flow time) value was constant over this period and equaled 10 s under laboratory conditions as well as at lower (–20°C) temperature.

Thus, the low-concentrated solution of polyfluorinated copolymer possesses a complex of important utilitarian properties: presumably high cutting-carrying capacity, stability of properties up to 100 days, low operation temperature. It may improve casing quality due to elimination of clay coating and prevent the payout bed contamination.

Solutions with similar characteristics are widely applied in oil and gas well-drilling in the Siberian region.

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