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Surface bound microgels on the basis of carboxymethylcellulose: preparation *via* the Ugi reaction and structural investigation using fluorescent and spin labels

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Abstract

A microgel with an average diameter of 368±4 nm was obtained by adding a small amount of polyvinylamine (PVAm) to a 0.3% aqueous solution of carboxymethylcellulose (CMC). The CMC/PVAm microgel particles were deposited on a layer of pure PVAm, which in turn was located on a glass substrate. Four-component Ugi condensation in aqueous solutions at pH 5.0–5.5 was applied to fix the resulted structures. A water-insoluble layer of PVAm gel with CMC/PVAm microgel particles distributed over its surface was obtained. It was shown that at pH > 8 the CMC/PVAm gel particles swell, more completely covering the surface of the PVAm gel layer applied to a glass substrate. Fluorescent labels (aminofluorescein moiety) and spin labels (amino-TEMPO moiety) were introduced into the CMC structure in order to monitor this process using fluorescence microscopy and EPR spectroscopy.

Keywords

microgels
carboxymethylcellulose
polyvinylamine
Ugi reaction
coating
spin label
fluorescent label

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Key findings

- A method for obtaining the surface bound microgels based on CMC was developed.
- Fluorescent and spin labels were used to determine swelling properties.
- Synthesis conditions were found that ensure optimal swelling of CMC microgels at pH > 8.

Supplementary materials

1. Introduction

Microgels based on cellulose derivatives have become a popular subject of research in the field of materials science in recent years [1]. This is primarily due to the biocompatibility of cellulose-based materials and the possibility of their utilization without causing significant harm to nature [2, 3]. However, other factors, such as a huge raw material base, low carbon footprint, ease of processing and low price also play a major role [4]. Among the useful properties of cellulose materials, it is worth highlighting the formation of densely packed structures due to hydrogen bonds between individual glucose units. This allows the creation of submicron structures with unique properties, such as high adhesion to various materials, the ability to stabilize emulsions, and response to various stimuli [5].

Of particular interest are asymmetric structures such as patchy gels [6], Janus particles [7] and colloidal molecules [8], which allow obtaining unique materials on their basis. Thus, microgels attached to a solid surface by covalent bonds have an up-down direction, relative to which the gel differs in its properties [9]. Such microgels usually have a denser lower part sewn to the substrate and a less dense upper part, which swells and contracts depending on external stimuli. In this case, the surface easily changes its properties depending on external conditions [10]. The systems have recently been described where a macrogel is used as a surface. The resulting materials were used for cell adhesion, especially in vitro response of MC3T3-E1 cells [11]. Cellulose derivatives were also chosen as the starting materials for obtaining membranes assembled from microgel particles. In this case, the lower layer determined the mechanical properties of the resulting material, while the upper

layer formed an uneven surface with excellent adhesive properties [12]. At the same time, it should be noted that cellulose derivatives are not often used to obtain surface-bound microgels, unlike thermosensitive ones such as poly(N-isopropyl-acrylamide) (PNIPAm) and its copolymers [9].

In practical terms, polymer membranes and fibers containing covalently cross-linked microgels are used to control the filtration process and effectively separate various substances. For example, the permeability of polymer membranes can be controlled using microgel particles deposited on their surface. Thus, a PAA-based gel, which easily swells in an alkaline medium, was used to control the transport of amino acids and copper ions through a polymer membrane [13]. Moreover, permeability control in such systems can occur not only due to physical flow blocking, but also due to electrostatic interaction between the solution and the microgel [14]. In addition to changing the pH, the flow through the membrane can also be regulated using thermosensitive responsive gels based on PNIPAm [15]. Such systems are convenient for controlling water evaporation and creating fabrics permeable to evaporation [16]. Coatings with an antifouling effect for separating water and oil emulsions were obtained based on a gel containing cellulose nanofibrils chemically cross-linked with a polymer gel [17]. Thus, surface bound microgels can be successfully used to separate oil from water and create self-cleaning materials.

Previously, we investigated coatings based on carboxymethyl cellulose (CMC) and polyvinylamine (PVAm) applied to fiberglass by layer-by-layer application of polymers with opposite charges followed by chemical fixation with formaldehyde [18]. Depending on the conditions of application of this pair of polymers, the resulting materials can change their ability to be wetted by crude oil. In this work, we propose a new method for applying these polymers to a surface, when carboxymethyl cellulose is used in the form of a microgel. This approach allows us to obtain materials that change their properties depending on the pH of the external environment.

2. Materials and methods

Hexamethylene diisocyanide was synthesized according well-known procedure [19]. The spin label 4-amino-2,2,6,6-tetramethylpiperidine-N^1-oxyl (4-aminino TEMPO) was purchased from the laboratory of nitrogenous materials of the Institute of Organic Chemistry (Novosibirsk). Carboxymethyl cellulose (low viscosity polyanionic cellulose with degree of substitution 0.98, purity 95%, pH of 1% solution in water of 7.2 and apparent viscosity 19.4 mPa·s) was purchased from Henan Ocean Chemical Technology, China. Polyvinylamine (PVAm) of purity 98% was purchased from BASF, Germany in form of 30% solution of salt with formic acid in water. Other materials include: dialysis membrane of cutting molecular weights 8kDa (Orange Scientific, Belgium), fluoresceinamine isomer1 (Aldrich Chemistry, USA), N-N-dicyclohexylcabodiimide (Merck, Germany), organic reagents of analytical grade (Acros Organics, Belgium): toluene, acetonitrile, formaldehyde 35%, ethanol, dimethylformamide, hydrochloric acid, sodium hydroxide, phosphate buffer, acetic acid, deionized water. Standard blank slides for microscopy (75×25×1) were used.

2.1. Preparation of CMC labelled with aminofluorescein

A 20 mL solution of CMC in water with a concentration of 5% by weight was acidified with concentrated 10 M hydrochloric acid to pH 3 and then diluted with acetonitrile (50 mL). After washing with acetonitrile, the precipitate was redissolved in 20 mL of dimethylformamide (DMF). The solution of fluoresceinamine in DMF (3 mg in 1 mL) and an excess of dicyclohexylcarbodiimide (20 mg) were added to the resulting CMC solution in DMF. After a 24-hour reaction time in a dark environment, the resulting mixture was precipitated with acetonitrile. After centrifugation at 500 rpm, the resulting precipitate was dried at 50 °C. The yield of the isolated product was 850 mg. To achieve a final concentration of 1% w/v, the precipitate was dissolved in distilled water. A dialysis membrane with a molecular weight cutoff of 8 kDa was used to dialyze the resulting sample against distilled water at pH 4.

2.2. Preparation of CMC labelled with the 4-amino TEMPO

Method A. Similar to the previously mentioned method, except a solution of 4-amino TEMPO (5 mg in 1 ml) was added instead of fluoresceinamine.

Method B. CMC solution 1% (w/v) was prepared by dissolving 0.5 g of CMC in 50 mL of distilled water. Then, the CMC solution was diluted to 0.5% (w/v). The solution was acidified by gradually adding dilute HCl (150 μL 10 M HCl in distilled water, 10 mL). Then, 4-amino TEMPO solution 0.2% (w/v) and a mixture of formaldehyde (20 μL) and hexamethylene diisocyanide (20 μL) in acetonitrile (5 mL) were added dropwise into the CMC solution. Finally, the mixture was acidified with diluted HCl (80 μL of 10 M HCl in 5 mL of distilled water).

2.3. Preparation of CMC/PVAm microgel labelled with aminofluorescein

PVAm 0.1% (v/v), 700 μL, was added dropwise to the solution of cellulose labelled with aminofluorescein, 0.3% (w/v), 15 ml. The amount of PVAm was determined based on the analysis of the obtained microgel particles using the DLS method (2.12).

2.4. Deposition of the CMC/PVAm microgel labelled with aminofluorescein on the glass slides

PVAm solution 0.05% (v/v) was spread over the glass slide with a brush and then dried at 72 °C for 30 min. The resulting PVAm layer was immersed in a diluted (1:21 ratio)

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CMC/PVAm microgel sample for 5 seconds. Then, a mixture of 10 μL hexamethylene diisocyanide and 10 μL formaldehyde in 50 μL acetonitrile was dripped over the PVAm layer and washed with water Sample **8** was completely dried at room temperature before this.

2.5. Preparation of CMC/PVAm microgel labelled with amino TEMPO

Similar to the previously mentioned method 2.3, except that CMC labelled with amino TEMPO was used.

2.6. Deposition of the CMC/PVAm microgel labelled with amino TEMPO on the glass fiber

A glass fiber measuring 2×2 cm and 14 mg in weight was immersed in 0.25% (w/v) PVAm solution and then dried at 50 °C. The dried glass fibers were used as a substrate instead of glass slides. The glass fiber was immersed in a diluted (1:21 ratio) CMC/PVAm microgel sample for 5 sec. Then, a mixture of 10 μL hexamethylene diisocyanide and 10 μL formaldehyde in 50 μL acetonitrile was dripped over the PVAm layer and washed with water. Sample **10** was completely dried at room temperature before this.

2.7. Examination of the swelling capacity

All samples **7–10** were immersed in aqueous media with different pH values (3, 5, 7.5, 8, 10, 12, 14) for 1 h and used for examination of swelling capacity with fluorescent microscopy and EPR spectroscopy.

2.8. Nuclear magnetic resonance (NMR)

The CMC labelled with amino TEMPO was purified by dialysis membrane with the cut-off of 8 kDa. The solution after dialysis was evaporated and the dried material (8 mg) were added to 4 mg of sodium carbonate and sent for analysis. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer in D_2O at 70 °C.

2.9. Fourier-transform infrared spectroscopy

The spectrum of the CMC labelled with amino TEMPO was obtained by placing an amount of its powder in the infrared equipment (Bruker Alpha FT-IR Spectrometer) equipped with an attenuated total reflectance device and zinc selenite crystals. The sample was transferred directly into the attenuated total reflectance compartment, and the result was obtained by combining 24 scans. The spectrum was recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}.

2.10. Fluorescent microscopy

Samples **1-8** were observed directly on the blank slide glasses where they were obtained. A fluorescent lens was used for observation. Micrographs of microgel were captured at x40 magnification using the microscope Altami LUM 1.

2.11. EPR spectroscopy

EPR spectra of samples **9, 10** were recorded at room temperature (293 K) using a X-band continuous wave (CW) with a Bruker EMX-500 Plus EPR spectrometer. The sample was placed in a standard quartz EPR tube with an internal diameter of 3.5 mm. The tube was then inserted into the EPR resonator of the spectrometer. The conditions of EPR recording were: the power of 1 mW, the modulation amplitude of 0.1 mT. Computer simulation of the room temperature spectra was performed taking into account rotational mobility of the paramagnetic fragment. The ODFR4 software developed by Prof. A. Kh. Vorobiev (Chemistry Department, Moscow State University) was used [20].

2.12. Dynamic light scattering (DLS)

The CMC/PVAm microgel size and zeta potential were measured using the dynamic light scattering (DLS) instrument Zetasizer Nano ZS (Malvern Instrument, U.K.) at scattering angle of 173°, wavelength 632.8 nm, and at 25.2 C. Polydispersity index (PDI) was calculated from a Cumulants analysis of the DLS measured intensity autocorrelation function. PDI = $2a_2/(a_1)^2$, where a_1 is the first moment (cumulant), and a_2 is the second moment. The average hydrodynamic diameters were calculated by the non-negative least-squares (NNLS) method using Malvern General Purpose and Multiple Narrow Mode algorithm, which separated multimodal distribution.

3. Results and Discussion

In this paper, we focused on the selection of optimal conditions for obtaining mosaic gels based on two polymers: carboxymethyl cellulose (CMC) and polyvinylamine (PVAm). According to the general concept that was chosen for this study, microgel particles based on one polymer should be deposited on the surface of the gel formed by another polymer. Then, the microgel particles should be covalently linked to the surface of the macrogel, forming a layer consisting of a mixture of the two original polymers. As a result, a layer with surface bound microgel should be formed. When the pH changes, the lower part of the resulting structure, consisting of a denser gel, should be stable. At the same time, the upper part should swell, covering the surface. The general scheme of the process is shown in Figure 1. Thus, the resulting surface will change its properties depending on the pH and have the ability to self-clean.

To test this concept, we used PVAm macrogel as a bottom layer and microgel based on CMC/PVAm complex. The four-component Ugi reaction was chosen for fixing the structure and covalently attaching the microgel to the PVAm gel layer (Scheme 1).

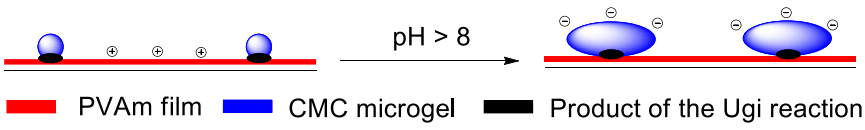

Figure 1 General approach to obtain the surface bound microgel based on CMC/PVAm.

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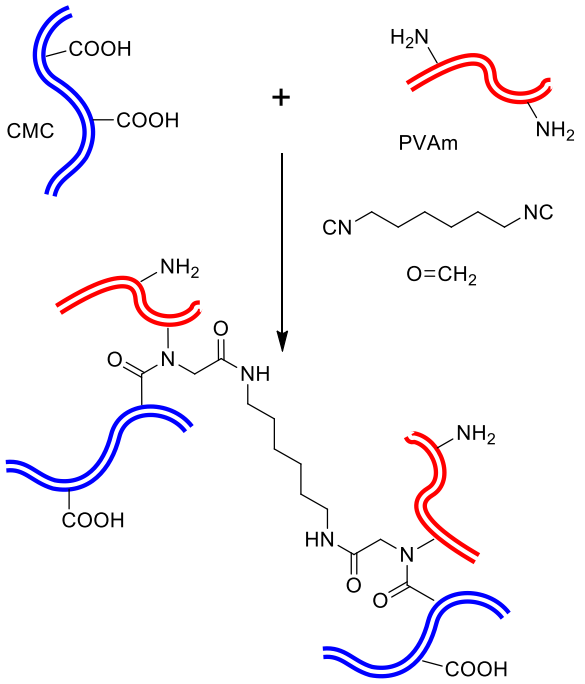

Scheme 1 Cross-linkage of surface bound microgels via the Ugi reaction.

Recently, we successfully used this reaction to obtain cage-like structures in two stages [21]. It is characterized by a high rate in aqueous solutions and high sensitivity to pH, which allows finely adjusting the process conditions. In addition, this reaction allows different cross-linking densities at the contact point of two polymers and each polymer separately. In this work, a glass slide was used as a substrate for easy identification of the formed structures using an optical microscope. A fluorescent dye was used to visualize the obtained structures. At the same time, a method based on the introduction of spin labels was used to determine the gel density in the formed structures. We previously used this method to evaluate polymer membranes obtained by layer-by-layer deposition on the surface of glass fiber [18].

The first stage of this study was to obtain a microgel stained with a fluorescent dye. For this purpose, the technique developed in our previous work [21] was used with minor modifications. CMC was redissolved in DMF and then reacted with fluoresceinamine in the presence of dicyclohexylcarbodiimide. After purification, CMC with an attached fluorescent label was dissolved in water and interacted with a dilute PVAm solution. After selecting an appropriate amount of PVAm, the CMC/PVam microgel was obtained. The results of dynamic light scattering showed that the distribution of particle had one maximum, the average particle diameter was 368±4 nm, and the polydispersity index was 0.27 (Figure 2).

The next stage of the study was the formation of a mosaic structure on the surface of the glass substrate. To do this, we varied the parameters of applying PVAm to the substrate and depositing the CMC/PVAm microgel on the resulting surface. The main difficulty is that PVAm is easily soluble in water. Therefore, when depositing the CMC/PVAm microgel on its surface, the integrity of the layer on the glass surface can be violated. To prevent this negative process, we pre-dried the gel layer on the glass surface, and the deposition was carried out under strictly controlled conditions for a certain period of time. The data on the optimization of the glass blank slides with PVAm gel and CMC/PVAm microgel deposition are given in Table 1. As can be seen from the data provided, a decrease in the concentration of PVAm in the solution and a decrease in the duration of contact with the CMC/PVAm microgel suspension had a positive effect on the properties of the resulting layer. Thus, sample **5** was selected for further experiments.

The initially formed coating was analyzed using a fluorescence microscope. It is evident from Figure 3a that the CMC/PVAm microgel particles are distributed relatively uniformly over the surface of the PVAm layer. By varying the concentration of these particles in the suspension, we achieved the optimal density of the CMC/PVAm microgel layer coating. The distance between the particles should be sufficient to freely accommodate the swollen gel particles. At the same time, after swelling of the gel particles, there should be no area left unoccupied by the gel. It is evident from Figure 3b that such arrangement of the CMC/PVAm microgel particles on the PVAm surface was achieved by diluting the initial suspension 21 times.

The resulting structures were fixed using the Ugi reaction, with the concentration of the cross-linking reagent (hexamethylene diisocyanide in combination with formaldehyde) selected to ensure good swelling of the resulting structures.

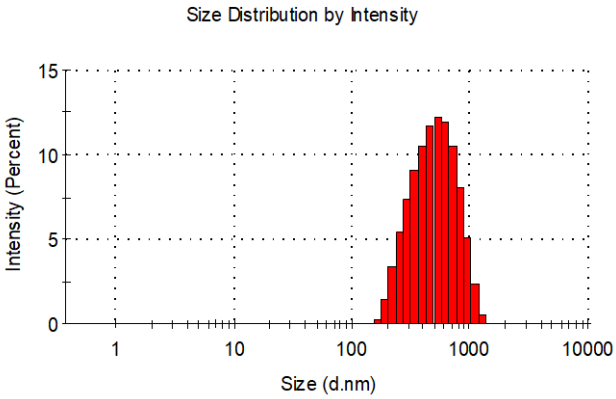

Figure 2 Distribution of CMC/PVAm microgel particles according light scattering data.

Table 1 Preparation conditions of PVAm layer with CMC/PVAm microgels deposited on it (samples **1-6**).

Sample	PVAm concentration, %	Drying time, min	Immersion time, s	Quality[a]
1	10	30	20	low
2	1	30	20	low
3	0.1	30	10	moderate
4	0.05	30	10	moderate
5	0.05	30	5	high
6	0.05	10	5	moderate

[a] The evenness of the surface, the absence of cracks, ridges and other defects were assessed under a microscope.

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For this purpose, sample **5** was immersed for 20 sec in an aqueous solution of the cross-linking reagent at a pH of 5–5.5, which is optimal for this reaction. Initially, when treated with the cross-linking reagent, a tough layer (sample **7**) was obtained that did not swell in aqueous solutions with a high pH. Pre-drying of sample **5** made it possible to obtain surface bound microgels with a high swelling capacity in alkaline solutions (sample **8**). Probably, the crosslinking reagent penetrates worse into the structure of the predried layer; therefore, sample **8** swells well in an alkaline solution, but does not dissolve in it. Figure 3b and 3c shows the photographs of the samples before and after treatment with a 3M NaOH solution. It is clearly seen that the intensity of the CMC/PVAm microgel spots increased significantly due to its swelling.

The study of the behavior of the CMC/PVAm microgel attached to the PVAm surface was continued using the EPR method. For this purpose, the amino-TEMPO spin label was covalently attached to the CMC polymer chain. Initially, we used a synthesis technique similar to the introduction of a fluorescent label. However, we encountered the fact that most of the label did not form a covalent bond with CMC and was removed during purification by dialysis. In this case, the amino TEMPO signal in the ^{1}H NMR spectrum was recorded at the noise level, and the IR spectrum did not contain absorption bands of the amide bond. Replacing dicyclohexylcarbodiimide with Ugi reaction components (hexamethylene diisocyanide in combination with formaldehyde) made it possible to significantly increase the label content in the sample and achieve the required signal intensity in the EPR spectra of the final samples. A technique close to that used in the case of CMC with a fluorescent label was used to prepare the samples of surface bound microgels. However, glass fiber was used as a substrate here in order to place the sample in the EPR spectrometer tube. We also changed the method of applying the PVAm layer, as we could not use a brush in this case. The conditions previously selected for immersion of CMC/PVAm particles on the glass surface remained unchanged. Therefore, we can compare the measurement results obtained on two glass surfaces (slide and fiber). The microphotographs presented in the section Supplementary materials confirm the presence of individual CMC/PVAm microgel particles on the fiber surface. Here we also used the method without drying (sample **9**) and the method with drying (sample **10**) in the processing of cross-linking reagent, as in the case of samples containing the fluorescent label.

Figure 4 shows the EPR spectra of the nitroxyl radical (amino TEMPO) covalently bound to the polymer chains of the CMC.

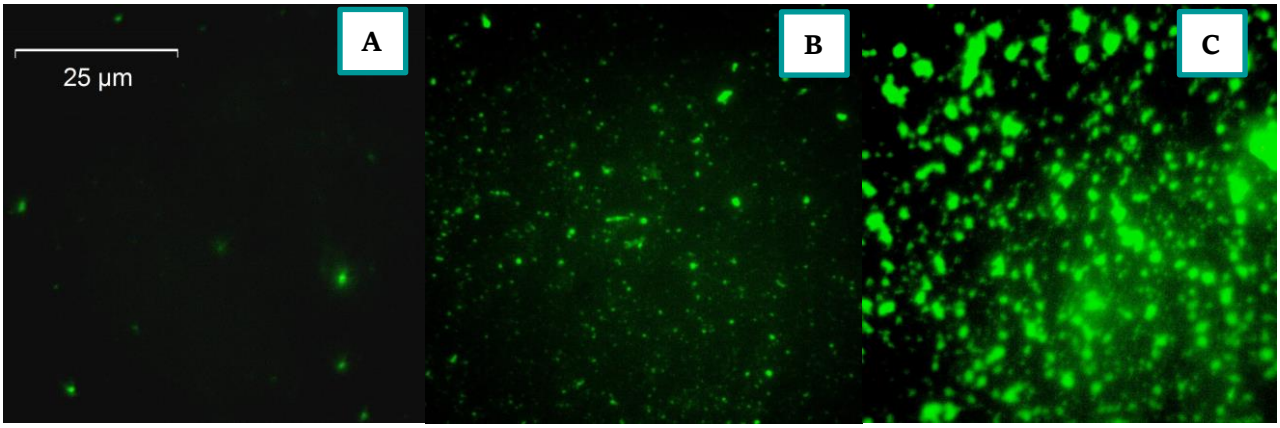

Figure 3 Microphotographs of the CMC/PVAm microgel on the PVAm gel layer located on blank slide: A –dilution in a ratio of 1:100; B-dilution in a ratio of 1:21; C-after treatment with alkali solution at pH 10.

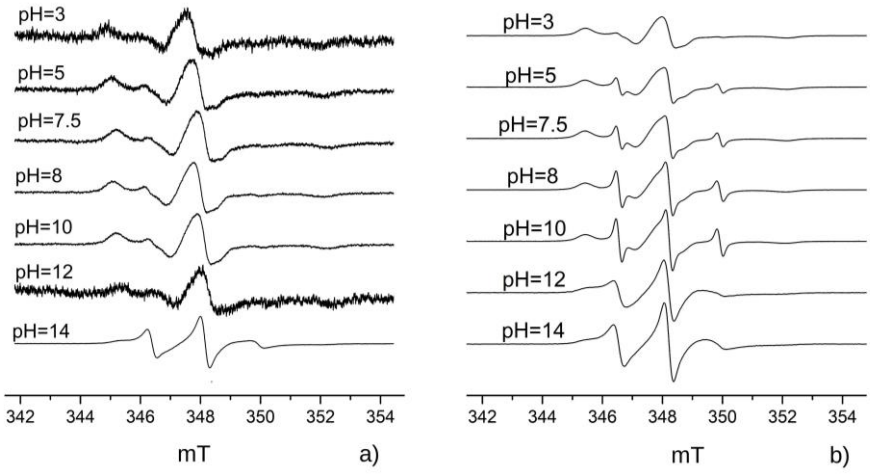

Figure 4 The dependence of the shape of the EPR lines of amino TEMPO covalently attached to the polymer chain of CMC on the pH of the external solution a) Sample **9** b) Sample **10**.

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Table 2 Preparation conditions of PVAm layer with CMC/PVAm microgels deposited on it (samples **7–10**).

Sample	PVAm concentration, %	Surface	Immersion time, s	Drying after immersion
7	0.05	blank slide	5	no
8	0.05	blank slide	5	yes
9	0.25	glass fiber	5	no
10	0.25	glass fiber	5	yes

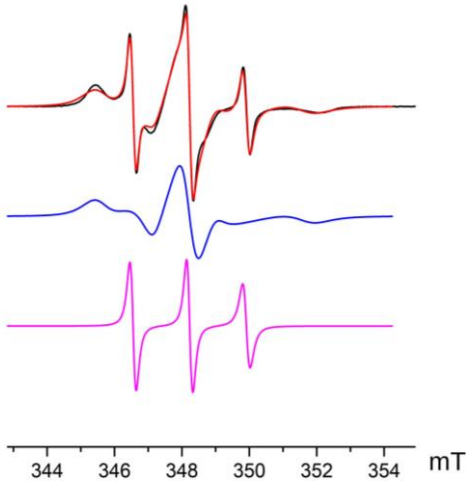

Figure 5 Experimental (in black) and simulated (in red) EPR spectra of sample **10** at pH = 10. Anisotropic signal (blue) and isotropic signal (magenta).

Table 3 The results of simulating the EPR spectra of amino TEMPO covalently attached to the polymer chain of CMC in sample **10** are presented.

pH	The type of EPR signal	Rotational correlation time , ns	Content ±3,%
3	isotropic	0.2	2
	anisotropic	10.4	98
5	isotropic	0.4	11
	anisotropic	12.8	89
7.5	isotropic	0.2	14
	anisotropic	16.7	86
8	isotropic	0.2	15
	anisotropic	12.8	85
10	isotropic	0.2	15
	anisotropic	11.1	85
12	isotropic	1.3	52
	anisotropic	9.3	48
14	isotropic	1.2	63
	anisotropic	9.2	37

The EPR spectra of sample **9** in the pH range from 3 to 12 represent an anisotropic signal of TEMPO, which indicates the low mobility of nitroxyl radical molecules. The EPR spectra of sample **10** at pH above 3 are a superposition of the anisotropic and isotropic signals of the nitroxyl radical (Figure 5). This type of spectrum indicates the presence of TEMPO with different mobility in the system. The proportion of the isotropic signal increases with increasing external pH values (Table 3). With increasing pH values, the gel swells and the nitroxyl radical, covalently cross-linked with the polymer chain of CMC, rotates freely.

At pH of the external solution above 12, the shape of the EPR spectrum lines of the nitroxyl radical covalently bound to the polymer changes (Table 3). The proportion of nitroxyl radical molecules giving an isotropic signal increases sharply. We propose that such behavior may indicate the maximum expansion of the gel matrix when the CMC chains are more mobile in a swollen polymer.

In general, the results obtained using both methods, fluorescence microscopy and EPR spectroscopy, correlate well with each other. Both methods show that with an increase in pH, the CMC/PVAm microgel particles swells and the mobility of the polymer chains increases. Their combination allows selecting the conditions for depositing the CMC/PVAm microgel on the PVAm layer and performing cross-linking with the help of the Ugi reaction. In this case CMC/PVAm microgel particles swell well, while the PVAm layer remains unchanged.

4. Limitations

The main limitation of this surface modification method is the tendency of CMC/PVAm microgels to associate. As a result, the surface is not covered uniformly, and clusters consisting of several particles are formed. In the course of this work, we also observed a similar phenomenon. Freshly prepared solutions were used to overcome particle association, and particle precipitation occurred within a few seconds. In the future, we plan to use stabilizers such as medium molecular weight polyethylene glycols to keep the particles in suspension.

5. Conclusions

Thus, in this work, the Ugi reaction was used for the first time to form surface bound microgels. We found that CMC/PVAm microgel easily precipitate on the surface of pre-dried PVAm gel. The deposition time was selected so that the positively charged PVAm gel did not have time to swell significantly and begin to dissolve. Using a fluorescent label it was found that CMC/PVAm microgel particles are distributed on the PVAm layer with the formation of mosaic structure. After the Ugi reaction CMC/PVAm microgel loses its solubility in water. However, with an optimal selection of the cross-linking reagent concentration, the surface bound microgels retain the ability to swell with changes in pH. The use of spin labels made it possible to determine the mobility of CMC chains at different pH values and, accordingly, select the synthesis conditions for obtaining CMC/PVAm microgel with swelling capacity. These studies provide the basis for the development of self-cleaning fiber, which can be used in various fields such as oil spill response, wastewater treatment and selective separation of organic compounds.

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• Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page.

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Visualization: A.R.S., A.D.O.
Writing – original draft: M.M.A., A.R.S.
Writing – review & editing: M.M.A., A.R.S., A.D.O.

• Conflict of interest

The authors declare no conflict of interest.

• Additional information

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