

OPTICAL PROPERTIES OF HYDROGELS FILLED WITH DISPERSED NANOPARTICLES

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Abstract. This paper reports on a study of novel heterohydrogel materials with regular inclusions of the dispersed phase such as polystyrene latex nanoparticles. Synthesized 3D hydrogel matrices contain a balanced number of cross-links and a defined amount of polystyrene nanoparticles with 50 or 85 nm in radius. This study has shown that the obtained hydrogel matrices are capable of changing the swelling degree and their optical properties depending on the size and concentration of the dispersed nanoparticles. The results of the performed studies revealed that the synthesized 3D hydrogels are sensitive for even small changes of glucose concentration and therefore are very promising materials for biosensors.

Keywords: hydrogel, nanoparticles, light scattering.

1. Introduction

Polymeric materials with specific stimuli responsive behavior are widely used for medical and biotechnological applications [1-4]. In particular, polymeric hydrogel systems have attracted great interest due to their soft and flexible consistency and their ability to absorb large amounts of water, keeping at the same time their three-dimensional stability [5, 6].

Many different hydrogel systems responsive to changes in temperature, pH, ionic strength, and concentration of a certain compound have been developed over the past decade [7-13]. The change in environmental stimuli mainly leads to either hydrogel collapse or increase/decrease of maximal swelling degree.

Previously we have described the synthesis of polyacrylamide hydrogels and studied their properties [14-

16]. Such hydrogels are promising as sensor-materials, providing the opportunity to measure the change in glucose concentration in the media of interest. The change in swelling degree is a parameter which is quite difficult to observe without specific registration devices. Therefore, there is a need to develop a simple method that would allow registering the changes under the influence of a certain factor in a narrow range of the change.

The change in the optical properties of the system can be used to obtain numeric values proportional to the swelling degree. One of these parameters is Rayleigh scattering of the short visible wavelengths occurring at the passage of the white light beam, when it goes through the dispersed system. According to the Rayleigh scattering law, its full intensity I_r (along with the whole cone) can be estimated using the following equation:

$$I_r = \frac{24p^3 \nu V^2}{I^4} \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 I_0 \quad (1)$$

According to this equation, the general scattering intensity is determined by the wavelength λ , the numeric concentration of scattering elements ν and the elements volume V . In addition, the ratio between the refractive index of the dispersion medium n_1 and the dispersed phase n_2 also affects the scattering intensity.

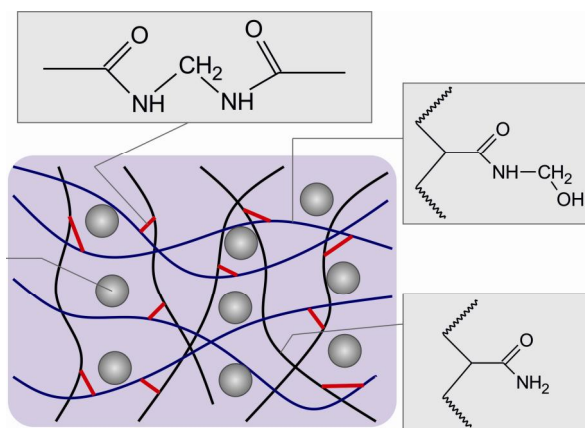


Fig. 1. Scheme of hydrogel matrix filled with polystyrene nanoparticles

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The passage of the light beam through the hydrogel systems promotes light scattering. However, the effect of the scattering change at a small degree of swelling change is too weak to build a clear analytical picture. In order to provide a sufficient optical effect, hydrogels were synthesized in the presence of spherical polystyrene nanoparticles of defined size, which were regularly distributed within the hydrogel volume (see Fig. 1). The nanoparticles were synthesized through free radical miniemulsion polymerization [18].

An objective of this study was to investigate optical effects caused by the Rayleigh scattering occurring at the passage of the white light beam through the modified polyacrylamide hydrogel filled with the polystyrene nanoparticles of 50 or 85 nm in radius.

2. Experimental

2.1. Materials

Polyacrylamide and poly-*N*-hydroxymethyl-acrylamide were synthesized using synthetic approaches described in [14]. Hydrophobic dispersed phase polystyrene nanoparticles of different sizes were obtained via miniemulsion polymerization as described in [18].

2.2. Methods

2.2.1. Synthesis of heterohydrogels

The synthesis of heterohydrogels was carried out using polyacrylamide (PAm) and poly-*N*-hydroxymethylacrylamide (PNHMAM) of different molecular weights with the ratio of PAm: PNHMAM = 1:1, then polystyrene particles of a certain size were added to the reaction mixture. The reaction mixture was stirred for 1 h, acidified with 10% nitric acid to the pH value of 2–3. After degassing the solution for 30 min, the composition

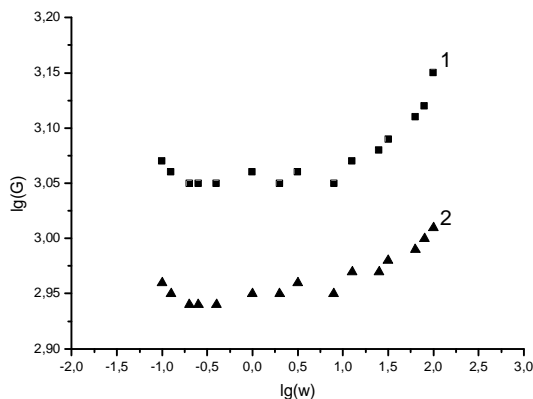


Fig. 3. Dependence of the dynamic modulus on the strain rate of hydrogel filled with 2 wt % polystyrene nanoparticles (50 nm) (2) and without a filler (1)

was heated at a given temperature (in the range between 313 and 343 K) within a defined time period.

2.2.2. The light transmittance technique

The hydrogel samples were prepared in plane-parallel cells ($l = 0.5$ cm) made of quartz optically transparent glass according to the procedure described in 2.2.1. The light transmittance (T , %) of the samples was measured using UNICO-1200.

3. Results and Discussion

As reported earlier [14, 15], the formation of PAm hydrogels via polycondensation mechanism proceeds according to Fig. 2.

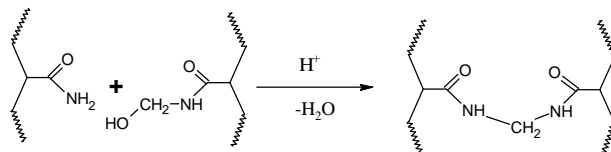


Fig. 2. Formation of polymer matrix of PAm hydrogel via polycondensation mechanism

Cross-linked hydrogel is formed from prepolymers of PAm and PNHMAM. Polystyrene nanoparticles can be incorporated into hydrogel polymer matrix by dispersing them on the stage of matrix formation.

In the beginning it was important to study the effect of particles presence on the hydrogel characteristics. The dependence of the dynamic modulus on the strain rate of hydrogels filled with nanoparticles and without them is shown in Fig. 3.

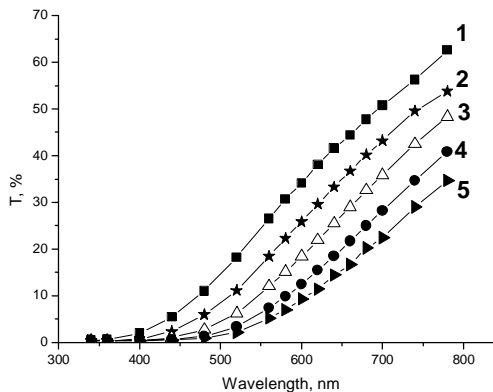


Fig. 4. Dependence of light transmittance of hydrogel samples filled with nanoparticles with average radius of 50 nm on the wavelength. The concentration of nanoparticles (wt% related to the amount of hydrogel) corresponds to (wt %): 0.11 (1); 0.15 (2); 0.21 (3); 0.26 (4) and 0.29 (5)

The analysis of these curves reveals that filled and non-filled hydrogels has the range where dynamic modulus does not depend on the strain rate. This peculiarity is specific of polymer materials with a network structure. These ranges and matching of their limits allow suggesting that dispersed particles with the radius size of 50 nm and concentration up to 2 wt % in the hydrogel matrix do not have a significant influence on the formation of hydrogel matrix. The increase of filler amount in hydrogel matrix leads to the rapid decrease of the dynamic modulus (Fig. 3). Thus, the position and the distribution of dispersed phase particles are to some extent controlled by the 3D hydrogel matrix.

Fig. 4 shows the dependence of light transmittance in the hydrogel samples, filled with different amounts of nanoparticles. The obtained curves demonstrate that hydrogel samples have different light transmittance at different wavelengths and number of nanoparticles. Thus, hydrogel samples containing dispersed phase diffuse the electromagnetic emission of the visible spectrum depending on the emission wavelength and amount of dispersed phase according to Eq. (1).

For the quantitative description of the dependencies the equation 1 should be presented in the form which includes the radius of nanoparticles determined by light scattering. In this case, we took into account that mass concentration of dispersed phase C (g/cm^3) can be presented as $C = \nu \cdot V \cdot d$, where d is the density of dispersed phase, V is the volume of one spherical particle $V = 4/3\pi r^3$ (cm^3) (r – particle radius). Eq. (1) will transform to:

$$\tau = I_r / I_0 = \frac{32\pi^4}{\lambda^4} \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 \frac{C \cdot r^3}{d} \quad (2)$$

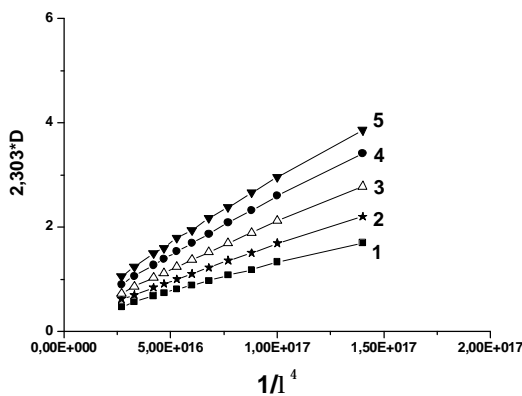


Fig. 5. Dependence of the optical density of hydrogel samples with a different number of nanoparticles on the fourth power of the inverse wavelength. The hydrogel sample was filled with nanoparticles with the average radius of 48 nm.

The concentration of nanoparticles (wt % related to the amount of hydrogel) corresponds to (wt %): 0.11 (1); 0.15 (2); 0.21 (3); 0.26 (4) and 0.29 (5)

The value of relative scattering intensity t at the certain emission wavelength is connected with the optical density D via the equation: $t = 2.303 \cdot D / l$, where l (cm) is the length of the light beam passing the sample. Hence, the optical density of the sample can be defined by equation:

$$D = 1353.491 \cdot K \cdot l \cdot r^3 \cdot C \cdot \frac{1}{\lambda^4} \quad (3)$$

where

$$K = \frac{1}{d} \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 \quad (4)$$

According to Eq. (4), if scattering corresponds to Rayleigh scattering, the optical density should decrease inversely to the fourth power of wavelength and increase proportionally to the particle concentration and the beam length in the sample. The size of dispersed nanoparticles is also a significant factor. The enlargement of particle size results in the increase of the third power of the optical density.

Figs. 5 and 6 demonstrate the dependences of the optical density of hydrogel samples (thickness – 0.5 cm) filled with different amounts of dispersed phase with average radius of 50 nm (Fig. 5) and 85 nm (Fig. 6) on the fourth power of the inverse wavelength. Curve alignment in these coordinates confirms that scattering corresponds to the Rayleigh one. Figures show that curves for samples with the radius of 50 nm are rectified for all studied concentrations of nanoparticles (0.11–0.29 wt %). However, curves for nanoparticles with the radius of 85 nm are rectified only for concentrations up to 0.15 wt %.

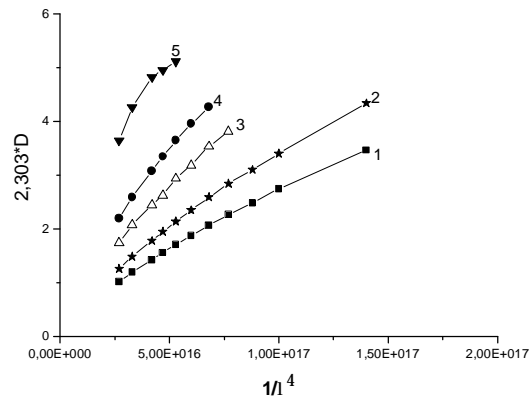


Fig. 6. Dependence of the optical density of hydrogel samples with a different number of nanoparticles on the fourth power of the inverse wavelength. The hydrogel sample was filled with nanoparticles with the average radius of 85 nm.

The concentration of nanoparticles (wt % related to the amount of hydrogel) corresponds to (wt %): 0.11 (1); 0.15 (2); 0.21 (3); 0.26 (4) and 0.29 (5)

It is known that the Rayleigh scattering is realized if the linear size of elements on which scattering takes place is much smaller than the emission wavelength. It is considered that the linear size should not exceed one tenth of the wavelength λ [19]. Polystyrene particles with the average radius of 50 nm meet this requirement, whereas the 85 nm particles significantly exceed it at any wavelengths of the visible emission and do not provide the realization of the Rayleigh scattering regime.

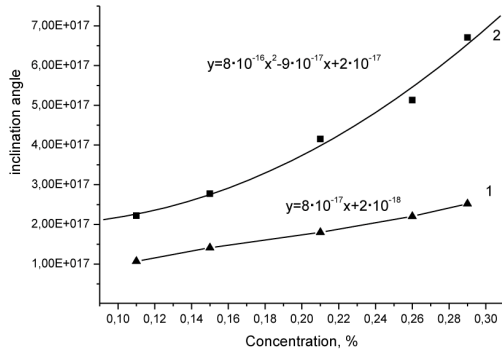


Fig. 7. Dependence of the tangent of the inclination angle (1) – for samples filled with nanoparticles of 50 nm (from Fig. 5) and (2) – for samples filled with 85 nm nanoparticles (from Fig. 6) on the concentration of dispersed phase particles in the hydrogel samples

The analysis of the tangent values of the inclination angle of the curves from Figs. 5 and 6 also confirms that the scattering does not correspond to Eq. (3). According to Eq. (3) these dependencies should be directly proportional and extrapolated to the origin of coordinates. All curves in Fig. 7 extrapolate to the origin of the coordinates; the dependence for the particles with the radius of 50 nm is directly proportional unlike it is for the particles with the radius of 85 nm.

The tangent of the inclination angle in Fig. 5 should be considered as numerical estimation of coefficient $1353,491 \cdot K \cdot r^3 \cdot C$ in Eq. (3), thus the fitted equation of line *b* in Fig. 7 can be substituted into this equation. As the equation was obtained for the samples with $l = 0.5$ cm it follows Eq. (5):

$$D_{\lambda} = (7.9 \pm 0.15) \cdot 10^{-17} \cdot \frac{C \cdot l}{\lambda^4} + \left[(1.2 \pm 0.1) + (4.2 \pm 0.3) \cdot 10^{-18} \cdot \frac{1}{\lambda^4} \right] \cdot l \quad (5)$$

The obtained equation describes the dependence of the optical density of the sample on the concentration of polystyrene nanoparticles (50 nm), the sample thickness and the wavelength. Also, it includes three summands that take into account different factors, which define the optical density of the sample: i) $1.2 \cdot l$ – concerns the optical density of the hydrogel medium

(compared with water); ii) $4.2 \cdot 10^{-18} \cdot l / \lambda^4$ – takes into consideration the inherent Rayleigh scattering of the hydrogel as the dispersed medium (inherent hydrogel scattering); iii) $7.9 \cdot 10^{-18} \cdot l \cdot C / \lambda^4$ – represents the Rayleigh scattering of the polystyrene nanoparticles.

The first and the third summand have with the biggest contribution to the scattering (95–97 %). The summand of the inherent hydrogel scattering is less than 5 %, and therefore it can be neglected in Eq. (5).

Rayleigh scattering can be used to register the effect of environmental factors on the hydrogel state. As the scattering intensity depends on the concentration of the dispersed nanoparticles, each factor that influences hydrogel swelling degree will also promote the change of the dispersed particles concentration.

To describe this effect numerically, we have introduced the term *contrast of scattering* X :

$$X = \frac{D_{580} - D_{750}}{D_{750}} \quad (6)$$

where D_{580} , D_{750} are the optical densities of the hydrogel sample at the wavelength of 580 and 750 nm respectively. This value shows the relative intensity of the scattering between the yellow and mid-red spectrum. Thus, the increase of X value points to the increasing scattering of the yellow and red spectra. In this case, the scattered rays will be orange and the intensity of the orange glow will depend on X .

After implementation of Eq. (5) without an insignificant summand into Eq. (6) and taking into account the dependence of the concentration on the gel swelling degree $C = n/n_0 \cdot C_0$, where C_0 is the particles concentration at the swelling degree n_0 (g of water per 1 g of gel-forming polymer), X can be estimated as:

$$X = \frac{4.48 \cdot n \cdot C_0}{1.20 \cdot n_0 + 2.50 \cdot n \cdot C_0} \quad (7)$$

This dependence allows relating the swelling degree and the contrast of scattering (Fig. 8).

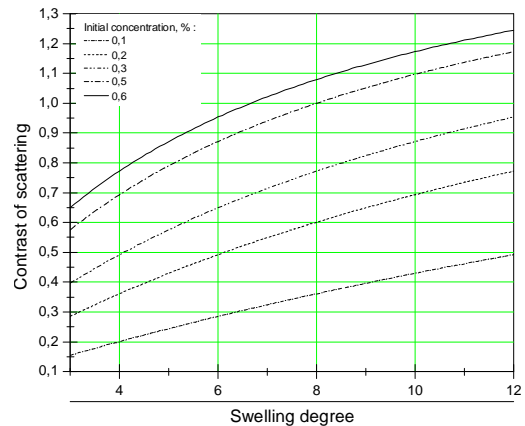


Fig. 8. Dependence of the contrast of scattering X on the swelling degree

Using these dependencies, one can make conclusions about the hydrogel state based on the scattering intensity data without immediate contact. This finding is an important factor for developing diagnostic systems based on the obtained hydrogel materials.

4. Conclusions

Controlled introduction of polystyrene nanoparticles into the hydrogel system can significantly affect its optical properties, in particular, it can create conditions for sustainable Rayleigh scattering in the visible spectrum. This property can be used for building diagnostic assays, for example to determine sugar in biological and biotechnological systems using glucose sensitive hydrogels.

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ОПТИЧНІ ВЛАСТИВОСТІ ГІДРОГЕЛІВ НАПОВНЕНИХ ДИСПЕРСНИМИ НАНОЧАСТИНКАМИ

Анотація. Вивчено нові гетерогідрогелеві матеріали з регулярними включеннями дисперсної фази, а саме полістирольними латексними наночастинками. Синтезовані 3D гідрогелеві матриці містять збалансоване число перехресних зв'язків і певну кількість наночастинок полістиролу з радіусом 50 або 85 нм. Встановлено, що отримані гідрогелеві матриці здатні змінювати ступінь набрякання та оптичні властивості залежно від розміру та концентрації дисперсних наночастинок. Показано, що синтезовані 3D гідрогелі є чутливими до невеликих змін концентрації глюкози, тому є дуже перспективними матеріалами для біосенсорів.

Ключові слова: гідрогель, наночастинки, світло-розсіювання.