

# Cross-Linked Polymer Hydrogels with Embedded Semiconductor Nanocrystals

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**Abstract** – Cross-linked hydrogels containing metal cations were synthesized via radical copolymerization of hydrophilic monomers and nanocomposite hydrogels were obtained on their basis using in situ sol-gel synthesis of semiconductor nanocrystals directly in hydrogel matrices. The influence of metal ions onto copolymerization kinetics and hydrogel cross-linking degree was studied. It was shown that nanocrystal size depends to a large extent on the density of hydrogel network.

**Keywords** – cross-linked hydrogels, copolymers, radical copolymerization, nanocomposites, semiconductor nanocrystals.

## I. Introduction

In recent years, nanocomposites based on semiconductor nanoparticles (NP) and polymeric matrices of various nature are attracting many researchers, since they can serve as substitutes for organic substances in optoelectronic devices, biological indicators, etc [1, 2]. Despite the existence of a number of methods for the formation of nanocomposite materials, the development of science and technology requires the creation of simple and accessible methods of obtaining polymer-mineral composites with improved characteristics. Among them, sol-gel methods of synthesis of mineral nanoparticles in conditions of limited growth of crystals in polymer matrices, which allow controlling the shape, size, size distribution of nanoparticles have attracted increasing attention.

## II. Experimental

Synthesis of cross-linked hydrogels based on acrylamide (AcAm) and acrylic acid (AA) as polymer matrix was carried out by radical copolymerization in water at 333K in the presence of metal salt  $\text{Cd}(\text{CH}_3\text{COO})_2$ . Structural agent N,N'-methylene-bis-acrylamide (MBA) (0.5-2% per monomers) was used to obtain structured hydrogels. The resulting hydrogels were placed in a desiccator over 10% aqueous  $\text{Na}_2\text{S}$  solution for 6 hours at 333 K. Due to the interaction of  $\text{Cd}^{2+}$  ions incorporated in the hydrogel with the gaseous  $\text{H}_2\text{S}$  CdS nanocrystals (NC) were formed in the hydrogel.

The elastic properties (compression ability) of structured hydrogels were determined as follows: samples of obtained hydrogels (cylinders with a diameter of 9 mm and a height of 10-12 mm) were placed under press. The height of the sample at different loads was measured. Relative deformation was determined by the equation:

$$\varepsilon = ((h_{in} - h_{compr}) / h_{in}) \cdot 100\%$$

where  $h_{in}$  is the height of a sample of a hydrogel without a load,  $h_{compr}$  is the height of the loaded sample.

Optical spectra of nanocomposite hydrogels were obtained using Specord-M40 spectrophotometer. The size of the CdS NC (D, nm) synthesized in the hydrogel was determined from absorption maximum values in optical spectra of samples of hydrogels (cylinders with a diameter of 9 mm and height of 2 mm) using the equation:

$$D = -6,6521 \cdot 10^{-8} \cdot \lambda^3 + 1,9557 \cdot 10^{-4} \cdot \lambda^2 - 9,2352 \cdot 10^{-2} \cdot \lambda + 13,29$$

where  $\lambda$  is the wavelength of the adsorption maximum in the absorption spectrum.

## III. Results and Discussion

The results of the study of copolymerization kinetics indicate (Fig. 1) that in the case of introduction of 10% cadmium acetate into reaction mixture the rate of copolymerization of acryl amide with acrylic acid decreased by 30-50%. And further increase of metal salt concentration up to 25% has a little effect on the kinetics of the process.

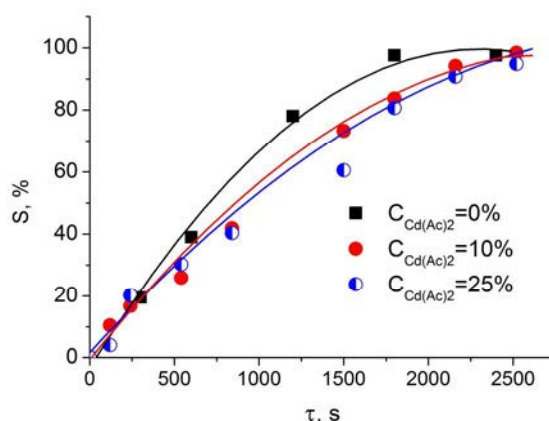


Fig. 1. Kinetics of copolymerization of AcAm with AA at different content of precursor  $\text{Cd}(\text{Ac})_2$ .  $[\text{AcAm}] : [\text{AA}] = 90 : 10$

The gel-fraction value of copolymers obtained in the presence of cadmium acetate was lower than in the case of its absence and was equal to 58-66% depending on MBA content. Taking into account that metal salt introduction decreased copolymerization rate one can conclude that cadmium acetate inhibited radical reaction of polymerization and cross-linking.

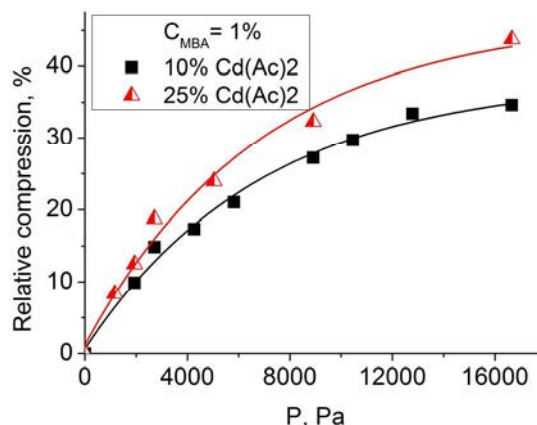


Fig. 2. Dependence of relative compression of p(AcAm-AA) hydrogels containing  $\text{Cd}^{2+}$  ions on  $\text{Cd}(\text{Ac})_2$  concentration

The curves of relative compression dependency of hydrogels containing Cd ions on load (Fig. 2) have classic look like those obtained for hydrogels without metal ions. But absolute values are essentially higher and increase with the increase of salt content that witness in favor of assumption about inhibiting influence of  $\text{Cd}(\text{Ac})_2$  on the process of hydrogel polymer cross-linking

As a result of the treatment of hydrogels containing  $\text{Cd}^{2+}$  ions with gaseous hydrogen sulfide CdS nanocrystals were formed in the volume of hydrogel that was proved by the change of sample color from colorless to yellow (Fig. 3). The color intensity increased with the growth of the concentration of cadmium acetate in initial reaction mixture



Fig. 3. Samples of structured poly(AcAm-AA) hydrogels filled with CdS nanoparticles ( $\text{Cd}(\text{Ac})_2 = 25\%$  (left), 10% (right))

Optical spectra of filled hydrogels proved the formation in them of CdS nanocrystals – the absorption bands in the range of 425-460 nm are present in spectra that corresponds to nanocrystal size of 4.3-5.7 nm (Table 1). Besides, with the increase of cross-linking agent concentration (i.e. enhancement of curing degree of hydrogels) we observed hypsochromic shift of absorption. The shift of this peak into the range of higher energies is caused by quantum-size effect of CdS NC and witnesses about the decrease of the size of nanocrystals embedded into hydrogel.

TABLE 1

DEPENDENCE OF CdS NC SIZE ON CONCENTRATION OF CROSS-LINKER MBA AND  $\text{Cd}(\text{Ac})_2$  PRECURSOR

| MBA content, % | $C_{\text{Cd}(\text{Ac})_2}$ , % | $\lambda_{\text{max}}$ , nm | $D_{\text{NC}}$ , nm |
|----------------|----------------------------------|-----------------------------|----------------------|
| 0,5            | 10                               | 437,3                       | 4,7                  |
| 0,5            | 25                               | 445                         | 5,1                  |
| 1,0            | 25                               | 440                         | 4,9                  |
| 2,0            | 10                               | 425,4                       | 4,3                  |

The values of relative compression for hydrogel with CdS nanoparticles are essentially higher than that for hydrogels with metal ions only (Fig. 4). On our point of view it can be due to the breaking at the formation of CdS NC of the salt and coordination bonds between  $\text{Cd}^{2+}$  ions and polar carboxylic groups of acrylic acid which also participate in the formation of 3D network. After breaking of these bonds the rigidity of mesh structure decreased

significantly that caused the ability of hydrogels to compression.

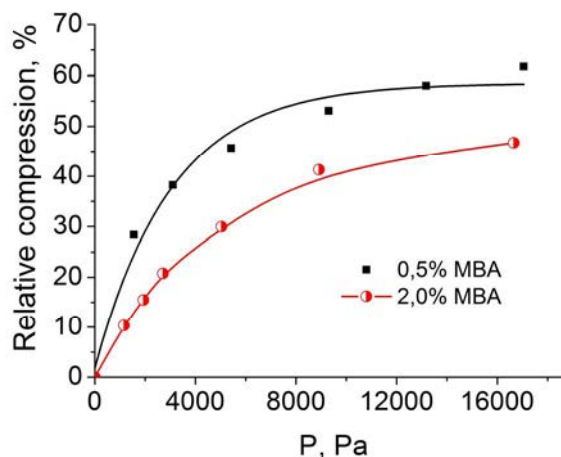


Fig. 4. Dependence of relative compression of p(AcAm-AA) hydrogels containing CdS NC on MBA concentration

But at the same time such samples are elastic and after unloading restored their size and shape (Fig. 5).

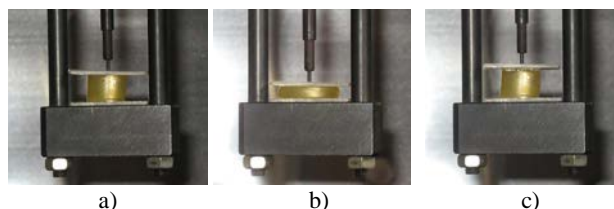


Fig. 5. Samples of p(AcAm-AA) hydrogel with CdS NC before loading (a); under pressure  $P=16,5$  kPa (b), after unloading (c)

## Conclusion

Thus, cross-linked nanocomposite hydrogels with embedded semiconductor nanocrystals were obtained via in situ synthesis of CdS nanocrystals in hydrogel polymer matrices. Studies of copolymerization kinetics indicate that the introduction of  $\text{Cd}^{2+}$  salt into monomer mixture reduces the rate of copolymerization and degree of hydrogel crosslinking. It is shown that the size of semiconductor nanocrystals is largely determined by the density of the hydrogel network. The formation of CdS NC leads to reduction in the stiffness of hydrogels due to the destruction of salt and coordination bonds between  $\text{Cd}^{2+}$  and the polar functional groups of copolymers.

## References

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