

UV POLYMERIZATION OF POLY (N-ISOPROPYLACRYLAMIDE) HYDROGEL

UV POLIMERIZACIJA POLI (N-ISOPROPILAKRILAMIDNEGA) HIDROGELA

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This contribution is focused on the determination of polymerization and crosslinking mechanism of poly (N-isopropylacrylamide) hydrogel and its swelling properties. Hydrogels were synthesized by environmental friendly UV polymerization method, from monomer N-isopropylacrylamide (NIPAM) and crosslinker N,N'-methylenebisacrylamide (BIS) of different concentrations. UV polymerization was performed in an UV chamber using UVA light with the wave length 350 nm. Surface morphology and pore structure analysis was carried out using SEM microscopy. The polymerization and crosslinking mechanism was determined by Fourier Transform Infrared spectroscopy (FT-IR). It was confirmed that crosslinker concentration influences the hydrogel structure and swelling properties. By increasing the crosslinker concentration the hydrogel structure changes from homogen to heterogen and the equilibrium degree of swelling decreases.

Keywords: poly (N-isopropylacrylamide) hydrogel, UV polymerization, FTIR, polymerization mechanism, swelling properties, SEM

V prispevku je predstavljen mehanizem polimerizacije in zamreženja poli(N-isopropilakrilamidnega) hidrogela in njegova sposobnost nabrekanja. Hidrogele smo sintetizirali z okolju prijazno metodo UV polimerizacije iz monomera N-isopropilakrilamida (NIPAM) in zamreževalca N,N'-metilenebisakrilamida (BIS) različnih koncentracij. UV polimerizacija je potekala v UV komori z UVA svetlobo valovne dolžine 350 nm. Površinsko morfolgijo in strukturo por smo spremljali s SEM mikroskopijo. Mehanizem polimerizacije in zamreženja smo določili na podlagi posnetih spektrov s Fourier Transform Infrardečo spektroskopijo (FT-IR). Ugotovili smo, da koncentracija zamreževalca vpliva na strukturo hidrogela in njegovo sposobnost nabrekanja. Z večanjem koncentracije zamreževalca pride do spremembe v strukturi hidrogela iz homogene v heterogeno, kar vpliva na zmanjšanje sposobnosti nabrekanja.

Ključne besede: poli (N-isopropilakrilamide) hidrogel, UV polimerizacija, FTIR, mehanizem polimerizacije, nabrekanje, SEM

1 INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks. Their most characteristic property is swelling in aqueous solutions¹. Hydrogels can be used for several applications including superabsorption in diapers and for contact-lenses, just to mention two well-established applications²⁻⁶. Recently, they have gained considerable attention also within the environmental field especially for wastewater treatments (dye and heavy metal adsorption)⁷.

Hydrogels are crosslinked during polymerization via condensation polymerization or free radical polymerization (thermal polymerization, radiation polymerization, photopolymerization or plasma polymerization)⁸⁻¹². Photopolymerization, in addition to its environmental-friendly aspect, offers a number of advantages, such as ambient temperature operations, location and time-control of the polymerization process and minimal heat production, in comparison with other techniques¹³. Photopolymerization can be induced by ultraviolet (100–400 nm), visible (400–700 nm) or infrared (780–20000 nm) radiation. Light quanta are absorbed by molecules via electronic excitation¹⁴. During photo-

polymerization process, photoinitiators are generally used having high absorption capacities at specific wavelengths of light thus enabling them to produce radically initiated species¹⁵.

Our work is focused on the preparation of nanocomposite hydrogels for water purification. This contribution represents preliminary studies that were performed for better understanding of synthesis mechanism of UV polymerized poly (N-isopropylacrylamide) hydrogel, which is essential for formation of nanocomposite hydrogel with defined properties.

2 EXPERIMENTAL

For the polymerization of poly (N-isopropylacrylamide) hydrogels we used N-isopropylacrylamide (NIPAM) as monomer, N,N'-methylenebisacrylamide (BIS) as crosslinker and Irgacure 2959 as photoinitiator. All chemicals were purchased from Sigma-Aldrich and their chemical structures are presented in **Figure 1**.

PNIPAM hydrogels were synthesized in aqueous solutions containing 1% of NIPAM monomer in the presence of different concentrations of N,N'-methylenebisacrylamide (0 – 5 wt%). NIPAM and BIS were kept

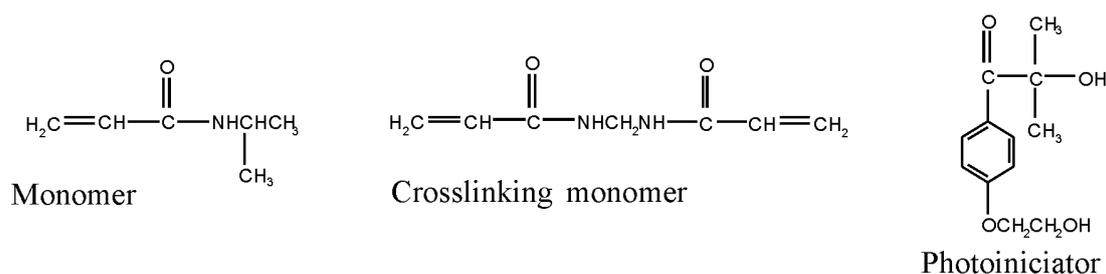


Figure 1: Chemical structure of monomer, crosslinker and photoinitiator
Slika 1: Kemijska struktura monomera, zamreževalca in fotoiniciatorja

under constant stirring for 1 hour at room temperature. After this period, Irgacure 2959 photoinitiator was added and the solution was kept under the same conditions for additional 30 minutes. Prepared solutions were pored in glass Petri dishes, bubbled with nitrogen for 5 minutes and covered. Petri dishes were placed on the sample holder in the middle of a UV chamber (Luzchem). Polymerization was carried out in UV chamber using 6 UVA lamps (centered at 350 nm) placed on top of the chamber with the distance to the sample 15 cm. Time of polymerization was 2 hours. After polymerization the hydrogels were washed with deionized water for 4 days (daily exchange of water). After washing, the hydrogels were dried at 40°C until a constant mass was reached.

For determination of an equilibrium degree of swelling (EDS) and equilibrium water content (EWC), we used pre-weighted hydrogel samples and immersed them into deionized water. Samples were removed from water every hour, wiped with filter paper in order to remove surface water, weighted and placed back into the water for further swelling. The equilibrium was reached when no mass difference was determined. EDS and EWC were calculated using these equations¹⁶:

$$EDS(\%) = \frac{W_s - W_d}{W_d} \cdot 100 \quad (1)$$

$$EWC(\%) = \frac{W_s - W_d}{W_s} \cdot 100 \quad (2)$$

where W_s and W_d are the masses of the gel in swollen and dried states, respectively.

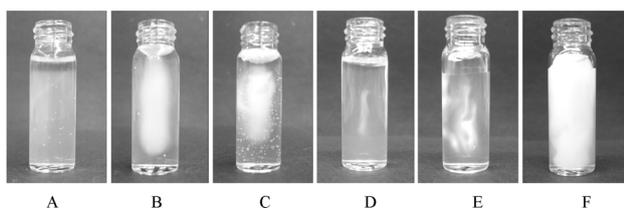


Figure 2: Polymerized hydrogels with different crosslinker concentrations (A:0 wt%, B:0.25 wt%, C:0.5 wt%, D: 1 wt%, E:2.5 wt%, F:5 wt% BIS regarding the monomer content)

Slika 2: Polimerizirani hidrogeli z različnimi koncentracijami zamreževalca (A:0 u.t.%, B:0,25 u.t.%, C:0,5 u.t.%, D: 1 u.t.%, E:2,5 u.t.%, F:5 u.t.% BIS glede na delež monomera)

The structural properties of the hydrogels were examined using the Perkin-Elmer Spectrum One FT-IR spectrophotometer. Hydrogel disks were cut into small pieces and dried at 40°C until a constant mass was reached. Spectra were recorded by placing a dried gel piece over the attenuated total reflectance crystal. Recording conditions were: 16 scans and an estimated resolution of 4 cm⁻¹.

The surface morphology of the hydrogels was studied using the scanning electron microscope FE-SEM-ZEISS Gemini Supra 35 VP. The samples were equilibrated in distilled water at room temperature and freeze-dried (Lyotrap freeze-drier) for 2 days prior to SEM analyses.

3 RESULTS AND DISCUSSIONS

Polymerized hydrogels with crosslinker concentrations less than 1 wt% regarding the monomer content form sticky gels that decay during the washing or subsequent swelling. At the cross-linker concentration of 1 wt% and above regarding the monomer content, polymerized hydrogels retained their structure also during the washing and swelling process. We assume that the ratio monomer/crosslinker under 100:1 is too small for the material to polymerize completely and form a firm and resistible hydrogel. In **Figure 2** it is demonstrated that hydrogel with crosslinker concentration of

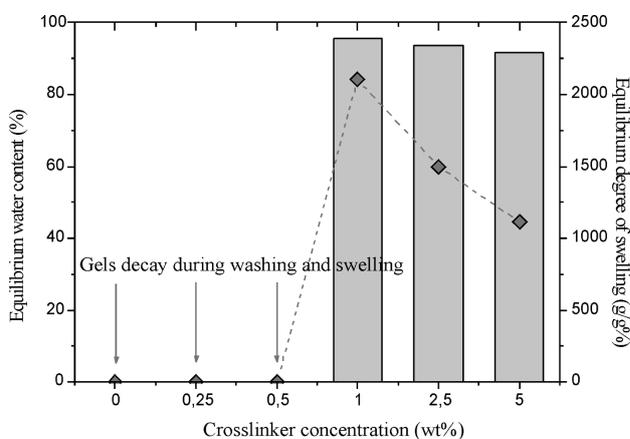


Figure 3: Equilibrium water content and equilibrium degree of swelling vs. crosslinker concentration

Slika 3: Delež vode v hidrogelu in stopnja nabrekanja v ravnatežju v odvisnosti od deleža zamreževalca v hidrogelu

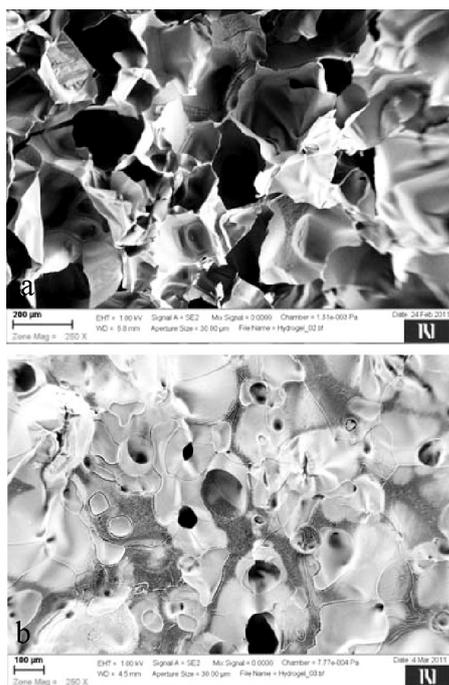


Figure 4: SEM micrographs of cross-section (A) and surface (B) of hydrogel with crosslinker concentration 1 wt% regarding the monomer content

Slika 4: SEM posnetki prereza (A) in površine (B) hidrogela s koncentracijo zamuževalca 1 u.t.% glede na delež monomera

1 wt% is transparent, which indicates that the crosslinking structure is homogeneous. Increased concentration of crosslinker causes formation of opaque segments, which indicate a formation of heterogen hydrogel structure (Figure 2).

When hydrogel is exposed to water, water molecules diffuse into hydrogel structure and consequently hydrogel swells. Hydrogel ability to swell or uptake water is one of the key characteristics. Therefore, the optimal monomer/crosslinker concentration ratio was determined in regard to the degree of swelling. Figure 3 represents the equilibrium degree of swelling and

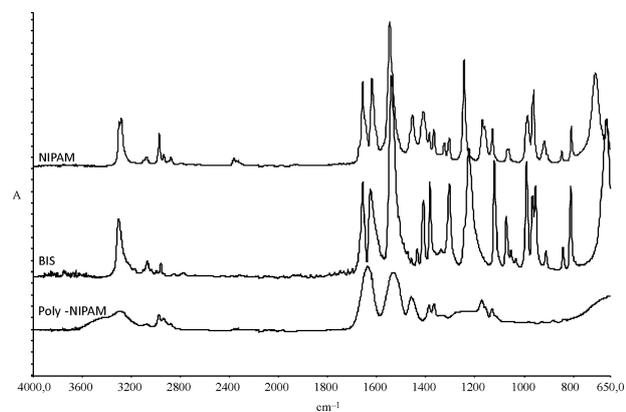


Figure 5: FTIR spectra of monomer (NIPAM), crosslinker (BIS) and synthesized hydrogel (poli-NIPAM – 1 wt% of BIS)

Slika 5: FTIR spektri monomera (NIPAM), zamuževalca (BIS) in polimernega hidrogela (poli-NIPAM –1 u.t.% BIS)

equilibrium water content for polymerized hydrogels with different concentrations of crosslinker.

It was established that when increasing the crosslinker concentration above 1 wt% the amount of water in equilibrium and consequently the degree of swelling starts to decrease. This decrease can be related to the formation of hydrogel heterogene structure. With the increase of crosslinker concentration we create a denser hydrogel structure which affects the water uptake. Water uptake represents the migration of water molecules into preformed gaps between polymer chains¹⁷. Denser hydrogel structure diminishes the accessibility of water molecules to hydrophilic parts of polymer molecules, therefore less water can penetrate into the hydrogel structure.

Figure 4 shows SEM micrographs of a cross-section and a surface of hydrogel with crosslinker concentration of 1 wt% regarding the monomer content. Samples were lyophilized after the equilibrium swelling has been reached at room temperature in order to preserve natural hydrogel structure in swollen state. Hydrogel cross-section (Figure 4a) shows very porous structure with several pores and wide pore size distribution. The pore structure has a sponge-like shape with spherical opens and interconnected cells. This porous microstructure is essential for a large active surface of hydrogel and assures the capillary effect of water uptake. Figure 4b shows a hydrogel surface. It is noticeable that hydrogel surface is covered with a surface layer with few smaller pores. Hydrogel surface differs from its interior probably due to the difference in effect of UV light. On the surface the UV intensity is higher in comparison to the interior and therefore it causes higher crosslinking efficiency and density on the surface. Therefore a core/shell structure is suggested for the polymerized hydrogels.

Unfortunately, however, neither the UV radiation intensity nor the penetration depth of the photons with the wavelength of 350 nm is known, so we can not give any quantitative estimation. Differences in SEM images between the surface of a porous sample and the bulk could be easily attributed to the artefact of the cutting technique. Namely, porous materials are inhomogeneous and thus difficult to cut and/or polish. The proper method for monitoring distribution of grains and/or

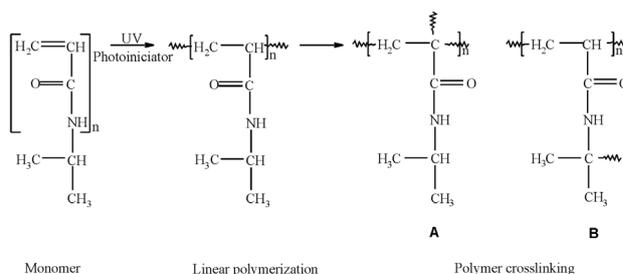


Figure 6: Mechanism of UV polymerization of poly (N-isopropylacrylamide) hydrogel

Slika 6: Mehanizem UV polimerizacije poli (N-isopropilakrilamidnega) hidrogela

pores inside a porous material is based on selective removal of the upper layers of materials. A common used method applies highly non-equilibrium gaseous plasma treatment. Gaseous particles interact with the surface material but not with the bulk. If proper parameters are taken, the material can be slowly removed without influencing the structure or composition below the surface. Such a method has been used for investigation of the structure of variety of composite materials^{18–25}. Unfortunately, however, this technology was not available at our experiments.

FTIR spektra of monomer, cross-linker and polymerized NIPAM hydrogel (poly-NIPAM) are presented in **Figure 5**. The FT-IR spectra of the monomer and crosslinker show typical absorption peaks that are summarized in **Table 1**. In comparison to FT-IR spectrum of poly (N-isopropylacrylamide) hydrogel several changes can be observed. First difference is observed in the spectrum from 3600–3100 cm^{-1} . In this part of the spectrum of monomer the absorption peak characteristic for N-H vibrations is located at 2970 cm^{-1} , while in spectrum of hydrogel this peak is much broader due to the overlapping with an absorption peak which is characteristic for O-H vibrations of water molecules. This change is attributed to the interactions of polymer molecules with neighbouring water molecules. Generally, the state of water in the polymer hydrogel can be divided into free water, freezing bound water and non-freezing bound water. Free water is the water which does not take part in hydrogen bonding with polymer molecules. Freezing bound water (intermediate water) is water which interacts weakly with polymer molecules. Non-freezing water (bound water) are the water molecules which are bound to polymer molecules through hydrogen bonds^{26–29}. Therefore the water that is presented in the FTIR spectrum of poly (NIPAM) hydrogel represents non-freezing bound water that remains in hydrogel structure also after extensive drying. The absorption peak at 1640 cm^{-1} is assigned to C=O stretching vibrations in $\text{C}=\text{O}\cdots\text{H}_2\text{O}$ and $\text{C}=\text{O}\cdots\text{H-N}$ hydrogen bonding with neighbouring water molecules.

Table 1: Characteristic absorption peaks in FTIR spectrum of monomer and crosslinker^{11,30,31}

Tabela 1: Značilni absorpcijski vrhovi FTIR spektra monomera in zamreževalca^{11,30,31}

Absorption peaks (cm^{-1})	Assignment
3280	N-H stretching of secondary amide
2970	Asymmetric and antisymmetric stretching of C-H bond
2876	
1656	C=O stretching of amide I bond
1620	
1540	N-H stretching of amide II bond
1387	Antisymmetric deformation of isopropyl $-\text{C}(\text{CH}_3)_2$ group
1367	

Due to the polymerization and crosslinking process of hydrogels, significant differences in absorption maxima of FTIR spectra were observed. Absorption peak at 2970 cm^{-1} in the hydrogel spectrum, that is characteristic for $=\text{C-H}$ vibrations, is higher in comparison to the same peak of the monomer spectrum, which indicates that a double bond of NIPAM is initiated by the photoinitiator radicals, resulting in the point of polymerization (**Figure 6** – linear polymerization). Absorption peaks at 1387 and 1367 cm^{-1} , characteristic for vibrations of isopropyl group, are lower in comparison to monomer spectra, what indicates that the isopropyl groups represent the crosslinking points. Crosslinking is formed on the tert-C atom of the side isopropyl group and tert-C atom of the main chain isopropyl group (**Figure 6** – polymer crosslinking). According to FTIR measurements proposed mechanism of UV polymerisation of poly (N-isopropylacrylamide) hydrogel is shown in **Figure 6**.

4 CONCLUSIONS

In the present study poly (N-isopropylacrylamide) hydrogels were UV polymerized. The method presented in this paper represents an environmental friendly alternative to conventional polymerization techniques. By the procedure elaborated here both the polymerization and crosslinking processes occur. Stable hydrogels were obtained, which are water insoluble but swell considerably in water. The optimal concentration of crosslinker in polymerization process of poly (NIPAM) hydrogel was found to be at about 1 wt% regarding the monomer content, where polymerized hydrogels form a rather homogeneous structure with the swelling degree of 2100% and the equilibrium water content of 95,5 %. An increase in crosslinker concentration influences the crosslinking point density in the hydrogel and, consequently, it becomes more heterogeneous. A heterogeneous structure is undesirable since it creates a fragile hydrogel causing a decrease of the swelling capacity.

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5 REFERENCES

- ¹ Osada Yoshihito, Kajiwara Kanji. Gels Handbook, Volume 1. London: Academic press, 2001
- ² Haraguchi Kazutoshi, Macromol. Symp., 256 (2007), 120–130
- ³ Haraguchi Kazutoshi, Curr. Opin. Solid. St. M., 11 (2007), 47–54
- ⁴ K. T. Nguyen, J. L. West, Biomaterials, 23 (2002), 4307–4314
- ⁵ K. Haraguchi, Macromol. Symp., 256 (2007), 120–130

- ⁶ Y. Bulut, G. Akcay, D. Elma, I.E. Serhatli, J. Hazard. Mater., 171 (2009), 717–723
- ⁷ Y. Liu, W. Wang, A. Wang, Desalination, 295 (2010), 258–264
- ⁸ Nguyen Kytai Truong, West L. Jennifer, Biomaterials, 23 (2002), 4307–4314
- ⁹ M. G. Neumann, C. C. Schmitt, F. Catalina, B. E. Goi, doi:10.1016/j.polymertesting.2006.09.012
- ¹⁰ D. He, H. Susanto, M. Ulbricht, Prog. Polym. Sci., 34 (2009), 62–98
- ¹¹ P.A. Tamirisa, J. Koskinen, D.W. Hess, Thin Solid Films, 515 (2006), 2618–2624
- ¹² Ortega, E. Bucio, G. Burillo, Polym. Bull., 58 (2007), 565–573
- ¹³ He Hongyan, Li Ling, Lee L. James, Polymer, 47 (2006), 1612–1619
- ¹⁴ Dongming, Susanto Heru, Ulbricht Mathias, Prog. Polym. Sci., 34 (2009), 62–98
- ¹⁵ Wang Dong. An, Elisseeff H. Jennifer. Photopolymerization. V: Encyclopedia of biomaterial and biomedical engineering. USA: Dekker, 2004, 1212–1225
- ¹⁶ L. Janovak, J. Varga, L. Kemeny, I. Dekany. Appl. Caly. Sci., 43 (2009), 260–270
- ¹⁷ V. Can, S. Absurrahmanoglu, O. Okay, Polymer, 48 (2007), 5016–5023
- ¹⁸ R. Kulcar, M. Friskovec, N. Hauptman, A. Vesel, M. Klanjsek-Gunde, Dyes Pigm., 86 (2010) 3, 271–277
- ¹⁹ A. Vesel, M. Mozetic, P. Panjan, N. Hauptman, M. Klanjsek-Gunde, M. Balat-Pichelin, Surf. Coat. Technol., 204 (2010) 9/10, 1503–1508
- ²⁰ M. Klanjšek Gunde, M. Kunaver, M. Mozetič, P. Pelicon, J. Simčič, M. Budnar, M. Bele, Surf. Coat. Int. B, Coat. Trans., 85 (2002) 2, 115–121
- ²¹ M. Kunaver, M. Klanjšek Gunde, M. Mozetič, A. Hrovat. Dyes Pigm., 57 (2003) 3, 235–243
- ²² I. Junkar, U. Cvelbar, A. Vesel, N. Hauptman, M. Mozetic, Plasma Processes Polym., 6 (2009) 10, 667–675
- ²³ M. Kunaver, M. Mozetič, M. Klanjšek Gunde, Thin Solid Films, 459 (2004) 1/2, 115–117
- ²⁴ M. Klanjšek Gunde, M. Kunaver, M. Mozetič, A. Hrovat, Powder Technol., 148 (2004) 1, 64–66
- ²⁵ M. Kunaver, M. Klanjšek Gunde, M. Mozetič, M. Kunaver, A. Hrovat, Surf. Coat. Int. B, Coat. Trans., 86 (2003) 3, 175–179
- ²⁶ S. J. Kim, S. J. Park, S. I. Kim, Reactive and functional polymers, 55 (2003), 53–59
- ²⁷ Ping Z. H., Nguyen Q. T., Chen S. M., Zhou J. Q., Ding Y. D., Polymer, 42 (2001), 8461–8467
- ²⁸ S. Sunm J. Hu, H. Tang, P. Wu, J. Phys. Chem. 114 (2010), 9761–9770
- ²⁹ Z. H. Ping, Q. T. Nguyen, S. M. Chen, J. Q. Zhou, Y. D. Ding, Polymer 42 (2001), 8461–8467
- ³⁰ R. da Silva, M. G. de Oliveira, Polymer 48 (2007), 4114–4122
- ³¹ Y. Bao, J. Ma, N. Li, Carbohy Polym, 84 (2011), 76–82