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Hydrogels of polyvinylpyrrolidone (PVP) and poly(acrylic acid) (PAA) synthesized by photoinduced crosslinking of homopolymers

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Abstract

A novel method of covalent crosslinking between polyvinylpyrrolidone (PVP) and poly(acrylic acid) (PAA) resulting in hydrogels has been developed. The hydrogels were formed by photocrosslinking in oxygen-free aqueous solutions containing hydrogen peroxide as a source of hydroxyl radicals. The crosslinking was achieved via irradiation within the broad wavelength range from 200 to 800 nm, as well as by the light cut-off at $\lambda > 300$ nm. The obtained PAA–PVP gels were sensitive to pH. Protonation of the PAA carboxylic groups with decreasing pH promoted hydrogen bonding between the PAA and PVP segments within the crosslinked structure and caused the gel to collapse. This property enabled the use of the hydrogels as a simple chemical sensor. When loaded with glucose oxidase, the PAA–PVP gel's opacity and sedimentation due to the clearly observable phase separation were triggered by the presence of glucose due to a drop in pH caused by the enzymatic reaction.

Keywords: Hydrogel; Crosslinking; Stimuli-sensitive

1. Introduction

Poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) are polyelectrolytes with the proton-donating carboxyls that are known to form interpolymer complexes (IPC) stabilized by hydrogen bonding with H-accepting neutral polymers such as poly(ethylene oxide) (PEO) and its copolymers, and polyvinylpyrrolidone (PVP) [1–7]. Complexation is reversible and occurs at low pH, where the dissociation degree of carboxylic groups is low enough to allow for cooperative H-bonding along a chain segment of a certain minimum length [8]. Similar complexation phenomena take place between chain segments of block, graft, and random copolymers consisting of H-donating and H-accepting polymers, such as p(MAA-*g*-EG) [9–14], p(MAA-*b*-EO) [15–17], p(MAA-*co*-VCL) [18], and p(AA-*co*-VP) [19], where MAA, EG, EO, VCL, AA, VP denotes methacrylic acid, ethylene glycol, ethylene oxide, vinylcaprolactone, acrylic acid and vinylpyrrolidone, respectively.

Formation and properties of PAA–PVP complexes have been studied in some detail [7,8,19–25]. These pH-sensitive materials have also been tested for applications such as pH-controlled drug delivery [26–28], ocular drug formulations [29], synthesis of mucoadhesive microspheres [28], and fabrication of polymer-ceramic composites [30].

Crosslinked random copolymer structures of AA and VP have previously been synthesized by UV-induced polymerization in the presence of crosslinking agents [31]. The pH-dependent formation of hydrogen bonds within the gel structure was indicated by FTIR spectroscopy, while parallel plate rheometry was used to determine the point at which the hydrogel breaks down; such a ''breakdown'' condition was found to be pH-dependent and also varied with molecular weight of the components. Another successful synthetic approach has been based on photoinitated grafting of acrylic acid on PVP chains in aqueous solutions in the presence of

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a crosslinker [32]. Hydrogels prepared by chain grafting and free-radical polymerization were applicable for the removal of heavy metal ions from aqueous solution and as reservoirs for pH-dependent drug release [33–36].

In the present work, we applied a simple alternative synthetic method leading to a previously untested gel structure built of PAA and PVP chains linked together by C–C bonds, rather than a network consisting of crosslinked AA–VP random copolymer chains. A conventional synthetic route toward a permanent polymer gel involves radical polymerization and crosslinking in a monomer system containing a crosslinker. While this method is very versatile and efficient, the products, especially when intended for biomedical use, may require careful post-synthesis treatment to remove the unreacted, hazardous monomeric compounds. Herein, the hydrogels are obtained via generating polymer radicals that are allowed to recombine, thus forming C–C bonds.

Such an approach, using polymers instead of monomers as substrates, has been used before to synthesize one-component polymer gels. Emami and co-workers [37–39] studied crosslinking of neat poly(ethylene oxide) in the molten state using thermal decomposition of peroxides as a mean of radical generation. Doytcheva et al. crosslinked solid PEO containing photoinitiators by UV light [40]. Direct UV irradiation ($\lambda = 254$ nm) of aqueous PVP solutions containing hydrogen peroxide has been shown to induce crosslinking [41,42] with the gel formation yield about 75%.

The present work is based upon our previous experience concerning syntheses of hydrogels in monomer and crosslinker-free aqueous solutions of polymers via OH-radical mediated crosslinking induced by ionizing radiation [43–50]. We have shown that PVP–PAA complexes could be crosslinked in dilute solutions by radiation to form nanogel particles [51]. Herein, we demonstrated similar effects induced by UV–vis light, leading to the formation of macroscopic PAA–PVP gels. Furthermore, we exploited the pH-sensitivity of the PAA–PVP hydrogels in order to obtain a sensitivity toward a neutral solute, glucose, by loading the gels with glucose oxidase. The hydrogels were able to respond, by deswelling, to the presence of glucose that caused a drop in the solution's pH.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA) with nominal weight-average molecular weight (M_w) of 50 kDa and polyvinylpyrrolidone, (PVP) with M_w of 650 kDa were obtained from Aldrich Chemical Co. and used as-received. To prepare solutions Nanopure-filtered water was used. The pH was adjusted with 1 M solutions of NaOH and HCl. Polymer concentrations are given in moles of repeating units per liter.

2.2. Hydrogel synthesis

PAA–PVP solutions were prepared by direct mixing of appropriate volume of PVP (1 M) and PAA (1 M) solutions to obtain the intended molar fraction of acrylic acid units expressed as $x_{AA} = [PAA]/([PAA] + [PVP])$. Irradiation of N_2-saturated PAA–PVP solutions of a chosen PAA molar fraction (total polymer concentration of 1 M, e.g., 0.5 M of PAA and 0.5 M PVP) with addition of H_2O_2 (100 mM) was carried out at pH 4.5 using a Thermo Oriel (Stratford, CT) illumination setup comprising a Model 6283 200-W mercury lamp mounted on a Model 66902 arc lamp housing and powered by a Model 68910 arc lamp power supply. Irradiation was performed either by full emission spectrum of the lamp (termed herein UV–vis irradiation) or by the far UV light cut-off using a filter transmitting at $\lambda > 300$ nm (termed near-UV–vis irradiation). The solution was placed in quartz cells (path length 1 cm) positioned in the front of the lamp set. This setting produced 58.35 mW cm^{-2} and 17.87 mW cm^{-2} flux for UV–vis and near-UV–vis irradiation, respectively. The absorbed doses were calculated on the basis of potassium tris(oxalato)-ferrate(III) (Hatchard–Parker) actinometer [52] taking into account the sample surface area of 2 cm^2.

2.3. Sol–gel analysis

After irradiation, the PAA–PVP hydrogels were equilibrated at 25 °C on average for 3 weeks with water change every 2 days using Nanopure-filtered, unbuffered water until constant gel weight was obtained. The sol fractions (s) were calculated as:

$$s = 1 - g \tag{1}$$

where g is the gel fraction, i.e., the ratio of dry gel weight after washing out the sol content to the initial polymer weight in the sample.

After reswelling, on the basis of dry (m_d) and swollen (m_s) gel weights equilibrium swelling degree (SD) has been calculated as:

$$\mathrm{SD} = \frac{m_s - m_d}{m_d} \tag{2}$$

2.4. Elemental analysis of PVP–PAA hydrogels

Composition of freeze-dried gels was determined by elemental analysis. For calculation of changes in PVP and PAA molar fraction after irradiation, percentage content of nitrogen (presented in PVP monomer unit) was measured with automatic EA Analyzer (Euro Vector). Sample of dry hydrogel was burned in oxygen atmosphere. Formed gas, after passing through catalyst, was separated on chromatographic columns and detected on thermal conductivity detector.

2.5. Glucose-induced deswelling of hydrogels

Freeze-dried gel ($x_{AA} = 0.5$, applied dose: 385 J) was equilibrium-swollen in an aqueous solution of glucose oxidase from *Aspergillus niger* (GOx, Sigma–Aldrich Co.). The enzyme concentration was chosen such that resulted in 500 units

of GOx per 1 g of swollen gel. Swollen gel (2 mL) was transferred to a test tube, and, after a pH determination with a microelectrode (Biotrode, Metrohm AG), 0.4 mL of glucose solution was added. Ratio of glucose to enzyme was equal to 0.02, 0.2 and 1 μmol per GOx unit. Response of the gel was followed in time by pH measurements and photography. The pH values were measured with a PHM 95 pH-meter (Radiometer Copenhagen).

3. Results and discussion

3.1. Photoinduced formation of PAA–PVP hydrogels

Direct UV irradiation of PVP solutions with no additives has been shown to induce crosslinking, albeit with limited yields [41]. The PAA–PVP complex has been stabilized by UV irradiation in a form of a film, presumably resulting in an insoluble, crosslinked structure [24]. In the present work, we irradiated oxygen-free PAA and PVP solutions at pH 4.5 in the presence of hydrogen peroxide. The pH of 4.5, close to the pK_a of the carboxyls, was selected as a compromise between the necessity of having a pH high enough to avoid turbidity persistent at very low pH, where PVP–PAA complexes precipitate, and yet low enough to avoid pronounced degradation processes known to occur when PAA radicals are generated in alkaline or neutral solutions [53,54].

In comparison to the UV irradiation process of an additive-free system [41], the presence of hydrogen peroxide is expected to significantly increase the crosslinking yield through generation of hydroxyl radicals ($^{\bullet}$OH) by the photo-homolysis of H_2O_2 [42]. The reactions of $^{\bullet}$OH radicals generated in our system with PVP and PAA are analogous to those taking place upon the treatment of deaerated solutions of these polymers with ionizing radiation [53–57], where the hydroxyl radicals are formed upon water radiolysis [58]. The hydroxyl radicals react with PVP and PAA at a diffusion-controlled rate by abstracting hydrogen atoms and giving rise to polymer radicals. The OH attack is not very selective, thus a polymer radical can be formed at any H-bearing carbon atom within the monomer unit. Recombination of such radicals located on separate chains leads to intermolecular crosslinking. The latter may be accompanied by other reactions, mainly intramolecular recombination, disproportionation, and chain scission (degradation). Effective gel formation requires that intermolecular crosslinking dominates over degradation.

In fact, upon the UV–vis or near-UV–vis irradiation of deoxygenated PAA + PVP solutions containing 100 mM hydrogen peroxide (pH 4.5, total polymers concentration 1 M), at both molar AA fractions used, i.e., 0.1 and 0.5, we observed the formation of transparent, strong hydrogels, which could be mechanically separated from the liquid phase.

Fig. 1 depicts changes in the gel fraction as a function of UV light radiation dose for PAA–PVP solutions with 0.1 and 0.5 AA unit molar fractions. In both cases the gel fraction increased with irradiation dose and reached relatively high values.

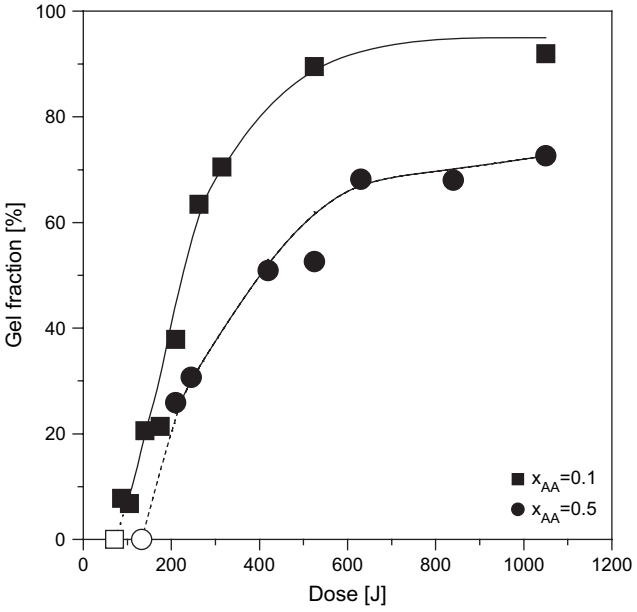


Fig. 1. Gel fraction as a function of dose during UV–vis irradiation, by a full spectrum of the high pressure Hg lamp, of aqueous PAA + PVP solutions at total polymers concentration of 1 M and AA unit molar fractions of: (■) 0.1 and (●) 0.5, [H_2O_2] = 100 mM. Empty symbols denote gelation doses calculated according to Eq. (3).

We used an expanded version [59–61] of the Charlesby–Pinner formula [62] for calculation of the gelation dose, D_g, (the dose necessary to produce the first insoluble gel fraction). Eq. (3) affords analysis for the crosslinking process in polymer samples of any initial molecular weight distribution:

$$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\left(\frac{D_v + D_g}{D_v + D}\right) \tag{3}$$

where s is the sol fraction, D is the absorbed dose, D_v is the virtual dose (a dose that would be necessary for converting the real sample into a sample of the most probable molecular weight distribution of $M_w/M_n = 2$, see Refs. [59–61]), p_0 is degradation density, i.e., average number of main chain scissions per monomer unit and per unit dose, q_0 is crosslinking density, i.e., fraction of monomer units crosslinked per unit dose.

Gelation dose depends on the molar fraction of AA, rising from ca. 71 J for $x_{AA} = 0.1$ up to ca. 133 J for $x_{AA} = 0.5$. The reason for this dependence can be several-fold as follows. The dose necessary to obtain a gel requires the formation of, on average, one crosslink per each polymer chain present initially in the solution [62]. The more chains are initially present per mass unit of the solution, the higher dose is needed for gelation, assuming no other factors are involved. In our system, due to varying molecular weights of monomer units and average molecular weights of PAA and PVP chains, changing the x_{AA} from 0.1 to 0.5 should increase the gelation dose by a factor of ca. 1.25.

The lower net crosslink efficiency at higher PAA content can be due to the tendency of the PAA-derived radicals to

undergo transformations leading to the breakage of polymer chains [53]. The balance between crosslinking and degradation of PAA is a function of pH, chain scission being more pronounced in neutral and alkaline solutions, where the linear charge density along the PAA chain is high. Coulombic repulsion between the negatively charged macromolecules results in a high energy barrier for two radical-bearing chain segments to come into proximity and react, thus recombination is slowed down to such extent that at pH 10 in deoxygenated PAA solutions the radical lifetime at RT amounts to minutes or even hours [53,54]. This very slow rate of recombination allows monoradical reactions such as chain scission to appear. We attempted to limit this effect by irradiating our system at pH 4.5, i.e., slightly below the pK_a of the PAA [63]. Still lower pH might lead to an onset of phase separation.

The gelation data were analyzed by finding D_g and D_v values, which provide the best fit according to Eq. (3), using a customized computer programme (free software available at http://mitr.p.lodz.pl/biomat/gelsol.html). As can be seen in Fig. 2, a reasonably good linear fit in terms of Eq. (3) can be obtained for both experimental series ($R^2 = 0.973$ and 0.982 for $x_{AA} = 0.1$ and 0.5, respectively). The calculation procedure results in gelation doses and p_0/q_0 values for both synthetic conditions.

The presence of scission reactions in our system at high PAA content is also reflected in the ratio of degradation vs. crosslinking density (p_0/q_0, see the intercepts in Fig. 2). For UV–vis-induced crosslinking of the PAA–PVP mixture at $x_{AA} = 0.1$, we obtain $p_0/q_0 \approx 0$. This indicates that at the given conditions the chain scission is negligible. In fact, it is known that in the absence of oxygen PVP-derived radicals have no tendency to rearrange with a C–C bond breakage [55,59]. With an increase in PAA concentration ($x_{AA} = 0.5$), the p_0/q_0 values rise to 0.49, indicating moderate contribution of degradation processes.

Values of the gelation doses and the p_0/q_0 parameter obtained in this work can be compared, by taking into account different irradiation geometry and conditions, with those reported previously [41,42] for UV irradiation ($\lambda_{max} = 254$ nm) of aqueous PVP solutions. The reported PVP concentrations were comparable to the sum of PAA and PVP concentrations herein, but the samples were not deoxygenated before irradiation. The presence of oxygen resulted in the p_0/q_0 values in the order of 0.1–0.3, indicating the presence of scission reactions. This is in line with earlier ionizing radiation experiments, where PVP degradation was observed in the presence of oxygen, but was negligible in its absence [55,59]. The gelation dose in the absence of H_2O_2, recalculated to unit volume of the irradiated system, was reported to be from 45 to 69 J cm^{-3} [41,42]. The latter value was reduced 5-fold, to 13 J cm^{-3}, when 20 mM of H_2O_2 was present [42], clearly indicating the advantage of using hydrogen peroxide as a photoinitiator. Our values for irradiation with unfiltered UV light were 35 and 76 J cm^{-3} for the polymers with $x_{AA} = 0.1$ and 0.5, respectively. The lower average molecular weights of our polymers, which require higher doses to be crosslinked, are expected to increase the gelation dose 2–3 times. Thus, these results

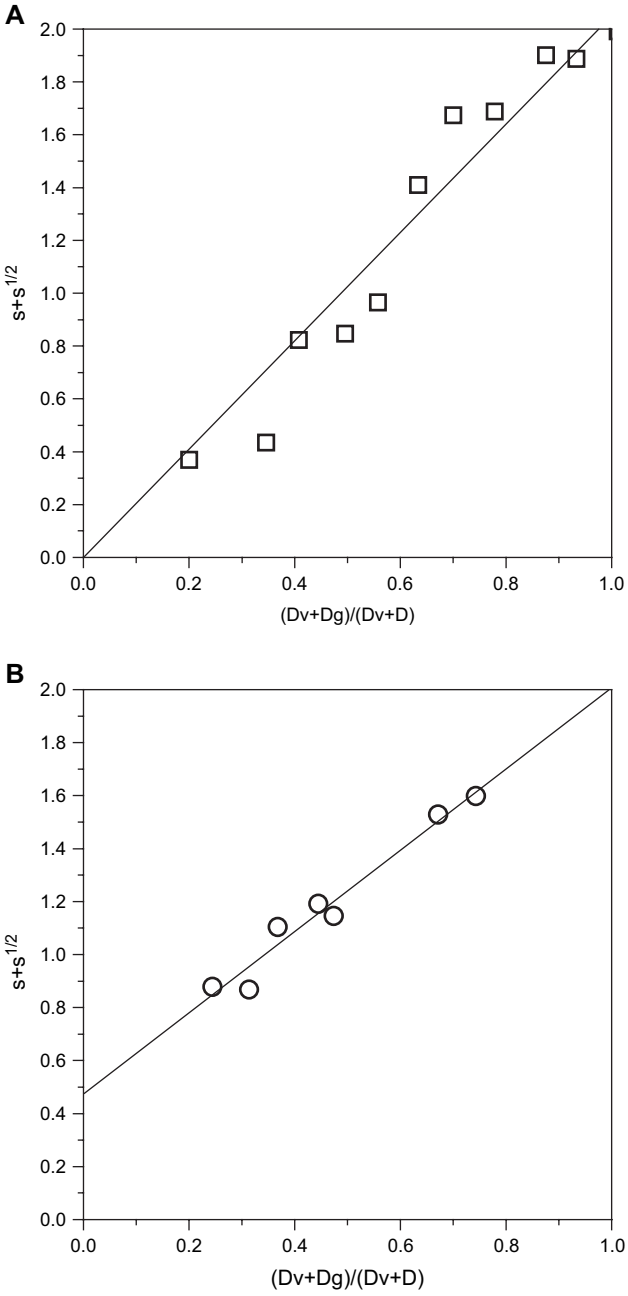


Fig. 2. Sol–gel data of Fig. 1 plotted in co-ordinates corresponding to Eq. (3): (A) $x_{AA} = 0.1$ and (B) $x_{AA} = 0.5$.

appear to be similar to those reported on PVP, indicating that the crosslinking efficiency in the PAA–PVP system is not significantly lower than in pure PVP, and the yield-reducing effect due to the chain scission related to the presence of PAA is relatively small.

Some difference between PVP and PAA in the effectiveness of crosslinking under our experimental conditions can also be inferred from the changes in gel composition. On the basis of hydrogel elemental analysis, namely nitrogen content in freeze-dried hydrogels, PVP molar fractions in hydrogels after irradiation have been calculated. Fig. 3 depicts changes in this value for hydrogels prepared from equimolar solutions ($x_{AA} = x_{VP} = 0.5$).

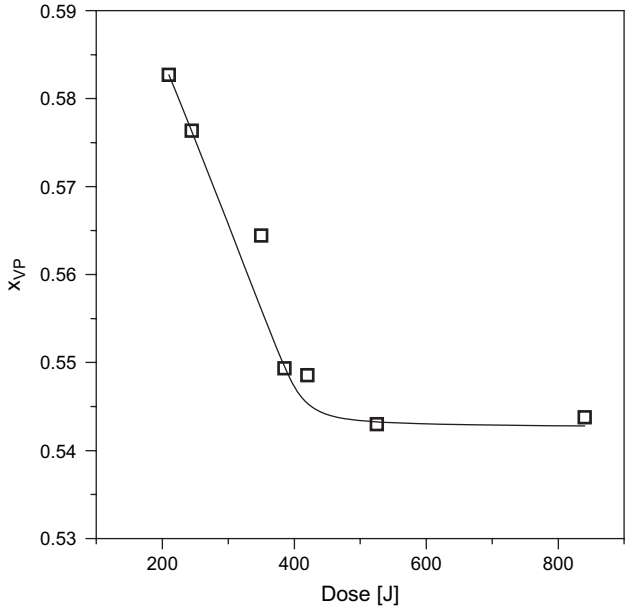


Fig. 3. Molar fraction of vinylpyrrolidone in the final product (x_{vp}) as a function of dose during UV–vis irradiation, by a full spectrum of the high pressure Hg lamp, of aqueous PAA + PVP solutions (total polymers concentration: 1 M, initial molar fraction of PAA: $x_{AA} = 0.5$, $[H_2O_2] = 100$ mM).

Hydrogels obtained at low doses (slightly higher than the gelation dose) contain almost 60% of polyvinylpyrrolidone ($x_{VP} = 0.58$, applied dose 210 J), while for higher doses PVP molar ratio decreases gradually toward the value of 0.5, corresponding to the initial substrate composition.

Next, we tested whether gelation in the PAA and PVP solutions could also be achieved using the near-UV–vis light in the range of 300–700 nm. Indeed, we observed gel formation under such conditions (Fig. 4(A)). For solutions with $x_{AA} = 0.5$, the gelation dose and p_0/q_0 values were equal to 1010 J and 0.23, respectively (Fig. 4(B)). The effective yield of crosslinking by the near-UV–vis light was found to be ca. 7-fold lower when compared to the UV–vis method. This still relatively high efficiency is due to the partial overlap of the hydrogen peroxide absorption spectrum and the spectral range of the light used for the irradiation. The difference in the p_0/q_0 values between the UV–vis and near-UV–vis irradiation may be due to a chain degradation by the UV–vis irradiation via direct absorption of the UV light by macromolecules, while such an effect is not expected to occur for irradiation at $\lambda > 300$ nm.

To the best of our knowledge, crosslinking of synthetic polymers in aqueous solutions by near-UV–vis light ($\lambda > 300$ nm) *devoid* of monomers, crosslinkers, Fenton-type reagents or specific chromophores in the polymer structure has not been reported in the literature. In the few works on additive-free photochemical crosslinking of polymers in aqueous solutions, medium or low-pressure Hg lamps ($\lambda_{max} = 254$ nm) have been used [41,42,64]. Formation of crosslinked structures by near-UV–vis light has been reported when a monomer (NIPAAm) solution containing H_2O_2 or persulfate with no added crosslinking agents was irradiated [65].

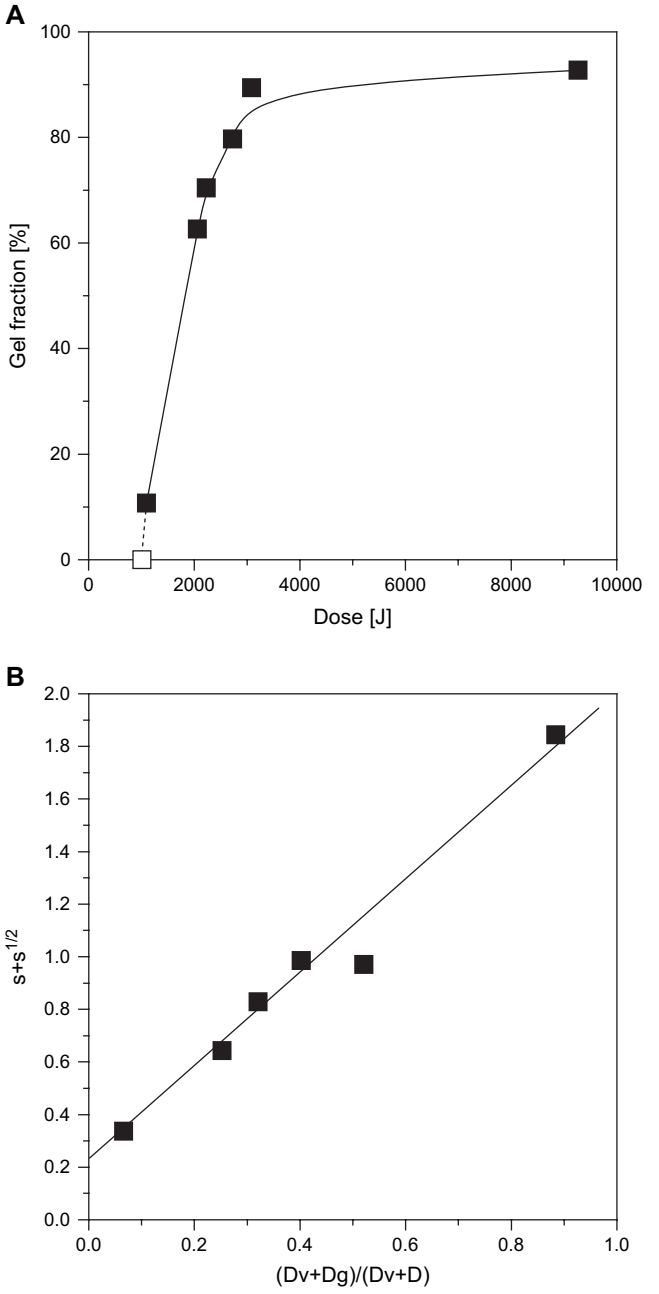


Fig. 4. (A) Changes in the gel fraction as a function of dose during near-UV–vis irradiation ($\lambda > 300$ nm) of aqueous PAA + PVP solutions (total polymers concentration: 1 M, $x_{AA} = 0.5$, $[H_2O_2] = 100$ mM). Empty symbol denotes gelation dose calculated according to Eq. (3). (B) The same data plotted in co-ordinates corresponding to Eq. (3).

To gain an insight into the structure of the obtained PAA–PVP hydrogels, the equilibrium swelling degree has been calculated with the use of Eq. (3).

Fig. 5 shows that the equilibrium swelling degree decreases with increasing dose i.e., with the number of crosslinks formed in the system. This dependency indicates that the parameters of the PAA–PVP hydrogels (swelling degree and also network mesh size correlated with this value) can be controlled by choosing appropriate irradiation conditions.

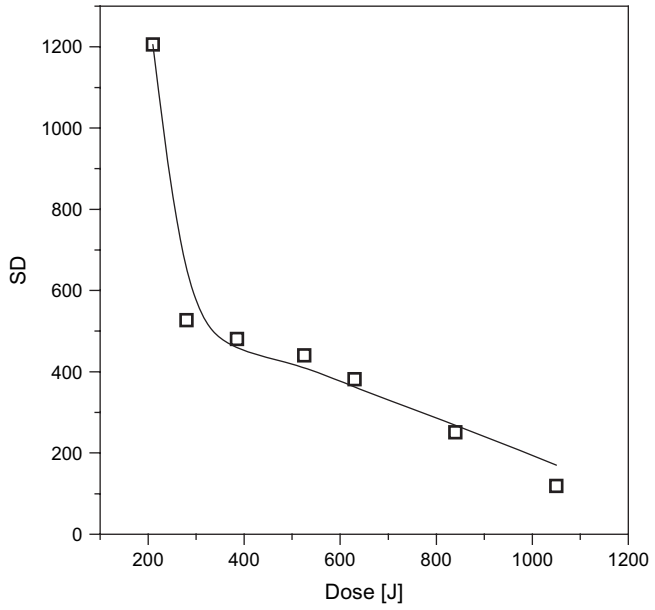


Fig. 5. Equilibrium swelling degree (SD) as a function of dose for hydrogels obtained by UV irradiation (full spectrum of the high pressure Hg lamp) of aqueous PAA and PVP solutions (total polymers concentration: 1 M, $x_{AA} = 0.5$, $[H_2O_2] = 100$ mM).

3.2. Swelling degree vs. pH

The effect of pH on swelling of the PAA–PVP hydrogel ($x_{AA} = 0.5$) is shown in Fig. 6. The swelling degree, $SD\% = 100 \times (m_s/m_d - 1)$, exhibited an abrupt drop at pH below ca. 4.5, irrespective of the dose used for irradiation (and thus irrespective of the crosslink density) of the PAA and PVP mixtures. The hydrogels lost ionization, collapsed, and became turbid at pH below 4.3, exhibiting phase separation. The transition in the PAA–PVP hydrogels appears to be somewhat different from the pH-induced deswelling of crosslinked PAA homopolymer, in that PAA hydrogels typically do not phase separate or become turbid [45,66,67].

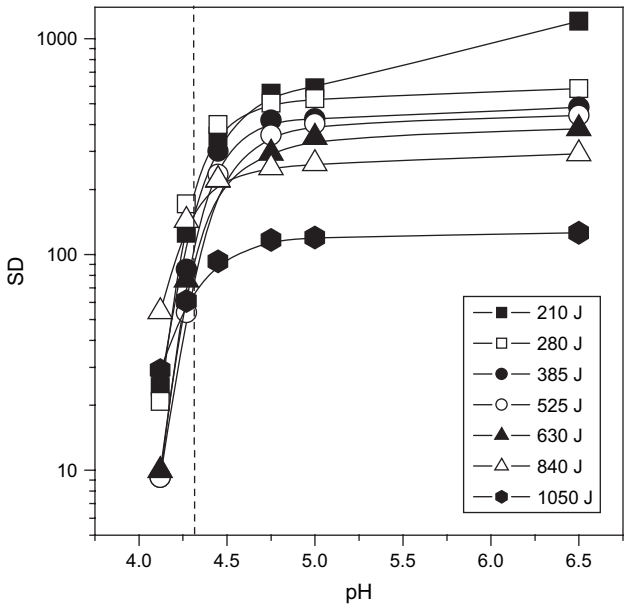


Fig. 6. Equilibrium swelling degree (SD) of the PAA–PVP hydrogels (AA unit molar fraction = 0.5) as a function of pH. Doses used for UV–vis irradiation (full spectrum of the high pressure Hg lamp) are shown in the plot. Broken line indicates change in transparency of the samples.

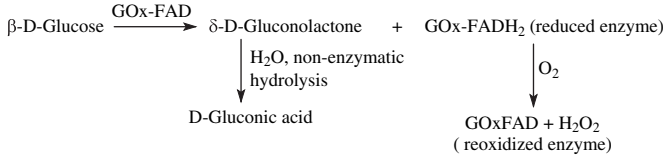
3.3. Glucose-induced changes in swelling degree and appearance of PAA–PVP–GOx hydrogels

Pronounced changes in volume and transparency of PAA–PVP gels in response to a decrease in pH may be utilized in potential applications of this material in stimuli-sensitive drug delivery systems or sensors. The latter function of pH-sensitive copolymer gel containing carboxylate functions can be based, e.g., on enzymatic acid generation [68]. We demonstrated the possibility of applying PAA–PVP hydrogel obtained by the above-described method as an indicator for detection of the glucose presence. This required loading of the gel with glucose oxidase (GOx). In the presence of glucose, the enzyme-mediated reactions lead to the formation of gluconic acid (Scheme 1), which yields a decrease in pH that affords the phase transition and collapse of the gel at pK below the pK_a of the gel carboxyls.

In preliminary series of experiments we observed that both UV–vis and near-UV–vis irradiation of the aqueous PAA and PVP mixtures containing GOx lead to significant (up to 50%) losses of the enzymatic activity. Therefore, we adopted a post-irradiation procedure of introducing the GOx into the gel. An equilibrium-swollen hydrogel was freeze-dried and then swollen in an aqueous solution of the glucose oxidase until equilibrium. This loading technique, where the enzyme was not exposed to the deleterious action of the irradiation, enabled a high activity of the enzyme embedded into the polymer network.

To test the applicability of the proposed system as glucose indicator, the freeze-dried samples of PAA–PVP hydrogel ($x_{AA} = 0.5$, UV–vis irradiation, dose 385 J) were swollen up to equilibrium in aqueous solutions of glucose oxidase. After this procedure, swollen particles (grains) of hydrogels filled with enzyme are obtained. The volume and concentration of enzyme solution was chosen to provide the final concentration of 500 GOx units per mL of swollen hydrogel. Changes in solution pH and appearance of the hydrogel after addition of glucose are given in Fig. 7. At the initial stage, the sample consists of a continuous, transparent and uniform phase of fully swollen gel grains with a slight excess of free water (Fig. 7(B), sample a).

One can see that upon glucose addition pH of the hydrogel-enzyme system decreases to reach, within 20 min, values



Scheme 1. Enzyme (GOx) mediated oxidation of glucose to gluconic acid.

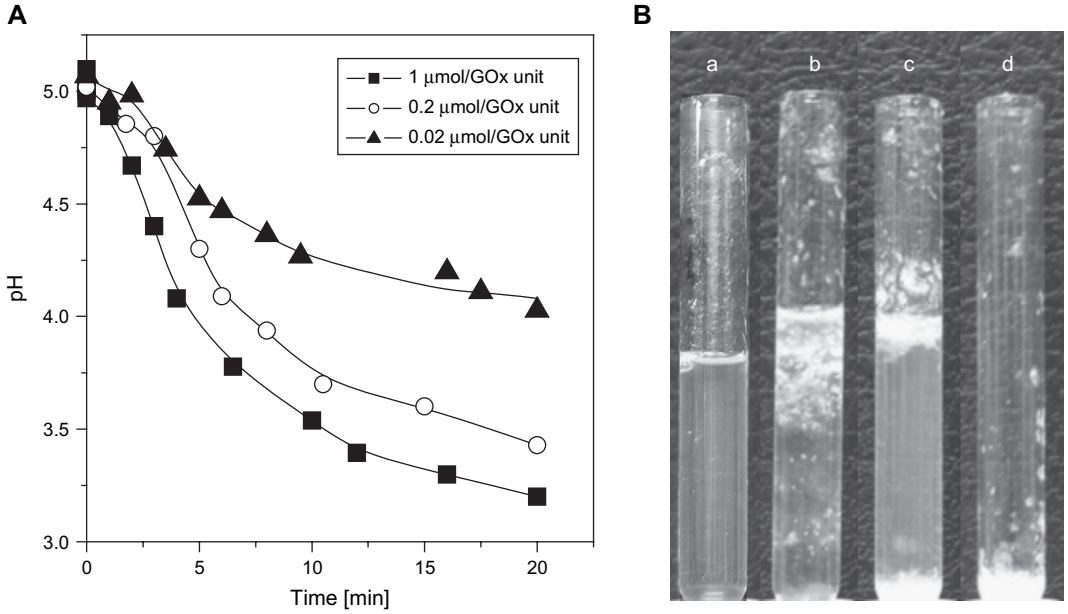


Fig. 7. (A) pH of the PAA–PVP hydrogels ($x_{AA} = 0.5$, dose = 385 J) as a function of time after glucose addition. Substrate-to-enzyme ratios are shown in the plot. (B) Changes in the appearance of the PAA–PVP hydrogels (AA unit molar fraction = 0.5, dose = 385 J) during glucose-induced deswelling (glucose/GOx = 0.2 μmol/unit) as a function of time: a – initial PAA–PVP–GOx gel sample (swollen, fully transparent gel grains with a slight excess of free water), b – 10 min after addition of glucose (formation of precipitate), c – 20 min after addition of glucose (precipitated gel particles, white, and excess of solvent), d – 20 min after addition of glucose (precipitated gel particles after decantation of excess solvent).

lower than those required to trigger phase separation in the PAA–PVP gel. As a result, the gel grains collapse, release water and separate from the solution in a form of white, non-transparent precipitate (Fig. 7(B), samples b–d). The rate of pH change depends on the substrate-to-enzyme ratio (Fig. 7(A)).

The use of pH-sensitive gels in combination with GOx has also been described by other authors (e.g. [68–72]), but, to our knowledge, the application of stimuli-sensitive hydrogels based on PVP–PAA system capable of reversible H-bonding as glucose sensors has not yet been explored. We believe that the easiness of hydrogel synthesis, the relatively short response time of prepared PAA–PVP–GOx system to low concentration of glucose (0.02 μmol/GOx unit) and easily observable, pronounced change in appearance are promising sign for the possibility of designing simple, single-use sensors based on the pH-responsive PAA–PVP gels.

4. Concluding remarks

Permanent, covalently crosslinked hydrogels consisting of PAA and PVP can be obtained by simple and reliable synthetic technique based on UV–vis photocrosslinking of these polymers in deoxygenated aqueous solutions (pH 4.5) containing H_2O_2 as a precursor of hydroxyl radicals. Moreover, we have demonstrated that near-UV–vis light ($\lambda > 300$ nm) can also be used for this purpose, although the required irradiation doses are significantly higher than for UV–vis.

Gelation data provide some insight into the mechanism of crosslinking, indicating that the PAA-derived radicals, formed by H-abstraction by OH radicals resulting from H_2O_2 photolysis, besides intermolecular recombination leading to gel formation, undergo transformations leading to the scission of the polymer chains, while the latter reaction is not observed in the case of PVP radicals. By selecting appropriate dose, one may influence the crosslink density and thus the swelling properties of the gels.

The observed phase separation and turbidity of the gels at pH below pK_a of the carboxylic groups are applicable in using PAA–PVP gels containing glucose oxidase as a glucose indicator. In the presence of 0.2 μmol of glucose per 1 enzyme unit, pH drops by 1.6 units and a complete phase separation takes place in the tested gel sample.

Acknowledgements

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