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Study of poly(acrylic acid)–poly(vinylpyrrolidone) complexes and their photostability

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Abstract

The poly(acrylic acid)(PAA)–poly(vinylpyrrolidone) (PVP) complexes with different stoichiometric ratio were obtained from aqueous solutions at different concentrations and pH values. The structure of complexes in solutions and in solid state has been studied using mainly FTIR spectroscopy. Least-square curve fitting method has been applied to calculate the contribution of different types of carbonyl groups (free and hydrogen bonded) in the PAA/PVP mixtures. Both polymers and their blends at different compositions were UV-irradiated ($\lambda = 254$ nm) in air. It has been found that PAA/PVP complexes are generally more photostable than pure polymers. This stabilisation effect was explained by the high amount of intermolecular hydrogen bonds reinforcing the polymer structure. Photocrosslinking is an additional factor influencing the stability of PAA/PVP complexes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(acrylic acid); Poly(vinylpyrrolidone); Photostability

1. Introduction

Numerous applications of polymer complexes have been described recently [1,2]. Studies of such complexes are interesting not only from chemical point of view, but they are also carried out in biochemistry, biology and medicine because of existence of such complexes in natural polymers, which play important functions in living organisms.

Most of recent works are devoted to polyelectrolyte complexes formed owing to ionic forces between two differently charged macrochains [1–8]. Introduction of even a small amount of ionic groups into incompatible polymers leads to proton transfer and it improves their compatibility through interactions between the macromolecules.

Besides strong Coulombic forces, weaker forces such as dipole–dipole, hydrogen bonds, van der Waals or hydrophobic interactions can be responsible for complex formation in polymers [9–15].

The structure of polymeric complexes in aqueous media depends on many factors — charge density, ionic strength, temperature, solution concentration and pH. These complexes can exist in completely homogenous solutions, turbid colloidal systems or two-phase compositions (containing insoluble gel) [1,2].

Among a variety of analytical methods for characterisation of polymer complexes, Fourier transform infrared spectroscopy (FTIR) technique seems to be very useful and more and more popular. Owing to continuous development of IR instruments, it is possible to monitor even very small differences in structure of system studied or small changes in absorption spectra during chemical reactions. Moreover, sophisticated computer programs allow evaluation of the data, for example, integration of peak absorption, spectra deconvolution or overlaying and resolving of complex bands onto components [16–18].

Recently, some interesting works concerning studies of specific interactions in polymer blends using FTIR spectroscopy have been published [19–23]. It was demonstrated in these articles that it is possible to calculate the concentration of hydrogen bonds and to determine quantitatively the fraction of “free” and bonded (associated) carbonyl and hydroxyl or amine groups in polymer mixtures. High sensitivity of novel IR spectrophotometers allowed to discover the new phenomenon in polymer blends called intramolecular screening effect [19,20,24]. This phenomenon explains why the number of intermolecular hydrogen bonds formed between donor and acceptor groups in miscible polymer blend is much smaller than that in analogous mixture of low molecular compounds.

Although the structure of polymer complexes is

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Table 1
Amount of insoluble complex after mixing of 1 wt% water solutions of PAA and PVP at different molar ratio (without buffer)

PAA/PVP	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
Amount of gel (%)	0	92	93	95	98	100	92	90	85	83	0

intensively studied, there is a lack of information about the stability of these unusual systems during UV irradiation.

The aim of this work was to study the structure of complexes of poly(acrylic acid) (PAA) with poly(vinylpyrrolidone) (PVP) formed in aqueous solutions and in solid state and to estimate their stability during short-wavelength UV irradiation ($\lambda = 254$ nm).

2. Experimental

2.1. Polymers

Poly(acrylic acid) was obtained in our laboratory by polymerisation of monomer (Reachim, USSR, purified by distillation under reduced pressure) in aqueous solution at 70°C using 30% hydrogen peroxide as initiator. The polymer obtained was dialysed to remove of monomer residue and water excess.

Poly(vinylpyrrolidone) (PVP) was purchased from International Enzymes Limted, Windsor, Berkshire, England.

2.2. Sample preparation

Polymeric complexes were prepared by mixing of suitable volumes of PAA and PVP aqueous solutions with the same concentrations, which varied from 0.01 to 1% (w/v). NaOH solution (0.02 mol/l) was used for the regulation of $[H^+]$. The polyacrylate buffer composed from PAA and its sodium salt was applied for fixing pH in acidic range of PAA/PVP blends. Only in case of pure PVP solution, pH = 4 was kept using acetate buffer.

Thin polymer films (~10–20 μm) were obtained by casting unneutralised or buffered solution onto quartz plate or CaF_2 spectrophotometric windows. After solvent evaporation, the samples were dried in vacuum at room temperature to a constant weight. Solutions and films were transparent (or a little hazy depending on concentration of the solution applied) and colourless.

2.3. UV irradiation

PAA, PVP and PAA/PVP films were exposed to a low-pressure mercury lamp (TUV30W, Philips, Holland) in air atmosphere. Samples of the same thickness and surface area were placed at 5-cm distance from the light source. The temperature at the film position was 30°C. Some experiments were also conducted in aqueous solution. The intensity of the incident light measured by IL 1400A Radiometer (International Light, USA) was 2.68 mW/cm^2; times of irradiation were 0.5, 1, 2, 4 and 6 h.

2.4. Methods of studies

FTIR spectra of samples before and after irradiation at ambient temperature were obtained using a Genesis II (Mattson, USA) spectrophotometer equipped with the WINFIRST 3.57 computer program (Mattson Instruments). One hundred scans at 400–4000 cm^{-1} were done for each spectrum; the resolution was 2 cm^{-1}. Intensity and area of absorption bands were calculated after baseline correction. Complex absorption bands were resolved applying the least-square fitting method and mixed Gaussian–Lorentzian functions. The number of absorption band components was deduced from second derivative plot of the spectrum and the deconvoluted spectrum [16–18].

The percentage change of carbonyl group content in UV-irradiated polymers was calculated from the formula:

$$\Delta[\mathrm{CO}] = \frac{S(\mathrm{CO})_t}{S(\mathrm{CO})_0} \times 100\%$$

where $S(\mathrm{CO})_t$ and $S(\mathrm{CO})_0$ are area of carbonyl peak after time t of irradiation, and before irradiation, respectively. The decrease of methylene group (CH_2) content in UV-irradiation was calculated in the same way.

The precipitated complexes were separated from solution by centrifugation, washed, dried and weighed. Each estimation was repeated three times.

The pH of polymer solutions was measured with an N-517 digital pH-meter (Mera-Elwro, Poland) with a glass–calomel electrode combination. The accuracy of measurement was ±0.01 pH unit.

3. Results and discussion

3.1. Preparation of PAA/PVP complexes

Mixing of unbuffered 1% PAA and 1% PVP aqueous solutions leads to immediate precipitation of complex. The percentage amount of insoluble complex with different molar ratio of PAA and PVP is very high: 100% with the 50/50 ratio and above 80–90% in other cases, even in mixtures with a minor fraction of one component (Table 1). It means that the amount of uncomplexed polymer is much less than the excess of this polymer in mixture. Such complexes are immediately and completely dissolved on adding NaOH solution (already at pH above 5).

The uncontrolled process of complex formation during

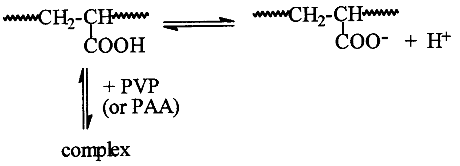
Table 2
Changes of pH during complexation of PAA and PVP at different molar ratios (measured after mixing of 0.1% water solutions of PAA and PVP (without buffer))

PAA/PVP	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
pH	3.45	3.55	3.68	3.86	4.06	4.44	4.80	4.81	4.86	4.94	6.08

mixing of relatively concentrated solutions can lead to its high inhomogeneity. Some parts of macrochains are inaccessible to the other polymer because of high sample gelation and trapping of functional groups in network. Thus, more mild conditions of complex preparation were applied. It was achieved by using more dilute solutions or buffers to fix pH and ionic strength.

Gradually diluting of PAA and PVP solutions (from 1 to 0.05%) without buffer addition, we found that the 0.1%(w/v) is a sufficiently low concentration to obtain clear mixtures at mole ratios from 1:9 to 9:1.

In these cases, a variation of pH was observed, depending on complex composition (Table 2). The pH changes arise from different ionisation degrees of the PAA. In the case of pure PAA, $[H^+] = 3.55 \times 10^{-4}$ mol/l, but in complexes $[H^+]$ decreases with the lowering of PAA content. In PAA/PVP 50/50, $[H^+]$ is about 10 times lower ($= 3.63 \times 10^{-5}$ mol/l) than that in PAA. For comparison, the blend containing the smallest amount of PAA (10/90) has $[H^+] = 1.15 \times 10^{-5}$ mol/l. This is caused by the moving of dissociation equilibrium of PAA to the left resulting from complexation of PAA macromolecules by PVP (reaction I). Such behaviour was reported by other authors [25]:



(I)

The shifting of equilibrium of above reaction can be also the reason of the increase of self-association in PAA.

The other set of PAA/PVP complexes was obtained at $pH = 4$, which assures the constant concentration of H^+ and macroions. Simultaneously, the concentration of undissociated carboxylic groups in PAA is also constant. The amount of insoluble complex formed at $pH = 4$ in 1% solutions changes with composition of PAA/PVP mixture but is also very high (for example, amount of gel obtained at $pH = 4$ in PAA/PVP 50/50 = 89%).

We have found that in alkaline solutions, where PAA is fully ionised, no insoluble complex is formed. The mixtures at every ratio are completely transparent even when concentrated solutions (1%) were used. The efficiency of insoluble PAA/PVP (50/50) complex formation dependent on pH is presented in Table 3. Only an acidic environment ($pH < 5$) enables gel formation and its amount increases with decrease in pH.

Table 3
The influence of pH on extent of insoluble PAA/PVP (50/50) complex formation in 1% solutions

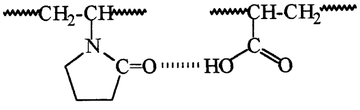
pH	5.00	4.84	4.42	4.00	3.70
% Gel	0	59.1	59.7	89.0	97.0

3.2. Structure of PAA/PVP complexes

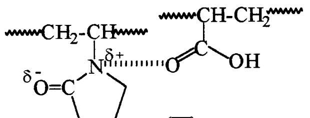
Mixing of polymeric hydrogen donors with polymers containing hydrogen acceptors (i.e. polyacid with polybase) causes formation of complexes with strong hydrogen bonds [12,13,25–30]. Such behaviour is shown by mixtures of PAA with PVP [12,25,31,32]. The structure of this complex is complicated because of numerous possibilities of interactions between macromolecules. At relatively low pH, PAA is non-ionised, hydrogen bonds and hydrophobic effects are dominant. In case of partial dissociation of PAA, the presence of carboxylate anions causes a rise to an attraction resulting from ion–dipole forces.

Thus, in PAA/PVP occur interactions between both components as well as different type of hydrogen bonds existing in pure PAA (including cyclic dimer, face-on fashion and lateral fashion), described in detail by Dong and co-workers [10] and in PVP alone [33].

PAA, which is a hydrogen donor, forms hydrogen bond with carbonyl group from PVP (structure II). Moreover, owing to partial positive charge on a nitrogen atom, the binding between N and C=O from PAA (as well as from C=O in another substituent of PVP) is formed (structure III):



(II)



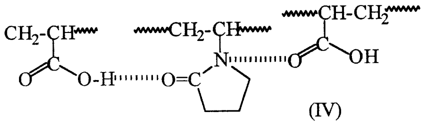
(III)

It is clear that structure II is formed more easily since there is a free access of OH groups from PAA to C=O groups in PVP. Structure III is less favoured because of inaccessibility of N atom due to steric hindrances of ring and macrochain.

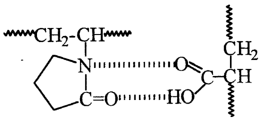
It is known that only undissociated carboxylic groups are capable to participate in hydrogen bonding. It is obvious because the charged groups in polyelectrolytes are surrounded by small oppositely charged counterions existing in aqueous solutions. The concentration of polyions in unneutralised and unbuffered system is very low because PAA is a weak acid ($pK_a = 5.32$ [34])

The evidence for complexation after mixing of relatively concentrated solutions (1%) of PAA with PVP was the instantaneous precipitation of insoluble gel.

Because the fraction of insoluble gel was very high in all PAA/PVP complexes obtained, we can assume that even a small addition of one polymer to second polymer induces not only the formation of interpolymer complexes but also strong interactions in both homopolymers: PAA and PVP. Probably the functional group from one polymeric unit participates in bonding two other groups belonging to different segments (structure IV). Two hydrogen bonds between one unit of PAA and PVP can also take place [31] (structure V):

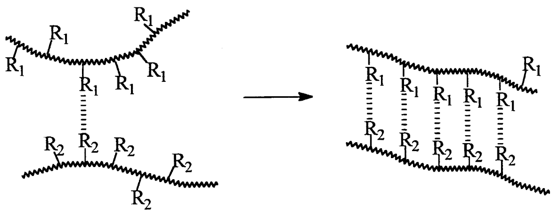


(IV)



(V)

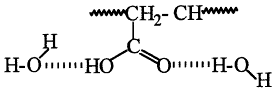
Moreover, one can suggest that the first hydrogen bond appearing between different polymers leads to fast zip formation of next interpolymer bonding from adjacent functional groups. It causes the conformational and energetic changes in polymer system. Thus, the structure similar to ladder polymers can be easily created between two macrochains (VI):



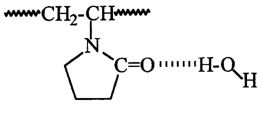
(VI)

It is necessary to remark that in pure PAA solution, gel appeared at higher concentration (~1.5 wt%). It means that the capacity of mutual binding of both polymers is very high and the interaction between them is stronger than that of hydrogen bonds formed during self-association in pure PAA in aqueous solution.

In more dilute solutions (0.05–0.10 wt.%), gel was not formed. Probably, in these mixtures, the hydrogen bonds between macromolecules (PAA or PVP) and water molecules dominate (structures VII and VII):

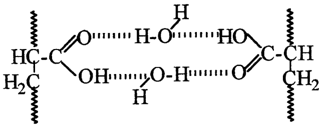


(VII)

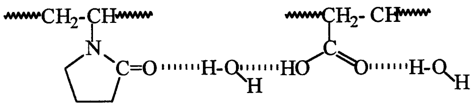


(VIII)

Interpolymer structures, in which PAA and PVP are associated through water molecules cannot be excluded (IX and X). Hydrates (IX) were found in pure PAA [35]:

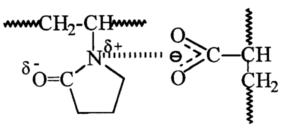


(IX)



(X)

In PAA/PVP mixtures obtained from solutions containing NaOH (added for fixing of pH), the different interactions appeared because of the presence of carboxylate groups. There are ion–ion or ion–dipole interactions (XI):

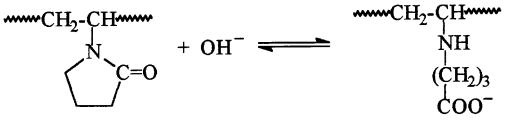


(XI)

In some privileged conformations, the following resonance between COOH and COO^- is possible, especially at low ionisation degrees [36]:

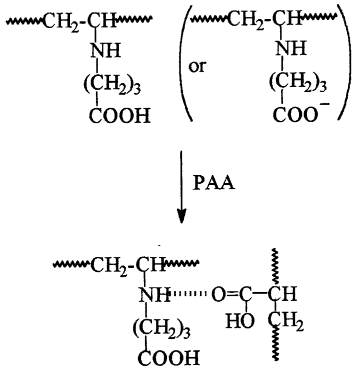
$$-COO^- \cdots\cdots HOOC- \longleftrightarrow -COOH \cdots\cdots {}^-OOC- \qquad \text{(XII)}$$

However, the PVP in alkali or acid can partially undergo ring opening reaction giving poly(γ-aminobutiric acid) [37]. In alkaline environment, the anionic form (XIII) is present:



(XIII)

Such PVP anions can participate in ionic interactions similarly to PAA carboxylates. Moreover, amine groups are capable of forming new hydrogen bonds with C=O from PAA or PVP segments:



(XIV)

pH of pure PVP aqueous solutions was always lower than 7, which indicates that a small amount of acidic groups is present in this polymer.

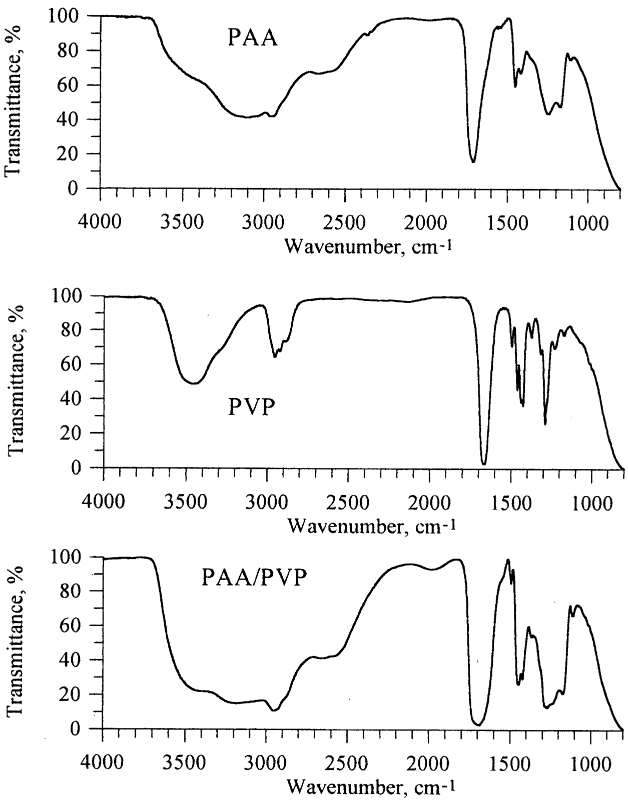


Fig. 1. FTIR spectra of PAA, PVP and PAA/PVP (50/50) complex obtained from 1% solutions without buffer (films on CaF_2 crystal).

3.3. FTIR studies of PAA/PVP complexes

IR spectra of PAA and PVP were interpreted in detail in the monograph by Molyneux [37] and references cited therein.

The interactions between both polymers were examined by FTIR. In Fig. 1 are shown spectra of PAA, PVP and chosen complex (50/50). The range of OH stretching vibration (3000–3700 cm^{-1}) is not considered because of the difficulty of removing the water residue completely. The long drying in vacuum at elevated temperature is dangerous for the polyacid structure because cyclic anhydride can be formed [37]. We can only say, that broad, intensive band characteristic of the stretching vibration of associated hydroxyl groups exists in all samples (Fig. 1). However, the lack of sharp band at ~3500 cm^{-1} due to free hydroxyl groups does not mean their absence in polymer. It was recently published that although there is no evidence of presence of such non-associated groups in mid-IR spectrum, they could be detected in near infrared region [10].

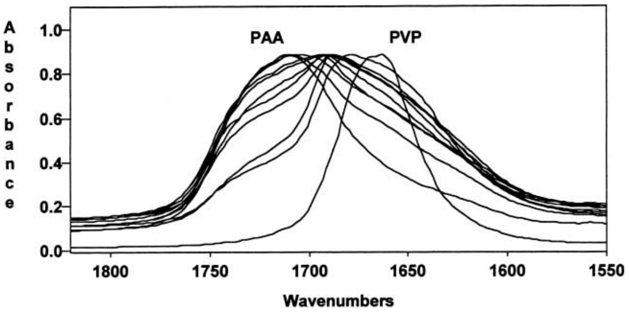


Fig. 2. Carbonyl band of PAA, PVP and their complexes at different molar ratio (from 90/10 to 10/90) obtained from 0.1% solutions without buffer; normalised.

After careful drying of samples, always in the same conditions, we studied carbonyl stretching region, keeping in mind the fact that residue of water can also cause red shift of C=O band [33].

The maximum of carbonyl stretching band in PAA lies at 1710 cm^{-1}, in PVP at 1662 cm^{-1} and its position is independent of polymer concentration. In case of partial neutralisation of PAA, the band due to carboxylate ions at 1547 cm^{-1} appeared.

The shape of C=O absorption bands for PAA/PVP blends depends on the way of their preparation. For PAA/PVP (50/50) complex obtained from 0.1% solutions without buffer, the maximum of this band appears at 1692 cm^{-1} but in other complexes, it is slightly shifted to lower or higher frequencies depending on the sample composition (Fig. 2, Table 4). Generally, the higher amount of PAA in mixture, the higher is the frequency of carbonyl bands in maximum. The carbonyl bands in complexes are broader than that in pure PAA and PVP, which is the evidence of strong interactions. As can be seen from Table 4, the position of peak is independent of the blend composition (with the exception of samples containing high amount of one component i.e. 90 mol%).

In samples with dominant amount of one component, the carbonyl band is composed of the band of complex and the band of non-complexed polymer in excess. We should remember that carbonyl band in our case is always the combination of a few branches corresponding to free and bonded carbonyl groups.

When PAA/PVP mixtures were prepared from more dilute (0.05%) solutions without buffer, more separated bands, which can be attributed to C=O from both components were seen (Fig. 3, Table 4). Probably, in this case, the phase separation occurs during slow water evaporation and the formation of solid interpolymer complex is hampered.

In case of blends prepared from dilute, buffered solutions (0.05%, pH = 4), besides the main carbonyl peak appearing at ~1660 cm^{-1}, the carboxylate band with maximum at 1565–1567 cm^{-1} exists (Fig. 4). In samples with prevalent amount of PAA in the blend (>50%), the branch typical for pure PAA at 1710 cm^{-1} is also clearly seen. The changes in position of C=O band dependent on blend composition are much regular when dilute solutions were used for their preparation (Table 4).

However, in all cases, IR spectrum of the blend is not the simple superposition of spectra of pure components. It means that even when mixtures were prepared from dilute and buffered solutions, the complex with strong interactions

Table 4
Main carbonyl peak position in PAA, PVP and their blends obtained in different conditions of preparation (IR spectra taken from films)

Sample composition (PAA/PVP)	Concentration of PAA and PVP solutions used for sample preparation and environment		
	0.1% (w/v) without buffer	0.05% (w/v) without buffer	0.05% (w/v) polyacrylate buffer (pH = 4)
100/0	1710	1710	1712; 1547
90/10	1705	1713; 1636	1666; 1570
80/20	1694	1714; 1636	1663; 1572
70/30	1692	1715; 1635	1660; 1572
60/40	1693	1718; 1637	1661; 1574
50/50	1692	1719; 1648	1661; 1572
40/60	1691	1720; 1655	1662; 1571
30/70	1689	1721; 1657	1661; 1570
20/80	1687	1721; 1659	1662; 1568
10/90	1679	1718; 1661	1661; 1576
0/100	1662	1662	1660[a]

[a] In acetate buffer.

between components was formed. Probably, the associated structures resulting from hydrogen bonds exist near hydrated but separated macromolecules of PAA and PVP.

3.4. Resolution of carbonyl absorption band of PAA and its complexes with PVP

Carbonyl absorption band is very complex in all studied samples (besides the pure PVP where single symmetric peak was observed). Therefore, in order to recognise better the composition of complexes, the curve fitting of carbonyl band was applied.

Three main separated peaks for PAA (obtained from solutions without buffer) were found, which indicate the coexistence of non-bonded and hydrogen-bonded C=O groups (Table 5, Fig. 5). According to previous findings [10], the narrower band appearing at higher wavenumbers (at 1739 cm^{-1}) can be attributed to free C=O. The fraction of free C=O in total amount of carbonyl groups in pure PAA is much smaller than the fraction of associated C=O (area of this peak = 7.6 or 11.8%, dependent on

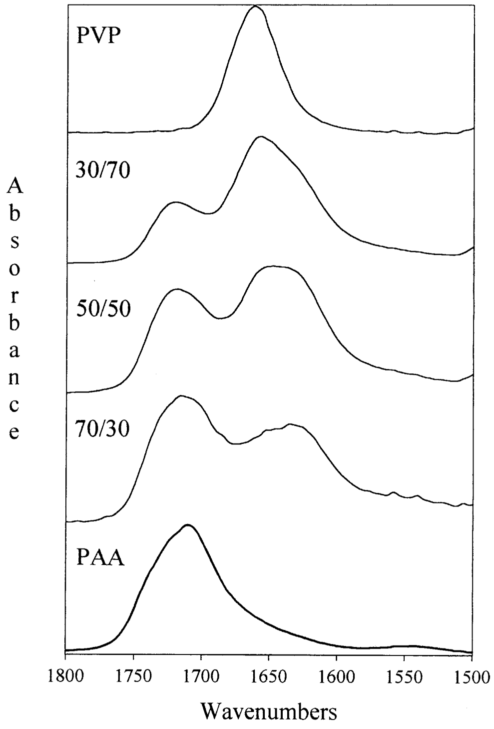


Fig. 3. Carbonyl band of PAA, PVP and their blends prepared from dilute solution (0.05%) without buffer.

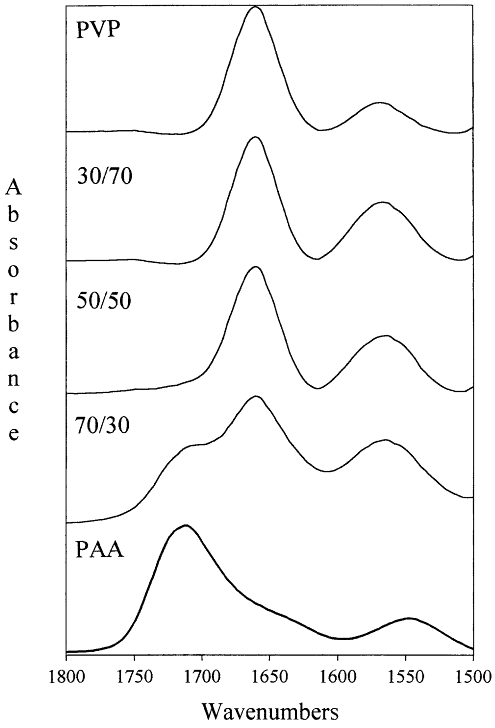


Fig. 4. Carbonyl band of PAA, PVP and their blends prepared from dilute solution (0.05%) at pH = 4.

Table 5
Resolution of carbonyl band (1550–1850 cm^{-1}) of PAA film obtained in different conditions (curve fitting method with 50 iterations and Gaussian + Lorenzian mixed function was used; number of bands, deduced from second derivative and deconvoluted spectra, was fixed)

Band assignment	Wavenumber (cm^{-1})	Height (abs. u.)[a]	Width (cm^{-1})	Area (a.u.)[b]
PAA (from 0.1% solution, without buffer)				
Free C=O	1739	0.17	27.4	4.97
PAA dimer	1712	0.56	49.8	29.88
C=O in lateral hydrogen bonds	1679	0.27	105.7	30.56
PAA (from 0.05% solution, without buffer)				
Free C=O	1739	0.38	31.4	12.85
PAA dimer	1711	1.04	42.9	50.41
C=O in lateral hydrogen bonds	1675	0.38	85.9	42.41
Carboxylate anion	1542	0.06	48.3	2.86
PAA (from 0.05% solution, pH = 4)				
PAA dimer	1716	0.43	49.4	22.83
C=O in lateral hydrogen bonds	1669	0.21	89.9	20.11
Carboxylate anion	1547	0.17	67.2	14.02

[a] abs. u. — absorption units.
[b] a.u. — arbitary units.

solution concentration). It can be seen from Table 5 that dimers formed from two carboxylic groups are prevalent structures in PAA obtained from dilute, unbuffered solution (area = 46.4%). Only negligible trace of carboxylate band was found in unneutralised PAA.

In PAA prepared from buffered solution (at pH = 4), the carboxylate band at 1547 cm^{-1} is present but without any constituent due to free C=O. The relatively large fraction of groups associated in PAA dimer (1716 cm^{-1}, area = 40.1%) was obtained from this calculation.

The shifting of maximum as well different width of C=O band in PAA obtained from unbuffered and buffered solutions arise from various surroundings of these groups. It is caused by the different type and amount of hydrogen bonds formed in both cases as discussed in Section 2.

In consideration of PAA/PVP complex, the following question appears: how many peaks should we expect for a correct description of overall carbonyl band? Assuming that, besides complexed structures (II–V, X), also free and hydrogen bonded C=O typical for pure polymers can be present in our complex, the number of components may be higher than in PAA and PVP alone.

The best fit for PAA/PVP (50/50) prepared from unbuffered 0.1% solutions was obtained for five bands, which can be assigned to carbonyl groups participating in intra- and intermolecular hydrogen bonds (Table 6, Fig. 6a). The amount of carbonyl groups engaged in hydrogen bonds in the complex is large (area of these components = 70.3%).

The carbonyl band of the same blend but obtained from more dilute solutions was also separated on different five peaks (Table 6, Fig. 6b). Probably only the highest constituent (at 1628 cm^{-1}) occupying 38.4% surface area of this envelope can be attributed to C=O associated in the intermolecular complex. In this mixture (contrary to the one obtained from 0.1% solutions), the band at 1711 cm^{-1} appears. It suggests that PAA dimers are formed instead of complex between PAA and PVP. Thus, we can conclude that the amount of intermolecular hydrogen bonds in PAA/PVP blends decreases with the decrease of solution concentration used. The contribution of C=O from carboxylate anion is small (area = 3.1%) and similar to that in pure PAA (2.6%).

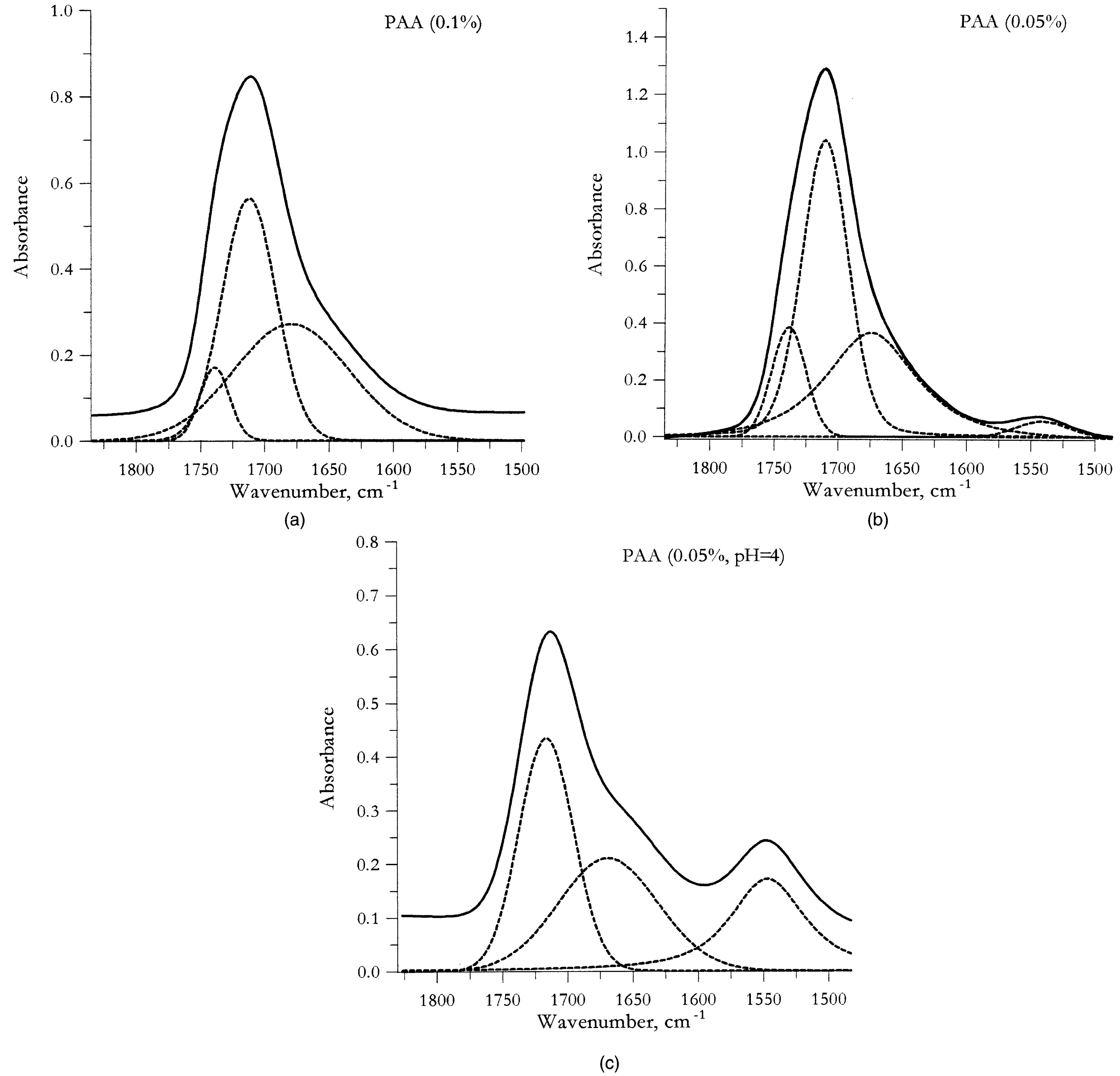
In case of PAA/PVP (50/50) blend obtained from 0.05% solution at fixed pH = 4 (Table 6, Fig. 6c), four peaks were found. The higher peaks at 1661 and 1561 cm^{-1} can be assigned to C=O band from PVP and to the band of carboxylate anion from PAA, respectively. Small components appearing at 1714 and 1593 cm^{-1} are probably due to C=O from PAA dimer and from associated COO^{-}.

3.5. Influence of UV irradiation on PAA/PVP

Thin films for photodegradation studies were obtained from PAA and PVP solutions (0.1 or 0.05%, without or with buffer assured pH = 4).

UV-irradiation of PAA/PVP complexes in solid state (films obtained from 1% unbuffered solutions) causes the increase of the amount of insoluble gel indicating that the further bonding of macromolecules takes place (Table 7). In pure PAA and PVP, where there was no gel before irradiation, high insoluble fraction (80%, 95%) appeared after 6 h exposure to UV. In order to check whether the gel separated from UV-irradiated samples was formed as a result of further hydrogen bonding or by crosslinking, it was treated by NaOH. It was found that in alkaline solution, the amount of gel decreases only at a slight rate. Thus, efficient photocrosslinking occurred in all samples and hydrogen bonds were replaced by covalent bonds. In fact, the analysis of IR spectra in carbonyl range (with their decomposition) indicates the significant decrease of hydrogen bonds in all samples after UV-irradiation.

The total amount of C=O groups in UV-irradiated



(a) (b) (c)

Fig. 5. Resolution of carbonyl absorption band in PAA obtained from 0.1% (a), 0.05% (b) solutions without buffer and from 0.05% solution at pH = 4 (c).

samples prepared from 0.1% solutions changes irregularly. In pure polymers, the decrease of C=O is observed, which indicates that side groups abstraction or other type of destruction in macromolecules does occur. The negative or positive changes of [C=O] in PAA/PVP blends suggest that besides the photodestruction, photooxidation also takes place. Generally, the changes of total amount of C=O in PAA/PVP are much lower than those in homopolymers (generally not higher than a few percent). It suggests the higher photostability of complexes in comparison to pure components.

In case of PAA/PVP blends obtained from more dilute solutions (0.05%), the changes in FTIR spectra were more regular. The systematic drop of all absorption bands was observed during UV exposure (Fig. 7). The amount of C=O decreases at the fastest rate in PAA, whereas in PVP significant drop was observed only at the beginning of degradation but after longer time of UV irradiation (>2 h), the changes were insignificant (Fig. 8). In all PAA/PVP samples [C=O] slightly but systematically decreases up to 8 h of UV irradiation.

Fig. 9 presents the C=O changes in all samples after 6 h of UV-irradiation against the blend composition. It is clearly seen that in case of samples obtained without buffer, the experimental curve (1) lies above the theoretical straight line characterising additive behaviour of components (dot

Table 6
Resolution of carbonyl band (1550–1850 cm^{-1}) of PAA/PVP blend (50/50) obtained in different conditions

Band assignment	Wavenumber (cm^{-1})	Height (abs. u.)[a]	Width (cm^{-1})	Area (a.u.)[b]
PAA/PVP (from 0.1% solution, without buffer)				
C=O from PAA	1732	0.92	40.3	39.71
C=O from complex	1695	1.24	47.8	63.37
C=O from PVP	1660	0.21	32.3	7.23
C=O from complex	1645	0.73	70.9	55.03
Carboxylate anion	1559	0.05	57.5	3.09
PAA/PVP (from 0.05% solution, without buffer)				
C=O from PAA	1732	0.13	30.1	4.26
PAA dimer	1711	0.27	45.3	13.57
C=O from PVP	1660	0.27	42.8	14.59
C=O from complex	1628	0.32	52.3	21.30
Carboxylate anion	1563	0.03	58.9	1.72
PAA/PVP (from 0.05% solution, pH = 4)				
PAA dimer	1714	0.03	37.8	1.47
C=O from PVP	1661	0.49	47.5	27.00
COO^- hydrogen bonded	1593	0.12	55.1	7.21
Free COO^-	1561	0.19	49.9	10.46

[a] abs. u. — absorption units.

[b] a.u. — arbitary units.

line). It means that photodestruction in all blends is less efficient than that in pure PAA or PVP.

However, the course of photodegradation of PAA/PVP was different when samples were prepared from buffered solutions at pH = 4. The changes of C=O concentration show that the blends with prevalent amount of PAA are more stable than other ones (Fig. 9, curve 2). When PAA is partially neutralised by NaOH, COO^- neighbour Na^+ counterions and electrostatic repulsion between macroanions decreases. It probably enhances macroradical recombination. Such a protective effect of salt on PAA photostability was described previously [38]. The blends with dominant amount of PVP were characterised by a lower photostability, which can be explained by the mutual interactions of free radicals and active centres formed during UV irradiation in both polymers.

From IR spectra in the region of methylene group absorption (deformation vibrations at 1380–1480 cm^{-1}), a small systematic decrease of intensity of this band can be seen during UV-irradiation of samples prepared from dilute solutions. The drop of methylene group concentration can be interpreted as an evidence of main chain scission. These changes after 6 h of UV-irradiation are smaller in all PAA/PVP blends than those in pure PAA or PVP (Fig. 10, curve 1). The shape of curve 1 in Fig. 10 is similar to that of curve 1 in Fig. 9 — in both cases, there is no additivity and the results indicate that PAA/PVP complexes are more stable compared to PAA and PVP. The course of photodegradation in samples obtained at pH = 4 is somewhat different — the decrease of $[CH_2]$ is generally smaller in blends than in separated polymers but in some cases, these differences are positive. It can be explained by the concurrence of the side-group abstraction and main chain scission. If the breaking away of side groups is a prevailing process, the increase of amount of methylene group can be observed.

Table 7
Changes in gel amount resulting of photocrosslinking in PAA/PVP complexes and NaOH treatment (samples prepared from 1% solutions without buffer)

Sample composition (PAA/PVP)	Amount of gel (%)		
	Before irradiation	After 6 h of UV irradiation	After NaOH treatment of UV-irradiated samples (pH = 9)
100/0	0	98	80
90/10	92	97	91
70/30	93	98	92
50/50	100	100	94
30/70	85	91	88
10/90	83	91	90
0/100	0	95	95

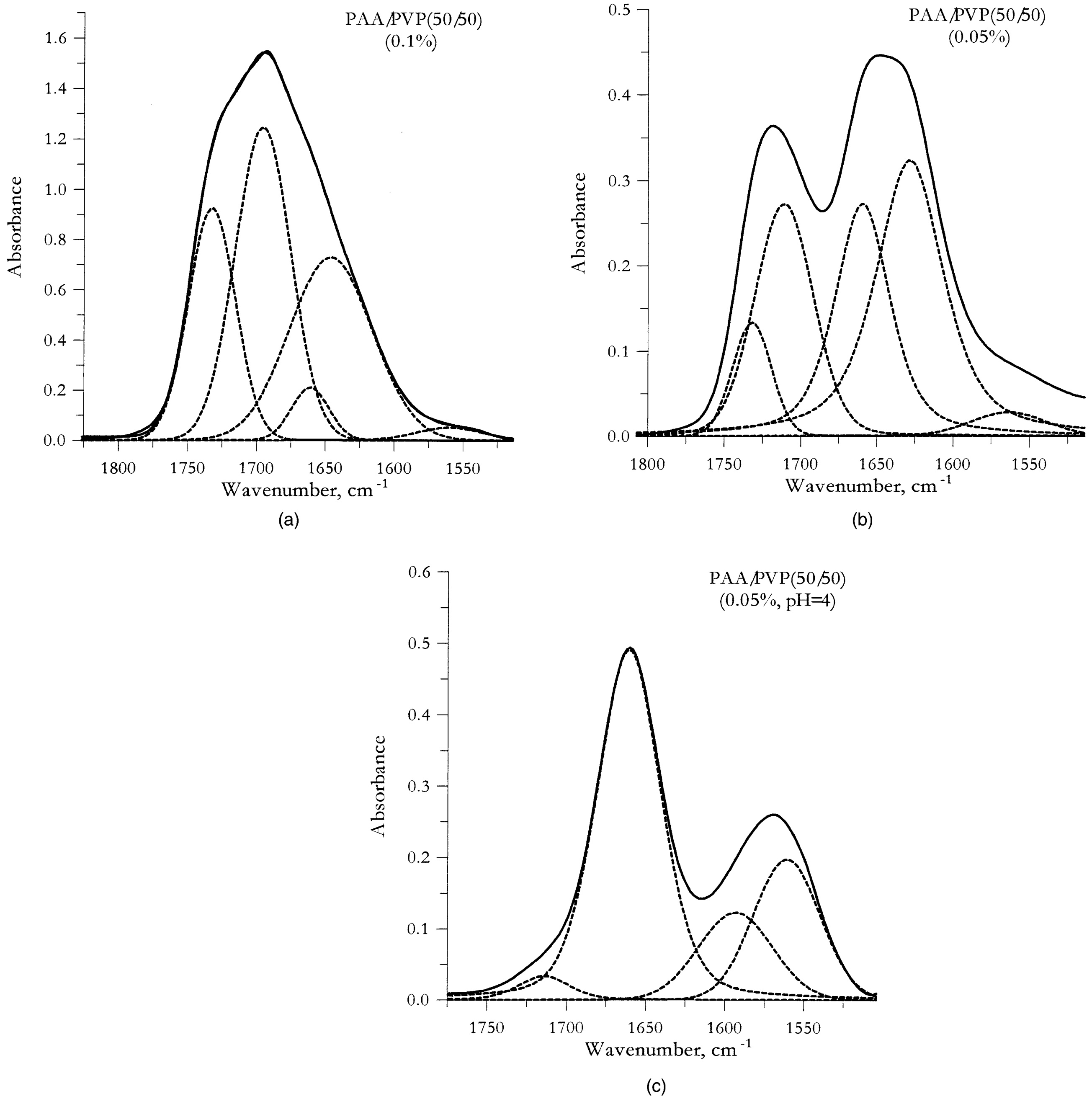
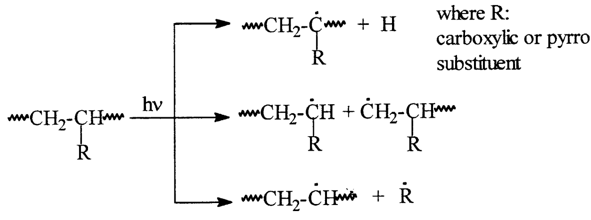


Fig. 6. Resolution of carbonyl absorption band in PAA/PVP (50/50) obtained from 0.1% (a), 0.05% (b) solutions without buffer and from 0.05% solution at pH = 4 (c).

3.6. Discussion of photodegradation mechanism

The mechanism of photooxidative degradation of PAA/PVP mixture can be considered on the basis of reactions occurring in pure polymeric components during its UV-irradiation [39–41]. It was described previously that during photoinitiation, the breaking of chemical bonds in the main chain as well as hydrogen abstraction are more important processes in PAA and PVP. Moreover, it was postulated that the abstraction of side groups takes place:



where R:
carboxylic or pyrrolidone substituent

(XV)

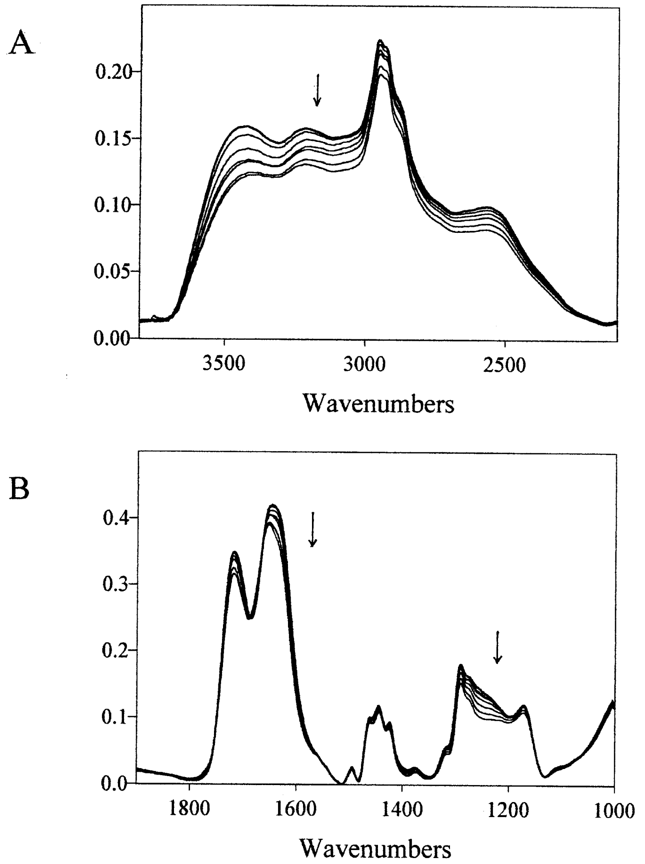
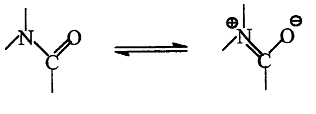


Fig. 7. Changes in FTIR spectrum upon UV-irradiation of PAA/PVP (50/50) blend obtained from dilute solutions (0.05%) without buffer: A — at 2100–3800 cm^{-1}, B — 1000–1900 cm^{-1} range.

From our results, we can conclude that abstraction of carboxylic groups in PAA is evident but there is no clear confirmation that pyrrolidone rings undergo elimination from PVP during 6 h UV-irradiation. However, it is very difficult to identify the tertiary nitrogen atom by IR. The most characteristic C–N vibrations lie in the range of C–H deformation vibrations and cannot be distinguished [43]. According to Rothschild's suggestion, PVP contains partially unsaturated bonds between nitrogen and carbon atoms (C=N), which absorb at 1425 cm^{-1} [33]:



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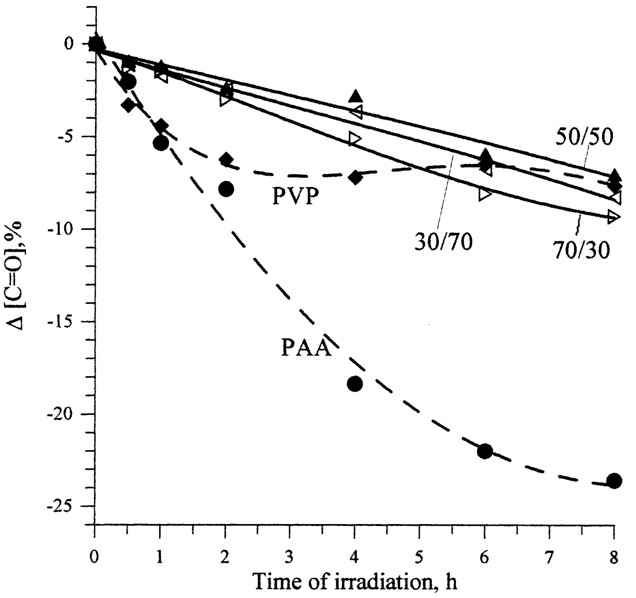
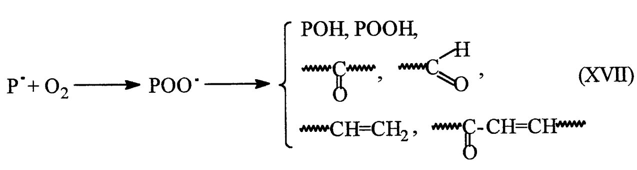


Fig. 8. Total amount of carbonyl groups in PAA, PVP and their blends (30/70, 50/50, 70/30; obtained from 0.05% solution without buffer) versus irradiation time.

We have found very small changes of that band (at 1424 cm^{-1}) in PVP during UV-irradiation (Fig. 7). Also our previous studies of PVP by means of elementary analysis indicated the small drop of nitrogen amount after UV-irradiation [42]. Thus, the abstraction of side groups in PVP cannot be excluded. However, these changes are not detectable in PAA/PVP complexes.

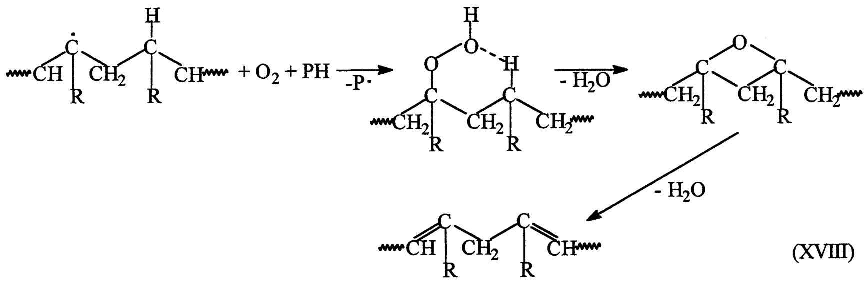
As all the experiments were conducted in air atmosphere, the next step is the reaction of macroradicals with oxygen leading to formation of macroperoxyradicals. These active species react with neighbouring macromolecules and as a result, some different products of photooxidative degradation (containing ketones, aldehydes and unsaturated groups) are formed [40,41]:



(XVII)

Photoprocesses leading to the formation of new carbonyl groups in PAA/PVP are hampered because of strong hydrogen bonds, which stabilise the structure of macromolecules.

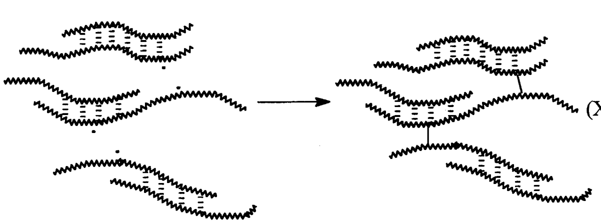
Oxidative degradation can also lead to the formation of double bonds with water elimination via cyclic intermediate [44]:



(XVIII)

The sensitivity of FTIR spectroscopy is too low to detect small amount of double bonds created in above processes (as well as in typical disproportionation) but UV–vis spectroscopy could be a very helpful method for this purpose.

Finally, recombination of macroradicals leads to the termination of polymer degradation and formation of three-dimensional, insoluble network:



(XIX)

4. Conclusions

Creation of complexes between PAA and PVP has been observed owing to the formation of hydrogen bonds of different types. It was found that in case of 1:1 molar ratio, polymers were completely bonded and 100% of insoluble gel was obtained in case of using 1% aqueous solutions. Even a small amount (~10%) of one polymer, added to other polymer, is a sufficient factor to initiate their binding and to form insoluble complexes with different stoichiometry. It seems reasonable to conclude that inter-associated hydrogen bonds dominate in PAA/PVP (1:1), whereas intramolecular hydrogen bonds prevail in mixtures with smaller amount of one of the components. Besides the hydrogen bonding, also ion–dipole and ion–ion interactions coexist in PAA/PVP systems, especially in case of partial neutralisation. PAA/PVP mixtures obtained from more dilute solutions (0.1%, 0.05%) without and with buffer do not form insoluble gel, but the specific interactions also exist in such samples.

On the basis of the above results, one can conclude that complexation of polymers studied enhances their resistance to UV-irradiation. Photooxidative degradation is hampered in PAA/PVP in comparison to that process going on in pure polymers. It suggests that intermolecular hydrogen bonds reinforce polymer structure. Probably, energy of incident

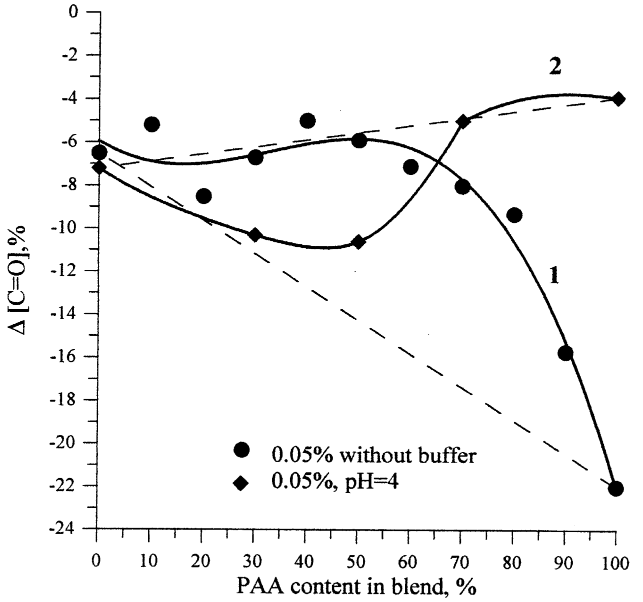


Fig. 9. Dependence of changes in total amount of carbonyl groups in PAA/PVP after 6 h UV-irradiation on blend composition: samples prepared from 0.05% solution without buffer (1), samples prepared from 0.05% solution at pH = 4 (2).

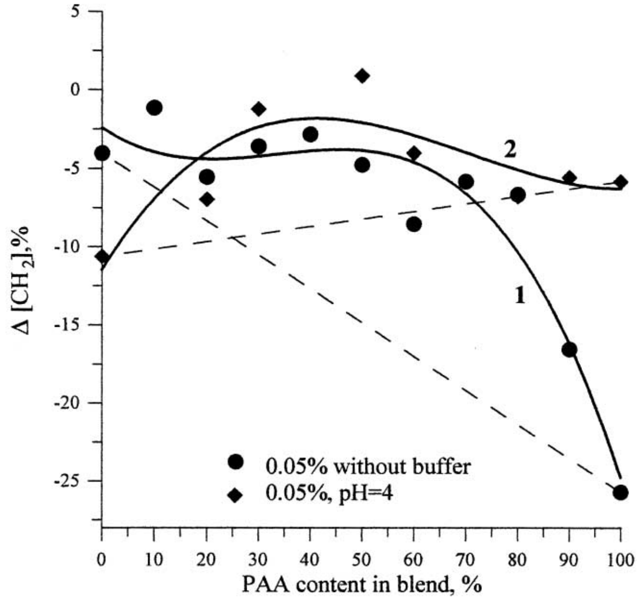


Fig. 10. Dependence of changes in methylene group amount in PAA/PVP after 6 h UV-irradiation on blend composition: samples prepared from 0.05% solution without buffer (1), samples prepared from 0.05% solution at pH = 4 (2).

radiation can be partially used-up in breaking the hydrogen bonds.

Photocrosslinking, occurring simultaneously in irradiated PAA/PVP complexes, additionally restrains the degradation by free radical mechanism. Moreover, the formed stiff network impedes the diffusion of oxygen into the polymer bulk, which is an important factor determining the rate of polymer oxidation.

PAA/PVP complexes prepared from solution at different concentrations and different pH values (changeable or fixed) exhibit different behaviour. Thus, changing the conditions of complex preparation, their photochemical properties can also be changed.

Thus, we can finally conclude that both hydrogen bonds and crosslinks play an important role in PAA/PVP stability and protect against chain scission or other harmful reaction.

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