The PVA-PAA$_N$ Intrapolymer Complexes as Sensors with Optical Response

Vladislav Yu. Kudrya, Valeriy M.Yashchuk, Ludmila P. Paskal',
Tetyana B. Zheltonozhskaya, Ol'ga V. Demchenko

Kyiv National Taras Shevchenko University, 6, Glushkova prosp., Kyiv, 03127,
Ukraine; e-mail: yashchuk@phys.univ.kiev.ua

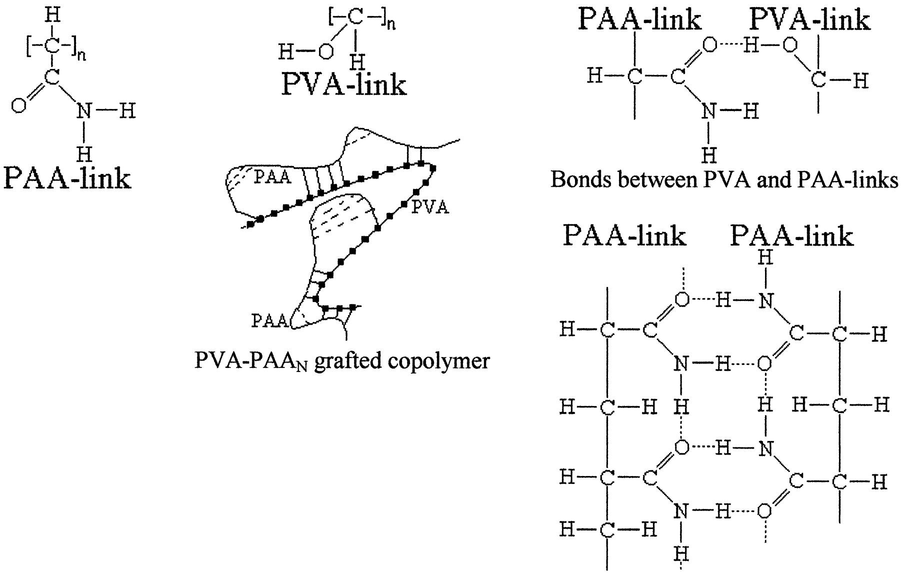
SUMMARY: Sorbtion of some impurities from aqueous solutions by polymer complex poly(vinylalcohol) with poly(acrylamide) grafted copolymers (PVA-PAA$_N$) was studied by means of spectrophotometry and steady-state fluorescence methods. The experiments showed that the PVA-PAA$_N$ films effectively sorbs impurities molecules of average benzene ring from water. Simultaneously, the processes of polymer films dissolving in water take place. The thermal annealing (with the help of special methods) PVA-PAA$_N$ film gives a possibility to obtain non-dissolving polymer films which possess high sorbtion ability. Such films are proposed to be used as the sensors with optical response.

Introduction

The grafted copolymers belong to the realm of promising polymer materials as their structure may be varied at will and be taylored to the required properties. This can be achieved by controlling the chemical nature, the length of the main chain as well as the length and quantity of grafted chains. Amongst the various graft copolymers a special group has been recently distinguished for its complexation properties: those displaying chemical complementary between the main chain and the grafted chains. Such grafted copolymers form a novel class of polymer compounds that may be designated as intramolecular polycomplexes (IntraPC) by analogy with interpolymer complexes (InterPC). Indeed, there is the possibility for the grafted chains to interact strongly (complexation) with the backbone, thus giving an unusual conformation, and correspondingly unusual properties. Hydrophilic and hydrophobic cavities are both created that may prove useful for trapping organic and inorganic molecules. As it was shown in our previous works [1-4] intramolecular polycomplexes based on poly(vinylalcohol) with poly(acrylamide) grafted copolymers (PVA-PAA$_N$) (fig.1) absorbed the molecules of some organic compounds effectively. But as it was observed simultaneously with absorbtion processes the processes of polymer films dissolving in water take place. Besides, we observed the oscillations of optical density of polymer films with time. The

CCC 1022-1360/00/$ 17.50+.50/0

reasons of such complex behaviour of polymer films, spectroscopic results obtained on PVA-PAA_N films (annealed and non-annealed) and possibility to create the polymer sensors with optical response were examined in present paper.



PVA-PAA_N grafted copolymer

Bonds between PVA and PAA-links

Bonds between PAA-links

Fig.1: Structure of PVA-PAA_N

Results and discussion

Fig.2 presents optical absorption spectra of PVA-PAA_N-film and changes in time dependence of optical density D(t) of PVA-PAA_N-film during sorbtion process in phenole solution in water. Two phenomena were observed: 1) decreasing the optical density of polymer films, 2) oscillations in optical absorption of polymer film connected with phenole molecule optical absorption. To our point of view that are connected with the fact that the process of polymer film dissolving in water takes place simultaneously with the phenole molecules sorbtion process by this polymer film. The similar situation is in luminescence (fig.3). Phenole is easy detected by luminescence methods because from typical water dissolving impurities only phenole molecules manifest strong luminescence (the peak is near 300 nm). But contrary to optical absorption of polymer films with phenole molecules sorbed the luminescence of these films is the result of two processes: own luminescence of phenole directly excited and luminescence of phenole which takes place due to electronic excitation energy transfer from polymer to phenole sorbed.

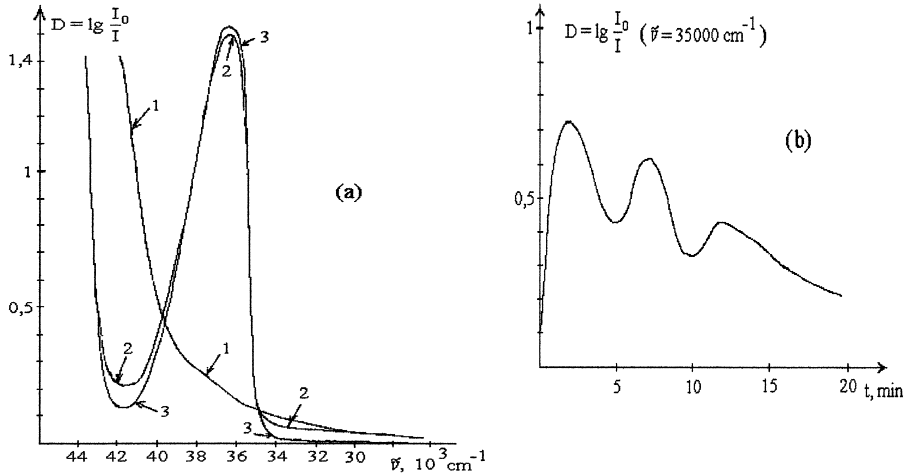


Fig.2: Optical absorption spectra (a) of: 1 - PVA-PAA$_N$ film; 2 - PVA-PAA$_N$ film after 2 minutes of exposition in phenole solution in water (C=10^{-2} g·cm^{-3}); 3 - phenole solution in water (C=10^{-4} g·cm^{-3}); (b): time dependence of optical density D(t) of PVA-PAA$_N$ film in phenole solution (C=10^{-2} g·cm^{-3}) at ν = 35000 cm^{-1}.

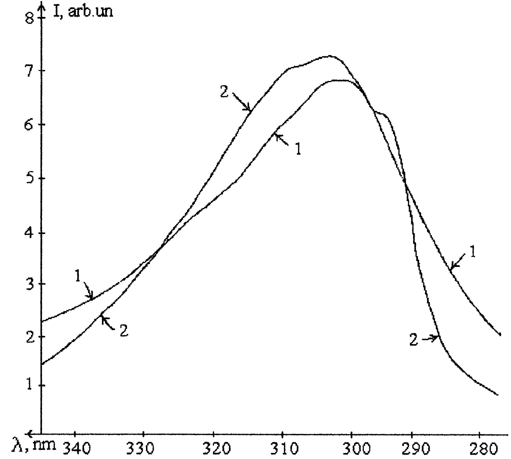


Fig.3: Luminescence (fluorescence) spectra of: 1 - PVA-PAA$_N$ film after 20 minutes of exposition in phenole solution in water (C=10^{-2} g·cm^{-3}); 2 - phenole solution in water (C=10^{-3} g·cm^{-3}).

With the aim to analyze the dual nature of the periodical process in phenole sorbtion by PVA-PAA$_N$ films the optical absorption spectra of these films during dissolving in distilled water and of this water after polymer film exposition were observed. Fig.4 shows that the optical density of PVA-PAA$_N$ film changes by some "jumps" ($t_j \approx 5$ min). That is why one can affirm that the dissolving of polymer film occurs by microlayers (step by step).

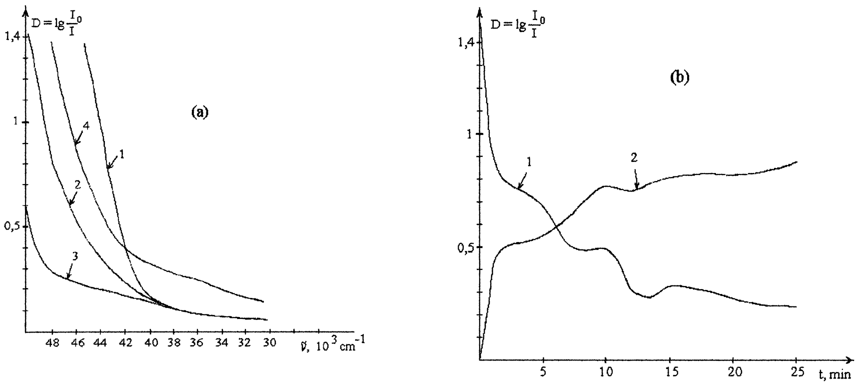


Fig.4: The dissolving of PVA-PAA$_N$ films in distilled water (the optical absorption specrta): a) 1- PVA-PAA$_N$ film before start of sorbtion; 2- PVA-PAA$_N$ film after 10 min. of sorbtion; 3- PVA-PAA$_N$ film after 25 min. of sorbtion; 4- water after PVA-PAA$_N$ film exposition (described in 3); b) 1-the dependence of PVA-PAA$_N$ film optical density on time of exposition in distilled water; 2- the dependence of resulted water optical density on time of polymer film dissolving.

The processes of dissolving PVA-PAA$_N$-films in water described above are the reason why the usage of PVA-PAA$_N$ investigated as the solid polymer sensor becomes impossible. One of the ways to solve this problem is presented.

With the aim to decrease the dissolving of PVA-PAA$_N$ the influence of thermoannealing on PVA-PAA$_N$ chemical and physical properties and sorbtion ability with respect to phenole were investigated. PVA-PAA$_N$ films were annealed at temperatures $T=140\div200°C$. This annealing reduce essentially dissolving of polymer films in water but do not change practically optical density of these films at 36000 cm^{-1} (phenole absorption peak). PVA-PAA$_N$ sample, which had been annealed at 180°C during 30 min, do not dissolve during exposition.

The phenole sorbtion process by annealed PVA-PAA$_N$ was studied by optical spectroscopy methods. Polymer films were exposed in phenole solutions and after that optical absorption spectra of these films were recorded. The phenole peak (36000 cm^{-1}) appeared already after the first second of polymer films exposure in phenole solution as in the case of non-annealed PVA-PAAN films [3]. Than, after several oscillation (negligible compared with non-annealed samples) there were no essential changes in optical density during exposure time (Fig.5).

Thus, thermo-annealing gives the possibility to propose PVA-PAAN films as sensors with optical response on phenole presence in water.

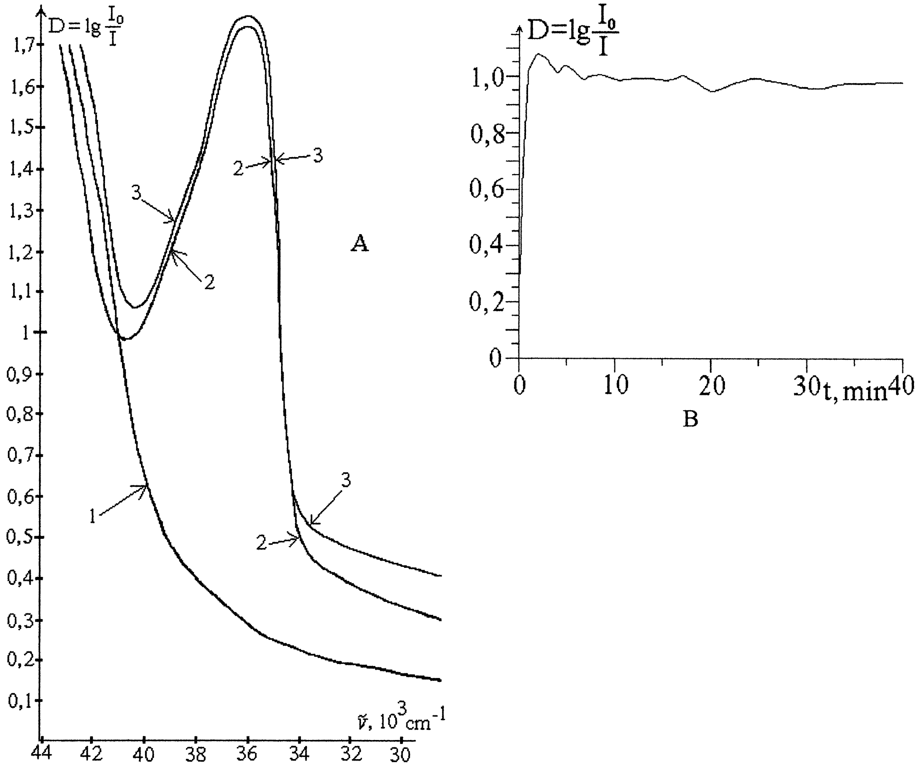


Fig.5: The absorption spectra (A) of PVA-PAA$_N$-film (annealed at 180°C during 30 min): 1-before exposition; 2- after 4 min exposition in phenole solution in water (C=10^{-2} g·cm^{-3}); 3- after 5 min exposition in phenole solution; the dependence of this PVA-PAA$_N$- (B) on exposition time in phenole solution with phenole concentration in water C=10^{-2} g·cm^{-3}.

References

1. T.B.Zheltonozhskaya, O.O.Romankevich, V.G.Syromyatnikov, L.A.Bulavin, V.Yu.Kudrya, T.Yu.Ogul'chansky, V.M.Yashchuk, *Macromolecular Symp.*, **114**, 263 (1997)
2. T.B.Zheltonozhskaya, V.G.Syromyatnikov, V.M.Yashchuk, V.Yu.Kudrya, O.V.Demchenko, I.V.Filimonova, *2nd International Conference "Electronic Processes in Organic Materials". Europhysics Conference Abstracts,* **22B**, 165 (1998)
3. T.B.Zheltonozhskaya, V.G.Syromyatnikov, V.M.Yashchuk, V.Yu.Kudrya, O.V.Demchenko, I.V.Filimonova, *Functional Materials*, **5**, N 3, 398 (1998)
4. T.B.Zheltonozhskaya, O.V.Demchenko, V.G.Syromyatnikov, N.V.Strelchuk, V.M.Yashchuk, V.Yu.Kudrya, *3rd International Conference "Electronic Processes in Organic Materials". Book of Abstracts,* 208 (2000)