Compacting of Poly(acrylamide)-Poly(vinyl alcohol) Grafted Copolymers in Aqueous Solution of Phenol and its Effect in the Copolymers Films Structure

Vladimir Syromyatnikov*, Tatyana Zheltonozhskaya*, Jean-Michel Guenet**, Iryna Rakovich*, Ol'ga Demchenko*, Nikolay Strelchuk***, Natalya Permyakova*

* Kiev Taras Shevchenko National University, Chemical Department,
Vladimirskaya St. 60, 01033 Kiev, Ukraine
** Institute Charles Sadron, CNRS UPS 22, 6, rue Boussingault, F-67083
Strasbourg Cedex France
***Institute of Nuclear Physic of NAS of Ukraine, Prospekt Nauki 47,
03028 Kiev, Ukraine

SUMMARY: The interaction of phenol with graft copolymers of poly(acrylamide) to poly(vinyl alcohol) (PVA-PAA$_N$) forming intramolecular polycomplexes (Intra PC), and also with PAA, is investigated by the methods of gel chromatography, viscometry, UV and IR spectroscopy. It is shown, that phenol connection with polymers is weak and carried out on the equilibrium mechanism. Under phenol influence the effect of compacting of polymer macromolecules is observed. It is revealed, in particular, by change of the ratio between different H-bonds structures in polymer films obtained at phenol presence. PVA-PAA$_N$ connect phenol more effectively, than PAA; the quantity of bound phenol grows with N.

Introduction

The ability of water-soluble polymers to connect of phenols is studied from different points of view [1-3]. The main purpose of these researches was to select of polymer with optimum chemical structure (them has appeared poly-N-(vinyl pyrrolidone)) for the maximal binding of the toxic phenol substances. Further, the creation of fragments containing pyrrolidones in cross-linked polymer sorbents was used for increase of their sorptional ability towards phenols [4]. In the decision of a problem of phenol binding the large prospects are opened by use of polymer-polymer complexes, which more effectively, than individual polymers connect various organic substances. The intermolecular polycomplexes (Inter PC) are most investigated in this plan [5]. But the intramolecular polycomlexes (Intra PC), in particular, graft copolymers with chemically complementary main and grafted chains, represent in a role of binders the much greater interest. Interacting polymer components are connected in Intra PC by covalent bonds. Therefore, Intra PC do not have the equilibrium on a macromolecular level, and in reactions of competitive interactions with organic substances they do not destroy up to individual polymers, as it happened with Inter PC [6]. In the present work the interaction of phenol with graft copolymers of poly(acrylamide) to poly(vinyl alcohol) (PVA-PAA$_N$) forming Intra PC, and also with PAA, is studied. Various aspects of phenol influence on a condition PVA-PAA$_N$ and PAA in solution are considered.

Behavior PVA-PAA$_N$ and PAA in aqueous-phenol solutions

Graft copolymers are obtained and identified according to Ref. [7]. The main characteristics of copolymers and PAA are submitted in Tab.1.

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Table 1. The molecular characteristics of PVA-PAA$_N$ and PAA.

Polymer sample	Mv_{PAA}•10^{-6}	Mv_{PVA}•10^{-6}	$M_{PVA-PAAN}$•10^{-6} a)	N
PVA-PAA$_N$1	0.372	0.08	9.385	25
PVA-PAA$_N$2	0.277	0.08	7.828	28
PVA-PAA$_N$3	0.163	0.08	6.939	42
PAA b)	4.400	-	-	-

a) This value as well as the grafted chains quantity N was determined by the data of elemental analysis.

b) The degree of hydrolysis of PAA links was lesser 1%.

Samples 1-3 differ by quantity N and length of grafts, but N is, in our opinion, by the major factor determining their properties. The methods of viscometry, gel chromatography, UV and IR spectroscopy are used in work. Viscosity is measured on viscometer such as Ostvald (τ_0=93.5 s at 298 K. Gel chromatography researches are carried out on a column 50x1 cm filled by gel Sephadex G-25. Polymer films (L~8 mcm) for IR spectroscopy are cast on fluorite glasses. Intra PC are formed in PVA-PAA$_N$ by means of hydrogen bonds between main and grafted chains [8] and are stabilized by H-bonds between PAA chains [8] and also by hydrophobic interactions [9]. PVA-PAA$_N$ macromolecules are associated in the diluted aqueous solutions, as the thermodynamic water quality towards them is close to the θ-solvent [9].

The additives of phenol in polymer solutions cause decrease of their reduced viscosity (Fig.1):

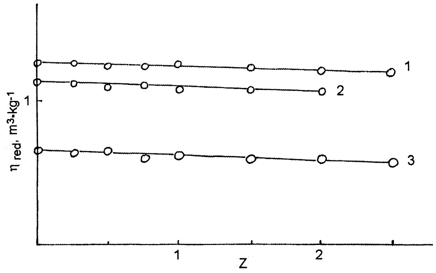


Fig. 1. Phenol influence on the reduced viscosity of solutions of PAA – 1, PVA-PAA$_N$1 – 2 and PVA-PAA$_N$3 – 3. $C_{polymer}$=1 kg•m^{-3}, Z the ratio mol of phenol/mol of PAA links, T=298 K.

This effect can be caused by several reasons. To make clear this question, a nature, value and mechanism of phenol binding with considered polymers are studied.

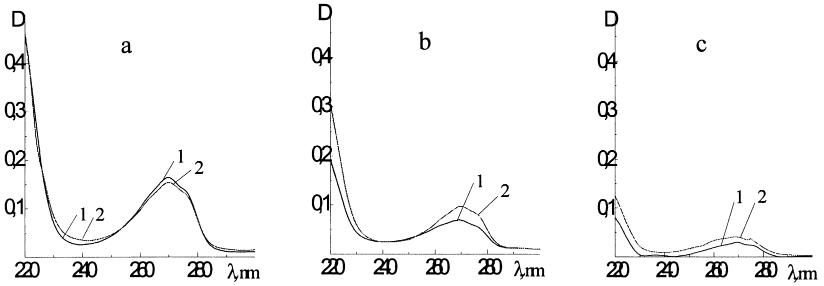


Fig. 2. UV spectra for individual water-phenol solutions (curves 1) and water-phenol solutions of PVA-PAA$_N$3 (curves 2) at Z=0.75 (a), 0.25 (b) and 0.15 (c) mol of phenol/mol of PAA links. T=293 K.

The participation of –OH groups of phenol in formation of H-bonds with polymers already was discussed 1). UV spectroscopy allows to characterize the force of such bonds by a change of intensity and position of phenol band at λ=270 nm. The example of UV spectra is shown in Fig.2 for aqueous-phenol mixtures in absence (curves 1) and at presence (curves 2) PVA-PAA$_N$3. The similar data are received for PVA-PAA$_N$1 and PAA.

At presence PAA, at any ratio Z phenol-polymer was not observed changes of a position and intensity of considered phenol band. But at presence of graft copolymers, especially of sample 3 with greatest N, the effect of small increase of the band intensity with reduction N (Fig.2b and c) is shown. This effect specifies formation of weak hydrogen bonds between copolymers and phenol. This data show also that H-bonds of phenol with PAA (if they exist) are on force weaker, than H-bonds between phenol and PVA-PAA$_N$.

IR spectroscopy method was used then to receipt the additional information about a nature of phenol binding with all polymers. The example of IR spectra for PVA-PAA$_N$3 films obtained from aqueous and aqueous-phenol solutions, is shown in Fig.3:

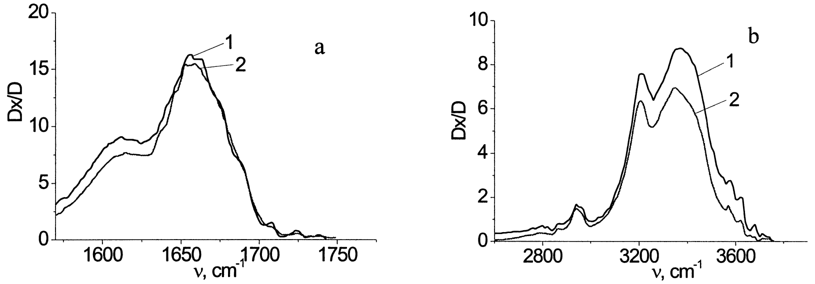


Fig. 3. IR spectra for PVA-PAA$_N$3 films obtained of water (curves 1) and of water-phenol solutions (curves 2) in region of amide 1, amide 2 (a) and of ν_{C-H}, ν_{N-H} and ν_{O-H} oscillations (b). T=293 K.

It is established, that in IR spectrum of diluted phenol solution in the inert solvent (Vaseline oil) there are two very strong bands $\nu_{C=C}$ oscillations of benzene ring at 1379 cm^{-1} and 1461 cm^{-1}. But in spectra of polymer films, obtained at phenol presence, both bands completely are absent. It appears, that phenol due to its high volatility and small thickness of films evaporates at a finish stage of films drying in vacuum. Thus, the direct bonds of phenol with polymers fail to be looked. However, the comparative analysis of IR spectra of films obtained from different solvents gives a unique opportunity to look after changes in structure of intramolecular bonds under phenol action. For detailed consideration of structure of H-bonds the division of overlapped bands of oscillations in amide 1 and amide 2 region by the method of splines 8) is carried out (the example is shown in Fig.4). The bands positions and corresponding H-bonds structures are submitted in Tab.2.

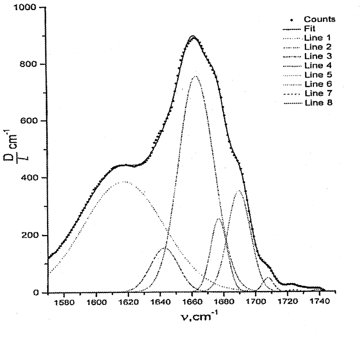
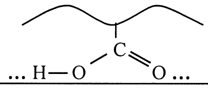
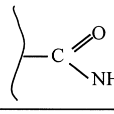
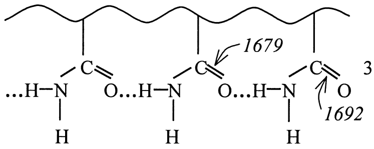
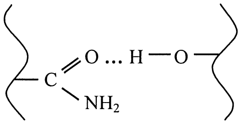
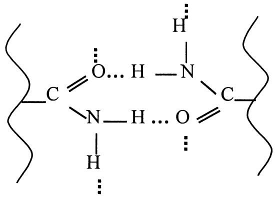


Fig. 4. The example of computer processing of IR spectra of PVA-PAAN1 in the region of amide 1 and amide 2 by the splines method. Experimental (···) and calculated (—) contours of bands.

Table 2. Oscillation bands in amide 1 and amide 2 region and hydrogen bonds structures for PVA-PAA$_N$ and PAA films.

Oscillation type	ν $^{a)}$ / cm^{-1}		The structure of chemical groups or hydrogen bonds
	Films from water	Films from water-phenol	
$\nu_{C=O}$	1722-1724	1723-1726	 1
$\nu_{C=O}$ amide 1	1707-1708	1708-1710	 2
	1689-1690 1676-1677	1689-1693 1677-1681	 3 *Trans*-multimers of amide groups
	1660-1663	1660-1664	 4 H-bonds between main and grafted chains (for graft copolymers)
			 5 *Cis-trans*-multimers of amide groups
δ_{O-H}	1641-1643	1642-1644	Absorbed water
δ_{O-H} amide 2	1615-1618	1614-1618	N-H groups associated in *trans*-position in relation to C=O groups

$^{a)}$ Line position.

The contributions of each type of oscillations to common absorption amide 1 and effective lengths of the *trans*-multimers of amide groups, are calculated using integrated intensities of separate bands obtained at the computer processing of spectra. As it is visible (Tab.3), the influence of phenol on structure of films has general character for all polymers. In particular, the relative quantity *cis-trans*-multimers of amide groups grows, but the quantity *trans*-multimers of amide groups and also free amide groups decreases. There is also some increase of effective length of *trans*-multimers for the majority of polymers. However, for PVA-PAA$_N$3 having maximal N, the reduction both of quantity and length of *trans*-multimers is observed. The described effects are caused by compacting of polymer macromolecules in aqueous-phenol solutions, which results in more dense packing of polymer segments in formed films. It is visible, that phenol renders the maximal influence on PAA.

Table 3. Contributions of individual bands of the amide groups $\nu_{C=O}$ oscillations to the common amide 1 absorption for films obtained by different ways.

Polymer	Solvent for the film forming	α a) / %				β b)
		~ 1662 cm^{-1}	~ 1679 cm^{-1}	~ 1690 cm^{-1}	~ 1708 cm^{-1}	
PAA	water	66.95	10.66	21.12	1.27	0.50
	water+phenol c)	77.78	7.97	13.06	1.18	0.61
PVA-PAA$_N$1	water	67.80	10.61	20.26	1.32	0.52
	water+phenol	69.26	13.75	15.72	1.27	0.87
PVA-PAA$_N$2	water	72.32	10.56	15.49	1.62	0.68
	water+phenol	73.96	11.11	13.58	1.34	0.82
PVA-PAA$_N$3	water	71.41	10.72	16.02	1.85	0.67
	water+phenol	76.48	8.51	14.44	0.58	0.59

a) The contribution in common integrated intensity.

b) $\beta=A_{1679}/A_{1691}$, the value characterizing the length of *trans*-multimers of amide groups.

c) The ratio between phenol and polymer Z=0.5 mol of phenol/mol of PAA links.

The data of gel-chromatography (the example for PVA-PAA$_N$3 is shown in Fig.5) confirm the fact of phenol connection with copolymers and PAA in solutions and allow to carry out the quantitative accounts, which based on gel chromatograms of polymers in aqueous-phenol solutions measured at λ=270 nm (Fig.5, curves 3), that is in such area of spectrum, where polymers have no bands of absorption. These researchers specify also the equilibrium mechanism of the process of phenol connection, as for all polymers and for all investigated values Z the intensive peak of unbound phenol on gel chromatograms is shown. The next two important conclusions follow from quantitative accounts (Tab.4):

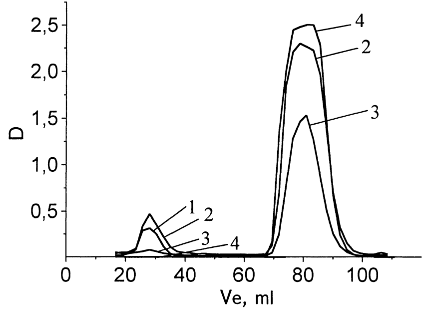


Fig. 5. Gel-chromatograms for PVA-PAAN3 in water (curve 1) and in water-phenol solution (curves 2, 3) at Z=0.5 mol of phenol/mol of PAA links, as well as for individual water-phenol solution (curve 4). λ=220 nm (1, 2) and 270 nm (3, 4).

One consists that graft copolymers more effectively, than PAA, connect phenol, and quantity of bound phenol grows with increase N. Other conclusion is that the quantity of bound phenol decreases with rising of its relative contents in a solution. Last result explains the reduction of spectral displays of phenol hydrogen bonds with growth Z (Fig.2), but contradicts the laws of chemical equilibrium, accordingly to which the increase of phenol concentration in a solution should to result in increase of its share, bound with polymers. However, the contradiction is eliminated, if to take into account the effect of compacting of polymer macromolecules at phenol presence, that should influence on equilibrium of complex formation.

Table 4. The quantity of phenol connected with graft copolymers and PAA in aqueous-phenolic solutions, according to the gel-chromatography data.

Polymer	Z mol of phenol/ mol of PAA links	n [a)] mol of phenol/ mol of polymer	n_0 [b)] mol of phenol/ graft chain	X [c)] %
PAA	0.5	330	-	0.53
	1.5	59	-	0.10
PVA-PAA_N1	0.5	896	36	0.68
	1.5	330	13	0.25
PVA-PAA_N2	0.5	1202	29	1.25
	1.5	192	5	0.20

[a)] The quantity of phenol connected with alone polymer macromolecule.

[b)] The number of phenol molecules connected with alone graft chain.

[c)] The degree of binding of acrylamide links of individual or graft PAA chain with phenol.

Conclusion

Thus, PVA-PAA_N in solution connect phenol more effectively, than PAA. In series of copolymers the degree of phenol binding rises with increase of quantity (density) of grafted chains. But as a whole, interaction of phenol with polymers is weak and carried out on the equilibrium mechanism. Under phenol influence the compacting of polymer macromolecules is observed, that can be caused by following. Proton-donor capacity -OH groups of phenol (pKa=9.89) is much higher, than –OH groups of multiatom alcohols (pKa=14.8-15.0), >NH groups of primary amides (pKa=15.1) and –OH groups of water (pKa=15.6). Therefore, phenol can actively compete with alcohol and amide groups of polymers participating in formation of H bonds, and it can evoke the destruction of a part of such bonds. Moreover, phenol molecules can substitute for molecules of water in solvating layers around macromolecules, lower around them the local dielectric permeability and aggravate in such a way the thermodynamic quality of the solvent.

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