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Properties of Poly(vinyl alcohol)-*graft*-Polyacrylamide Copolymers Depending on the Graft Length

1. Redistribution of Hydrogen Bonds and its Influence on the Copolymer Behavior in Aqueous Solution

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Summary: A series of poly(vinyl alcohol)-*graft*-polyacrylamide copolymers (PVA-*g*-PAA) with a constant number N but various molecular weights (lengths) of graft chains, which are intramolecular polymer-polymer complexes (intraPC), were investigated. The changes in the system of intramolecular hydrogen bonds and state of macromolecules in a solution are considered. The effect of partial detachment of PAA grafts from the main chain caused by the increase in molecular weight of grafts to a more than some critical value ($\overline{M}_{vPAAcrit} \approx 4.3 \cdot 10^5$ at N=9) has been revealed. When the length of grafts increases, the thermodynamic quality of water with respect to copolymers improves. The values of z-average radius of inertia, characteristic viscosity and the number of macromolecules in associate go through a minimum at $\overline{M}_{vPAA} = 4.3 \cdot 10^5$ and then sharply grow with increasing length of grafts.

Keywords: aqueous solution; associate; graft copolymer; H-bond; structure

Introduction

Graft copolymers with chemically complementary main and graft chains such as PVA-*g*-PAA, formed by polyacrylamide and poly(vinyl alcohol), are of great interest as a special type of polymer compounds[1] and as perspective functional materials.[2-4] The influence of the average number N of grafts per molecule (ranging from 25 to ~50) on the PVA-*g*-PAA structure in the bulk and in solution was considered in our previous works.[5,6] It is known that the length of grafts also influences properties of graft copolymers,[7] but the role of this

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factor in the behavior of graft copolymers forming intraPC have not been studied. That is why the aim of this work was to investigate a series of graft copolymers PVA-*g*-PAA with constant N but different molecular weight of grafts. The changes in the system of hydrogen bonds and state of macromolecules in a solution depending on the PAA molecular weight are considered.

Hydrogen Bonds and State of PVA-g-PAA in Solution

The characteristics of graft copolymers used in this work are detailed in Table 1.

Table 1. The copolymer molecular parameters (from viscometry and elemental analysis).

Copolymer	$\overline{M}_{vPAA}\cdot 10^{-6}$	$\overline{M}_{vPVA}\cdot 10^{-6}$	N	$M_{PVA\text{-}g\text{-}PAA}\cdot 10^{-6}$
PVA-*g*-PAA1	0.327	0.08	9	3.428
PVA-*g*-PAA2	0.430	0.08	9	3.950
PVA-*g*-PAA3	0.510	0.08	9	4.673

PVA-*g*-PAA1-3 samples were obtained by radical graft copolymerization[8] varying the ratio of concentrations of initiator (Ce^{IV} salt) and monomer (acrylamide). $\overline{M}_{vPAA}$ was determined according to Ref.[9] The number N of grafts was calculated on the basis of $\overline{M}_{vPAA}$ values, elemental analysis data[11] and taking into account the water content in a copolymer sample. PAA sample with $\overline{M}_v$=4.4·10^6 and the degree of hydrolysis of acrylamide units ~1% was also used. The structure of hydrogen bonds in PAA and PVA-*g*-PAA films ($l \approx 10$ μm) was characterized by IR spectroscopy. The $\nu_{C\text{-}H}$ vibration band of methylene groups at ~2945 cm^{-1} was used as the internal standard. Normalized IR spectra are shown in Figure 1.

For identification of overlapped bands in the amide I, amide II region (Figure 1a), the computer processing of spectra by the spline method,[11] was carried out. The well enough resolved $\delta_{C\text{-}H}$ vibration band at 1453 cm^{-1} was used as the calibration line. An example of computer deconvolution of the bands is given in Figure 2. The analysis of IR spectra shows that there are free amide groups (Table 2, structure II) and bound amide groups of *trans*-multimers (structure III) and *cis-trans*-multimers type in PAA and PVA-g-PAA films. There is also a small quantity of carboxylic acid groups, which form the open dimmer structures with neighboring amide groups (structure I). More detail description of separate bands in amide I region is considered earlier.[12] At the same time, in the spectra of all PVA-*g*-PAA samples, one more band at 1670 cm^{-1}, which is stipulated by the formation of H-bonds between the main and graft chains (Table 2, structure IV) manifests itself as a shoulder on the more intensive amide I band at 1661 cm^{-1} (Figure 2).

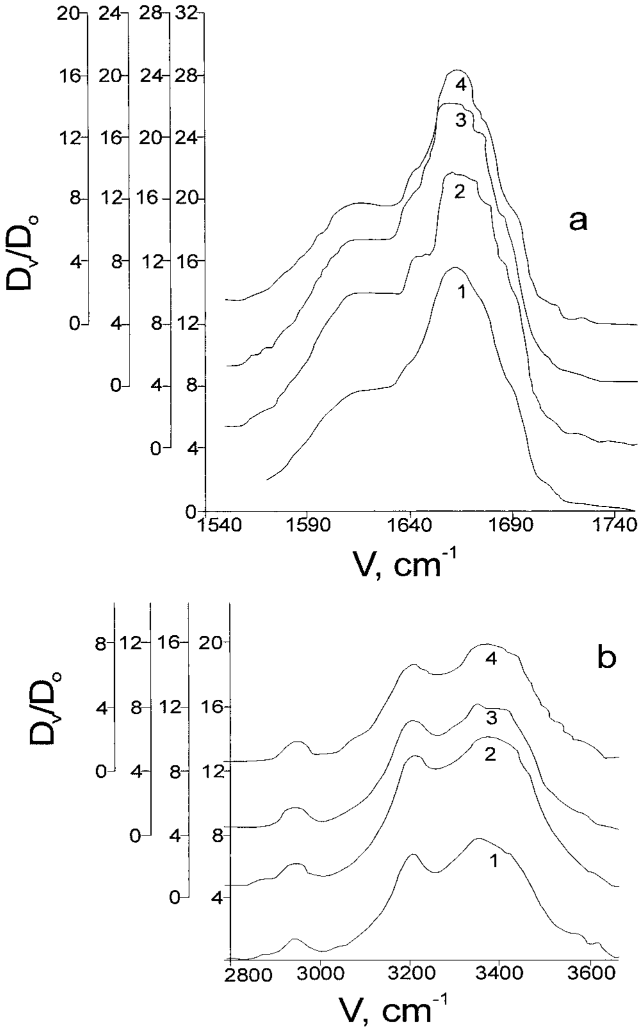


Fig. 1. Normalized IR spectra of PAA -*1*, PVA-*g*-PAA1 -*2*, PVA-*g*-PAA2 -*3*, PVA-*g*-PAA3 -*4* in the amide I and amide II regions (a) and ν_{C-H}, ν_{N-H}, ν_{O-H} regions (b).

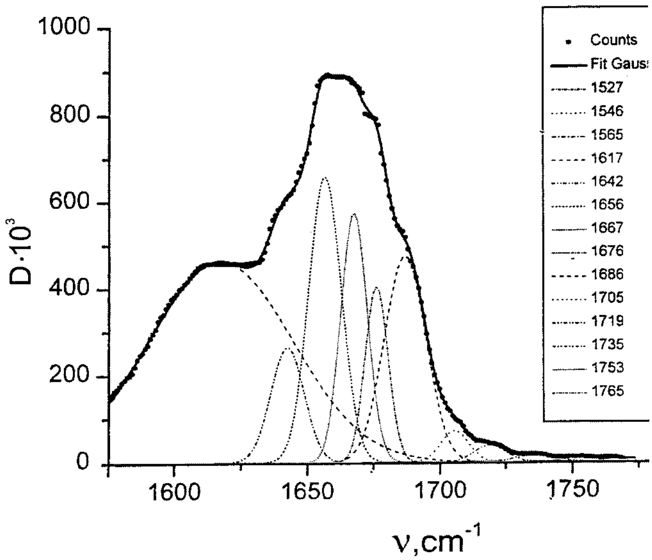
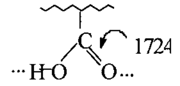
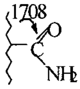
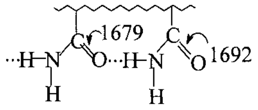
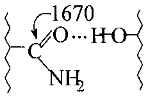
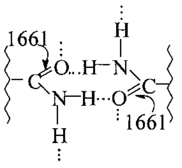


Fig. 2. An example of computer processing of IR spectrum of PVA-g-PAA2 in the amide I, amide II region. Experimental (…) and calculated (-) contours of bands.

Table 2. Structures of hydrogen bonds for PVA-*g*-PAA and PAA.

	I
	II
	III

	IV
	V

A comparison of the amount of amide groups which are in this or that state in the graft copolymer and PAA films, was carried out on the basis: i) the assumption on the absence of significant orientation effects in polymer films, ii) practically equal displacements (Δν) of the amide I bands of bound >C=O groups relative to the analogous band of free amide groups (in all the examined polymers), iii) the validity of the Buger-Lambert-Beer law:

$$B_i = A_i \cdot l \cdot C_i , \tag{1}$$

where B_i is the apparent integral absorption coefficient of i- the band in the spectrum, A_i is the actual integral absorption coefficient, l is the thickness of the film, C_i is molar concentration of the corresponding groups in the films.

The total concentration of amide groups is expressed the sum:

$$C = \sum_i \alpha_i \cdot C , \tag{2}$$

where α_i is the mole fraction of amide groups in the state i. Let us note that amide groups of PAA are in four different states, but in PVA-*g*-PAA sample, one more state (Table 2, structure IV) exists. After normalization of B_i values for separate amide I bands with the B_0 value for the internal standard band, we obtain:

$$\frac{B_i}{B_0} = \frac{A_i}{A_0} \cdot \frac{C}{C_0} \cdot \alpha_i = A_i^* \cdot X_{\mathrm{nPAA}} \cdot \alpha_i , \tag{3}$$

where A_i^* is the reduced integral absorption coefficient of the amide I i- the band, and X_{nPAA} is the mole fraction of acrylamide links in the given polymer. After rearrangement obtain the relation:

$$\frac{B_i}{B_0 \cdot X_{\mathrm{nPAA}}} = A_i^* \cdot \alpha_i \tag{4}$$

all the parameters of which on the left-hand side are easy to determine from a corresponding spectra and copolymer composition (Table 1). For PAA, $X_{\mathrm{nPAA}}=1$, but for copolymers $X_{\mathrm{nPAA}}<1$. Considering that for the same amide I band $A_i^*{}_{\mathrm{PAA}}=A_i^*{}_{\mathrm{PVA\text{-}g\text{-}PAA1\text{-}3}}$, it is possible to use the values on the left-hand side of relation (4) for estimation of changes in the distribution of amide groups between H-bond structures in the series of copolymers. The results of calculations are in Table 3.

It can be seen that high amount of *cis-trans*-multimers of amide groups (the ~1661 cm^{-1} band) is characteristic of PAA. In graft copolymers it decreases to a half and even more due to binding of a part of amide groups to the main chain (the ~1670 cm^{-1} band). Together with increase in the graft length, the amount of *cis-trans*-multimers decreases, reaches the minimum value in PVA-*g*-PAA2, and then somewhat grows. The amount of H-bonds between the main and grafted chains varies in opposite way: at first, with rising of the graft length, it somewhat increases, goes through a weak maximum and then essentially decreases. On the transition from PVA-*g*-PAA2 to PVA-*g*-PAA3 the amount of *trans*-multimers of amide groups also decreases 4.2 times (the ~1690 cm^{-1} band) but the length of *trans*-multimers, characterized by parameter β,[13] increases 4.8 times. This fact indicates a sharp rise in rigidity of graft chains. The described effects allow to conclude that in the series of PVA-*g*-PAA1-3, an increase in the graft length above some critical value results in their partial detachment and stretching to different sides from the main chain. The reason for this is probably the interaction of grafts at large distances from the main chain.

Table 3. Reduced apparent integral absorption coefficient of separate amide I bands and effective length of *trans*-multimers of amide groups for PAA and PVA-*g*-PAA.

Polymer	$B_i^{1)}/(B_0 \cdot X_{nPAA})$					$\beta = \frac{B_{1678}}{B_{1690}}$
	ν ~ 1661 cm^{-1}	ν ~ 1670 cm^{-1}	ν ~ 1678 cm^{-1}	ν ~ 1690 cm^{-1}	ν ~ 1707 cm^{-1}	
PAA	8.37	-	1.33	2.64	0.16	0.50
PVA-*g*-PAA1	4.22	2.38	2.26	3.59	0.39	0.63
PVA-*g*-PAA2	3.52	2.46	1.48	3.18	0.33	0.46
PVA-*g*-PAA3	3.62	1.94	3.23	1.46	0.44	2.21

1) Standard deviations of B_i values.of the 1661, 1670, 1678 and 1690 cm^{-1} bands after computer processing not exceeded.1.8 %.

The behavior of copolymers in solution was investigated by static light scattering and viscometry. The intensity of excess scattering of vertically polarized light by copolymer solutions was measured in the range θ=20-160 ° at λ=436 nm and T=293 K. The refractive index increment $\partial n/\partial C$ was determined by interferometry. In solutions of PVA and PAA the values $\partial n/\partial C$ were practically equal (0.157 and 0.163 $cm^3 \cdot g^{-1}$ respectively), which was confirmed by previous data.[14,15] One of the Zimm plots, calculated from the light scattering results,[16] is shown in Figure 3 and the copolymer characteristics are represented in Table 4.

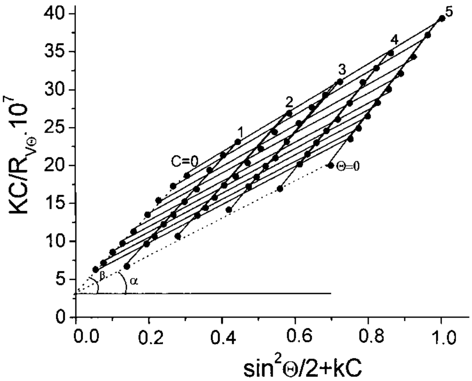


Fig. 3. Zimm diagram for PVA-*g*-PAA1 in the range $\theta \leq 65$ °. λ=436 nm, *T*=293 K. *C*= 0.2 -*1*, 0.4 -*2*, 0.6 -*3*, 0.8 -*4*, and 1.0 -*5* g·l^{-1}.

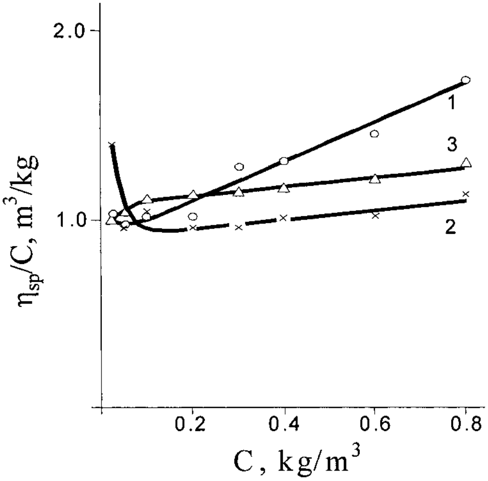


Fig. 4. Reduced viscosity *vs* concentration for PVA-*g*-PAA1-*1*, PVA-*g*-PAA2 -*2*, PVA-*g*-PAA3 -*3*. *T*=298 K.

Table 4. Characteristics of PVA-*g*-PAA$_N$ (by static light scattering).

Copolymer	$\partial n/\partial C$, cm^3/g	$M_w \cdot 10^{-6}$	$M_{PVA\text{-}g\text{-}PAA}$ $\times 10^{-6}$	N	$Z$$^{1)}$	$A_2 \cdot 10^6$ cm^3·mol/g^2	$\langle R^2 \rangle_z^{1/2}$ nm
PVA-g-PAA1	0.278	6.920	3.460	9	2	1.18	299
PVA-g-PAA2	0.232	3.812	3.812	9	1	1.55	253
PVA-g-PAA3	0.256	18.832	4.708	9	4	1.66	777

1) The number of macromolecules in the associate.

The parameters Z, N and $M_{\mathrm{wPVA}\text{-}g\text{-}\mathrm{PAA}}$ in Table 4 were determined comparing M_w values of scattering particles and $M_{\mathrm{PVA}\text{-}g\text{-}\mathrm{PAA}}$ (Table 1). When the graft length increases, the thermodynamic quality of water with respect to copolymers improves (the second virial coefficient A_2 grows monotonically). However, the values of Z and $<R^2>_z^{1/2}$ go through a minimum. Only PVA-*g*-PAA2 is molecularly dispersed in water. The macromolecules of other samples are associated in water, but these associates considerably differ from one another. The associates, containing two macromolecules of PVA-*g*-PAA1 have a dense compact structure (the low $<R^2>_z^{1/2}$ value in Table 4). A sharp decrease in the number of H-bonds between the main and graft chains in PVA-*g*-PAA3 macromolecules (Table 3) should result (and really results) in significant swelling in water, in removing the grafts into the solution bulk, farther from the main chain and in increase in the probability of contacts (pinnings) between swollen macrocoils.

The results of viscometric measurements (Figure 4, Table 5) performed on an Ostwald-type viscometer (τ_0=835 at T=298 K) are in accord with the light scattering data. In particular, in the series of PVA-*g*-PAA1-3, the value K decreases; therefore, the thermodynamic quality of water with respect to copolymers improves.

Table 5. Hydrodynamic parameters of the graft copolymers.

Copolymer	$[\eta]$, m^3/kg	$C^{*1)}$, kg/m^3	$K^{2)}$
PVA-*g*-PAA1	0.91	1.10	1.22
PVA-*g*-PAA2	0.90	1.11	0.29
PVA-*g*-PAA3	1.06	0.94	0.25

1) Crossover concentration.
2) Huggins viscometric constant.

The value of characteristic viscosity $[\eta]$, with increasing graft length, goes through a weak minimum and then somewhat increases. But there is also an important distinction: the discrepancy between the effects of $[\eta]$ and $<R^2>_z^{1/2}$ increases at the transition from PVA-*g*-PAA2 to PVA-*g*-PAA3. This fact confirms the destruction of friable associates of PVA-*g*-PAA3 under the action of even small flow rate gradients, which evolve in the capillary viscometer.

Conclusion

The effect of partial detachment of PAA-grafted from chemically complementary PVA main chain or the phenomenon of intraPC destruction caused by the increase in molecular weight of grafts higher than some critical value, is the most interesting and important result of the performed investigations. A significant swelling of PVA-*g*-PAA3 macrocoils in water compared with other copolymers and formation of fragile associates are consequences of the intraPC structure destruction. A dependence of $\overline{M}_{\text{crit}}$ on N can be expected. In the considered series of graft copolymers $\overline{M}_{\text{PAAcrit}} \approx 4.3 \cdot 10^5$ at N=9.

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