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

3. Benzene Solubilization by Solutions of the Copolymer

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Summary: The peculiarities of poly(vinyl alcohol)-*graft*-polyacrylamide copolymers (PVA-*g*-PAA), which are characterized by the equal average number (N=9), but various molecular weight (or length) of graft chains, in comparison with individual PAA and PVA, were investigated in aqueous medium. Sharp rise in benzene solubilization in PVA-*g*-PAA solutions at M_{PAA} higher than $4.3 \cdot 10^5$ has been established. It was shown that such effect is stipulated by the destruction of intramolecular polymer-polymer complex in the copolymer and increasing the benzene binding to separate PVA-g-PAA groups by means of hydrogen bonds.
The changes in the PVA-g-PAA solubilizing ability as the function of temperature were also investigated. The obtained results are discussed from the point of view of conformational transitions of intramolecular polymer-polymer complexes (intraPPC), which exist in copolymers, in dependence on the length of graft chains.

Keywords: benzene solubilization; graft copolymer; intramolecular polymer-polymer complexes; polyacrylamide; poly(vinyl alcohol)

Introduction

The influence of hydrophobic interactions between nonpolar parts of bound macromolecules in aqueous solutions on the stability of intermolecular polymer-polymer complexes (interPPC) is well known.[1,2] The substantial role of these interactions in stabilization of intramolecular polymer-polymer complexes (intraPPC) formed by polyacrylamide grafted to poly(vinyl alcohol) – (PVA-*g*-PAA), is also established.[3] It has been shown that in the series of PVA-*g*-PAA graft copolymers having commensurable length and various average numbers N of grafts, the volume of hydrophobic regions monotonically decreased with growing N. Such effect was explained with the increasing of steric hindrances what was accompanied by decreasing of hydrogen bonds between the main chain and the grafts. It was interesting to

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elucidate the hydrophobic interactions in a series of the same copolymers with constant N and variable length of the grafts.

It is known that in aqueous solution of PVA-*g*-PAA the reversible conformation transition such as *intraPPC ↔ segregated state*, occurs with rising temperature.[4] It is explained by breaking intramolecular hydrogen bonds between the main and graft chains and by different solubility of PVA and PAA in aqueous medium. This conformation transition is accompanied by a jump change in the copolymer viscosity in dependence on temperature.[4] Consequently, the changes in the PVA-*g*-PAA solubilizing ability with temperature were also investigated.

Hydrophobic Interactions in the Graft Copolymers Depending on Molecular Weight of Grafts and Temperature

The following graft copolymers were synthesized (according to ref.[5]) and used in the present work: N=9, $M_{\nu PVA}=8\cdot10^4$, $M_{\nu PAA}=3.27\cdot10^5$ (PVA-*g*-PAA1), $4.3\cdot10^5$ (PVA-*g*-PAA2) and $5.1\cdot10^5$ (PVA-*g*-PAA3). Additional characteristics are given in ref.[6] PVA sample (Japan) with $M_\nu=4\cdot10^4$ (33 % of the residual acetate groups) and PAA obtained by radical polymerization at room temperature with Ce^{IV} salt as initiator, were also used.

Investigation of benzene solubilization by aqueous copolymer solutions was carried out by refractometry method.[7] The solubilization value S was calculated from the relation:

$$S = \frac{\Pi_s - \Pi_{s+b}}{\Pi_{s+b} - \Pi_b} \cdot d_b \cdot 1000 \qquad (1)$$

where d_b is benzene density, $\Pi = (n^2-1)/(n^2+2)$, n is the refractive index and subscripts s, s+b and b, stand for the initial polymer solution, the polymer solution with benzene and pure benzene, respectively. The variation of the refractive index of PVA-*g*-PAA by addition of benzene was determined at constant polymer concentration C=3 kg·m^{-3}. The definite amount of benzene was added to copolymer solution, mixed and maintained in the closed glassware during 2 hours to reach thermodynamic equilibrium. Mixture was poured in measuring cuvette, closed and thermostabilized during 15 minutes. Then the refractive index of the aqueous layer was measured. Viscosity of graft copolymer solutions was measured with an Ostwald viscometer (τ_0=94 s at 298 K).

The curves of benzene solubilization with aqueous solutions of PVA, PAA and graft copolymers are shown in Figure 1. On the inflection points of curves 1-3 the values of limited solubilization, $S_{\rm lim}$, were found (Table 1).

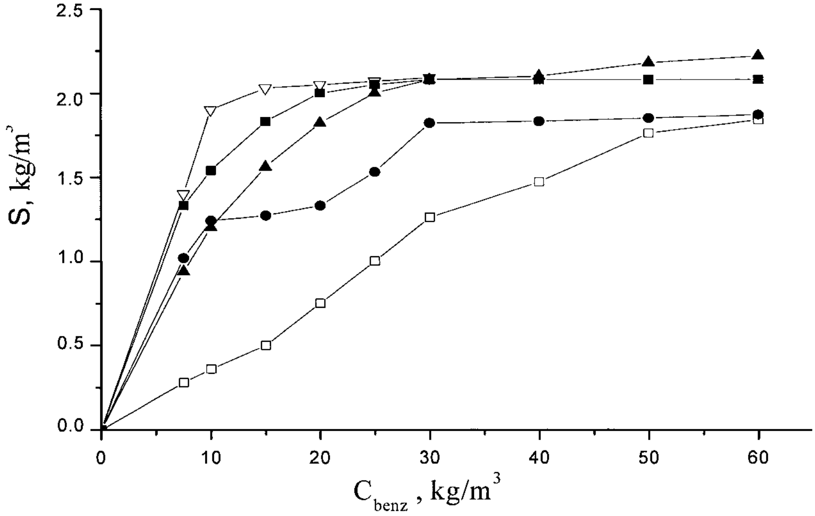

Fig. 1. Value of solubilization *versus* benzene concentration for: □ PVA, ● PAA, ▲ PVA-*g*-PAA1, ▽ PVA-*g*-PAA2, ■ PVA-*g*-PAA3. $T = 298$ K.

Table 1. Parameters of benzene solubilization with aqueous solutions of individual polymers and intraPPC.

Polymer	$S_{\rm lim}$ kg · m^{-3}	$S_{\rm red}$ kg · m^{-3}	n[1] mol$_{\rm benz}$/mol$_{\rm polym}$	V[2] nm^3
PVA	1.86	0.14	19	162
PAA	1.83	0.08	1505	135
PVA-*g*-PAA1	2.04	0.29	4251	382
PVA-*g*-PAA2	2.02	0.27	4588	410
PVA-*g*-PAA3	2.08	0.33	6586	593

[1] Number of benzene molecules bound by one polymer macromolecule.
[2] Size of hydrophobic regions.

The values of reduced solubilization $S_{\rm red}$ were calculated as the difference:

$$S_{\rm red} = S_{\rm lim} - S_{\rm o} \qquad (2)$$

where S_0 is benzene solubility in water at the temperature of experiment (S_0=1,75 kg·m^{-3} at T=278 K). Generally, it is possible to present $S_{\rm red}$ as the sum of two contributions:

$$S_{red} = S_H + S_D \qquad (3)$$

where S_H is the contribution due to the interaction of benzene π-electrons with proton- donor groups of polymer (hydrogen bonds),[8] and S_D is the contribution arising from benzene binding with hydrophobic regions of the polymer by dispersive forces.[7] It is clear that the most correct determination of hydrophobic domains evaluates the values S_D from Eq. (3). The experimental determination of this value in the presence of both types of interactions is quite a complicated problem.

The volume of hydrophobic domains V in macromolecules (Table 2) was calculated from the relation

$$V = n \cdot V_0 \qquad (4)$$

in which n is the number of benzene molecules bound by one macromolecule of polymer and V_0 is the size of one benzene molecule (0.09 nm^3). In most cases the value S_{red} was used for the calculation of hydrophobic domains size.

At the beginning of discussion, it is necessary to mark the two-step character of the solubilization curve for PAA (Figure 1, curve ●). This suggests the coiling of PAA macromolecules in the solubilization process reaching a definite benzene concentration in the mixture (~22 $kg \cdot m^{-3}$). Benzene solubilization by PVA solutions (curve □) is smaller than PAA and occurs at considerable excess of benzene introduced to polymer solution.

The second important moment is associated with the necessity of considering on S_H contribution to the S_{red} value, i.e. with the determination of the presence or absence of benzene binding to proton-donor groups of polymers due to hydrogen bonds. It is known that participation of the π-electron system of the benzene ring in the formation of hydrogen bonds results in a bathochromic shift of the characteristic benzene absorption band in UV spectrum at ~260 nm and or in an increase in intensity (integral absorption coefficient) of the band.[8] To clarify this question, UV spectra of benzene in water and in polymer solutions, were recorded (Figure 2). It can be seen that the presence of PAA in a water-benzene mixture does not influence the parameters of the absorption band at ~ 260 nm: its intensity and position in the spectrum do not change (curves ■, ●). In the presence of PVA-*g*-PAA3, a noticeable increase in the intensity of the absorption band at 260 nm, is observed (Figure 2, curve ▲), which points to the formation of weak hydrogen bonds between benzene and PVA-*g*-PAA3.

Let us compare the results of Table 1 with Figures 1 and 2. It can be observed that benzene solubilization in PAA solutions is weak. It becomes higher than the usual solubility of benzene in water only at C_{benz}>22 kg·m^{-3} (Figure 1, curve ●). According to data of Figure 2, such effect can be explained by the appearance of small hydrophobic domains in polymer structure. Actually, the formation of hydrophobic domains, which occurs due to the segregation of hydrophobic parts of polymer segments such as *cis–trans*-multimers of amide groups,[9] is initiated by benzene because it worsen the thermodynamic solvent quality relative to PAA.

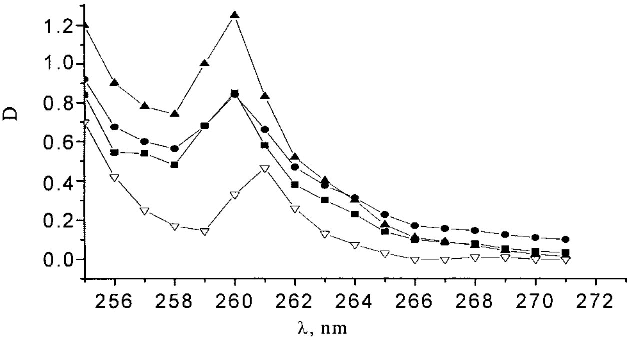

Fig. 2. Absorption spectra of benzene: ■ in water, ● in PAA solution, ▲ in PVA-*g*-PAA solution, ▽ in ethanol. C_{benz} = 1.53 kg·m^{-3}, C_{polym} = 3 kg·m^{-3}.

For PVA (Table 1), a very low quantity of bound benzene at the highest concentration (C_{benz}=60 kg·m^{-3}) is characteristic. It allows to assume that hydrophobic domains in PVA macromolecules in aqueous medium are absent. Such result is very interesting as it is known, that water relative to the polymer is practically a poor solvent.[10] In this case there is an insignificant binding of benzene to the hydroxy groups of PVA This is confirmed by the data of Figure 2 (curve ▽), by a bathochromic shift of the absorption band of benzene ($\pi \rightarrow \pi^*$) values at 260.5 nm of 1 nm. Thus, the low n and V for PVA in Table 1 correspond to the actual number and size of benzene molecules bound to PVA by hydrogen bonds.

In solutions of the graft copolymers, S_{red} and the size of hydrophobic regions increase sharply (Table 1). It is stipulated by specific structure of intraPPC in PVA-g-PAA.[3] The rise in the copolymer M_v(PAA) causes at first an insignificant increase of the size of hydrophobic domains but at M_v(PAA)>4.3·10^5, the V increases sharply. Such result contradicts the fact of improvement of the copolymer solubility in water when increasing the graft length that has been established by viscometry and static light scattering.[6] But taking into account the essential influence of PVA-*g*-PAA3 with largest grafts on UV spectrum of benzene (Figure 2, curve ▲), it is possible to conclude that for this sample the value V calculated using the summary value S_{red}, is only apparent. It is impossible in this case to neglect the contribution of S_H to S_{red}. It is natural to expect that this effect is stipulated not by an increase in the size of hydrophobic regions, but by increasing benzene quantity, bound by hydrogen bonds to PVA-*g*-PAA3 graft chains, which are most stretched in solution.

To obtain additional information on the structural changes that occur in PVA-*g*-PAA during the temperature transition, measurements of benzene solubilization for PVA-*g*-PAA4 sample (N=25, $M_{v(PVA)}=8\cdot10^4$, $M_{v(PAA)}=3.72\cdot10^5$) at various temperatures were carried out. The determined solubilization parameters are collected in Table 2. In the first column data on benzene solubility in water at each temperature of experiment are given. As can be seen, PVA-*g*-PAA4 macromolecules have the largest hydrophobic regions at T=281 K. With increasing temperature, these domains gradually diminish and at T=313 K they entirely disappear. It is interesting to compare the results with the temperature dependences of characteristic viscosity and Huggins viscometry constant for a copolymer sample, which is shown in Figure 3.

Table 2. The influence of temperature on the parameters of benzene solubilization by aqueous solutions of PVA-*g*-PAA4.

T	S_0 [1)] kg·m^{-3}	S_{red} kg·m^{-3}	S_{lim} kg·m^{-3}	n mol$_{benz}$/mol$_{polym}$	V nm^3
281	1.60	2.082	0.48	19240	1732
293	1.75	1.96	0.21	8418	758
313	1.96	1.96	0	-	-

1) Solubility of benzene in water at the temperature of experiment.

The temperature rise up to T~300 K causes decrease of K and increase of [η], which points out on the improvement of thermodynamic quality of a solvent and on swelling of macrocoils. This effect is associated with the break of a part of hydrogen bonds between the main and graft chains under the influence of temperature.[4] Thus, the decrease in size of hydrophobic domains in the given temperature interval is the direct corroboration of the fact that the intraPPC structure breaks during the conformational transition.

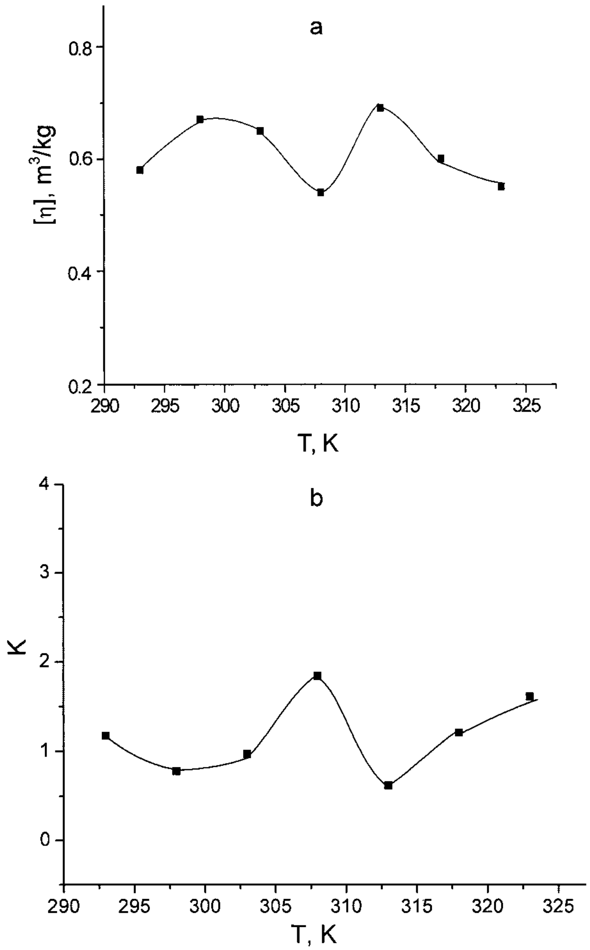

Fig. 3. Characteristic viscosity (a) and Huggins constant (b) *versus* temperature for PVA-*g*-PAA4.

In the narrow temperature interval $303 \leq T \leq 308$ K, the conformation transition of PVA-*g*-PAA macromolecules occurs, which results in the formation of polymer micelles.[4] Their cores are the segregated segments of PVA, which has poor solubility in water. On further temperature increase up to 313 K, the thermodynamic water quality with respect to PVA is improved[10] and the formed polymer micelles swell. The latter fact is confirmed by the decrease in K and increase in [η]. The described changes in the PVA-*g*-PAA structure correlate completely with zero values *n* and *V* at *T*=313 K (Table 2). Really, as shown above, the macromolecules of PVA do not form hydrophobic regions in water because the main type of intramolecular interactions is hydrogen bonds. In such case, it is impossible to expect conservation of hydrophobic regions in complete destruction of intraPPC structure and the conformational transition with the formation of polymer micelles, the cores of which are the segregated segments of PVA. The absence of hydrophobic regions in the structure of polymer micelles is also corroborated by the data on benzene solubilization.

Conclusion

The method of solubilization of hydrocarbons is a tool of research of polymer structure in solution, and also of structure changes of macromolecules, which occur under the influence of various factors. It is possible to conclude that the presence in PVA-*g*-PAA structure of hydrophobic domains and hydrophilic cavities (formed by links of polymer components) makes them practically universal binders of many organic substances, ions and colloid particles.[11,12]

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