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Structure and Properties of Intramolecular Polycomplexes Formed in Graft Copolymers with Chemically Complementary Polymer Components

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Summary: The structure in a bulk state and in a solution and also peculiarities of synthesis of the polyacrylamide to poly(vinyl alcohol) graft copolymers forming the intramolecular polycomplexes (IntraPC) are reviewed basing on the data of IR spectroscopy, dilatometry, DSC, QELS, static light scattering, rheology and some other methods. Influence of the quantity N and molecular weight of grafted chains and also the hydrogen bond system between the main chain and the grafts and between the grafted chains only on the IntraPC properties is highlighted. As illustration of the high binding ability of IntraPCs the results of studying of their complex formation with silica nanoparticles in aqueous medium are discussed.

Keywords: binding ability; graft copolymer; hydrogen bonds; intramolecular polycomplex; polymer-colloid complex; structure

Introduction

Binding properties of intermolecular polycomplexes (InterPC) with respect to low- and high-molecular-weight organic substances (first of all drugs and biopolymers), different ions, colloid particles and cells of living organisms are well known.[1-3] But as binders they have essential demerits conditioned by existence of the complex formation equilibrium at the macromolecular level. Really, InterPC can be irreversibly are destroyed up to individual macromolecules at a considerable dilution of a solution and pH alteration (if one or both polymer components are polyelectrolytes) and also at the action of more strong competitors or such factors as a temperature and additives of the inert low-molecular weight electrolytes.[1-3] In this connection the intramolecular polycomplexes (IntraPC) formed in macromolecules of block and graft copolymers by chemically complementary components are of special interest. Destruction of the cooperative system of bonds in such IntraPC is always reversible, that is why they have abnormally high binding ability.

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Peculiarities of a synthesis and structure in a bulk state and in a solution as well as factors of stabilization of IntraPCs formed in the polyacrylamide to poly(vinyl alcohol) graft copolymers (PVA-*g*-PAA$_N$, where N is the grafted chain number) are considered in the present paper. Their binding ability in respect of silica nanoparticles is demonstrated.

Properties and Binding Ability of Intramolecular Polycomplexes

Synthesis. Three series of PVA-*g*-PAA$_N$ copolymers were synthesized by free radical graft copolymerization with a Ce (IV) salt as the initiator according to Ref.[4] In a series of the PVA-*g*-PAA$_N$1-3 samples N was varied from 25 to 49 but molecular weights of the grafts were comparable ($M_v \sim 1 \cdot 10^5$).[5] In another series of the PVA-*g*-PAA$_N$4-6 copolymers N was changed from 25 to 42 and the molecular weight of the grafts was decreased from $3.72 \cdot 10^5$ to $1.63 \cdot 10^5$.[6] Then a series of PVA-*g*-PAA$_N$7-9 samples was prepared in which M_{vPAA} increased from $3.72 \cdot 10^5$ to $5.1 \cdot 10^5$ at the constant N=9.[6] Until recently the mechanism of grafting of PAA onto hydroxyl-containing polymers (including PVA) was believed to be well known.[8] But basing on thermodynamic affinity between PVA and PAA and also on the phenomenon of the matrix polymerization of monomers of the one chemical nature in the presence of complementary macromolecules of another chemical nature,[9] the idea about a matrix character of the PAA to PVA graft copolymerization has appeared. This assumption was examined in the kinetic studies of synthesis of the PVA-*g*-PAA$_N$1-3 and PVA-*g*-PAA$_N$7-9 copolymers, which were performed by dilatometry.[12] The rate of the graft copolymerization was shown in 2-4 times higher than that one of the acrylamide homopolymerization carried out in the same experimental conditions. Not only the kinetic matrix effect has been established in the PVA-*g*-PAA$_N$ synthesis, but also its relation to the density of the growing chains has been revealed. Really, when the quantity (density) of the growing grafts became too high (as in synthesis of PVA-*g*-PAA$_N$3) the kinetic matrix effect disappeared).[12]

The H-bond System Stabilizing IntraPC. Studying of the system of intramolecular bonds depending on the number (density) and molecular weight (length) of grafts is of fundamental importance for graft copolymers forming IntraPC because such system shapes already in the process of their synthesis (matrix effect). Hence, considerable attention has been given to this problem in researches of the PVA-*g*-PAA$_N$ graft copolymers. Careful quantitative analysis of the IR spectroscopy data basing on the computer separation of overlapping vibration bands in the Amide I and Amide II regions by the spline method was carried out. It was shown that IntraPC structure in the PVA-*g*-PAA_N macromolecules is stabilized by both H-bonds between the main chain and the grafts and also H-bonds between the units of the grafted chains (such as *cis-tras*-multimers of amide groups).[6,13,14] An increase in N in the series of PVA-*g*-PAA_N1-3 led to substantial changes in this H-bond system (Figure 1).

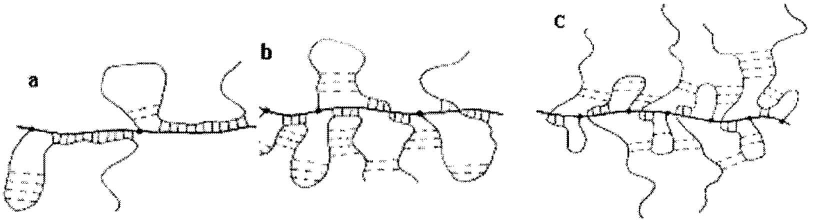
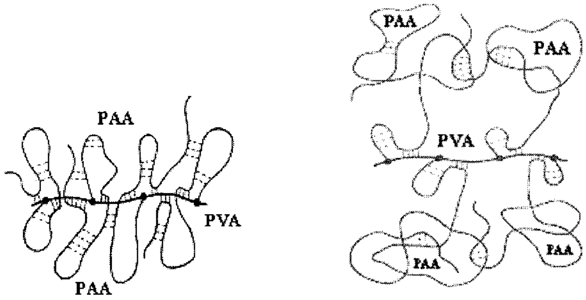


Figure 1. Redistribution of hydrogen bonds in the PVA-g-PAA_N copolymers depending on N.

Actually, the number of H-bonds such as the main chain – the grafts decreased with N growth whereas the number of H-bonds between the grafts increased.[14] At the same time, interesting effect of 'detachment' and stretching of the grafted chains in different directions away from the main chain was observed for the series of PVA-*g*-PAA_N7-9 copolymers when molecular weight (length) of the grafts became higher than some critical value M* (Figure 2): [6,13,14]

The changes in the hydrogen bond system with increasing N and M_{vPAA} were reflected in all the properties of PVA-*g*-PAA_N.



M_{vPAA}<M* **M_{vPAA}>M***

Figure 2. Schematic representation of the effect of 'detachment' of the grafts from the main chain.

Influence of Grafting Density. The bulk structures of the PVA-*g*-PAA$_N$1-3 graft copolymers with variable N were studied by DSC method.[15] It was found that the homogeneous amorphous copolymer structure characterized by alone glass transition remained up to some critical value of N (N^*~25). But at $N>N^*$ two glass transitions on the DSC thermograms appeared, that was conditioned by a microphase separation in the bulk structure of the graft copolymers. In this case side by side with the regions of full compatibility of the polymer components domains formed by the PAA segments, which do not interacted with the main chain because of steric hindrances, arise.

According to the data of static light scattering[5], water was practically the Θ-solvent in respect of the copolymers, but its thermodynamic quality was essentially improved with N growth. Such behavior of the graft copolymers in solution is consistent with the effect of a successive decrease in the number of the main chain-the grafts H-bonds in IntraPC. The contribution of hydrophobic interactions of bound parts of active groups of the polymer components to stabilization of IntraPC structures in water was estimated by benzene solubilization [14]. The results confirmed that such stabilization occurs and the role of this factor substantially decreases with increasing N. Actually, the volume of hydrophobic regions in the PVA-*g*-PAA$_N$ 1-3 series reduced from 794 to 98 nm^3.

Investigations of the changes in the state of the PVA-*g*-PAA$_N$1-3 and 4-6 macromolecules in solutions induced by factors capable to destroy the H-bond system in IntraPC were of special interest. Among these factors, the temperature[16] and hydrodynamic shear field[5] were examined. It was shown by viscometry and quasielastic laser scattering [16] that the copolymer macromolecules undergone the reversible conformational transition such as *IntraPC↔ segregated state* in the narrow temperature interval from 303 K to 308 K. Destruction of the H-bond system in IntraPC and essentially different solubility of PVA and PAA in water were the main reasons of such transition. The effect of hydrodynamic shear flow on the copolymer structure in solution was studied on a rheo-viscometer with coaxial cylinders [5]. Two levels of the copolymer reversible structure destruction, which were attributed to: i) destroying of a network of pinnings only (first level) at the shear rate gradient j lesser than some critical value j^* and at the copolymer concentration C higher than C^* and also ii) ruining of both the Intra PCs and their primary aggregates (second level) at $j>j^*$ and $C< C^*$, were revealed. Stability of PVA-*g*-PAA$_N$ structure to a hydrodynamic shear field reduced when N increased.

Influence of the Molecular Weight (Length) of Grafts. When studying the structure and behavior in solutions of the PVA-*g*-PAA$_N$7-9 samples with constant N but different molecular weight of the grafts the main interest was to elucidate how the effect of 'detachment' of the grafts from the main chain (which was revealed by IR spectroscopy) is displayed in the copolymer properties.[13,14,17] DSC researches confirmed the phenomenon of 'detachment' of the grafts by discovering of the state of microphase separation (two glass transitions in DSC thermograms) in the copolymer bulk structure at $M_{vPAA}>M^*$ in contrast with the homogeneous copolymer structure at $M_{vPAA} \leq M^*$.[17] Due to above-mentioned phenomenon, macrocoils of the PVA-*g*-PAA$_N$9 sample having M_{vPAA} higher than M^*, sharply swelled in aqueous solutions (comparing with the PVA-*g*-PAA$_N$7-8 samples) and formed the developed friable aggregates.[13] Additionally, basing on the investigations of benzene solubilization, the conclusion, about destroying of hydrophobic regions and a sharp increase in the amount of H-bond benzene in swollen coils of the PVA-*g*-PAA$_N$9 sample, was made.[18]

Binding Properties of the Intramolecular Polycomplexes. Graft copolymers forming IntraPC, such as PVA-*g*-PAA$_N$ are binders of new generation. Their particles in aqueous medium contain the hydrophobic regions and hydrophilic cavities formed by loops of non-bound polymer units (including active polymer groups), therefore they have practically universal binding ability. In particular, flocculants based on these graft copolymers can efficiently clear a river water on waterworks from pollutants of the natural and anthropic origin.[19,20] The interaction of PVA-*g*-PAA$_N$ with humic and fulvic acids (the main components of the humus substances in a river water) and also with phenol (one of the toxic substances in water) and the ions of stable and radioactive isotopes of cesium and strontium was considered earlier.[21,22] At the same time studying of the copolymer complex formation with smallest colloid particles are of great interest in order to show their binding possibilities. Two PVA-*g*-PAA$_N$2 and 3 samples were used to investigate their interaction with silica sol (R_{SiO_2}=11,2 nm), which was prepared from Aerosol A-175 ('Oriana', Ukraine), by viscometry, static light scattering and benzene solubilization. The polymer solutions were mixed with SiO_2 sol during 1 hour in the rations corresponding to 2 and 5 nanoparticles on every macromolecule. Formation of the polymer-colloid complexes (PCC) was accompanied by a sharp decrease of the reduced viscosity of the copolymer solutions (Figure 3). When the number of SiO_2 particles was higher the reduced viscosity decreasing ($\Delta\eta_{red}$) was greater. The PCCs appeared was stable in aqueous medium. In particular, they displayed greater stability to dilution of a solution than the initial IntraPCs (Figure 3, curves 2,3).

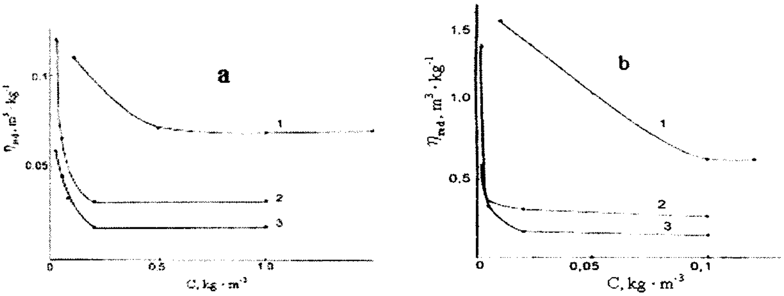


Figure 3. The reduced viscosity *vs* concentration for PVA-*g*-PAA$_N$2 (a) –*1*, PVA-*g*-PAA$_N$3 (b) –*1* and also for their polymer-colloid complexes with two –*2* and five –*3* SiO_2 particles.

The depolarization coefficients Δ_v and Δ_u (for vertically polarized and unpolarized falling light), which are sensitive to the smallest structural changes in macrocoils [23] were measured by instrument of the static light scattering FPS-3 (Russia) in the solutions of PVA-*g*-PAA$_N$2,3 and their mixtures with colloid nanoparticles (Figure 4).

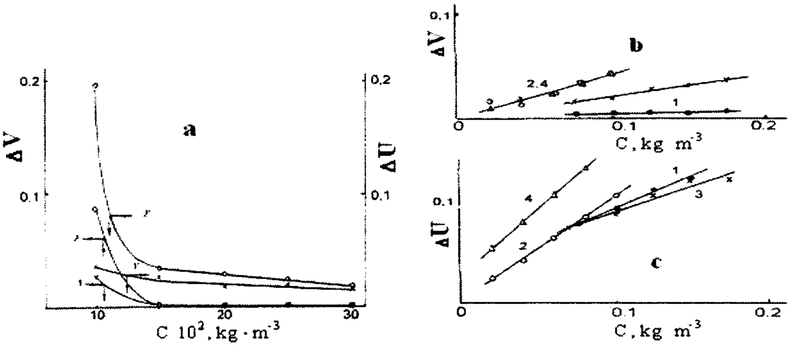


Figure 4. Depolarization coefficients *vs* concentration for PVA-*g*-PAA$_N$2 -*1,1'* (a), PVA-*g*-PAA$_N$3 -*2,2'* (a) and also for the mixtures PVA-*g*-PAA$_N$2+SiO_2 –*1,2* (b,c) and PVA-*g*-PAA$_N$3+SiO_2 –*3,4* (b,c) with two (*1,3*) and five (*2,4*) SiO_2 particles. $\Theta=90°$, $\lambda=436$ nm.

It is seen that the IntraPC structures in the graft copolymers are keeping into a wide region of their concentrations (Figure 4, a). However at $C < 0{,}15\ kg \cdot m^{-3}$ the sharp macrocoil swelling due to the IntraPC destruction occurs. Unlike to behavior of individual graft copolymers, their PCCs with 2 and 5 SiO_2 particles demonstrated full stability in the concentration region under study. The values of $\Delta\eta_{red}$ together with Δ_v^0 and Δ_u^0 found by extrapolation of the depolarization coefficients to C=0 are represented in Table 1. The values of Δ_h^0 and δ^2 (the third depolarization coefficient and the optical anisotropy parameter) in the table were calculated according to well-known relations placed under the table.

Table 1. Characteristics of PCCs formed by the graft copolymers with SiO_2 particles.

Copolymer	$n^{1)}$	$\frac{\Delta\eta_{red},}{m^3 \cdot kg^{-1}}$	Δ_V^o	Δ_u^o	$\Delta_h^{o\ 2)}$	$\delta^{2\ 3)}$
	-	-	0,006	0,030	4,030	0,052
PVA-g-PAA_N2	2	0.54	0,003	0,032	9,70	0,055
	5	0.74	0,003	0,030	9,03	0,052
	-	-	0,020	0,049	1,499	0,087
PVA-g-PAA_N3	2	0.58	0,001	0,024	23,02	0,042
	5	0.77	0,001	0,027	26,30	0,046

1) The number of SiO_2 particles in corresponding PCC.
2) $\Delta_u^o = (1 + \Delta_h^o) / [1 + (\Delta_v^o)^{-1}]$.
3) $\delta^2 = 10\ \Delta_u^o / (6 - 7\Delta_u^o)$. [23]

Note, that the depolarization coefficient Δ_v^0 is determined by the internal anisotropy of a polymer substance, whereas the depolarization coefficient Δ_h^0 depends on the anisotropy of macrocoils which is connected with their shape and large dimensions.[23] Finally, the parameter δ^2 characterizes the total anisotropy of polymer particles which is conditioned by both above-mentioned contributions.[23]

Let's consider with such point of view the data in Table 1. It is seen that the inside structure and shape of PVA-*g*-PAA_N2 macromolecules with lesser quantity (density) of the grafts (N=31) does not change enough in the complex formation with 2 and 5 SiO_2 particles. Such conclusion is based on a small alteration of the Δ_v^0, Δ_h^0 and δ^2 parameters in solution of PCCs comparing with solution of the graft copolymer. In this case the sharp decreasing of the η_{red} of the copolymer in the mixtures with SiO_2 particles can be attributed only to destroying of the PVA-*g*-PAA_N2 primary aggregates under influence of complex formation. Another situation is observed for the PVA-*g*-PAA_N3 sample with greater number of the grafts (N=49). The structure of its primary aggregates and individual macromolecules considerably change during the PCC formation. Really, the internal anisotropy and total anisotropy of macrocoils containing SiO_2 particles sharply decrease, but their size (or the coil asymmetry) grows.

The results of studying of the benzene solubilization in suspensions of individual SiO_2 particles and solutions of the PCCs (in comparison with the analogous data for the PVA-*g*-PAA$_N$2 and 3 samples) provide with additional information about complex formation between the graft copolymers and colloid particles. It was found that the PVA-*g*-PAA$_N$2 and 3 samples were able to connect in the solubilization process 3380 and 1090 mol_{benz}/mol_{cop} correspondingly. The value of adsorption of benzene by SiO_2 particles was equal to 869 mol_{benz}/particle. But all the polymer-colloid mixtures had no capability to solubilize benzene. Such experimental fact points on formation in these mixtures very dense PCC particles, in which the main part of active groups of both polymer components is bound with a surface of SiO_2 particles (Figure 5). It can be assume that the PVA and PAA chemical complementarity plays an important role in stabilization of the PCC structure.

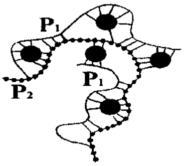


Figure 5. The scheme of the PCC structure.

Conclusion

Thus, the structure and properties and also binding ability of the PVA-*g*-PAA$_N$ graft copolymers which belong to a class of the intramolecular polycomplexes are determined not only by the number and molecular weight of the grafts (that is typical for all graft copolymers), but also by the system of hydrogen bonds such as *a main chain-a graft* and *a graft-a graft*. Formation of the H-bond system begins evidently in the synthesis of such graft copolymers because it has a matrix character. It was shown that there are certain critical values of the number and molecular weight of the grafts which ones are dependent from each other and determine the transfer from the homogeneous copolymer bulk structure to the state of microphase separation. Due to specific building the IntraPCs can efficiently bind different low- and high-molecular-weight organic substances, some inorganic (metal) ions and also hard nanoparticles, in particular, of silica sol. It was found that IntraPC structure undergoes a significant destruction in the complex formation with SiO_2 nanoparticles if the grafting density in PVA-*g*-PAA$_N$ is too large.

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