Peculiarities of Formation of Intermolecular Polycomplexes Based on Polyacrylamide, Poly(vinyl alcohol) and Poly(ethylene oxide)

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Summary: The phenomenon of self-assembly of aggregates formed by relatively short chains of poly(vinyl alcohol) (PVA) on the long macromolecules of polyacrylamide (PAA) in aqueous medium are discussed. PVA and PAA form intermolecular polycomplexes (InterPC) of a constant composition independently on a ratio of polymer components. The complex formation between high-molecular-weight PAA and relatively low-molecular-weight poly(ethylene oxide) (PEO) are considered also. PEO with $M \leq 4 \cdot 10^4$ $g.mol^{-1}$ weakly interacts with PAA. The polymer-polymer interaction can be intensified when the part of amide groups (~20 mol %) on PAA chain to transform into the carboxylic groups. InterPCs formed by PEO and initial or modified PAA have associative structure with friable packing of the polymer segments. They are stabilized by the hydrogen bond system.

Keywords: aggregates; hydrogen bonds; intermolecular polycomplexes; matrices; polyacrylamide; poly(ethylene oxide); poly(vinyl alcohol)

Introduction

In spite of numerous successes achieved at establishment of the main conformities of polymer-polymer interactions, researches of the intermolecular polycomplex (InterPC) structures connected with their properties remain an actual scientific problem. Polymer-polymer complexes stabilized mainly by the electrostatic interactions (the polyelectrolyte InterPC), today are widely studied.[1] InterPCs formed first of all by the hydrogen bonds are lesser known.[2,3] But such polycomplexes are used in designing of new medicines, as separating membranes, flocculants and other important functional materials.[4]

Processes of polymer-polymer interactions between very long (matrices) and relatively short ("oligomers") macromolecules are of special interest because they allow to find so called "the

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critical polymer chain length" which is necessary to achieve for the cooperative interaction between two polymers:[5]

$$P_1\,(\text{matrice}) + n{\cdot}P_2 \rightarrow \text{InterPC}\,(P_1 + n{\cdot}P_2)$$

In the present work complex formation in two pairs of hydrophilic polymers such as polyacrylamide (PAA) - poly(vinyl alcohol) (PVA) and PAA - poly(ethylene oxide) (PEO) are considered.

Reactions of formation and structure of InterPCs

The basic parameters of PVA, PAA and PEO samples under study are shown in Table 1-2.

Table1. Molecular parameters

System of PAA+PVA

Polymer	$M_v{\cdot}10^{-6}$	a1) %	b2) %
PVA 1	0.04	-	33
PVA 2	0.08	-	13
PVA 3	0.12	-	31
PAA 1	2.72	11	-
PAA 2	4.40	1	-

1)The degree of hydrolysis of acrylamide links.

2)The quantity of residual acetate groups in PVA.

Table 2. Molecular parameters

System of PAA+PEO

Polymer	$M_v{\cdot}10^{-5}$	a1) %
PAA3	9.80	1
P(AAm-*co*-AAc)	11.4	20
PEO 1	0.02	-
PEO 2	0.04	-
PEO 3	0.06	-
PEO 4	0.4	-
PEO 5	1.49	-

1)The degree of hydrolysis of acrylamide links.

It is seen that PAA length surpasses essentially the length of PVA or PEO chains. All the samples of PAA were synthesized by the acrylamide ("Merck", Germany) radical polymerization with using Ce^{IV} salt as initiator. The alkaline hydrolysis of PAA was carried out to obtain P(AAm-*co*-AAc) the random acrylamide with acrylic acid copolymer having the hydrolysis degree ~20%. The samples of PVA (Japan) and PEO ("Merck", Germany) were used also. The complex formation reactions were carried out by mixing of PAA with PVA or PEO in aqueous solutions during 1 hour.

System of PAA+PVA. The complex formation between PAA and PVA is displayed first of all in the viscometry data (Figure 1). Viscosity of polymer solutions was measured by Ostwald-type viscometer (τ_0=94 s at T=298 K). The deviation of the value $\eta_{sp\ mix}/\Sigma\eta_{sp\ i}$ from unity in a wide region of the mixture compositions testifies about the interaction of components. Positive deviations (curves 1, 2) point on to formation of InterPC particles with friable packing of the component segments, but negative ones (curves 3, 4) testifies to arising of the compact complex particles. The ratio φ between the component concentrations in

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extreme points of the curves can indicate on φ_{char} every InterPC, at which both polymers are connected quantitavely with each other. This assumption was confirmed earlier[6] for the compact particles in the PAA2+PVA1 mixture by gel chromatography.

In the present study validity of such assumption for the friable InterPC particles in the PAA1+PVA2 and PAA1+PVA3 mixtures by the high-speed sedimentation data (Figure 2,3; Table 3,4) was proved.

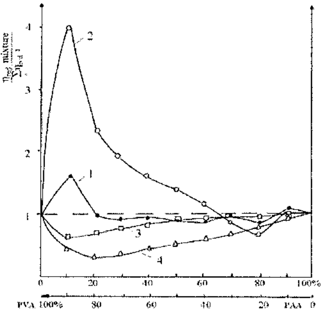

Figure 1. The ratio of η_{sp}mixture/$\sum\eta_{sp}$i *vs* mixture composition for PAA2+PVA1 – *1*, PAA1+PVA1 -*2*, PAA1+PVA2 -*3* and PAA1+PVA3 -*4*. T=298 K.

The sedimentation coefficients of individual polymers and their mixtures were determined with the use of analytical centrifuge MOM 3170 H (Hungary).

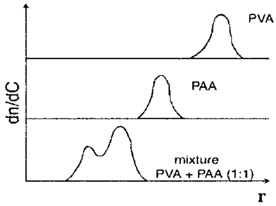

Figure 2. Sedimentograms of PVA2, PAA1 and their mixture (1:1) after 45 min centrifugation. $\omega=4\cdot10^4$ rs·min^{-1}, T=295 K, $C_{PVA}=C_{PAA}=0{,}5$ kg·m^{-3}.

Examples of sedimentograms are shown in Figure 2. Sedimentograms of the mixtures contained two peaks excluding the 9:1 ratio, which corresponds to φ_{char} (Table 4). The excess of bound PAA (matrice) for all the ratios $\varphi = C_{PVA}/C_{PAA} < \varphi_{char}$ was displayed as a separate sedimentation peak (Figure 2). The values of $1/S_c$ and Q (the area of the sedimentation peak) for the individual polymers linearly grow with concentration (Figure 3 a, Table 4), that is characteristic for the dense macrocoils, which do not change their state in viewed concentration field.[7] Q values for the 1-st peaks surpass considerably that ones for each component (Table 3) that allows to consider their as peaks of InterPC. The areas of the 2-nd peaks in both mixtures were lesser than peaks of separate components. The linear concentration dependences $1/S_c$ and Q for the 1-st peaks (Figure 3 b, lines 1,2; Table 4) were observed at all the mixture compositions. This fact allows concluding that the composition of both InterPCs in surveyed regions of concentrations and polymer ratios are constant. These peaks belong to unbound PAA. The linear dependence of $1/S_c$ for the 2-nd peaks from C_{PAA}, which are surplus concentration of PAA comparing with PAA concentration in corresponding InterPC (Figure 3 b, lines 3,4)

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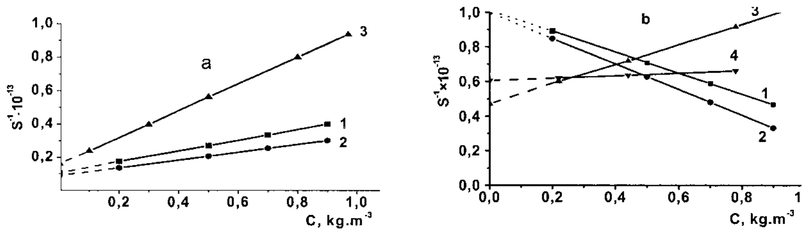

Figure 3. The inverse value of the sedimentation coefficient *vs* concentration for PVA2 –*1* (a), PVA3 –*2* (a), PAA1 –*3* (a) and mixtures of PVA2+PAA1 (1-st peak) –*1* (b), PVA3+PAA1 (1-st peak) - *2* (b), PVA2+PAA1 (2-nd peak) –*3* (b) and PVA3+PAA1 (2-nd peak) –*4* (b). T = 295 K.

confirms this conclusion. It is necessary to mark a negative declination of the line $1/S_c=f(C)$ for both InterPC (Figure 3 b, lines 1,2). Accordingly to Ref.[7], this effect is one more certificate to friable packing of polymer segments in formed InterPC. The comparison of S_0 values in Table 3 shows that complex formation of PAA1 with PVA2 and PVA3 is accompanied by destroying of their aggregates in aqueous solution. It is seen also that low-molecular-weight PVA is aggregated in initial state much more than high-molecular-weight PAA.

Table 3. Sedimentation coefficients for separate polymers and polymer mixtures

	S_c[1] x10^{13} s						
Composition	PVA 2	PVA 3	PAA 1	PAA1+PVA2		PAA1+PVA3	
w_{PVA}/w_{PAA}				1st peak	2nd peak	1st peak	2nd peak
9:1	2.50	3.32	4.22	2.14	-	3.01	-
7:3	3.19	3.93	2.51	1.70	1.66	2.08	1.61
5:5	3.84	4.82	1.78	1.41	1.39	1.59	1.57
2:8	5.70	7.32	1.25	1.12	1.09	1.18	1.51
1:30	-	-	1.06	-	0.97	-	-
S_0[2]x10^{13} s	9.39	11.11	6.42	0.99	2.12	1.00	1.65

[1] The concentration coefficient of sedimentation.

[2] The sedimentation coefficient, extrapolated to C=0.

Table 4. The areas of the sedimentation peaks for polymers and polymer mixtures

	Q in conditional units				
Composition	PVA2	PVA 3	PAA1	PAA1+PVA2	PAA1+PVA3
w_{PVA}/w_{PAA}				1st peak	2nd peak
9:1	57	44	6	67	68
7:3	44	34	20	64	59
5:5	32	24	28	47	36
2:8	13	9	47	21	15

The values of φ_{char} found in such a way are shown in Table 5.

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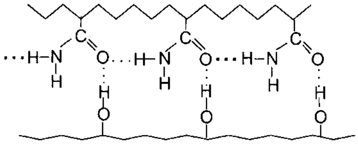
Table 5. The characteristic compositions of InterPCs

InterPC	φ_{char}			φ'_{char} 1)
	w_{PVA}/ w_{PAA}	$mole_{PVA}$/ $mole_{PAA}$	base-$mole_{PVA}$/ base-$mole_{PAA}$	$mole_{PVA}$/ $mole_{PAA}$
PAA1+PVA1	9	611	12	50
PAA1+PVA2	9	306	14	22
PAA1+PVA3	9	204	12	17
PAA2+PVA1	4	444	5	82

1) Calculated compositions of InterPC in the assumption of the full filling of PAA chain (a matrice) by the stretched PVA chains (1:1 base-$mole_{PVA}$/ base-$mole_{PAA}$).

It is seen that M_{vPVA} does not influence on φ_{char} of InterPC but it changes the packing density of the polymer segments. At the same time φ_{char} decreases and the packing density of segments in InterPC particles increases when M_{vPAA} grows. Characteristically that all the InterPCs studied contain a considerable excess of PVA. This fact and also the effect of destroying of the PVA aggregates during complex formation points on interaction of the long PAA macromolecules (matrices) with partially diminished aggregates of PVA. On the other hand, every InterPC have the constant φ_{char} value independently from the mixture composition. This results in appearance of the unbound PAA macromolecules in the range $\varphi<\varphi_{char}$. Hence, the diminished PVA aggregates are unevenly distributed among the PAA of matrices in the process of complex formation, that is the phenomenon of self-assembly of PVA aggregates on the matrices is observed.

It has been established by IR spectroscopy[6] that a major factor of formation of InterPC particles is the system of intermolecular hydrogen bonds such as:



Moreover, the hydrophobic interactions act as additional factor of stabilization of the InterPC compact particles. Really, it has been established by the benzene solubilization that such particles contain a developed hydrophobic regions.[6]

System of PAA+PEO. According to the viscometry data PEO with relatively short polymer chains ($M \leq 4\cdot10^4$) weakly interacts with PAA, that is why the specific viscosity of PAA solutions insignificantly increases at the PEO addition (Figure 4, curves 1,2). The appreciable growth of specific viscosity of PAA solutions at PEO addition begins at $M_{vPEO}>1\cdot10^5$

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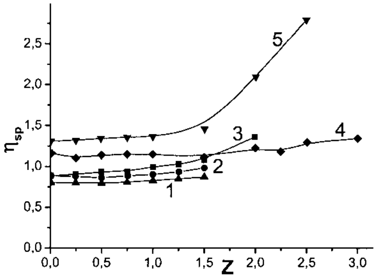

Figure 4. Specific viscosity *vs* mixture composition: for PAA3+PEO3 -*1*, PAA3+PEO4 -*2*, PAA3+PEO5 -*3* (C_{PAA3}=1 kg·m^{-3}) and P(AAm-*co*-AAc) +PEO3 -*4*, P(AAm-*co*-AAc)+PEO5 –*5* ($C_{P(AAm\text{-}co\text{-}AAc)}$=0.2 kg·m^{-3}). T=298 K.

(Figure 4, curve 3). It means that the critical M_{vPEO} ("critical PEO length") in the reaction with PAA is about $1 \cdot 10^5$. Such value large comparing with the critical M_{vPEO} value in reactions with poly(acrylic acid) and poly(methacrylic acid)[8] that is conditioned by more weak interaction of PEO with PAA.

In order to intensify the connection of PAA with PEO some part (~20 mol %) of the PAA amides groups were transformed into carboxylic groups by the reaction of alkaline hydrolysis, which was carried out at T=323 K during 4 hours (concentration of PAA C=10 kg·m^{-3}). More strong binding of modified PAA with PEO is reflected by the sharp growth of the η_{sp} *vs* Z (the ratio between base-mol PEO and base-mol initial or modified PAA in the mixture) in Figure 4, curve 5. Note that InterPC particles formed by the initial or modified PAA and PEO are characterized by friable packing of polymer segment.

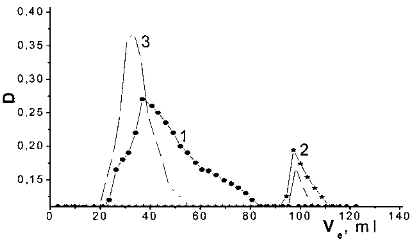

Figure 5. Gel chromatograms of aqueous solutions of P(AAm-*co*-AAc) -*1*, PEO3 -*2* and their mixture -*3* at Z=1.5; λ=220 nm, T=298 K.

Complex formation between P(AAm-*co*-AAc) and PEO is confirmed also by gel chromatography data (Figure 5). It is seen, that the elution peak of P(AAm-*co*-AAc) shifts to lower V_e values in the polymer mixture (curve 3). Simultaneously, the intensity of the PEO elution peak essentially reduces.

Existence of the H-bond system between P(AAm-*co*-AAc) and PEO was established by IR spectroscopy. The IR spectra of thin polymer films of PAA3 and P(AAm-*co*-AAc) and also the mixture P(AAm-*co*-AAc)+PEO5 on fluorite glasses (l=7-9 μm) were recorded on "Micolet NIXUS-475" spectrometer (USA) in the range 1000-4000 cm^{-1} (two examples in Figure 6). The separation of the strongly overlapped vibration bands in the Amide I, Amide II region was carried out by the spline method (Figure 7).[9] Note, that correct separation of the complicate band contour in this region was impossible taking into account only three most

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intense bands. That is why computer analysis of this region based on one wide band of the Amide II, two visible bands of $\nu_{C=O}$ vibration of COOH groups (at ν>1700 cm^{-1}) and three well known bands of the Amide I corresponding to *cis-trans-* and *trans*-multimers of amide groups.[10] Results of calculations ara presented in Table 6.

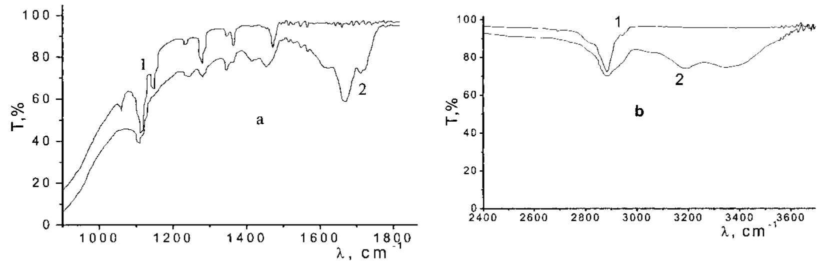

Figure 6. IR spectra of PEO5–*1* and the mixture P(AAm-*co*-AAc)+PEO5 –*2* in the regions of Amide I, Amide II and and ν_{C-O-C} vibrations (a) and also ν_{C-H}, ν_{N-H} and ν_{O-H} vibrations (b).

Table 6. The contributions (α) of separate $\nu_{C=O}$ bands of individual polymers and polymer mixture in common $\nu_{C=O}$ absorption

Sample	α %						$\beta^{1)}$
	ν~1662 cm^{-1}	ν~1678 cm^{-1}	ν~1690 cm^{-1}	ν~1708 cm^{-1}	ν~1711 cm^{-1}	ν~1723 cm^{-1}	
PAA3	66.9	10.7	21.1	1.3	-	0.1	0.50
P(AAm-*co*-AAc)	35.7	6.4	7.5	-	25.0	5.1	0.85
P(AAm-*co*-AAc)+ PEO5	38.8	10.4	5.0	-	20.9	24.9	2.10

$^{1)}$Effective length of *trans*-multimers of amide groups. $\beta=B_{1678}/B_{1690}$, where B_i is the apparent integral absorption coefficients.

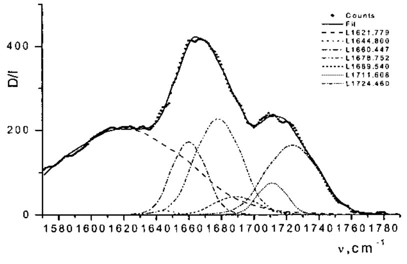

Figure 7. The example of computer processing of IR spectrum of P(AAm-*co*-AAc)+PEO5) mixture in the Amide I and Amide II region. Experimental (····) and calculated (–) vibration band contours.

The initial PAA3 as other PAA sample contained: i) the most contribution α from *cis-trans*-multimers of amide groups (the band of 1662 cm^{-1}), ii) lesser contribution from *trans*-multimers of amide groups (two bands at 1678 and 1690 cm^{-1}), iii) small contribution of free amide groups (the band of 1708 cm^{-1}) and iiii) very low contribution of COOH groups forming the

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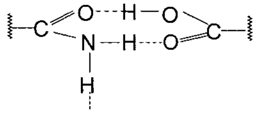
"open dimer" structure of H-bonds. In the P(AAm-*co*-AAc) sample the quantities of *cis*-*trans*- and *trans*-multimers of amide groups sharply decreased (Table 6), but that one of COOH groups grew. These groups formed not only "open dimers", but also the mixed cyclic dimmers with amide groups (the band of 1711-1712 cm^{-1})[11]:



Formation of the H-bond system between considered polymers was confirmed fist of all by noticeable lowering (in 6 cm^{-1}) of the $\nu_{C\text{-}O\text{-}C}$ vibration band of PEO in the polymer mixture (Figure 6 a). Moreover, the contribution α of the band of 1723 cm^{-1} and also the effective length of *trans*-multimers of amide groups in the polymer mixture sharply increases (Table 6). Such effects can be attributed to appearance of the continuous sequence of H-bonds between polymer components.

Conclusion

The effect of self-assembly of partially destroyed aggregates of the short PVA chains on PAA long macromolecules as on matrices is established. At mixing of PVA with PAA in aqueous medium InterPC of the constant composition φ_{char} is formed. The value φ_{char} does not depend on the polymer component ratio and is determined mainly by molecular parameters of PAA. Disaggregating of PVA and PAA macromolecules in the process of complex formation has been revealed.

PEO with relatively short polymer chains ($M \leq 4\cdot10^3$) weakly interacts with PAA. Polymer-polymer interaction is intensified when the part of amide groups on PAA chain is transformed in the carboxylic groups. InterPCs formed have associative structure with friable packing of segments of both polymer components.

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