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Interactions, Stabilizing the Structure of Intermolecular Polycomplex Between Poly(vinyl alcohol) and Poly(acrylamide)*

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The structure and properties of the intermolecular polycomplex, formed by cooperative intermolecular hydrogen bonds between poly(vinyl alcohol) and poly(acrylamide), were investigated. By viscometry, gel chromatography and differential scanning calorimetry the characteristic composition of polycomplex was established. The compatibility of polymers and structural peculiarities of polycomplex in a block state were characterized. Due to computer processing of the polycomplex IR spectra in amide I, amide II region by the spline method, the presence of the absorption band at 1668 cm^{-1}, related to hydrogen bonds between polymer pair, was shown. The developed hydrophobic regions in polycomplex structure in water, which additionally stabilize the polycomplex particles, were detected. The structure of such intermolecular polycomplexes is proposed.

Key words: intermolecular polycomplex, characteristic composition, hydrogen bonds, hydrophobic regions, cooperativity

The complex formation, the structure and properties of intermolecular polycomplexes, stabilized by the cooperative system of hydrogen bonds, are often described [1–3]. In particular, stoichiometric and nonstoichiometric polycomplexes formed by poly(acrylic acid), poly(methacrylic acid) on the one hand, and poly(acrylamide), poly(vinyl alcohol), poly(vinyl ethers) on the other hand, are well known [4,5]. Polycomplexes of the given type are of great interest in designing new medicines, in modeling of complex biochemical reactions, in applications as separating membranes and for other purposes [6]. Intermolecular polycomplexes of poly(vinyl alcohol) with poly(acrylamide) investigated in this paper consist a basis of high efficient flocculants **Unicomfloc**$^{\mathbf{inter}}$, which are perspective for purifying various colloid dispersions [7] and for clearing natural water [8]. In this connection, the processes of forming, the structural features and the factors of stabilization of polycomplex particles in an aqueous medium are investigated.

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EXPERIMENTAL

Materials. Poly(vinyl alcohol) (PVA) from Japan (more detailed information not available) with $\overline{M}_v = 4{\cdot}10^4$ and residual content of acetate groups 33% as well as poly(acrylamide) (PAA) with $\overline{M}_v = 4.4{\cdot}10^6$ and degree of hydrolysis of acrylamide links 1% (obtained by radical polymerization of acrylamide (AA) at T = 298 K with application of Ce(IV) salt, as the initiator), were used in the present work. The intermolecular polycomplex (InterPC) was obtained by mixing PVA with PAA in aqueous solutions during 1 hour.

Techniques. The characteristic composition φ_{char} of InterPC in aqueous medium, at which both polymers are connected quantitatively with each other, was determined by viscometry and gel chromatography. Viscosity of polymer dilute solutions was measured by an Ostwald type viscometer (τ_0 = 94 s at T = 298 K). The gel chromatography analysis of PVA, PAA and InterPC was carried out on a column (1×50) cm, filled with Dextran gel G-25 from "Pharmacia" (Sweden) at 298 K. The measurements of the optical density of eluted solutions were carried out on a spectrophotometer SF-16 from "Lomo" (Russia) at λ = 220 nm. 2 ml of PVA, PAA and InterPC solutions of concentration C = 2 $kg{\cdot}m^{-3}$ were introduced into a column.

Structural transitions in InterPC under temperature influence were studied by DSC at heat rate 16 $K{\cdot}min^{-1}$ by a DSC-210 microcalorimeter and thermoanalyzer 1090 from "Du Pont". The polymer blends of different composition for DSC investigations were prepared by mixing dilute polymer solutions (C = 1 $kg{\cdot}m^{-3}$) during 1 hour following a freeze – dry technique. Approximately 4–10 mg samples were investigated in open capsules to allow for water evaporation. The structure of bonds in individual PAA and InterPC (PVA + PAA) was investigated by IR spectroscopy. The IR spectra of thin polymer films (d = 7–9 μm) were recorded on a UR-20 spectrometer (Germany) in the range 1000–4000 cm^{-1}. The scanning rate was 10 $cm^{-1}{\cdot}min^{-1}$. The films were cast from aqueous solutions (C = 1.5 $kg{\cdot}m^{-3}$) on fluorite windows, air-dried, and then placed under vacuum above $CaCl_2$ for one week. The separation of the strongly overlapped vibration bands in the amide I, amide II region, determination of the positions, FWHM and integrated intensities of selected bands were carried out by means of the spline method [9,10] through computer processing of the stretched spectra on a scale 100 cm^{-1}/100 mm. The δ_{C-H} vibration band at 1452 cm^{-1} well enough resolved in spectra was used as a default line, which was inscribed in a complicated contour of overlapped bands.

The study of benzene solubilization by aqueous solutions of individual polymers and InterPC was carried out by refractometry [11]. The solubilization value S was calculated from the relation:

$$S = \frac{P_s - P_{s+b}}{P_{s+b} - P_b} \cdot d_b \cdot 1000 \quad (1)$$

where d_b is benzene density, $P = (n^2 - 1)/(n^2 + 2)$, (n is the refractive index) with subscripts s, s+b and b, are related to the initial polymer solution, the polymer solution with benzene and pure benzene, respectively. The variation of the refractive index of InterPC at φ_{char} by additions of benzene was determined at constant concentration of polycomplex (C = 5 $kg{\cdot}m^{-3}$) and of individual polymer components (C = 3 $kg{\cdot}m^{-3}$).

RESULTS AND DISCUSSION

Determination of InterPC composition: The complex formation in the PVA + PAA system in aqueous medium is testified first of all by viscometry. The deviation of $\eta_{sp\,mix}/\Sigma\eta_{sp\,i}$ from unity (Fig. 1) in a wide region of the polymer mixture compositions indicates the formation of intermolecular polycomplex.

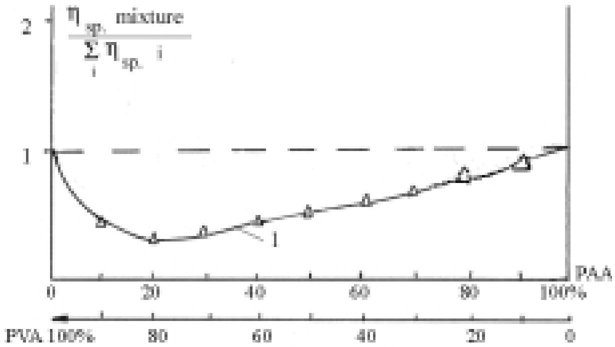


Figure 1. Plot of η_{sp}mixture/$\sum\eta_{sp}$ i *vs* mixture composition of polymers. T = 298 K.

At the same time, the character of this deviation allows to conclude about the formation of compact InterPC particles in a solution. The ratio of components in the extreme point corresponds to characteristic composition of InterPC $\varphi_{char} = 4\ w_{PVA}/w_{PAA}$. Both polymer components at this composition are connected quantitatively with each other. Quantitative binding of the polymers with each other in the extreme point of viscosity is confirmed by earlier obtained high-speed sedimentation data [12], and also by gel chromatography and DSC results, presented in this work. It is possible to assume that more high-molecular-weight PAA in relation to low-molecular-weight PVA becomes a matrix for the last one, whose molecular parameters define the characteristic composition of the polycomplex formed [13].

The gel chromatograms of individual polymers and their mixtures at the ratio $\varphi = 4\ w_{PVA}/w_{PAA}$ are shown in Fig. 2.

The PVA elution peak (curve 1) is displaced to lower values of V_e in relation to the PAA elution peak (curve 2). At the same time, InterPC is eluted practically at the same value of V_e (curve 3), as PAA. It is known that V_e is determined by hydrodynamic volume of eluted macromolecular particles, which is characterized by product $[\eta]\cdot M$, where $[\eta]$ is the characteristic viscosity, and M – molecular weight of particles [14].

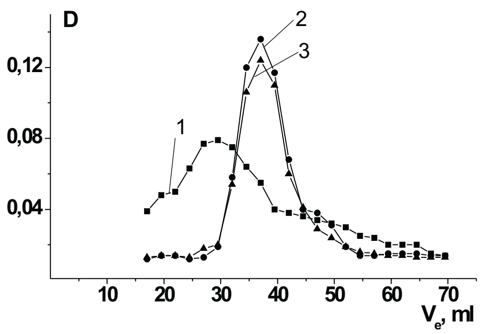


Figure 2. Gel chromatograms of water solutions of PVA – 1, PAA – 2 and InterPC at $\varphi = \varphi_{char}$ – 3 at λ = 220 nm. T = 298 K. .

Then V_e is the smaller the larger is the hydrodynamic volume of eluted coils. According to viscosity measurements of dilute water solutions $[\eta]_{PAA} = 0.864\ m^3 \cdot kg^{-1}$, $[\eta]_{PVA} = 0.032\ m^3 \cdot kg^{-1}$, but for the complex of composition $\varphi = 4\ w_{PVA}/w_{PAA}$ $[\eta] = 0.171\ m^3 \cdot kg^{-1}$. Because $\overline{M}_{vPVA} << \overline{M}_{vPAA}$, and $[\eta]_{PVA} << [\eta]_{PAA}$, the lower V_e value for PVA is connected only with its strong association in an aqueous medium [15]. Characteristically, the PVA associates are preserved in the elution process, but they are destroyed during the flow through viscometer.
Due to practically equal V_e values for PAA and InterPC, it is possible to write:

$$[\eta]_{PAA} \cdot \overline{M}_{vPAA} = [\eta]_{InterPC} \cdot \overline{M}_{vInterPC} \quad (2)$$

The $\overline{M}_{vInterPC}$ value calculated from (2) equals $22.23 \cdot 10^6$. On the other hand, if one considers $\varphi = 4$ as characteristic composition of InterPC, then the polycomplex particle should contain one PAA macromolecule and 444 molecules of PVA. $\overline{M}_{vInterPC}$ should be in this case equal to $22.16 \cdot 10^6$, that is practically the same value, as that from (2). Thus, the polymer ratio really corresponds to φ_{char} of InterPC in the point of viscosity minimum in Fig. 1.

DSC experiments: DSC thermograms for PVA, PAA and PVA + PAA blend of two compositions are shown in Fig. 3, while characteristics of structural transitions of the polymers and blends, which were determined from such thermograms, are represented in Table 1.

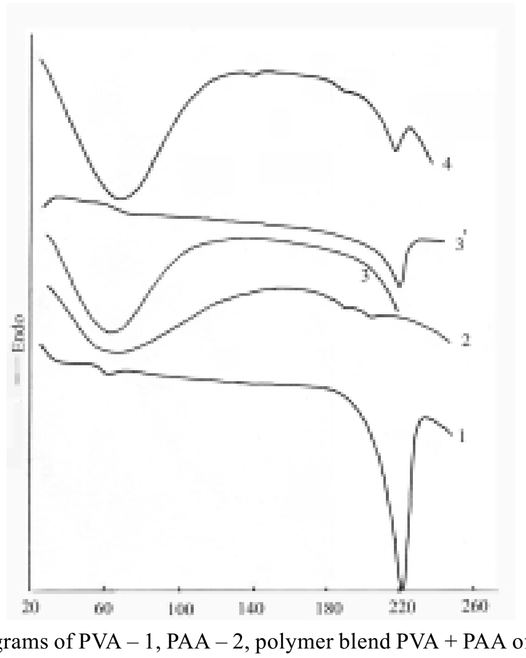


Figure 3. DSC thermograms of PVA – 1, PAA – 2, polymer blend PVA + PAA of composition $\varphi_{char} = 4$: 1-st run – 3, 2-nd run – 3′ and polymer blend PVA + PAA of composition $\varphi = 1$ – 4.

Table 1. Parameters of structural transitions in PVA, PAA and PVA + PAA blends.

Sample	T_g, °C	ΔT_g, °C	T_{11}, °C	ΔT_{11}, °C	T_m
PVA	58.5	8	–	–	222
PAA	185	13	206	14	–
PVA + PAA ($\varphi_{char} = 4$)	75	19	–	–	221
PVA + PAA ($\varphi = 1$)	139 188	6 8	–	–	219

The thermograms for amorphous PAA (curve 1) include a broad endothermic peak of water evaporation, subsequent jump of a thermal capacity, its center corresponding to the glass transition temperature T_g (α-transition) and further small endothermic peak, related to the liquid-liquid (ll) transition [16]. During ll-transition, the destruction of the most durable fragments of the initial structure, saved after glass transition, occurs. The thermogram of crystallized PVA (curve 2) contains a glass transition in the region of low temperatures, but in the range of considerably higher temperatures it reveals an intense endothermic melting peak (Table 1); its integration allows to estimate $\Delta H_m = 83.2\ J \cdot g^{-1}$. The thermograms of InterPC (PVA+PAA) at $\varphi_{char} = 4$ show first of all an intense endothermic peak, due to water evaporation (curve 3). Under this peak during repeated (second) scanning the glass transition was revealed (curve 3′), which temperature is higher than T_g for individual PVA, but lower than T_g for PAA (Table 1). The presence of a single T_g in polymer blends, in the range between T_g values for individual components, speaks about a compatibility of polymers at a molecular level [17–19]. However, on InterPC thermograms (curves 3, 3′) the small endothermic peak in the region of higher temperatures is well seen. It confirms the existence of small crystalline PVA domains in InterPC structure (Table 1). The glass transition for these domains was, however, not detected because of their relatively small weight contribution in a sample. Let us notice, that a similar phenomenon was discovered in blends of interacting polymers, such as poly(vinyl pirrolidone) (PVP) and PVA. In the structure of these blends the small crystalline PVA domains were preserved even at a PVP content over 80 w. % [20]. The fact of appearance of smallest crystalline domains of PVA in InterPC structure is worthy of special attention, if taking into account that the preparation of polymer blends for DSC investigations was carried out through a solution. But in a solution at $\varphi = \varphi_{char}$, PVA and PAA are quantitatively connected with each other, according to gel chromatography (Fig. 2) and high speed sedimentation data [21]. The thermogram for the PVA+PAA blend of composition $\varphi = 1$, which contains the excess of PAA in comparison with blend of composition φ_{char} (curve 4) is even more interesting. It includes the peak of water evaporation, two glass transitions and a melting peak of small crystalline PVA domains (Table 1). The first T_g characterizes the glass transition in amorphous domains of PVA and PAA compatibility in InterPC structure. The value of the second T_g practically coincides with T_g for PAA. Therefore, its appearance confirms the formation of a separate microphase of PAA excess in comparison with the stoichiometric quantity. This effect confirms once again the constant composition of InterPC, established earlier in the PVA + PAA system over a wide range of the ratios of polymer components [21]. In summary it is necessary to discuss the distinctions in T_g of domains of the polymers compatibility in InterPC structure and also noticeable depression of T_m of crystalline PVA microdomains with an increase of a PAA content in a blend (Table 1). The rise of T_g of the polymer compatibility amorphous domains at an excess of PAA content and at constant InterPC composition specifies on strengthening of interaction between polymers in these domains. The reasons for this can be: i) the increase of the number of hydrogen bonds between PVA and PAA and (or), ii) the formation of additional H-bonds between InterPC particles and fraction of PAA macromolecules which are in an excess [22]. Other phenomenon, namely the depression of T_m of PVA crystalline microdomains in InterPC structure with increasing the PAA content, is usual for compatible polymer blends, one component of which crystallizes, and another one is amorphous [17,23]. The theory of this phenomenon is well known [24]. According to it, the reason of the T_m depression of crystalline microdomains with increasing amorphous component fraction in a blend is the existence of specific interactions between polymers in an amorphous phase.

Hydrogen bonds as the main factor of InterPC formation: The structures of hydrogen bonds in individual PAA and in InterPC at $\varphi = \varphi_{char}$ were established by IR spectroscopy method. The IR spectra of films normalized to the internal standard, such as the ν_{C-H} vibration band of methylene groups at ~2940 cm^{-1}, in two major regions are shown in Fig. 4 a, b.

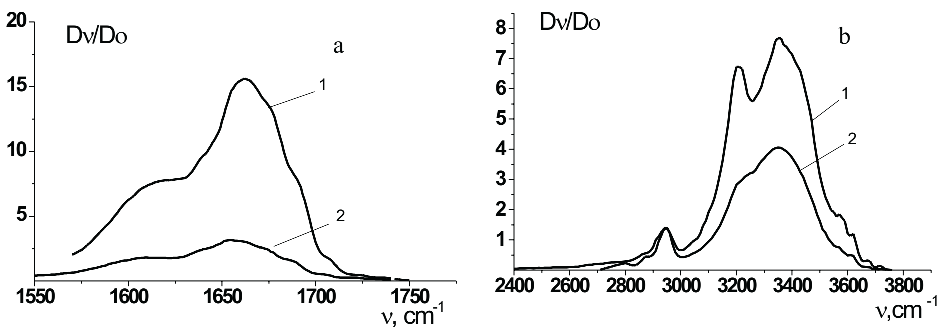


Figure 4. Normalized IR spectra of PAA – 1 and InterPC – 2 films in amide I, amide II regions (a) and ν_{C-H}, ν_{N-H}, ν_{O-H} (b) vibrations. T = 293 K.

It is seen that in the amide I and amide II region each spectrum is a superposition of a great number of strongly overlapped vibration bands, which correspond to the various states of both free and bound amide groups. The identification of separate bands in this region was achieved by computer processing of spectra by spline method [9]. As initial data the parameters of the default line (ν = 1452 cm^{-1}) and roughly estimated positions, intensities at maximum and FWHM of bands, detected in the analysed region as χ peaks, inflexion points or shoulders were introduced into the computer [10]. The results of computer deconvolution of spectra are represented in Fig. 5 a,b and Table 2.

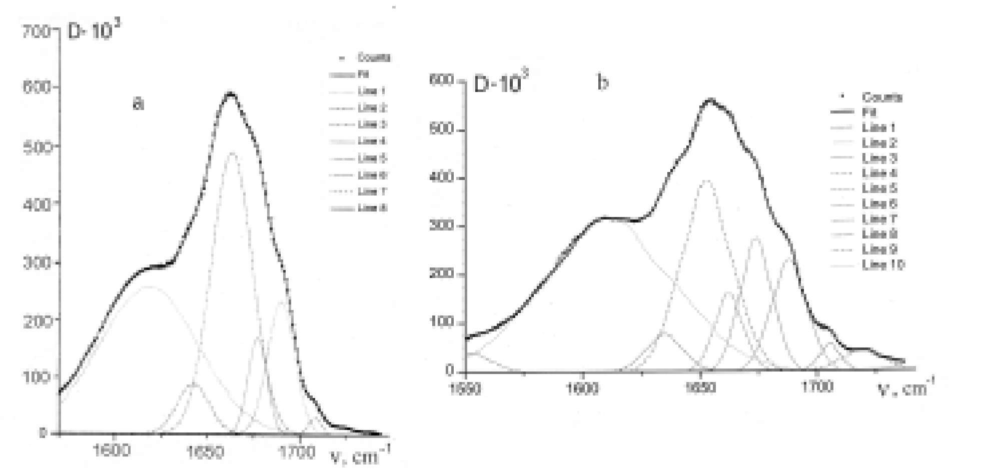


Figure 5. Computer processing of IR spectra of PAA (a) and InterPC of composition $\varphi = \varphi_{char}$ (b) in the amide I and amide II region. Experimental (···) and calculated (—) vibration band contours.

Table 2. Parameters of vibration bands determined by the computer processing of spectra.

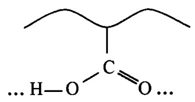
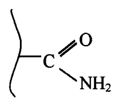
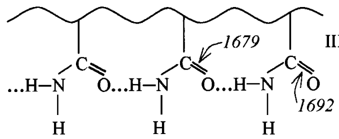
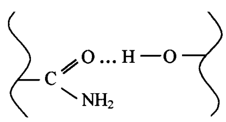
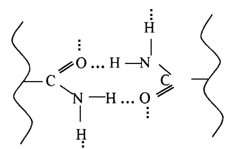
Polymer(s)	Line[1)] number	ν, cm^{-1}	SD[2)], cm^{-1}	FWHM, cm^{-1}	SD, cm^{-1}	B_i, cm^{-1}	SD, cm^{-1}	χ^2
PAA	1	1618.274	0.270	62.855	0.499	17.186	0.135	0.071
	2	1642.390	0.593	20.535	1.014	1.905	0.084	0.071
	3	1662.912	0.129	26.062	0.249	13.570	0.115	0.071
	4	1676.927	0.288	12.039	0.449	2.160	0.071	0.071
	5	1689.572	0.143	17.281	0.264	4.281	0.066	0.071
	6	1707.960	0.340	7.911	0.974	0.258	0.013	0.071
	7	1722.644	2.297	9.800	6.668	0.013	0.015	0.071
InterPC (PVA + PAA)	2	1616.908	0.151	61.759	0.488	21.393	0.167	0.076
	3	1640.791	0.347	17.503	1.576	1.478	0.094	0.076
	4	1659.003	0.105	24.638	0.400	10.561	0.132	0.076
	5	1668.481	0.472	13.831	0.738	2.435	0.094	0.076
	6	1680.203	0.143	15.315	0.402	4.588	0.094	0.076
	7	1692.205	0.097	16.933	0.373	4.236	0.076	0.076
	8	1708.483	0.515	9.706	0.614	0.586	0.040	0.076
	9	1723.511	1.612	18.928	0.920	0.878	0.030	0.076

[1)]The line number corresponds to separate bands in Fig. 5. [2)]The standard deviations of corresponding values.

The vibration bands in amide I and amide II region and corresponding hydrogen bonds structures of PAA and InterPC thin films are represented in Table 3.

The band at 1704–1708 cm^{-1} of low intensity, present both in PAA and InterPC spectra, is related to the group of amide I bands (overwhelming contribution of $\nu_{C=O}$ vibrations) and characterizes the stretching vibrations of the carbonyl group in a free amide group (structure II in Table 3). Such a conclusion is confirmed by the data on low-molecular-weight primary amides in an inert solvent CCl_4 [25]. According to [25], the free primary amide group also displays the bands of $\nu_{s\,N-H}$, ν_{asN-H} vibrations near 3415 and 3530 cm^{-1}, and the band amide II at 1588–1590 cm^{-1}, which is of mixed nature: the contribution of δ_{N-H} in-plane vibrations stands for ~60%, while the contribution of ν_{C-N} vibrations is ~40% (Table 3). However, these bands cannot be detected in considered spectra (Fig. 4) as they are overlapped and obliterated by more intense bands of ν_{N-H} and of δ_{N-H} vibrations of bound amide groups. Moreover, the bands of ν_{asN-H} vibrations of free amide groups are superimposed on the bands of ν_{O-H} vibrations related to bound water (3550–3750 cm^{-1}). Also, an intense band of ν_{O-H} vibrations of bound -OH groups is superimposed on the ν_{sN-H} band of vibrations in the InterPC spectrum (Figure 4 b). Note that the bands related to bound water, corresponding to ν_{O-H} and δ_{O-H} vibrations (the latter at 1638–1641 cm^{-1}), are seen in all spectra in spite of careful drying of the films (Table 3).

Table 3. Hydrogen bonds structures in PAA and InterPC (PVA + PAA).

Vibration type	PAA	InterPC	The structure of chemical groups or hydrogen bonds
$\nu_{C=O}$	1723	1724	 I
	1708	1708	 II
$\nu_{C=O}$ amide I	1690	1692	 III
	1677	1680	
	–	1668	 IV
	1663	1659	 V
δ_{O-H}	1642	1641	Adsorbed water
$\delta_{N-H} + \nu_{C-N}$ amide II	1618	1617	Associated N–H groups in *trans*-position to C=O groups

The involvement of >C=O and / or -NH_2 parts of amide groups in the formation of H-bonds is detected through the lowering of $\nu_{C=O}$ and ν_{N-H} frequencies, and through the rise of frequency of amide II band. It also causes an increase of intensity and of FWHM of the corresponding bands [26–30]. The drop of $\Delta\nu$ and an increase of the absorption coefficient depend on the H-bond structure (its strength) [28,29] and on the quantity of these groups in a continuous sequence of H-bonds, *i.e.* on the length of an appropriate associate [27,30,31].

The band at 1659–1663 cm^{-1} of highest intensity and of maximum value of $\Delta\nu$ is related to the amide I vibration ascribed to a cyclic *cis*-dimer or *cis-trans*-multimers (structure V in Table 3). It is known that such structures are formed by the low-molecular-weight primary and secondary amides under the condition that the creation of *trans*-associates is sterically impossible [25]. The intense band at 3210 cm^{-1} related to bound -NH_2 groups also confirms the existence of *cis*-dimers (*cis-trans*-multimers) in PAA and InterPC spectra (Fig. 4 b) [25].

The two vibration bands at 1676–1680 cm^{-1} and 1690–1692 cm^{-1}, observed in PAA and in InterPC spectra (Fig. 4,5) and showing sequentially decreasing $\Delta\nu$ values, are related to vibrations of bound and free >C=O groups in *trans*-associates (structure III in Table 3). The formation of *trans*-multimers was proved in N-mono-substituted low-molecular-weight amides and in polyamides, where the amide group possesses a planar *trans*-conformation [27,30–32]. The difference of the $\nu_{C=O}$ vibration frequency of the terminal carbonyl groups in *trans*-multimers with respect to carbonyl groups in free amide groups is expected [25]. In the region of ν_{N-H} vibrations the formation of *trans*-multimers is confirmed by two overlapped bands: a more intense of low-frequency band at 3350–3355 cm^{-1} (Fig. 4 b), related to hydrogen bonded-NH_2 groups, and a less intense but of higher frequency band (3400–3450 cm^{-1}), which characterizes vibrations of the terminal -NH_2 groups of *trans*-multimers [27,30]. Note that in this region of the spectrum two modes near 3100 cm^{-1} and 3300 cm^{-1} appear as small shoulders. The band at higher frequency may be probably assigned to the first overtone of the intense amide I band, and the band at lower frequency to the interaction of the first overtone of the amide I band with ν_{N-H} vibrations of hydrogen bonded -NH_2 groups (the Fermi resonance) [33].

The amide II band does not display a fine structure and appears as an uniform broad peak with maximum at 1616–1617 cm^{-1} (Fig. 5, Table 3). It is worth noting that in the region of $\nu_{C=O}$ vibrations a weak band is detected in PAA and InterPC spectra at 1721–1724 cm^{-1} (Fig. 5 a,b). Its appearance is possibly connected with the presence of small quantity of -COOH groups in individual PAA, which were formed as a result of hydrolysis of acrylamide links. This band in spectra of carboxyl compounds is related to $\nu_{C=O}$ vibration of bonded -COOH groups of the "open dimer" type [34] (structure I in Table 3). Such type of binding of carboxyl groups points toward their participation in the formation of *trans*-multimers of amide groups. Near 1740–1745 cm^{-1} (Fig. 5a, b) a hardly-noticeable band of $\nu_{C=O}$ vibrations is seen which is probably related to unbound carboxyl groups on PAA chain and/or to acetate groups of PVA [25,28].

The band at 1668 cm^{-1} can be undoubtedly related to $\nu_{C=O}$ vibrations of PAA amide groups bound with PVA hydroxyl groups (structure IV in Table 3). Indeed, IR spectra of dilute solutions of low-molecular-weight primary amides display a band at 1672 cm^{-1} when an inert solvent such as CCl_4 is replaced by methanol, which interacts with the carbonyl moiety of amide groups [25]. The appearance of a separate band near 1668 cm^{-1} in InterPC spectrum unlike PAA spectrum, related to H-bonds between PVA and PAA, confirms the formation of InterPC in polymer mixture.

In order to establish the changes in InterPC structure with respect to PAA, the different fractions of amide groups in different states (with various H-bond networks) were compared. The basis for quantitative calculations are: i) the proximity of $\Delta\nu$ values of separate amide I bands in InterPC and PAA spectra, ii) the assumption about the absence of significant orientation effects in the thin films and iii) the validity of the Buger-Lambert-Beer law:

$$B_i = A_i \cdot l \cdot C_i \qquad (3)$$

where B_i is the apparent integral absorption coefficient of the i-band in a spectrum, A_i is the actual integral absorption coefficient of the given band, l – the thickness of the film, and C_i – molar concentration of the chemical groups in various states. As shown in Table 3, the amide groups of individual PAA can exist in 4 states, while in InterPC another state occurs (structure IV). Thus it can be written:

$$C = C_1 + C_2 + \ldots + C_i = \alpha_1 \cdot C + \alpha_2 \cdot C + \ldots + \alpha_i \cdot C, \qquad (4)$$

where $C_1, C_2, \ldots, C_i$ and $\alpha_1, \alpha_2, \ldots, \alpha_i$ – mole concentrations and fractions of the amide groups, which are in various states, and C – total concentration of amide groups in a film. Let us carry out the normalization of the i-band in a spectrum to apparent integral absorption coefficient of the ν_{C-H} vibration band of methylene groups (B_0), selected as an internal standard:

$$B_i/B_0 = A_i/A_0 \cdot C/C_0 \cdot \alpha_i = A_i^* \cdot X_{PAA} \cdot \alpha_i, \qquad (5)$$

where $A_i^* = A_i/A_o$ is the reduced integral absorption coefficient of the i-band, and $X_{PAA} = C/C_0$ is the mole fraction of acrylamide links (for individual PAA $X_{PAA} = 1$, while for InterPC $X_{PAA} < 1$, as C_0 reflects the total concentration of PVA and PAA links). Let us divide both parts of ratio (5) on X_{PAA}:

$$B_i/(B_0 \cdot X_{PAA}) = A_i^* \cdot \alpha_i \qquad (6)$$

In such a way we obtain the relation (6), in which all values in the left part are known: B_i and B_0 are determined from corresponding spectrum, and X_{PAA} for InterPC are easily calculated from the φ_{char} value. Assuming further that for the same amide I band:

$$A_{i\,PAA}^* = A_{i\,InterPC}^* \tag{7}$$

it is possible to compare the change of amide group fraction in i-state of InterPC with that of PAA.

The reduced apparent integral absorption coefficient of amide I bands in PAA and InterPC spectra are shown in Table 4.

Table 4. Reduced apparent integral absorption coefficients of separate amide I bands and effective length of the amide groups *trans*-multimers for PAA and InterPC.

Sample	$B_i^{1)}/(B_0^{2)} \cdot X_{n\,PAA}^{3)})$					$\beta^{4)} = B_{1679}/B_{1692}$
	ν ~1661, cm^{-1}	ν ~1670, cm^{-1}	ν ~1679, cm^{-1}	ν ~1692, cm^{-1}	ν ~1707, cm^{-1}	
PAA	8.37	–	1.33	2.64	0.16	0.50
InterPC	5.69	1.31	2.47	2.28	0.32	1.08

[1)]Apparent integral absorption coefficient of i-band in amide I region.
[2)]Apparent integral absorption coefficient of ν_{C-H} band (2935–2940 cm^{-1}) in an appropriate spectrum.
[3)]Molecular part of amide groups (acrylamide links) in PAA or InterPC.
[4)]Effective length of *trans*-multimers of amide groups.

The parameter β in Table 4 characterizes an "effective length" of *trans*-multimers of amide groups because the intensity of band of terminal >C=O groups of *trans*-associates (~1692 cm^{-1}) is proportional to the total number of such structures, while the intensity of band of bound >C=O groups (~1679 cm^{-1}) is proportional to the total quantity of amide groups participating in the formation of *trans*-associates [27,30,31].

The observed distribution of amide groups between various states caused by complex formation is shown in Table 5.

Table 5. Change of the amount of amide groups, in various states in InterPC in comparison with pure PAA.

Sample	$\alpha_i^{1)}/\alpha_{i\,PAA}^{2)}$			
	ν ~1661, cm^{-1}	ν ~1679, cm^{-1}	ν ~1692, cm^{-1}	ν ~1707, cm^{-1}
InterPC	0.68	1.85	0.86	1.99

[1)]Fraction of amide groups in i-state in InterPC. [2)]Fraction of amide groups in i-state in PAA.

As follows from Tables 4 and 5 data, the largest amount of *trans*- and *cis*-*trans*-multimers of amide groups is contained in PAA, but the length of *trans*-associates are minimal. The distribution of amide groups between various structures of bonds in InterPC with respect to PAA changes noticeably. First, the new type of bond (structure IV) appears. Simultaneously, the number of amide groups participating in the formation of *cis-trans*-associates decreases by about 1.5 times. The quantity of *trans*-associates decreases little (by about 14%), but their length increases more than twice. The content of free groups also rises twice, that indicates on a decrease of their accessibility in InterPC structure as a result, of its higher rigidity.

Hydrophobic interactions as the additional factor of stabilization of InterPC structure: The important role of hydrophobic interaction in the stabilization effect of InterPC structure in aqueous medium is well known [35]. The influence of this factor on complex formation of PVA with PAA was determined by the method of benzene solubilization. An example of solubilization curve is shown in Fig. 6, and calculated from such curves volumes of hydrophobic regions are presented in Table 6.

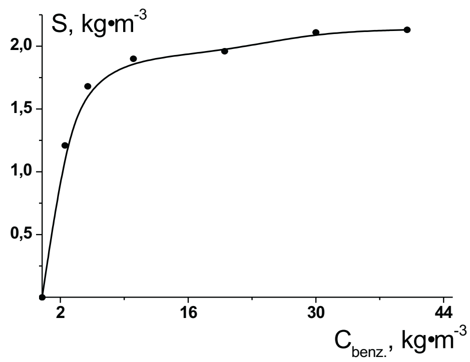


Figure 6. Solubilization curve for InterPC. T = 298 K.

Table 6. Solubilization parameters of PAA and InterPC.

Sample	S_{lim}, kg·m^{-3}	S_{red}[1)], kg·m^{-3}	N[2)]·10^{-3}	V[3)], nm^3
PVA	1.86	0.11	0.019	1.69
InterPC	1.83	0.08	4.543	408

[1)]$S_{red} = S_{lim} - S_0$, where S_0 is solubility of benzene in water (1.75 kg·m^{-3}).
[2)]The number of benzene moles connected with one mole of polymer or InterPC particle.
[3)]The size of hydrophobic regions V = V* · N, where V* = 0.09 nm^3 is a size of one benzene molecule.

Let us note that PAA is absent in Table 6, because it does not contain hydrophobic regions. However, InterPC possesses the developed hydrophobic regions that are evidenced by an additional contribution of hydrophobic interactions to stabilization of polycomplex particles in aqueous medium.

Two levels of cooperativity in PVA and PAA binding: It is known that in a dilute solution in reaction of the type:

P_1 (matrix) + P_2 $\Leftrightarrow$ Inter (P_1 + P_2),

where $Mp_1 >> Mp_2$, the formation of polycomplexes of constant composition φ_{char}, independently of the polymer component ratio proves the existence of two levels of cooperativity in polymer interaction [13]. The first level is connected with formation of the cooperative system of bonds between P_2 chains and appropriate parts of a matrix [36]. The second level is stipulated by an interaction of P_2 chains on a matrix. It is displayed in a disproportional distribution of P_2 between matrices during their filling [13]. In data of high speed sedimentation [12] for all relations of $C_{PVA}/C_{PAA} < \varphi_{char}$ the excess of unconnected PAA (matrices) was manifested on a sedimentograms as a separate peak. Two levels of cooperativity are also reflected in reaction between PVA and PAA. At the same time, all PVA chains do not contact with the matrix in InterPC, as shows the calculation. Really, one polycomplex particle at $\varphi_{char} = 4$ contains one PAA macromolecule and 444 PVA molecules. However, the quantity of short PVA chains, necessary for complete filling of PAA macromolecule is only 82. Therefore, the five-fold excess of PVA molecules comparing with necessary quantity is contained in the studied InterPC. The similar situation was observed when the complex between PVA and poly(acrylic acid) is formed [37].

The excess of PVA in the studied InterPC (PVA+PAA), and also in InterPC (PVA+poly(acrylic acid)) [37] can be explained as follows. In contrast to PAA (and poly(acrylic acid)) PVA has a small solubility in water, becoming worse at a great content of residual acetate groups. Therefore, the equilibrium of association of its molecules in aqueous medium:

$$n \cdot P_2 \Leftrightarrow (P_2)_n$$

is practically completely turned to the right. The interaction with PAA (or poly-(acrylic acid)) causes a destruction of PVA associates, as shown in Fig. 7.
However, this process is not completely accomplished. As a result, the small PVA associates are bound with PAA matrix and their additional interaction on the matrix (the second level of cooperativity) leads to a stability of the InterPC structure (Fig. 7). The interaction of PVA chains by H-bonds inside small associates on PAA matrix is confirmed by the intense absorption in IR spectrum of InterPC in the range of ν_{O-H} vibrations of bound hydroxyl groups (Fig. 4 b, curve 2). Really, according to φ_{char} of InterPC, D_ν/D_0 values in amide I region of InterPC spectrum (Fig. 4 a) are approximately four times less than analogous values (at the same frequencies) in PAA spectrum. But a different situation is observed in the other region (Fig. 4 b): D_ν/D_0 values of the band at 3350 cm^{-1} in spectra of InterPC and PAA differ only by about 2 times.

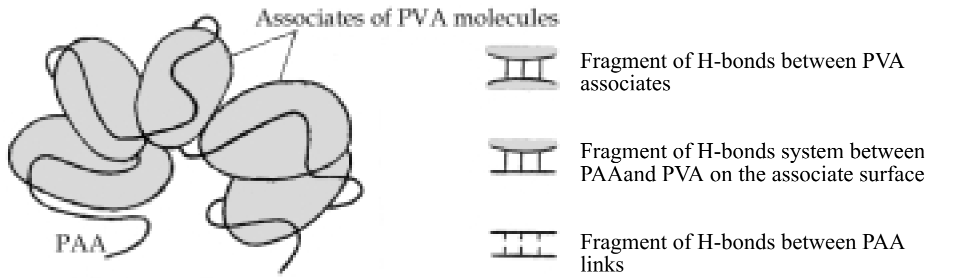


Figure 7. Schematic representation of InterPC (PVA + PAA) building.

Therefore, the band of ν_{O-H} vibration of PVA bonded –OH groups (at 3350 cm^{-1}) significantly contributies to the total absorption in this region. Note that the reaction between PVA and PAA resembles the process of self-assembly of the protein globules on a linear chain of a polyelectrolyte [38].

CONCLUSIONS

It is shown that when mixing PVA and PAA in water, InterPC of constant composition $\varphi_{char} = 4w_{PVA}/w_{PAA}$ is formed. The main factor of stabilization of InterPC particles is the system of hydrogen bonds between polymers. In IR spectra of InterPC, in contrast to PAA, a new amide I band ($\nu = 1668$ cm^{-1}), stimulated by hydrogen bonds between PVA and PAA, is detected. In InterPC structure the quantity of *cis-trans*--multimers of amide groups considerably decreases as compared with PAA, while the number of *trans*-multimers of amide groups is slightly reduced. However, the length of *trans*-associates is increased almost twice. The additional factor of stabilization of InterPC particles in aqueous medium is the hydrophobic interactions of non-polar parts of polymer components.

The complex formation between high-molecular-weight PAA (matrix) and considerably more lower- molecular-weight PVA results in partial destruction of associates of the latter. The two levels of cooperative effects characterize this reaction. The first level is promoted by formation of the cooperative system of H-bonds between PVA and PAA, and the second one is ruled by the interaction of PVA associates on the PAA matrix.

REFERENCES

1. Kabanov V.A. and Papisov I.M., *Vysokomolek. Soed. A*, **21**, 243 (1979).
2. Nikolaeva O.V., Budtova T.V., Kaluzhnaya L.M, Bel'nikevich N.G., Vlasova E.N. and Frenkel S.Ya., *Vysokomolek. Soed. A*, **41**, 1176 (1999).
3. Mun G.A., Nurkeeva Z.S., Chutoryansky V.V. and Mangazbaeva R.A., *Vysokomolek. Soed. B*, **43**, 552 (2001).

4. Mun G.A., Chutoryansky V.V., Nam I.K., Nukreeva Z.S. and Kudaibergenov S.E., *Vysokomolek. Soed. B*, **40**, 1403 (1998).
5. Annenkov V.V., Kruglova V.A. and Mazyar N.L., *J. Polym. Sci., Polym. Chem*., **34**, 597 (1996).
6. Pergushov D.V., Izumrudov V.A., Zezin A.B. and Kabanov V.A., *Vysokomolek. Soed. A*, **37**, 1739 (1995).
7. Zheltonozhskaya T.B., Kutsevol N.V., Momot L.N., Eremenko B.V. and Syromyatnikov V.G., Ukr. Pat. UA No 17242 A, (1997).
8. Zheltonozhskaya T.B, Momot L.N., Kutsevol N.V., Syromyatnikov V.G., Demchenko V.Ya. and Oleychenko V.M., Ukr. Pat. UA No 17814 A, (1997).
9. Alberg G., Nilson A. and Walsh G., Theoriya Splinov i Yeyo Prylozheniya, Mir, Moskwa 1972, 318 s.
10. Nurberger G., Approximation by Spline Function, Springer Verlag 1989, 243 p.
11. Izmailova V.N. and Rebinder P.A., Strukturoobrazovaniye v belcovykh systemakh, Nauka, Moskwa, 1974, 268 s.
12. Momot L.N., Zheltonozhskaya T.B., Permyakova N.M., Demchenko O.V., Romankevich O.O. and Syromyatnikov V.G., Abstracts of 7 Meeting of UK Polymer Colloids Forum, University of Surrey Guildford, 4–6 April 2001, England, 4P.
13. Papisov I.M., Baranovsky V.Yu. and Kabanov V.A., *Vysokomolek. Soed*., **17**, 2104 (1975).
14. Belenky B.G. and Vylentchik L.Z., Chromatographiya Polymerov, Moskwa 1978, 343 s.
15. Hong P.-D., Chow C.-M. and He C.-H., *J. Polymer*, **42**, 6105 (2001).
16. Bershtein V.A. and Yegorov V.M., Differentsyalnaya Skaniruyushchaya Kalorymetriya v Phyziko-Khimii Polymerov, Khimiya, Leningrad 1990, 256s.
17. Kuo S.W. and Chang F.C., *J. Macromol*., **34**, 4089 (2001).
18. Hseih D.-T. and Peiffer D.G., *J. Polymer*, **33**, 1210 (1992).
19. Zhang G., Jiang M., Zhu L. and Wu C., *J. Polymer*, **42**, 151 (2001).
20. Feng H., Feng Zh. and Shen L., *J. Polymer*, **34**, 2516 (1993).
21. Zheltonozhskaya T., Momot L., Permyakova N., Demchenko O., Phylypchenko S. and Syromyatnikov V., Abstracts of Polish – Ukrainian Conf. "Polymers of Special Applications", Radom Technical University. July 6–8 2000, Radom, Poland, p.132.
22. Zheleznova I.V., Shalbaeva G.B., Kaluzhnaya R.I., Zezin A.B. and Kabanov V.A., *Doklady AN SSSR*, **287**, 662 (1986).
23. Zhao W., Yu L., Zhong X., Zhang Yu. and Sun J., *J. Macromol. Sci. - Phys*., **B34**, 231 (1995).
24. Nishi T., *J. Macromol. Sci. - Phys*., **B17**, 517 (1980).
25. Dunkan A., Prymeneniye Spectroskopii v Khimii, Izd-vo inostr. lyter., Moskwa 1959, 159 s.
26. Skrovanek D.J., Howe S.E., Painter P.C. and Coleman M.M., *Macromol*., **18**, 1676 (1985).
27. Kuznetsov N.A., Moyiseenko V.M., Roganova L.A., Smolyansky A.L. and Shibaev V.P., *Vysokomolek. Soed. A*., **19**, 399 (1977).
28. Bellamy L., Noviye Danniye po IK Spectram Slozhnyh Molekul, Mir, Moskwa 1971, 320 s.
29. Molekularniye Vzaimodeystviya, Mir, Moskwa 1984, 600 s.
30. Kuznetsov N.A. and Smolyansky A.L., *Zhurn. priklad. spekt.*, **15**, 92 (1971).
31. Smolyansky A.L. and Shibaev V.P., *Vysokomolek. Soed. A*., **21**, 2221 (1979).
32. Hummel H. and Bonart R., *Makromol. Chem.*, **186**, 2049 (1985).
33. Lalov I.J., *Bolgarsky Phys. Zhurn.*, **12**, 560 (1985).
34. Zheltonozhskaya T.B., Harlanov V.M., Pop G.S. Eremenko B.V. and Uskov I.A., *Ukr. Chim. Zhurn.*, **59**, 987 (1993).
35. Mun G.A., Nurkeeva Z.S., Chutoryansky V.V., Kan, V.A., Sergazyev, A.D. and Shaichutdynov E.M., *Vysokomolek. Soed. B*, **43**, 1867 (2001).
36. Baranovsky V.Yu., Litmanovich A.A., Papisov I.M. and Kabanov V.A., *Europ. Polym. J*., **17**, 969 (1981).
37. Budtova T.V., Bel'nikevich N.G., Ivanova N.P., Kuznetsova V.A., Panarin Ye.F., Panov Yu.N., Sorokin A.Ya. and Frenkel S.Ya., *Vysokomolek. Soed. A*, **33**, 1664 (1991).
38. Izumrudov V.A., Kasayikin V.A. and Yermakova L.N., *Vysokomolek. Soed. A*, **23**, 1365 (1981).