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Polymer-colloid Complexes in Three-component System: Poly(styrene-*alt*-maleic acid)-Poly(ethylene oxide)-Silica Sol in Aqueous Medium

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Summary: Complex formation in the model three-component system, including polymer–polymer complex of poly(styrene-*alt*-maleic acid) (PSMA) and poly(ethylene oxide) (PEO), and also silica sol (SiO_2) in aqueous solution as a function of molecular weight of PEO and the order of component mixing, were investigated. The degree of binding of PSMA links with PEO and SiO_2 as well as the Gibbs energy of formation of the polymer–polymer complex and polymer-colloid complexes were defined. It was shown that the main factor of stabilization of the structure is hydrogen bonds. The conditions of three-component polymer-colloid system are practically independent of the order of component mixing. The spontaneous formation of polymer–colloid complexes between chemically complementary polymers and small dispersed particles is considered as the main reason for the abnormally high binding ability of colloid particles to the polymer–polymer complex.

Keywords: conformational transition; hydrogen bonds; intermolecular polycomplex; polymer-colloid complex; structure

Introduction

The interest in theoretical and experimental studies of polymer-colloid systems such as polymer-colloid particles-solvent[1-5] has increased in the last years. It is stipulated by establishment of the role of macromolecules as regulators of stability of dispersions of particles much smaller than the size of macrocoils[6,7] and also by intensive development of the new nanophase materials science,[8] based on technologies of assembling composites from nanoparticles.[9] Much less attention is given to multicomponent polymer-colloid systems, which contain, besides smallest dispersed particles, also chemically complementary polymers,

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forming the polymer-polymer complexes (PPC).[10] At the same time, the binding ability of intermolecular and intramolecular[11] PPC noticeably exceeds that of individual polymers.[12,13] Actually they are binders of new generation.

We started study the three-component polymer-colloid system containing chemically complementary poly(styrene-*alt*-maleic acid) (PSMA) and poly(ethylene oxide) (PEO) and also polydisperse silica (SiO_2) in aqueous and aqueous-salt media in the works.[14,15] In such systems, the competitive processes stipulated by various energy of pair interactions of components and by polydispersity of colloid particles, occurred. It was interesting to characterize the state of the same system in two limiting cases, when the size of macromolecules (and PPC particles) is much less than the size of the dispersed particles, $R_P \ll R_{SiO_2}$, and, on the contrary, when $R_P \gg R_{SiO_2}$. The former was described earlier from the colloid chemistry viewpoints.[16] The present work is devoted to investigation of the latter case from the viewpoints of polymer–colloid reactions.

Two- and Three-component Systems Including Polymers and Particles

PSMA sample with $M_v=2.18 \cdot 10^5$ was obtained by hydrolysis of high-molecular fraction of the alternating poly(styrene-*alt*-maleic anhydride).[17] PEO1 with $M=4 \cdot 10^4$ (Merc, Germany) and PEO2 with $M_v=1.49 \cdot 10^5$ (WSR-701, USA) were used. Based on Aerosil A-175 (Oriana, Ukraine) with the specific surface $S=1.75 \cdot 10^5$ $m^2 \cdot kg^{-1}$, SiO_2 sol with $R=11.2$ nm was prepared. Complex formation in two- and three-component systems was studied by potentiometric titration, IR spectroscopy and viscometry. The titration was carried out in thermostatted cuvette under argon at $T=298$ K.[14] The IR spectra of thin (~5-9 μm) films of PSMA were measured on fluorite windows and were recorded with a UR-20 instrument (Germany). In the region of $\nu_{C=O}$ vibrations, the widened spectra (100 cm^{-1}/100 mm) were recorded and the computer separation of the strongly overlapped bands by the spline method[23] was carried out. Viscosity of polymer solutions was measured with an Ostwald type viscometer ($\tau_0=91.8$ s at 298 K). The ratio of the polymers in the SiO_2-PSMA-PEO system in aqueous solution was equal to characteristic composition φ_{char} of PPC (composition at which polymers are quantitatively bound to each other). SiO_2 sol concentration corresponded to 1 particle per 1

PSMA macromolecule (or per 1 particle of PPC). The ratio of polymers to particles in binary systems was the same as in the three-component one.

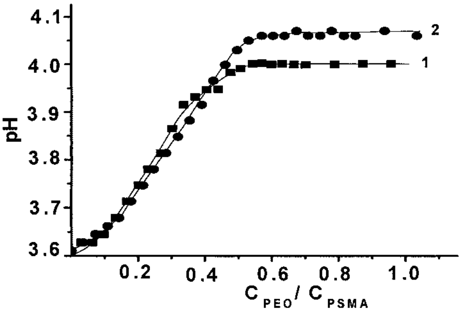
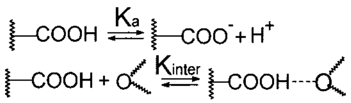


Fig. 1. pH in PSMA solution *vs* the relative concentration of *1* PEO1 and *2* PEO2. $C_{PSMA} = 0,7$ kg/m^3.

Let us consider first binary system. The complex formation of PEO with the non-fractionated PSMA sample was considered.[18,19] Interaction of PEO with a narrow PSMA fraction was studied similarly. The PPC formation was controlled by pH change of PSMA solution on addition of PEO solution (Figure 1). The φ_{char} value of PPC with PEO1 and PEO2 was determined on inflection points of curves 1, 2. The fraction of the polyacid bound with PEO, was determined by pH change in PSMA solution:[20]

$$C_b = C_0 - C, \theta = C_b / C_0, \tag{1}$$

where C_0, C and C_b are, consequently, the common concentration of PSMA links at some pH, and also concentrations of unbound and bound PSMA links in PPC at the same pH. Such calculation is based on the participation of PSMA COOH groups simultaneously in two complex equilibria: in the equilibrium of dissociation and in the equilibrium of formation of H-bonds with PEO:



The standard Gibbs energy of interaction of polymers $-\Delta G^0$ in PPC determined from the data of potentiometric titration of PSMA and PPC[21] (Figure 2a). PSMA is a polydibasic acid.[21]

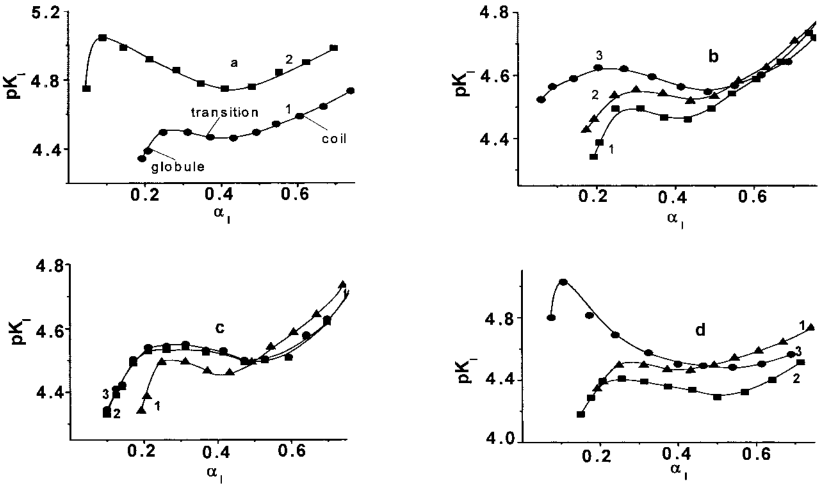


Fig. 2. Dependence of the negative logarithm of the effective dissociation constant of COOH groups of PSMA *vs* the dissociation degree for: *1* PSMA, *2* PPC (PSMA-PEO1) (a), *2* system PSMA+SiO_2 (φ=12.0) (b) and *3* PSMA+SiO_2 (φ=25.9 w_{SiO_2}/w_{PSMA}) (b), *2* system (SiO_2+PEO1)+PSMA (c) and *3* system (SiO_2+PSMA)+PEO1 (c), *2* system (PSMA+PEO1)+SiO_2 (d), *3* system (PSMA+PEO2)+SiO_2 (d) T=298 K.

In its macromolecules, at the first dissociation stage, the conformational transition such as globule-coil, occurs.[17,21] The transition manifests itself by three characteristic parts on the curves $pK_I=f(\alpha_I)$ (Figure 2 a, curve 1). The method of determination of the standard Gibbs energy of conformation transition, $\Delta G^o{}_I$ (or the standard Gibbs energy of a compact conformation of polyacids with opposite sign) is well known.[22] Using an analogous approach, the standard Gibbs energy of PSMA transition from the bound state in PPC to the isolated swelled coil $\Delta G^o{}_{(PPC\rightarrow PSMAcoil)}$ was determined from the curves $pK_I=f(\alpha_I)$ for PPC (Figure 2 a, curve 2). The extrapolation of initial parts of curves $pK_I=f(\alpha_I)$ to $\alpha_I=0$ was carried out by the Newton first interpolation formula. The parts of $pK_I=f(\alpha_I)$ curves corresponding to the titration of PSMA as isolated swelled coil, were extrapolated to low α_I values using the linear dependence between pH and $\log\alpha_I/(1-\alpha_I)$.[22] The Gibbs energy of interaction of the components in PPC was found by difference:

$$-\Delta G^o = -\Delta G^o{}_{(PPC\rightarrow PSMAcoil)} + \Delta G^o{}_{conf} \qquad (2)$$

The influence of M_{PEO} on PPC parameters is reflected by the data of Table 1. It is seen that the thermodynamic affinity between polymers in the followed interval of M_{PEO} grows.

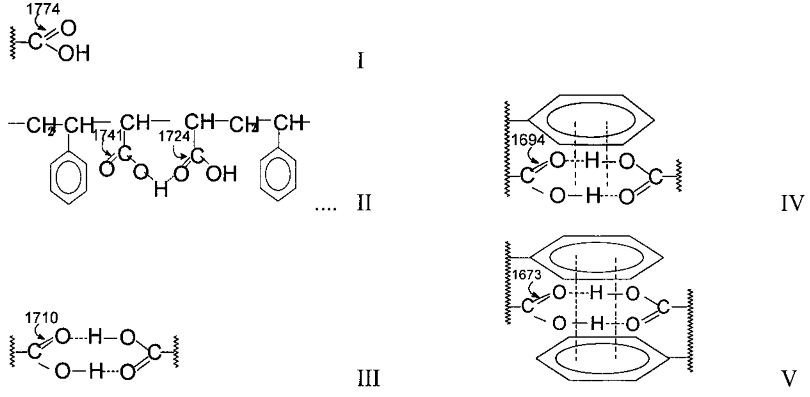
Table 1. Characteristics of PSMA compact conformation and InterPC (PSMA-PEO).

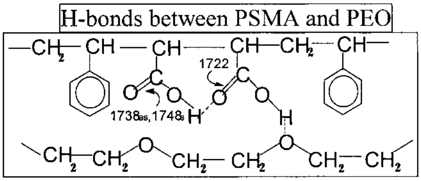
Polymer or PPC	φ_{char}, $w_{\mathrm{PEO}}/w_{\mathrm{PSMA}}$	φ_{char}, $\mathrm{mol_{PEO}/mol_{PSMA}}$	$pK_I^{0\ 1)}$	$[\eta]$, kg/m^3	θ, %	$-\Delta G^o$, kJ/mol
PSMA	-	-	2.62	-	-	0.226
PSMA+PEO1	0.39	1.95	2.71	0.011	54.4	0.675
PSMA+PEO2	0.52	2.60	2.57	0.012	65.6	0.74

1)Negative logarithm of the characteristic dissociation constant of COOH groups.

The structure of H-bonds in PSMA and PPC with various PEO was investigated earlier.[19] In a thin PSMA film a small part of COOH groups is free (Table 2, structure I), and the other groups participate in the formation of structures such as "open dimer" (structure II), cyclic dimer (structure III) and cyclic dimmer interacting with one (structure IV) or two (structure V) neighboring benzene rings. In IR spectra of PPC the splitting of the band 1741 cm^{-1} on symmetrical and anti symmetric components, and also the low-frequency shift and the sharp increase in integral absorption coefficient of the 1724 cm^{-1} band in the "open dimer" structure as a result of formation of intermolecular H-bonds (structure VI), were observed.

Table 2. PSMA COOH groups and hydrogen bonds.





VI

Complex formation between PSMA and SiO_2 sol is characterized by the data of Figure 2 b and Table 3. Previously, SiO_2 sol was mixed with PSMA solution during 24 h for the establishment of equilibrium of the complex formation. Parameters of polymer-colloid complexes (PCC) in Table 3 were determined by the above – mentioned method for Table 2. PSMA COOH groups and hydrogen bonds PPC. The correctness of such approach for the SiO_2-PSMA and SiO_2-PSMA-PEO systems was discussed in.[14] As it is seen (Figure 2 b, curve 2), the complex formation of PSMA with SiO_2 particles at $\varphi=12$ (w_{SiO_2}/w_{PSMA} 1 particle per 1 macromolecule) loosens the compact polyacid structure in solution (reduces the initial slope of a curve $pK_I=f(\alpha_I)$). However, it does not result in full destruction of such structure. In this case the Gibbs energy of interaction of components does not essentially exceed the $-\Delta G^0$ value for the compact PSMA conformation (Tables 1, 3). The fraction θ of the polyacid linked to SiO_2, is also insignificant. Further interaction of particles and macromolecules occurs when increasing the relative amount of particles in solution (up to $w_{SiO_2}/w_{PSMA}=\varphi=25.9$). This results in further swelling of the compact PSMA structure (Figure 2 b, curve 3) and increase in θ and $-\Delta G^0$ values (Table 3). At the same time the stability of a compact structure is still saved. These conclusions are confirmed by viscometric data (Figure 3, lines 1, 2).

Table 3. Parameters of PCC in water.

System	pK_I^0	Θ, %	$-\Delta G^0$, kJ/mol
PSMA-$SiO_2$$^{1)}$	3.93	32.1	0.265
PSMA-$SiO_2$$^{2)}$	4.74	71,5	0.718
(SiO_2-PEO1)-PSMA	3.92	45.3	0.784
(SiO_2-PSMA)-PEO1	3.93	46.0	0.779
PPC (PSMA-PEO1)-SiO_2	3.10	33.9	0.711
PPC (PSMA-PEO2)-SiO_2	3.45	55.0	1.302

$^{1)}$The SiO_2/PSMA weight ratio, $\varphi=12.0$ (1 particle per 1 macromolecule).
$^{2)}$$\varphi=25.9$ (more than 2 particles per macromolecule).

Structures of H-bonds between the copolymer and SiO_2 surface were determined by IR spectroscopy (Figure 4). By the most correct program of separation of overlapped bands based on the spline method,[23] more correct parameters of separate bands in the PSMA spectrum have been established (Table 4). The structures of H-bonds that correspond to these bands were already discussed (Table 2).[19] The 1673 cm^{-1} band that concerns to the structure V introduces the greatest contribution to the common absorption of carbonyl groups. The processing of PCC spectrum took into account: i) the relatively small degree of binding of PSMA to the surface (Table 3), and also ii) the possibility of formation with SiO_2 particles of similar H-bonds structures to those with PEO (structure IV). Therefore, among the established $\nu_{C=O}$ oscillations in PCC spectrum (Figure 4 b, Table 4), the bands of 1696, 1727, 1741 and 1765 cm^{-1}, it is possible to refer to PSMA links not connected to SiO_2, but to consider the appearance of other bands as the result of interaction between the copolymer and particles.

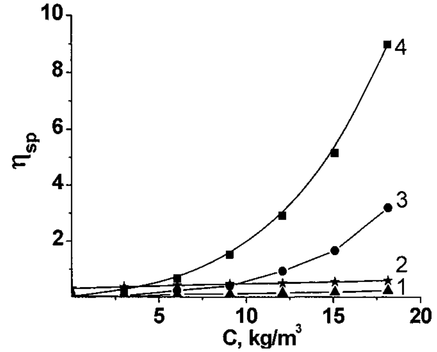
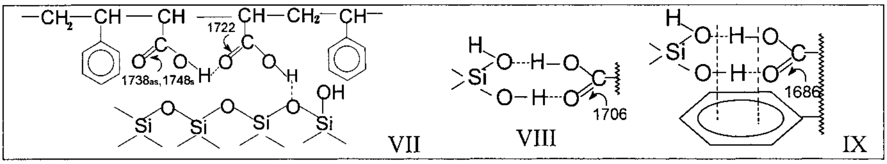
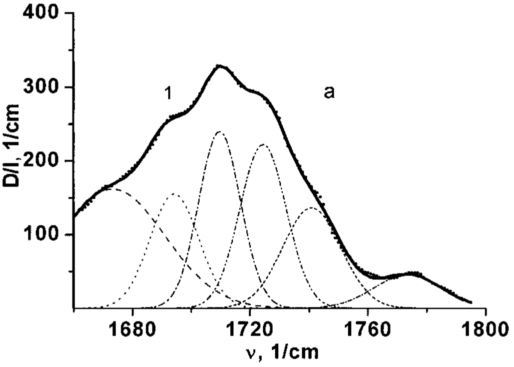
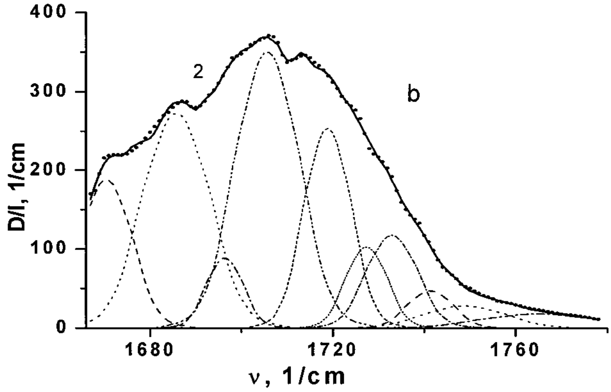


Fig. 3. Dependence of the specific viscosity of polymer-colloid systems *vs* concentration of SiO_2 for *1* sol, *2* PSMA-SiO_2, *3* PEO1-SiO_2 and *4* PPC (PSMA-PEO1)-SiO_2. T=298 K.

Thus in PCC spectrum, a low-frequency shift (3-8 cm^{-1}) of the $\nu_{C=O}$ bands of COOH groups, which are characteristic of cyclic structures of H-bonds (structure III-V in Table 2), is observed. The intensive band of 1719 cm^{-1} and two less intensive bands at 1733 and 1749 cm^{-1} appear. Besides, in the region of $\nu_{O\text{-}H}$ (Figure 4 c), the broad and most intensive 3230 cm^{-1} band stipulated by oscillations of ≡Si-OH groups forming hydrogen bonds,[24] appears. Simultaneously, in the $\nu_{C=C}$ region (Figure 4 d), the low-frequency shift and rise in the intensity of the benzene ring band are observed. The described changes in PCC spectrum allows to propose the following structures of H-bonds (structures VII-IX), between PSMA and SiO_2:







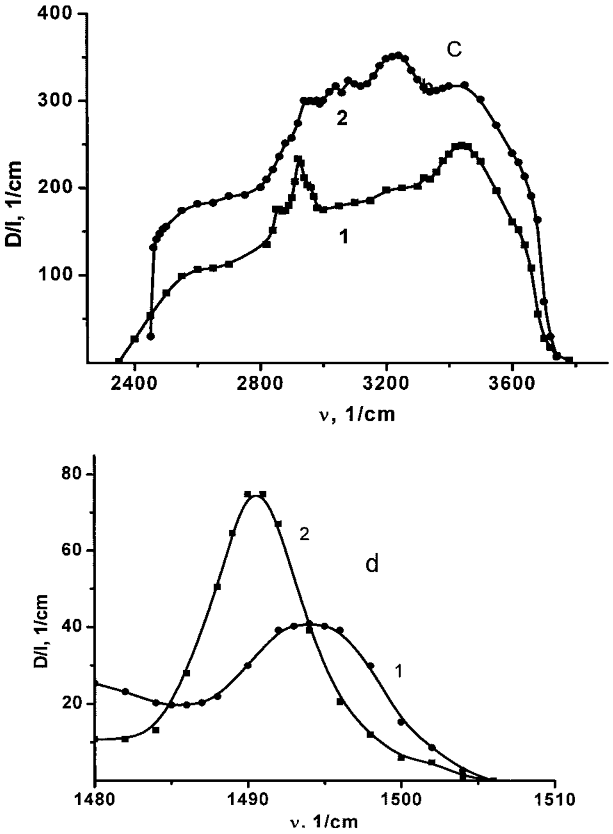


Fig. 4. IR spectra of *1* PSMA and *2* PCC (PSMA-S_iO_2) in the regions of $\nu_{C=O}$ (a, b), ν_{C-H}, ν_{O-H} (c) and $\nu_{C=C}$ (d) vibrations. Separate bands of $\nu_{C=O}$ vibrations are shown.

The ability of PEO to form H-bonds with the SiO_2 surface and to reduce its negative charge is well known.[24] At the same time, it was impossible to determine the Gibbs energy of complex formation of PEO with SiO_2 sol in such a way as in the system SiO_2-PSMA. Therefore, a more strong interaction of SiO_2 sol with the nonionic polymer is reflected only by a significant increase in PEO solution viscosity when raising the relative amount of SiO_2 particles (Figure 3, curve 3).

Table 4. Parameters of $\nu_{C=O}$ vibration bands in PSMA and PCC films.

Polymer or PCC	ν, 1) cm^{-1}	SD 2) cm^{-1}	FWHM, 3) cm^{-1}	SD cm^{-1}	B_i, 4) cm^{-2}	SD cm^{-2}	χ^2, 5) cm^{-2}	α, 6) %
PSMA	1673.3	0,5	42.1	1,0	7258	109	0.146	30.4
	1694.3	0,3	19.7	0,6	3248	86	0.146	13.6
	1709.7	0,3	16.8	0,5	4284	75	0.146	17.9
	1724.5	0,2	18.5	0,4	4395	85	0.146	18.4
	1741.0	0,3	23.3	0,5	3382	51	0.146	14.2
	1773.6	0,4	26.9	0,8	1320	35	0.146	5.5
PSMA-SiO_2	1670.5	0,4	12.9	0,9	2630	65	0.060	11.8
	1685.8	0,2	16.8	0,4	4969	67	0.060	22.2
	1696.3	0,2	9.4	0,3	896	79	0.060	4.0
	1705.7	0,1	16.0	0,3	6069	91	0.060	27.2
	1718.9	0,2	11.8	0,3	3242	76	0.060	14.5
	1727.4	0,3	10.4	0,6	1155	58	0.060	5.2
	1733.0	0,3	12.8	0,5	1627	59	0.060	7.3
	1741.3	0,4	11.5	0	585	39	0.060	2.6
	1748.9	0,8	20.7	0,5	624	38	0.060	2.8
	1765.0	1,1	28.1	0,1	550	30	0.060	2.5

1)Band position.

2)Standard deviations of corresponding values.

3)Band half-width.

4)Apparent integral absorption coefficient of a band. 5)Sum of squares of deviations of all calculated from experimental points. 6)Contribution of every B_i value in the total carbonyl absorption.

The three-component system SiO_2-PSMA-PEO is characterized by the potentiometric data (Figure 2, Table 3). In two cases, SiO_2 sol was mixed before titration with one of the polymers during 24 h. Then the other polymer was added and stirring was continued for 24 h. The use of PEO2 in these experiments resulted in sharp phase separation of the system on introducing the second polymer. That is why the data in Figure 2 and in Table 3 are shown only for PEO1. In the third case, SiO_2 sol was mixed during 24 h with PPC containing PEO1 or PEO2. It is seen, that in the two cases the curves $pK_I=f(\alpha_I)$ (curves 2, 3) and the parameters of the triple PCC calculated from them (Table 3) are practically the same. Therefore, the considered system does not depend on the order of introducing of polymer components. Note that θ and $-\Delta G^0$ values for triple PCC are higher than those for corresponding PPC (Table 1) and double PCC (SiO_2-PSMA). When the sol particles are added to PPC (PSMA-PEO1), the curve $pK_I=f(\alpha_I)$ (Figure 2 d) is similar to those obtained with the sequential addition of polymer components. However, the θ and $-\Delta G^0$ values for the triple PCC formed in this way are lower (Table 3). This means that the efficiency of interaction of the polymers and particles is reduced in the triple PCC formation. The rise in M_{PEO} in PPC is accompanied by a sharp increase in the stability of triple PCC. The change of the corresponding curve $pK_I=f(\alpha_I)$ in Figure 2 d, the growth of θ and $-\Delta G^o$ values in Table 3, and also the phase separation of the system confirm this.

Conclusion

In three-component system SiO_2 sol-PSMA-PEO in aqueous medium, a triple polymer-colloid complex is formed independently of the order of addition of components. In the complex, the energies of pair interactions essentially differ, therefore, it is thermodynamically most preferable. It can be assumed that a considerable scoring in entropy of the system is achieved in this case. The stability of the triple PCC grows with increasing M_{PEO}. The parameters of triple PCC such as θ and $-\Delta G^o$ do not depend on the order of addition of polymers to dispersed particles; however, they a decrease if the formed PPC is added to sol particles. The effect can be associated with the compact structure of PPC particles in water and advanced system of intermolecular H-bonds (Table 1). In this case the establishment of equilibrium in the triple PCC formation requires a greater time period, during which some H-bonds between PSMA and PEO are broken and small particles penetrate inside PPC. The spontaneous formation of the triple PCC in the system of chemically complementary polymers and small particles is a key to understanding an abnormally high binding ability of PPC colloid particles. Such effect is demonstrated, in particular, by the data of Figure 3 (curve 4).

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