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Interpolymer complexes between hydrophobically modified poly(methacrylic acid) and poly(*N*-vinylpyrrolidone)

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Abstract

The formation and structure of interpolymer complexes between amphiphilic multi-block copolymers—poly(dimethylsiloxane-*N*-vinylpyrrolidone) and poly(dimethylsiloxane-methacrylic acid)—were studied using potentiometric and conductometric titration, viscometry and fluorescence spectroscopy. The ratio of hydrophobic/hydrophilic groups in the copolymer and the molecular weight of each sequence were varied in order to establish the influence of these parameters on the interactions between the components. The complexation between pairs of block copolymers, of block copolymers and homopolymers as well as between homopolymer pairs was considered. The complexes were formed through the hydrogen bonding. They have a compact structure with a non-stoichiometric composition of pyrrolidone to methacrylic acid groups ratio around 0.6–0.7, with the exception of complexes formed between pairs of homopolymers and of copolymers with the shortest siloxane block. The difference between the new complexes and the ones formed from homopolymers, with equimolar composition, is explained by the spatial non-complementarity of the copolymers having a 'flower-like' structure in aqueous solutions.

Keywords: Interpolymer complex; Amphiphilic block copolymers; Hydrogen bonding

1. Introduction

Interpolymer complexes stabilised by hydrogen bonding have attracted much attention not only because they mimic the biological systems, but also because they present interesting solution and solid state properties, being good candidates for different technological applications such as carriers for enzymes and drugs, biological substrates, biosensors, light emitting diodes, etc. [1,2]. The complexes formed between poly(carboxylic acids) like poly(acrylic acid) or poly(methacrylic acid) (PMMA) and non-ionic proton accepting polymers like poly(ethylene oxide) or poly(*N*-vinylpyrrolidone) (PNVP) are the most studied ones. It was well established that complex formation in such systems is controlled by several critical factors such as minimal molecular weight, critical pH of complexation, minimal amount of active groups sequence, solvent nature, temperature, etc. [3–8]. It is also known that non-reacting groups may drastically change the complexation, i.e. if the amount of ionic groups exceeds 10% in a polyacid chain, the interpolymer complexation is prevented [9]. On the contrary, the introduction of hydrophobic groups may have different effects on the complexation ability, depending on the nature of the interacting polymers: it may prevent [9] or stabilise complexes [10,11] or shift the critical pH values [12].

The formation of complexes based on poly(methacrylic acid) and poly(*N*-vinylpyrrolidone) in aqueous medium was

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previously reported [1,2,6,13] and the influence of the molecular weight and temperature on the degree of complexation was discussed. It was shown that complexation occurs mainly through hydrogen bonding. However, it was assumed that hydrophobic and ion–dipole interactions should not be excluded, each type of bonding being more or less important depending on temperature. Using various investigation techniques, different authors reported two different compositions for PNVP+PMAA complexes, i.e. NVP/MAA=1/1 [2] and 3/2 [1,3]. The modification of PMAA or PNVP polymers through the introduction of hydrophilic but non-ionogenic groups leads to an important enhancement of complex stability [13]. Recent papers describe the influence of pH and polymer concentration on complexation and aggregation in aqueous PMAA+PNVP solutions [14,15]. The solid state behaviour of PMAA+PNVP complexes was also reported [16].

Considering the structure of PMAA and PNVP homopolymers and taking into account the interactions in poly(acrylic acid)+PNVP system described in Refs. [17,18], different types of interactions are supposed to be involved in the formation of PMAA+PNVP complexes, e.g. hydrogen bonding between COOH groups and carbonyl units of NVP cycles without or through the intermediate of water molecules, ion–dipole interactions between COO^- groups and polarised NVP cycles or involving NVP opened rings that could appear in acid or basic media.

In the present investigation the influence of hydrophobic chains attached to PMAA and PNVP on their complexation is studied. The presence of hydrophobic and flexible polydimethylsiloxane sequences (PDMS) in the new MAA or NVP containing block copolymers is expected to modify their complex formation ability. The influence of PDMS blocks on the characteristics of MAA and NVP copolymers in aqueous solutions had already been reported [19–21]. The present paper deals with complex formation between PDMS–PMAA and PDMS–PNVP segmented copolymers or/and between the mentioned copolymers and the corresponding mutually interacting homopolymers. Viscometry, potentiometry, conductometry and fluorescence spectroscopy were used to characterise the interactions between the (co)polymers in aqueous solutions.

2. Experimental

2.1. Materials and samples preparation

4,4′-Azobis(4-cyanovaleryl) chloride (ACVC) was synthesised according to the method proposed by Smith [22], starting from the corresponding diacid. *N*-vinyl-2-pyrrolidone (NVP) and methacrylic acid (MAA) monomers (Aldrich) were purified by vacuum distillation and kept under nitrogen in a refrigerator. $CHCl_3$, used for the solution polycondensation of ACVC with α,ω-bis(3-aminopropyl)-polydimethylsiloxanes ($SiO{-}NH_2$) was dried over P_2O_5 and distilled. Toluene was distilled over Na wire. Other solvents and reagents were high-grade commercial products and used without purification.

2.1.1. Sample preparation

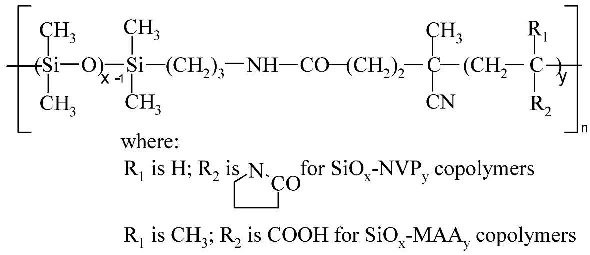
Poly(*N*-vinylpyrrolidone) (PNVP) of $M_n = 9\times10^4$ and poly(methacrylic acid) (PMAA) of $M_n = 2\times10^4$ were prepared by radical polymerisation of the corresponding vinyl monomers (concentration 20%) in the presence of 4,4′-azobis(4-cyanovaleric) acid in toluene solution. Their molecular weight was determined using GPC and viscometric methods (see details in Section 2.2).

The synthesis of amphiphilic poly(dimethylsiloxane-*b*-*N*-vinylpyrrolidone) and poly(dimethylsiloxane-*b*-methacrylic acid) block copolymers was performed through a multi-step procedure [23,24], implying the preparation of α,ω-bis(3-aminopropyl)polydimethylsiloxanes ($SiO_x{-}NH_2$) [25], of siloxane–amide macroazoinitiators (PSAA) and the radical polymerisation of vinyl monomers. In general, the radical polymerisation could result in a mixture of triblock (vinyl-SiO-vinyl) and multiblock copolymers $(\text{vinyl-SiO})_p$, due to the occurrence of two types of radical termination reactions-recombination and disproportionation. The ratio between the number average molecular weight M_n of the copolymers (obtained by GPC) and the calculated value of the siloxane-vinyl diblock sequence gives an average number of diblock segments, *n*, between 3 and 14. Thus, a multi-block structure of the synthesised copolymers has to be considered (Fig. 1).

The lengths of PDMS and vinyl sequences in the block copolymers are controlled through the preparation conditions of $SiO_x{-}NH_2$ precursor and by the concentration of azo groups with respect to the vinyl monomer, respectively [23,24]. The obtained samples are noted as $SiO_x{-}NVP_y$ (or $-MAA_y$) in the following, where *x* and *y* represent the polymerisation degrees of siloxane and vinyl sequences, respectively. The copolymer characteristics are presented in Table 1. The molecular weights of the copolymers determined by viscometry and GPC correlate well.

2.2. Methods

NMR technique (Bruker 400 spectrometer; BrukerBioSpin GmbH, Rheinstetten, Germany) was used to determine the ratio between siloxane and NVP or MAA sequences



$$\left[\left(\mathrm{Si(CH_3)_2{-}O}\right)_{x-1}\mathrm{{-}Si(CH_3)_2{-}(CH_2)_3{-}NH{-}CO{-}(CH_2)_2{-}C(CH_3)(CN){-}}\left(\mathrm{CH_2{-}CR_1R_2}\right)_y \right]_n$$

Fig. 1. Structure of amphiphilic siloxane-vinyl block copolymers.

Table 1
Characteristics of the (co)polymers

Sample	Siloxane block		Vinyl block		Vinyl/siloxane molar ratio	Vinyl block per 1 g of copolymer		M_v[a]	From GPC	
	DP[b]	M_n[c]	DP[d]	M_n[d]		(g)	(mol×10^{-2})		M_n	M_w/M_n
PNVP								90,000	52,900	1.60
PMAA								20,000	10,500	1.68
SiO_2–MAA_{76}	2.0	493	76	6600	38	0.93	1.081	189,800	115,400	1.52
SiO_{12}–MAA_{124}	12.4	1230	124	10,700	10	0.89	1.041	96,600	64,100	1.59
SiO_2–NVP_{71}	2.0	493	71	7900	35	0.94	0.847	26,500	27,100	1.49
SiO_2–NVP_{82}	2.0	493	82	9100	41	0.95	0.853	32,300	31,100	1.57

[a] Determined from viscometric experiments, see Section 2.2. for details.
[b] Obtained from ^{1}H NMR spectra of siloxane precursors.
[c] Calculated including the spacer.
[d] Calculated: $DP_{vinyl} = DP_{siloxane} \times$ vinyl/siloxane molar ratio; $M_n = DP_{vinyl} \times$ molecular weight of the structural unit.

from the integral ratio of characteristic peaks in ^{1}H NMR spectra (δ, ppm): (a) for SiO_x–NVP_y: 0.1 (Si–CH_3); 1.5–1.7 and 3.7–3.85 (PNVP chain); 1.5–1.7, 2.3–2.4 and 3.2–3.4 (PNVP cycle); (b) for SiO_x–MAA_y: 0.1 (Si–CH_3); 0.9–2.1 (–CH_2–C(CH_3)). The degree of polymerisation of siloxane sequence was established from ^{1}H NMR spectra of bis(3-aminopropyl)-terminated polydimethylsiloxane precursors (SiO_x–NH_2) and the degree of polymerisation of the vinyl sequence was calculated with the relation $DP_{vinyl} = DP_{siloxane} \times$ vinyl/siloxane molar ratio.

The GPC analysis was performed on a Waters Associates 440 apparatus (Polymer Laboratories, Shropshire, UK) in tetrahydrofuran, using polystyrene standards for both types of homo- and block copolymers. To avoid the polyelectrolyte effects, the MAA containing (co)polymers required a preliminary transformation of carboxylic groups into ester units by using diazomethane, according to a previously described procedure [19].

The surface tension was measured on a Processor K12 Tensiometer (Kruss, Hamburg, Germany) using the Wilhemy plate method. This technique was used to determine the critical aggregation concentration (CAC) [26]. The measurement interval varied between 1 and 500 mN/m with experimental error 0.01 mN/m. The surface tension decreases with the increase of (co)polymer concentration up to a constant value, thus showing two different slopes on the curve surface tension vs. (co)polymer concentration. The CAC value was determined as the abscissa of the intersection point of the two slopes. The surface tension values for SiO_x–NVP_y and SiO_x–MAA_y were around 37–39 and 47–48 mN/m, respectively. All analysed copolymers show a high efficiency in reducing the surface tension of water (72 mN/m for distilled water), though not as pronounced as in the case of cationic siloxane surfactants [27].

An Ubbelohde suspended-level capillary viscometer was used to perform viscosity measurements, both to determine the molecular weight, M_v, of the synthesised (co)polymers and to study interpolymer complex formation. In all cases the solvent flow time was long enough (higher than 2 min) for the kinetic energy and drainage corrections to be neglected. The intrinsic viscosities of the homo- and copolymers were determined for NVP containing polymers in water at 20 °C and for MAA containing polymers in 2 M $NaNO_3$ aqueous solutions at 25 °C. Considering that the content of SiO component in the copolymers is less than 10%, their viscosity average molecular weights (M_v) were calculated using Mark–Houwink equations established for the homopolymers, i.e. $[\eta] = kM_v^a$, where $k = 64 \times 10^{-5}$ mL/g, $a = 0.58$ for PNVP and $k = 44.9 \times 10^{-3}$ mL/g, $a = 0.65$ for PMAA [28]. This approximation was used earlier for other copolymers [29].

The interactions between components were studied as follows: the initial aqueous (co)polymer solutions of equal concentrations were mixed directly in the viscometer, under stirring, in different proportions and the flow time was measured. No buffer was used to modify mixture pH. For each mixture, two separate experiments were performed: (i) one component was diluted by another in the same viscometer up to the moment when the system became opaque, and (ii) the second component was diluted by the first one in the same way. This was done to avoid artefacts that could appear when continuing to measure an opaque mixture. The total (co)polymer concentration in the mixtures was kept in all cases constant at 0.2 g/dL. All experiments were performed at 25 °C. The experimental errors in the viscometric measurements were less than 3%.

Potentiometric and conductometric titrations were performed using a 716 DMS Titrine instrument (Metrohm, Herissau, Switzerland). The (co)polymer solutions were prepared in doubly-distilled water. The measurements were performed at 25 °C as follows: 25 mL of a dilute solution of one component (5×10^{-3} mol/L) was titrated with a more concentrated solution of the other component (5×10^{-2} mol/L) and pH or conductivity values were plotted vs. basic/acid active groups molar ratios. All experiments were performed at 25 °C.

Fluorescence spectra of pyrene in aqueous solutions of individual (co)polymers and of interpolymer complexes were measured at 25 °C as a function of polymer concentration using a LS50-B spectrofluorimeter (Perkin–Elmer, Optoelectronics, Wiesbaden, Germany). The optical path was 1 cm. Emission spectra were measured from 350 to 500 nm for identical sample volumes with the following parameters: $\lambda_{\text{excitation}} = 334$ nm; excitation slit width 2.5 nm; emission slit width—minimum 0 nm; emission filter 350 nm cut-off; scan speed 50 nm/min and two scans. The emission spectra recorded in the presence of the probe were corrected for the background signals. The sample preparation was previously described [19,20]. No buffer was used to modify mixture pH. CAC values were determined from the inflexion point of the ratio of the first to third vibronic bands I_1/I_3 of pyrene spectra vs. (co)polymer concentration. When I_1/I_3 of mixtures were studied as a function of mixture composition, the solutions initial concentrations were the same as in potentiometric and conductometric experiments: titrated solution of 5×10^{-3} mol/L and titrating solution of 5×10^{-2} mol/L.

3. Results and discussion

3.1. (Co)polymer properties

To follow the formation of interpolymer complexes between hydrophilic/hydrophobic block copolymers through hydrogen bonding, poly(dimethylsiloxane-*N*-vinylpyrrolidone) and poly(dimethylsiloxane-methacrylic acid) copolymers of different molecular weights and siloxane/vinyl ratios were prepared. The obtained SiO$_x$–NVP$_y$ copolymers are soluble in water, THF, chloroform, DMSO and DMF, while SiO$_x$–MAA$_y$ copolymers can be dissolved in toluene, alcohols, DMSO and water. The aqueous solutions of SiO$_x$–MAA$_y$ copolymers demonstrate polyelectrolyte properties, i.e. the increase of the reduced viscosity η_{sp}/C with copolymer dilution, as shown in Fig. 2 ($\eta_{sp} = \eta/\eta_0 - 1$, η being the solution viscosity, η_0, the solvent (water) viscosity; C, copolymer concentration in g/dL).

The overlap concentrations C^* of the SiO$_x$–MAA$_y$ and SiO$_x$–NVP$_y$ copolymers were determined from their intrinsic viscosities in 2 M NaNO$_3$ aqueous solutions at 25 °C and in water solutions at 20 °C, respectively, using the $C^* = 0.77/[\eta]$ relation [30] (Table 2). The values of C^* for all copolymers are in the 0.92–3.30 g/dL interval and depend on the nature of the vinyl block and on the molecular weight of the copolymers. The lowest C^* (and thus the highest intrinsic viscosity) value corresponds to SiO$_{12}$–MAA$_{124}$ sample that is characterised by the highest molecular weight and the smallest vinyl/SiO ratio.

The critical aggregation concentration for each copolymer was deduced through two methods: (a) the measurement of the surface tension of the copolymer aqueous solution [26], and (b) by using the polarity index I_1/I_3 determined from fluorescence spectra of pyrene in copolymer water solutions [31] (Table 2). Both methods gave reasonably similar values and the critical aggregation phenomena show the same dependence on vinyl/siloxane ratio in copolymers as the overlap concentration trend. Moreover, the CAC values for MAA containing multiblock copolymers are slightly higher as compared to the values previously obtained for triblock MAA-siloxane-MAA copolymers [19]. This difference between triblock and segmented copolymers could be explained by the formation in aqueous solution of inter-chain ‘clusters’ and of ‘flower-like’ micelle structures, respectively [20]. According to fluorescence studies in dilute solutions, PMAA sequences in ‘flowers’ appear to be more extended than in solutions of ‘cluster’-like triblock copolymers or of homopolymers at a given pH [19,20]. All interpolymer complexation studies performed in this work were carried out at concentrations between CAC and C^*.

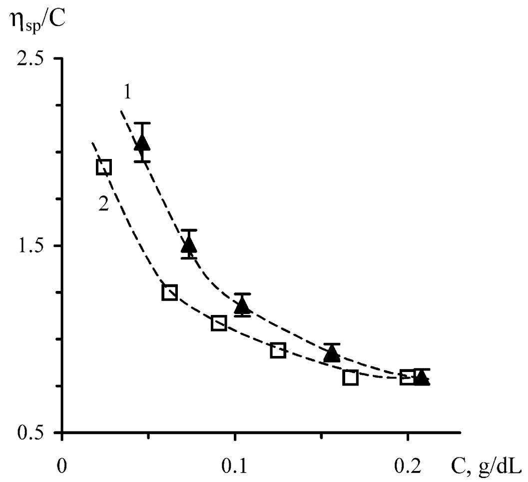


Fig. 2. Dependence of the reduced viscosity on polymer concentration for SiO$_2$–MAA$_{76}$ (1) and SiO$_{12}$–MAA$_{124}$ (2) copolymers. Lines are given to guide the eye.

3.2. Viscometric results

One of the simplest and widely used tests for the estimation of interactions in mixed polymer solutions is the measurement of mixture intrinsic viscosity vs. its composition. The experimental values of the mixture intrinsic viscosity have to be then compared with the calculated additive curve, which ignores the interactions between the components. Any deviations of experimental results from the additive curve would indicate the presence of specific interactions between the two polymers. This procedure is well known and has been described in many publications [9,10,32–36].

The classical way of calculating an additive curve is to measure the intrinsic viscosities of the initial components $[\eta]_1$ and $[\eta]_2$ and to calculate the mixture intrinsic viscosity at several compositions as follows: $[\eta]_{\text{add mix}} = W_1[\eta]_1 + W_2[\eta]_2$, where W_1 and W_2 are the weight fractions of each component in a given mixture (see, for example, Ref. [9]).

Table 2
Overlap C^* and critical aggregation CAC concentrations; each concentration is given in mol of active groups per litre and in grams of copolymer per dL

Smple	C^*		CAC			
			From superficial tension		From I_1/I_3	
	mol/L	g/dL	mol/L	g/dL	mol/L	g/dL
SiO_2–MAA_{76}	0.31	2.84	4.32×10^{-3}	4×10^{-2}	1.5×10^{-3}	1.3×10^{-2}
SiO_{12}–MAA_{124}	0.10	0.92	1.24×10^{-3}	1.2×10^{-2}	1.1×10^{-3}	1×10^{-2}
SiO_2–NVP_{71}	0.28	3.30	1.97×10^{-3}	2.3×10^{-2}	–	–
SiO_2–NVP_{82}	0.25	2.90	2.16×10^{-3}	2.5×10^{-2}	–	–

See Section 3.1 for details in C^* and CAC determination.

However, as far as one of the components (SiO_x–MAA_y) is a polyelectrolyte (Fig. 2), it is not possible to use the approach described above. In our case, the specific viscosities of mixtures $\eta_{\mathrm{sp\ mix}}$ of aqueous solutions at different compositions were measured. The additive curve was calculated using the following approximation:

$$\eta_{\mathrm{sp\ add}} = \eta_{\mathrm{sp\ 1}}(C_1) + \eta_{\mathrm{sp\ 2}}(C_2) \quad (1)$$

$\eta_{\mathrm{sp\ 1,2}}(C_{1,2})$ being the specific viscosity of each component at concentration C_1 and C_2 at which the copolymer is present in the mixture. The values of specific viscosities $\eta_{\mathrm{sp\ 1,2}}(C_{1,2})$ were measured in separate experiments by dilution of each component with water. The comparison of the measured and calculated values of the specific viscosities should give, in the first approximation, the indication of the interactions between the components. This procedure is described in several papers [32–36].

An example of the experimental dependencies of the mixture specific viscosity $\eta_{\mathrm{sp\ mix}}$ on the fraction of SiO_x–NVP_y copolymer in the mixture, $W_{SiOx\text{–}NVPy}+W_{SiOx\text{–}MAAy}=1$, is shown in Fig. 3 for the SiO_2–MAA_{76}+SiO_2–NVP_{71} and SiO_2–MAA_{76}+SiO_2–NVP_{82} mixtures (filled symbols represent experimental data, lines correspond to the additive dependences). The initial pH of SiO_x–MAA_y was 3.6. Other systems showed a very similar trend. It should be added that the complexation between homopolymers PMAA with PNVP were also tested using the viscometric method. It was practically impossible to measure the viscosity vs. mixture composition dependence due to immediate complex precipitation. Even at low initial polymer concentrations (0.1–0.2 g/dL) the addition of one solution to another induced strong increase in turbidity followed by precipitation. The interactions between homopolymers seem to be stronger as compared to those between block-copolymers.

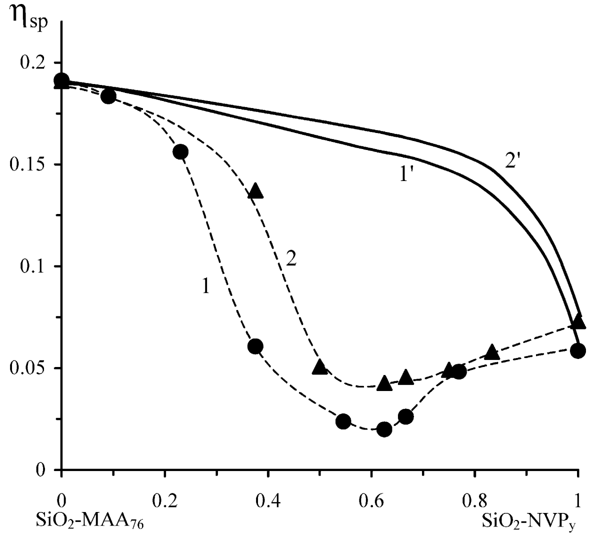


Fig. 3. Specific viscosity vs. mixture composition for SiO_2–MAA_{76}+SiO_2–NVP_{71} (1,1′) and SiO_2–MAA_{76}+SiO_2–NVP_{82} (2,2′) systems. Experimental data are shown with points (dashed lines are given to guide the eye); calculated additive curves are shown with solid lines (1′ and 2′). Total polymer concentration was 0.2 g/dL.

Eq. (1) for the additive dependence allows taking into account the real behaviour of the specific viscosity of each component with the decrease of its concentration during dilution in the mixture, in the case of the absence of any specific interaction. Due to the polyelectrolyte effect, the specific viscosity of SiO_x–MAA_y does not linearly decrease with dilution. That is why the calculated dependencies of $\eta_{\mathrm{sp\ add}}$ as a function of mixture composition (see solid lines in Fig. 3) show an upward curvature.

For all SiO_x–MAA_y+SiO_x–NVP_y studied mixtures there is a negative deviation of experimental data from the calculated additive viscosity values. Keeping in mind the results on homopolymer PNVP+PMAA complexation, one can conclude that an interpolymer complex of a compact structure is formed in the studied mixtures. It should be noted that at compositions in the range of $0.5<W_{SiOx\text{–}NVPy}<0.7$ the mixtures were opaque. This is also the indication that compact complexes are formed, like for homopolymer mixtures. Surprisingly, the block copolymer complexes are better soluble in water as compared to homopolymer complexes. This phenomenon can be explained by a higher spatial non-complementarity of SiO_x–MAA_y and SiO_x–NVP_y as compared to PMAA+PNVP system, caused by the presence of hydrophobic sequences that induce a specific conformation of the hydrophilic sequence in a selective solvent and may prevent reactive groups to interact with each other. As a result, some hydrophilic groups of the block copolymers remain not complexed and ‘help’ complexes dissolution.

The low concentrations of copolymers used in viscometric measurements were imposed by the low solubility limit of the interpolymer complexes. As a consequence, most of obtained specific viscosity values were low, between 0.03 and 0.1 inducing high experimental errors at minimum area, and it was not possible to precisely determine the ratio of NVP/MAA sequences in the complex. Thus, to further investigate the formation and composition of complexes between siloxane modified PMAA and PNVP polymers, potentiometry, conductometry and fluorescence spectroscopy were used.

3.3. Potentiometric/conductometric results

Fig. 4 presents typical curves of potentiometric and conductometric titration of acid (co)polymers with basic (co)polymers (curves 1 and 2) and of potentiometric titration of the inverse system (basic (co)polymers with acid (co)polymers, curve 3). The variations of pH and conductivity of aqueous solution of one (co)polymer were recorded during the addition of incremental amounts of a ten times more concentrated solution of the interacting partner.

The titration of acid copolymers with SiO_x–NVP_y copolymers (curves 1 and 2) results in hydrogen bonding interactions between COOH groups and pyrrolidone units. The formation of the complexes induces a displacement of the COOH dissociation equilibrium ($COOH \leftrightarrow COO^- + H^+$) to the undissociated form and, as a consequence, the concentration of H^+ in solution decreases, resulting in the increase of solution pH and the decrease of its conductivity up to constant values corresponding to the interpolymer complex composition. All studied systems, except the copolymer pair containing very short siloxane sequences (SiO_2–MAA_{76} + SiO_2–NVP_{82}), show non-stoichiometric complex compositions, contrary to the interpolymer complex formed through interacting PMAA and PNVP homopolymers (Table 3). Moreover, a non-stoichiometric composition was observed for the complex obtained by titration of a MAA copolymer having long siloxane chains (SiO_{12}–MAA_{124}) with PNVP homopolymer.

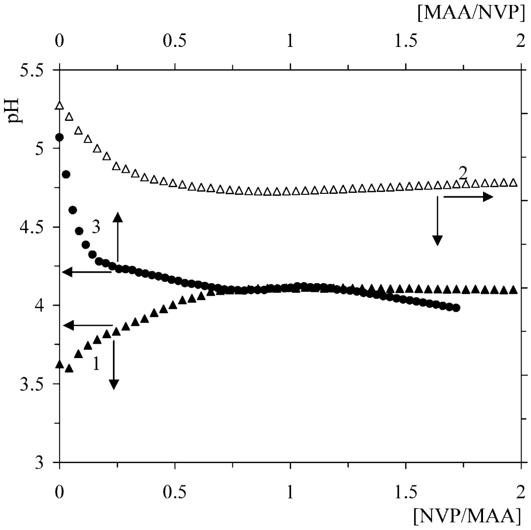


Fig. 4. Potentiometric (1, 3) and conductometric (2) curves for incremental addition of SiO_2–NVP_{71} to SiO_{12}–MAA_{124} (1,2) and for the inverse system (3). Titrated solution concentration is 5×10^{-3} mol/L and titrating solution concentration is 5×10^{-2} mol/L.

As far as (a) PNVP and PMAA form a stoichiometric complex and (b) vinyl sequences in multi-block copolymers are long enough to form interpolymer complexes (a critical molecular weight below which complexes are not formed is usually lower than 5×10^3), the most probable reason of the non-stoichiometric composition is a spatial one. The difference between the complexing behaviour of MAA and NVP homopolymers and that of siloxane-modified copolymers could be explained by the specific conformation of amhiphilic copolymers in water. Siloxane-MAA and siloxane-NVP copolymers were mixed at concentrations slightly higher than CAC. As reported earlier [20], in these conditions the copolymers adopt a 'flower-like' conformation, with a central part formed by the hydrophobic siloxane sequences and the external part consisting of a more or less extended coil of MAA segments. Due to steric and electrostatic repulsion effects, the flexibility of PMAA segments is lower as compared to that of PNVP chains. Thus, adding a flexible NVP copolymer over SiO_x–MAA_y should result in the accommodation of SiO_x–NVP_y along the sterically accessible part of the MAA copolymer, which is shorter than its total length.

In the inverse experiment, incremental amounts of a ten times more concentrated SiO_x–MAA_y copolymer solution were added over a dilute solution of NVP copolymer (Fig. 4, curve 3). First, the solution pH decreases drastically due to the accumulation of a not yet complexed polyacid. During dilution, some time is required for SiO_x–MAA_y micelles desaggregation, uncoiling of PMAA sequences and their accommodation to PNVP sequences. Thus, an induction period of the complexation process is needed. In the next stage, the slope of pH decrease is much lower because the COOH groups interact with pyrrolidone units and then it becomes constant, up to the complexation of all available NVP units (complex composition). The constant pH value corresponds to the same one obtained by titration of SiO_x–MAA_y copolymers with SiO_x–NVP_y copolymers (curve 1 in Fig. 4). Further addition of acid groups over the complex composition leads to a subsequent decrease of pH. Titrating base with acid (co)polymers results in complexes with MAA/NVP ratios similar to the ones obtained for the inverse systems (Table 3): they are close to equimolecular stoichiometry for the homopolymers and for the copolymers containing short siloxane chains (SiO_2–NVP_{82} + SiO_2–MAA_{76}) and slightly higher for the rest of the inverse systems.

3.4. Fluorescence analysis

Fluorescence measurements were carried out to obtain additional structural information of the complexes. Fig. 5

Table 3
Composition of complexes (NVP/MAA molar ratio) determined from potentiometric, conductometric and fluorescence measurements

Sample	Acid titrated with base			Base titrated with acid
	A	B	C	A
PMAA+PNVP	0.97	1.01	1.00	0.91
SiO_{12}–MAA_{124}+PNVP	0.66	0.71	–	0.75
SiO_2–MAA_{76}+SiO_2–NVP_{82}	1.10	1.02	1.01	1.00
SiO_{12}–MAA_{124}+SiO_2–NVP_{71}	0.71	0.74	–	0.85
SiO_{12}–MAA_{124}+SiO_2–NVP_{82}	0.62	0.72	0.50	0.74

A, from potentiometry; B, from conductometry; C, from fluorescence spectroscopy.

presents, as an example, the emission spectra of pyrene in aqueous solutions of a pure SiO_{12}–MAA_{124} copolymer (curve 1) and of SiO_{12}–MAA_{124}+SiO_2–NVP_{82} complex for 0.7 NVP/MAA molar ratio (curve 2). Both solutions had the same concentration of COOH groups (1.2×10^{-2} mol/L). The spectra of the pure copolymer solution and of the complex are very different. The emission intensity is significantly lower for the complex, indicating the change in pH value from low to higher values due to interpolymer complex formation (see Fig. 4, curve 1). The lowering of the emission intensity with the addition of SiO_x–NVP_y copolymer indicates a higher local polarity of the probe site and the final probe environment appears to be a result of intermolecular interactions of MAA with NVP groups leading to pH change.

The I_1/I_3 ratio of the intensities of the first to third vibronic bands of pyrene in SiO_x–MAA_y+SiO_x–NVP_y complex and in SiO_x–MAA_y aqueous solutions from fluorescence spectra gives a measure of the polarity of pyrene environment. The I_1/I_3 values, deduced from emission spectra as a function of [NVP]/[MAA] molar ratio for the complexes SiO_2–MAA_{76}+SiO_2–NVP_{82}, SiO_{12}–MAA_{124}+SiO_2–NVP_{82} and PMAA+PNVP are shown in Fig. 6. I_1/I_3 ratio shows fluctuations during the addition of a base (co)polymer to an acid (co)polymer due to conformational changes of polymers in the mixture, to pH variation and to the dynamic equilibrium of complexation. The last I_1/I_3 maxima values correspond to the complex composition (shown with arrows for each system, see the values given in Table 3). Curve 1 characterising the SiO_2–MAA_{76}+SiO_2–NVP_{82} mixture presents two maxima, the first one being probably due to the formation of a complex of another composition and having a conformation similar to the complex of higher composition, both of them almost equally excluding pyrene. Further increase of NVP/MAA ratio leads to the decrease of I_1/I_3 due to the accumulation of uncomplexed NVP (co)polymer, able to trap pyrene molecules. The complex stoichiometries obtained from fluorescence spectroscopy (Table 3) are quite similar to those determined by potentiometry/conductometry, i.e. compositions close to equimolecular values were obtained for complexes of homopolymers and of copolymers having short siloxane sequences and a non-stoichiometric composition was established for complexes with longer hydrophobic chains.

The I_1/I_3 ratio for the solutions at their complex compositions are higher than those obtained for the

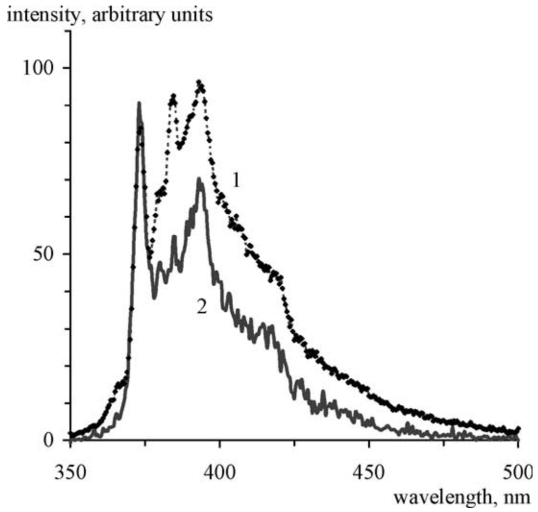


Fig. 5. Emission spectra of pyrene in an aqueous solution of SiO_{12}–MAA_{124} (1) and SiO_{12}–MAA_{124}+SiO_2–NVP_{82} complex (2) of 0.7 NVP/MAA molar ratio composition.

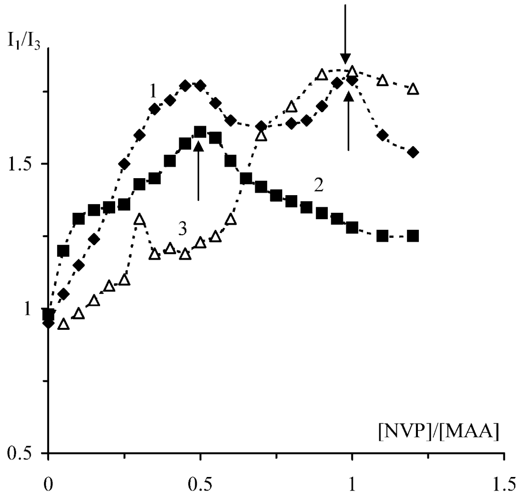


Fig. 6. The dependence of I_1/I_3 ratio on [NVP]/[MAA] for SiO_2–MAA_{76}+SiO_2–NVP_{82} (1), SiO_{12}–MAA_{124}+SiO_2–NVP_{82} (2) and PMAA+PNVP (3). Titrated solution concentration is 5×10^{-3} mol/L and titrating solution concentration is 5×10^{-2} mol/L.

Table 4
I_1/I_3 values for the initial (co)polymer solutions and for complexes; $C=2\times 10^{-2}$ mol of active groups

Sample	I_1/I_3
PMAA	1.15
SiO_2–MAA_{76}	0.98
SiO_{12}–MAA_{124}	0.88
PMAA + PNVP	1.82
SiO_2–MAA_{76} + SiO_2–NVP_{82}	1.79
SiO_{12}–MAA_{124} + SiO_2–NVP_{82}	1.61

corresponding solutions of pure (co)polymers (Table 4), but slightly lower than for pyrene in water solution (∼1.85), indicating that the complexes are able to solubilise small amounts of pyrene. The highest values for I_1/I_3 (1.82, 1.79) were observed for complexes obtained from PMAA and PNVP homopolymers and those containing short siloxane chains (SiO_{12}–MAA_{76} + SiO_2–NVP_{82}). These complexes are stoichiometric and thus very compact and exclude pyrene molecules to water environment. The complex containing MAA copolymer with longer siloxane sequences, SiO_{12}–MAA_{124} + SiO_2–NVP_{82}, is less compact as denoted by its lower I_1/I_3 value (1.61).

4. Conclusions

Non-stoichiometric hydrogen stabilised interpolymer complexes are formed between amphiphilic siloxane-*N*-vinylpyrrolidone and siloxane-methacrylic acid multi-block copolymers. These complexes are slightly better soluble in water than the ones formed from the corresponding homopolymers. The new complexes have a compact structure, the compactness decreasing with the increase of the length of the hydrophobic sequence. The molar composition of the complexes is non-stoichiometric, around NVP/MAA = 0.6–0.7, except for the pair composed of copolymers with the shortest siloxane blocks, where the complex has an equimolecular composition. The reason of the difference between complexes formed from homopolymers and from multi-block copolymers is the spatial non-complementarity of copolymers, the latter forming ‘flower-like’ micelles in aqueous solutions [20] at the studied concentrations.

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