Polymer 51 (2010) 122–128

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Comb-like poly(4-vilylpyridinium) salts with dodecylsulfate, sodium bis(2-ethylhexyl) sulfosuccinate and bromide counter ions. Small-angle X-ray scattering and dynamic light scattering study

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ARTICLE INFO

Article history:
Received 5 June 2009
Received in revised form
16 November 2009
Accepted 19 November 2009
Available online 26 November 2009

Keywords:
Comb-like polymer
Polyelectrolyte-surfactant complex
Poly(4-vinylpyridine)

ABSTRACT

Poly(4-vinylpyridine) derivatives alkylated with dimethylsulfate, octylbromide and dodecylbromide were synthesized. Bromide anions in the polymer salts were substituted with octylsulfate, dodecylsulfate or bis(2-ethylhexyl)sulfosuccinate (AOT) anions using ion-exchange reactions. The small-angle X-ray scattering (SAXS) studies of the structure of the comb-like polysalts demonstrated their highly-ordered structure. Loading the comb-like polycation with the surfactant anions leads to additional ordering of the polysalts structure. In the case of large AOT anions the transition from lamella to hexagonal structure is observed. Polyelectrolyte – surfactant complexes (PEC) of poly(4-vinyl-1-methylpyridinium) cation with octylsulfate and dodecylsulfate counter ions demonstrate a higher degree of order than the comb-like polymers having a similar chemical structure. The SAXS studies were complemented by dynamic light scattering study of the solutions of the polymers in chloroform. In the solution the comb-like polymers and their complexes with linear surfactants have coil conformations with the size of the coils close to that of the original poly-4-vinylpyridine. The conformations of PECs with octylsulfate and dodecylsulfate counter ions are more unfolded than those of the corresponding comb-like polymers.

1. Introduction

Self-assembly has recently become one of the main techniques for producing complex polymeric systems. Fragments of various lengths in this technique are bound via non-covalent bonds, such as ionic, hydrogen, and coordination bonds [1–4]. Self-assembly of biological macromolecules and amphiphiles is known to be a crucial prerequisite for life.

Complexes of linear or cross-linked polyelectrolytes and opposite-charged surfactants (polyelectrolyte–surfactant complexes – PSCs) form an important class of systems capable of self-assembly [5–12]. The growth of interest towards such systems during the recent decades is due to a series of very remarkable features. The ability of PSCs to self-assembly leading to formation of highly organized supramolecular nanostructures with various symmetry types is one of such features [13–27]. This class of systems also includes more intricate complexes, e.g. formed by two surfactants and one polyelectrolyte [28] or two polyelectrolytes and two surfactants [29]. The characteristics of self-assembled nanostructures can be determined by a series of various parameters, such as total concentration, ratio of charges, ionic force, chemical nature of the non-organic counter ion, pH, etc. The systems of this class also show structural and behavioral similarities with more complex biological macromolecular systems capable of self-assembly, such as lipoproteins and protein/DNA complexes [30,31]. Various practical applications of PSC are possible in such fields as microencapsulation and drug delivery, separation of proteins, stabilization and flocculation of colloidal dispersions, formation of separation membranes, coatings and responsive surfaces, and others [32–41]. We have used the ability of PSCs to form highly organized nanostructures, in particular, for creating nanoparticles of noble metals [42–46].

New PSCs have been synthesized recently, which are formed by comb-like polycations based on poly(4-vinylpyridine (P4VP)) and anionic surfactants (the original P4VP chains have been loaded with alkyl pendant groups and additionally complexed with surfactant). Fig. 1 shows that the obtained structures contain a high density of polymeric cationic groups (the counter ions located close

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doi:10.1016/j.polymer.2009.11.041

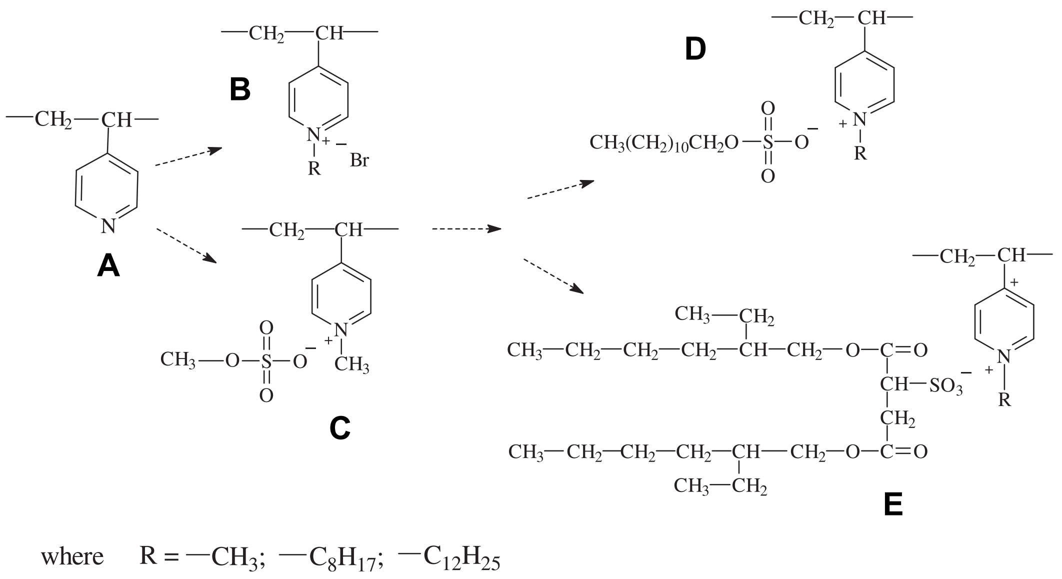

Fig. 1. Chemical structure of (A) P4VP; (B) P4VP alkylated with OB (R═C_8H_{17}, P4VPC8) or DDB (R═$C_{12}H_{25}$, P4VPC12), (C) P4VP alkylated with DMS (P4VPC1), (D) P4VPN (N = 1, 8, 12) with SDS (or OS) counter ion; (E) P4VPN (N = 1, 8, 12) with AOT counter ion.

to the main chain) and various quantities of long hydrocarbon residues (from one to three hydrocarbon chains per monomer unit of the polymer). The PSCs obtained were studied previously via scanning force microscopy (SFM) on a mica surface [47,48]. The results of the studies performed show a considerable increase in rigidity and unfolding of individual comb-like polycations upon their loading with large hydrocarbon residues of polycation chains and surfactants. At the same time the viscosimetry study of polymer solutions in chloroform has shown that the tendencies in changing the conformational state of the macromolecules in solution and on a flat surface of the anionic substrate are quite different [48]. The presence of 3D substitutes of cationic units of the polymer leads to a decrease in characteristic viscosity of the studied PSCs compared with that of the original neutral P4VP.

In the present work we continue the detailed study of conformational behavior of newly obtained PSCs using small-angle X-ray scattering (SAXS) as the major investigation tool to study the structural characteristics of the advanced nano-materials in the resolution range from about 1–2 to about 100 nm. The SAXS studies were complemented by dynamic light scattering measurements to provide a comprehensive description of the polyelectrolyte–surfactant complexes.

An important point in the study was also to compare the properties of comb-like polycations with those of similarly structured PSCs formed by the salt of the same original P4VP, but having shorter side substitutes and with surfactants as counter ions. It could be expected that, due to the labile nature of the ionic bonds between the surfactants and the polycations, the properties of the PSCs would differ from those of comb-like polymers.

2. Experimental section

2.1. Materials

P4VP ($M_w \approx 160{,}000$), sodium bis(2-ethylhexyl) sulfosuccinate (AOT), sodium octylsulfate (SOS), sodium dodecylsulfate (SDS), and dimethylsulfate (DMS) were obtained from “Fluka”, octylbromide (OB) and dodecylbromide (DDB), and also the organic solvents were obtained from “Aldrich”. Chloroform was distilled before use.

2.2. Synthesis of P4VP salts

Alkylation of P4VP with alkylbromides was performed in nitromethane under argon. The techniques for synthesis and rectification of the synthesized P4VP salts with octyl and dodecyl side groups (P4VPC8 and P4VPC12) are described in papers [47,48]. The techniques for exchanging the bromide anions with dodecylsulfate (SDS) and AOT are also given therein. The chemical structure of the synthesized polysalts is shown in Fig. 1. We shall use the following abbreviations for the polymeric salts: P4VPCNZ, where N is the number of carbon atoms in the alkyl groups of the pyridine ring, Z is the name of the surfactant anion. The structure of the synthesized polymers was verified via IR and NMR spectroscopy [47,48]. P4VP alkylated with DMS (P4VPC1) was synthesized by the reaction of the polymer with DMS in water-free ethanol solution at room temperature. Methylsulfate counter ions were exchanged for anions of OS, SDS, and AOT by the addition of 1.0 wt % solution of P4VPC1 in 1.0 wt % solution of the sodium salt of the surfactant. The charges of the polymer and of the surfactant were taken in equivalent amounts. The obtained precipitates were washed several times with 10^{-3} M solution of surfactant with 1-day intervals, and then with water. Upon centrifugation the precipitate was dried under vacuum up to constant weight at $T = 37\ ^\circ C$. In case of AOT synthesis a stable water suspension of polysalt was formed, which was coagulated via freezing at -5 °C. The properties of the obtained salts at room temperature are as follows: P4VPC8 and P4VPC12 are glass-like, P4VPC1AOT, P4VPC1SDS, P4VPC8SDS and P4VPC12SDS are wax-like, P4VPC8AOT and P4VPC8AOT are elastomers.

2.3. Fourier transform infrared (FTIR)

IR-spectroscopy measurements were performed on a “Bruker” “IRFS-113v” FTIR spectrophotometer equipped with a DTGS detector using samples prepared as KBr pellets. The spectra were recorded in the range of 1000–4000 cm^{-1} with the resolution of 2 cm^{-1}.

2.4. Dynamic Light Scattering (DLS)

Intensity correlation functions for the light scattered by the polymeric solutions were measured using the ALV-CGS-5000/6010 device for studying dynamic and static light scattering based on a 22 mW He–Ne laser (wavelength 632.8 nm). Mathematical processing of the correlation functions was performed with the CONTIN software package in order to obtain the distributions of relaxation times and hydrodynamic radii. All the dynamic light scattering experiments were set up for the 90° scattering angle using the solutions of the studied polymers in chloroform (viscosity is 0.54 mPa s) with polymer concentration of 1.0, 2.0, 3.0, and 4.0 g/l. Refraction index of chloroform is 1.44. The samples were freed from dust by filtering directly into the sample cell through “Millipore” membrane filters with average pore diameter of 0.45 microns.

2.5. *Scattering experiments and data analysis*

SAXS measurements were done on a laboratory diffractometer “AMUR-K”[49] (Institute of Crystallography, Moscow) at wavelength $\lambda = 0.1542$ nm in a Kratky-type (infinitely long slit) geometry [49] covered the range of momentum transfer $0.12 < s < 7.5\ \mathrm{nm}^{-1}$ (here, $s = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle). The thickness of the sample (about 1 mm) varied along the length of the sample holder so that the irradiated volume cannot be estimated and thus no absolute calibration was possible. The scattering profiles were corrected for the background scattering and primarily processed using standard procedures [50].

The quasi-periodic structures formed in the semi-crystalline materials (PSCs) gave rise to Bragg peaks in the isotropic scattering patterns. These peaks were analyzed to characterize the type of ordering following the standard procedures using the PRIMUS and PEAK software [50].

Lamellar structures were characterized by equidistant sequences of reflections: $s_n = 2\pi n/d_1$, $n = 1,2,3, \ldots$, where $d_1 = 2\pi/s_1$ is the periodicity of the ordered motifs computed from the position of the first peak in the scattering pattern. The two-dimensional hexagonal phase of long cylindrical micelles was determined by the sequence of Bragg reflections: $s_n = 2\pi(2/\sqrt{3})\sqrt{n}/d_1$, $n = (h^2 + k^2 + hk)$, where h, k are integer Miller indices, and the lateral separation between the micelles was calculated as $d_{\mathrm{hex}} = 2d_1/\sqrt{3}$. For the cubic phases, Bragg reflections occur at positions $s_n = 2\pi\sqrt{n}/d_1$, $n = (h^2 + k^2 + l^2)$, where h, k, and l are integers. The cubic cell periodicity is $d_c = d_1 = 2\pi/s_1$ (for the first observable reflection with Miller indices $hkl = 100$).

The mean long-range order dimension L (the size of crystallites) and the degree of disorder in the system Δ/d_1 were calculated as in paper [51]:

$$L = \frac{\lambda}{\beta_s \cos\theta_1} \tag{1}$$

$$\Delta/d_1 = \frac{1}{\pi}\sqrt{\frac{\beta_s \times d_1}{\lambda}} \tag{2}$$

where β_s is the full width at half-maximum intensity of the peak (in radians) observed at the mean scattering angle of $2\theta_1$ corresponding to the momentum transfer s_1, and Δ is the mean-square deviation of distances between the neighbouring regularly packed structure motifs.

3. Results and discussions

3.1. *Fourier transform infrared (FTIR)*

Fig. 2 shows FTIR spectra of P4VP and P4VPMe. Alkylation leads to complete disappearance of the bands corresponding to the valence oscillations in pyridine rings at 1597 and 1413 cm^{-1}, and to the appearance of the new bonds corresponding to the valence oscillations in the quarternized pyridine rings at 1644 and 1476 cm^{-1}. The strong absorbance at 1240 cm^{-1} indicates the presence of alkyl sulphate groups [48].

3.2. *Dynamic light scattering (DLS) technique*

The behavior of comb-like polycations and their salts with anionic surfactants on mica surface was previously studied with SFM [47,48]. It was shown that comb-like polycations adsorbed on the surface adopt much more extended conformations compared to those of the original P4VP. The increase (up to 2) of the number of hydrocarbon pendants per one charged unit of the backbone, when OS or SDS is the counter ion, leads to further unfolding of the polymeric salt macromolecule. The most extended conformations were observed when lipid-like AOT ions with two branched hydrocarbon groups were used as counter ions. Thus it could be expected that macromolecules of the corresponding polymers would have more extended conformations in solution, too. However, the viscosimetry data did not confirm this assumption. The intrinsic viscosities of polysalt solutions in chloroform were even somewhat less than that of the original flexible-chain P4VP.

DLS technique has a number of advantages compared to the viscosimetry studies. In particular, the viscosimetry technique causes a partial orientation of the macromolecules in the flux. DLS technique allows determining the relaxation time of the studied particles as well as their hydrodynamic radii. Besides, in the presence of electrostatic interactions between the soluble macromolecules, additional modes appear in the corresponding relaxation times distributions.

The shape of the self-correlation functions and relaxation time distributions is shown in Fig. 3 for P4VPC8. Correlation functions for all the samples with the exception of salts containing AOT as counter ions decrease monotonously, and the relaxation time distributions are unimodal curves. This indicates that the polymers in the solution form isolated polymeric coils. The dependences of the hydrodynamic radii of the studied samples vs. concentration are shown in Fig. 4. The interpolation of the concentration dependencies to zero concentration gives the values of R_{h}^{0} shown in Table 1. Fig. 4 and Table 1 show that the coil sizes obtained via DLS studies for comb-like salts P4VPC8 and P4VPC12 are somewhat greater, and those of P4VPC8SDS and P4VPC12SDS are somewhat smaller compared to the original P4VP. It can be assumed that the ion pairs in P4VPC8 and P4VPC12 are effectively solvated with chloroform which is moderately polar (dielectric permittivity ($\epsilon \sim 4.8$)), while in PEC the additional hydrocarbon groups of the surfactant ions ($\epsilon \sim 2.0$) completely screen ion pairs. As a result the effective affinity of the chains of P4VPC8 or P4VPC12 to the solvent is better than for PEC.

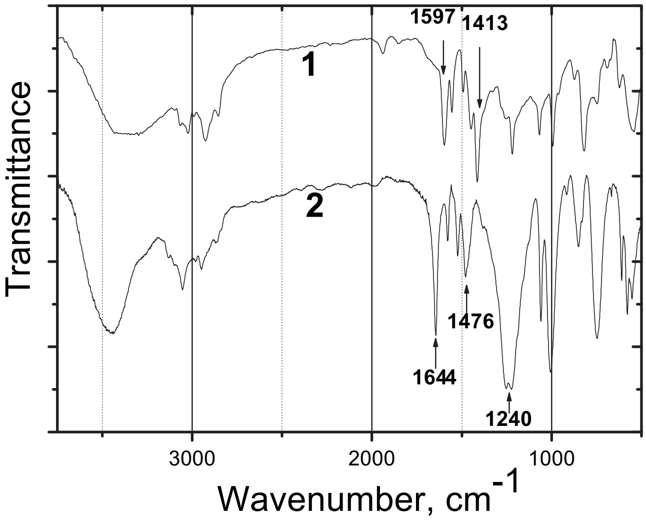

Fig. 2. FTIR spectra of P4VP and P4VPMe. The characteristic bands are shown with arrows.

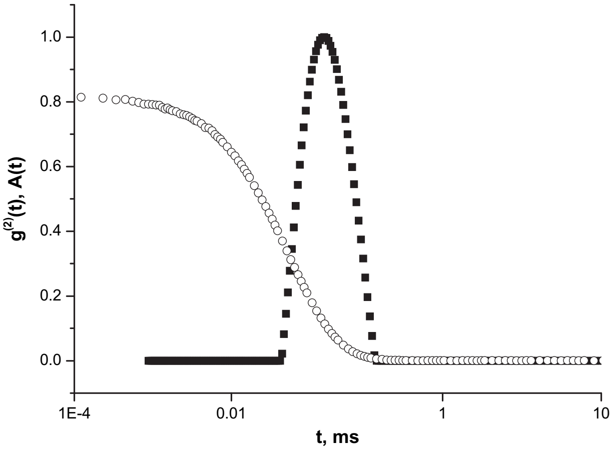

Fig. 3. Autocorrelation function and relaxation time distribution for P4VPC8. Concentration $c = 2.0$ g/l. Scattering angle $\theta = 90^{\circ}$.

The DLS study of the solutions of the comb-like polymer salts containing AOT counter ions have shown that correlation functions are not monotonously decreasing functions in the region of concentrations needed for the obtaining enough intensities for the DLS measurements. Moreover, the relaxation time distributions and calculated radius distributions are bi- or three-modal curves. The study of AOT containing salts is the subject of special investigation and the results will be published in the separate next paper.

The DLS technique was also used to study the solutions of P4VPC1OS and P4VPC1SDS in comparison with P4VPC12 and P4VPC8, respectively. The structure of PECs has much in common with that of comb-like polymers in respect of intermolecular interactions. In particular, ion pairs are formed in non-polar media by counter ions and cations of the backbone. The length of the surfactants' hydrocarbon chains equals that of the groups linked to the pyridine rings. Fig. 5(a, b) shows the size distribution for the P4VPC1OS and P4VPC8 (a) and for P4VPC1SDS and P4VPC12 (b) for sample concentration of 2.0 g/l. The distribution maxima for PECs are shifted towards greater R_h. The values of R_h^0 obtained from the DSL data shows that for polymer complexes P4VPC1OS and P4VPC1SDS, R_h^0 is 18 ± 2 nm, and 19 ± 2 nm, respectively. At the same time, similarly determined values for P4VPC8 and P4VPC12 are 15.3 ± 0.4 nm and 15.0 ± 0.5 nm, respectively (Table 1). Thus conformations of the P4VPC1OS and P4VPC1SDS PECs in chloroform solution are more extended than those of comb-like polymers with the same hydrocarbon residue. The observed difference can be explained by the mobility of the hydrocarbon fragments C8 and C12 in PECs. We assume that the ion pairs in PECs are more labile, so that they can be better solvated by chloroform, which has higher dielectric permittivity ($\epsilon \sim 4.8$) than ion pairs for the case P4VPC12 (P4VPC8) when hydrocarbon chain is chemically attached. Therefore the effective affinity of the chains P4VPC1SDS (P4VPC1OS) to the solvent molecules increases and the coil unfolds.

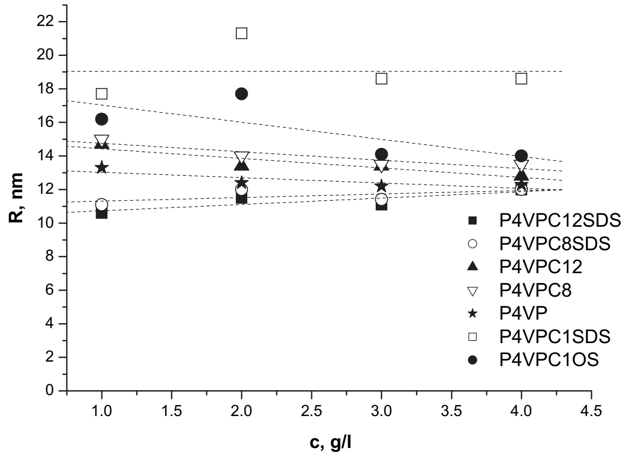

Fig. 4. Hydrodynamic radii of the polymer salts as a function of polymer concentration.

Table 1
The values of the hydrodynamic radius of the polymers under the study.

No.	Polymer	R_h^0, nm	Standard deviate, nm
1	P4VP	13.4	0.4
2	P4VPC8	15.3	0.4
3	P4VPC8SDS	11.0	0.5
4	P4VPC12	15.0	0.5
5	P4VPC12SDS	10.4	0.5
6	P4VPC1OS	18.0	2.0
7	P4VPC1SDS	19.0	2.0

3.3. Structural studies with small-angle X-ray scattering technique

Fig. 6 shows small-angle scattering diagrams for all the studied samples of salts of alkylated P4VP with octyl and dodecyl side groups and their complexes with SDS and AOT. Characteristic Bragg peaks can be seen in all the curves, which indicate the presence of

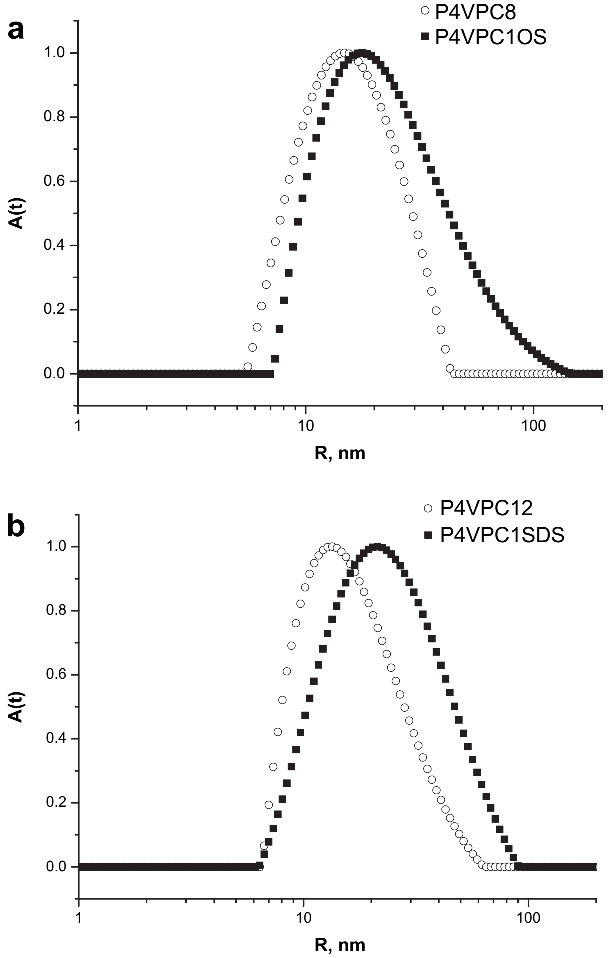

Fig. 5. Distribution functions of the hydrodynamic radii for P4VPC8 and P4VPC1OS (a), and P4VPC12 and P4VPC1SDS (b). $C = 2.0$ mg/ml, scattering angle $\theta = 90^{\circ}$.

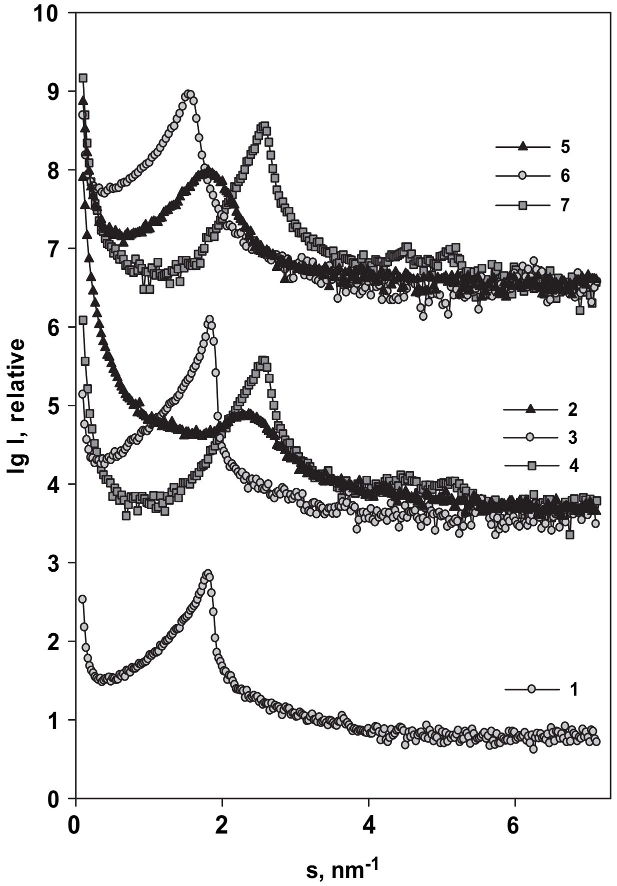

Fig. 6. Experimental curves for the small-angle scattering for the salts of alkylated derivatives of P4VP with octyl and dodecyl side groups and their complexes with SDS and AOT: 1, P4VPC1SDS; 2, P4VPC8; 3, P4VPC8AOT; 4, P4VPC8SDS; 5, P4VPC12; 6, P4VPC12AOT; 7, P4VPC12SDS.

periodical patterns in the samples. In case of the original polymers, where no surfactant ions like AOT or SDS are present (Fig. 6, curves 2 and 5), only a single Bragg peak is observed in each curve. These maxima are displaced with respect to each other on the angle scale: the maximum for P4VPC8 lies at 2.4 nm^{-1}, which corresponds to the quasi crystalline grid spacing of 2.6 nm, and the Bragg peak for P4VPC12 (Fig. 6, curve 5) corresponds to the wave vector of 1.85 nm^{-1} and grid spacing of 3.4 nm. The increase in the characteristic scale of the spatial polymeric network for P4VPC12 is most probably caused by an increase in the length of the hydrocarbon chains of the side groups, which separate the backbones. The other samples are characterized by the presence of three Bragg peaks in each curve, except for the P4VPC1SDS, which has two maxima. The first maxima for all the samples are rather well visible, whereas the other reflexes are very weak, especially for the P4VPC1SDS, P4VPC8AOT, and P4VPC12AOT, though their positions can be determined reliably enough.

In order to reduce the error in determining the structural characteristics based on Bragg peaks, the PEAK software was used at least 10 times for each sample with varying peak capture width, and the obtained parameters were averaged. The resulting calculation error was within 2%. The structural characteristics thus found are given in Table 2. The table shows that lamellar structure is characteristic for all the samples containing SDS, and the Miller indices obtained for comb-like polymers containing AOT can correspond either to cubic or hexagonal packing. The observed tendencies can be explained by the chemical structure of the studied compounds, which is shown in Fig. 1. The polycation chain and the ion pairs formed by pyridine cations and bromide anions or sulfogroups are located in the center. The chain is enveloped by a shell of hydrocarbon groups. It follows from the data in Table 2 that the decrease in length of the hydrocarbon substitute leads to a decrease of d from 3.4 down to 2.4 nm.

Note that the spacing d for all the polymeric salts studied having a single C12 group (chemically bound to the polymer or included into the counter ion molecule) are practically the same, $d = 3.4 - 3.5$ nm (Fig. 7). The length of the second group changing within the range from C1 to C8 does not affect the value of d. In case of P4VPC12SDS salt having two C12 chains, d increases up to 4.1 nm. This increase indicates the unfolding of the hydrocarbon chains due to their steric repulsion. Such steric interaction could be logically expected in case of a lamellar structure, when the polymer chains should be coplanar. In fact, lamellar structure is observed for all the studied PEC with linear hydrocarbon substituents. It was also observed in various studies for other PECs [14,20]. We suppose that the comb-like P4VPC8 and P4VPC12 having chemical structure close to that of P4VPC12SDS and P4VPC8SDS PECs also form lamellas with lower ordering degree.

The increase in volume and branching of the hydrocarbon substitute in case of AOT and a short methyl substitute do not lead

Table 2
Structural parameters of the synthesized polymer salts in bulk.

Sample	s, nm^{-1}	L, nm	$\Delta/\bar{d}$	s_n/s_1	Miller indexes		Type of packing and period, nm
P4VPC1AOT	2.45	90	0.06	1	100		Lamellar, $d_l = 2.6$
	4.95			2.0	200		Lamellar, $d_l = 3.5$
P4VPC1SDS	1.80	80	0.06	1	100		
	3.60			2.0	200		$d_1 = 2.6$
P4VPC8	2.40	20	0.12	–	–		
P4VPC8AOT	2.50	40	0.08	1	100	10	Cubic, $d_c = 2.5$; or hexagonal, $d_{hex} = 2.9$
	4.40			1.76	111	11	
	5.05			2.02	200	20	
P4VPC8SDS	1.90	80	0.06	1	100		Lamellar, $d_l = 3.4$
	3.80			2.0	200		
	5.60			2.95	300		
P4VPC12	1.85	20	0.12	–	–		$d_1 = 3.4$
P4VPC12AOT	2.50	50	0.07	1	100	10	Cubic, $d_c = 2.5$; or hexagonal, $d_{hex} = 2.9$
	4.40			1.76	111	11	
	5.10			2.04	200	20	
P4VPC12SDS	1.55	50	0.08	1	100		Lamellar, $d_l = 4.1$
	3.10			2.0	200		
	6.20			4.0	400		

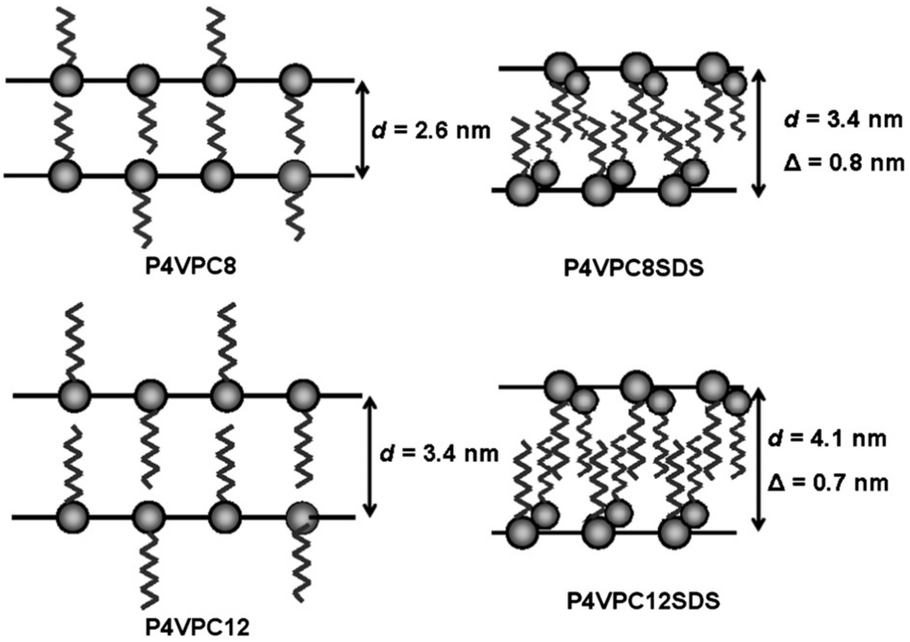

Fig. 7. Schematic representation of the structure of P4VP derivatives with octyl (P4VPC8) and dodecyl (P4VPC12) side groups and their complexes with dodecylsulfate.

to a change in the packing type of the PEC: the lamellar structure is preserved. However, addition of a second long hydrocarbon substitute (C8 or C12) causes a change in the symmetry type of polysalt. A limited number of secondary maxima in the small-angle scattering curves of the complexes of P4VPC8 and P4VPC12 with AOT do not allow determine unambiguously the type of their crystalline packing. However, based on the chemical structure of the polycation and AOT, we can suppose that the hexagonal phase is most probably formed. A schematic diagram of this structure for P4VPC12AOT is shown in Fig. 8. The polycation chain and the ion pairs formed by pyridine cations and anions of sulfogroups are located in the center of the cylinders. The chain is enveloped by a dense shell of hydrocarbon groups. It can be seen from the data in Table 2 that the distance between the centers of long cylindrical micelles (lateral component) does not depend on the length of the polymer's side chain and is determined only by the size of the micelles in the complex. Therefore we can assume that the conformations of side chains of the polycation are more winging in comparison with their conformations in the lamellas. The possible reason for the transition from lamella to hexagonal phases is stretching of the polymer chains due to volume interactions between the large side residues. Previously analogous effect of hexagonal phase formation was observed in the paper [12] for the zinc complex of P4VP derivative containing surfactant counter ions with two branched long hydrocarbon residues.

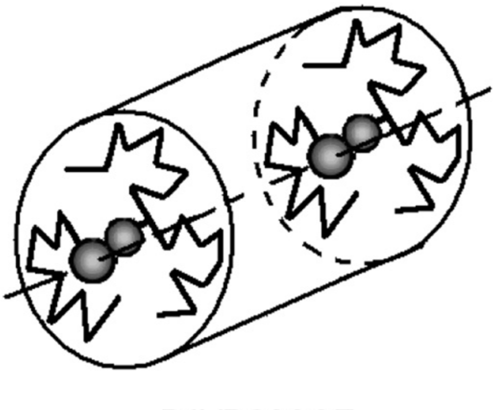

Fig. 8. Schematic representation of the hypothetical model of the structure of P4VP derivatives with alkyl side groups in complexes with AOT.

Note that the interaction of comb-like P4VP with amphiphilic molecules of AOT, OS, and SDS leads to a greater ordering in the system compared with the original polymers, which is expressed in a decrease of the parameter $\Delta/\overline{d}$ and so in an increase of the size of the crystallites. Thus complex formation is accompanied by an additional structuring of the samples. The latter assumption agrees well with the suggested hypothetical structure of the complexes. And finally, comparing the mean long-range order dimension *L* for P4VPC1SDS and for the similarly structured P4VPC12 demonstrates a greater ordering of the PEC. The latter is probably caused by the presence of a relatively labile ionic bond in the PEC.

4. Conclusion

This paper demonstrates that comb-like derivatives of alkylated P4VP salts and their complexes with OS, SDS, and AOT form highly-ordered structures in bulk. SAXS studies show that the length of the ordered domains increases markedly when the bromide counter ion of the polymer salts is substituted with OS or SDS anions. Loading of the comb-like macromolecules with large AOT anions leads to the transition from lamella to hexagonal structure. The density of the hydrocarbon shell around the macro ions with AOT counter ions is critical for the formation of the hexagonal packing. The decrease of the length of the polymer alkyl chain from 8–12 down to 1 results in the return to the lamellar structure of the polymer salt with AOT counter ion. In spite of the similarity in the chemical composition the structure of the comb-like bromide salts of alkylated P4VP is less ordered in comparison with that of polyelectrolyte complexes formed by P4VPC1 cations with octylsulfate and dodecylsulfate counter ions. This result is most probably due to the mobility of the counter ions of the surfactant in the complex. Dynamic light scattering investigation of the polymer solutions in chloroform has shown that the comb-like polymers and their complexes with linear surfactants have coil conformations with the size close to that of the original P4VP. The salts of the comb-like polymers containing AOT counter ions are an exception from this rule. Salts of P4VPC1 cations with octylsulfate and dodecylsulfate counter ions have more unfolded conformations. This result can be explained by better solvation of the mobile ionic pairs of the polysalts.

Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research (projects no. 07-03-91583 and 08-02-00555) for financial support. The work was also partially supported by the Leading Scientific School Program (project НШ-1955.2008.2).

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