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Polymerization of Dodecylammonium-2-acrylamido-2-methylpropane Sulfonate in Solvents with Different Dielectric Constants and Study of the Resulting Ionic Complexes

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Summary: Counterion polymerization of (DDA-AMPS) is suggested as a new route for preparation of organosoluble polyelectrolyte-surfactant complexes. The polymerization was performed in water and water-dioxane mixed solvent systems. Micellar properties of the monomer were studied. High molecular weight samples of the polymer complex (above 10^6) were obtained in solvent systems with high and small (0–5%) content of water. The complexes were studied in organic solutions by viscometry, isothermal diffusion, and by AFM on mica and as free films.

Keywords: counterion polymerization; dodecylammonium 2-acrylamido-2-methylpropane sulfonate; polyelectrolyte-surfactant complex; surfmers

Introduction

Complexes of polyelectrolytes and oppositely charged surfactants (polyelectrolyte-surfactant complexes – PSC) attract much attention due to their fundamental and practical interests.[1,2] Equimolar complexes are usually water-insoluble, but soluble in organic solvents, which enables to process them from organics for usage in water media.[3,4]

Formation of PSC is commonly realized by direct mixing of water solutions of surfactant and polyelectrolyte,[5] which leads to precipitation of the complex. This process is highly modular and cooperative.[6] Sometimes the process is complicated due to conformational changes of polyelectrolyte macromolecule and formation of microgels, which prevents complete conversion of interacting ionic groups.

The present work deals with a new approach to synthesis of PSC – polymerization of complex monomer consisting of surfactant molecule ionically bound with molecule of polymerizable organic compound in micellar or molecular solutions.

Polymerization in micellar solutions of ionic surfactants bearing polymerizable groups was first reported in 1958 by H.H. Fridman[7] and attracts much attention, especially over past decades.

Polymerizable surface active ionogenic monomers (surfmers) can be divided into three groups depending on the positioning of polymerizable group in their molecule. Locations of polymerizable groups in hydrophobic "tail" of surfactant molecule (T-type) and near to hydrophilic "head" - polar ionic groups (H-type) are most widespread and well-studied.[8] Polymerization of T-type surfmers results in formation of comb-like polyelectrolyte macromolecules with ionic group on the ends of lateral branches.[9] Polymerization of H-type surfmers gives also polyelectrolyte comb-like macromolecule, but ionic groups

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are located either in the main chain, or near to it. Molecules of both types are capable to form stable micelles in appropriate conditions, but they accept conformation of a random coil in non-micelle forming solvents.

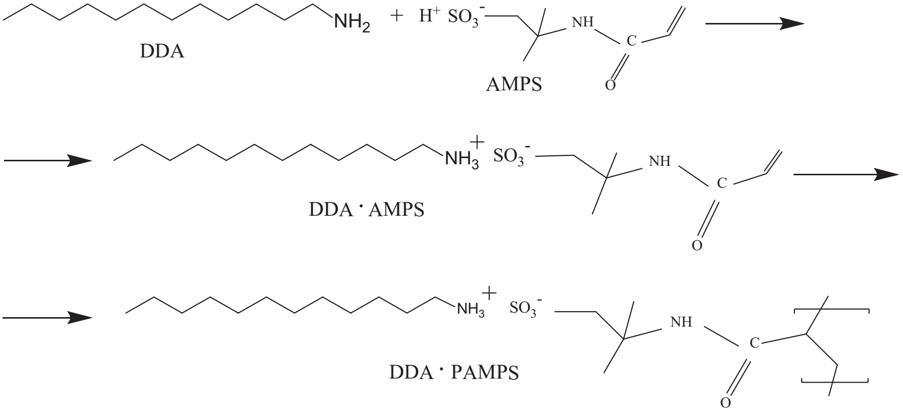
One more approach consists in location of polymerizable group in a counterion of surfmer molecule. It is presented in the literature much less. Polymerization of such monomers results in formation of polyelectrolyte-surfactant complexes which sometime can conserve structures and phase formed by surfmer. Authors[10,11] were the first to our knowledge, who reported surfmer counterion polymerization. They polymerized cetyltrimetylammonium metacrylate in direct micelles, which retain their shape. The product was not isolated and characterized. Yegorov[12] and Sanderson[13,14] polymerized concentrated solutions of dodecylammonium metacrylate and acrylate with conservation of the supramolecular structure. The products were insoluble in all tested solvents, which made unable molecular weight determination. Walker has published a set of papers dealing with synthesis and structural studies of polymer of three surmers with 4-vinylbenzoate counterion.[15–18] Water soluble nanoparticles have been formed as a result of the polymerization.

In this paper we report novel micelle-forming monomer dodecyl ammonium 2-acrylamido-2-methyl-1-propane sulfonate (DDA-AMPS), its micellar properties in water and water-dioxane mixed solution, polymerization in micellar and non-micellar states, and properties of the resulting products, including their solubility in different solvents and film-forming properties.

Generally DDA is used as surfactant with small chlorine or bromine counterions. DDA micelles association with acetate, chloroacetate and dicloroacetate were studied by M. Jansson[19] who showed that the highest degree of counterion binding displays the strongest dichloroacetic acid. Later the author studied degree of binding of DDA and location of organic counterions with respect to the micellar surface.[20]

Majority of counterion-polymerizable surfactants contain vinylbenzoate, acrylate or metacrylate weak anionic counterions. We have found no information about use of strong AMPS anion as polymerizable counterions.

We have not found also information about micellar properties of DDA-AMPS polymerizable surfactant salt. These properties were described in detail for its analogues – dodecylammonium alkylsulfonates (C_1-C_4).[21] Degree of counterion binding β at 30° was found to be 0.66 for C_1 and 0.79 for C_4. No information has been found concerning properties of the resulting polymerization product – poly(dodecylammonium 2-acrylamino-2-methylpropane-1-sulfonate). It is of interest to get answers for a set of questions concerning the above mentioned compounds.



Thus, the main aims of the work were synthesis and investigation of the monomer, its polymerization in solvent systems with different polarity (dielectric constant) and study of the polymer properties – solubility, molecular characteristics, film-forming properties etc.

Results and Discussion

Properties of the Monomer (DDA-AMPS)

DDA-AMPS is cationic surfactant consisting of hydrophobic tail and ammonium polar group with ionically bound polymerizable counterion AMPS. Conventional dodecylammonium surfactants (bromide, chloride) are known to form micelles in aqueous solution with cmc 13.1 mM (dodecylammonium chloride, DAC).[22] Cmc-1of dodecylammonium acrylate is 2 mM, cmc-2–270 mM and cmc-3–470 mM.[13]

We studied properties of DDA-AMPS solutions by viscometry, conductometry, and isothermal diffusion.

Viscometry study of DDA-AMPS aqueous solution shows two inflections on η_{red} – concentration plot which can be attributed to cmc-1 (0.5 g/dL, 12.7 mM) and cmc-2 (2 g/dL, 51 mM) (Figure 1).

Conductometry of DDA-AMPS aqueous solution has indicated cmc-1 at near the same concentration of 0.48 g/dL (12.2 mM) which is more accurate value (Figure 2a). The cmc-1value found for DDA-AMPS is very close to that of dodecylammonium chloride (DAC).

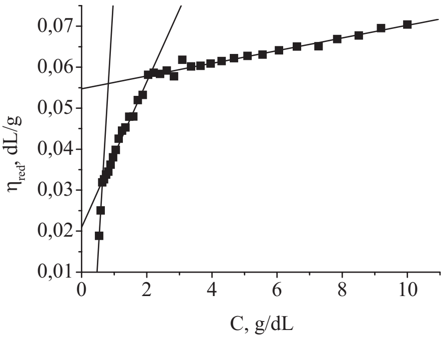


Figure 1.
Dependence of reduced viscosity on concentration of DDA-AMPS in water solution.

High solubility of DDA-AMPS in organic solvents (up to 30 g/dL in dioxane at 60 °C) makes possible formation of reversed micelles in non-polar media such as dioxane, THF, chloroform and dioxane-water mixtures. It is known that well organized reversed micelles are formed in non-polar media containing small amounts of water whereas only polydisperse aggregates formed in dry solvents.[23] Dioxane-water mixtures were chosen for this study to cover wide range of solvent dielectric permittivity (2.2 to 80).

In the mixtures containing more than 15% water characteristic inflections on conductivity vs concentration plot are observed (Figure 2b) which can be attributed to cmc-1, so micelle formation is suggested. Linear concentration dependence of conductivity is observed at 15% water content, which corresponds to

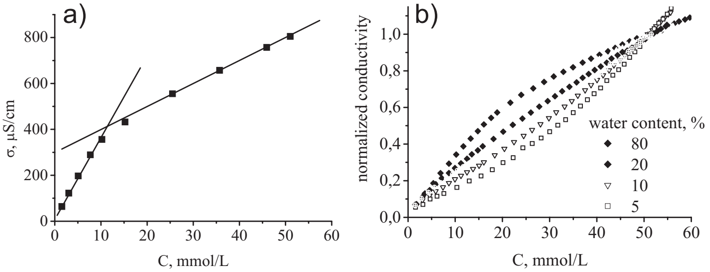


Figure 2.
Dependence of conductivity on concentration of water solutions of DDA-AMPS (a) and dependence of normalized conductivity on concentration of DDA-AMPS at different water content (b). All curves are normalized to conductivity of 50 mM solution.

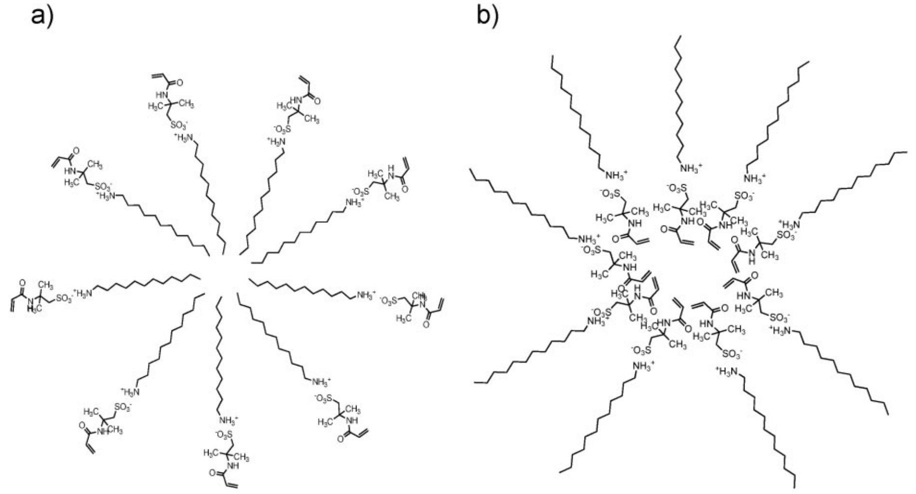


Figure 3.
Schematic presentation of suggested structures of direct (a) and reversed (b) micelles of DDA-AMPS in water and water-dioxane 5:95 respectively.

absence of structural changes in solution in this concentration range (no micelle formation). Solutions with low water content (below 15%) show quite different behavior: there are inflections on conductivity *vs* concentration, but in reverse direction. Formation of reversed micelle was suggested for these solutions (Figure 3b).

Pre-micellar S_1 and post-micellar S_2 slopes of conductivity vs concentration plot and their ratios $\alpha = S_2/S_1$ (micellar ionization degrees, 1-β) were calculated in dependence of water content in solution.[24,25] α value increased with decreasing of polarity of the solvent.

$\Delta G_{mic} = RT(2\text{-}\alpha)Ln(cmc/55.3)$, where 55.3 is molar concentration of water. Both α and ΔG_{mic} values are in good agreements with data reported data for dodecylammonium surfactants,[23] excepting calculations for reversed micelle systems.

To estimate sizes and micellar aggregation number of DDA-AMPS micelles diffusion coefficients in water were measured and hydrodynamic radii calculated using Stokes equation. Micellar mass and aggregation number were estimated suggesting dense spherical particles having density of 0.8 g/cm^3, data are summarized in Table 2.

Table 1.
Micellization parameters for AMPS-DDA in different conditions.

Water content, vol %	Cmc, mM	α	ΔG_{mic}, kJ/mol
100	10.5	0.37	−34
80	20	0.34	−32
80*	23.5	0.30	−46
70	25.5	0.48	−29
50	21.3	0.65	−26
30	21.5	0.68	−25
20	13.5	0.72	−26
18	–	–	
15	–	–	
12	30		
10	30.0		
5	33.2		

At 60 °C.

Table 2.
Hydrodynamic properties of DDA-AMPS in water.

	C = 4.3–8.4 mM/L	C = 17.8–25.5 mM/L
D, cm^2/s	41.7×10^{-7}	13.4×10^{-7}
R, nm	0.58	1.7
[η], dL/g	–	0,02
MM	394	9632
[a]N_{agg}	1	25

[a] Calculated using DDA-AMPS molecular mass of 392.

Polymerization Conditions and Polymer Properties

Polymerization of DDA-AMPS in water-dioxane mixtures was performed at 60 °C using azo-*bis*-cyanovaleric acid as an initiator at fixed concentration 1 mg/ml and monomer concentration 50 mg/ml (above cmc-2 in water) during 1 hour. A set of polymer samples were obtained in a whole range of water-dioxane volume ratios. Each sample was characterized by measuring intrinsic viscosity in chloroform at 25 °C in Ubbelohde viscometer.

Polymer (DDA-PAMPS) appeared to be insoluble in water, dioxane and their mixtures, and precipitated after 10 min of the reaction progress. Generally, polymerization in micellar state proceeds very fast, possible, due to high local concentration of polymerizable groups. We assume that this precipitation is the result of the disruption of the micelles during the polymerization. It occurs when the total conformational energy of the growing polymer chains exceeds the energy of micell formation.

Intrinsic viscosity values and yields of the polymer samples turned out dependent on water content in the reaction media and display evident minimum in the range of 10–30% water content. We assume that the monomer solution is disordered in this region, no micelles are formed.

Intrinsic viscosity values and yields of the polymer samples are higher and the highest are in pure water and pure dioxane, in presence of direct or reversed, micelles (Figure 4a,b).

Solubility of DDA-PAMPS Complexes

According to generally accepted opinion stoichiometric polyelectrolyte-surfactant complexes should be insoluble in water.[1,3,6] Nevertheless some examples of water-soluble stoichiometric PSC have been reported [10,16] and attract special interest due to the ability to form bicontinues and other complex phases.

Polymer-surfactant samples prepared in these works are completely insoluble in water in all range of water-dioxane ratios of solutions for polymerization. Moreover, DDA-PAMPS complexes precipitate at 10 mol% of DDA while titrate PAMPS-Na in water solutions with DAC. But the complexes were found to be soluble in wide range of organic solvents such as alcohols, formamides, chloroform and some other. Such PSC are of high interest during two past decades due to their ability to be processed from non-water solutions and their potential[6] and actual applications.[5]

Insolubility of the resulting polymers in water may be caused by several of the factors. The first one is the strength of electrostatic interactions between oppositely charged polyions and surfactant, which depends on the reduced linear charge density ζ of the chain:

$$\zeta = e^2/4\pi\varepsilon bkT,$$

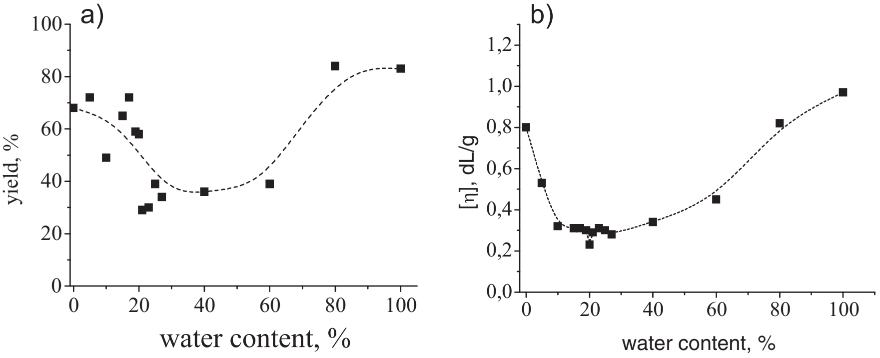


Figure 4.

Dependence of yields (a) and intrinsic viscosity ($CHCl_3$, 25 °C) (b) of DDA-PAMPS samples on water fraction (volume) in water-dioxane mixtures during polymerization.

where ε is the dielectric constant of the solvent and *b* is the distance between adjacent charges along the polymer chain.[25] Alkylammonium sulfonate is a salt group composed of enough strong alkylsulfonic acid and rather weak (comparing to quaternary ammoniun primary amino group. According to our results and literature data degree of ionic binding in monomeric micelles in water is about 0.7–0.8, the salt groups exist in immediate contact with the solvent, thus the salt groups are in equilibrium of dissociated, solvated and contact ionic pairs. Small radius of $R\text{-}NH_3^+$ ion assures strong Coulomb interaction with sulfonium anion. Linear charge density along the chain increases after reaching definite conversion degree during micellar polymerization as compared to charge density in rather labile micelle. Simultaneously density of hydrophobic tails increases. They can form hydrophobic shell around small and dense contact ionic pairs, which shields these pairs from contact with water, preventing their dissociation. And finally, formation of dense hydrophobic shell can increase rigidity of polymer backbone, which should result in decrease of solubility in water too.

Thus joint impact of all the factors makes DDA-PAMPS completely insoluble in water to such an extent, that the complex does not dissociate in highly acidic or basic media up to 1M HCl or 1M NaOH.

As opposed to water media, DDA-PAMPS complexes dissolve easily in many organic solvents, which enable studying their molecular properties and characteristics. Figure 5 shows dependence of reduced viscosity on concentration for the sample polymerized in water.

Solutions in polar organic solvents (methanol and butanol) display distinct polyelectrolyte effect, which can be suppressed by addition of LiCl. Presence of polyelectrolyte effect shows that dissociation of complex takes place. Solution in non-polar chloroform displays linear dependence of reduced viscosity on concentration with Huggins constants in range 0.3–0.5.

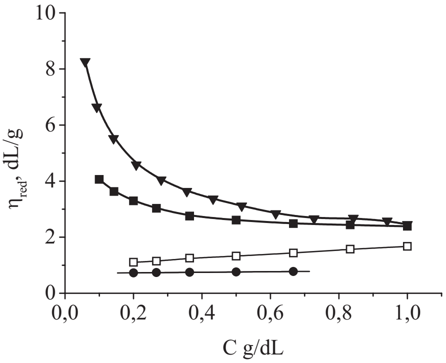


Figure 5.

Reduced viscosity of DDA-PAMPS *vs* concentration in different solvents: methanol -▼-; butanol-1 -■-; chloroform -□-; methanol +LiCl (3% mass.) -●-.

Molecular Characteristics of DDA-PAMPS Samples

We have not succeeded in determination of molecular mass of the complexes by SEC method, probably due to aggregation of the macromolecules.

In order to avoid these complications, we have disassembled of DDA-PAMPS to separate PAMPS-Na from the complex and to determine its molecular mass by MKH equation[26] and then to recalculate it in MKH for the complex. Walker has carried out similar "disassembling" of CTA-PVB complex to determine M of poly-4-vinyl benzoic acid.[16]

As mentioned above, the DDA-PAMPS complex could not be disassembled in water medium, but it was easily to do using methanol NaOH solution. For the experiment we used 5 samples of DDA-PAMPS complex with intrinsic viscosities in chloroform in a range 0.21–1.20 dl/g. After disassembling of the PSC, PAMPS-Na samples were obtained, their intrinsic viscosities were measured and molecular masses were calculated.

The following MKH equations[26] were used: for PAMPS in 5N NaCl: $[\eta] = 2.11 \times 10^{-5} M^{0.80}$; PAMPS-Na in 1N NaCl: $[\eta] = 3.6 \times 10^{-5} M^{0.77}$ (dL/g).

In the other way, several samples of DDA-PAMPS were prepared from dodecyl amine and pure PAMPS polymer of known

Table 3.
Intrinsic viscosities, degrees of polymerization and molecular masses of PAMPS, PAMPS-Na (obtained by DDA-PAMPS disassembling) and DDA-PAMPS.

Sample	[η] of PAMPS in 5M NaCl, dL/g	[η] of PAMPS-Na in 1M NaCl, dL/g	[η] of DDA-PAMPS in $CHCl_3$, dL/g	[a]DP	Mη $*10^{-3}$ PAMPS or PAMPS-Na	[b]Mη $*10^{-3}$ DDA-PAMPS
PAMPS	2.50		[c]4.20	10620	2198	4155
	1.95		[c]2.10	7784	1611	3051
	0.96		[c]1.46	3210	665	1260
	0.30		[c]0.48	750	155.3	394
DDA-PAMPS		1.28	1.20	3550	813	1394
		1.10	1.04	2917	668	1144
		0.71	0.60	1651	378	648
		0.64	0.47	1445	331	567
		0.24	0.21	404	92.5	159

[a]DP values for PAMPS chain calculated from Mη of PAMPS or PAMPS-Na.[b]Mη values for DDA-PAMPS calculated from DP of PAMPS chain.[c]samples obtained from PAMPS and DDA.

molecular mass, which was preliminary calculated using MKH equation. All data concerning viscometry and MKH calculations of PAMPS, PAMPS-Na and DDA-PAMPS are summarized in Table 3. Figure 6 shows logarithmic plot of intrinsic viscosity of DDA-PAMPS in chloroform *vs* its estimated molecular mass.

The data for samples obtained by DDA-AMPS polymerization and samples obtained from PAMPS are in a good agreement and lie on the same line.

From these data preliminary estimation of MKH constants could be as follows: K = 0,000011 dL/g, $\alpha = 0{,}83$. Rather high value of α – coefficient enables to suppose high rigidity of DDA-PAMPS macromolecules.

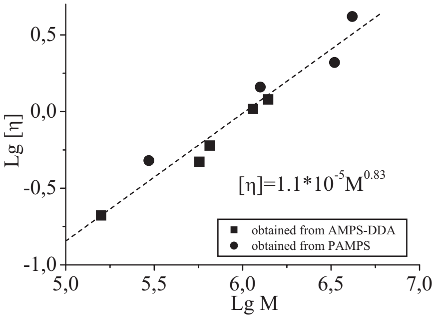


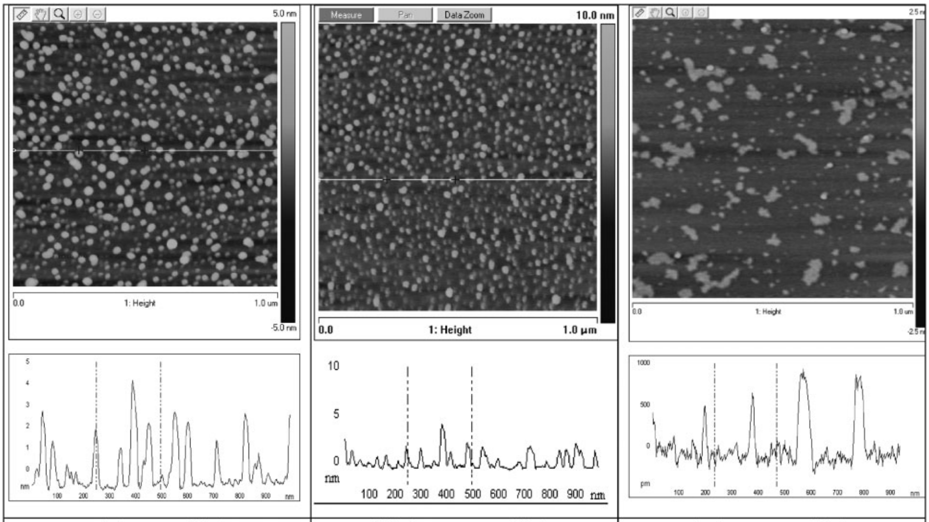
Figure 6.
Logarithmic plot of intrinsic viscosity of DDA-PAMPS in chloroform *vs* its molecular mass (■ – obtained from DDA-AMPS; ● – obtained from PAMPS.).

Atomic Force Microscopy Study of the Polymer Specimens

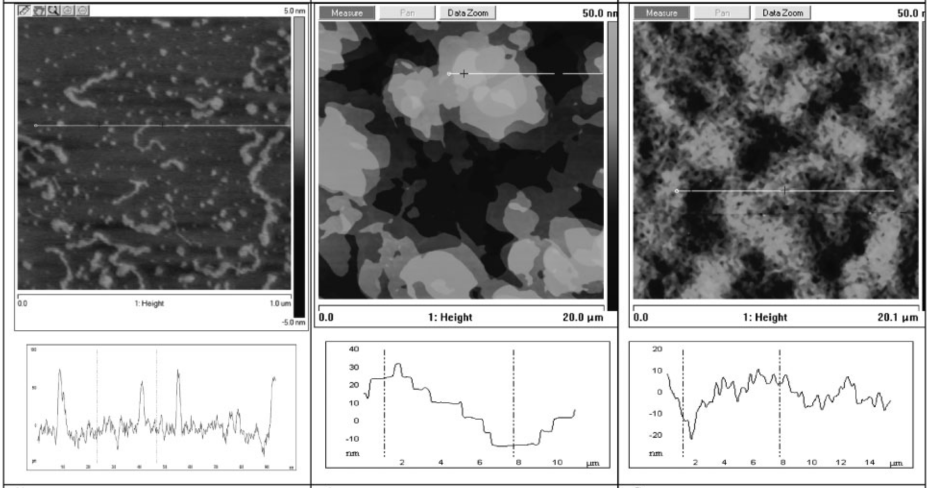
Atomic force microscopy is a powerful method for visualization of nano-dimensional objects.[27] Commonly freshly split mica is used as a support for sorption of the objects.

DDA-PAMPS samples were investigated by AFM method (tapping mode) using Veeco diNanoscope V instrument in two types of experiment (Figure 7a–d). Specimens of the first type were prepared by spin-coating from 0.02 g/L polymer solutions in butanol-1 on split mica. Other samples were polymer films prepared from solutions in different solvents.

There is distinct difference between samples of DDA-PAMPS obtained by polymerization in water, dioxane, water-dioxane mixtures and from PAMPS and DDA. One can find some similarities in polymers obtained in dioxane containing small amounts of water solvent systems. These polymers have been adsorbed on the mica as spherical particles. Polymers prepared in water have been adsorbed on the mica as shapeless particles of different size. AFM image of the samples derived from PAMPS and DDA differs considerably from images of the samples of both mentioned types (prepared in water-dioxane mixtures and in pure water). One can find large elongated aggregates in the picture of this polymer complex (Figure 7d). In order to



a) (0%, 1 dl/g) b) (19%, 0.2 dl/g) c) (100%, 2 dl/g)



d) (obtained from pre-synthesized PAMPS, 2.1 dl/g) e) – Free film from chloroform f) – Free film from methanol

Figure 7.

AFM images (topography and section) of DDA-PAMPS different samples on mika: a–d samples prepared from diluted solutions (water percentage in water-dioxane mixture during polymerization and polymer intrinsic viscosities measured in chloroform are given in parenthesis), e – free film from 20 g/L chloroform solution, f – free film from 20 g/L methanol solution (both films made of the polymer the same as for "c" sample).

understand difference in behavior of DDA-PAMPS prepared by polymerization of DDA-AMPS in different solvent systems and the samples prepared by direct interaction of DDA and PAMPS we perform study of their dilute solutions by hydrodynamic and dynamo-optical methods, which enable estimate conformational properties of macromolecules (to be published).

Free films of DDA-PAMPS appeared to be very interesting. The films were prepared from 20 g/L solution of the polymer in chloroform onto PTFE substrate. The solution was exposed at room temperature for 24 hours before casting.

The image of the film display distinct layered structure. Width of the layers is about 7–8 nm which may correspond to bilayer structure of the film. In contrast, the film cast from methanol had no layer motifs (Figure 7f).

Conclusion

We have investigated polymerization of novel ionic micelle forming monomer DDA-AMPS in water-dioxane mixtures with different values of dielectric permeability. The highest yields and molecular weights of polymer were observed in the conditions of presumable existence of direct or reversed micelles of the monomer. The polymer in all cases was insoluble in the reaction media; however it appeared to be soluble in chloroform, alcohols and other organic solvents. This made possible tentative estimation of MKH equation coefficients for DDA-PAMPS complex. Considerable difference has been shown in behavior of polymers synthesized in solvent systems of medium polarity and in water by AFM method.

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