Core Cross-Linked Polymerized Micelles and Dendronized Nanoparticles

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Summary: Polymerization of 11-acryloylaminoundecanoic acid and its copolymerization with diacrylic monomers were performed under different conditions in micellar (Na-salt in water) and non-micellar states. The effect of conditions of the syntheses on molecular mass of the polymers and hydrodynamic characteristics of their macromolecules was studied. Ionic complexes of core-cross-linked polymerized micelles with different dendrons bearing polymerizable peripheral groups were obtained and their trial polymerizations were performed.

Keywords: micelles; polymerization; self-assembly; supramolecular structures

Introduction

Polymerization of micelle-forming monomers is promising way for the synthesis of well-organized macromolecules and nanoparticles. Polymerizable ionic surfactant molecules and polymerized micelles, obtained from them, can be considered as building blocks in design of complex macromolecular objects being molecules and nanoparticles at once.

Polymers obtained from N-Acryloyl-11-aminoundecanoic acid (AAU) and its sodium salt (AAU-Na)[1–3] found their application in electrokinetic chromatography,[4] solubilization and drug delivery[5] etc. The first synthesis of PAAU refers to 1959.[6] A series of publications of Gan and Yeoh in 1989–1991 on acrylic surfactants[7–10] revealed some features of polymerization AAU-type monomers, some new applications of these polysoaps were suggested.[11,12] Roy and Dey[13–18] have performed recently extensive investigation of structure formation of AAU-derived surfactants in micellar state and their polymerization. The structure of AAU-Na associates in solution was studied in detail.[13]

Nevertheless, many questions remain unsolved concerning polymerization of AAU under different reaction conditions – concentration, solvent, ionic strength.

One more challenging problem remains unsolved – fixation of micelles structure and shape.

Even polymerized, micelles of polymerizable surfactant retain their dynamic nature – macromolecule is able to change its conformation upon changing environment.

We have reported[19] synthesis and results of preliminary investigation of polymerized micelles of PAAU and core-cross-linked polymerized micelles (cPAAU). In this paper we present the results of cPAAU investigation and further work on the construction of complex supramacromolecular objects based on cPAAU micellar core.

Results and Discussion

The monomer, AAU-Na is known to have cmc-1 at 0.042 mol/L (0.011%) in water.[7,11,13] The cmc of higher order up to now was not known for this substance. In [17] one can find the critical vesicle concentration (cvc, 3,45 mM, ~0.1%) with reference to [13] where

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no information on cvc was provided but presence of vesicles, rods and tubules in 2.5 mM solution of AAU-Na was stated. At concentration range from cmc-1 up to 0.3% (10mM/L) coexistence of spherical micelles, rods, tubules was shown by means of TEM, aggregation number at 2.5 mM/L (0.06%) was found to be 173. At concentrations above 0.3% only rod-like structures were observed.[13]

The aggregation number of these micelles is expected to grow significantly at the concentration range near ccm-2. We have found by means of viscometry that one of cmc's for AAU-Na is in the range of 2–4%.

Synthesis of PAAU in Different Conditions

The polymerization of AAU-Na was performed at different monomer concentration (from 3 mg/mL to 100 mg/mL) in water with ammonium persulfate as initiator. The concentration of initiator was fixed either to 1mg/mL or to constant monomer/initiator ratio of 1:50 mg/mg. In all cases the polymerization runs to 100% conversion which was proved by means of ^{1}H-NMR spectroscopy data. Yields of the polymers were close to 100%.

PAAU polymer is soluble in DMF, DMSO, aqueous THF, acetic acid, poorly soluble in ethanol (96%). It is insoluble in dry THF, chloroform, acetone, ethyl acetate, water.

The samples of PAAU isolated in carboxylic acid form were characterized by means of viscometry in DMF. Figs. 1 and 2 show dependence of reduced viscosities of the PAAU, obtained by free radical polymerization of AAU-Na in water at different concentrations of the monomer in range near cmc-2. Reduced viscosities (at $c = 0.5$ g/dL) and [η] increase with increasing monomer concentration that corresponds to polymer molecular mass increasing. Difference of reduced viscosities of the polymers obtained at constant initiator concentration and constant monomer/initiator ratio is shown in Fig. 2. It should be noted that the mechanism and kinetic features of micellar polymerization are not clear up to now and quantitative effect of initiator concentration on molecular mass of the polymer can not be predicted a priori. (In solution radical polymerization [20] M_n is proportional to $[M][I]^{-0.5}$, in emulsion polymerization – to $[M][I]^{-1}$, in some cases of microemulsion polymerization[21] is independent on [I]). It is clear from Figs. 1 and 2 that the monomer concentration affects greatly the molecular mass of the polymers.

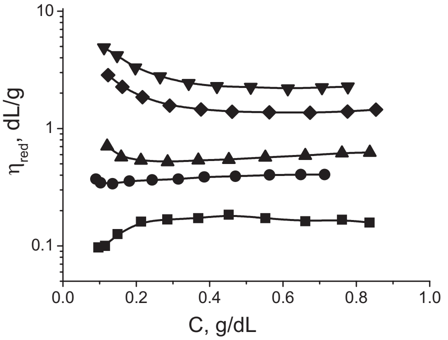


Figure 1.
Semilogarithmic plot of reduced viscosity vs concentration of PAAU solution in DMF depending on monomer concentration during polymer synthesis. ■0.3%, ●0.6%, ▲1%, ◆3%, ▼5% (in aqueous micellar solution).

One of the factors supposed to be responsible for polymer molecular mass increasing is increasing of micelle aggregation number in the concentration range near cmc-2. The other factor, which can be responsible for increasing of molecular

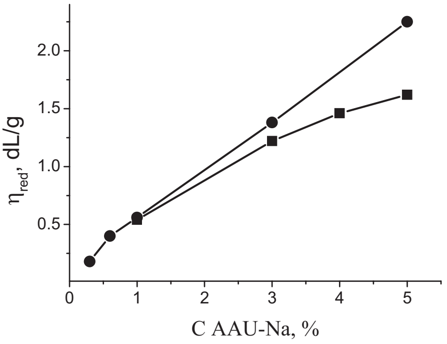


Figure 2.
Dependence of reduced viscosity (at $c = 0.5$ g/dL) of PAAU solution in DMF (at 0.5 g/dL) on monomer concentration during polymer synthesis ■ fixed monomer/initiator ratio, ● fixed initiator concentration.

mass, is the rate of dynamic exchange of monomer molecules between a micelle and solution[22]. Increasing of the ionic force of the solution leads to increasing of aggregation number of micelles and decreasing of the exchange rate. Fig. 3 shows the influence of KCl conctntration on reduced viscosities of the PAAU samples, obtained at different salt concentration up to 3 M (Monomer concentration was fixed to 10 mg/mL and initiator concentration was fixed to 1mg/mL). Molecular mass of the polymer increased with increasing of the ionic strength of the solution.

PAAU samples were obtained in non-micellar solution via polymerization of AAU-H monomer in DMF with AIBN initiator. Reaching 100% conversion takes 2h at 70 °C and 30% concentration of the monomer whereas in micellar solution 100% conversion takes only 22 min at much lower monomer concentrations.[7] Reduced viscosity of the polymer obtained in DMF was 0.2dL/g (at c = 0,5 g/dL).

Macromolecules of the polymers obtained from polymerizable surfactants behave as micelles in appropriate condition (i.e. polymer acid salts in water), but can turn into random coils in other condition (non-ionized state, i.e. polymer acid H-form in DMF).

In the first case macromolecules have the shape (macroconformation) of micelle (or vesicle) and their shape should remain unchanged upon dilution.

Table 1.
Dependence of AAU conversion on polymerization conditions (in DMF).

C (AAU-H), %	T, °C	conversion, %
5	60	<10
5	75	15
27	60	50
27	75	100

In the second case these polymers are typical polyelectrolytes, whose macromolecules uncurl upon dilution due to electrostatic interactions of ionic groups. In DMF most of the polymers (except low molecular mass samples obtained at concentration of 0.3 and 0.6%) display polyelectrolyte effect. This polyelectrolyte effect can be suppressed by adding LiCl to the DMF solution (Fig. 4) which is typical to polyelectrolytes.

Synthesis of the Cross-Linked Polymerized Micelles of PAAU

In our previous work[19] we have shown possibility to fix the shape of polymerized micelle so that changes in concentration or changes of conditions should not lead to changes in the shape of the macromolecule. Fixation of the shape of macromolecule can be achieved via intramolecular cross-linking, in this case it corresponds to cross-

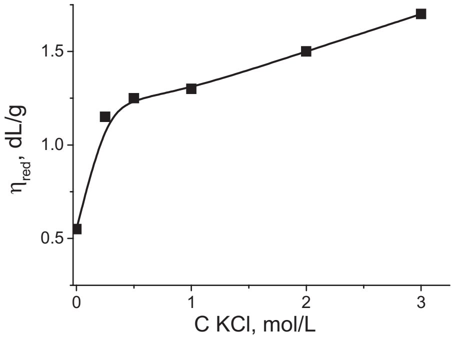


Figure 3.
Dependence of reduced viscosity of PAAU solution in DMF (at 0.5 g/dL) on KCl concentration during polymer synthesis.

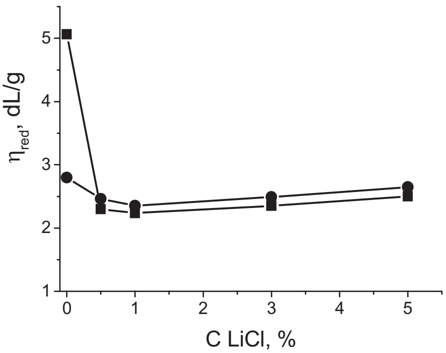


Figure 4.
Reduced viscosity of PAAU solution in DMF vs concentration of LiCl (PAAU concentration ● 0.2 g/dL, ■ 0.1 g/dL).

linking of the core of the micelle. In this work more detailed investigation of core-cross-linked PAAU micelles was performed.

For the core cross-linking we use oil-soluble cross-linkers hexamethylene diacrylate and resorcinol diacrylate, solubilized in AAU-Na micelles. Polymerization of AAU-Na in the presence of cross-linker results in formation of clear solutions. No gelation was observed. Core cross-linked poly(11-acryloylaminoudecanoic acid) cPAAU-H and cPAAU-Na were completely soluble in DMF and water, respectively. This indicates that micelles were formed and cross-linker was incorporated in the core area of these micelles.

Non cross-linked PAAU-H behaves as polyelectrolyte in DMF, displaying considerable polyelectrolyte effect (polyelectrolyte swelling) upon dilution. Macromolecules of the cPAAU-H, which have been cross-linked intramoleculary have no ability to swell (or uncurl) upon dilution which is clearly indicated by viscometric data (Fig. 5). cPAAU-H and PAAU-H have the same reduced viscosities in DMF and similar slopes of η_{red}-(C) at concentrations above 0.6 g/dl which corresponds to the same hydrodynamic radii of the molecules.

Chemical nature of cross-linker in cPAAU-H (diacryl ester) enables to perform selective hydrolysis of these cross-linking bonds. It would disassemble cross-linked micelles and turn them into the state similar to that of non cross-linked PAAU-H. After selective hydrolysis of ester bonds in cPAAU-H its rheological behavior in DMF becomes quite similar to that of PAAU-H (Fig. 5).

The load of cross-linker has some effect on the hydrodynamic behavior of cPAAU-H which is shown on Fig. 6. The more cross-linker is added to the polymer, the more compact macromolecules are obtained.

Molecular Characteristics of the Polymers

Molecular characteristics of the different PAAU samples were studied by means of isothermal diffusion, dynamic light scattering and MALDI-TOF MS.

The results of hydrodynamic measurements (in DMF solution) are summarized in Table 2.

Fig. 7 displays MALDI TOF spectrum of PAAU obtained in 0.3% micellar solution. The sample is virtually monodisperse with molecular mass 15800 which clearly indicates intra-micellar polymerization mechanism, but polymerization degree (62) is less than reported aggregation number value (171[13]). Fig. 8 shows MALDI TOF spectrum of PAAU sample obtained in DMF solution. The spectrum corresponds to the set of oligomers with polymerization degree from 8 up to 30. This spectrum is highly informative and allows obtaining information of mechanisms of

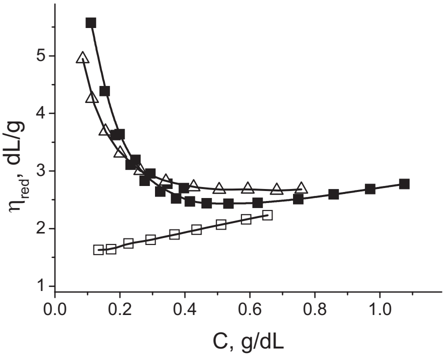


Figure 5.
Reduced viscosity vs. concentration for cPAAU-H (□), PAAU-H (■), and hydrolyzed cPAAU-H (Δ) in DMF solution.

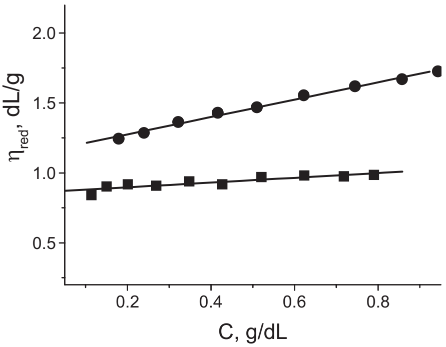


Figure 6.
Reduced viscosity vs concentration of cPAAU solution in DMF (resorcinol diacrylate concentration during synthesis ● 0.28 mg/mL, ■ 0.83 mg/mL).

Table 2.
Molecular characteristics of PAAU obtained in aqueous micellar solution.

	[a]C, *g/dL*	$[\eta]$ ±*0.1*, dL/g	$D \times 10^7$ ±*0.1*, cm^2/s	[b]$M_{D\eta} \times 10^{-3}$	[c]$D_Z \times 10^7$ ±*0.1*, cm^2/s	[d]R_H, nm
PAAU	0.3	0.12	10.5	9/12	8.9	2.4 ± 0.5
	0.6	0.35	8	7/9		3.4
	1	0.45	3	100/130	2.9	10.4 ± 0.9
	3	1.0	1.5	300/400		18
	5	1.8	1.4	250/330		19
cPAAU	[e]5	1.15	1.1	800/1070		25
	[f]5	0.85	1.3	650/870		21

[a]– concentration of monomer during polymerization.

[b]– calculated from Tsevetkov-Klenin equation $M_{D\eta} = (A_0 T/\eta_0 D)^3/[\eta]$ with $A_0 = 2.9 \times 10^{-17}$ J/K × mol$^{1/3}$ or $A_0 = 3.2 \times 10^{-17}$ J/K × mol$^{1/3}$.

[c]– from dynamic light scattering data.

[d]– calculated from Stokes-Einstein equation $D = kT/(6\pi\eta R_H)$.

[e]– cross-linker concentration 0.28 mg/mL.

[f]– cross-linker concentration 0.83 mg/mL.

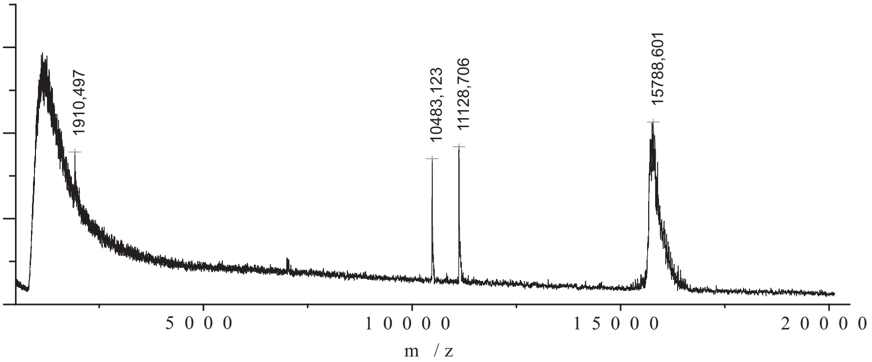


Figure 7.
Linear MALDI TOF spectrum of PAAU obtained in aqueous micellar solution (region of m/z 700–2000 contains signals of chemical noise).

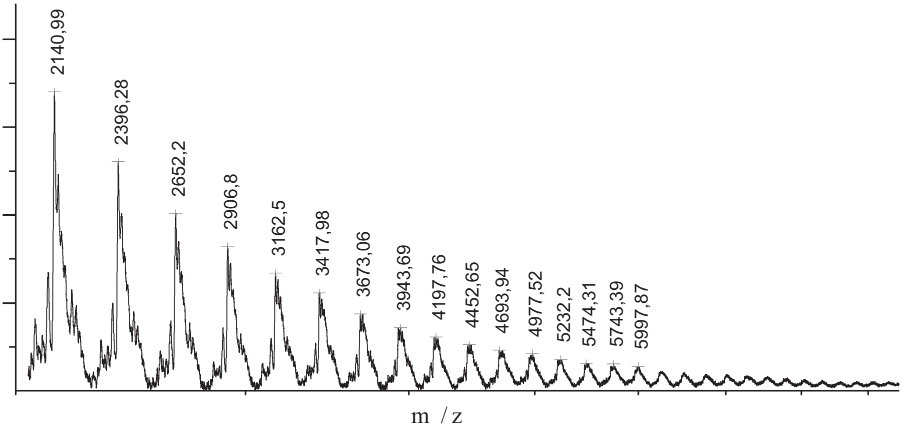


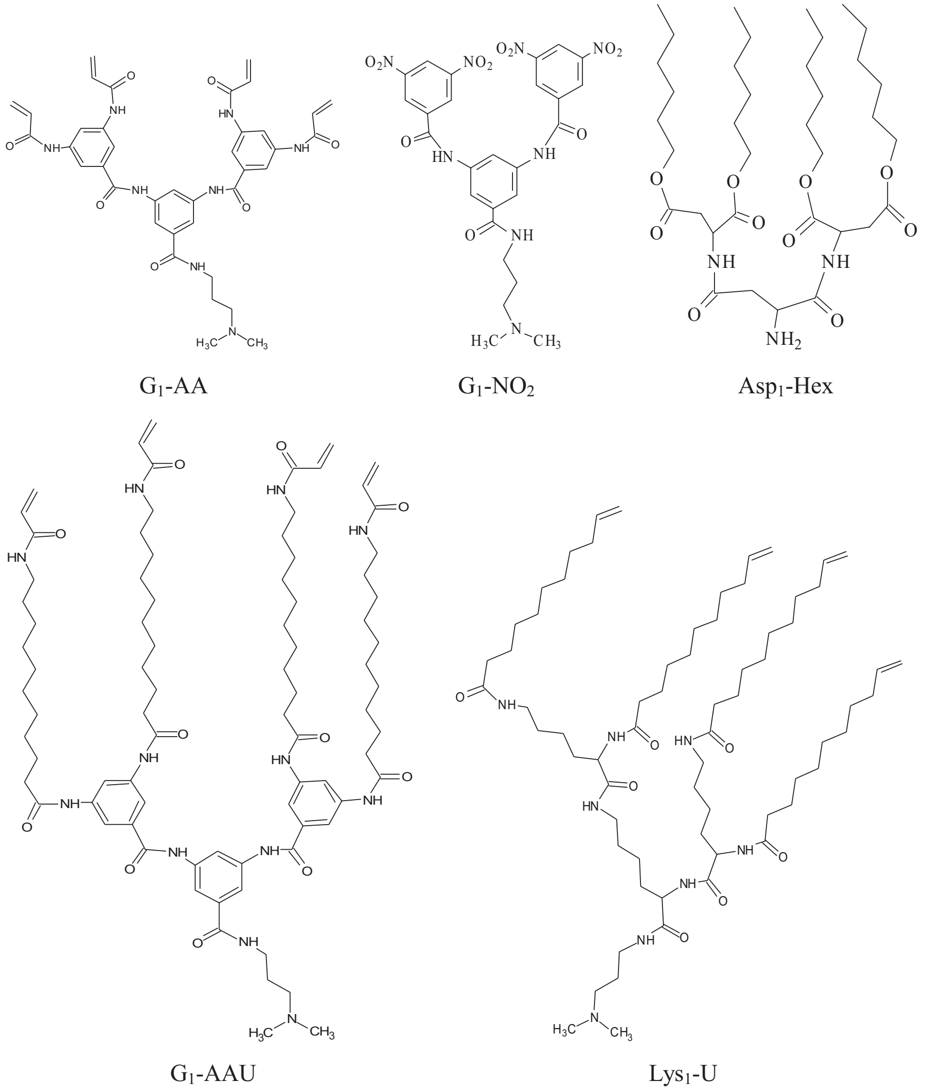
Figure 8.
Linear MALDI TOF spectrum of PAAU obtained in DMF solution.

chain transfer and termination in polymerization system. The detailed discussion of these data will be published elsewhere.

Functional (COOH) groups at the cross-linked micelle periphery could be used for layer-by-layer construction of complex nanoparticles by means of ionic bindig of appropriate building blocks bearing oppositely charged anchor groups. We used lysine or diaminobenzoic acid based dendrons (Fig. 9) bearing dimethylaminopropylamide focal group and 4–8 acrylamido peripheral groups to form ionic complexes with micellar cPAAU core. Ionic complexes formation proceed up to 100% binding in the case of cPAAU whose functional groups are located at the periphery, whereas non-cross-linked PAAU binds only about 30% of dendrons.

The binding degrees for the polymer – dendron complexes were calculated from CHN-analysis and ^{1}H-NMR data.

Trial template polymerizations were performed for acrylamido groups of the counterions at PAMPS, PAAU and


G_1-AA

G_1-NO_2

Asp_1-Hex

G_1-AAU

Lys_1-U

Figure 9.
Chemical structures of dendrons used in this study.

Table 3.
Binding degree (%) of ionic complexes with different polyelectrolyte core and dendritic counterion.

	polymerizable			model		
	G_1-AA	G_1-AAU	Lys_1-U	DCHA	G_1-NO_2	Asp_1-Hex
PAA	~30				~30	~30
PSS					~100	~100
PAMPS	~100					
PAAU	20–30			20–30		
cPAAU	~100	~100	>60			

cPAAU matrices. The polymerization proceeds at averaged concentrations of polymerizable groups in the range 0.01 to 0.0002 mol/L. No double bonds were detected by ^{1}H-NMR in soluble fraction (41%) after polymerization at lower concentration. Figure 10 presents AFM image of shell polymerized complex particles.

Experimental Part

Acryloyl chloride (Merck), 11-aminoundecanoic acid (Fluka), and DMF were used as received.

^{1}H-NMR spectra were recorded at Bruker DPX-300 spectrometer at 300 MHz.

Viscomeric measurements were performed at 25 °C using Ubbelohde or Cannon-Ubbelohde viscometers.

MALDI TOF mass spectra were recorded at Bruker UltraFlex spectrometer with 2,5-DHB matrix, samples were prepared from DMF solution.

AFM images were obtained on Veeco diNanoscope V operating in the tapping mode with RTESP nanoprobe tips. Samples were prepared by dipping freshly cleaned mica plates into 0.25 mg/mL complex DMSO solution for 5 min and subsequent washing the plate with DMSO and acetone.

AAU-H was synthesized via modified procedure [23]: 0.1 mol of 11-aminoundecanoic acid was dissolved in 200 ml 1N NaOH and solution of 0.1 mol of acryloyl chloride in 40 ml of CCl_4 was added dropwise under cooling and vigorous stirring. After 1 h the solution was acidified with 1 N HCl, white precipitate was filtered and washed conse-

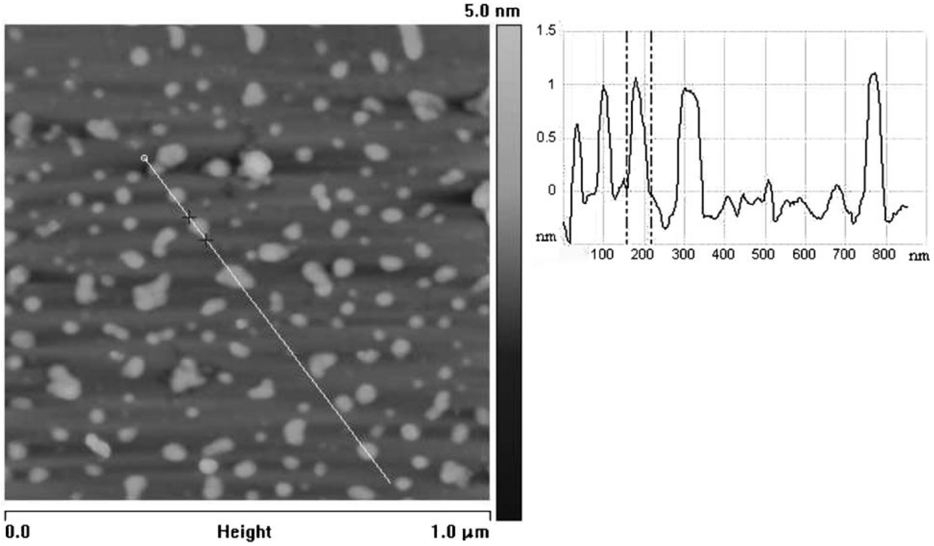


Figure 10.
AFM image of shell polymerized cPAAU – G_1-AAU complex.

quently with 0.5 N HCl and water. Crude product was recrystallized from ethyl acetate with neutral Al_2O_3. Mp. 79 °C.

CHN analysis calculated for $C_{14}H_{25}NO_3$ C: 65.85, H: 9.87, N: 5.49; Found C: 65.85, H: 9.84, N: 5.41.

^{1}H-NMR (DMSO-d6) 1.19-1.53 (16H) C_3-C_{10} alkyl; 2.16t (2H) C_2 alkyl; 3.1m (2H) C_{11} alkyl; 5.54dd (1H), 6.05dd (1H), 6.2dd (1H) acryloyl; 8.05t (1H) amide.

Sodium salt of AAU-H (AAU-Na) was obtained by dissolving of excess of the AAU-H in minimal volume of methanolic NaOH, filtering and precipitating in dry acetone.

CHN analysis calculated for $C_{14}H_{24}NNaO_3$ C: 60.63, H: 8.72, N: 5.05; Found C: 60.59, H: 8.72, N: 5.13.

Hexamethylene diacrylate was obtained by reacting of 0.021 mol of acryloyl chloride with 0.01 mol of hexane-1,6-diol in 10 ml fresh distilled dry N-methylpyrrolidone at −18 °C. After 2 days the reaction mixture was poured in 0.5 N HCl and extracted with petroleum ether. The solution was dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the residual oil was used without further purification.

^{1}H-NMR ($CDCl_3$) 1.42m (4H) C_3, C_4; 1.69m (4H) C_2, C_5; 4.12t (4H) C_1, C_6; 5.82dd (2H), 6.12dd (2H), 6.4dd (2H) acryloyl.

Resorcinol diarylate was obtained by reacting of 0.01 mol resorcinol in 20 ml 1N NaOH with 1.8 ml acryloyl chloride in 7 ml CCl_4, added dropwise. Reaction mixture was extracted with methylene chloride, extract was washed consequently with 0.5 M NaOH and water, dried over $MgSO_4$, the solvent was evaporated under reduced pressure, and the residual oil was used without further purification.

Polymerization of AAU-Na was carried out in aqueous solution at 60 °C for 45 min using ammonium persulfate (1mg/ml) as initiator. Sodium salt of AAU was prepared in situ by co-dissolving of calculated amounts AAU and Na_2CO_3 in water or aqueous KCl to obtain desired concentration of AAU-Na. After completion of the polymerization the solution was filtered and poured into 0.5 N HCl to obtain polymer in acid form (PAAU-H).

CHN analysis calculated for $C_{14}H_{25}NO_3$; C: 65.85, H: 9.87, N: 5.49; Found C: 64.40, H: 9.58, N: 5.37.

^{1}H-NMR (DMSO-d6) 1.0-1.5 (16H) C_3-C_{10} alkyl; 1.7-2.1 (1H) chain; 2.16t (2H) C_2 alkyl; 2.8-3.2 (2H) chain; 3.15-3.7 Water; 7.0-7.8 (1H) amide; 11.5-12.3 (1H) acid.

Polymerization with added solubilized cross-linker was carried out in similar manner. Cross-linker was added with the micro-syringe to the freshly prepared monomer solution and resulted mixture was sonicated for 15 min before polymerization.

PAMPS – G_1-AA complex was obtained by adding of 0.15 mmol of PAMPS ($M\eta = 25000$) in 0.5 ml methanol to the stirred solution of 0.22 mmol G_1-AA in 4 ml methanol. Precipitation of the complex begins in 5–10 min. After 24 h precipitated complex was collected by filtration and washed with methanol.

CHN analysis calculated for $C_{45}H_{53}N_9O_{11}S$ C: 58.25, H: 5.72, N: 13.59, S: 3.45, N/S: 3.94; Found C: 54.17, H: 5.88, N: 13.57, S: 3.38, N/S: 4.01.

cPAAU – G_1-AAU complex was obtained by adding of of 0.61 mmol of polymer in mixture of solvents (11.3 ml methanol, 1.9 ml THF, 0.56 ml H_2O) to the stirred solution of 0.92 mmol G_1-AA in 32 ml of hot methanol. Precipitation of the complex begins in 5–10 min. After 24 h precipitated complex was collected by filtration and washed with methanol.

CHN analysis calculated for $C_{96}H_{149}N_{13}O_{14}H$ C: 67.46, H: 8.79, N: 10.65; Found C: 66.28, H: 8.83, N: 10.60.

^{1}H-NMR (DMSO-d6) 1.1-1.3 (52H) C_3-C_8 alkyl; 1.3-1.45 (10H) C_2 alkyl; 1.45-1.7 (11H) C_9 alkyl and CH_2-C**H**$_2$-CH_2 spacer; 2.15 s (6H) N-C**H**$_3$, 2.2-2.4 (10H) C_{10} alkyl and CH_2-C**H**$_2$-N, 3.05-3.15 (8H) C_1 alkyl, 5.55 d (4H) C**H**$_2$=CH (cis $J^1 = 8$ Hz), 6.05 d (4H) C**H**$_2$=CH (trans $J^2 = 16$ Hz), 6.2 dd (4H) CH_2=C**H** ($J^1 = 8$ Hz, $J^2 = 16$ Hz), 7.79 s (4H) arom, 7.89 s (2H) arom, 8.06 bs (4H) amide aliph, 8.17 s (2H) arom, 8.29 s (1H) arom, 8.58 bs (1H) amide arom-aliph, 10.09 s (4H) amide aliph-arom, 10.49 s (2H) amide arom.

IR in KBr. 1605 cm^{-1} (ν, C=O), 1338 cm^{-1} (δ, O^-).

cPAAU – Lys_1-U complex was obtained by adding of 0.11 mmol of polymer in 1 ml THF_{aq} to the stirred solution of 0.17 mmol of dendron in 5 ml of methanol and 0.5 ml of water. The reaction mixture was concentrated and 10 ml of ether was added, after that precipitate was collected and washed with ethyl ether and ethyl acetate.

CHN analysis calculated for $C_{81}H_{147}N_9O_{10}$ C: 69.18, H: 10.46, N: 8.97; Found C: 66.32, H: 9.81, N: 8.30.

Polymerizations of cPAAU – G_1-AAU complex were performed under argon atmosphere in dioxane/DMSO (80/20) solution at concentrations 0.005 and 0.0001 mol/L using AIBN initiator at 70 °C for 6-8 h. In the thirst synthesis two products were obtained soluble (28%) and unsoluble (71%) in DMSO. Soluble fraction contained 8% residues double bonds. In the second synthesis only soluble product (41%) was obtained which does not contain double bonds.

Conclusion

Polymerized micelles of poly(11-acryloylaminoundecanoic acid) were obtained. Polymerization of AAU-Na in presence of solubilized oil-soluble cross-linker leads to intramoleculary cross-linked polymerized unimolecular micelles with fixed structure. Ionic complexes of core-cross-linked PAAU with dendrons bearing peripheral acrylamido groups were obtained with 100% degree of binding. Polymerization of surface double bonds of the above complex was performed.

Acknowledgements: This work was supported by Russian Foundation for Basic Research grant # 09-03-00968.

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