

Polymerized micelles. Fixation of micelle structure by the core cross-linking

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Summary

Polymerized micelles of poly(11-acryloylaminoundecanoic acid) were obtained via radical polymerization in micellar state. The structure of micelles was fixed by cross-linking of the micelle core using solubilized diacrylate co-monomer. Hydrodynamic behavior of both cross-linked and non cross-linked polymerized micelles was studied by means of viscometry.

Introduction

Polymerized micelles (or polymerized surfactants, surfmers) since their first synthesis in 1979 [1] find a lot of applications mostly in the field of electrokinetic chromatography [2]. Detailed review [3] gives clear representation of recent advances in the area of polymerized surfactants. However, a lot of questions remain concerning polymerization in different micellar phases, size, shape and hydrodynamic behavior of the polymerized micelles.

Results and discussion

Polymerization of ionogenic surfactants in micellar state is a way for obtaining comb-shaped polyelectrolytes or polymeric surfactants with nearly sharp molecular weight distribution (corresponding to monomer aggregation number in micelle). Polymerization in micellar state should lead to macromolecules each of those corresponds to one micelle. Macromolecules obtained are unimolecular micelles with the shape corresponding to that of the micelles formed by the monomer molecules. Cmc of the resulting polymerized surfactant equals to zero. Macromolecules of such polymers behave as micelle in appropriate condition (i.e. polymer acid salts in water), but can turn into random coil in other condition (non-ionized state, i.e. polymer acid H-form in DMF). (Similar to the hedgehog behavior). In the second case these polymers are typical polyelectrolytes, whose macromolecules uncurl upon dilution due to electrostatic interactions of ionic groups.

In this work we try 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

macromolecule (hedgehog can not uncurl). Fixation of the shape of macromolecule can be achieved via intramolecular cross-linking, in this case it corresponds to cross-linking of the core of the micelle.

So the objective of this work was to perform two polymerization experiments at exactly the same conditions (in micellar state of the monomer) and the only difference: in one case there should be cross-linking agent solubilized in the core of the monomer micelle.

For this experiment 11-acryloylaminoundecanoic acid (**AAU-H**) and its Na salt were chosen. **AAU-Na** readily undergoes radical polymerization in aqueous micellar solutions. Structure of **AAU-Na** micelles [4], kinetics of its polymerization [5, 6] and molecular characteristics of the polymer **PAAU-Na** [7] were studied earlier by Roy, Yeoh, and Fujimoto.

For the core cross-linking we use oil-soluble cross-linker hexamethylene diacrylate, solubilized in **AAU-Na** micelles. Polymerization of **AAU-Na** in the presence of 8% of cross-linker results in formation of clear solutions. No gelation was observed. Core cross-linked poly(11-acryloylaminoundecanoic acid) (**cPAAU-H**) and **cPAAU-Na** were completely soluble in DMF and water, respectively. This indicates that micelles were formed and all cross-linker was incorporated in the core area of these micelles.

Hydrodynamic behavior of **cPAAU-H** and non cross-linked **PAAU-H** was studied by means of viscometry.

Non cross-linked **PAAU-H** behaves as polyelectrolyte in DMF and DMSO (fig. 1), demonstrating considerable polyelectrolyte effect (polyelectrolyte swelling) upon dilution. In acetic acid the polyelectrolyte swelling is suppressed.

Macromolecules of the **cPAAU-H**, which have been cross-linked intramolecularly have no ability to swell (or uncurl) upon dilution which is clearly indicated by viscometric data.

Macromolecules of **cPAAU-H** have nearly the same reduced viscosity (which corresponds to the same hydrodynamic radius) at the same concentration (0.6 g/dl) in DMSO and DMF whereas macromolecules of **PAAU-H** have considerable higher reduced viscosity (higher hydrodynamic radius) in DMSO than in DMF. **cPAAU-H** and **PAAU-H** have the same hydrodynamic radii in DMF and similar slopes of $\eta_{red}(C)$ at concentrations above 0.6 g/dl.

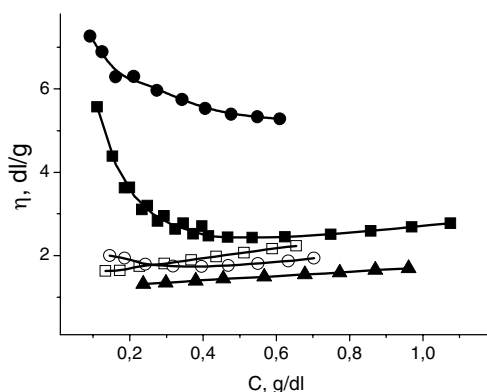


Figure 1 Reduced viscosity vs. concentration for **cPAAU-H** (□-DMF, ○-DMSO) and **PAAU-H** (■-DMF, ●-DMSO, ▲-AcOH) in different solvents.

Chemical nature of cross-linker in **cPAAU-H** (diacryl ester) allows us to perform selective hydrolysis of these cross-linking bonds. This 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. 2).

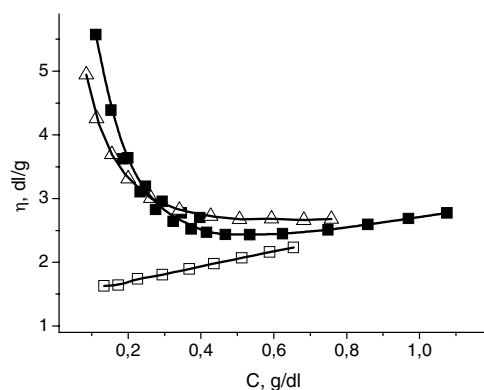


Figure 2 Reduced viscosity vs. concentration for **cPAAU-H** (□), **PAAU-H** (■), and hydrolyzed **cPAAU-H** (Δ) in DMF solution.

Experimental

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

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

Viscomeric measurements were performed at 25°C using Ubbelohde viscometer.

AAU-H was synthesized via modified procedure [8]: 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 solution was acidified with 1 N HCl, white precipitate filtered and washed consequently 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 $\text{C}_{14}\text{H}_{25}\text{NO}_3$ C: 65.85, H: 9.87, N: 5.49;

Found C: 65.85, H: 9.84, N: 5.41.

$^1\text{H-NMR}$ (DMSO- d_6) 1.19-1.53 (16H) C3-C10 alkyl; 2.16t (2H) C2 alkyl; 3.1m (2H) C11 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 $\text{C}_{14}\text{H}_{24}\text{NNaO}_3$ 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 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.

¹H-NMR (CDCl₃) 1.42m (4H) C3, C4; 1.69m (4H) C2, C5; 4.12t (4H) C1, C6; 5.82dd (2H), 6.12dd (2H), 6.4dd (2H) acryloyl.

Polymerization of AAU-Na was carried out in 80 mg/ml aqueous solution at 60°C for 1 h using ammonium persulfate (1mg/80mg **AAU-Na**). The resulting polymer solution was divided in two portions. The first one was filtered and poured into dry acetone to obtain polymer in sodium salt form (**PAAU-Na**). The second portion was filtered and poured into 0.5 N HCl to obtain polymer in acid form (**PAAU-H**).

CHN analysis calculated for C₁₄H₂₅NO₃: C: 65.85, H: 9.87, N: 5.49

Found C: 64.40, H: 9.58, N: 5.37

¹H-NMR (DMSO-d₆) 1.0-1.5 (16H) C3-C10 alkyl; 1.7-2.1 (1H) chain; 2.16t (2H) C2 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 (8 mass%) was carried out under vigorous stirring.

CHN analysis calculated for 11(C₁₄H₂₅NO₃)+(C₁₂H₁₈O₄): C: 65.69, H: 9.73, N: 5.08

Found: C: 64.56, H: 9.25, N: 4.95

Hydrolysis of cPAAU-Na was carried out in 1 N NaOH at 50°C for 3 days after that the polymer was treated with 0.5 N HCl and washed with water.

CHN analysis calculated for 11(C₁₄H₂₅NO₃)+2(C₃H₄O₂): C: 64.98, H: 9.64, N: 5.24

Found: C: 64.77, H: 9.50, N: 5.08;

Conclusions

Polymerized micelles of poly(11-acryloylaminoundecanoic acid) were obtained. Polymerization of AAU-Na in presence of solubilized oil-soluble cross-linker leads to intramolecular cross-linked polymerized unimolecular micelles with fixed structure. Selective hydrolysis of the cross-linked core enables obtaining of the polymer similar to that synthesized without cross-linker.

The more detailed investigation of core cross-linked polymerized micelles will be presented in the forthcoming paper.

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