



Macromolecules of poly-(12-acryloylaminododecanoic acid) in organic solvent: Synthesis and molecular characteristics



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ABSTRACT

The samples of poly(12-acryloylaminododecanoic acid) were synthesized in micellar solutions of the monomer. The possibility of obtaining polymeric ionogenic surfactants of different molecular masses by varying concentration of monomeric surfactant was demonstrated. Detailed studies of the obtained polymer were performed using macromolecular hydrodynamic methods, dynamic light scattering, scanning probe microscopy and flow birefringence. The parameter of equilibrium rigidity of macromolecules (the Kuhn segment length $A = 62 \times 10^{-8}$ cm) and their effective hydrodynamic diameter were determined in mixed solvent (dioxane-cyclohexanol). Contributions made by optical microform and macroform effects to the observed dynamic birefringence were analyzed in detail. The intrinsic optical anisotropy of the monomer unit was estimated; it correlates well with the corresponding values for comb-shaped polymers of similar structure.

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1. Introduction

Monomers and polymers capable of self-organization in dilute solutions are very interesting objects for fundamental science; besides, they also have great practical value due to their possible applications as surface-active micelle-forming agents, stabilizers for disperse systems, flocculants and drug carriers. There are several architectures of self-organizing monomers; the most convenient one is a classical ionic surfactant having linear hydrophobic part with ionic group attached to one end and polymerizable fragment attached to another end. These monomers undergo free-radical polymerization in micellar solutions to give “polymerized micelles” or comb-shaped polyelectrolytes capable of intramolecular hydrophobic association in water. Polymerization of micelle-forming monomers is a 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 at once molecules and nanoparticles. So far a large number of papers on synthesis and polymerization of anionic [1–7] and cationic [8–14] micelle-

forming monomers, and studies of “polymerized micelles” in aqueous solutions [15–21] have been published. However, little attention is paid to the specific behavior of these polymers in the nonionized state in organic solvents.

Hydrodynamic characteristics of comb-shaped molecules can be used in determining equilibrium rigidity of their main chains. Flexibility of the main chain decreases a little with increasing length of side moiety; this effect may be explained by the interaction between side chains which becomes stronger with increasing side chain length [22]. The method of dynamic light scattering allows getting information about the of the particles under investigation in water [23–25], and in other environments [26]. Flow birefringence studies of solutions of comb-shaped polymers allow us to obtain additional important information about conformational characteristics of both main and side chains, since the value and sign of anisotropy of the whole macromolecule are largely determined by the structure and anisotropy of its side radicals [27,28].

Recently we have published a number of papers concerning synthesis and studies of poly(11-acryloylaminoundecanoic acid) (PAAUA) and its cross-linked analogue in organic media [29]. It was found that these polymer chains possess rather high equilibrium rigidity ($A \approx 10$ nm). We have supposed that this phenomenon is caused by the presence of amide groups in side moieties of PAAUA macromolecules which are directly linked to the main polymer chain.

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The present work is focused on the investigation of a novel polymer synthesized from a micelle-forming monomer sodium 12-acryloylaminododecanoate. Comprehensive studies of poly(12-acryloylaminododecanoic acid) (PAADA) with long aliphatic fragment attached to the main chain via amide group were performed using molecular hydrodynamic and optical methods. The purpose of the investigation was to reveal mechanism of influence of side chains on physical parameters of macromolecules.

2. Experimental section

2.1. Materials

12-aminododecanoic acid and acryloyl chloride were purchased from Sigma–Aldrich.

2.1.1. Monomer synthesis and polymerization

The solution of 0.028 mol of acryloyl chloride in 5 ml of carbon tetrachloride was added drop-wise to a solution containing 0.023 mol of 12-aminododecanoic acid, NaOH (0.05 mol) and 5 ml of *n*-butanol in 50 ml of water; the procedure was carried out for 20 min under vigorous stirring and cooling with cold water bath. After addition of all acryloyl chloride solution, stirring was continued for 30 min at pH not less than 8; then the mixture was acidified with 2.5 ml of concentrated HCl. 12-Acryloylaminododecanoic acid was collected by filtration, washed with water, dried and crystallized from ethyl acetate. The yield was 82% and the melting point of the product was 96–98 °C.

Sodium salt of 12-acryloylaminododecanoic acid was obtained by dissolving 1.51 g (0.0056 mol) of the above acid in 20 ml of methanol containing 0.225 g (0.0056 mol) of NaOH, filtered and precipitated by pouring in large excess of acetone. Precipitate was filtered, washed with acetone and pentane, dried in vacuum desiccator over CaCl₂ and stored in desiccator over sulfuric acid. The yield was 82% and melting point was 220–222 °C. The results of elemental analysis were the following: calculated C% 61.83; H% 8.99; N% 4.81; Found C% 61.83; H% 9.50; and N% 4.79.

Typical procedure of polymerization was performed as follows: AAD-Na (300 mg) was dissolved in an appropriate amount of water to obtain the desired monomer concentration (ranging from 0.005 to 0.2 mol/L). Potassium persulfate was added to reach its concentration 1 g/L, and argon was bubbled through the reaction mixture for 15 min. Polymerization proceeded for 1 h in a thermostated bath at 60 °C, and product was isolated by pouring the reaction mixture into 100 ml of 0.5 N HCl. To isolate polymer as a Na-salt, precipitation in acetone was used. Polymer was washed with water and dried in desiccator over sulfuric acid. Polymerization runs carried out at various monomer concentrations yielded polymers with different degrees of polymerization.

Sodium salt of 12-acryloylaminododecanoic acid is a micelle-forming monomer, the next higher homolog of well-described 11-acryloylaminoundecanoic acid (AAU-Na). We did not try to measure CMC of AAD-Na supposing it should be 2–3 times lower than that of AAU-Na (4×10^{-4} mol/L) [6]. For AAU-Na, the existence of bilayered structures in solution, such as vesicles and tubules, was shown [30]; it can be expected that AAD-Na will demonstrate similar behavior. Even at high concentrations, monomer solutions were clear (or slightly turbid if contained a fraction of monomer in acid form) and non-viscous. Polymerization is characterized by a long induction period (up to 30 min depending on monomer concentration); after that, nearly 100% conversion is reached in a few minutes. All polymer solutions were clear and viscous.

The structure of monomer unit is given in Fig. 1.

Fig. 2 presents conversion curves for processes carried out at various initial monomer concentrations (conversions were

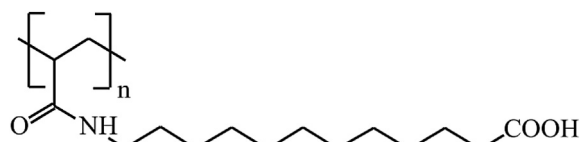


Fig. 1. Structural formula of PAADA monomer unit.

determined by spectrophotometry). The initial polymerization rates estimated using these curves were (567, 237, 113, 9) $\times 10^{-4}$ mol/(L \times min) at monomer concentrations of 0.2, 0.1, 0.05 and 0.01 mol/L, respectively. These data were used to determine the reaction order with respect to monomer (1.4). This value of the reaction order can be explained by low initiator efficiency. The monomer is present in the reaction mixture in the micellized state, the micelles possessing negative surface charge. The concentration of free monomer does not exceed CMC, i.e. is about 10^{-4} mol/L. In these conditions, initiation by negatively charged primary SO₄⁻ radicals can be realized only during interaction of radicals with free monomer molecules; thus, it is indeed ineffective. Chain growth starts after transferring the formed monomeric or oligomeric radical into monomer micelle and proceeds very fast with the formation, first, of polymer–monomer particle and then of “polymerized micelle”. Depending on molecular mass and concentration of the solution, PAAD-Na molecules can probably have various conformations (from micelle-like globules to loose coils); this process is controlled by competition between hydrophobic and charge interactions and requires special consideration.

Fig. 3(a–c) illustrates the data, observed by AFM for PAAD-Na molecules (analogues of PAADA-5 in Table 1) after rapid adsorption on mica surface from the solution at a concentration of 0.02 g/L. The AFM images show particles, similar to a hard sphere. Images allow us to determine the size of objects: the average height of $h = 1.8$ nm and a base diameter of $r = 80$ nm. This makes it possible to estimate the volume and molecular weight of the particles. Using the well-known equation for the volume segment of a sphere: $V = \pi \times h \times (3r^2 + h^2)/6$, where h is the height of the segment and r the diameter of its base, we can find the volume of the particle $V = 4530$ nm³. Thus the molecular weight of the particles can be assessed as $M = \rho V N_A = 2.7 \times 10^6$, assuming the particle density ρ close to 1 g/cm³. Taking into account the molecular weight of the macromolecule (see Table 1) we can assume that the observed particles at the AFM images are associates of approximately 4 macromolecules.

All studies of the polymer in the polyacid form were made in the mixed solvent (dioxane/cyclohexanol, volume ratio 1:1). Two

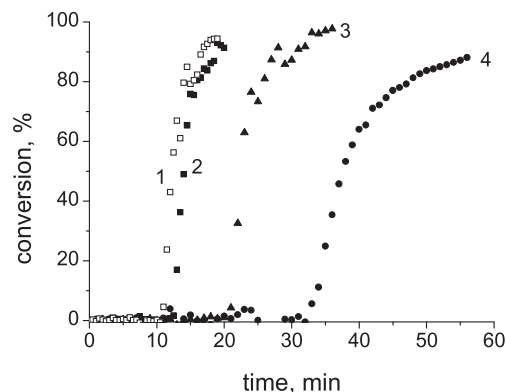


Fig. 2. Time-conversion curves for AAD-Na monomer at various concentrations: 1 – 0.2 mol/L; 2 – 0.1 mol/L; 3 – 0.05 mol/L; and 4 – 0.01 mol/L.

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