



# Polyelectrolyte-colloid complex formation via polymerization: reaction kinetics in direct micelles, inverted micelles, and homogeneous solution studied by NMR and conductometry

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## Abstract

Formation of polyelectrolyte-surfactant complexes (PESCs) in polymerization process of corresponding amphiphilic monomer is a promising way of pure stoichiometric PESC obtained in salt-free systems. Polymerization of micelle-forming monomer dodecylammonium 2-acrylamido-2-methylpropanesulfonate (DDA-AMPS) in different media was studied by means of <sup>1</sup>H-NMR and conductance measurements. Kinetics of polymerization in direct micelles, inverted micelles, and homogeneous solution was considered in terms of classical solution polymerization and microemulsion polymerization. Reaction orders on monomer and initiator were measured in water and dioxane. The rate of polymerization is strongly dependent on monomer micelle existence, being considerably higher in micellar solution than in homogeneous one.

**Keywords** Micellar polymerization · Microemulsion polymerization · Kinetics · Surfmer · Polyelectrolyte-surfactant complex

## Introduction

Polymerization of micelle-forming monomers in micellar state is widely investigated. Most of these works dealt with aqueous solutions of ionic surfactants bearing polymerizable group in the tail or in the head group of the molecule. Much less studies were devoted to micellar systems with polymerizable counterion [1–11] and very few—to inverted micellar polymerization [12–16]. Micellar polymerization usually proceeds with high rate and conversions close to 100%, which is explained by “monomer condensation” effect—increasing of local monomer concentration in the micelle core (up to bulk concentration values) and possible monomer molecule orientation favoring to polymerization [17].

Kinetic studies of polymerization in micellar state are limited to rather few papers [18–26] because of quite fast reaction at low concentrations having low volume effects.

Most results in these studies established classical kinetics regularities known for free-radical homogeneous polymerization. There are some papers considering mechanistic aspects of micellar polymerization for monomers with high and low cmc [24, 25]. Paper [26] treats micellar polymerization in terms of microemulsion regime described in Morgan and Kaler work [27].

In this paper, we describe micellar precipitation polymerization of micelle-forming monomer dodecylammonium 2-acrylamido-2-methylpropanesulfonate (DDA-AMPS) having hydrophobic cation and hydrophilic polymerizable anion. Polymerization of such monomer leads to formation of polyelectrolyte-surfactant complex (PESC)—a special kind of macromolecular substances, which are usually obtained by mixing together solutions of polyelectrolyte and surfactant. Synthesis of PESC by direct polymerization of micelle-forming monomer [1–9, 16] or of the ionic monomer in surfactant solution [28] makes it possible to control molecular weight and dispersity of the resulting polymer [1, 6, 29] and in some cases—morphology of the polymer in the solid state [16]. PESCs obtained by mixing of aqueous solutions of a polyelectrolyte and an oppositely charged surfactant can form different structures in the solid states [30]. Kinetic studies of PESC formation in polymerization process are practically absent in the literature. Most of PESCs are insoluble in water and the

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polymerization proceeds in precipitation regime that is additional complication for precise kinetic measurements. In this direction, probably the most interesting results were obtained by Walker and Kline [1–6] for the polymerization of cetyltrimethylammonium 4-vinylbenzenecarboxylate, which after polymerization formed stable PESC solution in water. The kinetics of structural changes of micellar solutions during polymerization in that works was monitored by SANS [5] but no correlations of these data with monomer conversion were presented.

In our previous papers, we described synthesis of a series of PESC-forming amphiphilic ionic monomers with polymerizable counterion [16, 31], their micelle-forming properties in media of different polarity [32, 33], their polymerization in such media, and the properties of the resulting polymers [34, 35]. The current paper is focused on the polymerization kinetics of a micelle-forming monomer, in which polymerizable group is located in counterion, actually, monomer is AMPS acid anion with about 0.6 degree of binding to the micelles [33]. Polymerization was performed in different states of monomer solution—direct micelles in water and inverted micelles in dioxane and in homogeneous solution in water/dioxane mixture, all under precipitation polymerization conditions. In each case, polymerization resulted in great structural rearrangements of solution [5] originated from the concurrence of hydrophobic interactions of surfactant tails and Coulomb interactions of charged groups to adopt most stable conformation of polymer chain [35]. Direct NMR spectroscopy measurements were used to determine monomer conversion in the course of polymerization.

## Experimental section

Dodecylamine (98%, Merck), 2-acrylamido-2-methylpropanesulfonic acid (99%, Merck), potassium persulfate (special purity grade, Vekton, Russia), and azo-bis-cyanovaleric acid (98%, Sigma-Aldrich) were used as received. 1,4-Dioxane (Vekton, Russia) was distilled above potassium hydroxide prior to use. Deionized water with a specific resistance not less than 16 MOh was used for all preparations.

Monomer DDA-AMPS was prepared as described previously [15].

Conductivity measurements were performed using an Expert-002 (Russia) conductometer equipped with Mettler Toledo InLab-710 platinum probe; conductivity values were taken every 10 s.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance III 500 spectrometer at 500 MHz.

Polymerizations were carried out in standard 5-mm NMR tubes in non-deuterated solvents. Measuring cell was preheated to temperature 60 °C. Shimming and locking were performed using a sample tube with corresponding deuterated pure solvent. Monomer and initiator solution of desired

concentration were placed in the NMR tube and bubbled with argon for 15 min prior to heating. After placing the tube into the spectrometer, shimming (without lock) was performed again and  $^1\text{H}$  NMR spectra were recorded every 18 s (4 scans per spectrum). Monomer conversion was calculated from the decreasing intensity of signals corresponding to the double-bond hydrogens at 6.50, 6.38, and 5.94 ppm (Figs. 1 and 2). Signal of methyl group (from dodecylamine) at 0.9 ppm was used as internal standard for calculation of conversion. Conversion was calculated as  $p = (1 - I_1/I_7) \times 100\%$ , where  $I_1$  and  $I_7$  are integral intensities of hydrogen signals of double bond ( $I_1$ , 3H) and methyl group ( $I_7$ , 3H). The data was processed with Bruker Topspin Dynamics Centrum software.

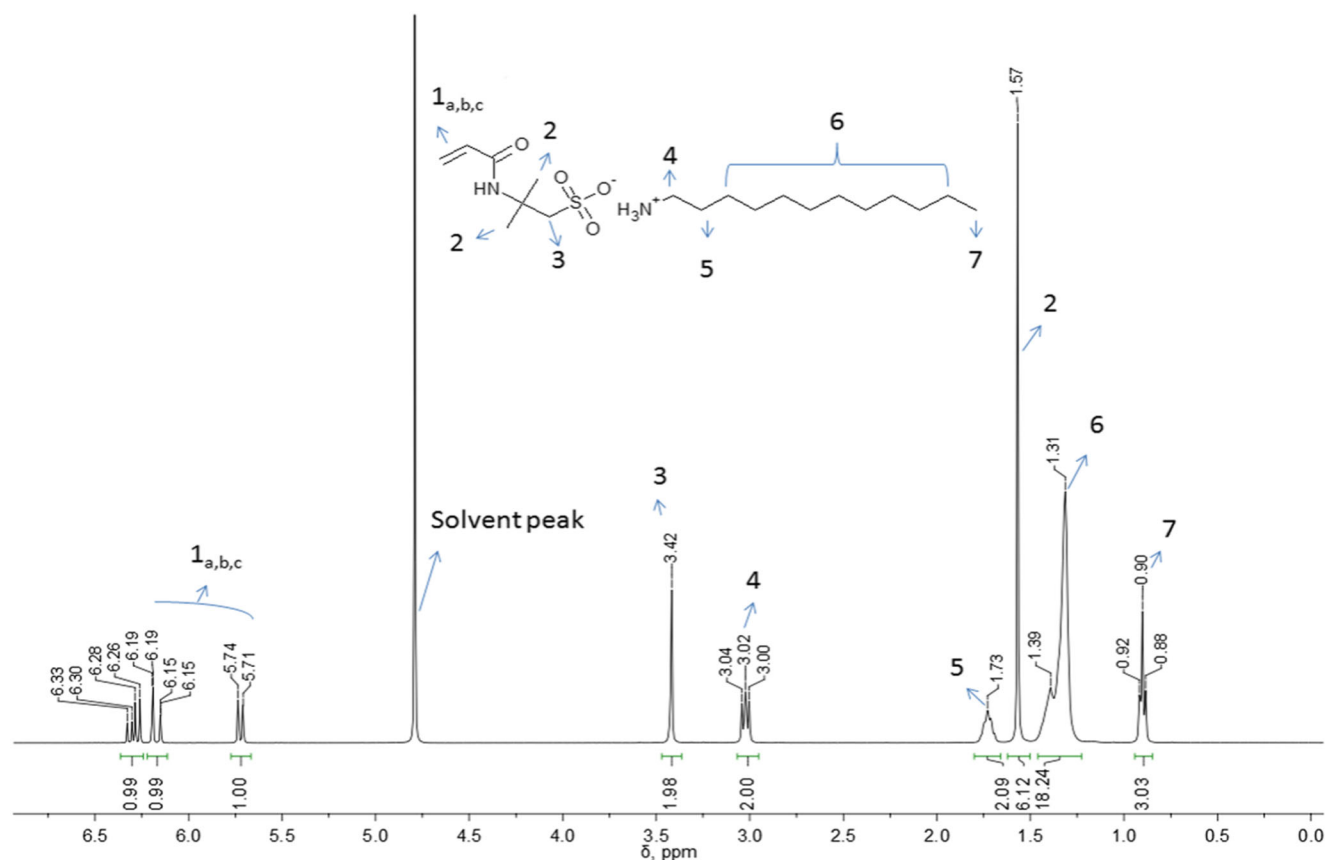
Visual effect of polymerization was that polymer precipitated from solution but it was found from NMR and conductance measurements that precipitation started from metastable polymer solution when conversion of monomer was quite high (more than 60–70%), so polymerization proceed quicker than it seems from visual observation and it is possible to perform conversion measurements in macroscopically homogeneous solution before precipitation starts.

After polymerization, DDA-PAMPS was isolated by filtration and washed with acetone. To convert it to PAMPS-Na form, the polymer sample was dissolved in methanol containing 20% stoichiometric excess of NaOH and stirred for 24 h then precipitated in diethyl ether, and washed with acetone. Resulting PAMPS-Na was dissolved in water, filtered through a 0.45- $\mu\text{m}$  syringe filter, and freeze-dried. The completeness of ion exchange was checked by NMR by the absence of signals corresponding to the dodecylammonium tail. Chromatographic analysis was performed on Shimadzu LC-20AD apparatus equipped with a refraction detector and TSKgel SuperAW5000 column calibrated according to pullulan standards (Shodex,  $M_w = 5 \times 10^3 - 8 \times 10^5$ ). Aqueous 0.5 M  $\text{NaNO}_3$  with 0.05%  $\text{NaN}_3$  was used as eluent at 30 °C, flow rate 0.5 mL/min, and pressure 1.8 MPa. Sample concentration was 3 g/L.

## Results and discussion

DDA-AMPS is micelle-forming monomer which can form direct and inverted micelles in appropriate media; its aggregation behavior and polymerization in micellar state and in homogeneous solution were studied in detail [16]. In water, DDA-AMPS forms micelles having hydrodynamic radius of 2.4 nm, aggregation number of about 100, and cmc of  $1.1 \times 10^{-2}$  mol/L at 25 °C.

Polymerization of DDA-AMPS proceeds very fast and with high yields in micelles and with considerably lower yields in homogeneous regime. Recently we have published new results [26] for kinetic study of micellar polymerization with semi-empirical model of microemulsion polymerization



**Fig. 1** <sup>1</sup>H NMR spectrum of AMPS-DDA in D<sub>2</sub>O (signals of NH and NH<sub>3</sub> are not shown)

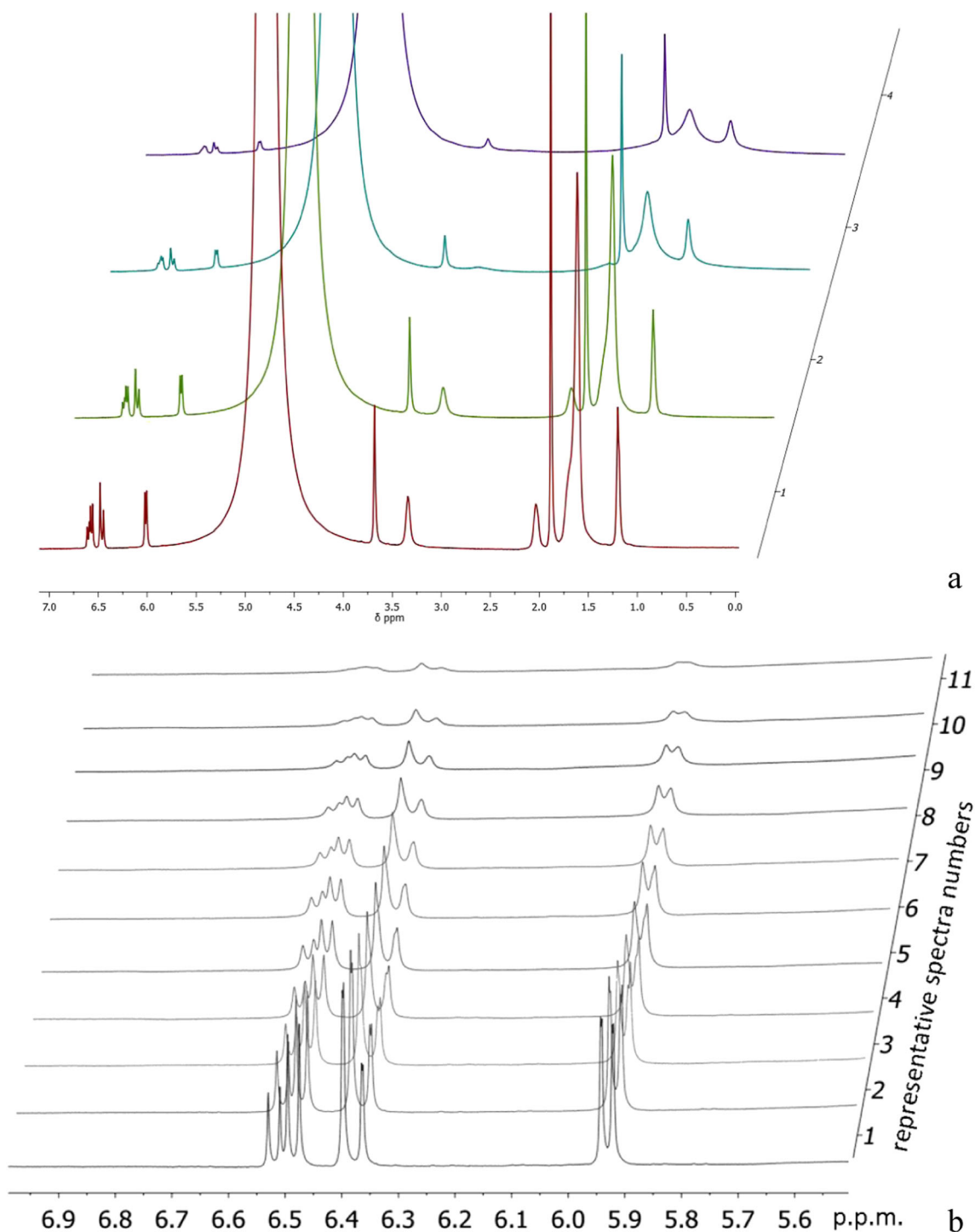
[27] adopted for the case of pure micelle-forming monomer. Conversion data for polymerization rate calculations in that paper were obtained from UV-spectroscopy measurements. Here we tried to use NMR real-time spectroscopy for investigation of DDA-AMPS polymerization. NMR-spectroscopy allows obtaining directly the data of monomer conversion in the course of polymerization in various media.

Polymerization of DDA-AMPS in water was performed in monomer concentration range 0.013–0.25 mol/L at constant potassium persulfate concentration ( $3.7 \times 10^{-3}$  mol/L) or at constant monomer concentration 0.25 mol/L and initiator concentration range  $2\text{--}11 \times 10^{-3}$  mol/L. Conversion vs time curves are shown in Fig. 3 a and c.

In all cases, some induction period (1–2 min) was observed after which polymerization started and completed in several minutes. Rates of polymerization were calculated from conversion data (from linear region of conversion curves: 10–70% conversion) and plotted against concentration (Fig. 3b, d). From these plots, reaction orders were calculated:  $1.13 \pm 0.04$  with respect to monomer and  $0.46 \pm 0.08$  with respect to initiator. These values appeared to be in good agreement with classical theory of free-radical polymerization and previously reported data for polymerization of the micelle-forming monomer alkyldimethyl-4-vinylbenzylammonium chloride in water [24, 25].

In dioxane, DDA-AMPS forms inverted micelles with cmc about  $3.3 \times 10^{-2}$  mol/L (value obtained by conductance measurements in dioxane containing 5% water). Polymerization in dioxane was performed in similar way as in water; azo-bis-cyanovaleric acid was used as initiator. Conversion curves (Fig. 4) in dioxane appeared to be very similar to those in water indicating high rate of polymerization retained up to 80% conversion, which is characteristic to micellar or microemulsion type of polymerization [26, 36]. Reaction order with respect to monomer appeared to be  $1.32 \pm 0.16$  that is close to value obtained in water.

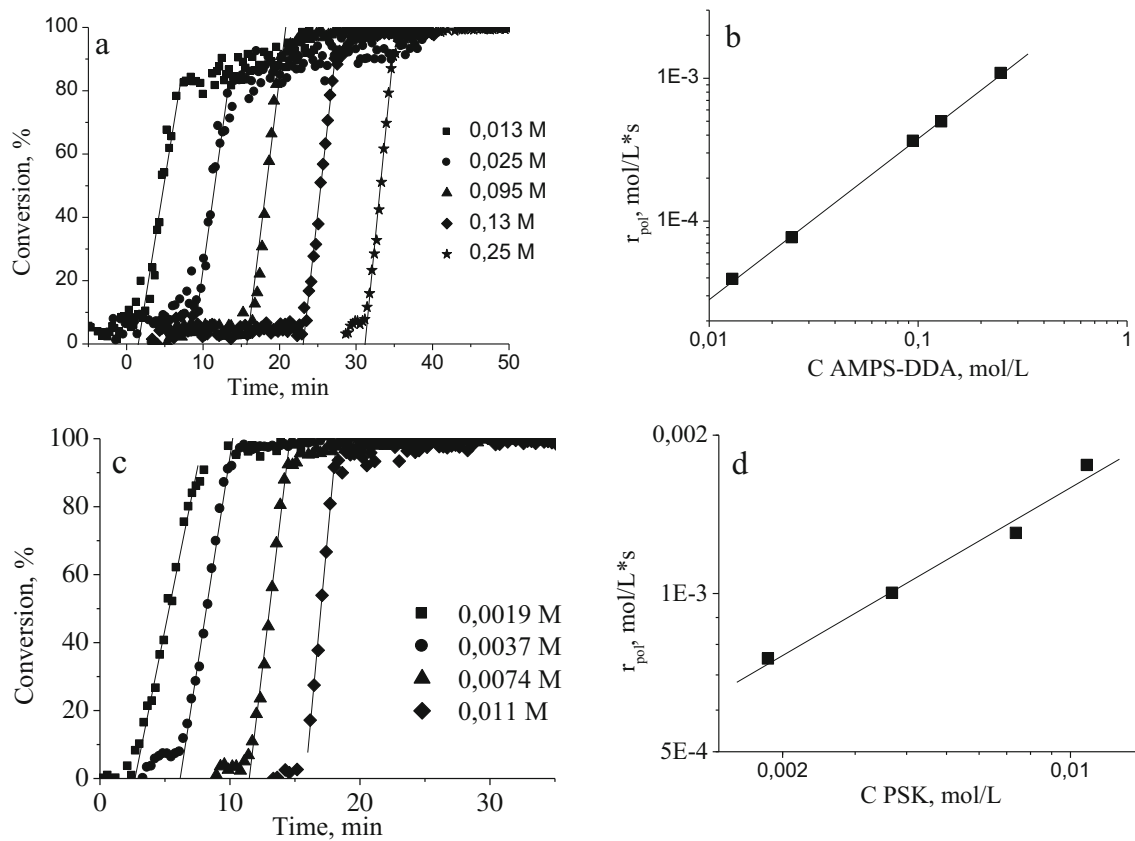
Polymerization of DDA-AMPS in dioxane containing 20% of water proceeds considerably different. These conditions correspond to homogeneous monomer solutions; no micelles formed. The rate of polymerization ( $8.5 \times 10^{-5}$  mol/L  $\times$  s) compared with that in water ( $1.0 \times 10^{-3}$  mol/L  $\times$  s) or in pure dioxane ( $6.1 \times 10^{-4}$  mol/L  $\times$  s) is much lower (at the other conditions being equal) and after 1 h of reaction proceeding conversion was not higher than 70% (Fig. 5a). It seems that differences between polymerization in micellar state (pure water, pure dioxane) and homogeneous solution are just quantitative, but there are some observations indicating qualitative distinction between micellar and homogeneous polymerizations.



**Fig. 2** Evolution of  $^1\text{H}$  NMR spectra of DDA-AMPS during polymerization in water **a** full spectrum and **b** double-bond hydrogen signals

Conversion data can be treated in the terms of microemulsion polymerization kinetics theory proposed by Morgan and Kaler [27] and used for micellar polymerization characterization. In this approach, dome-shaped dependences of  $dp/dt$  on  $p$  appeared to be characteristic for microemulsion regime of polymerization having maximum

of  $dp/dt$  at conversion value of 39%. In homogeneous regime, this dependence extincts to straight line. As it can be seen from Fig. 5b, in pure water and pure dioxane, conversion curves in Morgan-Kaler coordinates have distinct dome shapes, whereas conversion points in water-dioxane mixture drop to linear array.

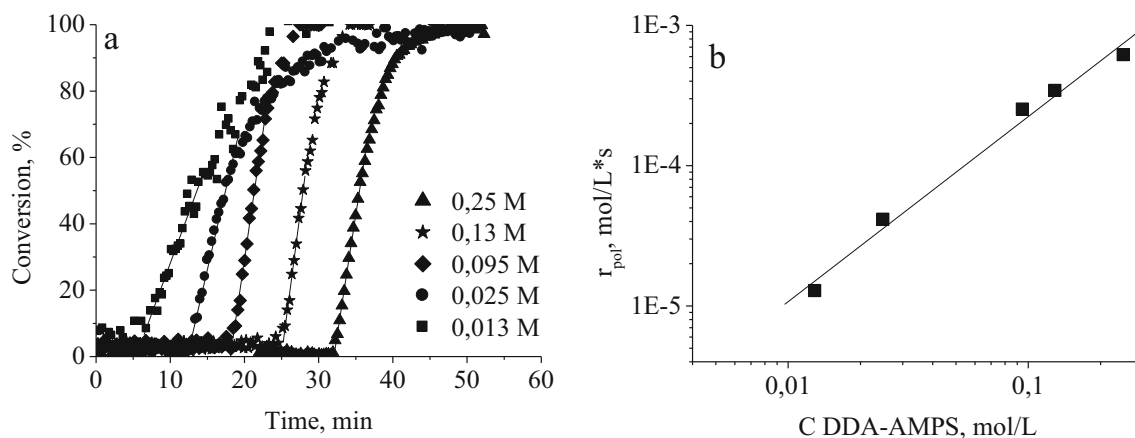


**Fig. 3** Kinetic data for DDA-AMPS polymerization in water. Conversion curves (**a**, **c**) are shifted by 500 s from each other for distinct representation. **a** Conversion vs time dependences at different monomer concentrations. **b** Polymerization rate vs monomer concentration

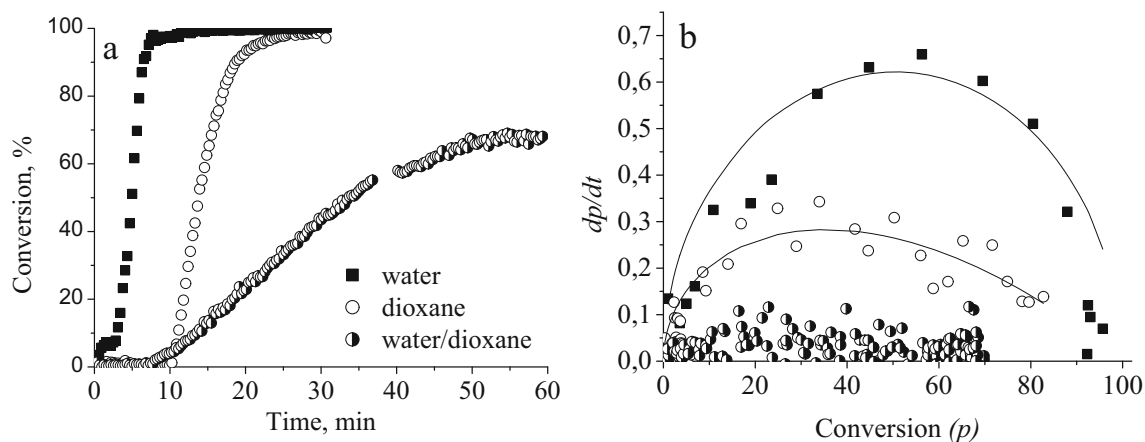
dependence. **c** Conversion vs time dependences at different initiator (PSK) concentrations. **d** Polymerization rate vs initiator concentration dependence

The main equation for micellar polymerization  $\frac{\partial p}{\partial t} = (1-p)^\alpha \sqrt{-2A^* \ln(1-p)}$  having two fitting parameters  $A^*$  and  $\alpha$  were used to fit experimental data of DDA-AMPS conversion (lines on Fig. 5b). In the Morgan-Kaler model, parameter  $A = \frac{2fk_d I k_p C_0}{M_0}$  combines the rate constants of initiator decomposition ( $k_d$ ) and propagation ( $k_p$ ) reaction, initial monomer

( $M_0$ ), and initiator ( $I$ ) gross concentration and local concentration of monomer in the particles at the moment of the particle formation ( $C_0$ ). In this case, empirical parameter  $A^* = AM_0/2$  accounting dependence of initiation efficiency  $f$  on monomer concentration  $f \approx k_i[M] \approx k_i M_0(1-p)$ , where  $k_i$  is relative rate constant of primary radical reaction with monomer. Parameter  $\alpha$  corresponds to initiation efficiency and radical transfer from



**Fig. 4** Kinetic data for DDA-AMPS polymerization in dioxane. **a** Conversion vs time dependences at different monomer concentrations (curves are shifted by 500 s from each other for distinct representation). **b** Polymerization rate vs monomer concentration dependence



**Fig. 5** Conversion vs time dependences (a) and polymerization rate vs conversion plots (b) for DDA-AMPS polymerization in water, dioxane, and water/dioxane mixture (1:4) at monomer concentration 0.25 mol/L

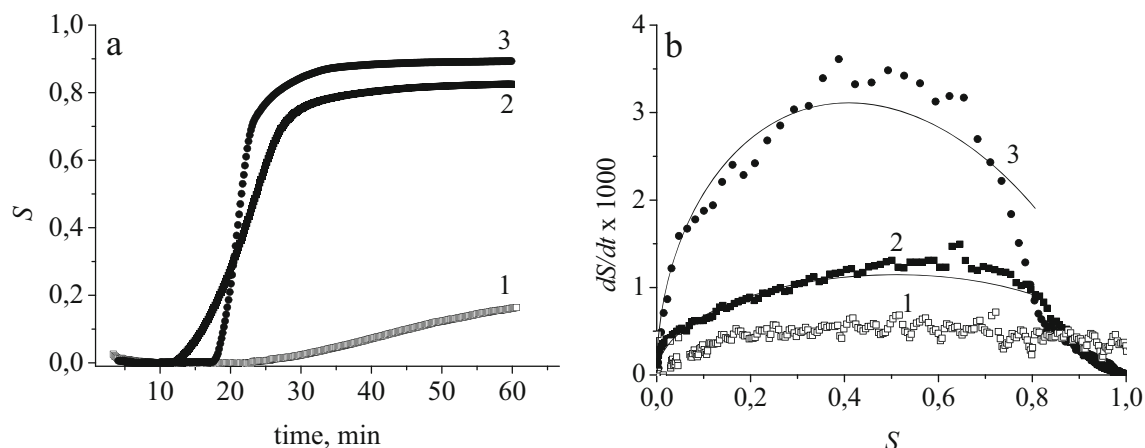
solution to the micelles [19, 21]. Here  $A^* = 0.75$  and  $\alpha = 0.7$  in water and  $A^* = 0.25$  and  $\alpha = 1.15$  in dioxane. In the case of DDA-AMPS, the polymerization was complicated by polymer precipitation and this might disturb basic regularity, but in general, in all cases of micellar polymerization, we observed dome-shaped curves in Morgan-Kaler plots for NMR-based (or UV-based) conversion data and for conductance changes during polymerization.

Polymerization of DDA-AMPS and some related monomers was studied by means of conductance measurements. Conductance changes during polymerization (Fig. 6a) retrace conversion curves when plotted in appropriate coordinates (normalized conductance  $S$  vs time,  $S = 1 - \frac{\chi - \chi_f}{\chi_0 - \chi_f}$ , where starting value of conductance  $\chi_0$  taken as a datum and final value of conductance  $\chi_f$  taken as unity) [26]. Real-time conductance measurements are quite simple and substantially cheaper than NMR. In our case, the data obtained by means of conductometry appeared to be in good agreement with

NMR observations and the kinetics model (Fig. 6b) at the early stages of polymerization (up to 40–50% conversion, until large amount of polymer was formed, affecting conductance due to increasing viscosity or precipitation).

### Molecular characteristic of the polymers

Since DDA-PAMPS is PESC, it is relatively complicated object for chromatographic characterization due to its high adsorption. Some DDA-PAMPS polymers obtained in micellar regime (direct or inverted micelles) and in homogeneous solution were converted to polyelectrolyte form (PAMPS-Na) and analyzed by means of SEC. Results are shown in Table 1. One can see that molecular weights of the polymers obtained in micellar regime appeared to be considerably higher than those of the polymers obtained in homogeneous solution, whereas dispersity of the polymers had comparable values of 1.9–3.3. Such values of dispersities are common for free-radical polymerization, but a



**Fig. 6** Conductometric study of polymerization in water at 0.25 M monomer and 1 g/L CVA concentration. (1) AMPS-Na; (2) DDA-AMPS; (3) hexadecylammonium-AMPS. a normalized conductance ( $S$ ) vs time dependence. b Rate of normalized conductance change vs normalized conductance

**Table 1** Molecular characteristics of PAMPS-Na, isolated from samples of DDA-PAMPS obtained in different conditions

Solvent system	Solution appearance	$M_w \times 10^{-3}$	$\bar{D}$
Water	*	618	4.0
Water	Direct micelles	1068	3.3
Water/dioxane 4/1	Direct micelles	666	2.2
Water/dioxane 1/4	Homogeneous	111	1.9
Water/dioxane 1/19	Inverted micelles	256	2.1
Dioxane	Inverted micelles	592	3.1

\*Obtained from AMPS-Na in aqueous solution without DDA

little bit higher than those (1.2–1.7) obtained for polymers of  $\omega$ -N-acryloylaminoalkanoates in micellar regime [37]. Probably, in this case, some dispersity in molecular weights may be caused by coexistence of two possible mechanisms of polymerization and PESC formation—the first (and the main) is polymerization of AMPS anion bound to dodecylammonium micelles (degree of binding about 60% [33]) and the second is polymerization of “free” AMPS anion with subsequent binding with micelles. Precipitation of the polymer during polymerization also may contribute to polymer dispersity.

## Conclusion

Micellar polymerization and its kinetics are of great interest because of their academic and applied significance. PESC formation via polymerization of tailored amphiphilic monomers in appropriate media allows obtaining pure stoichiometric products with controllable molecular weights. Thus, it becomes clear from the results of NMR experiments presented in this paper that polymerization of DDA-AMPS (micelle-forming alkylammonium salt of ionic monomer AMPS) proceeds in micellar regime in both direct micelles (in water) and inverted micelles (in dioxane) and can be treated in terms of microemulsion polymerization theory. Molecular weights of the polymers obtained in micellar regime are higher than those of polymers obtained in homogeneous solution. No considerable differences in dispersity of “micellar” or “homogeneous” polymers were observed for DDA-AMPS.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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