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Ananiy Kohut[1], Andriy Voronov[2] and Stanislav Voronov[1]

MICELLIZATION AND ADSOLUBILIZATION OF AMPHIPHILIC INVERTIBLE POLYESTERS

[1] Lviv Polytechnic National University
12, S. Bandery str., 79013 Lviv, Ukraine; ananiy.kohut@gmail.com
[2] North Dakota State University
1735 NDSU Research Park Dr., Fargo, ND, 58102, USA

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Abstract. Using surface tension measurements, solubilization, and fluorescence spectroscopy, polyesters based on aliphatic dicarboxylic acids and PEG-1000 have been shown to form monomolecular micelles in aqueous solutions at the concentrations of 10^{-7}–10^{-4} %. With increasing concentration, the monomolecular micelles have been revealed to aggregate to afford polymolecular micelles. The amphiphilic polyesters have been demonstrated to possess invertibility and thus respond to the change in a medium polarity as well as adsorb at hydrophilic and hydrophobized dispersed silica surface. Using 2-naphthol, the adsorbed amphiphilic polyester layers have been shown to solubilize sparingly water-soluble organic compounds.

Keywords: amphiphilic polymers, micellization, invertibility, adsorption, adsolubilization.

1. Introduction

Adsolubilization (also referred to as surface solubilization) is the incorporation of sparingly water-soluble organic compounds (solutes) into surfactant layers adsorbed at the solid/solution interface, though the solutes themselves hardly adsorb at the interface [1]. This phenomenon has been widely used in the development of various industrial products such as paints [2], pharmaceuticals [3], cosmetics, and health care products [4], preparation of polymer thin films [5], and wastewater treatment to collect and remove organic pollutants [6-13]. Adsolubilization has been reported to be applied in electrochemically assisted photocatalysis [14] and to determine perfluorinated compounds in river water [15] and herbicides in drinking water [16].

Adsolubilization characteristics have been reviewed previously [17] as a function of the chemical structure of surfactants used as an adsorbate [6, 18, 19], a kind of substrate [20, 21], a type of solute [7, 18, 22, 23], temperature [24, 25], and pH in solution [8, 22, 26]. It has been recently reported that surfactant mixtures present great possibilities for enhancing the adsolubilization efficiency of sparingly water-soluble compounds as a result of the formation of a closely packed adsorbed layer at the solid/solution interface [4].

However, one of the problems of using surfactant-modified adsorbents in adsolubilization is the loss of surfactant because of desorption caused by the replacement of the solution phase [27-29]. This desorption necessarily results in the subsequent release of the adsolubilized solutes. From this point of view, the use of polymeric surfactants as an adsorbate is more practical for adsolubilization. Recently, polymerizable surfactants have been used to minimize surfactant losses by polymerization of the adsorbed micellar structure to help secure it to the solid oxide surface [27]. Tsurumi *et al.* [28, 29] used nonionic surface active triblock copolymers as a polymeric adsorbate to study adsolubilization into the adsorbed layers at the silica/solution interface. The block copolymers formed core-shell micellar aggregates in an aqueous solution [30]. The core-forming blocks provided an adsolubilization site for sparingly water-soluble organic compounds, whereas the hydrophilic blocks anchored at the surface of the hydrophilic silica particles [28]. Previously, surface micellar structures have also been observed for short-chain nonionic surfactants adsorbed at the silica surface [31-33].

In fact, the adsorption behavior of nonionic block copolymeric surfactants is of particular interest itself and in terms of adsolubilization. Most copolymer adsorption studies have been performed with the use of diblock copolymers. The adsorption of triblock copolymers has been less extensively investigated, but there are many articles dealing with this issue from both experimental and theoretical viewpoints [34-38]. Thus, the interfacial behavior of poly(ethylene oxide-tetrahydrofuran-ethylene oxide) triblock copolymers at both hydrophilic [37] and hydrophobized [38] silica surfaces has been studied in terms of adsorption isotherms, layer thicknesses, and kinetics of adsorption and desorption. Most of the published work on the adsorption of block copolymers concerns triblock ethylene oxide-propylene oxide-ethylene oxide copolymers adsorbed at silica surfaces [35, 36]. These copolymers are generally referred to by the trade name Pluronics. The adsorption of different Pluronics and pure poly(ethylene oxide) on dispersed silica particles and flat silica substrates has been measured, and the adsorbed layer thickness has been determined [35]. The experimental data have been interpreted with a modified mean-field theory [35].

Due to the copolymers unique properties, Pluronics have been the subject of a wide variety of recent publications [39, 40]. Variation in the molecular characteristics (molecular weight, poly(ethylene oxide)/poly(propylene oxide) ratio) of Pluronics during synthesis allows the fabrication of surfactants for diverse uses, including detergency, dispersion stabilization, foaming, emulsification, lubrication, etc. along with more specialized applications in pharmaceutics, bioprocessing, and separations [39]. Similar to ionic surfactants, Pluronics form micelles above the critical concentration in water with liquid crystals frequently occurring at a higher concentration [41]. The macromolecules of Pluronics have been shown to aggregate in aqueous solutions to form polymolecular micelles mostly at elevated temperatures, with a core presumably dominated by poly(propylene oxide) segments [42, 43]. A parameter of great importance for the aggregation is the critical micelle concentration (cmc), at which micelles start to form [42]. Pluronics macromolecules typically form aggregates of spherical micelles [44, 45] as well as rod-like micelles and possibly layered forms. The aggregate structure depends on the specific molecular design [45] and thermodynamic parameters [40, 44]. In the high-concentrated regimes, micellar aggregates constitute the basis for a variety of crystalline mesophases [46].

Nevertheless, despite the interesting properties of Pluronics, their application is rather restricted, particularly in medicine. Pluronics are not biodegradable, and their macromolecules aggregate in solutions and form complex architectures often at the elevated temperature.

Recently, we described amphiphilic invertible polyesters prepared by a polycondensation reaction from PEG of a molar weight of 300 or 600 g/mol (hydrophilic constituent) and aliphatic dicarboxylic acids (sebacic or dodecanedioic, hydrophobic constituent) [47]. The hydrophilic and hydrophobic fragments are alternately distributed along the polyester backbone. The amphiphilic invertible macromolecules form micellar architectures in solvents strongly differing by polarity and demonstrate a unique switching behavior with changing environment polarity [48-55]. The possibility of conformational switching for the polyesters has been reached with a controllable presence of hydrophobic and hydrophilic fragments and oxygen atoms in the polymer main backbone. The amphiphilic invertible polyesters have been used as nanoreactors for the synthesis of smart nanoparticles with a protective shell made from both the hydrophilic and hydrophobic polymeric fragments and thus very stable both in polar and non-polar environments [48-52].

As a further development of our previous experimental findings, two new amphiphilic polyesters based on longer PEG (molar weight 1000 g/mol) and the same aliphatic dicarboxylic acid components (sebacic and dodecanedioic) have been synthesized and used in an adsolubilization study of poorly soluble (in water) substances upon deposition on solid, dispersed substrates strongly differing by polarity. The new amphiphilic polyesters differ in molecular weight and the hydrophilic-lipophilic balance (HLB) of the repeating units. It is evident that the amphiphilic polyesters based on PEG-1000 are more hydrophilic and, hence, more soluble in water compared to those synthesized from PEG-300 or PEG-600.

We assume that the higher hydrophilicity of the new amphiphilic polyesters can expand their potential use in aqueous media, including biomedical and agricultural application, drug delivery across cell membranes, etc. In the present paper, we describe an original way for the development of hybrid adsorbents based on polymers that are able to adsorb both on polar and non-polar solid substrates and further adsolubilize hydrophobic substances into the adsorbed layer. For this purpose, new amphiphilic polyesters have been characterized in terms of their surface activity and self-assembly upon the changing concentration in aqueous solution. The critical aggregation concentration of the polyesters has been determined, their solubilization ability has been analyzed, and the polarity of the micellar sites responsible for the solubilization in an aqueous solution has been estimated. To this end, the factors that contribute to the polymolecular micelle formation in an aqueous solution (PEG : aliphatic acid length ratio, polyester concentration, hydrophilic–lipophilic balance) have been examined. Adsorption of the new amphiphilic polyesters on both hydrophilic and hydrophobized silica nanoparticles and adsolubilization of 2-naphthol into an adsorbed polyester layer has been studied. The relationship between the HLB value of the amphiphilic polyesters and their adsorption and adsolubilization behavior has been investigated.

2. Experimental

2.1. Materials

Poly(ethylene glycol) with a molecular weight of 1000 g/mol (PEG-1000, Sigma-Aldrich), sebacic acid (Aldrich), dodecanedioic acid (TCI), pyrene (Alfa Aesar), tannic acid (Sigma-Aldrich), 2-naphthol (Aldrich), and a buffer solution with pH 9.0 (BDH) were used as received. Hydrophilic fumed silica AEROSIL® OX50 and hydrophobically modified silica AEROSIL® NAX50, treated with hexamethyldisilazane, were kindly supplied by Evonik Degussa Corporation. The average primary particle size and specific surface area (BET) of AEROSIL® OX50 were 40 nm and 50 ± 15 m^2/g, respectively, as reported by the supplier. The specific surface area (BET) of AEROSIL® NAX50 was 30–50 m^2/g.

Synthesis of the polyesters. A three-necked flask fitted with a nitrogen inlet, a thermometer, and a Dean-Stark trap with a reflux condenser was charged with 0.1 mol of poly(ethylene glycol) PEG-1000, 0.1 mol of dicarboxylic (sebacic or dodecanedioic) acid, and toluene. A 1:3 (w/v) monomer mixture/toluene solution was used. The Dean-Stark trap was filled with toluene. The reactive mixture was agitated and heated to dissolve the dicarboxylic acid completely. Then 0.1 ml of 75 % sulfuric acid was added to catalyze the polycondensation reaction. The mixture was refluxed under nitrogen for about 20 h. To neutralize H_2SO_4, 0.175 ml of a NaOH solution (40 %) was added, and the mixture was stirred at room temperature for 12 h. Sodium sulfate that formed was separated by centrifugation. Toluene was removed under reduced pressure. Polymers were dried in vacuum at 333 K for at least 24 h.

2.2. Characterization

The specific viscosity of the polyester solutions was measured with an Ubbelohde viscometer. The polyester solutions with the concentration of 1 g/100 ml were prepared by dissolving the polyesters in a corresponding solvent. The solutions were left for at least 16 h to equilibrate at room temperature before being measured.

The average molecular weights and polydispersity index (PDI) were determined by GPC using a Waters 515 HPLC pump with an Ultrahydrogel™ 500 7.8×300 mm Column (Waters) and a Waters 2410 refractive index detector. Tetrahydrofuran was used as eluent at a flow rate of 1.0 ml/min; 200 μl of a 1 mg/ml THF solution were injected for each sample. All samples were filtered before running through a 0.45 μm THFE filter (Nalgene). A molecular weight calibration curve was generated with polystyrene standards of low polydispersity (Polymer Laboratories, USA).

Fourier transform infrared spectra were taken with a Thermo Scientific Nicolet 8700 spectrometer with a resolution of 4 cm^{-1}.

^1H NMR spectra were recorded at 400 MHz on a Varian VXR-400 NMR spectrometer.

The surface tension measurements were performed by drop shape analysis on a pendant drop with a Contact Angle/Surface Tension Analyzer from First Ten Angstroms (FTÅ125). Measurements were carried out at room temperature for the polyester solutions of various concentrations (10^{-7}–10 % w/v). Aqueous polyester solutions were prepared by dissolving the polyester in a buffer solution with pH 9.0 and diluting to the desired concentration. All glassware was washed in a 1 N NaOH bath and thoroughly rinsed with distilled water before use.

Fluorescence spectroscopy measurements were used to determine the critical aggregation concentrations (cac). First, a solution of pyrene in acetone with a concentration of $5 \cdot 10^{-4}$ mol/l was prepared. Each sample was prepared by adding the pyrene solution (20 µl) into an empty vial, evaporating the acetone for 2 h at room temperature, adding the polyester solution (20 ml), and stirring the solution for at least 24 h. The final pyrene concentration in water reached $5 \cdot 10^{-7}$ mol/l, which is slightly below the pyrene saturation concentration in water at room temperature. For the fluorescence measurements, the solution (ca. 3 ml) was placed in a 1.0x1.0 cm^2 cell. All spectra were taken using a Fluoromax-3 Fluorescence Spectrometer (Jobin Yvon Horiba) with 90° geometry and a slit opening of 0.5 nm. For fluorescence excitation spectra, λ_{em} = 390 nm was chosen. Spectra were accumulated with an integration time of 0.5 nm/s.

Tannic method developed by Nuysink and Koopal [56] was used to measure polyester concentration in aqueous solutions. This method is based on a principle that turbidity caused by complexation between tannic acid and PEG chains of the polyesters based on PEG-1000 becomes proportional to the concentration of a particular polyester. A linear calibration equation of the absorbency of the polyester and tannic acid complex as a function of the polyester concentration was obtained first in the following manner: 3 ml of the polyester solution of different concentrations was added into a 7 ml glass vial containing 1 ml of water. A 0.5 ml volume of 1 M NaCl solution was added, and the vial was shaken up and down 20 times. A 0.5 ml volume of 2 g/l tannic acid was added to give a total volume of 5.0 ml. The vial was shaken for 10 s, and the absorbency of the polyester and tannic acid complex was measured immediately with a Varian Cary 5000 UV-Vis-NIR spectrophotometer at a wavelength of 600 nm. The amount of free polyester in the solution was measured by the absorbance of the polyester and tannic acid complex.

Calculations of the hydrodynamic radius and section of the macromolecular architectures. From the viscosity data, the volume fraction of macromolecules in solution was calculated according to Newton's equation for spherical particles:

$$w = (h/h_o - 1)/a$$

where h and h_o are the viscosities of the polymer solution and pure solvent respectively, and a is the coefficient equal to 2.5 for spherical particles.

The volume of macromolecular architectures was calculated according to the following equation:

$$V_m = wM/(cN_A)$$

where M is polymer molecular weight, c is polymer concentration, and N_A is Avogadro's number.

Hydrodynamic radius of macromolecular architectures was calculated according to the following equation:

$$R_m = (\tfrac{3}{4}pV_m)^{\frac{1}{3}}$$

Hydrodynamic section of macromolecular architectures was calculated according to the following equation:

$$S_m = (36pV^2)^{\frac{1}{3}}$$

2.3. Adsorption Study

Silica particles (0.1 g) were shaken with 10 ml of polyester solutions of various concentrations for 24 h to achieve adsorption equilibrium. The silica particles were separated by centrifugation (60 min, 9000 rpm). The polyester concentration in the supernatant was measured by referring to the tannic acid method, and the adsorbed amount of the polyester was calculated from the difference in the concentration before and after adsorption.

2.4. Adsolubilization Study

After equilibration of the polyester adsorption on silica, the supernatant was replaced by 10 ml of a 0.4 mM aqueous solution of 2-naphthol, and the resulting suspension was shaken for 24 h. The silica particles were separated by centrifugation (60 min, 9000 rpm). The concentration of 2-naphthol in the supernatant was determined by measuring the absorbance at 328 nm using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The adsolubilized amount of 2-naphthol was calculated from the difference in the concentration before and after adsolubilization.

2.5. Desorption Study

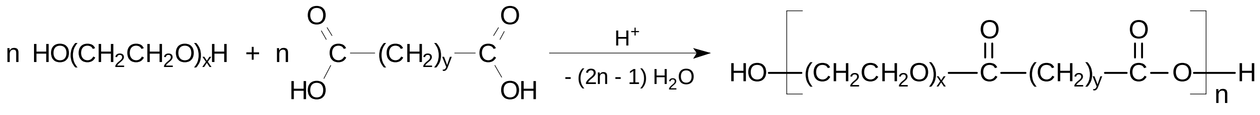
The desorbed amount of the polyester was calculated from the concentration of free polyester in the supernatant after the adsolubilization stage (*i.e.*, after the supernatant replacement). The concentration of free polyester was measured in a manner similar to that mentioned above.

3. Results and Discussion

3.1. Synthesis and Characterization of the Amphiphilic Polyesters

The polyesters of poly(ethylene glycol) with a molecular weight of 1000 g/mol (PEG-1000) and decanedioic (sebacic) acid ($PEG_{1000}S$) or dodecanedioic acid ($PEG_{1000}D$) have been synthesized *via* polycondensation (Fig. 1). The polycondensation of dicarboxylic acids with diols is known to be an equilibrium process; therefore, the water evolved during the reaction must be continuously removed from the reactive mixture to shift the equilibrium toward the desired polyester formation. Hence, the acylation of PEG-1000 by dicarboxylic acids has been carried out in toluene as an azeotrope former; a Dean-Stark trap has been used to remove water. The reaction has been performed in the presence of catalytic amounts of sulfuric acid (1.25 mol %). The progress of the reaction has been monitored by the amount of water released during polycondensation.

The characteristics and composition of the polyesters are shown in Table 1.



$$n\ HO(CH_2CH_2O)_xH + n\ HOOC-(CH_2)_y-COOH \xrightarrow[-(2n-1)\,H_2O]{H^+} HO\left[(CH_2CH_2O)_x-\overset{O}{\overset{\|}{C}}-(CH_2)_y-\overset{O}{\overset{\|}{C}}-O\right]_n H$$

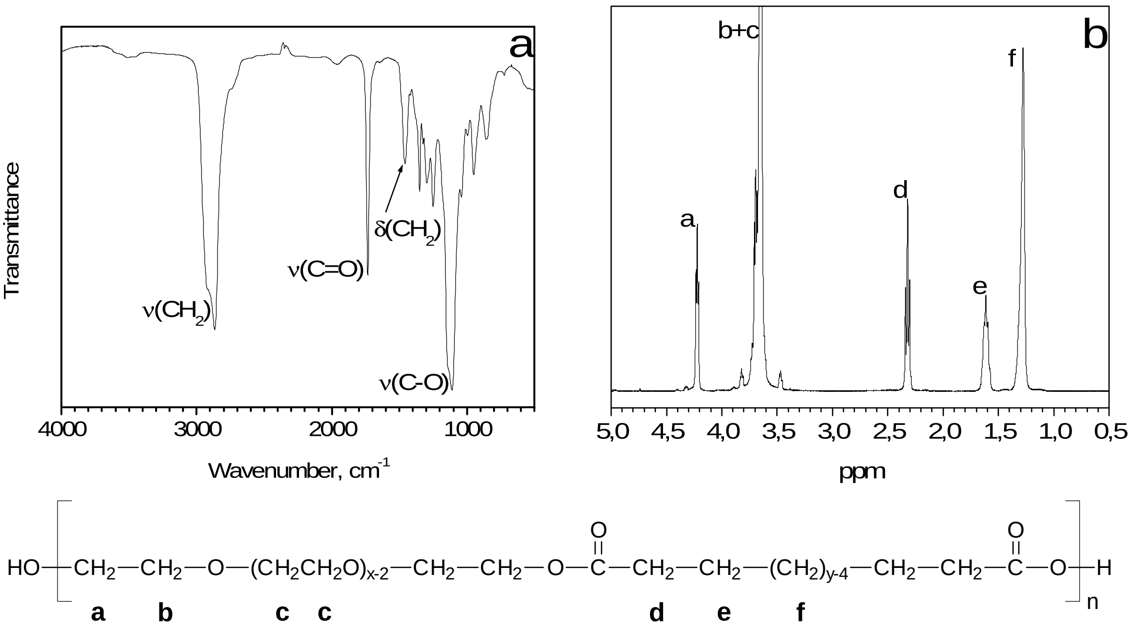
Fig. 1. Polycondensation reaction of the synthesis of amphiphilic polyesters

Table 1

Composition and characteristics of the amphiphilic polyesters

Polyester	Molecular weight / Polydispersity index	Hydrophilic–lipophilic balance (HLB)[a]	Polyester composition
$PEG_{1000}S$	11 700 / 1.95	15.4	x = 22.3; y = 8; n = 10.0
$PEG_{1000}D$	7600 / 1.53	14.4	x = 22.3; y = 10; n = 6.4

[a] Calculated according to Ref. [57]



$$HO-\left[CH_2-CH_2-O-(CH_2CH_2O)_{x-2}-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-(CH_2)_{y-4}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O\right]_n-H$$

Fig. 2. FTIR (a) and ^1H NMR (b) spectra of $PEG_{1000}D$.
The letters on ^1H NMR spectra correspond to letters on the polyester structural scheme

The chemical structure of the synthesized polyesters has been confirmed by FTIR and ^1H NMR spectroscopy (Fig. 2). The following absorption bands have been found in a typical FTIR spectrum (the polyester $PEG_{1000}D$): a very intensive band at 1110 cm^{-1}, which belongs to valence oscillations of C–O bonds in the PEG fragments; an intense absorption band at 1735 cm^{-1}, indicating the presence of ester carbonyl groups (C=O); and absorption bands at 2865 cm^{-1} and 1460 cm^{-1} corresponding to the valence and deformation oscillations of $–(CH_2)_n–$ groups, respectively. In a typical ^1H NMR spectrum (the polyester $PEG_{1000}D$), peaks appeared at 3.64 ppm (m, ~85H, PEG fragments) and 1.28 ppm (m, 12H, $(CH_2)_6$), which have been in agreement with those of PEG and dodecanedioic acid. At 4.22 ppm, a triplet absorption peak that can be attributed to the methylene protons of the acylated PEG end unit has been observed (t, 4H, $COOCH_2CH_2O$). The spectrum shows a triplet peak at 2.32 ppm and a pentet peak at 1.61 ppm corresponding to the methylene groups in an α- and β-position in relation to the carbonyl groups in the dodecanedioic acid moieties (4H, CH_2CH_2COO and 4H, CH_2CH_2COO, respectively).

To confirm the ability of $PEG_{1000}S$ and $PEG_{1000}D$ to respond to polarity changing, the specific viscosity of both polyesters has been measured in different solvents at the same polymer concentration (1 g/100 ml), and the hydrodynamic radius of the macromolecular architectures has been determined. Four solvents of varying polarity have been selected: tetrachloromethane, toluene, acetone, and water (normalized E_T^N values characterizing solvent polarity are 0.052, 0.099, 0.355, and 1.000 [58], respectively) (Fig. 3). For both investigated polymers, the specific viscosity of the CCl_4 solution has been the highest, indicating that tetrachloromethane is a good solvent for these amphiphilic polyesters. This implies that both the hydrophilic (PEG) and hydrophobic (acid moieties) fragments of the macromolecules are extended in this medium. Obviously, the polyester macromolecules thus occupy a larger volume, and viscosity increases. In contrast, the lowest viscosity values have been determined for the aqueous solutions of the polyesters. Interestingly, the viscosity of the more hydrophobic polyester $PEG_{1000}D$ in water has been much lower than those of the acetone and toluene solutions, whereas for the more hydrophilic $PEG_{1000}S$, the viscosity of the aqueous solution has been only slightly lower than that of the acetone and toluene solutions. This could be explained by the fact that water is a selective solvent for the hydrophilic PEG fragments of the polyester macromolecules. In an aqueous medium, the $PEG_{1000}D$ macromolecules build up micelles with a dense non-polar core due to the hydrophobic interaction of the long dodecanedioic acid moieties. As a result, the volume occupied by the $PEG_{1000}D$ macromolecules in water becomes smaller, decreasing the viscosity. The hydrophobic interaction of the shorter sebacic acid moieties of the polyester $PEG_{1000}S$ in water is weaker than that of $PEG_{1000}D$. Evidently, water is a better solvent for $PEG_{1000}S$ than for $PEG_{1000}D$, and the macromolecules of $PEG_{1000}S$ possess a more extended conformation in an aqueous solution than the macromolecules of $PEG_{1000}D$. As shown in Fig. 3, an increase in solvent polarity leads to the decrease in the hydrodynamic radius of the macromolecular architectures in solution. Thus, the synthesized amphiphilic polymers reveal invertibility that could be correlated to their chemical structure.

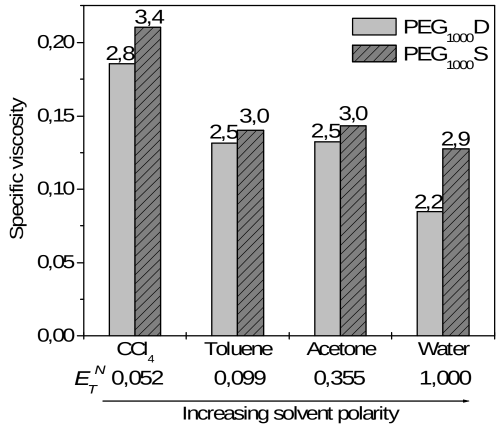


Fig. 3. Viscosity data for amphiphilic polyester solutions in solvents of different polarity (*C* = 0.01 g/ml). The numbers over the bars show the calculated hydrodynamic radius (in nm) of the macromolecular architectures in a corresponding solvent

To evaluate the polyesters surface activity and show the ability to build micelles, we have tried to determine the critical aggregation concentrations (cac) in the polyester aqueous solutions with surface tension measurements. Typically, the surface tension of an aqueous surfactant solution decreases as the surfactant concentration increases. The surface tension reaches a constant value (critical micelle concentration) that does not change if the surfactant concentration increases. Obviously, the situation is more complicated in the case of the amphiphilic invertible polyesters studied here.

Surface tension data for various aqueous polyester solutions plotted semi-logarithmically are presented in Fig. 4. It appears that both polyesters are surface active and decrease the surface tension of water up to 45 mN/m. At very low concentrations of PEG$_{1000}$D and PEG$_{1000}$S, the surface tension of their solutions slightly decreases up to the first critical aggregation concentration (cac$_1$) and then drops rapidly. It is assumed that by very low concentrations in water (from 10^{-7} to approximately 10^{-4} %) the amphiphilic polyester macromolecules form intramolecular micelles having lipophilic pockets composed from the dicarboxylic acid moieties and an external hydrophilic shell containing the PEG fragments. The intramolecular micelle formation is facilitated by the hydrophobic interaction of the dicarboxylic acid moieties and the flexibility of the polyester macromolecule due to the presence of oxygen atoms in the backbone chain. Following fast decrease of surface tension indicates the formation of a monomolecular adsorption layer at the air/water interface and monomolecular micelle aggregation into polymolecular micelles (cac$_1$). Similar behavior has been observed for the amphiphilic invertible polyesters based on the same aliphatic dicarboxylic acid and shorter PEGs (*i.e.*, PEG-300 and PEG-600) that have demonstrated a clear low-concentration break point [59]. Conspicuously, a change in the chemical composition of PEG$_{1000}$D and PEG$_{1000}$S (length of hydrophobic fragment in the macromolecule), and therefore their hydrophilic–lipophilic balance, results in a difference in the behavior of the surface tension isotherm at the high concentrations recorded for PEG$_{1000}$D in comparison to PEG$_{1000}$S. The slope on the surface tension *vs.* concentration plot is well expressed for the more hydrophobic PEG$_{1000}$D and a second break point (second critical aggregation concentration cac$_2$) can be determined for PEG$_{1000}$D. The cac$_2$ point implies the formation of polymolecular micelles, their adsorption at the interface that is accompanied with the structural rearrangements in the adsorbed layer. Afterwards, the surface activity of the PEG$_{1000}$D macromolecules does not change anymore. On the contrary, the experimental data are not so convincing for the recorded surface tension data of PEG$_{1000}$S. To this end, an alternative approach based on solubilization of pyrene has been used for the determination of critical aggregation concentrations.

Pyrene is a well-known fluorescent probe for studying the aggregation behavior of amphiphilic polymer macromolecules [60, 61]. Depending on the environment of pyrene, a bathochromic shift in the spectral band with enhanced excitation intensity is observed due to the migration of the probe from the hydrophilic phase to the lipophilic phase of the polymer micelles. Thus, it is possible to investigate the macromolecular aggregation behavior and to determine the cac of polymeric surfactants.

Fig. 5a depicts the fluorescence spectra of pyrene in aqueous solution over a wide range of PEG$_{1000}$S concentrations. We have succeeded in obtaining cac measurements for both PEG$_{1000}$D and PEG$_{1000}$S by adsolubilization of pyrene. With the increase in PEG$_{1000}$S concentration from 10^{-7} to 10 %, the excitation spectra have exhibited a bathochromic shift from 333.5 to 336.5 nm with an enhanced excitation intensity by a factor of 6.3. The intensity ratio $I_{336.5}/I_{332.5}$ from the excitation spectra plotted against the concentration of the polyester (both PEG$_{1000}$S and PEG$_{1000}$D) is shown in Fig. 5b. Low $I_{336.5}/I_{332.5}$ intensity ratios calculated for dilute solutions indicate a hydrophilic surrounding of pyrene while higher ones indicate a more hydrophobic surrounding due to the formation of aggregates (*i.e.*, polymolecular micelles). The second critical aggregation concentration values for each polyester (cac$_2$) have been determined by a sigmoidal fit of the measured data. The amphiphilic polyester PEG$_{1000}$S shows spontaneous self-aggregation into micelles at a concentration of about 0.05 %, whereas PEG$_{1000}$D does so at 0.003 %. The fluorescence spectroscopy data show that the aggregation of amphiphilic polyesters is favored by the hydrophobic inter-

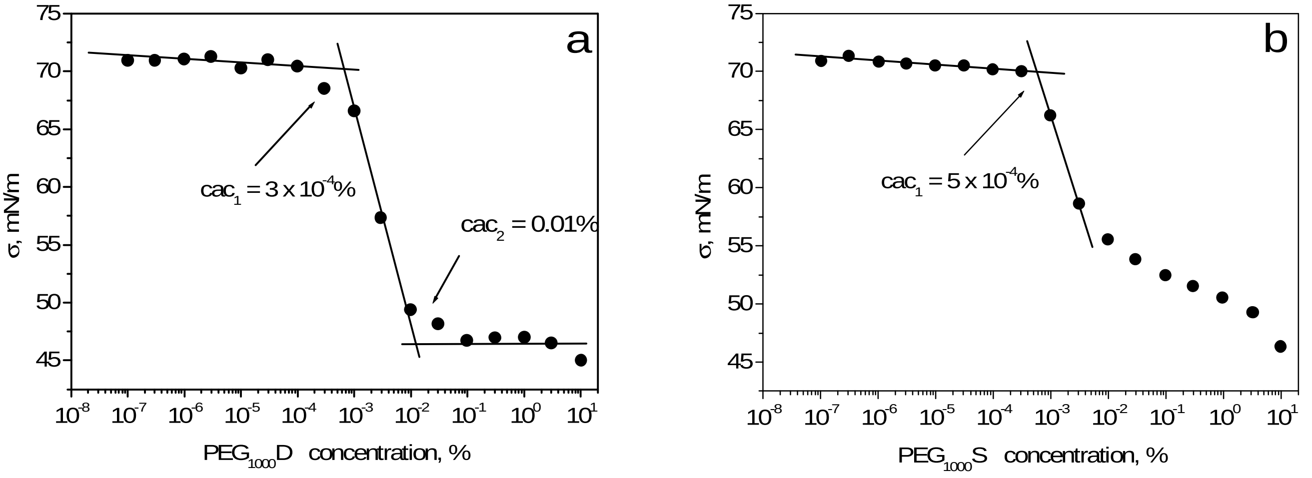


Fig. 4. Surface tension isotherms for aqueous solutions of the PEG$_{1000}$D (a) and PEG$_{1000}$S (b) polyesters

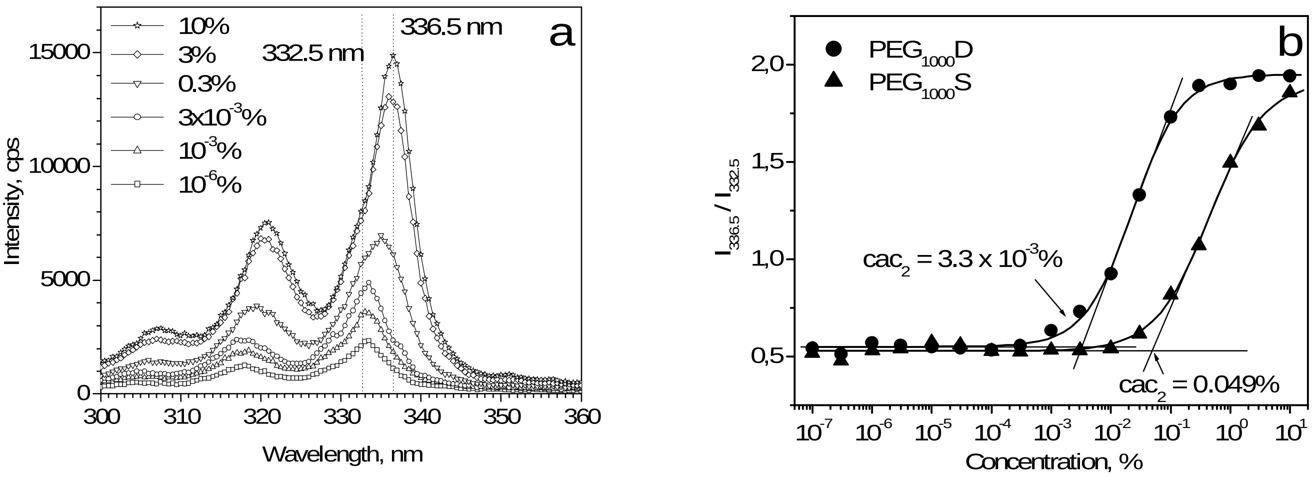


Fig. 5. Excitation spectra of pyrene in the polyester PEG$_{1000}$S aqueous solutions at different concentrations (a); the intensity ratio $I_{336.5}/I_{332.5}$ of the excitation spectra of pyrene in polyester solutions *vs.* polyester concentration (b)

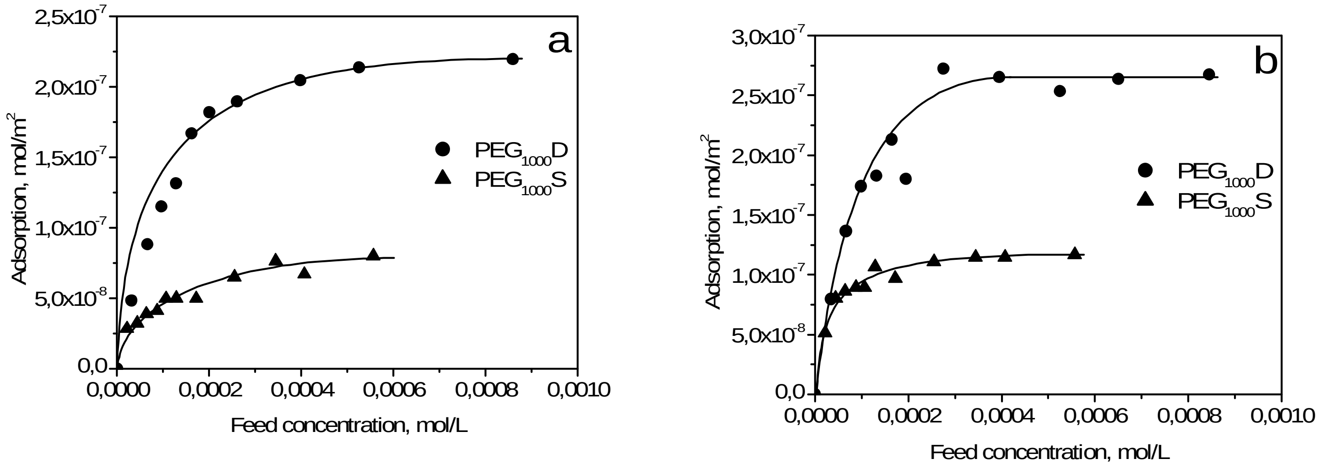


Fig. 6. Adsorption isotherm of the amphiphilic polyesters on hydrophilic (a) and hydrophobized (b) silica particles

action. The polyester PEG$_{1000}$D with longer lipophilic fragments starts to build up the polymolecular micelles at a lower concentration due to the self-aggregation process of the lipophilic parts of the macromolecule. Conversely, PEG$_{1000}$S (having shorter lipophilic fragments) tends to form unimolecular micelles instead of building up aggregates at lower concentrations. Formation of aggregates begins only when the PEG$_{1000}$S concentration reaches 0.05 %. These data show that a small change in the lipophilic fragment length, and therefore in the hydrophilic–lipophilic balance, results in an essential variation in the surface active properties of the amphiphilic polyesters.

Since the critical aggregation concentrations of PEG$_{1000}$S and PEG$_{1000}$D have been easily and unambiguously determined by comparing the intensity ratio $I_{336.5}/I_{332.5}$ from the pyrene excitation spectra in the polyester solutions exactly, these cac values have been used in further calculations.

3.2. Polyester Adsorption

Fig. 6a shows the adsorption isotherms of the polyesters PEG$_{1000}$S and PEG$_{1000}$D on conventional hydrophilic silica particles AEROSIL® OX50. The adsorbed amount of the polyesters increases as the concentration increases and reaches plateau values of about $0.8 \cdot 10^{-7}$ and $2.2 \cdot 10^{-7}$ mol/m^2 for PEG$_{1000}$S and PEG$_{1000}$D, respectively. Comparing the adsorption behavior and adsorbed amount of the amphiphilic polyesters at the plateau region, one can see that the polyester chemical composition (length of the hydrophobic fragment) is obviously one of the key factors in this adsorption. That is, the adsorbed amount obtained at the plateau region is found to be higher for the more hydrophobic PEG$_{1000}$D than that of PEG$_{1000}$S. It is assumed [62] that the adsorption of nonionic poly(ethylene glycol)-based surfactants on the oxide surfaces is governed by forces such as hydrogen bonding and hydrophobic interaction. The former force acts between the surfactant molecule and the oxide surface, whereas a subsequent buildup of the adsorbed layer is driven by the latter force. The adsorbed amount of the nonionic surfactants therefore varies with the ratio of the poly(ethylene glycol) chain length to the alkyl chain length – in other words, the adsorbed amount varies with the hydrophilic lipophilic balance (HLB) value.

The higher adsorption amount for the polyester with longer hydrophobic sequences (PEG$_{1000}$D) indicates that, due to energetically less favorable contact with water, the polyester more readily adsorbs onto the polar silica surface compared to the more hydrophilic PEG$_{1000}$S. However, we found these results intriguing because a very small change in the hydrophobic alkyl fragment length (and, thus, a small change in the HLB value of PEG$_{1000}$D) resulted in its significantly different adsorption amount compared to PEG$_{1000}$S.

Similar adsorption experiments with polyesters PEG$_{1000}$D and PEG$_{1000}$S have been carried out on hydrophobized silica AEROSIL® NAX50. Noteworthily, as it is hydrophobized silica, it cannot be easily dispersed in water and remains floating at the air/water interface. Yet when hydrophobized silica has been added to the polyester aqueous solution and then agitated, dispersion has been formed within 24 h. Fig. 6b shows the adsorption isotherms of the PEG$_{1000}$D and PEG$_{1000}$S on hydrophobized silica nanoparticles recorded after 7 days of agitation. A much faster increase in the adsorption amount is observed for each polyester compared to the adsorption on the conventional hydrophilic silica. Such adsorption behavior is generally observed when polymers possess high affinity to a solid substrate surface. To this end, we have assumed that, opposite of the adsorption on polar silica, when PEG fragments in polyesters are mainly responsible for the formation of physical bonding between polyester and substrate, PEG$_{1000}$D and PEG$_{1000}$S are adsorbed on hydrophobized silica due to the interaction between the hydrophobic alkyl fragments and the substrate. The higher adsorption amount for the more hydrophobic polyester can be explained by the higher surface activity of polyester PEG$_{1000}$D resulting obviously in the adsorption of more compact micellar architectures than in the case of bulkier PEG$_{1000}$S micellar adsorption.

Another important conclusion here is that the amphiphilic polyester macromolecules can adsorb readily onto the diffuse solid substrates strongly differing in surface polarity. The dominant driving force for the adsorption on the hydrophobized silica is obviously the hydrophobic interaction between the sebacic/dodecanedioic acid moieties and the hydrophobized silica surfaces (opposite of the adsorption on polar silica, where adsorption occurs due to the interaction of the PEG fragments with a polar substrate). The length of the acid fragment in the polyester macromolecule is another important factor in this process. Indeed, the adsorption has been found to depend on the length of the hydrophobic fragment in the polymer composition. The adsorbed amount is higher for the more hydrophobic polyester PEG$_{1000}$D than for the more hydrophilic PEG$_{1000}$S.

3.3. Adsolubilization of 2-Naphthol into Adsorbed Amphiphilic Polyesters

Sparingly water-soluble 2-naphthol has been chosen for our experiments to show the ability of the amphiphilic polyesters (being adsorbed onto the solid, dispersed substrates strongly differing by surface polarity) to adsolubilize hydrophobic substances. This experiment is important in order to confirm the capability of the silica-polyester hybrid to act as an adsorbent in an aqueous medium.

Fig. 7 shows an amount of 2-naphthol adsolubilized into the adsorbed amphiphilic polyester on the hydrophilic and hydrophobized silica as a function of the polyester concentration. Hydrophobic 2-naphthol do not adsorb onto polar silica nanoparticles [28]. In separate experiments, we have determined the adsorption amount of 2-naphthol on hydrophobized silica as $9.3 \cdot 10^{-5}$ mmol/m^2. In the presence of the adsorbed amphiphilic polyesters, successful adsolubilization has been observed for both polar and non-polar substrates. For both PEG$_{1000}$D and PEG$_{1000}$S, adsorbed either on polar or non-polar silica, the amount of adsolubilized 2-naphthol increases as the polyester concentration increases and reaches plateau values. Similar behavior has been described in other previously reported adsolubilization studies [28, 29]. The data show that the amount of adsolubilized 2-naphthol is higher for the more hydrophobic polyester PEG$_{1000}$D than for PEG$_{1000}$S, irrespective of substrate polarity. Nevertheless, there is a significant difference in adsolubilization behavior between the polyesters adsorbed on hydrophilic silica in comparison to the polyesters adsorbed on the hydrophobized substrate. Hence, similar to polyester adsorption isotherm behavior, there is a slow increase in adsolubilized 2-naphthol once PEG$_{1000}$D and PEG$_{1000}$S are adsorbed on polar silica (Fig. 7a). If the amphiphilic polyesters are adsorbed on the hydophobized substrate, then the adsolubilized amount increases very rapidly and reaches plateau values at significantly smaller polyester concentrations (Fig. 7b).

It is necessary to note that we have observed and monitored partial desorption of both PEG$_{1000}$D and PEG$_{1000}$S from silica during the adsolubilization. The desorption data are shown in Fig. 8. For the amphiphilic polyesters adsorbed on hydrophilic silica, the desorption of more hydrophilic PEG$_{1000}$S has been higher, as expected, in comparison to PEG$_{1000}$D. However, the situation changes once desorption from hydrophobized silica is analyzed. Here, the desorption of more hydrophobic PEG$_{1000}$D practically has not changed while almost three times less polyester PEG$_{1000}$S has been desorbed from the hydrophobic substrate. These results confirm that different fragments in the amphiphilic polyester macromolecules are responsible for the interaction between the macromolecules and substrates during the adsorption. Moreover, one can conclude that significantly weaker physical bonding is formed when PEG fragments interact with a hydrophilic substrate compared to the bonding formed between the polyesters' alkyl fragments and hydrophobized silica surface.

From the cac$_2$ values determined by the fluorescence spectroscopy, changes in Gibbs energy ΔG_{agg} associated with the polymolecular micelle formation (*i.e.*, aggregation) were calculated through

$$\Delta G_{agg} = RT \cdot \ln \mathrm{cac}_2$$

and the obtained data are shown in Table 2. The higher (in comparison to PEG$_{1000}$D) free energy of the aggregation of the polyester PEG$_{1000}$S indicates more extended conformation. These data are very consistent with the viscosity measurements (Fig. 3) that revealed the weaker hydrophobic interaction of the shorter sebacic acid moieties of PEG$_{1000}$S in water and, hence, the formation of more extended micelles of PEG$_{1000}$S.

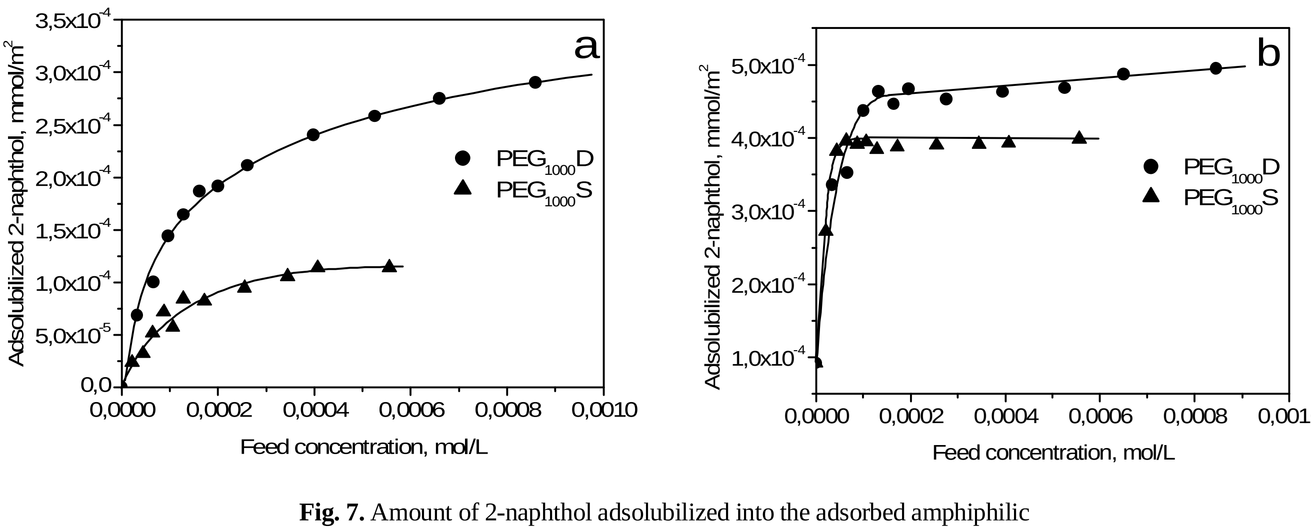


Fig. 7. Amount of 2-naphthol adsolubilized into the adsorbed amphiphilic polyester layer on hydrophilic (a) and hydrophobized (b) silica nanoparticles

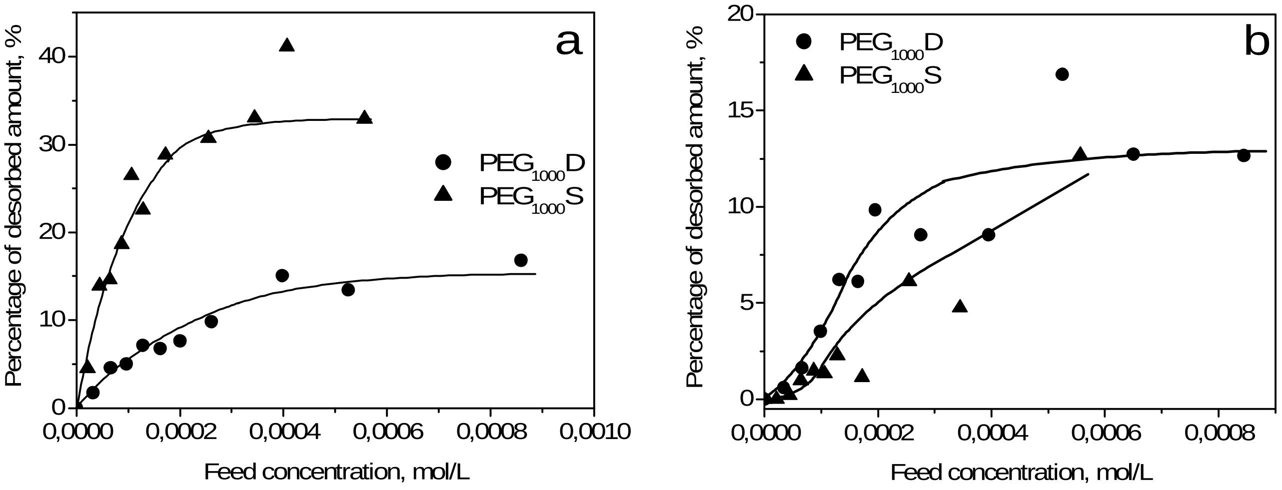


Fig. 8. Desorption of the amphiphilic polyesters from hydrophilic (a) and hydrophobized (b) silica *vs.* feed polymer concentration

Table 2

Second critical aggregation concentration and free energy of aggregation of the polyesters

Polyester	cac$_2$		Free energy of aggregation ΔG_{agg}, kJ/mol	Surface concentration G, mol/m^2	Area per molecule S, nm^2
	%	mol/l			
PEG$_{1000}$D	$3.0\cdot10^{-3}$	$3.9\cdot10^{-6}$	-30.3	$3.03\cdot10^{-6}$	0.55
PEG$_{1000}$S	0.049	$4.2\cdot10^{-5}$	-24.6	$2.74\cdot10^{-6}$	0.61

Table 3

Adsorption and area per molecule of the polyesters at the interfaces

Polyester	Hydro-dynamic section, nm^2	Water – air interface		Hydrophilic silica – water		Hydrophobized silica – water	
		Surface conc. Γ, mol/m^2	Area per molecule S, nm^2	Surface conc. Γ, mol/m^2	Area per molecule S, nm^2	Surface conc. Γ, mol/m^2	Area per molecule S, nm^2
PEG$_{1000}$D	79	$3.0\cdot10^{-6}$	0.55	$2.2\cdot10^{-7}$	7.5	$2.7\cdot10^{-7}$	6.2
PEG$_{1000}$S	104	$2.7\cdot10^{-6}$	0.61	$8.0\cdot10^{-8}$	20.1	$1.2\cdot10^{-7}$	13.8

Information on the conformation of the polyester macromolecules at the air/water interface is necessary for understanding micellar aggregation. To this end, areas per molecule of polyester have been calculated from the surface tension data using the simple form of the Gibbs adsorption isotherm that relates the surface (excess) concentration of the surfactant (G) to the surface tension and the surfactant chemical potential:

$$G = -(1/RT)\,(ds\,/d\ln c)$$

where the area per molecule (S) is equal to $(GN_A)^{-1}$, s is the surface tension, N_A is Avogadro's number, R is the molar gas constant, and T is the absolute temperature.

The calculated values of S are presented in Table 3. The data confirmed the more extended conformation of the polyester PEG$_{1000}$S macromolecules at the interface. Interestingly, the values of area per polyester macromolecule are very close to those described in the literature for Pluronics [63].

One of the objectives in the presented study is a demonstration of the unique ability of the amphiphilic polyester macromolecules to be deposited on both polar and non-polar solid, dispersed substrates and adsolubilize sparingly water-soluble hydrophobic compounds. For this purpose, adsorption of PEG$_{1000}$S and PEG$_{1000}$D on both conventional (hydrophilic) silica nanoparticles and hydrophobized (silanized) silica nanoparticles was carried out. Upon adsorption, polymer–modified silica nanoparticles have been separated from the polyester solution and redispersed in water containing poorly water-soluble 2-naphthol.

From the adsorption isotherms (Fig. 6), the saturation adsorption amount (*i.e.*, surface concentration Γ) of the amphiphilic polyesters PEG$_{1000}$D and PEG$_{1000}$S on hydrophilic and hydrophobically modified silica particles have been determined. In fact, the saturation adsorption is the adsorbed amount of the polyesters at the plateau region. The value of the surface area per one macromolecule upon polyester adsorption on both polar and non-polar silica has been calculated from the saturation adsorption amount and compared with the hydrodynamic section calculated from the viscosity (Table 3). For all experiments, the surface area occupied during the adsorption on the substrate has been significantly smaller than the hydrodynamic section of the macromolecule in solution. It was clearly seen that the area occupied per polyester macromolecule is much higher for the more hydrophilic PEG$_{1000}$S in comparison to PEG$_{1000}$D in adsorption on the hydrophilic and hydrophobized silica substrates. This indicates that PEG$_{1000}$D is adsorbed in a more compact conformation than PEG$_{1000}$S. Noticeably, the area per macromolecule almost has not changed if PEG$_{1000}$D adsorption on hydrophilic silica is compared to adsorption on a hydrophobic substrate. In turn, the area occupied by the PEG$_{1000}$S macromolecule is smaller once this polyester is adsorbed on the hydrophobized silica. This indicates the higher flexibility of the PEG$_{1000}$S macromolecules, resulting presumably from the higher molecular weight.

Considering the equilibrium adsorption, one can apply the Langmuir equation to describe the experimental data recorded in the adsorption and adsolubilization stages, respectively:

$$c_e/A = k_d/k_a + 1/A_m\, c_e$$

where A is the polymer adsorption at the first stage (polyester adsorption) (A_1) and at the second stage (adsolubilization of 2-naphthol) (A_2), k_a and k_d are the rate constants of polymer adsorption/desorption, and A_m is the maximum polymer adsorption on the silica surface.

The equilibrium concentration c_e at the first stage (polyester adsorption) can be calculated according to the following equation:

$$c_e = c_f - Ac_{s1}$$

where c_f is a feed polymer concentration, A is the polyester adsorption at the first stage, and c_{s1} is the silica content in the mixture at the first stage.

The equiliblrium concentration c_e at the second stage (adsolubilization of 2-naphthol) can be calculated according to the following equation:

$$c_e = (A_1 - A_2)c_{s2}$$

where c_{s2} is the silica content in the mixture at the second stage.

Figs. 9 and 10 show that the experimental data for both the first (polyester adsorption) and second (2-naphthol adsolubilization) stages can be described by straight lines in the coordinates of the Langmuir equation. The correlation coefficients, equilibrium constants, and values of A_m are presented in Table 4.

A comparison of the area per molecule values in Tables 3 and 4 indicates that the adsorption layer is saturated when PEG$_{1000}$S is adsorbed on the hydrophobized silica substrate and partially unsaturated in the rest of the experiments. The area per molecule values are close for PEG$_{1000}$D being adsorbed on the hydrophilic and hydrophobized substrates, both after adsorption and adsolubilization. This indicates that no changes in PEG$_{1000}$D conformation occur upon adsolubilization of hydrophobic 2-naphthol. In turn, the surface area per macromolecule of PEG$_{1000}$S is changed when 2-naphthol is incorporated into the adsorbed PEG$_{1000}$S layer. This indicates conformational changes in PEG$_{1000}$S and, in fact, weaker bonding between the PEG$_{1000}$S macromolecules and silica. This effect is less pronounced for the PEG$_{1000}$S adsorbed on the hydrophobized substrate where stronger bonding between the alkyl fragments and the substrate is formed in comparison to the PEG fragments that form the bond with the polar silica.

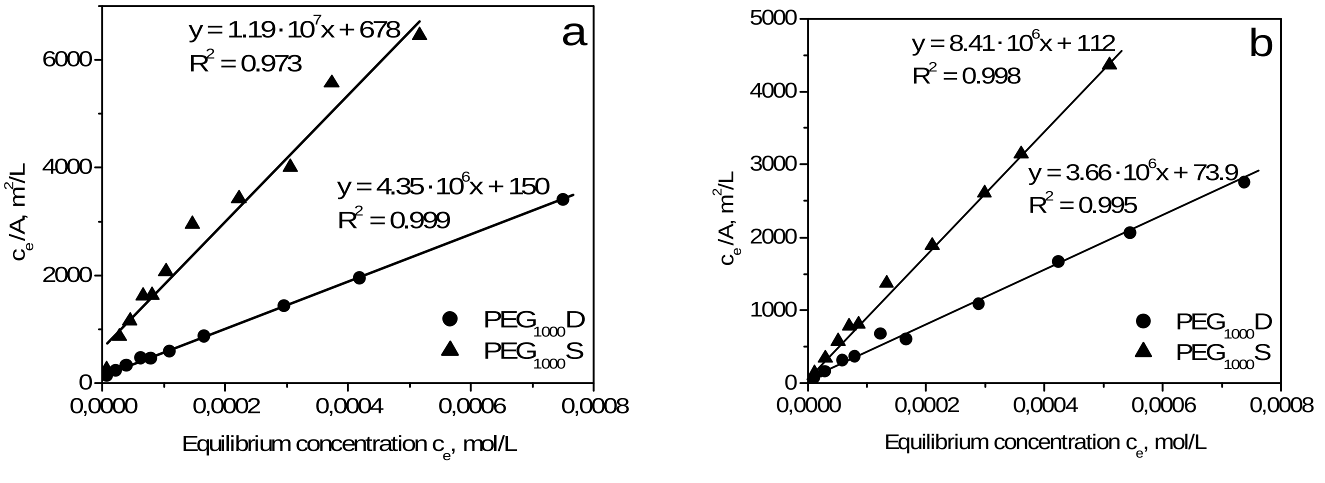


Fig. 9. Polymer adsorption *vs*. equilibrium polymer concentration at the first stage (amphiphilic polyester adsorption on hydrophylic (a) and hydrophobized (b) silica substrate)

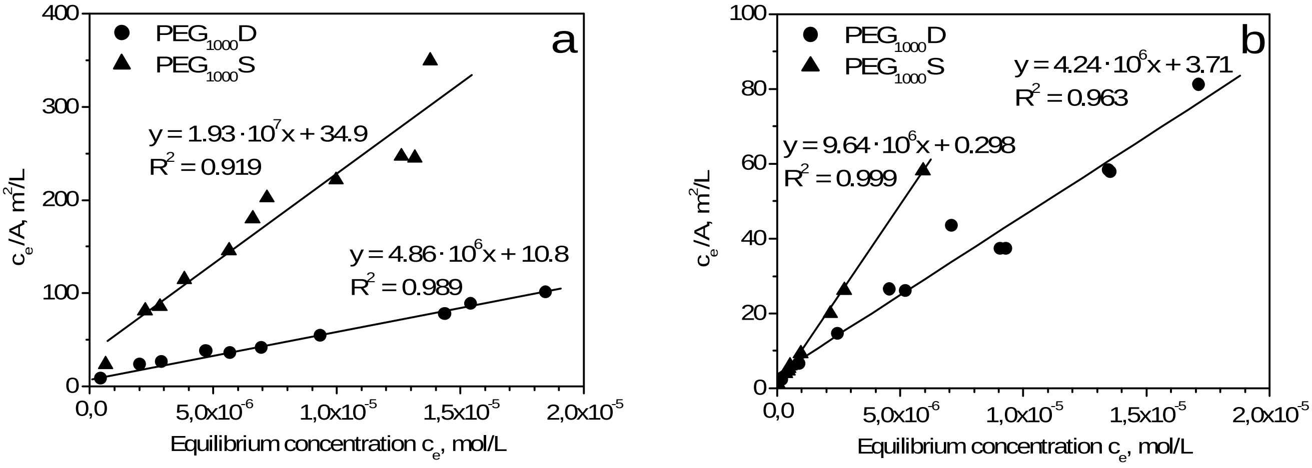


Fig. 10. Polymer adsorption *vs.* equilibrium polymer concentration at the second stage (adsolubilization of 2-naphthol on hydrophylic (a) and hydrophobized (b) silica substrate)

Table 4

Correlation coefficients, equilibrium constants and A_m for amphiphilic polyester adsorption on hydrophylic and hydrophobized silica substrate

Polyester	Silica	R^2	k_d/k_a, m^2/l	A_m^{-1}, m^2/mol	Area per molecule, nm^2
Polyester adsorption (first stage)					
PEG$_{1000}$S	Hydrophilic	0.973	678	1.19·10^7	19.8
PEG$_{1000}$S	Hydrophobized	0.998	112	8.41·10^6	14.0
PEG$_{1000}$D	Hydrophilic	0.999	150	4.35·10^6	7.2
PEG$_{1000}$D	Hydrophobized	0.995	73.9	3.66·10^6	6.1
2-Naphthol adsolubilization (second stage)					
PEG$_{1000}$S	Hydrophilic	0.919	34.9	1.93·10^7	32.1
PEG$_{1000}$S	Hydrophobized	0.999	0.3	9.64·10^6	16.0
PEG$_{1000}$D	Hydrophilic	0.989	10.8	4.86·10^6	8.1
PEG$_{1000}$D	Hydrophobized	0.963	3.7	4.24·10^6	7.0

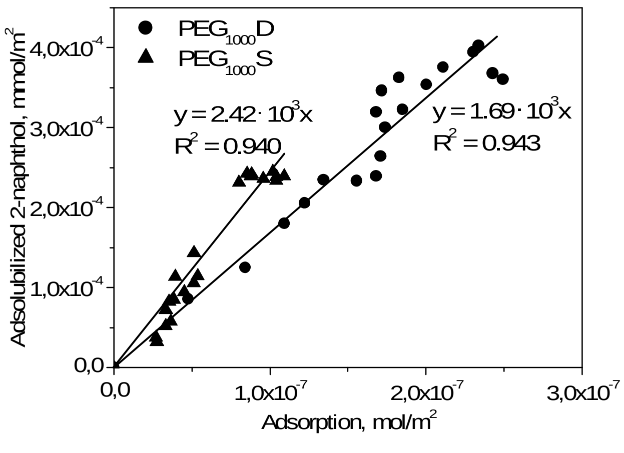


Fig. 11. Adsolubilized amount of 2-naphthol *vs.* amphiphilic polyester adsorption

Finally, higher k_d/k_a values for PEG$_{1000}$S adsorbed on the hydrophilic silica confirm that PEG$_{1000}$S macromolecules are more mobile in the adsorption layer in comparison to the PEG$_{1000}$D ones. In addition, the adsolubilization of 2-naphthol into the amphiphilic polyester fragments changes the macromolecular conformation in the polyester adsorption layer and, obviously, the nature of bonding between the macromolecules and the substrate, thus decreasing the k_d/k_a as well as the rate of polymer desorption.

Fig. 11 shows the amount of adsolubilized 2-naphthol in the amphiphilic polyesters adsorbed on both the hydrophilic and hydrophobized silica substrates *vs.* polyester concentration (PEG$_{1000}$S and PEG$_{1000}$D). Remarkably, the adsolubilization experimental stage can be described by straight lines for both PEG$_{1000}$S and PEG$_{1000}$D, thus indicating that adsolubilization behavior does not depend on the substrate nature. The calculated correlation coefficients are about 0.94 for both polyesters, and the tangents of the slope angles are given as 2.42·10^3 for PEG$_{1000}$S and 1.69·10^3 for PEG$_{1000}$D. The tangents indicate higher adsolubilization ability for $PEG_{1000}S$, which has a longer macromolecular chain. In fact, the amount of adsolubilized hydrophobic 2-naphthol by the amphiphilic polyesters does not show any dependence on the polymer composition (length of the hydrophobic fragment) and depends only on the molecular weight of the polymers.

4. Conclusions

A new way to make amphiphilic adsorbents from silica nanoparticles that differ greatly in their surface polarity and smart amphiphilic invertible polymers is proposed. The polymers are synthesized from PEG-1000 as a hydrophilic constituent and sebacic or dodecanedioic acids as a hydrophobic constituent. The hydrophilic and hydrophobic fragments are alternatingly distributed along the macromolecules. The polymers reveal inverse behavior and adaptive properties correlating to the hydrophilic-lipophilic balance of the macromolecules. Due to the amphiphilic nature and inverse behavior, the polymers successfully adsorb onto a hydrophilic and hydrophobized silica substrate. It has been found that different fragments of the amphiphilic polymers are responsible for adsorption on polar and non-polar particulate substrates. Obviously, PEGs interact with hydrophilic silica and facilitate polymer adsorption there, while alkyl fragments form physical bonding between the macromolecules and the hydrophobic substrate. Furthermore, adsolubilization of sparingly water-soluble 2-naphthol into adsorbed polymer layers on both hydrophilic and hydrophobized silica has been carried out. Although amphiphilic polymer macromolecules possess different surface activity depending on polymer composition (length of the hydrophobic fragment), the adsolubilized amount of 2-naphthol into the polymer layer depends neither on the substrate polarity nor on the length of the hydrophobic fragment in the amphiphilic polymers. It is expected that mainly the hydrophobic fragments of the polymers interact with 2-naphthol and facilitate the adsolubilization. The amount of adsolubilized 2-naphthol depends primarily on the total length of the adsorbed amphiphilic polymer macromolecules.

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МІЦЕЛІЗАЦІЯ Й АДСОЛЮБІЛІЗАЦІЯ АМФІФІЛЬНИХ ІНВЕРТАБЕЛЬНИХ ПОЛІЕСТЕРІВ

Анотація. *Методами вимірювання поверхневого натягу, солюбілізації і флуоресцентної спектроскопії показано, що поліестери на основі аліфатичних дикарбонових кислот і ПЕГ-1000 у водному розчині при концентраціях* 10^{-7}–10^{-4} *% формують мономолекулярні міцели, які з підвищенням концентрації агрегують з утворенням полімолекулярних міцел. Досліджувані амфіфільні поліестери мають інвертабельні властивості, завдяки чому здатні реагувати на зміну полярності середовища й адсорбуватись на поверхні гідрофільних і гідрофобізованих частинок силіки. На прикладі 2-нафтолу показано, що адсорбовані шари амфіфільних поліестерів здатні солюбілізувати органічні речовини, малорозчинні у воді.*

Ключові слова: *амфіфільні полімери, міцелоутворення, інвертабельність, адсорбція, адсолюбілізація.*