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# MONOMOLECULAR MICELLES BASED ON AMPHIPHILIC INVERTIBLE POLYMERS

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**Abstract.** Using surface tension measurements, solubilization of dimethyl yellow dye and solvatochromic dye $E_t30$, and fluorescence spectroscopy, amphiphilic polyesters containing alternated hydrophilic poly(ethylene glycol) fragments and lipophilic dicarboxylic acid or polytetrahydrofuran moieties in the polymer backbone have been shown to form monomolecular micelles in aqueous solutions at the concentrations of $10^{-7}$–$10^{-4}$ %. These monomolecular micelles have been demonstrated to possess invertibility and respond to the change in a medium polarity.

**Keywords:** amphiphilic polymers; monomolecular micelles; invertibility; surface tension; solubilization.

## 1. Introduction

The use of amphiphilic polymers in various branches of science and technology (*e.g.*, experimental medicine, pharmaceutics, biology, optics, electronics, tribology, *etc.*) has a long history and is expecting rapid development [1]. The primary reason for this is that the size of both the hydrophilic and the hydrophobic section can be varied at will; the molecular weight of the polymer can be changed within a wide range while maintaining constant hydrophilic-lipophilic balances; the properties and function of amphiphilic polymers at interface, *e.g.* oil-water, can be controlled through changes in polymer structure, and more importantly, both hydrophilic and hydrophobic section can be chemically engineered towards specific application.

One of the earliest works on the synthesis, characterization, micellization, and solubilization of amphiphilic polymers are papers published by the Strauss group [2, 3]. Unlike low-molecular weight surfactants, no critical concentration of a synthesized amphiphilic polymer was necessary for micelle formation [4-6]. The authors have concluded that “intramolecular micelles” consisting of one macromolecule have been formed in this case. For the first time, the term “monomolecular micelle” has been introduced by Sadron [7], who studied the properties of A–B diblock-copolymer solutions with A and B parts of different polarity which have different solubilities in given solvents. Sadron has revealed that these “non-uniformly soluble macromolecules” form micelles in solutions (Fig. 1a). He has also suggested shape and size of the monomolecular micelles. Dobry and Boyer-Kawenoki have investigated the influence of solvent, concentration, molecular weight and constitution of the macromolecules on the properties of polymer solutions using fourteen polymers dissolved in thirteen solvents [8]. Certain macromolecule blocks have been found to undergo the microphase separation in very dilute solutions in a selective solvent. An insoluble block builds up a micellar core whereas a soluble one assures the formation of a micellar shell. The authors have considered the mutual incompatibility of the macromolecule blocks as another important factor determining the structure of monomolecular micelles. Spherical micelles have been found to be mainly formed in aqueous dilute solutions [9]. Hence, the shape of monomolecular micelles depends on the solvation of different macromolecule blocks and their incompatibility. Bresler *et al.* [10] have shown that the use of selective solvents for a block copolymer consisting of five polystyrene blocks and four polyisoprene blocks leads to the microphase separation of a polymer chain and the formation of monomolecular micelles in nonaqueous media (Fig. 1b). Micellization in an organic solvent (pentane) has been also examined in Ref. [11] and a new technique to identify the monomolecular micelles of ethylene–propylene random copolymers has been developed. The concept of monomolecular micelles has been considered by Pop [12, 13] and Boyko [14].

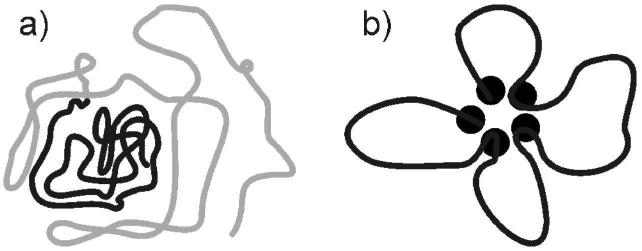


**Fig. 1.** Scheme of a monomolecular micelle of an A–B diblock-copolymer according to Sadron where an outer layer is the hydrophilic block of a macromolecule and a core is the lipophilic block of a macromolecule (a) and scheme of a nine-block copolymer macromolecule of polystyrene-*co*-isoprene in a selective solvent according to Bresler where ● is precipitated blocks and — is solvated blocks of the macromolecule (b)

Therefore, if particular blocks of a macromolecule are immiscible then phase separation occurs in polymer solutions on a small scale although it is impossible for the entire system. The phase separation leads to the formation of a domain (microphase) structure with domains of certain sizes and shapes. In the event of aqueous solutions, an almost anhydrous lipophilic phase (micellar core) and a hydrophilic phase soaked with water (micellar shell) are formed [15]. As a further development of these works, Alexander Kabanov *et al.* have studied the micellization of amphiphilic triblock copolymers in aqueous solutions [16]. The copolymers (Pluronics) are composed of a central lipophilic poly(propylene oxide) block (PPO) flanked by two hydrophilic poly(ethylene oxide) blocks (PEO). The authors have shown that the Pluronic macromolecules form “unimers” (*i.e.*, monomolecular micelles) in dilute aqueous solutions. The separate Pluronic unimers have been observed to aggregate to multimolecular micelles (aggregates) under certain conditions (temperature and concentration). Depending on the type of Pluronic (length of the hydrophilic PEO blocks and the lipophilic PPO block), the multimolecular micelles have had an average hydrodynamic diameter ranging from about 15 nm to about 35 nm, a molecular weight of about 200,000 g/mol, and aggregation numbers ranging from a few macromolecules to several tens. The formation of monomolecular micelles [7] or, according to Kabanov, “unimers” with an ordered lipophilic core and a hydrophilic shell is widely investigated and discussed to date but this issue still remains moot [17]. Nevertheless, Fabio Ganazzoli *et al.* [18, 19] have proven the development of monomolecular micelles from amphiphilic polymers due to the formation of a compact core composed from lipophilic blocks and an outer shell built up from polar blocks. Thus, the existence of monomolecular micelles has been evidently confirmed for both aqueous solutions and nonpolar organic solvents.

The unique feature of amphiphilic polymers is the ability of their lipophipilic blocks to aggregate in aqueous solutions leading to the development of monomolecular micelles. Intramolecular micelles have been demonstrated to appear in very dilute solutions at concentrations that are significantly lower than the critical aggregation concentration (cac) [4, 12, 18, 20].

One of the peculiarities of monomolecular micelle behavior is slow decrease of the surface tension at the air/water interface. Monomolecular micelles change the macromolecular conformation and arrange themselves at the air/water interface; this process determines the value of the drop in the surface tension. The further increase in the amphiphilic polymer concentration results in a sudden decrease of the surface tension corresponding to the globular structure development since macromolecules having a globular conformation are less hydrated and, therefore, more readily absorb at the air/water interface. In this case, not only a perfectly closed packed array of amphiphilic macromolecules on the surface is been formed, as it has been shown by Kulman [21]. This process is accompanied by either a macromolecular conformational change leading to the formation of optimized structures or an intramolecular interaction of the amphiphilic macrochains or both of them [13, 20, 22, 23]. The surface tension decrease ends in a cac point indicating the formation of multimolecular micelles (aggregates). Hence, the mechanism of a drop in the surface tension is different for traditional (low-molecular weight) surfactants and macromolecular ones.

This work aims at ascertaining a possibility that amphiphilic polyester macromolecules form monomolecular micelles in aqueous solutions via studying their surface active properties (*viz.* decrease of surface tension and solubilization of lipophilic dyes). A further objective of the present work is to prove the invertibility of the polyester macromolecules having hydrophilic and lipophilic fragments alternatingly distributed along the polymer macrochain.

## 2. Experimental

### 2.1. Materials

The polyesters **1-4** (Table 1) were synthesized *via* the polycondensation of poly(ethylene glycol) with a molecular weight of 300 g/mol (PEG-300) with sebacic (polyester $PEG_{300}S$) or dodecanedioic (polyester $PEG_{300}D$) acids and poly(ethylene glycol) PEG-600 (molecular weight of 600 g/mol) with sebacic (polyester $PEG_{600}S$) or dodecanedioic (polyester $PEG_{600}D$) acids using previously reported methods [26]. The polyesters **5-10** (Table 1) were synthesized *via* the polycondensation of polytetrahydrofuran, poly(ethylene glycol), and succinic anhydride as described in Ref. [28]. Submicrometer-size dispersed titania (rutile) with a mean particle size of 340 nm and a specific surface area of 8.5 $m^2/g$ was purchased from Sachtleben (Germany).

*Table 1*

**Composition and characteristics of investigated polyesters**

| No. | Polyester | Molecular weight / Polydispersity index | Hydrophilic-lipophilic balance (HLB) | Polyester composition |
|---|---|---|---|---|
| 1 | $PEG_{300}S$ | 6700 / 1.43 | 10.1 | x = 6.4; y = 8; n = 14.4 |
| 2 | $PEG_{600}S$ | 6400 / 1.45 | 12.4 | x = 13.2; y = 8; n = 8.4 |
| 3 | $PEG_{300}D$ | 5500 / 1.44 | 9.2 | x = 6.4; y = 10; n = 11.1 |
| 4 | $PEG_{600}D$ | 17 700 / 1.81 | 11.4 | x = 13.2; y = 10; n = 22.3 |
| 5 | $PEG_{1000}PTHF_{250}$ | 7100 / 1.51 | 20.1 | x = 22.3; y = 3.2; n = 5.0 |
| 6 | $PEG_{600}PTHF_{250}$ | 8900 / 1.39 | 17.1 | x = 13.2; y = 3.2; n = 8.8 |
| 7 | $PEG_{300}PTHF_{250}$ | 12 000 / 1.45 | 14.9 | x = 6.4; y = 3.2; n = 16.8 |
| 8 | $PEG_{1000}PTHF_{1000}$ | 6300 / 1.50 | 13.9 | x = 22.3; y = 13.6; n = 2.9 |
| 9 | $PEG_{600}PTHF_{650}$ | 9700 / 1.52 | 13.8 | x = 13.2; y = 8.8; n = 6.9 |
| 10 | $PEG_{300}PTHF_{650}$ | 11 100 / 1.57 | 11.6 | x = 6.4; y = 13.6; n = 10.0 |

## 2.2. Methods

*The surface tension measurements* of aqueous polyester solutions at different concentrations were performed with an automatic K12 tensiometer from Krüss, Germany. The experiments were carried out at 298 K using the Wilhelmy plate technique. The solutions were prepared by dissolving the polyesters in a tetraborate buffer (pH 9.22).

*Dimethyl yellow solubilization* was performed at 298 K by adding a small amount of the solid dye to aqueous polyester solutions of various concentrations. The UV-Vis-measurements were performed with a Cary 100 Scan (Varian) spectrophotometer, operated at 2 nm resolution. The critical aggregation concentration was determined using the absorbance band intensity at 444 nm.

*Reichardt's dye solubilization.* Absorption spectra for the solvatochromic dye $E_t30$ in aqueous polyester solutions at increasing polymer concentrations in sodium tetraborate buffer were recorded with a Cary 100 Scan (Varian) spectrophotometer. First, 0.0025 g of the solvatochromic dye $E_t30$ was dissolved in 3 ml of methanol. Then, 150 µl of the dye solution was added to the polyester solutions of various concentrations and stirred for 15 min. The UV-Vis-measurements were performed after at least 24 h of equilibration at 298 K.

*Pyrene solubilization.* 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 amphiphilic 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, $l_{em}$ = 390 nm was chosen. The spectra were accumulated with an integration time of 0.5 nm/s. Critical aggregation concentration values were determined after fitting the semi-logarithmic plots of intensity ratio $I_{336.5}/I_{333}$ *versus* log concentration to the sigmoidal curve.

*For the contact angle measurements*, a drop of bidistilled water or diiodomethane ($CH_2I_2$) was placed on the surface of silicon wafers. Thin films of polystyrene (PS) and polyvinylpyridine (PVP) were deposited onto polished silicon wafers by spin-coating from chloroform (3 mg/ml) and dried. The polyester films were spincoated (from acetone solution, 3 mg/ml, on PS film and from toluene solution, 3 mg/ml on PVP film) on PS and PVP. An advanced contact angle (Θ) was measured immediately after the drop was settled. Measurements were done with a Contact Angle SystemOCA15 plus instrument with a precision of ± 0.1°. An average value of the contact angles measured from the left and right sides of at least ten drops has been accepted.

*Reaction of toluene diisocyanate (TDI) with titania particles.* TDI (0.6 g, 3.4 mmol) was added to a mixture of titania (6.0 g) in toluene (60 ml). The resulting suspension was heated to and held at 353 K for 4 h under nitrogen. After cooling to room temperature, the suspension was centrifuged. To remove the unreacted TDI, the precipitate of modified titania was washed with a fresh portion of toluene (about 25 ml) and subsequently centrifuged; this procedure was repeated three times. The modified titania was dried in a vacuum oven at 333 K until a constant weight was obtained.

*Attachment of $PEG_{600}S$ to the titania surface modified with TDI.* A mixture of $TiO_2$ particles (6.0 g) modified with TDI and $PEG_{600}S$ (1.0 g) in toluene (50 ml) was thoroughly stirred at 353 K for 7 h under nitrogen. Then, the suspension was centrifuged, and the excess unreacted polyester was removed as described above for the case of TDI grafting.

*The Fourier transform infrared (FTIR) spectra* were recorded for the samples of bare titania, TDI-modified titania, and $PEG_{600}S$-grafted titania pilled with KBr powder by a Varian Excalibur FTS 3100 spectrometer with a resolution of 4 $cm^{-1}$ using the EasiDiff diffuse reflectance accessory. The obtained spectra were converted into the absorbance-like spectra by performing Kubelka-Munk transformation of the recorded data.

## 3. Results and Discussion

Micelles and micellar structures built up from common surfactants are widely used in various industrial applications, medicine, biology, pharmaceuticals, and cosmetics. On the other hand, there is still a strong need for developing monomolecular micelles which could undergo macromolecular conformational changes in response to changing medium polarity. In this context, the term “invertibility of a macromolecular chain” has been recently introduced [24-26]. The invertibility of a macromolecular chain is defined as a reversible change of its conformation, depending on environmental polarity, due to the selective solvation of some blocks of an amphiphilic macromolecule leading to the microphase separation of the macromolecular blocks [27] and development of certain architectures. If a micelle formed of an amphiphilic polymer is located in water, then its core is lipophilic because of hydrophobic interactions whereas an outer shell is hydrophilic similarly to traditional surfactants. On the contrary, an outer micellar shell is lipophilic and a core is hydrophilic in a nonpolar medium. The uniqueness of the invertible structure allows, for instance, solubilizing lipophilic drugs in the aqueous solution of an amphiphilic polymer and delivering drugs within a hydrophilic body medium (blood). A micelle, loaded with a certain drug, could interact through micellar lipophilic fragments with a hydrophobic cell membrane during their contact that could result in delivery of the lipophilic drug into the cell [27]. Therefore, an invertible macromolecule should consist of (i) hydrophilic and lipophilic moieties somehow distributed along the macromolecular chain, (ii) oxygen atoms in the polymer backbone (chiefly due to the presence of the ether or ester groups), which provide segmental mobility for the macromolecules and enhance their flexibility. This enables rapid conformational switching of the amphiphilic macromolecules induced by changes in the environment polarity (Fig. 2).

For the study of monomolecular micelle development the following structures of amphiphilic polyesters were suggested, containing:

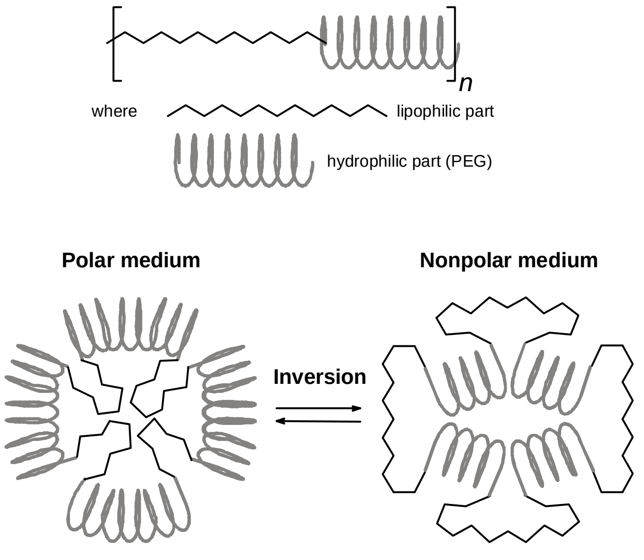


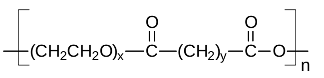
**Fig. 2.** Scheme of architectures of amphiphilic invertible polyester macromolecules in polar and nonpolar media

1) hydrophilic poly(ethylene glycol) (PEG) fragments and lipophilic moieties of dicarboxylic acids [sebacic (decanedioic) and dodecanedioic] alternatingly distributed along the polymer macrochain [26];

2) hydrophilic poly(ethylene glycol) and lipophilic polytetrahydrofuran (PTHF) fragments alternatingly distributed along the polymer macrochain [28].

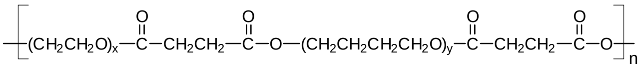
Because of limited experimental possibilities for imaging micelles and the investigation of adsorption layers at the liquid interfaces, both the study of surface tension changes for the aqueous solutions of amphiphilic polymers and the solubilization of substances which are insoluble in water are of great interest. Indeed, the decrease of free surface energy is observed in the course of spontaneous physical adsorption, which confirms the localization of the surface active groups or segments of macromolecules right at the interface [21]. Moreover, a lipophilic microphase appears in the system during the micellization that can colloidally dissolve (*i.e.*, solubilize) hydrophobic substances.

In the present paper, the surface active properties of amphiphilic polyesters based on polyols (hydrophilic poly(ethylene glycol), lipophilic polytetrahydrofuran) and dicarboxylic acids (succinic, sebacic, dodecanedioic) have been investigated:



$$\left[ (CH_2CH_2O)_x - \overset{O}{\overset{\|}{C}} - (CH_2)_y - \overset{O}{\overset{\|}{C}} - O \right]_n$$

Polyester **1-4**



$$\left[ (CH_2CH_2O)_x - \overset{O}{\overset{\|}{C}} - CH_2CH_2 - \overset{O}{\overset{\|}{C}} - O - (CH_2CH_2CH_2CH_2O)_y - \overset{O}{\overset{\|}{C}} - CH_2CH_2 - \overset{O}{\overset{\|}{C}} - O \right]_n$$

Polyester **5-10**

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

For the study of polyesters surface active properties and the formation of monomolecular micelles from the polyesters, two methods have been employed, *i.e.* surface tension measurements and the solubilization of hydrophobic dyes. Typically, the aqueous solution surface tension of low-molecular weight surfactant decreases with increasing surfactant concentration. It indicates the increase of activity of the surfactant in the solution under coverage of air/water interface with surfactant. The surface tension reaches the constant value (cmc) that does not change with an increase of surfactant concentration. Obviously, the situation is more complicated in the case of amphiphilic polyesters studied here. It reflects the features of polymer surfactant micellization in an aqueous environment.

Surface tension data for various aqueous solutions of the amphiphilic polyesters plotted semi-logarithmically are presented in Fig. 3. It appears that each of the polyesters demonstrates high surface activity and is able to decrease the surface tension of water up to 43–45 mN/m. At a very low concentration of PEG$_{300}$S, PEG$_{300}$D, and PEG$_{600}$D, the surface tension of their solutions slightly decreases up to the first critical aggregation concentration (cac$_1$) and then drops rapidly (Fig. 3a-c). It is assumed that by this concentration in water (from $10^{-7}$ to $10^{-4}$ % w/v depending on polyester) the polyester macromolecules form intramolecular micelles (Fig. 3d) having lipophilic pockets composed from the dicarboxylic acid moieties and an external hydrophilic shell containing the PEG fragments (Fig. 2). 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. Formation of similar thermodynamically stable structures from the copolymers has been shown theoretically and experimentally in the literature both for the polar and nonpolar solvents at low concentration [7, 11, 18, 19]. Similar behavior has been observed for Pluronics, which was demonstrated by two clear break points and two different slopes appearing when the surface tension of aqueous solution of Pluronics is plotted as a function of the concentration [29-31].

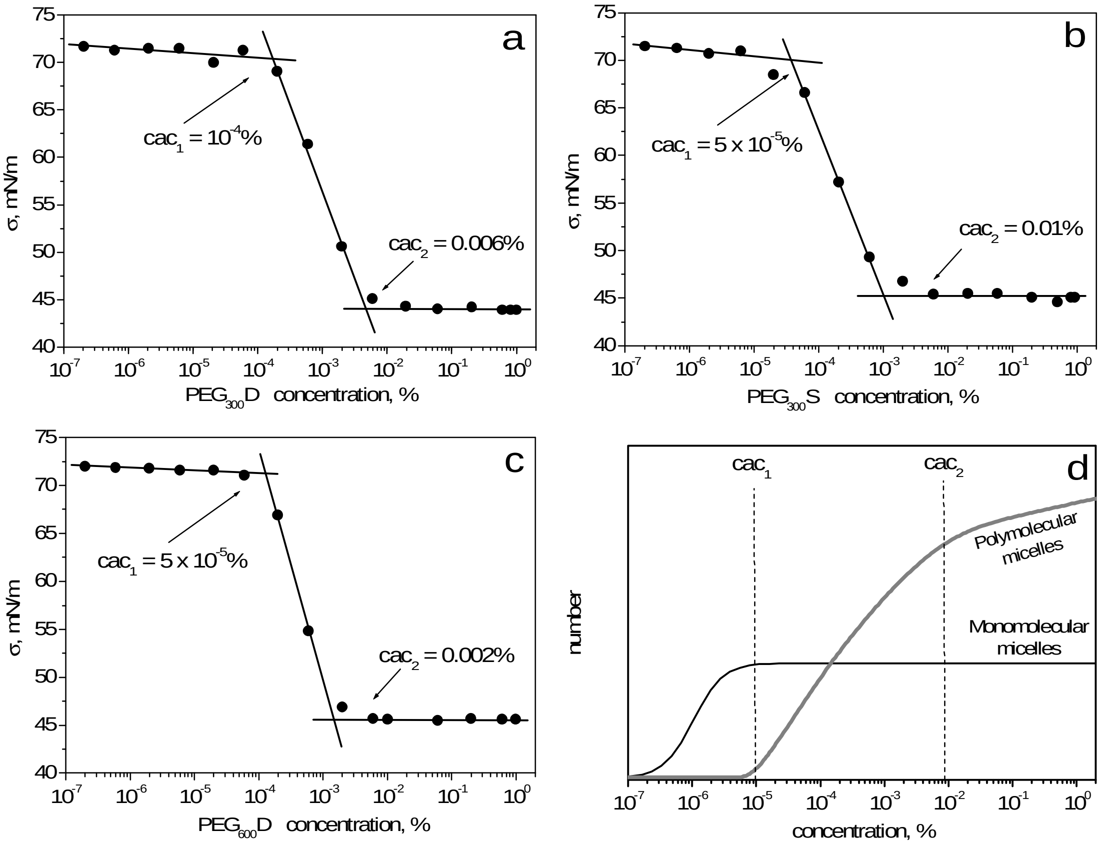


**Fig. 3.** Surface tension isotherms for aqueous solutions of the PEG$_{300}$D (a), PEG$_{300}$S (b), PEG$_{600}$D (c) polyesters at 298 K and a schematic representation of the number of mono- and polymolecular micelles plotted as a function of polyester concentration (d)

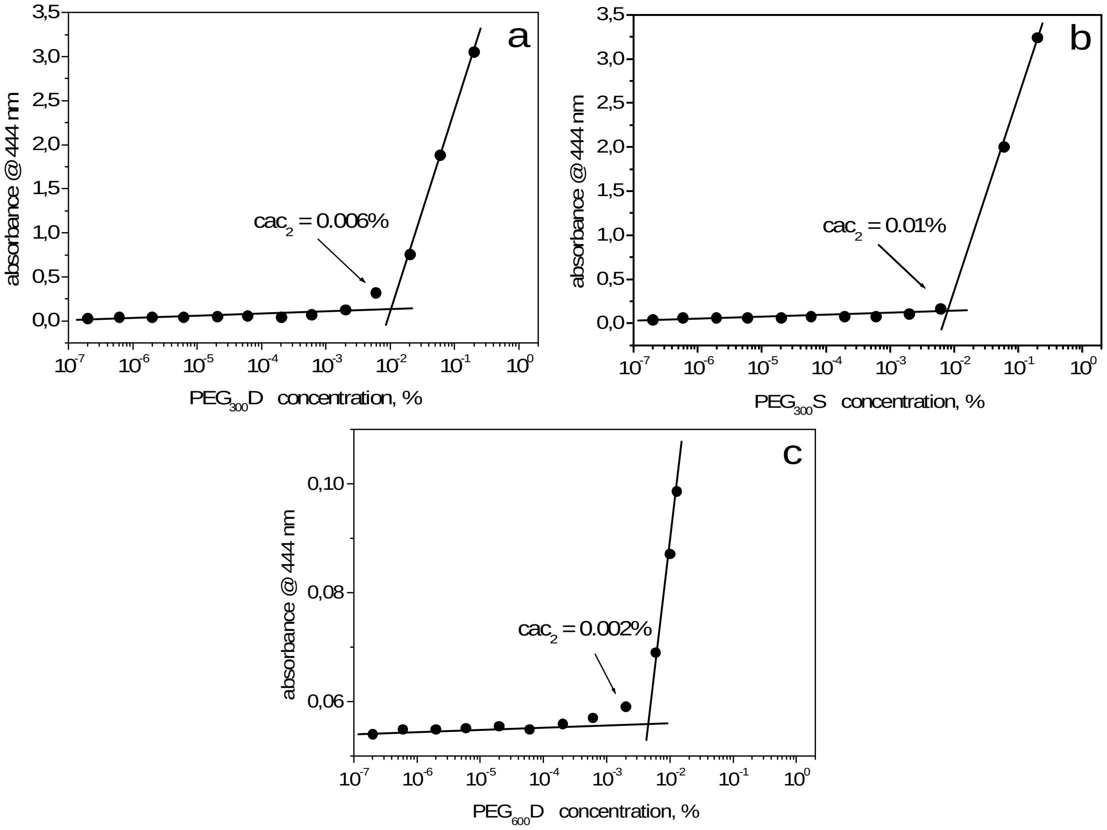


**Fig. 4.** Changes of absorption intensity at 444 nm for aqueous solutions of the PEG$_{300}$D (a), PEG$_{300}$S (b) and PEG$_{600}$D (c) polyesters with solubilized dimethyl yellow dye *vs*. concentration of polyester

The relatively gentle slope at low concentrations of PEG$_{300}$S, PEG$_{300}$D, and PEG$_{600}$D indicates the migration of the macromolecular micellar structures (*i.e*., monomolecular micelles) to the interface and their adsorption at the air/water interface in an extended conformation of the macromolecules. The same phenomenon has been reported for amphiphilic Pluronic macromolecules [32]. Remarkably, PEG$_{300}$S, PEG$_{300}$D, and PEG$_{600}$D have different slopes at low concentrations, which imply differences in their surface activity. The slopes are steeper for more hydrophobic PEG$_{300}$S and PEG$_{300}$D polyesters as compared with more hydrophilic PEG$_{600}$D (Fig. 3a-c). Hence, both PEG$_{300}$S and PEG$_{300}$D exhibit higher surface activity than PEG$_{600}$D.

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$_1$) as schematically shown in Fig. 3d. The decrease ends in the cac$_2$ point (second critical aggregation concentration) implying the adsorption of polymolecular micelles at the interface and the simultaneous structural rearrangements in the adsorbed layer. Afterwards, the surface activity of polyester macromolecules does not change anymore. The lowest cac$_2$ value observed for the polyester PEG$_{600}$D may be explained by the highest polyester molecular weight. Pluronics of higher molecular weight have been shown to form polymolecular micelles more readily, *i.e*. at lower concentrations and the surface activity of polymer surfactants decreases with an increase of their molecular weight [17, 33].

The monomolecular micelle formation at low concentrations of the amphiphilic polyesters and the critical aggregation concentration values obtained from the surface tension measurements have been additionally confirmed by the solubilization of dimethyl yellow (*p*-dimethylaminoazobenzene) (Fig. 4). The slight increase of absorption intensity at 444 nm (characteristic value of dimethyl yellow dye) in optical spectroscopy has been observed through cac$_1$ to cac$_2$ for each of the polyesters implying solubilization of the dye initially by monomolecular micelles and afterwards by aggregates based on monomolecular micelles (*i.e*., polymolecular micelles). The rapid increase of the absorption intensity at 444 nm after cac$_2$ indicates an increase of the amount of the solubilized dye and the appearance of a larger number of the polymolecular micelles. From the inflection points in the absorbance at 444 nm plotted as a function of amphiphilic polyester concentration, critical aggregation concentrations (cac$_2$) have been determined for PEG$_{300}$S,

$PEG_{300}D$, and $PEG_{600}D$. The $cac_2$ values obtained from the surface tension measurements and the dimethyl yellow solubilization coincide for the studied amphiphilic polyesters (Figs. 3 and 4).

Therefore, the formation of monomolecular micelles by the amphiphilic polyesters in an aqueous medium at very low concentrations ($10^{-7}$–$10^{-4}$ %) has been revealed by two different techniques. The monomolecular micelles aggregate with increasing polyester concentration to afford more complex macromolecular assemblies – polymolecular micelles (aggregates). Such monomolecular micelles are expected to have a core-shell architecture. In an aqueous environment, the micellar core is lipophilic whereas an outer shell is hydrophilic as confirmed by the dimethyl yellow solubilization. Obviously, the polymolecular micelles (aggregates) have similar structures in aqueous solutions.

In order to verify the structure of both the monomolecular micelles and their aggregates, we studied the core composition and its changes by the increase of each of the polyester concentrations in solution. To this end, solvatochromic dye $E_t30$ has been used for the solubilization in polyester solutions. This dye is one of the most established polarity probes for media where it is localized [34]. The dye has been widely used to investigate Pluronics micelles and liposomes [35]. The $E_t30$ solvatochromic band shifts from the maximum at 453 nm in water to 810 nm in lipophilic diphenyl ether. This absorption band is attributed to a charge transfer process from phenoxide oxygen. At pH lower than 9 the oxygen protonation results in the disappearance of the solvatochromic properties. For this reason, the polarity measurements have been conducted in a tetraborate buffer at pH 9.22. The optical absorption spectra for the polyesters along with the increase of their concentration in solution have been recorded. The changes of absorption intensity are shown in Figs. 5a and 5b. In general, optical adsorption have been found to increase almost linearly at low polyester concentration meaning appearance of the lipophilic microphase of the monomolecular micelles (cores) where solvatochromic dye $E_t30$ localizes. This fact confirms the monomolecular micelle formation under these conditions. At the $cac_2$, the optical adsorption jumps rapidly, which indicates increasing of the lipophilic core and the polymolecular micelle (aggregate) formation. Determined $l_{max}$ changes for each of the polyesters can be classified in two different types. For polyester $PEG_{300}D$, this value ranges from 454 to 471 nm with a rapid increase of $l_{max}$ after the $cac_2$ to 552 nm (Fig. 5c). These changes of $l_{max}$ with the polyester concentration indicate the formation of monomolecular micelles which build up aggregates at high concentrations. Similarly, polyester $PEG_{300}S$ shows maxima values from 452 to 463 nm and a rapid increase of $l_{max}$ after the $cac_2$ to 562 nm (Fig. 5d) implying the development of monomolecular micelles at low polyester concentrations and aggregates at high concentrations.

The data recorded from the solubilization of $E_t30$ in $PEG_{300}D$ and $PEG_{300}S$ solutions show that the exterior of the polyester micelle structures (shell, Fig. 2) mainly contains more polar fragments. For comparison, the values of $l_{max}$ measured for the solutions of $E_t30$ in ethanol and methanol are equal to 550 and 515 nm, respectively. Therefore, the micelle interior (core) is obviously composed from more lipophilic aliphatic fragments. The $l_{max}$ of polyester solutions changes (increases) with an increase of polyester concentration. We believe that with concentration increase the lipophilic interior (core) also increases resulting in the increase of $l_{max}$. The rapid jump of $l_{max}$ at $cac_2$ for both $PEG_{300}S$ and $PEG_{300}D$ confirms the appearance of a new lipophilic microphase.

To evaluate the surface activity of the polyesters based on PEG and PTHF and show their ability to build micelles, we studied the micellization in the polyester aqueous solutions using fluorescence spectroscopy.

Pyrene is a well-known fluorescent probe for studying the aggregation behavior of amphiphilic polymer macromolecules [36, 37]. Depending on the environment of the pyrene, a bathochromic shift in the absorption 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.

In our experiments, pyrene excitation spectra were monitored in the 300–360 nm wavelength region over a wide range of polyester concentrations ($10^{-6}$–3 %) (Fig. 6a). From the pyrene excitation spectra, the intensity ratios $I_{336.5}/I_{333}$ were plotted as a function of amphiphilic polyester concentration (Fig. 6b). A bathochromic shift of the fluorescence excitation spectra and enhanced excitation intensity with an increasing polyester concentration in aqueous solution indicates the transfer of pyrene molecules from water to a lipophilic interior (core) of the monomolecular micelles and the solubilization of pyrene within the micelles. The sharp increase in the intensity ratio $I_{336.5}/I_{333}$ indicates a more hydrophobic surrounding of pyrene due to the formation of aggregates (*i.e.*, polymolecular micelles) and corresponds to the critical aggregation concentration for each polyester. The cac values correlate with the chemical structure of the amphiphilic polyesters. Changing length of both hydrophilic and lipophilic fragments and their ratio in the macromolecules results in a significant difference in recorded cac values. The cac increases with an increasing HLB of polymers and varies between $3.5 \cdot 10^{-4}$ % for the most lipophilic $PEG_{600}PTHF_{650}$ and 0.067 % for the most hydrophilic $PEG_{1000}PTHF_{250}$. Thus, the fluorescence spectroscopy data show that the amphiphilic polyester macromolecules tend to form monomolecular micelles in an aqueous environment at the concentrations below the cac value.

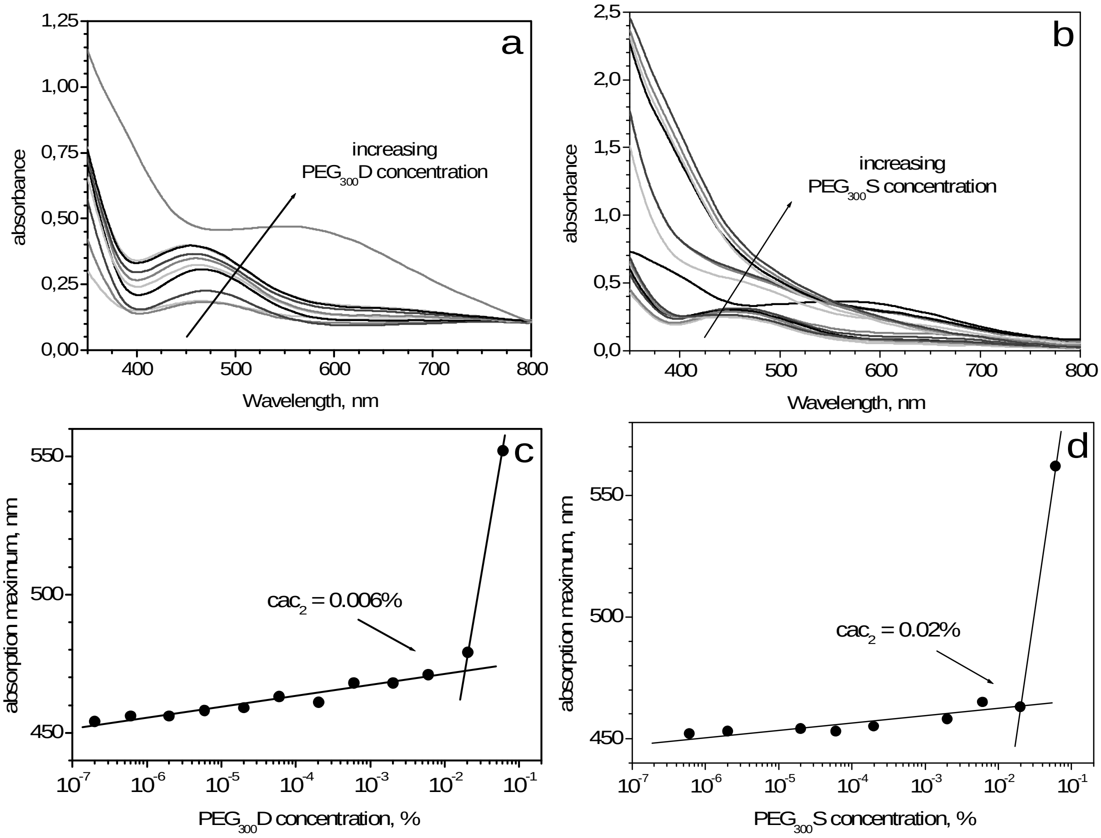


**Fig. 5.** Absorption spectra for the solvatochromic dye Et30 in polyester $PEG_{300}D$ (a) and $PEG_{300}S$ (b) solutions and absorption maximum changes with a concentration of polyester $PEG_{300}D$ (c) and $PEG_{300}S$ (d).

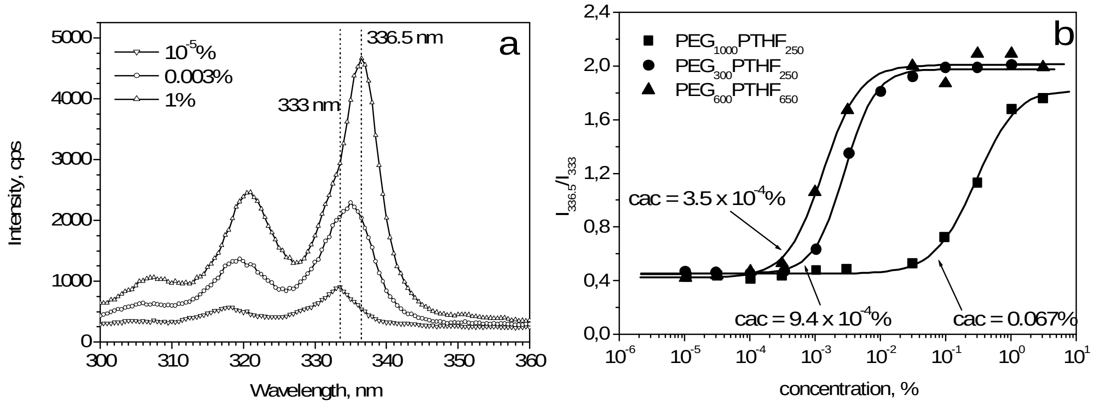


**Fig. 6.** Excitation spectra of pyrene in the polyester $PEG_{600}PTHF_{650}$ aqueous solutions at different concentrations (a); the intensity ratio $I_{336.5}/I_{333}$ of the excitation spectra of pyrene in polyester solutions *vs* polyester concentration (b)

**Fig. 7.** Invertibility of amphiphilic polyesters on a flat surface

To confirm the invertibility and adaptive properties of the amphiphilic polyester macromolecules, the measurements of water and diiodomethane contact angles has been carried out using silicon wafers modified with the polyesters. To this end, polystyrene (PS) and polyvinylpyridine (PVP) films have been initially deposited onto silicon wafers by spin-coating. Then polyester $PEG_{600}S$ thin films have been spin-coated onto the top of the PS or PVP films.

The contact angle data and the calculated polar and dispersive constituents of surface energy [38] are presented in Table 2. The data clearly show that the top layer macromolecules of the polyester film changes their conformation upon exposure to either a polar or nonpolar environment. When water contact angles were determined, poly(ethylene glycol) fragments dominated at the top of the film (Fig. 7, left). When diiodomethane was used as a wetting liquid, nonpolar dicarboxylic acid moieties came to the top (Fig. 7, right), and the surface changed its energetic state through the change of the chemical nature of the surface. The switchability on the order of a few seconds has been found for the polyester deposited on a PS film as well as on more polar PVP.

The macromolecules of the studied amphiphilic polyesters contain alternatingly distributed hydrophilic and lipophilic fragments of a certain length and they possess invertible properties. This favors a reversible change of the macromolecular conformation, depending on environmental polarity, due to the selective solvation of some blocks of an amphiphilic macromolecule leading to the microphase separation of the macromolecular blocks and development of certain architectures.

*Table 2*

**Advanced contact angles of wetting the modified silicon wafers with water and diiodomethane**

| Sample | Contact angle with water (Θ°) | Contact angle with $CH_2I_2$ (Θ°) | $g^d_s$, mJ/m$^2$ | $g^p_s$, mJ/m$^2$ |
|---|---|---|---|---|
| PS film | 90.0 | 11.2 | 50.9 | 0.2 |
| PVP film | 60.5 | 40.1 | 19.2 | 12.3 |
| $PEG_{600}S$ on PS | 17.3 | 9.0 | 35.1 | 37.2 |
| $PEG_{600}S$ on PVP | 18.4 | 15.1 | 34.0 | 37.5 |

Moreover, in order to confirm the invertibility of amphiphilic polyester macromolecules immobilized at a dispersed surface, the macromolecules have been covalently grafted onto the particulate titania surface and their ability to reversibly change conformation has been examined according to the known technique [39]. Grafting amphiphilic polyester macromolecules has been conducted *via* a two-step process. In the first step, titania particles are treated with a toluene solution of toluene diisocyanate as a coupling agent in order to functionalize their surface. It can be assumed that in this case TDI grafting occurs due to the interaction of hydroxyl groups usually present on the titanium dioxide surface [39] with only one isocyanate group of toluene diisocyanate molecule. In the second step, the remaining isocyanate groups immobilized at the solid titania surface have reacted with the terminated functionalities of the invertible polyester, which led to tethering the macrochains onto the surface.

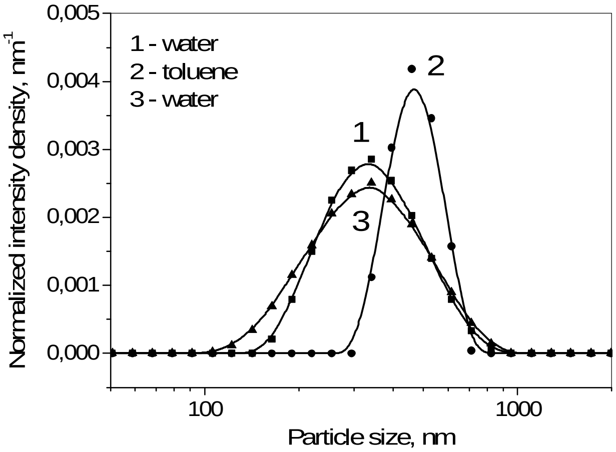


**Fig. 8.** Size distribution of titania particles, modified with the $PEG_{600}S$ amphiphilic polyester, in redispersion cycles in water and toluene

Both Fourier transform infrared spectroscopy and thermogravimetric analysis have been employed to prove grafting amphiphilic polyester macromolecules onto the solid titania surface. As compared to the spectrum of bare titania, the new characteristic absorption bands appear in the TDI-modified titania spectrum at 1654 cm$^{-1}$ (urethane), 1545 cm$^{-1}$ (amide II), 1604 and 1508 cm$^{-1}$ (aromatics), indicating that the reaction of toluene diisocyanate with hydroxyl groups on the titanium dioxide surface takes place through the formation of a urethane bond. According to thermogravimetric analysis, the amount of toluene diisocyanate grafted from the 1 % toluene solution on the titania surface is 0.67 % w/w. Apart from those bands mentioned above, in the spectrum of titania with grafted amphiphilic polyester, absorption peaks at 2928 and 2870 cm$^{-1}$ arise, which belong to the $CH_2$ stretch vibration. A new absorption band at 1735 cm$^{-1}$ indicates the appearance of carbonyl groups on the titania surface. It should be mentioned that both $CH_2$ and C=O groups are present in the structure of the amphiphilic polyester. Therefore, we assumed that the presence of these new absorption bands imply successful covalent grafting of the polyester macromolecules onto the particulate titania surface *via* TDI coupling. The amount of the amphiphilic polyester grafted from the 2 % toluene solution on the titania surface functionalized with the isocyanate groups is 0.88 % w/w as determined from thermogravimetric analysis.

To prove invertible properties of the amphiphilic polyester macromolecules grafted onto the particulate titania surface, the stability of titania suspensions in solvents of various polarity (toluene and water) has been studied. Fig. 8 shows the change in the particle size distribution during the redispersion of a dried titania powder both in a polar medium (water) and in a nonpolar medium (toluene). It should be noted that a mean particle size of the bare titania is 340 nm and the particles form rather stable suspensions in water. The titania particles have not lost their stability in an aqueous medium after grafting amphiphilic polyester macromolecules to the particulate surface since the mean particle size in water has not significantly changed after the modification (420 nm – *curve* 1 in Fig. 8). After dispersion in water, the titania particles modified with the amphiphilic polyester have been isolated by the centrifugation, dried, and redispersed in toluene. The formation of a stable suspension has been observed. The normalized intensity density plot (*curve* 2 in Fig. 8) shows the maximum at about 550 nm. Interestingly, the investigated titania particles in the absence of the polymer coating do not form any stable suspension in toluene and settle down as soon as the stirring is stopped. After isolation from the toluene medium and drying, these particles are able again to be redispersed in water to give a stable suspension with a particle size of 410 nm (*curve* 3 in Fig. 8). These results confirm the ability of the amphiphilic polyester macromolecules grafted to the solid surface to change their conformation in response to changing medium polarity via a certain location of the hydrophilic and lipophilic fragments (Fig. 2). Upon exposure to toluene (a nonpolar medium), the amphiphilic macrochains form an outer layer built up from the dicarboxylic acid moieties. Thus, the particulate titania surface becomes hydrophobic, which enhances particle compatibility with the nonpolar environment and facilitates suspension stability in toluene. Upon the transfer of the modified titania particles to water, the shell at the titania surface undergoes inversion. The polar poly(ethylene glycol) fragments of the grafted macromolecules form a hydrophilic outer layer. As a result, the particulate titania surface becomes hydrophilic in an aqueous medium, which provides particle stability in a polar environment.

As a rough approximation, the grafted macromolecular chains of the amphiphilic invertible polyesters could be obviously considered as tethered monomolecular invertible micelles. The surface occupied by one tethered monomolecular micelle has been determined to be about 15 nm$^2$ and this value supports our suggestion. Thus, both the contact angle measurements and the particulate titania surface modification *via* grafting the amphiphilic invertible polyester macromolecules clearly indicate that the lipophilic and hydrophilic fragments of the macromolecules alternatingly distributed along the polymer backbone rapidly respond to changing medium polarity and undergo rearrangement and inversion while adapting to a new environment.

## 4. Conclusions

Amphiphilic polyester macromolecules form monomolecular micelles in an aqueous medium at concentrations that are significantly lower than the critical aggregation concentration ($10^{-7}$–$10^{-4}$ %), adsorb at the air/water interface, decrease surface tension, and solubilize hydrophobic substances, *e.g.* dyes (dimethyl yellow, solvatochromic Reichardt's dye, pyrene). Due to the presence of alternatingly distributed hydrophilic and lipophilic fragments in the macromolecular structure, the macromolecules acquire invertibility, *i.e.* the ability to change their conformation in response to changing medium polarity that leads to the formation of certain macromolecular architectures.

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## МОНОМОЛЕКУЛЯРНІ МІЦЕЛИ НА ОСНОВІ АМФІФІЛЬНИХ ІНВЕРТАБЕЛЬНИХ ПОЛІМЕРІВ

***Анотація.*** *Методами вимірювання поверхневого натягу, солюбілізації барвника диметилового жовтого, сольватохромного барвника* $E_t30$ *і флуоресцентної спектроскопії показано, що амфіфільні поліестери, які містять гідрофільні фрагменти поліетиленгліколю і ліпофільні залишки аліфатичних дикарбонових кислот або політетрагідрофурану, альтернатно розташовані в полімерному макроланцюзі, утворюють мономолекулярні міцели у водному розчині при концентраціях* $10^{-7}$*–*$10^{-4}$ *%. Показано, що мономолекулярні міцели такої будови мають інвертабельні властивості і реагують на зміну полярності середовища.*

***Ключові слова:*** *амфіфільні полімери; мономолекулярні міцели; інвертабельність; поверхневий натяг; солюбілізація.*