

# The miscibility of poly(D,L-lactide-co-glycolide) with amphiphilic molecules at air/water interface

Lu Sun, Hui Zhang, Miao Xu, Lijun Ma, Yuqing Wu, Lixin Wu\*

Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130023, PR China

Available online 30 November 2004

## Abstract

The miscibility of mixtures of poly(D,L-lactide-co-glycolide) (PLG) with two amphiphilic molecules was investigated when they were spread at air/water interface. The plateau in the  $\pi$ -A isotherms of the PLG mixture with cationic amphiphile, C<sub>12</sub>AzoC<sub>6</sub>PyBr, became short with gradually increasing the proportion of the amphiphile and the aggregates appeared in LB film became more uniform, both in scale and in shape, in comparing with the wormlike aggregation of pure PLG, by atomic force microscopy (AFM). However, the  $\pi$ -A isotherm of the PLG mixed with non-ionic amphiphile, C<sub>16</sub>AzoPy, showed no obvious changes corresponding to pure polymer except the molecular area increasing in some extent, and the domains with different heights on the LB film were clearly observed. Combing the results of UV-vis spectra, it is concluded that the PLG is basically miscible with C<sub>12</sub>AzoC<sub>6</sub>PyBr but is not with C<sub>16</sub>AzoPy, which is favorable to be a carrier for anionic biomolecules.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Miscibility; PLG; Amphiphile; LB film

## 1. Introduction

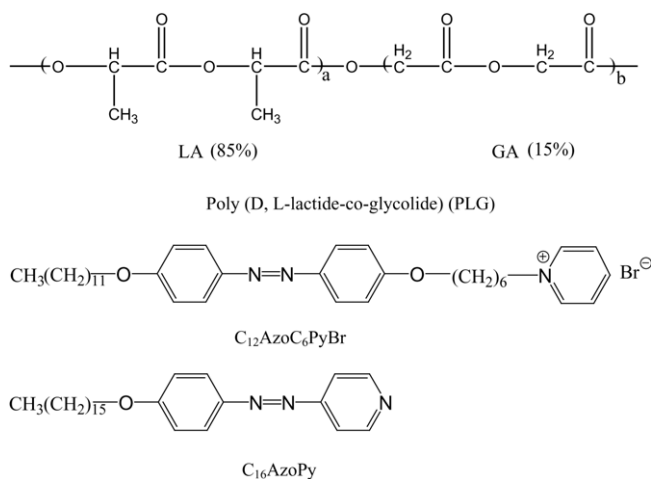
Poly(D,L-lactide-co-glycolide) (PLG) and its derivatives as synthetic polymers have recently received much attention due to their biodegradable, biocompatible and non-toxic features [1], and have been applied to bio/medical materials such as tissue engineering materials, cell supporting scaffolds and matrixes of drug release [2–4]. However, they are basically water-insoluble and their aggregates lack of recognition sites and cell compatibility so that it is difficult to use them directly in aqueous solutions [5]. In order to overcome these disadvantageous features, it is necessary to increase surface energy, affinity and fusion capability of PLG to the cell as well as hydrophilic properties. Versatile methods have been exploited for these purposes by improving chemical structure [6–8], inserting hydrophilic block covalently, introducing additional components, surface coating, plasma treating to the surface of PLG and so on.

By blending poly(lactide-co-glycolide) with some surfactants such as cetyltrimethylammoniumbromide, the formed cationic microparticle exhibits merits as a carrier for DNA adsorbing on electrostatically. Furthermore, such a composite has been employed to be substantially more potent than corresponding naked DNA vaccines in the transfection process into cells [9].

In addition, during the process of protein encapsulation using PLG, surfactants play an important role in protecting the protein during the freeze-drying steps [10,11]. PLG monolayers at air/water interface have been investigated in the past few years, [12,13] which presented an insight into the effect of the polymer structure on the monolayer interfacial behavior, whereas few researches related to the interaction of PLG with amphiphilic molecules. Herein, we try to elucidate the miscibility of PLG at air/water interface with two different surfactants, cationic azobenzene containing amphiphile, C<sub>12</sub>AzoC<sub>6</sub>PyBr, and non-ionic azobenzene containing amphiphile, C<sub>16</sub>AzoPy, as shown in Scheme 1, and meanwhile the relationship between aggregation of the amphiphiles and the miscibility was discussed.

\* Corresponding author.

E-mail address: wulx@jlu.edu.cn (L. Wu).



Scheme 1. Chemical structures of PLG and the two amphiphilic molecules.

## 2. Experimental

### 2.1. Materials

The surfactant  $\text{C}_{12}\text{AzoC}_6\text{PyBr}$  and amphiphile  $\text{C}_{16}\text{AzoPy}$  were synthesized according to the procedures as described in the literature [14,15] and characterized by  $^1\text{H}$  NMR, IR and elemental analysis. Poly(D,L-lactide-co-glycolide) (PLG, 85:15, M.W. 90000–120000) was purchased from Sigma Chemical Co. and used as received. Organic solvents were analytical reagents. The pure water (Milli-Pore  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was used in the experiments. The mixture was prepared by simply mixing PLG and surfactant with molar ratio of glycolide group in the PLG to the surfactant at 1:0.3, 1:0.5, 1:0.8 and 1:1. The concentration for both pure PLG and its mixture with two small molecules in chloroform solution maintained at 0.74 mg/ml.

### 2.2. Preparation and measurements

A Nima 622D trough, equipped with a Wilhelmy balance as surface pressure sensor, was employed for  $\pi$ -A isotherm measurements and the deposition of Langmuir–Blodgett (LB) films. The chloroform solution of PLG or the mixture of PLG with surfactant (concentration of PLG is 0.74 mg/ml) was spreaded onto the pure water sub-phase (pH 6–7). After spreading sample solution, the monolayer was kept at air/water interface for 15 min to make the evaporation of the solvent completely and then compressed with a constant barrier rate,  $20 \text{ cm}^2/\text{min}$ , to get  $\pi$ -A isotherms. Area is expressed in terms of area per monomer unit. We attributed an average value for the monomer weight, taking into account the weight of lactic and glycolic acid and the percentage of each unit in the polymer. This gave 140 for PLG and mixtures. The temperature of the sub-phase was kept at  $20^\circ\text{C}$ . For the transferred LB films, the monolayers were prepared under the same conditions as getting  $\pi$ -A isotherms. After they were

allowed to equilibrate for 20 min at the setup value, the condensed monolayers were deposited by the vertical dipping method onto mica for AFM and quartz for UV-vis spectral measurements.

The topological images of the single monolayer LB films on mica sheets were performed on an ex situ atomic force microscopy (AFM) (Digital Instrument, Dimensional 3000) with tapping mode in air. Images were minimally flattened, and a single low-pass filter to diminish high frequency noise was used to facilitate data analysis.

## 3. Results and discussion

### 3.1. $\pi$ -A isotherms of PLG and its mixture with surfactants

There is a plateau at surface pressure about 5 mN/m, which emerged in the range of liquid expand (LE) phase after the molecular area large than  $0.17 \text{ nm}^2$ , in the  $\pi$ -A isotherms of pure PLG on water surface, as shown in Fig. 1A(a). It is quite similar to the previous result in literature [12,16,17]. The plateau could be explained from the conformation change of PLG under compression and this change should be reversible because after a compressing–expanding cycle the plateau could appear again. For the mixture (1:0.3) of PLG with cationic surfactant  $\text{C}_{12}\text{AzoC}_6\text{PyBr}$ , quite different  $\pi$ -A isotherms were observed, where the starting area with surface pressure rising became larger, while the plateau became shorter and a phase transition emerged at 10 mN/m during compression. Increasing the molar ratio of the  $\text{C}_{12}\text{AzoPyC}_6\text{Br}$  to PLG would result in the increase of the surface pressure, at which phase transition took place and the decrease of plateau gradually. This indicates that the addition of  $\text{C}_{12}\text{AzoC}_6\text{PyBr}$  restrains conformation change of PLG and implies that the surfactant has dispersed into the polymer. From the plots of molecular area versus molar ratio of surfactant, as shown in Fig. 1B, we could observe that the actual areas of PLG with the addition of the surfactant is increasing linearly under low surface pressure and the molecular area of  $\text{C}_{12}\text{AzoC}_6\text{PyBr}$  is estimated to be about  $0.3 \text{ nm}^2$ , in good agreement with that extrapolated from the  $\pi$ -A isotherm of pure surfactant. But the actual area is smaller than that of the ideal one under high surface pressure such as 20 mN/m. It means that there is strong interaction between cationic surfactant and PLG at this pressure [18–20]. The negative influence of surface pressure on the molecular area derives probably from a few of surfactant molecules being extruded into water as the pressure getting high due to its strong hydrophilic property. The expanding–compression cycles, as shown in Fig. 1C, supports the analysis. However, with the addition of  $\text{C}_{16}\text{AzoPy}$ , the  $\pi$ -A isotherm of the polymer mixture showed no obvious change corresponding to that of pure PLG even though the molar ratio of the amphiphile to the polymer reached 1:1, as shown in Fig. 1D, indicative of that the conformation change of the polymer in the mixed Lang-

Download English Version:

<https://daneshyari.com/en/article/9676016>

Download Persian Version:

<https://daneshyari.com/article/9676016>

[Daneshyari.com](https://daneshyari.com)