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Delivery of hydrophobic substances from an aqueous environment into polyesters using micelles

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Appendix 1. Experimental section

Materials

Polylactide (PLA) brand PLA4032D (M_w 140 kDa, $Đ$ 1.82, T_g 60–63 °C, mp 167 °C) from Nature Works LLC, USA, poly-ε-caprolactone (PCL) (M_w 170 kDa, $Đ$ 1.50, T_g −60 °C, mp 60 °C) by Sigma-Aldrich, USA; poly(ethylene glycol) methyl ether-*block*-poly(D,L-lactide) (PLA–PEG) with polyethylene glycol block M_n = 2000 and polylactide block M_n = 2000 and $Đ$ < 1.4 (Sigma-Aldrich, USA) were used as received.

Isotropic PLA and PCL films measuring 60 × 45 mm and 100 μm thick were obtained from polymer granules by hot pressing at a temperature of 190 °C for PLA and 90 °C for PCL under a pressure of 150–170 kgf cm^{-2} with quenching in a cold water bath (~15 °C), avoiding direct contact of the film sample surface with water. Under these conditions, regardless of the sample thickness, the PLA films were practically amorphous (degree of crystallinity from 0 to 3%), and the PCL films were partially crystalline (degree of crystallinity 50–55%). To obtain porous samples based on partially crystalline PLA, the initial amorphous films were pre-annealed in an SNOL thermostat (Umega, Lithuania) at 50 °C for 30 min to obtain samples with a crystallinity degree of about 40%.

PLA–PEG micelles (PLAMs) were prepared as follows. A copolymer sample (20 mg) was placed in a round-bottomed flask and dissolved in THF (2 ml). The solvent was then removed using a vacuum rotary evaporator, and the resulting film was dispersed in water (2 ml). The solution was then ultrasonicated for 10 min while continuously cooling with water. This resulted in a micellar solution with a PLA–PEG concentration of 10 mg ml^{-1}. Pyrene (Merck, USA) was used as a model hydrophobic compound and fluorescent dye. Pyrene-labeled PLAMs were obtained as described above by adding a methanol solution of pyrene to the THF solution of the copolymer so that the dye content was 1 wt%. The size of the obtained individual micelles and micelles with a fluorophore, measured by dynamic light scattering, was 20–30 nm.

Methods

Impregnation of films with PLAMs. The PLA and PCL films with S ~ 0.5 cm^2 subjected to uniaxial deformation *via* the crazing mechanism and then kept in a solution with an excess of PLAMs at a concentration of 3 mg ml^{-1} while stirring in a Multi-Vortex V-32 mixer (Biosan, Latvia) for 15 min. The films were then removed, immersed in bidistilled water to rinse off unadsorbed particles, and placed in the mixer for 5 min in pulse mode. The water was then changed, and the procedure was repeated. After five repetitions of the ‘shaking–water change’ cycle, the modified films were further examined.

Mechanical testing of polymer film samples was conducted on a Thümler Z3-X500 universal testing machine (Germany) with a 1 kN Nordic Transducer (Denmark) strain gauge at room temperature. Test specimens were cut from the films using double-sided blades 10 mm long and 5.2 mm wide. The strain rate was 10 mm min^{-1} for PCL and 2.5 mm min^{-1} for PLA.

The surface characteristics of the polymer films were determined by measuring the contact angle using a TRACKERTM Standard Drop Tensiometer (Teclis Scientific, Lyon, France).

Appendix 2. Results section

After crazing and subsequent impregnation with pyrene-labeled PLAMs, the PLA and PCL films were examined using fluorescence techniques. The impregnated films were rinsed with distilled water and air-dried. Photographs of the PLA and PCL films are shown in Figure S1(*a*) and Figure S1(*b*), respectively. The films were exposed to UV irradiation using a UV laser. As a result, a uniform violet fluorescence was observed for both samples, reflecting the distribution of pyrene in the films [see Figure S1(*c*) and Figure S1(*d*)].

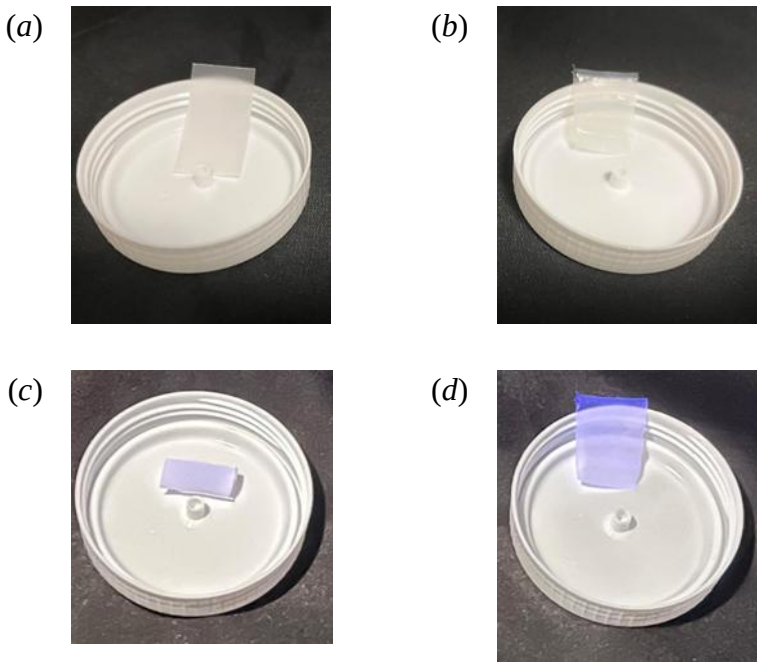

Figure S1 Photographs of PLAM- impregnated (*a*),(*c*) PLA and (*b*),(*d*) PCL films under (*a*),(*b*) visible light and (*c*),(*d*) UV irradiation.

To investigate the stability of the absorbed dye in polymer films, the release kinetics of pyrene-labeled micelles from the polymer films was studied using fluorescence spectroscopy. The dependence of the PLAM suspension fluorescence on the concentration of pyrene-labeled PLAMs is shown in Figure S2. Samples (1 cm^2 area) of PLA and PCL films impregnated with pyrene-labeled PLAMs were placed in water (1.5 ml), after which the fluorescence in the aqueous solution was analyzed at an excitation wavelength of 342 nm and an emission wavelength of 383 nm. After one week of incubation, the fluorescence of the water supernatant was analyzed. No detectable fluorescence was recorded for both samples.

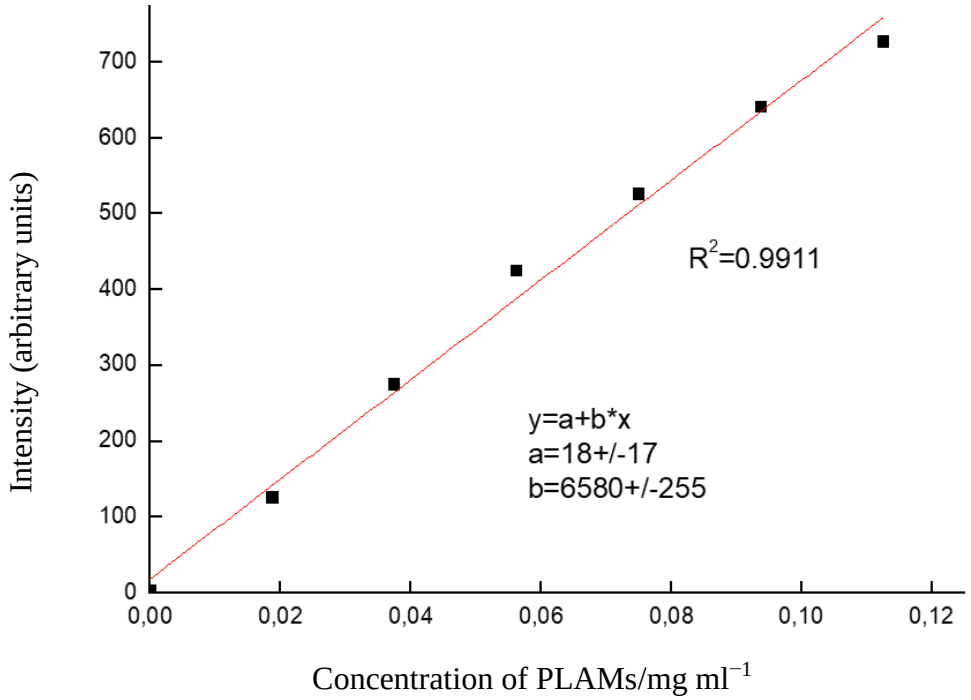

Figure S2 Dependence of the fluorescence intensity of an aqueous suspension of pyrene-labeled micelles on their concentration (λ_{ex} = 342 nm, λ_{em} = 383 nm).