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Temperature-dependent interfacial properties of hydrophobically end-modified poly(2-isopropyl-2-oxazoline)s assemblies at the air/water interface and on solid substrates

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A B S T R A C T

We describe herein the properties at the air/water (A/W) interface of hydrophobically end-modified (HM) poly(2-isopropyl-2-oxazoline)s (PiPrOx) bearing an *n*-octadecyl chain on both termini (telechelic HM-PiPrOx) or on one chain end (semitelechelic HM-PiPrOx) for different subphase temperatures and spreading solvents using the Langmuir film balance technique. The polymer interfacial properties revealed by the π–A isotherms depend markedly on the architecture and molecular weight of the polymer. On cold water subphases (14 °C), diffusion of PiPrOx chains onto water takes place for all polymers in the intermediate compressibility region (5 mN m^{-1}). At higher subphase temperatures (36 and 48 °C), the HM-PiPrOx film exhibited remarkable stability with time. Brewster angle microscopy (BAM) imaging of the A/W interface showed that the polymer assembly was not uniform and that large domains formed, either isolated grains or pearl necklaces, depending on the polymer structure, the concentration of the spreading solution and the subphase temperature. The Langmuir films were transferred onto hydrophilic substrates (silica) by the Langmuir–Blodgett (LB) technique and onto hydrophobic substrates (gold) by Langmuir–Schaefer (LS) film deposition, resulting in the formation of adsorbed particles ranging in size from 200 to 500 nm, depending on the polymer architecture and the substrate temperature. The particles presented "Janus"-like hydrophilic/hydrophobic characteristics.

1. Introduction

Many practical applications of thermoresponsive polymers rely on the reversible heat-induced transition from hydrophilic to hydrophobic, and vice versa, of a wet polymer/air interface. Commercial devices that rely on the sharpness, tunability, reversibility, and reliability of this transition are now available in areas as varied as chromatography [1,2], microfluidics [3], cell culture, and tissue engineering [4,5]. These achievements have spurred a renewed interest in fundamental studies of polymer self-assembly at the air/water (A/W) interface particularly in the case of amphiphilic diblock copolymers [6–8]. Less attention has been given to the interfacial properties of telechelic hydrophobically-modified (HM) polymers which consist of a hydrophilic backbone, mostly poly(ethylene oxide) (PEO), carrying an alkyl group at each chain end. These polymers have found applications as rheology modifiers for fluids used in cosmetics, foodstuff, pharmaceutical formulations, and coatings [9]. Most fundamental studies on telechelic HM-polymers focus on the "bulk" properties of their aqueous solutions, rather than on their interfacial characteristics. A number of reports demonstrate that PEO chains modified with hydrophobic substituents, such as *n*-alkyl [10], perfluoro [11], polyhedral oligomeric silsesquioxanes [12], or double-chained lipids [13] are able adsorb at the A/W interface upon end-group modification. End-modified HM-poly(*N*-isopropylacrylamide) (PNIPAM) derivatives [14] also form Langmuir films at the A/W interface. The morphology, thickness, density and stability of the films depend markedly on the subphase temperature, in particular in the vicinity of 32 °C, the lower critical solution temperature of PNIPAM in bulk water [15].

The work reported here pertains to a family of telechelic HM-poly(2-isopropyl-2-oxazoline)s PiPrOx (Fig. 1), in which the main chain is PiPrOx, a water-soluble polymer which undergoes a phase transition in water as the solution temperature exceeds a critical value ranging from 45 °C ($M_n = 6000$ g mol^{-1}) to 70 °C ($M_n = 2000$ g mol^{-1}) [16]. This polymer, together with its homologs poly(2-ethyl-2-oxazoline) and poly(2-methyl-2-oxazoline), is

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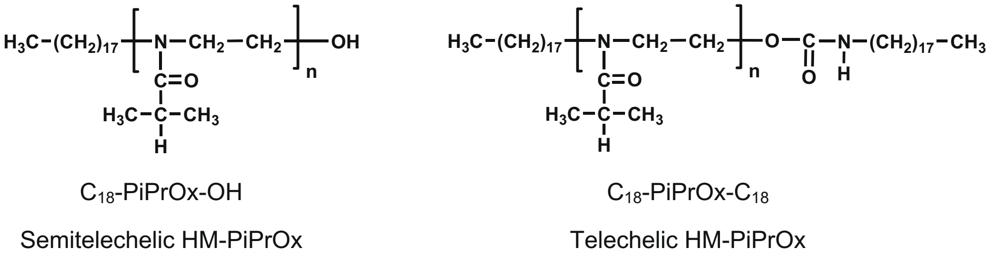

Fig. 1. Chemical structure of the polymers investigated.

biocompatible, biodegradable, and possesses stealth characteristics in vitro and in vivo comparable to those of PEO [17]. Poly(2-alkyl-2-oxazoline) are assessed currently as biomaterials, hydrogels, and drug carriers [18–20]. Studies of the interfacial properties of amphiphilic diblock copolymers with a (2-alkyl-2-oxazoline) block-indicate the propensity of poly(2-alkyl-2-oxazoline) to adsorb at the A/W interface [21]. A poly(2-methyl-2-oxazoline) or a poly(2-ethyl-2-oxazoline) carrying a dialkyl phospholipid on one chain end (lipopolymer) also adsorb at the A/W interface, forming a quasi two-dimensional physical network as a result of strong hydrophobic interactions between the phospholipid-groups aligned in the air-phase, coupled with water mediated organization of the tethered poly(2-alkyl-2-oxazoline) chains in the subphase [22–26].

We present here the temperature-dependent A/W interfacial behavior of semitelechelic and telechelic HM-PiPrOX samples bearing one or two *n*-octadecyl chains, respectively, with various PiPrOx chain lengths. The polymers were recently prepared with a view towards their use in thermoresponsive systems [27,28]. The Langmuir films were characterized by surface pressure measurements, including isotherms, hysteresis profiles and relaxation data, and Brewster angle microscopy (BAM), as a function of the composition and concentration of the spreading solution and of the subphase temperature. The morphologies of the Langmuir–Blodgett and the Langmuir–Schaeffer films transferred onto hydrophilic silica substrates and on hydrophobic butanethiol-coated gold substrates were analyzed by atomic force microscopy. The water contact angle of the transferred films was determined as a function of temperature.

2. Experimental section

2.1. Materials

Water was deionized with a Millipore Milli-Q system. All solvents were reagent grade and used as received. The HM-PiPrOx samples were prepared and characterized as described previously [27]. Their molecular characteristics are listed in Table 1. HPLC grade chloroform ($CHCl_3$) (Aldrich, 99.8%) and anhydrous ethyl alcohol (EtOH) (Commercial Alcohols Inc.) were used for the preparation of HM-PiPrOx solutions.

Table 1
Physical properties of the polymers investigated.

Polymer	M_n[a]	M_w/M_n[a]	n[b]	T_{cp}[c]
C_{18}–PiPrOx–OH 7 K	6700	1.21	57	32.5
C_{18}–PiPrOx–OH 10 K	9900	1.17	85	33.2
C_{18}–PiPrOx–OH 13 K	12,800	1.16	111	39.0
C_{18}–PiPrOx–C_{18} 7 K	7000	1.15	57	31.6
C_{18}–PiPrOx–C_{18} 10 K	10,300	1.15	85	32.1
C_{18}–PiPrOx–C_{18} 13 K	13,100	1.18	111	34.9

[a] M_n and M_w: number- and weight-average molecular weight from GPC analysis.
[b] n: average number of monomer units.
[c] T_{cp}: cloud point, from turbidity measurements (polymer concentration: 1.0 g L^{-1}, Ref. [27]).

2.2. Langmuir isotherms

Surface pressure–area (π–A) isotherms were obtained using a KSV Minitrough kept in a dust shield enclosure. The total trough surface area was 364×75 mm^2 with a trough volume ~300 mL. The trough area was robotically controlled by two hydrophobic barriers that compressed the spread film symmetrically and bilaterally at a rate of 20 mm min^{-1} (30 cm^2 min^{-1}; $\cong$4 Å^2 per monomer unit min^{-1}). The Wilhemly plate was placed in the middle of the trough facing (parallel to) the moving barriers. All measurements were made at 14 °C unless otherwise noted. Prior to each trial, the water surface was cleaned by aspiration, such that the measured surface pressure remained <0.20 mN m^{-1} over a full compression. Surface pressure measurements were made from a roughened platinum Wilhemly plate, which was flame-cleaned prior to each trial. HM-PiPrOx solutions were spread on the subphase using a gas-tight Hamilton syringe (the spreading volume ranged from 10 to 40 μL). Spreading solutions were prepared 24 h prior to use to allow for equilibration and were used within 2 days. Solutions of HM-PiPrOx in chloroform had a concentration of about 0.275 g L^{-1} and in $CHCl_3$/EtOH (50:50, v/v) a concentration of 0.275 or 0.55 g L^{-1}. The spreading solution was deposited dropwise at regularly spaced locations on the trough. In all trials, a 20 min evaporation period was maintained prior to compression. Each measurement was repeated at least three times to check the reproducibility of the isotherms, which in all cases was reproducible with deviations of less than ±1 Å^2 per monomer unit.

2.2.1. Hysteresis compression-expansion studies

Hysteresis measurements consisted of one compression/expansion cycle for HM-PiPrOx films deposited at the A/W interface by spreading 10 or 40 μL of a polymer solution prepared in $CHCl_3$ on the water subphase. The expansion was performed immediately after the compression was completed at the same barrier speed rate on the order of 4 Å^2 per monomer unit min^{-1}.

2.2.2. Isobaric creep measurements

Measurements were conducted at a constant surface pressure of 5 mN m^{-1} for different subphase temperatures (14, 36, and 48 °C). The spreading solution ($CHCl_3$, 40 μL) on the water subphase was compressed at a rate of 4 Å^2 per monomer unit min^{-1} at a constant surface pressure (5 mN m^{-1}). The change in the mean molecular area (MMA) was monitored as a function of time. At the end of the experiment, the area of the surface film (A) was compared to the initial area obtained at time zero (A_0). The difference $\Delta A = A - A_0$ was used to determine the change in the MMA as a function of time.