



Thermo-responsiveness of poly(*N,N*-diethylacrylamide) polymers at the air–water interface: The effect of a hydrophobic block

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ABSTRACT

The poly(*N,N*-diethylacrylamide) (h-PDEA) homopolymer and the poly(*N*-decylacrylamide)-*b*-PDEA (PDcA₁₁-*b*-PDEA₂₃₁) diblock copolymer were studied in the range of 10 to 40 °C, at the air–water interface. The π -*A* isotherms of h-PDEA appear nearly invariant with temperature while the π -*A* isotherms of PDcA₁₁-*b*-PDEA₂₃₁ deviate significantly to lower areas with the temperature increase evidencing the thermo-responsiveness of this diblock copolymer at the interface. For the copolymer, the limiting area per segment *versus* temperature shows a break point around 29 °C, slightly lower than the lower critical solution temperature (LCST) of h-PDEA in water (31–33 °C). AFM images of LB monolayers transferred at 40 °C revealed for both polymers the presence of hydrophobic aggregates due to the conformational changes (collapse) of chains that occur at the LCST. Differences in the morphology of these aggregates, flat irregular structures for h-PDEA and round-shaped domains for PDcA₁₁-*b*-PDEA₂₃₁, were related with the condensing effect of the hydrophobic block. The PDcA₁₁ block, anchoring the polymer to the interface, ensures a better stability and cohesion to the film and preserves the thermo-sensitivity of the h-PDEA at the interface.

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1. Introduction

The interest in stimuli responsive polymers increased enormously during the past years motivated by the potential applications of these materials [1]. Polymers can be prepared to be responsive to different stimulus (temperature [2,3], pH [4,5], ionic strength [6], light [7] and electric field [8]) but those responsive to temperature and pH in water are the most suitable for biomedical applications [9]. It is well known that several *N*-substituted poly(acrylamides) undergo an entropic driven transition from a well solvated *coil* to a *globule* by increasing the temperature around the physiological temperature [10–18]. Nevertheless, other thermodynamically stable intermediates were found between the two states showing that the polymer does not go directly from a random coil to a globular state [19–21]. The *coil*-to-*globule* transition induces polymer aggregation and phase separation. The lowest temperature at which phase separation occurs in the concentration–temperature plot is the lower critical solution temperature (LCST). The LCST depends on the subtle balance

between the polymer ability to form hydrogen bonds with water through the amide groups and the hydrophobic interactions due to the hydrocarbon backbone and the side-chain alkyl groups. At temperatures below the LCST, a homogeneous solution of hydrated polymer chains in a random coil conformation exists. By increasing the temperature above the LCST, the amide–water hydrogen bonds disrupt, the collapse of the chain into a globule occurs releasing the bound and structured water. The LCST can be tuned by the introduction of lateral chains or end groups with different lengths and structure [22–25]. Generally, the incorporation of hydrophobic comonomers leads to a lower LCST, while hydrophilic comonomers increase the LCST [26].

The capability of thermo-responsive polymers to alternate from hydrophilic to hydrophobic by adjusting the temperature has been used to create intelligent surfaces with applications namely in chromatography [27,28], microfluidic devices [29], and cell culture and engineering [30–32].

Poly(*N*-isopropylacrylamide) (PNIPAM) is certainly the most studied thermo-responsive polymer in aqueous solutions [10] and at the air–water interface [33–37]. The coil of long polymer chains shrinks to a globule with a drastic variation of volume in water, around 32 °C. The steady-state surface tension of aqueous PNIPAM solutions is independent of the bulk concentration and

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slightly changes with temperature ($\gamma = 43.1 \text{ mNm}^{-1}$, at 25°C , and 40.2 mNm^{-1} , at 40°C) [35]. Nevertheless, the thickness and the number density of segments of the PNIPAM layer at the interface increase with temperature. In spite of the large discrepancies between the values obtained by ellipsometry [36] and neutron reflectivity [37] techniques, this suggests that conformational changes occur at the air–water interface by temperature variation without significant changes of the surface tension. Furthermore, good agreement was found between the steady-state surface tension and the plateau surface pressure of spread monolayers at the air–water interface [36].

The π - A isotherms of PNIPAM are rather insensitive to temperature around the LCST of PNIPAM in water [33,36]. However, hydrophobically modified thermo-sensitive polymers and copolymers composed of hydrophobic moieties show significant variations of their isotherms with temperature [33–41]. The few studies known show that the thermo-responsiveness of these copolymers at the air–water interface depends on the content of hydrophobic moieties attached as terminal blocks or introduced as comonomers in the polymer backbone. Polymers, with a very low content of hydrophobic groups introduced in the polymer backbone of PNIPAM [38] or attached at the ends of the poly(2-isopropyl-2-oxazoline) (PIPOZ) thermo-responsive block [39] present deviations to lower molecular areas with temperature increase. An opposite trend was observed when the hydrophobic block is similar or longer than the thermo-responsive block. Deviations to higher molecular areas were observed when the temperature increased above the LCST for a diblock copolymer with a long hydrophobic block attached to PNIPAM (with a thermo-responsive component of 46 mol%) [41] and for the pentablock copolymer composed of a central pluronic (PEO–PPO–PEO) block with two thermo-responsive poly(diethylaminoethyl methacrylate) (PDEAEM) blocks at both ends with a 15 mol% content [42]. Further studies are needed in order to clarify the influence of the molecular composition and structure of thermo-responsive materials at the air–water interface.

This work studies the thermo-responsive behavior of the poly(*N,N*-diethylacrylamide) homopolymer (h-PDEA) and the poly(*N*-decylacrylamide)-*b*-PDEA (PDCA₁₁-*b*-PDEA₂₃₁) copolymer at the air–water interface. The interest in PDEA has been increasing in the last years because it is biocompatible [43–45] and like PNIPAM shows a LCST around the physiological temperature. The thermo-responsiveness of both the h-PDEA and the PDCA₁₁-*b*-PDEA₂₃₁ was studied in the 10–40 °C temperature interval. The π - A isotherms were recorded to acquire information on the polymer conformational changes that should occur with temperature increase above the polymer LCST in water. The significant differences observed between the h-PDEA and the hydrophobically modified PDEA copolymer were ascribed to the PDCA hydrophobic block (3 mol%). *In situ* observation by BAM and the AFM analysis of Langmuir–Blodgett (LB) monolayers on mica substrates were performed to follow the

formation of aggregates with temperature increase. These aggregates are discussed in the context of the phase separation undertaken by thermo-responsive polymers above the LCST.

2. Experimental

2.1. Materials

N,N-diethylacrylamide (DEA) was purchased from Monomer-Polymer & Dajac Labs and distilled under reduced pressure in the presence of hydroquinone. *N*-decylacrylamide (DCA) was synthesized as previously described [46]. The initiators 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65) (WAKO, 98%) and 2,2'-azobis(isobutyro-nitrile) (AIBN) (Fluka, 98%) were purified by recrystallization from ethanol. The *tert*-butyl dithiobenzoate (*t*BDB) was synthesized following the procedure described in [47], and the *N*-(4-(9-phenanthrenyl)butyl)-2-[[2-phenyl-1-thioxo]thio]-propanamide (PBTP) was prepared from 4-(9-phenanthrenyl)butyl amine hydrochloride [48] using the procedure reported by Bathfield et al. [49]. 1,4-Dioxane (Acros, 99%) was distilled over LiAlH₄ (110 °C), dimethylsulfoxide (DMSO) (Aldrich, anhydrous, 99.9%), tetrahydrofuran (THF) (SDS, 99%) tetrabutylammonium bromide (TBAB) (Fluka, 99%) and trioxane (Acros, 99%) were used as received.

2.2. Synthesis of PDEA

The thermo-sensitive homopolymer (h-PDEA) was obtained from the RAFT polymerization of DEA in the presence of *t*BDB as a chain transfer agent. DEA (1.22 g, 9.6 mmol), *t*BDB (5.8 mg, 27.6 μmol), AIBN (0.5 mg, 2.74 μmol), DMSO (6 mL), and trioxane (0.07 g, 0.08 mmol, the ¹H NMR internal reference) were introduced in a Schlenk tube equipped with a magnetic stirrer. The mixture was degassed by five freeze–evacuate–thaw cycles and then heated under nitrogen in a thermostated oil bath (90 °C). Periodically, aliquots of the polymerization medium were withdrawn to determine the monomer conversion by ¹H NMR. Typically, 400 μL of acetone-*d*₆ was added to 200 μL of each sample and the NMR spectrum was recorded using a Bruker AC 200 spectrometer. Monomer consumption was determined from the area of vinylic protons using trioxane (5.1 ppm) as the internal reference. The polymer (obtained at 74% conversion) was diluted ten times in H₂O Millipore and purified by dialysis at 4 °C for 5 days using a dialysis cassette (Slide-A-Lyzer[®]) from Pierce with a cut-off of 3500 Da.

2.3. Synthesis of PDCA₁₁-*b*-PDEA₂₃₁

The block copolymer with the molecular structure shown in Chart 1, was synthesized by sequential reversible addition-fragmentation chain transfer (RAFT) polymerization. The PDCA

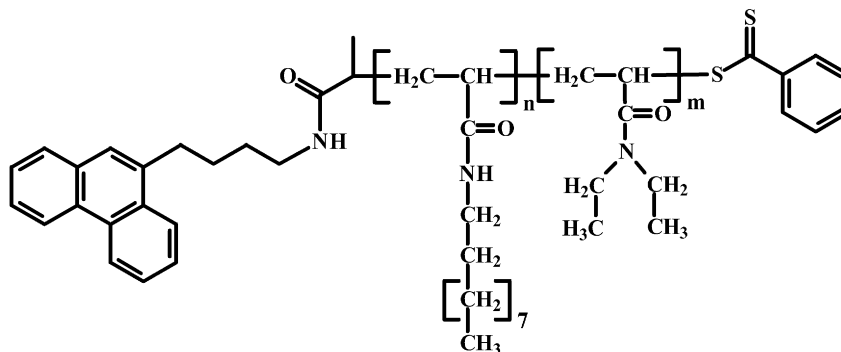


Chart 1. Chemical structure of the PDCA₁₁-*b*-PDEA₂₃₁ copolymer.

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