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Fluorescent sensibility of microarrays through functionalized adhesive polydiacetylene vesicles

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ABSTRACT

We present a design of 'smart' gluing interfaces with combined adhesive properties and intrinsic fluorescent sensing properties. Therefore, polymer–peptide amphiphiles with adhesive functional head-groups were coupled to a diacetylene tail and polymerized after formation of small vesicles. The vesicles were immobilized and confined into micro-arrays created by a photo-patterned perfluorinated film onto the substrate. Fluorescent properties of the vesicles in aqueous suspension were quantified to build standard curves for fluorescent intensity as a function of vesicle concentration. The fluorescent properties of surface-confined vesicles were quantified for different vesicle concentration and external normal load, by using a micro-chip reader. A combination of fluorescent microscopy and image processing was applied to demonstrate the fluorescent sensitivity of the adhesive micro-arrays as a function of vesicle composition, concentration and thermal annealing. These observations allow estimating the quality of the adhesive interface. Finally, the fluorescent sensitivity of the adhesive micro-array to mechanical solicitations such as normal load, internal shear under parallel and rotational sliding was investigated. The observations serve as a proof-of-concept for the fluorescent sensitivity of the adhesive bond as a function of the operational conditions. In future, this design may serve as an assessment tool for optimization or detection of local defects and device failure, e.g. in integrated microsystem components.

1. Introduction

Soft materials are good candidates for novel sensing applications as they are flexible and elastically deformable, allowing them to easily adapt their morphology (on macroscopic scale) and conformation (on molecular level) to the environment and react upon external stimuli. As an example, conjugated polymer systems such as polydiacetylenes occur as a blue- or red-colored phase, depending on the effective molecular conjugation length [1] and planarity of the backbone in the polymerized network [2]. A shift between both color states may be initiated by perturbations in the molecular structure under temperature, pH, binding of analytes, chemical environment or stress and the transition may be reversible [3], or irreversible [4]: therefore, polydiacetylenes do not need further labeling and are favorably used in various sensing and imaging systems [5], including sensors for biology [6], chemistry [7], temperature [8] or mechanics [9].

Simultaneously, it is known that polydiacetylenes in the red color state are fluorescent in contrast with the blue form as studied for oligomeric diacetylenes molecules with different chain length [10]. Initially, the fluorescent states of partially polymerized diacetylene single crystals were characterized, and attributed to local fluorescent centers connected to the polymer chain either near the end groups or accompanied by a significant relaxation of the C=C bond [11]. The fluorescent properties of polydiacetylene were further evaluated for monolayers [12], and bilayers [13]. As the stability and brittleness of such films are a main drawback, new methods for deposition of thin polydiacetylene films with uniform fluorescence were developed [14]. Ultrathin films with three adjacent monolayers of polymerized diacetylene were organized into crystalline domains and exhibit significant fluorescence in the red form [15]: the fluorescent emission is reduced at elevated temperatures likely due to thermal effects in the

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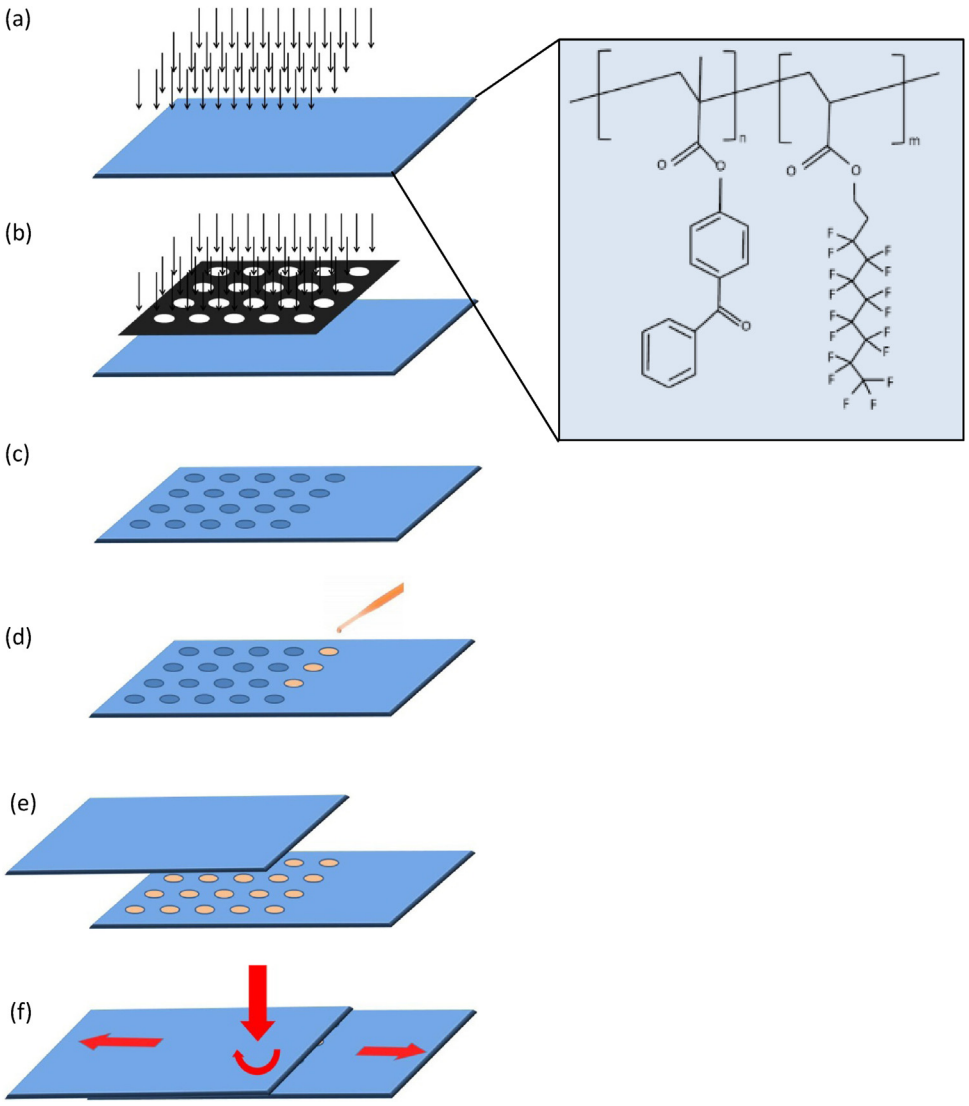

Fig. 1. Fabrication of adhesive micro-arrays onto PMMA substrates, (a) photo-chemical attachment of perfluoride thin film, (b) photo-ablation of perfluoride thin film through mask, (c) patterned PMMA substrate, (d) drop-casting of adhesive into micro-array spots, (e) formation of adhesive interface with PMMA counterface, (f) testing of adhesive interface.

hydrocarbon side chain, but the absorption remains unchanged. An energy barrier between both states was determined by time-resolved fluorescence experiments. Recently, supramolecular structures with amphiphilic diacetylenes organized in fibers [16] or liposomes [17–21] were used for fluorescent imaging. In order to more precisely localize the fluorescent sensing properties onto a substrate, the polydiacetylene films were directly patterned by photolithography [22] or the monomers were embedded in a polymer film that was further illuminated through a photomask [23]. Finally, a sensor chip platform was developed by direct photomasked irradiation of immobilized diacetylene vesicles on glass plates [24]. Similar micro-arrays were developed for sensing volatile organic compounds [25]. The organization of polydiacetylenes in droplets by means of hydrodynamic instabilities in a microfluidic flow channel allowed for detection of variations in temperatures by fluorescent response [26]. Besides the favorable fluorescent properties inherent to the molecular structure of polydiacetylene, the emission can be further enhanced through fluorophore addition [27].

An interesting possibility that opens with a large number of different diacetylenic amphiphiles is the chemical modification of the reactive head-group of such diacetylene monomers for coupling of specific functional groups. As such, specific selectivity of polydiacetylene-based sensors can be achieved by modification of a recognition group [28]. Especially, the intrinsic fluorescent properties can be combined with a dedicated interaction mechanism for biological receptivity or general adhesion purposes [29]. For the latter, e.g. peptide–polymer amphiphiles including diacetylene with modified functional head-groups can be synthesized and polymerized into vesicular nanostructures [30], including specific peptide sequences exhibiting adhesive properties, such as a GRGDSP hexapeptide [31] or mussel-inspired DOPA-adhesives [32]. The polymerization process allows better stability of the diacetylene structure as sensing material and ensures precise organization of the adhesive groups over its surface. Moreover, the use of such vesicles as reliable and stable sensing mechanism should allow for a controllable localization of the sensing elements within a system. Therefore, the sensing elements should be immobilized onto the substrate in a reproducible, precise and stable manner. In one of the first examples, polymerized diacetylenic vesicles exposing a thiol-group at the surface could be immobilized on gold substrates, although the thermal stability of the generated