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Colorimetric sensing properties of catechol-functional polymerized vesicles in aqueous solution and at solid surfaces

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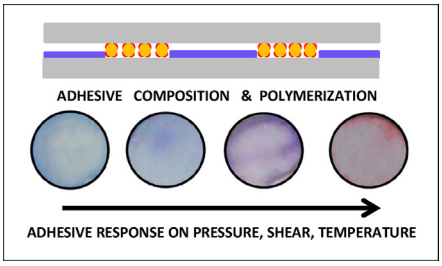
HIGHLIGHTS

- Polymerized vesicles with combined adhesive properties and colorimetric response available in aqueous dispersion.
- Color of vesicles depends on polymerization conditions, composition and thermal curing.
- Confinement of vesicles into adhesive spots onto solid substrates.
- Color of surface adsorbed vesicles depends on normal pressure and shear.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymerized vesicles containing adhesive amphiphiles with dihydroxyphenylalanine (DOPA) groups coupled to diacetylenes, allow to combine a well-controlled presentation of adhesive functions over the surface and intrinsic colorimetric sensing properties upon external stimuli. In this study, the colorimetric response of such polymerized adhesive vesicles is first evaluated after synthesis in aqueous solution as a function of vesicle compositions and polymerization times under UV light. The development of blue to red color serves as a qualitative measure for the successful formulation of the adhesive vesicles. In a second step, the colorimetric response of adhesive vesicles adsorbed onto solid surfaces was quantified. Therefore, the adhesive vesicles were confined into a spot by drop casting the aqueous solution onto lithographically patterned model substrates and subsequent drying. The colorimetric response of such an adhesive spot was studied as a function of the vesicle composition or polymerization conditions, with comparable behavior to the vesicles in dispersed state. Interestingly, the colorimetric response varies linearly within certain ranges of vesicle concentration. Finally, the color sensitivity of an adhesive spot after thermal curing and mechanical solicitation under normal load and shear load was demonstrated, indicating favorable sensitivity to heating temperature, heating time and loading levels. In this study, a potential tool has been developed for quality assessment and failure analysis of adhesive interfaces in future.

1. Introduction

The miniaturization of microsystem elements requires new strategies for local adhesive bonding at the nanoscale. While gluing is a most versatile method, current problems in dispensing small adhesive droplets should be resolved through the application of low-viscous media (e.g. aqueous environment) and the

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adhesive should be firmly located in contact with solid surfaces. The smallest adhesive contact theoretically happens by mechanical and chemical interactions at single-molecular [1] or atomic scale [2]. In one example, the lock-and-key mechanisms in biological systems have specifically inspired researchers to investigate adhesion more fundamentally at small scales [3]. In another example, micro- to nanoscale adhesion in plaques of blue mussels is mediated by specific proteins [4]. The constituents and adhesive properties of mussel foot proteins were investigated extensively [5,6] and mimicked with artificial materials [7,8], reporting the key role of catechol groups in 3,4-dihydroxy-L-phenyl-alanine (DOPA).

In order to further exploit the adhesive properties of DOPA-function for technological applications, the catechol groups should be incorporated into a stable matrix and presented to solid surfaces in a well-defined manner. One idea to address this challenge is the conjugation of amino acid groups and/or short peptides into nano-objects of defined size and surface chemistry. The large surface area of nanoscale adhesive objects allow for the precise presentation of adhesive groups over the surface and consequently high efficiency in the contribution to the overall adhesion. Moreover, the failure of an adhesive interface with discrete nanoscale objects is supposed to be delayed in comparison to a homogeneous and continuous adhesive film, as the propagation of a crack through the adhesive layer is locally hindered. The formulation of adhesive nano-objects can be achieved by modular functionalization of the surface of polymerized vesicles by precise synthesis and co-assembly of different functional amphiphiles. In one example, amino acids and short peptide sequences could be coupled to a polymerizable diacetylenic fatty acid [9]. The latter also includes the synthesis of a polymerizable amphiphile with DOPA-functional head-group [10]. Such functional polydiacetylene molecules provide a favorable system for assembly into further interesting nanostructures, such as micro- and nanocrystals, polydiacetylene networks, or mono- and multilayered films [11–14].

Another feature of polydiacetylenic vesicles is their inherent property to react to external stimuli with distinct chromatic responses [15]. The optical response of polydiacetylene upon environmental stimuli makes them ideal candidates for bio- and chemosensors [16]. The absorption in the VIS-range changes upon temperature [17], pH [18], shear-stress [19], chemical environment [20–22], anionic surfactant [23], or specific interaction of biological agents with function exposed at the surface of polydiacetylenic assemblies [24]. As a result, polydiacetylenes have been studied in responsive nanocomposite films [25], sensor applications [26], optical waveguides [27], displays [28] or molecular electronics [29]. The thermochromism of polydiacetylenes, in particular, can be used for developing reversible [30–32] or non-reversible [33,34] chromatic sensors. The transition of the stimulus-response kinetics is generally characterized by a blue-to-red color change with an intermediate metastable purple phase [35]. In general, the color of polydiacetylenes is determined by the effective conjugation length [36] and planarity of the backbone in the polymerized network [37]. On theoretical level, the color transition mechanisms for polydiacetylenes were studied by molecular dynamics and electronic structure calculations and related to out-of-plane conformational transitions due to internal stresses induced by interfacial perturbation, torsion or binding [38]. The color change is influenced by presence of metal ions by formation of organic/inorganic hybrids [39], and depends on charge-induced rearrangements of the headgroup that disturbs the backbone assembly [40]. The occurrence of a specific color phase initially depends on the polymerization conditions [41], the diacetylene position [42], the role of side chains [43], and the positioning of specific moieties to the diacetylene amphiphiles [44]. The polydiacetylenes are also known for mechanochromic response upon various mechanical stress, as first observed by compressing single crystals [45]. Later, the polydiacetylene-based materials were embedded as sensing elements into an elastomeric matrix and loaded under tensile strains [46]. The influence of mechanical solicitations under shear was described on a nanometer scale [47], by using molecular trilayer films of polymerized pentacosadiynoic acid in tribological contacts [48]. Finally, the thermal and mechanical stability and colorimetric response of polydiacetylene fibrous materials received interest from theoretical and practical viewpoints [49].

As polydiacetylenic vesicles can be conveniently synthesized with tailored surface chemistry and exhibit inherent “in-built” colorimetric response, it is interesting to explore the colorimetric sensitivity of adhesive vesicles with DOPA-functional groups for use in adhesive joints. The color changes upon various stimuli would provide a unique tool for in situ quality estimation and post-mortem failure analysis of technological applications: e.g., variations in the adhesive composition and curing, or local mechanical stress concentrations or may be assessed to optimize the design of an adhesive interface. This becomes critical in miniaturized devices where, e.g., high temperatures or mechanical solicitations are present. Besides designing and tailoring polymerized vesicles with respect to size and composition, it is furthermore important to control their deposition onto a solid substrate, i.e. to adjust the number of vesicles per surface area. Therefore, the vesicles should be applied into single spots by using micro-patterned surfaces that can conveniently be prepared, e.g., with perfluorinated monolayers that are chemically attached and structured onto solid substrates by lithography [50].

In this paper, we study the feasibility of nanoscale vesicles for simultaneous use as adhesive and colorimetric sensing elements. First, we will evaluate the colorimetric performance of adhesive DOPA-functional polymerized vesicles in a low-viscous aqueous solution as this can be taken as an indication for successful polymerization and further adhesive performance. A critical study on the assembly and polymerization for different amphiphilic compositions and polymerization times allows to optimize the stability and sensitivity by maximizing the backbone conjugation length, specifically for these adhesive vesicles. Next, the adhesive vesicles were deposited onto a solid surface and their colorimetric properties were evaluated more quantitatively. Therefore, the vesicles were confined in a so-called “adhesive spot” for quantitative colorimetric studies as a function of concentration, temperature and mechanical stress. While it is obvious that the concentration (number of deposited vesicles) will influence the adhesive strength, also thermal curing of the vesicles further enhances the adhesion. Therefore, the colorimetric response of adhesive spots upon vesicle concentration and temperature can be used as an estimate for the quality of the adhesive bonding. Upon successful demonstration and quantification of the colorimetric properties, the adhesive vesicles may be used for quality inspection and failure assessment of adhesive spots in future.

2. Experimental

2.1. Materials

For synthesis of adhesive nanoparticles, 10,12-tricosadiynoic acid (TDA) was received from GFS Chemicals (Powell, OH), glycine methyl ester (H-Gly-OMe·HCl) was received from Advanced ChemTech (Louisville, KY), 2-hydroxyethylamine-2-chlorotrityl resin (Novasyn TGT), 1-hydroxy-benzotriazole (HOBT), 2-(1-hydroxy-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU), Fmoc-DOPA (acetonid)-OH, and Fmoc-NH-$(PEG)_2$-OH were received from Merck Chemicals Ltd. (Nottingham, UK). The monomeric TDA was purified by dissolving in chloroform and filtering through a 0.45 μm PTFE filter. The