

# Preparation and thermally induced adhesion properties of a poly(vinyl alcohol)-*g*-*N*-isopropylacrylamide copolymer membrane

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## ABSTRACT

In the work described here, poly(vinyl alcohol)-*g*-*N*-isopropylacrylamide was prepared via graft polymerisation of *N*-isopropylacrylamide (NIPAM) onto poly(vinyl alcohol) (PVA). The structure and components of the polymer were characterised by differential thermogravimetry (DTG), differential scanning calorimetry (DSC), <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) and fourier transform infrared spectroscopy (FT-IR) testing, respectively. The T-type peel adhesion strengths and water contact angles of the prepared graft copolymer membranes were determined at different temperatures. The results indicated that the membrane has an obvious change in adhesion and water contact angle around the lower critical solution temperature (LCST) of the thermosensitive PNIPAM, regardless of the composition of the copolymers. Based on the scanning electron microscope (SEM) and energy dispersive spectrometric (EDS) analysis of freeze-dried graft copolymer membranes swollen in water at various temperatures, a mechanism for the thermally induced adhesion properties of the graft copolymer was proposed.

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## 1. Introduction

Conventional adhesives are applied as a low-viscosity liquid and transform into a strong and tough solid that bond two surfaces together. Generally, this liquid–solid transformation is irreversible. Oftentimes, we require a bond or an adhesive that is not permanent, and the adhesive joint needs to be “debonded” at a pre-determined time. An emerging area of adhesives research is the development of reversible adhesives. These adhesives enable facile debonding and separation of the bonded surfaces when the adhesion is no longer required [1]. Uses for non-permanent adhesives, non-structural applications include items, such as removable labels, surface protection films, easily placeable and removable notepaper and bonding credit cards to mailers. Additionally, structural applications for non-permanent adhesives include tooling placement, prototyping, and disassembly of parts for reuse and repositioning. Ideally, adhesive reversibility should be achieved with minimal sacrifice of adhesive strength in the bonded state, relative to the irreversible case. To develop reversible adhesives, various strategies have been reported. First, the micro- or nano-structured dry adhesive surfaces with the hierarchical structure of a gecko foot have been widely studied [2,3].

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Second, several researchers utilised the shape memory effect to induce either a microscopic transition of the surface topology [4,5] or a macroscopic change in the geometry [6] as a means to be able to “self-peel”. Third, some chemical reactions have been used to prepare reversible adhesives. A thermally removable adhesive using the reversible Diels–Alder reaction was reported [7]. Adducts can form between a furan and a maleimide below approximately 60 °C. However, adducts open above approximately 90 °C, resulting in both a low molecular weight and a low modulus. The modulus can be many orders of magnitude lower than a conventional adhesive heated above its glass transition temperature. A self-healing polymer blend composed of poly(ε-caprolactone) (PCL) and a diglycidyl ether of bisphenol-A (DGEBA) was determined to undergo polymerisation-induced phase separation. The resulting product possesses a reversible adhesive behaviour when it is alternatively heated and cooled [8]. A triblock copolymer with poly(methyl methacrylate) end blocks and a poly(*n*-butyl acrylate) midblock was determined to exhibit reversible adhesive behaviour based on the adhesion of the thermally reversible gel to solid surfaces [9]. A reversible adhesive based on a well-known thermosensitive polymer, poly(*N*-isopropylacrylamide) (PNIPAM), has also been reported. PNIPAM shows a thermally reversible transition in conformation around the lower critical solution temperature (LCST) [10], which results in a sudden transformation of the PNIPAM chains from exhibiting hydrophilicity below LCST to exhibiting hydrophobicity above LCST [11]. This temperature-induced conformational

switch of PNIPAM can be used in bioscience applications for controlling protein or cell adhesion. PNIPAM-functional films with adhesion-sensitive properties are dehydrated and kept hydrophobic to be suitable for cell or protein attachment when the external temperature is above the LCST. However, when the temperature is below the LCST, the surface is hydrated and hydrophilic and exhibits detachment of the cell or protein [12,13]. There are various PNIPAM-based polymers, such as PNIPAM surface brushes [14,15], PNIPAM and poly(2-vinyl pyridine) [16] or poly(dimethylamino) ethyl methacrylate surface brushes [17], PNIPAM-*b*-PS diblock copolymer brushes [18], a copolymer of PNIPAM with hydroxypropyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate [19], PNIPAM nanohydrogel [20] and film hydrogel [21] that can be used in determining controlled protein or cell adhesion/detachment. Although some strategies for the preparation of reversible adhesives have been reported, to the best of our knowledge, a strategy based on the use of a poly(vinyl alcohol) (PVA)-*g*-NIPAM copolymer has not been reported.

It is well known that poly(vinyl alcohol) (PVA) possesses unique characteristics, such as excellent film-forming, and film properties, such as remarkable flexing resistance and adhesive strength [22]. PVA has a long history of use in various industrial applications [23,24]. As an adhesive, PVA is commonly used for non-structural applications, such as laminating and bonding or binding porous materials. Additionally, PVA exhibits very good wet tack properties for laminating, sufficient water resistance for most interior applications, and excellent resistance to grease and oil. Taking into consideration the adhesive feature of PVA and the properties of the temperature-induced conformational switch of PNIPAM, a film with reversible adhesion may be obtained by combining both the advantages of PVA and PNIPAM into one film. In this study, a PVA-*g*-NIPAM graft copolymer was prepared and characterised to first verify the feasibility of this idea (Scheme 1A). Moreover, the effects of the grafting ratio on the adhesion strengths and the thermosensitivities of the prepared films were investigated. Although the PVA-*g*-NIPAM copolymer has been prepared to obtain a membrane with the temperature dependence of the permeation of

solutes [25–28], research on temperature dependence of the adhesion of this copolymer is rarely reported in literature. We hope the results reported here in this paper will be beneficial and help to apply this new reversible adhesive film.

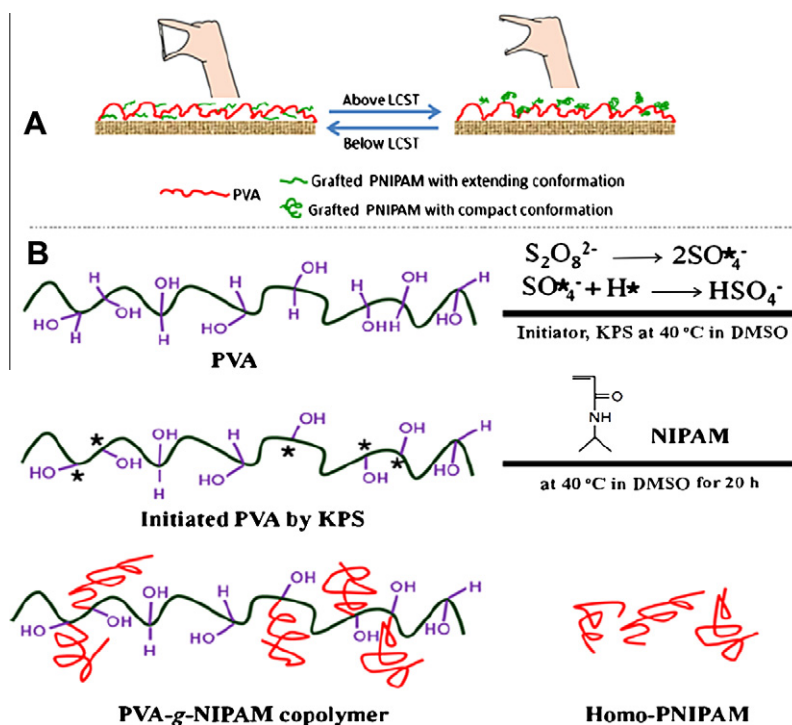
## 2. Experimental

### 2.1. Materials

*N*-isopropylacrylamide (NIPAM) was purchased from Aldrich and purified twice by recrystallisation using *n*-hexane. Poly(vinyl alcohol) (PVA, >99% hydrolysed with  $M_w = 89,000 - 98,000$  g/mol, from Aldrich) was dried at 40 °C for 24 h prior to use. Potassium persulfate (KPS, from Aldrich) was recrystallised twice using water. Other chemicals were of AR grade and used as received.

### 2.2. Synthesis of PVA-*g*-NIPAM graft copolymers

The PVA-*g*-NIPAM graft copolymer was prepared through introduction of PNIPAM side chains onto the PVA backbone via the radical-initiated “grafting-from” method [25–28]. In a typical synthesis, PVA was dissolved in dimethyl sulfoxide (DMSO) into a Schlenk flask, three vacuum-purge argon fill cycles were performed, and a solution of monomer NIPAM and initiator KPS in DMSO were added into the flask under argon. An amount of 20 mL of DMSO was dissolved into the Schlenk flask and then deoxygenated by passing argon through the mixture for a minimum of 30 min at room temperature. After sealing the flask, the polymerisation process was performed at 40 °C for 20 h with stirring before being quenched by exposure to air and cooling. The copolymer in the solution of DMSO was precipitated in acetone. The ungrafted homo-PNIPAM formed during the graft copolymerisation was removed partially by washing the crude copolymer with acetone several times. To ensure its complete removal, the crude copolymer was Soxhlet extracted for approximately 4 days. The disappearance of the peak of homo-PNIPAM detected by gel permeation chromatography



**Scheme 1.** Illustration of the PVA-*g*-NIPAM graft copolymer with temperature dependence of the adhesion (A) and synthesis of PVA-*g*-NIPAM graft copolymer (B).

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